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Cationic Manganese(I) Dihydrogen and Dinitrogen Complexes Derived from a Formally 16-Electron Complex with a Bis-Agostic Interaction, $[Mn(CO)(Ph_2PC_2H_4PPh_2)_2]^+$

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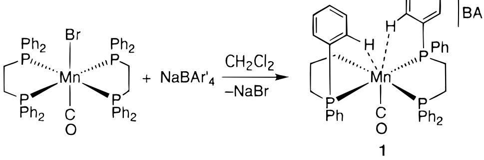
The synthesis and characterization of metal−η^2-dihydrogen complexes has provided great insight into the catalytic and stoichiometric activation of H_2 by transition metals.[1] The fine line of stability of H_2 complexes toward either dissociation of H_2 or oxidative addition to a dihydride is governed by the degree of backbonding the H_2 receives from the metal center.[1] Systematic variation of the electronegativity of the metal center in L_nM-H_2 by changing the donor/acceptor properties of the ancillary ligands and the metal allow exploration of the reaction coordinate for addition of H_2 to metals. To this end, we have synthesized a new 16-electron precursor $[Mn(CO)(dppe)_2]BAr'_4$ (**1**) capable of binding small molecules (dppe = $Ph_2PC_2H_4PPh_2$; BAr'_4 = $B[C_6H_3(3,5\text{-}CF_3)_2]_4$[2]). This species has yielded the first well-characterized cationic manganese−H_2 complex, $[Mn(H_2)(CO)(dppe)_2]BAr'_4$. The complexes $MnH_3(R_2PC_2H_4PR_2)_2$ [R = Me (dmpe), Et (depe)] were proposed to contain H_2 ligands,[3a] and $CpMn(CO)_2(H_2)$ was recently isolated.[3b] We also report that N_2 reaction with **1** gives an extremely labile N_2 complex characterized by ^{15}N NMR.

Complex **1** forms on reaction of $Mn(CO)(dppe)_2Br$[4] with the sodium salt of the large noncoordinating anion, $NaBAr'_4$, in CH_2Cl_2 followed by filtration to remove NaBr.[5] Cationic complexes $[Mn(CO)(L)(dppe)_2][PF_6]$ (L = NCR or CNR) have been prepared by reaction of $Mn(CO)(dppe)_2Br$ and $TlPF_6$ in the presence of L. However, reaction in the absence of L yielded only the decomposition product, $[Mn(CO)_2(dppe)_2][PF_6]$.[6] The deep blue, extremely air and moisture sensitive **1** is thus apparently stabilized by $BAr'_4{}^-$. It is soluble in aromatic solvents and CH_2Cl_2 but insoluble in hydrocarbons and crystallizes from toluene as a solvate containing 0.7 toluene after drying in vacuo. The complex can be obtained toluene-free by preparation in CH_2Cl_2 followed by filtration and solvent removal in vacuo.



(1)

1

The X-ray structure of the **1** cation is formally five-coordinate square-pyramidal (Figure 1). The notable feature is the presence of *two* agostic interactions from *ortho*-hydrogen atoms (H12, H18) located on separate phenyl rings of mutually *trans*-phosphines.[7] This contrasts with the $Mo(CO)(dppe)_2$ analogue which contains only one such interaction.[8] The double interaction most likely results from the reduced Mn-P-*ortho*-phenyl-H ring size as compared to the Mo system, preventing full interaction of the C−H bond. The Mn···H distances are much longer (2.89(6), 2.98(6) Å) than that found for the single agostic interaction in $Cr(CO)_3(PCy_3)_2$ (2.240(1) Å)[9] and similar to that in the Mo analogue (2.98(11) Å),[8] a larger-radius metal. Although multiple agostic interactions are rare, a similar double phenyl-H interaction has been observed in $M(PPhBu^t{}_2)_2$ (M = Pt, Pd), which also contain two M-*tert*-butyl-H interactions.[10]

