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Activation of H_2 with Dinuclear Manganese(I)-Phosphido Complexes

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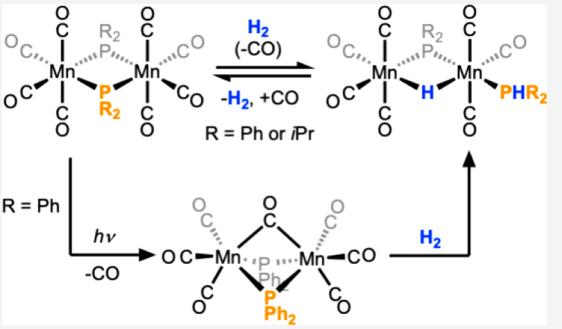
ABSTRACT: There are few reports of activation of H_2 across metal−phosphido linkages, and all of the first-row metal examples use N-heterocyclic phosphido donors. In this report, we highlight the discovery of H_2 activation using first-row transition-metal phosphido complexes with alkyl and aryl substituents. The complex $[Mn(CO)_4(\mu\text{-}PPh_2)]_2$ (**1**) was treated with H_2 (125 °C, 33 h), affording $[\{Mn(CO)_4\}(\mu\text{-}H)(\mu\text{-}PPh_2)\text{-}\{Mn(CO)_3(Ph_2PH)\}]$ (**2**). Treating **2** with $Mn_2(CO)_{10}$ leads to PH bond activation and formation of $[\{Mn(CO)_4\}(\mu\text{-}H)(\mu\text{-}PPh_2)\{Mn(CO)_4\}]$ (**3**). The interconversion of **1** to **3** is reversible, as indicated by the treatment of **3** with free Ph_2PH, giving **2** at 80 °C or **1** and H_2 at 120 °C. The isopropyl analogue of **1**, $[Mn(CO)_4(\mu\text{-}P(iPr)_2)]_2$ (**5**), was synthesized by the oxidative addition of $[(iPr)_2PP(iPr)_2]$ (**4**) with $Mn_2(CO)_{10}$. The reactivity of **5** is analogous to that of **1**, forming $[\{Mn(CO)_4\}(\mu\text{-}H)(\mu\text{-}P(iPr)_2)\{Mn(CO)_3((iPr)_2PH\}]$ (**6**) on treatment with H_2, which in turn reacts with $Mn_2(CO)_{10}$, quantitatively affording $[\{Mn(CO)_4\}(\mu\text{-}H)(\mu\text{-}P(iPr)_2)\{Mn(CO)_4\}]$ (**7**). The chemistry diverges upon use of the *t*Bu substituent. Treating $Na[Mn(CO)_5]$ with $Cl(tBu)_2P$ results in formation of the bis-(tBu_2P) hexacarbonyl complex $[Mn(CO)_3(\mu\text{-}PtBu_2)]_2$ (**8**), a dark green compound with a formal M−M double bond (2.5983(5) Å). **8** reacts sluggishly with H_2 to form free tBu_2PH and $[MnH(CO)_4(HPtBu_2)]$ (**10**). The activation of H_2 with **1** is incomplete even at high temperatures. In contrast, facile activation of H_2 occurs with $[\{Mn(CO)_3(\mu\text{-}PPh_2)\}_2(\mu\text{-}CO)]$ (**1**-CO) to yield **2** (84%, 70 °C, 10 h), implicating thermally demanding CO dissociation from **1** as the first step in the H_2 activation. PCl bond activation under hydrogenative conditions was also examined. The reactions between $Mn_2(CO)_{10}$ and $ClPh_2P$ or $Cl(iPr)_2P$ under 1 atm of H_2 gave **3** (R = Ph) or **7** (R = *i*Pr) in 50−60% yield, indicating the intermediacy of bisphosphido compounds. When $Cl(tBu)_2P$ was used instead, the compounds *cis*-$[Mn(CO)_4(H)((tBu_2)P)_2H)]$ (**10**), $[Mn(CO)_3(H)((tBu_2)P)_2H]$ (**11**), and *diaxial*-$[Mn(CO)_4((tBu_2)PH)]_2$ (**12**) were isolated, indicating PCl bond hydrogenation to phosphines using H_2 and $Mn_2(CO)_{10}$.



INTRODUCTION

Metal−ligand cooperative (MLC) based dihydrogen activation is important for its utility in organic synthesis and implications in hydrogen storage.[1] A majority of transition-metal-based systems that use the MLC paradigm rely on H_2 activation across M−amido linkages (Figure 1, top), and only a handful of examples use M−phosphido linkages. The vast majority of these rely on second- and third-row transition metals (M = Zr,[2] Hf,[3] Ru,[4,5] Ir[6]) or alkali metals.[7] Examples with first-row metals are even more rare,[8−10] and so far, these have all relied on N-heterocyclic phosphido (NHP) donor groups. The NHP ligands temper the basicity of phosphido ligands (Figure 1, middle), but this strategy precludes readily available diaryl- and dialkylphosphido groups in MLC with first-row metals.

