# Metal-Metal (MM) Bond Distances and Bond Orders in Binuclear Metal Complexes of the First Row Transition Metals Titanium Through Zinc 

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ABSTRACT: This survey of metal-metal (MM) bond distances in binuclear complexes of the first row 3d-block elements reviews experimental and computational research on a wide range of such systems. The metals surveyed are titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc, representing the only comprehensive presentation of such results to date. Factors impacting MM bond lengths that are discussed here include (a) the formal MM bond order, (b) size of the metal ion present in the bimetallic core $\left(\mathrm{M}_{2}\right)^{n+}$, (c) the metal oxidation state, (d) effects of ligand basicity, coordination mode and number, and (e) steric effects of bulky ligands. Correlations between experimental and computational findings are examined wherever possible, often yielding good agreement for MM bond lengths. The formal bond order provides a key basis for assessing experimental and computationally derived MM bond lengths. The effects of change in the metal upon MM bond length ranges in binuclear complexes suggest trends for single, double, triple, and quadruple MM bonds which are related to the available information on metal atomic radii. It emerges that while specific factors for a limited range of complexes are found to have their expected impact in many cases, the assessment of the net effect of these factors is challenging. The combination of experimental and computational results lead us to propose for the first time the ranges and "best" estimates for MM bond distances of all types (Ti-Ti through $\mathrm{Zn}-\mathrm{Zn}$, single through quintuple).

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## 1. INTRODUCTION

Transition metal (TM) complex chemistry began with Werner's coordination theory treating primarily a ligand array around a single metal center. ${ }^{1,2}$ Such complexes can contain two or more metal atoms but no direct metal-metal bonds. In 1957, evidence of the first metal-metal (MM) bonds was seen in the binuclear metal carbonyls $\mathrm{M}_{2}(\mathrm{CO})_{10}(\mathrm{M}=\mathrm{Mn}, \mathrm{Re}) .^{3}$ This was the year that one of the authors (RBK) of this review started his doctoral work at Harvard University. In the only slightly more than six decades from the definitive identification of the first MM bond between d-block metals, this field has mushroomed into a very rich area of chemistry with well characterized binuclear d-block metal molecules having all possible integral formal bond orders between 1 and 5 .

The mid-60's saw the first recognition of MM multiple bonds in the quadruple Re-Re bond of the $\left(\mathrm{Re}_{2} \mathrm{Cl}_{8}\right)^{2-}$ anion. ${ }^{4,5}$ Prior to this, many TM complexes had been synthesised which only later were shown to have MM multiple bonds, including $\mathrm{Cr}-\mathrm{Cr},{ }^{6} \mathrm{Mo}-\mathrm{Mo},{ }^{7} \mathrm{~W}-\mathrm{W},{ }^{8} \mathrm{Pt}-\mathrm{Pt},{ }^{9} \mathrm{Nb}-$ $\mathrm{Nb},{ }^{10}$ and $\mathrm{Ta}-\mathrm{Ta}^{11}$ bonds. The anion $\mathrm{Re}_{3} \mathrm{Cl}_{12}{ }^{2-}$ was the first instance of metal-metal multiple bond recognition by MO analysis, in the $\mathrm{Re}_{3}$ triangle with three $\mathrm{Re}=\mathrm{Re}$ double bonds. ${ }^{12,13}$ Since then, the chemistry of MM bonded TM complexes has been documented in many monographs. ${ }^{14,15,16,17,18}$ Thousands of TM complexes with MM bonds are now known and experimentally characterized over the three TM periods, spanning elements from groups 4 to 12. Figure 1 depicts structures of a mononuclear complex $\mathbf{A}$, of a bimetallic complex $\mathbf{B}$ without an MM bond, and of a binuclear complex $\mathbf{C}$ with a metal-metal covalent bond. In general, this review is focused on complexes of the type $\mathbf{C}$ with metal-metal bonds.


A


B


C

Figure 1. Mononuclear, non-MM-bonded binuclear, and MM-bonded binuclear complexes

### 1.1. Metal-Metal (MM) Bonds in Binuclear Complexes

Metal-metal distances are key experimentally measurable features of binuclear or polynuclear metal complexes. This survey of MM bond distances in homobinuclear metal complexes of the first row 3d-block elements derives much from experimental structure determinations, mostly X-ray diffraction studies. Heteronuclear MM bonds are also well known ${ }^{19}$ but are not dealt with here. Cluster complexes with three or more metal atoms are also not discussed in detail here. Extended metal atom chain complexes with up to an infinite number of metal centers also fall outside the scope of this review.

Computational (mainly density functional) studies furnish a wealth of information on MM bond lengths predicted for a wide variety of binuclear and other complexes. Theory often corroborates experiment and provides reasonable predictions for species not yet synthesized. Unequivocal experimental studies on the geometrical structure of a complex provide a benchmark against which the reliability of computational findings may be gauged.

Metal-metal interactions in binuclear complexes include (a) covalent MM bonds involving overlap between metal orbitals, (b) weak interactions supported mainly by bridging ligands, (c) metal-to-metal dative bonds, (d) antiferromagnetic coupling between metal centers, (f) three-center two-electron bonds via ligand atoms not invoking direct metal-metal bonding,
and (f) no discernible metal-metal interaction at all in systems with widely separated metal centers. This survey focuses on MM interactions with predominantly covalent bonding.

Various structural and electronic factors influence MM covalent bond distances including the following: (a) the atomic and covalent radii of the metal, (b) the oxidation state of the metal atoms and the formal charge on the $\left(\mathrm{M}_{2}\right)^{n+}$ core ( $n$ ranging from 0 to 8 ), (c) the formal MM bond order, (d) the basicity and electron-releasing capacity of the ligands, (e) the spatial arrangement of the ligands around the $\left(\mathrm{M}_{2}\right)^{n+}$ core, (f) the effects of steric bulk and crowding, (g) stereoelectronic factors like the "bite" angle of bidentate ligands, (h) the mode of metalligand bonding which includes a number of distinct types, (i) the spin state of the complex, and (j) crystal packing forces, discussed in more detail later.

### 1.2. Scope of This Survey

This review focuses on homonuclear bimetallic complexes with well-defined covalent MM bonds. The metal M is restricted to the first row 3d-block elements $(\mathrm{M}=\mathrm{Ti}, \mathrm{V}, \mathrm{Mn}, \mathrm{Cr}, \mathrm{Fe}$, $\mathrm{Co}, \mathrm{Ni}, \mathrm{Cu}$, and Zn ). Binuclear metal complexes are also well known for second and third row transition metals, $\mathrm{Rh}, \mathrm{Mo}, \mathrm{Re}$ and Ru being the most thoroughly studied in this respect. ${ }^{20}$

The 3d-block element scandium is not a genuine TM, and not known to form complexes with $\mathrm{Sc}-\mathrm{Sc}$ covalent bonds. However, metallic $\mathrm{Sc}-\mathrm{Sc}$ bonding was found by Corbett and coworkers in clusters with an $\mathrm{Sc}_{7} \mathrm{Cl}_{10}$ system ${ }^{21}$ or based on an ScCl system, ${ }^{22}$ and in infinite chain $\mathrm{Sc}_{4} \mathrm{Cl}_{6} \mathrm{Z}$ systems $(\mathrm{Z}=\mathrm{B}, \mathrm{N}){ }^{23}$ The $\mathrm{Sc}-\mathrm{Sc}$ distances fall outside the $\mathrm{Sc}-\mathrm{Sc}$ single bond distance of $2.96 \AA$ expected from an estimate of $1.48 \AA$ for the Sc single covalent bond radius. ${ }^{24} \mathrm{An} \mathrm{Sc-Sc}$ distance of $3.24 \AA$ expected from the metallic bonding radius of $1.62 \AA^{25}$ is more consistent with these $\mathrm{Sc}-\mathrm{Sc}$ distances. The $\mathrm{Sc}-\mathrm{Sc}$ bond length in the scandium dimer $\mathrm{Sc}_{2}$ is not yet experimentally known, although a dissociation energy $D_{0}$ of $1.65 \pm 0.22 \mathrm{ev}$ (Gingerich ${ }^{26}$ ) and a harmonic vibrational frequency of $239.9 \mathrm{~cm}^{-1}$ (Moskovitz ${ }^{27}$ ) have been
reported. The Sc -Sc distance in $\mathrm{Sc}_{2}$ has been estimated at 2.20 to $2.42 \AA^{28,29}$ using empirical formulas. ${ }^{30,31,32}$ Density functional methods gave $\mathrm{Sc}-\mathrm{Sc}$ bond lengths ranging from 2.562 to $2.663 \AA,{ }^{33,34}$ with a configuration pointing to a covalent $\mathrm{Sc}=\mathrm{Sc}$ double bond.

Zinc is also not properly a TM since, in its $\mathrm{Zn}^{+2}$ oxidation state, it has the $\mathrm{d}^{10}$ configuration with no half-filled 3d orbitals. $\mathrm{Zn}-\mathrm{Zn}$ covalent bonds are well-established, however, in inorganic and organometallic complexes. Section 12 deals with the prospect for $\mathrm{Zn}-\mathrm{Zn}$ bonds in a variety of binuclear complexes studied experimentally and computationally.

In this review, the MM bond distance is referred to as $R_{M M}$ (in angstrom). Experimental $R_{M M}$ values can span a wide range even for a given metal. We also focus on MM bond orders, covering single, double, triple, quadruple, and quintuple MM bonds, with brief mention of the possibility of sextuple bonds. The monographs edited by Cotton, Walton and Murillo ${ }^{14-16}$ dealt chiefly with triple and quadruple bonds. The formal bond order (fBO) takes on integral values (1, 2, 3 etc.) for an integral number of shared electron pairs between the two metal centers. Half-integral fBOs can arise if an unpaired electron is involved in MM bonding. Further, the involvement of single electrons in an MM bond in two orbitals orthogonal to each other is described by the concept of "half-bonds" of the $\pi$ or $\delta$ types, where the full bond is denoted as $2 / 2 \pi$ or $2 / 2 \delta$.

MO theory in a single determinantal framework can assign fBO values on the basis of occupancy of the molecular orbitals (bonding and antibonding) by electrons associated with the metal. Multi-configurational approaches, however, may call into question the very concept of a bond order between two atoms, although the computation of an "effective bond order" (eBO) can be carried out in such approaches.

The 18 -electron rule ${ }^{35,36,37}$ provides a basis for assigning MM formal bond orders in TM binuclear complexes, where, for 3d block elements, an electronic configuration of the $n=3$ shell corresponding to a noble gas-like population of 18 electrons around each metal centre is
regarded as ideal and designated as $(18,18)$. Electron counting is performed by firstly filling in electrons to the metal centres according to their oxidation state. After considering bonding with the ligands and the presence of any unpaired electrons, the remaining electrons go to constitute the MM bond, being counted to assign the formal MM bond order fBO. This works well for mononuclear complexes like metal carbonyls and organometallics when the d-orbital splitting between bonding and anti-bonding orbitals is large. Low valence states of the metal centres and the presence of $\pi$-acceptor ligands favor adherence to this rule. However, this qualitative rule of thumb, along with the effective atomic number rule, ${ }^{38}$ often meets with exceptions, so that $(18,16),(17,17)$ and other configurations may be assigned in some binuclear complexes. This can occur with first row TM complexes having ligands ranking low in the spectrochemical series. The electron counting method to arrive at formal MM bond orders is illustrated for some representative complexes in the Supplementary Information.

Such broad qualitative descriptions may contrast with the quantitative estimates of bond strength used in computational chemistry, such as the Wiberg bond index ${ }^{39}$ and a host of other indices computed by appropriate treatments of the electron density between two atoms. ${ }^{40}$ Such estimates include the effective bond order (eBO) computed in a multiconfigurational context. These numerical indices are not restricted to integral or half-integral values, but accommodate a continuum of values. All these quantitative non-integral indices of bond strength are broadly referred to here as "computed bond orders" (cBO). While fBO values are arrived at by inspection, cBO values are derived from computations using quantum mechanical electronic structure theories. Bond dissociation energies may also be considered as descriptors of MM bond strengths. MM bond dissociation energies are less often estimated experimentally, but may be computed using the methods of molecular quantum mechanics.

This review contains extensive tables with experimentally determined MM bond distances gathered from the literature on binuclear first row metal complexes, most derived from X-ray
diffraction studies. This review also gathers MM bond distances obtained from the results of quantum chemical theoretical studies on binuclear metal complexes. Hundreds of such complexes have been studied using a wide range of theoretical methods, most frequently DFT methods. For MM bond lengths in 3d-block binuclear complexes, the database of computational predictions exceeds considerably the database of experimental results.

### 1.3 Some Critical Observations

All 3d-block metals except scandium have shown evidence for homonuclear metal-metal bonds in their binuclear complexes, with formal MM bond orders from 0.5 to 5.0. Chromium shows the most proclivity for multiple MM bonding, but experimental and computational results indicate that vanadium and manganese are also capable of having MM multiple bonds in their binuclear complexes. For first row metals after manganese, computational studies predict MM bonds of high bond order only in some high energy isomers of some complexes.

The synthesis of viable binuclear complexes with MM bonds of high order (quadruple and quintuple) is challenging due to the high energy content of the multiple MM bond. Other outcomes like addition reactions, disproportionation, bond dissociation, and isomerism to complexes with MM bonds of lower order, etc., can all detract from the desired result. This requires special strategies like steric protection of the highly reactive MM multiple bond.

Computational analysis of metal-metal bonds has revealed some aspects of the nature of metal-metal bonds in binuclear complexes. The symmetry type ( $\sigma, \pi$, and $\delta$ ) and relative strengths of the components of quadruple and quintuple MM bonds in Group 6 binuclear complexes have been made evident through MO and DFT approaches. Covalent MM bonding usually involves the 3 d orbitals, but can also involve the 4 s and 4 p orbitals as well, as in the $\mathrm{Zn}-\mathrm{Zn}$ bonds in some dizinc complexes. The covalent aspect of MM bonding via metal orbital overlap is thus quite well understood. Other aspects of metal-metal bonding like
ferro- and antiferromagnetic coupling between metal centers, two-electron three-center bonding through bridging ligands, metal $\rightarrow$ metal dative bonding, effects of metal electropositivity upon MM bonding, metal $\rightarrow$ ligand backbonding in carbonyl complexes, etc. have received so far only limited attention. There also has been a relaxation of rigor and accuracy in the theoretical models used to study MM bonds in binuclear complexes, due largely to the size of the systems involved. Lastly, for first row metals, most of the attention given through computational approaches has so far focused on binuclear complexes that contain carbonyl ligands. There are very few DFT studies on non-carbonyl complexes such as binuclear paddlewheel complexes.

Although scientific intuition would presuppose an inverse sort of correlation between MM bond length and MM bond order, a comprehensive analysis of the results is still lacking. There has yet been no attempt to propose limits or ranges for MM bond lengths within a given MM bond order (single to quintuple) in binuclear complexes of any given metal.

### 1.4 Some Challenges

The synthesis of binuclear complexes with MM bonds of high order (quadruple or quintuple) can present a real challenge. The goal of arriving at a stable structure of this kind is often overturned by the high reactivity associated by the MM multiple bond, for which protective strategies have to be devised. From the theoretical side, true minima (often of high energy) for unknown complexes having quadruple or even quintuple MM bonds have been identified. Whether or not they are synthetically viable remains to be established by experiment.

A proper theoretical description of metal-metal bonding also presents challenges. Some cases (like the $\mathrm{Zn}-\mathrm{Zn}$ bond in dizinc complexes) lend themselves quite amenable to treatment by theory. Other cases, notably the highly correlated MM bonds of multiple order (such as in dichromium bis(terphenyl) complexes), would require a degree of rigor and sophistication of
method which is very compute-intensive for systems of even modest size. A complicating factor is the involvement of factors in MM bonding which are not derived directly from metal-metal orbital overlap, such as three-center two-electron bonds, electrostatic and dispersive interactions, antiferromagnetic coupling, etc. Also related to these issue is the question of whether less demanding approaches like DFT can give reasonably good predictions regarding the geometry of the complex and the MM bond length, the ground state magnetic and spectral properties, etc., of MM bonded complexes.

One challenge that is faced in this review concerns the systematic proposal of well-defined ranges or "best" values for MM bond distances in binuclear complexes having MM bonds of various orders (one to five) and covering the whole range of the 3d block metals. Such a task would require an extensive database to be statistically significant. Unfortunately, for the 3d block binuclear metal complexes, the experimental database is often insufficient or lacking. Computational (DFT) studies have led to a much more extensive collection of such results, and are much laid recourse to in this review, especially for binuclear complexes containing carbonyl ligands.

### 1.5. Objectives of This Review

The objectives of this review on metal-metal bond lengths and bond orders in binuclear MMbonded 3d-block metal complexes may be delineated as follows:

1. To present systematically and comprehensively, together for the first time, a large body of results on metal-metal bond distances in binuclear complexes of all of the 3dblock metals as gathered from experimental and computational studies.
2. To seek for qualitative trends regarding the influence of one or more of the factors described above upon metal-metal bond lengths within a series of related complexes.
3. To observe how computational predictions of metal-metal bond lengths compare with the available experimental conclusions in order to gauge the reliability and applicability of the computational methodologies used.
4. To seek relationships between MM bond lengths and bond orders wherever possible, and on this basis to suggest limits within which MM bond lengths of a given formal bond order for a given metal may belong.

## 2. FACTORS INFLUENCING METAL-METAL BOND DISTANCES

Various structural and electronic features of the complex may have their impact upon the MM bond distance found experimentally or predicted by theory, as discussed below:

### 2.1. Size of the Metal Atom/Ion

The electronic configurations $[\mathrm{Ar}] 3 \mathrm{~d}^{\mathrm{n}} 4 \mathrm{~s}^{\mathrm{m}}$ of the neutral atoms of the 3 d -block metals are given in Table 1, written simply as $3 d^{n} 4 \mathrm{~s}^{\mathrm{m}}(\mathrm{n}=1$ to $10 ; \mathrm{m}=1,2)$. The size of the metal atom or ion may, according to context, be expressed as the atomic, covalent, or ionic radius. Table 1 presents for the 3d-block metals the values of
(a) the covalent radii $\mathrm{R}_{\text {cov }}$ derived by Cordero et al. ${ }^{41}$ from crystallographic data in the Cambridge Structural Database;
(b) the non-bonded atomic radii $\mathrm{R}_{\text {cal }}$ computed by Clementi et al. ${ }^{42}$;
(c) the single-bond covalent radii $\mathrm{R}_{\mathrm{cv}}(1)$ of Pyykkö and Atsumi; ${ }^{24}$
(d) the double-bond covalent radii $\mathrm{R}_{\mathrm{cv}}(2)$ of Pyykkö and Atsumi; ${ }^{43}$
(e) the triple-bond covalent radii $\mathrm{R}_{\mathrm{cv}}(3)$ of Pyykkö; ${ }^{44}$
(f) the metallic radii $\mathrm{R}_{\text {met }}$ of Pauling. ${ }^{25}$

Apart from the above, other estimates relevant for discussion of MM covalent bonds in TM complexes have been made by Pauling. ${ }^{45,46,47}$ Each set of values has its own area of
applicability. Estimated values of atomic and covalent radii can vary widely depending upon the criteria used for defining them.

The set of covalent radii $\mathrm{R}_{\text {cov }}$ does not specify the metal valence state. Different sets of covalent radii, considering whether the metal is singly, doubly, or triply bonded to the other atom(s), have proposed by Pyykkö, viz., the $\mathrm{R}_{\mathrm{cv}}(1), \mathrm{R}_{\mathrm{cv}}(2)$ and $\mathrm{R}_{\mathrm{cv}}(3)$ values of Table 1, , 24,43,44 where, as expected, for any metal, $\mathrm{R}_{\mathrm{cv}}(1)>\mathrm{R}_{\mathrm{cv}}(2)>\mathrm{R}_{\mathrm{cv}}(3)$. These are much shorter than the generalized covalent radii $\mathrm{R}_{\text {cov }}$ obtained by Cordero et al. ${ }^{41}$ and the radii $\mathrm{R}_{\text {met }}$ for atoms in the metallic state. This review most often uses the $\mathrm{R}_{\mathrm{cov}}$ values of Cordero et al. as the reference for MM bond lengths rather than the $\mathrm{R}_{\mathrm{cv}}(1), \mathrm{R}_{\mathrm{cv}}(2)$ and $\mathrm{R}_{\mathrm{cv}}(3)$ values of Table 1. This is because MM bond length estimates based upon the $\mathrm{R}_{\text {cov }}$ values are often more consistent with experimental data on MM single bond distances.

Table 1. Neutral Atom Configurations and Atomic Radii ( $\AA$ ) of 3d-Block Metals

| Metal | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Config- <br> uration $^{a}$ | $3 \mathrm{~d} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{2} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{3} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{5} 4 \mathrm{~s}^{1}$ | $3 \mathrm{~d}^{5} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{6} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{7} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$ | $3 \mathrm{~d}^{10} 4 \mathrm{~s}$ | $3 \mathrm{~d}^{10} 4 \mathrm{~s}^{2}$ |
| $R_{\text {cov }}{ }^{b}$ | $1.70(7)$ | $1.60(8)$ | $1.53(8)$ | $1.39(5)$ | $1.39(5)$ | $1.32(3)$ | $1.26(3)$ | $1.24(4)$ | $1.32(4)$ | $1.22(4)$ |
| $R_{c a l}$ | 1.84 | 1.76 | 1.71 | 1.66 | 1.61 | 1.56 | 1.52 | 1.49 | 1.45 | 1.42 |
| $R_{c v}(1)$ | 1.48 | 1.36 | 1.34 | 1.22 | 1.19 | 1.16 | 1.11 | 1.10 | 1.12 | 1.18 |
| $R_{c r}(2)$ | 1.16 | 1.17 | 1.12 | 1.11 | 1.05 | 1.09 | 1.03 | 1.01 | 1.15 | 1.20 |
| $R_{c r}(3)$ | 1.14 | 1.08 | 1.06 | 1.03 | 1.03 | 1.02 | 0.96 | 1.01 | 1.02 | - |
| $R_{m e t}$ | 1.62 | 1.47 | 1.34 | 1.28 | 1.27 | 1.26 | 1.25 | 1.24 | 1.28 | 1.34 |

[^0]Any MM covalent bond in a homonuclear bimetallic complex is expected to be approximately equal to or shorter than twice the covalent radius for the metal. The intrinsic degree of length or shortness of homonuclear MM covalent bonds in binuclear complexes may be expressed as the formal shortness ratio (FSR), ${ }^{48}$ expressed as

$$
\begin{equation*}
\mathrm{FSR}=R_{M M} / 2 R_{M} \tag{1}
\end{equation*}
$$

where $R_{M M}$ is the MM bond length in the given molecule and $R_{M}$ is the covalent radius of the element M as derived from the compilations of Cordero et al. ${ }^{41}$ The formal shortness ratio may be used to compare intrinsic MM bond strength between related as well as unrelated binuclear complexes.

### 2.2. Metal Oxidation States

Formal oxidation states of each atom in bimetallic complexes generally range from 0 to +4 , leading to formal net charges of 0 to +8 on the bimetallic core. Lower oxidation states may increase the scope for higher MM bond orders by disfavouring binding to basic or negatively charged ligands, leaving the electrons on each metal atom available to form MM bonds of higher order. Thus the design of bis(terphenyl) dichromium complexes with formal quintuple MM bonds used a low metal formal oxidation state of +1 . Higher metal oxidation states tend to drive the metal atoms further apart through electrostatic repulsion, promoting longer MM bond distances. For metals early in the period, the size of the metal center varies widely with change of oxidation state, an effect less evident in the later metals.

### 2.3. Influences of Ligands

The number of ligands present can affect MM bond distances. The maximum coordination number of 3d-block transition metals is nine corresponding to the $\mathrm{sp}^{3} \mathrm{~d}^{5}$ manifold. However, nona-coordinated TM complexes like the $\mathrm{ReH}_{9}{ }^{2-}$ anion of Ginsberg ${ }^{49}$ are rare. Unsaturation arises when the full complement of ligands is not attained, which can lead to higher MM
bond orders. This is analogous to the hydrocarbon series $\mathrm{C}_{2} \mathrm{H}_{6}, \mathrm{C}_{2} \mathrm{H}_{4}$ and $\mathrm{C}_{2} \mathrm{H}_{2}$, where the carbon-carbon bond order increases as the number of hydrogen atoms decreases.

Ligands may coordinate to the bimetallic core $\left(\mathrm{M}_{2}\right)^{n+}$ in various ways. Many ligands bind by donating an electron pair to one of the metal centres forming a sigma bond. Metal-ligand pi bonds occur in complexes with hydrocarbon or other ligands having multiple bonds, although the designation "pi or $\pi$-type" is now not often used to describe such metal-ligand binding modes. Pi donor ligands may coordinate to the metal center with varying hapticity. The hapticity $n$ of a ligand as it coordinates to a metal center through $n$ atoms of the ligand is expressed as $\eta^{n}$, e.g., the $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$ ligand coordinates to the metal through all five carbons. Pi acid ligands like CO can receive electron density into their antibonding orbitals through metal $\rightarrow$ ligand backbonding, an effect noted to have MM bond lengthening effects. Terminal ligands coordinate to only one metal center, while bridging ligands (designated by the symbol $\mu)$ coordinate to both metal centers, where coordination may be through the same or different atoms. Semi-bridging ligands (designated by the symbol $s \mu$ ) have significantly different distances between the bridging atom and each of the metal atoms. The presence of bridging ligands can often lead to some ambiguity about the formal bond order for the MM bond and also about the formal oxidation states of the two metal centers.

For a given MM bond order, higher ligand basicity may shorten MM bond lengths by electron donation decreasing electrostatic repulsion between the metal atoms. Ligand basicity depende on the formal charge as well as the electronegativity of the binding ligand atom.

Steric effects are seen in bidentate ligands of the $(\mathrm{X}-\mathrm{C}=\mathrm{Y})$ type which coordinate to the metal centers through the atoms X and Y . The bite angle $\angle[\mathrm{X}-\mathrm{C}-\mathrm{Y}]$, if narrow, tends to decrease the MM bond distance, and vice versa. For some ligands, this angle is flexible so that a fairly wide range of MM bond lengths can be accommodated. Sterically cumbersome substituents in the terphenyl ligands coordinated to a dichromium core maintain the high
(quintuple) bond order and the short $\mathrm{Cr}-\mathrm{Cr}$ bond distance by preventing oligomerization and addition reactions.


a

e

f

j

k

I

m

Figure 2. Various kinds of ligands occurring in bimetallic complexes

Figure 2 depicts some ligands with structures more complex than simple ligands like water, halide or amines. The monanionic bidentate ( $\mathrm{X}-\mathrm{C}=\mathrm{Y}$ ) type (a) coordinates through the X and Y atoms $(\mathrm{X}, \mathrm{Y}=\mathrm{N}, \mathrm{O}, \mathrm{S}$ or C$)$, and include the amidinate (b), guanidinate (c), aminopyridinate (d), carboxamidate (e), carboxylate (f), dithiocarboxylate (g) and alkoxyphenyl (h) ligands. Also shown are the $\alpha$-diimine type (i), the N -heterocyclic carbene (NHC) ligand type exemplified by ( j ) with an imidazole-based ring, the diphosphinoalkane type (k), the terphenyl ligand type (l) present in some complexes with MM bonds of high order, and the $\eta^{\mathrm{n}}$-carbocyclic type typified by the cyclopentadienyl anion (m). The NHC is written as $\operatorname{IR}$ or $\mathrm{IR}_{2}$, where R is the N -substituent group, and as SIR or $\mathrm{SIR}_{2}$ if the heterocycle is saturated, e.g., $\mathrm{I}^{i} \mathrm{Pr}$ or $\mathrm{I}^{i} \mathrm{Pr}_{2}$ (unsaturated case) and $\mathrm{SI}^{i} \mathrm{Pr}$ or $\mathrm{SI}^{i} \mathrm{Pr}_{2}$ (saturated case).

Some kinds of ligand arrays for binuclear complexes with an MM core are schematically depicted in Figure 3. The digonal and tetragonal arrangements with bidentate $(\mathrm{X}-\mathrm{C}=\mathrm{Y})^{-}$type ligands are shown in (a) and (b). The square parallelepiped type (c) is typified by the $\mathrm{Cr}_{2} \mathrm{Me}_{8}^{2-}$ anion. Others are the dimetallocene type (d) and type (e) with bridging bicyclic carbocyclic ligands. The bridged homoleptic carbonyl type (f) and the binuclear carbonyl type (g) with other ligands (here, the $\eta^{5}$-cyclopentadienyl ligand) are also shown. Type (h) is the $\mathrm{L}_{3} \mathrm{M}=\mathrm{ML}_{3}$ type which, however, is not found among the first row 3d-block elements.

a

b


C

d

e

f

g

h

Figure 3. MM-bonded binuclear complexes of various types

### 2.4. Other Effects

The spin state often depends on the bimetallic core configuration rather than on the ligands (usually closed-shell systems). Different spin states for a given isomer can result in different MM bond lengths. Different low-lying spin states close to one another in energy can lead to a spin-state equilibrium with the different spin states having comparable populations. This can result in systems having interesting magnetic properties.

Crystal packing forces may create differences in MM bond distances even among related complexes. These can affect molecular conformations, so that a conformational minimum in the solid state may not be a minimum in the gas phase. ${ }^{50}$ It is conceivable that differences in hydrogen-bonding or ligand bridging patterns among similar binuclear complexes may lead to crystal packing effects which create differences in the metal-metal distances.

### 2.5. Different Influences in Tandem

The net effect of different factors operating in tandem is, of course, difficult to determine on an a priori basis. It may be possible to have a series of complexes where the effects of one given factor are discerned more clearly if the other factors are comparable. For instance, the effects of coordination number may be examined in a series of homoleptic binuclear metal carbonyl complexes with a varying number of ligands, since the ligand and the metal oxidation state are the same for all members of the series. The effects of ligand change upon MM bond length may likewise be seen in paddlewheel complex series $\mathrm{M}_{2}(\mu-\mathrm{L})_{4}$ for a given metal M with different L ligands. Change in the metal itself in a series of isostructural complexes with different metals can lead to observations on how the identity of the metal affects the MM bond length. Finally, the effects of formal MM bond order may be discerned by assigning ranges of metal-metal bond distances associated with a given formal bond order.

## 3. THEORETICAL DESCRIPTIONS OF METAL-METAL BONDS

Together with the experimental results gathered here on MM bond distances, extensive computational results on MM bond lengths are surveyed here. This review does not, however, present detailed or sophisticated understandings on the nature of metal-metal bonding, quite a different topic in fact. A brief overview of the various theories used to study binuclear metal complexes may be in order here, along with general comparisons of the various methods.

### 3.1. Theories of Metal-Metal Bonding

In early years, coordination complexes were treated using crystal field theory and ligand field theory to predict their overall shapes and physical properties. The MM bonds in binuclear complexes have been treated by a variety of theoretical models, among which molecular orbital (MO) theory and density functional theory (DFT) are most prominent. MO methods used range from estended H ckel theory to rigorous ab initio methods treating electron correlation. Since most binuclear complexes are quite large, their study by highly accurate methods is very compute-intensive. DFT reduces computational cost without much sacrifice of accuracy, and has been the most widely used theoretical approach for mono-, bi- and polynuclear metal complexes. The B3LYP and BP86 methods with the DZP basis set have been the most extensively used DFT approaches to date. However, M06-L and still newer functionals (e.g., $\omega \mathrm{B} 97 \mathrm{XD}$ ) have become more prominent in more recent years.

A large body of computational results is availablee on MM and metal-ligand bond lengths, assigned MM bond orders, vibrational spectra, charge distribution and computed bond orders, besides some thermochemical data on complex stability with respect to ligand lability or dissociation of the MM bond. All these theoretical results may be compared with the limited experimental findings, and the effectiveness of the theory assessed.

### 3.2. Metal-Metal Covalent Bonds of Various Orders

With the unit of formal MM bond order defined as one shared electron pair between two metal centers, the number of shared electrons may range from 1 to 12 (the limiting case of the chromium dimer according to some descriptions). This implies MM bond orders from 0.5 to 6. MM bonds may be of the sigma ( $\sigma$ ), pi $(\pi)$ and delta ( $\delta$ ) types, where the degree of overlap and bond strength is most often in the order $\sigma>\pi>\delta$. There is also scope for a shared electron pair to consist of two "half" bonds ( $2 / 2 \pi$ or $2 / 2 \delta$ ), like the bond in triplet dioxygen.

MM bonds in first row metal binuclear complexes are treated as involving metal 3 d or 4 s and 4 p orbital overlap. Metal orbitals are also used for bonding to the ligands. The number of electrons on the metal centers remaining after bonding to ligands and the spin state are considered determines the MM formal bond order. MM bonding competes with metal-ligand bonding, and the synthetic outcome depends on which is favoured. This might be a reduction in the MM bond order with greater scope for metal-ligand bonding, even to the extent that no binuclear complex is formed.

Single $M-M$ bonds are of the $\sigma$ type, nvolving metal $3 d, 4 s$ or 4 p orbitals. Double $M=M$ bonds have a $\sigma$ bond and a $\pi$ bond, the $\pi$ bond sometimes being of the $2 / 2 \pi$ type with two unpaired electrons in the $\mathrm{M}=\mathrm{M}$ bond. Several types of $\mathrm{M} \equiv \mathrm{M}$ triple bonds are possible, including the $\sigma+2 \pi$ type and the $\sigma+\pi+\delta$ type, as well those incorporating "half" bond types. Quadruple MM bonds are commonly of the $\sigma+2 \pi+\delta$ type, along with the "half" bond alternatives. A quintuple MM bond is of the $\sigma+2 \pi+2 \delta$ type. A sextuple bond, as in $\mathrm{Cr}_{2}$ and $\mathrm{W}_{2}$, involves five $d$ electrons and one $s$ electron of each centre, leading to a $2 \sigma+2 \pi+2 \delta$ type of bonding situation.

In the context of paddlewheel complexes, several possibilities can arise. ${ }^{51}$ An M-M single bond has the "electron-rich" configuration $\sigma^{2} \pi_{1}^{2} \pi_{2}^{2} \delta^{2} \delta^{* 2} \pi_{1}{ }^{* 2} \pi_{2}{ }^{* 2}$. An $M=M$ double bond has the configuration $\sigma^{2} \pi_{1}{ }^{2} \pi_{2}{ }^{2} \delta^{2} \delta^{* 2} \pi_{1}{ }^{*} \pi_{2}{ }^{*}$. The two possible configurations for an $\mathrm{M} \equiv \mathrm{M}$ triple
bond are the "electron poor" $\sigma^{2} \pi_{1}{ }^{2} \pi_{2}{ }^{2}$ configuration or the "electron rich" $\sigma^{2} \pi_{1}{ }^{2} \pi_{2}{ }^{2} \delta^{2} \delta^{* 2}$ configuration, depending upon the number of electrons available. Half-integral bonds involve an unpaired electron in the $\delta$ or $\delta^{*}$ orbital (for bond order 3.5), in the $\pi_{1} *$ orbital (for bond order 2.5), in the $\pi_{2}{ }^{*}$ orbital (for bond order 1.5), and in the $\sigma^{*}$ orbital (for bond order 0.5).

The metal-metal quadruple bond, first recognized in the $\mathrm{Re}_{2} \mathrm{Cl}_{8}{ }^{2-}$ anion, ${ }^{4,5}$ consists of a $\sigma$ bond, two mutually perpendicular $\pi$ bonds, and a $\delta$ bond. The $\sigma$ bond, arising from overlap of the $d_{z 2}$ orbitals of the metal atoms, forms the strongest component of the quadruple bond. One $\pi$ bond involves the $d_{x z}$ orbitals, while the other calls for overlap of the $d_{y z}$ orbitals. Overlap between the $\mathrm{d}_{x y}$ orbitals constitutes the $\delta$ bond, the weakest component of the quadruple bond. The electronic configuration is thus $\sigma^{2} \pi_{1}^{2} \pi_{2}^{2} \delta^{2}$. The $\delta$ component affects the conformation of the ligands around the $\mathrm{M}_{2}{ }^{+\mathrm{n}}$ core, and accounts for the eclipsed structure of the anion.

The discovery of quintuple MM bonds in bis(terphenyl) dichromium complexes and many other dichromium complexes (see Section 6) prompted discussion on the nature of five-fold MM bonding. The qualitative picture of the quintuple $\mathrm{Cr}-\mathrm{Cr}$ bond recognizes it as being of the $\sigma+2 \pi+2 \delta$ type, arising from metal 3d orbital overlap. Such a multiple MM bond of high order is promoted by low ligand coordination number and low formal metal oxidation state. In quintuply bonded dichromium complexes, each metal center (oxidation state +1 ) coordinates through a sigma bond to the carbon or nitrogen atom of the ligand. The steric bulk of ligand substituents protects the quintuple bond preventing reactions which reduce the bond order, such as oligomerization, solvation, further ligand coordination, or rearrangement.

### 3.3. DFT Methods for Binuclear Carbonyl Complexes

The computational studies of Schaefer, King, Xie, and co-workers, mostly on bimetallic carbonyl derivatives, using DFT methods, constitute a substantial body of research done over the past 18 years, often on systems yet unknown to experiment and hence of much predictive
value. These studies focused on a large number of series of binuclear complexes with each member of a given stoichiometry yielding various minima, isomers, and spin states. Usually, only minima within $10 \mathrm{kcal} / \mathrm{mol}$ above the global minimum are considered in this review. The energy level of a local minimum above the global minimum ( $\Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$ ) is often mentioned. The MM bond length $R_{M M}$ for each separate structure is given along with the spin multiplicity ( $\mathrm{S}, \mathrm{T}, \mathrm{Q}$, and H for singlet, triplet, quintet and septet, respectively). Each minimum is numbered with regard to its relative energy as $1,2,3$ etc., where 1 refers to the global minimum, and 2,3 , etc. to successively higher energy minima. Thus, for instance, S-1 means a singlet global minimum, while T-3 is the third lowest energy minimum that is a triplet electronic state. Stationary points with one or more imaginary vibrational frequencies are excluded from consideration, except when very small values arise from constraints in numerical computing. The formal bond orders ( fBO ) as derived from electron counting and pertinent remarks (like ligand binding modes) are also presented in the tables. The electronic configuration around the two metal atoms in the bimetallic core is written as $(N, N)$, where $N$ is the number of electrons assigned to each metal center. The favoured $(18,18)$ configuration is most often not mentioned, while other types of configurations like $(17,17)$ or $(16,18)$ are sometimes noted.

DFT methods have proven effective for studying mononuclear transition metal complexes, notably organometallics, ${ }^{52,53,54,55,56,57,58,59,60,61,62,63,64,65}$ at low computational cost. The B3LYP method ${ }^{66,67}$ and the BP86 method ${ }^{68,69}$ have been the variants most frequently used for the study of binuclear metal complexes. The B3LYP method is a hybrid Hartree-Fock approach combining the Becke functional B3 incorporating exact exchange with three calibrated parameters along with the Lee-Yang Parr generalized gradient correlation functional. The BP86 method combines Becke's 1988 functional (B) with Perdew's 1986 gradient corrected correlation functional (P86) and incorporates no exact exchange. In general, the BP86 DFT
method is the one regarded as more reliable in this context, and the results tabulated here mainly arise from computations using this method. The DZP (double zeta plus polarization) basis sets were the most commonly used in the DFT studies reviewed here. In these basis sets various d functions are added to the standard Huzinaga-Dunning contracted DZ set ${ }^{70,71}$ or the Dunning DZ set. ${ }^{72}$ Metal atoms are commonly described by a loosely contracted DZP basis set (the Wachters primitive set ${ }^{73}$ with added p and d functions and suitably contracted. ${ }^{74}$

### 3.4. Assessment of Theoretical Methods

Theories of chemical bonding vary in rigor and degree of success in predicting experimental fndings. The gamut of theoretical methods used to study MM bonds in binuclear complexes ranges from those only qualitatively meaningful to those whose sophistication is high or whose accuracy in predicting MM bond lengths is quite noteworthy. The large size of most binuclear complexes generally precludes their study using rigorous methods with adequate treatment of electron correlation. DFT methods have proved successful in predicting good structures and energies of such systems, along with infrared spectra and magnetic properties. The B3LYP and BP86 DFT methods with the DZP basis set have been widely applied in this context since about 2000. They can often reproduce experimental MM bond lengths to a remarkable degree of accuracy. How far DFT methods can properly describe correlated MM bonds is a moot question. However, the notable success of DFT methods in predicting good geometries and MM bond lengths in a large number of bimetallic complexes leads to a degree of confidence in such approaches.

## 4. TITANIUM-TITANIUM BONDS

Titanium belongs with zirconium and hafnium in the Group 4 transition metals, whose metalmetal bonded chemistry was reviewed by Gade in $2015 .{ }^{75}$ Group 4 metals show scarcely any proclivity for forming homobimetallic complexes, and very few binuclear titanium complexes exhibit any evidence of MM covalent bonding. However, heterobimetallic complexes with metal-metal bonds containing the Group 4 metals are known and have been extensively reviewed. ${ }^{75}$ A neutral titanium atom has the $[\mathrm{Ar}] 3 \mathrm{~d}^{2} 4 \mathrm{~s}^{2}$ configuration, while the $\mathrm{Ti}(\mathrm{I}), \mathrm{Ti}(\mathrm{II})$, and $\mathrm{Ti}(\mathrm{III})$ oxidation states have the $3 \mathrm{~d}^{2} 4 \mathrm{~s}, 3 \mathrm{~d}^{2}$ and $3 \mathrm{~d}^{1}$ configurations, respectively. Titanium in such oxidation states could in principle have the capacity for a $\mathrm{Ti}-\mathrm{Ti}$ metal bond through 3d orbital overlap. For a given formal bond order, any putative $\mathrm{Ti}-\mathrm{Ti}$ bond would be longer than the corresponding MM covalent bonds in any other TM binuclear complex since Ti has the largest covalent radius among all transition metals. The estimated Ti covalent radius ${ }^{41}$ of $1.60 \AA$ suggests a covalent Ti-Ti single bond length around $3.2 \AA$. Most known binuclear $\mathrm{Ti}(\mathrm{III})$ complexes are paramagnetic with $\mathrm{Ti} \cdots \mathrm{Ti}$ distances too long to indicate $\mathrm{Ti}-\mathrm{Ti}$ covalent bonding. This Section deals with the $\mathrm{Ti}_{2}$ dimer, experimentally known dititanium complexes, and the binuclear cyclopentadienyltitanium carbonyls studied by DFT, the results all being given in Table 2.

### 4.1. Titanium Dimer

The dimer $\mathrm{Ti}_{2}\left(\mathbf{0 1}\right.$, Table 2) with a triplet ground state has a $\mathrm{Ti}-\mathrm{Ti}$ bond length (Doverstå ${ }^{76}$ ) of $1.943 \pm 0.001 \AA$ determined by resonant two-photon ionization and a dissociation energy (Morse ${ }^{77}$ ) of 1.349 eV . DFT methods predict a $\left(3 d \sigma_{g}\right)\left(3 d \pi_{u}\right)^{4}\left(3 d \delta_{g}\right)\left(4 s \sigma_{g}{ }^{*}\right)^{2}$ configuration and a triplet ground state ${ }^{3} \Delta_{\mathrm{g}}$ with Ti-Ti bond lengths ranging from 1.861 to $1.950 \AA \AA^{33}$ with the BLYP value of $1.950 \AA$ being the best estimate. Four DFT methods gave Ti-Ti bond lengths from 1.880 to $1.989 \AA .{ }^{34}$ Values from 1.92 to $1.99 \AA$ were obtained ${ }^{28}$ based on the Pauling,

Badger and Guggenheimer empirical formulas. ${ }^{30-32} \mathrm{~A} \mathrm{Ti}=\mathrm{Ti}$ double bond for the titanium dimer is indicated by the electronic configuration. ${ }^{33}$ Experiment and DFT methods lead to similar results, suggesting a rather simple less correlated nature of the MM bonding in $\mathrm{Ti}_{2}$.

### 4.2. Experimentally Known Dititanium Complexes

Amidinate ligands can promote short MM bond distances in paddlewheel type complexes. The complex 02 (Table 2; Figure 4a) with four dicyclohexylformamidinate ligands was prepared by Gambarotta and coworkers ${ }^{78}$ in anticipation of a Ti-Ti covalent bond. However, this diamagnetic complex is not of the paddlewheel type seen in dichromium paddlewheel complexes with two axial ligands, having bridging, not axial, chloride ligands. The Ti-Ti bond length of $2.942 \AA$ (Table 2) suggests a single bond, corroborated by HF/STO-3G results on the model complex $\mathbf{0 3}$ giving a computed bond order value of 0.96 . Ti-Ti bonds of order higher than two are not known experimentally, but have been studied computationally.

Table 2 lists the experimentally known $\left(U_{t k o}{ }^{79}\right.$, Horacek $^{80}$, Cotton ${ }^{81}$ ) binuclear titanium complexes 04, 05 (Figure 4b) and 06 (Figure 4c). Their $R_{M M}$ values range from 2.362 to 2.599 $\AA$, less than that of $\mathbf{0 2}$. Like $\mathbf{0 2}$, complexes $\mathbf{0 4}$ and $\mathbf{0 5}$ have bridging ligands and supported $\mathrm{Ti}-$ Ti interactions. These diamagnetic complexes may involve antiferromagnetic coupling mediated by the bridging ligands. Computational analysis of $\mathbf{0 4},{ }^{79}$ however, showed weak electron localization functional maxima indicative of some degree of direct Ti-Ti bonding, which should, by analogy, as well apply to $\mathbf{0 5}$ with a similar $R_{M M}$ value. For $\mathbf{0 6}$, the bridging cyclooctatetraene ligands may play a role in forcing the Ti centres to approach each other closely, as seen in the $R_{M M}$ value of $2.362 \AA$ suggesting a $\mathrm{Ti}=\mathrm{Ti}$ double bond. ${ }^{80}$ The trinuclear complex 06 has a chloride ligand bridging each of the three $\mathrm{Ti}(\mathrm{II})-\mathrm{Ti}(\mathrm{II})$ bonds, with the $R_{M M}$ value of $2.872 \AA$ on the high side. ${ }^{81}$

Table 2. Ti-Ti Bond Lengths in $\mathrm{Ti}_{2}$, Experimentally Known Complexes and the $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO}){ }_{n}$ Series ${ }^{a}$

| Label Complex | State | $R_{M M}(\AA)$ | fBO | Remarks | References |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Ti2 dimer |  |  |  |  |  |
| $01 \mathrm{Ti}_{2}$ | T | 1.9429 | - | experimental | 76 |
|  | T | 1.950 | 2 | BLYP | 33 |
|  | T | 1.92-1.99 | - | empirical formulae | 28 |
| Experimentally known dititanium complexes |  |  |  |  |  |
| $02[\mathrm{CyNC}(\mathrm{H}) \mathrm{NCy}] 4 \mathrm{Ti}_{2} \mathrm{Cl}_{2} .2 \mathrm{THF}$ | S | 2.942(2) | 1 | XRD; diamagnetic | 78 |
| $03[\mathrm{MeNC}(\mathrm{H}) \mathrm{NCMe}]_{4} \mathrm{Ti}_{2} \mathrm{Cl}_{2}$ | S | - | 1 | HF/STO-3G; eBO $=0.96$ | 678 |
| 04 (THF) $3_{3}(\mu-\mathrm{OMe})_{2}(\mu-\mathrm{Cl}) \mathrm{Ti}(\mathrm{III})_{2} \mathrm{Cl}_{2}$ | S | 2.543(1) | 1 | average in two units | 79 |
| 05 (THF) $\left.3^{( } \mu-\mathrm{OEt}\right)_{2}(\mu-\mathrm{Cl}) \mathrm{Ti}(\mathrm{III})_{2} \mathrm{Cl}_{2}$ | S | 2.599(1) | 1 | cf. 04 | 79 |
| $06\left\{\mu-1,6-\left(\mathrm{SiMe}_{3}\right)_{2}-\mathrm{C}_{8} \mathrm{H}_{6}\right\}_{2} \mathrm{Ti}_{2}$ | S | 2.362(2) | 2 | $\eta^{5}: \eta^{5}$-COT; Ti=Ti bond | 80 |
| $07\left(\mathrm{Me}_{2} \mathrm{PCH}_{2} \mathrm{CH}_{2} \mathrm{PMe}_{2}\right)_{3}(\mu-\mathrm{Cl})_{3} \mathrm{Ti}_{3}$ | S | 2.872(3) | 1 | trinuclear $\mathrm{Ti}(\mathrm{II})$ cluster | 81 |
| Binuclear cyclopentadienyltitanium carbonyls (BP86 results) |  |  |  |  | 82,83 |
| $08 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{8}$ | S-1 | 3.909 | 1 | weak Ti-Ti bond |  |
| $09 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{7}$ | S-1 | 3.734 | 1 | glob. min.; $1 \eta^{2}-\mu-\mathrm{CO}$ |  |
|  | S-2 | 3.378 | 2 | $(18,18) ; \Delta \mathrm{E}=6.3$ |  |
|  | S-3 | 3.667 | 1 | $\Delta \mathrm{E}=7.5 ; 1 \eta^{2}-\mu-\mathrm{CO}$ |  |
| $10 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{6}$ | S-1 | 2.795 | 3 | glob. min.; 2 s $\mu$-CO |  |
|  | S-2 | 2.820 | 3 | $\Delta \mathrm{E}=6.3 ; 2 \mathrm{~s} \mu$-CO |  |
| $11 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{5}$ | S-1 | 2.809 | 3 | glob. min.; $1 \eta^{2}-\mu-\mathrm{CO}$ |  |
|  | S-2 | 3.139 | 1 | $\Delta \mathrm{E}=6.1 ; 2 \eta^{2}-\mu-\mathrm{CO}$ |  |
| $12 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{4}$ | S-1 | 3.219 | 1 | glob. min.; $2 \eta^{2}-\mu$-CO; (1 | (16,16) |
|  | T-2 | 3.108 | 2 | $\Delta \mathrm{E}=2.3 ; 2 \eta^{2}-\mu-\mathrm{CO} ;(17,17)$ | (17) |
|  | S-3 | 3.012 | 1 | $\Delta \mathrm{E}=2.8 ; 2 \eta^{2}-\mu-\mathrm{CO} ;(16,16)$ | (16,16) |
|  | T-4 | 3.046 | 2 | $\Delta \mathrm{E}=4.6 ; 2 \eta^{2}-\mu-\mathrm{CO}$; $(17,17)$ | (17) |
| $13 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{3}$ | S-1 | 3.031 | 1 | glob. min.; $3 \eta^{2}-\mu$-CO; (1 | $(16,16)$ |
| $14 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{2}$ | S-1 | 2.752 | 3 | glob. min.; $2 \eta^{2}-\mu$-CO; (1 | $(16,16)$ |
| $15 \mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})$ | S-1 | 2.364 | 3 | glob. min.; $1 \eta^{2}-\mu-\mathrm{CO}$; (1 | $(14,14)$ |
|  | T-2 | 2.782 | 3 | $\Delta \mathrm{E}=6.3 ; 1 \eta^{2}-\mu-\mathrm{CO} ;(17,17)$ | ,17) |

[^1]

b (05)


d (12, T-2)

e (11, S-1)

f(14)

Figure 4. Some experimentally known ( $\mathbf{a}, \mathbf{b}, \mathbf{c}$ ) and computationally studied (d, e, f) binuclear titanium complexes (labels in brackets refer to Table 2)

### 4.3. Binuclear Titanium Carbonyl Complexes

Table 2 reports BP86 results for the series of binuclear cyclopentadienyltitanium carbonyls $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{n}\left(\mathrm{Cp}=\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5} ; n=8,7,6,5,4,3,2,1\right)$ treated by the BP86 and B3LYP DFT methods, ${ }^{82,83}$ giving MM bond lengths $R_{M M}$ and formal bond order (fBO) values for the various minima located, as well as the values of $\Delta \mathrm{E}$ (energy of a given minimum above the global minimum). The BP86 predictions suggest Ti-Ti bonding possibilities, some of which are multiple. The only low-energy structure found for $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{8}$ has its two $\mathrm{CpTi}(\mathrm{CO})_{4}$ fragments held together by a weak Ti-Ti single bond of length $3.909 \AA$. This $R_{M M}$ value exceeds the Ti-Ti single bond value of $3.20 \AA$ expected from the estimate of $1.60 \AA$ for the Ti covalent radius, so doubt may be cast on the covalent nature of the $\mathrm{Ti} \cdots \mathrm{Ti}$ interaction here. This weak $\mathrm{Ti} \cdots \mathrm{Ti}$ bond is also associated with a low dissociation energy of $9.3 \mathrm{kcal} / \mathrm{mol}$ into two $\mathrm{CpTi}(\mathrm{CO})_{4}$. Single Ti-Ti bond orders are assigned in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{7}$ (minima $\mathrm{S}-1$ and $\mathrm{S}-2$ ), in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{5}$ (minimum $\mathrm{S}-2$ ), in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{4}$ (minima S-1 and $\mathrm{S}-3$ ), and in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{3}$. These $\mathrm{Ti}-\mathrm{Ti}$ single bonds are noticeably shorter ( 3.031 to $3.734 \AA$ ) than that in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{8}$ owing to the presence of four-electron donor $\eta^{2}-\mu-\mathrm{CO}$ groups. The increase in the number of such groups from 1 to 3 results in progressive shortening of the $\mathrm{Ti}-\mathrm{Ti}$ single bond.

The bond shortening effect of $\eta^{2}-\mu$-CO groups is also seen in the shorter lengths of the formal double $\mathrm{Ti}=\mathrm{Ti}$ bonds in the triplet minima of $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{4}$ with two $\eta^{2}-\mu-\mathrm{CO}$ groups (Figure 4 d ) than in minimum S-2 of $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{7}$ (with none). $\mathrm{Ti}=\mathrm{Ti}$ double bond lengths here range from 3.046 to $3.378 \AA$, which are much longer than the $\mathrm{Ti}=\mathrm{Ti}$ double bond length of $1.9429 \AA$ in the titanium dimer. ${ }^{76}$ Formal $\mathrm{Ti}=\mathrm{Ti}$ triple bond lengths ranging from 2.752 to $2.820 \AA$ are seen in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{6}$, in the global minimum S-1 of $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{5}$ (Figure 4e), and in $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{2}$ with two $\eta^{2}-\mu$-CO groups (Figure 4 f ). No low-energy isomer of any of these complexes has a quadruple bond. Apart from the $(18,18)$ configuration around each Ti atom in complexes with $5,6,7$, and 8 CO groups, the $(14,14)$ and $(16,16)$ configurations are
assigned to singlet minima with $1,2,3$, or 4 CO groups. The $(17,17)$ configuration assigned to each Ti atom in the triplet minima is consistent with a $\sigma+2 / 2 \pi$ bonding type (having two "half" $\pi$ bonds) similar to that in the triplet electronic ground state of $\mathrm{O}_{2}$.

### 4.4. Ti-Ti Bond Length Ranges

The few experimentally derived lengths for $\mathrm{Ti}-\mathrm{Ti}$ interactions interpreted as formal single bonds, such as in the non-carbonyl complexes $\mathbf{0 2}, \mathbf{0 4}, \mathbf{0 5}$, and $\mathbf{0 7}$ of Table 2, range from 2.599 to $2.872 \AA$. The $\mathrm{Ti}-\mathrm{Ti}$ single bond lengths in the above DFT studies on binuclear cyclopentadienyltitanium carbonyls range from 3.031 to $3.734 \AA(3.38 \pm 0.35 \AA$ ), which is often longer than the estimate of $3.20 \AA$ from the titanium covalent radius of $1.60 \AA$, and much longer than the experimental $\mathrm{Ti}-\mathrm{Ti}$ single bond lengths of Table 2. The presence of successively zero, 1, 2 and 3 bridging CO ligands results in successive decrease of the $\mathrm{Ti}-\mathrm{Ti}$ bond length. BP86 $\mathrm{Ti}=\mathrm{Ti}$ double bond lengths have the range $3.21 \pm 0.17 \AA$, which is much longer than the experimental $\mathrm{Ti}=\mathrm{Ti}$ double bond length in complex $\mathbf{0 6}$ of Table 2 or the $R_{M M}$ value of $1.942 \AA$ in $\mathrm{Ti}_{2}$. $\mathrm{BP} 86 \mathrm{Ti} \equiv \mathrm{Ti}$ triple bond lengths are found in the range $2.79 \pm 0.03 \AA$. The BP86 method might appear to overestimate Ti-Ti bond lengths, especially for single and double MM bonds. However, it may also be that the $\pi$-acid CO ligands present in the binuclear titanium complexes of these DFT studies impart an MM bond lengthening effect owing to back-bonding of electrons from the metal $3 d$ orbitals into the ligand anti-bonding orbitals. This does not occur with the more basic ligands present in the experimentally characterized non-carbonyl complexes of Table 2. Lastly, a Ti-Ti quadruple bond of length $2.646 \AA$ (BP86 value) was predicted for the triplet ground state of the dititanium analogue $\mathrm{Cp}_{2} \mathrm{Ti}_{2}\left(\mathrm{C}_{8} \mathrm{H}_{8}\right)$ in a series of non-carbonyl binuclear dicyclopentadienyl cyclooctatetraene complexes. ${ }^{84}$ However, such bonds are unknown experimentally in dititanium complexes.

## 5. VANADIUM-VANADIUM BONDS

Vanadium, the first row member of the Group 5 transition elements $(\mathrm{V}, \mathrm{Nb}, \mathrm{Ta})$ has a neutral atom configuration of $[\mathrm{Ar}] 3 \mathrm{~d}^{3} 4 \mathrm{~s}^{2}$. Group 5 complexes have been reviewed by Murillo ${ }^{85}$ and by Ghosh and Roy. ${ }^{86}$ Covalent radius estimates of $1.53 \AA^{41}$ and $1.34 \AA^{24}$ have been made for vanadium. This suggests a $\mathrm{V}-\mathrm{V}$ covalent single bond length of about $3.06 \AA$, considering the $\mathrm{R}_{\text {cov }}$ value of Table 1 , or about $2.68 \AA$ by the $\mathrm{R}_{\mathrm{cv}}(1)$ value. This Section reviews the $\mathrm{V}_{2}$ dimer, some experimentally known divanadium complexes (including the paddlewheel type with bidentate ligands, some carbonyl complexes, complexes with nitrogen and carbocyclic ligands, vanadoboranes, and complexes with chalcogen ligands) as well as two series of binuclear vanadium carbonyl complexes studied by computational methods (DFT).

### 5.1. Vanadium Dimer

The $V_{2}$ dimer (01, Table 3) has a V-V bond length estimated at $1.783 \AA,{ }^{87}$ and also at $1.77 \AA$ with a dissociation energy of $2.753 \pm 0.001 \mathrm{eV} .{ }^{88} \mathrm{~A}$ DFT study ${ }^{33}$ using six functionals predicted a triplet ${ }^{3} \Sigma^{-} \mathrm{g}$ ground state and a $\left(3 d \sigma_{g}\right)^{2}\left(3 d \pi_{u}\right)^{4}\left(3 d \delta_{g}\right)^{2}\left(4 s \sigma_{g}{ }^{*}\right)^{2}$ configuration with V-V bond lengths from 1.707 to $1.786 \AA$, with the BP86 value of $1.773 \AA$ being closest to experiment. Another study using four DFT methods gave V-V bond distances ranging from 1.708 to $1.786 \AA$. $^{34}$ Empirical formulas based on vibrational frequencies gave values from 1.65 to $1.90 \AA$, Error! Bookmark not defined. the Guggenheimer value being the best at $1.76 \AA$. The $\mathrm{V} \equiv \mathrm{V}$ bond here is assigned a bond order of three on the basis of the $\mathrm{V}_{2}$ configuration. ${ }^{33}$ As will be seen later, this $\mathrm{V} \equiv \mathrm{V}$ triple bond is atypical compared to other $\mathrm{V} \equiv \mathrm{V}$ triple bonds, notably those predicted in DFT studies on binuclear vanadium carbonyl complexes.

Table 3. V-V Bond Lengths in $V_{2}$ and Some Experimentally Known Binuclear Vanadium Complexes

| Label Complex | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Vanadium Dimer |  |  |  |
| $01 \mathrm{~V}_{2}$ | $\begin{aligned} & 1.783 \\ & 1.77 \\ & 1.773 \\ & 1.65-1.90 \end{aligned}$ | $\begin{aligned} & 87 \\ & 88 \\ & 33 \\ & 28 \end{aligned}$ | Experimental <br> Experimental BP86 DFT method Empirical formulae |
| With $V_{2}{ }^{+4}$ core $(\mathrm{fBO}=3)$ |  |  |  |
| $02 \mathrm{~V}_{2}(\mathrm{hpp})_{4}$ | 1.932(1) | 89 | Guanidinate type ligand |
| $03 \mathrm{~V}_{2}(\mathrm{ap})_{4} \cdot 2 \mathrm{C}_{6} \mathrm{H}_{6}$ | 1.942(1) | 90 | Aminopyridinate ligand |
| $04 \mathrm{~V}_{2}(\mathrm{TPG})_{4} \cdot 4 \mathrm{C}_{6} \mathrm{H}_{6}$ | 1.952(1) | 91 | Guanidinate type ligand |
| $05 \mathrm{~V}_{2}(\mathrm{DCyF})_{4}$ | 1.968(2) | 91,92 | Formamidinate ligand |
| $06 \mathrm{~V}_{2}(\mathrm{DTolF})_{4} \cdot$ toluene | 1.978(2) | 93 | Tetragonal |
| $07 \mathrm{~V}_{2}(\mathrm{DTolF})_{4}$ | 1.974(4) | 94 | Orthorhombic |
| $08 \mathrm{~V}_{2}\left(\mathrm{D}^{\mathrm{Cl}} \mathrm{PhF}\right)_{4}$ | $\begin{aligned} & 1.974(1) \\ & 1.982(1) \end{aligned}$ | 90 | Formamidinate ligand |
| $09 \mathrm{~V}_{2}(\mathrm{DPhF})_{4}$ | $\begin{aligned} & 1.978(1) \\ & 1.979(1) \end{aligned}$ | 90 | Formamidinate ligand |
| $10 \mathrm{~V}_{2}(\mathrm{DAniF})_{4}$ | 1.988(1) | 90 | Formamidinate ligand |
| $11 \mathrm{~V}_{2}(\mathrm{DMP})_{4}$ | 2.200(2) | 95 | Bioctahedron; $\sigma^{2} \pi^{2} \delta^{2}$ |
| $12 \mathrm{~V}_{2}(\mathrm{TMP})_{4}$ | 2.223(2) | 97 | Bioctahedron; $\sigma^{2} \pi^{2} \delta^{2}$ |

With $\mathrm{V}_{2}{ }^{+3}$ core $(\mathrm{fBO}=3.5)$
$13\left[\mathrm{~K}(\mathrm{THF})_{3}\right]^{+}\left[\mathrm{V}_{2}(\mathrm{DPhF})_{4}\right]^{-}$
1.929(1) 90,98
Paddlewheel; $\sigma^{2} \pi^{4} \delta$
$14\left[\mathrm{~K}(18 \text {-crown-6)(THF) })_{2}\right]\left[\mathrm{V}_{2}(\mathrm{DPhF})_{4}\right]$
1.924(1) 90
Paddlewheel; $\sigma^{2} \pi^{4} \delta$

With $\mathrm{V}_{2}{ }^{+2}$ core

| $\mathbf{1 5}$ | $\mathrm{V}_{2}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{~s} \mu-\mathrm{CO})_{2}(\mathrm{CO})_{3}$ | $2.462(2)$ | 99 | 2 s $\mu-\mathrm{CO} ; \mathrm{fBO}=3$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1 6}$ | $\mathrm{~V}_{2}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{5}$ | $2.459(3)$ | 100 | same as $\mathbf{1 5}$ |
| $\mathbf{1 7}$ | $\mathrm{V}_{2}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{4} \mathrm{PPh}_{3}$ | $2.466(1)$ | 100 | cf. $\mathbf{1 5}$ above; $\mathrm{fBO}=3$ |
| $\mathbf{1 8}$ | $\mathrm{~V}_{2}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}\left(\mathrm{C}_{8} \mathrm{H}_{8}\right)$ | 2.439 | 101 | COT ligand; $\mathrm{fBO}=3$ |
| $\mathbf{1 9}$ | $\mathrm{~V}_{2}(\mathrm{CO})_{8}\left(\mu-\mathrm{PMe}_{2}\right)_{2}$ | 2.733 | 102 | long $\mathrm{V}=\mathrm{V}$ double bond |
| $\mathbf{2 0}$ | $\mathrm{V}_{2}\left(\mathrm{PMePh}_{2}\right)_{4}\left(\mathrm{H}_{2} \mathrm{ZnH}_{2} \mathrm{BH}_{2}\right)_{2}$ | $2.400(2)$ | 103 | short $\mathrm{V}=\mathrm{V}$ double bond |


a (9)

b (11)

c (15)

d (18)

e (20)

Figure 5. Some experimentally known binuclear vanadium complexes (labels in brackets refer to Table 3)

### 5.2. Binuclear Vanadium Complexes with Bidentate and Carbonyl Ligands

Numerous binuclear vanadium complexes have been synthesized. ${ }^{85}$ Experimentally characterized complexes with V-V bonds have the metal in lower oxidation states with the $\left(\mathrm{V}_{2}\right)^{n+}$ core having $n$ values of 4, 3 and 2 . Many known $\mathrm{V}_{2}$ complexes are of the paddlewheel type with a $\mathrm{V}_{2}{ }^{4+}$ or $\mathrm{V}_{2}{ }^{3+}$ core having four bidentate ligands around it. Vanadium probably ranks just after chromium among first row transition metals in its capacity to form multiple metal-metal bonds. Bond orders of 2, 3 and 3.5 have been assigned to V-V bonds in experimentally characterized binuclear vanadium complexes, but quadruple $\mathrm{V}-\mathrm{V}$ bonds are yet to be discovered.

Table 3 shows V-V bond lengths obtained experimentally by X-ray diffraction (XRD) studies for binuclear vanadium complexes with $\mathrm{V}_{2}{ }^{+4}, \mathrm{~V}_{2}{ }^{+3}$ and $\mathrm{V}_{2}{ }^{+2}$ cores. Complexes $\mathbf{0 2}$ to $\mathbf{1 0}$ with $\mathrm{V}_{2}{ }^{+4}$ cores are of the paddlewheel type and diamagnetic, having bidentate ligands with an $\mathrm{N}-\mathrm{C}-\mathrm{N}$ moiety and a bond order of 3 assigned to the $\mathrm{V} \equiv \mathrm{V}$ bonds, taken to be of the $\sigma^{2} \pi^{4}$ type. ${ }^{89,90,91,92,93,94}$ In Figure 5, structure a shows the paddlewheel complex $09 \mathrm{~V}_{2}(\mathrm{DPhF})_{4}$. The $\mathrm{V} \equiv \mathrm{V}$ triple bonds have lengths from 1.968 to $1.988 \AA$ for structures $\mathbf{0 5}$ to $\mathbf{1 0}$ (all with formamidinate ligands). Complexes $\mathbf{0 2}, \mathbf{0 3}$ and $\mathbf{0 4}$ with shorter $R_{M M}$ values ( 1.924 to $1.952 \AA$ ) have aminopyridinate or guanidinate ligands with a relatively small bite angle that promotes shorter MM bonds. These $R_{M M}$ values are noticeably higher than the triple bond length (1.77 or $1.783 \AA$ ) noted above for the vanadium dimer. This may be an effect of the higher metal oxidation states in the complexes as compared with the zero oxidation state in $V_{2}$. Complexes 11 (Figure 5b) and $\mathbf{1 2}$ differ from $\mathbf{0 2}$ to $\mathbf{1 0}$ in having an edge-sharing bioctahedral (not paddlewheel) structure ${ }^{95,96,97}$ and longer V-V bond lengths, owing to the $\sigma^{2} \pi^{2} \delta^{2}$ configuration assigned to the triple bonds in $\mathbf{1 1}$ and 12; the ligands also differ, being of the alkoxyphenyl type with V-C bonds. The weak $\delta$ bond in $\mathbf{1 1}$ and $\mathbf{1 2}$ instead of the $\pi$ bond in $\mathbf{0 2}$ to $\mathbf{1 0}$ may be a factor lengthening the MM bonds in $\mathbf{1 1}$ and $\mathbf{1 2}$ compared to those in $\mathbf{0 2}$ to $\mathbf{1 0}$.

Reduction of $\mathbf{0 9}$ leads to $\mathbf{1 3}$ with a $\mathrm{V}_{2}{ }^{+3}$ core, an $R_{M M}$ value of $1.929 \AA$, and a V-V bond order of $3.5 .{ }^{90,98}$ Complex $\mathbf{1 4}$ resembles $\mathbf{1 3}$ with its $\mathrm{V}_{2}{ }^{+3}$ core, an $R_{M M}$ value of $1.924 \AA$, and a bond order of 3.5. The decrease of $\sim 0.05 \AA$ in V-V bond length upon reduction of 09 to 13 goes along with an increase in bond order from 3.0 to 3.5 and a decrease in oxidation state of the $V_{2}$ core, where $\mathbf{1 3}$ and $\mathbf{1 4}$ are paramagnetic. Complexes $\mathbf{0 2}$ to $\mathbf{1 0}$ along with $\mathbf{1 3}$ and $\mathbf{1 4}$ have $R_{M M}$ values below $2.0 \AA$, like the supershort quadruple $\mathrm{Cr}-\mathrm{Cr}$ bonds of sub-section 6.3. These have very small formal shortness ratio (FSR) values of 0.631 to 0.650 , using the rather high estimate of $3.06 \AA$ for a V-V single bond length based on the $\mathrm{R}_{\text {cov }}$ value in Table 1.

Complexes $\mathbf{1 5}$ to $\mathbf{2 0}$ (Table 3) have reduced $\mathrm{V}_{2}{ }^{+2}$ cores with each vanadium atom in the +1 formal oxidation state. Two structural studies (Cotton ${ }^{99}$, Huffman ${ }^{100}$ ) of dicyclopentadienylpentacarbonyldivanadium (Figure 5d) gave $\mathrm{V} \equiv \mathrm{V}$ bond lengths around 2.46 $\AA$ close to that in the $\mathrm{PPh}_{3}$ derivative $17 .{ }^{100}$ The cyclooctatetraene derivative 18 (Figure 5d) with a tub-shaped COT ligand has an $R_{M M}$ value (Elschenbroich ${ }^{101}$ ) of $2.439 \AA$. These $\mathrm{V} \equiv \mathrm{V}$ bonds may be assigned a bond order of three, where $\mathbf{1 5}$ to $\mathbf{1 7}$ have two semibridging carbonyl ligands. The $\mathrm{V}=\mathrm{V}$ bonds in 19 and in 20 (Figure 5e) are described as formal double bonds
 triple bonds in $\mathbf{1 5}$ to $\mathbf{1 8}$ are longer than the $\mathrm{V}=\mathrm{V}$ double bond in $\mathbf{2 0}$, and much longer than the $\mathrm{V} \equiv \mathrm{V}$ triple bonds in $\mathrm{V}_{2}$ and the paddlewheel complexes 02 to $\mathbf{1 2}$. Metal $\rightarrow$ carbonyl backbonding effects in $\mathbf{1 5}$ to $\mathbf{1 7}$ and the COT ligand conformation in $\mathbf{1 8}$ may increase MM bond lengths. The long $\mathrm{V}=\mathrm{V}$ double bond in $\mathbf{1 9}$ may be a consequence of the large number of CO ligands with their metal-metal bond lengthening effects.

### 5.3. Binuclear Vanadium Complexes with Nitrogen and Carbocyclic Ligands

Table 4 lists V-V bond lengths for binuclear vanadium complexes with nitrogen ligands, including ligands of the $\left(\mathrm{NR}_{2}\right)^{-}$amido type, the NR imido type and the $(\mu-\mathrm{N})$ nitrido type. In general, V-V bond orders are not given here, although oxidation states of the vanadium centers are often mentioned in the literature. Complexes 01 (Figure 5c) to 03 have $\left(\mathrm{V}_{2}\right)^{4+}$ cores with $R_{M M}$ values ranging from 2.399 to $2.563 \AA$ (Berno and Gambarotta ${ }^{104}$, Howard and coworkers ${ }^{105}$, Haddad et al. ${ }^{106}$ ) while structure $\mathbf{0 4}$ has a short V-V distance of $2.324 \AA$ (Buijink ${ }^{107}$ ). The cluster 05 has a cubane-like centre with four vanadium atoms, each pair separated by $2.674 \AA$ (Abernethy ${ }^{108}$ ), while structure $\mathbf{0 6}$ has a bridging azide ligand and an $R_{M M}$ value of $2.563 \AA .{ }^{106} \mathbf{0 7}$ to $\mathbf{0 9}$ have amido ligands (Gambarotta ${ }^{109,110,111}$ ) and $R_{M M}$ values ranging from 2.640 to $2.857 \AA$ ), which are longer than those in this list with imido or nitrido
ligands. Complex 10 is of interest for the short V-V single bond length of $2.460 \AA$ and a $\left(\mathrm{V}_{2}\right)^{8+}$ core (Ruiz et al. ${ }^{112}$ ). This high oxidation state of +4 is also present in $\mathbf{1 1}$ with a similar $R_{M M}$ value of $2.467 \AA$ (Preuss et al. ${ }^{113}$ ).

