Comparative Binding of H_2, N_2, and Related Ligands to $[Mn(CO)_3(PCy_3)_2]^+$ and Other 16e Electrophiles. N_2 Does Not Coordinate, and H_2 Is the Most Versatile Weak Ligand†

Andreas Toupadakis*,‡

Chemistry Department, University of Crete, Iraklio, Crete, Greece

Gregory J. Kubas,* Wayne A. King, Brian L. Scott, and Jean Huhmann-Vincent

Los Alamos National Laboratory, CST-18, MS-J514, Los Alamos, New Mexico 87545

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The photochemical reaction of $Mn(CO)_5Br$ with PCy_3 in toluene proceeds with the fast evolution of CO. The complex formed, $MnBr(CO)_3(PCy_3)_2$, **1**, readily reacts with NaA (A = $B[C_6H_3(3,5\text{-}CF_3)_2]_4$) to form the dark green salt $[Mn(CO)_3(PCy_3)_2][A]$, **2**, which has an agostic interaction of a cyclohexyl C−H with manganese. The light yellow η^2-H_2 complex, $[Mn(H_2)(CO)_3(PCy_3)_2][A]$, **3**, forms at room temperature by placing solutions of **2** under 1 atm of H_2. The H_2 ligand is labile and readily dissociates when the H_2 atmosphere is removed in vacuo. ^{31}P NMR clearly shows that at 25 °C under 1 atm of H_2, **3** exists in equilibrium with **2**. At −78 °C and under <1 atm of H_2, only **3** is observed. The synthesis of the new tricarbonyl complex $[Mn(CO)_3(PCy_3)_2]^+$ provides an excellent system of comparison for the binding of small molecules to similar known 16e fragments such as $M(CO)_3(PCy_3)_2$ (M = Cr, Mo, W, Re^+) and $M(CO)(dppe)_2$ (M = Mo, Mn^+). The cationic manganese complex **2** appears to give somewhat more stable binding of H_2 than the isoelectronic neutral chromium congener, which would not have been expected on the basis of relative back-bonding ability of the metal centers. Thus it is clear that increased σ-donation more than compensates for decreased back-bonding in the relative metal−H_2 bonding energies. Surprisingly, binding of N_2, ethylene, or silanes to **2** was not observed in solution even at low temperature and SO_2 binds only weakly. By comparison with other similar systems, it is clear that H_2 becomes an increasingly better ligand than N_2 as the electrophilicity of the metal increases. Thus nonclassical H_2 is a more versatile ligand than most classical ligands in its ability to adjust to a larger range of electronic situations.

Introduction

We have recently concentrated our efforts on developing unsaturated, highly electrophilic, *cationic* fragments such as $[Mn(CO)(R_2PC_2H_4PR_2)_2]^+$, $[PtH(PR_3)_2]^+$, and $[Re(CO)_4(PR_3)]^+$ for binding of H_2, silanes, and, potentially, alkanes.[1] The positive charge here favors η^2-coordination over oxidative addition, and the degree of activation of the H−H bond in these and other cationic or dicationic H_2 complexes is remarkably similar to that in neutral analogues as judged by H−H distance, J(HD), and stability. For example, despite their increasing electrophilicity, the isostructural and isoelectronic 16e fragments $Mo(CO)(dppe)_2$,[2] $[Mn(CO)(dppe)_2]^+$,[1a] and $[M(CO)(diphosphine)_2]^{2+}$ (M = Fe, Ru, Os)[3] all bind H_2 with H−H distances near 0.88 Å and J(HD) = 32−34 Hz (dppe = $Ph_2PC_2H_4PPh_2$). It is now clear that there is a tradeoff in the $H_2 \rightarrow M$ σ-donation bonding component, E_D, with the back-donation component, E_{BD} (Scheme 1); that is, increased electrophilicity at the metal increases σ-donation at the expense of back-bonding, but the effects balance out to enable H_2 to adapt to virtually any electronic situation.