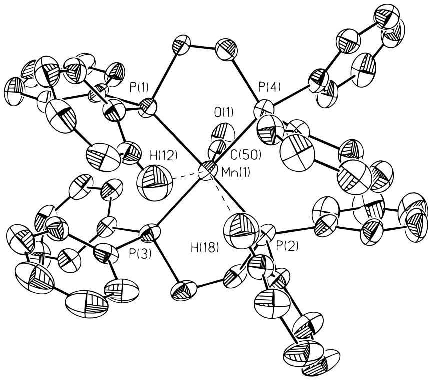


Figure 1. ORTEP drawing (50% probability ellipsoids) of $[MnCO)(dppe)_2]^+$. Selected bond lengths (Å): Mn(1)−C(50), 1.733(7); Mn(1)−P(1), 2.278(2); Mn(1)−P(2), 2.280(2); Mn(1)−P(3), 2.321(2); Mn(1)−P(4), 2.335(2); Mn(1)−H(12), 2.89(6); Mn(1)−H(18), 2.98(6). Selected bond angles (deg): C(50)−Mn(1)−P(1), 92.3(2); C(50)−Mn(1)−P(2), 90.8(2); C(50)−Mn(1)−P(3), 96.1(2); C(50)−Mn(1)−P(4), 97.2(2); P(1)−Mn(1)−P(4), 82.67((7); P(2)−Mn(1)−P(3), 82.90(7); P(1)−Mn(1)−P(3), 95.68(7); P(2)−Mn(1)−P(4), 98.02(7).

The ^1H NMR resonances for the anion in **1** are unremarkable and consistent with those observed in related $[Re(PR_3)_2(CO)_3]$-BAr'_4.[11] The most diagnostic ^1H signal is that for the PC_2H_4P bridge, which gives a broad multiplet indicative of both ^{31}P and

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(5) $[Mn(CO)(dppe)_2]BAr'_4\cdot 0.7$toluene:$CH_2Cl_2$ (20 mL) was vacuum transferred onto $Mn(CO)(dppe)_2Br$ (0.65 mmol) and $NaBAr'_4$ (0.84 mmol) at −78 °C. The solution was placed under Ar and allowed to warm to 25 °C. After 30 min, the CH_2Cl_2 was removed in vacuo from the deep-blue solution. The solids were extracted with warm toluene (25 mL), and the solution was reduced to 10 mL and allowed to stand for 16 h. The blue crystalline precipitate was isolated by decantation, washing with toluene, and drying in vacuo. Yield: 0.93 g (79%). ^1H NMR (CD_2Cl_2) d 7.72 (s, $C_6H_3(3,5\text{-}CF_3)_2$, 8H, *ortho*); 7.56, (s, $C_6H_3(3,5\text{-}CF_3)_2$, 4H, *para*); 7.3−7.0-(m), 6.16(m) (C_6H_5 of toluene and phosphine, 43.5H); 2.79 (m, PCH_2CH_2P, 8H); 2.34 (CH_3, toluene, 2H); ^{31}P NMR{^1H} (CD_2Cl_2) d 82.6; IR (cm^{-1}) ν(CO) 1839 (CH_2Cl_2), 1862 (Nujol).

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(7) X-ray quality crystals were grown from toluene. $[Mn(CO)(dppe)_2]BAr'_4\cdot 1.5$toluene: aquamarine, rectangular, 0.21 × 0.25 × 0.45 mm, M_r = 1881.16; space group $P\bar{1}$; a = 12.956(2) Å; b = 16.935(3) Å; c = 20.568(4) Å, a = 89.50°, b = 75.63°, g = 86.33°; V = 4362(1) $Å^3$; Z = 2; D_{calc} = 1.432 g/cm^3; Siemens P4PC diffractometer; 173 K; Mo Ka radiation (l = 0.710 73 Å); scan method $2\theta-\theta$; θ range for data collection 2.53 to 29.54°; total number of data measured, 13 173; number of independent reflections, 11 341 (R_{int} = 3.54%); number of observed reflections, 7405 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares procedures to give final residuals of R = 0.0753 and R_w = 0.1754. From final difference Fourier maps, residual electron densities of 1.140 and −0.719 e/$Å^3$ were present. Hydrogen atoms H(12) and H(18) were located and refined with temperature factors fixed at 0.08 $Å^2$. All other hydrogen atoms included the final refinement were fixed at idealized positions. All atoms other than hydrogen were refined with anisotropic thermal parameters with the exception of toluene carbons.