Table 4. Experimental V-V Distances in Binuclear Vanadium Complexes with Nitrogen Ligands (Amido, Imido and Nitride) and with Carbocyclic Ligands

Label Complex
----------------------------

| $\mathbf{0 1}\left[\mathrm{V}_{2}(\mu-\mathrm{H})_{3}\left(\mathrm{PMe}_{3}\right)_{6}\right]^{+}\left[\mathrm{V}_{2}(\mu-\mathrm{N})_{2}\left(\mathrm{SiMe}_{3}\right)_{4}\right]^{-}$ | $2.399(1)$ | 104 | $\left(\mathrm{~V}_{2}\right)^{4+}$ core in cation |
| :--- | :--- | :--- | :--- |
| $\mathbf{0 2}[\mathrm{CpV}(\mu-\mathrm{N}-\mathrm{p}-\mathrm{tolyl})(\mu-\mathrm{Me})]_{2}$ | $2.5095(6)$ | 105 | $\left(\mathrm{~V}_{2}\right)^{4+}$ core; imido ligand |
| $\mathbf{0 3}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{~V}_{2}(\mu-\mathrm{N})_{2} \mathrm{Cl}_{2}$ | $2.561(2)$ | 106 | $\left(\mathrm{~V}_{2}\right)^{4+}$ core; nitrido ligand |
| $\mathbf{0 4} \mathrm{V}_{2}\left\{\mu-\left(2,6-\mathrm{Me}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}\right\}_{2}(\mu-\mathrm{Me}) \mathrm{Cp}_{2}$ | $2.324(1)$ | 107 | imido ligand |
| $\mathbf{0 5}\left[\mathrm{Cp} * \mathrm{~V}\left(\mu_{3}-\mathrm{N}\right)\right]_{4}$ cluster | $2.674(8)$ | 108 | cubane-like cluster |
| $\mathbf{0 6}\left[\mathrm{Cp} * \mathrm{~V}(\mu-\mathrm{N})\left(\mathrm{N}_{3}\right)\right]_{2}$ | $2.5633(14)$ | 106 | azide ligand |
| $\mathbf{0 7} \mathrm{V}_{2}\left(\mathrm{Cy}_{2} \mathrm{~N}\right)_{2}\left(\mu^{3}, \eta^{1}-\mathrm{O}\right)\left(\mu^{2}, \eta^{1}: \eta^{1}-\mathrm{CMe}\right]$ | $2.640(2)$ | 109 | amido ligand |
| $\mathbf{0 8}\left[\left\{\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~N}\right\} \mathrm{V}\right\}_{2}(\mu-\mathrm{S})_{2}$ | $2.857(1)$ | 110 | amido ligand |
| $\mathbf{0 9} \mathrm{V}_{2}\left\{\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~N}\right\}_{2}\left(\mu-\mathrm{Me}_{3} \mathrm{SiN}^{2} . \mathrm{SiMe}_{2} . \mathrm{CH}_{2}\right)_{2}$ | $2.736(2)$ | 111 | amido ligand; $\left(\mathrm{V}_{2}\right)^{6+}$ core |
| $\mathbf{1 0}\left[\mathrm{V}\left\{\eta^{2}-\mathrm{C}\left(\mathrm{Mes}^{2}\right)=\mathrm{NBu}_{3}^{\mathrm{t}}\right\}_{3}\right]$ reduced form | $2.460(1)$ | 112 | $\mathrm{~V}-\mathrm{V}$ single bond; $\left(\mathrm{V}_{2}\right)^{8+}$ core |
| $\mathbf{1 1}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{~V}_{2}\left(\mu-\eta^{1}-\mathrm{Te}_{2}\right)\left(\mu-\mathrm{N}^{\mathrm{t}} \mathrm{Bu}_{2}\right.$ | $2.4665(8)$ | 113 | $\left(\mathrm{~V}_{2}\right)^{8+}$ core; imido ligand |

With carbocyclic ligands

| $\mathbf{1 2}\left[\left(\eta^{6}-\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}\right) \mathrm{V}(\mathrm{CO})_{2}\right]_{2}$ | $2.388(2)$ | 114 | $\left(\mathrm{~V}_{2}\right)^{0}$ core; $\mathrm{fBO}=3$ |
| :--- | :--- | :--- | :--- |
| $\mathbf{1 3} \mathrm{~V}_{2}\left(\mathrm{C}_{5} \mathrm{Me}_{4} \mathrm{R}\right)_{2}(\mu-\mathrm{Br})_{4}$ | $2.565(1)$ | 115 | $\left(\mathrm{~V}_{2}\right)^{6+}$ core |
| $\mathbf{1 4} \mathrm{V}_{2}(\mathrm{thf})_{2}(\text { salophen })_{2}{ }^{a}$ | $2.406(3)$ | 116 | $\left(\mathrm{~V}_{2}\right)^{6+}$ core; $\mathrm{V}=\mathrm{V}$ bond |
| $\mathbf{1 5}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{4} \mathrm{Et}\right)_{2} \mathrm{~V}_{2}\left(\mu, \eta^{6}: \eta^{6}-\mathrm{P}_{6}\right)$ | $2.627(2)$ | 117 | triple decker sandwich |
| $\mathbf{1 6}\left(\eta^{6}-\mathrm{C}_{6} \mathrm{H}_{6}\right)(\mathrm{CpVH})_{2}$ | $2.425(1)$ | 118 | $\left(\mathrm{~V}_{2}\right)^{4+} ;$ bridging $\mathrm{C}_{6} \mathrm{H}_{6}$ and H |
| $\mathbf{1 7}\left(\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{~V}_{2}$ | $2.1689(5)$ | 119 | $\left(\mathrm{~V}_{2}\right)^{4+} ;$ pentalene; $\mathrm{fBO}=3$ |
| $\mathbf{1 8}(\mathrm{CpV})_{2}\left(\mu-\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{H}_{6}\right)$ | 2.538 | 120 | $\left(\mathrm{~V}_{2}\right)^{4+} ;$ two $\mathrm{Cp} ; \mathrm{fBO}=3$ |
| $\mathbf{1 9}\left(\mu-\eta^{5}, \eta^{6}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{~V}_{2}$ | 2.351 | 121 | $\left(\mathrm{~V}_{2}\right)^{2+} ;$ indenyl ligand |

[^2]Binuclear vanadium complexes with carbocyclic ligands are also included in Table 4 (apart from those given in Table 3). Churchill and coworkers ${ }^{114}$ have shown that complex $\mathbf{1 2}$ with a $\left(\mathrm{V}_{2}\right)^{0}$ core has a $\mathrm{V} \equiv \mathrm{V}$ triple bond length of $2.388 \AA$. Complexes $\mathbf{1 3}$ and $\mathbf{1 4}$ with $\left(\mathrm{V}_{2}\right)^{6+}$ cores have rather short $R_{M M}$ values of 2.565 and $2.406 \AA$ respectively. The latter value is consistent with the assigned $\mathrm{V}=\mathrm{V}$ double bond. ${ }^{115,116}$ Complex $\mathbf{1 5}$ is a triple decker sandwich complex with a central $\mathrm{P}_{6}$ ring, in which the V-V distance of $2.602 \AA$ (Scherer ${ }^{117}$ ) may allow for some metal-metal interaction. Complex 16 with a $\eta^{6}$-benzene ligand has an $R_{M M}$ value of $2.425 \AA$ (Jonas and coworkers ${ }^{118}$ ) not far from those in the Cp complexes $\mathbf{1 5}$ to $\mathbf{1 7}$ of Table 3. Complex 17 is the vanadium analogue in a series (Ashley et al. ${ }^{119}$ ) of binuclear dipentalene complexes $\left(\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{M}_{2}(\mathrm{M}=\mathrm{V}, \mathrm{Cr}, \mathrm{Mn}, \mathrm{Co}, \mathrm{Ni})$ in which the very short MM bond of 2.169 $\AA$ (formal shortness ratio $\mathrm{FSR}=0.71$ ) in the $\left(\mathrm{V}_{2}\right)^{4+}$ core is given a formal bond order $(\mathrm{fBO})$ of 3 (of the $\sigma+\pi+\delta$ type). This is confirmed by the computed bond order (cBO) value of 2.83. Complex 18 has one pentalene ligand with two Cp ligands (Jones and $\mathrm{O}^{\prime} \mathrm{Hare}^{120}$ ), giving a longer $R_{M M}$ value of $2.538 \AA$ owing to the distance between the two Cp ligands, but the same fBO of 3 . The MM bond in complex 19 with an indenyl ligand (length $2.351 \AA$, Jonas ${ }^{121}$ ) is also assigned an fBO value of 3 .

### 5.4. Divanadaboranes and Complexes with Chalcogen Ligands

Table 5 presents $R_{M M}$ values for some vanadaborane complexes and for some divanadium complexes with chalcogen ligands ( $\mathrm{S}, \mathrm{Se}$ and Te ). Dimetallaboranes with vanadium and Group 5 metals are limited in number, and only five divanadaboranes are mentioned here. In complexes 01 to 05 , the boron centres of the borane ligands bridge the two metal atoms, where the V-V distances of 2.759 to $2.859 \AA$ (Bose et al. ${ }^{122}$, Roy et al. ${ }^{123}$ ) are consistent with single bonds.

Table 5. Experimental V-V Distances in Divanadoboranes and Binuclear Vanadium Complexes with Chalcogen-Based Ligands

| Label Complex | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Divanadoboranes |  |  |  |
| $01\left[(\mathrm{CpV})_{2}\left(\mathrm{~B}_{2} \mathrm{H}_{6}\right)_{2}\right]$ | 2.787(2) | 122 | V(III)-V(III) bond |
| $02\left[(\mathrm{CpV})_{2} \mathrm{~B}_{5} \mathrm{H}_{11}\right]$ | 2.7604(10) | 123 | $\mathrm{V}-\mathrm{V}$ single bond |
| $03\left[(\mathrm{CpV})_{2} \mathrm{~B}_{3} \mathrm{H}_{8}\left(\mu_{3}-\mathrm{OEt}\right)\right]$ | $2.7589(10)$ | 123 | edge-fused cluster |
| $04\left[(\mathrm{CpV})_{2}\left(\mathrm{BH}_{3} \mathrm{~S}\right)_{2}\right]$ | 2.777(2) | 123 | $\mathrm{V}-\mathrm{V}$ single bond |
| $05 \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mu-\mathrm{TePh})_{2}\left(\mu_{3}-\mathrm{Te}\right) \mathrm{BH} . \mathrm{THF}$ | 2.8587(9) | 123 | divanadatelluraborane |
| With chalcogen ligands |  |  |  |
| $06\left[\mathrm{Cp}^{*} \mathrm{~V}(\mathrm{CO})_{2}(\mu-\mathrm{SPh})\right]_{2}$ | 3.07 | 124 | CO ligands; long V...V |
| $07\left[\mathrm{Cp}^{*} \mathrm{~V}(\mathrm{CO})_{2}(\mu-\mathrm{TePh})\right]_{2}$ | 3.29 | 124 | CO ligands; long V...V |
| $08\left[\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{5} \mathrm{~V}_{5} \mathrm{~S}_{6}\right]\left[(\mathrm{TCNQ})_{2}\right]^{a}$ | 3.110 | 125 | long V...V distance |
| $09\{\mathrm{CpV}(\mu-\mathrm{SePh})\}_{2}(\mu-\mathrm{Se})$ | 2.74 | 129 | bridging selenide |
| $10(\mathrm{CpV})_{2} \mathrm{~S}_{4}\left(\mu-\eta^{1}-\mathrm{S}_{2}\right)$ | 2.665 | 130 | V-V single bond |
| $11\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{2} \mathrm{~V}_{2} \mathrm{~S}_{5}$ | 2.658(1) | 126 | substd. Cp |
| $12\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4}{ }^{i} \mathrm{Pr}\right)_{2} \mathrm{~V}_{2} \mathrm{~S}_{4}$ | 2.610(1) | 128 | substd. Cp |
| $13\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{2} \mathrm{~V}_{2} \mathrm{~S}_{2}\left\{\mathrm{~S}_{2} \mathrm{C}_{2}\left(\mathrm{CF}_{3}\right)_{2}\right\}$ | 2.574 | 128 | substd. Cp |
| $14\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{2} \mathrm{~V}_{2} \mathrm{~S}_{3} \mathrm{Fe}(\mathrm{CO})_{3}$ | 2.510 | 126 | substd. Cp |
| $15\left(\mathrm{CH}_{3} \mathrm{CS}_{2}\right)_{4} \mathrm{~V}_{2} \mathrm{~S}_{4}$ | 2.800 | 131 | dithioacetate ligand |
| $16\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{4} \mathrm{~V}_{4} \mathrm{~S}_{4}$ | 2.873 | 132 | cubane structure |
| $17\left[\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{4} \mathrm{~V}_{4} \mathrm{~S}_{4}\right]^{+}\left[\mathrm{BF}_{4}\right]^{-}$ | 2.854 | 132 | cation moiety |
| $18\left({ }^{\mathrm{B}} \mathrm{Bu}_{2} \mathrm{NCS}_{2}\right)_{4} \mathrm{~V}_{2}\left(\mathrm{~S}_{2}\right)_{2}$ | 2.851 | 133 | V(IV)-V(IV) bond |
| $19\left(\mathrm{~V}_{2} \mathrm{~S}_{4}\right)^{4+}$ moiety | 2.852 | 134 | $\mathrm{PV}_{2} \mathrm{~S}_{10}$ cluster |
| $20\left[\mathrm{~V}_{2}\left(\mathrm{Se}_{2}\right)_{2}\right]^{4+}$ moiety of cluster | $2.779(5)$ | 135 | ( $\left.\mathrm{V}_{2} \mathrm{Se}_{13}\right)^{-}$cluster |
| $21\left[\mathrm{~V}_{2} \mathrm{O}_{2}(\mu-\mathrm{S})_{2}(\mathrm{EtNCS})_{2}\right]^{2-}$ | 2.78-2.81 | 136 | various cations |
| $22\left[\mathrm{~V}_{2} \mathrm{O}_{2}(\mathrm{Se})\left(\mathrm{Se}_{4}\right)_{2}\right]^{2-}$ | 2.90-2.96 | 137 | various cations |
| $23\left[\mathrm{~V}_{2} \mathrm{O}_{2}(\mu-\mathrm{Se})_{2}(\mathrm{Se})_{2}\left(\mathrm{Se}_{4}\right)_{2}\right]^{2-}$ | 2.958(7) | 137 | polyselenide |
| $24\left[\mathrm{~V}_{2}(\mathrm{O})(\mathrm{S})_{4}(\mathrm{edt})\right]^{3-}$ | 2.977(1) | 138 | ethanedithiolato ligand |

[^3]Complexes with chalcogenide ligands include divanadium and polyvanadium clusters as well as oxovanadium complexes having monochalcogen and dichalcogen ligands. Structures 06, 07 and 08 (Herberhold et al. ${ }^{124}$, Bolinger et al. ${ }^{125}$ ) have long V-V distances (3.11 to 3.29 $\AA$ ) which may not indicate metal-metal covalent interactions. Complexes 09 to $\mathbf{1 4}$ have significantly shorter $R_{M M}$ values of 2.510 to $2.74 \AA$, which are more typical of V-V covalent bonds (Bolinger et al..$^{126}$, Rheingold ${ }^{127,128}$, Bose et al. ${ }^{129,130}$ ). Complexes $\mathbf{1 5}$ to $\mathbf{1 9}$ present longer V-V separations of about $2.80 \AA,{ }^{111,132,133,134}$ while structure 20 with a $\mathrm{V}_{2} \mathrm{Se}_{4}$ moiety has an $R_{M M}$ value of $2.779 \AA$ close to this range (Ibers ${ }^{135}$ ). The complex anions 21 to 24 reflect the affinity of vanadium for oxygen and exhibit long $R_{M M}$ values from 2.78 to $2.977 \AA$ (Zhu et al. ${ }^{136}$, Kanatzidis ${ }^{137}$, Christou ${ }^{138}$ ). Rather long V-V distances seem characteristic of this group of binuclear and cluster chalcogenide complexes (apart from 09 to 14), suggesting weak V-V single bonds or no covalent bonds at all.

### 5.5. Computational Studies on V-V Bonded Complexes

The scope for multiple V-V bonds in three divanadium complexes was examined using ab initio theory. ${ }^{139}$ These Hartree-Fock-Roothaan studies on singlet ground state $\mathrm{V}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4}$ with a fixed $\mathrm{V}-\mathrm{V}$ bond distance of $2.20 \AA$ led to the conclusion that the $\mathrm{V} \equiv \mathrm{V}$ bond is triple with a $\sigma^{2} \pi^{4}$ configuration, as in the complexes $\mathbf{0 2}$ to $\mathbf{1 0}$ of Table 3. Studies using the FenskeHall approximation to HF theory ${ }^{140}$ predicted a V-V bond length between 2.0 and $2.1 \AA$, which is not very different from the 1.9 to $2.0 \AA$ range found experimentally for the paddlewheel complexes $\mathbf{0 2}$ to $\mathbf{1 0}$ (Table 3). This study, however, suggested that divanadium tetracarboxylates might not be viable synthetic targets unlike their $\mathrm{N}-\mathrm{C}=\mathrm{N}$ type ligand analogues. The Fenske-Hall method predicted the V-V bond in $\mathrm{V}_{2}(\mathrm{DMP})_{4}$ to have a $\sigma^{2} \pi^{2} \delta^{2}$ configuration instead of $\sigma^{2} \pi^{4}$ consistent with its edge-shared bioctahedral structure (cf. 11 and 12 of Table 3). On modelling complex 18 of Table 3 by replacing the substituted phosphine n41
ligands by $\mathrm{PH}_{3}$, the Fenske-Hall studies concluded that making the P-V-P moiety linear would increase the V-V bond order from double to quadruple but the resulting structure is not competitive energetically.

An SCF/CI study on the cyclooctatetraene complex $(\mathrm{CpV})_{2}\left(\mathrm{C}_{8} \mathrm{H}_{8}\right)$ (Figure 5 d ; $\mathbf{1 8}$ of Table 3) predicted a $\mathrm{V}-\mathrm{V}$ single bond, ${ }^{141}$ the other d electrons being involved in vanadium-ligand bonding. Inclusion of nondynamic correlation, ${ }^{142}$ however, yielded a $\mathrm{V} \equiv \mathrm{V}$ triple bond involving the six 3 d electrons, with a delocalized $\pi$ component and also weak $\sigma / \delta$ and $\pi$ components pointing to antiferromagnetic coupling. A similar picture was predicted for the related butanediyl divanadium(III) complex $(\mathrm{CpV})_{2}\left(\mathrm{C}_{4} \mathrm{H}_{8}\right)_{2}$ by SCF/CI studies and inclusion of a multireference SDCI expansion, ${ }^{143}$ where the antiferromagnetic coupling involves four localized 3d electrons leading to a $\mathrm{V}=\mathrm{V}$ double bond.

A series of DFT studies on binuclear vanadium carbonyl complexes focused on homoleptic as well as Cp-substituted cases. Table 6 presents BP86 values of V-V bond lengths for minima of the $\mathrm{V}_{2}(\mathrm{CO})_{n}$ series $(n=12,11,10,9,8)^{144,145,146}$ and of the binuclear cyclopentadienylvanadium carbonyl complexes $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{n}(n=7,6,5,4,3,2,1),{ }^{147,148}$ indicating the fBO associated with each structure along with its $\Delta \mathrm{E}$, the energy of a minimum above the global minimum. The series $\mathrm{V}_{2}(\mathrm{CO})_{n}$ has a formally neutral $\mathrm{V}_{2}$ core with both metal atoms in the zero formal oxidation state, while the $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{\mathrm{n}}$ series has a $\left(\mathrm{V}_{2}\right)^{+2}$ core with each vanadium atom in the formal +1 oxidation state. Table 6 also describes the type of CO group ( $\mu-\mathrm{CO}, \mathrm{s} \mu-\mathrm{CO}$ or $\eta^{2}-\mu-\mathrm{CO}$ ) and often the configuration around the two metal atoms, e.g., the $(17,17)$ configuration associated often with binuclear triplet state structures. The ranges shown by the $\mathrm{V}-\mathrm{V}$ bond lengths of different orders (single, double and triple) are discussed in the next sub-section.

Table 6. DFT-derived V-V Bond Lengths in Binuclear Vanadium Carbonyl Complexes ${ }^{a}$

| Label Complex | State $R_{M M}(\AA)$ fBO Remarks |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Homoleptic divanadium carbonyls (BP86 results; Refs. 144-146) |  |  |  |  |
| $01(\mathrm{CO})_{6} \mathrm{~V}_{2}(\mathrm{CO})_{6}$ | S-1 | 3.334 | 1 | no $\mu$-CO |
| $02(\mathrm{CO})_{5} \mathrm{~V}(\mu-\mathrm{CO}) \mathrm{V}(\mathrm{CO})_{5}$ | S-1 | 3.376 | 1 | $1 \mu$-CO |
| $03(\mathrm{CO})_{3}(\mathrm{~s} \mu-\mathrm{CO})_{3} \mathrm{~V}_{2}(\mathrm{CO})_{4}$ | S-1 | 2.510 | 3 | $1 \mathrm{~s} \mu-\mathrm{CO}$ |
| $04(\mathrm{CO})_{4}(\mathrm{~s} \mu-\mathrm{CO})_{2} \mathrm{~V}_{2}(\mathrm{CO})_{3}$ | T-1 | 2.482 | 3 | glob min.; $(17,17)$ |
| $(\mathrm{CO})_{2}(\mathrm{~s} \mu-\mathrm{CO})_{3} \mathrm{~V}_{2}(\mathrm{CO})_{4}$ | S-2 | 2.486 | 3 | $\Delta \mathrm{E}=1.5 ;(18,16)$ |
| $(\mathrm{CO})_{3}(\mathrm{~s} \mu-\mathrm{CO})_{3} \mathrm{~V}_{2}(\mathrm{CO})_{3}$ | S-3 | 2.447 | 3 | $\Delta \mathrm{E}=1.7$; $(18,16)$ |
| $(\mathrm{CO})_{3}(\mathrm{~s} \mu-\mathrm{CO})_{2} \mathrm{~V}_{2}(\mathrm{~s} \mu-\mathrm{CO})(\mathrm{CO})_{3}$ | T-4 | 2.418 | 3 | $\Delta \mathrm{E}=2.8$ ( 17,17 ) |
| $(\mathrm{CO})_{3}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{2}(\mu-\mathrm{CO}) \mathrm{V}_{2}(\mathrm{CO})_{3}$ | S-5 | 2.981 | 1 | $\Delta \mathrm{E}=3.8$; $(16,16)$ |
| $(\mathrm{CO})_{4} \mathrm{~V}(\mu-\mathrm{CO})_{2} \mathrm{~V}(\mathrm{CO})_{3}$ | S-6 | 2.478 | 3 | $\Delta \mathrm{E}=5.6$ |
| $(\mathrm{CO})_{4}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{V}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{3}$ | T-7 | 2.841 | 1 | $\Delta \mathrm{E}=7.1 ;(17,17)$ |
| $05 \mathrm{~V}_{2}(\mathrm{CO})_{8}$ | S-1 | 2.858 | 1 | $(16,16)$ |

Cyclopentadienyl divanadium carbonyls (BP86 results; Refs.147,148)
$06 \mathrm{Cp}(\mathrm{CO})_{3}(\mu-\mathrm{CO}) \mathrm{V}_{2}(\mathrm{CO})_{3} \mathrm{Cp} \quad \mathrm{S}-1 \quad 3.306 \quad 1 \quad$ unstable w.r.t. dissociation
$07\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{~V}_{2}(\mathrm{CO})_{6}$
$08 \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{5}$
$09 \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{4}$
$10 \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{3}$
$11 \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{2}$
$12 \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})$
S-1 $2.847 \quad 2 \quad 2 \mu$-CO; $(18,18)$
T-2 $2.936 \quad 1 \quad 2 \mathrm{~s} \mu-\mathrm{CO} ;(17,17)$
S-3 $3.150 \quad 1 \quad 1 \eta^{2}-\mu$-CO; $(18,18)$
S-1 $2.452 \quad 3 \quad$ cf. expt. data (Refs. 99, 100)
S-2 $2.5293 \Delta \mathrm{E}=5.5$
T-1 $2.444 \quad 3 \quad 2 \mathrm{~s} \mu-\mathrm{CO} ;(17,17)$
S-2 $2.547 \quad 3 \quad \Delta \mathrm{E}=1.2 ; 1 \mathrm{~s} \mu-\mathrm{CO} ; 1 \eta^{2}-\mu-\mathrm{CO}$
T-1 $2.532 \quad 3 \quad 2 \mathrm{~s} \mu$-CO; $(17,17) ; 1 \eta^{2}-\mu-\mathrm{CO}$
S-2 $2.5593 \quad \Delta \mathrm{E}=9.8 ; 1 \mu-\mathrm{CO} ; 2 \eta^{2}-\mu-\mathrm{CO}$
S-3 $2.480 \quad 3 \quad \Delta \mathrm{E}=9.9 ; 2 \mathrm{~s} \mu-\mathrm{CO} ; 1 \eta^{2}-\mu-\mathrm{CO}$
S-1 $2.414 \quad 3 \quad$ glob $\min ; 2 \eta^{2}-\mu$-CO ligands
S-2 $2.423 \quad 3 \quad \Delta \mathrm{E}=0.6 ; 2 \eta^{2}-\mu-\mathrm{CO}$
T-3 $2.584 \quad 3 \quad \Delta \mathrm{E}=2.5 ; 2 \eta^{2}-\mu-\mathrm{CO}$
T-4 $2.605 \quad 3 \quad \Delta \mathrm{E}=2.9 ; 2 \eta^{2}-\mu-\mathrm{CO}$
S-5 $2.631 \quad 3 \quad \Delta \mathrm{E}=6.1 ; 2 \eta^{2}-\mu-\mathrm{CO}$
Q-1 $2.528 \quad 3$ glob min; $\eta^{2}-\mu$-CO
T-2 $2.4003 \quad \Delta \mathrm{E}=2.5 ; \eta^{2}-\mu-\mathrm{CO}$

[^4]
### 5.6. V-V Bond Length Ranges

For the experimentally characterized complexes of Tables 3, 4 and 5, the V-V bond lengths span wide ranges for any given formal bond order. Beginning with formal $\mathrm{V} \equiv \mathrm{V}$ triple bonds, the naked $\mathrm{V}_{2}$ dimer represents the shortest known V-V separation ( $1.77 \AA$ ). This is a unique case of a very short $\mathrm{V} \equiv \mathrm{V}$ triple bond, which is even shorter than the $\sigma^{2} \pi^{4} \mathrm{~V} \equiv \mathrm{~V}$ triple bonds of paddlewheel complexes $\mathbf{0 2}$ to $\mathbf{1 0}$ of Table 3 ranging from 1.93 to $1.98 \AA$. Structures $\mathbf{0 2}$ to $\mathbf{1 0}$ may have longer $\mathrm{M} \equiv \mathrm{M}$ triple bonds owing to their V (II) oxidation state contrasted with the $\mathrm{V}(0)$ oxidation state in $\mathrm{V}_{2}$. The $\mathrm{V}-\mathrm{V}$ bonds of order 3.5 in complexes $\mathbf{1 3}$ and $\mathbf{1 4}$ are shorter at 1.92 to $1.93 \AA$, while the $\mathrm{V} \equiv \mathrm{V}$ triple bonds of the $\sigma^{2} \pi^{2} \delta^{2}$ type in $\mathbf{1 1}$ and $\mathbf{1 2}$ are longer at 2.20 to $2.22 \AA$. Complexes $\mathbf{1 5}$ to $\mathbf{1 8}$ of Table 3 along with $\mathbf{1 2}, \mathbf{1 7}$ and $\mathbf{1 8}$ of Table 4 have $\mathrm{V} \equiv \mathrm{V}$ triple bonds ranging from 2.169 to $2.538 \AA(2.35 \pm 0.19 \AA)$. There the variations arise from effects of the CO, cyclooctatetraene, and pentalene ligands as well as of the vanadium formal oxidation state $(0,+1$ and +2$)$. These experimental $\mathrm{V} \equiv \mathrm{V}$ triple bond lengths may be compared with the $\mathrm{V} \equiv \mathrm{V}$ triple bond lengths predicted by DFT on two series of binuclear vanadium carbonyl complexes, as discussed below.

For $\mathrm{V}=\mathrm{V}$ double bond lengths, the non-carbonyl complexes $\mathbf{2 0}$ (Table 3) and $\mathbf{1 4}$ (Table 4) have $R_{M M}$ values around $2.40 \AA$, while the carbonyl complex 19 (Table 3) shows a longer $\mathrm{V}=\mathrm{V}$ bond length of $2.733 \AA$, which may be a lengthening effect from CO back-bonding.

The V-V single bond estimate of $3.06 \AA$ (based on the $\mathrm{R}_{\text {cov }}$ value in Table 1) seems on the high side, and the other estimate of $2.68 \AA$ based on $\mathrm{R}_{\mathrm{cv}}(1)$ is in better agreement with many of the longer V-V bond distances in Table 4. The $R_{M M}$ values of structures $\mathbf{0 5}$ to $\mathbf{1 0}$ and $\mathbf{1 5}$ (Table 4) approach this estimate, and may be consistent with $\mathrm{V}-\mathrm{V}$ single bonds in the absence of more definitive information. The short V-V single bond length of $2.460 \AA$ in $\mathbf{1 0}$ may be linked to the small metal ion size in the high V(IV) oxidation state present.

The V-V bonds in the vanadaboranes of Table 5 may be considered as formal single bonds consistent with the assignments for $\mathbf{0 1}, \mathbf{0 2}$, and $\mathbf{0 4}$. These $\mathrm{V}-\mathrm{V}$ bonds span the range from 2.759 to $2.787 \AA$, which is not too far from the V-V single bond estimate of $2.68 \AA$. Apart from $\mathbf{0 6}$ to $\mathbf{0 8}$ and $\mathbf{2 2}$ to $\mathbf{2 4}$ with long $\mathrm{V} \cdots \mathrm{V}$ interactions, most of the remaining complexes in Table 5 have $R_{M M}$ values from 2.610 to $2.873 \AA$ consistent with single bonds. Including structure $\mathbf{1 0}$ of Table 4 gives a range of $2.667 \pm 0.206 \AA$ for experimental V-V single bond lengths for the complexes of Tables 4 and 5.

The computational DFT results seen in Table 6 yield estimates of single, double and triple V-V bond length ranges. V-V bonds described as single have lengths ranging from 2.841 to $3.376 \AA$ in $\mathrm{V}_{2}(\mathrm{CO})_{12}, \mathrm{~V}_{2}(\mathrm{CO})_{11}$, isomers $\mathrm{S}-5$ and $\mathrm{T}-7$ of $\mathrm{V}_{2}(\mathrm{CO})_{9}$, in $\mathrm{V}_{2}(\mathrm{CO})_{8}$, in $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{7}$ and in isomers T-2 and S-3 of $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{6}$. Complexes $\mathrm{V}_{2}(\mathrm{CO})_{12}, \mathrm{~V}_{2}(\mathrm{CO})_{11}$ and $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{7}$ have $R_{M M}$ values much longer than the estimate of about $3.06 \AA$ for a V-V single bond, which may not indicate MM covalent bonds proper, especially for the unstable $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{7}$. The single bond $R_{M M}$ value of $2.858 \AA$ for $\mathrm{V}_{2}(\mathrm{CO})_{8}$ is more consistent with a V-V single bond length, although somewhat longer than the estimate of $2.68 \AA$ for a V-V single bond length based on $\mathrm{R}_{\mathrm{cv}}(1)$. This may be an effect of $\mathrm{V} \rightarrow \mathrm{CO}$ back-bonding.

Triple bond orders are assigned to shorter $\mathrm{V} \equiv \mathrm{V}$ bond distances ( 2.418 to $2.631 \AA$ ) in the two binuclear vanadium carbonyl series (Table 6). This DFT-derived range is consistent with the $\mathrm{V} \equiv \mathrm{V}$ triple bond lengths of structures $\mathbf{1 5}$ to $\mathbf{1 7}$ of Table 3, although somewhat longer than the $\mathrm{V} \equiv \mathrm{V}$ triple bond length for $\mathbf{1 2}$ in Table 4 . The $\mathrm{V} \equiv \mathrm{V}$ triple bond distance of $2.452 \AA$ predicted here for $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{5}$ (the global minimum S-1) by the BP86 DFT method is very close to the Huffman experimental bond length of $2.459 \AA$ in this complex. ${ }^{100}$ The $\mathrm{V} \equiv \mathrm{V}$ triple bond lengths predicted for these carbonyl complexes with a neutral $\mathrm{V}_{2}$ or a $\mathrm{V}_{2}{ }^{+2}$ core are markedly longer than the experimental V-V triple bond lengths for the paddlewheel complexes of Table 3 with $\left(\mathrm{V}_{2}\right)^{+4}$ cores. The strong electron-donating capacity of the
bidentate ligands in the complexes of Table 3 may contribute towards reducing the effective charge of the $\left(\mathrm{V}_{2}\right)^{4+}$ core, while metal-to-ligand back-bonding in the carbonyl complexes may increase positive charge on the core. There is also a difference in oxidation states of the metal centres, being 0 for the homoleptic carbonyl complexes, +2 for the paddlewheel complexes, and +1 for the carbonyl complexes with Cp ligands.

Experiment fails to yield any examples of species containing a V-V formal quadruple bond, unlike the tetragonal dichromium paddlewheel complexes associated with $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds. Computationally, a V-V quadruple bond was seen in a high energy isomer of $\mathrm{V}_{2}(\mathrm{CO})_{9}$ and in a singlet minimum noted for $\mathrm{Cp}_{2} \mathrm{~V}_{2}\left(\mathrm{C}_{8} \mathrm{H}_{8}\right)$ which gave a BP 86 value of $2.333 \AA$ for the V-V quadruple bond. ${ }^{84}$ Furthermore, unsaturated bimetallic complexes with carbonyl groups do not favour quadruple metal-metal bonds. The need for quadruple V-V bonds in these species to give each vanadium atom the favored 18 -electron configuration is obviated by the presence of four-electron donor CO groups, or simply by leaving "holes" in the ligand array around the metal atoms for the highly unsaturated cases.

In summary, higher vanadium oxidation states in the binuclear $\mathrm{V}_{2}$ core are seen to promote shorter distances for V-V bonds of a given order. The presence of carbonyl ligands has the opposite effect of lengthening V-V bond distances owing to $\mathrm{M} \rightarrow \mathrm{CO}$ back-bonding. In addition, there is also the unexamined possibility of three-centre two-electron bonds for the carbonyl complexes with bridging CO ligands similar to those in $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ and $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ (see Sections 8 and 9).

## 6. CHROMIUM-CHROMIUM BONDS

Chromium is the first-row transition metal most thoroughly studied so far with respect to binuclear complexes and MM bonding. Much experimental and theoretical or computational work has been carried out on complexes with $\mathrm{Cr}-\mathrm{Cr}$ bonds, mostly multiple bonds. Atomic chromium has the $[\mathrm{Ar}] 3 \mathrm{~d}^{5} 4 \mathrm{~s}^{1}$ configuration and, like the other group 6 metals molybdenum and tungsten, has a marked capacity for MM multiple bonds in its binuclear complexes. Thus $\mathrm{Cr}-\mathrm{Cr}$ bond orders of three, four and five are encountered in the laboratory. The covalent radius of chromium ( $\mathrm{R}_{\text {cov }}$ estimated at $\left.1.39 \AA\right)^{41}$ gives a length of about $2.78 \AA$ for a covalent chromium-chromium single bond. Another covalent radius estimate of $1.22 \AA\left[\mathrm{R}_{\mathrm{cv}}(1)\right.$ of Table 1$]^{24}$ seems short in the face of the many multiply-bonded dichromium complexes with $R_{M M}$ values greater than $2.44 \AA$.

Binuclear chromium complexes with multiple bonds have been amply reviewed by Cotton, ${ }^{149}$ chiefly with regard to tetragonal paddlewheel complexes. A review by Chisholm and Patmore deals with more recent developments. ${ }^{150}$ The chemistry of metal-metal multiplybonded compounds actually dates back to 1844 , long before any understanding of chemical bonding whatsoever, when Peligot reported the synthesis of a hydrated chromium carboxylate complex, now believed to have been $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CCH}_{3}\right)_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ containing a $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond. ${ }^{6}$ The dark red color of this binuclear chromium(II) acetate is striking in view of the light blue aqueous $\mathrm{Cr}(\mathrm{II})$ solution from which it is precipitated by addition of acetate. Further work, notably by Herzog and Kalies, ${ }^{151,152,153,154,155,156}$ led to the synthesis of more dichromium tetracarboxylate complexes, later recognized as having $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds. The scope of binuclear complexes with $\mathrm{Cr}-\mathrm{Cr}$ multiple bonds studied experimentally or computationally now extends beyond the dichromium tetracarboxylates to include other paddlewheel complexes with various bidentate ligands of the ( $\mathrm{X}-\mathrm{C}=\mathrm{Y}$ ) type. Tetragonal paddlewheel complexes with four bidentate ligands often have very short $\mathrm{Cr}-\mathrm{Cr}$ bond lengths,
incorporating the alkoxyphenyl, 2-oxopyridinate, carboxamidate, amidinate and guanidinate ligand types, and all are recognized as having $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds.

Much more recently the chemistry of species containing formal $\mathrm{Cr}-\mathrm{Cr}$ quintuple bonds has received considerable attention. Thus, following the original discovery of the $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond in a bis(terphenyl) dichromium derivative, numerous quintuply bonded dichromium complexes with ever-decreasing $\mathrm{Cr}-\mathrm{Cr}$ bond lengths were characterized. $\mathrm{Cr}-\mathrm{Cr}$ bond distances span a very wide range from about 1.71 to about $2.60 \AA$ within the general assignment of formal quadruple or quintuple bond orders. The limit in short $\mathrm{Cr}-\mathrm{Cr}$ bond lengths is seen in the diatomic $\mathrm{Cr}_{2}$ molecule, with a $\mathrm{Cr}-\mathrm{Cr}$ bond length of $1.679 \AA$ and an assigned formal bond order of six. This Section reviews chromium-chromium bond lengths in a variety of systems, including the chromium dimer, tetragonal dichromium paddlewheel complexes, quintuply bonded dichromium complexes, and binuclear chromium carbonyl complexes (homoleptic and with other ligands), drawing from experimental and computational results.

### 6.1. Chromium Dimer

The chromium dimer $\mathrm{Cr}_{2}$ is probably the most intensively studied transition metal dimer, presenting a challenge to theoreticians and computational chemists. Table 7 shows estimates of the MM distance in $\mathrm{Cr}_{2}$. The experimental $\mathrm{Cr}-\mathrm{Cr}$ bond length (Bondybey and English ${ }^{157}$, Moore ${ }^{158}$ ) of $1.679 \AA$, as determined by laser-induced fluorescence spectroscopy, is the shortest metal-metal contact known so far among transition metals. Estimates of the $\mathrm{Cr}-\mathrm{Cr}$ bond order range from sextuple to possibly no covalent bond at all (Politzer ${ }^{159}$ ). Assignment of a sextuple bond order to $\mathrm{Cr}_{2}$ arises out of the $\left(3 d \sigma_{g}\right)^{2}\left(3 d \pi_{u}\right)^{4}\left(3 d \delta_{g}\right)^{4}\left(4 s \sigma_{g}\right)^{2}$ configuration associated with the ${ }^{1} \Sigma^{+}$g ground state. ${ }^{160}$ However, the six-fold nature of this MM bond has been questioned (Goodgame and Goddard ${ }^{161}$ ) owing to the rather low dissociation energy of
$1.53 \pm 0.06 \mathrm{eV}$ (Simard and coworkers ${ }^{162}$ ), with a second-law estimate of $1.44 \pm 0.05 \mathrm{eV}$ (Hilpert and Ruthardt ${ }^{163}$ ). One minimum proposed for $\mathrm{Cr}_{2}$ has the 3d orbitals antiferromagnetically coupled, ${ }^{164,165,166}$ calling for broken symmetry calculations when using hybrid and many non-hybrid DFT methods to obviate an unbound situation. ${ }^{167}$

Table 7. Chromium-Chromium Bond Length in the Chromium Dimer $\mathbf{C r}_{2}$

| Method | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Experiment | 1.6788 | 157,158 | Laser fluorescence spectroscopy |
| DFT BLYP | 1.647 | 33 | Best DFT estimate |
| CASPT2 | 1.713 | 34 | Closest to experiment in this study |
| Empirical formulae | 1.74-1.81 | 28 | Pauling, Badger \& Guggenheimer formulae |

Six DFT methods predicted Cr-Cr distances in $\mathrm{Cr}_{2}$ from 1.605 to $1.647 \AA$, all shorter than the experimental value, the BLYP value being the closest (Table 7). ${ }^{33}$ Another study using four DFT methods yielded values from 1.562 to $1.632 \AA$, while the CASPT2 value of 1.713 $\AA \AA$ is also fairly close to the experimental value. ${ }^{34}$ The empirical formulas of Pauling, Badger and Guggenheimer yielded values from 1.74 to $1.81 \AA$, the Pauling value being the most realistic, ${ }^{28}$ though still on the high side. Roos summarized some computational findings on the $\mathrm{Cr}_{2}$ dimer while reporting his CASPT2 results. He describes the difficulties in treating this system where multireference character is predominant. ${ }^{168}$

### 6.2 Quadruply-Bonded Dichromium Tetracarboxylates

Dichromium paddlewheel complexes involve an array of four bidentate ligands coordinated to a $\mathrm{Cr}(\mathrm{II})-\mathrm{Cr}(\mathrm{II})$ or $\left(\mathrm{Cr}_{2}\right)^{4+}$ core. Such ligands include the carboxylate, alkoxyphenyl, 2oxopyridinate, carboxamidate and formamidate ligands shown in Figure 2. Figure 6 depicts general structures of tetragonal dichromium complexes, namely the bare and the axially
dicoordinated dichromium tetracarboxylates (a) and (b), and complexes without axial ligands like dichromium tetraformamidinate (c), dichromium tetracarboxamidate (d), dichromium tetra(alkoxyphenyl) (e) and dichromium tetra(2-oxopyridinate) (f). Dichromium tetragonal complexes are associated with $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds of the type $\sigma+2 \pi+\delta$, analogous to the quadruple bond in the $\mathrm{Re}_{2} \mathrm{Cl}_{8}{ }^{2-}$ anion, as briefly described in Section 2. However, this anion, along with other Group 7 quadruply MM-bonded systems, has a square parallelepiped structure and not the paddlewheel structure treated here and in sub-section 6.3.

a

b
e



c

d

f

Figure 6. Experimentally known dichromium paddlewheel complex types

Dichromium tetracarboxylates are often unstable in air and in solution, requiring an inert atmosphere for their preparation and study. Over 40 such complexes had their structures elucidated between 1970 to 2005, yielding a wide range of $\mathrm{Cr}-\mathrm{Cr}$ bond lengths ranging from about 1.9 to $2.5 \AA$ (Cotton, Chisolm and coworkers) presented in Table 8. ${ }^{169,170,171,172,173,}$ 174,175,176,177,178,179,180,181,182,183,184 They may display weak paramagnetism, owing to a small population of the triplet excited state. Many of these structures have axial ligands $\mathbf{L}$ and the general formula $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4} \mathrm{~L}_{2}$, with $\mathrm{Cr}-\mathrm{Cr}$ bond lengths ranging from 2.2 to $2.5 \AA$. The absence of axial ligands gives the bare $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ complexes which have markedly shorter $\mathrm{Cr}-\mathrm{Cr}$ bonds of lengths around $1.97 \AA\left(\right.$ Koktar and Fink $^{185}$, Cotton $\left.{ }^{175}\right)$.

Table 8 lists $\mathrm{Cr}-\mathrm{Cr}$ bond lengths and metal-axial ligand bond lengths $\mathrm{Cr}-\mathrm{L}$ for the tetracarboxylate complexes $\mathbf{0 1}$ to $\mathbf{4 3} .{ }^{149}$ Most such complexes have axial ligands L, while those that do not are either bare molecules $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ or exist in infinite chains with the carboxylate O -atoms of one molecule coordinated to the metal center of another. Column $\mathbf{R}$ refers to the $\mathbf{R}$ group in the carboxylate ligand $\mathbf{R}-\mathrm{COO}^{-}$, while column $\mathbf{L}$ refers to the axial ligands. $\mathrm{Cr}-\mathrm{Cr}$ bond lengths range from $2.176 \AA$ (complex 32) to $2.541 \AA$ (complex 15). The Cr-L bonds involve a wide variety of ligands with lengths from 2.210 to $2.736 \AA$, excluding cases with arene ligands where Cr-L distances are much longer (complexes 31, 32 and 33).

Effects of $\mathbf{R}$ group in the carboxylate ligand. The tetraformate complexes $\mathbf{0 1}$ to $\mathbf{0 5}(\mathbf{R}=\mathrm{H})$ have $\mathrm{Cr}-\mathrm{Cr}$ bond lengths ranging from 2.360 to $2.443 \AA$, while those in the tetraacetate complexes $\mathbf{0 6}$ to $\mathbf{1 3}(\mathbf{R}=\mathrm{Me})$ range from 2.295 to $2.411 \AA$. The $\mathrm{Cr}-\mathrm{Cr}$ bond length ranges in the tetrapivalate complexes $\mathbf{2 1}$ to $\mathbf{2 4}\left(\mathbf{R}=\mathrm{CMe}_{3}\right)$ and in the tetra(triphenylacetate) complexes 29 to $\mathbf{3 3}\left(\mathbf{R}=\mathrm{CPh}_{3}\right)$ are, respectively, 2.327 to $2.379 \AA$ and 2.176 to $2.383 \AA$. The trend here is that a greater electron-donating capacity of the $\mathbf{R}$ group in the carboxylate ligands tends to shorter $R_{M M}$ values in the order $\mathrm{H}>\mathrm{Me}>\mathrm{CMe}_{3}>\mathrm{CPh}_{3}$.

Table 8. Cr-Cr and Cr-L Bond Lengths in Dichromium Tetracarboxylates

| Label R group |  | Ligand (L) | $R_{M M}(\AA)$ | $R_{M L}(\AA)$ | References |
| :---: | :---: | :---: | :---: | :---: | :---: |
| A. $\mathrm{Cr}_{2}(\mathrm{OOCR}) \mathrm{L}_{2}$ |  |  |  |  |  |
| 01 | H | $\mathrm{H}_{2} \mathrm{O}^{\text {a }}$ | $\begin{aligned} & 2.373(2) \\ & 2.360(2) \end{aligned}$ | $\begin{aligned} & 2.268(4) \\ & 2.210(6) \end{aligned}$ | 169 |
| 02 | H | py | 2.408(1) | 2.308(3) | 170 |
| 03 | H | $\mathrm{HCO}_{2}{ }^{-}$ | 2.451(1) | 2.224(2) | 170 |
| 04 | H | 4-NMe 2 -py | 2.443 (1) | 2.270(4) | 171 |
| 05 | H | 4-CN-py | 2.385(3) | 2.34(1) | 171 |
| 06 | $\mathrm{CH}_{3}$ | $\mathrm{CH}_{3} \mathrm{COOH}$ | 2.300 (1) | 2.306(3) | 172 |
| 07 | $\mathrm{CH}_{3}$ | $\mathrm{H}_{2} \mathrm{O}$ | $2.362(1)$ | 2.272(3) | 173 |
| 08 | $\mathrm{CH}_{3}$ | piperidine | 2.342(2) | 2.338(7) | 172 |
| 09 | $\mathrm{CH}_{3}$ | pyridine | 2.369(2) | $2.335(5)$ | 174 |
| 10 | $\mathrm{CH}_{3}$ | (pyrazine) $2 / 2{ }^{\text {b }}$ | 2.295(5) | $2.314(10)$ | 174 |
| 11 | $\mathrm{CH}_{3}$ | 4-CN-py | $2.315(2)$ | 2.327(4) | 171 |
| 12 | $\mathrm{CH}_{3}$ | 4-NMe 2 -py | 2.411(1) | 2.279(4) | 171 |
| 13 | $\mathrm{CH}_{3}$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 2.389(2) | 3.326(2) | 175 |
| 14 | TIPP ${ }^{\text {c }}$ | $\mathrm{CH}_{3} \mathrm{CN}$ | 2.395(1) | 2.326(6) | 175 |
| 15 | $\mathrm{CF}_{3}$ | $\mathrm{Et}_{2} \mathrm{O}$ | 2.541(1) | 2.244(3) | 170 |
| 16 | Ph | PhCOOH | 2.352(3) | 2.295(7) | 170 |
| 17 | 2-phenyl-Ph | THF | 2.316 (3) | 2.275(6) | 176 |
| 18 | 9-anthracenyl | $\left(\mathrm{MeOCH}_{2} \mathrm{CH}_{2} \mathrm{OMe}\right)_{2 / 2}$ | 2.283(2) | 2.283(5) | 170 |
| 19 | $\mathrm{O}^{d}$ | $\mathrm{H}_{2} \mathrm{O}$ | 2.214(1) | $2.300(3)$ | 172 |
| 20 | $\mathrm{OCMe}_{3}$ | THF | 2.367(3) | 2.268(7) | 177 |
| 21 | $\mathrm{CMe}_{3}$ | pyridine | 2.359(3) | 2.325(8) | 171 |
| 22 | $\mathrm{CMe}_{3}$ | 4- $\mathrm{NH}_{2}$-py | 2.379(1) | 2.282(2) | 171 |
| 23 | $\mathrm{CMe}_{3}$ | $4-\mathrm{CN}-\mathrm{py}$ | $2.335(1)$ | 2.334(2) | 171 |
| 24 | $\mathrm{CMe}_{3}$ | 2-CN-py | 2.327(1) | 2.388(4) | 171 |
| 25 | $\mathrm{NEt}_{2}$ | $\mathrm{Et}_{2} \mathrm{NH}$ | 2.384(2) | 2.452(8) | 178 |
| 26 | $\mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}$ | Cl | 2.524(1) | 2.581(1) | 179 |
| 27 | $\mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}$ | Br | 2.513(1) | 2.736(1) | 179 |
|  |  | n52 |  |  |  |


| 28 | $\mathrm{C}_{2} \mathrm{H}_{5}$ | NCS | 2.467(3) | 2.249(3) | 180 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 29 | $\mathrm{CPh}_{3}$ | $\mathrm{Et}_{2} \mathrm{O}$ | 2.303(4) | 2.30(1) | 181 |
| 30 | $\mathrm{CPh}_{3}$ | ${ }^{1 / 2}$ pyridine | 2.383(4) | 2.31(4) | 181 |
| 31 | $\mathrm{CPh}_{3}$ | $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2 / 2}$ | 2.256(4) | $3.299(2)^{e}$ | 181 |
| 32 | $\mathrm{CPh}_{3}$ | $\left(1,4-\mathrm{F}_{2} \mathrm{C}_{6} \mathrm{H}_{4}\right)_{2 / 2}$ | 2.176 (3) | $3.388(2)^{e}$ | 181 |
| 33 | $\mathrm{CPh}_{3}$ | $\left(1,4-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{4}\right)_{2 / 2}$ | 2.291(3) | $3.310(2)^{e}$ | 181 |
| 34 | $\mathrm{CClH}_{2} / \mathrm{CH}_{3}$ | pyridine | 2.367(2) | $2.366(6)$ | 171 |
| 35 | $\mathrm{CClH}_{2}$ | 4-CN-py | 2.408(4) | 2.23(2) | 171 |
| 36 | $\mathrm{CF}_{2} \mathrm{H}$ | 4-NMe ${ }_{2}$-py | 2.500 (1) | 2.246 (9) | 171 |
| 37 | $\mathrm{CF}_{2} \mathrm{H}$ | 4-CMe ${ }_{3}$-py | 2.514(1) | 2.299(9) | 171 |
| 38 | $\mathrm{CpFe}(\mathrm{CO})_{2}$ | $2 \mathrm{CpFe}(\mathrm{CO})_{2} \mathrm{CH}_{2} \mathrm{COOH}$ | $2.307(1)$ | 2.246(2) | 182 |
| B. $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ chains |  |  |  |  |  |
| 39 | $\mathrm{CH}_{3}$ | - | 2.288(2) | 2.327(4) | 183 |
| 40 | $\mathrm{CMe}_{3}$ | - | 2.388(4) | 2.44(1) | 184 |
| 41 | 2-Ph-C6 $\mathrm{H}_{4}$ | - | 2.348(2) | $2.309(5)$ | 176 |
| C. Bare $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ molecules |  |  |  |  |  |
| 42 | $\mathrm{CH}_{3}$ | - | 1.966(14) | - | 185 |
| 43 | TIPP ${ }^{\text {c }}$ | - | 1.9662(5) | - | 175 |

[^5]Complexes 01, 07 and 19 are also comparable, having, respectively, the formate, acetate and carbonate ligands with $\mathrm{H}_{2} \mathrm{O}$ as the common axial $\mathbf{L}$ ligand. Increasing the electronrichness of the $\mathbf{R}$ groups ( $\mathrm{H}, \mathrm{CH}_{3}$ and O ) gives the order $\mathrm{HCOO}^{-}>\mathrm{CH}_{3} \mathrm{COO}^{-}>\mathrm{CO}_{3}^{2-}$ for the $R_{M M}$ distances with respect to the ligand. In contrast, the electron-poor $\mathrm{CF}_{3}$ group in the ligands of $\mathbf{1 5}$ leads to the longest $\mathrm{Cr}-\mathrm{Cr}$ bond length ( $2.541 \AA$ ) in this list. This is consistent with the long Cr-Cr bonds in 26, 27, 36 and $\mathbf{3 7}$ ( 2.500 to $2.524 \AA$ ), all with electron-poor $\mathbf{R}$ groups. Structure $\mathbf{1 5}$ may be compared with the analogous $\mathbf{2 9}$ having $\mathbf{R}=\mathrm{CPh}_{3}$ (both with $\mathbf{L}$ $=\mathrm{Et}_{2} \mathrm{O}$ ), where the electron-rich ligand in 29 gives a shorter $\mathrm{Cr}-\mathrm{Cr}$ bond length ( $2.303 \AA$ ).

Complexes 04, 12, $\mathbf{2 2}$ and 36, all having $\mathbf{L}=4-\mathrm{NMe}_{2}$-py, give $R_{M M}$ values in the order $\mathrm{CF}_{2} \mathrm{H}$ $>\mathrm{H}>\mathrm{CH}_{3}>\mathrm{CMe}_{3}$, consistent with the electron-donating capacity of $\mathbf{R}$. Complexes $\mathbf{0 5}, \mathbf{2 3}$ and $\mathbf{3 5}$ all having $\mathbf{L}=4$-CN-py give the order $\mathrm{CF}_{2} \mathrm{H}>\mathrm{H}>\mathrm{CMe}_{3}$ for their $R_{M M}$ values as expected from the electronic properties of the $\mathbf{R}$ group (though $\mathbf{1 1}$ with $\mathbf{R}=\mathrm{Me}$ is anomalous here). Likewise, $\mathbf{0 2}, \mathbf{0 9}$ and $\mathbf{2 1}$ with $\mathbf{L}=$ pyridine have the order $\mathrm{H}>\mathrm{Me}>\mathrm{CMe}_{3}$ for their $R_{M M}$ values. Comparison of $\mathbf{1 3}$ with $\mathbf{1 4}$ and $\mathbf{1 7}$ with $\mathbf{2 0}$ also reflects such trends.

Effects of axial ligands. In general, electron-rich axial ligands $\mathbf{L}$ lead to shorter Cr-L bond lengths, in turn leading to longer $\mathrm{Cr}-\mathrm{Cr}$ bond distances. This arises from ligand back-bonding into the dimetal antibonding orbitals such as those of the $\sigma^{*}$ type. Complexes 01, 02, 03, 04 and $\mathbf{0 5}$ (all with $\mathbf{R}=\mathrm{H}$ ) exhibit the order of $R_{M M}$ values with respect to $\mathbf{L}$ as $\mathrm{HCO}_{2}^{-}>4$ -$\mathrm{NMe}_{2}-$ py $>$ py $>4-\mathrm{CN}-$ py $>\mathrm{H}_{2} \mathrm{O}$ in accord with the relative electron-donating capacities of these $\mathbf{L}$ ligands. Complexes $\mathbf{0 6}$ to $\mathbf{0 9}$ and $\mathbf{1 1}$ to $\mathbf{1 3}$ (all with $\mathbf{R}=\mathrm{CH}_{3}$ ) give this order as 4- $\mathrm{NH}_{2}$-py $>\mathrm{CH}_{3} \mathrm{CN}>$ py $>\mathrm{H}_{2} \mathrm{O}>$ piperidine $>4-\mathrm{CN}-$ py $>\mathrm{CH}_{3} \mathrm{COOH}$, in accord with the availability of coordinating electron pairs in these ligands. Complexes 21, 22, 23 and $\mathbf{2 4}$ with $\mathbf{R}=\mathrm{CMe}_{3}$ exhibit the order for their $R_{M M}$ values as $4-\mathrm{NH}_{2}$-py $>$ py $>4-\mathrm{CN}-\mathrm{py}>2-\mathrm{CN}-\mathrm{py}$, consistent with such expectations. Pi complexation of arene ligands to the $\mathrm{Cr}_{2}$ unit leads to shortening of the $\mathrm{Cr}-\mathrm{Cr}$ bonds, as seen in 31, $\mathbf{3 2}$ and $\mathbf{3 3}$ as compared with structures $\mathbf{2 9}$ and 30 (all with $\mathbf{R}=\mathrm{CPh}_{3}$ ).
$\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ chain complexes. $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ systems have a very strong tendency to acquire two axial ligands. Thus syntheses of dichromium tetracarboxylates in coordinating solvents result in solvation at the two chromium centers. Structural data are available for the
 although other such complexes have been reported without structure determination. These complexes display an infinite chain structure, with the oxygen atoms of one molecule coordinated to the metal center of another, which means axial coordination does occur, but
from one molecule in the chain to the next. The unsolvated chain complexes $\mathbf{3 9}$ and 40 have Cr-Cr bond lengths of 2.288 and $2.388 \AA$, respectively. Use of $\mathbf{R}=2$-phenylphenyl with crystallization from toluene yielded complex 41 as a dimer having axial positions on the $\mathrm{Cr}_{2}$ units occupied by oxygen atoms, and giving a $\mathrm{Cr}-\mathrm{Cr}$ bond length of $2.348 \AA$. The $\mathrm{Cr}-\mathrm{Cr}$ bond length of $2.316 \AA$ in complex $\mathbf{1 7}$ with two axial THF ligands attached may be compared with that of structure 41. Using $\mathbf{R}=\mathrm{CPh}_{3}$ with crystallization from benzene led to $\mathbf{3 1}$ having an infinite chain arrangement with an $R_{M M}$ value of $2.256 \AA$. Though the $\mathrm{Cr}-\mathrm{Cr}$ bond lengths in structures 39, 40, 41 and 31 are on the short side, they do not truly represent the total absence of axial coordination.

Bare $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ complexes. The difficulties in arriving at viable syntheses and structural analyses of bare $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ complexes with no axial ligands have been discussed ${ }^{149}$ along with measures taken towards this goal. Such complexes are expected to have markedly shorter $\mathrm{Cr}-\mathrm{Cr}$ bond lengths owing to the lack of axial coordination. Electron diffraction studies in the vapour phase on bare $\mathrm{Cr}_{2}(\mathrm{OOCMe})_{4}$ required sophisticated methods (Ketkar and Fink ${ }^{185}$ ) to finally determine the $\mathrm{Cr}-\mathrm{Cr}$ bond length as $1.966(14) \AA$ for this complex $\mathbf{4 2}$. XRD analysis of bare $\mathrm{Cr}_{2}(\mathrm{OOCTPIP})_{4} 43$ (TIPP is 2,4,6-triisopropylphenyl) gave an $R_{M M}$ value of $1.966 \AA .{ }^{175}$ These bond lengths, which are much shorter than those for the infinite chain complexes described above, are the shortest found so far in any dichromium tetracarboxylate, arising from total absence of axial coordination. Addition of two $\mathrm{CH}_{3} \mathrm{CN}$ axial ligands to $\mathbf{4 3}$ to give $\mathbf{1 4}$ increases the $\mathrm{Cr}-\mathrm{Cr}$ bond length to $2.395 \AA .{ }^{175}$

The very short $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond lengths in $\mathbf{4 2}$ and $\mathbf{4 3}$ came in the face of a consensus based on theoretical studies ${ }^{186,187,188,189}$ that absence of axial coordination would not appreciably affect the $\mathrm{Cr}-\mathrm{Cr}$ bond lengths in these tetragonal dichromium systems. Ab initio results from Wiest and Benard ${ }^{186}$ on $\mathrm{Cr}_{2}(\mathrm{NHCHO})_{4}$ and $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4}$ had yielded $R_{M M}$ values of 1.92 and $2.53 \AA$ respectively. Further computational studies predicted an $R_{M M}$ value of 2.4
$\AA$ for $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4} .{ }^{187} \mathrm{~A}$ second theoretical study by Kok and Hall ${ }^{188}$ predicted the nature of the bridging bidentate ligand to be the major factor influencing $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond lengths in such complexes. Another theoretical study by Davy and Hall ${ }^{189}$ proposed an $R_{M M}$ range of 2.05 to $2.10 \AA$ for bare $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CR}\right)_{4}$ complexes. It is apparent that inadequate treatment of electron correlation led to such conclusions, now proven unjustifiable by experimental results. The latter place the $R_{M M}$ range for the bare tetracarboxylates as similar to that for dichromium paddlewheel complexes with other $(\mathrm{X}-\mathrm{C}=\mathrm{Y})$ type ligands like formamidinate, alkoxyphenol, guanidinate, and 2-oxopyridinate (Tables 9 and 10), where absence of axial coordination leads to shorter MM bond lengths.

This list of tetracarboxylate complexes with quadruple MM bonds demonstrates that (a) electron-donating $\mathbf{R}$ groups in the $\mathbf{R C O O}$ ligands decrease $\mathrm{Cr}-\mathrm{Cr}$ bond distances, (b) greater coordinating capacity of axial ligands (with $\mathrm{Cr}-\mathrm{L}$ bond length shortening) increases $\mathrm{Cr}-\mathrm{Cr}$ bond distances, (c) absence of axial ligands can allow for intermolecular axial coordination which does not appreciably decrease $\mathrm{Cr}-\mathrm{Cr}$ bond lengths, and (d) total absence of axial coordination of any kind has the effect of dramatically reducing $\mathrm{Cr}-\mathrm{Cr}$ bond lengths.

### 6.3. Other Dichromium Paddlewheel Complexes

Besides the carboxylate ligand, other bidentate ligands of the ( $\mathrm{X}-\mathrm{C}=\mathrm{Y}$ ) type ( $\mathrm{X}, \mathrm{Y}=\mathrm{C}, \mathrm{O}, \mathrm{N}$; Figure 2) include the alkoxyphenyl, 2-oxopyridinate, carboxamidate and formamidinate ligand types. Paddlewheel dichromium complexes with these ligands (Figure 6) display short $\mathrm{Cr}-\mathrm{Cr}$ bond distances associated with formal $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds. Table 9 shows paddlewheel dichromium complexes containing alkoxyphenyl, 2-oxopyridinate, and carboxamidate ligands, including the $R_{M M}$ values. The formamidinate complexes are listed in Table 10. Most of these compounds have four bidentate ligands in a tetragonal array around the $\mathrm{Cr}_{2}{ }^{4+}$ metal core, and are associated with quadruple metal-metal bonds. In most cases,
axial ligands are not present, thereby leading to short $\mathrm{Cr}-\mathrm{Cr}$ bonds. The presence of axial ligands or solvation leads to longer $\mathrm{Cr}-\mathrm{Cr}$ bonds, as shown above for the tetracarboxylates.

## Table 9 Cr-Cr Bond Lengths in Dichromium Complexes with ( $\mathbf{X}-\mathbf{C}=\mathbf{Y}$ ) Type Ligands

| Label Complex | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Alkoxyphenyls |  |  |  |
| $01 \mathrm{Cr}_{2}(\mathrm{DMP})_{4}$ | 1.847(1) | 190,191 | disubstituted ligand |
| $02 \mathrm{Cr}_{2}(\mathrm{TMP})_{4}$ | 1.849(2) | 191,192 | trisubstituted ligand |
| $03 \mathrm{Li}_{6} \mathrm{Cr}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{O}\right)_{4} \cdot \mathrm{Br}_{2} .6 \mathrm{Et}_{2} \mathrm{O}$ | 1.830(4) | 193 | oxyphenyl ligand |
| $04 \mathrm{Cr}_{2}\left(2-\mathrm{MeO}-5-\mathrm{MeC}_{6} \mathrm{H}_{3}\right)_{4}$ | 1.828(2) | 194 | disubstituted ligand |
| $05 \mathrm{Cr}_{2}\left(2-\mathrm{Bu}_{\mathrm{t}} \mathrm{OC}_{6} \mathrm{H}_{4}\right)_{2}(\mathrm{OOCMe})_{2}$ | 1.862(1) | 195 | 2 carboxylate ligands |
| 2-Oxopyridinates |  |  |  |
| $06 \mathrm{Cr}_{2}(\mathrm{mhp})_{4}$ | 1.889(1) | 196 |  |
| $07 \mathrm{Cr}_{2}(\mathrm{map})_{4}$ | 1.870(3) | 197 |  |
| $08 \mathrm{Cr}_{2}(\mathrm{dmhp})_{4}$ | 1.907(3) | 198 |  |
| $09 \mathrm{Cr}_{2}(\mathrm{chp})_{4}$ | 1.955(2) | 199 |  |
| $10 \mathrm{Cr}_{2}(\mathrm{fhp})_{4}(\mathrm{THF})$ | 2.150(2) | 200 | 1 axial THF ligand |
| Carboxamidates |  |  |  |
| $11 \mathrm{Cr}_{2}[\mathrm{PhNC}(\mathrm{Me}) \mathrm{O}]_{4}$ | 1.873(4) | 201,202 | phenyl N -substituent |
| $12 \mathrm{Cr}_{2}\left[\mathrm{Me}_{3} \mathrm{CNC}(\mathrm{Me}) \mathrm{O}\right]_{4}$ | 1.866(2) | 203 | tert-butyl substituent |
| $13 \mathrm{Cr}_{2}\left[\left(2,6-\mathrm{Me}_{2} \mathrm{Ph}\right) \mathrm{NC}(\mathrm{Me}) \mathrm{O}\right]_{4}$ | 1.937(2) | 204 | aryl N -substituent |
| $14 \mathrm{Cr}_{2}[\mathrm{PhNC}(\mathrm{PhNH}) \mathrm{O}]_{4}$ | 1.873(4) | 205 | Ph N-substituent |
| $15 \mathrm{Cr}_{2}[\mathrm{PhNC}(\mathrm{Me}) \mathrm{O}] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ | 1.949(2) | 206 | solvated |
| $16 \mathrm{Cr}_{2}\left[\left(2,6-\mathrm{Me}_{2} \mathrm{Ph}\right) \mathrm{NC}(\mathrm{Me}) \mathrm{O}\right]_{4} \cdot \mathrm{CH}_{2} \mathrm{Br}_{2}$ | 1.961(4) | 204 | solvated |
| $17 \mathrm{Cr}_{2}\left[\left\{2,6-\mathrm{Me}_{2} \mathrm{Ph}\right) \mathrm{NC}(\mathrm{Me}) \mathrm{O}\right]_{4} \cdot \mathrm{THF}$ | 2.023(1) | 207 | 1 axial ligand |
| $18 \mathrm{Cr}_{2}\left[\left(\mathrm{Me}_{2} \mathrm{NC}_{6} \mathrm{H}_{4}\right) \mathrm{NC}(\mathrm{Me}) \mathrm{O}\right]_{4} \cdot \mathrm{THF}$ | 2.006(2) | 207 | 1 axial ligand |
| $19 \mathrm{Cr}_{2}\left[\left\{2,6-\mathrm{Me}_{2} \mathrm{Ph}\right) \mathrm{NC}(\mathrm{Me}) \mathrm{O}\right]_{4} \cdot 2 \mathrm{THF}$ | 2.221(3) | 207 | 2 axial ligands |
| $20 \mathrm{Cr}_{2}\left[\left\{2,6-\mathrm{Me}_{2} \mathrm{Ph}\right) \mathrm{NC}(\mathrm{Me}) \mathrm{O}\right] 4 \cdot 2 \mathrm{Py}$ | 2.354(5) | 207 | 2 axial ligands |
| $21 \mathrm{Cr}_{2}[\mathrm{PhNC}(\mathrm{PhNH}) \mathrm{O}]_{4} \cdot 2 \mathrm{THF}$ | 2.246(2) | 205 | 2 axial ligands |

The tetraalkoxyphenyl complexes $\mathbf{0 1}$ to $\mathbf{0 5}$ (Table 9) contain organometallic chromiumcarbon bonds, ${ }^{190,191,192,193,194}$ and exhibit $R_{M M}$ values of 1.828 to $1.849 \AA$ that are shorter than those in other dichromium paddlewheel complexes, and of clear $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond character. This may be linked to the absence of axial ligands as well as the highly basic carbanionic ligand type. At the time of discovery of $\left.\mathrm{Li}_{6} \mathrm{Cr}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{O}\right)\right)_{4} \cdot \mathrm{Br}_{2} .6 \mathrm{Et}_{2} \mathrm{O}$ ( 03 in Table 9), its "super-short" $\mathrm{Cr}-\mathrm{Cr}$ bond length ( $1.830 \AA$ ) was the shortest metal-metal bond known (Cotton and Koch) ${ }^{193}$ in any TM complex. The alkoxyphenyl ligand has a capacity for inducing short $\mathrm{Cr}-\mathrm{Cr}$ distances surpassing that of the carboxylate ligand, linked to a smaller bite angle and presence of a Cr-C bond. Replacement of two alkoxyphenyl ligands by two carboxylate ligands in structure $\mathbf{0 5}$ leads to a $\mathrm{Cr}-\mathrm{Cr}$ bond length of $1.862 \AA,{ }^{195}$ intermediate between those of the tetraalkoxyphenyl complexes $\mathbf{0 1}$ to $\mathbf{0 4}$ and the tetracarboxylate complexes of Table 8 .

