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Special Issue

Dinuclear Mn(I) Complexes with Phosphido and Hydrido Bridges: Synthesis, Reactivity, and Hydrogenative Catalysis

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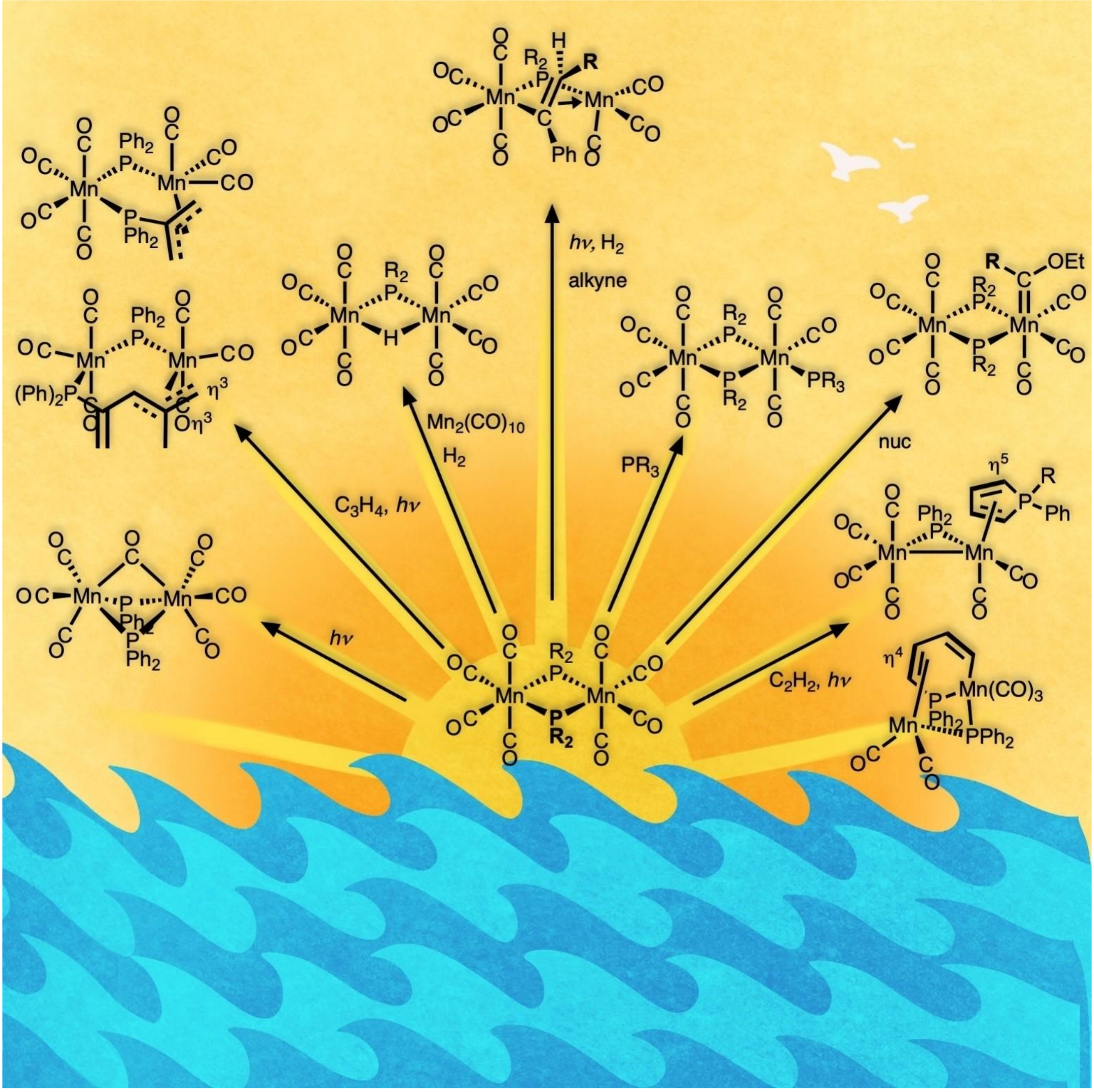

Abstract: A class of organomanganese hydrogenation catalysts was recently rediscovered. These are simple dinuclear Mn(I) carbonyl compounds with phosphido (PR_2^-) and hydrido (H^-) bridges. This class of compounds has been known since the 1960's, and they have rich coordination chemistry and reactivity. Given their recently discovered potential for catalytic applications, a fresh look at this class of compounds was necessary. Hence, this Review comprehensively covers the synthesis, reactivity, and catalysis of this interesting class of molecules.

1. Introduction

Manganese(I) and Ru(II) share similar electronic structure and ionic radii.[1,2] These similarities and the need for sustainable metal chemistry in synthesis[3] has led to serious research efforts to develop catalysts that use Mn(I) in areas where Ru(II) is typical. In the arena of pharmaceutical chemical synthesis, Ru complexes are often used as hydrogenation catalysts,[4] and this is one area where replacement with Mn has been actively studied. In addition the low-abundance of Ru in the earth crust, there are also issues of metal toxicity[5,6] that further justifies the pursuit of researching Mn catalysts.

The first example of a well-defined molecular Mn(I) hydrofunctionalization catalysts was reported by Sappa and coworkers for alkyne hydrogenation,[7] and these molecules were of the dinuclear Mn(I) phosphido/hydrido class (see below). Pratt and coworkers reported the first examples for alkene hydrosilylation.[8,9] Additionally, the early work of Halpern[10] and Baird[11] on the mechanism of stoichiometric alkene hydrogenation with $Mn(CO)_5H$ is notably relevant.[12] The field of Mn(I) hydrofunctionalization catalysis laid relatively dormant for some time until it witnessed a resurgence of interest following the work of Ozerov,[13] Trovitch,[14] Boncella,[15] Milstein,[16] Beller,[17] Kirchner,[18] Kempe,[19] and others who explored simple and ligated Mn(I) complexes leading to an explosion of research in Mn-catalyzed (de)hydrogenative and hydroelementation applications and mechanisms.[20] The area of Mn(I) hydrofunctionalizations has additionally benefited from the burgeoning field of CH activations using Mn(I) complexes.[21,22] While progress in developing Mn catalysts using simple ligands and precursors is notable,[2327] continued advances are needed because organomanganese starting materials are surprisingly expensive given the high abundance of Mn in the earth crust. In part, this is a problem rooted in difficulties preparing organomanganese(I) compounds from ore and Mn(II) starting materials compared to other metals.[28] Until this challenge is solved, using simple ligands and catalytic systems is one way to achieve low-cost organomanganese catalyzed hydroelementations.

We were therefore attracted by the simplicity of Sappa's system, noted above, that used a bench-stable complex, $[\{Mn(CO)_4\}_2(\mu\text{-}PPh_2)(\mu\text{-}H)]$ (**2**^{Ph}), and H_2 for *trans*-selective semihydrogenation of diphenylacetylene (dpa),[7] and this system was recently investigated in more detail.[12] For instance, it was recently discovered that Mn–PR_2 moieties are reactive toward H_2 and,[29] intriguingly, that *cis*-vinyl inserted Mn(I) intermediate complexes react with H_2 to form a *trans*-alkene product, exclusively, without *cis* to *trans* isomerization.[30] This selectivity mode is in contrast to the normal *cis* to *trans* isomerization mode in mononuclear catalysts.[12,31] It was further demonstrated that the catalytic platform can be assembled in situ directly from $Mn_2(CO)_{10}$ and phosphine (R_2PH) without the need for isolation. Such drop-in catalyst formation is ideal for applications in pharmaceutical synthesis industry. Given (*i*) the simplicity of the catalysts, (*ii*) their bench-stability, and (*iii*) potential utility in hydrogenation catalysis one can anticipate a fruitful area of research using dinuclear systems. While the chemistry of phosphido ligands on other elements has been reviewed,[32,33] it has not been for manganese. Phosphinidine (RP^{2-}) bridged binuclear complexes has been reviewed.[28a,34] Therefore, the following review is an undertaking to survey the synthesis of the class of manganese compounds (Scheme 1) that generally can be described as dinuclear Mn(I) phosphido and hydride complexes, and aspects of their reactivity that make them relevant to hydrogenative catalysis. In addition, the germane PP-clipped dimanganese(I) dihydride complexes are also covered.

2. Synthesis of dinuclear Mn(I) complexes with phosphido bridges

2.1. Synthesis of 1^{R} by oxidative addition of P–Cl bonds

Complexes such as **1**^{R} can be synthesized via oxidative addition of P–Cl bonds in ClR_2P by pentacarbonylmanganate, $[Mn(CO)_5]^-$ (the anion is often prepared by reduction of $Mn_2(CO)_{10}$ with sodium amalgam,[35] although reduction with NaK or $Li[Et_3BH]$ in THF are good mercury-free alternatives[26,36,37]). Green reported the synthesis of **1**^{Ph} ("small yields") and **2**^{Ph} (2%) using this strategy,[38] and to our knowledge represents the first preparation of this class of molecules; the source of the hydride in **2**^{Ph} was likely adventitious moisture in the reaction (see below in oxidative addition of P–H bonds).[39] Later, Hayter reported a synthesis of **1**^{Ph} and **1**^{Me} via the same strategy but in much higher yields, likely owing to the use of more forcing conditions (Scheme 2).[40] Following Hayter's procedure, Basato prepared the **1**^{Et} complex and studied the ligand substitution kinetics

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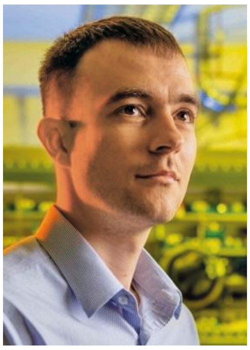
with $n\mathrm{Bu}_3\mathrm{P}$ that will be described in section 3.1.[41] Although this strategy is broadly applicable for the synthesis of various analogues of $\mathbf{1}^{\mathrm{R}}$, the yields are often limited by the steric bulks of the phosphine substituents. Attempts to prepare the bulkier octacarbonyl *i*Pr and *t*Bu analogs of $\mathbf{1}^{\mathrm{Ph}}$ using this P–Cl oxidative addition strategy resulted in very low yields or none at all, respectively.[29] For instance, when $\mathrm{Na[Mn(CO)_5]}$ was reacted with $\mathrm{Cl}i\mathrm{Pr_2P}$, the main product was $i\mathrm{Pr_2P{-}P}i\mathrm{Pr_2}$ with only small amounts of $\mathbf{1}^{i\mathrm{Pr}}$. Furthermore, $\mathrm{Cl}t\mathrm{Bu_2P}$ and $\mathrm{Na[Mn(CO)_5]}$ gave a mixture of two compounds, one of which is the hexacarbonyl analog of $\mathbf{1}^{\mathrm{R}}$ ($\mathbf{1}^{t\mathrm{Bu}}$) and a monophosphido bridged $\mathrm{[Mn(CO)_4]_2}$ anion, $[\mathbf{2}^{t\mathrm{Bu}}\text{-H}]^-$ (Scheme 2, bottom). The latter of these likely forms from the comproportionation of a mononuclear intermediate $t\mathrm{Bu_2P{-}Mn(CO)_{4/5}}$ and $\mathrm{Na[Mn(CO)_5]}$, making dimer $[\mathbf{2}^{t\mathrm{Bu}}\text{-H}]^-$, which in turn is competent to oxidatively add across another equivalent of $t\mathrm{Bu_2PCl}$ (Scheme 2, bottom).

This oxidative addition mechanism is supported by two special cases that use highly reactive P–Cl bonds. For example, the room temperature reaction of $\mathrm{Na[Mn(CO)_5]}$ with (2,3,4,5-tetraphenyl)-cyclobutadienephospholylchloride (Ph$_4$phosphole-Cl) furnished the mononuclear complex $\mathrm{[Mn(CO)_5(Ph_4phosphole)]}$ (**4**) (Scheme 3, top).[42] This pentacarbonyl readily loses one CO to form the dinuclear complex $\mathbf{1}^{\mathrm{Ph4phosphole}}$ (Scheme 3, top).[42,43] Neither $\mathbf{1}^{\mathrm{Ph4phosphole}}$ nor **4** is the thermodynamic product, as with further heating or use of vacuum the complexes convert into $[\mathrm{Mn(CO)_3}(\eta^5\text{-(Ph}_4\text{phosphole)}]$ (**5**).