We hypothesized that the use of highly electron deficient metal centers, or those substantially compensated with a plethora of electron-withdrawing supporting ligands, could stabilize phosphido groups enough to enable H_2 activation across M−P linkages. We recognized that dinuclear Mn(I) complexes bearing phosphido bridges such as $[Mn(CO)_4(\mu\text{-}PR_2)]_2$ (**1**, R = Ph; **5**, R = *i*Pr) are well-suited to this end.

Such dinuclear Mn(I) phosphido complexes have been known for a long time now. For instance, **1** was prepared first in 1964 by Hayter by reacting $Mn_2(CO)_{10}$ with $Ph_2P−PPh_2$ or treating $Na[Mn(CO)_5]$ with $ClPh_2P$,[11] and since then some alternative syntheses for **1** and related compounds have been discovered.[12−14] Although some reactions surrounding the chemistry of **1** have been reported,[15] its reaction with dihydrogen has not been studied. We therefore endeavored to test the hypothesis that **1** can activate H_2 in an MLC-type mode. We investigated the coordination and H_2 activation chemistry of **5**, the isopropyl analogue of **1**, and found it to be very similar. However, the bulkier *tert*-butyl phosphidos gave different results. For instance, a unique dinuclear compound with a formal Mn−Mn double bond (complex **8**) was isolated. In addition, we discovered that $Mn_2(CO)_{10}$, under an H_2

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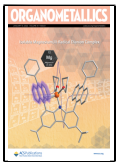

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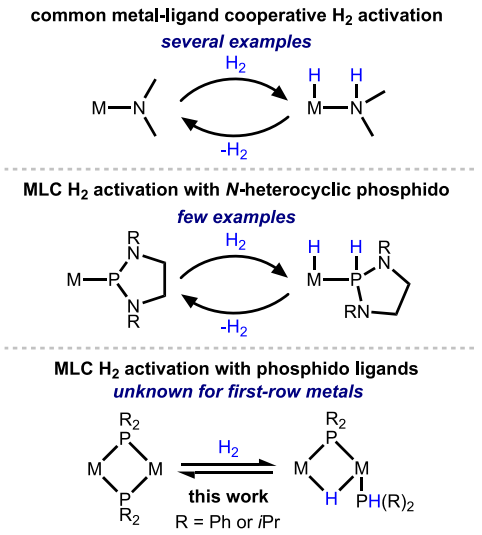


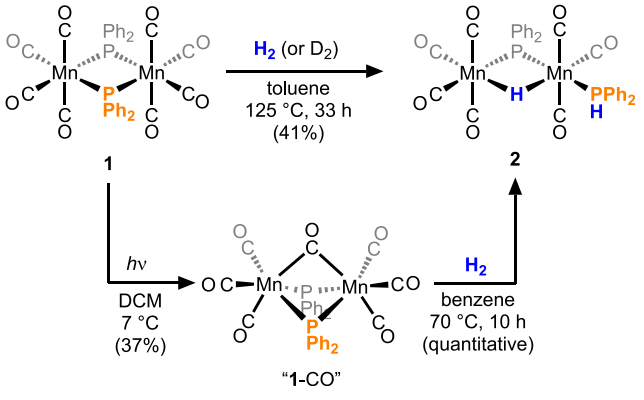
Figure 1. (top) Conventional metal−ligand cooperative (MLC) activation occurs across M−amido linkages. (middle) First-row metals known to activate H_2 across M−P bonds rely on N-heterocyclic phosphido (NHP) ligands. (bottom) This work describes the first example of M−PR_2 MLC activation of H_2 where M = first-row metal and R = alkyl or aryl substituent.

atmosphere, will reduce P−Cl bonds in $ClPR_2$ (R = Ph, *i*Pr, *t*Bu) to form either bridging phosphido/hydrido complexes or complexes bearing reduced dialkylphosphine ligands. While other methods of PCl bond reduction use strong hydride donors (DIBAL-H, $LiAlH_4$, etc.),[16] the reaction described herein uses molecular dihydrogen and commercially available Mn complexes.