The tetra(2-oxopyridinate) complexes $\mathbf{0 6}$ to $\mathbf{0 9}$ have $R_{M M}$ values ranging from 1.870 to $1.955 \AA,{ }^{196,197,198,199}$ which are longer than those for the tetra(alkoxyphenyl) complexes above, since the 2-oxopyridinate ligands coordinate through the ring nitrogen lone pair, and not through Cr-C bonds. Note that structure $\mathbf{1 0}$ (Table 9) with axial coordination by THF gives a longer $R_{M M}$ value of $2.150 \AA .{ }^{200}$

The dichromium tetracarboxamidates $\mathbf{1 1}$ to $\mathbf{1 6}$ without axial ligands show $R_{M M}$ values from 1.873 to $1.961 \AA .{ }^{201,202,203,204,205}$ Similar to the tetracarboxylates, introduction of axial ligands (THF, dihalomethane, or Py) increases $R_{M M}$ values, seen in $\mathbf{1 5}$ to 21 ( 1.949 to $2.354 \AA$ ), where two axial ligands $(\mathbf{1 9}, \mathbf{2 0}$ and 21) have a stronger effect than the single axial ligands in 15 to 18. ${ }^{205,206,207}$

Table 10. Cr-Cr Bond Distances in Dichromium Formamidinate Complexes

| Label $\mathbf{R}$ group in $\mathbf{R N C}(\mathrm{H}) \mathrm{NR}$ | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Tetraformamidinates |  |  |  |
| 01 p-tolyl | 1.930(2) | 208 |  |
| 02 -fluorophenyl | 1.968(2) | 209 | ortho substituted |
| 03 -fluorophenyl | 1.916(1) | 209 |  |
| 04 p-fluorophenyl | 1.917(6) | 209 |  |
| 05 pentafluorophenyl | 2.012(1) | 209 |  |
| 06 3,5-difluorophenyl | $1.906(1)$ | 209 |  |
| 07 o-tolyl | 1.925(1) | 210 | ortho substituted |
| 08 cyclohexyl | 1.913(3) | 211 | non-aromatic $\mathbf{R}$ |
| 09 p-chlorophenyl | 1.907(1) | 212 |  |
| 10 3,5-dichlorophenyl | 1.916(1) | 212 |  |
| 11 m-trifluoromethylphenyl | 1.902(1) | 212 |  |
| 12 m-methoxyphenyl | 1.918(1) | 212 |  |
| 13 o-methoxyphenyl | $2.140(2)$ | 210 | ortho substituted |
| 14 o-chlorophenyl | 2.208(2) | 210 | ortho substituted |
| 15 o-bromophenyl | 2.272(2) | 210 | ortho substituted |
| $16 p$ - $\mathrm{C}_{6} \mathrm{H}_{5}$ phenyl | 1.928(2) | 211 | biphenyl group |
| Formamidinate complexes with other ligands; guanidinate complexes (full formulae) |  |  |  |
| $17\left[\left(o-\mathrm{ClC}_{6} \mathrm{H}_{4}\right) \mathrm{NC}(\mathrm{H}) \mathrm{N}\left(o-\mathrm{ClC}_{6} \mathrm{H}_{4}\right)\right]_{3}\left(\mu-\mathrm{Cl}^{2}\right) \mathrm{Cr}_{2}$ | 1.940(1) | 213 | 3 formamidinates |
| $18\left[\left(o-\mathrm{BrC}_{6} \mathrm{H}_{4}\right) \mathrm{NC}(\mathrm{H}) \mathrm{N}\left(o-\mathrm{BrC}_{6} \mathrm{H}_{4}\right)\right]_{3}(\mu-\mathrm{Cl}) \mathrm{Cr}_{2}$ | 1.940(2) | 210 | 3 formamidinates |
| $19\left[\left({ }^{i} \mathrm{Pr}\right) \mathrm{NC}(\mathrm{H}) \mathrm{N}\left({ }^{( } \mathrm{Pr}\right)\right]_{3}\left(\mu-\mathrm{BH}_{4}\right) \mathrm{Cr}_{2}$ | 1.844(2) | 214 | 3 formamidinates |
| $20 \begin{aligned} & \text { cis-[(o-MeOC} \left.\left.{ }_{6} \mathrm{H}_{4}\right) \mathrm{NC}(\mathrm{H}) \mathrm{N}\left(o-\mathrm{MeOC}_{6} \mathrm{H}_{4}\right)\right]_{2} \\ & \left(\mathrm{O}_{2} \mathrm{CMe}\right)_{2} \mathrm{Cr}_{2} \end{aligned}$ | 2.037(1) | 215 | 2 formamidinates <br> 2 carboxylates |
| $21[(\mathrm{Xyl}) \mathrm{NC}(\mathrm{H}) \mathrm{N}(\mathrm{Xyl})]_{2}\left(\mathrm{O}_{2} \mathrm{CMe}\right)_{2} \mathrm{Cr}_{2}(\mathrm{THF})_{2}$ | 2.612(1) | 215 | 2 axial ligands |
| $22(\mathrm{hpp})_{4} \mathrm{Cr}_{2}{ }^{a}$ | 1.852(1) | 216 | 4 guanidinates |
| 23 [PhNC(THP)NPh] $4_{4} \mathrm{Cr}_{2}{ }^{\text {b }}$ | 1.903(4) | 217 | 4 guanidinates |
| $24\left[\mathrm{CyNC}\left\{\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right\} \mathrm{NCy}\right]_{2}(\mathrm{Me})_{2} \mathrm{Cr}_{2}$ | 1.773(1) | 218 | 2 guanidinates |

[^6]For the tetraformamidinate complexes $\mathbf{0 1}$ to $\mathbf{1 6}$ of Table 10 (Cotton ${ }^{208,209,210}$, Gambarotta and coworkers ${ }^{211}$, Carlton-Day and coworkers ${ }^{212}$ ), the $\mathrm{Cr}-\mathrm{Cr}$ bond lengths are longer than those for the tetraalkoxyphenyl complexes, owing to absence of the organometallic Cr-C bond. The tetraformamidinate complexes display a wider range of $R_{M M}$ values ranging from 1.902 to $2.272 \AA$, probably linked to a more flexible bite angle in the formamidinate ligands. Apart from $\mathbf{0 8}$ with $\mathbf{R}=$ cyclohexyl, all of these complexes have substituted phenyl groups as the $\mathbf{R}$ group in the ( $\mathbf{R}-\mathrm{N}=\mathrm{CH}-\mathrm{N}-\mathbf{R}$ ) ligand. The position of the phenyl group substituent has a distinct effect. Meta-substituted phenyl groups (including 3,5-disubstituted phenyl groups) lead to $\mathrm{Cr}-\mathrm{Cr}$ bond lengths from 1.902 to $1.918 \AA$, while the para-substituted phenyl groups lead to $\mathrm{Cr}-\mathrm{Cr}$ bond lengths from 1.907 to $1.930 \AA$. However, complexes containing orthosubstituted phenyl groups (except for the o-tolyl group in 07), namely, 02, 13, $\mathbf{1 4}$ and $\mathbf{1 5}$ having $\mathrm{F}, \mathrm{OMe}, \mathrm{Cl}$ and Br substituents, respectively, exhibit increased $R_{M M}$ values, ranging from 1.968 to $2.272 \AA$, where the pentafluorophenyl complex $\mathbf{0 5}$ may also be included.

Complexes 17, 18 and 19 in Table 10 have three formamidinate ligands along with one bridging ligand $\left(\mathrm{Cl}\right.$ or $\left.\mathrm{BH}_{4}\right)$, where the effect of bridging is to decrease the $R_{M M}$ value, especially noted for the $\mu-\mathrm{BH}_{4}$ ligand in $19 .{ }^{213,210,214}$ The steric effect of the $N$-isopropyl substituents in 19 contributes to the very short $R_{M M}$ value of $1.844 \AA$. The presence of two carboxylate ligands increases the $R_{M M}$ value of structure 20, while axial coordination in $\mathbf{2 1}$ further increases the $\mathrm{Cr}-\mathrm{Cr}$ bond length to $2.612 \AA .{ }^{215}$

Complexes 22 and 23 feature 4 tricyclic guanidinate ligands in tetragonal array around the $\left(\mathrm{Cr}_{2}\right)^{4+}$ core. ${ }^{216,217}$ These have short $R_{M M}$ values ( 1.852 and $1.903 \AA$ ), where the $R_{M M}$ value for 23 increases to $1.925 \AA$ upon oxidation to a $\left(\mathrm{Cr}_{2}\right)^{5+}$ core. ${ }^{218}$ The digonal bis(guanidinate) complex 24 features the shortest $\mathrm{Cr}-\mathrm{Cr}$ bond length in a $\left(\mathrm{Cr}_{2}\right)^{+4}$ complex known to date, namely, $1.773 \AA$ (Horvath, Gorelsky, Gambarotta, and Korobkov ${ }^{219}$ ). Complex 24 has the unusual feature of two methyl ligands bridging the central $\mathrm{Cr}_{2}$ unit through four-center
agostic interactions. The short $R_{M M}$ value for the $\mathrm{Cr}-\mathrm{Cr}$ formal quadruple bond in $\mathbf{2 2}$ is in fact shorter than the $R_{M M}$ values for some complexes containing quintuple $\mathrm{Cr}-\mathrm{Cr}$ bonds.

A rather different example of a quadruple $\mathrm{Cr}-\mathrm{Cr}$ bond studied computationally by the DFT BP86 method is the dibenzene dichromium sandwich. ${ }^{220}$ The two $\eta^{6}-\mathrm{C}_{6} \mathrm{H}_{6}$ ligands attached to the neutral $\mathrm{Cr}_{2}$ core yield a $D_{2 \mathrm{~h}}$ global minimum with the $D_{6 \mathrm{~h}}$ structure as a transition state. The $\mathrm{Cr}-\mathrm{Cr}$ bond is assigned a bond order of four with a length of $1.701 \AA$. In line with many DFT and other computational results for $\mathrm{Cr}-\mathrm{Cr}$ multiple bonds (see sub-sections 6.5 and 6.6), this value may be on the low side. The experimental value is not available for this dichromium complex, since it has not yet been synthesized.

### 6.4. Quintuply Bonded Dichromium Complexes

Although the triple bond is the upper limit for bond orders in p-element compounds, numerous examples of quadruple bonds have been found in binuclear complexes of d-block metals, particularly dichromium, dimolybdenum and dirhenium complexes, following the original discovery of $\mathrm{Re}_{2} \mathrm{Cl}_{8}{ }^{2-}$. The quest for even higher formal bond orders involved efforts like the computational prediction of a quintuple $\mathrm{U}-\mathrm{U}$ bond in the hypothetical $\mathrm{U}_{2}$ molecule (Gagliardi and Roos ${ }^{221}$ ) and the assignment of a sextuple bond in the diatomic $\mathrm{Cr}_{2}$ species (see above). Quintuple (or five-fold) bond orders have been assigned to $\mathrm{Cr}-\mathrm{Cr}$ bonds in a variety of experimentally characterized dichromium complexes, namely bis(terphenyl) dichromiums, bis(formamidinate) and tris(formamidinate) dichromiums, and bis(guanidinate) dichromiums. Steric effects play an important role in maintaining the five-fold character of the very short $\mathrm{Cr}-\mathrm{Cr}$ bonds as suggested by the bulky substituents in all such complexes. Representative such complexes include a bis(terphenyl) dichromium complex (Figure 7a) and a bis(formamidinate) dichromium complex (Figure 7b). Sub-section 3.2 dealt briefly with the nature of quintuple metal-metal bonds in such systems.

a

b

Figure 7 Two types of quintuply-bonded dichromium complexes

Table 11 notes first bis(terphenyl) dichromium complexes which have been synthesized and characterized. The $\mathrm{Cr}-\mathrm{Cr}$ bonds in such complexes are designated as quintuple or fivefold of the $\sigma+2 \pi+2 \delta$ type. A quintuple metal-metal bond was first discovered in the bis(terphenyl)dichromium complex 01, synthesized by Power's group ${ }^{222}$ via the $\mathrm{KC}_{8}$ reduction of a bridged dichlorobis(terphenyl)dichromium complex. The quintuple $\operatorname{Cr}(\mathrm{I})-\mathrm{Cr}(\mathrm{I})$ bond of length $1.8351 \AA$ here uses the five 3d orbitals of each chromium centre leading to five shared electron pairs with the configuration $\sigma^{2} \pi^{4} \delta^{4}$. Complex 01 exhibits a trans bent structure with a weak temperature-independent paramagnetism, though the main contribution is from the singlet ground state. The five-fold nature of the $\mathrm{Cr}-\mathrm{Cr}$ bond was corroborated by DFT computational analysis ${ }^{223}$ (see sub-section 6.6 below).

Table 11. Quintuple Cr-Cr Bond Lengths in Diaryldichromium Complexes and Related Compounds

| Label Complex | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Experimental bond lengths |  |  |  |
| $01\left[2,6-\left\{\left(2,6-{ }^{-} \mathrm{Pr}_{2}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right\}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right]_{2} \mathrm{Cr}_{2}$ | 1.8351(4) | 222 | First quintuple MM bond |
| 02 [2,6- $\left.\left.\left.{ }^{(2,6}{ }^{-} \mathrm{Pr}_{2}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right\}_{2}-4-\mathrm{X}-\mathrm{C}_{6} \mathrm{H}_{2}\right]_{2} \mathrm{Cr}_{2}$ | 1.8077(7) | 224 | $\mathrm{X}=\mathrm{SiMe}_{3}$ |
|  | 1.8160(5) | 224 | $\mathrm{X}=\mathrm{OMe}$ |
| $04\left[2,6-\left\{\left(2,6-{ }^{-} \mathrm{Pr}_{2}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right]_{2}-4-\mathrm{X}-\mathrm{C}_{6} \mathrm{H}_{2}\right]_{2} \mathrm{Cr}_{2}$ | 1.831(2) | 224 | $\mathrm{X}=\mathrm{F}$ |
| $05\left(\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{Cr}_{2}$ | 2.1494(7) | 119 | $\left(\mathrm{Cr}_{2}\right)^{4+}$; sandwich |
| $06\left(\mu-\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{H}_{4}-1,4-\mathrm{Pr}_{3} \mathrm{Si}_{2}\right)_{2} \mathrm{Cr}_{2}$ | 2.251 | 225 | $\left(\mathrm{Cr}_{2}\right)^{4+}$; sandwich |
| $07 \mathrm{Cp}_{2} \mathrm{Cr}_{2}\left(\mathrm{C}_{8} \mathrm{H}_{8}\right)$ | 2.390 | 226 | COT ligand; $\mathrm{fBO}=3$ |
| Computed bond lengths |  |  |  |
| 08 linear PhCrCrPh | 1.678 | 223 | CASPT2 |
| 09 trans bent PhCrCrPh | 1.752 | 223 | CASPT2 |
| 10 linear PhCrCrPh | 1.560 | 223 | BLYP/TZ2P (ZORA) |
| 11 trans bent $\mathrm{PhCrCrPh}\left(C_{2 h}\right)$ | 1.658 | 223 | BLYP/TZ2P (ZORA) |
| $\left.12\left[2,6-\left(2,6-{ }^{-} \mathrm{Pr}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)\right]_{2} \mathrm{Cr}_{2}$ | 1.609 | 223 | BLYP/TZ2P (ZORA) |
| $13\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{2} \mathrm{Cr}_{2}$ | 1.660 | 224 | B3LYP/CRENBEL |
| $14\left(\mathrm{C}_{6} \mathrm{H}_{4}-4-\mathrm{SiMe}_{3}\right)_{2} \mathrm{Cr}_{2}$ | 1.660 | 224 | B3LYP/CRENBEL |
| $15\left(\mathrm{C}_{6} \mathrm{H}_{4}-4-\mathrm{OMe}\right)_{2} \mathrm{Cr}_{2}$ | 1.662 | 224 | B3LYP/CRENBEL |
| $16\left(\mathrm{C}_{6} \mathrm{H}_{4}-4-\mathrm{F}\right)_{2} \mathrm{Cr}_{2}$ | 1.660 | 224 | B3LYP/CRENBEL |
| $17\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{2} \mathrm{Cr}_{2}$ | 1.684 | 224 | TZP/BVP86/ZORA |
| $18\left(2,6-\mathrm{Ph}_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2} \mathrm{Cr}_{2}$ | 1.725 | 224 | TZP/BVP86/ZORA |
| 19 [2,6-( $\left.\left.\left.2,6-{ }^{-} \mathrm{Pr}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)\right]_{2} \mathrm{Cr}_{2}$ | 1.725 | 224 | TZP/BVP86/ZORA |
| 20 [2,6-(2,4,6- $\left.\left.\mathrm{Pr}_{3}-\mathrm{C}_{6} \mathrm{H}_{2}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right]_{2} \mathrm{Cr}_{2}$ | 1.721 | 224 | TZP/BVP86/ZORA |
| $21 \mathrm{HCrCrH}\left(C_{2 h}\right)$ | 1.71 | 229 | BLYP |
| $22 \mathrm{FCrCrF}\left(D_{\infty}\right)$ | 1.64 | 229 | BLYP |
| $23 \mathrm{ClCrCrCl}\left(D_{\infty}\right)$ | 1.64 | 229 | BLYP |
| $24 \mathrm{BrCrCrBr}\left(D_{2 h}\right)$ | 1.69 | 229 | BLYP |
| $25 \mathrm{MeCrCrMe}\left(C_{s}\right)$ | 1.72 | 229 | BLYP |
| $26 \mathrm{CNCrCrCN}\left(C_{2 h}\right)$ | 1.74 | 229 | BLYP |

Unlike the six-fold bonded $\mathrm{Cr}_{2}$ species, this five-fold bonded diaryldichromium complex is stable at room temperature. Note, however, that the five-fold $\mathrm{Cr}-\mathrm{Cr}$ bond of $\mathbf{0 1}$ is longer than the quadruple $\mathrm{Cr}-\mathrm{Cr}$ bond of some dichromium complexes like $\mathbf{4 6}$ and $\mathbf{4 7}$ of Table 9. This is another indication that MM bond length as such is not always commensurate with the assigned formal bond order. Substituted derivatives of 01, namely, 02, $\mathbf{0 3}$ and $\mathbf{0 4}$ having $\mathrm{SiMe}_{3}$, OMe and F substituents in the coordinating terphenyl group, were also synthesized and structurally characterized by Power ${ }^{224}$ and found to have shorter $R_{M M}$ values of 1.8077, 1.816 and $1.831 \AA$, respectively. The effect of the 4 -substituent on the $\mathrm{Cr}-\mathrm{Cr}$ bond length follows the order $\mathrm{SiMe}_{3}<\mathrm{OMe}<\mathrm{F}<\mathrm{H}$. This bis(terphenyl) dichromium complex series thus yields $R_{M M}$ values within the range $1.8214 \pm 0.0137 \AA$, which is significantly shorter than the quadruply-bonded paddlewheel dichromium complexes of Tables 8 to 10 .

Table 11 also presents $\mathrm{Cr}-\mathrm{Cr}$ bond lengths of three dichromium complexes with carbocyclic ligands having formal double and triple rather than quintuple $\mathrm{Cr}-\mathrm{Cr}$ bonds. The (bis)pentalene dichromium complexes $\mathbf{0 5}$ and $\mathbf{0 6},{ }^{119,225}$ have short $R_{M M}$ values of 2.149 and $2.251 \AA$ respectively, with $\mathrm{Cr}=\mathrm{Cr}$ double bonds consistent with an $(18,18)$ configuration, confirmed by the cBO values of 1.98 and 1.67. Complex 07 (Elschenbroich ${ }^{226}$ ) has a tub-shaped COT ligand, where the $\mathrm{Cr}=\mathrm{Cr}$ triple bond length of $2.390 \AA$ is somewhat longer than that for the binuclear cyclopentadienylchromium carbonyls of Table 13 (see sub-section 6.6).

Table 11 reports computational results on $\mathrm{Cr}-\mathrm{Cr}$ bonds in diaryl or bis(terphenyl) dichromium complexes studied using quantum chemical theoretical methods, including the DFT and CASPT2 approaches. The prototype diarylchromium PhCrCrPh was studied in linear and trans bent structures, along with the full complex 01, by the CASPT2 method and the BLYP/TZ2P/ZORA strategy. ${ }^{223}$ The trans bent structure is preferred over the linear one in accord with the predictions of Landis and Weinhold. ${ }^{227,228}$ The CASPT2 results gave
longer $\mathrm{Cr}-\mathrm{Cr}$ bond lengths than the DFT results, but still fell short of the experimental bond length range for diaryldichromium complexes. Other DFT methods were used ${ }^{224}$ to study a series of diaryl dichromium complexes $\mathbf{1 3}$ to $\mathbf{2 0}$, where the TZP/BVP86/ZORA approach yielded better $\mathrm{Cr}-\mathrm{Cr}$ bond lengths. A series of hypothetical $\mathrm{Cr}-\mathrm{Cr}$ quintuply-bonded LCrCrL compounds ( $\mathrm{L}=\mathrm{H}, \mathrm{F}, \mathrm{Cl}, \mathrm{Br}, \mathrm{Me}, \mathrm{CN}$ ) were studied $\left(\mathrm{Hoffmann}^{229}\right)$ by the BLYP method, giving $R_{M M}$ values for the most stable minimum in each case in Table 11 ( 1.64 to $1.74 \AA$ ). In general, these computational studies confirmed the quintuple nature of the $\mathrm{Cr}-\mathrm{Cr}$ bond in all of these modelled systems, even for the simplest case of HCrCrH . However, the $R_{M M}$ values fell short of the experimental range even for the systems where the steric bulk of the ligand substituent is considered. This may be a consequence of inadequate treatment of correlation effects for these MM multiple bonds.

Other quintuply bonded binuclear chromium complexes contain sterically encumbered bridging nitrogen ligands quite unlike the monodentate organometallic terphenyl ligands described above. Table 12 gives experimental and computational $\mathrm{Cr}-\mathrm{Cr}$ bond data for a series of binuclear chromium complexes containing substituted diazadiene, amidinate, aminopyridinate and guanidinate ligands. The low oxidation state $\operatorname{cr}(\mathrm{I})$ and low coordination number serve to promote the five-fold nature of the $\mathrm{Cr}-\mathrm{Cr}$ bond. The bulky substituents are important in sterically maintaining the five-fold character of the $\mathrm{Cr}-\mathrm{Cr}$ bond by preventing reactions such as oligomerization, rearrangement, or addition to the multiple bond. Bulky substituents may also enable ligands of the anionic $(\mathrm{X}-\mathrm{C}=\mathrm{Y})$ type to reduce or maintain their small bite angles with consequent effects including shortening of the MM bond. All of these complexes have $R_{M M}$ values within a range that is shorter than that for the bis(terphenyl) dichromium complexes described above. The bidentate ligands in these complexes demonstrate a flexible pincer-like effect which accommodates $\mathrm{Cr}-\mathrm{Cr}$ bonds with lengths ranging from 1.729 to $1.803 \AA$.

Table 12. Experimental and Computational Quintuple $\mathrm{Cr}-\mathrm{Cr}$ Bond Lengths in Dichromium Complexes with Diazadiene, Formamidinate, Aminopyridinate and Guanidinate Ligands

| Label Complex | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| Experimentally Characterized |  |  |  |
| $01\left[1,4-\left(2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right)_{2} \mathrm{NCH}=\mathrm{CHN}\right]_{2} \mathrm{Cr}_{2}$ | 1.8028(9) | 230 | Diazadiene ligands |
| $02\left[\left\{\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{Xyl}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{Xyl}}\right\}_{3} \mathrm{Cr}_{2}\right]^{-a}$ | 1.7397(9) | 231 | $\mathrm{BO}=5.0 ; \mathrm{Cr}^{+2}$ core |
| $03\left[\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{Xyl}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{Xyl}}\right]_{3} \mathrm{Cr}_{2}{ }^{a}$ | 1.8169(7) | 231 | $\mathrm{BO}=4.5 ; \mathrm{Cr}^{+3}$ core |
| $04\left[\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{I}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{1}\right]_{2} \mathrm{Cr}_{2}$ | 1.7404(8) | 232 | $\mathrm{Ar}^{\mathrm{I}}=2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$ |
| $05\left[\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{I}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{1}\right]_{2} \mathrm{Cr}_{2}$ | 1.7454(1) | 232 | $\mathrm{Ar}^{\mathrm{I}}=2,6-\mathrm{Et}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ |
| $\begin{array}{r} \mathbf{0 6}\left[\mu-\eta^{2}-\operatorname{Ar}^{\mathrm{l}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{I}}\right]_{2} \mathrm{Cr}_{2} \\ {\left[\mu-\eta^{2}-\operatorname{Ar}^{\mathrm{I}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{1}\right]_{2} \mathrm{Cr}_{2}} \end{array}$ | $\begin{aligned} & 1.7472(10) \\ & 1.7492(1) \end{aligned}$ | 232 | $\begin{aligned} & \mathrm{Ar}^{\mathrm{I}}=2,6--^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \\ & \mathrm{Ar}^{\mathrm{I}}=2,6-\mathrm{C}^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \end{aligned}$ |
| $07\left[\mu-\eta^{2}-\operatorname{Ar}^{\mathrm{r}} \mathrm{NC}(\mathrm{Me}) \mathrm{NAr}^{1}\right]_{2} \mathrm{Cr}_{2}$ | 1.7395(7) | 232 | $\mathrm{Ar}^{\mathrm{I}}=2,6-{ }^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ |
| 08 ( $\mu-\eta^{2}$-TippPyNMes) $2_{2} \mathrm{Cr}_{2}{ }^{\text {b }}$ | 1.749(2) | 235 | Aminopyridinate ligands |
| 09 ( $\left.\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{Xyl}} \mathrm{PyNDipp}\right)_{2} \mathrm{Cr}_{2}{ }^{\text {a }}$ c | 1.750(1) | 236 | Aminopyridinate ligands |
| $10\left[\mu-\eta^{2}\right.$-DippNC( $\mathrm{NMe}_{2}$ ) $\mathrm{NDipp}_{2} \mathrm{Cr}_{2}{ }^{c}$ | 1.7293(12) | 237 | Guanidinate ligands |
| $11\left[\mu-\eta^{2}-\mathrm{DippNC}\left\{\mathrm{N}(\mathrm{dmp})_{2}\right\} \mathrm{NDipp}\right]_{2} \mathrm{Cr}_{2}{ }^{c}$ | 1.7056(12) | 238 | Shortest MM bond so far |
| $12\left[\mu-\mathrm{HC}\left(\mathrm{N}-2,6-\mathrm{Me}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}\right]_{2} \mathrm{Cr}_{2}$. ${ }^{\text {(THF) }} 2$ | 1.8115(12) | 239 | 2 axial ligands |
| $13\left[\mu-\mathrm{HC}\left(\mathrm{N}-2,6-\mathrm{Me}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)_{2}\right]_{2} \mathrm{Cr}_{2}$. ${ }^{\text {(MeTHF) }}$ | 1.7635(5) | 239 | 1 axial ligand |
| Computational Results |  |  |  |
| $14\left[\left\{\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{Xyl}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{Xyl}}\right\}_{3} \mathrm{Cr}_{2}\right]^{-}$ | 1.755 | 234 | DFT; $\mathrm{Cr}^{+2}$ core; cf. 02 |
| $15\left[\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{Xy}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{Xyl}}\right]_{3} \mathrm{Cr}_{2}$ | 1.802 | 234 | DFT; $\mathrm{Cr}^{+3}$ core; cf. 03 |
| $16\left[\mu-\eta^{2}-\operatorname{Ar}^{\mathrm{I}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{I}}\right]_{2} \mathrm{Cr}_{2}$ | 1.749 | 234 | DFT; $\mathrm{Ar}^{\mathrm{I}}=2,6-{ }^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ |
| $17\left[\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{E}} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{\mathrm{E}}\right]_{2} \mathrm{Cr}_{2}$ | 1.764 | 240 | $\mathrm{DFT}^{*}{ }^{d} ; \mathrm{Ar}^{\mathrm{E}}=2,6-\mathrm{Et}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ |
| 18 [ $\left.\left\{\mu-\eta^{2}-\mathrm{PhNC}(\mathrm{H}) \mathrm{NPh}\right\}_{3} \mathrm{Cr}_{2}\right]^{-}$ | 1.738 | 240 | DFT*; model for $\mathbf{0 2}$ |
| $19\left[\mu-\eta^{2}-\mathrm{PhNC}(\mathrm{H}) \mathrm{NPh}\right]_{3} \mathrm{Cr}_{2}$ | 1.806 | 240 | DFT*; model for 03 |
| 20 ( $\left.\mu-\eta^{2}-\mathrm{PhPyNPh}\right)_{2} \mathrm{Cr}_{2}$ | 1.777 | 240 | DFT*; model for $\mathbf{0 8}$ |
| $21\left[\mu-\eta^{2}-\mathrm{DippNC}\left(\mathrm{NMe}_{2}\right) \mathrm{NDipp}_{2} \mathrm{Cr}_{2}\right.$ | 1.752 | 240 | DFT*; cf. 09 |
| $22\left[\mu-\eta^{2}-\mathrm{Ar}^{\mathrm{Xyl}} \mathrm{NC}\left(\mathrm{NMe}_{2}\right) \mathrm{NAr}^{\mathrm{Xyl}}\right]_{2} \mathrm{Cr}_{2}$ | 1.772 | 240 | DFT*; model for 09 |
| ${ }^{a} \mathrm{Ar}^{\mathrm{Xyl}}=2,6-(\mathrm{Me})_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ <br> ${ }^{b}$ TippPyNMes $=6$-( $2,4,6$-triisopropylphenyl) pyr <br> ${ }^{c}$ Dipp $=2,6-\left({ }^{( } \mathrm{Pr}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{3} ; \mathrm{dmp}=2,6$-dimethylpipe <br> ${ }^{d}$ DFT $^{*}=$ CASPT2 with B3LYP/DZP | ridin-2-yl-2,4 <br> eridine | 6-trimeth | lphenylimide |

DFT analysis on the diazadiene complex 01 with an experimentally determined short $R_{M M}$ value of $1.803 \AA$ (Theopold ${ }^{230}$ ) confirmed the essentially five-fold nature of the $\mathrm{Cr}-\mathrm{Cr}$ bond (see sub-section 6.6). Complexes $\mathbf{0 2}$ and $\mathbf{0 3}$ contain three amidinate ligands, where $\mathbf{0 3}$ is the oxidized form of the anion $\mathbf{0 2}$ (Tsai et al. ${ }^{231}$ ). Anion $\mathbf{0 2}$ with a $\left(\mathrm{Cr}_{2}\right)^{+2}$ core has a formal bond order of 5 and an $R_{M M}$ value of $1.740 \AA$, which is shorter than the $R_{M M}$ value of $1.817 \AA$ in 03 with a $\mathrm{Cr}-\mathrm{Cr}$ bond order of 4.5.

The search was on for ever-decreasing metal-metal bond lengths, which was commented on by Wagner, Noor, and Kempe. ${ }^{232}$ The series of complexes $\mathbf{0 4}$ to $\mathbf{0 7}$ incorporating two substituted amidinate ligands showed $R_{M M}$ values from 1.740 to $1.747 \AA \AA^{233}$ structure $\mathbf{0 7}$ was re-characterized with an $R_{M M}$ value of $1.749 \AA .{ }^{234}$ Incorporation of two aminopyridinate ligands in 08 and 09 resulted in $R_{M M}$ values of 1.749 and $1.750 \AA$ (Kempe and coworkers ${ }^{235,236}$ ). Complexes $\mathbf{1 0}$ and $\mathbf{1 1}$ have guanidinate ligands noted for their capacity to shorten MM multiple bonds, where the shortest MM bond known so far in a transition metal complex was found in $\mathbf{1 1}$ with an $R_{M M}$ value of $1.706 \AA$ (Kempe ${ }^{237,238}$ ) with an FSR value of 0.613. Steric effects in $\mathbf{1 1}$ are enhanced by the central cyclopropyl N -substituents. Axial coordination by THF and 2-methyltetrahydrofuran in structures $\mathbf{1 2}$ and $\mathbf{1 3}$ has the effect of lengthening the $\mathrm{Cr}-\mathrm{Cr}$ distance, ${ }^{239}$ similar to the effect of axial coordination upon quadruply bonded dichromium paddlewheel complexes. This is more evident when two axial ligands are present, as compared with systems having only a single axial ligand.

Computational estimates of $R_{M M}$ values in some dichromium complexes with bidentate nitrogen ligands (including some model compounds) are provided in Table 12. Complexes 02,03 and 06 were optimized by the B3LYP method to give $\mathbf{1 4}, \mathbf{1 5}$ and 16 with $R_{M M}$ values of $1.755,1.802$, and $1.749 \AA$ respectively, ${ }^{234}$ close to the experimental values, especially for 06 corresponding to 16. A strategy combining DFT and CASPT2 approaches (labelled DFT*
in Table 12) was used to optimize the structures of several dichromium complexes and their model compounds. ${ }^{240}$ Complexes $\mathbf{0 5}$ and $\mathbf{0 9}$ were modelled by structures $\mathbf{1 7}$ and $\mathbf{2 1}$ with $R_{M M}$ values of 1.764 and $1.752 \AA$, respectively, where $\mathbf{0 9}$ and $\mathbf{2 1}$ have shorter $\mathrm{Cr}-\mathrm{Cr}$ bond lengths than 05 and 17. Complexes $02,03,08$ and 09 were modelled by structures 18, 19, 20 and 21 respectively with theoretical $R_{M M}$ values fairly close to the experimental values. The longer $R_{M M}$ value of $\mathbf{0 3}$ over $\mathbf{0 2}$ is reflected in the longer $R_{M M}$ value of $\mathbf{1 9}$ over $\mathbf{1 8}$.

### 6.5. Theoretical Analysis of Dichromium Quadruple and Quintuple Bonds

Chromium-chromium bonds in quadruply and quintuply bonded dichromium complexes and in the $\mathrm{Cr}_{2}$ dimer present a challenging task to computational and theoretical chemists owing to the highly correlated nature of their metal-metal bonding. It is evident that a single determinantal description is inadequate, calling for a multi-configurational approach. The need for mixing of configurations may be also reflected in the observation that many dichromium paddlewheels with short $\mathrm{Cr}-\mathrm{Cr}$ bond lengths are weakly paramagnetic owing to small populations of the triplet excited state. Ab initio methods have been used to investigate the nature of metal-metal bonding in dichromium paddlewheel and quintuply bonded dichromium complexes with a variety of results.

The failure of early $a b$ initio computational approaches to yield satisfactory predictions of the $\mathrm{Cr}-\mathrm{Cr}$ bond lengths in dichromium tetracarboxylates ${ }^{186-189}$ has been mentioned earlier. The SCF Hartree-Fock approach cannot even give a correct description of the MM multiple bond in $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right) 4 \cdot 2 \mathrm{H}_{2} \mathrm{O},{ }^{241}$ where the ground state with the $\sigma^{2} \delta^{2} \delta^{* 2} \sigma^{* 2}$ configuration led to no $\mathrm{Cr}-\mathrm{Cr}$ bond at all. The SCF results showed small energy separations between the no-bond ground state and multiple bond configurations for the $\left(\mathrm{Cr}_{2}\right)^{4+}$ core. Assignment of a $\mathrm{Cr}-\mathrm{Cr}$ multiple bond order to $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4}$ led to instabilities in the single determinantal HF wave function. ${ }^{242}$ In another study, configuration mixing using an antisymmetric product of
orthogonal geminals gave an MM bond order of only 1.6 for the isolated $\left(\mathrm{Cr}_{2}\right)^{4+}$ species and 1.0 for $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O},{ }^{243}$ still not yet arriving at a more complete description.

A limited CI wave function identified ${ }^{244}$ the $\sigma^{2} \pi^{4} \delta^{2}$ configuration as a leading term in the expansion for $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}, \mathrm{Cr}_{2} \mathrm{Me}_{8}{ }^{4-}$ and $\mathrm{Cr}_{2} \mathrm{Cl}_{8}{ }^{4-}$. $\mathrm{For}_{2} \mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4}$, addition of axial water ligands did not materially affect the Cr-Cr bond strength. The old SCF-X $\alpha-\mathrm{SW}$ method assigned a quadruply bonded $\sigma^{2} \pi^{4} \delta^{2}$ configuration to the ground state of some second and third series transition metal tetragonal binuclear complexes. ${ }^{245,246,247} \mathrm{X} \alpha-\mathrm{SW}$ studies on $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4}$ also yielded the correct quadruply-bonded ground state configuration. ${ }^{248} \mathrm{An}$ extensive CI approach revealed the dominant role of antiferromagnetic coupling rather than covalent overlap between the metal centres of the square parallelepiped $\mathrm{Cr}_{2} \mathrm{Cl}_{8}{ }^{4-}$ system. ${ }^{249}$ Ab initio studies at various levels on $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{4}{ }^{250}$ showed the importance of quadruple excitations in the CI expansion, where correlation effects are necessary to describe the 3d ionizations. Such considerations figured in further discussions on MM multiple bonds in binuclear complexes. ${ }^{251,252}$ A multiconfigurational approach was used to study the relation between MM bond lengths and $\mathrm{d} \rightarrow \mathrm{d}^{*}$ orbital transitions in Group 6 and $\operatorname{Re}($ III $)$ octamethyldimetalate anions (square parallepiped complexes). ${ }^{253}$

DFT methods have not been used with much regularity to study dichromium paddlewheel complexes. In view of the remarkable reproduction by DFT of transition metal complex geometries and MM bond lengths in many documented cases, it is a moot question as to whether DFT approaches can suffice to furnish a reasonably accurate description of the nature of the quadruple bond in such systems, along with the equilibrium MM bond length. Due to the relative dearth of optimized geometries for dichromium paddlewheel complexes, more reliable theoretical studies of $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds are needed.

Quintuple $\mathrm{Cr}-\mathrm{Cr}$ bonds in known binuclear chromium complexes and their model counterparts have been subjected to theoretical analyses. ${ }^{223,224,231,235,241}$ The five d orbitals on
one $\operatorname{Cr}(\mathrm{I})$ centre of such complexes can overlap with the five d orbitals on the other and contribute to the formation of molecular orbitals dominated by metal d orbital character. Computational studies on the quintuple bond in bis(terphenyl) dichromium complexes ${ }^{223}$ reveal that the five highest occupied MOs (HOMO to HOMO-4) are dominated by overlap between the 3d orbitals of one chromium atom with those of the other. The orbitals HOMO-4 and HOMO-3 are Cr-Cr $\pi$ MO's (non-degenerate) arising from $d_{x z}-d_{x z}$ and $d_{y z}-d_{y z}$ overlap. HOMO-2 is a $\mathrm{Cr}-\mathrm{Cr} \sigma$ MO arising from $d_{z^{2}}-d_{z^{2}}$ overlap. HOMO and HOMO-1 are $\mathrm{Cr}-\mathrm{Cr} \delta$ MO's arising from $d_{x y}-d_{x y}$ and $d_{x} 2-y 2-d_{x 2-y 2}$ overlap. The extent of AO overlap follows the order $\sigma>\pi>\delta$, so the $\delta$ component of the five-fold bond is the weakest (as in quadruple bonds). This leads to an effective bond order value approaching the formal bond order of 5 .

The quintuple bond in the dichromium diazadiene complex $\mathbf{0 1}$ of Table 12 shows a different picture, ${ }^{230}$ where $\mathrm{Cr}-\mathrm{Cr} 3 \mathrm{~d}$ orbital overlap is prominent in the orbitals HOMO-1 down to HOMO-5. HOMO-5 and HOMO-4 represent $\pi$ bonds arising from $d_{x z}-d_{x z}$ and $d_{y z}-d_{y z}$ overlap. HOMO-3 is a $\sigma$ bonding MO involving $d_{z 2}-d_{z} 2$ overlap. HOMO-2 is more delocalized but significantly involves $\delta$ bonding between 3d orbitals on each centre. HOMO-1 represents overlap between sd hybrids on each Cr centre leading to a side-on $s d-\pi$ bond. The lack of localization of all 5 electron pairs between the chromium centres leads to an effective bond order lower than 5 .

Computational studies by Power and coworkers ${ }^{254}$ show that secondary metal-arene inteactions in bis(terphenyl) binuclear complexes differentiate dichromium complexes from their diiron and dicobalt counterparts, contributing towards maintaining the MM quintuple bond in the former. The $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond in the dichromium complex $\mathbf{0 1}$ of Table 11 was analyzed by Ndambuk and Ziegler ${ }^{255}$ on the basis of combined natural orbitals for chemical valence and an extended transition state method.

### 6.6. Binuclear Chromium Carbonyl Complexes

This sub-section describes computational results on the structural and bonding possibilities for binuclear chromium carbonyl complexes and derivatives as presented in Tables 13 and 14. This body of work covers homoleptic binuclear chromium carbonyls as well as organometallic derivatives with cyclopentadienyl, cycloheptatrienyl, and azulene ligands.

Homoleptic binuclear chromium carbonyls in the series $\mathrm{Cr}_{2}(\mathrm{CO})_{n}(n=11,10,9,8)$ have been studied by DFT methods. The BP86 results are summarised in Table 13. ${ }^{256,257}$ This series has a neutral $\mathrm{Cr}_{2}$ core with two $\mathrm{Cr}(0)$ centres. While the saturated $\mathrm{Mn}_{2}(\mathrm{CO})_{10}, \mathrm{Fe}_{2}(\mathrm{CO})_{9}$ and $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ analogues are well-known, the saturated dichromium analogue $\mathrm{Cr}_{2}(\mathrm{CO})_{11}$ with a $\mathrm{Cr}-\mathrm{Cr}$ single bond is unknown experimentally. The potential energy surface of $\mathrm{Cr}_{2}(\mathrm{CO})_{11} \mathbf{0 1}$ is flat with the global minimum having one bridging carbonyl group and a $\mathrm{Cr}-\mathrm{Cr}$ distance of $3.148 \AA$. This Cr-Cr distance is well beyond the estimate of $\sim 2.78 \AA$ for a $\mathrm{Cr}-\mathrm{Cr}$ covalent bond based on the covalent radius of $1.39 \AA$ for chromium; ${ }^{41}$ this may suggest resonance between a $\mathrm{Cr}-\mathrm{Cr}$ single bond and a $\mathrm{Cr}-\mathrm{Cr}$ no bond. This structure was predicted as disfavored by $1.7 \mathrm{kcal} / \mathrm{mol}$ with respect to dissociation into mononuclear fragments. The lower energy structure $(\mathrm{CO})_{5} \mathrm{Cr}-(\mathrm{OC})-\mathrm{Cr}(\mathrm{CO})_{5}$ with a bridging isocarbonyl group and no $\mathrm{Cr}-\mathrm{Cr}$ bond is, however, viable with respect to dissociation. ${ }^{258}$ The binuclear metal carbonyls $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ and $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ were suggested by theoretical studies to have no direct covalent MM bonds (see Sections 8 and 9 ), but this is yet to be determined for $\mathrm{Cr}_{2}(\mathrm{CO})_{11}$. Although the experimentally characterized $\left[\mathrm{Cr}_{2}(\mathrm{CO})_{10}(\mu-\mathrm{H})\right]^{-}$anion has a $\mathrm{Cr} \cdots \mathrm{Cr}$ distance of $\sim 3.39 \AA$ indicating no covalent MM bond, ${ }^{259,260}$ this anion is predicted to be clearly viable towards dissociation by the DFT results. ${ }^{258}$

The BP86 results on $\mathrm{Cr}_{2}(\mathrm{CO})_{10}$ (02) gave a singlet global minimum with two $\eta^{2}-\mu$ - CO groups, ${ }^{258,261}$ interpreted as a hybrid between a structure with a $\mathrm{Cr}=\mathrm{Cr}$ double bond and one having a weak $\mathrm{Cr} \cdots \mathrm{Cr}$ interaction, leading to a $\mathrm{Cr}-\mathrm{Cr}$ distance of $2.832 \AA$. Triplet $\mathrm{Cr}_{2}(\mathrm{CO})_{10}$
lies $\sim 10 \mathrm{kcal} / \mathrm{mol}$ higher in energy with a $\mathrm{Cr}=\mathrm{Cr}$ distance of $2.726 \AA$ corresponding to a weak double bond of the $\sigma+2 / 2 \pi$ type. The $\left[\mathrm{Cr}_{2}(\mathrm{CO})_{10}\right]^{2-}$ dianion $\mathbf{0 3}$ was shown experimentally to be an unbridged structure with a Cr-Cr bond length of 2.98 to $3.00 \AA$ (Hey-Hawkins ${ }^{262}$, Lee, Geib and Cooper ${ }^{263}$, Schrobilgen ${ }^{264}$ ). This Cr-Cr bond length is shorter than that predicted for $\mathrm{Cr}_{2}(\mathrm{CO})_{11}$.

a (04)

b (05, S-2)

c (04)

d (07)

e (08)

f(10)

Figure 8. Some computationally studied binuclear chromium complexes (labels for $\mathbf{a}$ and $\mathbf{b}$ refer to Table 13; labels for $\mathbf{c}$ to $\mathbf{f}$ refer to Table 14)

Table 13. Computational and Experimental Data on $\mathbf{C r}-\mathrm{Cr}$ Bonds in Binuclear Chromium Carbonyls (Homoleptic and with Cyclopentadienyl Ligands) ${ }^{a}$

| Label Complex | State $R_{M M}(\AA)$ fBO $\begin{gathered}\text { Refer- } \\ \text { ences }\end{gathered}$ | Remarks |
| :---: | :---: | :---: |

Homoleptic chromium carbonyls (BP86 results)

| $\mathbf{0 1}(\mathrm{CO})_{4}(\mathrm{~s} \mu-\mathrm{CO})_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-1$ | 3.148 | $<1$ | 256,257 | unstable |
| :--- | :---: | :--- | :--- | :--- | :--- |
| $\mathbf{0 2}(\mathrm{CO})_{4}(\mu-\mathrm{CO}) \mathrm{Cr}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.832 | $<2$ | 257,258 | unstable |
| $(\mathrm{CO})_{5} \mathrm{Cr}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~T}-2$ | 2.726 | 2 | 261 | $\sigma+2 / 2 \pi$ bond |
| $\mathbf{0 3}\left[\mathrm{Cr}_{2}(\mathrm{CO})_{10}\right]^{2-}$ anion | - | $2.98-3.00$ | 1 | $262-264$ | experimental |
| $\mathbf{0 4}(\mathrm{CO})_{3}(\mu-\mathrm{CO}) \mathrm{Cr}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.285 | 3 | 257,265 | stable |
| $\mathbf{0 5 ( \mathrm { CO } ) _ { 2 } ( \mu - \mathrm { CO } ) \mathrm { Cr } _ { 2 } ( \mu - \mathrm { CO } ) _ { 2 } ( \mathrm { CO } ) _ { 3 }}$ | $\mathrm{S}-1$ | 2.276 | 3 | 257,266 | small $i v ;(18,16)$ |
| $(\mathrm{CO})_{3}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Cr}_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.469 | 2 | 266 | $\Delta \mathrm{E}=7.5$ |

Binuclear cyclopentadienylchromium carbonyls (experimental and BP86 results)

| $06\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{4} \mathrm{Cr}_{2}$ | S | 2.239 | 3 | 269 | XRD exptl. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $07\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2}(\mathrm{CO})_{4} \mathrm{Cr}_{2}$ | S | 2.280(2) | 3 | 271,272 | XRD exptl. |
| $08\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2}(\mathrm{CO})_{4} \mathrm{Cr}_{2}$ | S | 2.272 | 3 | 273 | BP86; cf. 07 |
| $09 \mathrm{CpCr}_{2}(\mathrm{~s} \mu-\mathrm{CO})_{3} \mathrm{Cp}$ | T-1 | 2.295 | 3 | 273 | BP86; $(17,17)$ |
| $\mathrm{Cp}(\mu-\mathrm{CO}) \mathrm{Cr}_{2}(\mathrm{~s} \mu-\mathrm{CO})_{2} \mathrm{Cp}$ | T-2 | 2.271 | 3 | 273 | BP86; $\Delta \mathrm{E}=5.4$ |
|  | S-3 | 2.191 | 4 | 273 | BP86; $\triangle \mathrm{E}=11.5$ |
| $10\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{3}$ | T-1 | 2.319 | 3 | 273 | BP86; $(17,17)$ |
|  | S-2 | 2.215 | 4 | 273 | BP86; $\triangle \mathrm{E}=11.7$ |
| $11 \mathrm{Cp}_{2}(\mathrm{CO})_{2} \mathrm{Cr}_{2}$ | T-1 | 2.311 | 3 | 273 | BP86; $(16,16)$ |
| $\mathrm{Cp}_{2}(\mathrm{CO})_{2} \mathrm{Cr}_{2}$ | Q-2 | 2.353 | 3 | 273 | BP86; $(16,16)$ |
| $\mathrm{Cp}_{2}(\mathrm{CO})_{2} \mathrm{Cr}_{2}$ | H-3 | 2.615 | 2 | 273 | $\Delta \mathrm{E}=16.1$; $(15,15)$ |
| $12\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{2}$ | T-1 | 2.346 | 3 | 273 | BP86; $(16,16)$ |
| $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{2}$ | Q-2 | 2.363 | 3 | 273 | BP86; $\triangle \mathrm{E}=2.7$ |
| $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{2}$ | H-3 | 2.598 | 2 | 273 | $\Delta \mathrm{E}=11.9$ ( 15,15 ) |

[^7]The global minimum for the fluxional species $\mathrm{Cr}_{2}(\mathrm{CO})_{9}$ (structure 04, Figure 8a) has two s $\mu$-CO ligands and an endothermic dissociation energy of $43 \mathrm{kcal} / \mathrm{mol}$ into $\mathrm{Cr}(\mathrm{CO})_{5}$ and $\mathrm{Cr}(\mathrm{CO}) 4,{ }^{258,265}$ suggesting a possible synthetic target. The $\mathrm{Cr}=\mathrm{Cr}$ distance of $2.285 \AA$ suggests a formal triple bond, comparable to that in $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}$ (see below). The octacarbonyl $\mathrm{Cr}_{2}(\mathrm{CO})_{8}(\mathbf{0 5})$ has a viable triply bridged singlet structure with a dissociation energy of $44 \mathrm{kcal} / \mathrm{mol} .{ }^{258,266} \mathrm{The} \mathrm{Cr} \equiv \mathrm{Cr}$ triple bond length of $2.276 \AA$ here suggests an $(18,16)$ configuration for the $\mathrm{Cr}_{2}$ core. Another singlet $\mathrm{Cr}_{2}(\mathrm{CO})_{8}$ structure lying $7.5 \mathrm{kcal} / \mathrm{mol}$ higher in energy has two four-electron donor bridging $\eta^{2}-\mu$-CO groups (Figure 8 b ), leading to a $\mathrm{Cr}=\mathrm{Cr}$ double bond length of $2.469 \AA$.

These homoleptic binuclear chromium carbonyls thus exhibit weak $\mathrm{Cr} \cdots \mathrm{Cr}$ interactions of around $3 \AA$ in length, $\mathrm{Cr}=\mathrm{Cr}$ double bond lengths from 2.47 to $2.73 \AA$, and $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bond lengths of $\sim 2.28 \AA$. The thermodynamic instability of many of these systems with respect to dissociation may help explain why so far no homoleptic binuclear chromium carbonyl has been synthesised. However, DFT has predicted that binuclear chromium carbonyls may be stabilized by substitution of thiocarbonyl groups for carbonyl groups. ${ }^{267}$

Binuclear cyclopentadienylchromium carbonyls have been studied both experimentally and computationally (Table 13). The compound $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{6}$ has an experimental $\mathrm{Cr}-\mathrm{Cr}$ bond distance of $3.281 \AA\left(\mathrm{Adams}^{268}\right)$, which is very long for a covalent $\mathrm{Cr}-\mathrm{Cr}$ bond. The experimentally characterized structures $\mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}(\mathbf{0 6})^{269}$ and $\mathrm{Cp}^{*}{ }_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}(\mathbf{0 7})$ (Efraty and coworkers ${ }^{270,271,272}$ ) have singlet ground states with $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bond lengths of 2.239 and $2.280 \AA$, respectively. Table 13 presents experimental and computational (BP86) results for the series $\mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{n}$ and $\mathrm{Cp}^{*}{ }_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{n}\left(\mathrm{Cp}=\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5} ; \mathrm{Cp}^{*}=\eta^{5}-\mathrm{Me}_{5} \mathrm{C}_{5} ; n=3,2\right) .{ }^{273}$ The ground state triplet tricarbonyl $\mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{3}$ has an $R_{M M}$ value of $2.295 \AA$ interpreted as a $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bond, while the higher energy singlet has an $R_{M M}$ value of $2.191 \AA$, interpreted as a quadruple Cr - Cr bond. Similar results are seen for the permethylated $\mathrm{Cp}^{*}{ }_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{3}$. The
dicarbonyls $\mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{2}$ and $\mathrm{Cp}^{*} \mathrm{Cr}_{2}(\mathrm{CO})_{2}$ both have triplet global minima with triple bond $R_{M M}$ values of 2.311 and $2.346 \AA$, respectively. This DFT study predicts $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bond lengths from 2.272 to $2.363 \AA$ for various minima, which are close to the experimental (Curtis and Butler ${ }^{269}$, Efraty ${ }^{270,272}$, King $^{271}$ ) triple bond $R_{M M}$ values of 2.239 and $2.280 \AA$ for $\mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}$ and $\mathrm{Cp}_{2}{ }_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}$ respectively.

Binuclear cycloheptatrienyl chromium carbonyl complexes of the series $\left(\mathrm{C}_{7} \mathrm{H}_{7}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{n}$ ( $n=1$ to 6 ) have been studied by DFT methods (BP86 results in Table 14). ${ }^{274}$ These structures have two cycloheptatrienyl ligands each bonded to one Cr centre of the MM core. The cycloheptatrienyl rings display variable hapticity, with heptahapto coordination in lower energy structures seen only for $n=1$. Lower hapticity leads to bent $\mathrm{C}_{7} \mathrm{H}_{7}$ rings. The global minima all have formal $\mathrm{Cr}=\mathrm{Cr}$ triple bonds with lengths from 2.411 to $2.480 \AA$, longer than those in binuclear homoleptic chromium carbonyls and cyclopentadienylchromium carbonyls (Table 13). Figure 8c shows the tricarbonyl 04 with two bridging CO groups. The dimetallocene type $\left(\eta^{7}-\mathrm{C}_{7} \mathrm{H}_{7}\right)_{2} \mathrm{Cr}_{2}$ species 07 with no CO ligands (Figure 8 d ) has a $\mathrm{Cr}=\mathrm{Cr}$ distance of $2.265 \AA$, which is described as a triple bond, consistent with a $(16,16)$ core configuration (cf. $\mathbf{0 6}$ and $\mathbf{0 7}$ of Table 13).

The series of binuclear azulene chromium carbonyls $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{n}(n=1$ to 6$)$ was studied by DFT methods; the BP86 results are given in Table 14. ${ }^{275}$ These complexes have each ring of the azulene ligand pi-bonded with variable hapticity to one of the two Cr centres of the MM core. The hexacarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{6} 08$ (Figure 8e) has an experimental $\mathrm{Cr} \cdot{ }^{\circ} \mathrm{Cr}$ distance of $3.26 \AA\left(\right.$ Edelman $\left.^{276}\right)$ close to the BP86 value of $3.325 \AA$ and suggesting only a weak MM single bond. The pentacarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{5}(09)$ exhibits a global minimum S-1 with a $\mathrm{Cr}=\mathrm{Cr}$ double bond and an $R_{M M}$ value of $2.664 \AA$; the range from 2.606 to $2.880 \AA$ is seen for $\mathrm{Cr}=\mathrm{Cr}$ double bond lengths in the various structures of this series. The $\mathrm{Cr}=\mathrm{Cr}$ triple bond lengths range from 2.416 to $2.455 \AA$ in this series, including singlet and

Table 14. Distances for Cr-Cr Bonds in Binuclear Chromium Carbonyl Complexes with Cycloheptatrienyl and Azulene Ligands ${ }^{a}$
Label Complex

Binuclear cycloheptatrienylchromium carbonyls (BP86 results; Ref. 274)

| $\mathbf{0 1}$ | $\left(\eta^{5}-\mathrm{C}_{7} \mathrm{H}_{7}\right)(\mathrm{CO})_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}\left(\eta^{1}-\mathrm{C}_{7} \mathrm{H}_{7}\right)$ | $\mathrm{S}-1$ | 2.473 | 3 | glob. min. |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 2}$ | $\left(\eta^{3}-\mathrm{C}_{7} \mathrm{H}_{7}\right)(\mathrm{CO})_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{3}\left(\eta^{2,1}-\mathrm{C}_{7} \mathrm{H}_{7}\right)$ | $\mathrm{S}-1$ | 2.472 | 3 | glob. min. |
|  | $\left(\eta^{3}-\mathrm{C}_{7} \mathrm{H}_{7}\right)(\mathrm{CO})_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{3}\left(\eta^{2,1}-\mathrm{C}_{7} \mathrm{H}_{7}\right)$ | $\mathrm{T}-1$ | 2.498 | 3 | $\Delta \mathrm{E}=8.5 ;(18.16)$ |
| $\mathbf{0 3}$ | $\left(\eta^{5}-\mathrm{C}_{7} \mathrm{H}_{7}\right)_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \mathrm{Cr}_{2}$ | $\mathrm{~S}-1$ | 2.433 | 3 | glob. min. |
| $\mathbf{0 4}$ | $\left(\eta^{2}-\mathrm{C}_{7} \mathrm{H}_{7}\right)_{2}(\mu-\mathrm{CO})_{2} \mathrm{Cr}_{2}(\mathrm{CO})$ | $\mathrm{S}-1$ | 2.480 | 3 | glob. min. |
| $\mathbf{0 5}$ | $\left(\eta^{2,1}-\mathrm{C}_{7} \mathrm{H}_{7}\right)(\mathrm{CO}) \mathrm{Cr}_{2}(\mu-\mathrm{CO})\left(\mathrm{C}_{7} \mathrm{H}_{7}\right)$ | $\mathrm{S}-1$ | 2.480 | 3 | glob. min. |
|  | $\left(\eta^{2,1}-\mathrm{C}_{7} \mathrm{H}_{7}\right)(\mathrm{CO}) \mathrm{Cr}_{2}(\mu-\mathrm{CO})\left(\mathrm{C}_{7} \mathrm{H}_{7}\right)$ | $\mathrm{S}-2$ | 2.459 | 3 | $\Delta \mathrm{E}=10.7$ |
| $\mathbf{0 6}$ | $\left(\eta^{7}-\mathrm{C}_{7} \mathrm{H}_{7}\right)_{2} \mathrm{Cr}_{2}(\mu-\mathrm{CO})$ | $\mathrm{S}-1$ | 2.411 | 3 | heptahaptic ligand |
| $\mathbf{0 7}$ | $\left(\eta^{7}-\mathrm{C}_{7} \mathrm{H}_{7}\right)_{2} \mathrm{Cr}_{2}$ | $\mathrm{~S}-1$ | 2.265 | 3 | $D_{7 h} ;$ no CO ligand; $(16,16)$ |

Binuclear azulene chromium carbonyls (BP86 results; Ref. 275)

| 08 | cis $-\left[\left(\eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{6}\right.$ | S-1 | 3.325 | 1 | glob. min.; unstable |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | cis-[ $\left[\eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{6}$ | S | 3.26 | 1 | exptl. XRD; Ref. 276 |
| 09 | cis $-\left[\left(\eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})\right.$ | S-1 | 2.664 | 2 | glob. min. |
|  | cis-[( $\left.\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{4}(\mathrm{~s} \mu-\mathrm{CO})$ | T-2 | 2.784 | 2 | $\Delta \mathrm{E}=4.5$ |
|  | cis-[ $\left[\eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{5}$ | T-3 | 2.880 | 2 | $\Delta \mathrm{E}=5.4$ |
| 10 | $c i s-\left[\left(\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{3}(\mu-\mathrm{CO})\right.$ | S-1 | 2.455 | 3 | glob. min. |
| 11 | $c i s-\left[\left(\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})\right.$ | T-1 | 2.447 | 3 | glob. min. $(17,17)$ |
|  | cis-[( $\left.\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})$ | S-2 | 2.424 | 3 | $\Delta \mathrm{E}=3.9$; $(18,16)$ |
|  | cis $-\left[\left(\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})\right.$ | T-3 | 2.282 | 4 | $\Delta \mathrm{E}=6.3 ; \sigma+2 \pi+2 / 2 \delta$ |
|  | cis- $\left[\left(\eta^{5}, \eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})\right.$ | S-4 | 1.993 | 5 | $\Delta \mathrm{E}=18.1$ |
| 12 | cis $-\left[\left(\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CO}\right)\right.$ | T-1 | 2.606 | 2 | glob. min. $(15,15)$ |
|  | cis-[( $\left.\eta^{5}, \eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CO}\right)$ | Q-2 | 2.708 | 2 | $\Delta \mathrm{E}=1.7$ |
| 13 | $c i s-\left[\left(\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}(\mu-\mathrm{CO})\right.$ | T-1 | 2.416 | 3 | glob. min. $(15,15)$ |
|  | cis-[( $\left.\eta^{5}, \eta^{7}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Cr}_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)$ | Q-2 | 2.467 | 3 | $\Delta \mathrm{E}=8.8$; (16.16) |

[^8]triplet minima, as seen in $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4}$ (Figure 8 f$)$. This range of $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bonds lengths is similar to that in the binuclear cyclopheptatrienylchromium carbonyl series described above. Of interest also are the $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond $(2.282 \AA$ ) and the $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond (1.993 $\AA$ ) appearing in higher lying minima of the tricarbonyl (11), where the quintuply bonded minimum is clearly inaccessible energetically ( $\Delta \mathrm{E}=18.1 \mathrm{kcal} / \mathrm{mol}$ ).

## 6.7. $\mathrm{Cr}-\mathrm{Cr}$ Bond Length Ranges

The experimental and computational findings for $\mathrm{Cr}-\mathrm{Cr}$ bond lengths may be related to the assigned $\mathrm{Cr}-\mathrm{Cr}$ bond orders by noting limits or ranges for the MM distances for $\mathrm{Cr}-\mathrm{Cr}$ bonds of increasing bond orders from single to quintuple. This is carried out for the various classes of dichromium species treated here, with comparisons between computational and experimental results.

The BP86-derived $\mathrm{Cr}-\mathrm{Cr}$ single bond lengths for binuclear chromium carbonyl complexes range from 3.148 to $3.325 \AA$, or $3.24 \pm 0.09 \AA$, which may be compared with the experimental values of 2.98-3.00 $\AA$ for $\mathbf{0 3}$ of Table 13 and $3.26 \AA$ for $\mathbf{0 8}$ of Table 14. The BP86 values of $\mathrm{Cr}=\mathrm{Cr}$ double bonds span the range $2.60 \pm 0.13 \AA$, for which experimental data are lacking. The BP86 values for $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bond distances fall in the range $2.39 \pm 0.11 \AA$, which is comparable to the experimental $R_{M M}$ values of 2.239 and $2.280 \AA$ noted for the carbonyl complexes $\mathbf{0 6}$ and $\mathbf{0 7}$ of Table 13. These results suggest that BP86 ranges for $\mathrm{Cr}-\mathrm{Cr}$ single and $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bond lengths in binuclear chromium carbonyl complexes compare well with the corresponding experimental ranges. However, the BP86 values tend to be somewhat higher than those exhibited in the very limited set of experimental structures. The BP86 median values of $3.236 \AA, 2.597 \AA$ and $2.385 \AA$ for $\mathrm{Cr}-\mathrm{Cr}$ single, double and triple bonds correspond to formal shortness ratios (FSR) values of $1.164,0.934$ and 0.858 respectively.
$\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds in binuclear chromium carbonyl complexes are not known experimentally. The BP86 values for $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds in binuclear chromium carbonyl complexes (two cases only) span the range $2.236 \pm 0.045 \AA$. This rather unrepresentative range may be compared to the experimental ranges for the non-carbonyl paddlewheel complexes of Tables 8 to 10 as follows. The doubly axially coordinated $\mathrm{Cr}_{2}\left(\mathrm{O}_{2} \mathrm{CR}\right)_{4} \mathrm{~L}_{2}$ series (Table 8) has the $R_{M M}$ range $2.38 \pm 0.16 \AA$, while bare tetracarboxylates have $R_{M M}$ values of $1.966 \AA$. The dichromium tetra(alkoxyphenyl) complexes without axial ligands have the lowest $R_{M M}$ value range $(1.85 \pm 0.02 \AA)$. For other complexes without axial ligands (Tables 9 and 10), the tetra(2-oxopyridinate) series has the $R_{M M}$ range $1.91 \pm 0.04 \AA$, the tetra(carboxamidate) series exhibits the same $R_{M M}$ range, while tetraformamidinates yield the broader $R_{M M}$ range $2.09 \pm 0.19 \AA$. Axial coordination always has the effect of increasing $\mathrm{Cr}-\mathrm{Cr}$ bond distances in these paddlewheel complexes. The BP86 quadruple bond lengths for binuclear chromium carbonyl complexes are comparable to those in the tetracarboxylate series with two axial ligands. These $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond lengths are markedly longer than those in experimentally known paddlewheel complexes without axial ligands. The latter span the range 1.828 to $2.272 \AA(2.05 \pm 0.22 \AA)$, where the median $R_{M M}$ values follow the increasing order alkoxyphenyl $<$ carboxamidate $<2$-oxopyridinate $<$ carboxylate $<$ formamidinate, with FSR values ranging from 0.66 to 0.75 .

Quintuple Cr-Cr bonds in the dichromium bis(terphenyl) complexes (Table 11) have experimental lengths in the range $1.821 \pm 0.014 \AA$. Computational estimates lead to lower $R_{M M}$ values for diaryldichromium or RCrCrR complexes in general. Experimental quintuple $\mathrm{Cr}-\mathrm{Cr}$ bond lengths in dichromium diazadiene, formamidinate and guanidinate complexes (Table 12) fall in the range $1.75 \pm 0.05 \AA$. The overall range for all types of quintuply-bonded dichromium complexes is $1.77 \pm 0.07 \AA$, which is significantly shorter than the range $(2.05 \pm 0.22 \AA)$ found in the paddlewheel dichromium complexes assigned $\mathrm{Cr}-\mathrm{Cr}$ bonds of
quadruple order. The median $R_{M M}$ value of $1.770 \AA$ here gives an FSR of 0.64 . The sole quintuple $\mathrm{Cr}-\mathrm{Cr}$ bond length reported for a carbonyl complex (1.993 $\AA$; BP86 value) is noticeably higher than the experimental quintuple bond ranges in non-carbonyl systems.

It is predicted that the presence of carbonyl ligands in dichromium complexes leads to longer $\mathrm{Cr}-\mathrm{Cr}$ multiple bond lengths. This is inferred by comparing BP86 Cr-Cr quadruple and quintuple bond length ranges in four series of binuclear chromium carbonyl complexes (Tables 13 and 14) with the experimental $\mathrm{Cr}-\mathrm{Cr}$ quadruple and quintuple bond length ranges for paddlewheel complexes (Tables 8 to 10) and for dichromium bis(terphenyl), diazadiene, formamidinate and guanidinate complexes (Tables 11 and 12). This is probably more related to the $\mathrm{Cr}-\mathrm{Cr}$ bond lengthening effect of the back-bonding CO ligands in the computationally studied systems than to any systematic inadequacy of the BP86 method. The binuclear titanium carbonyl complexes of Section 4, however, probably suffered more from systematic errors of the BP86 and B3LYP methods than from back-bonding effects of the CO ligands.

## 7. MANGANESE-MANGANESE BONDS

Manganese, along with technetium and rhenium, has the $d^{5} \mathrm{~s}^{2}$ configuration of the Group 7 metals, whose MM bonds were reviewed by Poineau, Sattelberger, Lu and Liddle. ${ }^{277}$ Manganese can give rise to low spin and high spin structures for its complexes. The covalent radius of $1.39 \AA$ estimated for manganese ${ }^{41}$ suggests a length around $2.78 \AA$ for an $\mathrm{Mn}-\mathrm{Mn}$ covalent single bond. Relatively few binuclear dimanganese complexes with MM covalent bonds have been experimentally characterized. This Section deals with the loosely bonded manganese dimer, experimentally characterized dimanganese complexes, homoleptic binuclear manganese carbonyls, binuclear manganese carbonyl complexes containing hydride, fluoroborylene and phospholyl $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)$ ligands, and binuclear manganese carbonyl complexes having the cyclobutadienyl, cyclopentadienyl, benzene, pentalene, and azulene ligands. A survey is then made of trends in MM bond lengths in these dimanganese systems, drawing further data from DFT studies on other series of dimanganese complexes. Owing to the relative paucity of experimental data on $\mathrm{Mn}-\mathrm{Mn}$ bond lengths, most of the MM bond length data discussed here is taken from computational results.

### 7.1. Manganese Dimer

Some experimental and theoretical results for the Mn-Mn distance in the manganese dimer are listed in Table 15. $\mathrm{Mn}_{2}$ was detected by Weltner and coworkers ${ }^{278,279}$ as a van der Waals dimer by electron spin resonance studies, with an Mn-Mn separation of $\sim 3.4 \AA$. This experimental value comes close to the UHF value of $3.5 \AA$ for the high spin state, ${ }^{280}$ the B3LYP DFT value of $3.500 \AA$ for the ${ }^{11} \Sigma^{+}$uigh spin state, ${ }^{34}$ the spin-polarized $\mathrm{X} \alpha$ value of $3.4 \AA$ for an anti-ferromagnetically coupled state,,${ }^{281}$ and the value of $3.34 \AA$ from the Pauling empirical formula. ${ }^{28}$ Four unrestricted DFT methods along with the MP2 method predicted unbound states for the low-spin ${ }^{1} \Sigma^{+} \mathrm{g}$ state of $\mathrm{Mn}_{2} .{ }^{34}$ Four out of six DFT methods in another
study ${ }^{33}$ could not locate the ${ }^{11} \Sigma^{+}$u high spin state, although $\mathrm{Mn}-\mathrm{Mn}$ bond lengths of 1.609 to $1.703 \AA$ were predicted for the ${ }^{1} \Sigma^{+}{ }_{\mathrm{g}}$ state by these DFT methods. It is concluded that the MnMn contact in $\mathrm{Mn}_{2}$ does not involve $4 s$ orbitals but relies on weaker $3 d$ orbital interactions, where the ${ }^{11} \Sigma^{+}{ }_{u}$ high spin state with longer $\mathrm{Mn}-\mathrm{Mn}$ separations is slightly higher in energy than the ${ }^{1} \Sigma^{+} \mathrm{g}$ state. This high spin state with a long Mn $\cdots \mathrm{Mn}$ interaction is reflected in the experimental and empirically derived $R_{M M}$ values. The non-covalently bonded nature of $\mathrm{Mn}_{2}$ is difficult to treat adequately by single-determinant DFT approaches, although the B3LYP value of $R_{M M}$ in the high-spin ${ }^{11} \Sigma^{+}$ustate is quite close to the experimental value.

### 7.2. Experimentally Known Binuclear Manganese Complexes

Covalent MM bonds in dimanganese complexes are not so common, although hundreds of compounds with $\mathrm{Mn}-\mathrm{Mn}$ interactions are listed in the Cambridge Structural Database (512 hits in the CSD version 03/2014, mostly multi-metal clusters). Table 15 lists some experimental $\mathrm{Mn}-\mathrm{Mn}$ distances in binuclear manganese complexes which are shorter than 3.0 $\AA$ and thus more recognizable as $\mathrm{Mn}-\mathrm{Mn}$ bonds. Dimanganese decacarbonyl (structure 02, Figure 9a) was the first known dimanganese complex (1954, Brimm, Lynch and Sesny ${ }^{282}$ ) whose experimental Mn-Mn bond lengths are given in Table 15. XRD studies by Vaida and by Dahl gave $R_{M M}$ values of 2.93 and $2.895 \AA,,^{283,284,285}$ while a gas phase electron diffraction study by Almenningen ${ }^{286}$ gave a distance of $2.98 \AA$ (cf. the BP86 values in Table 16). These suggest $\mathrm{Mn}-\mathrm{Mn}$ interactions of limited strength, with an $\left(\mathrm{Mn}_{2}\right)^{0}$ core. Conversely, the $\left(\mathrm{Mn}_{2}\right)^{4+}$ core in the ketimide complex $\mathbf{0 3}$ has a shorter $R_{M M}$ value of $2.596 \AA$ (Lewis et al. ${ }^{287}$ ), with the magnetic data suggesting antiferromagnetic coupling between the two Mn (II) centres.

