

Higher Spin States in Some Low-Energy Bis(Tetramethyl-1,2-diaza-3,5-diborolyl) Sandwich Compounds of the First Row Transition Metals: Boraza Analogues of the Metallocenes

Jianlin Chen,^{a*} Hao Feng,^a Yaoming Xie,^b R. Bruce King,^{a,b*} Henry F. Schaefer^b

^a*School of Science, Research Center for Advanced Computation
Xihua University, Chengdu, China 610039*

^b*Department of Chemistry and Center for Computational Chemistry
University of Georgia, Athens, Georgia 30602, USA
E-mail: rbking@chem.uga.edu, chenjianlin2000@163.com*

Abstract

The known sandwich compound $[\eta^5\text{-(CH}_2)_3\text{N}_2\text{(BPh)}_2\text{CMe}]_2\text{Fe}$ in which adjacent C_2 units are replaced by isoelectronic BN units can be considered as a boraza analogues of ferrocene similar to borazine, $\text{B}_3\text{N}_3\text{H}_6$, considered as a boraza analogue of benzene. In this connection, the related bis(1,2,3,5-tetramethyl-1,2-diaza-3,5-diborolyl) derivatives $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ ($\text{M} = \text{Ti, V, Cr, Mn, Fe, Co, Ni}$) for all of the first row transition metals have been optimized using density functional theory for comparison with the isoelectronic tetramethylcyclopentadienyl derivatives $(\text{Me}_4\text{C}_5\text{H})_2\text{M}$. Low-energy sandwich structures having parallel $\text{B}_2\text{N}_2\text{C}$ rings in a *trans* orientation are found for all seven metals. The 1,2-diaza-3,5-diborolyl ligand appears to be a weaker field ligand than the isoelectronic cyclopentadienyl ligand as indicated by higher spin ground states for some $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ sandwich compounds relative to the corresponding metallocenes $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{M}$. Thus $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Cr}$ has a quintet ground state in contrast to the triplet ground state of $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Cr}$. Similarly, the sextet ground state of $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Mn}$ lies ~ 18 kcal/mol below the quartet state in contrast to the doublet ground state of the isoelectronic $(\text{Me}_4\text{C}_5\text{H})_2\text{Mn}$. These sandwich compounds are potentially accessible by reaction of 1,2-diaza-3,5-diborolide anions with metal halides analogous to the synthesis of $[\eta^5\text{-(CH}_2)_3\text{N}_2\text{(BPh)}_2\text{CMe}]_2\text{Fe}$.

1. Introduction

Replacement of adjacent pairs of carbon atoms in cyclic hydrocarbons with isoelectronic BN units leads to inorganic boraza analogues of familiar hydrocarbons. For example, borazine or “inorganic benzene,” $B_3N_3H_6$, is the boraza analogue of benzene obtained by complete replacement of the three C_2 units in the six-membered ring of benzene with BN units. Molecular orbital calculations and experimental results for the transmission of substituent effects through the B_3N_3 ring indicate only partial delocalization of the π electrons in borazine as compared with their complete delocalization in benzene [1, 2]. Nevertheless, hexamethylborazine forms a stable chromium tricarbonyl complex (η^6 -Me₆B₃N₃)Cr(CO)₃ (Figure 1) [3, 4] analogous to the well-known benzene chromium tricarbonyl (η -C₆H₆)Cr(CO)₃ and its derivatives.

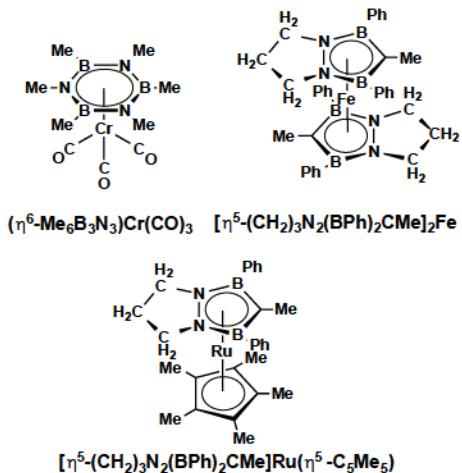


Figure 1. Metal complexes of borazine and diazadiborolyl ligands that have been synthesized.

This paper explores the structures and spin states of the boraza analogues of the metallocenes. An initial step in this direction was taken in 2002 by Fu and coworkers [5]. They used indirect synthetic methods to replace a pair of carbon atoms in one of the cyclopentadienyl rings of ferrocene by an BN pair to give the pentahapto 1,2-azaborolyl-iron derivatives $[\eta^5\text{-C}_3\text{H}_3\text{N}(\text{tBu})\text{BX}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ (X = H, F, allyl, OMe, NMe₂, etc.). More extensive substitution of adjacent carbon pairs in ferrocene with BN units to the limit of a ($\eta^5\text{-R}_5\text{B}_2\text{N}_2\text{C}$)₂Fe derivative was achieved by Roesler and coworkers [6, 7]. They synthesized a diazadiborolyl anion, which was subsequently used to prepare a substituted boraza analogue of ferrocene, namely $[\eta^5\text{-}(\text{CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$ as well as the mixed ruthenium sandwich compound $[\eta^5\text{-}(\text{CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)$ (Figure 1) [8].

The laboratory availability of the $[\eta^5\text{-}(\text{CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]^-$ anion suggests the possibility of synthesizing boraza analogues of the entire series of the first row transition metal metallocenes similar to the ferrocene analogue $[\eta^5\text{-}(\text{CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$. We report here the use of density functional theory to explore the preferred structures and spin states of the boraza metallocene analogues $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). The diazadiborole ligand with methyl substituents on the boron and nitrogen atoms was chosen as the simplest reasonable model for the experimental systems.

Experimental studies by Roesler and coworkers on $[\eta^5\text{-}(\text{CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$ [6] as well as the earlier studies by Fu and coworkers [5] showed the boraza analogues of the cyclopentadienyl ligand to be more electron-donating than the cyclopentadienyl ligand itself. In this connection our studies on the $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ metallocene analogues predict a greater preference for higher spin states relative to the $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}$ and $(\eta^5\text{-Me}_4\text{C}_4\text{H})_2\text{M}$ metallocenes. Particularly noteworthy is the energetic preference for a sextet spin state for the manganese derivative $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Mn}$ by nearly 18 kcal/mol. In addition a quintet spin state for the chromium derivative $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Cr}$ is found to be energetically competitive with the triplet spin state, which is the clear ground state for the cyclopentadienyl analogues $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}$ [9] and $(\eta^5\text{-Me}_4\text{C}_4\text{H})_2\text{Cr}$.