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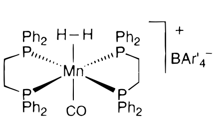
S0002-7863(96)00499-4 CCC: $12.00

^{55}Mn coupling. This shows that **1** is fluxional at 298 K which is consistent with the closely related neutral Mo(CO)($R_2PC_2H_4PR_2$)$_2$ (R = Ph, Bz).[1e,f,8] No significant changes in the PC_2H_4P resonances are observed on cooling to 198 K, indicating no reduction in symmetry, i.e., the agostic interactions have not been frozen out. The phenyl region consists of two distinct sets of multiplets containing both phosphine and toluene−solvate phenyl protons. The first ranges from 7.3−7.0 ppm, and the second is significantly upfield of the first at 6.16 ppm, integrating as 8 H against the PC_2H_4P protons. The latter feature is also present in the toluene-free system and is remarkably similar to that observed for Mo(CO)[$Bz_2PC_2H_4PBz_2$]$_2$.[1] In contrast to the latter, no collapse of the resonance into the base line is seen down to 198 K, indicating **1** is more fluxional. The resonance did sharpen (from 92 Hz at 298 K to 74 Hz at 198 K, FWHM, 500 MHz) and shifted slightly to 6.05 ppm, indicating octahedrally-coordinated Mn in which the site trans to CO interacts with[8] rapidly exchanging agostic hydrogens. The $^{31}P\{^1H\}$ NMR shows a singlet at both 298 and 198 K, consistent with a highly fluxional complex.

The H_2 complex forms by placing solutions of **1** under H_2.



[Mn(H_2)(CO)(dppe)$_2$]BAr′$_4$[12] is light yellow with solubility similar to **1**. The H_2 is extremely labile and readily dissociates when the H_2 atmosphere is removed or the complex is warmed. At 298 K, the ^1H resonances of PC_2H_4P show two multiplets consistent with H_2 trans to CO. The upfield phenyl resonance collapses into the phenyl multiplet at 7.3−7.0 ppm. The H_2 resonance is broad with no ^{31}P coupling and displays a field dependent width at −7.21 ppm (27 Hz, 300 MHz; 62 Hz, 500 MHz), integrating as 2 H relative to PC_2H_4P. On cooling to 168 K, the H_2 signal greatly broadens (540 Hz, 300 MHz). Mo(H_2)(CO)(dppe)$_2$ does not display this temperature dependence, although the signal is already very broad at 298 K (∼300 Hz, 300 MHz). The more electron-rich complex, Mo(H_2)(CO)($Bz_2PC_2H_4PBz_2$)$_2$, shows very similar behavior to the Mn complex.[1] A single temperature independent resonance was observed for $^{31}P\{^1H\}$ NMR consistent with H_2 trans to CO and no observable dihydrogen-dihydride equilibrium. The HD complex prepared from HD gas gives an HD coupling constant of 32 Hz in accord with a short H−H distance.[1]

The H−H distance was determined by solid-state NMR measurements[13] to be 0.89(2) Å in [Mn(H_2)(CO)(dppe)$_2$]BAr′$_4$ prepared by exposing solid toluene-free **1** to H_2. This compares favorably to H−H NMR distances observed in Mo(H_2)(CO)$_3$(PCy$_3$)$_2$ (0.87 Å)[13a] and FeH(H_2)(dppe)$_2^+$ (0.86 Å)[14] and correlates with the large J_{HD}. The distance in MnH_3(dmpe)$_2$ was estimated from solution NMR T_1 to be 0.90 or 1.13 Å depending on fast or slow H_2 rotation.[3] Remarkably, the H−H length in Mo(H_2)(CO)(dppe)$_2$ (0.88 Å)[13b] is nearly identical to the Mn system despite the fact that backbonding from the first row Mn cation should be less than from the second row neutral Mo. This should give a shorter H−H in the Mn system because of less donation of electron density to the σ^* H_2 orbital. The similarity of H−H distances in the Mn and Mo systems may result from the much more electrophilic Mn center ($\nu_{CO} = 1862$ cm^{-1} in **1** versus 1723 cm^{-1} in Mo(CO)(dppe)$_2$) weakening H−H primarily by drawing electron density away from the H−H σ-bonding orbital rather than by backbonding.