David C. Lacy: David Lacy obtained his B.S. in chemistry from Colorado State University (2007), a Ph.D. in chemistry from the University of California-Irvine (2012), and he performed postdoctoral work at Caltech (2012-2015). He started his independent career in 2015 at the University at Buffalo (UB), the State University of New York (USA), where he is currently an Associate Professor. Prof. Lacy has developed a research program that seeks to invent new reagents that are useful in preparative pharmaceutical and medicinal chemistry. This work focuses on transition metals including low- and high-valent manganese compounds, studying their reactivity, and pursuing applications.

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Similarly, the activated *N*-heterocyclic phosphine (NHP) chloride precursor activates at room temperature to afford the mononuclear $\mathbf{4}^{\mathrm{NHP}}$ (Scheme 3, bottom).[44] This species in turn is photolabile, releasing one CO to form half an equivalent of heptacarbonyl $\mathbf{1}^{\mathrm{NHP}}$, an unsymmetrical dimer.

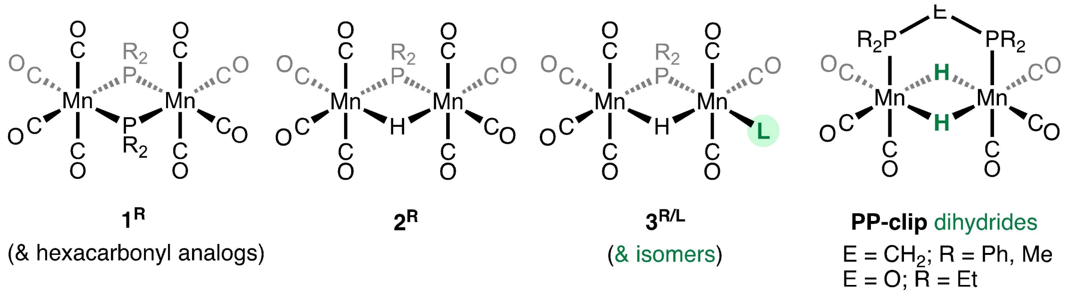
2.2. Electronic structure of dinuclear Mn complexes with phosphido bridges

An alternative formalism to the oxidative addition leading to a Mn(I) ion with anionic phosphido is a salt metathesis between Mn(−1) phosphine chloride and loss of NaCl. Both formalisms are relevant. In the case of **4**, which has five CO ligands, the 18-e$^-$ complex is best described as Mn(I)-phosphido. In contrast, the tetracarbonyl complex $\mathbf{4}^{\mathrm{NHP}}$ is best viewed as an 18-e$^-$ Mn(−1)-phosphenium compound and is an isoelectronic and structural analog of the trigonal bipyramidal $\mathrm{Fe(CO)_5}$. $\mathbf{4}^{\mathrm{NHP}}$ is reactive toward nucleophiles at the phosphido ligand making new P–Nu bonds (Nu = hydride, methyl anion). The two formalisms for phosphido ligands have been extensively covered elsewhere (Figure 1).[45]

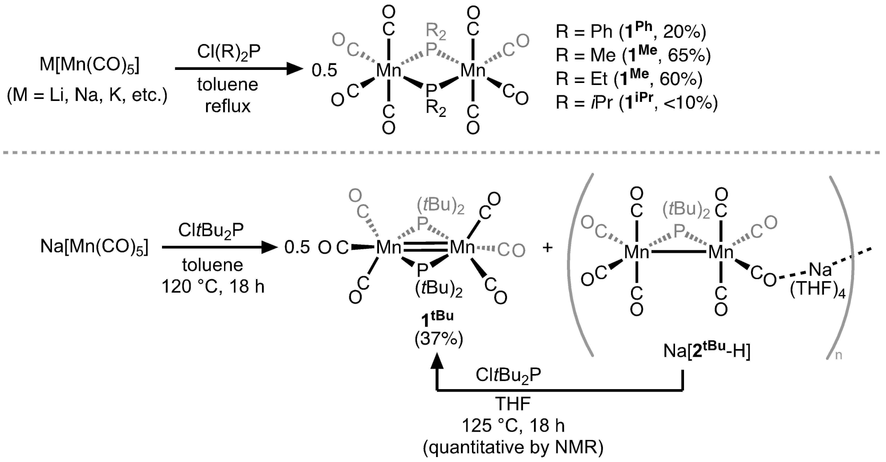
In much of the literature describing dinuclear Mn(I) complexes with phosphido bridges, the compounds are described as unsaturated having M–M bonds. However, electron counting formalisms dictate that the octacarbonyl dinuclear Mn compounds do not have M–M bonds; this includes those with bridging hydride ligands.[46] Removal of a proton from $\mathbf{2}^{\mathrm{R}}$ forms anions like $[\mathbf{2}^{t\mathrm{Bu}}\text{-H}]^-$ which does contain formal M–M bonding (section 3.3). Similarly, removal of CO ligands from the octacarbonyl compounds leads to formal M–M bonding, as in $\mathbf{1}^{t\mathrm{Bu}}$. Aside from electron counting formalisms, the Formal Shortness Ratio (FSR), defined as the ratio of the distance between two atoms to the addition of their atomic radii, can be used to as an additional empirical factor in deducing M–M character.[47] An FSR ≥ 1 implies no M–M bonding and anything <1 is generally indicative of a bond. As an illustrative example, $\mathbf{1}^{i\mathrm{Pr}}$ has an FSR = 1.37, and $\mathbf{1}^{t\mathrm{Bu}}$ has FSR = 0.94.

2.3. Synthesis of $\mathbf{1}^{\mathrm{R}}$ by oxidative addition across P–P bonds

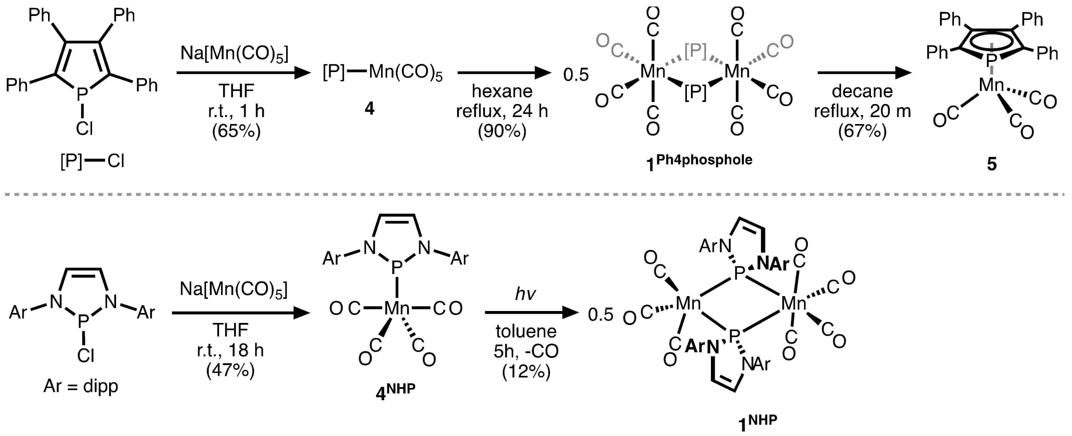
Complexes $\mathbf{1}^{\mathrm{R}}$ can be synthesized via the oxidative addition of $\mathrm{Mn_2(CO)_{10}}$ across $\mathrm{R_2P{-}PR_2}$. The reaction requires high-temperatures and hydrocarbon solvents such as toluene, xylene or decalins (Scheme 4, left). $\mathbf{1}^{\mathrm{Ph}}$ was synthesized in moderate yields (46 %) in a reaction between in situ generated tetraphenyl bisphosphide ($\mathrm{Ph_2P{-}PPh_2}$) and $\mathrm{Mn_2(CO)_{10}}$ in refluxing toluene.[40] A higher yielding synthesis (84 %) of $\mathbf{1}^{\mathrm{Ph}}$ with $\mathrm{Ph_2P{-}PPh_2}$ was recently achieved by employing $\mathrm{Me_3NO}$ as a reagent prior to addition of the bisphosphide.[29] Returning to the phosphole system described above, when $\mathrm{Mn_2(CO)_{10}}$ and tetrakis-(2,3,4,5-tetraphenyl)-bis-phosphole were allowed to react, only the η^5



Scheme 1. The main class compounds discussed in this review are presented using the following abbreviations: $[\{Mn(CO)_4\}(\mu\text{-}PR_2)]_2$ (**1^R**); $[\{Mn(CO)_4\}_2(\mu\text{-}PR_2)(\mu\text{-}H)]$ (**2^R**); $[\{Mn(CO)_4\}(\mu\text{-}PR_2)(\mu\text{-}H)\{Mn(CO)_3(L)\}$ (**$3^{R/L}$**). There are few variants of each class. For example, the number of carbonyl ligands (**1^{tBu}**), or bromido in pace of hydrido (**$2^{DBP/Br}$**), or a disubstituted compound (**$3^{Cy/(PMe3)2}$**). In such instances, the differences are indicated in the text where the complex is described, or they are simply given a new number. Finally, the mono- and bis-PP-clip dimanganese(I) dihydrides are described and reactivity compared against that of the phosphido complexes.



Scheme 2. Synthesis of 1^R using R_2PCl reagents.[38,40,29]



Scheme 3. Synthesis of dinuclear Mn(I) complexes with NHP–Cl reactants.[42]

complex **5** was obtained (Scheme 3);[42] presumably this reaction occurred through intermediacy of **$1^{Ph4phosphole}$** or **4**. Bottomley and coworkers used a dibenzophosphole (DBP) reagent to form dimanganese complex **1^{DBP}** (Scheme 4).[48] Bulkier tetra-alkyl bisphosphide such as $iPr_2P\text{–}PiPr_2$ is not effective at generating the species **1^{iPr}** ($\leq 7\%$).[29] $Me_2P\text{–}PMe_2$ has been used to prepare **1^{Me}**.[49] The hydride $HMn(CO)_5$ was also used in a reaction with $(CF_3)_2P\text{–}P(CF_3)_2$ to prepare **1^{CF3}** and the mononuclear pentacarbonyl $Mn(CO)_4P(CF_3)_2$ (**4^{CF3}**),[50] although neither of these have been completely characterized.

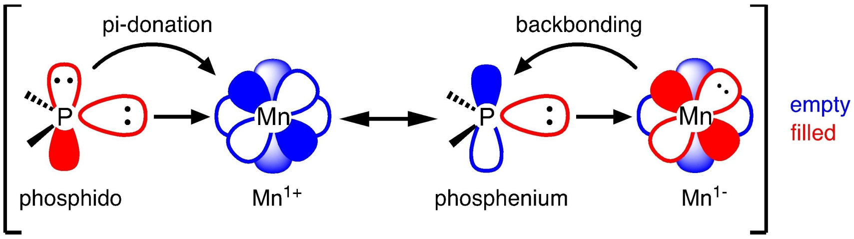
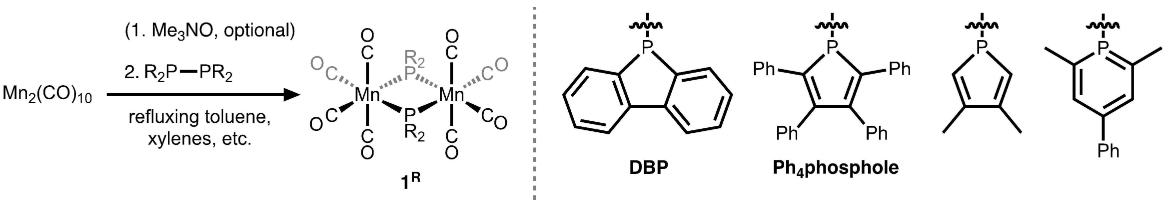


Figure 1. Qualitative orbital description of the two limiting Mn–PR_2 resonance structures. Sometimes the molecular structure determined using X-ray diffraction provides clear indicators of the dominant formalism.[45]



Scheme 4. Left: Synthesis of 1^R by means of oxidation of addition of bisphosphide reagents with $Mn_2(CO)_{10}$. Right: Examples of phosphole reagents used to prepare 1^R.[42,43,48,51]

It is also possible to use the bisphosphidesulfide reagents (i.e., $R_2P(S)–P(S)R_2$) in preparation of $\mathbf{1}^R$ (R=Me, Et, *n*Pr, *n*Bu), but yields are diminished (≈20%) and are contaminated with Mn complexes containing dialkylthiophosphinate ($P(S)R_2^-$) groups.[52] This is not a significant problem though because, given that $\mathbf{1}^R$ are typically bench-stable (Figure 2), the products can be separated using column chromatography. This method might be useful in generating complexes of $\mathbf{1}^R$ where the reduced bisphosphide reagent is difficult to prepare and/or handle.