2. Theoretical Methods

Density functional theory (DFT), including electron correlation effects, is a powerful computational tool that has been successfully used in organotransition metal chemistry [10,11,12,13,14,15,16]. Two DFT methods were used for this work. The first method is the hybrid HF/DFT functional B3LYP* [17,18], which is the modified B3LYP functional [19,20] in order to provide electronic state orderings in good agreement with experiment [21]. The second method is a meta-GGA DFT method M06-L developed by Truhlar's group [22]. The M06-L method is found to predict energy differences close to the experimental values for the transition metal chemistry [23]. We discuss the M06-L results in the text, while the B3LYP* results are listed in the Supporting Information. In fact, the energy orderings predicted by the B3LYP* method are generally consistent with those predicted by the M06-L method.

The double- ζ plus polarization (DZP) basis sets used in this paper for the boron, carbon, and nitrogen atoms add one set of pure spherical harmonic d functions with orbital exponents, $\alpha_d(\text{B}) = 0.70$, $\alpha_d(\text{C}) = 0.75$, and $\alpha_d(\text{N}) = 0.80$, to the standard Huzinaga-Dunning contracted DZ sets and are denoted as $(9s5p1d/4s2p1d)$ [24, 25]. For hydrogen, a set of p polarization functions $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga-Dunning DZ sets. For the transition metal atoms, our loosely contracted DZP basis set

(14s11p6d/10s8p3d) uses the Wachters' primitive set [26] augmented by two sets of p functions and one set of d functions contracted following Hood, Pitzer, and Schaefer [27].

All computations were carried out using the Gaussian 09 program [28]. For the M06-L functional the (120,974) grid was used for numerical evaluation of the integrals. In the present paper the $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ structures are designated using the format **M-x-n**, where **M** stands for the transition metal, **x** for the spin state, and **n** for the angle in degrees between the H-CB₂N₂ bond in each ring projected onto a plane of the other ring. The spin multiplicities are indicated by **s**, **d**, **t**, **q**, **p**, and **x** for singlets, doublets, triplets, quartets, quintets, and sextets, respectively. Thus, the triplet $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ structure with a *trans* relationship between the two B₂N₂C rings is designated as **Ti-t-180**. The corresponding metallocene $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{M}$ structures are designated as **c-M-x-n**. Thus, the triplet $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Ti}$ structure with a *cis* relationship between the two cyclopentadienyl rings is designated as **c-Ti-t-0**.

3. Results and Discussion

3.1 $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$

Four low-energy $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ structures (two singlets and two triplets) were found by the DFT methods (Figure 2). Quintet structures were found to lie at least 50 kcal/mol in energy above the lowest energy structure. They thus do not appear to be chemically significant and therefore are not discussed in this paper. In the triplet $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ structure **Ti-t-180** the two B₂N₂C rings are parallel. In the other three structures the two B₂N₂C rings are not parallel, but have dihedral angles of $\sim 30^\circ$ for the two singlet structures and $\sim 15^\circ$ for the triplet **Ti-t-144**. Thus the O-Ti-O' angle for **Ti-t-144** is 166.6° whereas the O-Ti-O' angles for **Ti-s-144** and **Ti-s-0** are 150.7° and 152.6° , respectively where O and O' represent the centers of the two rings. Since the B₂N₂C ring is a five-electron donor like the cyclopentadienyl ligand, the titanium atom in the $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ complexes has a 14-electron configuration.

The lowest-energy $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ structure is the *C*₂ triplet **Ti-t-144** with a rotation angle of 144° between the two B₂N₂C rings (Figure 2). A *C*_s triplet structure **Ti-t-180** lies only 1.4 kcal/mol in energy above **Ti-t-144**. Structure **Ti-t-180** has a very small $15i\text{ cm}^{-1}$ imaginary vibrational frequency (M06-L) that may be regarded as arising from numerical integration errors. Following the normal mode corresponding to the imaginary vibrational frequency of **Ti-t-180** leads to **Ti-t-144**.

The two singlet $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ structures **Ti-s-144** (*C*₂) and **Ti-s-0** (*C*_s) are significantly higher energy structures, lying 12.3 and 16.0 kcal/mol, respectively, above

Ti-t-144 (M06-L). These two singlet structures have similar geometries, differing only by the rotation of one $\text{B}_2\text{N}_2\text{C}$ ring relative to the other (Figure 2).

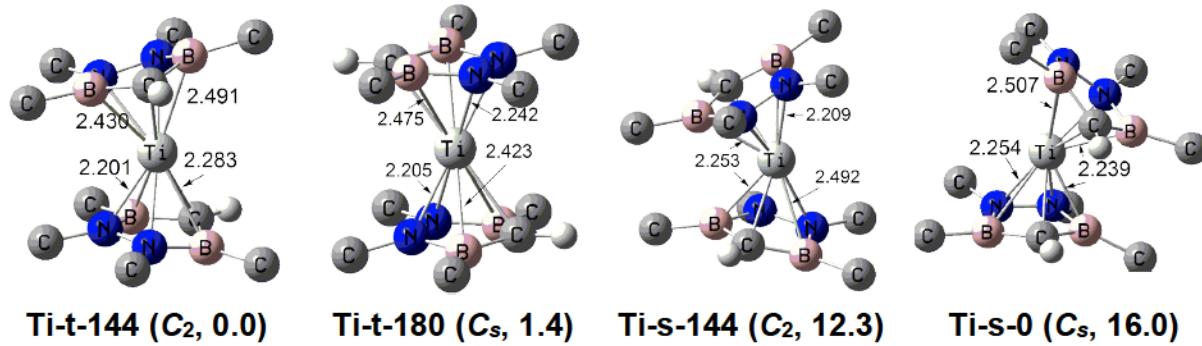


Figure 2. The low-energy $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ti}$ structures using the M06-L method. In Figures 2 to 15, the bond distances are in Å. The relative energies without ZPVE correction (ΔE , in kcal/mol) are given in parentheses. For clarity, the hydrogen atoms in the methyl groups are not shown.

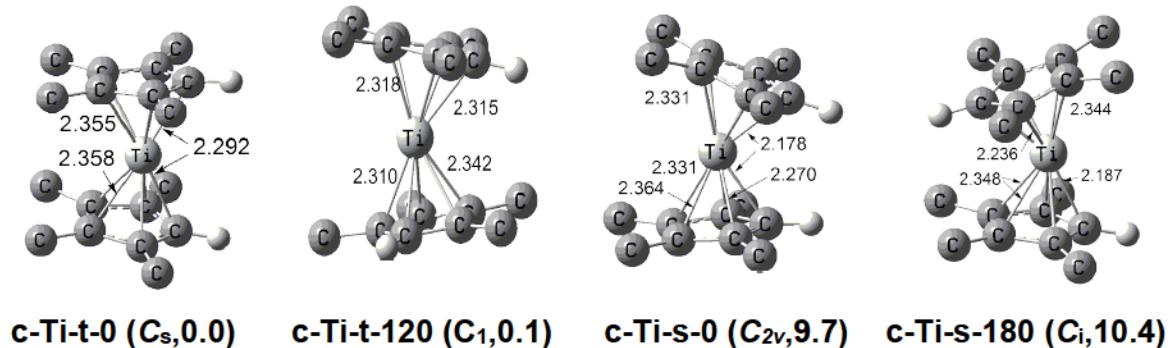


Figure 3. The low-energy $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Ti}$ structures using the M06-L method.