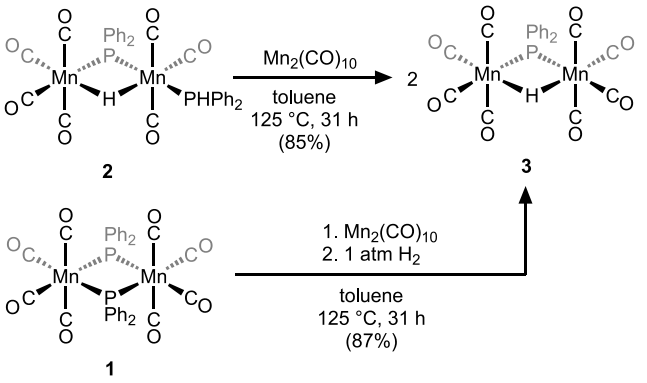
RESULTS AND DISCUSSION

To test H_2 activation across Mn−P bonds, **1** was subjected to heating under 1 atm of H_2, which resulted in the formation of **2** in moderate yields (Scheme 1). The ^{1}H NMR spectrum of **2** contains a resonance at −16.17 ppm (1H, dd, J_{PH} = 30, 30 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **2** contains two resonances, one at 43.9 ppm (bs) corresponding to the L-type diphenylphosphine and another at 166.0 ppm (bs) corresponding to the bridging phosphido group. The ^{1}H NMR spectrum also contains a doublet at 6.78 ppm with a large coupling (J_{PH} = 350 Hz) indicative of a P−H bond. Since the ^{31}P and $^{31}P\{^1H\}$ spectra show broad singlets ($\Delta w_{1/2}$ = 100 Hz), the J_{P-P} coupling constants were not determined; similar peak broadening induced by neighboring Mn nuclei (I = 5/2) is well-documented for related compounds.[17,24] Collectively, along with the ATR-FTIR spectrum, the formulation of **2** is $[\{Mn(CO)_4\}(\mu\text{-H})(\mu\text{-}PPh_2)\{Mn(CO)_3(Ph_2PH)\}]$ (Scheme 2). The characterization data also match the spectroscopic

Scheme 1. H_2 Activation with a Dinuclear Mn/P System



Scheme 2. PH Bond Activation with a Dinuclear Mn/P System



assignment for the same compound isolated by Mays as an intermediate during the photolytic reaction of $[(Cp)(CO)_2Ru-Mn(CO)_5]$ with diphenylphosphine (Ph_2PH).[18]

To verify H_2 activation across the Mn−PPh_2 moiety in **1** (as opposed to adventitious water or other processes not involving dihydrogen), D_2 was used and the formation of $[\{Mn(CO)_4\}(\mu\text{-D})(\mu\text{-}PPh_2)\{Mn(CO)_3(Ph_2PD)\}]$ (**2**^{D}) was confirmed by ^{2}H, ^{1}H, ^{31}P, and $^{31}P\{^1H\}$ NMR experiments (Figures S31−S33).

The moderate yield of the H_2 activation reaction with **1** is partially due to the insolubility of **1** in the reaction medium and also the reversibility of the reaction (*vide infra*). We also reasoned that a thermally difficult CO dissociation was the first step toward hydrogen activation, which dictated the harsh conditions required for H_2 activation with **1**. Therefore, we hypothesized that a coordinatively unsaturated version of **1**, such as $[\{Mn(CO)_3(\mu\text{-}PPh_2)\}_2(\mu\text{-CO})]$ (**1**-CO), would open a path for H_2 activation under less forcing conditions. Hence, we synthesized the known heptacarbonyl complex **1**-CO[19] via the CO photolysis of **1** and monitored its reaction with H_2 as a function of temperature. **1**-CO was essentially unreactive toward H_2 below 60 °C, but at 70 °C complete consumption of **1**-CO occurred (10 h) with formation of **2** (84%) and **1** (16%) (Figure S34 and Scheme 1). Under identical conditions there is no reaction between **1** and H_2. Overall, these results indicate a required vacant site for H_2 coordination and subsequent activation of the H_2 across the Mn−P bond in what can be considered a σ-complex-assisted metathesis (σ-CAM) reaction.[20]

Since radical-based pathways involving Mn(I)-hydrides are known,[21] we investigated whether the hydrogen activation observed was a result of H atom abstraction involving **1**. For example, heating a solution of **1** at 120 °C in the presence of an excess of 9,10-dihydroanthracene (10 equiv) or TEMPO-H (5 equiv) did not lead to the formation of **2** or **3**. These data strongly support a non-radical-based pathway.

The monodentate phosphine in **2** can be further carried on in useful chemistry (Scheme 2). For instance, the known complex $[\{Mn(CO)_4\}(\mu\text{-H})(\mu\text{-}PPh_2)\{Mn(CO)_4\}]$ (**3**) is typically prepared by reacting $Mn_2(CO)_{10}$ with diphenylphos-

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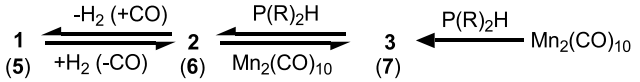
phine (Ph_2PH).[22] To demonstrate the utility of **2** as a phosphine synthon, **2** was allowed to react with $Mn_2(CO)_{10}$ and the product was **3**, isolated in 85% yield. Likewise, a mixture of **1**, $Mn_2(CO)_{10}$, and H_2 resulted in the direct formation of **3** in 87% yield (Scheme 2).