Table 15. Mn-Mn Bond Distances for the $\mathbf{M n}_{2}$ Dimer and Experimentally Known Binuclear Manganese Complexes

| Label Species |  | $R_{M M}(\AA)$ | Remarks | Refer- |
| :---: | :---: | :---: | :---: | :---: |
| 01 | $\mathrm{Mn}_{2}$ | $\sim 3.4$ | van der Waals dimer 27 | 278,279 |
|  |  | 3.5 | UHF; high spin | 280 |
|  |  | 3.4 | spin-polarized $\mathrm{X} \alpha$ | 281 |
|  |  | 2.932 | UHF; ${ }^{1}{ }^{+}{ }_{\mathrm{g}}$ | 280 |
|  |  | 1.656 | B3LYP DFT; ${ }^{1} \Sigma^{+}{ }_{\mathrm{g}}$ | 33 |
|  |  | 3.500 | B3LYP DFT; high spin ${ }^{11} \Sigma^{+}{ }_{u}$ | 33 |
|  |  | 2.663 | B3LYP DFT; high spin ${ }^{11} \Pi_{u}$ | 33 |
|  |  | 3.34 | empirical formula | 28 |
| 02 | $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ | 2.92 | XRD | 284 |
|  |  | 2.895 | XRD | 285 |
|  |  | 2.98 | electron diffraction | 286 |
| 03 | $\left[\mathrm{Li}(12-\mathrm{crown}-4)_{2}\right]\left[\mathrm{Mn}_{2}\left(\mathrm{~N}=\mathrm{C}^{\prime} \mathrm{Bu}_{2}\right)_{5}\right]$ | $2.5965(7)$ | $\left(\mathrm{Mn}_{2}\right)^{4+}$; antiferromagnetic | 287 |
| 04 | $\left(\mu-\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{Mn}_{2}$ | 2.277(5) | $\left(\mathrm{Mn}_{2}\right)^{2+}$; sandwich; $\mathrm{fBO}=1$ | 119 |
| 05 | $\left(\mu-\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{H}_{4}-1,4-{ }^{i} \mathrm{Pr}_{3} \mathrm{Si}_{2}\right)_{2} \mathrm{Mn}_{2}$ | 2.609 | $\left(\mathrm{Mn}_{2}\right)^{2+} ;$ sandwich; $\mathrm{fBO}=1$ | 288 |
| 06 | $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mu-\mathrm{CO})_{3}$ | 2.170 | $\left(\mathrm{Mn}_{2}\right)^{2+} ; \mathrm{Mn} \equiv \mathrm{Mn}$ triple bond | 289 |
| 07 | $\mathrm{Cp} *(\mathrm{CO})_{2} \mathrm{Mn}\left(\mu-\mathrm{CH}_{2}\right) \mathrm{Mn}(\mathrm{CO})_{2} \mathrm{Cp}^{*}$ | 2.799 | $\left(\mathrm{Mn}_{2}\right)^{2+}$; bridging carbene ligan | and 291 |
| 08 | $\mathrm{Cp}(\mathrm{CO})_{2} \mathrm{Mn}\left(\mu-\mathrm{CH}_{2}\right) \mathrm{Mn}(\mathrm{CO})_{2} \mathrm{Cp}$ | 2.779 | $\left(\mathrm{Mn}_{2}\right)^{2+}$; bridging carbene ligan | and 291 |
| 09 | $\mathrm{Cp}(\mathrm{CO})_{2} \mathrm{Mn}(\mu-\mathrm{BR}) \mathrm{Mn}(\mathrm{CO})_{2} \mathrm{Cp}$ | 2.79-2.85 | $\left(\mathrm{Mn}_{2}\right)^{2+}$; borylene; $\mathrm{R}=\mathrm{OEt}, \mathrm{Me}$ | - 293 |
| 10 | $\left[\mathrm{Mn}_{2}\left\{\mu-\kappa^{2}-N, N^{\prime}-\mathrm{Me}_{2} \mathrm{Si}(\mathrm{NDipp})_{2}\right\}\right]^{2-}$ | 2.7871(8) | $\left(\mathrm{Mn}_{2}\right)^{2+} ;\left[\mathrm{K}(2,2,2 \text {-cryptant })_{2}\right]^{2+}$ | ${ }^{2+} 294$ |
| 11 | $\left[\mathrm{Mn}_{2}\left\{\mu-\kappa^{2}-N, N^{\prime}-\mathrm{Me}_{2} \mathrm{Si}(\mathrm{NDipp})_{2}\right\}\right]^{-}$ | 2.6848(8) | $\left(\mathrm{Mn}_{2}\right)^{3+} ;\left[\mathrm{K}(18-\text { crown-6)(thf) })_{2}\right.$ | $2]^{+} 294$ |
| 12 | $\left[\mathrm{Mn}_{2}\left\{\mu-\kappa^{2}-N, N^{\prime}-\mathrm{Me}_{2} \mathrm{Si}(\mathrm{NDipp})_{2}\right\}\right]^{-}$ | 2.6851(9) | $\left(\mathrm{Mn}_{2}\right)^{3+} ;\left[\mathrm{K}(2,2,2 \text {-cryptant })_{2}\right]^{+}$ | + 294 |
| 13 | $\left\{\left[\mathrm{HC}(\mathrm{CMeNDipp})_{2}\right] \mathrm{Mn}\right\}_{2}$ | 2.721(1) | $\left(\mathrm{Mn}_{2}\right)^{2+} ; \beta$-diketiminate ligand | d 295 |
| 14 | $\left[\mathrm{Mn}\left\{\eta^{1}: \eta^{3}-\mathrm{N}: \mathrm{C}_{3}-\left({ }^{(t \mathrm{Bu}}\right) \mathrm{C}(\mathrm{NDipp})_{2}\right\}\right]_{2}$ | 2.7170 (9) | $\left(\mathrm{Mn}_{2}\right)^{2+} ;$ high spin; $\mathrm{S}_{1}=\mathrm{S}_{2}=5 / 2$ | 2296 |
| 15 | $\mathrm{Mn}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})\left(\mu-\mathrm{S}_{2}\right)$ | $2.6745(5)$ | $\left(\mathrm{Mn}_{2}\right)^{2+}$; cf. Ref. (299) | 297 |
| 16 | $\mathrm{Mn}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})\left(\mu-\mathrm{S}_{2}\right)\left(\mathrm{RhCp}^{*}\right)$ | 2.7886 (9) | $\left(\mathrm{Mn}_{2}\right)^{2+}$; from 14; $\eta^{5}-\mathrm{Cp}{ }^{*}$ | 298 |
| 17 | $\mathrm{Mn}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})\left(\mu-\mathrm{S}_{2}\right)(\mathrm{CoCp})$ | 2.7714(7) | $\left(\mathrm{Mn}_{2}\right)^{2+}$; from $14 ; \eta^{5}-\mathrm{Cp}$ | 298 |
| 18 | $\mathrm{Mn}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})\left(\mu-\mathrm{Se}_{2}\right)\left(\mathrm{PPh}_{3}\right)$ | 2.702(2) | $\left(\mathrm{Mn}_{2}\right)^{2+}$ | 300 |
| 19 | $\left[\mathrm{PPh}_{3}(\mathrm{CO})_{2} \mathrm{Mn}\right]_{2}(\mu-\mathrm{CO})(\mu-\mathrm{EPh})_{2}$ | 2.64-2.69 | $\mathrm{E}=\mathrm{S}, \mathrm{Se}$; thiolate \& selenolat | ate 301 |
| 20 | $(\mathrm{CO})_{3} \mathrm{Mn}_{2}\left(\eta^{6}, \eta^{4}-\mathrm{C}_{10} \mathrm{H}_{6} \mathrm{Me}_{2}\right)(\mathrm{CO})_{2}$ | 2.9239(8) | $\left(\mathrm{Mn}_{2}\right)^{0}$; bridging PAH ligand | 303 |
| 21 | $(\mathrm{CO})_{3} \mathrm{Mn}_{2}\left(\eta^{6}, \eta^{4}-\mathrm{C}_{16} \mathrm{H}_{10}\right)(\mathrm{CO})_{2}$ | 2.933(3) | $\left(\mathrm{Mn}_{2}\right)^{0}$; bridging PAH ligand | 303 |


a (Tab 15-02)

b (Tab 15-04)

c (Tab 15-06)

d (Tab 15-10)

g (Tab 17-09)

e (Tab 15-15)

h (Tab 18-03)


i (Tab 18-10)

Figure 9. Some experimentally known and computationally studied dimanganese complexes (giving Table number with label)

Complexes $\mathbf{0 4}$ to $\mathbf{0 9}$ and $\mathbf{1 2}$ to $\mathbf{1 7}$ have $\left(\mathrm{Mn}_{2}\right)^{2+}$ cores. The permethylpentalene complex $\left(\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{Mn}_{2} \mathbf{0 4}$ (Figure 9b) has a short $R_{M M}$ value of $2.277 \AA$ suggesting a multiple bond, although the fBO value is 1 from the 18 -electron rule. ${ }^{119}$ DFT results yield a cBO value of 1.13. The similar complex $\mathbf{0 5}$, however, has a longer $\mathrm{Mn}-\mathrm{Mn}$ distance of $2.609 \AA$ consistent with a $\mathrm{Mn}-\mathrm{Mn}$ single bond. ${ }^{288}$ The shortest $\mathrm{Mn}-\mathrm{Mn}$ bond length known to date is $2.170 \AA$ in $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3} 06$ (Figure 9c), consistent with an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond (Herrmann ${ }^{289,290}$ ). Binuclear cyclopentadienylmanganese carbonyl complexes with a bridging carbene ligand (structures 07 and 08, Herrmann ${ }^{291,292}$ ) or with borylene ligands BR (structure $\mathbf{0 9}, \mathrm{R}=\mathrm{OEt}$, Mes, Braunschweig ${ }^{293}$ ) give much longer $R_{M M}$ values ( 2.78 to $2.85 \AA$ ), where the $\mathrm{Mn}-\mathrm{Mn}$ fBO may be assigned as unity. A similar value of $2.787 \AA$ is seen in structure $\mathbf{1 0}$ with $\mathrm{Me}_{2} \mathrm{Si}(\mathrm{NDipp})_{2}$ ligands (Figure 9d), although an increase in charge of the $\mathrm{Mn}_{2}$ core to +3 in $\mathbf{1 1}$ and $\mathbf{1 2}$ results in shorter Mn-Mn distances of $2.685 \AA$ (Tsai and coworkers ${ }^{294}$ ).
$\mathrm{Mn}-\mathrm{Mn} R_{M M}$ values around $2.72 \AA$ are seen in the $\beta$-ketiminate complex 13 and the high spin complex 14 (Gatteschi ${ }^{295}$, Jones ${ }^{296}$ ). Complexes 15 (Figure 9e), 16 and 17 have ( $\mu-\mathrm{S}_{2}$ ) ligands, where addition of the $\mathrm{RhCp} *$ and CoCp moieties increases the $R_{M M}$ value of $2.675 \AA$ in $\mathbf{1 5}$ to $2.789 \AA$ and $2.771 \AA$ in $\mathbf{1 6}$ and $\mathbf{1 7}$ (Ermenko ${ }^{297}$, Adams ${ }^{298}$ ). The Mn-Mn interaction in $\mathbf{1 5}$ is weaker than the $\mathrm{Fe}-\mathrm{Fe}$ interaction in the similar $\mathrm{Fe}_{2}(\mathrm{CO})_{6}\left(\mu-\mathrm{S}_{2}\right)$ according to QTAIM analyses. ${ }^{299}$ Complex 18 and 19 contain the $\mathrm{PPh}_{3}$ ligand, where 18 with a ( $\mu-\mathrm{Se}_{2}$ ) ligand has an $R_{M M}$ value of $2.702 \AA$ ( Belletti $^{300}$ ) while the complexes in entry 19 with thiolate and selenolate ligands have $\mathrm{Mn}-\mathrm{Mn}$ distances ranging from 2.64 to $2.69 \AA$ (Reyes-Lezama ${ }^{301,302}$ ).

The above dimanganese complexes in Table 15 exhibit an upper $R_{M M}$ limit of about $2.8 \AA$. Most of these have an $\left(\mathrm{Mn}_{2}\right)^{2+}$ core, where the $R_{M M}$ values are often not far from the $2.78 \AA$ distance for an $\mathrm{Mn}-\mathrm{Mn}$ single bond estimated by doubling the manganese covalent radius. Most of these structures may be regarded as containing Mn-Mn single bonds of varying strengths. However, complexes $\mathbf{0 4}$ and $\mathbf{0 6}$ have short $R_{M M}$ distances of 2.28 and $2.17 \AA$,
respectively, suggesting Mn-Mn multiple bonds. Longer Mn-Mn distances of 2.92 and $2.93 \AA$ are found in the $\left(\mathrm{Mn}_{2}\right)^{0}$ complexes 20 and 21 containing binuclear and tetranuclear PAH ligands (Overly and coworkers ${ }^{303}$ ) comparable to the $\mathrm{Mn}(0)-\mathrm{Mn}(0)$ length in $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$. An oxo bridged binuclear $\mathrm{Mn}(\mathrm{III})$ complex with tridentate ONO ligands has an $R_{M M}$ distance of $2.994 \AA$ (Yahsi and Kara ${ }^{304}$ ). Even longer $R_{M M}$ distances of 3.15 to $3.26 \AA$ are found in a series of binuclear manganese complexes containing bridging carboxylate and oxo groups. ${ }^{305}$ The $\mathrm{Mn}-\mathrm{Mn}$ distance of $3.275 \AA$ in a binuclear $\mathrm{Mn}(\mathrm{III})$ complex with a bridging 2-salicyloylhydrazono-1,3-dithiane ligand ( $\mathrm{Welter}^{306}$ ) approaches the non-covalently bonded distance of $3.4 \AA$ in the van der Waals manganese dimer. Such $R_{M M}$ values of over $3 \AA$ do not suggest strong covalent $\mathrm{Mn}-\mathrm{Mn}$ bonding.

### 7.3. Homonuclear Binuclear Manganese Carbonyl Complexes

Table 16 lists BP86 Mn-Mn bond lengths and corresponding formal bond orders for the homoleptic binuclear manganese carbonyls $\mathrm{Mn}_{2}(\mathrm{CO})_{n}(n=10,9,8,7,6) .{ }^{307,308}$ Experimental $R_{M M}$ distances for $\mathrm{Mn}_{2}(\mathrm{CO})_{10} 01$ (Table 15) range from 2.90 to $2.98 \AA,{ }^{284-286}$ comparing well with the BP86 result of $2.954 \AA$ for the ground state singlet $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ (Table 16) having a $\mathrm{Mn}-\mathrm{Mn}$ single bond and no bridging CO ligands.

The enneacarbonyl $\mathrm{Mn}_{2}(\mathrm{CO})_{9} \mathbf{0 2}$ has been suggested (Dunkin et al. ${ }^{309}$, Church $^{310}$ ) as a photolysis product of $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$. The global minimum S-1 with an $\mathrm{Mn}-\mathrm{Mn}$ single bond length of $2.914 \AA$ has 4 terminal CO groups on each Mn atom and a four-electron donor $\eta^{2}-\mu-$ CO group bridging the $\mathrm{Mn}_{2}$ unit. The $\mathrm{Mn}_{2}(\mathrm{CO})_{9}$ isomer $\mathrm{S}-2$, lying $9.2 \mathrm{kcal} / \mathrm{mol}$ in energy above S-1, has a long $\mathrm{Mn}=\mathrm{Mn}$ double bond of length $2.704 \AA$ in a zwitterionic structure $(\mathrm{CO})_{5} \mathrm{Mn}^{+}=\mathrm{Mn}^{-}(\mathrm{CO})_{4}$. The lowest energy triplet $\mathrm{Mn}_{2}(\mathrm{CO})_{9}$ structure $\mathrm{T}-3$ has an $\mathrm{Mn}=\mathrm{Mn}$ double bond of length $2.413 \AA$ of the $\sigma+2 / 2 \pi$ type similar to triplet $\mathrm{O}_{2}$.

Table 16. BP86 Mn-Mn Bond Distances in Binuclear Manganese Carbonyl Complexes (Homoleptic and with Hydride, Fluoroborylene and $\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}$ Ligands) ${ }^{a}$
Label Complex - -------------------------------------------------------------------------------------------------------------------

Homoleptic binuclear manganese carbonyls (BP86 results; Refs.307,308)

| $\mathbf{0 1}$ | $(\mathrm{CO})_{5} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-1$ | 2.954 | 1 | BP86; cf. exptl. data (Table 15) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 2}$ | $(\mathrm{CO})_{4}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{\mathrm{Mn}_{2}(\mathrm{CO})_{4}}$ | $\mathrm{~S}-1$ | 2.914 | 1 | global min. |
|  | $(\mathrm{CO})_{4} \mathrm{Mn}=\mathrm{Mn}(\mathrm{CO})_{5}$ | $\mathrm{~S}-2$ | 2.704 | 2 | $\Delta \mathrm{E}=7.2 ;$ no $\mu-\mathrm{CO}$ |
|  |  | $\mathrm{T}-3$ | 2.413 | 2 | $\sigma+2 / 2 \pi$ type |
| $\mathbf{0 3}$ | $(\mathrm{CO})_{4} \mathrm{Mn} \equiv \mathrm{Mn}(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.300 | 3 | $\mathrm{No} \mu-\mathrm{CO}$; cf. Ref. 311 |
|  | $(\mathrm{CO})_{3} \mathrm{Mn} \equiv \mathrm{Mn}(\mathrm{CO})_{5}$ | $\mathrm{~S}-2$ | 2.341 | 3 | $\Delta \mathrm{E}=2.6$; dative Mn-Mn bond |
|  | $(\mathrm{CO})_{3}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-3$ | 2.720 | 1 | $\Delta \mathrm{E}=5.8$ |
|  | $(\mathrm{CO})_{3}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-4$ | 2.731 | 1 | $\Delta \mathrm{E}=9.6$ |
| $\mathbf{0 4}$ | $(\mathrm{CO})_{3}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.207 | 4 | $\sigma+2 \pi+\delta$ |
|  | $(\mathrm{CO})_{3}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.324 | 4 | $\Delta \mathrm{E}=3.0 ; \sigma+2 \pi+\delta$ |
| $\mathbf{0 5}$ | $(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.527 | 3 | $\mathrm{~T}-\mathrm{CO}$ groups trans |
|  | $(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-2$ | 2.572 | 3 | $\mathrm{~T}-\mathrm{CO}$ groups cis; $\Delta \mathrm{E}=1.2$ |
|  | $(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~T}-3$ | 2.456 | 3 | $\Delta \mathrm{E}=2.8$ |
|  | $(\mathrm{CO})_{2}(\mu-\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}(\mathrm{CO})_{2} \mathrm{~T}-4$ | 2.305 | 3 | $\Delta \mathrm{E}=3.4 ;(15,17)$ |  |
|  | $(\mathrm{CO})_{3} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-5$ | 2.173 | 4 | $\Delta \mathrm{E}=6.0 ;(16,18)$ |

Binuclear manganese carbonyl hydrides (BP86 results; Ref. 312)

| $\mathbf{0 6}$ | $(\mathrm{CO})_{5} \mathrm{Mn}_{2}\left(\eta^{2}-\mathrm{H}_{2}\right)(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.933 | 1 | $\Delta \mathrm{E}=0.0 ;$ no $\mu-\mathrm{CO} ; \mathrm{H}_{2}$ ligand |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  | $(\mathrm{CO})_{5}(\mu-\mathrm{H}) \mathrm{Mn}_{2}(\mathrm{CO})_{4} \mathrm{H}$ | $\mathrm{S}-2$ | 3.095 | 1 | $\Delta \mathrm{E}=8.3$; weak single bond |
| $\mathbf{0 7}$ | $(\mathrm{CO})_{4}(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.703 | 2 | $\Delta \mathrm{E}=0.0 ; 2(\mu-\mathrm{H})$ groups |
| $\mathbf{0 8}$ | $(\mathrm{CO})_{4}(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.341 | 3 | $\Delta \mathrm{E}=0.0 ; 2(\mu-\mathrm{H})$ groups |
| $\mathbf{0 9}$ | $(\mathrm{CO})_{3}(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{~s} \mu-\mathrm{CO})(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.377 | 3 | $\Delta \mathrm{E}=0.0 ; 3$ bridging groups |
|  | $(\mathrm{CO})_{3}(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.522 | 3 | $\Delta \mathrm{E}=5.6 ; 2(\mu-\mathrm{H})$ groups |
|  | $(\mathrm{CO})_{3}(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-3$ | 2.296 | 4 | $\Delta \mathrm{E}=6.6 ; 2(\mu-\mathrm{H})$ groups |
|  | $(\mathrm{CO})_{3}(\mathrm{~s} \mu-\mathrm{CO})(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~T}-3$ | 2.382 | 3 | $\Delta \mathrm{E}=6.7 ; 2(\mu-\mathrm{H})$ groups; $(17,17)$ |

Fluoroborylene dimanganese carbonyls (BP86 results; Ref. 313)

| 10 | $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{9}$ | $\mathrm{~S}-1$ | 2.787 | 1 | $\Delta \mathrm{E}=0.0 ; \mu-\mathrm{BF}$ |
| :---: | :--- | :--- | :--- | :--- | :--- |
|  |  | $\mathrm{S}-2$ | 2.931 | 1 | $\Delta \mathrm{E}=3.6 ;$ no bridging |
|  |  | $\mathrm{S}-3$ | 3.035 | 1 | $\Delta \mathrm{E}=6.9 ;$ no bridging |
| $\mathbf{1 1}$ | $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{8}$ | $\mathrm{~T}-1$ | 2.497 | 1 | $\Delta \mathrm{E}=2.4 ; \mu-\mathrm{BF}$ |
|  |  | $\mathrm{T}-2$ | 2.467 | 2 | $\Delta \mathrm{E}=3.2 ; \mu-\mathrm{BF} ; 2 \mu-\mathrm{CO}$ |
|  |  | $\mathrm{T}-3$ | 2.641 | 1 | $\Delta \mathrm{E}=7.6 ; \mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
| $\mathbf{1 2}$ | $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{7}$ | $\mathrm{~T}-1$ | 2.449 | 2 | $\Delta \mathrm{E}=7.7 ; \mu-\mathrm{BF}, \mu-\mathrm{CO} ;(17,17)$ |
|  |  | $\mathrm{T}-2$ | 2.492 | 1 | $\Delta \mathrm{E}=9.8 ; \mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
|  |  | $\mathrm{T}-3$ | 2.534 | 1 | $\Delta \mathrm{E}=7.9 ; \mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
| $\mathbf{1 3}$ | $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{6}$ | $\mathrm{~T}-1$ | 2.548 | 1 | $\Delta \mathrm{E}=0.0 ; \mu-\mathrm{BF}, \mu-\mathrm{CO} ;(17,17)$ |
|  |  |  | n 86 |  |  |


| $\mathrm{S}-2$ | 2.291 | 3 | $\Delta \mathrm{E}=4.7 ; \mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{T}-3$ | 2.548 | 1 | $\Delta \mathrm{E}=4.9 ; \mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
| $\mathrm{T}-4$ | 2.318 | 3 | $\Delta \mathrm{E}=5.6 ; \mu-\mathrm{BF}$ |
| $\mathrm{T}-5$ | 2.242 | 3 | $\Delta \mathrm{E}=8.0 ; \mu-\mathrm{BF}$ |

Binuclear phospholyl manganese carbonyls (BP86 results; Ref. 314)
$14\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$
S-1 $2.167 \quad 3 \quad \Delta \mathrm{E}=0.0 ; 2 \mu-\mathrm{CO}$
$15\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$
T-1 $2.920 \quad 1 \quad \Delta \mathrm{E}=0.0 ;\left(\eta^{5}-\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2} ;(17,17)$
T-2 $2.1523 \quad \Delta \mathrm{E}=1.0 ; \eta^{5}, \eta^{1}$-mode; $\mu-\mathrm{CO}$
T-3 $2.196 \quad 3 \quad \Delta \mathrm{E}=3.7 ; 2 \mu-\mathrm{CO} ;(17,17)$
S-4 $2.068 \quad 3 \quad \Delta \mathrm{E}=6.0 ; 2 \mu-\mathrm{CO} ;(18,18)$
S-5 $2.067 \quad 3 \quad \Delta \mathrm{E}=6.3 ; 2 \mu-\mathrm{CO} ;(18,18)$

[^9]For the octacarbonyl $\mathrm{Mn}_{2}(\mathrm{CO})_{8} \mathbf{0 3}$, the global minimum $\mathrm{S}-1$ is the symmetrical unbridged (CO) ${ }_{4} \mathrm{Mn} \equiv \mathrm{Mn}(\mathrm{CO})_{4}$ with an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond length of $2.300 \AA$, close to the results of another DFT study (Barckholtz and Bursten ${ }^{311}$ ). A slightly higher energy isomer S-2, has an unsymmetrical $(\mathrm{CO})_{3} \mathrm{Mn} \equiv \mathrm{Mn}(\mathrm{CO})_{5}$ structure with a dative $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length $2.341 \AA$. The still higher energy $\mathrm{Mn}_{2}(\mathrm{CO})_{8}$ structures $\mathrm{S}-3$ and $\mathrm{S}-4$ have two $\eta^{2}-\mu-\mathrm{CO}$ groups and $\mathrm{Mn}-\mathrm{Mn}$ single bonds of lengths 2.720 and $2.731 \AA$, respectively. The $\eta^{2}-\mu-\mathrm{CO}$ groups shorten the $\mathrm{Mn}-\mathrm{Mn}$ single bonds in the minima S-3 and S-4 of $\mathrm{Mn}_{2}(\mathrm{CO})_{8}$, and in the global minimum S-1 of $\mathrm{Mn}_{2}(\mathrm{CO})_{9}$, as compared with the $\mathrm{Mn}-\mathrm{Mn}$ single bond length of unbridged $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$.

The heptacarbonyl $\mathrm{Mn}_{2}(\mathrm{CO})_{7} \mathbf{0 4}$ has two minima $\mathrm{S}-1$ and $\mathrm{S}-2$ with quadruple $\mathrm{Mn}-\mathrm{Mn}$ bonds of the $\sigma+2 \pi+\delta$ type of lengths 2.207 and $2.324 \AA$, respectively. For the hexacarbonyl $\mathrm{Mn}_{2}(\mathrm{CO})_{6}(\mathbf{0 5})$ the two lowest energy minima S-1 and S-2 are cis and trans isomers, both with two four-electron donor $\eta^{2}-\mu$-CO groups and $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds of lengths 2.527 and $2.572 \AA$, respectively. The triplet $\mathrm{Mn}_{2}(\mathrm{CO})_{6}$ structure T-3 with two bridging CO ligands has an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length $2.456 \AA$, while T-4 with a $(15,17)$ configuration also has a $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length $2.305 \AA$. The unbridged $\mathrm{Mn}_{2}(\mathrm{CO})_{6}$ isomer S-5, lying
$6.0 \mathrm{kcal} / \mathrm{mol}$ in energy above $\mathrm{S}-1$, is unusual in having a very short quadruple $\mathrm{Mn}-\mathrm{Mn}$ bond of length $2.173 \AA$ corresponding to a $(16,18)$ core configuration.

### 7.4. Binuclear Manganese Carbonyl Complexes with Hydride, BF, and $\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}$ Ligands

 BP86 studies have been carried out on binuclear manganese carbonyl complexes incorporating the hydride, fluoroborylene, and phospholyl $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)$ ligands (Table 16). In the binuclear manganese carbonyl hydrides $\mathrm{Mn}_{2} \mathrm{H}_{2}(\mathrm{CO})_{n}(n=9,8,7,6),{ }^{312}$ a preference for bridging hydride (or dihydrogen) ligands over bridging carbonyl ligands is predicted. The complex $\mathrm{H}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{9} \mathbf{0 6}$ has a bridging dihydrogen $\left(\eta^{2}-\mathrm{H}_{2}\right)$ ligand in the global minimum S-1 with an $R_{M M}$ value of $2.933 \AA$, indicating an $\mathrm{Mn}-\mathrm{Mn}$ single bond. The higher energy $\mathrm{Mn}_{2} \mathrm{H}_{2}(\mathrm{CO})_{9}$ minimum S-2 with one bridging hydride ligand has a somewhat longer $\mathrm{Mn}-\mathrm{Mn}$ single bond length of $3.095 \AA$. All of the other members of this series have two bridging hydride $(\mu-\mathrm{H})$ ligands. The $\mathrm{Mn}_{2} \mathrm{H}_{2}(\mathrm{CO})_{8}$ compound 07 (Figure 9f) has the structure $(\mathrm{CO})_{4}(\mu-\mathrm{H})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ and an $\mathrm{Mn}=\mathrm{Mn}$ double bond length of $2.703 \AA$. The $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond lengths in the $\mathrm{Mn}_{2} \mathrm{H}_{2}(\mathrm{CO})_{n}$ series range from 2.341 to $2.522 \AA$. The $\mathrm{Mn}-\mathrm{Mn}$ quadruple bond in S-3 for $\mathrm{Mn}_{2}(\mu-\mathrm{H})_{2}(\mathrm{CO})_{6}$ has an $R_{M M}$ value of $2.296 \AA$. The two bridging hydride ligands in $\mathbf{0 7}, \mathbf{0 8}$, and $\mathbf{0 9}$ effectively protonate the $\mathrm{Mn}-\mathrm{Mn}$ multiple bonds. These complexes are predicted to be viable with respect to dissociation into mononuclear fragments suggesting possible synthetic targets.BP86 predictions for the dimanganese fluoroborylene carbonyl series $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{n}(n=$ $9,8,7,6)^{313}$ are given in Table 16. The $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{9}$ system $\mathbf{1 0}$ has three singlet minima within $6.9 \mathrm{kcal} / \mathrm{mol}$, with $\mathrm{Mn}-\mathrm{Mn}$ single bond lengths ranging from 2.787 to $3.035 \AA$. The $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{8}$ system 11 has three triplet minima within $7.6 \mathrm{kcal} / \mathrm{mol}$, where $\mathrm{T}-1$ and $\mathrm{T}-3$ have $\mathrm{Mn}-\mathrm{Mn}$ single bonds of lengths 2.497 and $2.641 \AA$, respectively, while T-2 has an $\mathrm{Mn}=\mathrm{Mn}$ double bond length of $2.467 \AA$. The $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{7}$ system 12 has four triplet
minima within $9.0 \mathrm{kcal} / \mathrm{mol}$. The lowest energy such triplet structure $\mathrm{T}-1$ has an $\mathrm{Mn}=\mathrm{Mn}$ double bond length of $2.449 \AA$. The higher energy $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{7}$ structures T-2 and T-3 have $\mathrm{Mn}-\mathrm{Mn}$ single bonds of lengths 2.492 and $2.534 \AA$, respectively. The $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{6}$ system $\mathbf{1 3}$ has one singlet and four triplet minima within $8.0 \mathrm{kcal} / \mathrm{mol}$, all with bridging BF ligands. The lowest energy triplet $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{6}$ structures $\mathrm{T}-1$ and $\mathrm{T}-3$ have $\mathrm{Mn}-\mathrm{Mn}$ single bonds of length $2.548 \AA$, while the $\mathrm{Mn}_{2}(\mathrm{BF})(\mathrm{CO})_{6}$ structures $\mathrm{S}-2, \mathrm{~T}-4$ and $\mathrm{T}-5$ have $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds with lengths ranging from 2.291 to $2.242 \AA$.

The BP86 results for the binuclear phospholylmanganese carbonyl series $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2}(\mathrm{CO})_{n}\left(\right.$ Table 16) cover only the tricarbonyls and dicarbonyls $(n=3,2) .{ }^{314}$ The sole singlet $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2}(\mathrm{CO})_{3}$ minimum has an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length $2.167 \AA$, close to Herrmann's experimental $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond length ${ }^{289}$ of $2.170 \AA$ in $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mu-\mathrm{CO})_{3}$ (structure 06 of Table 15). For the dicarbonyl $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2}(\mathrm{CO})_{2}$, only the ground state triplet has an $\mathrm{Mn}-\mathrm{Mn}$ single bond ( $2.920 \AA$ ), while the other five minima have $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds ranging from 2.067 to $2.196 \AA$ in length.

### 7.5. Binuclear Manganese Carbonyl Complexes with Carbocyclic Ligands

DFT studies have been reported on binuclear manganese carbonyl complexes incorporating a variety of cyclic organometallic ligands including cyclobutadiene, cyclopentadienyl, benzene, pentalene and azulene (Table 17). The cyclobutadiene series $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2}(\mathrm{CO})_{n}$ series ( $n=6$, $5,4,3)^{315}$ has one low-energy singlet minimum 01 for $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2}(\mathrm{CO})_{6}$ with a long $\mathrm{Mn} \cdots \mathrm{Mn}$ separation of $3.037 \AA$, comparable to that in the homoleptic $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$. The $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2}(\mathrm{CO})_{5}$ system 02 has minima $\mathrm{T}-1$ and $\mathrm{S}-2$ with long $\mathrm{Mn}=\mathrm{Mn}$ double bonds ( $2.650 \AA$ ), T-3 with a long Mn-Mn single bond ( $3.058 \AA$ ), and the high energy S-4 with an $\mathrm{Mn}=\mathrm{Mn}$ double bond $(2.605 \AA)$. The $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2}(\mathrm{CO})_{4}$ system 03 has a triplet global minimum T-1 with an Mn-Mn single bond of length $2.860 \AA$ and minima S-2 and S-3 with
$\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds of lengths 2.210 and $2.310 \AA$, respectively. The $\mathrm{Mn}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2}(\mathrm{CO})_{3}$ system 04 has a triplet global minimum with an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length $2.433 \AA$.

Table 17. Mn-Mn Bond Distances in Binuclear Manganese Carbonyl Complexes with Cyclobutadiene and Cyclopentadienyl Ligands ${ }^{a}$
Label Complex

Binuclear cyclobutadiene manganese carbonyls (B3LYP results; Ref. 315)

| $\mathbf{0 1}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{6}$ | $\mathrm{~S}-1$ | 3.037 | 1 | $\Delta \mathrm{E}=0.0 ; 2 \mu-\mathrm{CO}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 2}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~T}-1$ | 2.650 | 2 | $\Delta \mathrm{E}=0.0 ; 2 \mu-\mathrm{CO}$ |
|  | $\mathrm{S}-2$ | 2.650 | 2 | $\Delta \mathrm{E}=1.9 ; 2 \mu-\mathrm{CO}$ |
|  | $\mathrm{T}-3$ | 3.058 | 1 | $\Delta \mathrm{E}=4.2 ; 2 \mu-\mathrm{CO}$ |
| $\mathbf{0 3}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ | $\mathrm{~S}-4$ | 2.605 | 2 | $\Delta \mathrm{E}=10.5 ; 2 \mu-\mathrm{CO}$ |
|  | $\mathrm{T}-1$ | 2.860 | 1 | $\Delta \mathrm{E}=0.0 ; 4 \mu-\mathrm{CO} ;(17,17)$ |
| $\mathbf{0 4}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.210 | 3 | $\Delta \mathrm{E}=3.3 ;$ no bridging |
|  | $\mathrm{S}-3$ | 2.310 | 2 | $\Delta \mathrm{E}=7.9 ;$ no bridging |
|  | $\mathrm{T}-1$ | 2.433 | 3 | $\Delta \mathrm{E}=0.0 ; \eta^{5}, \eta^{1}-\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} ;(17,17)$ |

Binuclear cyclopentadienyl manganese carbonyls (BP86 results; Ref. 316)

```
05 Cp}2\mp@subsup{\textrm{Mn}}{2}{(\mu-CO)(s\mu-CO)2(CO)2
    cis }\mp@subsup{\textrm{Cp}}{2}{}\mp@subsup{\textrm{Mn}}{2}{(}(\mu-\textrm{CO})(\textrm{s}\mu-\textrm{CO})(\textrm{CO}\mp@subsup{)}{3}{
06 trans }\mp@subsup{\textrm{Cp}}{2}{}\mp@subsup{\textrm{Mn}}{2}{}(\textrm{s}\mu-\textrm{CO}\mp@subsup{)}{2}{}(\textrm{CO}\mp@subsup{)}{2}{}\quad\textrm{S}-1\quad2.509 2 global min.
    trans }\mp@subsup{\textrm{Cp}}{2}{}\mp@subsup{\textrm{Mn}}{2}{}(\textrm{s}\mu-\textrm{CO})44 T-2 2.457 2 \DeltaE=1.0; small iv
    Cp}\mp@subsup{\mp@code{2Mn}}{2}{}(\textrm{s}\mu-\textrm{CO}\mp@subsup{)}{4}{}\quad\mathrm{ T-3 2.461 2 
```




```
    (\eta}\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{5}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Mn}}{2}{}(\mu-\textrm{CO}\mp@subsup{)}{3}{
08 Cp}\mp@subsup{2}{2}{}\mp@subsup{\textrm{Mn}}{2}{(}\mu-\textrm{CO}\mp@subsup{)}{2}{
    Cp2Mn}2(\mu-CO)
09 Cp}\mp@subsup{2}{2}{}\mp@subsup{\textrm{Mn}}{2}{}(\mp@subsup{\eta}{}{2}-\mu-\textrm{CO}
    Cp2}\mp@subsup{\textrm{Mn}}{2}{}(\mp@subsup{\eta}{}{2}-\mu-\textrm{CO}
    Cp2}\mp@subsup{\textrm{Mn}}{2}{}(\mp@subsup{\eta}{}{2}-\mu-\textrm{CO}
    Cp2Mnn}(\mu-\textrm{CO}
    S-1 2.167 3 BP86
S-1 2.202 3 global min.; (17,17); small iv
T-2 2.067 4 \DeltaE=3.3; small iv
T-1 2.191 3 (16,16)
H-2 2.523 1 (15,15)
Q-3 2.109 3 (16,16)
S-4 1.879 5 
```

[^10]BP86 predictions for $\mathrm{Mn}-\mathrm{Mn}$ bond lengths in the binuclear cyclopentadienylmanganese carbonyl series $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{n}\left(n=5,4,3,2 ; \mathrm{Cp}=\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$ are given in Table 17. ${ }^{316}$ The $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ system 05 has the singly bridged $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})$ structure $\mathrm{S}-1$ as the global minimum with an $R_{M M}$ value of $2.804 \AA$ consistent with an $\mathrm{Mn}-\mathrm{Mn}$ single bond. The BP86 $v(\mathrm{CO})$ data suggests that the transient species detected by Poliakoff in the laser photolysis of $\mathrm{CpMn}(\mathrm{CO})_{3}$ has this structure. ${ }^{317}$ The $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ structure S-2, lying 7.4 $\mathrm{kcal} / \mathrm{mol}$ in energy above $\mathrm{S}-1$, has an $\mathrm{Mn}-\mathrm{Mn}$ single bond length of $2.846 \AA$. The $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ system 06 has two singlet and two triplet minima, all with $\mathrm{Mn}=\mathrm{Mn}$ double bonds ranging in length from 2.457 to $2.509 \AA$. The lowest energy structure in the $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ system 07 is the triply bridged $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mu-\mathrm{CO})_{3}$ structure $\mathrm{S}-1$ with a BP86 $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond length of $2.167 \AA$, which is very close to the Herrmann experimental value of $2.170 \AA .{ }^{290}$ The $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ system 08 has a singlet global minimum with an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond length of $2.202 \AA$, while the higher energy triplet T-2 has an $\mathrm{Mn}-\mathrm{Mn}$ quadruple bond length of $2.067 \AA$. BP86 results on the monocarbonyl $\mathrm{Cp}_{2} \mathrm{Mn}_{2} \mathrm{CO}$ gave a variety of minima with $R_{M M}$ values as follows: T-1 (2.191 $\AA$ ), H-2 (2.523 $\left.\AA\right), \mathrm{Q}-3(2.109 \AA)$, and S-4 (1.879 $\AA$ ). The $\mathrm{Cp}_{2} \mathrm{Mn}_{2} \mathrm{CO}$ structure S-4 (Figure 9h), lying $11.1 \mathrm{kcal} / \mathrm{mol}$ in energy above the global minimum T-1, is of interest since it has a formal $\mathrm{Mn}-\mathrm{Mn}$ quintuple bond of length $1.879 \AA$, somewhat longer than the $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond in the first known quintuply bonded MM complex synthesized by Power and coworkers. ${ }^{222}$

All of the low-energy structures in the benzene series ${ }^{318} \mathrm{Mn}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{n}(n=4,3,2,1)$ have the benzene ligands as hexahapto $\eta^{6}-\mathrm{C}_{6} \mathrm{H}_{6}$ ligands (Table 18). The $\mathrm{Mn}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{4}$ system 01 has three singlet minima with $\mathrm{Mn}-\mathrm{Mn}$ single bond distances ranging from 2.654 to
 global singlet minimum with an $\mathrm{Mn}=\mathrm{Mn}$ double bond of length $2.447 \AA$. A higher energy triplet $\mathrm{Mn}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{3}$ structure T-2 has an $\mathrm{Mn}-\mathrm{Mn}$ single bond of length $2.570 \AA$, while

Table 18. Mn-Mn Bond Distances for Binuclear Manganese Carbonyl Complexes with Benzene, Pentalene and Azulene Ligands ${ }^{a}$


Binuclear pentalene manganese carbonyls (BP86 results; Ref. 319)

| $\mathbf{0 5}$ cis- $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{3} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 3.204 | 1 | Weak bond; $(18,18)$ |
| :---: | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 6}\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.873 | 1 | Glob. min. |
| $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{3} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~T}-2$ | 2.958 | 1 | $(17,17)$ |
| $\mathbf{0 7}\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.246 | 3 | $\mathrm{No} \mu-\mathrm{CO}$ |
| $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})(\mu-\mathrm{CO}) \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-2$ | 2.734 | 1 | $\Delta \mathrm{E}=5.9 ;(18,16)$ |
| $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{2} \mathrm{Mn}(\mu-\mathrm{CO}) \mathrm{Mn}(\mathrm{CO})$ | $\mathrm{T}-3$ | 2.445 | 2 | $\Delta \mathrm{E}=6.2 ;(17,17) ;$ dipolar MM bond |
| $\mathbf{0 8}\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Mn}(\mu-\mathrm{CO}) \mathrm{Mn}(\mathrm{CO})_{2}$ | $\mathrm{~T}-1$ | 2.274 | 3 | $(17,17)$ |
| $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}_{2}(\mathrm{CO})$ | $\mathrm{T}-2$ | 2.602 | 2 | $\Delta \mathrm{E}=1.0 ;(17,17)$ |
| $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{Q}-3$ | 2.583 | 2 | $\sigma+2 / 2 \pi$ |
| $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{2} \mathrm{Mn}_{2}(\mathrm{CO})$ | $\mathrm{S}-4$ | 2.289 | 4 | $\Delta \mathrm{E}=5.4 ;$ dipolar MM bond |

Binuclear azulene manganese carbonyls (BP86 results; Ref. 320)

| $\mathbf{0 9} \mathrm{C}_{10} \mathrm{H}_{8} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-1$ | 3.025 | 1 | $\Delta \mathrm{E}=0.0 ; \eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}(c i s)$ |
| :--- | :--- | :--- | :--- | :--- |
|  | $\mathrm{S}-2$ | 2.969 | 1 | $\Delta \mathrm{E}=1.5 ; \eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}(c i s)$ |
| $\mathbf{1 0} \mathrm{C}_{10} \mathrm{H}_{8} \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ | $\mathrm{~T}-1$ | 2.758 | 1 | $\Delta \mathrm{E}=0.0 ; \eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8} ; \mu-\mathrm{CO} ;(17,17)$ |
|  | $\mathrm{S}-2$ | 2.763 | 2 | $\Delta \mathrm{E}=7.2 ; \eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8}$ |
| $\mathbf{1 1} \mathrm{C}_{10} \mathrm{H}_{8} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.359 | 3 | $\Delta \mathrm{E}=0.0 ; \eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8} ; \mu-\mathrm{CO}$ |
|  | $\mathrm{S}-2$ | 2.707 | 2 | $\Delta \mathrm{E}=4.3 ; \eta^{5}, \eta^{5}-\mathrm{C}_{10} \mathrm{H}_{8} ; \mu-\mathrm{CO}$ |
| $\mathbf{1 2} \mathrm{C}_{10} \mathrm{H}_{8} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~T}-3$ | 2.768 | 1 | $\Delta \mathrm{E}=7.2 ; \eta^{5}, \eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8} ; \mu-\mathrm{CO}(17,17)$ |
|  | $\mathrm{T}-1$ | 2.605 | 2 | $\Delta \mathrm{E}=0.0 ; \eta^{5}, \eta^{2}-\mathrm{C}_{10} \mathrm{H}_{8} ; \mu-\mathrm{CO}(17,17)$ |

[^11]the still higher energy $\mathrm{Mn}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{3}$ structures $\mathrm{S}-3$ and T-4 have $\mathrm{Mn}=\mathrm{Mn}$ double bonds of lengths 2.366 and $2.349 \AA$, respectively. The dicarbonyl $\mathbf{0 3}$ has closely lying dibridged singlet and triplet minima, where the singlet $\mathrm{S}-1$ (Figure 9h) has a short $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond length of $2.156 \AA$, while the triplet $\mathrm{T}-2$ has a longer $\mathrm{Fe}=\mathrm{Fe}$ double bond. Of interest is the quadruple $\mathrm{Mn}-\mathrm{Mn}$ bond in the global minimum of the monocarbonyl $\mathbf{0 4}$ with a very short $\mathrm{Mn}-\mathrm{Mn}$ distance of $1.915 \AA$. Apart from the weak $\mathrm{Mn}-\mathrm{Mn}$ bond of $\mathrm{S}-3$ in $\mathrm{Mn}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{4}$ 01, this benzene series has Mn-Mn bond lengths on the shorter side, suggesting that the benzene ligands here have an $\mathrm{Mn}-\mathrm{Mn}$ bond shortening effect.

BP86 results on the pentalene dimanganese carbonyl series ${ }^{319} \mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{n}(n=6,5,4$, 3) are given in Table 18. The $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{6}$ system 05 has an $R_{M M}$ value of $3.204 \AA$, which is significantly longer than that expected from the manganese covalent radius, thereby suggesting a weak $\mathrm{Mn}-\mathrm{Mn}$ interaction. The $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ system $\mathbf{0 6}$ has a singlet global minimum $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ with an $R_{M M}$ value of $2.873 \AA$, and a higher energy triplet minimum $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)(\mathrm{CO})_{3} \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ with an $R_{M M}$ value of $2.958 \AA$, both suggesting $\mathrm{Mn}-\mathrm{Mn}$ single bonds. The $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ system $\mathbf{0 7}$ has an unbridged singlet global minimum with an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length of $2.246 \AA$. Higher energy $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ minima include $\mathrm{S}-2$ with an $\mathrm{Mn}-\mathrm{Mn}$ single bond length of $2.734 \AA$, and the singly bridged T-3 with an $\mathrm{Mn}=\mathrm{Mn}$ dipolar double bond of length $2.44 \AA$. The $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ system 08 has a triplet global minimum with the $(17,17)$ configuration and an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond length of $2.274 \AA$. Higher energy $\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ minima include the triplet T-2 with an $\mathrm{Mn}=\mathrm{Mn}$ double bond length of $2.602 \AA$, the quintet $\mathrm{Q}-3$ with an $\mathrm{Mn}=\mathrm{Mn}$ double bond length of $2.583 \AA$, and the singlet S-4 with a dipolar quadruple Mn-Mn bond length of $2.289 \AA$.

BP86 predictions for the azulene series $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{n}(n=5,4,3,2)^{320}$ show mainly $\eta^{5}, \eta^{5}$-coordination modes for the bicyclic ligand, except for two triplet minima (Table 18).

The $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ system 09 has two singlet minima with long $\mathrm{Mn}-\mathrm{Mn}$ single bonds of lengths 3.025 and $2.969 \AA$. The $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{4}$ system $\mathbf{1 0}$ has a CO-bridged triplet global minimum T-1 with an Mn-Mn single bond length of $2.758 \AA$, and a higher energy minimum S-2 (Figure 9i) with a long $\mathrm{Mn}=\mathrm{Mn}$ double bond of length $2.763 \AA$. The $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{3}$ system 11 has a singlet global minimum with an $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bond of length $2.359 \AA$, whereas the higher energy isomers S-2 and T-3 have double and single MM bonds of lengths 2.707 and $2.768 \AA$, respectively. The triplet $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Mn}_{2}(\mathrm{CO})_{2}$ minimum 12 has a long $\mathrm{Mn}=\mathrm{Mn}$ double bond of length $2.605 \AA$. The overall breadth of the bicyclic azulene ligand leads to rather long $\mathrm{Mn}-\mathrm{Mn}$ distances in this series.

### 7.5. Mn-Mn Bond Length Ranges

The experimental and computational $\mathrm{Mn}-\mathrm{Mn}$ bond distances reviewed in this Section cover dimanganese complexes with and without carbonyl ligands. The experimental results of Table 15 show effects of the metal oxidation state upon $R_{M M}$ values for $\mathrm{Mn}-\mathrm{Mn}$ bonds judged as single. The $R_{M M}$ range of 2.90 to $2.98 \AA$ seen for $\mathrm{Mn}(0)-\mathrm{Mn}(0)$ bonds in $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ and complexes 20 and 21 with PAH ligands points to weak Mn-Mn interactions within an fBO value of 1 with formal shortness ratio (FSR) values from 1.052 to 1.072 based on the estimate of $2.78 \AA$ for a $\mathrm{Mn}-\mathrm{Mn}$ covalent single bond. $R_{M M}$ values greater than $3 \AA$ become too long for $\mathrm{Mn}-\mathrm{Mn}$ covalent bonds as they approach the value of $3.5 \AA$ for the van der Waals dimer $\mathrm{Mn}_{2}$. The experimental dataset of Table 15 suggests a range of 2.609 to $2.85 \AA(2.73 \pm 0.12 \AA)$ for $\mathrm{Mn}(\mathrm{I})-\mathrm{Mn}(\mathrm{I})$ single bonded species apart from the singular example of $\left(\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{Mn}_{2} \mathbf{0 4}$. Species 11 and $\mathbf{1 2}$ with an $\left(\mathrm{Mn}_{2}\right)^{3+}$ core have an $R_{M M}$ single bond distance of $2.685 \AA$, while 03 with an $\left(\mathrm{Mn}_{2}\right)^{4+}$ core has an $R_{M M}$ value of $2.597 \AA$. The trend seems to be that increasing the charge $n$ leads towards shorter $\mathrm{Mn}-\mathrm{Mn}$ single bonds. There is no evidence of a formal $\mathrm{Mn}=\mathrm{Mn}$ double bond in this experimental dataset. The very short $\mathrm{Mn} \equiv \mathrm{Mn}$ bond length in $\mathbf{0 6}$,
however, suggests an MM triple bond. The absence or presence of CO ligands does not have any consistent effect on the ranges of $\mathrm{Mn}-\mathrm{Mn}$ bond lengths in this experimental dataset.

The remaining results of this sub-section are compiled from computational (BP86) results where some consistent trends are discernible in Tables 16 to 18 for various series of binuclear manganese carbonyl complexes. Further results for other series of dimanganese carbonyl complexes are not tabulated here, for which the trends are simply summarized below.

The homoleptic binuclear manganese carbonyl series ${ }^{308,309}$ (Table 16) has the following ranges for MM bond lengths: $2.84 \pm 0.12 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ single bonds; $2.704 \AA$ for the sole $\mathrm{Mn}=\mathrm{Mn}$ double bond; $2.44 \pm 0.14 \AA$ for $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds; and $2.25 \pm 0.08 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ quadruple bonds. The binuclear mangantese carbonyl hydride series ${ }^{312}$ (Table 16) has the ranges: $3.01 \pm 0.08 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ single bonds (relatively weak); $2.703 \AA$ for the sole $\mathrm{Mn}=\mathrm{Mn}$ double bond; $2.43 \pm 0.09 \AA$ for $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds; $2.296 \AA$ for the only example of a MnMn quadruple bond. The binuclear manganese fluoroborylene carbonyl series ${ }^{313}$ (Table 16) has the ranges: $2.91 \pm 0.12 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ single bonds in singlets; $2.57 \pm 0.07 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ single bonds in triplets; $2.50 \pm 0.05 \AA$ for $\mathrm{Mn}=\mathrm{Mn}$ double bonds; and $2.26 \pm 0.03 \AA$ for $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds. The binuclear manganese phospholyl carbonyl series ${ }^{314}$ has the ranges: $2.920 \AA$ for the sole example of a $\mathrm{Mn}-\mathrm{Mn}$ single bond; $2.11 \pm 0.06 \AA$ for $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds. The presence of the hydride ligand leads to longer single, double and triple Mn-Mn bonds than in the fluoroborylene and phospholyl series, being more comparable with the homoleptic carbonyl series. There is thus an overall trend towards steady decrease in MM bond length with increase in bond order for these complexes of Table 16.

The trends are as follows for the five series of binuclear manganese carbonyls with carbocyclic ligands. For the cyclobutadiene ligand series ${ }^{315}$ (Table 17), the ranges are: $2.63 \pm 0.02 \AA$ for $\mathrm{Mn}=\mathrm{Mn}$ double bonds; $2.32 \pm 0.01 \AA$ for $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds. The cyclopentadienyl ligand series ${ }^{316}$ (Table 17) has the ranges: $2.83 \pm 0.02 \AA$ for single bonds
(one quintet minimum giving $2.523 \AA$ ); $2.48 \pm 0.03 \AA$ for double bonds; $2.16 \pm 0.05 \AA$ for triple bonds; $2.067 \AA$, and $1.879 \AA$ for the sole examples of quadruple and quintuple bonds, respectively, with the latter being a high energy minimum not likely to be experimentally realizable. For the benzene ligand series ${ }^{318}$ (Table 18), the ranges are: $2.75 \pm 0.18 \AA$ for single bonds; $2.38 \pm 0.07 \AA$ for double bonds; $2.156 \AA$ for the sole example of a triple bond. The pentalene ligand series ${ }^{319}$ (Table 18) gives the ranges: $2.85 \pm 0.11 \AA$ for single bonds (one long interaction aside); $2.52 \pm 0.08 \AA$ for double bonds; $2.26 \pm 0.01 \AA$ for triple bonds; $2.289 \AA$ for the sole example of a dipolar quadruple bond. The azulene series ${ }^{320}$ (Table 18) has the ranges: $2.76 \pm 0.01 \AA$ for single bonds (weak interactions apart); $2.68 \pm 0.08 \AA$ for double bonds; 2.359 $\AA$ for the sole example of a triple bond.

BP86 Mn-Mn bond length ranges for other series of binuclear manganese carbonyl complexes not tabulated here are summarised as follows. The diphosphacyclobutadiene series has 3.037, 2.634, and $2.343 \AA$ for single, double and triple $\mathrm{Mn}-\mathrm{Mn}$ bond lengths, respectively. The thiocarbonyl series ${ }^{321}$ has the ranges: $3.02 \pm 0.10 \AA$ for weaker single bonds ( $>2.90 \AA$ ) $2.79 \pm 0.04 \AA$ for other single bonds; $2.58 \pm 0.03 \AA$ for double bonds. The thionitrosyl series ${ }^{322}$ has the ranges: $2.77 \pm 0.17 \AA$ for single bonds, and $2.55 \pm 0.11 \AA$ for double bonds.

Comparison with the homoleptic binuclear manganese carbonyl series predicts a general trend toward shortening of $\mathrm{Mn}-\mathrm{Mn}$ bond lengths when some of the carbonyl groups are replaced by other ligands. Increased electron donation by such ligands towards the bimetallic core may reduce the positive charge on each metal center thereby serving to draw them closer to each other. The hydride ligand does not exert as much an effect here as other ligands. The benzene ligand exerts the maximal MM bond shortening effect for single and double bonds.

In the computational set (Tables 16 to 18 and untabulated data) for the binuclear manganese carbonyl complexes, the DFT results closely correspond to experiment for
$\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ and $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mu-\mathrm{CO})_{3}$. The remaining theoretical results are not yet substantiated experimentally. This is a testimony to the relative paucity of experimental data on $\mathrm{Mn}-\mathrm{Mn}$ bond distances. The DFT data on $\mathrm{Mn}-\mathrm{Mn}$ single bonds suggest that $R_{M M}$ values around $3 \AA$ or above indicate weaker interactions, while the range for proper $\mathrm{Mn}-\mathrm{Mn}$ single bonds in singlet minima emerges as 2.654 to $2.954 \AA$, or $2.80 \pm 0.15 \AA$, comparable to the estimate of $2.78 \AA$ for an $\mathrm{Mn}-\mathrm{Mn}$ single bond derived from the manganese covalent radius of $1.39 \AA,{ }^{41}$ and not too far from the experimental range of $2.73 \pm 0.12 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ single bonds (Table 15). For $\mathrm{Mn}=\mathrm{Mn}$ double bonds, the DFT range is rather wide at $2.53 \pm 0.23 \AA$. For $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds, the range is also wide at $2.32 \pm 0.26 \AA$, while for the few Mn-Mn quadruple bonds, the range is narrower at $2.20 \pm 0.13 \AA$. The sole case of an $\mathrm{Mn}-\mathrm{Mn}$ quintuple bond gives an $R_{M M}$ value of $1.879 \AA$, which is very short but longer than known $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond lengths. The trend towards shorter $\mathrm{Mn}-\mathrm{Mn}$ bond lengths with increase in formal bond order is thus seen in this computational domain. $\mathrm{Mn}-\mathrm{Mn}$ bond orders of 4 and 5 are rare, and occur usually in higher energy minima. It is also apparent that the presence of CO ligands in binuclear manganese complexes does not generally have a shortening effect on $\mathrm{Mn}-\mathrm{Mn}$ single bond lengths, although this effect was discerned for single, double and triple $\mathrm{Ti}-\mathrm{Ti}$ bonds (Section 4), for V-V bonds of various orders (Section 5), and for multiple $\mathrm{Cr}-\mathrm{Cr}$ bonds (Section 6) in their various binuclear complexes.

## 8. IRON-IRON BONDS

Iron along with the other Group 8 metals ruthenium and osmium has the $\mathrm{d}^{6} \mathrm{~s}^{2}$ neutral atom configuration. Iron exhibits oxidation states of zero, $+1,+2$ and +3 in its experimentally known binuclear complexes, reviewed by Murillo ${ }^{323}$ and by Tereniak and Lu. ${ }^{324}$ Iron-iron bonds are also known in the naked iron dimer $\mathrm{Fe}_{2}$ and in the metallic state. This Section deals with experimental and computational estimates of $\mathrm{Fe}-\mathrm{Fe}$ bond lengths in various diiron complexes, with brief mention of some tri- and polyiron clusters having carbonyl ligands. Binuclear iron complexes with three and four bidentate ligands were synthesized following the discovery of paddlewheel complexes with various other binuclear $\left(\mathrm{M}_{2}\right)^{+\mathrm{n}}$ cores. Many experimentally characterized diiron complexes do not have carbonyl ligands. Instead they have anionic bidentate ligands of the $(\mathrm{X}-\mathrm{C}=\mathrm{Y})$ type, or various nitrogen, phosphinoamide, oxo, N-heterocyclic carbene, and carbon ligands. Bi- and polynuclear iron complexes with carbonyl ligands are known but less numerous. Computational DFT studies have largely treated binuclear iron carbonyl complexes, including the homoleptic series, and those with carbon ligands like acetylene, butadiene, cyclobutadiene, cyclopentadienyl, pentalene, indenyl, azulene etc., as well as various series having boron-based ligands. This Section analyzes results for $\mathrm{Fe}-\mathrm{Fe}$ bond distances and bond orders from experimental and computational sources.

### 8.1. Iron Dimer

Table 19 includes results for the iron dimer $\mathrm{Fe}_{2}$ with an $\mathrm{Fe}-\mathrm{Fe}$ bond length of $2.02 \AA$ derived by Purdum and coworkers from X-ray absorption fine structure studies. ${ }^{325}$ This may be compared with DFT estimates of 1.96 to $2.03 \AA$ for the $\mathrm{Fe}-\mathrm{Fe}$ distance in the septet ${ }^{7} \Delta_{u}$ ground state of $\mathrm{Fe}_{2}$ with the $\left(3 d \sigma_{g}\right)^{2}\left(3 d \pi_{u}\right)^{4}\left(3 d \delta_{g}\right)^{3}\left(3 d \delta_{u}{ }^{*}\right)^{2}\left(3 d \pi_{g}{ }^{*}\right)^{2}\left(3 d \sigma_{u}{ }^{*}\right)\left(4 s \sigma_{g}\right)^{2}$ configuration. ${ }^{33}$ This configuration leads to a formal bond order of 3. In another study, four

DFT methods gave Fe -Fe bond length values from 1.989 to $2.077 \AA$ for this ground state. The BP86 value $(2.013 \AA)$ is the best, whereas the MP2 value is noticeably lower. ${ }^{34}$ The septet ${ }^{7} \Sigma^{+}{ }_{u}$ state was found only by the UHF approach ${ }^{33}$ and by the B3LYP functional, ${ }^{35}$ having appreciably longer Fe-Fe distances. Empirical formulas yield Fe-Fe bond distances from 2.06 to $2.12 \AA .{ }^{28}$ Ground state $\mathrm{Fe}_{2}$ may be described as a septet, where DFT methods give reasonable predictions for the Fe - Fe triple bond length.

### 8.2. Experimentally Known Binuclear Iron Complexes (Non-Carbonyl)

Table 19 presents experimental MM bond lengths for non-carbonyl binuclear iron complexes with trigonal, tetragonal, and other arrangements, which have been extensively reviewed. ${ }^{323,324}$ The experimentally characterized diiron complexes $\mathbf{0 2}$ to 09 have nitrogen ligands and $\left(\mathrm{Fe}_{2}\right)^{n+}$ cores with $n=2,3,4,5$. The digonal $\left(\mathrm{Fe}_{2}\right)^{2+}$ paddlewheel $\mathbf{0 2}$ $\mathrm{Fe}_{2}\left[\mathrm{ArNC}\left(\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{~N}\right) \mathrm{NAr}\right]_{2}$ (Figure 10a) has the shortest $\mathrm{Fe}-\mathrm{Fe}$ contact known in any diiron complex, with an fBO of $3,{ }^{326}$ although CASSCF/PT2 results give a computed bond order (cBO) value of only 1.19. Trigonal paddlewheels with an $\left(\mathrm{Fe}_{2}\right)^{3+}$ core include the tris(aminidinate) complexes 03 (Figure 10b) and $\mathbf{0 4}$ (with the DPhF and DPhBz ligands) which also have short Fe - Fe bonds. ${ }^{327,328}$ These paramagnetic systems were treated by $a b$ initio theory using the model $\mathrm{Fe}_{2}(\mathrm{HNC}(\mathrm{H}) \mathrm{NH})_{3}$ which gave an fBO of 1.5 from the configuration $\sigma^{2} \pi^{4} \pi^{* 2} \sigma^{* 1} \delta^{2} \delta^{* 2}$ with 7 unpaired electrons. ${ }^{329}$ CASSCF/PT2 studies on the full $\mathrm{Fe}_{2}(\mathrm{DPhF})_{3}$ molecule confirmed the same with an effective bond order of $1.15 .{ }^{330}$ The short Fe-Fe bond lengths in complexes $\mathbf{0 2}$ to $\mathbf{0 5}$ with an fBO of only 1.5 contrast with the longer Fe-Fe bonds found in some carbonyl complexes having higher bond orders of 2 or even 3, as shown later for computationally studied series of diiron carbonyl systems.

Table 19. Fe -Fe Bond Lengths for $\mathrm{Fe}_{2}$ and Experimentally Known Binuclear Iron Complexes Without Carbonyl Ligands

| Label Species | $R_{M M}(\AA)$ | Remarks | References |
| :---: | :---: | :---: | :---: |
| $01 \mathrm{Fe}_{2}$ | 2.02 | X-ray absorption fine structure | 325 |
|  | 2.013 | ${ }^{7} \Delta_{u}$; DFT BP86 | 33 |
|  | 2.010 | ${ }^{7} \Delta_{u}$; DFT PW91 | 34 |
|  | 2.06-2.12 | Empirical formulas | 28 |
| $02 \mathrm{Fe}_{2}\left[\mathrm{ArNC}\left(\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{~N}\right) \mathrm{NAr}\right]_{2}$ | $2.1270(7)$ | $\left(\mathrm{Fe}_{2}\right)^{2+}$ core; guanidinate ligands; $\mathrm{fBO}=3$ | 326 |
| $03 \mathrm{Fe}_{2}(\mathrm{DPhF})_{3}$ | 2.2318(8) | $\left(\mathrm{Fe}_{2}\right)^{3+} ; \mathrm{fBO}=1.5 ;$ paramagnetic | 327 |
| $04 \mathrm{Fe}_{2}(\mathrm{DPhBz})_{3}$ | 2.198(2) | $\left(\mathrm{Fe}_{2}\right)^{3+}$ core; very short; $\mathrm{fBO}=1.5$ | 328 |
| $05 \mathrm{Fe}_{2}(\mathrm{DPhF})_{3}$ | 2.27 | $\left(\mathrm{Fe}_{2}\right)^{3+}$; computational; octet; $\mathrm{eBO}=1.15$ | 329,330 |
| $06 \mathrm{Fe}_{2}(\mathrm{DPhF})_{4}$ | 2.462(2) | $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; $D_{2 h}$; distorted tetragonal | 331 |
| $07 \mathrm{Fe}_{2}(\mathrm{DPhBz})_{4}$ | > 3.0 | $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; no Fe-Fe bond | 331 |
| $08 \mathrm{Fe}_{2} \mathrm{Cl}$ (py ${ }_{3}$ tren) | 2.2867(5) | $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; $S=3 ; \mathrm{eBO}=0.73$ | 332 |
| $09\left[\mathrm{Fe}_{2}\left(\mathrm{~N}=\mathrm{C}^{\prime} \mathrm{Bu}_{2}\right)_{5}\right]^{-} \mathrm{L}^{+}$ | 2.443(1) | $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; $\mathrm{L}=\left[\mathrm{Li}(12-\text { crown } 4)_{2}\right] ; \mathrm{fBO}=2$ | 2286 |
| $10 \mathrm{Fe}_{2}(\mathrm{tim})_{2}$ | 2.6869(6) | $\left(\mathrm{Fe}_{2}\right)^{5+}$ core; bridging; $\mathrm{fBO}=0.5$ | 333 |
| $\begin{gathered} 11\left\{\begin{array}{l} \left\{\eta^{2}-\mathrm{C}(\mathrm{Mes})=\mathrm{N}^{\prime} \mathrm{Bu}\right\}_{2} \mathrm{Fe}_{2}- \\ \left\{\mu-\mathrm{C}(\mathrm{Mes})=\mathrm{N}^{\prime} \mathrm{Bu}\right\}_{2} \end{array}\right. \end{gathered}$ | 2.371(4) | ketimide ligand; not paddlewheel | 334 |
| $12 \mathrm{Fe}\left(\mathrm{NMesP}^{\text {P }} \mathrm{Pr}_{2}\right)_{3} \mathrm{FeCl}$ | 2.5855(4) | phosphinoamide ligand; $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; $S=3$ | 335 |
| $13 \mathrm{Fe}_{2}\left(\mathrm{~N}^{i} \mathrm{PrP}^{\text {P }} \mathrm{Pr}_{2}\right)_{3} \mathrm{Cl}$ | 2.6112(7) | phosphinoamide ligand; $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; $S=3$ | 335 |
| $14 \mathrm{Fe}_{2}\left(\mathrm{PrNPPh}_{2}\right)_{3} \mathrm{PMe}_{3}$ | 2.4545(5) | $\left(\mathrm{Fe}_{2}\right)^{3+}$ core; $S=7 / 2$ (suggested) | 336 |
| $15 \mathrm{Fe}_{2}\left({ }^{( } \mathrm{PrNPPh}_{2}\right)_{3} \mathrm{PPh}_{3} \mathrm{NH}^{\text {i }} \mathrm{Pr}$ | 2.4694(3) | $\left(\mathrm{Fe}_{2}\right)^{3+}$ core; $S=7 / 2$ (suggested) | 336 |
| $16\left({ }^{( } \mathrm{PrNPPh}_{2}\right)_{3} \mathrm{Fe}_{2} \equiv \mathrm{NR}$ | 2.54-2.56 | $\mathrm{R}=\mathrm{t} \mathrm{Bu}, \mathrm{Ad}, \mathrm{Mes} ; S=5 / 2$ | 336 |
| $17 \mathrm{Fe}_{2}\left(\mathrm{OOCAr}^{\text {tol }}\right)_{4} \cdot\left(4-\mathrm{Bu}^{\text {t }} \text {-py }\right)_{2}$ | 2.823 (1) | $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; $\mathrm{BO}<1$; paramagnetic | 337 |
| $18\left[\mathrm{Fe}_{2}(\mathrm{O})-2,6-\mathrm{Me}_{3}-\mathrm{TPA}_{2}\right]^{2+}$ | 2.71 | $\mu-\mathrm{O} ;\left(\mathrm{ClO}_{4}\right)^{-}$anions | 338 |
| $19\left[\mathrm{Fe}_{2}(\mathrm{O})(\mathrm{OH})(\mathrm{BPEEN})_{2}\right]^{2+}$ | 2.81 | $\mu-\mathrm{O} ;\left(\mathrm{ClO}_{4}\right)^{-}$anions | 338 |
| $20 \mathrm{Fe}_{2}(\mathrm{Mes})_{4}$ | 2.617(1) | $\left(\mathrm{Fe}_{2}\right)^{4+}$ core; not paddlewheel | 339 |
| $21 \mathrm{Fe}_{2}\left(\mathrm{Ar}^{\mathrm{T}}\right)_{2}$ | 2.515(9) | $\mathrm{Ar}^{\mathrm{T}}=2,6-\left(2,6-\mathrm{PrC}_{6} \mathrm{H}_{3}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}$ | 340 |
| $22 \mathrm{Fe}_{2}\left\{\mu-\eta^{1}(\mathrm{c}): \eta^{6}(\mathrm{Mes}) \mathrm{IMes}\right\}_{2}$ | 2.621 | NHC ligand; $S=2 ;\left(\mathrm{Fe}_{2}\right)^{0}$ core | 341 |
| $23 \mathrm{Fe}_{2}\left\{\mu-\eta^{1}(\mathrm{c}): \eta^{6}\left({ }^{( } \mathrm{Pr}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)\right\}_{2}$ | 2.583 | carbene ligand; $S=0 ;\left(\mathrm{Fe}_{2}\right)^{0}$ core | 341 |
| $\begin{aligned} & 24 \text { (IMes) } \mathrm{Fe}(\mu-\mathrm{NAd})_{2} \mathrm{Fe} \\ & \left(\eta^{2}-\mathrm{N}_{4} \mathrm{Ad}_{2}\right) \end{aligned}$ | 2.390 | NHC ligand; $\left(\mathrm{Fe}_{2}\right)^{0}$ core; $\mathrm{fBO}=1$ | 341 |


a (02)

b (03)

c (06)



Figure 10. Some experimentally known non-carbonyl diiron complexes (labels in brackets refer to Table 19)

Complexes 06 to 09 have $\left(\mathrm{Fe}_{2}\right)^{4+}$ cores, all with nitrogen ligands. The $D_{2 h}$ tetragonal paddlewheel $06 \mathrm{Fe}_{2}(\mathrm{DPhF})_{4}($ Figure 10c) has a longer $\mathrm{Fe}-\mathrm{Fe}$ bond ( $2.462 \AA$ ) between the two Fe (II) atoms arising from greater repulsion between the core metal atoms, and an fBO value of $1 .{ }^{331}$ Complex $\mathbf{0 7}$ with the DPhBz ligand has an $R_{M M}$ value longer than $3.0 \AA$ suggesting a negligible $\mathrm{Fe} \cdots \mathrm{Fe}$ interaction. Complex $08 \mathrm{Fe}_{2} \mathrm{Cl}\left(\right.$ py $y_{3}$ tren $)$ has one heptadentate ligand of interesting structure (trideprotonated N,N,N-tris(2-(2-pyridyl-amino)ethyl)amine) and a short $R_{M M}$ value of $2.287 \AA$, although the cBO value of 0.73 is small. ${ }^{332}$ The ketimide complex 09
(Hayton et al. ${ }^{287}$ ) also has only nitrogen ligands (two bridging, two terminal) with an $\left(\mathrm{Fe}_{2}\right)^{4+}$ core, where the $R_{M M}$ value of $2.443 \AA$ fits in with the fBO value of two assigned to the $\mathrm{Fe}=\mathrm{Fe}$ bond here. Complex $10 \mathrm{Fe}_{2}(\mathrm{tim})_{2}$ with an $\left(\mathrm{Fe}_{2}\right)^{5+}$ core and an $\mathrm{Fe}(\mathrm{II})-\mathrm{Fe}$ (III) bond is a dimer of two tetragonal monoiron complexes with an $\mathrm{N}_{4}$-macrocyclic ligand (tim) and a long $R_{M M}$ value of $2.687 \AA,{ }^{333}$ which fits in with the low $\mathrm{Fe}-\mathrm{Fe}$ bond order of 0.5 .

Complexes $\mathbf{1 1}$ to $\mathbf{1 6}$ in Table 19 have ligands with N -coordination along with coordination to a C -atom or a P -atom. Complex 11 (Figure 10d) has four $\left[\mathrm{C}(\mathrm{Mes})=\mathrm{NBu}^{\mathrm{t}}\right]$ ligands (two $\eta^{2}$ type and two $\mu$-type) with C-coordination along with N -coordination (Klose et al. ${ }^{334}$ ) where the $R_{M M}$ value $(2.371 \AA$ ) may suggest multiple $\mathrm{Fe}-\mathrm{Fe}$ bonding. Complexes $\mathbf{1 2}$ to $\mathbf{1 6}$ have phosphinoamide anionic ligands with coordination from P- as well as N-atoms. Structures 12 and 13 have $\left(\mathrm{Fe}_{2}\right)^{3+}$ cores $(S=3)$ and $R_{M M}$ values ( 2.59 and $2.61 \AA$, Thomas and coworkers ${ }^{335}$ ), longer than $\mathbf{1 4}$ and $\mathbf{1 5}$ which have $\left(\mathrm{Fe}_{2}\right)^{4+}$ cores $(S=7 / 2)$ and shorter $R_{M M}$ values ( 2.45 and $2.47 \AA$ ). ${ }^{336}$ Entry 16 in Table 19 has complexes with the $\mathrm{Fe}=$ NR moiety, where $S=5 / 2$ and $R_{M M}$ values are intermediate ( 2.54 to $2.56 \AA$ ). ${ }^{336}$

Complexes $\mathbf{1 7}$ to 19 have O -atoms coordinating to the $\mathrm{Fe}_{2}$ core. $\mathrm{Fe}_{2}\left(\mathrm{OOCAr}^{\text {tol }}\right)_{4} \cdot \mathrm{Py}_{2}$ (complex 17) has four bulky carboxylate ligands $\left(\mathrm{Ar}^{\text {tol }}=2,6\right.$-ditolylphenyl) along with two axial pyridine ligands (cf. dichromium tetracarboxylates with axial ligands). The long $\mathrm{Fe}-\mathrm{Fe}$ distance of $2.823 \AA$ in $\mathbf{1 7}$ and similar complexes (Lippard ${ }^{337}$ ) may indicate absence of a covalent $\mathrm{Fe}-\mathrm{Fe}$ bond in contrast to the short quadruple MM bonds in most dichromium tetracarboxylate compounds. Somewhat lower $R_{M M}$ values (2.71 and $2.81 \AA$ ) are seen in structures 18 and 19 with bridging oxo groups (Feng ${ }^{338}$ ).