The 16e manganese cations, $[Mn(CO)(R_2PC_2H_4PR_2)_2]^+$, are also of interest because they have been found to contain multiple agostic interactions,[1a,d] whereas the neutral Mo analogues[4] and the tricarbonyl complexes, $M(CO)_3(PR_3)_2$, (M = Cr, W, Re^+),[5] all show only one such interaction (Scheme 2).

† Dedicated to Professor Warren Roper on his 60th birthday.

‡ Current address: Lawrence Livermore National Laboratory, POB 808, Mail Stop L-092, Livermore, CA 94551.

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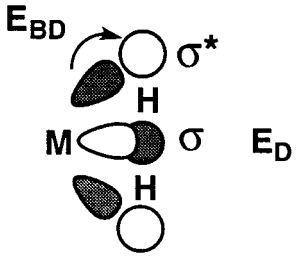
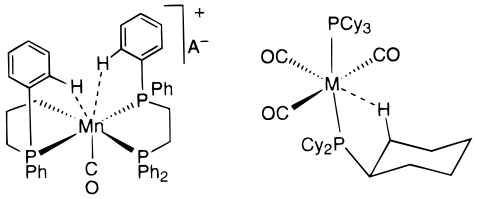
Scheme 1



Scheme 2

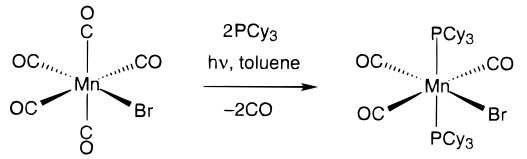


The cationic rhenium complexes, $[Re(CO)_3(PR_3)_2]^+$, were found by Heinekey to coordinate H_2 as well as or perhaps even better than the neutral analogue, $W(CO)_3(PR_3)_2$.[5d] We now report here preparation of the first-row manganese congener, $[Mn(CO)_3(PCy_3)_2]^+$, to further compare the binding and activation of X−H bonds (X = H,[1−7] Si,[6h,i,o] and Ge[8]) on two ongoing interrelated series of isostructural and isoelectronic 16e complexes, $M(CO)_3(PR_3)_2$ and $M(CO)(diphosphine)_2$, where M = group 6 (neutral),[2,4,5a,b,6,8] group 7 (cationic),[1,5c,d,7] and group 8 (dicationic, diphosphine).[3] All 16e members of the group 6−7 series are now known except the Cr and Re^+ diphosphines and the Tc[9] complexes. All give H_2 complexes except $W(CO)(dppe)_2$[10] and $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = alkyl), which oxidatively add H_2 because of the higher electron richness of these fragments.

A general past observation is that H_2 and N_2 coordinate to the same transition metal fragments. In several systems that will be discussed below, H_2 binds more strongly than N_2, and in some cases this is due to an entropic advantage for H_2. However, a few cationic fragments were noted not to form isolatable N_2 complexes in solution at room temperature,[1b,11] even under 3 atm of N_2 in the case of $[Re(CO)_2(triphos)]^+$.[11b] These observations were very qualitative (equilibrium binding possibly occurs), but we are now able to make a more informative correlation between the relative binding abilities of H_2, N_2, and other π-acceptor ligands on the large array of group 6−8 neutral and cationic complexes. The first-row cationic $[Mn(CO)_3(PCy_3)_2]^+$ is one of the most electrophilic complexes in this series, and as will be shown, also demonstrates little or no propensity to bind N_2 and related ligands compared to H_2. It appears that electrophilic *cationic* systems clearly favor H_2 binding, while coordination of N_2 and even stronger π-acceptors such as SO_2 is weak or nonexistent on positively charged fragments. Although H_2 and N_2 are generally considered to be "weak" ligands with binding enthalpies similar to ethers and H_2O (pure σ-donors), the highly amphoteric nature of H_2 bonding to transition metals (σ-base and/or π-acid) makes H_2 much more versatile than N_2 and virtually any other ligand.

Results and Discussion

Synthesis and Structure of $MnBr(CO)_3(PCy_3)_2$, 1. The synthetic precursor *trans*-$MnBr(CO)_3(PCy_3)_2$, **1**, is prepared by photochemical reaction of $Mn(CO)_5Br$ with PCy_3, which proceeds with rapid evolution of CO (eq 1).