As was noted earlier, the formation of **2** from **1** and dihydrogen does not go to completion and some possible reasons include the poor solubility of **1** and the sluggish loss of CO. In addition, there also appears to be reversibility that precludes complete conversion (Scheme 3). To test the

Scheme 3. Observed Reversibility of Mn−P/H_2 Activation

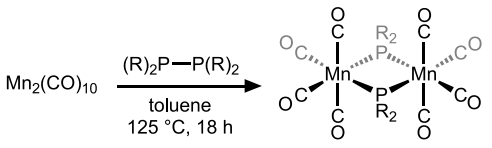


reversibility, we examined the reverse transformation of **3** into **2** into **1** with loss of H_2. When **3** is treated with 1 equiv of free diphenylphosphine (Ph_2PH) at 80 °C, clean and near-quantitative conversion to **2** is observed (Figure S38). When the reaction is carried out at 120 °C instead, **1** is detected as the major product along with **2** and H_2 (Figures S39 and S40).

This reversibility is akin to what has been observed for a somewhat related osmium-phosphido/phosphine complex.[23] However, the closely related cyclohexyl analogue of **2** appears not to exhibit reversibility.[24] Thus, we suspect reversible P−H/H_2 bond activation with Mn-phosphidos is likely controlled by the steric bulk of the phosphorus substituents (*vide infra*).

To further test this hypothesis, we sought to prepare bulkier analogues of **1** using *i*Pr and *t*Bu substituents instead of Ph. By a procedure analogous to that used to prepare **1**, oxidative addition of tetraisopropylbisphosphide [$(iPr)_2P-P(iPr)_2$] (**4**) across $Mn_2(CO)_{10}$ shows the formation of **5** but only in low

Scheme 4. Preparation of Bisphosphido Complexes



yields (Scheme 4). Complex **5** was characterized using ^1H and $^{31}P\{^1H\}$ NMR spectra and ATR-FTIR (Figure S14−S16), and an XRD analysis of crystals suitable for diffraction (Figure 2) confirms the assigned structure.

Although **5** is a thermally stable species, it proved relatively difficult to synthesize in comparison to the phenyl analogue **1**. For instance, when **5** was prepared by treating $Na[Mn(CO)_5]$ and $Cl(iPr)_2P$, by procedures similar to those for $[Mn(CO)_4(\mu\text{-}PR_2)]_2$ (R = Ph, Me),[11] **5** was only a minor product and instead **4** was the major product (Figure S41). We suspect that **5** is the initial product but that it reductively eliminates **4**. We also attempted to synthesize **5** via a P−H bond activation method, akin to the route used to prepare $[Mn(CO)_4(\mu\text{-}PCy_2)]_2$.[25] Heating a mixture of $Mn_2(CO)_{10}$ and 2 equiv of diisopropylphosphine $(iPr)_2PH$ in xylene resulted in a mixture of $[\{Mn(CO)_4\}(\mu\text{-}H)(\mu\text{-}P(iPr)_2)\{Mn(CO)_3((iPr)_2PH\}]$ (**6**) and $[\{Mn(CO)_4\}(\mu\text{-}H)(\mu\text{-}P(iPr)_2)\{Mn(CO)_4\}]$ (**7**) and minor quantities of **5** (Scheme 5). A GC analysis of the

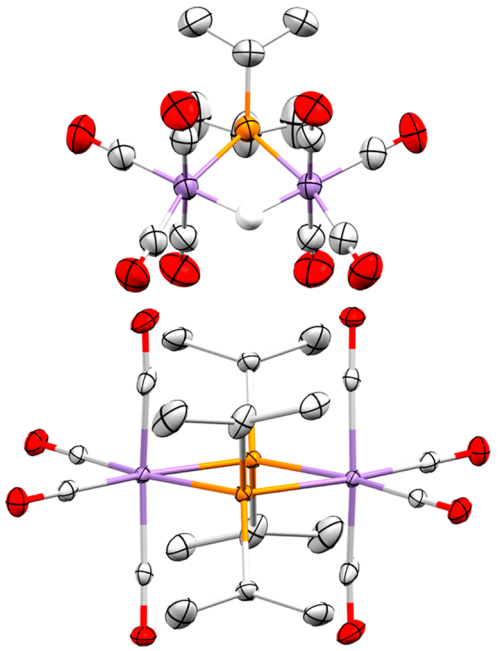
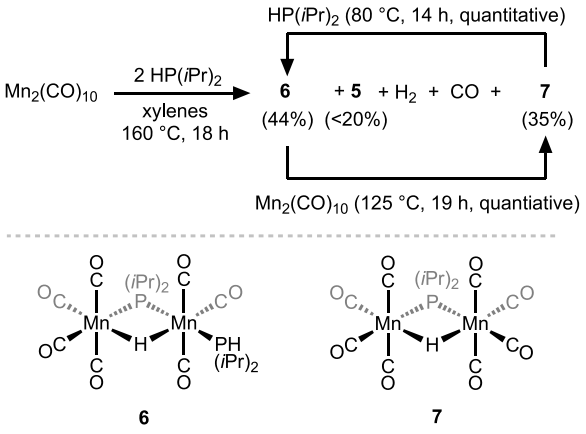