Four low-energy $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Ti}$ structures (two triplets and two singlets) were found (Figure 3). The lowest-energy structure is the C_s triplet **c-Ti-t-0**. Another triplet structure **c-Ti-t-120** (C_1) lies only 0.1 kcal/mol in energy above **c-Ti-t-0**. The two singlet $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Ti}$ structures **c-Ti-s-0** (C_{2v}) and **c-Ti-s-180** (C_i) are of higher energy, lying 9.7 and 10.4 kcal/mol (M06-L), respectively, above **c-Ti-t-0**. In **c-Ti-t-0** the two cyclopentadienyl rings are almost parallel. However, in the other three $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Ti}$ structures the two cyclopentadienyl rings are not parallel, but have a dihedral angle of $\sim 30^\circ$ for the two singlet structures and $\sim 15^\circ$ for the triplet structure, similar to **Ti-t-144**, **Ti-s-144**, and **Ti-s-0**.

3.2 $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{V}$

Only one low-energy quartet ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{V}$ structure **V-q-180** (C_{2h}) was found (Figure 4). The corresponding doublet ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{V}$ structure **V-d-180** is a high-energy structure, lying 32.3 kcal/mol in energy above **V-q-180**. Structure **V-q-180** is a genuine minimum adopting the expected parallel sandwich geometry. In **V-q-180** the V-C distances are ~ 2.33 Å, the V-B distances are ~ 2.38 Å, while the V-N distances are significantly shorter at 2.16 Å (M06-L). These distances suggest a five-electron donor pentahapto $\text{B}_2\text{N}_2\text{C}$ ring thereby giving the vanadium atom in **V-q-180** a 15-electron configuration.

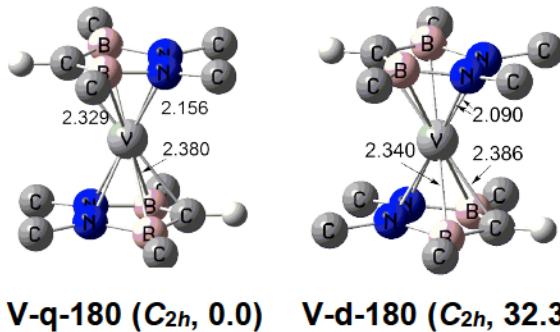


Figure 4. The low-energy $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{V}$ structures using the M06-L method.

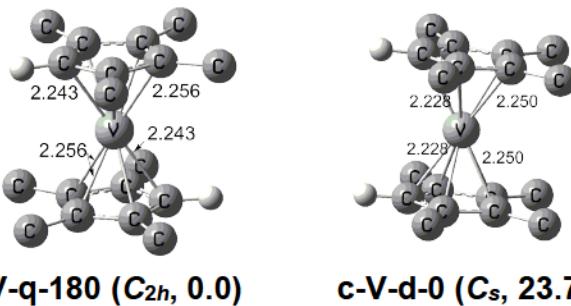


Figure 5. The low-energy $(\text{Me}_4\text{C}_5\text{H})_2\text{V}$ structures using the M06-L method.

Two low-energy ($\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{V}$ structures were found (Figure 5). The quartet structure **c-V-q-180** (C_{2h}) is a genuine minimum adopting the expected parallel sandwich geometry. Another minimum, the doublet **c-V-d-0** (C_s) is of higher energy, lying 23.7 kcal/mol above **c-V-q-180** (M06-L). In the two ($\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{V}$ structures the V-C distances range from 2.22 to 2.26 Å, which are close to the experimental V-C distances of 2.280 Å in vanadocene, ($\eta^5\text{-C}_5\text{H}_5$)₂V. [29]

3.3 (η^5 -Me₄B₂N₂CH)₂Cr

Five low-energy (η^5 -Me₄B₂N₂CH)₂Cr structures (three quintets and two triplets), all with parallel B₂N₂C rings, were found by the DFT methods (Figure 6). The lowest-energy such structure is the C_i quintet **Cr-p-180**. The two C_2 quintet conformers **Cr-p-144** and **Cr-p-36** have energies within 0.8 kcal/mol (M06-L) of **Cr-p-180**. In the three quintet structures the Cr-C distances range from 2.23 to 2.26 Å, the Cr-B distances from 2.32 to 2.50 Å, and the Cr-N distances from 2.14 to 2.40 Å. These interatomic distances indicate two pentahapto B₂N₂C ligands to give each chromium atom a 16-electron configuration. The two triplet (η^5 -Me₄B₂N₂CH)₂Cr structures **Cr-t-180** and **Cr-t-72** are higher energy structures than their quintet isomers, lying 7.9 and 12.0 kcal/mol, respectively, above **Cr-p-180** (M06-L). They also have pentahapto B₂N₂C ligands and thus 16-electron configurations for the chromium atoms.

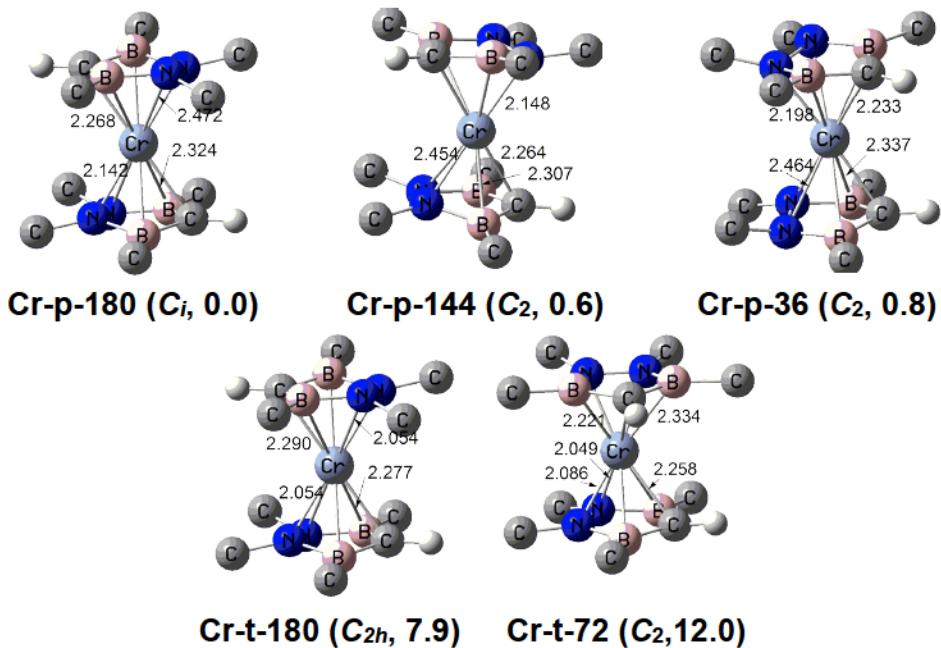


Figure 6. The low-energy ($\text{Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Cr structures using the M06-L method.