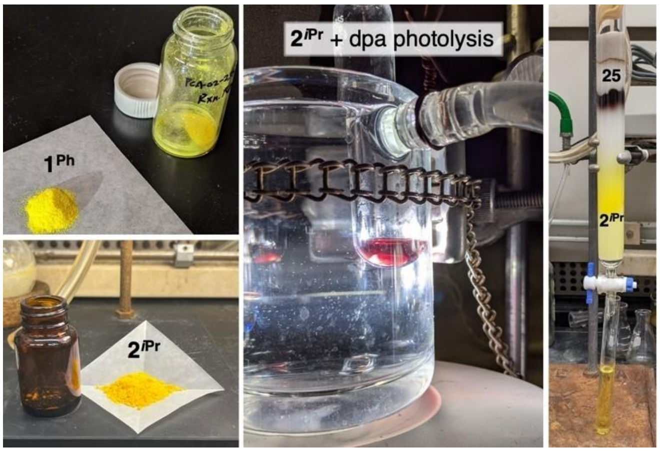
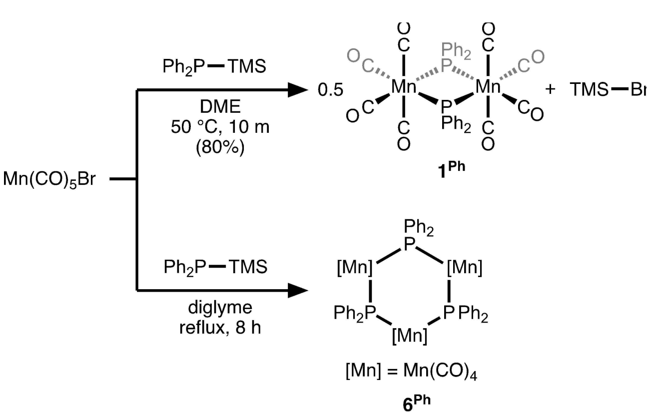


Figure 2. Air stability of the phosphido complexes demonstrated with $\mathbf{1}^{Ph}$ (top left), $\mathbf{2}^{iPr}$ (bottom left), photolysis for synthesis of **25** (center image) followed by its isolation by column chromatography on the bench (right). The unreacted starting material $\mathbf{2}^{iPr}$ shown here was recovered and reused.

2.4. Synthesis of 1^R by transmetallation using $R_2P–SiR'_3$ or lithiated phosphidos

$\mathbf{1}^{Ph}$ can be synthesized in high yields (yield=80%) by transmetallation of $Mn(CO)_5Br$ and $Me_3Si–PPh_2$. Transmetallation uses significantly milder conditions compared to those described earlier (the reaction is complete within 10 min at 50 °C) (Scheme 5).[53] However, the reaction is temperature and time dependent. For example, the trinuclear complex $[\{Mn(CO)_3\}(\mu\text{-}PPh_2)]_3$ ($\mathbf{6}^{Ph}$) forms if the reaction is carried out in refluxing diglyme for 8 h.[53]

Following similar strategy, $\mathbf{1}^H$ was prepared through transmetallation of $Mn(CO)_5Cl$ and $Me_3Si–PH_2$.[54] This system behaved similarly to that shown in Scheme 5. $\mathbf{1}^H$ reacts with CX_4 to yield $\mathbf{1}^X$, where X=Cl, Br, and I. The trinuclear complex $\mathbf{6}^H$ reacts with CCl_4 to make $\mathbf{6}^{Cl}$, and is thermally unstable, converting into $\mathbf{1}^{Cl}$ when heated. Additionally, $\mathbf{1}^X$ (or $\mathbf{6}^{Cl}$) react



Scheme 5. Synthesis of $\mathbf{1}^{Ph}$ and $[\{Mn(CO)_3\}(\mu\text{-}PPh_2)]_3$ ($\mathbf{6}^{Ph}$) from transmetallation.

with $AgBF_4$ to form 1^F (or 6^F). These halogenated reagents might be useful precursors for a variety of other compounds.

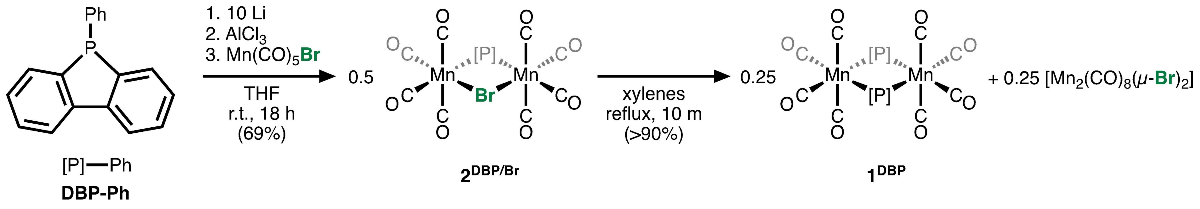
Another transmetallation strategy is to use lithiated phosphide reagents and $Mn(CO)_5Br$. This was accomplished by Bottomley and coworkers using lithiated dibenzophosphole (DBP) to make the mixed bromide/DBP octacarbonyl $2^{DBP/Br}$, which at elevated temperatures disproportionates in high yield to 1^{DBP} and the known dimer $[Mn_2(CO)_8(\mu\text{-}Br)_2]$ (Scheme 6).[48]

2.5. Synthesis of 2^R and 1^R by oxidative addition across P–H bonds

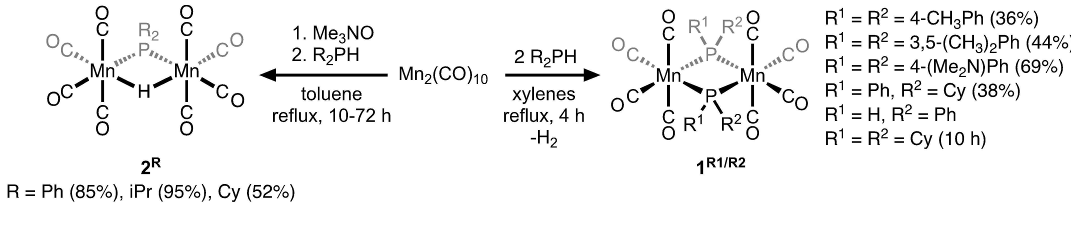
Complexes of the form $[\{Mn(CO)_4\}_2(\mu\text{-}PR_2)(\mu\text{-}H)]$ (2^R) can be synthesized via the oxidative addition of P–H bonds in R_2PH using $Mn_2(CO)_{10}$ (Scheme 2, left-bottom). Hayter was the first to report the synthesis of 2^{Ph} via this strategy, albeit in low yield (12 %).[40] An improved synthesis for 2^{Ph} using refluxing decalins was found (85 %), suggesting that the reaction requires high temperatures.[55] Similarly, reacting Cy_2PH and $Mn_2(CO)_{10}$ in refluxing xylenes resulted in formation of 2^{Cy} (52 %).[56] When $CyPH_2$ is used instead, the result is a mixture of *cis*- and *trans*-$[\{Mn(CO)_4\}_2(\mu\text{-}H)(\mu\text{-}P(H)Cy)]$ ($2^{Cy,H}$).[57]

As will be discussed later, the high temperatures employed to synthesize 1^R and 2^R are likely required to force CO dissociation. Consistent with this hypothesis use of Me_3NO accelerates the reaction and allows for a synthesis at lower temperatures. For example, the preparation of 2^{Ph} in high yield (85 %) can be accomplished in toluene at 120 °C when Me_3NO is included as a co-reactant.[29] This is a vast improvement and does not require the high temperatures associated with refluxing decalin (b.p. = 190 °C). This strategy is general and has been employed for the synthesis of other 2^R, including 2^{iPr} (Scheme 7, left).[29] Further evidence for the dissociative hypothesis is noted by the use of light in the synthesis of $2^{N(iPr)2}$, which was prepared by photolysis of a mixture $Mn_2(CO)_{10}$ and $(iPr_2N)_2PH$ in THF 70 °C (50 %).[58]

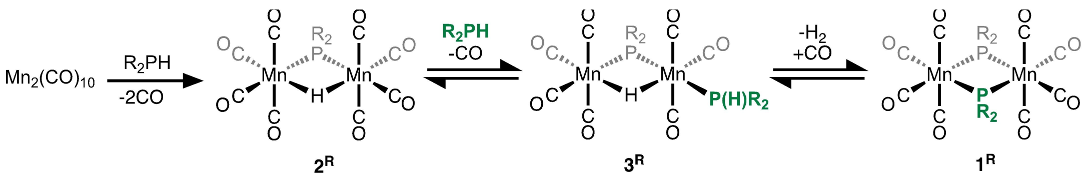
The reaction between $Mn_2(CO)_{10}$ and R_2PH does not always furnish 2^R as the sole product. Sometimes, 1^R is a corresponding byproduct,[57] or the main product when two equivalents of R_2PH are used (Scheme 7, right). This was demonstrated by Westerhausen and others in the synthesis of several mixed $1^{R1,R2}$ complexes.[59–63] In Westerhausen's report, it was noted that H_2 was a byproduct in these instances. It was demonstrated that this occurs through a series of reactions involving $3^{R/L}$ as an intermediate when R = Ph or *i*Pr (Scheme 8).[29] For instance, after P–H bond activation by $Mn_2(CO)_{10}$ to form 2^R, ligand substitution between 2^R and the second equivalent of R_2PH results in loss of CO and $3^{R/L}$. This latter species, when heated, loses H_2 and forms 1^R as the main product. This series of reactions can be reversed by addition of H_2 to 1^R (Scheme 8), a reaction described in more detail in section 3.2. Jones reported that $Mn_2(CO)_{10}$ and two equivalents of Cy_2PH afforded $3^{Cy/P(H)Cy2}$, and that sustained refluxing in toluene or xylenes did not lead to formation of 1^{Cy} (60 %).[64] Therefore, the conversion between



Scheme 6. Synthesis of 1^{DBP} by transmetallation with lithiated phosphide.



Scheme 7. Products that can result from oxidative addition of P–H bonds by $Mn_2(CO)_{10}$.



Scheme 8. Summary of P–H bond activation reactions with $Mn_2(CO)_{10}$ and 3^R (demonstrated for R = Ph and iPr).

these species as shown in Scheme 8 does not always proceed and is highly ligand dependent.

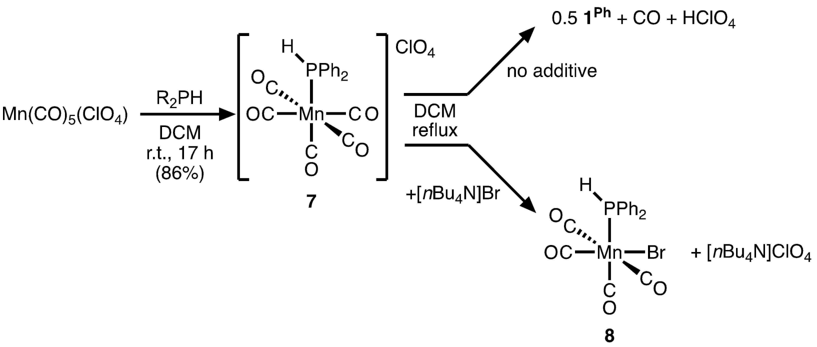
Another example of P–H oxidative addition is exemplified by the reactivity of the mononuclear cationic complex [Mn(CO)$_5${P(H)Ph$_2$}]ClO$_4$ (**7**) (Scheme 9).[65] **7** was synthesized by the reaction of Mn(CO)$_5$(ClO$_4$) and Ph$_2$PH at r.t. in DCM. When heated, it converts quantitatively into **1**$^{\mathbf{Ph}}$ and HClO$_4$. A plausible mechanism for the formation of **1**$^{\mathbf{Ph}}$ is as follows: (*i*) **7** dissociates a CO, (*ii*) intramolecular oxidative addition (alpha-hydride elimination) from the phosphine, (*iii*) reductive elimination (deprotonation) forming HClO$_4$ and **4**$^{\mathbf{Ph}}$, (*iv*) finally subsequent dimerization of the intermediate **4**$^{\mathbf{Ph}}$. This mechanism is circumstantially supported by the fact that if a nucleophile (e.g., Br$^-$) is included in the heating of **7**, it traps the unsaturated species before oxidative addition occurs leading to exclusive formation of **8** (Scheme 9).[65] It should be possible to interconvert **1**$^{\mathbf{Ph}}$ and **8** by addition of HBr and AgX, respectively.