Complexes 20 to 24 in Table 19 incorporate only carbon-Fe ligand-metal interactions. Complexes 20 and 21 are quite different in structure, but have rather similar $R_{M M}$ values of 2.617 and $2.516 \AA$. Complex 20 (Muller ${ }^{339}$ ) has the $\mathrm{Fe}(\mathrm{II})$ oxidation state with four aryl ligands, while 21 (Figure 10e) has two terphenyl ligands and two Fe(I) centers ( $\mathrm{Power}^{340}$; cf.
the quintuply bonded dichromium complexes of sub-section 6.4). Electron counting assigns an $\mathrm{Fe} \equiv \mathrm{Fe} \mathrm{fBO}$ of 3 to the terphenyl complex 21. Complexes $\mathbf{2 2}$ to $\mathbf{2 4}$ have $\left(\mathrm{Fe}_{2}\right)^{0}$ cores with carbene ligands (Tatsumi ${ }^{341}$ ). $R_{M M}$ values of 2.621 and $2.583 \AA$ are found in complexes 22 and 23, while 24 has a shorter $\mathrm{Fe}(0)-\mathrm{Fe}(0)$ bond length of $2.390 \AA$.

### 8.3. Binuclear Iron Carbonyl Complexes (Homoleptic and with $\mathrm{C}_{2} \mathrm{H}_{2}$ Ligands)

Table 20 presents experimental and computational results for homoleptic binuclear iron carbonyls as well as those with acetylene and terphenyl ligands. Diiron enneacarbonyl $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ (Figure 11a) has an experimental $\mathrm{Fe}-\mathrm{Fe}$ bond length of 2.523(1) $\AA .^{342}$ The substituted acetylene complex $\mathbf{0 2}$ has a tetrahedral structure with two $\mathrm{Fe}(0)$ atoms and the two carbon atoms as apices, and an $\mathrm{Fe}=\mathrm{Fe}$ double bond length of $2.316 \AA\left(\right.$ Cotton $\left.^{343,344}\right)$. The $R_{M M}$ value of $2.594 \AA$ in the substituted acetylide complex $\mathbf{0 3}$ (Green and $\operatorname{Bryan}^{345}$ ) is longer than for $\mathbf{0 2}$, having two $\mathrm{Fe}(\mathrm{I})$ centers. The black and violet forms $\mathbf{0 4}$ and $\mathbf{0 5}$ of another substituted acetylene complex with an $\left(\mathrm{Fe}_{3}\right)^{0}$ core contain $\mathrm{Fe}-\mathrm{Fe}$ distances (Dodge and Schomaker ${ }^{346}$ ) of 2.43 and $2.46 \AA$ which fall within the range for $\mathrm{Fe}-\mathrm{Fe}$ covalent bonds. Complex 06 (Figure 11b) has a terphenyl ligand and a short $\mathrm{Fe}(\mathrm{I})-\mathrm{Fe}(\mathrm{I})$ bond length of $2.393 \AA .{ }^{347}$ Computational studies on structure $\mathbf{0 6}$ give a small cBO value of 0.36 and a charge separation between the metal centers suggesting a dative $\mathrm{Fe} \rightarrow \mathrm{Fe}$ bond.

Assorted diiron and polyiron carbonyl complexes like $\left(\mathrm{AsCH}_{3}\right)_{4} \mathrm{Fe}_{2}(\mathrm{CO})_{6}(2.68 \AA$, Gatehouse), ${ }^{348} \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5}\left(2.63 \AA\right.$, Vahrenkamp), ${ }^{349} \mathrm{CO} . \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3} \mathrm{PtFe}_{2}(\mathrm{CO})_{8}$ (2.78 $\AA$, Mason), ${ }^{350} \mathrm{Fe}_{3}(\mathrm{CO})_{11} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\left(2.57,2.68\right.$ and $2.71 \AA$, Dahn and Dobson), ${ }^{351}$ $\mathrm{Fe}_{5}(\mathrm{CO})_{15} \mathrm{C}_{6}(2.64 \AA, \mathrm{Dahl}),{ }^{352}$ and the cluster anion $\left[\mathrm{Fe}_{6}(\mathrm{CO})_{16 \mathrm{C}}\right]^{2-}(2.67 \AA$, Churchill and Wormald) ${ }^{353}$ show $R_{M M}$ values longer than those seen in the carbonyl complexes above. However, since these $R_{M M}$ values are similar to the $R_{M M}$ value of $2.64 \AA$ expected for an $\mathrm{Fe}-\mathrm{Fe}$ covalent bond from the iron covalent radius of $1.32 \AA$, the possibility of weaker $\mathrm{Fe}-\mathrm{Fe}$
single bonds may not be excluded. The Fe-Fe distance (Weaver and Woodward ${ }^{354}$ ) of $2.51 \AA$ in $\left[\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right] \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ is a little shorter than that in $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ and may indicate an $\mathrm{Fe}-\mathrm{Fe}$ single bond. However, the prospect of three-centre two-electron bonding in these complexes with bridging CO ligands must also be considered, as discussed later.



c (21-03)

d (23-01)

e (23-02)

f (24-06, S-1)
Figure 11. Some binuclear iron complexes containing carbonyl ligands (table number and label given in brackets).

Table 20. Fe-Fe Bond Distances in Binuclear Iron Carbonyl Complexes (Homoleptic and Those with Acetylene Ligands (Experimental and Computational Data) a

| Label Complex |  | $R_{\text {MM }}(\AA) \mathrm{f}$ | O | Remarks | References |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Experimentally characterized |  |  |  |  |  |
| $01 \mathrm{Fe}_{2}(\mathrm{CO})_{9}$ | S | 2.523(1) | - | XRD; homoleptic | 342 |
| $02(\mathrm{CO})_{3} \mathrm{Fe}-\left(\mu-\mathrm{C}_{2} \mathrm{Bu}^{\mathrm{t}}\right) \mathrm{-}-\mathrm{Fe}(\mathrm{CO})_{3}$ | S | 2.316 | 2 | tetrahedrane | 343,344 |
| $03 \mathrm{Cs}_{2}\left[\pi-(3)-1,2-\mathrm{C}_{2} \mathrm{~B}_{9} \mathrm{H}_{11} \mathrm{Fe}(\mathrm{CO})_{2}\right]_{2}$ | S | 2.591(5) | - | ethyne ligand | 345 |
| $04\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}_{3}(\mathrm{CO})_{8}$ black | S | 2.43 | - | ethyne ligand | 346 |
| $05\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}_{3}(\mathrm{CO})_{8}$ violet | S | 2.46; 2.59 | - | ethyne ligand | 346 |
| 06 (3,5- ${ }^{-} \mathrm{Pr}_{2} \mathrm{Ar}^{*}$ ) $\mathrm{Fe}_{2} \mathrm{Cp}(\mathrm{CO})_{2}$ | S | 2.3931(8) | - | $\mathrm{Ar}^{*}=$ terphenyl | 347 |
| Homoleptic diiron carbonyls (DFT results) |  |  |  |  |  |
| $07 \mathrm{Fe}_{2}(\mathrm{CO})_{9}$ (tribridged) | S | 2.519 | 1 | BP86 | 355 |
|  | S | 2.525 | 1 | B3LYP/DZP | 356 |
|  | S | 2.524 | 1 | B3LYP/LAN2DZ | 356 |
| $08 \mathrm{Fe}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})_{2}$ | S | 2.447 | 2 | BP86; $C_{2 v}$ | 355 |
| $\mathrm{Fe}_{2}(\mathrm{CO})_{8}$ (unbridged) | S | 2.551 | 1 | BP86; $D_{2 h} ; 2 i v$ | 355 |
| $\mathrm{Fe}_{2}(\mathrm{CO})_{8}$ (unbridged) | S | 2.585 | 1 | BP86; $C_{2 h} ; 1 \mathrm{iv}$ | 355 |
| $09 \mathrm{Fe}_{2}(\mathrm{CO})_{5}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{2}$ | S | 2.235 | 3 | BP86 | 355 |
| $\mathrm{Fe}_{2}(\mathrm{CO})_{4}\left(\eta^{2}-\mu-\mathrm{CO}\right)_{3}$ | S | 2.206 | 3 | BP86 | 355 |
| $10 \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ | S | 2.029 | 4 | BP86; $D_{3 h}$ | 355 |
|  | S | 2.434 | 2 | BP86; glob. min. | 355 |
| With $\mathrm{C}_{2} \mathrm{H}_{2}$ ligands (BP86 results) |  |  |  |  |  |
| $11 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ | S-1 | 2.398 | 2 | glob. min. | 366 |
| $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ | S-2 | 2.803 | 1 | $(16,16) ; \Delta \mathrm{E}=9.8$ | 366 |
| $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ | T-3 | 2.545 | 1 | $(17,17) ; \Delta \mathrm{E}=8.4$ | 366 |
| $12 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\eta 2-\mu-\mathrm{CO})(\mathrm{CO})_{4}$ | S-1 | 2.349 | 2 | glob. min. | 366 |
| $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{4}$ | T-2 | 2.382 | 2 | $(17,17) ; \Delta \mathrm{E}=2.4$ | 366 |

[^12]Table 20 also gives $\mathrm{Fe}-\mathrm{Fe}$ bond characteristics from DFT studies on homoleptic binuclear iron carbonyls. Only $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ has been characterized by XRD. ${ }^{342}$ The BP86 method was used to study the series $\mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=9,8,7,6),{ }^{355}$ where a decrease in the number of CO groups ( $n$ ) would result in $\mathrm{Fe}-\mathrm{Fe}$ formal bond orders increasing up to four if both iron atoms have the favored 18 -electron configuration. The experimental $\mathrm{Fe}-\mathrm{Fe}$ bond distance in $\mathrm{Fe}_{2}(\mathrm{CO})_{9} \mathbf{0 7}$ is well-reproduced by DFT results, ${ }^{356,357}$ especially by the B3LYP/DZP method, being less than twice the iron covalent radius of $1.32 \AA$. This $\mathrm{Fe}-\mathrm{Fe}$ interaction is described as a single bond by the 18 -electron rule. This assumption was challenged by orbital interaction analysis ${ }^{356}$ and by atoms-in-molecules analysis which gave no MM bond path or bond critical point. ${ }^{358}$ Domain averaged Fermi hole analysis proposed one 3-center 2-electron bond spread over all three $\mathrm{Fe}-\mathrm{C}$-Fe bridges through resonance ${ }^{356}$ as in the $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ case, ${ }^{359}$ which now emerges as the most viable picture. It may be possible to extend such a picture to other binuclear iron carbonyl complexes (even those with other ligands) if bridging CO ligands are present, especially for cases having $\mathrm{Fe}-\mathrm{Fe}$ distances on the longer side.

Diiron octacarbonyl $\mathbf{0 8}$ was detected and characterized as a transient species (Poliakoff and Turner ${ }^{360,361}$, Moskovits ${ }^{362}$ ) and studied theoretically as well. ${ }^{363,364,365}$ BP86 results show that $\mathrm{Fe}_{2}(\mathrm{CO})_{8}$ has a doubly bridged global minimum with $C_{2 v}$ symmetry and an $\mathrm{Fe}=\mathrm{Fe}$ double bond length of $2.447 \AA$, which corresponds to the most stable isomer reported experimentally (Poliakoff and Turner ${ }^{360}$ ). A higher energy $D_{2 h}$ unbridged $\mathrm{Fe}_{2}(\mathrm{CO})_{8}$ structure has an $\mathrm{Fe}-\mathrm{Fe}$ bond length of $2.551 \AA$ and corresponds to the structure predicted by Hoffmann. ${ }^{363}$ There is also a $C_{2 h}$ unbridged structure with an $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.585 \AA$. Diiron heptacarbonyl 09 has a global minimum with two semibridging carbonyl groups and an $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond length of $2.235 \AA$. A higher energy $\mathrm{Fe}_{2}(\mathrm{CO})_{7}$ structure has three bridging carbonyl groups and an $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond of length $2.206 \AA$. The hexacarbonyl $\mathrm{Fe}_{2}(\mathrm{CO})_{6} \mathbf{1 0}$ has a global minimum with an $\mathrm{Fe}=\mathrm{Fe}$ double bond length of $2.434 \AA$. A higher energy $D_{3 h}$
unbridged $\mathrm{Fe}_{2}(\mathrm{CO})_{6}$ isomer has an $\mathrm{Fe}-\mathrm{Fe}$ quadruple bond of length $2.029 \AA$ of the $\sigma+2 \pi+\delta$ type. However, this higher energy $\mathrm{Fe}_{2}(\mathrm{CO})_{6}$ structure is predicted not to be viable.

Table 20 also presents BP86/DZP computational results on binuclear iron carbonyl complexes $\mathbf{1 0}$ and $\mathbf{1 1}$ with an acetylene $\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)$ ligand $\eta^{2}-\mu$ coordinated to the $\mathrm{Fe}(0)$ atoms, ${ }^{366}$ forming the tetrahedrane structure noted above for $\mathbf{0 2}$. Three minima of $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6} \mathbf{1 1}$ lie within $9.8 \mathrm{kcal} / \mathrm{mol}$ of the ground state singlet $\mathrm{S}-1$. The global minimum $\mathrm{S}-1$ has an $\mathrm{Fe}=\mathrm{Fe}$ double bond of length $2.398 \AA$ comparing fairly well with Cotton's experimental $R_{M M}$ value of $2.316 \AA$ in the substituted acetylene complex $\mathbf{0 2} .{ }^{343,344} \mathrm{The}_{2} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ singlet $\mathrm{S}-2$ has a long $\mathrm{Fe}-\mathrm{Fe}$ distance of $2.803 \AA$ described as a single bond. The triplet $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ structure T-3 with a $(17,17)$ core configuration has an $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.545 \AA$. The pentacarbonyl $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{Fe}_{2}(\mathrm{CO})(\mathrm{CO})_{4} \mathbf{1 2}$ has a singlet ground state $\mathrm{S}-1$ with an $R_{M M}$ value of $2.349 \AA$ and a triplet state T-2 with an $R_{M M}$ value of $2.382 \AA$, both consistent with $\mathrm{Fe}=\mathrm{Fe}$ double bonds.

### 8.4. Binuclear Iron Carbonyl Complexes With $\mathrm{C}_{4} \mathrm{H}_{4}$ and $\mathrm{C}_{4} \mathrm{H}_{6}$ Ligands

Table 21 gives BP86 results on the binuclear cyclobutadiene iron carbonyl series $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=5,4,3,2,1) .{ }^{367}$ The tricarbonyls $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ and $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{Me}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ are experimentally known, though uncharacterized (Fischler ${ }^{368}$ and Herrmann ${ }^{369}$ ), showing that a transient species like cyclobutadiene can be stabilized by metal coordination. All complexes here have the cyclobutadiene ligands coordinated to the $\mathrm{Fe}(0)$ atoms as tetrahapto $\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}$ ligands. The pentacarbonyl complex $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5}$ has one bridging carbonyl ligand and an $R_{M M}$ value of $2.743 \AA$ corresponding to a long $\mathrm{Fe}-\mathrm{Fe}$ single bond. The tetracarbonyl $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ has the doubly CO-bridged $\left(\eta^{4}-\right.$ $\left.\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ structure in the S-1, S-2 and T-3 minima with $R_{M M}$ values of 2.615 , 2.629 and $2.386 \AA$, respectively, all indicating $\mathrm{Fe}=\mathrm{Fe}$ double bonds. The shorter value for T-3
is consistent with the $\sigma+2 / 2 \pi$ double bond type. The tricarbonyl $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ (Figure 11c) is a singlet with three bridging carbonyl ligands and an $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond length of $2.148 \AA$, corresponding to the experimentally known compound. The infrared vibrational frequencies computed here for $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ indicate three bridging CO groups, thereby correcting the structure originally suggested by the discoverers (Fischler et al. ${ }^{368}$ ) who interpreted their data to assign only two bridging carbonyl groups. The dicarbonyl $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ has two bridging carbonyl ligands in both the global minimum T-1 and the singlet minimum $\mathrm{S}-1$, with $\mathrm{Fe}=\mathrm{Fe}$ triple bonds of lengths 2.216 and $2.310 \AA$, respectively. The triplet T-1 $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ structure is assigned a $(17,17) \mathrm{MM}$ configuration. The monocarbonyl system $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)$ has singlet, triplet, and quintet minima with $R_{M M}$ values of 2.471, 2.370 and $2.424 \AA$ respectively, all consistent with $\mathrm{Fe}=\mathrm{Fe}$ double bonds.

The results on cyclobutadiene diiron carbonyls prompted comparison of their open chain analogues containing butadiene ligands. DFT M06-L results are given in Table 21 for a series of complexes $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right){ }_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=3,4,5,6,7) .{ }^{370}$ These bis(butadiene) complexes all have bridging CO ligands, with $\mathrm{C}_{4} \mathrm{H}_{6}$ ligands coordinated to the neutral $\mathrm{Fe}_{2}$ core through one or both of their $\mathrm{C}=\mathrm{C}$ double bonds. The tricarbonyl $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ has a singlet global minimum S-1 with three bridging carbonyl groups and a short $R_{M M}$ value of $2.164 \AA$ that is consistent with an $\mathrm{Fe}=\mathrm{Fe}$ triple bond. The triplet $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ structure T-2 has two bridging carbonyl groups and an $R_{M M}$ value of $2.329 \AA$ corresponding to an $\mathrm{Fe}=\mathrm{Fe}$ double bond with a $(17,17)$ core configuration. The tetracarbonyl $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ is represented by the doubly bridged $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ structure with a global minimum $\mathrm{T}-1$ and a singlet minimum $\mathrm{S}-2$ having $\mathrm{Fe}=\mathrm{Fe}$ double bond lengths of 2.429 and $2.541 \AA$, respectively. The pentacarbonyl $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5}$ has a singly bridged structure for the global minimum with a long $\mathrm{Fe}-\mathrm{Fe}$ distance of $2.763 \AA$ interpreted as a single bond. The hexacarbonyl $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ also has a singly bridged structure with a long Fe - Fe distance of $2.723 \AA$.

The global minimum S-1 of $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{7}$ has a triply bridged structure with an $R_{M M}$ value of $2.507 \AA$, while the higher energy structure S-2 has a singly bridged structure with an $R_{M M}$ value of $2.694 \AA$, both interpreted as $\mathrm{Fe}-\mathrm{Fe}$ single bonds.

Table 21. Fe-Fe Distances ${ }^{a}$ in Binuclear Iron Carbonyl Complexes Containing Cyclobutadiene and Butadiene Ligands

| No Complex | State $R_{\text {MM }}$ | fBO Remarks |
| :---: | :---: | :---: |
| Binuclear cyclobutadieneiron carbonyls (BP86 results; Ref. 367) |  |  |
| $01\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})$ | S-1 2.743 | 1 long Fe-Fe distance |
| $02\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ | S-1 2.615 | 2 long $\mathrm{Fe}=\mathrm{Fe}$ bond |
| $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ | S-2 2.629 | $2 \Delta \mathrm{E}=4.6$ |
| $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ | T-3 2.386 | $2 \Delta \mathrm{E}=4.6 ; \sigma+2 / 2 \pi$ |
| $03\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | S-1 2.148 | 3 experimentally known; Ref. 368 |
| $04\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}$ | T-1 2.216 | 3 triplet global min.; $(17,17)$ |
| $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}$ | S-2 2.301 | $3 \Delta \mathrm{E}=7.7$; $(18,18)$ |
| $05\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)$ | T-1 2.471 | - triplet global min. |
| $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)$ | T-2 2.370 | - $\Delta \mathrm{E}=0.1$ |
| $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right)$ | Q-3 2.424 | - $\Delta \mathrm{E}=3.5$ |

Binuclear butadiene iron carbonyls (M06-L results; Ref. 370)

| $06\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.164 | 3 | $(18,18)$ |
| :---: | :---: | :--- | :--- | :--- |
| $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})(\mu-\mathrm{CO})_{2}$ | $\mathrm{~T}-2$ | 2.329 | 2 | $(17,17)$ |
| 07 trans $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ | $\mathrm{~T}-1$ | 2.419 | 2 | long $\mathrm{Fe}=\mathrm{Fe}$ bond |
|  |  | $\mathrm{S}-2$ | 2.541 | 2 |
|  | long $\mathrm{Fe}=\mathrm{Fe}$ bond |  |  |  |
| $\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})$ | $\mathrm{S}-1$ | 2.763 | 1 | long $\mathrm{Fe}-\mathrm{Fe}$ bond |
| $09\left(\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{6}\right)\left(\eta^{2}-\mathrm{C}_{4} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5}(\mu-\mathrm{CO})$ | $\mathrm{S}-1$ | 2.723 | 1 | long Fe-Fe bond |
| $10\left(\eta^{2}-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.507 | 1 | global min. |
| $\left(\eta^{2}-\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})$ | $\mathrm{S}-2$ | 2.694 | 1 | long Fe-Fe bond |

[^13]
### 8.5. Binuclear Iron Carbonyl Complexes With Cyclopentadienyl and $\mathrm{C}_{5} \mathrm{~F}_{6}$ Ligands

Binuclear cyclopentadienyliron carbonyls have been known since the 1950s. Table 22 gives experimentally derived Fe - Fe bond distances in complexes 01 to 09 which span a wide structural variety. ${ }^{371,372,373,374,375,376,377,378,379}$ Complexes $\mathbf{0 1}$ to $\mathbf{0 8}$ have Fe-Fe bond lengths from 2.49 to $2.59 \AA$ which are consistent with single bonds. Complexes $\mathbf{0 6}$ and $\mathbf{0 7}$ are trans and cis isomers of the doubly bridged tetracarbonyl $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ with very similar $\mathrm{Fe}-\mathrm{Fe}$ single bond lengths and coexisting in equilibrium in solution. ${ }^{376,377} \mathrm{~A}$ crystal structure study (Milcher, Rees, and Lehmann ${ }^{378}$ ) of $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ gave an $\mathrm{Fe}-\mathrm{Fe}$ bond distance of $2.539 \AA$. Complex 09 is the permethylated tricarbonyl $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ with a short $\mathrm{Fe}=\mathrm{Fe}$ double bond length of $2.265 \AA$ and a triplet ground state. ${ }^{379}$ This corresponds to an $(18,18)$ configuration for the $\mathrm{Fe}_{2}$ core with the two unpaired electrons of the triplet ground state in the single-electron $\pi$ "half-bonds" of a $\sigma+2 / 2 \pi$ double bond. The unsubstituted $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ is also known (Casper and Moyer ${ }^{380}$, Wrighton ${ }^{381}$ ) but its structure has not been determined by X-ray crystallography.

Table 22 also presents BP 86 results on the series $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=4,3,2,1),{ }^{382}$ in which each Cp ligand binds in $\eta^{5}$-fashion The tetracarbonyl $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4} \mathbf{1 0}$ has three singlet minima, where $\mathrm{S}-1$ and S-2 are trans and cis isomers of $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$. The $\mathrm{Fe}-\mathrm{Fe}$ distance of $2.540 \AA$ in S-1 is very close to the experimental lengths of Bryan and Green for the trans isomer 06 and for $08 .{ }^{376,377}$ The cis isomer has two small imaginary frequencies and an $\mathrm{Fe}-\mathrm{Fe}$ bond length close to that in $\mathbf{0 7}$. The higher energy $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ structure $\mathrm{S}-3$ is an unbridged structure with a long $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.713 \AA$. The tricarbonyl $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3} 11$ has a triplet global minimum T-1 with the two unpaired electrons in a formal $\mathrm{Fe}=\mathrm{Fe} \sigma+2 / 2 \pi$ double bond of length $2.264 \AA$ remarkably close to the experimental value of $2.265 \AA$ for the permethyl derivative 09. The dicarbonyl $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2} \mathbf{1 2}$ has singlet and triplet minima $\mathrm{S}-1$ and $\mathrm{T}-2$, both with $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds. $\mathbf{1 2}$ is a proposed intermediate n110
(King ${ }^{383}$ ) for the formation of $\mathrm{Cp}_{4} \mathrm{Fe}_{4}(\mathrm{CO})_{4}$, obtained (Bursten ${ }^{384}$ ) by pyrolysis of $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$. The highly unsaturated monocarbonyl $\mathrm{Cp}_{2} \mathrm{Fe}_{2} \mathrm{CO} 13$ is yet unknown, but noteworthy for its ultrashort $\sigma+2 \pi+2 / 2 \delta$ quadruple Fe-Fe bond of length $2.069 \AA$.

Table 22. Fe-Fe Bond Lengths in Binuclear Cyclopentadienyliron Carbonyls ${ }^{\boldsymbol{a}}$

Label Complex \begin{tabular}{l}
State $R_{\mathrm{MM}}(\AA) \mathrm{fBO}$ Remarks

 

Refer- <br>
ences
\end{tabular}

Experimentally characterized
$01 \mathrm{Fe}_{2}\left(\pi-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{2} \mathrm{CNPh} \quad-\quad 2.53 \quad 1$ isonitrile ligand 371
$02 \mathrm{Fe}_{2}\left(\pi-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{2}\left(\mathrm{COAlEt}_{3}\right)_{2} \quad$ - $2.49(1) \quad 1 \quad \eta^{2}-\mu$-CO ligands 372
$03 \mathrm{Fe}_{2}(\mathrm{CO})_{4}\left[\left(\pi-\mathrm{C}_{5} \mathrm{H}_{4}\right) \mathrm{CH}\left(\mathrm{NMe}_{2}\right)\right]_{2} \quad-\quad 2.510(2) \quad 1$ diamine ligand 373
$04\left[\mathrm{Fe}_{2}\left(\pi-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{2}\right]_{2}\left(\mathrm{Ph}_{2} \mathrm{PC}\right)_{2} \quad-\quad 2.54 \quad 1$ diphosphine acetylene 374
05 cis $-\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3} \mathrm{SO}_{2} \quad-\quad 2.59 \AA 1$ sulfur dioxide ligand 375
06 trans $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \quad-\quad 2.534(2) \quad 1 \quad 2$ bridging CO ligands 376
07 cis $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \quad-\quad 2.531(2) \quad 1 \quad$ cf. trans isomer $06 \quad 377$
$\mathbf{0 8} \mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \quad-\quad 2.539 \quad 1 \quad$ cf. $\mathbf{0 6}$ and $\mathbf{0 7} 378$
$09\left(\eta^{5}-\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3} \quad$ T $2.265(1) \quad 2 \quad \sigma+2 / 2 \pi$ bonds $\quad 379$
Binuclear cyclopentadienyliron carbonyls (BP86 results; Ref. 382)

| 10 trans $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.540 | 1 | cf. 06 above (Ref. 376$)$ |
| :---: | :---: | :---: | :---: | :--- |
| cis $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-2$ | 2.545 | 1 | 2 small $i v ;$ cf. Refs. 377,378 |
| trans $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ | $\mathrm{~S}-3$ | 2.713 | 1 | $\Delta \mathrm{E}=9.1 ;$ long single MM bond |
| $\mathbf{1 1} \mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | $\mathrm{~T}-1$ | 2.264 | 2 | cf. Ref. $379 ;(18,18)$ |
| $\mathbf{1 2} \mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.120 | 3 | global min. |
| $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}$ | $\mathrm{~T}-2$ | 2.214 | 3 | $\Delta \mathrm{E}=3.3$ |
| $\mathbf{1 3} \mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})$ | $\mathrm{T}-1$ | 2.069 | 4 | $\sigma+2 \pi+2 / 2 \delta$ bonds |

Binuclear hexafluorocyclopentadiene iron carbonyls (BP86 results; Ref. 385)

| $\mathbf{1 4}\left(\eta^{3}, \eta^{1}-\mu-\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.802 | 1 | sole min. |
| ---: | :--- | :--- | :--- | :--- |
| $\mathbf{1 5}\left(\eta^{3}, \eta^{1}-\mu-\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.558 | 2 | global min. |
| $\left(\eta^{3}, \eta^{1}-\mu-\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{3}$ | $\mathrm{~T}-2$ | 2.459 | 2 | $\sigma+2 / 2 \pi ; \Delta \mathrm{E}=9.1$ |
| $\mathbf{1 6}\left(\eta^{1}, \eta^{3}-\mu-\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.337 | 2 | $(16,18)$ |
| $\left(\eta^{2}, \eta^{2}-\mu-\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{2}$ | $\mathrm{~S}-2$ | 2.278 | 3 | bis(dihapto); $\Delta \mathrm{E}=10.0$ |

[^14]Table 22 also gives BP86 results for the hexafluorocyclopentadiene diiron carbonyl series $\left(\mathrm{C}_{5} \mathrm{~F}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=8,7,6,5)^{385}$ among which the octacarbonyl $\left(\mathrm{C}_{5} \mathrm{~F}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{8}$ is known (Banks and Hazeldine ${ }^{386}$ ) experimentally. These complexes have a neutral $\mathrm{Fe}_{2}$ core. The BP86 results predict bis(dihapto) $\left(\eta^{2}, \eta^{2}\right)$ as well as $\left(\eta^{3}, \eta^{1}\right)$ bridging modes for ligand binding. The octacarbonyl has bis(dihapto) binding with no direct $\mathrm{Fe}-\mathrm{Fe}$ bond, and is not listed. The heptacarbonyl $\left(\eta^{3}, \eta^{1}-\mu-\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{4} 14$ has a long $\mathrm{Fe}(0)-\mathrm{Fe}(0)$ single bond distance of $2.802 \AA$. The hexacarbonyl $\mathbf{1 5}$ has $\left(\eta^{3}, \eta^{1}\right)$ bridged structures for the S-1 and T-2 minima with rather long $\mathrm{Fe}=\mathrm{Fe}$ double bonds of lengths 2.558 and $2.459 \AA$, respectively, with the latter $\mathrm{Fe}=\mathrm{Fe}$ double bond being of the $\sigma+2 / 2 \pi$ type $)$. The pentacarbonyl $\left(\mathrm{C}_{5} \mathrm{~F}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5} \mathbf{1 6}$ has a singlet global minimum $\mathrm{S}-1$ with an $\mathrm{Fe}=\mathrm{Fe}$ bond length of $2.337 \AA$, while a higher energy isomer S-2 has a bis(dihapto) structure with an $\mathrm{Fe}=\mathrm{Fe}$ triple bond length of $2.278 \AA$.

### 8.6. Binuclear Iron Carbonyl Complexes With Fused Carbocyclic Ligands

Table 23 gives experimental and computational $\mathrm{Fe}-\mathrm{Fe}$ bond distances for binuclear iron carbonyl complexes having fused carbocycles (pentalene, indenyl, and azulene) as ligands. The permethylated pentalene diiron complex (Weidemuller and Hafner ${ }^{387}$ ) cis ( $\eta^{5}, \eta^{5}$ $\left.\mathrm{C}_{8} \mathrm{Me}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5} \mathbf{0 1}$ (Figure 11d) has an $\mathrm{Fe}-\mathrm{Fe}$ distance of $2.687 \AA$, which may be described as a single bond. Other known binuclear complexes with the $\mathrm{C}_{8} \mathrm{Me}_{6}$ ligand include the dicobalt complex $\mathrm{C}_{8} \mathrm{Me}_{6} \mathrm{Co}_{2}(\mathrm{CO})_{4}$ and the series $\left(\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{M}_{2}(\mathrm{M}=\mathrm{V}$, $\mathrm{Cr}, \mathrm{Mn}, \mathrm{Co}, \mathrm{Ni}) .{ }^{119}$ Although binuclear indenyliron carbonyls have not been structurally characterized, a dicobalt bis(indenyl) derivative is known (Hung-Low and Bradley ${ }^{388}$ ). The azulene carbonyl complex cis $\left(\eta^{5}, \eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5} \mathbf{0 2}$ (Figure 11e) has an $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.782 \AA$ (Churchill ${ }^{389}$ ). The complex 03 (Pettit ${ }^{390}$ ) has a cyclooctatetraene (COT) ligand with an $\mathrm{Fe}-$ Fe single bond of length $2.742 \AA$.

Table 23. Fe-Fe Bond Distances for Binuclear Iron Carbonyls Containing Pentalene, Indenyl and Azulene Ligands ${ }^{a}$

| Label Complex | State $R_{M M}(\AA)$ fBO Remarks/References |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Experimentally characterized |  |  |  |  |
| 01 cis $\left(\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{Me}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5}$ | S | 2.687 | 1 | pentalene; XRD; Ref. 387 |
| 02 cis $\left(\eta^{5}, \eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{Fe}_{2}(\mathrm{CO})_{5}\right.$ | S | 2.782 | 1 | azulene; XRD; Ref. 389 |
| $03\left(\eta^{5}, \eta^{3}-\mathrm{C}_{8} \mathrm{H}_{8} \mathrm{Fe}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO})\right.$ | S | 2.742 | 1 | COT; XRD; Ref. 390 |

Binuclear pentaleneiron carbonyls (BP86 results; Ref. 391)


```
05 cis (\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{8}{}\mp@subsup{\textrm{H}}{6}{})\mp@subsup{\textrm{Fe}}{2}{}(\textrm{CO}\mp@subsup{)}{4}{}(\mu-\textrm{CO})\quad\mathrm{ S-1 
```



```
    cis (\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{8}{}\mp@subsup{\textrm{H}}{6}{})\mp@subsup{\textrm{Fe}}{2}{}(\textrm{CO}\mp@subsup{)}{4}{
T-2 2.499 2 (18,18); \DeltaE=0.6;\sigma+2/2\pi
    cis (\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{3}-\mp@subsup{\textrm{C}}{8}{}\mp@subsup{\textrm{H}}{6}{})\mp@subsup{\textrm{Fe}}{2}{(}(\mu-\textrm{CO})(\textrm{CO}\mp@subsup{)}{3}{
S-3 2.568 2 \DeltaE=1.3
S-1 2.304 3 (18,18)
```

Binuclear indenyliron carbonyls (BP86 results; Ref. 392)

| $\mathbf{0 8}\left(\eta^{3}, \eta^{3}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6}$ | $\mathrm{~S}-1$ | 2.771 | 1 | no $\mu-\mathrm{CO}$ |
| :---: | :---: | :---: | :--- | :--- |
| $\mathbf{0 9}\left(\eta^{5}, \eta^{5}-\mu-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-1$ | $>3.0$ | 0 | no Fe-Fe bond |
| $\left(\eta^{5}, \eta^{1}-\mu-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.610 | 1 | $\Delta \mathrm{E}=6.8$ |
| $\left(\eta^{5}, \eta^{3}-\mu-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-3$ | 2.971 | 1 | long Fe-Fe bond; $\Delta \mathrm{E}=6.9$ |
| $\mathbf{1 0}\left(\eta^{5}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.556 | 1 | global min. |
|  | $\mathrm{S}-2$ | 2.556 | 1 | $\Delta \mathrm{E}=1.8$ |
| $\mathbf{1 1}\left(\eta^{5}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | $\mathrm{~S}-3$ | 2.539 | 1 | $\Delta \mathrm{E}=2.8$ |
| syn $\left(\eta^{5}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | $\mathrm{~T}-1$ | 2.253 | 2 | global min.; $\sigma+2 / 2 \pi$ |
| anti $\left(\eta^{5}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.299 | 2 | $\Delta \mathrm{E}=2.2$ |
| $\left(\eta^{5}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})$ | $\mathrm{S}-3$ | 2.286 | 2 | $\Delta \mathrm{E}=3.7$ |
| $\mathbf{1 2}\left(\eta^{5}-\mu-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~T}-4$ | 2.372 | 2 | $\Delta \mathrm{E}=7.4 ; \sigma+2 / 2 \pi$ |
| $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.866 | 1 | $9-\mathrm{e}$ bridging indenyl |
| $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-2$ | 2.084 | 3 | $\Delta \mathrm{E}=9.0$ |
| $\mathbf{1 3}\left(\mu-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})$ | $\mathrm{S}-3$ | 2.127 | 3 | $\Delta \mathrm{E}=9.5$ |
| $\left(\eta^{4}, \eta^{5}-\mu-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe} 2(\mathrm{CO})$ | $\mathrm{T}-1$ | 2.789 | 1 | global min. |
| $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})$ | $\mathrm{S}-2$ | 2.539 | 1 | $9-\mathrm{e}$ bridging indenyl |
|  | T-3 | 1.991 | 4 | $\Delta \mathrm{E}=18.6$ |

Binuclear azuleneiron carbonyls (BP86 results; Ref. 395)

| $\mathbf{1 4}\left(\eta^{4}, \eta^{4}-\mu-\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.730 | 1 | . |
| :--- | :---: | :---: | :---: | :---: |
| $\mathbf{1 5}\left(\eta^{5}, \eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-1$ | 2.793 | 1 | cf. 02; Ref. 389 |

```
16(\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{3}-\mu-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{}(\textrm{CO}\mp@subsup{)}{2}{}(\mu-\textrm{CO}\mp@subsup{)}{2}{}\quad\textrm{S}-1\quad2.482\quad2 global min.
    (\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{3}-\mu-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{2}(\textrm{CO}\mp@subsup{)}{3}{}(\mu-\textrm{CO})\quad\mathrm{ T-2 2.515 2 
17(\eta
18(\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{8}{\prime}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{(}(\textrm{CO}\mp@subsup{)}{2}{
    (\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{}(\textrm{CO}\mp@subsup{)}{2}{
    (\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{H}{8}{\prime})2\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{(CO}\mp@subsup{)}{2}{
19(\eta}\mp@subsup{\eta}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{(}(\textrm{CO}
    (\eta
    (\eta}\mp@subsup{}{}{5},\mp@subsup{\eta}{}{5}-\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{)}{2}{}\mp@subsup{\textrm{Fe}}{2}{}(\textrm{CO}
\begin{tabular}{llll} 
S-1 & 2.482 & 2 & global min. \\
T-2 & 2.515 & 2 & \(\sigma+2 / 2 \pi ; \Delta \mathrm{E}=6.6\)
\end{tabular}
T-1 2.577 1 dative single bond; (17,17)
Q-1 2.408 2 glob min.; \sigma+2/2\pi; (17,17)
T-2 2.437 2 \sigma 
S-3 2.256 3 (18,18); \DeltaE=6.6
Q-1 2.324 3 global min.
T-2 2.308 3 \DeltaE=4.1
S-3 2.416 2 \DeltaE=6.6;(16,16)
```

${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

Table 23 gives BP 86 results on $\mathrm{Fe}-\mathrm{Fe}$ bond lengths for the three series of pentalene, indenyl, and azulene diiron carbonyl complexes. A BP86 study on the pentalene complexes treated the series $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=6,5,4,3){ }^{391}$ exhibiting varying ligand hapticity in binding to the $\mathrm{Fe}_{2}$ core. The cis isomer of the hexacarbonyl $\left(\eta^{5}, \eta^{1}-\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{5} \mathbf{0 4}$ is slightly lower in energy than the corresponding trans isomer, and has an $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.646 \AA$, where the ligand is a 6 -electron donor. The pentacarbonyl $\left(\eta^{5}, \eta^{5}-\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{4}(\mu-\mathrm{CO}) 05$ has a long $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.753 \AA$, a little higher than the experimental value of $2.687 \AA$ for the permethylated derivative. ${ }^{387}$ The tetracarbonyl $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{4} \mathbf{0 6}$ has a triplet global minimum with an $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.629 \AA$. Higher energy $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ structures include $\mathrm{T}-2$ with an $\mathrm{Fe}=\mathrm{Fe} \sigma+$ $2 / 2 \pi$ type double bond of length $2.499 \AA$, and $\mathrm{S}-3$ with an $\mathrm{Fe}=\mathrm{Fe}$ double bond length of 2.568 $\AA$. The unbridged tricarbonyl $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{3} \mathbf{0 7}$ has an $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond of length $2.304 \AA$. BP86 results (Table 23) on the binuclear indenyliron carbonyls $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=6,5$, $4,3,2,1)^{392}$ reveal varying hapticity for binding of the indenyl ligands to the $\left(\mathrm{Fe}_{2}\right)^{+2}$ core. The carbonyl-rich structures $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=5,6)$ are not thermodynamically viable. The hexacarbonyl $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{6} \mathbf{0 8}$ has each indenyl group bonded as a trihapto ligand to each Fe atom with an $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.771 \AA$. The pentacarbonyl n114
$\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{5} 09$ has three singlet minima $\mathrm{S}-1, \mathrm{~S}-2$, and $\mathrm{S}-3$ with varying indenyl hapticities, respectively having no $\mathrm{Fe} \cdots \mathrm{Fe}$ bond, an $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.610 \AA$, and a long Fe-Fe single bond of length $2.971 \AA$. The doubly bridged tetracarbonyl $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \mathbf{1 0}$ has been synthesized; ${ }^{393}$ the BP86 results on this system predict three singlet minima S-1, S-2 and S-3. All three of these singlet structures have similar energies suggesting a fluxional situation, with very similar $\mathrm{Fe}-\mathrm{Fe}$ single bond lengths of $2.556,2.556$, and $2.539 \AA$, respectively. Two isomers of the tricarbonyl $\mathbf{1 1}$ $\left(\eta^{5}, \eta^{5}-\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ have been found by infrared spectroscopy of the $v(\mathrm{CO})$ frequencies. ${ }^{394}$ The BP86 results show several minima (T-1, S-2, S-3 and T-4) for the $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ system, differing in CO bridging modes, and with $\mathrm{Fe}=\mathrm{Fe}$ double bond lengths from 2.253 to $2.370 \AA$. The $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ global minimum $\mathrm{T}-1$ has an $\mathrm{Fe}=\mathrm{Fe}$ double bond length of $2.253 \AA$, close to the value of $2.265 \AA$ for the cyclopentadienyl counterpart $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$. The dicarbonyl $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2} \mathbf{1 2}$ has a singlet global minimum with the indenyl ligand acting as a nine-electron donor bridging ligand, giving an $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.866 \AA$. Higher energy singlet $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ structures S-2 and S-3 have $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond lengths of 2.084 and $2.127 \AA$, respectively. The monocarbonyl $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO}) \mathbf{1 3}$ has a triplet global minimum T-1 with an $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.789 \AA$ and a higher energy singlet minimum $\mathrm{S}-2$ with an $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.539 \AA$. Of special interest is the triplet $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})$ structure T-3, lying $18.6 \mathrm{kcal} / \mathrm{mol}$ above the global minimum, with an ultrashort $\mathrm{Fe}-\mathrm{Fe}$ quadruple bond of length $1.991 \AA$.

Table 23 also lists BP86 predictions for the binuclear azuleneiron carbonyl series $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}(n=6,5,4,3,2,1),{ }^{395}$ showing variable hapticity for the azulene ligand binding to the neutral $\mathrm{Fe}_{2}$ core. The hexacarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{6} \mathbf{1 4}$ has $\eta^{4}, \eta^{4}$ hapticity for the bridging azulene ligand and a global minimum $\mathrm{S}-1$ with an $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.730 \AA$. The pentacarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5} \mathbf{1 5}$ has $\eta^{5}, \eta^{3}$ hapticity for azulene coordination
in the global minimum S-1 where the $\mathrm{Fe}-\mathrm{Fe}$ single bond length of $2.793 \AA$ is very close to the experimental value (Churchill ${ }^{389}$ ) of $2.782 \AA$. The tetracarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{4} \mathbf{1 6}$ has minima S-1 and T-2 showing $\eta^{4}, \eta^{4}$ hapticity of azulene coordination and different CO ligand binding modes, with $\mathrm{Fe}=\mathrm{Fe}$ bond lengths of 2.482 and $2.515 \AA$, respectively. The tricarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{3} \mathbf{1 7}$ is a ground state triplet with an $\mathrm{Fe} \rightarrow \mathrm{Fe}$ dative single bond of length $2.577 \AA$ and a $(17,17)$ configuration of the $\mathrm{Fe}_{2}$ core. The dicarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{2} \mathbf{1 8}$ and monocarbonyl $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right) \mathrm{Fe}_{2}(\mathrm{CO}) 19$ both have quintet global minima $\mathrm{Q}-1$ with double and triple $\mathrm{Fe}-\mathrm{Fe}$ bonds respectively, and higher energy minima $\mathrm{S}-2$ and $\mathrm{T}-3 . \mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds are seen in S-3 of the dicarbonyl and in structures S-2 and T-3 of the monocarbonyl.

### 8.7. Binuclear Iron Carbonyl Complexes with Boron-based Ligands

Table 24 gives BP86 predictions of $\mathrm{Fe}-\mathrm{Fe}$ bond lengths in three series of binuclear iron carbonyl complexes containing boron-based ligands, where singlet and triplet structures are numbered separately in order of increasing energy. The ligand coordination modes are indicated in the second column. The diiron boronyl carbonyl $\mathrm{Fe}_{2}(\mathrm{BO})_{2}(\mathrm{CO})_{8} \mathbf{0 1},{ }^{396}$ isoelectronic with $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$, gives three singlet minima all with long $\mathrm{Fe}-\mathrm{Fe}$ single bonds ranging from 2.837 to $2.976 \AA$ in length.

In the diiron fluoroborylene carbonyl series $\mathrm{Fe}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{n}(n=5,4),{ }^{397}$ the pentacarbonyl 02 has two singlet minima with $\mathrm{Fe}=\mathrm{Fe}$ double bonds of lengths 2.406 and $2.476 \AA$ and two triplet minima with slightly longer $\mathrm{Fe}-\mathrm{Fe}$ single bonds of lengths 2.500 and $2.541 \AA$ (Table 24). These triplets have $(17,17)$ configurations of the central $\mathrm{Fe}_{2}$ unit. The tetracarbonyl $\mathrm{Fe}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{4} \mathbf{0 3}$ has three triplet minima with different MM core configurations. Thus T-1 has a long dative $\mathrm{Fe}-\mathrm{Fe}$ bond of length $2.708 \AA$ ), $\mathrm{T}-2$ has an $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond of length $2.304 \AA$, and T-3 has a short $\mathrm{Fe}-\mathrm{Fe}$ bond of length $2.492 \AA$. The singlet $\mathrm{Fe}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{4}$ structure S-2 has a short $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond of length $2.304 \AA$.

Table 24. Fe-Fe Bond Lengths in Binuclear Iron Carbonyl Complexes Containing Boron-Based Ligands (DFT Values) ${ }^{a}$

| Label Species | State $R_{M M}(\AA)$ fBO Remarks |
| :---: | :---: |

Binuclear iron boronyl carbonyls (BP86 results; Ref. 396)
$01 \mathrm{Fe}_{2}(\mathrm{BO})_{2}(\mathrm{CO})_{8}$
S-1 $\quad 2.878 \quad 1 \quad c f . \mathrm{Mn}_{2}(\mathrm{CO})_{10}$
$\mathrm{Fe}_{2}(\mathrm{BO})_{2}(\mathrm{CO})_{8}$
S-2 $2.837 \quad 1$
$\mathrm{Fe}_{2}(\mathrm{BO})_{2}(\mathrm{CO})_{8}$
S-3 $2.976 \quad 1$

Binuclear fluoroborylene iron carbonyls (BP86 results; Ref. 397)

| $\mathbf{0 2} \mathrm{Fe}_{2}(\mu-\mathrm{BF})(\mathrm{BF})\left(\eta^{2}-\mu-\mathrm{CO}\right)(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.406 | 2 | glob. min. $(\mathrm{BP} 86)$ |
| :---: | :---: | :---: | :---: | :--- |
| $\mathrm{Fe}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{3}(\mathrm{CO})_{2}$ | $\mathrm{~S}-2$ | 2.476 | 2 | $(18,16)$ |
| $\mathrm{Fe}_{2}(\mu-\mathrm{BF})_{2}(\mathrm{CO})_{5}$ | $\mathrm{~T}-1$ | 2.500 | 1 | $(17,15)$ |
| $\mathrm{Fe}_{2}(\mu-\mathrm{BF})_{2}(\mathrm{CO})_{5}$ | $\mathrm{~T}-2$ | 2.541 | 1 | $(17,17) ; \mathrm{Fe}^{+}-\mathrm{Fe}^{+}$bond |
| $\mathbf{0 3} \mathrm{Fe}_{2}\left(\eta^{1}-\mu-\mathrm{BF}\right)(\mathrm{BF})(\mu-\mathrm{CO})(\mathrm{CO})_{3}$ | $\mathrm{~T}-1$ | 2.708 | 2 | $(17,17) ;$ dative $\mathrm{Fe} \leftarrow \mathrm{Fe}$ bond |
| $\mathrm{Fe}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{4}$ | $\mathrm{~T}-2$ | 2.304 | 3 | $(18,16) ; \Delta \mathrm{E}=1.0$ |
| $\mathrm{Fe}_{2}(\mu-\mathrm{BF})_{2}(\mathrm{CO})_{4}$ | $\mathrm{~T}-3$ | 2.492 | 1 | $(15,15) ; \Delta \mathrm{E}=5.0$ |
| $\mathrm{Fe}_{2}\left(\mu-\mathrm{B}_{2} \mathrm{~F}_{2}\right)(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.287 | 3 | $(18,16)$ |

Binuclear dimethylaminoborole iron carbonyls (BP86 results; Ref. 398)

| 04 trans $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{4}$ | S-1 | 2.786 | 1 | glob. min.; no $\mathrm{N} \rightarrow \mathrm{Fe}$ bond |
| :---: | :---: | :---: | :---: | :---: |
| trans $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right) \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{4}$ | S-2 | 2.808 | 1 | no $\mathrm{N} \rightarrow \mathrm{Fe}$ bond |
| cis $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{4}$ | S-3 | 2.839 | 1 | no $\mathrm{N} \rightarrow \mathrm{Fe}$ bond |
| $05\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{2}$ | S-1 | 2.542 | 2 | glob. min.; $\mathrm{N} \rightarrow$ Fe bond |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{2}$ | S-2 | 2.570 | 2 | $\mathrm{N} \rightarrow \mathrm{Fe}$ bond |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})_{2}$ | S-3 | 2.580 | 2 | $\mathrm{N} \rightarrow \mathrm{Fe}$ bond |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{3}$ | T-1 | 2.475 | 2 | $\sigma+2 / 2 \pi$ |
| $06\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{3}$ | S-1 | 2.219 | 3 | glob. min. |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{2}$ | S-2 | 2.218 | 3 |  |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{CO})$ | T-1 | 2.347 | 2 | $(17,17)$ |
| $07\left(\mu-\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ | S-1 | 2.769 | 1 | glob. min.; $2 \mathrm{~N} \rightarrow$ Fe bonds |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})$ | T-1 | 2.303 | 3 | $(17,17)$ |
| $\left(\mu-\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2}$ | T-2 | 2.690 | 1 | $(17,17) \mathrm{N} \rightarrow$ Fe bond |
| $\left(\mu-\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})_{2}$ | T-3 | 2.238 | 3 | $(17,17)$ |
| $\mathbf{0 8}\left(\mu-\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})$ | T-1 | 2.397 | 2 | glob. min.; (17,17) |
| $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mu-\mathrm{CO})(\mathrm{CO})$ | S-1 | 2.632 | 2 | $2 \mathrm{~N} \rightarrow \mathrm{Fe}$ bonds |

[^15]The dimethylaminoborole carbonyl series $\mathrm{Fe}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2}(\mathrm{CO})_{n}(n=5,4,3,2,1)^{398}$ exhibits many examples of $\mathrm{N} \rightarrow \mathrm{Fe}$ dative bonds, and some structures in which where the aminoborole ligand bridges the central $\mathrm{Fe}_{2}$ unit (Table 24). The $\mathrm{Fe}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2}(\mathrm{CO})_{5}$ system 04 has three singlet minima with long $\mathrm{Fe}-\mathrm{Fe}$ single bonds of lengths ranging from 2.786 to $2.839 \AA$. The $\mathrm{Fe}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2}(\mathrm{CO})_{4}$ system 05 has three singlet minima with $\mathrm{Fe}=\mathrm{Fe}$ double bonds of lengths 2.542 to $2.580 \AA$ and a triplet electronic state with an $\mathrm{Fe}=\mathrm{Fe}$ bond of length $2.475 \AA$. The $\mathrm{Fe}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2}(\mathrm{CO})_{3}$ system 06 (Figure 11f) has two singlet minima with $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds of lengths $\sim 2.22 \AA$ and one triplet with an $\mathrm{Fe}=\mathrm{Fe}$ double bond of length $2.347 \AA$. The $\mathrm{Fe}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}\right)_{2}(\mathrm{CO})_{2}$ system $\mathbf{0 7}$ has a singlet global minimum with an $\mathrm{Fe}-\mathrm{Fe}$ single bond of $2.769 \AA$, two triplet minima with $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds of lengths 2.303 and $2.238 \AA$, and a triplet structure with an $\mathrm{Fe}-\mathrm{Fe}$ single bond of length $2.690 \AA$. The $\mathrm{Fe}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right)_{2}(\mathrm{CO})$ system $\mathbf{0 8}$ has a triplet global minimum and a singlet minimum both with an $\mathrm{Fe}=\mathrm{Fe}$ double bond of lengths 2.397 and $2.632 \AA$, respectively.

### 8.8. Fe-Fe Bond Distances and Bond Orders

The experimentally derived $\mathrm{Fe}-\mathrm{Fe}$ distances for $\mathrm{Fe}_{2}$ and various diiron complexes in Tables 19, 20, 22, and 23 lead to the following analysis as to how $\mathrm{Fe}-\mathrm{Fe}$ bond length ranges change with formal bond order. The $\mathrm{Fe} \equiv \mathrm{Fe}$ bond of length about $2.02 \AA$ in the iron dimer is assigned an fBO of 3, which may be also assigned to the $\mathrm{Fe} \equiv \mathrm{Fe}$ bond of length $2.127 \AA$ in $\mathbf{0 2}$ of Table 19, and to the $\mathrm{Fe} \equiv \mathrm{Fe}$ bond of length 2.148 in $\mathbf{0 3}$ of Table 21. This gives a range from 2.02 to $2.148 \AA$ (or $2.08 \pm 0.06 \AA$ ) for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds from these limited results, excluding the $R_{M M}$ value of $2.519 \AA$ for the proposed $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond in $\mathbf{2 1}$ of Table 19.

An fBO value of 2 is assigned to the $\mathrm{Fe}=\mathrm{Fe}$ bond lengths of $2.443 \AA$ in $\mathbf{0 9}$ of Table 19, of $2.316 \AA$ in $\mathbf{0 2}$ of Table 20, and of $2.265 \AA$ to $\mathbf{0 9}$ 0f Table 22, giving a range of $2.35 \pm 0.09 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds in carbonyl and non-carbonyl diiron complexes. The range 2.198 to
$2.232 \AA(2.21 \pm 0.02 \AA)$ for $R_{M M}$ values in complexes $\mathbf{0 3}$ and $\mathbf{0 4}$ of Table 19 is associated with an fBO value of 1.5 . An fBO value of 1 assigned to some non-carbonyl complexes of Table 19 is associated with $R_{M M}$ values of $2.462 \AA$ in $\mathbf{0 6}, 2.390 \AA$ in $\mathbf{2 4}$, and values up to $2.621 \AA$ for structures deemed to have $\mathrm{Fe}-\mathrm{Fe}$ single bonds. This gives the $R_{M M}$ range $2.51 \pm 0.12 \AA$ for diiron non-carbonyl complexes. For binuclear iron carbonyl complexes, the $R_{M M}$ values of $2.523 \AA$ in $\mathrm{Fe}_{2}(\mathrm{CO})_{9}, 2.49$ to $2.59 \AA$ for $\mathbf{0 1}$ to $\mathbf{0 8}$ in Table 22, and 2.687 and $2.787 \AA$ for $\mathbf{0 1}$ and $\mathbf{0 2}$ in Table 23 are linked to an fBO of 1 . This gives a range of $2.64 \pm 0.15 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bond lengths in binuclear iron carbonyl complexes, although this range includes structures described as having 3-centre 2 -electron bonds. An $R_{M M}$ value of $2.687 \AA$ is linked to the BO of 0.5 in $\mathbf{1 0}$ of Table 19. $R_{M M}$ values higher than about $2.8 \AA$ in $\mathbf{0 7}$ and $\mathbf{1 7}$ of Table 19 suggest the absence of an $\mathrm{Fe}-\mathrm{Fe}$ covalent bond. Only the $R_{M M}$ values related to an fBO of 1.5 do not fit the trend here of increasing experimental $\mathrm{Fe}-\mathrm{Fe}$ bond length with decrease in assigned formal bond order.

The following paragraphs describe trends and ranges of $\mathrm{Fe}-\mathrm{Fe}$ bond lengths for binuclear iron carbonyl complexes obtained from DFT (mostly BP86) results. Table 25 presents ranges for single, double and triple MM bonds in various series of binuclear iron carbonyl complexes studied computationally. Fe-Fe bond lengths of higher order are also mentioned in the discussion. The homoleptic binuclear iron carbonyl series $\mathrm{Fe}_{2}(\mathrm{CO})_{n}$ (Table 20) ${ }^{355}$ yields an $R_{M M}$ value of $2.525 \AA$ (B3LYP/DZP) for the $\mathrm{Fe}-\mathrm{Fe}$ single bond in $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$, very close to the Cotton and Troup ${ }^{342}$ experimental value of $2.523 \AA$, although this iron-iron interaction does not necessarily involve a direct $\mathrm{Fe}-\mathrm{Fe}$ bond as discussed above. $\mathrm{Fe}=\mathrm{Fe}$ double bond lengths (BP86) have the range $2.49 \pm 0.06 \AA$ and $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds have the range $2.22 \pm 0.02$ $\AA$. The sole quadruple $\mathrm{Fe}-\mathrm{Fe}$ bond is shorter at $2.029 \AA$. The expected trend single $>$ double $>$ triple > quadruple in $\mathrm{Fe}-\mathrm{Fe}$ bond lengths is thus evident in these MM bond ranges.

The effects of hydrocarbon ligands in binuclear iron carbonyls was studied by the BP86 method for the acetylene, cyclobutadiene, butadiene, cyclopentadienyl, hexafluorocyclopentadiene, pentalene, indenyl and azulene ligands. The acetylene $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ systems ${ }^{366}$ (Table 20) exhibit the following length ranges for iron-iron bonds: $2.67 \pm 0.13 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds and $2.37 \pm 0.03 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds. The cyclobutadiene $\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{367}$ (Table 21) exhibit the following length ranges for iron-iron bonds: $2.743 \AA$ for the sole example of a $\mathrm{Fe}-\mathrm{Fe}$ single bond, $2.51 \pm 0.12 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.25 \pm 0.08 \AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds. The butadiene $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{370}$ (Table 21) exhibit the following length ranges for iron-iron bonds: $2.63 \pm 0.13 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.43 \pm 0.11$ $\AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.164 \AA$ for the only example of a $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond. The cyclopentadienyl $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{382}$ (Table 22) exhibit the following length ranges for iron-iron bonds: $2.63 \pm 0.09 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.264 \AA$ for the sole example of an $\mathrm{Fe}=\mathrm{Fe}$ double bond, $2.16 \pm 0.05 \AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds, and $2.069 \AA$ for the sole example of a Fe - Fe quadruple bond. The hexafluorocyclopentadiene $\left(\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{385}$ (Table 22) exhibits the following length ranges for iron-iron bonds: $2.802 \AA$ for the sole example of an $\mathrm{Fe}-\mathrm{Fe}$ single bond, $2.45 \pm 0.11 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.278 \AA$ for the sole example of an $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond. The pentalene $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{391}$ (Table 23) exhibits the following length ranges for iron-iron bonds: $2.69 \pm 0.06 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.47 \pm 0.17$ $\AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.304 \AA$ for the sole example of an $\mathrm{Fe}=\mathrm{Fe}$ triple bond. The indenyl $\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{392}$ (Table 23) exhibit the following length ranges for iron-iron bonds: $2.70 \pm 0.16 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.31 \pm 0.06 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, $2.11 \pm 0.03$ $\AA$ for $\mathrm{Fe}=\mathrm{Fe}$ triple bonds, and $1.991 \AA$ for the sole example of an $\mathrm{Fe}-\mathrm{Fe}$ quadruple bond. Finally, the $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ azulene series ${ }^{395}$ (Table 23) exhibit the following length ranges for iron-iron bonds: $2.68 \pm 0.11 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.46 \pm 0.05 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.29 \pm 0.04 \AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds.

Table 25. Iron-Iron Bond Length ( $\AA$ ) Ranges in Various Series of Binuclear Iron Carbonyl Complexes (DFT Results)

| No Series | Refer- | Single bond | Double bond | Triple bond |
| :---: | :---: | :---: | :---: | :---: |
| $01 \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 355 | 2.519 | $2.495 \pm 0.052$ | $2.221 \pm 0.015$ |
| $02 \mathrm{C}_{2} \mathrm{H}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 366 | $2.674 \pm 0.129$ | $2.374 \pm 0.025$ | - |
| $03\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 367 | 2.743 | $2.508 \pm 0.122$ | $2.225 \pm 0.077$ |
| $04\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 370 | $2.635 \pm 0.128$ | $2.432 \pm 0.109$ | 2.164 |
| $05\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 382 | $2.627 \pm 0.087$ | 2.264 | $2.167 \pm 0.047$ |
| $06\left(\mathrm{C}_{5} \mathrm{~F}_{6}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 385 | 2.802 | $2.448 \pm 0.111$ | 2.278 |
| $07\left(\mathrm{C}_{8} \mathrm{H}_{6}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 391 | $2.691 \pm 0.062$ | $2.467 \pm 0.163$ | 2.304 |
| $08\left(\mathrm{C}_{9} \mathrm{H}_{7}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 392 | $2.703 \pm 0.164$ | $2.313 \pm 0.060$ | $2.106 \pm 0.022$ |
| $09\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 395 | $2.685 \pm 0.108$ | $2.462 \pm 0.054$ | $2.290 \pm 0.034$ |
| $10(\mathrm{BO})_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{8}$ | 396 | $2.907 \pm 0.070$ | - | - |
| $11(\mathrm{BF})_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 397 | $2.517 \pm 0.024$ | $2.441 \pm 0.085$ | $2.296 \pm 0.009$ |
| $12(\mathrm{BS})_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 399 | $2.718 \pm 0.104$ | - | - |
| $13\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BH}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 400 | $2.736 \pm 0.128$ | $2.406 \pm 0.097$ | $2.209 \pm 0.043$ |
| $14\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BCH}_{3}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 401 | $2.713 \pm 0.104$ | $2.453 \pm 0.056$ | $2.206 \pm 0.029$ |
| $15\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BNMe}_{2}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 398 | $2.765 \pm 0.075$ | $2.490 \pm 0.143$ | $2.261 \pm 0.043$ |
| $16\left(\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{BCH}_{3}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 401 | $2.593 \pm 0.002$ | $2.379 \pm 0.099$ | - |
| $17\left(\mathrm{Me}_{4} \mathrm{~B}_{2} \mathrm{~N}_{2} \mathrm{CH}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 403 | $2.571 \pm 0.008$ | $2.389 \pm 0.094$ | - |
| $18\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 404 | $2.568 \pm 0.066$ | - | - |
| $19\left(\mathrm{CF}_{3} \mathrm{NC}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 405 | $2.631 \pm 0.124$ | $2.531 \pm 0.029$ | - |
| $20\left(\mathrm{CF}_{2}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 406 | $2.559 \pm 0.089$ | $2.430 \pm 0.100$ | - |
| $21\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | 407 | $2.621 \pm 0.149$ | $2.314 \pm 0.046$ | $2.141 \pm 0.002$ |

The BP86 results on various series of binuclear iron carbonyl complexes with boron-based ligands are also summarized this way, using the predictions tabulated in Table 24. More information is also available from untabulated data. The $\mathrm{Fe}-\mathrm{Fe}$ single bonds in the boronyl $\mathrm{Fe}_{2}(\mathrm{BO})_{2}(\mathrm{CO})_{8}$ series ${ }^{396}$ exhibit the range $2.91 \pm 0.07 \AA$. The $\mathrm{Fe}-\mathrm{Fe}$ single bonds in the
thioboronyl $\mathrm{Fe}_{2}(\mathrm{BS})_{2}(\mathrm{CO})_{n}$ series ${ }^{399}$ are shorter than those in the corresponding boronyl derivatives, falling in the range $2.72 \pm 0.10 \AA$. The fluoroborylene $\mathrm{Fe}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{n}$ series ${ }^{397}$ exhibits the following length ranges for iron-iron bonds: $2.52 \pm 0.02 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.44 \pm 0.09 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.30 \pm 0.01 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ triple bonds. The borole $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BH}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{400}$ exhibits the following length ranges for iron-iron bonds: $2.74 \pm 0.13 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.40 \pm 0.10 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.21 \pm 0.04 \AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds. The methylborole $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{BCH}_{3}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{401}$ gives the following length ranges for iron-iron bonds: $2.71 \pm 0.10 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.45 \pm 0.06 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, $2.21 \pm 0.03 \AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds and $2.12 \pm 0.03 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ quadruple bonds. The dimethylaminoborole $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{NBMe}_{2}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{398}$ exhibits the following length ranges for iron-iron bonds: $2.77 \pm 0.08 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds, $2.49 \pm 0.14$ $\AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds, and $2.26 \pm 0.04 \AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds. The methylborabenzene $\left(\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{BCH}_{3}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series $^{402}$ shows the following length ranges for iron-iron bonds: $2.59 \pm 0.01 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds and $2.38 \pm 0.10 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds. In the methylsubstituted 1,2-diaza-3,5-dibororyl $\left(\mathrm{Me}_{4} \mathrm{~B}_{2} \mathrm{~N}_{2} \mathrm{CH}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{403}$ the range for iron-iron single bond lengths is $2.57 \pm 0.01 \AA$, and $2.39 \pm 0.09 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bond lengths.

Other series are as follows: $\mathrm{Fe}-\mathrm{Fe}$ single bonds in the acetonitrile $\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{404}$ fall in the range $2.59 \pm 0.07 \AA$. The isocyanide $\left(\mathrm{CH}_{3} \mathrm{NC}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{405}$ exhibit the following length ranges for iron-iron bonds: $2.63 \pm 0.12 \AA$ for $\mathrm{Fe}-\mathrm{Fe}$ single bonds and $2.53 \pm 0.03 \AA$ for $\mathrm{Fe}=\mathrm{Fe}$ double bonds. In the difluorocarbene $\left(\mathrm{CF}_{2}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series ${ }^{406}$ $\mathrm{Fe}-\mathrm{Fe}$ single bonds fall in the range $2.56 \pm 0.09 \AA$ and $\mathrm{Fe}=\mathrm{Fe}$ double bonds fall in the range $2.43 \pm 0.10 \AA$. Finally, in the phospholyl $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{P}\right)_{2} \mathrm{Fe} 2(\mathrm{CO})_{n}$ series ${ }^{407} \mathrm{Fe}-\mathrm{Fe}$ single bonds fall in the range $2.62 \pm 0.15 \AA, \mathrm{Fe}=\mathrm{Fe}$ double bonds fall in the range $2.31 \pm 0.05 \AA$, and $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds fall in the range $2.14 \pm 0.01 \AA$.

The BP86 MM bond length ranges in the binuclear iron carbonyl complexes of Tables 20 to 24 along with untabulated data are summarised as follows: $\mathrm{Fe}-\mathrm{Fe}$ single bonds overall have lengths ranging from 2.492 to $2.878 \AA$. We may exclude $\mathrm{Fe}-\mathrm{Fe}$ bond lengths exceeding, say $2.70 \AA$, since these may relate to weaker $\mathrm{Fe} \cdots \mathrm{Fe}$ interactions. This then yields $\mathrm{Fe}-\mathrm{Fe}$ single bond lengths from 2.492 to $2.690 \AA$, or $2.59 \pm 0.10 \AA$, not too far from the experimental $R_{M M}$ value of $2.523 \AA$ for $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ or the experimental range $2.63 \pm 0.16 \AA$ noted above for binuclear iron carbonyl complexes (for many cases of which, however, the $\mathrm{Fe}-\mathrm{Fe}$ interaction is believed to be not covalent). This is longer than the experimental $R_{M M}$ range of $2.51 \pm 0.12$ $\AA$ noted above for $\mathrm{Fe}-\mathrm{Fe}$ single bonds in non-carbonyl complexes. BP86 $\mathrm{Fe}=\mathrm{Fe}$ double bond lengths range from 2.264 to $2.629 \AA$ or $2.45 \pm 0.19 \AA$, longer than the experimental $\mathrm{Fe}=\mathrm{Fe}$ double bond length range of $2.35 \pm 0.09 \AA$ noted above. BP86 Fe $\equiv \mathrm{Fe}$ triple bond lengths fall within the range $2.19 \pm 0.11 \AA$, somewhat longer than the experimental $R_{M M}$ range $2.08 \pm 0.07$ $\AA$ for $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bond lengths given above for non-carbonyl complexes. Shorter $\mathrm{Fe}-\mathrm{Fe}$ distances of 1.991 to $2.069 \AA$, or $2.03 \pm 0.04 \AA$, are described as quadruple MM bonds, which are unknown experimentally. Thus, an overall decrease in $R_{M M}$ value with increasing $\mathrm{Fe}-\mathrm{Fe}$ bond order is evident in this summary of BP86 results on binuclear iron carbonyl complexes.

These BP86 $R_{M M}$ value ranges for single, double and triple iron-iron bonds in carbonyl complexes are seen to be higher than the experimental value ranges noted above. It is a moot question whether this implies a tendency of the BP86 functional to overestimate iron-iron bond lengths. Such may also be the case for the binuclear titanium carbonyl complex series (Table 2) studied by the BP86 and B3LYP methods. However, it is more likely that the $\mathrm{Fe} \rightarrow \mathrm{CO}$ back-bonding characterizing the carbonyl complexes of Tables 20 to 24 is responsible for their longer $\mathrm{Fe}-\mathrm{Fe}$ bond distances compared to those in non-carbonyl diiron complexes. This effect was also found to occur in divanadium and dichromium complexes, but not generally in dimanganese complexes.

## 9. COBALT-COBALT BONDS

Cobalt along with rhodium and iridium of the group 9 transition metals has the $d^{7} s^{2}$ configuration. Metal-metal bonds in group 9 metals have been reviewed ${ }^{408}$ and binuclear complexes of cobalt and iridium have been also described. ${ }^{323}$ Oxidation states of cobalt in binuclear complexes generally range from zero to +2 . This Section deals with cobalt-cobalt distances in the naked cobalt dimer $\mathrm{Co}_{2}$, a number of dicobalt paddlewheel complexes and related compounds with bi- and polydentate ligands, homoleptic binuclear cobalt carbonyl and trifluorophosphine complexes, and binuclear cobalt carbonyl complexes having organic ligands. A few examples of tri- and polycobalt cluster complexes are also discussed. Experimental findings on cobalt-cobalt bond distances are discussed for the relatively few binuclear cobalt complexes which have been structurally characterized. The results of computational DFT studies on several series of binuclear cobalt complexes are also presented. Some idea of cobalt-cobalt bond length ranges within variously assigned Co-Co bond orders is also provided by surveying the experimental and computational results.