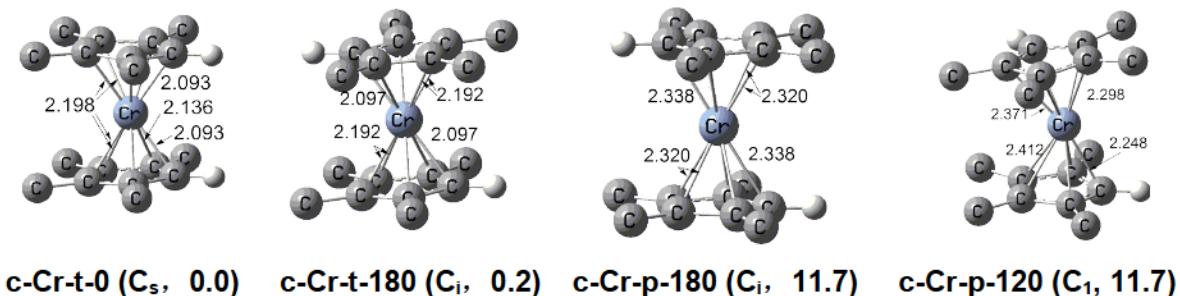


Figure 7. The low-energy ($\text{Me}_4\text{C}_5\text{H}$)₂Cr structures using the M06-L method.

Four low-energy ($\eta^5\text{-Me}_4\text{C}_5\text{H}$)₂Cr structures were found (Figure 7). The lowest energy ($\eta^5\text{-Me}_4\text{C}_5\text{H}$)₂Cr structure is the C_s triplet **c-Cr-t-0**. A triplet structure **c-Cr-t-180** (C_i) lies only 0.2 kcal/mol in energy above **c-Cr-t-0**. The two quintets **c-Cr-p-180** (C_i) and **c-Cr-p-120** (C_1) are of higher energy, lying 11.7 kcal/mol above **c-Cr-t-0**. This is different from the ($\text{Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Cr system for which the quintet structures of lower energies than their triplet isomers. In the two triplet structures the Cr-C distances range from 2.10 to 2.20 Å, which are shorter than those in the quintet structures. The Cr-C distances range from 2.09 to 2.19 Å. This is in reasonable agreement with the experimental Cr-C distances (2.169 Å) in chromocene, ($\eta^5\text{-C}_5\text{H}_5$)₂Cr. [29]

3.4 ($\text{Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn

Five low-energy ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn structures (one sextet, one doublet, and three quartets) have been optimized using the DFT methods (Figure 8). All five structures are predicted to have the expected parallel sandwich structure. The C_2 sextet ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn structure **Mn-x-144** is the lowest energy structure. It is a very favorable structure since it lies ~18 kcal/mol in energy below the next lowest energy ($\text{Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn structure. Such a high spin sextet ground state is favored by the half-filled d-shell in the d^5 configuration of the central Mn(II) atom in the sandwich compound ($\text{Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn.

The C_i doublet structure **Mn-d-180** lies 21.6 kcal/mol in energy above **Mn-x-144** (M06-L). The three quartet structures **Mn-q-180** (C_i), **Mn-q-36** (C_2), and **Mn-q-144** (C_2) lie 17.9, 18.9, and 24.6 kcal/mol, respectively, above **Mn-x-144** (M06-L). In the five ($\text{Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn structures the Mn-C distances range from 2.15 to 2.19 Å, the Mn-B distances range from 2.17 to 2.53 Å, and the Mn-N distances range from 2.01 to 2.51 Å indicating pentahapto $\text{B}_2\text{N}_2\text{C}$ ligands in all cases. Since each $\text{Me}_4\text{B}_2\text{N}_2\text{CH}$ ligand is a five-electron donor like the isoelectronic cyclopentadienyl ligand, the manganese atoms in the five structures all have 17-electron configurations. The low energy of the sextet ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Mn structure **Mn-x-144** relative to isomers with lower spin states clearly indicates that the $\text{B}_2\text{N}_2\text{C}$ ligand is a weaker field ligand than the cyclopentadienyl or substituted cyclopentadienyl ligands as well as other five-electron cyclic donor ligands forming similar manganese sandwich complexes [30].

Four low-energy ($\eta^5\text{-Me}_4\text{C}_5\text{H}$)₂Mn structures (one doublet, two sextets, and one quartet) have been optimized using the DFT methods (Figure 9). The lowest energy structure is the doublet **c-Mn-d-0**. Two sextet ($\eta^5\text{-Me}_4\text{C}_5\text{H}$)₂Mn structures **c-Mn-x-90** and **c-Mn-x-180** lie 6.0 and 7.6 kcal/mol, respectively, above **c-Mn-d-0**. The quartet

structure **c-Mn-q-0** (C_{2v}) lies 14.9 kcal/mol above **c-Mn-d-0** ($M06-L$). In three of the $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Mn}$ structures, the two cyclopentadienyl rings are almost parallel, while in structure **c-Mn-x-90** the two cyclopentadienyl rings have a dihedral angle of 30° . In the doublet **c-Mn-d-0** the Mn-C distances range from 2.05 to 2.13 Å, while in the quartet **c-Mn-q-0** the Mn-C distances range from 2.13 to 2.33 Å. These results are significantly shorter than the experimental Mn-C distances (2.380 Å) in manganocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}$ [31]. This difference appears to be a consequence of the sextet spin state of unsubstituted manganocene and the doublet spin state of **c-Mn-d-0**.

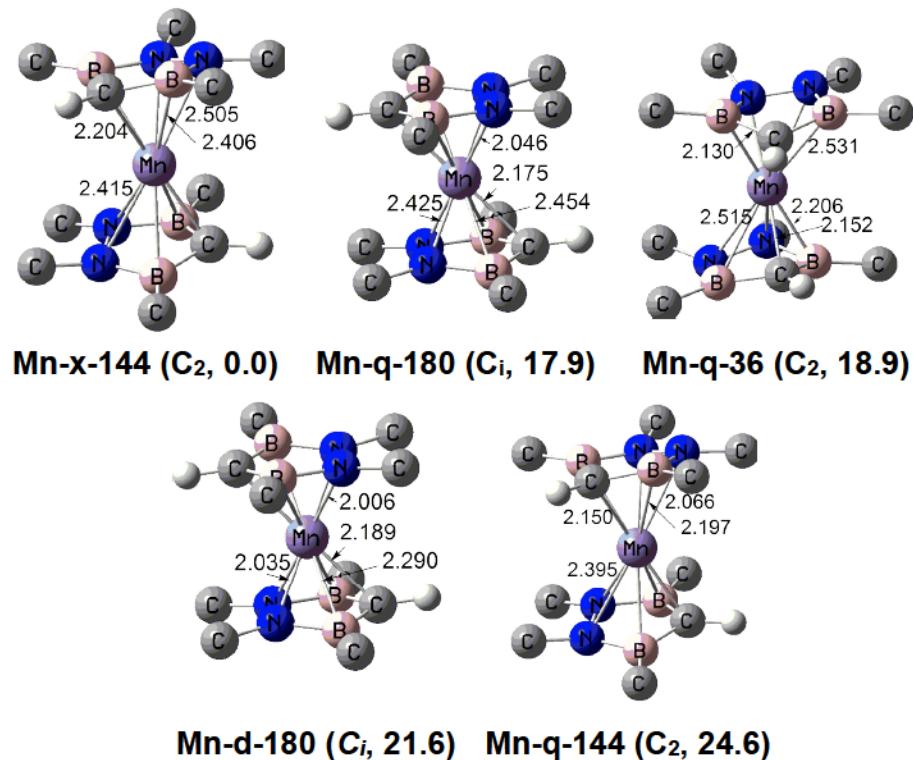


Figure 8. The low-energy $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Mn}$ structures using the $M06-L$ method.