3. Reactivity of dinuclear Mn(I) phosphido systems

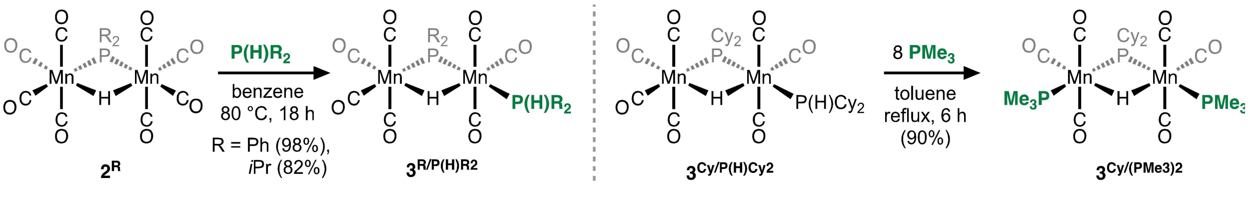
3.1. Substitution of CO ligands

Ligand substitution with PR$_3$ in complexes like **1**$^{\mathbf{R}}$, **2**$^{\mathbf{R}}$, and **3**$^{\mathbf{R/L}}$ typically occurs in the plane formed by the diamond core.[41] For instance, the reaction between **2**$^{\mathbf{Ph}}$ and one equivalent of Ph$_2$PH affords **3**$^{\mathbf{Ph/P(H)Ph2}}$ with Ph$_2$PH ligand *trans* to the phosphido and *cis* to hydride (Scheme 10, left).[29,66] Also, treatment of **3**$^{\mathbf{Cy/P(H)Cy2}}$ with excess PMe$_3$ results in the formation of **3**$^{\mathbf{Cy/(PMe3)2}}$ (90%) with the stereochemistry shown in Scheme 10 (right).[64]

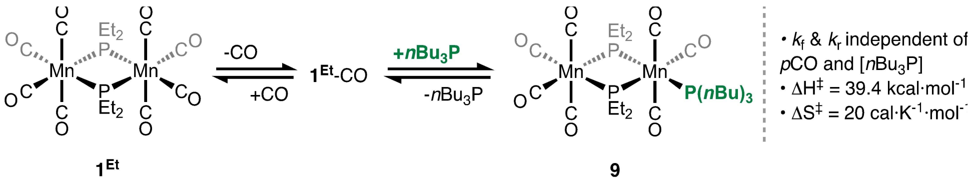
The mechanism of ligand substitution for the bis-phosphido complex **1**$^{\mathbf{Et}}$ with phosphine nucleophile *n*Bu$_3$P to afford *cis-trans*-[{Mn(CO)$_4$(μ-PEt$_2$)$_2${Mn(CO)$_3$(*n*Bu$_3$P)}] (**9**) was studied in detail by Basato (Scheme 11).[41] The reaction has the hallmarks of a dissociative ligand substitution since the rate is independent of *p*CO and [*n*Bu$_3$P]; the reverse reaction of **9** and CO is similarly dissociative in nature. Furthermore, the activation parameters closely resemble those for dissociative ligand substitution with Mn$_2$(CO)$_{10}$ and MnX(CO)$_5$ ($\Delta H^{\ddagger} = 39.4$ kcal·mol^{-1} and $\Delta S^{\ddagger} =$ 20 cal·(K·mol)$^{-1}$ for **1**$^{\mathbf{Et}}$ and *n*Bu$_3$P).[67,68] The stereochemistry of the product (**9**) was determined to be *cis-trans*, meaning that



Scheme 9. Reactive landscape of [Mn(CO)$_5${P(H)Ph$_2$}]ClO$_4$ leading to **1**$^{\mathbf{Ph}}$ and other products.



Scheme 10. The most common position of substitution is in the plane formed by the Mn and bridging atoms.



Scheme 11. Dissociative ligand substitution reaction with **1**$^{\mathbf{Et}}$ and nBu$_3$P.

the *n*Bu_3P ligand is in the plane of the diamond core (Scheme 11). **9** can also react further with *n*Bu_3P to afford the disubstituted product with both *n*Bu_3P ligands in the diamond core plane (the respective *cis* or *trans* stereochemistry of the two *n*Bu_3P groups with respect to each other was not determined).

The stereochemistry in **9** and similar substitution patterns in other compounds might indicate that the labile CO originates from the position of substitution. However, several lines of evidence suggest otherwise. First, substitution with isonitriles, among other ligands, explored in detail by Mays and coworkers, indicates that a range of stereochemical positions are accessible (Scheme 12).[55]

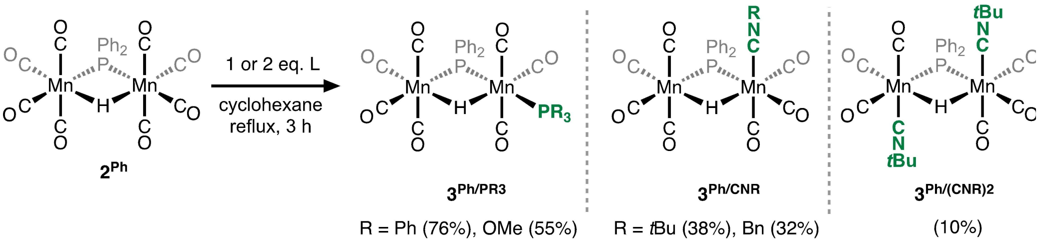
As expected, the substitution pattern for a variety of phosphine ligands gave products with the new PR_3 ligand in the position *trans* to phosphido and *cis* to the hydride. However, the isonitrile substitution pattern for $\mathbf{3}^{\mathbf{Ph/CNR}}$ is *cis* to both phosphido and hydride, and they are mutually *trans* to each other in the bis-substituted product $\mathbf{3}^{\mathbf{Ph/(CNtBu)2}}$. The structures of the complexes shown in Scheme 12 were determined using a combination of FTIR and ^1H and ^{13}C NMR spectroscopies, and the molecular structure of $\mathbf{3}^{\mathbf{Ph/(CN\mathit{t}Bu)2}}$ was determined using X-ray diffraction.

Secondly, the heptacarbonyl complex $[\{Mn(CO)_3(\mu\text{-}PPh_2)\}_2(\mu\text{-}CO)]$ ($[\mathbf{1}^{\mathbf{Ph}}\text{-CO}]$) has been isolated by CO photolysis of $\mathbf{1}^{\mathbf{Ph}}$ and does not contain information about which CO was lost (Scheme 13).[29,69] Rather, $[\mathbf{1}^{\mathbf{Ph}}\text{-CO}]$ has a bridging CO ligand, and this means that an incoming nucleophile can attack at various positions leading to different stereochemical outcomes. Similarly, the heptacarbonyl $\mathbf{1}^{\mathbf{NHP}}$ adopts a configuration where one unsaturated *fac*-$Mn(CO)_3$ can nominally lead to various stereochemical outcomes (Scheme 3).[44] Finally, density functional theory was used to determine which of the three possible vacant positions furnished the lowest energy heptacarbonyl isomer $[\{Mn(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}PMe_3)(\mu\text{-}H)]$, $[\mathbf{2}^{\mathbf{Me}}\text{-CO}]$.[30] The calculated Mn–CO bond dissociation energies (BDFE) shown in Scheme 13 are for the elevated temperatures that were used in experiments for $\mathbf{2}^{\mathbf{iPr}}$ to drive CO dissociation (refluxing toluene); calculations for the BDFEs at r.t. gave same ordering and were about 4 to 6 kcal/mol higher. Collectively, these data suggest the following general mechanism for substitution reactions in this class of compounds: (*i*) dissociation of CO occurs from the *cis*-labilized position, a supposition fully consistent with other six-coordinate Mn(I) centers;[70] (*ii*) the heptacarbonyl intermediate can adopt a structure similar to the one known for $[\mathbf{1}^{\mathbf{Ph}}\text{-CO}]$ or $\mathbf{1}^{\mathbf{NHP}}$ (Scheme 13 and Scheme 3); (*iii*) attack by the nucleophilic ligand is governed by steric properties; (*iv*) finally, since ligand substitution is reversible and also dissociative in nature (Scheme 11), the thermodynamic product is observed with specified stereochemistry.

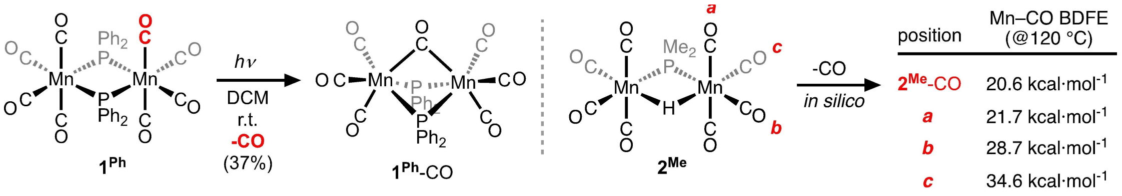
3.2. Reactivity of Mn–PR_2 moieties with H_2

Lacy and coworkers demonstrated Mn-phosphido complexes can activate H_2 across the Mn–P bond (Scheme 14).[29] This was shown by the reaction of $\mathbf{1}^{\mathbf{Ph}}$ and H_2 in toluene at elevated temperatures to yield $\mathbf{3}^{\mathbf{Ph/P(H)Ph2}}$. The reaction is slow (33 h) even with relatively forcing conditions (125 °C), and conversion to product was only ≈40% with unreacted $\mathbf{1}^{\mathbf{Ph}}$ remaining. The sluggishness was hypothesized to be the result of the difficulty in the thermal liberation of CO and was tested by treating $[\mathbf{1}^{\mathbf{Ph}}\text{-CO}]$ with H_2. This reaction only required heating at 70 °C for 10 h for near quantitative conversion to the same $\mathbf{3}^{\mathbf{Ph/P(H)Ph2}}$. The reactions with H_2 appear general, as they were also repeated using the $\mathbf{1}^{\mathbf{\mathit{i}Pr}}$ analog, which exhibits the reversibility shown in Scheme 8. Note that $\mathbf{2}^{\mathbf{R}}$ complexes do not appear to be reactive toward H_2 (1 atm, toluene, 125 °C).

It is also possible to generate $\mathbf{2}^{\mathbf{R}}$ (R = Ph, *i*Pr) by reacting ClR_2P and $Mn_2(CO)_{10}$ with H_2 (1 atm, 125 °C) (Scheme 14, right).29

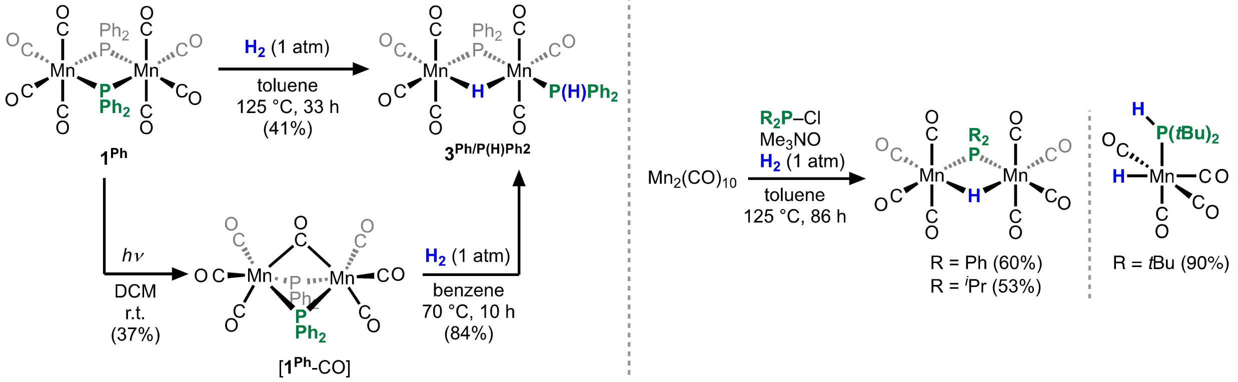


Scheme 12. Substitution of CO in $\mathbf{2}^{\mathbf{Ph}}$ with L-type ligands leading to mono-and di-substituted products.



position	Mn–CO BDFE (@120 °C)
$\mathbf{2}^{\mathbf{Me}}$-CO	20.6 kcal·mol^{-1}
a	21.7 kcal·mol^{-1}
b	28.7 kcal·mol^{-1}
c	34.6 kcal·mol^{-1}

Scheme 13. (left) Generation of heptacarbonyl $[\mathbf{1}^{\mathbf{Ph}}\text{-CO}]$. (right) DFT computed energy of Mn–CO bond dissociation free energy (BDFE) from $\mathbf{2}^{\mathbf{Me}}$. Note, the energies for entry "**a**", "**b**", and "**c**", the Mn–CO dissociation is for the product with a vacant site and no bridging CO.