### 9.1. Cobalt Dimer

The electronic ground state of the cobalt dimer $\mathrm{Co}_{2}$ is not yet known, and its equilibrium CoCo bond length is also yet undetermined. ${ }^{33} \mathrm{~A}$ third-law estimate of $1.7 \pm 0.3 \mathrm{eV}$ has been made for the dissociation energy of $\mathrm{Co}_{2},{ }^{409}$ and the $\mathrm{Co}_{2}$ vibrational frequency determined by Lombardi ${ }^{410}$ as $297 \pm 1 \mathrm{~cm}^{-1}$. Table 26 gives some computed values for the Co-Co distances in $\mathrm{Co}_{2}$ in various states, which are generally markedly shorter than the values 2.52 and $2.50 \AA$ (twice the covalent and metallic radii assigned to cobalt. ${ }^{41,25}$ Various LSDA DFT studies yielded values of the equilibrium Co-Co distance from 1.92 to $2.04 \AA,,^{411,412,413}$ in line with a Badger's rule estimate of $2.02 \AA$ (not judged as very reliable). ${ }^{29}$ These compare fairly well with empirically derived estimates (derived from force constants) ranging from 2.05 to
$2.11 \AA .{ }^{28}$ However, a CI study with 1084 determinants yielded a longer distance of $2.56 \AA .{ }^{414}$ Various DFT methods predicted Co-Co bond lengths ranging from 2.373 to $2.503 \AA$ for the ${ }^{5} \Sigma^{+}{ }_{g}$ state with the configuration ${ }^{33,34}\left(3 d \sigma_{g}\right)\left(3 d \pi_{u}\right)^{4}\left(3 d \delta_{g}\right)^{3}\left(3 d \delta_{u}{ }^{*}\right)^{3}\left(3 d \pi_{g}{ }^{*}\right)^{4}\left(3 d \sigma_{u}{ }^{*}\right)\left(4 s \sigma_{g}\right)^{2}$. The ${ }^{5} \Sigma^{+}{ }_{g}$ state with the configuration $\left(3 d \sigma_{g}\right)^{2}\left(3 d \pi_{u}\right)^{4}\left(3 d \delta_{g}\right)^{2}\left(3 d \delta_{u}{ }^{*}\right)^{2}\left(3 d \pi_{g}{ }^{*}\right)^{4}\left(3 d \sigma_{u}{ }^{*}\right)^{2}\left(4 s \sigma_{g}\right)^{2}$ gave shorter distances ( 2.303 and $2.356 \AA$ ).$^{33}$ The ${ }^{5} \Delta_{g}$ state gave even lower values ( 1.946 to 2.049 $\AA$ ) which are closer to the LSDA predictions and empirical estimates. The MP2 prediction for the ${ }^{5} \Sigma^{+}{ }_{g}$ ground state of $\mathrm{Co}_{2}$ is $2.406 \AA$ and the SDCI value is $2.56 \AA .{ }^{34}$ It emerges that different methods predict different ground states. The ${ }^{5} \Sigma^{+} g$ state is associated with longer CoCo bond lengths, and the ${ }^{5} \Delta_{g}$ state with shorter distances. The assignment of a reliable Co-Co bond length in the cobalt dimer based on accurate theory depends on identification of its true ground state.

### 9.2. Experimentally Known Binuclear Cobalt Complexes

The experimental results on binuclear cobalt complexes with a variety of ligands were reviewed by Murillo ${ }^{323}$ and also by Dunbar and coworkers. ${ }^{408}$ These included trigonal and tetragonal paddlewheel complexes, besides those with other ligand alignments, as well as some with unsupported Co-Co bonds. Table 26 presents experimentally derived Co-Co bond lengths $R_{M M}$ and other data for such dicobalt complexes, where the $\left(\mathrm{Co}_{2}\right)^{n+}$ core has $n=2,3$, 4, 5. The shortest known Co-Co bonds (Aldridge and coworkers ${ }^{415}$ ) are found in the digonal complexes $\mathbf{0 2}$ [a bis(amidinate), Figure 12a] and $\mathbf{0 3}$ [a bis(guanidinate)] with $R_{M M}$ values of only 2.140 and $2.135 \AA$. These have $\left(\mathrm{Co}_{2}\right)^{2+}$ cores, where the low oxidation state and small bite angle could lead to the short $R_{M M}$ values. These structures indicate strong MM covalent bonds, although CASPT2 studies could not assign a formal MM bond order owing to the high degree of multi-configurational character. Electron counting leads to an fBO value of $\mathbf{2}$ for $\mathbf{0 2}$ and 03.

Table 26. Co-Co Bond Lengths for $\mathrm{Co}_{2}$ and for Non-Carbonyl Dicobalt Complexes

| Label Complex | $R_{M M}(\AA)$ | fBO | References and Remarks |
| :---: | :---: | :---: | :---: |
| $01 \mathrm{Co}_{2}$ | $\begin{aligned} & 1.984 \text { to } 2.007 \\ & 2.373 \text { to } 2.438 \\ & 1.92-2.04 \\ & 2.56 \\ & 2.02 ; 2.05-2.11 \end{aligned}$ |  | 33; DFT data for ${ }^{5} \Delta_{g}$ state 34; DFT data for ${ }^{5} \Sigma^{+}{ }_{g}$ state 411-413; LSDA DFT data 414; CI (1084 determinants) 28; empirical formulae |
| $02 \mathrm{Co}_{2}\left(\mathrm{NN}^{\mathrm{tBu}}\right)_{2}$ | 2.1404(10) | 2 | 415; $\left(\mathrm{Co}_{2}\right)^{2+}$ core; $S=2$ |
| $03 \mathrm{Co}_{2}\left(\mathrm{NN}^{\mathrm{NCy2}}\right)_{2}$ | $2.1345(7)$ | 2 | 415; $\left(\mathrm{Co}_{2}\right)^{2+}$ core; $S=2$ |
| $04 \mathrm{Co}_{2}(\mathrm{DPhF})_{3}$ | $2.385(1)$ | 0.5 | 416,417; $\mathrm{Co}_{2}{ }^{3+}$ core; $S=5 / 2$ |
| $05 \mathrm{Co}_{2}(\mathrm{DPhBz})_{3}$ | 2.3201(9) | 0.5 | 417; $\mathrm{Co}_{2}{ }^{3+}$ core (high spin) |
| $06 \mathrm{Co}_{2}(\mathrm{DAniF})_{3}$ | $2.3773(5)$ | 0.5 | 418; $\mathrm{Co}_{2}{ }^{3+}$ core (high spin) |
| $07 \mathrm{Co}_{2}\left(\mathrm{~L}^{\mathrm{Ph}}\right)$ | 2.2943 (7) | 0.5 | 419; $\mathrm{Co}_{2}{ }^{3+}$ core; $S=5 / 2 ; C_{3}$ |
| $08 \mathrm{Co}_{2}$ (DTolA) $4.2 \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}$ | 2.265(2) | 1 | 420; $\mathrm{Co}_{2}{ }^{4+}$ core; amidinate |
| $09 \mathrm{Co}_{2}(\mathrm{DPhF})_{4}$ | $2.3735(1)$ | 1 | 421; $\mathrm{Co}_{2}{ }^{4+}$ core |
| $10 \mathrm{Co}_{2}(\mathrm{DPhBz})_{4}$ | $2.302(1)$ | 1 | 422; $\mathrm{Co}_{2}{ }^{4+}$ core |
| $11 \mathrm{Co}_{2}(\mathrm{DAniF})_{4}$ | $2.3580(16)$ | 1 | 418; $\mathrm{Co}_{2}{ }^{4+}$ core |
| $12 \mathrm{Co}_{2}(\mathrm{DPhBz})_{4} \cdot \mathrm{PF}_{6}{ }^{a}$ | 2.322(2); 2.332(2) | 1.5 | 421; $\mathrm{Co}_{2}{ }^{5+}$ core |
| $13\left[\mathrm{Co}_{2}\left(\mu-\mathrm{NC}^{t} \mathrm{Bu}\right)_{3}\left(\mathrm{NC}^{t} \mathrm{Bu}\right)_{2}\right]^{-}$ | 2.4097(7) | 1 | 287; $\left(\mathrm{Co}_{2}\right)^{4+}$ core |
| $14 \mathrm{Co}_{2}$ (py ${ }_{3}$ tren) Cl | 2.4986(4) | 1 | 332; $\mathrm{eBO}=0.22 ;$ axial Cl |
| $15 \mathrm{Co}_{2}\left(\mathrm{MesNP}^{i} \mathrm{Pr}_{2}\right)_{2}\left(\mathrm{PMe}_{3}\right)_{2}$ | 2.5536(3) | - | 424; $\left(\mathrm{Co}_{2}\right)^{2+} ; 2$ axial $\mathrm{PMe}_{3}$ |
| $16\left[\mathrm{Co}_{2}\left(\mathrm{MesNP}^{i} \mathrm{Pr}_{2}\right)_{2}\left(\mathrm{PMe}_{3}\right)(\mathrm{THF})\right]^{+}$ | 2.4864(6) | - | 424; $\left(\mathrm{Co}_{2}\right)^{3+}$; axial ligands |
| $17 \mathrm{Co}_{2}\left[\mathrm{HN}\left(\mathrm{PPh}_{2}\right)_{2}\right]_{2}\left(\mu-\mathrm{PPh}_{2}\right)_{2}$ | $2.3857(5)$ | 2 | 425; $\sigma+\delta$ bonds |
| $18 \mathrm{Co}_{2}\left(\mathrm{O}_{2} \mathrm{CPh}\right)_{4} \cdot 2 \mathrm{Qu}{ }^{b}$ | 2.830 | - | 426; $\mathrm{Co}_{2}{ }^{4+}$ core |
| $19 \mathrm{Ba}_{3}\left[\mathrm{Co}_{2}(\mathrm{CN})_{10}\right] \cdot 13 \mathrm{H}_{2} \mathrm{O}^{c}$ | 2.798(2); 2.794(2) | - | 427,428; $\mathrm{Co}_{2}{ }^{4+}$ core |
| $20\left[\mathrm{Co}_{2}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{10}\right]\left(\mathrm{ClO}_{4}\right)_{4}$ | 2.73(1) | - | 429; $\mathrm{Co}_{2}{ }^{4+}$ core |
| $21\left(\mu-\eta^{5}, \eta^{3}-\mathrm{C}_{8} \mathrm{Me}_{6}\right) \mathrm{Co}_{2}$ | 2.491(2) | 1 | 119; $\left(\mathrm{Co}_{2}\right)^{4+}$; sandwich |

[^16]







g (01)

h (03)

Figure 12. Some experimentally characterized dicobalt complexes (bracketed labels for $\mathbf{a}$ to $\mathbf{f}$ refer to Table 26, and for $\mathbf{g}$ and $\mathbf{h}$ to Table 27)

Trigonal paddlewheel complexes containing $\left(\mathrm{Co}_{2}\right)^{3+}$ cores include the tris(amidinate) complexes $\mathrm{Co}_{2}(\mathrm{DPhF})_{3}$ (Figure 12b), $\mathrm{Co}_{2}(\mathrm{DPhBz})_{3}$, and $\mathrm{Co}_{2}(\mathrm{DAniF})_{3}(\mathbf{0 4}, \mathbf{0 5}$, and 06) along with $\mathrm{Co}_{2}\left(\mathrm{~L}^{\mathrm{Ph}}\right)\left(\mathbf{0 7}\right.$, Figure $12 \mathrm{c} ; \mathrm{L}^{\mathrm{Ph}}$ is a multidentate ligand) with short $R_{M M}$ distances (Cotton ${ }^{416,417,418}$, Zall et al. ${ }^{419}$ ) of 2.385, 2.320, 2.377 and $2.294 \AA$, respectively. Here the average +1.5 oxidation state of cobalt necessarily has a paramagnetic electronic configuration
with an MM fBO of 0.5 which may appear small considering the short Co-Co distances. Tetragonal complexes with a $\left(\mathrm{Co}_{2}\right)^{4+}$ core include $\mathbf{0 8}$ (Figure 12d), 09, $\mathbf{1 0}$ and $\mathbf{1 1}$ having azenido and amidinate ligands, with $R_{M M}$ distances (Cotton ${ }^{420,421}$, Bear and coworkers ${ }^{422}$ ) of $2.265,2.374,2.302$, and $2.358 \AA$, respectively. The Co-Co bond lengths here follow the order $\mathrm{DTolA}<\mathrm{DPhF}<\mathrm{DPhBz}$ with respect to the ligand, like the corresponding dirhodium complexes. ${ }^{423} \mathrm{CI}$ studies predict domination of the single bond configuration $\sigma^{2} \sigma^{* 0}$ in the CI expansion, so that a Co-Co single $\sigma$ bond may be assigned to these complexes with a $\left(\mathrm{Co}_{2}\right)^{4+}$ core. The formal bond order of 0.5 in the trigonal complexes as compared to the fBO of 1 in tetragonal complexes leads to a longer MM bond in 04 than in $\mathbf{0 9}$, in 05 than in 10, and in 06 than in 11. The oxidized complex $\mathrm{Co}_{2}(\mathrm{DPhBz})_{4} \cdot \mathrm{PF}_{6} 12$ has a $\left(\mathrm{Co}_{2}\right)^{5+}$ core and a BO of $1.5,{ }^{421}$ although its $R_{M M}$ value $(2.322 / 2.332 \AA)$ is not shorter than that in $\mathrm{Co}_{2}(\mathrm{DPhBz})$. This may be a result of increased cobalt atom charges (electrostatic repulsive effect) or the presence of an axial ligand $\left(\mathrm{PF}_{6}\right)^{-}$(a possible MM bond lengthening effect as in dichromium paddlewheels). The ketamide complex $\mathbf{1 3}^{287}$ also has a $\left(\mathrm{Co}_{2}\right)^{4+}$ core with an $R_{M M}$ value of $2.4097 \AA$. $\mathrm{Co}_{2}$ (py3tren) 14 (Figure 12e) with a multidentate ligand and a chloride axial ligand may be considered as having a $\operatorname{Co}(\mathrm{I})-\mathrm{Co}(\mathrm{III})$ core, with a longer $R_{M M}$ value of $2.499 \AA^{332}$ and an fBO value of 1 , although CASSCF/CASPT2 results give an effective BO value of only 0.22 .

The phosphinoamide complex 15 with a $\left(\mathrm{Co}_{2}\right)^{2+}$ core has an $R_{M M}$ value of $2.554 \AA,{ }^{424}$ which is much longer than for the $\left(\mathrm{Co}_{2}\right)^{+4}$ complexes $\mathbf{1 3}$ and 14 . One-electron oxidation of $\mathbf{1 5}$ yields 16 (Figure 12 f ) with a $\left(\mathrm{Co}_{2}\right)^{3+}$ core in which the Co -Co bond length shortens to 2.486 $\AA$. The 18 -electron rule assigns an fBO of 1 to $\mathbf{1 5}$ and 1.5 to $\mathbf{1 4}$. Complex $\mathbf{1 7}$ is a phosphidobridged compound with a short Co-Co bond of length $2.387 \AA$, to which Hey-Hawkins and coworkers ${ }^{425}$ assigned a bond order of 2 by a DFT study, involving a $\sigma$ bond and a $\delta$ bond.

Complexes 18, 19 and 20, all having $\left(\mathrm{Co}_{2}\right)^{4+}$ cores, exhibit long $\mathrm{Co} \cdots \mathrm{Co}$ distances which may not be classifiable as covalent Co-Co bonds,. The axially disubstituted tetracarboxylate
complex $\mathbf{1 8}$ has a Co $\cdots$ Co distance of $2.83 \AA^{426}$ indicating a weak MM interaction, possibly owing to the axial quinuclidine ligands. $\left(\mathrm{Co}_{2}\right)^{+4}$ complexes with long unsupported $\mathrm{Co}-\mathrm{Co}$ bonds include the complex anion present in 19, and the complex tetracation present in 20, having $R_{M M}$ distances $\left(\right.$ Dahl $^{427}$, Raymond ${ }^{428}$, Cotton ${ }^{429}$ ) of 2.798 (or 2.794) and 2.73(1) $\AA$ respectively.

Complex 21 is the cobalt member of the $\left(\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{M}_{2}$ series, ${ }^{119}$ where the $R_{M M}$ value of $2.491 \AA$ is consistent with a Co-Co single bond. The fBO value of 1 , however, does not arise from assigning an $(18,18)$ configuration to the bimetallic core. The unmethylated $\left(\mathrm{C}_{8} \mathrm{H}_{6}\right)_{2} \mathrm{Co}_{2}$ species, however, was predicted by computational studies to have a longer $R_{M M}$ value of $2.60 \AA$ with no significant Co-Co covalent bond. ${ }^{288}$ Permethylation could result in greater basicity of the pentalene ligands with possible effects on the strength of Co-Co bonding.

The experimental MM bond lengths and the bond orders discussed above suggest that some relationship between formal Co-Co bond order and bond length may be discerned for closely related systems. An increased cobalt oxidation state often appears to have an MM bond lengthening effect in such systems. Otherwise, the variations in Co-Co bond distances are difficult to explain. Metal atom charge, spin, ligand basicity and steric effects can all influence MM bond lengths. Sub-section 9.7 deals further with bond length limits within a given bond order, drawing from the computational and available experimental findings for numerous series of dicobalt complexes with a variety of ligands and metal oxidation states.

### 9.3. Binuclear Cobalt Carbonyls and Cobalt Cluster Carbonyls

Table 27 lists experimental $R_{M M}$ values for some dicobalt carbonyl complexes along with tricobalt and polycobalt clusters. The well-known dicobalt octacarbonyl $\mathrm{Co}_{2}(\mathrm{CO})_{8} \mathbf{0 1}$ (Figure 12 g ) may be regarded as the prototype species for binuclear cobalt carbonyl complexes in general including those with other ligands. The crystal structure (Sumner ${ }^{430}$, Coppens ${ }^{431}$,

Table 27. Experimental Co-Co Bond Distances in Binuclear Cobalt and Cobalt Cluster Carbonyl Complexes

| Label | Species | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: | :---: |
| 01 | $\mathrm{Co}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})_{2}$ | 2.528 | 430-432 | homoleptic |
| 02 | $\mathrm{Co}_{2}(\mathrm{CO})_{8} . \mathrm{C}_{60}$ | 2.700 | 435 | no bridging CO; fullerene ligand |
| 03 | $\mathrm{Ph}_{2} \mathrm{C}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{6}$ | 2.47 | 436 | acetylene ligand |
| 04 | $\mathrm{OC}\left[\mathrm{CCo}_{3}(\mathrm{CO})_{9}\right]_{2}$ | 2.47 | 437 | 6 Co centres; acetone derivative |
| 05 | $\mathrm{H}_{3} \mathrm{CC}\left[\mathrm{Co}(\mathrm{CO})_{3}\right]_{3}$ | 2.47 | 438 | 3 Co atoms; triply bridged carbon |
| 07 | $\mathrm{Co}_{4}(\mathrm{CO})_{9}(\mu-\mathrm{CO})_{3}$ | 2.50 | 439 | tetracobalt dodecacarbonyl |
| 08 | $\mathrm{Co}_{6}(\mathrm{CO})_{15}$ | 2.49 | 440 | hexacobalt cluster |
| 09 | $\left[\mathrm{HC}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{6}\right]_{3} \mathrm{As}$ | 2.47 | 441 | acetylide ligand; arsine |
| 10 | $\mathrm{C}_{6} \mathrm{Co}_{8}(\mathrm{CO})_{24}$ | 2.47 | 442 | methinyl tricobalt derivative |
| 11 | $\left[\mathrm{CCo}_{3}(\mathrm{CO})_{9}\right]_{2}$ | 2.45 | 443 | methinyl tricobalt derivative |

$\operatorname{Braga}^{432}$ ) gives a Co-Co distance of $2.528 \AA$ in a doubly bridged $\mathrm{Co}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})_{2}$ structure with three terminal CO groups on each $\operatorname{Co}(0)$ centre. The simple 18 -electron rule would assign a Co-Co single bond to this structure as for the isoelectronic $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$. This, however, as for $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$, is challenged by Bader's analysis of the electron density which located no bond path nor any bond critical point between the Co atoms. ${ }^{361,433,434}$ Ponec et al. ${ }^{358}$ used a domain averaged Fermi hole analysis to treat the Co $\cdots$ Co interaction as a three-centre twoelectron $\mathrm{Co}-\mathrm{C}(\mu-\mathrm{CO})$-Co bond delocalized over the two bridging CO groups and not involving direct $\mathrm{Co}-\mathrm{Co}$ bonding in a fashion analogous to their treatment of the $\mathrm{Fe} \cdots \mathrm{Fe}$ interaction in $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$. The complex adduct $\mathbf{0 2}$ of $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ with the fullerene $\mathrm{C}_{60}$, however, does not have bridging CO groups and no $3 \mathrm{c}-2 \mathrm{e}$ bond over such, resulting in a longer $\mathrm{Co} \cdots \mathrm{Co}$ distance of $2.700 \AA \AA^{435}$. The $R_{M M}$ value for $\mathrm{Co}_{2}(\mathrm{CO})_{6}\left(\mathrm{Ph}_{2} \mathrm{C}_{2}\right) \mathbf{0 3}$ (Figure 12h) is $2.47 \AA^{436}$ which may indicate Co-Co bonding, being less than twice the covalent radius of $1.26 \AA$ for

Co. ${ }^{35}$ The other structures in Table 27 are tri- and polynuclear complexes. ${ }^{437,438,439,440,441,442,443}$ These all contain Co-Co distances ranging from 2.47 to $2.50 \AA$, which could indicate either covalent bonding or three-centre two-electron bonds through bridging carbonyl ligands.

### 9.4. Homoleptic Binuclear Cobalt Complexes

A DFT study on homoleptic dicobalt carbonyls focused on the series $\mathrm{Co}_{2}(\mathrm{CO})_{n}(n=5,6,7$, 8), ${ }^{444}$ for which BP86 predictions for Co-Co bond distances are given in Table 28. Dicobalt octacarbonyl, $\mathrm{Co}_{2}(\mathrm{CO})_{8}$, has been well-characterized by experiment, and evidence has been found for the existence of $\mathrm{Co}_{2}(\mathrm{CO})_{7}$ and possibly $\mathrm{Co}_{2}(\mathrm{CO})_{6}$. The 18 -electron rule ascribes single, double, and triple bond orders to the $\mathrm{Co}-\mathrm{Co}$ bonds in $\mathrm{Co}_{2}(\mathrm{CO})_{8}, \mathrm{Co}_{2}(\mathrm{CO})_{7}$ and $\mathrm{Co}_{2}(\mathrm{CO})_{6}$, respectively. The doubly bridged structure $\mathrm{Co}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})_{2}$ for the octacarbonyl 01 (Figure 12 g ) has an XRD-derived $R_{M M}$ value of $2.528 \AA,{ }^{432}$ close to the BP86 value of $2.550 \AA$ for the $C_{2 v}$ doubly bridged isomer, and not far from the experimental and DFT $R_{M M}$ values for $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$. The validity of assigning a Co-Co covalent single bond to this structure has been discussed earlier. An unbridged $D_{3 d} \mathrm{Co}_{2}(\mathrm{CO})_{8}$ isomer that has been deduced to coexist with the doubly bridged structure in solution has a longer BP86 $R_{M M}$ distance of $2.692 \AA$ (Noack ${ }^{445,446}$, Bor ${ }^{447}$, Koelle ${ }^{448}$ ). Another unbridged $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ isomer of $D_{2 d}$ symmetry was proposed by Sweany and Brown ${ }^{449}$ with a BP86 $R_{M M}$ value of $2.629 \AA \mathrm{Co}_{2}(\mathrm{CO})_{8}$ may be viewed as a highly fluxional molecule, since the BP86 energy separations between isomers are small. The presence of bridging CO groups shortens the Co-Co distance, while also providing the possibility of three-centre two-electron metal-metal bonding.

The experimentally detected unbridged structure for dicobalt heptacarbonyl $\mathbf{0 2}^{450}$ under $C_{2 v}$ symmetry constraints gave a BP86 structure with one imaginary frequency and an $R_{M M}$ value of $2.490 \AA$ suggesting a Co-Co single bond. However, one BP86 minimum (Figure 13a) had an $R_{M M}$ value of $2.398 \AA$ suggesting a $\mathrm{Co}=\mathrm{Co}$ double bond. The doubly bridged dicobalt hexacarbonyl (03; Figure 13b), the existence of which is suggested from IR measurements, n131
has a $D_{2 h}$ singlet minimum with a short $\mathrm{BP} 86 R_{M M}$ value of $2.255 \AA$ consistent with a $\mathrm{Co} \equiv \mathrm{Co}$ triple bond. Higher energy triplet minima have $\mathrm{Co}=\mathrm{Co}$ double bond lengths of 2.286 and $2.404 \AA$. The unknown $\mathrm{Co}_{2}(\mathrm{CO})_{5}(\mathbf{0 4})$ has a singly bridged singlet structure with a short $R_{M M}$ distance of $2.173 \AA$ consistent with a quadruple Co-Co bond. A triply bridged triplet $\mathrm{Co}_{2}(\mathrm{CO})_{5}$ structure has an $R_{M M}$ value of $2.249 \AA$, suggesting a bond order less than four.

a (02)

b (03)




f ( $05, \mathrm{~S}-1$ )

g(06)

h (07)

Figure 13. Some computationally studied binuclear cobalt complexes (labels a to e refer to Table 28; labels $\mathbf{f}$ to $\mathbf{h}$ refer to Table 30)

Table 28. DFT Co-Co Bond Lengths for Homoleptic Binuclear Cobalt Carbonyl and Trifluorophosphine Complexes and for Dicobalt Thiocarbonyl Carbonyl Complexes ${ }^{a}$

| Label Species | State $R_{M M}(\AA)$ fBO Remarks |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Homoleptic binuclear cobalt carbonyl complexes (BP86 data; Ref. 444) |  |  |  |  |
| $01 \mathrm{Co}_{2}(\mathrm{CO})_{6}(\mu-\mathrm{CO})_{2}$ | S | 2.550 | 1 | $C_{2 v}$; cf. crystal structure |
| $\mathrm{Co}_{2}(\mathrm{CO})_{8}-$ unbridged | S | 2.692 | 1 | $D_{3 d}$; cf. Refs. 444-448 |
| $\mathrm{Co}_{2}(\mathrm{CO})_{8}-$ unbridged | S | 2.629 | 1 | $D_{2 d}$; cf. Ref. 449 |
| $02(\mathrm{CO})_{3}(\mu-\mathrm{CO}) \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | S | 2.398 | 2 | $C_{s}$; glob. min. |
| $(\mathrm{CO})_{4} \mathrm{Co}_{2}(\mathrm{CO})_{3}-$ unbridged (39i) | S | 2.490 | 1 | $C_{2 v}$; cf. Ref. 450 |
| $03(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$ | S | 2.255 | 3 | $D_{2 h}$ |
| $(\mathrm{CO})_{3} \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | T | 2.286 | 2 | $D_{3 d}$; staggered |
| $(\mathrm{CO})_{2}(\mathrm{~s} \mu-\mathrm{CO})_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$ | T | 2.404 | 2 | $\mathrm{C}_{2 \mathrm{v}}$; partly dibridged |
| $04(\mathrm{CO})_{2} \mathrm{Cr}_{2}(\mu-\mathrm{CO})(\mathrm{CO})_{2}$ | S | 2.173 |  | $C_{2 v} ; 1$ iv |
| $(\mathrm{CO})(\mu-\mathrm{CO})_{3} \mathrm{Co}_{2}(\mathrm{CO})$ | T | 2.249 | < 4 | $C_{2 v}$ |
| $(\mathrm{CO})(\mu-\mathrm{CO})_{3} \mathrm{Co}_{2}(\mathrm{CO})$ | T | 2.247 | < 4 | $D_{3 h}$ |

Homoleptic binuclear trifluorophosphine cobalt complexes (BP86 results; Ref. 451)

| $\mathbf{0 5}\left(\mathrm{PF}_{3}\right)_{4} \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{4}$ | $\mathrm{~S}-1$ | 2.742 | 1 | sole structure; unbridged |
| :---: | :---: | :---: | :---: | :--- |
| $\mathbf{0 6}\left(\mathrm{PF}_{3}\right)_{4} \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{3}$ | $\mathrm{~T}-1$ | 2.425 | 1 | global min; $(18,16)$ |
| $\left(\mathrm{PF}_{3}\right)_{4} \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{3}$ | $\mathrm{~S}-2$ | 2.526 | 2 | $\Delta \mathrm{E}=8.5 ;(18,18)$ |
| $\mathbf{0 7}\left(\mathrm{PF}_{3}\right)_{4} \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{2}$ | $\mathrm{~T}-1$ | 2.468 | 2 | global min. |
| $\left(\mathrm{PF}_{3}\right)_{3}\left(\mu-\mathrm{PF}_{3}\right) \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{3}$ | $\mathrm{~S}-2$ | 2.199 | 3 | $(18,18)$ |
| $\mathbf{0 8}\left(\mathrm{PF}_{3}\right)_{2}\left(\mu-\mathrm{PF}_{2}\right)\left(\mu-\mathrm{F}_{3} \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{2}\right.$ | $\mathrm{T}-1$ | 2.705 | 1 | $(17,17)$ |
| $\left(\mathrm{PF}_{3}\right)_{2}\left(\mu-\mathrm{PF}_{2}\right)\left(\mu-\mathrm{F}_{2} \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{2}\right.$ | $\mathrm{S}-2$ | 2.750 | 1 | $(18,18)$ |
| $\left(\mathrm{PF}_{3}\right)_{2}\left(\mu-\mathrm{PF}_{3}\right) \mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{2}$ | $\mathrm{~S}-3$ | 2.103 | 3 | $(18,18)$ |

Binuclear cobalt carbonyl thiocarbonyl complexes (BP86 results; Ref. 452)

| $09 \mathrm{Co}_{2}(\mu-\mathrm{CS})\left(\mu-\mathrm{S}_{2} \mathrm{C}_{2} \mathrm{R}_{2}\right)(\mathrm{CO})_{3}(\mu-\mathrm{dppm})$ | S | 2.449 | 1 | Exptl. XRD (Ref. 453) |
| :---: | :---: | :---: | :---: | :--- |
| $\mathbf{1 0}(\mathrm{CO})_{3}(\mu-\mathrm{CS})_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.497 | 1 | glob. min.; cf. $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ |
| $(\mathrm{CO})_{2}(\mathrm{CS})(\mu-\mathrm{CS})(\mu-\mathrm{CO}) \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.528 | 1 | $\Delta \mathrm{E}=4.8$ |
| $\mathbf{1 1} \mathrm{CO}(\mathrm{CS})\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mathrm{s} \mu-\mathrm{CO}) \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.668 | 1 | glob. min. |
| $\mathrm{CO}(\mathrm{s} \mu-\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CS}\right) \mathrm{Co}_{2}(\mathrm{CO})_{2} \mathrm{CS}$ | $\mathrm{S}-2$ | 2.659 | 1 | $\Delta \mathrm{E}=0.6$ |
| $(\mathrm{CO})_{2}(\mathrm{~s} \mu-\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CS}\right) \mathrm{Co}_{2}(\mathrm{CO})_{2} \mathrm{CS}$ | $\mathrm{S}-3$ | 2.678 | 1 | $\Delta \mathrm{E}=1.2$ |
| $(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CS}\right)_{2}\left(\eta^{2}-\mu-\mathrm{CO}\right) \mathrm{Co}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-4$ | 2.351 | 2 | tribridged; $\Delta \mathrm{E}=7.2$ |
| $\mathbf{1 2}(\mathrm{CO})_{2}(\mu-\mathrm{CS})_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.383 | 1 | glob. min. |
| $(\mathrm{CO})_{2}(\mu-\mathrm{CO})(\mu-\mathrm{CS}) \mathrm{Co}_{2}(\mathrm{CS})(\mathrm{CO})$ | $\mathrm{S}-2$ | 2.404 | 1 | $\Delta \mathrm{E}=4.1 ;(16,16)$ |
| $\mathbf{1 3}(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CS}) \mathrm{CO}$ | $\mathrm{S}-1$ | 2.422 | 1 | glob. min.; $(16,16)$ |

[^17]BP86 results on the homoleptic dicobalt trifluorophosphine series $\mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{n}(n=8,7,6$, 5) ${ }^{451}$ are also included in Table 28. In these systems the electronegative fluorine atoms on the ligating phosphorus atom makes the $\mathrm{PF}_{3}$ ligand an electron acceptor like CO . For $\mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{8}$ (05), a long Co-Co single bond length of $2.742 \AA$ in an unbridged structure is seen in the sole minimum (Figure 13c). For $\mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{7}(\mathbf{0 6})$, the triplet global minimum T-1 has a short single Co-Co bond of length $2.425 \AA$, while the singlet minimum S-2 has a long $\mathrm{Co}=\mathrm{Co}$ double bond of length $2.526 \AA$. For $\mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{6}(\mathbf{0 7})$, the triplet global minimum T-1 (Figure 13d) has a $\mathrm{Co}=\mathrm{Co}$ double bond of length $2.468 \AA$, while the singlet minimum S-2 has a $\mathrm{Co} \equiv \mathrm{Co}$ triple bond of length $2.199 \AA$. For $\mathrm{Co}_{2}\left(\mathrm{PF}_{3}\right)_{5}(\mathbf{0 8})$, the minima T-1 and S-2 both have long single Co-Co bonds, while minimum S-3 (Figure 13e) has a $\mathrm{Co} \equiv \mathrm{Co}$ triple bond length of $2.103 \AA$.

### 9.5. Binuclear Cobalt Carbonyl Complexes with Inorganic Ligands

This sub-section presents DFT results on three series of binuclear cobalt carbonyl complexes having inorganic ligands (thiocarbonyl, nitrosyl, and fluoroborylene). The BP86 results on the dicobalt carbonyl thiocarbonyl series $\mathrm{Co}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{n}(n=6,5,4,3)^{452}$ are given in Table 28. For $\mathrm{Co}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{6}$, minima S-1 and S-2 (different bridging ligands) have $\mathrm{Co}-\mathrm{Co}$ single bonds, where the $R_{M M}$ value of $2.497 \AA$ for S-1 is close to the experimental (Morris ${ }^{453}$ ) single bond length of $2.449 \AA$ in the complex $\mathrm{Co}_{2}(\mu-\mathrm{CS})\left(\mu-\mathrm{S}_{2} \mathrm{C}_{2} \mathrm{R}_{2}\right)(\mathrm{CO})_{3}(\mu-\mathrm{dppm})$. The bridging thiocarbonyl ligands in S-1 have an MM bond shortening effect greater than that of the bridging CO ligands in $\mathrm{Co}_{2}(\mathrm{CO})_{8}$. For $\mathrm{Co}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{5}$, minima $\mathrm{S}-1, \mathrm{~S}-2$ and $\mathrm{S}-3$ present a fluxional system with rather long Co-Co single bond lengths ( $2.668 \pm 0.010 \AA$ ), while the higher energy minimum S-4 has a $\mathrm{Co}=\mathrm{Co}$ double bond of length $2.351 \AA$. For $\mathrm{Co}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{4}$, minima $\mathrm{S}-1$ and $\mathrm{S}-2$ have rather short $\mathrm{Co}-\mathrm{Co}$ single bonds, where the bridging CS ligand leads to a shorter $R_{M M}$ value than does the bridging CO ligand. For $\mathrm{Co}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{3}$, the minimum S-1 has a single bond length of $2.422 \AA$.

Table 29. DFT Co-Co Bond Distances for Binuclear Cobalt Carbonyl Complexes Containing Nitrosyl and Fluoroborylene Ligands

| No Complex | State | $R_{M M}$ <br> ( $\AA$ ) | $\underset{\{\mathrm{kcal} / \mathrm{mol})}{\Delta \mathrm{E}} \mathrm{fBO}^{\mathrm{f}}$ | Remarks |
| :---: | :---: | :---: | :---: | :---: |

Binuclear cobalt nitrosyl carbonyls (BP86 results; Ref. 454)

| $01 \mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{5}$ | S-1 | 2.581 | 0.0 | 1 | $\mu-\mathrm{NO}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | S-2 | 2.646 | 0.5 | 1 | $\mu-\mathrm{CO}$ |
|  | S-3 | 2.650 | 4.9 | 1 | $\mu-\mathrm{CO}$ |
|  | S-4 | 2.583 | 4.5 | 1 | $\mu-\mathrm{NO}$ |
|  | S-5 | 2.638 | 4.9 | 1 | $\mu-\mathrm{NO}$ |
|  | S-6 | 2.577 | 6.4 | 1 | $2 \mu$-CO |
| $\left.02 \mathrm{Co}_{2}(\mathrm{NO})_{2} \mathrm{CO}\right)_{4}$ | S-1 | 2.508 | 0.0 | 2 | $2 \mu-\mathrm{CO}$ |
|  | S-2 | 2.529 | 0.3 | 2 | $2 \mu$-CO |
|  | S-3 | 2.413 | 2.8 | 2 | $2 \mu-\mathrm{CO}, \mu-\mathrm{NO}$ |
|  | S-4 | 2.382 | 5.2 | 2 | $2 \mu$-NO |
|  | S-5 | 2.541 | 7.1 | 1 | $2 \mu-\mathrm{CO} ;(16,16)$ |
| $03 \mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{3}$ | S-1 | 2.182 | 0.0 | 3 | $3 \mu$-CO |
| $04 \mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{2}$ | S-1 | 2.392 | 0.0 | 3 | $2 \mu$-CO, $\mu$-NO; $(18,16)$ |
|  | S-2 | 2.243 | 0.5 | 3 | $2 \mu-\mathrm{CO} ;(18,18)$ |
|  | T-1 | 2.403 | 9.8 | 3 | $2 \mu-\mathrm{CO}, \mu-\mathrm{NO} ;(17,17)$ |
| $05 \mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})$ | S-1 | 2.323 | 0.0 | 2 | $2 \mu-\mathrm{CO}$ |

Binuclear cobalt fluoroborylene carbonyl complexes (BP86 results; Ref. 455)

| $\mathbf{0 6} \mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{7}$ | $\mathrm{~S}-1$ | 2.605 | 0.0 | 1 | $\mu-\mathrm{CO}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 7} \mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{6}$ | $\mathrm{~S}-1$ | 2.620 | 0.0 | 1 | $2 \mu-\mathrm{BF}$ |
| $\mathbf{0 8} \mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{5}$ | $\mathrm{~S}-1$ | 2.505 | 0.0 | 1 | $2 \mu-\mathrm{BF} ;(16,16)$ |
|  | $\mathrm{S}-2$ | 2.539 | 0.4 | 1 | $2 \mu-\mathrm{BF}$ |
|  | $\mathrm{S}-3$ | 2.392 | 2.5 | 1 | $2 \mu-\mathrm{BF}$ |
|  | $\mathrm{S}-4$ | 2.350 | 4.9 | 1 | $2 \mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
| $\mathbf{0 9} \mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{4}$ | $\mathrm{~S}-5$ | 2.457 | 9.6 | 1 | $\mu-\mathrm{BF}, \mu-\mathrm{CO}$ |
|  | $\mathrm{S}-1$ | 2.365 | 0.0 | 2 | $2 \mu-\mathrm{BF}, \mu-\mathrm{CO} ;(16,16)$ |
| $\mathbf{1 0} \mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-2$ | 2.407 | 7.5 | 2 | $2 \mu-\mathrm{BF} ;(18,16)$ |
|  | $\mathrm{S}-1$ | 2.361 | 0.0 | 2 | $\eta^{2}-\mathrm{CO} ;(16,16)$ |
|  | $\mathrm{S}-2$ | 2.432 | 5.6 | 1 | $2 \mu-\mathrm{BF}$ |

Table 29 gives the BP86 results for the binuclear cobalt nitrosyl carbonyl series $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{n}(n=5,4,3,2,1) .{ }^{454}$ For $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{5}$, six minima are located, all with bridging NO or CO groups. These all have single Co-Co bonds ranging in length from 2.577 to $2.650 \AA$, with the shortest Co-Co bond occuring in S-6 with two bridging carbonyl groups. For $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{4}$, all five minima have at least two bridging ligands. Minima S-1 to $\mathrm{S}-4$ all have $\mathrm{Co}=\mathrm{Co}$ double bonds with $R_{M M}$ values ranging from 2.382 to $2.529 \AA$, whereas minimum S-5 has a Co-Co single bond of length $2.541 \AA$. For $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{3}$, the single minimum is a triply bridged structure with a short $\mathrm{Co} \equiv \mathrm{Co}$ triple bond of length $2.182 \AA$. For $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{2}$, the singlet global minimum has a $\mathrm{Co} \equiv$ Co triple bond of length $2.392 \AA$, while S-2 has a Co-Co quadruple bond of length $2.243 \AA$. These two singlet minima are close in energy, but differ in the bridging ligands. The higher energy $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})_{2}$ structure T-3 has a $\mathrm{Co} \equiv \mathrm{Co}$ triple bond $2.403 \AA$ in length. For $\mathrm{Co}_{2}(\mathrm{NO})_{2}(\mathrm{CO})$, the global minimum has a $\mathrm{Co}=\mathrm{Co}$ double bond of length $2.323 \AA$.

Table 29 presents the BP86 data for the binuclear cobalt fluoroborylene carbonyl series $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{n}(n=7,6,5,4,3,2) .{ }^{455}$ For $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{7}$, only the global minimum has Co-Co covalent bonding with a Co-Co single bond of length $2.605 \AA$; other $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{7}$ minima have long Co ${ }^{\cdots}$ Co separations. For $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{6}$, the sole low-energy minimum S1 has a Co-Co single bond of length $2.620 \AA$. For $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{5}$, the five singlet minima all have at least two bridging ligands, and all have Co-Co single bonds with lengths ranging from 2.350 to $2.539 \AA$; S-4 with the shortest $R_{M M}$ value has a triply bridged structure. For $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{4}$, the two singlet minima have $\mathrm{Co}=\mathrm{Co}$ double bonds of lengths 2.365 and $2.407 \AA$. For $\mathrm{Co}_{2}(\mathrm{BF})_{2}(\mathrm{CO})_{3}$, the global minimum $\mathrm{S}-1$ has a $\mathrm{Co}=\mathrm{Co}$ double bond of length $2.362 \AA$ while S-2 has a short Co-Co single bond of length $2.432 \AA$.

### 9.6. Binuclear Cobalt Carbonyl Complexes with Carbon Ligands

Table 30 presents DFT predictions concerning Co-Co bonds in three series of dicobalt carbonyl complexes containing carbon ligands, namely the butadiene, cyclopentadienyl, and trimethylenemethane ligands. BP86 results for the bis(butadiene) dicobalt carbonyl series $\mathrm{Co}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{n}(n=4,3,2,1)^{456}$ yield four singlet minima within around $10 \mathrm{kcal} / \mathrm{mol}$ of the global minimum for the tetracarbonyl $\mathrm{Co}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{4}$ (complex 01). These four structures all have two bridging carbonyl groups and $\mathrm{Co}-\mathrm{Co}$ single bonds in the narrow distance range from 2.539 to $2.575 \AA$. The tricarbonyl $\mathrm{Co}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{3}$ system $\mathbf{0 2}$ has minima S-1 and S-2 with relatively short Co-Co single bonds of lengths 2.470 and $2.452 \AA$, respectively, along with the minima $\mathrm{S}-3$ and $\mathrm{T}-4$ containing $\mathrm{Co}=\mathrm{Co}$ double bonds of lengths 2.282 and $2.449 \AA$, respectively. The $\mathrm{Co}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}(\mathrm{CO})_{2}$ system 03 has minima S-1 and S-2 with $\mathrm{Co} \equiv \mathrm{Co}$ triple bonds of lengths 2.299 and $2.252 \AA$, respectively, while minima S-3 and S-4 have $\mathrm{Co}-\mathrm{Co}$ single bonds of 2.548 and $2.478 \AA$. $\mathrm{The}_{\mathrm{Co}_{2}\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2}(\mathrm{CO}) \text { system } 04 \text { contains }}$ short Co-Co quadruple bonds for S-1 and S-2 with lengths 2.142 and $2.130 \AA$, respectively.

BP86 predictions for the binuclear cyclopentadienylcobalt carbonyl series $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{n}$ ( $n$ $=3,2,1)^{457}$ are also given in Table 30 . The tricarbonyl $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}$ system 05 has the minima S-1 and S-2 (Figure 13f), with Co-Co single bonds of lengths 2.506 and $2.352 \AA$ respectively, where the triple bridging in the latter may be linked to the shorter $R_{M M}$ value. The $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$ complex 06 has one doubly bridged singlet minimum $\mathrm{S}-1$ (Figure 13g) with a $\mathrm{Co}=\mathrm{Co}$ double bond of length $2.346 \AA$. The $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})$ complex 07 has two minima S-1 (Figure 13h) and S-2, both with $\mathrm{Co} \equiv$ Co triple bonds of lengths 2.050 and $2.298 \AA$. S-1 has one $C p$ ligand $\eta^{5}$-coordinated to each Co atom, while S-2 has both $C p$ ligands $\eta^{1}, \eta^{2}$ coordinated to both Co centres.

Table 30. DFT Co-Co Bond Lengths for Binuclear Cobalt Carbonyl Complexes Containing Carbon Ligands

| Label | Complex | State | $R_{M M}$ <br> (A) | $\Delta \mathrm{E}$ (kcal/mol) | fBO | Remarks |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Binuclear butadiene cobalt carbonyl complexes (BP86; Ref. 456) |  |  |  |  |  |  |
| 01 | $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Co}_{2}(\mathrm{CO})_{4}$ | S-1 | 2.568 | 0.0 | 1 | $2 \mu$-CO |
|  |  | S-2 | 2.575 | 0.5 | 1 | $2 \mu$-CO |
|  |  | S-3 | 2.539 | 9.8 | 1 | $2 \mu$-CO |
|  |  | S-4 | 2.559 | 10.2 | 1 | $2 \mu$-CO |
| 02 | $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | S-1 | 2.470 | 0.0 | 1 | $2 \mu$-CO |
|  |  | S-2 | 2.452 | 0.2 | 1 | $2 \mu$-CO |
|  |  | S-3 | 2.282 | 2.4 | 2 | $3 \mu$-CO |
|  |  | T-4 | 2.449 | 9.0 | 2 | $2 \mu$-CO |
| 03 | $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$ | S-1 | 2.299 | 0.0 | 3 | $2 \mu$-CO |
|  |  | S-2 | 2.252 | 4.2 | 3 | $2 \mu$-CO |
|  |  | S-3 | 2.548 | 6.3 | 1 | no bridging; $(16,16)$ |
|  |  | S-4 | 2.478 | 6.6 | 1 | no bridging; $(16,16)$ |
| 04 | $\left(\mathrm{C}_{4} \mathrm{H}_{6}\right)_{2} \mathrm{Co}_{2}(\mathrm{CO})$ | S-1 | 2.142 | 0.0 | 4 | $\mu$-CO |
|  |  | S-2 | 2.130 | 4.8 | 4 | $\mu-\mathrm{CO}$ |
|  |  | S-3 | 2.277 | 7.8 | 3 | $\eta^{4}-\mathrm{C}_{4} \mathrm{H}_{6}$ |
|  |  | T-4 | 2.223 | 10.8 | 3 | $\mu$-CO |

Binuclear cyclopentadienylcobalt carbonyls (BP86; Ref. 457)

| $\mathbf{0 5}$ | $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}$ | $\mathrm{~S}-1$ | 2.352 | 0.0 | 1 | $3 \mu-\mathrm{CO}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  |  | $\mathrm{S}-2$ | 2.506 | 1.8 | 1 | $\mu-\mathrm{CO}$ |
| $\mathbf{0 6}$ | $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.346 | 0.0 | 2 | $2 \mu-\mathrm{CO}$ |
| $\mathbf{0 7}$ | $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})$ | $\mathrm{S}-1$ | 2.050 | 0.0 | 3 | $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$ to each Co |
|  |  | $\mathrm{S}-2$ | 2.298 | 9.6 | 3 | $\eta^{2}, \eta^{1}-\mathrm{C}_{5} \mathrm{H}_{5}$ to both Co |

Binuclear trimethylenemethane cobalt carbonyls (M06-L; Ref. 458)

| $\mathbf{0 8}$ | $\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}\right.$ | $\mathrm{S}-1$ | 2.290 | 0.0 | 3 | $\mu-\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 9}$ | $\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}\right.$ | $\mathrm{S}-1$ | 2.419 | 0.0 | 2 | no bridging |
|  |  | S-2 | 2.408 | 1.4 | 2 | $2 \mu$-CO |
|  |  | $\mathrm{T}-3$ | 2.231 | 3.3 | 2 | $3 \mu$-CO |
| $\mathbf{1 0}$ | $\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2} \mathrm{Co}_{2}(\mathrm{CO})_{4}$ | $\mathrm{~S}-1$ | 2.504 | 0.0 | 1 | $2 \mu$-CO |
|  |  | S-2 | 2.507 | 0.4 | 1 | $2 \mu$-CO |
|  |  | $\mathrm{S}-3$ | 2.678 | 1.7 | 1 | no bridging |
| $\mathbf{1 1}$ | $\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{5}\right.$ | S-1 | 2.698 | 0.0 | 1 | $\mu$-CO |
| $\mathbf{1 2}$ | $\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{6}\right.$ | S-1 | 2.770 | 0.0 | 1 | no bridging |

The M06-L DFT method has been used to study the binuclear cobalt trimethylenemethane carbonyl series $\left.\mathrm{Co}_{2}\left[\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}(\mathrm{CO})_{n}(n=2,3,4,5,6) .{ }^{458}$ The dicarbonyl $\left.\mathrm{Co}_{2}\left[\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}(\mathrm{CO})_{2}$ (08) has a single low-energy structure $\mathrm{S}-1$, which has a bridging trimethylenemethane ligand, as well as a $\mathrm{Co} \equiv \mathrm{Co}$ triple bond of length $2.290 \AA$. The tricarbonyl $\left.\mathrm{Co}_{2}\left[\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}(\mathrm{CO})_{3}(\mathbf{0 9})$ has the minima $\mathrm{S}-1, \mathrm{~S}-2$ and $\mathrm{T}-3$ with $\mathrm{Co}=\mathrm{Co}$ double bond lengths of 2.419, 2.408, and $2.231 \AA$, respectively. The tetracarbonyl $\left.\mathrm{Co}_{2}\left[\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}(\mathrm{CO})_{4}(\mathbf{1 0})$ has three singlet minima within $2 \mathrm{kcal} / \mathrm{mol}$ of the global minimum, all with $\mathrm{Co}-\mathrm{Co}$ single bond lengths from 2.504 to $2.678 \AA$. The pentacarbonyl $\left.\mathrm{Co}_{2}\left[\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}(\mathrm{CO})_{5} \mathbf{1 1}$ and hexacarbonyl $\left.\mathrm{Co}_{2}\left[\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right]_{2}(\mathrm{CO})_{6} \mathbf{1 2}$ have singlet minima with Co-Co single bonds of lengths 2.698 and $2.770 \AA$. The Co-Co single bonds become longer as the number of CO ligands increases (entries 10, 11 and 12).

### 9.6. Co-Co Bond Length Ranges

The estimate of about $2.52 \AA$ for a Co-Co single bond length arises from the value of $1.26 \AA$ for the cobalt covalent radius. This estimate is significantly longer than the experimental Co-Co single bond lengths in the paddlewheel complexes $\mathbf{0 4}, \mathbf{0 5}$ and $\mathbf{0 6}$ of Table 26, which range from 2.265 to $2.374 \AA$. Some idea of the range of Co-Co bond lengths with change in MM bond order may be drawn from the limited experimental structures of Table 26. A bond order of 0.5 is associated with Co-Co distances from 2.320 to $2.385 \AA(2.35 \pm 0.03 \AA)$, while a bond order of 1 is assigned to the Co-Co bond length range of $2.32 \pm 0.06 \AA$. A bond order of 1.5 is attributed to one complex with an average $R_{M M}$ value of $2.327 \AA$. A bond order of 2 is assigned to the Co-Co bond length range of $2.26 \pm 0.13 \AA$.

The Co-Co single bond estimate of about $2.52 \AA$ given above is more consistent with the experimental MM bond length range of 2.45 to $2.50 \AA$ noted for the dicobalt and cobalt cluster carbonyl complexes $\mathbf{0 3}$ to $\mathbf{1 1}$ of Table 27. The carbonyl ligand leads to Co-Co bond lengthening through back-bonding, unlike the bidentate electron donor amidinate ligands of

Table 26. Furthermore, bridging CO groups provide the possibility for three-centre twoelectron bonding thereby bypassing two-center MM covalent bonding. The $R_{M M}$ values for $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ (Table 28) may thus not be representative of $\mathrm{Co}-\mathrm{Co}$ covalent single bond lengths owing to the arguments for $3 \mathrm{c}-2 \mathrm{e}$ bonding. $R_{M M}$ values above $2.550 \AA$ in CO-bridged dicobalt carbonyl complexes may then not indicate true localized cobalt-cobalt covalent bonding.

Except for such systems, the BP86 results for two series of binuclear cobalt complexes (the homoleptic carbonyl and trifluorophosphine series of Table 28) exhibit the range $2.52 \pm 0.03 \AA$ for Co-Co single bond lengths, which seem more consistent with a covalent cobalt-cobalt single bond. The DFT results for $\mathrm{Co}=\mathrm{Co}$ double bond lengths present the range $2.38 \pm 0.09 \AA$, while the range for $\mathrm{Co} \equiv \mathrm{Co}$ triple bonds is $2.18 \pm 0.08 \AA$. A BP86 value of $2.173 \AA$ was predicted for a quadruple Co-Co bond in a high energy isomer of dicobalt pentacarbonyl. A successive decrease in bond length range with increasing bond order is thus noted for these carbonyl complexes.

Binuclear cobalt carbonyl complexes with inorganic ligands (thiocarbonyl, nitrosyl and fluoroborylene) present the following ranges of $R_{M M}$ values (inclusive of those higher than $2.550 \AA$ ). The thiocarbonyl series (Table 28) exhibits the range $2.53 \pm 0.15 \AA$ for $\mathrm{Co}-\mathrm{Co}$ single bonds and $2.351 \AA$ for the sole example of a $\mathrm{Co}=\mathrm{Co}$ double bond. The nitrosyl series (Table 29) exhibits the range $2.60 \pm 0.06 \AA$ for $\mathrm{Co}-\mathrm{Co}$ single bonds; $2.43 \pm 0.10 \AA$ for $\mathrm{Co}=\mathrm{Co}$ double bonds; $2.29 \pm 0.11 \AA$ for $\mathrm{Co} \equiv \mathrm{CO}$ triple bonds; $2.243 \AA$ for the sole example of a MM quadruple bond. The fluoroborylene series (Table 29) yields the range $2.49 \pm 0.14 \AA$ for CoCo single bonds and $2.38 \pm 0.02 \AA$ for $\mathrm{Co}=\mathrm{Co}$ double bonds.

Three series of binuclear cobalt carbonyl complexes (Table 30) with the carbon ligands butadiene, cyclopentadienyl, and trimethylenemethane exhibit ranges of $R_{M M}$ values as follows (inclusive of those higher than $2.550 \AA$ ). The butadiene series exhibits the ranges $2.51 \pm 0.06 \AA$ for Co-Co single bonds; $2.37 \pm 0.08 \AA$ for $\mathrm{Co}=\mathrm{Co}$ double bonds; $2.26 \pm 0.04 \AA$ for
$\mathrm{Co} \equiv \mathrm{CO}$ triple bonds; $2.14 \pm 0.01 \AA$ for Co-Co quadruple bonds. The cyclopentadienyl series (Table 28) exhibits the range $2.63 \pm 0.07 \AA$ for Co -Co single bonds; $2.346 \AA$ for the sole example of a $\mathrm{Co}=\mathrm{Co}$ double bond; $2.17 \pm 0.12 \AA$ for $\mathrm{Co} \equiv \mathrm{Co}$ triple bonds. The trimethylenemethane series gives the range $2.63 \pm 0.13 \AA$ for $\mathrm{Co}-\mathrm{Co}$ single bonds; $2.33 \pm 0.09 \AA$ for $\mathrm{Co}=\mathrm{Co}$ double bonds; $2.290 \AA$ for the sole $\mathrm{Co} \equiv \mathrm{Co}$ triple bond.

The expected general trend towards shorter Co-Co bonds with increasing MM bond order is demonstrated by this limited set of experimental and computational results for binuclear cobalt complexes. The experimental results for non-carbonyl complexes appear to be in a category of their own, distinct from the experimental and theoretical structures for carbonyl complexes. This could be a consequence of the MM bond lengthening effect of CO ligands arising from their metal $\rightarrow$ ligand back-bonding.

## 10. NICKEL-NICKEL BONDS

The group 10 metals nickel, palladium and platinum have the neutral atom configuration $\mathrm{d}^{8} \mathrm{~s}^{2}$. Binuclear group 10 metal complexes have been reviewed by Murillo ${ }^{459}$ and by Lu and Liddle. ${ }^{460}$ Binuclear nickel complexes are experimentally known with nickel in the $0,+1$ and +2 oxidation states. In their common $\mathrm{M}^{2+}$ oxidation states, the group 10 metals have stable $\mathrm{d}^{8}$ configurations, and a few paddlewheel complexes having a $\left(\mathrm{Ni}_{2}\right)^{+4}$ core with bidentate ligands are known. This Section reviews the nickel dimer $\mathrm{Ni}_{2}$, various sets of experimentally characterized binuclear nickel complexes, and also computational (DFT) studies on binuclear nickel complexes. Ni-Ni bond lengths in experimentally studied binuclear nickel complexes are presented according to the oxidation state of the metal centres, without much reference to the formal MM bond orders present. An attempt is made to establish ranges for $\mathrm{Ni}-\mathrm{Ni}$ bond lengths as a function of MM bond order for some series of computationally studied binuclear nickel complexes. An estimate of around $2.48 \AA$ derived from the covalent radius of $1.24 \AA$ for nickel ${ }^{41}$ may serve as a reference here for discerning the presence of $\mathrm{Ni}-\mathrm{Ni}$ covalent bonding in binuclear nickel complexes.

### 10.1. Nickel Dimer

The nickel dimer $\mathrm{Ni}_{2}$ has not been easy to characterize experimentally or computationally. ${ }^{33}$ Around 59 distinct electronic configurations have been described as lying within 0.84 eV of the ground state (Morse, Smalley, and coworkers ${ }^{461}$ ). The ground state has not been clearly defined, although a point charge and spin-orbit model based on ligand field theory suggested a $0_{g}{ }^{+}$ground state. ${ }^{462}$ Table 31 presents some experimental and computational estimates of the $\mathrm{Ni}-\mathrm{Ni}$ distance in the nickel dimer. Low-resolution resonant two-photon ionization studies by Morse and coworkers ${ }^{463}$ yielded an equilibrium Ni-Ni distance of $2.1545 \pm 0.0004 \AA$ for the Hund's case (c) ground state $\Omega=0^{+} g$ or $0^{\sim}{ }_{u}$. Empirical formulas gave values from 2.11 to
$2.23 \AA .{ }^{28}$ Although single configuration DFT methods cannot be expected to give definitive results for a multireference system like $\mathrm{Ni}_{2}$, the B3P86 method gave a very reasonable equilibrium Ni-Ni bond length of $2.175 \AA$ for the ${ }^{1} \Sigma^{+} g$ ground state ${ }^{33}$ comparable with the experimental value. One of four DFT methods gave a value of $2.133 \AA$ for the ${ }^{3} \Sigma^{\sim} g$ state. ${ }^{34}$ Higher level theoretical results include the value of $2.289 \AA$ for the ${ }^{3} \Sigma^{2} \mathrm{~g}$ state from an CASSCF/IC-ACPF study, ${ }^{464}$ and the values of 2.228 and $2.231 \AA$ for the mixed singlet and triplet states from a CASPT2/ANO study ${ }^{465}$ using a perturbation theory-based relativistic one-electron Darwin contact term.

### 10.2. Binuclear Nickel Complexes with $\mathrm{Ni}(\mathrm{O})$ Centers

The electron-rich $\mathrm{Ni}(0)$ oxidation state with the $3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$ configuration is present in relatively few known dinickel complexes, presented in Table 31. Ligands include the dppa, dppm, isocyanide, $\mathrm{Ga}(\mathrm{I})$, and olefin groups. The nature of MM bonding and the interaction between the two $\mathrm{d}^{8}$ centres is not clear, nor are formal MM bond orders suggested. Computational studies should be useful here. Complexes 02 (Figure 14a) to 06 (Figure 14b) have $\mathrm{Ni}(0)$ $\mathrm{Ni}(0)$ bond lengths from 2.483 to $2.572 \AA\left(\right.$ Kubiak $^{466,467}$, Fischer ${ }^{468}$, Seifert and Linti ${ }^{469}$ ), while structure $\mathbf{0 7}$ has a shorter $R_{M M}$ value of $2.437 \AA\left(\right.$ Power $\left.^{470}\right)$.

Complexes 08 (Figure 14c), 09 and 10 have a $\left(\mathrm{Ni}_{2}\right)^{+}$core with two $\alpha$-diimine ligands L [ L $=\mathrm{N}, \mathrm{N}^{\prime}-\operatorname{dipp}_{2}(\mathrm{NC}(\mathrm{Me}) \mathrm{C}(\mathrm{Me}) \mathrm{N}$ in various radical and/or anionic states] and the countercations $\left[\mathrm{Na}\left(\mathrm{Et}_{2} \mathrm{O}\right)\right]^{+}$and $\mathrm{Na}^{+}{ }^{471}$ These exhibit $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(0)$ bonds of length 2.338, 2.445 , and $2.465 \AA$, respectively. The mixed-valent dications $\mathbf{1 1}$ and $\mathbf{1 2}$ have $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(0)$ bond lengths $\left(\mathrm{Kubiak}^{472}\right.$ ) of 2.393 and $2.481 \AA$, while the monocation $\mathbf{1 3}$ with a $\left(\mathrm{Ni}_{2}\right)^{+}$core and a $\mathrm{Ni}(0.5)-\mathrm{Ni}(0.5)$ bond has a longer $2.588 \AA \mathrm{Ni}-\mathrm{Ni}$ distance. However, there is no simple general relation between $\mathrm{Ni}-\mathrm{Ni}$ bond length and Ni oxidation state in these complexes.

Table 31. Ni-Ni Bond Lengths in $\mathrm{Ni}_{2}$ and Binuclear Nickel Complexes with Ni(0) Centres

| Label Species | $R_{M M}(\AA)$ | References and Remarks |
| :---: | :---: | :---: |
| 01 Nickel dimer | 2.1545 | 463; experimental |
|  | 2.11-2.23 | 28; empirical formulae |
|  | 2.175 | 33; ${ }^{1}{ }^{+}{ }^{\text {g }}$; B3P86 DFT |
|  | 2.133 | 34; ${ }^{3} \Sigma^{-} g$; BOP DFT |
|  | 2.289 | 464; ${ }^{3} \Sigma^{-}$g ; CASSCF |
|  | 2.228 | 465; ${ }^{1} \Sigma^{+}{ }^{\text {g }}$; CASPT2/ANO |
|  | 2.231 | 465; ${ }^{3} \Sigma_{g} ;$ CASPT2/ANO |

Binuclear nickel complexes with one or two $\mathrm{Ni}(0)$ centres

| $02 \mathrm{Ni}_{2}(\mu \text {-dppa })_{2}(\mu$-CNMe $)(\mathrm{CNMe})_{2}$ | 2.5174(9) | 466; $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ |
| :---: | :---: | :---: |
| $03 \mathrm{Ni}_{2}(\mu-\mathrm{dppm})_{2}(\mu-\mathrm{CNMe})(\mathrm{CNMe})_{2}$ | 2.572(1) | 467; $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ |
| $04 \mathrm{Ga}\left[\{\mathrm{N}-(\mathrm{dipp}) \mathrm{NC}(\mathrm{Me})\}_{2} \mathrm{CH}\right] \mathrm{Ni}_{2}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)_{4}$ | 2.5051(18) | 468; $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ |
| $05 \mathrm{Ga}\left[\{\mathrm{N}-(\mathrm{dipp}) \mathrm{NC}(\mathrm{Me})\}_{2} \mathrm{CH}\right] \mathrm{Ni}_{2}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)_{3}$ | 2.4830 (14) | 469; $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ |
| $06 \mathrm{Ni}_{2}(\mu-\mathrm{Ga}-\mathrm{tmp})_{3}(\mathrm{Ga}-\mathrm{tmp})_{4}{ }^{\text {a }}$ | 2.522(1) | 469; $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ |
| $07 \mathrm{Ni}_{2}\left(\mathrm{GaAr}^{\prime}\right)_{2}\left(\eta^{1}: \eta^{1}-\mu^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)^{b}$ | 2.437(5) | 470; $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ |
| $08\left(\mathrm{Ni}_{2}\right)^{+}\left(\mu-\mathrm{L}^{-{ }^{-}}\right)_{2}{ }^{\text {c }}$ | 2.3383 (14) | 471; bridged $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(0)$ |
| $09\left(\mathrm{Ni}_{2}\right)^{+}\left(\mathrm{L}^{2-}\right)\left(\mathrm{L}^{+-}\right)^{c}$ | 2.4453(5) | 471; $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(0)$ |
| $10\left(\mathrm{Ni}_{2}\right)^{+}\left(\mathrm{L}^{2-}\right)^{c}$ | 2.4649(8) | 471; $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(0)$ |
| $11\left[\mathrm{Ni}_{2}\left\{\mu-\mathrm{CH}_{2}\left(\mathrm{PPh}_{2}\right)_{2}\right\}_{2}\left(\mathrm{CN'Bu}_{3}\right]^{2+}\right.$ | 2.3931(13) | 472; $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(0)$ |
| $12\left[\mathrm{Ni}_{2}\left\{\mu-\mathrm{CH}_{2}\left(\mathrm{PPh}_{2}\right)_{2}\right\}_{2}\left\{\mathrm{CN}\left(2,6-\mathrm{Me}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right)\right\}_{3}\right]^{2+}$ | 2.4813 (10) | 472; $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(0)$ |
| $13\left[\mathrm{Ni}_{2}\left\{\mu-\mathrm{CH}_{2}\left(\mathrm{PPh}_{2}\right)_{2}\right\}\left(\mu-\mathrm{CN}^{\mathrm{t}} \mathrm{Bu}\right)\left(\mathrm{CN}^{\mathrm{tBu}}\right)_{2}\right]^{+}$ | 2.5879(8) | 472; $\mathrm{Ni}(0.5)-\mathrm{Ni}(0.5)$ |

[^18]
a (31-02)

c (31-08)



d (32-02)


Figure 14. Some experimentally known dinickel complexes having $\mathrm{Ni}(0)$ and $\mathrm{Ni}(\mathrm{I})$ centers (brackets refer to Table number and label)

### 10.3. Binuclear Nickel Complexes with $\mathrm{Ni}(\mathrm{I})$ Centers

A significant number of binuclear nickel complexes with $\mathrm{Ni}(\mathrm{I})$ centers have been experimentally characterized (Table 32). The $\mathrm{d}^{7}$ metal configuration allows for covalent MM bonding in the $\left(\mathrm{Ni}_{2}\right)^{+2}$ core. Such binuclear complexes with $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ bonds may contain ligands of the anionic bidentate ( $\mathrm{X}-\mathrm{C}=\mathrm{Y}$ ) type, aromatic rings, bridging halides, azadienes and N-heterocyclic carbenes (NHC), besides others. Here again, the trends shown by the lengths of the $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ bonds present ranging from 2.291 to $2.605 \AA$ are not easy to rationalize on a general basis.

Complexes 01 to 04 contain bidentate ( $\mathrm{X}-\mathrm{C}=\mathrm{Y}$ ) type ligands (amidinate, guanidinate and carboxylate) and exhibit $R_{M M}$ values ranging from 2.291 to $2.563 \AA$. The small bite angles of the amidinate ligands in 01 and guanidinate ligands in 02 (Figure 14d) result in very short $\mathrm{Ni}-\mathrm{Ni}$ bond lengths around $2.29 \AA$ (Eisen ${ }^{473}$, Jones ${ }^{474}$ ). Complex $\mathbf{0 2}$ is paramagnetic with NiNi antiferromagnetic coupling, for which computational studies give a triplet ground state and a Ni-Ni bond index value of 0.62 . Complex $\mathbf{0 4}\left(\right.$ Fischer $\left.^{475}\right)$ has one acrylate ligand, where this carboxylate ligand with its larger bite angle leads to a longer $R_{M M}$ value of $2.563 \AA$. The $\alpha$-diimine complex $\mathbf{0 5}$ has a very short $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ bond distance of $2.296 \AA, 475$ shorter than the derivatives $\mathbf{0 8}, \mathbf{0 9}$, and $\mathbf{1 0}$ of Table 31 with longer $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(0)$ bonds.

Complexes $\mathbf{0 6}$ to $\mathbf{1 1}$ have aromatic ring ligands and exhibit $R_{M M}$ values from 2.392 to $2.447 \AA\left(\right.$ Zagarin $^{476}$, Beck and Johnson ${ }^{477}$, Brudvig $\left.{ }^{478}\right)$. Most of these complexes have one bridging chloride ligand, while $\mathbf{1 0}$ and $\mathbf{1 1}$ also contain N -heterocyclic carbene (NHC) ligands. Complex $\mathbf{1 2}$ with a borabenzene ring ligand has an appreciably longer Ni-Ni bond of $2.605 \AA$ (Macha et al. ${ }^{479}$ ). Complexes $\mathbf{1 3}$ to $\mathbf{1 8}$ incorporate bi/polyphenyl ligands (e.g. 15; Figure 14e) with $R_{M M}$ values ranging from 2.320 to $2.525 \AA$ (Velian ${ }^{480}$, Keen and Johnson ${ }^{481}$, Agapie ${ }^{482,483}$, Beck and Johnson ${ }^{484}$ ). Among these complexes, 16 with two bridging chloro

Table 32. Ni-Ni Bond Lengths in Binuclear Nickel Complexes with Two Ni(I) Centres

| Label Species | $R_{M M}(\AA)$ | References and Remarks |
| :---: | :---: | :---: |
| $01 \mathrm{Ni}_{2}\left\{\mu-\mathrm{Me}_{3} \mathrm{SiNC}(\mathrm{Ph}) \mathrm{NSiMe}_{3}\right\}_{2}$ | 2.2938(12) | 473; 2 amidinate ligands |
| $\left.02 \mathrm{Ni}_{2}\left\{\mathrm{dippNC}\left({ }^{( } \mathrm{Pr}_{2} \mathrm{~N}\right) \mathrm{Ndipp}\right)\right\}_{2}$ | 2.2908(11) | 474; 2 guanidinate ligands |
| $\left.03 \mathrm{Ni}_{2}(\mu-\mathrm{CO})_{2}\left\{\mathrm{dippNC}\left({ }^{( } \mathrm{Pr}_{2} \mathrm{~N}\right) \mathrm{Ndipp}\right)\right\}_{2}$ | 2.437(1) | 474; 2 amidinate, 2 CO |
| $04 \mathrm{Ni}_{2}\left(\mu-\mathrm{PPh}_{2}\right)(\mu-\mathrm{dppm})(\mathrm{dppm})_{2}\left(\mu-\mathrm{O}_{2} \mathrm{CCH}=\mathrm{CH}_{2}\right)$ | 2.563(1) | 475; 1 acrylate ligand |
|  | 2.2957(6) | 471; $\alpha$-diimine ligand |
| $06 \mathrm{Ni}_{2}\left(\mu-\mathrm{PPh}_{2}\right)\left(\mathrm{PPh}_{3}\right)_{2}\left(\eta^{4}-\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{BPh}_{3}\right)$ | 2.4471(11) | 476; phenyl ligand |
| $07 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})\left(\mathrm{P}^{i} \mathrm{Pr}_{3}\right)_{2}\left(\eta^{2}: \eta^{2}-\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{BPh}_{3}\right)$ | 2.4255(9) | 477; phenyl ligand |
| $08 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})\left(\mathrm{P}^{\mathrm{i}} \mathrm{Pr}_{3}\right)_{2}\left(\eta^{2}: \eta^{2}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$ | 2.3995 (10) | 477; cyclopentadienyl |
| $09 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})\left(\mathrm{P}^{i} \mathrm{Pr}_{3}\right)_{2}\left(\eta^{2}: \eta^{2}-\mathrm{C}_{9} \mathrm{H}_{7}\right)$ | 2.3918(8) | 477; indenyl ligand |
| $10 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})\left(\mathrm{Pr}_{2}\right)_{2}\left(\eta^{2} \cdot \eta^{2}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$ | 2.4015 (3) | 478; $\mathrm{NHC}^{\text {IPr }}{ }_{2}$ |
| $11 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})\left(\mathrm{SIPr}_{2}\right)_{2}\left(\eta^{2}: \eta^{2}-\mathrm{C}_{9} \mathrm{H}_{7}\right)$ | 2.4425(6) | 478; $\mathrm{NHC} \mathrm{SIPr}_{2}$ |
| $12 \mathrm{Ni}_{2}\left[\left(\eta^{6}-\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~B}\right) \mathrm{P}^{\prime} \mathrm{Bu}_{2}\right]_{2}$ | $2.605(1)$ | 479; borabenzene |
| $13 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})_{2}\left\{1,4-\left(\mathrm{o}-{ }^{-} \mathrm{Pr}_{2} \mathrm{P}-\mathrm{C}_{6} \mathrm{H}_{4}\right)_{2}\left(\eta^{2}: \eta^{2}-\mathrm{C}_{6} \mathrm{H}_{4}\right)\right\}$ | 2.36580 (16) | 480; terphenyl phosphine |
| $14 \mathrm{Ni}_{2}\left\{1,4-\left(\mathrm{o}^{-} \mathrm{Pr}_{2} \mathrm{P}-\mathrm{C}_{6} \mathrm{H}_{4}\right)_{2}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right)\right\}\left(\mathrm{C}_{6} \mathrm{H}_{4} . \mathrm{C}_{6} \mathrm{H}_{4}\right)$ | 2.44266(19) | 480; biphenyl ligand |
| $15 \mathrm{Ni}_{2}\left[\left\{3,4-\mathrm{F}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{3}\right)\right\} \cdot\left\{3,4-\mathrm{F}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{3}\right)\right\}\right]\left(\mathrm{PEt}_{3}\right)_{4}$ | 2.3710 (5) | 481; biphenyl ligand |
| $16 \mathrm{Ni}_{2}\left[\left\{o-\mathrm{P}^{i} \mathrm{Pr}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right)\right\}_{2}\left(\eta^{2}: \eta^{2}-\mathrm{C}_{6} \mathrm{H}_{6}\right)\right](\mu-\mathrm{Cl})_{2}$ | 2.3201(2) | 482; $\mathrm{C}_{6} \mathrm{H}_{6}$ is dien-1,4-diyl |
| $17 \mathrm{Ni}_{2}\left[1,3,5-\left\{\left(o-\mathrm{P}^{i} \mathrm{Pr}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right)\right\}_{3}\left(\mathrm{C}_{6} \mathrm{H}_{3}\right)\right](\mu-\mathrm{Cl})\right.$ | 2.5248(3) | 483; molecular hinge |
| $18\left(\mu-\mathrm{C}_{6} \mathrm{H}_{4} \cdot \mathrm{C}_{6} \mathrm{H}_{4} \cdot \mathrm{C}_{6} \mathrm{H}_{4} . \mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{Ni}_{2}\left(\mathrm{P}^{i} \mathrm{Pr}_{3}\right)_{2}$ | 2.3352(6) | 484; tetraphenylene |
| $19\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{Ni}_{2}\left[\mu-\mathrm{S}\left\{1,3,5-i \mathrm{Pr}_{3}\left(\mathrm{C}_{6} \mathrm{H}_{2}\right)\right\}\right]_{2}$ | 2.3510(3) | 485; thiolate ligand |
| $20\left(\mu-{ }^{-} \mathrm{Pr}_{2} \mathrm{PCH}_{2} \mathrm{P}^{\mathbf{i}} \mathrm{Pr}_{2}\right)\left\{\left({ }^{2} \mathrm{Pr}_{2}\right)_{2} \mathrm{CH}\right\} \mathrm{Ni}_{2} \mathrm{Br}$ | 2.408(2) | 486; Ni-C bond |
| $21 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})_{2} \mathrm{I}^{\mathrm{i}} \mathrm{Pr}_{2}$ | 2.5194(5) | 487; NHC ligand $\mathrm{I}^{\mathrm{i}} \mathrm{Pr}_{2}$ |
| $22 \mathrm{Ni}_{2}(\mu-\mathrm{Cl})_{2} \mathrm{Si}^{i} \mathrm{Pr}_{2}$ | 2.5099(6) | 487; NHC ligand $\mathrm{SI}^{\prime} \mathrm{Pr}_{2}$ |
| $23 \mathrm{Ni}_{2}(\mu-\mathrm{NO})(\mu-\mathrm{I}) \mathrm{I}^{i} \mathrm{Pr}_{2}$ | 2.314(1) | 488; NHC ligand $\mathrm{I}^{\mathrm{I} \mathrm{Pr}_{2}}$ |
| $24 \mathrm{Ni}_{2}\left(\mu-\mathrm{I}^{\prime} \mathrm{Bu}\right)_{2}\left(\mathrm{I}^{\prime} \mathrm{Bu}_{2}\right)_{2}$ | 2.4354(9) | 489; 2 NHC anions |
| $25\left(\mathrm{Ni}_{2}\right)^{2+}\left\{2,5-\left(\mathrm{PPh}_{2} \mathrm{CH}_{2}\right)_{2}\left(\mathrm{C}_{4} \mathrm{H}_{2} \mathrm{~N}\right)^{-}\right\}_{2}$ | 2.3259(2) | 490; pincer ligand |
| $26 \mathrm{Ni}_{2}\left\{1-\left(\mathrm{PPh}_{2} \mathrm{NH}\right)-2-\left(\mathrm{PPh}_{2} \mathrm{~N}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right)\right\}_{2}$ | 2.4152(6) | 491; $\mathrm{Ni}_{2} \mathrm{P}_{2} \mathrm{~N}_{2}$ core |
| $27\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Ni}_{2}(\mathrm{CO})_{2}$ | 2.390(1) | 492 |
| $28\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{Me}\right)_{2} \mathrm{Ni}_{2}(\mathrm{CO})_{2}$ | $2.363(1)^{a}$ | 492 |

[^19]ligands has a short $R_{M M}$ value of $2.320 \AA\left(\mathrm{C}_{6} \mathrm{H}_{6}\right.$ is the cyclohexa-1,3-dien-diyl moiety). Complex 17 functions as a molecular hinge.