(1)

1

The reaction is complete within 15 min, and the yield of analytically pure yellow product is 32%. Complexes of this type with other phosphines have previously been prepared by thermal displacement of CO,[12] e.g. reflux in chloroform for 16−24 h. Attempts to prepare **1** by refluxing $Mn(CO)_5Br$ and excess PCy_3 in $CHCl_3$ resulted in a metal carbonyl complex inseparable from the excess phosphine. Complex **1** isolated from eq 1 was characterized by NMR, IR, and X-ray crystallography. ν_{CO} bands were observed at 1885(s), 1925(s), and 2015(m) cm^{-1} in KBr, which compare favorably with those for the PPr^i_3 analogue[12a] in $CHCl_3$ solution (1887(m), 1932(s), and 2019(w) cm^{-1}). These are consistent with a mer-CO arrangement.[12c] $^{31}P\{^1H\}$ NMR in toluene showed a single resonance at δ 46.44 in accord with a *trans*-phosphine structure (comparable data for other congeners were not found). X-ray crystallography confirmed this structure, which contains a center of inversion (Figure 1, Tables 1 and 2). The closest other known structure of this type is for *trans*-$MnBr(CO)_3$-

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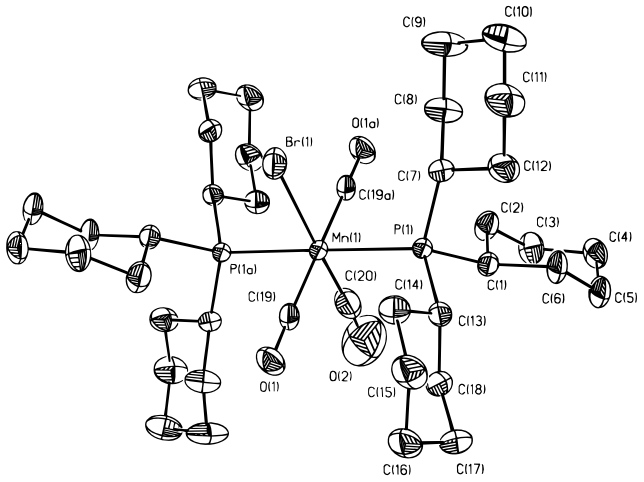


Figure 1. ORTEP diagram for $MnBr(CO)_3(PCy_3)_2$ (50% probability ellipsoids).

Table 1. Crystal Data and Structure Refinement for $Mn(PCy_3)_2(CO)_3Br$, 1

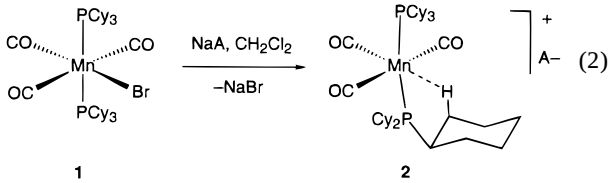
formula	$C_{39}H_{66}BrMnO_3P_2$
cryst size, mm	0.21 × 0.21 × 0.08
temp, K	293(2)
wavelength, Å	0.710 73
space group	triclinic, $P\bar{1}$
a, Å	9.852(2)
b, Å	10.492(2)
c, Å	11.011(2)
α, deg	115.80(3)
β, deg	108.01(3)
γ, deg	91.98(3)
Z	1
μ, mm^{-1}	1.510
2*θ* range, deg	2.80−24.99
no. of reflns collected	3838
no. of independent reflns	3216 (R_{int} = 0.0341)
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0466, wR2 = 0.0953
R indices (all data)	R1 = 0.0831, wR2 = 0.1116