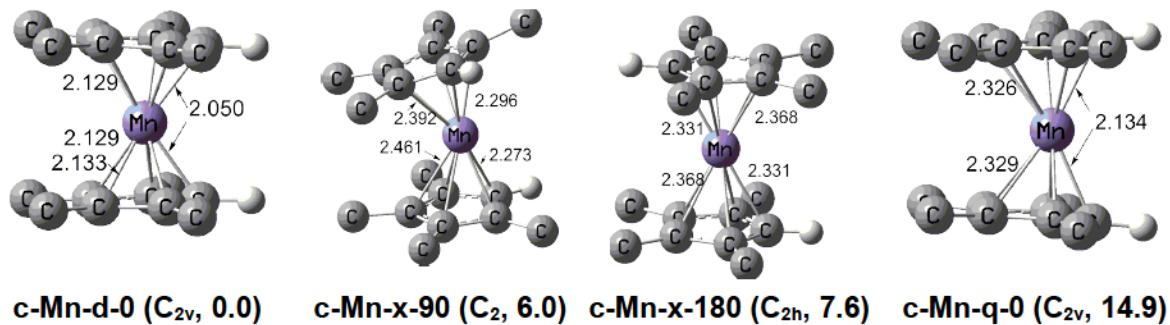


Figure 9. The lowest-energy $(\text{Me}_4\text{C}_5\text{H})_2\text{Mn}$ structures using the $M06-L$ method.

3.5 $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Fe}$

Six low-energy $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Fe}$ structures (two singlets, one quintet, and three triplets) were found (Figure 10). All six structures are predicted to have the expected sandwich structure with parallel $\text{B}_2\text{N}_2\text{C}$ rings. The global minimum $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Fe}$ structure is the C_{2h} singlet structure **Fe-s-180**. The other singlet $(\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Fe}$ structure **Fe-s-72** lies 3.5 kcal/mol (M06-L) in energy above **Fe-s-180**. (Figure 10), Our predicted Fe-N distances (~ 1.97 Å), Fe-C distances (~ 2.15 Å) and Fe-B distances (~ 2.17 Å) in the singlet $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Fe}$ structures **Fe-s-180** and **Fe-s-72** are in very good agreement with the experimental Fe-N, Fe-C, and Fe-B distances of ~ 1.97 , 2.17, and ~ 2.20 Å, respectively, in $[\eta^5\text{-(CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$, as determined by X-ray crystallography [8]. The B-C, B-N, and N-N bond distances in the $\text{B}_2\text{N}_2\text{C}$ rings are also in very good agreement with corresponding experimental values (Figure 10). X-ray crystallography of $[\eta^5\text{-(CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$ shows that the angle between the $\text{B}_2\text{N}_2\text{C-CH}_3$ bonds is not 180° , but close to the angle between the $\text{B}_2\text{N}_2\text{C-H}$ bonds of structure **Fe-s-72**. This could be a consequence of increased steric hindrance of the phenyl groups in a $[\eta^5\text{-(CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$ structure of the type **Fe-s-180** relative to a structure of the type **Fe-s-72**.

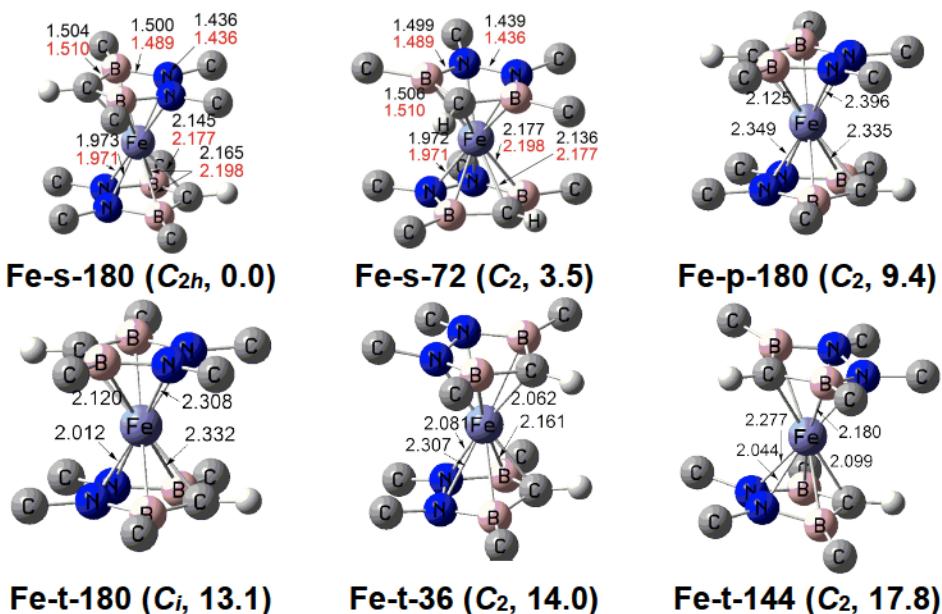


Figure 10. The low-energy $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Fe}$ structures using the M06-L method. The lower numbers in red for structures **Fe-s-180** and **Fe-s-72** are the corresponding experimental values for the $[\eta^5\text{-(CH}_2)_3\text{N}_2(\text{BPh})_2\text{CMe}]_2\text{Fe}$ [8].

The C_{2h} quintet (η^5 -Me₄B₂N₂CH)₂Fe structure **Fe-p-180** lies 9.4 kcal/mol above **Fe-s-180** (Figure 10). The triplet (η^5 -Me₄B₂N₂CH)₂Fe structures **Fe-t-180** (C_i), **Fe-t-36** (C_2), and **Fe-t-144** (C_2) are even higher energy structures, lying 13.1, 14.0, and 17.8 kcal/mol (M06-L), respectively, above **Fe-s-180**. In the triplet (η^5 -Me₄B₂N₂CH)₂Fe structures the Fe-C distances are 2.06 to 2.23 Å, the Fe-B distances are 2.16 to 2.33 Å, and the Fe-N distances are 2.01 to 2.31 Å, suggesting pentahapto Me₄B₂N₂CH ligands. This gives the iron atoms in even these higher spin state (η^5 -Me₄B₂N₂CH)₂Fe structures the favored 18-electron configurations.