Scheme 14. H_2 activation across Mn-phosphido moieties.

It was proposed that 1^R forms as an intermediate after a P–Cl bond activation (for instance, see Scheme 6 for reactivity of Mn(μ-Br)(μ-PR_2) species), which then activates H_2 as described immediately prior for 1^{Ph}. Bulkier Cl(tBu)$_2$P reacted differently to afford numerous products including free (tBu)$_2$PH and (tBu)$_2$PH manganese carbonyl complexes (Scheme 14, right).

N-heterocyclic phosphido (NHP) manganese complexes have reactivity with elimination of H_2. This was demonstrated by Gudat using 4^{NHP} (Scheme 15),[44] which was treated sequentially with a hydride and proton reagent to yield **10** and **11**, respectively. The latter undergoes H_2 photolysis upon irradiation at r.t. in benzene to reform 4^{NHP}.

3.3. Acid/base chemistry of hydrido ligand in Mn–PR_2 complexes

The bridging hydrido ligand in 2^R is acidic. For instance, Mays and coworkers synthesized bench-stable PPN[{Mn(CO)$_4$}(μ-PPh$_2$)-{Mn(CO)$_4$}] (PPN[2^{Ph}-H]) by reacting 2^{Ph} with $NaBH_4$ or methanolic KOH followed by salt metathesis with [PPN]Cl (Scheme 16, top).[39,71] The crystal structure of PPN[2^{Ph}-H] has a Mn–Mn bond distance of 2.87 Å, similar to the 2.78 Å distance in the tBu$_2$P analog Na[2^{tBu}-H] (Scheme 2).[29] The [2^{Ph}-H]$^-$ anion reacts with a host of metal-halide complexes to form hetero-multimetallic complexes **12** (Scheme 16),[71–73] exemplifying the importance of the Mn(−1) formalism discussed earlier.[45]

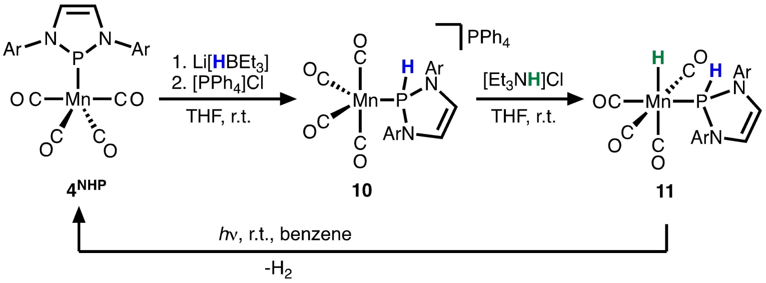
Deprotonation of $2^{Cy,H}$ with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) leads to the formation of an anion, which was not isolated, that reacted with various auric-chloride complexes to yield hetero-bimetallic complexes where the Au atom resides on the P-atom or as a bridge to the two Mn ions (Scheme 16, bottom).[56,57,74] Other related higher nuclearity clusters have been prepared, although they are not discussed further because they commonly degrade into homodinuclear complexes like 1^R or 3^R.[66,75,76]

Unsurprisingly, treatment of the anionic octacarbonyl complexes [2^R-H]$^-$ with acids yield the corresponding neutral bridging hydrides 2^R. This was shown by the protonation of [2^{Cy}-H]$^-$ with $Et_2O\cdot HBF_4$ in DCM, as shown in Scheme 17.[77]

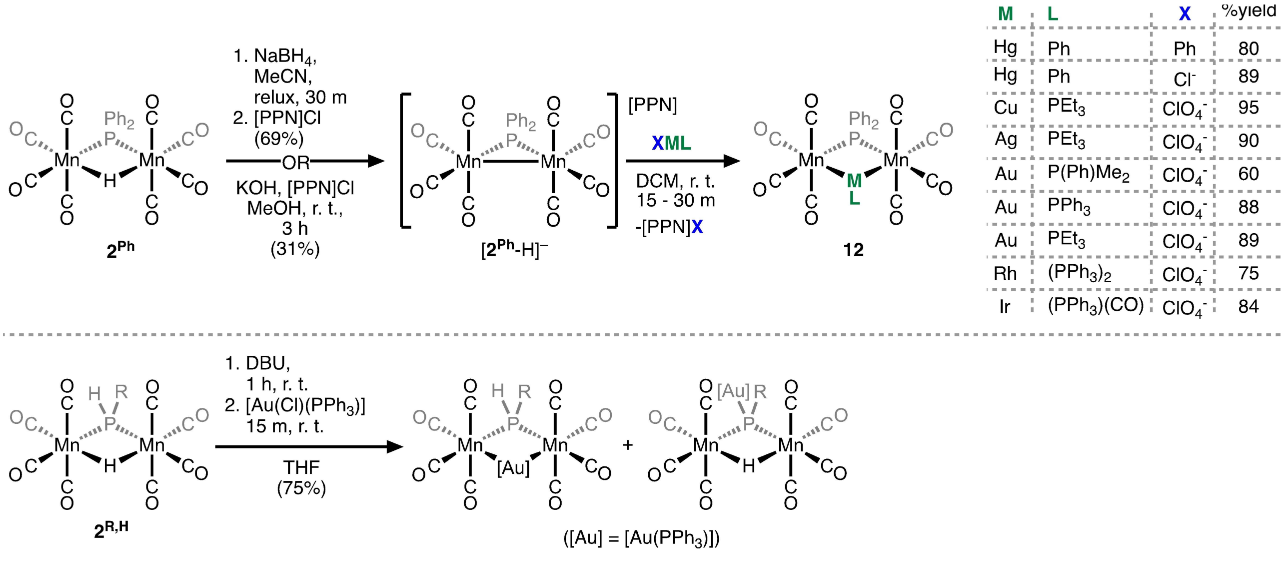
3.4. Synthesis and reactivity of Mn–PR_2-vinyl compounds and relevance in catalysis

3.4.1. Synthesis of Mn–PR_2-vinyl compounds

The reaction of alkynes with 2^R is typically slow or does not occur at room temperature. Furthermore, complicated mixtures result when reactions are carried out at elevated temperatures. Therefore, the reactions leading to vinylic inserted complexes (**13**–**26**) are driven photochemically near room temperature; several examples derived from R^1CCR^2 and 2^{Ph} are shown in Scheme 18,[55,78] and two have been derived from 2^{iPr}.[30]

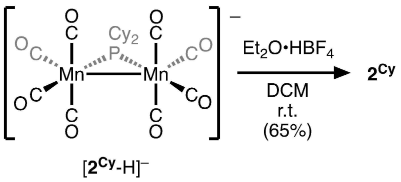


Scheme 15. H_2 elimination to form a phosphido-Mn complex.



M	L	X	%yield
Hg	Ph	Ph	80
Hg	Ph	Cl^-	89
Cu	PEt_3	ClO_4^-	95
Ag	PEt_3	ClO_4^-	90
Au	$P(Ph)Me_2$	ClO_4^-	60
Au	PPh_3	ClO_4^-	88
Au	PEt_3	ClO_4^-	89
Rh	$(PPh_3)_2$	ClO_4^-	75
Ir	$(PPh_3)(CO)$	ClO_4^-	84

Scheme 16. Acid/Base chemistry of 2^R.

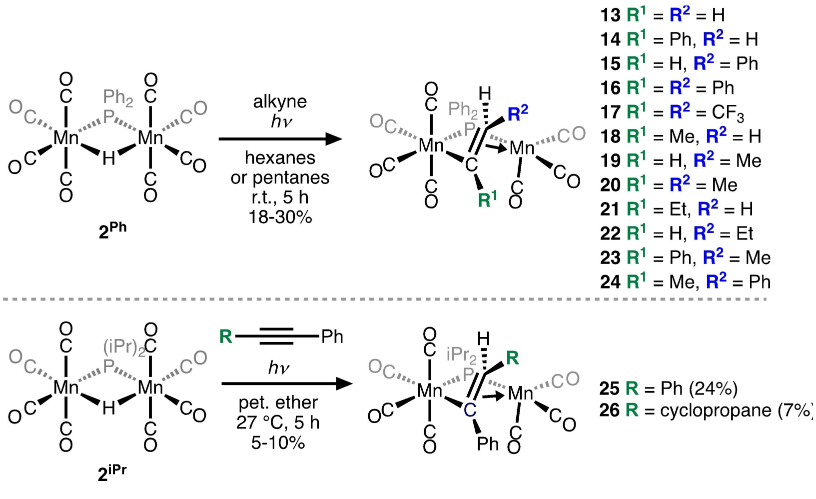


Scheme 17. Protonation of anionic $[2^R\text{-}H]^-$ leads to 2^R.

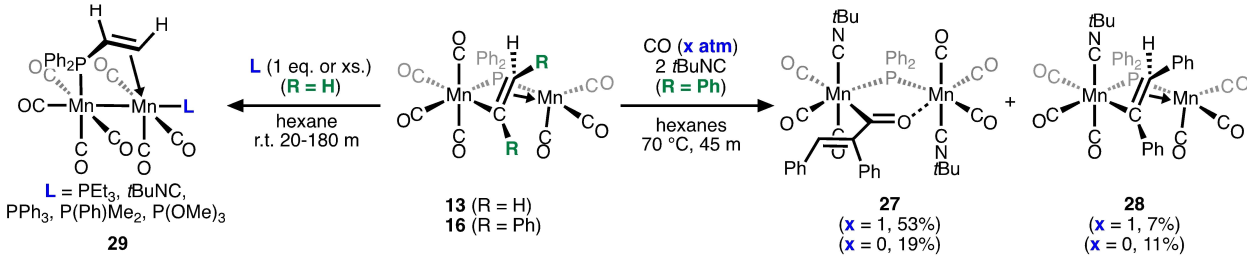
Conveniently, they are typically air and moisture stable enabling purification from unreacted 2^R using column chromatography (Figure 2). A possible mechanism for formation of **13**–**26** is as follows: dissociative ligand substitution from 2^R to afford a coordinated alkyne (not observed); migratory insertion leading to **13**–**26**. Another possibility is a bimolecular "molecular-assisted" homolysis as determined for $Mn(CO)_5H$ and alkenes.[10,11] However, a non-radical process was demonstrated through the use of a cyclopropyl functionalized alkyne and isolation of the product with an in-tact cyclopropyl ring in **26** (Scheme 18, bottom).[30] Another possibility is protonation of the alkyne prior to coordination (section 3.3). Given the use of light to drive CO dissociation near room temperature, the dissociative migratory insertion reaction seems most probable.

3.4.2. Reactivity of Mn–PR₂-vinyl compounds with nucleophiles, alkynes, and allene

The vinyl-Mn complexes can undergo a variety of transformations. One possibility is migratory CO insertion to form α,β-unsaturated acyl-bridged complex **27** by addition of *t*BuNC to **16** (Scheme 19, right).[79,80] Another product of this reaction is



Scheme 18. Photochemically driven insertion of alkynes with 2^R.