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $MnBr(CO)_3(PCy_3)_2$, 1

Mn(1)−C(20)	1.691(14)
Mn(1)−C(19)	1.841(4)
Mn(1)−P(1)	2.3965(13)
Mn(1)−Br(1)	2.512(3)
O(1)−C(19)	1.141(4)
O(2)−C(20)	1.25(2)
C(20)−Mn(1)−C(20)#1	180.0(1)
C(20)−Mn(1)−C(19)#1	88.1(4)
C(20)−Mn(1)−C(19)	91.9(4)
C(19)#1−Mn(1)−C(19)	180.0
C(20)−Mn(1)−P(1)#1	88.1(4)
C(19)−Mn(1)−P(1)#1	87.98(12)
C(20)−Mn(1)−P(1)	91.9(4)
C(19)−Mn(1)−P(1)	92.02(12)
P(1)#1−Mn(1)−P(1)	180.0
C(20)−Mn(1)−Br(1)	178.3(3)
C(19)#1−Mn(1)−Br(1)	86.88(13)
P(1)#1−Mn(1)−Br(1)	89.26(4)
C(19)−Mn(1)−Br(1)	93.12(13)
P(1)−Mn(1)−Br(1)	90.74(4)

$[P(OMe)_2Ph]_2$, which contains smaller phosphonite ligands instead of PCy_3 and disorder in the Br ligand.[13] The Mn−Br distance in **1** is 2.512(3) and 2.528(8) Å in the latter, while the respective Mn−P distances are 2.3965(13) and 2.264(8) Å (av). The much longer M−P distances in **1** no doubt result from a combination of steric and electronic differences between the P-donor ligands.

Synthesis and Structure of $[Mn(CO)_3(PCy_3)_2][A]$, 2. **1** readily reacts (eq 2) with NaA (A = $B[C_6H_3(3,5\text{-}CF_3)_2]_4$) to form in 80% yield the dark green cationic complex $[Mn(CO)_3(PCy_3)_2][A]$, **2**.



(2)

$^{31}P\{H\}$NMR in CD_2Cl_2 shows a singlet at δ 51.6 compared to similar resonances at δ 63.6 and 27.2 for the neutral Cr[6b] and cationic Re[5c,d] analogues, respectively. Chemically equivalent phosphines at room temperature have previously been observed in these systems because of the highly fluxional nature of their agostic interactions.[6m] Variable-temperature $^{31}P\{^1H\}$ NMR (25 to −90 °C, CD_2Cl_2) of **2** also shows only the one singlet (δ 50.5 ppm at −90 °C), unlike the Mo, W, and Re^+ analogues that give decoalescence below 0 °C to a new weaker resonance with an AB pattern in addition to the (shifted) main singlet.[5d,6m] One proposed rationale for the appearance of the AB signal centered on the existence of hindered rotation of the bulky PCy_3 ligands about the M−P bonds, resulting in a conformer with inequivalent P atoms. However this explanation now appears to be less likely since the smaller first-row metal should have even closer contacts between cyclohexyl groups on opposite sides of the metal (M−P distances are 2.35 Å for Mn and 2.48 Å for W). On the other hand, the fluxionality in the agostic interaction and the overall internal dynamics in this and related systems are exceedingly complex, a fact that is not usually emphasized. There are 24 hydrogens on 12 *β*-carbons on six Cy rings that potentially can interact with the metal. There can be synchronous or asynchronous rotation of eight chemical bonds (2 M−P and 6 P−C) and conformational changes (chair-boat) in the Cy rings. Multiple agostic interactions could occur in solution. Thus, equivalency or inequivalency in the phosphorus atoms could result from any number of temperature-dependent factors here. The rationale[6m] that the AB signal is due to a nonagostic geometric isomer with inequivalent phosphines for the second- and third-row systems but (apparently) not the first-row also remains a possibility.

Low-temperature $^{13}C\{^1H\}$ NMR (−75 °C, CH_2Cl_2) of **2** shows no CH_2Cl_2 binding to the Mn center, as also found for the Re analogue. In contrast, the more electron-rich neutral group 6 analogues react irreversibly with halogenated solvents, presumably forming oxidative addition products. Crystals of **2** are air sensitive and slowly form the tetracarbonyl complex *trans*-$[Mn(CO)_4(PCy_3)_2][A]$ upon exposure to air for more than 5 min or so, analogous to the group 6 systems. The tetracarbonyl shows ν(CO) at 1981 cm^{-1} (Nujol) and a $^{31}P\{^1H\}$ NMR (CD_2Cl_2) resonance at δ 59.3. Storage of **2** at room temperature under He gives approximately 10% disproportionation to the latter, but the crystals were stable for weeks at −30 °C in the drybox freezer.