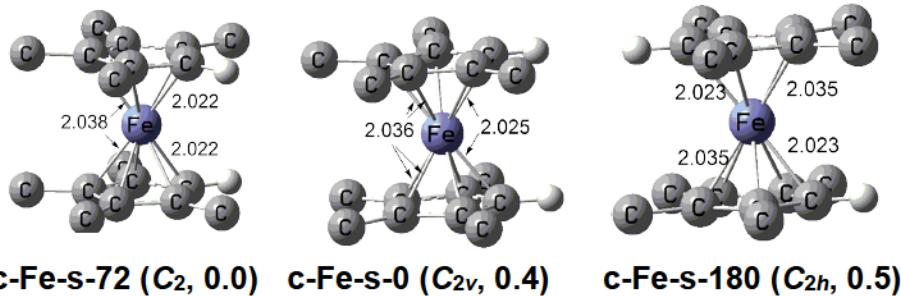


Figure 11. The lowest-energy (Me₄C₅H)₂Fe structures using the M06-L method.

Only three low-energy (η^5 -Me₄C₅H)₂Fe structures were found, all singlets with the favored 18-electron configuration (Figure 11). The triplet and quintet isomers were found to lie least 30 kcal/mol higher in energy and thus are not discussed in this paper. These three low-lying structures are predicted to have the expected parallel sandwich geometry similar to ferrocene. The lowest energy (η^5 -Me₄C₅H)₂Fe structure **c-Fe-s-72** has C_2 symmetry, while the other isomers **c-Fe-s-0** (C_{2v}) and **c-Fe-s-180** (C_{2h}) have only slightly higher energies of 0.4 and 0.5 kcal/mol, respectively (M06-L). In these three singlet (η^5 -Me₄C₅H)₂Fe structures the Fe-C distances are in a narrow range from 2.02 to 2.03 Å, which are close to the corresponding experimental Fe-C distances (2.064 Å) of the well-known ferrocene, (η^5 -C₅H₅)₂Fe [32].

3.6 (Me₄B₂N₂CH)₂Co

Four low-energy (η^5 -Me₄B₂N₂CH)₂Co structures (two doublets and two quartets) were found (Figure 12). All four structures adopt the expected parallel sandwich structures. The global minimum is the C_{2h} doublet structure **Co-d-180**. The other doublet (η^5 -Me₄B₂N₂CH)₂Co structure **Co-d-36** is a C_2 structure lying 1.7 kcal/mol in energy above **Co-d-180**. The quartet (η^5 -Me₄B₂N₂CH)₂Co structures **Co-q-180** (C_{2h}) and **Co-q-36** (C_2) are higher energy structures, lying 8.7 and 13.6 kcal/mol (M06-L),

respectively, in energy above **Co-d-180**. In these $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Co}$ structures the Co-C distances range from 2.08 to 2.15 Å, the Co-B distances range from 2.15 to 2.33 Å, and the Co-N distances range from 1.96 to 2.30 Å (M06-L). This indicates pentahapto $\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$ ligands, thereby giving each cobalt atom a 19-electron configuration.

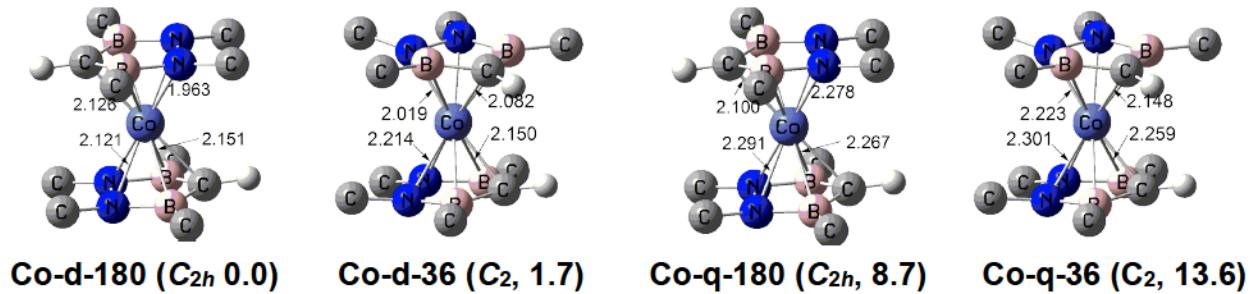


Figure 12. The low-energy $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Co}$ structures using the M06-L method.

Three low-energy ($\eta^5\text{-Me}_4\text{C}_5\text{H}$)₂Co structures have been located with closely spaced relative energies. The C_{2h} structure **c-Co-d-180** has the lowest energy, but structures **c-Co-d-0** (C_{2v}) and **c-Co-d-36** (C_2) lie only 0.7 and 1.2 kcal/mol, respectively, above **c-Co-d-180**. All three structures are doublet spin state structures, predicted to have the expected parallel sandwich structure (Figure 13). The Co-C distances in these structures range from 2.05 to 2.13 Å (M06-L) in agreement with the corresponding experimental Co-C distances in (2.119 Å) of cobaltocene, ($\eta^5\text{-C}_5\text{H}_5$)₂Co [33].

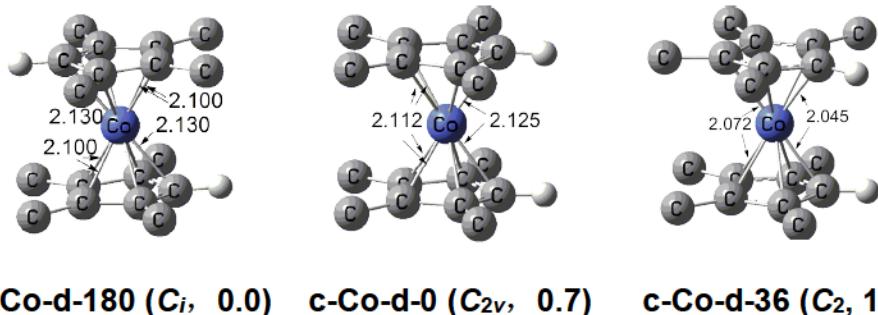


Figure 13. The lowest-energy $(\text{Me}_4\text{C}_5\text{H})_2\text{Co}$ structures using the M06-L method.

3.7 $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ni}$

Only two low-energy ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$)₂Ni structures **Ni-s-180** (C_{2h}) and **Ni-t-180** (C_{2h}) were found (Figure 14). These structures adopt the expected parallel sandwich geometry and are almost identical in energy with the singlet structure **Ni-s-180** lying 1.2 kcal/mol below the triplet structure **Ni-t-180**. Both $\text{B}_2\text{N}_2\text{C}$ rings in the two $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ni}$ structures are pentahapto $\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$ ligands, thereby giving the

nickel atoms 20-electron configurations similar to the well-known nickelocene $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$.