Figure 2. Molecular structures of **7** (top) and **5** (bottom) with H atoms (except the bridging hydride) omitted for clarity. Thermal ellipsoids are shown at 50% probability. Color scheme: white, H; gray, C; red, O; orange, P; purple, Mn. Selected distances (Å) and angles (deg) for **7**: Mn···Mn = 2.9378(5); Mn1−P = 2.2991(5); Mn2−P = 2.2994(6); Mn1−P−Mn2 = 79.41(2). Selected distances (Å) and angles (deg) for **5**: Mn···Mn = 3.838(2); Mn−P = 2.401(2); P···P = 2.695(3); Mn−P−Mn = 109.9(1); P−Mn−P = 70.13(9).

reaction headspace shows the presence of CO and H_2 (Figure S44), indicative of the formation of **5** from **6** via H_2 elimination.

Scheme 5. Reversibility of H_2 and PH Activation with *i*Pr Phosphido Ligands



Independent hydrogen activation with **5** was also investigated. In a reaction analogous to **1**, heating a solution of **5** under an H_2 atmosphere led to activation across the Mn−P bond, resulting in the formation of **6** (Figure S35). Overall, this and the reactivity of the *i*Pr-substituted compounds are consistent with the reversible H_2 and P−H bond activation chemistry associated with **1** (Scheme 3).

To confirm the identity of **6** and **7**, we synthesized these new complexes independently. Complex **7** was prepared in high

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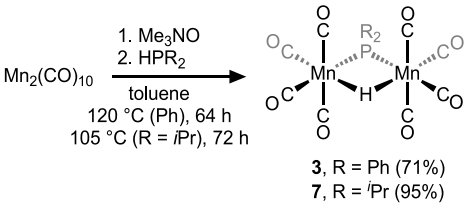
yield by the direct P−H activation of $(i\mathrm{Pr})_2\mathrm{PH}$ across $Mn_2(CO)_{10}$ with Me_3NO as a promoter (Scheme 6). The

Scheme 6. Independent Synthesis of 3 and 7

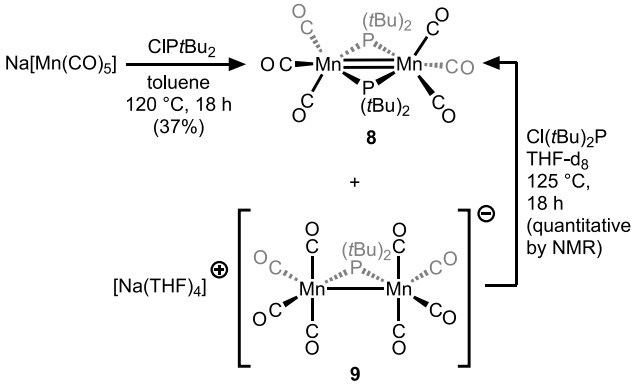


presence of a bridging hydride in **7** was confirmed by a doublet at −16.76 ppm (J_{P-H} = 30 Hz) in the ^1H NMR, and the bridging phosphido group shows a downfield resonance at 190.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Figures S22 and S23), consistent overall with the known analogues and **3**.[24,26] Additionally, the structure was confirmed using single-crystal XRD (Figure 2, top). Both Mn(I) centers are hexacoordinated with a Mn···Mn distance of 2.94 Å, which is comparable to the Mn···Mn distance reported for **3** (2.95 Å) and other dialkylphosphido-bridged analogues.[19,27] However, this short distance is not a M−M bond but a three-center−two-electron bond in the usual formalism for bridging hydride ligands.

Treatment of **7** with 1 equiv of $(i\mathrm{Pr})_2\mathrm{PH}$ at 80 °C leads to the near-quantitative formation of the new complex **6** (Scheme 5, top arrow) (Figures S17−S21). Complexes **6** and **7** behave similarly to **2** and **3** (see Schemes 1−3), except that attempts to convert **7** into **5** (analogous to conversion of **3** to **1**) give a significantly lower yield (Figures S45 and S46).

The even bulkier phosphine $Cl(t\mathrm{Bu})_2P$ was used in attempts to prepare the *t*Bu derivative of **1** and **5**. However, the hexacarbonyl complex $[Mn(CO)_3(\mu\text{-}Pt\mathrm{Bu}_2)]_2$ (**8**) and the octacarbonyl complex $[Na(THF)_4][\{Mn(CO)_4\}_2(\mu\text{-}Pt\mathrm{Bu}_2)]$ (**9**) formed instead (Scheme 7). A closer inspection of the *i*Pr