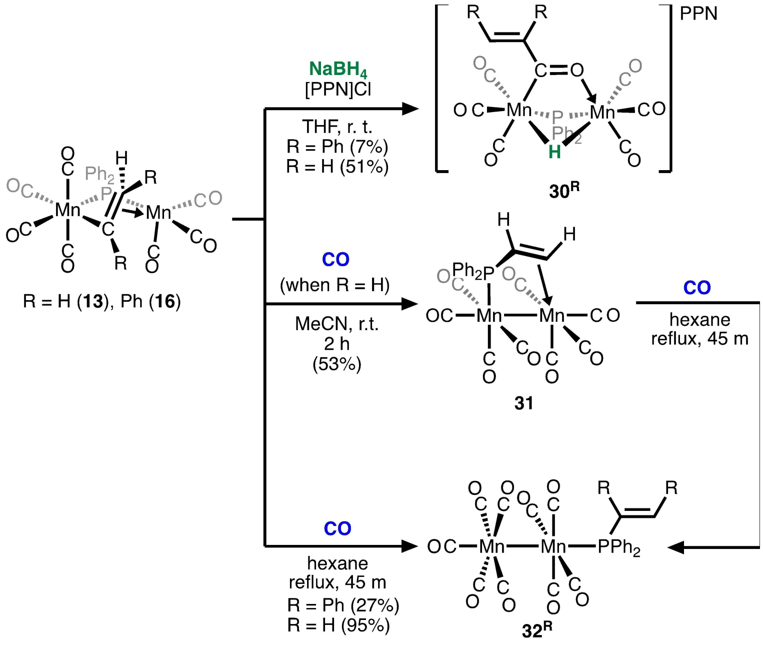


Scheme 19. Reactivity of Mn-vinyl-PR$_2$ compounds **13** and **16** (R=H, Ph) with nucleophiles (isonitriles and phosphines).

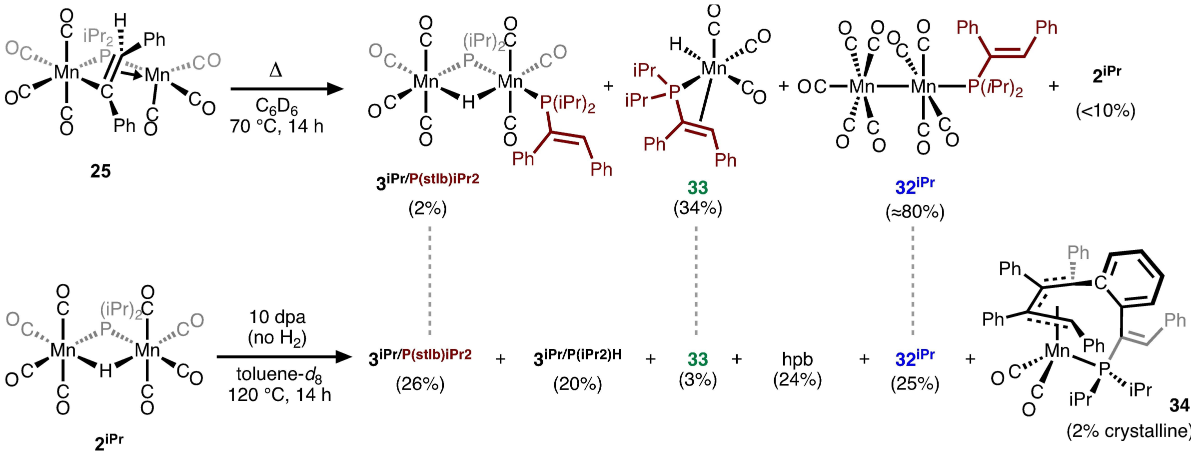
the substituted compound **28**, yet its formation is inhibited if the reaction between **16** and *t*BuNC is carried out under CO atmosphere. This notable result indicates that the Mn(CO)$_3$ side of **13**–**26** is not the site of substitution, and that ligand substitution on compounds like **13**–**26** is dissociative in nature occurring on the Mn(CO)$_4$ side of the complex. This becomes important in describing the reactivity of **25** and **26** with H$_2$ later. The acetylene derived vinyl complex **13** is much more reactive toward nucleophiles. For example, **16** is unreactive toward *t*BuNC or phosphine ligands at room temperature, but **13** reacts readily at room temperature. The coordination reactions with **13** induce a P–C bond reductive elimination to afford **29** (Scheme 19, left).

Treatment of **13** or **16** (R=H, Ph) with NaBH$_4$ leads to a different CO-inserted complex **30^R** that has a new bridging hydride ligand (Scheme 20). Addition of CO to **13** or **16** induces P–C reductive elimination, just like it did for reaction of phosphine ligands with **13**. The products contain the vinylic phosphines in either a bridging motif, as in **31**, or in terminal position, as in **32^R** (Scheme 20).[79,80]

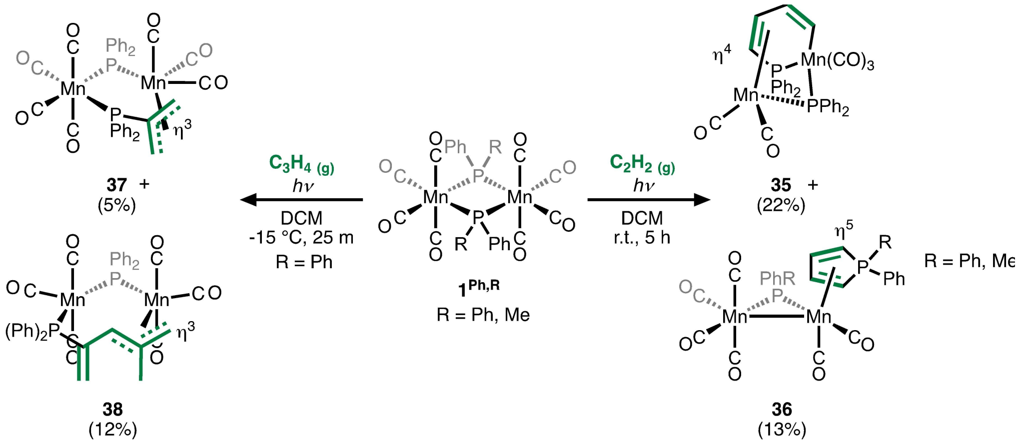
It was noted in section 3.4.1 that reactions between alkynes and **2^R** at elevated temperatures give complicated mixtures, and that preparation of **13**–**26** required photolysis near room temperature. The complicated mixtures arise from the thermal instability of **13**–**26**, as was demonstrated for **25** and **26**.[30] For example, synthesis and isolation of **25** was accomplished using broadband irradiation at 27 °C. Heating **25** led to formation of **3$^{iPr/P(stlb)iPr2}$**, **32^{iPr}**, and **33** resulting from P–C bond reductive elimination (Scheme 21). A similar mixture of byproducts resulted when **2^{iPr}** was heated in the presence of 1 equiv. dpa at 80 °C, but this reaction was sluggish and mostly contained unreacted **2^{iPr}** (90 % remained after 44 h). Driving the reaction by addition of more dpa and at higher temperatures gave a slightly different set of compounds but with overall similar results to heating **25** (Scheme 21). All of these results are consistent with a dissociative mechanism involving loss of CO, coordination of the alkyne and then insertion, with the resulting vinyl species undergoing degradation through P–C bond reductive elimination.



Scheme 20. Additional reactivities of Mn-vinyl-PR$_2$ compounds **13** and **16** (R=H, Ph) with hydride and CO reactants.

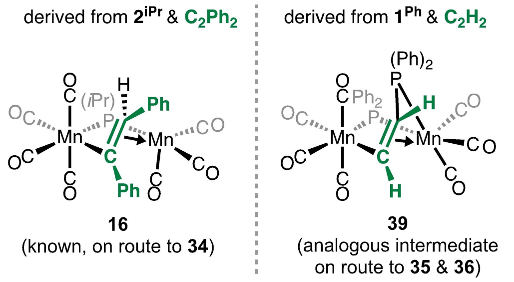


Scheme 21. Thermal instability of Mn-vinyl-PR$_2$ compound **25** yields similar mixture of compounds when **2^{iPr}** is allowed to react with dpa at elevated temperatures. Yield of hpb (hexaphenylbenzene) is relative to dpa.



Scheme 22. Reaction of **1^{Ph,R}** with acetylene (right) and allene (left).

The reactions of the non-hydride complex **1^{Ph}** with acetylene and allene (propadiene) have also been explored.[61,81] With acetylene, **1^{Ph}** was unreactive up to 90 °C, but with UV irradiation at room temperature gave at least nine different products, all in low yields. Two products, **35** and **36** were characterized with XRD and these contained new P–C bonds resulting from reductive elimination of transiently formed inserted intermediates (Scheme 22, right); intermediate **39** was proposed to be involved in the second insertion step leading to **35** and **36** (Scheme 23).[61] When the same reaction was carried out with allene instead of acetylene, at least 15 products were obtained, with only **37** and **38** isolated and characterized by XRD (Scheme 22, left). Products **34**–**38** highlight how, in addition to P–C bond reductive elimination, dinuclear Mn(I) vinyl compounds are subject to subsequent insertion reactions when there is excess unsaturated hydrocarbon substrate present.



Scheme 23. Proposed intermediate **39** in the double insertion products leading to **35** and **36**.

3.4.3. Reactivity of Mn–PR$_2$-vinyl compounds with H$_2$ and catalysis with the Mn–PR$_2$ system

The reaction with **25** and H$_2$ has also been explored in detail.[30] The organic product is, intriguingly, exclusively *trans*-stilbene, along with **2^{iPr}** as the major organomanganese product in addition to other byproducts associated with decomposition of

25 (Scheme 24). Unfortunately, the reaction with H_2 and **25** occurs at the same temperature where thermal decomposition begins, and this complicated a kinetic analysis.

It was proposed that the reaction of **25** and H_2 leading to *trans*-stilbene proceed through an H_2 adduct, **25**-H_2, and then H_2 insertion. The H_2 insertion step could give rise to an organomanganese product with coordinated *cis*-alkene **3**$^{iPr/cis-stlb}$ with eventual dissociation of stilbene, which was expected given the *cis*-configuration of the vinyl group(s) in **25**. However, *trans*-stilbene is the only product in the reaction with **25** and H_2, so this was deemed unlikely.[30] Furthermore, **25** and **2**^{iPr} do not isomerize *cis*-stilbene in time frames associated with *trans*-stilbene formation rates. Therefore, alternative mechanisms that did not produce *cis*-stilbene species were considered.

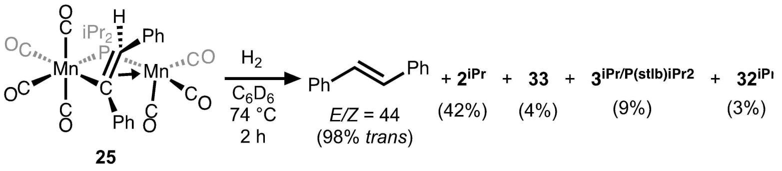
One possibility considered was a carbenoid species (**40**) (Scheme 25). Subsequent reactions with **40** might include an insertion to afford an alkyl intermediate (**43**), which would then allow for rotation about the single bond and β-hydride elimination giving *trans*-stilbene from **3**$^{iPr/trans-stlb}$. The carbenoid intermediate **40** is akin to the geminal addition products using Cp*Ru catalysts in *trans*-selective alkyne semihydrogenation.[82] Similar carbenoid intermediates have been invoked to account for *trans*-selective alkyne hydrosilylation reactions as well.[83,84] Some structurally related carbene complexes on Mn for which the structures have been determined with XRD have been prepared. These include the Fisher carbene complexes **41** and **42** derived from nucleophilic attack on CO ligands in **1**^{Ph} (Scheme 25).[85]

These reactions were combined to provide a mechanism of the catalytic alkyne semihydrogenation reaction by **2**^{R} (Scheme 26); the mechanism shown was calculated for **2**^{Me} by Lacy and coworkers.[30] However, considering the reactions described in this review so far, a few important alterations should be discussed. First, consistent with the CO dissociative paradigm for this class of compounds, it seems appropriate that the first step is loss of CO to afford an unsaturated intermediate **2**^{Me}-CO. The inclusion of this species in Scheme 26 is the only difference from the one in the literature, which contained the unsymmetrical isomer(s) described in Scheme 13. Second, H_2 addition to **25** was originally postulated to result in an H_2 adduct on the "unsaturated" $Mn(CO)_3$ side (shown). However, the reaction with **16** with *t*BuNC yielding **28** (Scheme 19) and the similarly elevated temperatures required suggests that H_2 addition is dissociative in nature leading to a $Mn_2(CO)_6(vinyl)(H_2)$ adduct. The relative energy of this species compared to **25** + H_2 was computed using DFT, and they only differed by 2 kcal/mol. The one presented in the literature, **25** + H_2, was the lower energy of the two and hence was included. As noted in the preceding paragraph, insertion could give rise to the expected *cis*-stilbene coordinated product **3**$^{Me/cis-stlb}$, but since *cis*-stilbene was not observed in careful stoichiometric reactions, the geminal H-addition carbenoid intermediate **40** was considered. This avoids the formation of *cis*-stilbene and offers one plausible explanation for the highly selective nature of the system that otherwise cannot catalyze *cis*-*trans* alkene isomerization.