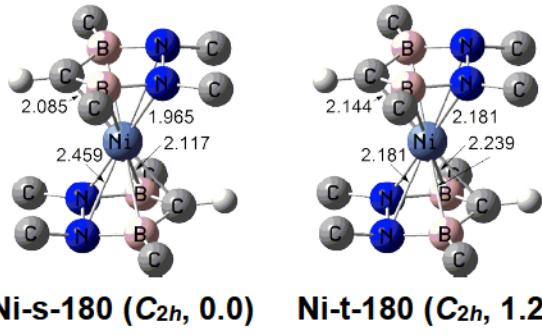


Figure 14. The low-energy $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Ni}$ structures using the M06-L method.

Four low- energy $(\eta^5\text{-Me}_4\text{C}_5\text{H})_2\text{Ni}$ structures (two singlets and two triplets) were found (Figure 15). All four structures adopt the expected parallel sandwich geometry. The two triplet structures **c-Ni-t-180** and **c-Ni-t-0** have almost the same energies (within 0.05 kcal/mol), whereas the two singlet structures **c-Ni-s-180** (C_i), **c-Ni-s-0** (C_{2v}) have significantly higher energies at 15.2 and 17.4 kcal/mol (M06-L), respectively, above the triplet structure **c-Ni-t-180**. In both triplet structures **c-Ni-t-180** and **c-Ni-t-0**, the Ni-C distances range from 2.16 to 2.17 Å (M06-L) in reasonable agreement with the corresponding experimental Ni-C distances of 2.196 Å in nickelocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}$ [34].

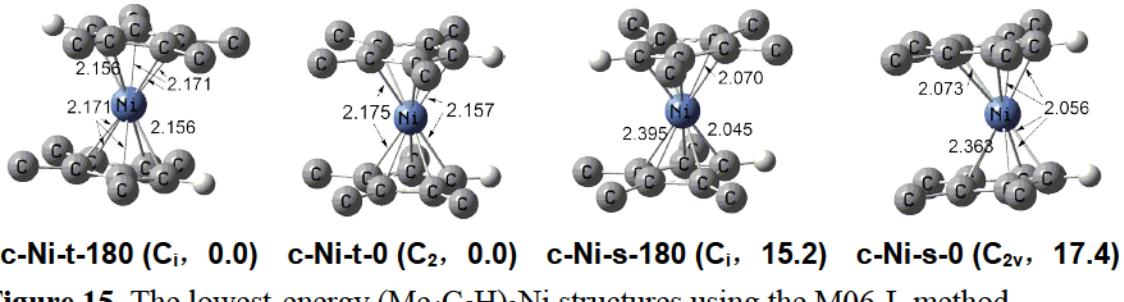
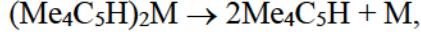
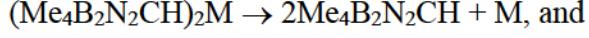


Figure 15. The lowest-energy $(\text{Me}_4\text{C}_5\text{H})_2\text{Ni}$ structures using the M06-L method.

3.8 Dissociation Energies

In order to study the stability of complexes under study, we have explored the dissociation energies for the following reactions:



where M = Ti, V, Cr, Mn, Fe, Co, and Ni are the free atoms in their electronic ground states. All of the dissociation energies are found to be substantial (Figure 16). Thus

the DE values for the $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ compounds are in the range from 127 to 193 kcal/mol, while those for the $(\text{Me}_4\text{C}_5\text{H})_2\text{M}$ compounds are in the range from 127 to 204 kcal/mol.

In both cases, the DE values do not monotonously decrease, but have minima at $(\text{Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{Mn}$ and $(\text{Me}_4\text{C}_5\text{H})_2\text{Mn}$. This is similar to the behavior for the experimental mean bond dissociation enthalpies (i.e., half of the total bond dissociation enthalpy) for the metallocenes, which are 88 (V), 68 (Cr), 51 (Mn), 71 (Fe), 64 (Co), 59 (Ni) kcal/mol and thus have a minimum at manganese.³⁵

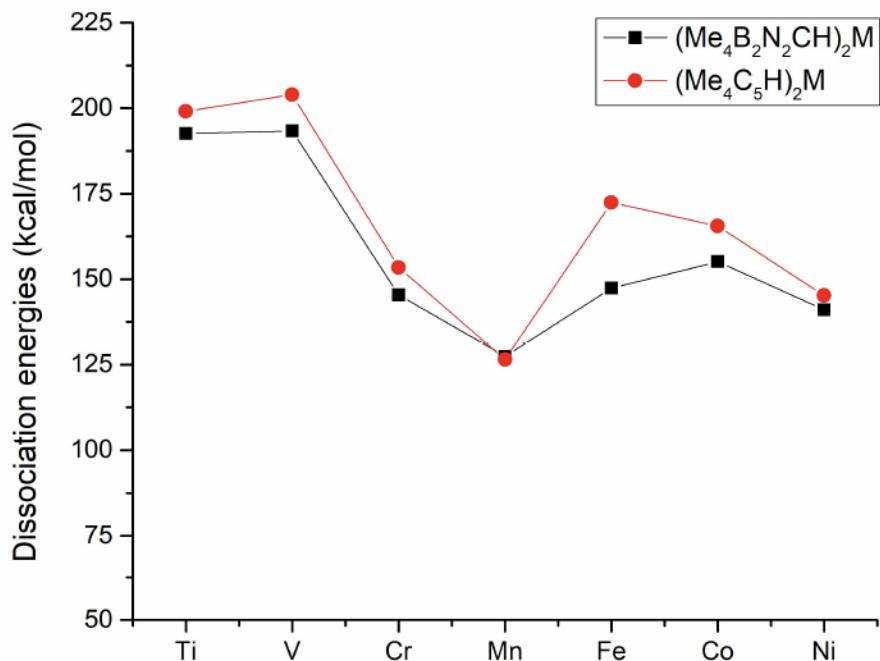


Figure 16. The dissociation energies for the $(\text{Me}_4\text{C}_5\text{H})_2\text{M}$ compounds ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) using the M06-L method.

4. Conclusion

All seven first-row transition metal atoms form low-energy ($\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH})_2\text{M}$ sandwich structures with a *trans* (or nearly *trans* for Mn and Ti) orientation of parallel $\text{B}_2\text{N}_2\text{C}$ rings corresponding to a 180° (or 144° for Mn and Ti) angle between the C–H subunits of the $\text{Me}_4\text{B}_2\text{N}_2\text{CH}$ rings. Furthermore, the π -electrons in these heterocyclic $\text{B}_2\text{N}_2\text{C}$ rings are necessarily more localized than those in the homocyclic $\eta^5\text{-C}_5\text{H}_5$ cyclopentadienyl ligand. Thus the five electrons donated by a neutral $\eta^5\text{-Me}_4\text{B}_2\text{N}_2\text{CH}$ ligand to a metal atom can at least formally originate from lone pairs on each of the nitrogen atoms and one electron from the carbon atom. The 180° orientation of the

B_2N_2C rings in these structures leads to a formal localized octahedral coordination of the central transition metal forming two M–N bonds and one M–C bond to each ring with two *trans* N–M–N units and one *trans* C–M–C unit.