Our attempts to evaluate the role of backbonding in **1** and related fragments compelled us to investigate the dinitrogen complex, [Mn(N_2)(CO)(dppe)$_2$]BAr′$_4$, formed by placing CH_2Cl_2 solutions of **1** under N_2 at −78 C.[15] The blue solution turns yellow on N_2 addition. On warming to room temperature in a closed system, the solution turns blue-green. $^{31}P\{^1H\}$ NMR of [Mn(N_2)(CO)(dppe)$_2$]BAr′$_4$ at 198 K in CH_2Cl_2 reveals a resonance at 75.7 ppm. On warming to 298 K a second resonance associated with the 16-electron complex grows in at 82.6 ppm, and the resonance associated with the N_2 complex is observed at 75.0 ppm. Both peaks broaden, indicating exchange is beginning to take place. Integration reveals 37% of the Mn centers contain bound N_2. ^1H NMR at 200 K consists of two multiplets for PC_2H_4P, consistent with N_2 trans to CO. The resonance at 6.16 ppm associated with the *ortho*-phenyl protons disappears on N_2 addition, and a new multiplet grows in at 6.47 ppm integrating as eight protons relative to those of the anion. On warming to 25 °C, the ^1H resonances associated with the N_2 complex decrease in intensity, and those associated with **1** increase. Most notably the PC_2H_4P resonances collapse to a single broad multiplet with a slight upfield shoulder.

In order to determine if N_2 binding is bridging or terminal, an ^{15}N NMR study was performed on the complex prepared with 99.9% ^{15}N-enriched N_2 (Isotec Inc). At 200 K, two multiplets occur at −27.9 and −56.2 ppm (external reference: nitromethane). Although these could not be assigned (Mn-*N*N vs Mn−N*N*) because broadening from ^{55}Mn coupling destroyed ^{31}P and ^{15}N coupling information, two resonances are consistent with terminal rather than μ-N_2. On warming to 300 K, the resonances shift to −25.1 and −56.1 ppm and broaden slightly.

Precipitation from CH_2Cl_2 with pentane at −78 °C was used to trap [Mn(N_2)(CO)(dppe)$_2$]BAr′$_4$ in the solid state.[16] This gave an opportunity to observe ν_{NN} and ν_{CO} in IR of solid mulls to confirm terminal rather than μ-N_2 as in [Mo(CO)(depe)$_2$]$_2$(μ-N_2)[17] and also to gauge backbonding. Both ν_{NN} and ν_{CO} (2167 and 1911 cm^{-1}) are much higher than those for Mo(N_2)(CO)(dppe)$_2$ (2090 and 1809 cm^{-1}), confirming significantly less backbonding in [Mn(N_2)(CO)(dppe)$_2$]BAr′$_4$ than Mo(N_2)(CO)(dppe)$_2$. By comparison, MnH(N_2)(dmpe)$_2$ is much more basic with $\nu_{NN} = 1947$ cm^{-1},[3] which is 220 cm^{-1} lower than for Mn(N_2)(CO)(dppe)$_2^+$ and below the usual range[1b] (2060−2160 cm^{-1}) observed for stable H_2 binding to the analogous metal fragment.

We are continuing to explore coordination to **1**, which is unique among first-row metals in giving isolable agostic, H_2, and N_2 adducts. Preliminary results show that organosilanes also interact but more weakly than in Mo(η^2-SiR$_n$H$_{4-n}$)(CO)(dppe)$_2$.[18] We will examine the effects of using other low-interacting anions and varying co-ligands, e.g., depe versus dppe.

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Supporting Information Available: X-ray diffraction data (15 pages). Ordering information is given on any current masthead page.

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(15) ^1H NMR data for [Mn(N_2)(CO)(dppe)$_2$]BAr′$_4$ system in CD_2Cl_2: 200 K: d 7.73 (s, C_6H_3(3,5-CF_3)$_2$, 8H, *ortho*); 7.53, (s, C_6H_3(3,5-CF_3)$_2$, 4H, *para*); 7.4−7.0 (m), 6.47 (m) (C_6H_5, toluene and phosphine, 43.5H); 2.57 (m, PCH_2CH_2P, 4H); 2.42 (m, PCH_2CH_2P, 4H); 2.28 (CH_3, toluene, 2H). 298 K: d 7.73 (s, C_6H_3(3,5-CF_3)$_2$, 8H, *ortho*);7.56, (s, C_6H_3(3,5-CF_3), 4H, *para*); 7.3−7.1 (m), 6.67(m) (C_6H_5, toluene and phosphine, 43.5H); 2.67 (m, PCH_2CH_2P, 8H); 2.34 (CH_3, toluene, 2H).

(16) The orange-yellow precipitate was found to be a mixture of [Mn(N_2)(CO)(dppe)$_2$]BAr′$_4$ and **1** by IR of a Nujol mull.

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