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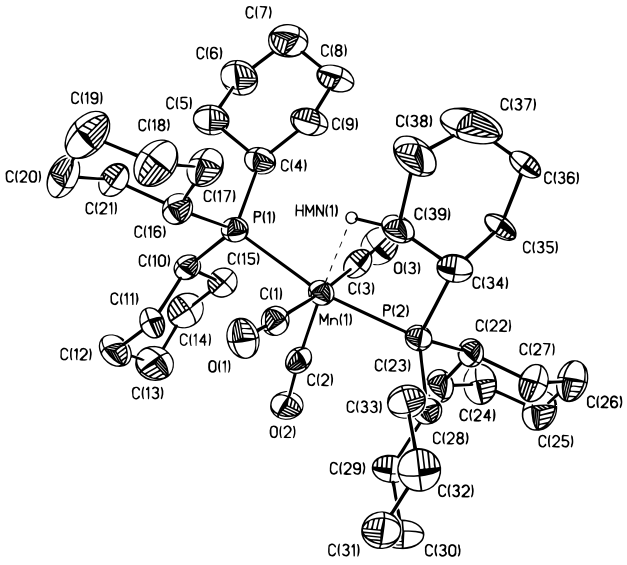


Figure 2. ORTEP diagram for the cation of $[Mn(CO)_3(PCy_3)_2][A]\cdot CH_2Cl_2$ (50% probability ellipsoids). Relevant distances (Å) and angles (deg): Mn(1)−C(1), 1.865(8); Mn(1)−C(2), 1.761(7); Mn(1)−C(3), 1.839(9); Mn(1)−P(2), 2.317(2); Mn(1)−P(1), 2.391(2); P(2)−Mn(1)−P(1), 168.94(8); C(28)−P(2)−Mn(1), 122.5(2); C(34)−P(2)−Mn(1), 98.0(3); C(22)−P(2)−Mn(1), 116.3(3); C(39)−C(34)−P(2), 106.4(6).

Table 3. Metal−Agostic Distances for $[M(CO)_3(PCy_3)_2]^{0,+}$

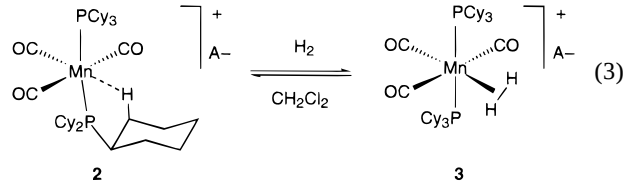
fragment	M···H, Å	M···C, Å
$Cr(CO)_3(PCy_3)_2$	2.240(1)	2.884(1)
$[Mn(CO)_3(PCy_3)_2]^+$	2.01(9) [1.880, 2.072][a] (idealized)	[2.65(3), 2.849(14)][a]
$[Re(CO)_3(PCy_3)_2]^+$		2.89(5)
$W(CO)_3(PCy_3)_2$	2.27 (idealized)	2.945(6)

[a] For disordered carbon positions C39′ and C39, respectively.

By comparison the Cr analogue of **2** is more stable, although $Cr(CO)_3(PPr^i_3)_2$, which contains the slightly less bulky PPr^i_3, could not even be isolated upon H_2 removal from $Cr(CO)_3(PPr^i_3)_2(H_2)$,[6d] demonstrating that there is a fine line of stability here.