Scheme 7. Synthesis of 8 and 9



groups in **5** makes it obvious that there is no more room to accommodate the extra methyl groups in a *t*Bu derivative, and we therefore suspect that the disparity in products is solely a result of steric bulk. Dark green crystals of **8** suitable for diffraction were obtained, and the XRD analysis (Figure 3, top) was consistent with its spectroscopic characterization (Figures S25−S28). **9** was also characterized spectroscopically (Figures S29 and S30), and the structure was corroborated with XRD analysis (Figure 3, bottom). **9** reacts with equimolar

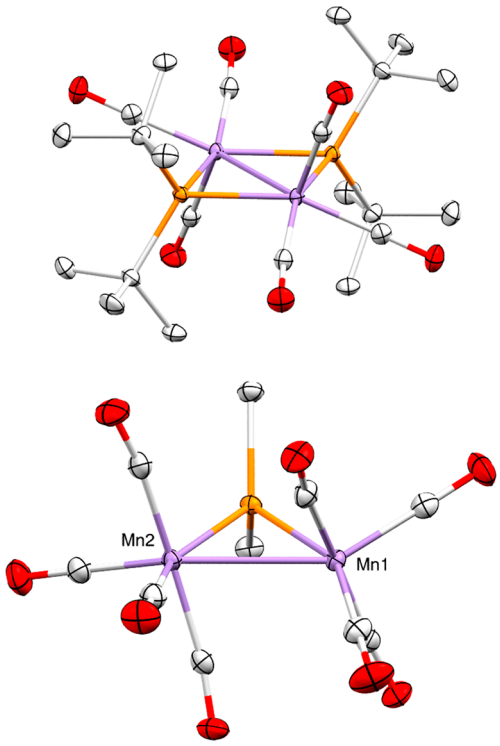


Figure 3. Molecular structures of **8** (top) and **9** (bottom) with H atoms, $[Na(THF)_4]$ countercation, and disordered toluene molecule omitted for clarity. The *tert*-butyl methyl carbons in **9** have been removed for clarity. Thermal ellipsoids are shown at 50% probability. Color scheme: white, H; gray, C; red, O; orange, P; purple, Mn. Selected distances (Å) and angles (deg) for **8**: Mn−Mn = 2.5983(5); Mn−P = 2.2706(4); Mn−P−Mn = 69.80; P−Mn−P = 110.20. Selected distances (Å) and angles (deg) for **9**: Mn1···Mn2 = 2.7793(6); Mn1−P = 2.3099(7); Mn2−P = 2.3070(7); Mn1−P−Mn2 = 74.03(2).

$Cl(t\mathrm{Bu})_2P$ to form **8**, among other products (Figures S54 and S55).

Complex **8** is surprisingly air stable, despite the fact that it contains two coordinatively unsaturated Mn centers. Furthermore, the octacarbonyl complexes (and essentially most other formally monovalent Mn complexes in this report) are yellow to orange. However, **8** is a deep green and has a dramatically shortened M···M distance of 2.5983(5) Å. On the basis of electron-counting formalism, **8** contains a rare formal double Mn−Mn bond having two d^6 centers.[28,29]

The $^{31}P\{^1H\}$ NMR spectrum of **8** contains a very downfield resonance at 404.3 ppm, which is indicative of M−M bond character as discussed by Riera and co-workers.[30] An inspection of the canonical MOs obtained from a single-point calculation at the PBE0/def2-TZVPP level reveals a M−M σ bond (HOMO-6) and M−M π bond (HOMO). Gas-phase TD-DFT calculations at the def2-SVP level predict a band at 576 nm with a major contribution (79%) from the HOMO to the LUMO. On the basis of the canonical MOs the transition is qualitatively a Mn−Mn π to Mn−Mn π^* transition (Figure 4). An experimental candidate for this predicted transition is at 694 nm (ε = 4600 M^{-1} cm^{-1}) (Figure S28). This band does not shift upon a change in solvent, indicating that it is not a charge transfer band, and we assign this to the same Mn−Mn π to Mn−Mn π^* transition.

The activation of H_2 with **8** required forcing conditions and did not go to completion (20% at 120 °C for 48 h). The

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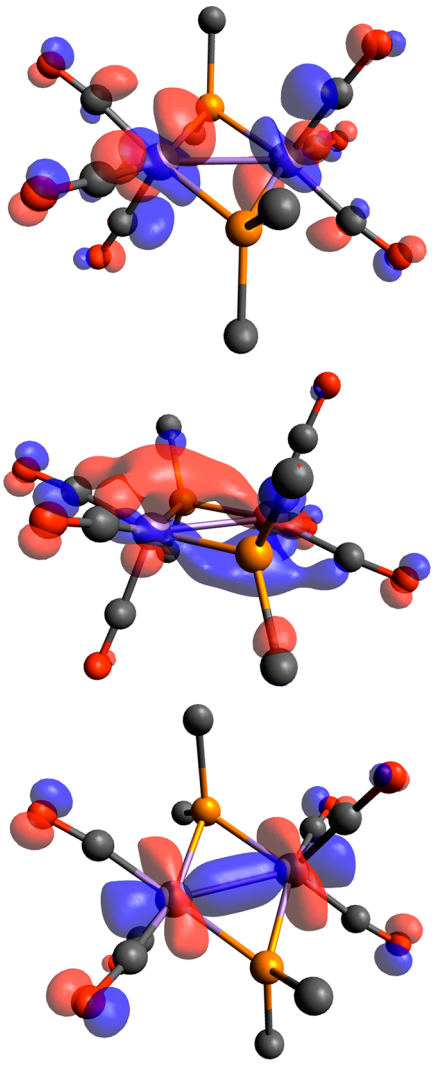