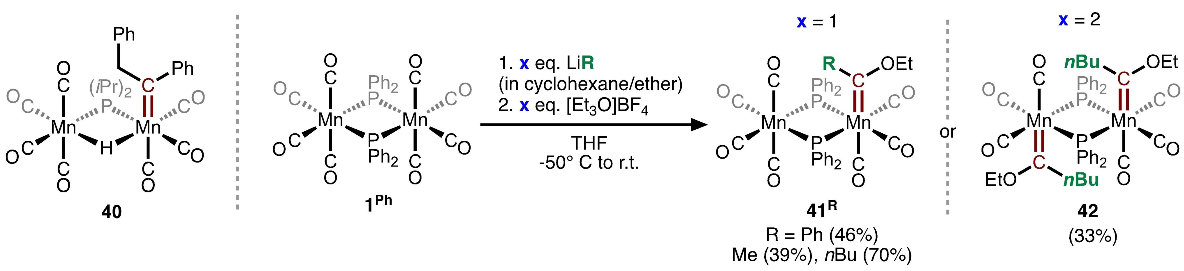
A radical-based mechanism was considered because Halpern and Baird demonstrated $Mn(CO)_5H$ hydrogenates alkenes through a bimolecular molecular-assisted radical mechanism.[10,11] In contrast however, the dinuclear system appears to operate via a non-radical path and this was tested using a cyclopropyl inserted species **26**, which upon treatment with H_2 resulted in exclusive formation of the *trans*-alkene with cyclopropyl ring intact (Scheme 27). Furthermore, **25** did not react with TEMPOH, indicating that Mn-vinyl bond homolysis is not an important process in the reactions discussed so far.

3.4.4. Involvement of Mn–PR$_2$-vinyl compounds in catalysis

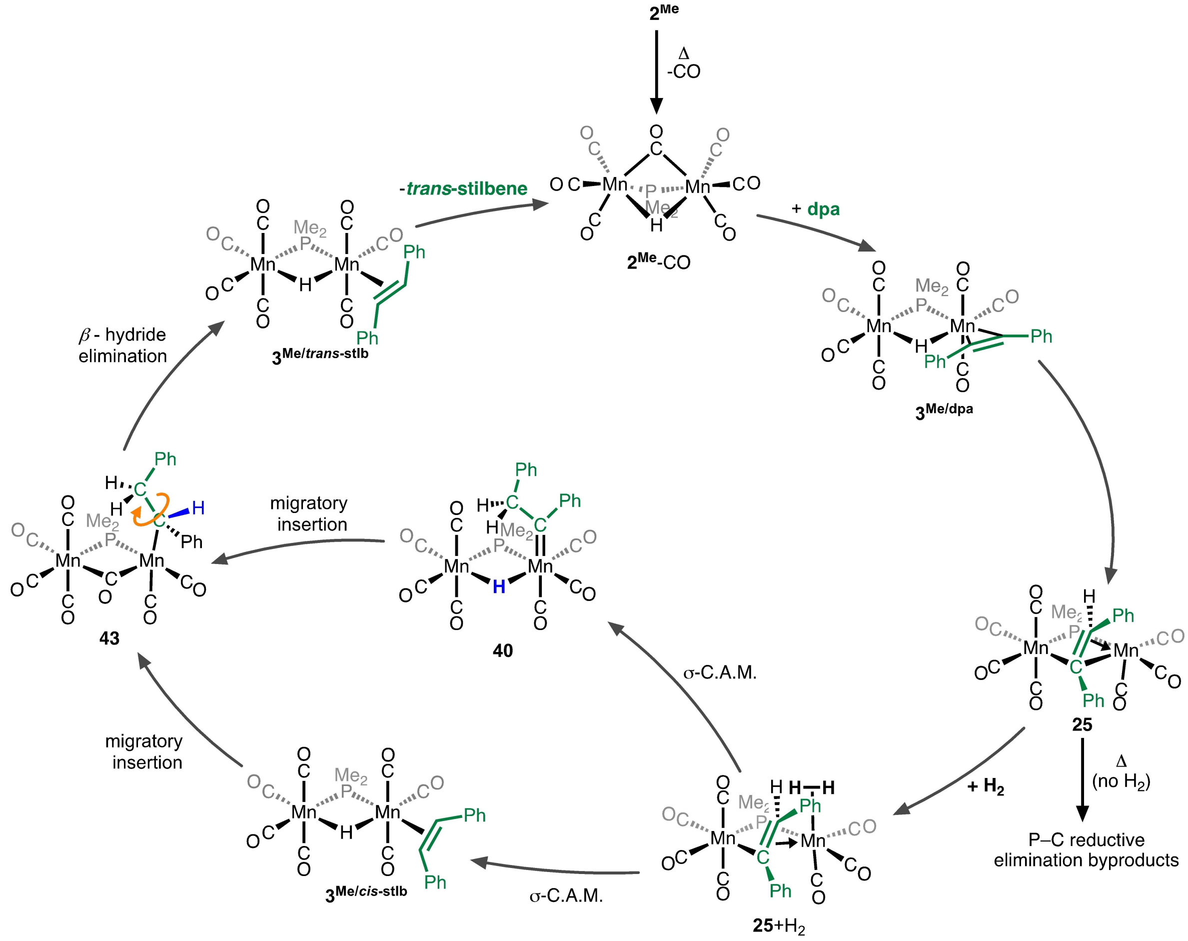
Alkyne semihydrogenation catalysis with the dinuclear platform has been attempted by Sappa and Lacy.[7,30] Sappa and co-



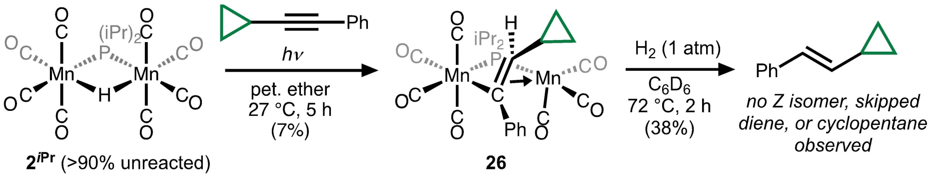
Scheme 24. Reaction of **25** with H_2 leads to formation of trans-stilbene.



Scheme 25. Proposed intermediate **40** (left). Synthesis of known Fisher carbene complexes **40** and **41** (right).



Scheme 26. Mechanism of E-selective alkyne semihydrogenation.



Scheme 27. Stepwise semihydrogenation of (cyclopropylethynyl)benzene indicate a non-radical mechanism.

workers investigated the catalytic activity of the dinuclear Mn(I) complexes **1**^{Ph}, **2**^{Ph}, and **2**$^{Ph/H}$ and the dinuclear Mn(0) complex *eq*-[Mn(CO)$_9$(HPPh$_2$)] for alkyne semi-hydrogenation. Their preliminary findings show that dinuclear Mn-complexes are capable of *E*-selective alkyne semi-hydrogenation (*E*-SASH) using diphenyl acetylene (dpa) as substrate, albeit with low efficiency. They demonstrated that amongst the compounds investigated, **2**^{Ph} was the best catalyst showing the highest efficiency (% yield of *trans*-stilbene = 50 %) and the selectivity (*E*/*Z* = 4) at elevated temperatures under 34 atm of H_2 over 48 h. Although these initial data are not the state-of-the-art, they demonstrate the capacity of the system to catalyze hydrogenations (via H_2 activation) and is the first reported example of a Mn(I) hydrogenation catalyst. The authors of this review further explored this hydrogenation in more detail to shed light on the mechanism involved.[30] They reported improved efficiency with the use of **2**^{iPr} as the catalyst for dpa *E*-SASH with high efficiency (% yield of *trans*-stilbene = 76 %) and selectivity under comparatively benign conditions (1 atm, 120 °C, 14 h). However, the substrate scope was limited under the conditions investigated. The experimental and theoretical mechanistic investigations support a nonradical operative mechanism, with **25** as catalytically active species and the rich coordination chemistry and reactivity possible on this platform (see above).

4. Synthesis and reactivity of PP-clipped dimanganese(I) dihydrides

4.1. Synthesis of dimanganese(I) dihydride complexes supported with "PP-clips"

All of the compounds described so far have had phosphido ligands, or were precursors or products of reactions involving dimanganese-phosphido complexes. Another similar class of compounds are the dinuclear manganese carbonyl dihydrides supported with one or two "PP-clips" (e.g diphenylphosphinomethane (dppm), or diethylphosphinomethane (depm), or tetraethyl diphosphite (tedip)); the synthesis and reactivity of this class of compounds was pioneered by Ruiz, Riera, and coworkers in addition to others. The hydride molecules in this class are typically synthesized by reduction of the bridging dihalide with $LiAlH_4$ or $Li[Et_3BH]$, and three selected examples are provided in Scheme 28.[86–89]

4.2. Reactivity of the PP-clipped dimanganese(I) dihydrides

4.2.1. Overview

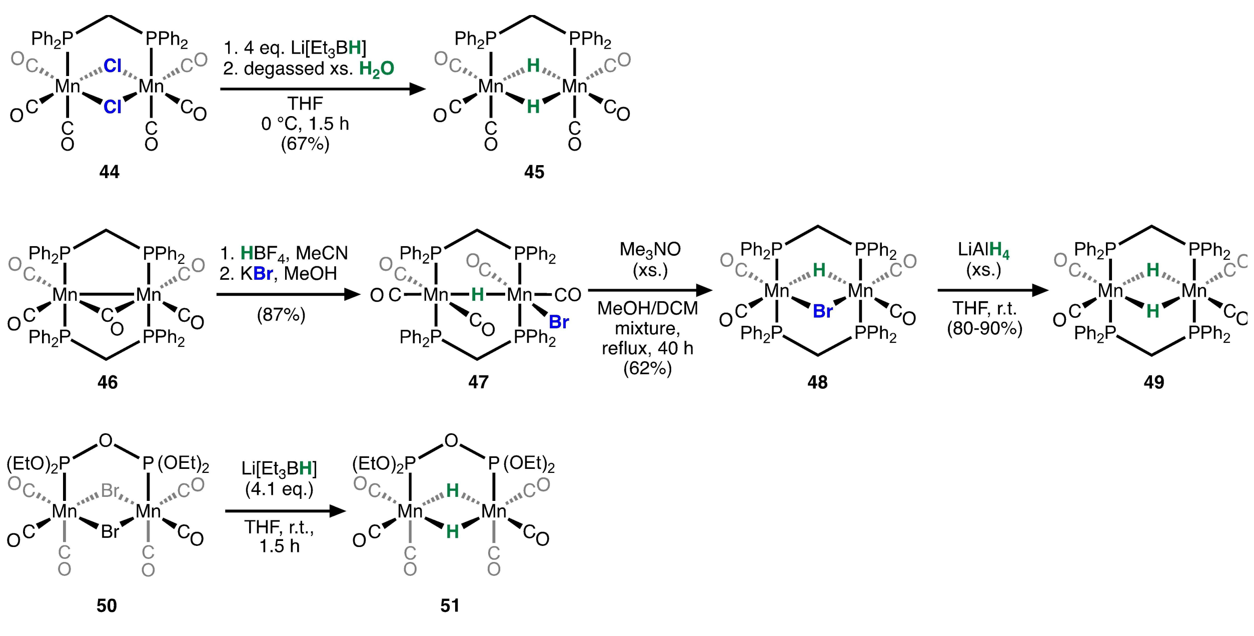
The reactivity of the hydrides in this class of molecules, such as **45**, **49**, and **51** generally mirrors the reactivity of the phosphido hydrides $\mathbf{2}^{R}$. This includes acid/base chemistry[90] and the propensity of the anions to form clusters like in Scheme 16,[88,91] insertion reactions with alkynes,[92] insertion reactions with nitriles and isonitriles,[87,93] reactions with neutral M-carbonyls (M=Fe, Cr, Mo, W) to yield higher nuclearity clusters,[94] reactions with main group hydrides,[89,95] and small molecule activations such as with elemental sulfur,[96] CO_2 and formic acid,[97,98] and oxides of nitrogen,[99] and reactions with R_2PH.[100] To avoid redundancy and to keep the discussion focused on reactions with specific relevance to the phosphido/hydrides discussed earlier, only the reactions with alkynes, nitriles, phosphines, and CO will be discussed. The reader is directed to the literature cited above for more details on the other systems.