X-ray crystallography of **2**·CH_2Cl_2 (Figure 2) shows a relatively strong agostic interaction of a cyclohexyl C−H bond with manganese very similar to those in the Cr, W, and Re^+ analogues. The P−Mn−P angle, 168.94(8)°, and the C(34)−P(2)−Mn(1) angle, 98.0(3)°, are both smaller than normal to facilitate the agostic interaction. There is an unusual type of disorder present in a few of the atom positions in the structure, including the agostic carbon (C39, C39′) resulting in a high R1 = 0.1025 (see Supporting Information), but it was possible to refine the H atom of the proton attached to it (all other H's were fixed). The refined Mn···H distance is 2.01(9) Å, while the idealized positions are 1.880 (Mn−H39′) and 2.072 Å (Mn−H39) for C39−H39 and C39′−H39′ set to 0.96 Å. These distances are significantly shorter than that in the Cr analogue, 2.240(1) Å. The M···C distances are 2.65(3) (Mn−C39′) and 2.849(14) Å (Mn−C39) versus 2.884(1) and 2.89(5) Å for the Cr and Re^+ analogues (Table 3). Thus the agostic interaction appears to be stronger in the cationic group 7 system than in the neutral group 6 system, although differences in van der Waals radii and other factors may play a role here. Presumably stronger σ-donation from the C−H bond to the more electrophilic cations is occurring. In the diphosphine system, $[Mn(CO)(R_2PC_2H_4PR_2)_2]^+$, multiple agostic interactions (two for R = Ph, four for R = Et) are present, and the Mn···H distances are much longer (>2.9 Å).[1a,d] The more rigid chelating phosphine substituents are apparently more constrained in their ability to approach the tight coordination sphere of the first-row metal, so the unsaturated metal obtains smaller amounts of electron density from more than one CH bond.

Synthesis and Properties of $[Mn(H_2)(CO)_3(PCy_3)_2]$-[A], 3. The light yellow H_2 complex $[Mn(H_2)(CO)_3(PCy_3)_2][A]$, **3**, readily forms at room temperature by placing solutions of **2** under 1 atm of H_2 (eq 3).

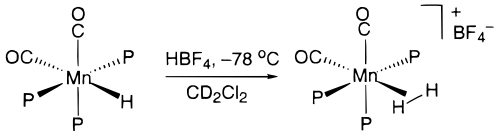


(3)

2 **3**

The H_2 ligand is labile and readily dissociates when the H_2 atmosphere is removed in vacuo to regenerate the dark green solution of **2**. At room temperature this cycling could be applied three times with no observable decomposition. That there is an equilibrium between the agostic complex and the H_2 complex is proven unequivocally by the ^{31}P NMR experiments. At −78 °C and under <1 atm of H_2, a singlet is observed at δ 63.29 for the H_2 complex in CD_2Cl_2. However at 25 °C two peaks are observed, one at δ 63.47 (for the hydrogen complex) and the other at δ 51.6 (for the agostic complex). Under 0.8 atm of H_2 at 35 °C, the dark green solution of $[Mn(CO)_3(PCy_3)_2]^+$ turned immediately to pale yellow, and 72% of the latter is coordinated by H_2 from integration of ^{31}P NMR resonances. At −10 °C, 95% of the complex is bound to H_2.

The importance of the low-interacting $B[C_6H_3(3,5\text{-}CF_3)_2]_4$ anion in complexes **2** and **3** is underscored by the recent work of Albertin[7] on similar systems containing phosphite ligands. In this case the hydrides $MnH(CO)_n(P)_{5-n}$ (n = 2, 3) were protonated as in eq 4 with strong acids with coordinating anions such as HBF_4 and triflic acid.



(4)

P = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2OEt

In eq 4 the resulting H_2 complexes were unstable above 0 °C and could not be isolated, although NMR data showed H_2 binding at low temperature. The tricarbonyl complexes were even more unstable, and H_2 instantly evolved on protonation at low temperature. The use of triflic acid resulted in isolation of triflate complexes $Mn(\eta^1\text{-}OSO_2CF_3)(CO)_3(P)_2$. Clearly the anion immediately displaced transiently bound H_2, which was never observed. Although 16e $[Mn(CO)_n(P)_{5-n}]^+$ complexes were claimed to have been isolated as yellow BPh_4^- salts and postulated to have an agostic interaction based on ^{31}P NMR data, crystallographic evidence was not obtained to rule out anion coordination. Pro-

Table 4. Comparison of Small Molecule Binding Relative[a] to H_2 on Various Metal Fragments in Approximate Order of Decreasing Electrophilicity