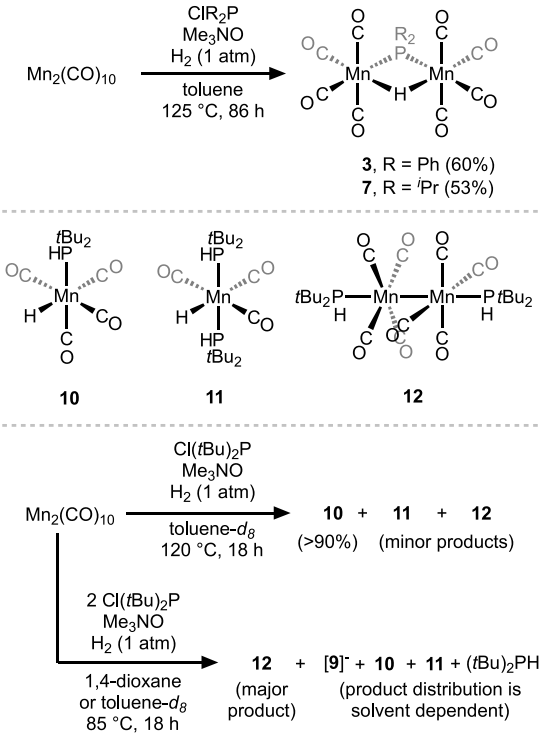
Figure 4. Selected MOs of **8** at the PBE0/def2-TZVPP level with hydrogens omitted for clarity (isovalue 0.05): (bottom) Mn−Mn σ bond, HOMO-6; (middle) Mn−Mn π bond, HOMO; (top) Mn−Mn π^*, LUMO. Color scheme: Mn, purple, C, gray, P, orange, O, red. The TD-DFT electronic transition at 576 nm is predominantly HOMO to LUMO.

products were identified as free $(t\mathrm{Bu})_2\mathrm{PH}$ (20% yield) and [*cis*-$\mathrm{MnH(CO)_4((t\mathrm{Bu}_2)PH)}$] (**10**) (<1%) (see below for description) (Figure S36).

In contrast, **5** is fully consumed with H_2, forming **6** (120 °C, 18 h), indicating that the H_2 activation across Mn−P bonds is not unique to phenyl-substituted phosphines (Figure S35). The lack of reactivity of H_2 with **8**, in contrast to **1** and **5**, and the milder conditions required for **1**-CO together point to a mechanism where a vacant site is required for H_2 activation on a heptacarbonyl intermediate. **8**, however, having only six carbonyl ligands, forms two M−M bonds and is effectively rendered inert toward H_2 until forcing conditions are achieved.

We also tested the ability of $Mn_2(CO)_{10}$ to activate P−Cl bonds (Scheme 8, top). Chlorodiphenylphosphine ($ClPh_2P$) does not react with $Mn_2(CO)_{10}$ at temperatures lower than 90 °C. Exceeding 90 °C results in paramagnetic broadening of the ^{1}H NMR spectrum, and at 125 °C complete consumption of the $ClPh_2P$ and formation of **1** as the major product results (isolated yield, 25% based on $Mn_2(CO)_{10}$). In contrast,

Scheme 8. P−Cl Bond Reduction with H_2 and $Mn_2(CO)_{10}$



repeating the same experiment but with H_2 (125 °C) leads to the formation of **3** in 60% yield along with other yellow byproducts, including **1** (<5%); no unreacted chlorophosphine remained. Similar results were obtained with $Cl(i\mathrm{Pr})_2P$ and H_2, yielding **7** (53%). The source of the H atom was confirmed to arise from H_2 by repeating the experiment with D_2, yielding [$\{\mathrm{Mn(CO)_4}\}(\mu\text{-D})(\mu\text{-PPh}_2)\{\mathrm{Mn(CO)_4}\}$] (**3**$^{\mathrm{D}}$) (Figures S51−S53).