Complex 19 (Tatsumi ${ }^{485}$ ) has a bridging thiolate ligand, giving an $R_{M M}$ value of $2.351 \AA$, while structure 20 (Vicic et al. ${ }^{486}$ ) with a Ni-Ni distance of $2.408 \AA$ contains Ni-C bonds. Complexes 21 to 24 also have Ni-C bonds with NHC ligands and $R_{M M}$ values (Arif ${ }^{487}$, Varonka and Warren ${ }^{488}$, Caddick ${ }^{489}$ ) from 2.314 to $2.519 \AA$. The bridging NO group in 23 (Figure 14f) is found to have a marked MM bond shortening effect. Such a bond shortening effect is also present in structure $\mathbf{2 5}$ (Gade ${ }^{490}$ ) having a pincer ligand. Complex $\mathbf{2 6}$ with two bis(phosphamino)benzene ligands has a longer Ni-Ni bond distance (Hey-Hawkins ${ }^{491}$ ) of $2.415 \AA$. This complex is unusual because of the Dewar-benzene type structure of its $\mathrm{Ni}_{2} \mathrm{P}_{2} \mathrm{~N}_{2}$ backbone.

Complexes 27 and 28 (Dahl ${ }^{492}$ ) synthesised by the method of King, ${ }^{493}$ were determined to have $R_{M M}$ values of $2.390 \AA$ (for 27) and of 2.363 and $2.351 \AA$ (for 28), where a $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ bond order of 1 was assigned to both complexes. Like the $R_{M M}$ values for many other complexes of Table 32, these are on the short side when compared with the estimate of 2.48 $\AA$ for a $\mathrm{Ni}-\mathrm{Ni}$ single bond as per the covalent radius value of $1.24 \AA$ assigned to nickel. ${ }^{41}$

### 10.4. Binuclear Nickel Complexes with $\mathrm{Ni}(\mathrm{II})$ and $\mathrm{Ni}($ III $)$ Centers

Binuclear nickel complexes having $\mathrm{Ni}(\mathrm{II})$ and $\mathrm{Ni}(\mathrm{III})$ centres are less numerous. Table 33 presents $R_{M M}$ values for a series of $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(\mathrm{II})$ complexes $\mathbf{0 1}$ to $\mathbf{1 2}$ and for a few with $\mathrm{Ni}($ III $)$ centers. The $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(\mathrm{II})$ complexes 01 (Figure 15a) to $\mathbf{0 4}$ are of the paddlewheel type with bidentate X-C $=\mathrm{Y}$ ligands. Their $R_{M M}$ values (Cotton ${ }^{494,495}$, Eisen $^{496}$, Bellitto ${ }^{497}$, Kobayashi ${ }^{498}$ ) range from 2.448 to $2.564 \AA$, where structures $\mathbf{0 1}$ and $\mathbf{0 2}$ have $\mathrm{Ni}-\mathrm{N}$ bonds with $\mathrm{Ni}-\mathrm{Ni}$ bond lengths of 2.485 and $2.448 \AA$, the former having two axial $\mathrm{H}_{2} \mathrm{O}$ ligands. The tetrakis(dithioacetate) complex $\mathrm{Ni}_{2}\left(\mathrm{~S}_{2} \mathrm{CCH}_{3}\right)_{4} \mathbf{0 3}$ with $\mathrm{Ni}-\mathrm{S}$ bonds has an $R_{M M}$ value of 2.564
$\AA$, described as a weak interaction. ${ }^{497}$ This is oxidized to an infinite chain complex $\left[\mathrm{Ni}_{2}\left(\mathrm{~S}_{2} \mathrm{CCH}_{3}\right)_{4} \mathrm{I}\right]_{\infty}$ with a $\mathrm{Ni}-\mathrm{Ni}$ separation of $2.514 \AA$. Complex 04 is also an infinite chain with dithiopropionate ligands and a similar Ni-Ni distance of $2.527 \AA .{ }^{498}$

a (01)

c (12)

d (16)

Figure 15. Some experimentally known dinickel complexes with $\mathrm{Ni}(\mathrm{II})$ and $\mathrm{Ni}($ III $)$ centers (labels in brackets refer to Table 33)

Table 33. Experimental Ni-Ni Distances in Binuclear Nickel Complexes with Ni(II) and Ni(III) Centers

| Label Species | $R_{M M}(\AA)$ | References and Remarks |
| :---: | :---: | :---: |
| $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(\mathrm{II})$ complexes |  |  |
| $01\left[\mathrm{Ni}_{2}(\mathrm{DTolF})_{4}\right]\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ | 2.485(2) | 495; formamidinate ligands |
| $02 \mathrm{Ni}_{2}\left\{\mu-\left(\mathrm{Me}_{2} \mathrm{C}_{7} \mathrm{H}_{5} \mathrm{CH}_{2}\right) \mathrm{NC}(\mathrm{Ph}) \mathrm{NH}\right\}_{4}$ | 2.4484(13) | 496; benzamidinate paddlewheel |
| $03 \mathrm{Ni}_{2}\left(\mu-\mathrm{S}_{2} \mathrm{CCH}_{3}\right)_{4}$ | 2.564(1) | 497; dithioacetate paddlewheel |
| $04 \mathrm{Ni}_{2}\{\mu-\mathrm{SC}(\mathrm{Et}) \mathrm{S}\}_{4}$ | $2.5267(10)$ | 498; infinite chain |
| $05 \mathrm{Ni}_{2}(\mu-\mathrm{NAd})(\mathrm{Me}$-nacnac) $){ }^{a}$ | $2.506(1)$ | 499; paramagnetic |
| $06 \mathrm{Ni}_{2}\left(\mu\right.$-NAd)(Me-nacnac*) ${ }_{2}{ }^{b}$ | 2.4872(7) | 500; cf. 05 |
| $07 \mathrm{Ni}_{2}\left(\mu-\mathrm{NMes}^{2}\right) \mathrm{Cl}_{2}\left(\mathrm{I}^{i} \mathrm{Pr}_{2}\right)_{2}$ | $2.5767(15)$ | 501; $\mathrm{NHC} \mathrm{I}^{\text {i }} \mathrm{Pr}_{2}$ |
| $08\left[\mathrm{Ni}_{2}(\mu-\mathrm{NMes})(\mu-\mathrm{Cl})\left(\mathrm{I}^{i} \mathrm{Pr}_{2}\right)_{2}\right]$ | $2.3284(5)$ | $501 ; \mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{II})$ bond |
| $09\left[\mathrm{Ni}_{2}(\mu-\mathrm{NMes})(\mu-\mathrm{Cl})\left(\mathrm{I}^{\mathrm{i}} \mathrm{Pr}_{2}\right)_{2}\right]^{+}$ | 2.2911(8) | 501; $\left.\mu-\mathrm{Cl} ; \mathrm{B}^{\mathrm{F}} \mathrm{Ar}_{4}\right]^{-}$anion |
| $10\left[\mathrm{Ni}_{2}(\mu-\mathrm{NMes})\left(\mu-\mathrm{CPh}_{2}\right)\left(\mathrm{I}^{2} \mathrm{Pr}_{2}\right)_{2}\right]^{+}$ | $2.4312(10)$ | 502; bridging carbene |
| $11\left[\mathrm{Ni}_{2}\left(\mu-\mathrm{NMes}^{2}\right)\left(\mu-\mathrm{CHSiMe}_{3}\right)\left(\mathrm{I}^{\mathrm{i}} \mathrm{Pr}_{2}\right)_{2}\right]^{+}$ | 2.4385(9) | 502; bridging carbene |
| $12 \mathrm{Ni}_{2}\left(\mu-\mathrm{CH}_{2}\right)\left(\eta^{5}-\mathrm{C}_{5}{ }^{\text {P }} \mathrm{Pr}_{4} \mathrm{H}\right)_{2}$ | $2.3158(10)$ | 503; $\mu$-carbene; $\mathrm{Ni}=\mathrm{Ni}$ bond |
| $13\left(\mu-\eta^{3}, \eta^{3}-\mathrm{C}_{8} \mathrm{Me}_{6}\right) \mathrm{Ni}_{2}$ | 2.569 (1) | 119; sandwich; $(16,16)$ |
| With $\mathrm{Ni}(\mathrm{III})$ centers |  |  |
| $14\left[\mathrm{Ni}_{2}(\mathrm{DTolF})_{4}\right]^{+}\left(\mathrm{BF}_{4}\right)^{-}$ | 2.418(4) | 495; Ni(2.5); paddlewheel |
| $15\left[\mathrm{Ni}_{2}\left\{\mathrm{Ar}^{1} \mathrm{NC}(\mathrm{H}) \mathrm{NAr}^{1}\right\} 4\right]^{+}\left(\mathrm{BF}_{4}\right)^{-}$ | 2.3703(4) | 504; $\mathrm{Ni}(2.5) ; \mathrm{Ar}^{1}=4-\mathrm{OMeC}_{6} \mathrm{H}_{4}$ |
| $16\left[\mathrm{Ni}_{2}\{\mathrm{PhNC}(\mathrm{NHPh}) \mathrm{NPh}\}_{4}\right]^{+}\left(\mathrm{BF}_{4}\right)^{-}$ | $2.3298(6)$ | 504; two $\mathrm{Ni}(2.5)$ centers |
| $17 \mathrm{Ni}_{2}\left\{\left(1-\mathrm{S}-2-\mathrm{SiMe}_{3}-\mathrm{C}_{6} \mathrm{H}_{3}\right)_{3} \mathrm{P}\right\}_{2}$ | 2.6026(7) | 505; two Ni(III) centers |

[^20]Complexes $\mathbf{0 5}$ to $\mathbf{1 1}$ have the bridging imide ligands NAd and NMes along with other ligands. Complexes 05 and 06 with the NAd ligand have the similar ligands (Me-nacnac) and (Me-nacnac*) with $R_{M M}$ distances (Warren ${ }^{499,500}$ ) fairly close to each other (2.506 and 2.487 $\AA$ ). Complexes $\mathbf{0 7}$ to $\mathbf{1 1}$ (Laskowski and Hillhouse ${ }^{501,502}$ ) all have a bridging NMes ligand along with the N -heterocyclic carbene ligand $\mathrm{I}^{i} \mathrm{Pr}_{2}$, where the bridging Cl or carbene ligands tend to decrease $R_{M M}$ values relative to structure $\mathbf{0 7}$ (Figure 15b). Oxidation of $\mathbf{0 8}$ with an $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{II})$ bond gives 09 with a very short $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(\mathrm{II})$ bond of length $2.291 \AA$ (cf. the $R_{M M}$ values for 01, 02 and 05 in Table 32). Complex 12 (Sitzmann ${ }^{503}$ ) with a bridging carbene ligand and a substituted cyclopentadienyl ligand (Figure 15c) has a short $\mathrm{Ni}=\mathrm{Ni}$ double bond distance of $2.316 \AA$. The sandwich bis(pentalene) complex $\mathbf{1 3}$ is the nickel analogue in the $\left(\mathrm{C}_{8} \mathrm{Me}_{6}\right)_{2} \mathrm{M}_{2}$ series ${ }^{119}$ showing a $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(\mathrm{II})$ single bond length of $2.569 \AA$.

Complexes $\mathbf{1 4}$ to $\mathbf{1 6}$ have mixed-valent $\mathrm{Ni}_{2}{ }^{+5}$ cores with $\mathrm{Ni}(\mathrm{II})$ and $\mathrm{Ni}(\mathrm{III})$ centres that may be regarded as $\mathrm{Ni}(2.5)$ centres owing to symmetry. The Cotton ${ }^{495}$ complex $\left[\mathrm{Ni}_{2}(\mathrm{DTolF})_{4}\right]^{+}\left[\mathrm{BF}_{4}\right]^{-}(\mathbf{1 4})($ Figure 15 d$)$ has an $R_{M M}$ value of $2.418 \AA$, which is shorter than in $\left[\mathrm{Ni}_{2}(\mathrm{DTolF})_{4}\right]\left(\mathrm{H}_{2} \mathrm{O}\right)_{2} \mathbf{0 1}$ with an $\mathrm{Ni}_{2}{ }^{+4}$ core, perhaps due to axial ligation in 01. Complex $\mathbf{1 5}$ (Lee et al. ${ }^{504}$ ) is also a tetragonal formamidinate complex with an $R_{M M}$ value of $2.330 \AA$, while the tetragonal guanidinate complex $\mathbf{1 6}$ has an $R_{M M}$ value of $2.370 \AA$. Oxidation of a binuclear bis(triphenylphosphine) nickel complex with a $\left(\mathrm{Ni}_{2}\right)^{4+}$ core $\left(R_{M M}=2.5808(8) \AA\right)$ gives structure $\mathbf{1 7}$ with a $\left(\mathrm{Ni}_{2}\right)^{6+}$ core, in which the long $R_{M M}$ value of $2.603 \AA$ precludes $\mathrm{Ni}-$ Ni bonding (Berry et al. ${ }^{505}$ ).

### 10.5. Computational Studies on Binuclear Nickel Complexes

Dinickelocene, $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Ni}_{2}$, was studied by the B3LYP method ${ }^{506}$ after the first dimetallocene $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{Zn}_{2}$ was discovered. Coaxial $D_{5 h}$ and perpendicular structures were explored, where the latter structure has the $\mathrm{Ni}-\mathrm{Ni}$ axis perpendicular to the axis perpendicular to the $\mathrm{C}_{5} \mathrm{H}_{5}$
rings and running through the midpoint of the $\mathrm{Ni}-\mathrm{Ni}$ bond. The coaxial structure has a $\mathrm{Ni}-\mathrm{Ni}$ bond length of $2.062 \AA$ suggesting a triple bond consistent with the favored $(18,18)$ configuration for each Ni atom. The perpendicular dinickelocene structure has a $\mathrm{Ni}-\mathrm{Ni}$ bond length of $2.226 \AA$ and lies $52 \mathrm{kcal} / \mathrm{mol}$ lower in energy than the coaxial isomer. The perpendicular isomer is suggested to be a synthetically more viable target than the coaxial isomer through decarbonylation of appropriate $\mathrm{Ni}_{2}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}(\mathrm{CO})_{\mathrm{n}}$ precursors or use of bulky substituents to prevent trimerization.

The homoleptic binuclear nickel carbonyl and trifluorophosphine complexes studied by the BP86 method all have the $\mathrm{Ni}(0)$ oxidation state (Table 34). BP86 values of $\mathrm{Ni}-\mathrm{Ni}$ bond lengths for the homoleptic binuclear nickel carbonyls $\mathrm{Ni}_{2}(\mathrm{CO})_{\mathrm{n}}(n=7,6,5)^{507}$ show that decreasing the number of carbonyl groups ( $n$ ) from 7 to 5 increases the number of bridging CO groups from 1 to 3 . All three systems gave singlet global minima with $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ bonds of length 2.521 to $2.672 \AA$ of orders 1, 2, and 3 respectively. BP86 results on the homoleptic binuclear nickel trifluorophosphine series $\mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{\mathrm{n}}(n=6,5,4)^{508}$ gave singlet global minima for the three systems with $n=6,5$ and 4 , each with two bridging $\mathrm{PF}_{3}$ ligands. The singlet structure $\mathrm{S}-1$ for $\mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{6}$ has a $\mathrm{Ni}(0)=\mathrm{Ni}(0)$ double bond of length $2.483 \AA$. The lowest energy $\mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{5}$ structure $\mathrm{S}-1$ exhibits a short $\mathrm{Ni} \equiv \mathrm{Ni}$ triple bond length of $2.238 \AA$, while the lowest energy $\mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{4}$ structure $\mathrm{S}-1$ has a $\mathrm{Ni}=\mathrm{Ni}$ double bond of length $2.338 \AA$.

BP86 results for the binuclear nickel thiocarbonyl carbonyl complexes $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{n}(n=$ $5,4,3,2)^{509}$ are reported in Table 34. The $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{5}$ system 07 has three nearly degenerate singlet minima with $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ single bond lengths in the range $2.62 \pm 0.02 \AA$ which could suggest three different conformational minima. The singly bridged $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{5}$ minima S-4 and S-5 exhibit longer single bond $R_{M M}$ distances of 2.688 and $2.665 \AA$. The $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{4}$ system $\mathbf{0 8}$ has six singlet minima where all but $\mathrm{S}-3$ exhibit $\mathrm{Ni}=\mathrm{Ni}$ double bond lengths from 2.461 to $2.545 \AA$. The $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{4}$ structure $\mathrm{S}-3$ has an
$\mathrm{Ni}-\mathrm{Ni}$ single bond length of $2.546 \AA$. The $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{3}$ system 09 exhibits two singlet minima, each with a $\eta^{2}$-bridging CS ligand and $\mathrm{Ni}=\mathrm{Ni}$ double bond lengths of 2.428 and $2.469 \AA$. The $\mathrm{Ni}_{2}(\mathrm{CS})_{2}(\mathrm{CO})_{2}$ system $\mathbf{1 0}$ has three variously bridged singlet minima with $\mathrm{Ni}=\mathrm{Ni}$ double bonds of lengths 2.384 to $2.422 \AA . \mathrm{Ni}=\mathrm{Ni}$ double bonds are common in this series, where all minima listed are singlets.

Table 34. DFT Ni-Ni Bond Distances in Homoleptic Binuclear Nickel Carbonyl and Trifluorophosphine Complexes and in Binuclear Nickel Thiocarbonyl Carbonyl Complexes

| Label Species | State $R_{M M}(\AA)$ fBO Remarks |
| :---: | :---: |

Homoleptic binuclear nickel carbonyls (BP86; Ref. 507)

| $\mathbf{0 1 ~ N i} i_{2}(\mathrm{CO})_{7} ;(\mathrm{CO})_{3}(\mu-\mathrm{CO}) \mathrm{Ni}_{2}(\mathrm{CO})_{3}$ | S | 2.672 | 1 | $1 \mu-\mathrm{CO}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 2} \mathrm{Ni}_{2}(\mathrm{CO})_{6} ;(\mathrm{CO})_{2}(\mu-\mathrm{CO})_{2} \mathrm{Ni}_{2}(\mathrm{CO})_{2}$ | S | 2.521 | 2 | $2 \mu-\mathrm{CO}$ |
| $\mathbf{0 3 ~} \mathrm{Ni}_{2}(\mathrm{CO})_{5} ;(\mathrm{CO})(\mu-\mathrm{CO})_{3} \mathrm{Ni}_{2}(\mathrm{CO})$ | S | 2.521 | 3 | $3 \mu-\mathrm{CO}$ |

Homoleptic binuclear nickel trifluorophosphine complexes (BP86; Ref. 508)

| $\mathbf{0 4} \mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{6}$ | $\mathrm{~S}-1$ | 2.483 | 2 | $1 \mu$ and $1 \mathrm{~s} \mu \mathrm{PF}_{3}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{0 5} \mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{5}$ | $\mathrm{~S}-1$ | 2.238 | 3 | $2 \mu \mathrm{PF}_{3}$ |
| $\mathbf{0 6} \mathrm{Ni}_{2}\left(\mathrm{PF}_{3}\right)_{4}$ | $\mathrm{~S}-1$ | 2.338 | 2 | $2 \mathrm{~s} \mu \mathrm{PF}_{3} ;(16,16)$ |

Binuclear nickel thiocarbonyl carbonyls (BP86; Ref. 509)

| $\mathbf{0 7}(\mathrm{CO})_{3}(\mu-\mathrm{CS}) \mathrm{Ni}_{2}(\mathrm{CO})_{2}(\mathrm{CS})$ | $\mathrm{S}-1$ to | 2.618 | 1 | Almost degenerate; |
| :---: | :--- | :--- | :--- | :--- |
| $(\mathrm{CS})(\mathrm{CO})_{2}(\mu-\mathrm{CO}) \mathrm{Ni}_{2}(\mathrm{CO})_{2}(\mathrm{CS})$ | $\mathrm{S}-3$ | $\pm 0.017$ |  | $1 \mu-\mathrm{CS}$ |
| $(\mathrm{CO})_{3}(\mu-\mathrm{CS}) \mathrm{Ni}_{2}(\mathrm{CO})_{2}(\mathrm{CS})$ | $\mathrm{S}-4$ | 2.688 | 1 | $\Delta \mathrm{E}=3.5 ; 1 \mu-\mathrm{CO}$ |
| $\mathbf{0 8}(\mathrm{CO})_{2}(\mu-\mathrm{CS})_{2} \mathrm{Ni}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-5$ | 2.665 | 1 | $\Delta \mathrm{E}=3.9 ; 1 \mu-\mathrm{CS}$ |
| $(\mathrm{CO})(\mathrm{CS})(\mu-\mathrm{CS})(\mu-\mathrm{CO}) \mathrm{Ni}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-1$ | 2.461 | 2 | $2 \mu-\mathrm{CS}$ |
| $(\mathrm{CO})(\mathrm{CS})\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CO}) \mathrm{Ni}_{2}(\mathrm{CO})_{2}$ | $\mathrm{~S}-3$ | 2.502 | 2.546 | 1 |
| $(\mathrm{CO})(\mathrm{CS})(\mu-\mathrm{CO})_{2} \mathrm{Ni}_{2}(\mathrm{CO})(\mathrm{CS})$ | $\mathrm{S}-4$ | 2.538 | 2 | $1 \eta^{2}-\mu-\mathrm{CS} ; 1 \mu-\mathrm{CO} ; \Delta \mathrm{E}=4.2$ |
| $(\mathrm{CO})(\mathrm{CS})(\mu-\mathrm{CO})_{2} \mathrm{Ni}_{2}(\mathrm{CO})(\mathrm{CS})$ | $\mathrm{S}-5$ | 2.545 | 2 | $2 \mu-\mathrm{CO} ; \Delta \mathrm{E}=8.1$ |
| $\mathbf{0 9}(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CS}) \mathrm{Ni}_{2}(\mathrm{CO})$ | $\mathrm{S}-1$ | 2.428 | 2 | global min. |
| $(\mathrm{CO})_{2}\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CS}) \mathrm{Ni}_{2}(\mathrm{CO})$ | $\mathrm{S}-2$ | 2.469 | 2 | $1 \eta^{2}-\mu-\mathrm{CS} ; \Delta \mathrm{E}=4.1$ |
| $\mathbf{1 0}(\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CS}) \mathrm{Ni}_{2}(\mathrm{CO})$ | $\mathrm{S}-1$ | 2.384 | 2 | $1 \eta^{2}-\mu-\mathrm{CS} ;(18,16)$ |
| $(\mathrm{CO})\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CO}) \mathrm{Ni}_{2}(\mathrm{CS})$ | $\mathrm{S}-2$ | 2.422 | 2 | $(18,16) ; \Delta \mathrm{E}=5.2$ |
| $(\mathrm{CS})\left(\eta^{2}-\mu-\mathrm{CS}\right)(\mu-\mathrm{CO}) \mathrm{Ni}_{2}(\mathrm{CO})$ | $\mathrm{S}-3$ | 2.422 | 2 | $(18,16) ; \Delta \mathrm{E}=6.1$ |

### 10.6. Ni-Ni Bond Length Ranges

The experimental Ni-Ni bond lengths in Tables 31, 32 and 33 are described in the context of the formal oxidation states of the metal centres without assigning fBO values in most cases. In Table 31, the $\mathrm{Ni}(0)-\mathrm{Ni}(0)$ bonds in complexes $\mathbf{0 2}$ to $\mathbf{0 7}$ are all supported by bridging ligands, and the role of the $3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$ configuration of each $\mathrm{Ni}(0)$ centre for $\mathrm{Ni}-\mathrm{Ni}$ bonding is not clear. The prospect of three-centre two-electron bonding through bridging ligands cannot be excluded. Nevertheless, the range of $R_{M M}$ values for these systems of 2.437 to $2.572 \AA$ is not far from the estimate of $2.48 \AA$ for a Ni-Ni covalent bond based on the $\mathrm{R}_{\text {cov }}$ value (Table 1 ). Complexes 08 to 12, regarded as combining $\mathrm{Ni}(\mathrm{I})$ and $\mathrm{Ni}(\mathrm{II})$ centres with an $\mathrm{Ni}(0)$ centre, may contain Ni-Ni covalent bonds, since the $R_{M M}$ values range from 2.393 to $2.481 \AA$. The longer MM bond in $13(2.588 \AA)$ is interpreted as an $\mathrm{Ni}(0.5)-\mathrm{Ni}(0.5)$ interaction.

The $\mathrm{Ni}(\mathrm{I})$ oxidation state with its $3 \mathrm{~d}^{9}$ configuration provides more facile opportunities for $\mathrm{Ni}-\mathrm{Ni}$ covalent bonding. The series of $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ bonded complexes of Table 32 exhibit a wide range of $R_{M M}$ values, from 2.291 to $2.605 \AA$. A range of shorter Ni-Ni bonds from 2.291 to $2.326 \AA$ (or $2.31 \pm 0.02 \AA$ ) is seen in complexes $\mathbf{0 1}, \mathbf{0 2}, \mathbf{0 5}, \mathbf{1 6}, \mathbf{1 8}, \mathbf{2 3}$, and $\mathbf{2 5}$. Complex $\mathbf{0 2}$ is paramagnetic with a triplet ground state, in which electron counting can give a $\mathrm{Ni}(\mathrm{I})=\mathrm{Ni}(\mathrm{I})$ double bond with a $(17,17)$ core configuration. Conversely, the $\mathrm{Ni}-\mathrm{Ni}$ interaction could be antiferromagnetic as indicated by magnetic studies. If such a description is extended to the above seven complexes by analogy, they may be assigned fBO values of 2 consistent with a triplet state, or else described in terms of $\mathrm{Ni}-\mathrm{Ni}$ antiferromagnetic coupling. Note the $\mathrm{Ni}(\mathrm{II})=\mathrm{Ni}(\mathrm{II})$ double bond length of $2.316 \AA$ for complex $\mathbf{1 2}$ of Table 33 also falls within this range ( 2.29 to $2.33 \AA$ ), which may be taken as being consistent with $\mathrm{Ni}=\mathrm{Ni}$ double bonds.

The $3 \mathrm{~d}^{9} \mathrm{Ni}(\mathrm{I})$ oxidation state in the other complexes of Table 32 can lead to to longer $R_{M M}$ distances. Complexes with $\mathrm{Ni}-\mathrm{Ni}$ distances within the range 2.400 to $2.525 \AA(2.46 \pm 0.06 \AA)$ may contain $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ covalent single bonds if the given complex is diamagnetic, since this
range is not far from the $\mathrm{Ni}-\mathrm{Ni}$ covalent single bond estimate of $2.48 \AA$. The $\mathrm{Ni}(\mathrm{I})$ configuration here could also provide possibilities for $\mathrm{Ni}-\mathrm{Ni}$ antiferromagnetic coupling.

The $\mathrm{Ni}(\mathrm{II})$ oxidation state ( $3 \mathrm{~d}^{8}$ configuration) presents problems since a first approach to the $\mathrm{Ni}-\mathrm{Ni}$ bonding situation in the $\left(\mathrm{Ni}_{2}\right)^{4+}$ core leads to no $\mathrm{Ni}-\mathrm{Ni}$ bond at all. Although the very short $\mathrm{Ni}(\mathrm{II})-\mathrm{Ni}(\mathrm{II})$ bonds found in complexes $\mathbf{0 8}, \mathbf{0 9}$ and $\mathbf{1 2}$ of Table 33 ( $R_{M M}$ from 2.291 to $2.328 \AA$ ) by reason of length may be consistent with $\mathrm{Ni}=\mathrm{Ni}$ double bonds, this is not evident in the MO analysis of the model $\mathrm{Ni}_{2}(\mathrm{HNCHNH})_{4}$ which showed no appreciable 3d covalent interactions. ${ }^{494}$ Stereoelectronic effects from the ligands or the domination of $4 s$ and $4 p$ antibonding interactions by bonding ones may serve to bring the $\mathrm{Ni}(\mathrm{II})$ centres together. The paramagnetic system 05 (and, by analogy, 06) with longer $R_{M M}$ distances of 2.506 and $2.487 \AA$ may exhibit Ni-Ni antiferromagnetic coupling.

With the diversity present in the experimentally known binuclear nickel complexes covered in this Section, it is clear that the Ni-Ni interactions are of many kinds, including antiferromagnetic coupling, covalent bonding, and possibly three-centre two-electron bonding. Different examples need to be treated theoretically in an appropriate manner to discern the bonding situation on an individual basis. Given this lack of a uniform MM bonding picture, and the inapplicability of the very concept of a formal covalent bond order in many cases, the search for relationships between MM bond distances and MM bond orders appears to be very difficult for the binuclear nickel complexes for which the experimental MM bond lengths are compiled in this Section.

The DFT bond length data of Table 34 cover two series of binuclear nickel carbonyl complexes and one series of binuclear nickel trifluorophosphine complexes. Experimentally characterized binuclear nickel carbonyl complexes include structures 03, 27 and $\mathbf{2 8}$ of Table 32, all with $\mathrm{Ni}(\mathrm{I})-\mathrm{Ni}(\mathrm{I})$ bonds. The presence of two bridging carbonyl ligands in $\mathbf{0 3}$ increases the $R_{M M}$ value relative to the similar complex $\mathbf{0 2}$. The CO and $\mathrm{PF}_{3}$ ligands can be electron
acceptors with scope for metal $\rightarrow$ ligand back-bonding which may lengthen MM bond distances. This effect is more pronounced for the CO ligand than for the $\mathrm{PF}_{3}$ ligand. BP86 results on homoleptic binuclear nickel carbonyls and on homoleptic binuclear nickel trifluorophosphine complexes suggest the range 2.546 to $2.688 \AA(2.62 \pm 0.07 \AA)$ for $\mathrm{Ni}-\mathrm{Ni}$ single bonds and 2.384 to $2.502 \AA(2.44 \pm 0.06 \AA)$ for $\mathrm{Ni}=\mathrm{Ni}$ double bonds. These ranges appear to be on the higher side compared to experimental distances available here on $\mathrm{Ni}-\mathrm{Ni}$ interactions classifiable as single and double bonds (itself much subject of discussion as to the nature of bonding present). The experimentally derived MM single bond range of $2.46 \pm 0.06 \AA$ arrived at above, and the double bond range of $2.31 \pm 0.02 \AA$ suggested above may be presented for comparison, both being on the lower side. These differences may be linked to the MM bond lengthening effects of the CO and $\mathrm{PF}_{3}$ ligands, for which further theoretical studies would be in order.

## 11. COPPER-COPPER BONDS

Copper along with silver and gold has the $\mathrm{d}^{10} \mathrm{~s}^{1}$ electronic configuration. Binuclear complexes of the Group 11 metals were reviewed by Gray and Sadighi. ${ }^{510}$ Binuclear copper complexes are mostly known with the copper centers in the $\mathrm{Cu}(\mathrm{I})$ oxidation state, along with some multinuclear systems as well. There is also some evidence for the existence of the saturated dicopper carbonyl $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$ with Cu in the zero oxidation state. $\mathrm{The} \mathrm{Cu}(\mathrm{II})$ oxidation state is present in the cupric acetate dimer. Some species with mixed valent copper centres involving $\mathrm{Cu}-\mathrm{Cu}$ covalent bonds are also known (e.g., in some metalloproteins). The covalent radius of $1.32 \AA$ for copper ${ }^{41}$ suggests a value around $2.64 \AA$ for a $\mathrm{Cu}-\mathrm{Cu}$ covalent bond length, while the $\mathrm{Cu}-\mathrm{Cu}$ distance in metallic copper is $2.56 \AA . \mathrm{Cu}-\mathrm{Cu}$ separations with values quite shorter than these are encountered in many dicopper complexes. This Section deals with copper dimer $\mathrm{Cu}_{2}$, numerous $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ complexes, cupric acetate dimer, some mixed valent cases, and a series of homoleptic dicopper carbonyl complexes.

### 11.1. Copper Dimer

Table 35 provides some estimates for the MM bond length in $\mathrm{Cu}_{2}$. The ${ }^{1} \Sigma^{+}{ }_{\mathrm{g}}$ ground state for the copper dimer $\mathrm{Cu}_{2}$ is well-established, ${ }^{33}$ where the $\mathrm{Cu}-\mathrm{Cu}$ single bond essentially involves only the single $4 s$ electrons of each Cu atom, leading to a $4 s \sigma_{\mathrm{g}}$ configuration and a $\mathrm{Cu}-\mathrm{Cu}$ bond order of one. Fourier-transform emission spectroscopy (Bernath ${ }^{511}$ ) determined the $\mathrm{Cu}-$ Cu distance as $2.219 \pm 0.001 \AA$ and the dissociation energy was reported by Rohlfing and Valentini ${ }^{512}$ as $2.08 \pm 0.02 \mathrm{eV}$. This is quite a short length for a first row MM single bond. A $\mathrm{Cu}-\mathrm{Cu}$ bond length of $2.267 \AA$ with a dissociation energy of 1.74 eV was predicted by the modified coupled-pair functional method. ${ }^{513}$ Unrestricted Møller-Plesset theory with infinite extrapolation predicted a bond length of $2.274 \AA .{ }^{514}$ A CASPT2/ANO study yielded a bond length of $2.215 \AA$ and a dissociation energy of $1.97 \mathrm{eV},{ }^{465}$ the best theoretical estimate so far.

A DFT study with six functionals predicted bond length values of 2.179 to $2.306 \AA$, of which the B3P86 value of $2.248 \AA$ was the best. ${ }^{33}$ Four DFT methods in another study ${ }^{34}$ predicted bond lengths from 2.233 to $2.267 \AA$ of which the PW91 value was the closest to experiment. Empirical estimates range from 2.08 to $2.17 \AA$ of which the Pauling value of $2.17 \AA$ seems the best. ${ }^{28}$ The electronically less complex nature of the MM bonding in $\mathrm{Cu}_{2}$ allows for computational estimates of the MM bond length to be quite accurate.

### 11.2. Some $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ Complexes

The $\mathrm{Cu}(\mathrm{I})$ oxidation state is the oxidation state most commonly found in experimentally known binuclear copper complexes. With its $\mathrm{d}^{10}$ configuration, the possibility of covalent MM bonding would seem diminished. Dispersive and sometimes electrostatic interactions are believed to play a role here in some cases. With bridging ligands, three-center two-electron bonding through the bridging center may obviate the need for direct $\mathrm{Cu}-\mathrm{Cu}$ covalent interactions. Table 35 lists $\mathrm{Cu}-\mathrm{Cu}$ bond lengths for numerous experimentally characterized binuclear copper complexes, mostly with the metal centers in the $\mathrm{Cu}(\mathrm{I})$ oxidation state.

The early Brown and Dunitz ${ }^{515}$ example of bis(1,3-diphenyltriazenido) dicopper 02 gave an $R_{M M}$ value of $2.45 \AA$, which is close to the Lappert ${ }^{516}$ value of $2.42 \AA$ in tetrakis(trimethylsilylmethylcopper) $\mathbf{0 3}$ in which the interactions were described as being of the three-center two-electron type. The tris(1,5-di-p-tolyl-pentazenido) tricopper complex 04 gave two different $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ distances (Becke and Strahle ${ }^{517}$ ) of 2.348 and $2.358 \AA$. These short distances were ascribed to dispersive interactions between the $\mathrm{d}^{10}$ centers by ab initio studies. ${ }^{518}$

Complexes $\mathbf{0 5}$ to $\mathbf{1 0}$ have bridging ligands through which three-centre two-electron bonds can form without direct $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ interactions. $\mathrm{The} \mathrm{Cu}_{2}(\mu-\mathrm{H})_{2}$ structure 05 with two bridging hydrides was studied computationally by the MP2 method, ${ }^{519}$ by which the very
short $R_{M M}$ value of $2.155 \AA$ was found to arise from strong three-center two-electron interactions. ${ }^{520,521}$ The hydride-bridged $\mathrm{Cu}_{2}\left\{\mathrm{MeC}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{3}\right\}_{2}(\mu-\mathrm{H})_{2} \mathbf{0 6}$ exhibits a $\mathrm{Cu}-\mathrm{Cu}$ distance (Mankad and coworkers ${ }^{522}$ ) of $2.371 \AA$. For $\mathrm{Cu}_{2}(\mu-\mathrm{I})_{2}\{\mathrm{ICHC}(\mathrm{Me}) \mathrm{Frcp}\} \mathbf{0 7}$ with an N -heterocyclic carbene ligand $\left[\mathrm{Frcp}=\left\{2-\left(\mathrm{PPh}_{2}\right) \mathrm{C}_{5} \mathrm{H}_{3}\right\}-\mathrm{Fe}-\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)\right]$ the $R_{M M}$ value is $2.356 \AA$ (Gischig and Togni ${ }^{523}$ ), where three-centre two-electron interactions can occur through the carbene centre and the two bridging iodide groups. Complexes $\mathbf{0 8}$ (Figure 16a) to $\mathbf{1 0}$ (Figure 16b) have longer $\mathrm{Cu}-\mathrm{Cu}$ distances (Warren ${ }^{524,525}$, Tilley ${ }^{526}$, Wyss ${ }^{527}$ ), in which the threecentre two-electron interactions occur through one bridging atom in each case (carbene, nitrogen and hydride). The presence of more than one bridging ligand in complexes $\mathbf{0 5}$ to 07 is seen to shorten the $\mathrm{Cu}-\mathrm{Cu}$ distance.



c (11)

d (13)

Figure 16. Some binuclear copper complexes (labels in brackets refer to Table 35)

Table 35. Experimental and Computational $\mathbf{C u}-\mathrm{Cu}$ Bond Lengths in Copper Dimer $\mathrm{Cu}_{2}$ and Some Binuclear Copper Complexes

| Label Species | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| 01 Copper dimer $\mathrm{Cu}_{2}$ |  |  |  |
| Fourier-transform emission | $2.219 \pm 0.001$ | 511 | experimental |
| Couple-paired functional | 2.267 | 513 | high level ab initio |
| UMP2 infinite extrapolation | 2.274 | 513 | high level ab initio |
| Various DFT methods | 2.179-2.306 | 33 | B3P86 value best |
| Various DFT methods | 2.233-2.267 | 34 | PW91 value best |
| CAST2/ANO method | 2.215 | 465 | best theoretical value |
| Empirical methods | 2.08-2.17 | 28 | Pauling value 2.17 |
| $02 \mathrm{Cu}_{2}(\mathrm{PhNNNPh})_{2}$ | 2.45 | 514 | $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ bond |
| $03\left[\left(\mathrm{Me}_{3} \mathrm{Si}\right)(\mathrm{Me}) \mathrm{Cu}\right]_{4}$ | 2.42 | 516 | $\mathrm{Cu}(\mathrm{I})$ tetramer |
| $04 \mathrm{Cu}_{3}\left(p-\mathrm{MeC}_{6} \mathrm{H}_{5}-\mathrm{N}_{5}-p-\mathrm{MeC}_{6} \mathrm{H}_{5}\right)_{3}$ | $\begin{aligned} & 2.348(2) \\ & \text { and } 2.358(2) \end{aligned}$ | 517 | pentazenido ligands |
| $05 \mathrm{Cu}_{2}(\mu-\mathrm{H})_{2}$ | 2.155 | 518 | MP2 results |
| $06 \mathrm{Cu}_{2}\left\{\mathrm{MeC}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{3}\right\}_{2}(\mu-\mathrm{H})_{2}$ | 2.371(2) | 522 | bridging hydride |
| $07 \mathrm{Cu}_{2}(\mu-\mathrm{I})\{\mathrm{ICHC}(\mathrm{Me}) \mathrm{Frcp}\}$ | 2.3561(13) | 523 | NHC ligand |
| $\left.\mathbf{0 8}\left\{\mathrm{Ar}^{\prime} \mathrm{NCMe}\right)_{2} \mathrm{CH}\right\}_{2} \mathrm{Cu}_{2}\left(\mu-\mathrm{CPh}_{2}\right)$ | 2.4635(7) | 524 | Ar' $=2,4,6-\mathrm{Cl}_{3}-\mathrm{C}_{6} \mathrm{H}_{2}$ |
| 09 \{2,7-(py $\left.\left.\mathrm{y}_{2} \mathrm{CMe}\right)_{2}-\mathrm{NPTh}\right\} \mathrm{Cu}(\mathrm{MeCN})$ | 2.4457(4) | 525 | bridging N -atom |
| $10\left\{(\mathrm{IDipp})_{2} \mathrm{Cu}_{2}(\mu-\mathrm{H})\right\}^{+}\left(\mathrm{BF}_{4}\right)^{-}$ | $\begin{aligned} & 2.5331(15) ; \\ & 2.5354(15 \end{aligned}$ | 526 | 2 molecules; NHC ligand |
| $11\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Cu}_{2}-$ coaxial | 2.216 | 506 | BP86 DFT; triplet |
| $12\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Cu}_{2}$ - perpendicular | 2.467 | 506 | BP86; more stable |
| $13 \mathrm{Cu}(\mathrm{II})$ acetate dimer | 2.64 | 528 | Experimental; XRD |
|  | 2.619 | 529 | More recent XRD |
|  | 2.617 | 537 | DFT broken symmetry |

The discovery of a zinc-zinc bond in the dizincocene $\left(\eta^{5}-\mathrm{Me}_{5} \mathrm{C}_{5}\right)_{2} \mathrm{Zn}_{2}$ (see Section 12) prompted a DFT study on dicuprocene $\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Cu}_{2} .{ }^{506}$ The triplet coaxial structure (Figure 16c) has a $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ distance of $2.216 \AA(\mathrm{BP} 86)$ suggesting a $\mathrm{Cu}=\mathrm{Cu}$ double bond of the $\sigma+^{2} / 2 \pi$ type, close to the $\mathrm{Cu}-\mathrm{Cu}$ single bond length in the dimer $\mathrm{Cu}_{2}$. The singlet perpendicular structure, described as $\mathrm{Cu}_{2}\left(\eta^{2}-\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\eta^{3}-\mathrm{C}_{5} \mathrm{H}_{5}\right)$, was predicted to be $75 \mathrm{kcal} / \mathrm{mol}$ lower in energy than the co-axial structure and found to have a $\mathrm{Cu}-\mathrm{Cu}$ single bond length of 2.467 Á.

### 11.3. Cupric Acetate Dimer and Mixed Valent Dicopper Complexes

Attention was drawn early to the possibility of a $\mathrm{Cu}-\mathrm{Cu}$ bond in the dimer of cupric acetate hydrate $\left[\mathrm{Cu}(\mathrm{II})\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}\right]_{2} \mathbf{1 3}$ (Figure 16 d ), a paddlewheel complex characterized by XRD as having a $\mathrm{Cu}-\mathrm{Cu}$ distance of $2.64 \AA \AA,{ }^{528}$ and more recently as $2.619 \AA \AA^{529}$ In 1956, Figgis and Martin ${ }^{530}$ deduced that the antiferromagnetism of this dimer arises from metalmetal bonding, while Bleaney and Bowers ${ }^{531}$ as early as 1952 explained the ESR spectrum on the basis of spin coupling in a pair of $\mathrm{Cu}(\mathrm{II})$ ions. In 1965 , Royer ${ }^{532}$ used the values of the nuclear quadrupole splitting of ${ }^{63} \mathrm{Cu}$ in the single crystal dimer between $77-156 \mathrm{~K}$ to establish a $\delta \mathrm{Cu}-\mathrm{Cu}$ single bond as proposed by Ross (1959) ${ }^{533}$ rather than a $\sigma$ bond as proposed earlier. The 1969 theoretical treatment of Jotham and Kettle ${ }^{534}$ incorporated spin-exchange functions to predict ferromagnetic contributions although the overall energy patterns suggest antiferromagnetism. Cannon (1981) ${ }^{535}$ estimated the aqueous phase metal-metal bond energy in chromium(II) acetate dimer as higher by about $45 \mathrm{~kJ} \mathrm{~mol}^{-1}$ than in copper(II) acetate dimer. This rather weak $\mathrm{Cu}-\mathrm{Cu}$ interaction may be described as a $\delta$ bond arising from overlap between the two copper $d_{\mathrm{x} 2-\mathrm{y} 2}$ orbitals (a Cu (II)- Cu (II) single bond). A DFT study on Cu (II)$\mathrm{Cu}(\mathrm{II})$ bonding in the model paddlewheel dicopper complex $\mathrm{Cu}_{2}(\mathrm{HNNNH}) 4^{536}$ gave a structure similar to $\mathrm{Cr}_{2}\left(\mathrm{OCOCH}_{3}\right)_{4}$, where strong antiferromagnetic $\mathrm{Cu}-\mathrm{Cu}$ coupling was
invoked. A recent (2015) broken symmetry study ${ }^{537}$ on $\mathrm{Cu}_{2}(\mathrm{OAc})_{4}$ gave an $R_{M M}$ value of 2.617 Á, fortuitously close to the XRD value of 2.619 Á.

Mixed valent $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{II})$ cores have been found in metalloproteins such as cytochrome c oxidase, nitrous oxide reductase, and methane monooxygenase. These enzyme centres have also been modelled by synthetic and theoretical studies. $\mathrm{A} \mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{II})$ core with bridging cysteine thiolate ligands is present in cytochrome c oxidase and nitrous oxide reductase with a $\mathrm{Cu}-\mathrm{Cu}$ separation of about $2.5 \AA .{ }^{538}$ EPR and other spectroscopic studies (Solomon ${ }^{539}$ ) indicated a fully delocalized $\mathrm{Cu}(1.5)-\mathrm{Cu}(1.5)$ core. A thiolate-bridged dicopper model system for these metalloprotein centres was synthesized $\left(\operatorname{Tolman}^{540}\right)$ with a long $R_{M M}$ value of 2.931 $\AA$, which is much longer than in the metalloprotein itself.
$\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{II})$ octaazacryptate complexes were also synthesized (Barr et al. ${ }^{541}$ ) to help understand structure and bonding in metalloproteins, where a short $\mathrm{Cu}-\mathrm{Cu}$ bond of length $2.364 \AA$ was reported. Half-paddlewheel $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{II})$ complexes with sterically bulky carboxylate ligands and axial THF ligands showed an $R_{M M}$ value (Tolman ${ }^{542}$ ) of $2.395 \AA$. In all of these mixed valent systems the $\mathrm{Cu}-\mathrm{Cu}$ interaction is described as a half bond $(\mathrm{fBO}=$ 0.5 ) between a $\mathrm{d}^{10}$ centre and a $\mathrm{d}^{9}$ centre. Since the $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{II})$ core is delocalized, these systems are best described as $\mathrm{Cu}(1.5)-\mathrm{Cu}(1.5)$ systems. Such mixed valent complexes arise from one-electron oxidation of $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ precursors.

### 11.4. Homoleptic Binuclear Copper Carbonyls

Systematic theoretical studies on a series of homoleptic dicopper carbonyls $\mathrm{Cu}_{2}(\mathrm{CO})_{n}(n=6$, $5,4,3,2,1)^{543}$ used four functionals. The BP86 predictions are presented in Table 36. Experimental evidence for $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$ was found $\left(\mathrm{Ozin}^{544}\right.$ ) by condensation of Cu atoms with CO using matrix isolation IR and UV-visible methods, and confirmed by low temperature studies (Kasai and Jones ${ }^{545}$ ) and spectroscopic studies (Mile and Howard ${ }^{546,547}$ ) in inert
matrices at 77 K . By the 18 -electron rule, $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$ should have a $\mathrm{Cu}-\mathrm{Cu}$ single bond. The above noted BP86 study ${ }^{543}$ did not propose an MM fBO for any of the species studied in the series, and avoided precise descriptions of MM multiple bonds for all of the unsaturated cases. The filled $\mathrm{d}^{10}$ shell of a $\mathrm{Cu}(0)$ atom could lead to difficulties in the formation of $\mathrm{Cu}-\mathrm{Cu}$ multiple bonds. All minima were treated as ground state singlets. All species shown here are unbridged, since bridged structures were found to be of high energy ( $\Delta \mathrm{E}>10 \mathrm{kcal} / \mathrm{mol}$ ).

## Table 36. Cu-Cu Bond Lengths in Homoleptic Binuclear Copper Carbonyls ${ }^{543}$



The canonical saturated dicopper hexacarbonyl, $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$, has an ethane-like structure. The staggered conformer lies lower in energy than the eclipsed structure, these having $R_{M M}$ values of 2.602 and $2.636 \AA$, respectively. Dicopper pentacarbonyl, $\mathrm{Cu}_{2}(\mathrm{CO})_{5}$, is like the ethyl radical with a $\mathrm{Cu}-\mathrm{Cu}$ bond length of $2.499 \AA$. Dicopper tetracarbonyl, $\mathrm{Cu}_{2}(\mathrm{CO})_{4}$, has a methylcarbene-like global minimum $\left(R_{M M}=2.382 \AA\right)$ and two higher energy ethylene-like minima ( $R_{M M}=2.408$ and $2.636 \AA$ ). Dicopper tricarbonyl, $\mathrm{Cu}_{2}(\mathrm{CO})_{3}$ has a methylcarbyne-
like global minimum $\left(R_{M M}=2.360 \AA\right.$ ) and a higher energy structure analogous to the vinyl radical $\left(R_{M M}=2.365 \AA\right)$. Dicopper dicarbonyl, $\mathrm{Cu}_{2}(\mathrm{CO})_{2}$, has bent acetylene-like minima ( $R_{M M}=2.324$ and $2.327 \AA$ ) and a higher energy vinylidene-like structure $\left(R_{M M}=2.331 \AA\right)$. Dicopper monocarbonyl, $\mathrm{Cu}_{2}(\mathrm{CO})$ has a linear triatomic structure $\left(R_{M M}=2.257 \AA\right)$.

### 11.5. Cu-Cu Bond Length Ranges

The experimental $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ distances described in Table 35 range from 2.348 to $2.535 \AA$ and are regarded as not being due to covalent bonding through $\mathrm{Cu}-\mathrm{Cu}$ orbital overlap. Some cases are ascribed to the dispersion interaction between the two $\mathrm{d}^{10}$ centres, while systems with bridging ligands are attributed to three-centre two-electron bonding without direct Cu Cu bonding. The $\mathrm{Cu}(\mathrm{II})-\mathrm{Cu}(\mathrm{II})$ interaction in the cupric acetate dimer is longer at $2.64 \AA$ and involves some degree of $3 d$ orbital overlap, leading to a formal MM single bond. The single bond in copper dimer arises from strong $4 s$ orbital overlap and is much shorter. No definitive relationship can be established between formal bond order and $\mathrm{Cu}-\mathrm{Cu}$ bond length in these cases.
$\mathrm{Cu}-\mathrm{Cu}$ bond lengths in the homoleptic dicopper carbonyl series range from $2.257 \AA$ for $\mathrm{Cu}_{2}(\mathrm{CO})$ to $2.636 \AA$ for $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$, where only the latter is assigned a formal bond order. The trend for global minima in the six $\mathrm{Cu}_{2}(\mathrm{CO})_{n}$ systems $(n=6,5,4,3,2,1)$ is towards a steady decrease of the $R_{M M}$ value as $n$ decreases. The 18 -electron rule, if straightforwardly applied, would also predict a steady increase in formal bond order for these unbridged minima.

## 12. ZINC-ZINC BONDS

Zinc along with cadmium and mercury has the $\mathrm{d}^{10} \mathrm{~s}^{2}$ configuration, and is not a transition metal proper. Group 12 metal-metal bonds have been reviewed by Wu and Harder. ${ }^{548}$ Zinc is known to form $\mathrm{Zn}-\mathrm{Zn}$ covalently bonded molecules, mostly in its $\mathrm{Zn}^{+}$oxidation state, while the $\mathrm{Zn}(0)$ oxidation state is present in the $\mathrm{Zn}_{2}$ dimer. A rough idea of the possible length for a $\mathrm{Zn}-\mathrm{Zn}$ single bond may be obtained from twice the covalent radius of $1.22 \AA$ assigned to zinc, ${ }^{41}$ i.e., a value of about $2.44 \AA$. This Section reviews $\mathrm{Zn}-\mathrm{Zn}$ bond lengths found in zinc dimer, in a series of inorganic $\mathrm{Zn}_{2} \mathrm{X}_{2}$ molecules, and in some dizinc complexes with larger ligands (organometallic and N -ligands).

### 12.1. Zinc Dimer and $\mathrm{Zn}_{2} \mathrm{X}_{2}$ Molecules

Table 37 summarizes mostly theoretical results on $\mathrm{Zn}-\mathrm{Zn}$ bond lengths, $\mathrm{Zn}-\mathrm{Zn}$ bond dissociation energies (BDE), and the metal-ligand bond lengths $R_{M X}$ for a series of inorganic dizinc compounds. The zinc dimer $\mathrm{Zn}_{2}$ is known ${ }^{549}$ as a van der Waals dimer like $\mathrm{Mn}_{2}, \mathrm{Cd}_{2}$ and $\mathrm{Hg}_{2}$, with a $\mathrm{Zn} \cdots \mathrm{Zn}$ separation of $4.19 \AA$ and a binding energy of only $0.80 \mathrm{kcal} / \mathrm{mol}$ (Table 37). A series of DFT methods used to study this dimer along with other dizinc species and rare gas dimers led to an M05-2X value of $3.85 \AA$ for the $\mathrm{Zn} \cdots \mathrm{Zn}$ distance and a binding energy of $0.77 \mathrm{kcal} / \mathrm{mol}$ (the best DFT estimate). ${ }^{550}$ Empirical formulas yield values from 4.20 to $4.40 \AA$ for the $\mathrm{Zn} \cdots \mathrm{Zn}$ distance, ${ }^{28}$ among which the Pauling formula gives the result most concordant with experiment.

Simple dizinc molecules studied computationally include $\mathrm{Zn}_{2} \mathrm{H}, \mathrm{Zn}_{2} \mathrm{H}^{+}, \mathrm{Zn}_{2} \mathrm{H}_{2}$ and the dizinc dihalides ${ }^{551,552,553}$ (Table 37). The ab initio methods used were MP2 and PP-MP2, along with LDF (local density functional with relativistic effects). Upon combining the results of these approaches to cover all systems, the $R_{M M}$ values in the $\mathrm{Zn}_{2} \mathrm{X}_{2}$ series $(\mathrm{X}=\mathrm{H}, \mathrm{F}$, $\mathrm{Cl}, \mathrm{Br}, \mathrm{I}$ ) are found to range from 2.293 to $2.375 \AA$. These give the sequence $\mathrm{F}<\mathrm{Cl}<\mathrm{Br}<\mathrm{I}$
$<\mathrm{H}$ with respect to X , and the reverse sequence for the magnitude of the dissociation energy, where the electronegativity of X is a deciding factor. In a similar manner, the order $\mathrm{F}<\mathrm{Cl}<$ H is seen for $\mathrm{Zn}-\mathrm{Zn}$ bond lengths in $\mathrm{Zn}_{2} \mathrm{X}_{2}(\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{H})$ and the reverse order for the bond dissociation energies, as studied by the MP2 method. ${ }^{553}$ The trends are as expected, and predict $\mathrm{Zn}-\mathrm{Zn}$ single bond lengths that are well within the estimate of around $2.44 \AA$ for a $\mathrm{Zn}-\mathrm{Zn}$ covalent bond length.

Table 37. Zn-Zn Distances and Other Data in Inorganic Zinc-Zinc-Bonded Molecules


[^21]
### 12.2. Binuclear Zinc Complexes with Organometallic and Nitrogen Ligands

Table 38 gives $\mathrm{Zn}-\mathrm{Zn}$ bond lengths for dizinc complexes with organometallic and nitrogen ligands. The first dimetallocene discovered (Carmona and coworkers ${ }^{554}$ ) was dizincocene $\left(\eta^{5}-\mathrm{Me}_{5} \mathrm{C}_{5}\right)_{2} \mathrm{Zn}_{2}(\mathbf{0 1})$ (Figure 17a) obtained by allowing $\left(\eta^{5}-\mathrm{Me}_{5} \mathrm{C}_{5}\right)_{2} \mathrm{Zn}$ to react with $\mathrm{Et}_{2} \mathrm{Zn}$. Shortly thereafter a related dizincocene $\left(\eta^{5}-\mathrm{Me}_{4} \mathrm{C}_{5} \mathrm{Et}_{2}\right)_{2} \mathrm{Zn}_{2}$ was synthesized, also by Carmona. ${ }^{555}$ The $\mathrm{Zn}-\mathrm{Zn}$ axis in $\mathbf{0 1}$ is collinear with the centroids of the two ligand rings and the $\mathrm{Zn}-\mathrm{Zn}$ bond length is 2.305(3) $\AA$. DFT results gave a $\mathrm{Zn}-\mathrm{Zn}$ bond dissociation energy of $67.7 \mathrm{kcal} / \mathrm{mol} .{ }^{556} \mathrm{~B} 3 \mathrm{LYP}$ studies on $\left(\eta^{5}-\mathrm{Me}_{5} \mathrm{C}_{5}\right)_{2} \mathrm{Zn}_{2}$ did not predict a true minimum with the $\eta^{5}$-coordination mode, but gave an $\eta^{3}$-coordinated structure $\mathbf{0 2}$ as a minimum on a flat surface with a $\mathrm{Zn}-\mathrm{Zn}$ distance of $2.331 \AA .{ }^{557}$ The related doubly hydride-bridged complex $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{Zn}(\mu-\mathrm{H})_{2} \mathrm{Zn}^{2}\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$ was not found to be a minimum, instead optimizing freely to a non-covalently bonded dimer of $\mathrm{Zn}\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right) \mathrm{H}$. Analysis of the $\mathrm{Zn}-\mathrm{Zn}$ bond in $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{Zn}_{2}$ predicted an almost pure 4 s character, while the Zn 4 p orbitals interact with the cyclopentadienyl ring. The $\mathrm{Zn}-\mathrm{Zn}$ bond dissociation energy was estimated at $62.1 \mathrm{kcal} / \mathrm{mol}$ ( $62.5 \mathrm{kcal} / \mathrm{mol}$ for $\mathrm{Cp}_{2} \mathrm{Zn}_{2}$ ). BP86 results on the unsubstituted $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Zn}_{2}$ structure $\mathbf{0 3}$ gave a $\mathrm{Zn}-\mathrm{Zn}$ single bond of almost pure 4 s character, ${ }^{506}$ with a $\mathrm{Zn}-\mathrm{Zn}$ bond length of 2.315 $\AA ́$ close to the experimental value for the permethylated complex. The doubly bridged hydride $\mathrm{CpZn}(\mu-\mathrm{H})_{2} \mathrm{ZnCp}$ was predicted as fleeting, dissociating to monomeric CpZnH fragments.

Another type of complex with a $\mathrm{Zn}-\mathrm{Zn}$ bond $\mathrm{RZn}-\mathrm{ZnR} 04$ was characterized by Robinson and coworkers, ${ }^{558}$ where R is a $\beta$-diketiminate ligand $\left[\left\{\left(2.6-\mathrm{Pr}^{i}{ }_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}(\mathrm{Me}) \mathrm{C}\right\}_{2} \mathrm{CH}\right]^{-}$(Figure 17b). Steric effects of the isopropyl groups help protect the $\mathrm{Zn}-\mathrm{Zn}$ bond with the two ligands almost perpendicular to each other. The $\mathrm{Zn}-\mathrm{Zn}$ bond length of $2.359 \AA$ in this complex contrasts with the longer $R_{M M}$ value of $2.451 \AA$ in the doubly hydride-bridged $\mathrm{RZn}(\mu-\mathrm{H})_{2} \mathrm{ZnR}$
structure 06 (Roesky, Schmidt and coworkers ${ }^{559}$ ). The metal-ligand $\mathrm{Zn}-\mathrm{N}$ bonds are among the longest such known. B3LYP and BP86 studies on the $D_{2 d}$ model species R'Zn-ZnR' $[\mathrm{R}$ ' $\left.=(\mathrm{HNCH})_{2} \mathrm{CH}\right]$ gave a non-planar structure with an $R_{M M}$ value of $2.366 \AA(\mathrm{BP} 86$ value $)$, close to the experimental value for the original complex $\mathrm{RZn}-\mathrm{ZnR}$. The doubly hydridebridged model complex $\mathrm{R}^{\prime} \mathrm{Zn}(\mu-\mathrm{H})_{2} \mathrm{ZnR}$ ' has a longer $\mathrm{Zn}-\mathrm{Zn}$ distance of $2.412 \AA$ (BP86), so that hydride bridging is seen to lengthen the $\mathrm{Zn}-\mathrm{Zn}$ bond. In all these complexes, the $\mathrm{Zn}-\mathrm{Zn}$ bond is found to be a single $\sigma$-bond, which is weaker in the doubly bridged structures.



b (04)

c (08)

d (13)

Figure 17. Some experimentally characterized dizinc complexes (labels in brackets refer to Table 38)

Table 38. Zn-Zn Bond Lengths in Other Dizinc Complexes

| Label Species | $R_{M M}(\AA)$ | References | Remarks |
| :---: | :---: | :---: | :---: |
| $01\left(\eta^{5}-\mathrm{Me}_{5} \mathrm{C}_{5}\right)_{2} \mathrm{Zn}_{2}$ | 2.305(3) | 554 | Experimental; XRD |
| $02\left(\eta^{3}-\mathrm{Me}_{5} \mathrm{C}_{5}\right)_{2} \mathrm{Zn}_{2}$ | 2.331 | 557 | B3LYP |
| $03\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Zn}_{2}$ | 2.315 | 506 | BP86 |
| 04 RZnZnR | 2.3586 | 558 | $\mathrm{XRD} ; \mathrm{R}=\left[\left\{\left(2.6-\mathrm{Pr}^{i}{ }_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}(\mathrm{Me}) \mathrm{C}\right\}_{2} \mathrm{CH}\right]^{-}$ |
| 05 R'Zn-ZnR' | 2.366 | 558 | BP86; $\left.\mathrm{R}^{\prime}=(\mathrm{HNCH})_{2} \mathrm{CH}\right]$ |
| $06 \mathrm{RZn}(\mu-\mathrm{H})_{2} \mathrm{ZnR}$ | 2.4513(9) | 559 | XRD; $\mathrm{R}=\left[\left\{\left(2.6-\mathrm{Pr}^{i}{ }_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}(\mathrm{Me}) \mathrm{C}\right\}_{2} \mathrm{CH}\right]^{-}$ |
| $07 \mathrm{R}{ }^{\prime} \mathrm{Zn}(\mu-\mathrm{H})_{2} \mathrm{ZnR}{ }^{\prime}$ | 2.412 | 559 | BP86; $\left.\mathrm{R}^{\prime}=(\mathrm{HNCH})_{2} \mathrm{CH}\right]$ |
| 08 Ar'ZnZnAr' | 2.3591 | 560 | XRD; Ar' $=\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\left(\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\mathrm{Pr}^{\text {i }} 2\right.$ |
| 09 Ar' $\mathrm{Zn}(\mu-\mathrm{H})_{2} \mathrm{ZnAr}{ }^{\prime}$ | 2.4084(8) | 560 | XRD; $\left.\mathrm{Ar}^{\prime}=\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\left(\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\mathrm{Pr}^{\text {i }}\right)^{2}\right)_{2}$ |
| $\left.10 \mathrm{Ar}^{\prime} \mathrm{Zn}(\mu-\mathrm{Na}) \mu-\mathrm{H}\right) \mathrm{ZnAr}{ }^{\prime}$ | 2.352(2) | 560 | XRD; Ar' $=\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\left(\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\mathrm{Pr}^{\text {i }}{ }_{2}\right)_{2}$ |
| $11\left[\mathrm{Na}(\mathrm{THF})_{2}\right]_{2} \cdot[\mathrm{LZn}-\mathrm{ZnL}]$ | 2.3994(6) | 561 | XRD; $\left.\mathrm{L}=\left[\left(2,6-\operatorname{Pr}^{i} \mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}(\mathrm{Me}) \mathrm{C}\right)_{2}\right]_{2}{ }^{-}$ |
| $12\left[\mathrm{~K}(\mathrm{THF})_{2}\right]_{2} \cdot[\mathrm{LZn}-\mathrm{ZnL}]$ | 2.3934(8) | 562 | XRD; $\left.\mathrm{L}=\left[\left(2,6-\mathrm{Pr}^{i} \mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}(\mathrm{Me}) \mathrm{C}\right)_{2}\right]_{2}{ }^{-}$ |
| 13 [(dipp-bian)Zn] ${ }_{2}{ }^{\text {a }}$ | $\begin{aligned} & 2.3321 \\ & 2.3386 \end{aligned}$ | $\begin{aligned} & 563 \\ & 563 \end{aligned}$ | XRD; crystallized in $\mathrm{Et}_{2} \mathrm{O}$ XRD; crystallized in toluene |
| 14 [(phen-bian) Zn$]_{2}{ }^{\text {b }}$ | 2.315 | 563 | B3LYP; model for $\mathbf{1 3}$ |

[^22]The search for a dizinc complex with each metal centre having a coordination number of only one led Power and coworkers ${ }^{560}$ to the discovery of the Ar'ZnZnAr' complex 08 [ $\mathrm{Ar}{ }^{\prime}=$ $\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\left(\mathrm{C}_{6} \mathrm{H}_{3}-2,6-\mathrm{Pr}^{i}\right)_{2}$ ] (Figure 17c) and its derivatives. The $\mathrm{Zn}-\mathrm{Zn}$ bond distance here is $2.359 \AA$, which is $0.05 \AA$ longer than that in the cyclopentadienyl complex described above, but close to that in the $\beta$-ketiminate complex. The almost orthogonal alignment of the Ar ' ligands helps protect the $\mathrm{Zn}-\mathrm{Zn}$ bond. The $\mathrm{Zn}-\mathrm{Zn}$ distance is $2.408 \AA$ in the doubly bridged
$(\mu-\mathrm{H})_{2}$ derivative, which lacks a true covalent $\mathrm{Zn}-\mathrm{Zn}$ bond. The $(\mu-\mathrm{Na})(\mu-\mathrm{H})$ doubly bridged derivative of unprecedented structure has a $\mathrm{Zn}-\mathrm{Zn}$ bond length of $2.353 \AA$. Single point B3LYP/6-31G* results for Ar' ZnZnAr ' showed the major role of the $\mathrm{Zn} 4 \mathrm{p}_{z}$ orbitals to form the $\mathrm{Zn}-\mathrm{Zn}$ single bond (unlike the dizinc complexes described above) while the 4 s orbitals are involved in binding to the terphenyl ligands. However, in the $(\mu-\mathrm{Na})(\mu-\mathrm{H})$ doubly bridged derivative, the Zn 4 s orbitals are involved in both the $\mathrm{Zn}-\mathrm{Zn}$ bond and the $\mathrm{Zn}-\mathrm{H}$ bonds. The 4 p character of the $\mathrm{Zn}-\mathrm{Zn} \sigma$ bond here arises from differences in the orientation of binding between the bimetallic core and the ligands.

Later synthetic research led to the discovery of $\left[\mathrm{Na}(\mathrm{THF})_{2}\right]_{2} \cdot[\mathrm{LZn}-\mathrm{ZnL}]^{561}$ and its potassium analogue ${ }^{562}$ where L is the dianionic $\alpha$-diimine ligand $\left.\left[\left(2,6-\mathrm{Pr}^{i}{ }_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{N}(\mathrm{Me}) \mathrm{C}\right)_{2}\right]_{2}{ }^{-}$, having $R_{M M}$ values of $2.399 \AA$ and $2.393 \AA$ respectively, close to that in the doubly bridged $\operatorname{Ar}^{\prime} \mathrm{Zn}(\mu-\mathrm{H})_{2} \mathrm{ZnAr}^{\prime} .{ }^{560}$ BP86 studies on the model systems $\mathrm{Na}_{2}\left[(\mathrm{CHNH})_{2} \mathrm{Zn}-\mathrm{Zn}(\mathrm{CHNH})_{2}\right]$ and $\mathrm{K}_{2}\left[(\mathrm{CHNH})_{2} \mathrm{Zn}-\mathrm{Zn}(\mathrm{CHNH})_{2}\right]$ gave $\mathrm{Zn}-\mathrm{Zn}$ distances of $2.373 \AA$ and $2.396 \AA$, respectively, close to the experimental values for the full experimentally synthesized complexes. The $\mathrm{Zn}-\mathrm{Zn}$ bond is almost pure 4 s in character, with the ligand dianions $\pi$ bonded by solvated $\mathrm{Na}^{+}$or $\mathrm{K}^{+}$ions. Both zinc atoms are in the +2 oxidation state since the neutral dimine ligands are reduced to dianions during synthesis.