	π-acceptor strength				
metal fragment	SO_2	silanes	C_2H_4	N_2	Et_2O/CH_2Cl_2
$[trans\text{-}PtH(PR_3)_2]^+$	no			no	stronger
$[Fe(CO)(dppe)_2]^{2+}$				no	
$[Re(CO)_4(PR_3)]^+$		weak	stronger	no	stronger
$[Mn(CO)_3(PR_3)_2]^+$	reversible	no (−70 °C)	no (−70 °C)	no (−58 °C)	no
$[Re(CO)_3(PR_3)_2]^+$				weaker	no
$[Re(CO)_2(triphos)]^+$				no (3 atm)	
$[Mn(CO)(dppe)_2]^+$	reversible	no (−70 °C)		weaker	no
$[RuCl(dppe)_2]^+$				no	no
$Cr(CO)_5$	strong	stronger	stronger[b]	weaker	
$Cr(CO)_3(PR_3)_2$		no		weaker[c]	no
$W(CO)_3(PR_3)_2$	strong	OA[d]	yes	stronger	no
$Mo(CO)(dppe)_2$	strong	yes[e]	yes	stronger	no
$TcCl(dppe)_2$				yes	no

[a] *Weaker* or *stronger* than H_2 in terms of ΔG of binding at room temperature. Terminology: *strong* = irreversible coordination; *no* = binding not observed at ambient temperature and pressure; *yes* = similar to H_2 binding but relative stabilities not determined; blank entry = not reported. [b] $Cr(CO)_5(C_2H_4)$ has been isolated as a solid (Banister, J. A.; Lee, P. D.; Poliakoff, M. *Organometallics* **1995**, *14*, 3876. [c] At pressures above 1 atm. [d] OA = oxidative addition. [e] Complex rearranges to isomer with silane cis to CO.

tonation with $H(OEt_2)_2A$ would probably give stable H_2 and agostic complexes here with no possibility of anion interaction.

The H_2 binding to $[Mn(CO)_3(PCy_3)_2]^+$ is similar to that in the neutral congener $Cr(CO)_3(PCy_3)_2$ that also gave equilibria between agostic and dihydrogen complexes in toluene solution. Similar chemical shift differences were seen in the ^{31}P NMR for the latter (δ 63.6 for agostic versus δ 73.5 for H_2 complex).[6b] However, hydrogen gas pressures upward of 20 atm were required to drive the equilibrium completely to the H_2 complex at room temperature, and very little binding occurred at atmospheric pressure. Thus the cationic manganese system appears to give somewhat more stable binding of H_2 than the isoelectronic neutral chromium complex. This would never have been expected solely on the basis of relative back-bonding ability of the metal centers, which should be far lower for the positively charged manganese. Thus it is clear that increased σ-donation more than compensates for decreased back-bonding. The J(HD) coupling for the HD isotopomer of **3** is 33 Hz and is 35 Hz for $Cr(HD)(CO)_3(PPr^i_3)_2$,[6d] indicating that the H−H bond is actually longer (0.87−0.89 Å based on J(HD)[14]) and held more strongly in the Mn cation than in neutral $Cr(H_2)(CO)_3(PR_3)_2$ (R = Cy, 0.85 Å (solid NMR[6d]); R = Pr^i, 0.84−0.85 Å[14]). This increasing (or nearly equal) binding strength with increasing positive charge has also been seen in the $[M(CO)(dppe)_2]^{n+}$ (n = 0−2) systems as stated in the Introduction. J(HD) for the dicarbonyl phosphite complex $[Mn(H_2)(CO)_2\{P(OEt)_3\}_3]^+$ is also 33 Hz,[7] once again demonstrating as we have previously shown[1d] that the nature of the cis-ligand set does not have significant influence on H_2 activation in comparison to that of the trans ligand (CO).