4.2.2. Reactivity with alkynes and nitriles

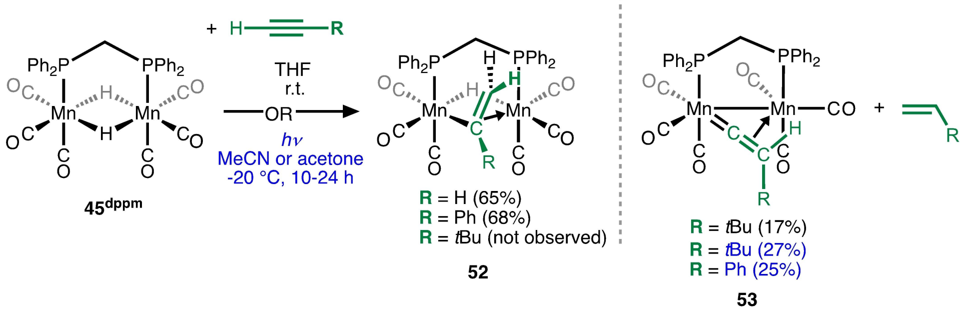
A major difference is that reactions do not always need such forcing conditions. This can be observed by the facile insertion reaction with 1-alkynes using **45** (Scheme 29).[92] In contrast to $\mathbf{2}^{R}$ which was virtually unreactive at room temperature with substituted alkynes, **45** reacts at room temperature to afford the inserted vinyl compound **52**, analogous to those obtained with light for **13**–**26** (Scheme 18). The chemistry shown in Scheme 29 is a snapshot of the many different compounds that were isolated from the complicated mixtures using different 1-alkynes, such as alkenylidene (e.g., **53**) and alkynyl (not shown) compounds, demonstrating a versatile reaction landscape. Analogous products were obtained for nitrile insertion reactions using benzonitrile to afford **54** or acetonitrile to afford **55** (Scheme 30).[93]

4.2.3. Reactivity with CO and phosphines

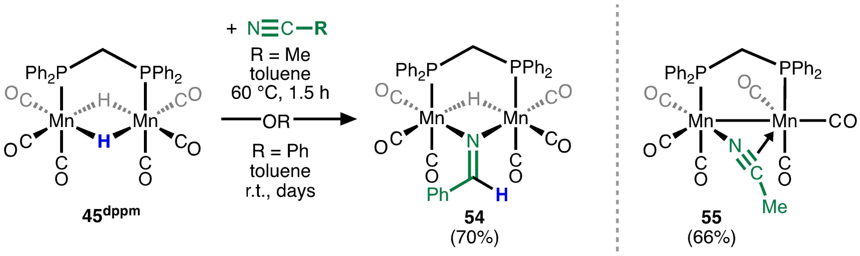
The dihydride complexes are susceptible to reductive elimination of H_2 in the presence of excess L-type ligands such as CO (20 bar) or trimethyl phosphite (Scheme 31).[87] For instance, the reaction of **49** with $P(OMe)_3$ resulted in the phosphine substituted version of **46**, **56**. Also, the reaction with 20 atm CO



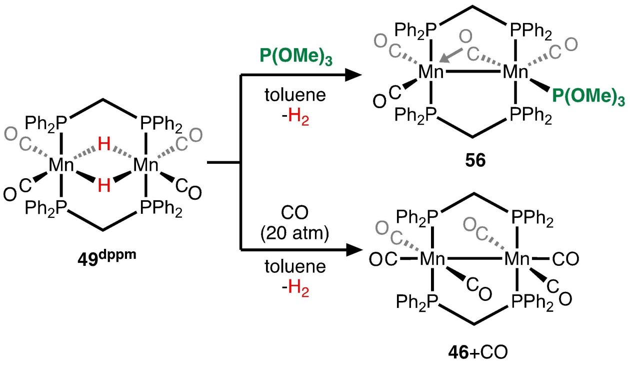
Scheme 28. Synthesis of mono- and bis-PP-clipped dimanganese(I) carbonyl dihydrides.



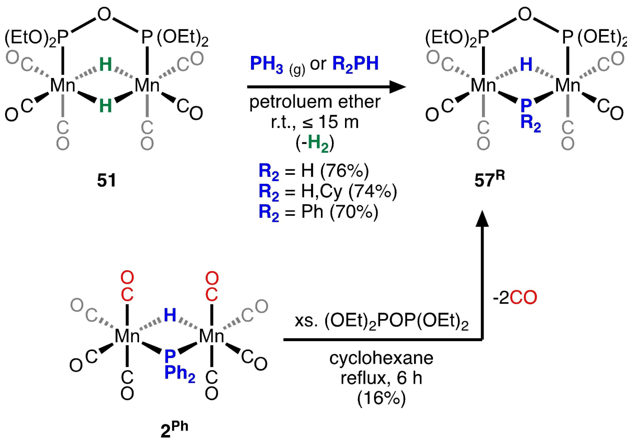
Scheme 29. Reaction of PP-clipped dimanganese(I) dihydride with 1-alkynes.



Scheme 30. Reaction of PP-clipped dimanganese(I) dihydride with nitriles.



Scheme 31. Ligand induced reductive elimination of H_2 from PP-clipped dimanganese(I) dihydride complexes.



Scheme 32. Reaction of PP-clipped dimanganese(I) dihydride with phosphines (top). Ligand substitution of **2**^{Ph} with chelating tedip ligand.

caused elimination of H_2 and formation of the fully saturated complex **46** + CO.

A similar reductive elimination of H_2 in **51** can be driven by the reaction with disubstituted phosphines (also PH_3) and affords new complexes **57**^{R} (Scheme 32).[100] The mechanism likely involves an adduct of the phosphine that induces H_2 elimination affording an adduct complex analogous to **56** (Scheme 31). Then, following a similar mechanism to the one shown in Scheme 8 for PH activation, the final product is **57**^{R}; in support of this, the use of excess phosphine in these reactions led to diminished yields. Intriguingly, attempts to form the same **57**^{Ph} complex by simple ligand substitution with tedip and **2**^{Ph} required forcing conditions and only afforded the product in 16% yield,[55] as opposed to room temperature Ph_2P–H activation in petroleum ether (70%).[100] This reactivity difference (*i*) reinforces the difficult dissociative substitution paradigm discussed above for the phosphido octacarbonyl complexes and (*ii*) that substitution reactions on the PP-clipped dihydrides is substantially more facile. The phosphine induced reductive eliminations shown in Scheme 32 were also performed using **45** giving similar results except with lower yields of the resulting dppm analogs of **57**^{R}.[100]

5. Conclusion

It was the ease of access to a wide range of complexes, diverse chemical reactivity, and bench-stability that attracted our attention to this compound-class as an attractive candidate for applications in synthesis and catalysis. However, at the time of this writing, applications are on the horizon. To jumpstart progress in developing potential applications, we have summarized the research of nearly six decades, reaching as far back as the discovery of **1**^{Ph} & **2**^{Ph} and extending to contemporary studies involving mechanism and catalysis with **2**^{iPr}. Compiling this comprehensive review uncovered underlying reactivity paradigms that permeate the dinuclear Mn(I) phosphido/hydrido class, and these are as follows:

(i) Ligand substitution of $Mn_2(\mu\text{-}X)_2(CO)_8$ with nucleophiles is dissociative and typically requires light, Me_3NO, or high temperatures to proceed at appreciable rates/conversions.
(ii) Reactions involving the "unsaturated" vinyl compounds, like **13**–**26**, likewise appears to proceed by ligand dissociation prior to attack by nucleophiles or addition of H_2.
(iii) The PP-clipped dihydride compounds are substantially more reactive, perhaps because of (*a*) an ability to reductively eliminate H_2 and/or (*b*) enhanced substitutional lability of CO and/or PP-clip.
(iv) **1**^{R} has phosphido bridges but only one of these is reactive toward H_2. The phosphido ligands in **2**^{R} and **3**^{R} appear inert toward H_2 under the conditions described in this review.
(v) The phosphido ligands are chemically non-innocent. For example, they engage in P–C bond coupling from the vinyl-phosphido complexes **13**–**26**. This reaction may be detrimental in many catalytic applications, but it is also important for potential hydrophosphination applications.
(vi) Likewise, the CO ligands are chemically non-innocent in certain cases, especially toward strong nucleophiles (generating carbenes, **41** and **42**) or toward migratory insertion from Mn-vinyl moieties (generating acyls, **27** and **30**)

Thinking forward, the coordination chemistry and resulting ligand effects on reactivity have not been exhausted on the dinuclear phosphido platform, especially in the arena of hydrogenative and hydroelementation catalysis. Additionally, although a complete synthetic cycle for hydrophosphination has been demonstrated, putting this together for catalytic hydrophosphination has yet to be accomplished. The possibility of Ru-like carbenoid intermediates in catalysis is furthermore an exciting possibility that could enable sustainable catalysis in selective transformations. Overall, there are many avenues remaining to explore with this interesting class of compounds.

6. Appendix: Details on computations

DFT methods from reference [30] were used to compute another isomer of the heptacarbonyl **2**^{Me}-CO (namely, $[\{Mn(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}PMe_3)(\mu\text{-}H)]$). The geometry was optimized using the M06 functional[101] and the def2-SVP[102] basis set, with atom-pairwise dispersion correction, Becke-Johnson zero-damping,[103] and solvation effects were incorporated using the conductor-like polarizable continuum (C-PCM) implicit solvation model (toluene was used as the solvent) in ORCA 4.2.1.[104] Energy minimum was confirmed for the optimized structure by the absence of imaginary frequencies. Thermochemical calculations were performed at 1 atm pressure and 393.15 K. Gas phase single point energy of the optimized geometry was calculated at the def2-TZVPP[102] level and the solvated energy at the def2-TZVPP level was computed by combining the single point energy with correction factors from the thermochemical calculations at the def2-SVP level.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: organomanganese · manganese(I) · hydrogenation catalysis · dinuclear · metal carbonyl complexes

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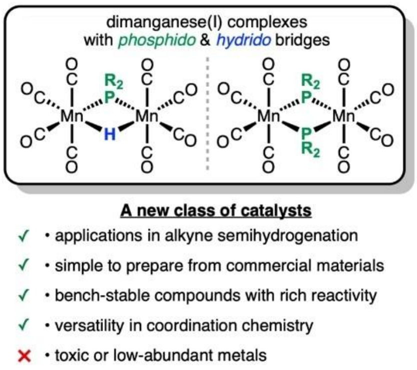
REVIEW

The simple class of dinuclear Mn(I) carbonyl compounds with phosphido (PR_2^-) and hydrido (H^-) bridges has been known since the 1960's. Only recently were they discovered to have potential catalytic applications. This Review is a fresh look the synthesis, reactivity, and catalysis of this interesting class of molecules.



A new class of catalysts

- ✓ • applications in alkyne semihydrogenation
- ✓ • simple to prepare from commercial materials
- ✓ • bench-stable compounds with rich reactivity
- ✓ • versatility in coordination chemistry
- ✗ • toxic or low-abundant metals

Prof. Dr. D. C. Lacy, Dr. P. C. Abhyankar*

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Dinuclear Mn(I) Complexes with Phosphido and Hydrido Bridges: Synthesis, Reactivity, and Hydrogenative Catalysis