This theoretical study shows that this type of octahedral coordination of the two diazadiborolyl rings in sandwich compounds leads to a weaker field ligand than the cyclopentadienyl ligand. This is manifest in higher spin states for the lowest energy $(\eta^5\text{-Me}_4B_2N_2CH)_2M$ sandwich structures compared with the corresponding metallocenes $(\eta^5\text{-Me}_4C_5H)_2M$. This effect is most noticeable in the manganese derivative $(\eta^5\text{-Me}_4B_2N_2CH)_2Mn$ for which the sextet structure **Mn-x-144** (Figure 5) lies ~ 18 kcal/mol in energy below the lowest energy quartet structure. The special stability of the half-filled d^5 shell of manganese(II) is evident here. This contrasts with the complicated magnetic behavior of $(\eta^5\text{-C}_5H_5)_2Mn$, the doublet ground state of $(\eta^5\text{-Me}_5C_5)_2Mn$ found experimentally [30], and the doublet spin state structure of $(\eta^5\text{-Me}_4C_5H)_2Mn$ predicted in this work to lie ~ 6 kcal/mol in energy below the lowest energy sextet spin state structure (Figure 9). The chromium derivative $(\eta^5\text{-Me}_4B_2N_2CH)_2Cr$ also has a high-spin quintet ground state in **Cr-p-180** (Figure 4) as compared with the triplet ground state [9] found experimentally for $(\eta^5\text{-C}_5H_5)_2Cr$ and predicted theoretically for $(\eta^5\text{-Me}_4C_5H)_2Cr$ (Figure 7). Even for the ferrocene analogue $(\eta^5\text{-Me}_4B_2N_2CH)_2Fe$ the high-spin quintet structure **Fe-p-180** lies only ~ 9 kcal/mol in energy above the singlet ground state **Fe-s-180** (Figure 6).

The only bis(1,2-diaza-3,5-diborolyl)metal sandwich compound that has been synthesized is the substituted ferrocene analogue $[\eta^5\text{-(CH}_2)_3N_2(BPh)_2CMe]_2Fe$, obtained by Roesler and co-workers from the 1,2-diaza-3,5-diborolyl anion and $FeCl_2(\text{thf})_4$ [8]. Related sandwich compounds of the other first-row transition metals should be accessible by analogous synthetic methods.

Acknowledgment. This research was supported by Funds for Sichuan Distinguished Scientists (Grant No. 2015JQ0042) and Funds for the Youth Innovation Team of the Education Department of Sichuan Province (Grant No. 14TD0013) in China.

There are no conflicts of interest to declare.

Supporting Information. Tables S1 to S7: Total energies (E in hartree), relative energies (ΔE in kcal/mol), and numbers of imaginary vibrational frequencies (N_{img}) for the $(\text{Me}_4B_2N_2CH)_2M$ structures; Tables S8 to S35: Atomic coordinates of the optimized structures for the $(\text{Me}_4B_2N_2CH)_2M$ complexes.

Literature References

- [1] Boyd, R. J.; Choi, S. C.; Hale, C. C. *Chem. Phys. Lett.* **1984**, *112*, 136.
- [2] Kiran, B.; Phykan, A. K.; Jemmis, E. D. *Inorg. Chem.*, **2001**, *40*, 3615.
- [3] Prinz, R.; Werner, H. *Angew. Chem. Int. Ed.*, **1967**, *6*, 91.
- [4] Werner, H.; Prinz, R.; Deckelmann, E., *Chem. Ber.*, **1969**, *102*, 95.
- [5] Liu, S.-Y.; Lo, M. M-C.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 174.
- [6] Ly, H. V.; Forster, T. D.; Maley, D.; Parvez, M.; Roesler, R. *Chem. Commun.*, **2005**, 4468.
- [7] Ly, H. V.; Forster, T. D.; Corrente, A. M.; Eisler, D. J.; Konu, J.; Parvez, M.; Roesler, R. *Organometallics*, **2007**, *26*, 1750.
- [8] Ly, H. V.; Moilanen, J.; Tuononen, H. M.; Parvez, M.; Roesler, R. *Chem. Commun.*, **2011**, *47*, 8391.
- [9] Gordon, K. R.; Warren, K. D., *J. Organometal. Chem.* **1976**, *117*, C27.
- [10] Ziegler, T.; Autschbach J. *Chem. Rev.*, **2005**, *105*, 2695.
- [11] Bühl, M.; Kabrede, H. *J. Chem. Theory Comput.*, **2006**, *2*, 1282.
- [12] Brynda, M.; Gagliardi, L.; Widmark, P. O.; Power, P. P.; Roos, B. O. *Angew. Chem. Int. Ed.*, **2006**, *45*, 3804.
- [13] Sieffert, N.; Bühl, M. *J. Am. Chem. Soc.*, **2010**, *132*, 8056.
- [14] Schyman, P.; Lai, W.; Chen, H.; Wang, Y.; Shaik, S. *J. Am. Chem. Soc.*, **2011**, *133*, 7977.
- [15] Adams, R. D.; Pearl, W. C.; Wong, Y. O.; Zhang, Q.; Hall, M. B.; Walensky, J. R. *J. Am. Chem. Soc.*, **2011**, *133*, 12994.
- [16] Lonsdale, R.; Olah, J.; Mulholland, A. J.; Harvey, J. N. *J. Am. Chem. Soc.*, **2011**, *133*, 15464.
- [17] Reiher, M.; Salomon, O.; Hess, B. A. *Theor. Chem. Acc.* **2001**, *107*, 48.
- [18] Harvey, J. N.; *Structure and Bonding*, **2004**, *112*, 151.
- [19] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- [20] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, **1988**, *37*, 785.
- [21] Salomon, O.; Reiher, Hess, M. B. A. *J. Chem. Phys.* **2002**, *117*, 4729.
- [22] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
- [23] Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757.
- [24] Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
- [25] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
- [26] Wachters, A. J. H., *J. Chem. Phys.* **1970**, *52*, 1033.
- [27] Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 705.

- [28] Frisch, M. J. et al. Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
- [29] Gard, E.; Haaland, A.; Novak, D. P.; Seip, R. *J. Organomet. Chem.* **1975**, *88*, 181.
- [30] Hebendanz, N.; Koehler, F. H.; Mueller, G.; Riede, J. *J. Am. Chem. Soc.* **1986**, *108*, 3281.
- [31] Haaland, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 267.
- [32] Haaland, A. *Top. Curr. Chem.* **1975**, *53*, 1.
- [33] Almenningen, A.; Gard, E.; Haaland, A. *J. Organomet. Chem.* **1976**, *107*, 273.
- [34] Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1970**, *53*, 1228.
- [35] Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71