Using $Cl(t\mathrm{Bu})_2P$ instead gives a different set of results. Heating $Mn_2(CO)_{10}$ with 1 equiv of $Cl(t\mathrm{Bu})_2P$ at 120 °C under H_2 (1 atm) leads to the formation of **10** (>90%). The formulation of **10** as [*cis*-$\mathrm{MnH(CO)_4\{(tBu_2)PH\}}$] is based on the ^{1}H NMR spectrum, which contained a Mn−H resonance at −7.88 ppm (d, $^2J_{\mathrm{P-H}}$ = 36 Hz), a P−H resonance at 3.84 ppm (d, $J_{\mathrm{P-H}}$ = 321 Hz), and a ^{31}P resonance at 85.1 ppm (d, $J_{\mathrm{P-H}}$ = 322 Hz) (Figures S56 and S57); the *cis* confirmation and mononuclear assignment are consistent with these data. The data are also consistent with those of analogous compounds reported elsewhere.[31]

Using 2 equiv of $Cl(t\mathrm{Bu})_2P$ leads to a mixture of **10**, $\mathrm{[Mn(H)(CO)_3((tBu_2)PH)_2]}$ (**11**), and *diaxial*-$\mathrm{[Mn(CO)_4((tBu_2)PH)]_2}$ (**12**) (Scheme 8, bottom). Crystals of **11** and **12** suitable for diffraction were retrieved from the mixture, and an X-ray analysis confirmed their structure (Figure 5). A ^{1}H and ^{31}P{^{1}H} NMR spectroscopic analysis of the solution agrees with the assigned structure (Figures S59 and S60); the separation of these products was not pursued. These reactions unambiguously demonstrate the reduction of P−Cl bonds, but the variation in products obtained is heavily dictated by steric factors.

■ CONCLUSION

To summarize, we demonstrated herein the first example of H_2 activation in first-row transition-metal dialkyl- and diarylphosphido complexes. We confirmed this using simple Mn

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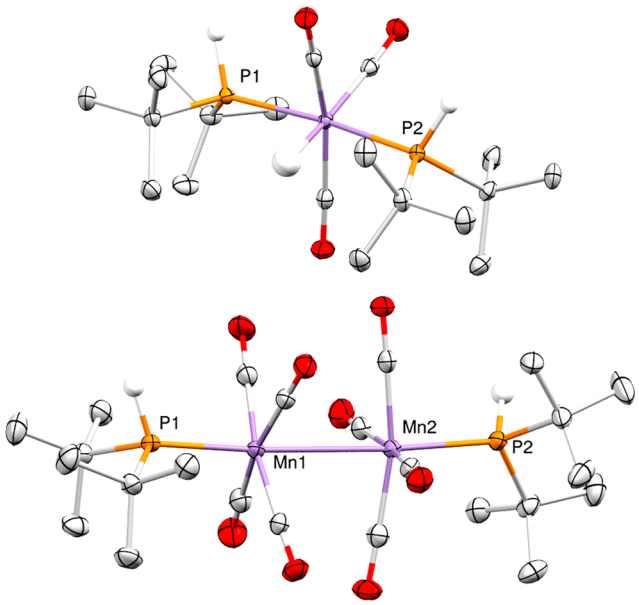

Figure 5. Molecular structures for **11** (top) and **12** (bottom). All H atoms except those directly bound to P and Mn atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Color scheme: white, H; gray, C; red, O; orange, P; purple, Mn. Selected distances (Å) and angles (deg) for **11**: Mn−P1 = 2.2935(4); Mn−P2 = 2.2873(4); P2−Mn−P1 = 172.15(2). Selected distances (Å) and angles (deg) for **12**: Mn1−Mn2 = 2.9333(7); P1−Mn1 = 2.2949(9); P2−Mn2 = 2.2941(9); P1−Mn1−P2 = 175.71(3); Mn1−Mn2−P2 = 176.33(3).

and phosphine starting materials, showing that NHPs are not necessary to engender the stability required for H_2 activation using first-row metal phosphido groups. The reaction mechanism between **1** and H_2 is consistent overall with CO dissociation followed by σ-CAM, affording **2**. The coordinated phosphine that results from H_2 activation can be further activated (P−H bond activation) by treatment with $Mn_2(CO)_{10}$, yielding the octacarbonyl μ-phosphido μ-hydrido complexes. The chemistry discussed herein is heavily influenced by steric properties, as indicated from studies with bulkier substituents, such as *i*Pr and *t*Bu. The *i*Pr substituent behaved similarly to Ph, but the *t*Bu substituent resulted in the formation of an unsaturated hexacarbonyl dimer with a M═M bond exhibiting substantially slower and different H_2 activation chemistry. Additionally, P−Cl reduction was affected by the substituents on phosphorus. Ph- and *i*Pr-disubstituted $Cl(R)_2P$ substrates were reduced to μ-phosphido μ-hydrido complexes, implicating bis-phosphido intermediates resulting from thermally induced P−Cl bond activation by $Mn_2(CO)_{10}$, but no PH bonds were formed. In contrast, tBu_2PCl hydrogenation to tBu_2PH was accomplished using H_2 (1 atm) and $Mn_2(CO)_{10}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00603.

Procedures and characterization data for novel compounds (PDF)

Accession Codes

CCDC 2091720 and 2114649−2114653 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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