A biradical dizinc complex with radical anion ligands [(dpp-bian) $\mathrm{Zn}-\mathrm{Zn}(\mathrm{dpp}-\mathrm{bian})]$ (dppbian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) (Figure 17d) was synthesized by Fedushkin ${ }^{563}$, with $R_{M M}$ values of 2.332 and $2.339 \AA$ in crystals from $\mathrm{Et}_{2} \mathrm{O}$ and toluene, respectively. B3LYP/6-31G* results on a model with unsubstituted phenyl rings gave a triplet ground state with the two ligands perpendicular to each other and an $R_{M M}$ value of $2.315 \AA$. However, the coplanar conformation, lying $2.3 \mathrm{kcal} / \mathrm{mol}$ higher in energy, is the structure found by XRD. The $\mathrm{Zn}-\mathrm{Zn}$ bond here is $95 \% 4 s$ in character with zinc atoms coordinated to nitrogen atoms.

### 12.4. Zn -Zn Bond Length Ranges

Experimental and theoretical results thus give a range of 2.28 to $2.40 \AA$ for the $\mathrm{Zn}-\mathrm{Zn}$ single bonds in all of the above-discussed structures, where all except the carbon-coordinated complexes have $\mathrm{Zn}-\mathrm{Zn}$ bonds of almost pure 4 s character. These $\mathrm{Zn}-\mathrm{Zn}$ distances are all shorter than the sum $2.44 \AA$ of the Zn covalent radii, ${ }^{41}$ suggesting the covalent $\mathrm{Zn}-\mathrm{Zn}$ bonding present. Most of these complexes have the dizinc centre in the $\mathrm{Zn}^{+}$oxidation state, with only two examples in the $\mathrm{Zn}^{2+}$ oxidation state. In general, good agreement is observed between experimental data and computational results when comparisons can be made.

## 13. VARIOUS METAL-METAL BOND LENGTHS COMPARED

This Section deals with the effects of changes in the identity of the metal $M$ in the binuclear core $\left(\mathrm{M}_{2}\right)^{n+}$ within a series of similar or related complexes having different metals M. A large part of the survey in the preceding Sections was concerned with how different ligands or different series of related ligands operate to affect the MM bond distances in binuclear complexes, where some reasonable trends could be discerned. Effects which are inherently characteristic of the metal include the size of the atom/ion, the metal oxidation state, and the electropositivity of the metal. A study of the effects of the metal upon MM bond lengths must necessarily first categorize the MM bonds by their formal bond orders (single, double, etc.). In order to describe meaningfully the effects of a change in the metal $M$ in a series of binuclear complexes, all factors extraneous to the metal need to be kept as uniform or as comparable as possible. This entails a judicious choice of the binuclear complexes. Owing to the relative paucity of available experimental data on such series of complexes which span a wide range of metals, all too often such an analysis would need to resort to the more abundant data that are available from the results of computational (mostly DFT) studies. In view of the sufficient reliability of such methods with regard to the geometries and MM bond lengths in bimetallic complexes, amply attested to in the surveys above, this recourse to DFT results for such an analysis appears justifiable.

Suitable series of bimetallic complexes for this purpose include the series of homoleptic binuclear carbonyls $\mathrm{M}_{2}(\mathrm{CO})_{n}$ with metals ranging from titanium to copper, and the series of binuclear cyclopentadienylmetal carbonyls $\mathrm{Cp}_{2} \mathrm{M}_{2}(\mathrm{CO})_{n}$ covering a wide range of first row d-block metals. These series provide coherent datasets based on thoeretical results. Besides these two series, the MM bond length ranges given in the final sub-sections of Sections 4 to 12 are summarized in this Section, and the effects of change in metal upon the $R_{M M}$ ranges for
single, double, and triple MM bonds in binuclear complexes are also discussed. The $R_{M M}$ ranges noted for quadruple and quintuple MM bonds are also summarized and discussed.

### 13.1 Binuclear Homoleptic Metal Carbonyls

Earlier Sections have presented BP86/DZP results on various binuclear homoleptic metal carbonyl series $\mathrm{M}_{2}(\mathrm{CO})_{n}$ covering the first row d-block metals $\mathrm{M}\left(\mathrm{M}=\mathrm{V},{ }^{144-146} \mathrm{Cr},{ }^{258} \mathrm{Mn},{ }^{308}\right.$ $\mathrm{Fe},{ }^{355} \mathrm{Co},{ }^{444} \mathrm{Ni},{ }^{509}$ and $\mathrm{Cu}^{543}$ ). All of these complexes have the metal in the zero oxidation state $\mathrm{M}(0)$, a feature facilitating comparisons. Comparisons are made here within the categories of single, double, and triple MM bonds. The saturated members of each of these seven series have global minima with MM formal single bonds, namely $\mathrm{V}_{2}(\mathrm{CO})_{12}, \mathrm{Cr}_{2}(\mathrm{CO})_{11}$, $\mathrm{Mn}_{2}(\mathrm{CO})_{10}, \mathrm{Fe}_{2}(\mathrm{CO})_{9}, \mathrm{Co}_{2}(\mathrm{CO})_{8}, \mathrm{Ni}_{2}(\mathrm{CO})_{7}$, and $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$. Note is also taken of members of each series with one CO ligand less than in the previous group, namely $\mathrm{Cr}_{2}(\mathrm{CO})_{10}, \mathrm{Mn}_{2}(\mathrm{CO})_{9}$, $\mathrm{Fe}_{2}(\mathrm{CO})_{8}, \mathrm{Co}_{2}(\mathrm{CO})_{7}, \mathrm{Ni}_{2}(\mathrm{CO})_{6}$, and $\mathrm{Cu}_{2}(\mathrm{CO})_{5}$, which have minima with $\mathrm{M}=\mathrm{M}$ double bonds. Finally, we include members of these series with two CO ligands less than in the first group, namely $\mathrm{V}_{2}(\mathrm{CO})_{10}, \mathrm{Cr}_{2}(\mathrm{CO})_{9}, \mathrm{Mn}_{2}(\mathrm{CO})_{8}, \mathrm{Fe}_{2}(\mathrm{CO})_{7}, \mathrm{Co}_{2}(\mathrm{CO})_{6}, \mathrm{Ni}_{2}(\mathrm{CO})_{5}$, and $\mathrm{Cu}_{2}(\mathrm{CO})_{4}$, which have minima with $\mathrm{M} \equiv \mathrm{M}$ triple bonds. One must note, however, that in the DFT study on the dicopper carbonyl series, the formal MM bond orders are not mentioned in the original paper. Most of these structures have bridging CO ligands, referred to as $\mu-\mathrm{CO}, \eta^{2}-\mu-\mathrm{CO}$, and s $\mu-\mathrm{CO}$. The presence and number of such bridging CO ligands is a complicating factor, also affecting MM bond lengths apart from the inherent nature of the metal itself. Although most of these homoleptic binuclear metal carbonyls are unknown experimentally, this extensive body of computational data furnishes a good opportunity for discerning effects of changing the metal upon the MM bond lengths in binuclear complexes.

Table 39. BP86 MM Bond Lengths ( $\AA$ ) (Single, Double and Triple) in Binuclear Homoleptic Metal Carbonyls

M-M single bonds
Complex $\quad \mathrm{V}_{2}(\mathrm{CO})_{12} \quad \mathrm{Cr}_{2}(\mathrm{CO})_{11} \quad \mathrm{Mn}_{2}(\mathrm{CO})_{10} \quad \mathrm{Fe}_{2}(\mathrm{CO})_{9} \quad \mathrm{Co}_{2}(\mathrm{CO})_{8} \quad \mathrm{Ni}_{2}(\mathrm{CO})_{7} \quad \mathrm{Cu}_{2}(\mathrm{CO})_{6}$ Ligands no $\mu$-CO 1 s $\mu$-CO $\quad$ no $\mu$-CO $\quad 3 \mu$-CO $\quad 2 \mu$-CO $\quad 1 \mu$-CO $\quad$ no $\mu$-CO

| $R_{M M}$ | 3.334 | 3.148 | 2.954 | 2.519 | 2.550 | 2.672 | 2.602 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

$\mathrm{M}=\mathrm{M}$ double bonds
Complex $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{6} \mathrm{Cr}_{2}(\mathrm{CO})_{10} \quad \mathrm{Mn}_{2}(\mathrm{CO})_{9} \quad \mathrm{Fe}_{2}(\mathrm{CO})_{8} \quad \mathrm{Co}_{2}(\mathrm{CO})_{7} \quad \mathrm{Ni}_{2}(\mathrm{CO})_{6} \quad \mathrm{Cu}_{2}(\mathrm{CO})_{5}$
Ligands $\quad 2 \mu$-CO no $\mu$-CO $\quad 1 \eta^{2}$-CO $\quad 2 \mu$-CO $\quad 1 \mu$-CO $\quad 2 \mu$-CO $\quad$ no $\mu$-CO

| $R_{M M}$ | 2.847 | 2.726 | 2.704 | 2.447 | 2.423 | 2.521 | 2.499 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

$\mathrm{M} \equiv \mathrm{M}$ triple bonds

| Complex | $\mathrm{V}_{2}(\mathrm{CO})_{10}$ | $\mathrm{Cr}_{2}(\mathrm{CO})_{9}$ | $\mathrm{Mn}_{2}(\mathrm{CO})_{8}$ | $\mathrm{Fe}_{2}(\mathrm{CO})_{7}$ | $\mathrm{Co}_{2}(\mathrm{CO})_{6}$ | $\mathrm{Ni}_{2}(\mathrm{CO})_{5}$ | $\mathrm{Cu}_{2}(\mathrm{CO})_{4}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ligands | $1 \mathrm{~s} \mu-\mathrm{CO}$ | $3 \mu-\mathrm{CO}$ | no $\mu-\mathrm{CO}$ | $2 \eta^{2}-\mathrm{CO}$ | $2 \mu-\mathrm{CO}$ | $3 \mu-\mathrm{CO}$ | no $\mu-\mathrm{CO}$ |
| $R_{M M}$ | 2.510 | 2.285 | 2.300 | 2.235 | 2.255 | 2.521 | 2.382 |

Table 39 presents MM single, double and triple bond lengths for selected members of the three series of homoleptic binuclear metal carbonyls mentioned above, also giving the number and type of bridging carbonyl ligands.

The $\mathrm{M}-\mathrm{M}$ single bonds in the first series (saturated carbonyls) range in length from 3.334 to $2.519 \AA$. In the absence of results for homoleptic binuclear titanium carbonyls, the unbridged $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{8}\left(R_{M M}=3.909 \AA\right)^{82}$ is taken as representative. The $R_{M M}$ values for these $\mathrm{M}-\mathrm{M}$ single bonds decrease along with the $\mathrm{R}_{\mathrm{cov}}$ values of Table 1 in the following monotonic trend with respect to metal: $\mathrm{Ti}>\mathrm{V}>\mathrm{Cr}>\mathrm{Mn}>\mathrm{Cu}>\mathrm{Co}$, in which nickel and iron fall somewhat outside this trend (Figure 18a). A similar correlation between $R_{M M}$ and the single bond covalent radii $\mathrm{R}_{\mathrm{cv}}(1)$ of Table 1 is shown in Figure 18 b , in which the nickel and iron cases fall outside the trend.

(a)

(b)

Figure 18. Plots of $\mathrm{M}-\mathrm{M}$ single bond lengths $R_{M M}$ for $\mathrm{M}_{2}(\mathrm{CO})_{n}$ series versus (a) metal covalent radius $\mathrm{R}_{\mathrm{cov}}$, and (b) single bond covalent radius $\mathrm{R}_{\mathrm{cv}}(1)$

The more electron-rich nature of the later transition metals and the effects of changes in electropositivity are factors that are not considered here. Also, the number and coordination mode of the bridging CO ligands, though noted down, do not enter into the reckoning here, e.g. the three $\mu$-CO ligands in $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$. Furthermore, we cannot also discount the scope for three-centre two-electron bonding via bridging ligands which obviate the covalent nature of metal-metal bonding in such complexes, as described for $\mathrm{Fe}_{2}(\mathrm{CO})_{9}$ and $\mathrm{Co}_{2}(\mathrm{CO})_{8}$ in theoretical studies. ${ }^{356-359}$

The $\mathrm{M}=\mathrm{M}$ double bonds in the second series of Table 39 range in length from 2.847 to $2.423 \AA$, where the case for divanadium is represented by the non-homoleptic $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{6}$ in the absence of an MM double-bonded homoleptic binuclear vanadium carbonyl. ${ }^{147}$ The dititanium case is likewise represented by the MM double-bonded complex $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{7}$ (not the global minmum) with an $R_{M M}$ value of $3.378 \AA . .^{82}$ The correlation between $R_{M M}$ for these $\mathrm{M}=\mathrm{M}$ double bonds and the double bond metal radii $\mathrm{R}_{\mathrm{cv}}(2)$ values of Table 1 is shown in Figure 19a. The bond distance trend with respect to metal is: $\mathrm{Ti}>\mathrm{V}>\mathrm{Cr}>\mathrm{Mn}>\mathrm{Co}$, where the copper, iron and nickel cases appear out of place in the overall plot.

The $\mathrm{M} \equiv \mathrm{M}$ triple bond lengths in the third series of Table 39 range from 2.795 to $2.235 \AA$, where the doubly-bridged MM triple-bonded $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{6}$ is taken as representative of the dititanium case. ${ }^{82}$ The formal MM bond order of 3 in complexes $\mathrm{V}_{2}(\mathrm{CO})_{10}$ to $\mathrm{Cu}_{2}(\mathrm{CO})_{4}$ is concomitant with a steady decrease in the number of CO ligands from 10 to 4 . From the dititanium case down to $\mathrm{Fe}_{2}(\mathrm{CO})_{7}$, the decrease in $R_{M M}$ goes with a decrease in the triple bond metal covalent radius $\mathrm{R}_{\mathrm{cv}}(3)$ of Table 1 . Figure 19b portrays the overall correlation, which shows anomalies for the cobalt, nickel and copper cases.

(a)

(b)

Figure 19. Plots of (a) $\mathrm{M}=\mathrm{M}$ double bond lengths $R_{M M}$ for homoleptic $\mathrm{M}_{2}(\mathrm{CO})_{n}$ vs. double bond metal covalent radius $\mathrm{R}_{\mathrm{cv}}(2)$, and (b) $\mathrm{M} \equiv \mathrm{M}$ triple bond lengths $R_{M M}$ for homoleptic $\mathrm{M}_{2}(\mathrm{CO})_{n}$ vs. triple bond metal covalent radius $\mathrm{R}_{\mathrm{cv}}(3)$

It emerges that these theoretical results predict that the size of the metal atom figures prominently in influencing MM single, double, and triple bond distances, especially for the earlier transition metals. However, other factors such as effects of bridging ligands, electron population around the metal centers, and metal electropositivity require attention. Morever, the assumption that the metal-metal interactions are covalent may need to be challenged in light of three-centre two-electron bonding, which discounts direct metal-metal overlap. This is a distinct possibility for binuclear systems with bridging CO ligands.

### 13.2 Binuclear Cyclopentadienylmetal Carbonyl Complexes

Another group of complexes which presents an opportunity for gauging effects of change in the metal upon MM bond lengths is the various series of binuclear cyclopentadienylmetal carbonyls that have been extensively studied by DFT methods including the BP86/DZP method. Previous sections have presented computational results on such series of complexes, covering the metals titanium, ${ }^{82,83}$ vanadium, ${ }^{147,148}$ chromium,,${ }^{273}$ manganese, ${ }^{316}$ iron, ${ }^{382}$ and cobalt. ${ }^{457}$ Table 40 presents theoretical predictions for MM single, double and triple bond lengths in complexes taken from the series $\mathrm{Cp}_{2} \mathrm{M}_{2}(\mathrm{CO})_{n}(\mathrm{M}=\mathrm{Ti}, \mathrm{V}, \mathrm{Cr}, \mathrm{Mn}, \mathrm{Fe}$ and Co$)$, giving the species, the bridging ligands, and the $R_{M M}$ values, where the dichromium case is taken from experimental data, ${ }^{273}$ and the other cases from BP86 results.

Table 40. BP86 Metal-Metal Bond Lengths ( $\AA$ ) (Single, Double and Triple) in Binuclear Cyclopentadienylmetal Carbonyls

| Core | Ti ${ }_{2}$ | $\mathrm{V}_{2}$ | $\mathrm{Cr}_{2}$ | $\mathrm{Mn}_{2}$ | $\mathrm{Fe}_{2}$ | $\mathrm{Co}_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{M}-\mathrm{M}$ single bond lengths |  |  |  |  |  |  |
| Species | $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{8}$ | $\mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{7}$ | - | $\mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{5}$ | $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{4}$ | $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}$ |
| Ligands | no $\mu$-CO | $1 \mu$-CO | - | $1 \mu ; 2 \mathrm{~s} \mu$-CO | $2 \mu$-CO | $3 \mu$-CO |
| $R_{M M}$ | 3.909 | 3.306 | - | 2.804 | 2.540 | 2.352 |

$\mathrm{M}=\mathrm{M}$ double bond lengths
Species $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{4} \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{6} \mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{2} \mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{4} \mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3} \mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{2}$

| Ligands | $2 \eta^{2}-\mathrm{CO}$ | $2 \mathrm{~s} \mu-\mathrm{CO}$ | no $\mu-\mathrm{CO}$ | $2 \mathrm{~s} \mu-\mathrm{CO}$ | $3 \mu$-CO | $2 \mu$-CO |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $R_{M M}$ | 3.108 | 2.847 | 2.615 | 2.509 | 2.264 | 2.346 |

$\mathrm{M} \equiv \mathrm{M}$ triple bond lengths
Species $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{6} \mathrm{Cp}_{2} \mathrm{~V}_{2}(\mathrm{CO})_{5} \mathrm{Cp}_{2} \mathrm{Cr}_{2}(\mathrm{CO})_{4} \mathrm{Cp}_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{3} \mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{2} \mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})$
Ligands $2 \mu$-CO $2 \mathrm{~s} \mu$-CO $3 \mu$-CO $2 \mu$-CO $1 \mu$-CO
$\begin{array}{lllllll}R_{M M} & 2.795 & 2.452 & 2.239^{a} & 2.167 & 2.120 & 2.050\end{array}$

[^23]The M-M single bond lengths in the first series of Table 40 are taken from systems that are as saturated as possible, subject to the available results. From $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{8}$ to $\mathrm{Cp}_{2} \mathrm{Co}_{2}(\mathrm{CO})_{3}$, the decrease in the number of CO ligands is monotonic. The decrease in $R_{M M}$ values from the dititanium system to the dicobalt system follows the decrease in the values of the atomic radii $\mathrm{R}_{\mathrm{cov}}$ and $\mathrm{R}_{\mathrm{cv}}(1)$ of Table 1. In general, the number of bridging CO ligands increases across the series, which may be a complicating factor. The presence of the two Cp ligands might diminish the scope for three-center two-electron bonding, imparting more covalent character to the MM bonds.

(a)

(b)

Figure 20. Plots of (a) $\mathrm{M}=\mathrm{M}$ double bond lengths $R_{M M}$ for the $\mathrm{Cp}_{2} \mathrm{M}_{2}(\mathrm{CO})_{n}$ series vs. double bond metal covalent radius $\mathrm{R}_{\mathrm{cv}}(2)$, and (b) $\mathrm{M} \equiv \mathrm{M}$ triple bond lengths $R_{M M}$ for the $\mathrm{Cp}_{2} \mathrm{M}_{2}(\mathrm{CO})_{n}$ series vs. triple bond metal covalent radius $\mathrm{R}_{\mathrm{cv}}(3)$

The $\mathrm{M}=\mathrm{M}$ double bond lengths in the second series of Table 40 are taken from data which do not present uniformity of trend in structure, namely a uniform decrease with the number of CO ligands. The monotonic decrease in $\mathrm{M}=\mathrm{M}$ double bond $R_{M M}$ values goes along with the decrease in the double bond atomic radii $\mathrm{R}_{\mathrm{cv}}(2)$ (Table 1), except for $\mathrm{Cp}_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{3}$ (Figure 20a).

The $\mathrm{M} \equiv \mathrm{M}$ triple bond lengths in the third series of Table 40 are taken from systems which together display uniformity of structure with a steady decrease in the number of CO ligands from 6 to 1 across the row. The monotonic decrease in $\mathrm{M} \equiv \mathrm{M}$ triple bond $R_{M M}$ distances from the dititanium system to the dicobalt system follows the decrease in the triple bond metal radii $\mathrm{R}_{\mathrm{cv}}(3)$ (Table 1), as shown in Figure 20 b .

### 13.3 Single, Double, and Triple MM Bond Length Ranges

As a result of the comprehensive survey of MM bond lengths given in the last sub-sections of Sections 4 to 12 (titanium to zinc), as gathered from experimental and computational sources, a general overview is now made of the MM bond distance ranges for single, double, and triple MM bonds in binuclear complexes of the metals titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper. Table 41 presents these results for the sake of discerning changes in MM bond lengths with given bond orders with different metals M . The experimental MM bond length ranges are emphasized in bold.

The experimental $\mathrm{Ti}-\mathrm{Ti}$ single bond length range of $2.74 \pm 0.14 \AA$ is drawn from a small group of non-carbonyl dititanium complexes (Table 2) and fits in closer with the Ti-Ti single bond estimate of $2.96 \AA$ based on the $\mathrm{R}_{\mathrm{cv}}(1)$ value of $1.48 \AA$ than with the longer estimate of $3.20 \AA$ based on the $\mathrm{R}_{\text {cov }}$ value of $1.60 \AA$ (Table 1 ). The sole experimental $R_{M M}$ value for a $\mathrm{Ti}=\mathrm{Ti}$ double bond in a complex ( $2.362 \AA ; \mathbf{0 6}$ of Table 2) is much longer than $\mathrm{Ti}=\mathrm{Ti}$ double bond length of $1.942 \AA$ in the bare dimer $\mathrm{Ti}_{2}$. The markedly higher computationally
derived ranges for $\mathrm{Ti}-\mathrm{Ti}$ single, double, and triple bond lengths in the $\mathrm{Cp}_{2} \mathrm{Ti}_{2}(\mathrm{CO})_{n}$ series exemplify the MM bond lengthening effect of CO ligands and possibly suggest an overestimation of Ti-Ti bond distances by the BP86 method. Binuclear titanium complexes with CO ligands are not yet known experimentally.

The experimental ranges for vanadium-vanadium single, double, and triple bonds in noncarbonyl binuclear vanadium complexes show the expected trend single $>$ double $>$ triple. The $R_{M M}$ range for $\mathrm{V}-\mathrm{V}$ single bonds here is more consistent with the single bond length estimate derived from the $\mathrm{R}_{\mathrm{cv}}(1)$ value of $1.34 \AA$ than the $\mathrm{R}_{\mathrm{cov}}$ value of $1.53 \AA$ (Table 1). The $R_{M M}$ value of $2.733 \AA$ for the $\mathrm{V}=\mathrm{V}$ double bond in the carbonyl complex $\mathbf{1 9}$ of Table 3 is higher than the single bond length range for non-carbonyl complexes here. Paddlewheel complexes lead to shorter $(1.96 \pm 0.03 \AA) \mathrm{V} \equiv \mathrm{V}$ triple bonds than those in the vanadoborane, chalcogenide and other divanadium complexes of Tables 5 and 6 . This may be related to the higher basicity of the bidentate ligands in the paddlewheel complexes. The BP86 predictions for vanadium-vanadium bonds in binuclear vanadium carbonyls yield the expected bond length trend, namely single $>$ double $>$ triple, where the values for each bond order are higher than those for the corresponding results in non-carbonyl complexes based on experimental findings.

Experimental findings on $\mathrm{Cr}-\mathrm{Cr}$ single bonds are thus far limited to the $\left[\mathrm{Cr}_{2}(\mathrm{CO})_{11}\right]^{-}$ anion, ${ }^{262-264}$ whose $R_{M M}$ value is appreciable longer than the $\mathrm{Cr}-\mathrm{Cr}$ single bond length estimate derived from the $\mathrm{R}_{\text {cov }}$ value of $1.39 \AA$ (Table 1). This is longer than the experimental range for $\mathrm{Cr}=\mathrm{Cr}$ double bonds in non-carbonyl binuclear chromium complexes, in turn longer than the experimental range for $\mathrm{Cr} \equiv \mathrm{Cr}$ triple bonds in carbonyl and non-carbonyl binuclear chromium complexes. The theoretical results yield longer ranges for single, double and triple bond lengths in dichromium carbonyl complexes, following the expected order single $>$ double $>$ triple.

Table 41. MM Single, Double and Triple Bond Length Ranges in $\AA$ for First Row $d$ Block Binuclear Complexes (Experimental Ranges in Bold)

| Metal | Single M-M bonds | Double $\mathrm{M}=\mathrm{M}$ bonds | Triple $\mathrm{M} \equiv \mathrm{M}$ bonds |
| :---: | :---: | :---: | :---: |
| Titanium |  |  |  |
| Exptl. range | $2.73 \pm 0.14$ | 2.362 |  |
| Remarks | Exptl.; non-carbonyl | Exptl.; 06 (Table 2) | No exptl. data |
| BP86 range <br> Remarks | $3.38 \pm 0.35$ <br> carbonyl complexes | $3.21 \pm 0.17$ <br> carbonyl complexes | $2.79 \pm 0.04$ <br> carbonyl complexes |
| Vanadium |  |  |  |
| Exptl. range | $2.66 \pm 0.21$ | $\begin{aligned} & 2.40 \pm 0.01^{b} \\ & 2.733^{d} \end{aligned}$ | $\begin{aligned} & 1.96 \pm 0.03{ }^{c} \\ & 2.35 \pm 0.19^{e} \end{aligned}$ |
| Remarks | Exptl. (non-carbonyl) | ${ }^{b}$ Exptl. (non-CO) <br> ${ }^{d}$ Exptl.; carbonyl | ${ }^{c}$ Exptl. (paddlewheel) <br> ${ }^{e}$ Exptl. (others) |
| BP86 range <br> Remarks | $2.99 \pm 0.16$ <br> carbonyl complexes | $2.847$ <br> carbonyl complexes | $2.45 \pm 0.06$ <br> carbonyl complexes |
| Chromium |  |  |  |
| Exptl. range | $2.99 \pm 0.01$ | $\mathbf{2 . 2 0} \pm \mathbf{0 . 0 5}$ | $\mathbf{2 . 3 1} \pm \mathbf{0 . 0 8}$ |
| Remarks | Expt1.; carbonyl | Exptl.; non-CO | Exptl.; CO and non-CO |
| BP86 range Remarks | $3.23 \pm 0.09$ <br> carbonyl complexes | $2.59 \pm 0.13$ <br> carbonyl complexes | $2.38 \pm 0.12$ <br> carbonyl complexes |
| Manganese |  |  |  |
| Exptl. range | $\begin{aligned} & 2.94 \pm 0.04{ }^{f} \\ & 2.72 \pm 0.08 \end{aligned}$ | - | 2.170 |
| Remarks | $\begin{aligned} & { }^{f} \text { For }\left(\mathrm{Mn}_{2}\right)^{0} \text { cases } \\ & { }^{g}\left(\mathrm{Mn}_{2}\right)^{n+} \text { cases, } n=1-3 \end{aligned}$ | - | Exptl.; CO complex |
| BP86 range | $2.83 \pm 0.12$ | 2.704 | $2.43 \pm 014$ |
| Remarks | $\mathrm{Mn}_{2}(\mathrm{CO})_{\mathrm{n}}$ series | $\mathrm{Mn}_{2}(\mathrm{CO})_{\mathrm{n}}$ series | $\mathrm{Mn}_{2}(\mathrm{CO})_{\mathrm{n}}$ series |
| BP86 range <br> Remarks | $\begin{aligned} & 2.74 \pm 0.18 \\ & \left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{n} \end{aligned}$ | $\begin{aligned} & 2.37 \pm 0.08 \\ & \left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{n} \end{aligned}$ | $\begin{aligned} & 2.156 \\ & \left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{n} \end{aligned}$ |
| BP86 range | $2.76 \pm 0.19$ | $2.50 \pm 0.20$ | $2.36 \pm 0.21$ |
| Remarks | All CO complexes | All CO complexes | All CO complexes |
| Iron |  |  |  |
| Exptl. range | $2.51 \pm 0.12{ }^{h}$ | $\mathbf{2 . 3 5} \pm \mathbf{0 . 0 9}$ | $\mathbf{2 . 0 9} \pm \mathbf{0 . 0 7}$ |
|  | $2.62 \pm 0.17^{i}$ |  |  |
| Remarks | ${ }^{h}$ Exptl.; non-carbonyl <br> ${ }^{i}$ Exptl.; carbonyl | Exptl.; CO and non-CO n 183 | Exptl.; non-carbonyl |


| DFT range | $2.55 \pm 0.04$ | $2.49 \pm 0.06$ | $2.22 \pm 0.02$ |
| :---: | :---: | :---: | :---: |
| Remarks | DFT; $\mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | BP86; $\mathrm{Fe}_{2}(\mathrm{CO})_{n}$ | BP86; $\mathrm{Fe}_{2}(\mathrm{CO})_{n}$ |
| BP86 range Remarks | $\begin{aligned} & 2.51 \pm 0.03 \\ & (\mathrm{BF})_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n} \end{aligned}$ | $\begin{aligned} & 2.31 \pm 0.06 \\ & \left(\mathrm{C}_{9} \mathrm{H}_{7}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n} \end{aligned}$ | $\begin{aligned} & 2.10 \pm 0.03 \\ & \left(\mathrm{C}_{9} \mathrm{H}_{7}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{n} \end{aligned}$ |
| BP86 range Remarks | $\begin{aligned} & 2.91 \pm 0.07 \\ & (\mathrm{BO})_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n} \end{aligned}$ | $\begin{aligned} & 2.51 \pm 0.12 \\ & \left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n} \end{aligned}$ | $\begin{aligned} & 2.30 \pm 0.01 \\ & (\mathrm{BF})_{2} \mathrm{Fe}_{2}(\mathrm{CO})_{n} \end{aligned}$ |
| BP86 range <br> Remarks | $2.74 \pm 0.24$ <br> All CO complexes | $2.44 \pm 0.19$ <br> All CO complexes | $2.20 \pm 0.11$ <br> All CO complexes |
| Cobalt |  |  |  |
| Exptl. range | $\begin{aligned} & 2.38 \pm 0.11^{j} \\ & 2.49 \pm 0.04^{k} \end{aligned}$ | $2.26 \pm 0.13$ | - |
| Remarks | ${ }^{j}$ Exptl.; non-carbonyl <br> ${ }^{k}$ Exptl.; carbonyl | Exptl.; non-carbonyl | - |
| BP86 range Remarks | $2.56 \pm 0.18$ <br> homoleptic carbonyl | $2.45 \pm 0.16$ <br> homoleptic carbonyl | $2.18 \pm 0.08$ <br> homoleptic carbonyl |
| BP86 range | $2.51 \pm 0.16$ | $2.43 \pm 0.10$ | $2.29 \pm 0.11$ |
| Remarks | CO with inorg. ligands | CO with inorg. ligands | CO with inorg. ligands |
| DFT range | $2.51 \pm 0.09$ | $2.34 \pm 0.11$ | $2.18 \pm 0.13$ |
| Remarks | CO with organic ligands | CO with organic ligands | CO with org. ligands |
| BP86 range | $2.58 \pm 0.16$ | $2.38 \pm 0.15$ | $2.23 \pm 0.18$ |
| Remarks | All CO complexes | All CO complexes | All CO complexes |
| Nickel |  |  |  |
| Exptl. range | $2.51 \pm 0.07^{l}$ | $2.31 \pm 0.02$ | - |
|  | $\mathbf{2 . 4 6} \pm 0.06{ }^{\text {m }}$ |  |  |
| Remarks | ${ }^{l}$ Exptl.; $\left(\mathrm{Ni}_{2}\right)^{0}$ core ${ }^{m}$ Exptl.; $\left(\mathrm{Ni}_{2}\right)^{2+}$ core | Exptl.; $\left(\mathrm{Ni}_{2}\right)^{2+}$ core | - |
| BP86 range | $2.62 \pm 0.07$ | $2.44 \pm 0.06$ | $2.38 \pm 0.04$ |
| Remarks | homoleptic CO and $\mathrm{PF}_{3}$ | homoleptic CO and $\mathrm{PF}_{3}$ | homoleptic $\mathrm{CO} \& \mathrm{PF}_{3}$ |
| Copper |  |  |  |
| Exptl. range | $2.44 \pm 0.09^{\boldsymbol{n}} \boldsymbol{;} \mathbf{2 . 6 1 1}{ }^{\text {o }}$ |  |  |
| Remarks | ${ }^{n}$ Exptl.; $\left(\mathrm{Cu}_{2}\right)^{+2}$ core <br> ${ }^{o}$ Exptl.; $\mathrm{Cu}_{2}(\mathrm{OAc})_{4} .2 \mathrm{H}_{2} \mathrm{O}$ |  |  |
| DFT range | $2.55 \pm 0.08$ | 2.216 |  |
| Remarks | $\mathrm{Cu}(0), \mathrm{Cu}(\mathrm{I}), \mathrm{Cu}(\mathrm{II})$ | BP86; $\mathrm{Cp}_{2} \mathrm{Cu}_{2}$ (coaxial) |  |
| Zinc |  |  |  |
| Exptl. range | $2.38 \pm 0.07$ |  |  |
| Remarks | Exptl., $\mathrm{Zn}(\mathrm{I})$ and $\mathrm{Zn}(\mathrm{II})$ |  |  |
| Theor. range | $2.38 \pm 0.07$ |  |  |
| Remarks | MP2 and BP86 |  |  |

Experimental results for $R_{M M}$ ranges are available for $\mathrm{Mn}-\mathrm{Mn}$ single bonds and $\mathrm{Mn} \equiv \mathrm{Mn}$ triple bonds, but not for $\mathrm{Mn}=\mathrm{Mn}$ double bonds. The experimental $\mathrm{Mn}-\mathrm{Mn}$ single bond ranges indicate a higher $R_{M M}$ range for complexes with an $\left(\mathrm{Mn}_{2}\right)^{0}$ core than for those with an $\left(\mathrm{Mn}_{2}\right)^{n+}$ core ( $n=1,2,3$ ). These single bond length ranges are not too far from the $R_{M M}$ value of 2.78 $\AA$ estimated from the $\mathrm{R}_{\mathrm{cov}}$ value (Table 1). The BP86-derived $R_{M M}$ ranges in the homoleptic $\mathrm{Mn}_{2}(\mathrm{CO})_{n}$ series give the expected trend single $>$ double $>$ triple. Introduction of other ligands into binuclear manganese carbonyl complexes leads to shorter $R_{M M}$ values, e.g., in the $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2} \mathrm{Mn}_{2}(\mathrm{CO})_{n}$ series where the benzene ligand leads to the shortest $\mathrm{Mn}-\mathrm{Mn}$ bond length ranges among all the binuclear manganese carbonyl compound series. The overall $R_{M M}$ range for all binuclear manganese carbonyl series is also given.

Binuclear iron complexes give experimental $R_{M M}$ ranges that show the expected trend single $>$ double $>$ triple. Experimental $R_{M M}$ ranges for $\mathrm{Fe}-\mathrm{Fe}$ single bonds are shorter for complexes with no carbonyl ligands than those with carbonyl ligands. The latter range is close to the estimate of $2.64 \AA$ derived from the $\mathrm{R}_{\text {cov }}$ value (Table 1). The trend single $>$ double $>$ triple is also seen in the $\operatorname{BP} 86 R_{M M}$ range for the homoleptic $\mathrm{Fe}_{2}(\mathrm{CO})_{n}$ series and its derivatives, where some MM bond-lengthening effect of the carbonyl ligands is discernible for $\mathrm{Fe}=\mathrm{Fe}$ double and $\mathrm{Fe} \equiv \mathrm{Fe}$ triple bonds when compared with the experimental ranges for non-carbonyl complexes. BP86-derived single, double and triple bond $R_{M M}$ ranges for binuclear iron carbonyl complexes with a variety of non-carbonyl ligands are also shown, giving the lowest ranges and the highest ranges (noting the particular series from which these ranges are taken). Finally, the overall BP86-derived single, double and triple bond $R_{M M}$ ranges for all binuclear iron carbonyl complexes and their derivatives are also shown.

Experimental information is available for $\mathrm{Co}-\mathrm{Co}$ single bonds and $\mathrm{Co}=\mathrm{Co}$ double bonds, but not for cobalt-cobalt bonds of higher order. The estimate of $2.52 \AA$ for a Co-Co single
bond length derived from the $\mathrm{R}_{\mathrm{cov}}$ value (Table 1) comports better with the computational data for binuclear cobalt carbonyl complexes than with the experimental data. The $R_{M M}$ range for $\mathrm{Co}-\mathrm{Co}$ single bonds is predictably higher than that for $\mathrm{Co}=\mathrm{Co}$ double bonds, and a bondlengthening effect of CO ligands may be inferred for Co-Co single bonds. The BP86 predictions for the $R_{M M}$ ranges in the homoleptic $\mathrm{Co}_{2}(\mathrm{CO})_{n}$ series and its derivatives yield the expected trend single $>$ double $>$ triple. $R_{M M}$ ranges are also given for binuclear cobalt carbonyl complexes with inorganic ligands and with organic ligands. Complexes with organic ligands show lower $R_{M M}$ ranges, expecially for double and triple cobalt-cobalt bonds. The overall ranges for all series of dicobalt carbonyl complex derivatives are also given.

Experimental results yielding $R_{M M}$ ranges for binuclear nickel complexes are available only for $\mathrm{Ni}-\mathrm{Ni}$ single bonds and $\mathrm{Ni}=\mathrm{Ni}$ double bonds. The $R_{M M}$ range for complexes with a $\left(\mathrm{Ni}_{2}\right)^{0}$ core is somewhat higher than that for complexes with a $\left(\mathrm{Ni}_{2}\right)^{+2}$ core. These experimental ranges for $\mathrm{Ni}-\mathrm{Ni}$ single bond lengths in non-carbonyl complexes compare well with the estimate of $2.48 \AA$ derived from the $\mathrm{R}_{\mathrm{cov}}$ value (Table 1). BP86 data on $R_{M M}$ ranges for single, double, and triple MM bonds in homoleptic dinickel carbonyls and trifluorophosphines (subsection 10.6) shows the expected trend, namely single $>$ double $>$ triple, where the ranges here for MM single and double bonds are noticeably higher than the experimental ranges for non-carbonyl complexes.

The experimental $R_{M M}$ range of $2.44 \pm 0.09 \AA$ for $\mathrm{Cu}(\mathrm{I})-\mathrm{Cu}(\mathrm{I})$ distances in non-carbonyl binuclear copper complexes (Table 35) is lower than twice the covalent radius $\mathrm{R}_{\text {cov }}$ of $1.32 \AA$ (Table 1). However, this experimental range is not related to covalent copper-copper bonding, but to MM interactions from other effects. The $\mathrm{Cu}-\mathrm{Cu}$ single bond length estimate of $2.64 \AA$ is quite close to the experimental $R_{M M}$ value in the copper(II) acetate dimer and the BP86 $R_{M M}$ value for $\mathrm{Cu}_{2}(\mathrm{CO})_{6}$, both of which may exhibit at least some degree of covalent $\mathrm{Cu}-\mathrm{Cu}$ bonding. The DFT range of $2.55 \pm 0.08 \AA$ for $\mathrm{Cu}-\mathrm{Cu}$ single bond lengths is taken from
the computational results in Tables 35 and 36 for complexes having Cu oxidation states of 0 , +1 and +2 . This range is longer than the BP86-derived $\mathrm{Cu}=\mathrm{Cu}$ double bond length of $2.216 \AA$ in the coaxial $\mathrm{Cp}_{2} \mathrm{Cu}_{2}$ complex.

The zinc-zinc bonds in binuclear zinc complexes are all single. The experimental and computational results agree quite closely, and together give an $R_{M M}$ range of $2.38 \pm 0.07 \AA$. This range is somewhat lower than the $R_{M M}$ estimate of $2.44 \AA$ derived from the $\mathrm{R}_{\mathrm{cov}}$ value, but closer to the estimate of $2.36 \AA$ derived from the $\mathrm{R}_{\mathrm{cv}}(1)$ value for zinc (Table 1). The experimental range of $2.378 \pm 0.073 \AA$ for $\mathrm{Zn}-\mathrm{Zn}$ single bond lengths is taken from XRD results tabulated in Table 38, and covers complexes with zinc in the $\mathrm{Zn}(\mathrm{I})$ and $\mathrm{Zn}(\mathrm{II})$ oxidation states. The computationally derived range of $2.383 \pm 0.073 \AA$ pertains to MP2 and DFT results on a variety of complexes tabulated in Tables 37 and 38.

One general feature of these MM bond length ranges is the MM-bond lengthening effect of the carbonyl ligands in many cases, as noted in the experimental and the computational data sets. This effect is noted for single, double and triple bonds, being particularly marked in the earlier transition metals, but noticeably less evident for binuclear manganese complexes. The binuclear iron, cobalt, and nickel complexes also exhibit this effect. Previous sections have mentioned the back-bonding effect of pi acid ligands like CO, which may be a primary factor responsible for the lengthening of MM bonds in binuclear carbonyl complexes.

### 13.4 Quadruple and Quintuple MM Bond Length Ranges

While single, double and triple MM bonds are found in binuclear complexes of all the metals titanium to nickel (either experimentally or computationally), this is not so for MM quadruple and quintuple bonds. Experimentally, among the first row transition metals, MM bonds of such high order have been discovered experimentally among 3d block complexes only for binuclear chromium complexes (sub-sections 6.3, 6.4 and 6.5 ), and these have been well
studied by computational and theoretical approaches (sub-section 6.6). Computational studies have predicted quadruple and quintuple MM bonds in isolated cases of binuclear complexes having other metals like titanium, vanadium, manganese, and iron. The MM bond length ranges are given in Table 42, with the experimental ranges being highlighted in bold.

Table 42. MM Quadruple and Quintuple Bond Length Ranges for First Row d-Block Binuclear Complexes (Experimental Ranges in Bold) ${ }^{a}$

| Metal | Quadruple bond length range | Quintuple bond length range |
| :---: | :---: | :---: |
| Titanium | 2.646 (DFT value) |  |
| Vanadium | 2.333 (DFT value) |  |
| Chromium |  |  |
| Exptl. range Remarks | $2.05 \pm 0.22$ <br> Paddlewheels (no axial ligands) | 1.77 $\pm \mathbf{0 . 0 . 0 7}$ <br> All known complexes |
| Exptl. range Remarks | $2.38 \pm 0.16$ <br> Paddlewheels with axial ligands | $1.82 \pm 0.01$ <br> Bis(terphenyl) complexes |
| Exptl. range Remarks | $\begin{aligned} & \mathbf{1 . 8 5} \pm \mathbf{0 . 0 2} \\ & \text { Tetra(alkoxyphenyl)s } \end{aligned}$ | $1.75 \pm 0.05$ <br> With two N -ligands |
| Exptl. range Remarks | $2.09 \pm 0.19$ <br> Tetraformamidinates |  |
| BP86 range Remarks | $2.24 \pm 0.05$ <br> With carbonyl ligands | 1.993 <br> With carbonyl ligands |
| Manganese |  |  |
| BP86 range | $2.20 \pm 0.13$ (carbonyl complexes) | 1.879 (carbonyl complex) |
| Iron |  |  |
| BP86 range | $2.03 \pm 0.04$ (carbonyl complexes) |  |

[^24]BP86 results predicted a Ti-Ti quadruple bond in the dicyclopentadienyl cyclooctatetraene dititanium complex $\mathrm{Cp}_{2}(\mathrm{COT}) \mathrm{Ti}_{2},{ }^{84}$ having an $R_{M M}$ value of $2.646 \AA$. This study also found a

V-V quadruple bond in a singlet minimum of the corresponding divanadium complex with a shorter $R_{M M}$ value of $2.333 \AA$.

The experimental $R_{M M}$ range for $\mathrm{Cr}-\mathrm{Cr}$ quadruple bonds in all dichromium tetragonal paddlewheel complexes with bidentate $(\mathrm{X}-\mathrm{C}=\mathrm{Y})^{-}$type ligands and without axial ligands is found to be $2.050 \pm 0.222 \AA$. The lowest range here is seen in the tetra(alkoxyphenyl) series $(1.845 \pm 0.017 \AA)$ and the highest in the tetraformamidinate series $(2.087 \pm 0.185 \AA)$. Axial ligands in dichromium tetracarboxylates and carboxamidates lengthen $R_{M M}$ values by about $0.42 \AA$. No computational studies have yielded any global geometry optimizations of any non-carbonyl dichromium paddlewheels, so precise computationally-derived values for $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond lengths in this particular set of complexes are not yet available. Experimental $R_{M M}$ ranges or values for MM quadruple bonds in binuclear non-carbonyl complexes given in Table 42 thus follow the general order $\mathrm{Ti}>\mathrm{V}>\mathrm{Cr}$, which is in line with the $\mathrm{R}_{\text {cov }}$ values of Table 1.

Regarding MM quadruply bonded binuclear carbonyl complexes, BP86 studies predict the $R_{M M}$ range $2.24 \pm 0.05 \AA$ for $\mathrm{Cr}-\mathrm{Cr}$ quadruple bond lengths in two binuclear chromium carbonyl complexes, which is longer than the experimental range for the above non-carbonyl paddlewheel complexes. The BP86 results for binuclear manganese carbonyl complexes gives the $R_{M M}$ range $2.20 \pm 0.13 \AA$ for $\mathrm{Mn}-\mathrm{Mn}$ quadruple bonds. The BP86 range for iron-iron quadruple bond lengths in binuclear iron carbonyl complexes is lower at $2.03 \pm 0.04 \AA$. MM quadruple bonds in binuclear cobalt, nickel, copper, and zinc complexes are yet unknown experimentally and computationally. The $R_{M M}$ ranges for MM quadruple bonds in binuclear metal carbonyl complexes thus follow the order $\mathrm{Cr}>\mathrm{Mn}>\mathrm{Fe}$, which is in line with the $\mathrm{R}_{\mathrm{cov}}$ values of Table 1.

Quintuple bond length ranges in dichromium complexes are also shown in Table 42. The shortest MM bond known in any experimentally known binuclear complex is seen in the
dichromium bis(formamidinate) complex $\mathbf{0 7}$ of Table 12, with an $R_{M M}$ value of only 1.704 $\AA .{ }^{238}$ The first type of quintuply-bonded dichromium complexes - the bis(terphenyl) type yields the experimental range $1.82 \pm 0.01 \AA$. The second type - with substituted $N$-ligands like diazadiene, formamidinate and guanidinate - gives shorter $\mathrm{Cr}-\mathrm{Cr}$ quintuple bonds whose lengths fall within the range $1.75 \pm 0.05 \AA$. The overall experimental range for $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond lengths in dichromium complexes is thus $1.77 \pm 0.07 \AA$. As discussed above, $\mathrm{Cr}-\mathrm{Cr}$ quintuple bond lengths derived from computational studies on these two types of dichromium non-carbonyl complexes are shorter than the corresponding experimental values. However, for one dichromium carbonyl complex (structure 11 of Table 14), the BP86 value for the Cr Cr quintuple bond length is $1.993 \AA$, longer than the above experimental ranges. Apart from dichromium complexes, DFT studies predict a $\mathrm{Mn}-\mathrm{Mn}$ quintuple bond in a dimanganese carbonyl complex (structure $\mathbf{0 7}$ of Table 17) with a length of $1.879 \AA$.

### 13.5 Effects of Change in Metal upon MM Bond Length Ranges

The experimental and computational data of Tables 41 and 42 may be used to discern effects of change in the metal M of the bimetallic core $\left(\mathrm{M}_{2}\right)^{n+}$ upon the range of MM bond distances in first row binuclear complexes for MM bond orders ranging from single to quintuple. The limited number of systems from which data can be drawn may, however, in many cases, prevent us from attaching much statistical significance to these inferences.

Experimental MM single bond length ranges for non-carbonyl complexes give the steady trend $\mathrm{Ti}>\mathrm{V}>\mathrm{Fe}>\mathrm{Co}$ which is consistent with the trends for the $\mathrm{R}_{\mathrm{cov}}$ and $\mathrm{R}_{\mathrm{cv}}(1)$ values (Table 1). No experimental example of a $\mathrm{Cr}-\mathrm{Cr}$ single bond is known in a non-carbonyl system, and the binuclear manganese systems present an anomaly here. Binuclear nickel complexes also give higher single MM bond ranges than binuclear cobalt complexes. However, the trend $\mathrm{Ni}>\mathrm{Cu}>\mathrm{Zn}$ does seem evident for MM single bond length ranges.

The experimental MM double bond length ranges do not present very consistent trends. Apart from the sole dititanium example and the lack of dimanganese examples, the trend (mostly for non-carbonyl complexes) from divanadium onwards is as follows: $\mathrm{V}>\mathrm{Cr}<\mathrm{Fe}$ (CO and non-CO) $>\mathrm{Co}<$ Ni. Here, the trends $\mathrm{Cr}<\mathrm{Fe}$ and $\mathrm{Co}<\mathrm{Ni}$ do not follow the trends seen in the $\mathrm{R}_{\mathrm{cv}}(2)$ values of Table 1, where the trends are $\mathrm{Cr}>\mathrm{Fe}$ and $\mathrm{Co}>\mathrm{Ni}$.

Experimental MM triple bond length ranges are available for vanadium, chromium, manganese, and iron. Excluding the dimer $\mathrm{V}_{2}$ and divanadium paddlewheels, the trend is $\mathrm{V}>$ $\mathrm{Cr}>\mathrm{Mn}$ (one case) $>\mathrm{Fe}$, consistent with values of the triply bonded metal covalent radii $\mathrm{R}_{\mathrm{cv}}(3)$ of Table 1.

From the computational side, the MM single bond length ranges predicted from theoretical (mostly DFT) results follow the trend $\mathrm{Ti}>\mathrm{V}<\mathrm{Cr}>\mathrm{Mn}>\mathrm{Fe}>\mathrm{Co}<\mathrm{Ni}>\mathrm{Cu}>\mathrm{Zn}$. These ranges pertain to binuclear metal complexes with carbonyl ligands for most cases, except for Cu and Zn . The overall ranges for all carbonyl-containing complex series are taken for Mn , Fe and Co . The range for chromium seems anomalous since only weakly-bonded dichromium systems are available from computations, but the experimental $R_{M M}$ value of $2.99 \AA$ for the $\left[\mathrm{Cr}_{2}(\mathrm{CO})_{10}\right]^{2-}$ anion may seem more in place. The trend $\mathrm{Co}<\mathrm{Ni}$ also does not follow the trend shown by the $\mathrm{R}_{\mathrm{cov}}$ and $\mathrm{R}_{\mathrm{cv}}(1)$ values of Table 1 .

The MM double bond length ranges, mostly for binuclear metal carbonyl complexes, as predicted from BP 86 , follow the trend $\mathrm{Ti}>\mathrm{V}>\mathrm{Cr}>\mathrm{Mn}>\mathrm{Fe}>\mathrm{Co}<\mathrm{Ni}>\mathrm{Cu}$. Here the overall ranges for all carbonyl-containing complex series are taken for $\mathrm{Cr}, \mathrm{Mn}, \mathrm{Fe}$, and Co , while the two homoleptic nickel complex series and the solitary case of coaxial $\mathrm{Cp}_{2} \mathrm{Cu}_{2}$ represent Ni and Cu respectively. This trend is consistent with that shown by the $\mathrm{R}_{\mathrm{cv}}(2)$ values of Table 1, except for the binuclear nickel carbonyls, where the trend is $\mathrm{Co}<\mathrm{Ni}$.

The MM triple bond length ranges for binuclear metal carbonyl complexes, as derived from BP86 results, follow the trend: $\mathrm{Ti}>\mathrm{V}>\mathrm{Cr} \approx \mathrm{Mn}>\mathrm{Fe}<\mathrm{Co}<\mathrm{Ni}$, where the ranges for
$\mathrm{Mn}, \mathrm{Fe}$, and Co cover all carbonyl-containing complex series. Upon comparing with the $\mathrm{R}_{\mathrm{cv}}(3)$ values, only the trend $\mathrm{Fe}<\mathrm{Co}$ seems anomalous. The increased range for binuclear nickel carbonyls reflects the increase in the $\mathrm{R}_{\mathrm{cv}}(3)$ value of nickel as compared with cobalt.

It is thus evident that size of the metal atom, as indicated by the covalent radius (whether for single, double or triple bonds), has an appreciable impact upon MM bond length ranges for single, double, and triple MM bonds, especially for the earlier transition metals. Other effects like metal electropositivity and oxidation state are not treated here, and may be linked with anomalies shown, especially for cobalt and nickel.

Experimental MM quadruple and quintuple bond length ranges are available only for dichromium complexes among the first transition metal series. Comparisons may be made between the experimental results for axially ligated dichromium paddlewheels and the limited theoretical predictions for binuclear manganese and iron complexes, where the trend $\mathrm{Cr}>\mathrm{Mn}$ $>$ Fe may be discerned, which is in line with the general estimates for covalent radii of these metals.

## 14. BOLD OR FOOLHARDY FINAL ESTIMATES OF METAL-METAL BOND DISTANCES

The patient reader will understand that we have been cautious in assigning specific bond distances to particular metal-metal bonds. This may be seen in the many error bars used and the discussion surrounding these uncertainties.

However, most good chemists know that carbon-carbon single, double and triple bonds have lengths of about $1.54,1.35$ and $1.21 \AA$, respectively. Quite naturally, many chemists have wanted similar unambiguous distances for metal-metal bonds.

Therefore, we now throw caution to the wind and propose such distances. These final estimates are given in Table 43. We hope that this Table will encourage experimental scientists to press on toward synthesizing, for example, an organometallic complex with a vanadium-vanadium quadruple bond. And we challenge theorists to use high level theoretical methods to improve upon our estimates for these metal-metal bond distances.

Table 43. "Best" Distances (in $\AA$ ) for Metal-Metal Bonds (Single to Quintuple) in Binuclear Complexes of Metals Titanium through Zinc, with Values for Non-Carbonyl Complexes without Brackets and for Carbonyl Complexes within Brackets.

| $\mathrm{MM} \mathrm{BO}^{a}$ | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Single | $\begin{gathered} 2.74 \\ (3.35) \end{gathered}$ | $\begin{gathered} 2.67 \\ (3.00) \end{gathered}$ | $(\stackrel{\ddot{c}}{(2.99)}$ | $\begin{gathered} 2.74 \\ (2.76) \end{gathered}$ | $\begin{gathered} 2.51 \\ (2.74) \end{gathered}$ | $\begin{aligned} & 2.38 \\ & (2.49) \end{aligned}$ | $\begin{aligned} & 2.46 \\ & (2.62) \end{aligned}$ | $\begin{gathered} 2.44 \\ (2.55) \end{gathered}$ | $\begin{aligned} & 2.38 \\ & (. . .) \end{aligned}$ |
| Double | $\begin{aligned} & 2.36 \\ & (3.21) \end{aligned}$ | $\begin{gathered} 2.40 \\ (2.85) \end{gathered}$ | $\begin{gathered} 2.20 \\ (2.60) \end{gathered}$ | $(2.51)$ | $\begin{gathered} 2.35 \\ (2.44) \end{gathered}$ | $\begin{aligned} & 2.26 \\ & (2.38) \end{aligned}$ | $\begin{aligned} & 2.31 \\ & (2.44) \end{aligned}$ | $\begin{aligned} & 2.22 \\ & (. .) \end{aligned}$ | ( .. ) |
| Triple | (2.78) | $\begin{gathered} 2.35 \\ (2.43) \end{gathered}$ | $\begin{gathered} 2.31 \\ (2.39) \end{gathered}$ | $(2.36)$ | $\begin{gathered} 2.09 \\ (2.20) \end{gathered}$ | $(2.23)$ | (2.38) | ( ... ) | ( .. ) |
| Quadruple | $\begin{aligned} & 2.65 \\ & (. .) \end{aligned}$ | $\begin{aligned} & 2.33 \\ & (. .) \end{aligned}$ | $\begin{gathered} 2.05 \\ (2.34) \end{gathered}$ | $(2.20)$ | (2.03) |  |  |  |  |
| Quintuple | $\binom{. .}{(. .}$ | ( ... ) | $\begin{gathered} 1.77 \\ (1.99) \end{gathered}$ | $(1.88)$ |  |  |  |  |  |

[^25]Table 43 contains entries for non-carbonyl binuclear complexes (without brackets) and for binuclear complexes with carbonyl ligands (within brackets). This distinction is made on the basis of the marked MM bond lengthening effect of carbonyl ligands. In most cases, these values are derived from the median value within a given range, as noted in the previous Sections for experimentally characterized as well as computationally studied series of binuclear complexes. In some cases, the value entered is taken from a single example.

Estimates for $\mathrm{Ti}-\mathrm{Ti}$ bond distances are proposed here for single, double, triple and quadruple $\mathrm{Ti}-\mathrm{Ti}$ bonds. The $\mathrm{Ti}-\mathrm{Ti}$ single and double bond length estimates for non-carbonyl complexes are taken from the ranges given in Table 41 for experimentally characterized noncarbonyl complexes. While there is no result on $\mathrm{Ti} \equiv \mathrm{Ti}$ triple bond lengths in non-carbonyl complexes, the $\mathrm{Ti} \equiv \mathrm{Ti}$ quadruple bond length estimate for non-carbonyl complexes is based on a single example studied by DFT. For carbonyl complexes, the estimates for Ti-Ti single, double, triple, and quadruple bond distances are derived from the DFT results of Table 2, since no binuclear titanium complex with carbonyl ligands is experimentally known.

Estimates for V-V bond distances are given for single, double, triple and quadruple bonds. For non-carbonyl complexes, the estimates for single, double, and triple bond lengths are based on the ranges entered in Table 41 for experimentally characterized structures, extended to include the $\mathrm{V} \equiv \mathrm{V}$ triple bond length range $2.43 \pm 0.04 \AA$ for two carbonyl complexes. The quadruple bond length estimate is taken from a single example studied by DFT. For carbonyl complexes, the estimates for single, double, and triple bond lengths are derived from the DFT results of Table 6. Note that, as for titanium, no quadruple or quintuple bonds have been found in binuclear vanadium carbonyl complexes.

Estimates for $\mathrm{Cr}-\mathrm{Cr}$ bond distances span the range from single to quintuple bonds. The estimates for non-carbonyl complexes cover $\mathrm{Cr}-\mathrm{Cr}$ bonds from double to quintuple, and are
based on experimental results. For carbonyl complexes, the estimates are taken from DFT results as well as experimental studies (mostly the former).

Estimates for $\mathrm{Mn}-\mathrm{Mn}$ bond distances span the range from single to quintuple bonds. For non-carbonyl complexes, bond length estimates are available only for single $\mathrm{Mn}-\mathrm{Mn}$ bonds, and based on experimental results. For carbonyl complexes, bond length estimates are given for single, double, triple, quadruple, and quintuple Mn-Mn bonds, being taken from DFT results.

Estimates for $\mathrm{Fe}-\mathrm{Fe}$ bond distances are given for single, double, triple, and quadruple Fe Fe bonds, where $\mathrm{Fe}-\mathrm{Fe}$ quintuple bonds are unknown experimentally and theoretically. For non-carbonyl complexes, the estimates for single, double, and triple bond lengths are taken from experimental results. For carbonyl complexes, bond length estimates span the range from single to quadruple bonds, these being derived from DFT results.

Estimates for Co-Co bond distances and for $\mathrm{Ni}-\mathrm{Ni}$ bond distances are given only for single, double, and triple bonds. For non-carbonyl complexes, the estimates are based on experimental results for single and double bonds. For carbonyl complexes, the estimates are derived from DFT results.

Estimates for $\mathrm{Cu}-\mathrm{Cu}$ bond distances are available for single and double bonds. The single bond length estimate for non-carbonyl complexes is taken from experimental results, while that for carbonyl complexes is derived from DFT studies. The estimate for double bonds is taken from DFT studies (a single example of a non-carbonyl complex).

The estimate for the $\mathrm{Zn}-\mathrm{Zn}$ single bond length in non-carbonyl complexes is taken from experimental studies. No binuclear zinc complex with carbonyl ligands is known.

It may be deduced by inspection of Table 43 that, for the dichromium and dimanganese series of carbonyl complexes, the bond length estimates follow the order of magnitude: single
$>$ double $>$ triple $>$ quadruple $>$ quintuple. For the metals vanadium, iron, cobalt, and nickel, the expected trend single $>$ double $>$ triple may be discerned.

Across the row, the monotonic trend with respect to metal is $\mathrm{Ti}>\mathrm{V}>\mathrm{Cr}>\mathrm{Mn}>\mathrm{Fe}>\mathrm{Co}$, which is seen for single, double and triple bonds in carbonyl complexes. This trend is not continued for the metals $\mathrm{Ni}, \mathrm{Cu}$ and Zn , which disruption of trend is also noted for the various covalent radii of Table 1.

Finally, the MM bond-lengthening effects of carbonyl ligands are clearly made evident by comparing these bond length estimates for non-carbonyl complexes with those for carbonyl complexes. The bond lengths for non-carbonyl complexes are invariably longer than those for carbonyl complexes, where the increase in bond length ranges from 0.07 to $0.33 \AA$. This does not, however, seem to apply to $\mathrm{Mn}-\mathrm{Mn}$ single bond lengths, for which the estimate for noncarbonyl complexes is quite close to that for carbonyl complexes.

## 15. SUMMARY AND CONCLUSIONS

This review constitutes the only comprehensive collection to date of both experimental and theoretical results for metal-metal bond distances for binuclear 3d block metal complexes. In fact, such a collection has not yet been made available for complexes of the second and third period d-block metals, nor for any other group of metal complexes. A variety of factors impacting MM bond lengths are discussed and some trends discerned. The results of computational studies, based largely on DFT methods, provide reliable predictions of metalmetal distances that go far beyond the relatively limited information available on experimentally known binuclear first row transition metal derivatives through structure determinations by X-ray crystallography. Such information provides an opportunity to enhance considerably our understanding of the metal-metal bonding in such systems. From this information the following factors affecting metal-metal distances in binuclear derivatives of the first row transition metals from titanium to zinc have been identified:
(a) the formal MM bond order (assigned by inspection) which enables observation of the expected trend that, for a given metal, the MM bond length range (represented by the median value) decreases as the bond order increases.
(b) size of the metal ion present in the bimetallic core $\left(\mathrm{M}_{2}\right)^{n+}$, which shows a general trend of longer MM bond lengths with larger metal covalent radius, seen more in the earlier transition metals than in the later (for which effects like electropositivity may need to be also taken into consideration).
(c) the metal oxidation state, where higher oxidation states tend to promote shorter MM bond lengths for the earlier 3d metal cases (due to decreased ionic size) but longer MM bond lengths for the later 3d metal cases (due to electrostatic repulsion effects).
(d) effects of the ligand, which include the MM bond lengthening effect of the CO ligand due to $\mathrm{M} \rightarrow \mathrm{CO}$ back bonding, MM bond shortening effects of basicity for electron donor ligands, MM bond lengthening of axial ligands in paddlewheel complexes, and steric effects of bulky ligands which can promote high bond orders and short MM distances.

It emerges that while specific factors for a limited range of metal complexes are found to have their expected impact in many cases, the net effect of these factors together is challenging to assess on an a priori basis for a wide range of diverse binuclear transition metal complexes. Computational methods may be used to monitor the various factors individually by studies on various series of structurally related complexes, each series dealing with just a single factor.

Correlations between experimental and computational data often exhibit close coincidences between experimental and computationally derived MM bond lengths. Computational approaches have enabled study of the effects of change in the metal upon MM bond length ranges in binuclear complexes which suggest trends for single, double, triple, and quadruple MM bonds which are related to the available data on metal atomic radii. The final estimates for MM bond distances for all the MM bonds reviewed here (single to quintuple, titanium through zinc), proposed here for the first time, would be of interest to synthetic and structural chemists, as well as to computational chemists.

Finally, the following points may be made concerning some directions and prospects that lie ahead for the field of binuclear metal complexes:
(1) Computational methods of greater rigor and accuracy will eventually provide new insights into the nature of the MM bond in binuclear complexes. Such studies would be able to characterize the presence of covalent, dative and polar MM bonding, besides analyzing ligand bridging interactions like three-centre two-electron bonding or probing the nature of antiferromagnetic interactions. This largely remains as a challenge to date.
(2) Computational studies may also help move towards the design of synthetically viable binuclear complexes through predictions of kinetic and thermodynamic stability.
(3) The approaches developed here for 3d block metal binuclear complexes may be extended and applied to 4 d and 5d block metal complexes, besides tri- and polynuclear metal complexes of all three TM periods, as well as such complexes of the 4 f block elements.
(4) Applications of the chemistry of binuclear metal complexes can continue to be developed for use in the fields of catalysis, design of complex molecular architectures, as well as material science.

## SUPPLEMENTARY INFORMATION

Details of how formal bond orders for metal-metal bonds in 3d metal binuclear complexes may be derived by electron counting are incorporated for some representative cases. This material is available free of charge at http://pubs.acs.org.

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## ABBREVIATIONS

| Ad | 1-adamantyl |
| :--- | :--- |
| ANO | atomic natural orbital |
| ap | dianion of 2-anilinopyridine |
| $\mathrm{Ar}^{\mathrm{Xyl}}$ | 2,6-dimethylphenyl |
| CASPT2 | multiconfigurational second order perturbation method |
| CASSCF | complete active space self-consistent field |
| cBO | computed bond order |
| chp | 6-chloro-2-hydroxypyridine anion |
| CI | configuration interaction |
| COT | cycloocta-1,3,5,7-tetraene |
| Cp | $\eta^{5}$-C5 $\mathrm{H}_{5}$ (cyclopentadienyl) |
| Cp | $\eta^{5}$-C ${ }_{5} \mathrm{Me}_{5}$ (permethylcyclopentadienyl) |
| Cy | cyclohexyl |
| DAniF | $\mathrm{N}, \mathrm{N}^{\prime}$-di-p-anisylformamidinate anion |
| $\mathrm{D}^{\mathrm{Cl}} \mathrm{PhF}$ | $\mathrm{N}, \mathrm{N}^{\prime}$-di- $p$-chlorophenylformamidinate anion |
|  |  |


| DCyF | N.N'-dicyclohexylformamidinate anion |
| :---: | :---: |
| DFT | density functional theory |
| Dipp | 2,6-diisopropylphenyl |
| DMP | 2,6-dimethoxyphenyl anion |
| dmhp | 2,4-dimethyl-6-hydroxypyrimidine anion |
| DPhF | N,N'-diphenylformamidinate anion |
| dppa | bis(diphenylphosphino)amine |
| dppm | bis(diphenyl |
| DTolA | N,N'-di-p-tolylamidinate anion |
| DTolF | N.N'-di-p-tolylformamidinate anion |
| DZP | double zeta plus polarization |
| eBO | effective bond order |
| edt | ethanedithiolate |
| fBO | formal bond order |
| fhp | 6-fluoro-2-hydroxypyridine anion |
| FSR | formal shortness ratio |
| HF | Hartree-Fock |
| hpp | anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine |
| $L^{\text {Ph }}$ | a phenyl substituted tris(amidinato)amine ligand |
| LSDA | local spin density approximation |
| M05-2X | Minnesota 05 global hybrid functional (56\% HF exchange) |
| M06-L | Minnesota 06 local functional (0\% HF exchange) |
| map | 6-methyl-2-aminopyridine anion |
| Mes | 2,4,6-trimethylphenyl (mesityl) |
| mhp | 6-methyl-2-hydroxypyridine anion |
| NHC | N-heterocyclic carbene |
| $\mathrm{NN}^{\text {tBu }}$ | 2-tert-butylformamidinate |
| NN ${ }^{\text {NCy2 }}$ | N2,N2-dicyclohexylguanidinate |
| PAH | polycyclic aromatic hydrocarbon |
| $\mathrm{py}_{3}$ tren | trideprotonated N,N,N-tris(2-(2-pyridyl-amino)ethyl)amine |
| $\mathrm{R}_{\text {cal }}$ | atomic radii from Clementi ${ }^{42}$ |
| $\mathrm{R}_{\text {cov }}$ | covalent radii from Cordero et al. |
| $\mathrm{R}_{\mathrm{cv}}(1)$ | single-bond covalent radii |

$\mathrm{R}_{\mathrm{cv}}(2) \quad$ double-bond covalent radii
$\mathrm{R}_{\mathrm{cv}}(3) \quad$ triple-bond covalent radii
$\mathrm{R}_{\text {met }} \quad$ metallic radii
RHF restricted Hartree-Fock
QTAIM Bader's quantum theory of atoms in molecules
SCF self-consistent field
SDCI single and double-excitation configuration interaction
THF tetrahydrofuran
TIPP 2,4,6-triisopropylphenyl
TM transition metal
TMP 2,4,6-trimethoxyphenyl anion
tmp 2,2,6,6,-tetramethylpiperidine
TPG $\mathrm{N}, \mathrm{N}$ ', N "-triphenylguanidinate anion
TZ2P triple zeta double polarization
UHF unrestricted Hartree-Fock
XRD X-ray diffraction
Xyl xylyl
ZORA zero-order regular approximation (relativistic Hamiltonian)

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[^0]:    ${ }^{a}$ Abbreviation for configuration [Ar] $3 d^{m} 4 s^{\mathrm{m}}$
    ${ }^{b}$ Numbers in brackets refer to standard deviations

[^1]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^2]:    ${ }^{a}$ salophen $=N, N^{\prime}$-o-phenylene-bis(salicylideneiminato)

[^3]:    ${ }^{a} \mathrm{TCNQ}=$ tetracyanoquinodimethane

[^4]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^5]:    ${ }^{a}$ Two crystallographically independent $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ molecules in the cell
    ${ }^{b}$ Notation indicates one axial ligand connects $\mathrm{Cr}_{2}(\mathrm{OOCR})_{4}$ molecules
    ${ }^{c}$ 2,4,6-triisopropylphenyl ${ }^{d}$ Carbonate anion $\quad{ }^{e} \mathrm{Cr}$ to ring center

[^6]:    ${ }^{a} \mathrm{hpp}=$ a bicyclic guanidinate $\quad{ }^{b} \mathrm{THP}=$ tetrahydropyrrol $-N$-ide

[^7]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^8]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^9]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^10]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^11]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^12]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^13]:    * $R_{M M}$ values in angstrom; $\Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^14]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^15]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^16]:    ${ }^{a}$ Two independent crystal structure determinations
    ${ }^{b} \mathrm{Qu}=$ quinuclidine
    ${ }^{c}$ Two independent molecules

[^17]:    ${ }^{a} \Delta \mathrm{E}$ in $\mathrm{kcal} / \mathrm{mol}$

[^18]:    ${ }^{a} \mathrm{tmp}=$ 2,2,6,6-tetramethylpiperidino
    ${ }^{b}$ Ar' $=2,6$-bis(2,6-diisopropylphenyl)(phenyl)
    ${ }^{c} \mathrm{~L}=\mathrm{N}, \mathrm{N} \cdot$ - $\operatorname{dipp}_{2}(\mathrm{NC}(\mathrm{Me}) \mathrm{C}(\mathrm{Me}) \mathrm{N}$ (an $\alpha$-diimine ligand)

[^19]:    ${ }^{a}$ One Ni-Ni bond length; the other is 2.351 (1) $\AA$

[^20]:    ${ }^{a}$ Me-nacnac $=\left\{\left(2,6-\mathrm{Me}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{NC}(\mathrm{Me})\right\}_{2} \mathrm{CH}$
    ${ }^{b}$ Me-nacnac* $=\left\{\left(2,4,6-\mathrm{Me}_{3}-\mathrm{C}_{6} \mathrm{H}_{3}\right) \mathrm{NC}(\mathrm{Me})\right\}_{2} \mathrm{CH}$

[^21]:    ${ }^{a}$ Single point ANO-QCISD(T) results

[^22]:    ${ }^{a}$ dipp-bian $=1,2$-bis[(2,6-diisopropylphenyl)imino]acenaphthene
    ${ }^{b}$ phen-bian $=1,2$-bis $[($ phenyl $)$ imino $]$ acenaphthene

[^23]:    ${ }^{a}$ Experimental value (Ref. 269)

[^24]:    ${ }^{a}$ Bond distances in $\AA$

[^25]:    ${ }^{a}$ Metal-metal bond order