Comparison of H_2, N_2, SO_2, and Other Small Molecule Coordination to 2 and Other Fragments. Several other small molecules were reacted with **2** in order to compare relative binding abilities of this cationic fragment with isoelectronic fragments, including neutral species. At the same time, relative coordination strengths of various common ligands can be assessed on the various fragments. Most surprisingly, the normally strong ligand SO_2,[15] which is a stronger π-acceptor than CO, was found to be very weakly bound. Not only was an SO_2 complex unable to be isolated as a solid, it was only detectable as an equilibrium species by ^{31}P NMR, and IR frequencies for SO stretches could not be determined. At room temperature, addition of 0.8 atm of SO_2 (excess) to **2** in CD_2Cl_2 gave a mixture of **2** (51.6 ppm) and SO_2 complex (56.9 ppm) in a ratio of 1/0.7. When cooled to −40 °C, conversion to the SO_2 complex was complete, but in comparison, SO_2 *irreversibly* binds to the neutral $M(CO)_3(PCy_3)_2$ analogues at room temperature.[15c] Steric factors should not play a role here since SO_2 prefers electronically to lie in the plane between the bulky phosphines to receive maximum back-donation.

Nearly as surprising, no evidence for *any* N_2 binding to **2** under 0.8 atm of $^{15}N_2$ was seen by ^{15}N NMR in CD_2Cl_2 solution, even when the temperature was lowered to −58 °C, which favors binding of weak external ligands here (the 10 kcal/mol entropic advantage that internal agostic CH binding holds over external ligand binding is reduced at lower temperatures). Only a strong signal for free N_2 was observed, whereas for $[Mn(CO)(dppe)_2(N_2)]^+$ the expected two resonances for end-on-coordinated N_2 were clearly observed by this method at −73 °C up to room temperature.[1a] The complete lack of N_2 binding to **2** is also surprising because the Re congener, $[Re(CO)_3(PCy_3)_2]^+$, was 50% coordinated by N_2 (0.8 atm) at room temperature.[5c]

The explanation for the above disparity goes beyond the simple rationale that third-row metals are better π-donors than first-row metals and N_2 is a moderate π-acceptor. In this regard it is particularly informative to compare H_2, N_2, and other ligand coordination on a large array of cationic and neutral fragments. Table 4 lists relevant 16e fragments, all of which bind H_2, in roughly estimated decreasing order of electrophilicity and whether they bind N_2 and other common ligands discussed below. In some cases direct comparisons to

(14) Calculated from and bracketed by the empirical relationships r_{HH} = 1.42 − 0.0167J(HD) (Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396) and r_{HH} = 1.44 − 0.0168J(HD) (Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127).

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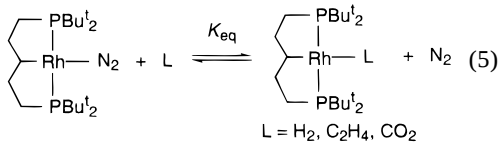
the binding strength of H_2 can be made (denoted by "weaker" or "stronger"). As mentioned in the Introduction, N_2 also does not coordinate to the 16e dicarbonyl complex, $[Re(CO)_2(triphos)]^+$, at room temperature under 3 atm N_2. This fragment is believed to have an agostic interaction trans to one of the phosphine arms. The H_2 ligand replaces the agostic interaction and is moderately labile in the solid state, but the complex is isolatable. In the neutral $M(CO)_3(PCy_3)_2$ system, coordination of H_2 and N_2 is far more competitive and is nearly isoenergetic. N_2 binding to $Cr(CO)_3(PCy_3)_2$ was not seen in solution at room temperature, but partial coordination occurred when the pressure of N_2 was raised to ca. 2 atm and higher (100% binding required 100 atm).[6a] Thermodynamic measurements showed that H_2 binding to Cr was stronger, but by only about 1 kcal/mol in terms of ΔG and primarily for entropic reasons; ΔH actually favors N_2 binding by 2 kcal/mol here. Entropy can play a large role in weakly coordinating ligands because $T\Delta S$ can rival ΔH in magnitude, and as the temperature is lowered, the relatively small absolute entropy of H_2 increasingly favors binding of H_2 as compared to other ligands.[6n] For the cationic $[Mn(CO)_3(PCy_3)_2]^+$ congener however, H_2 binding is clearly favored *enthalpically* over N_2 since at −58 °C there is essentially no N_2 coordination and complete H_2 coordination, while for Cr partial binding of both H_2 and N_2 is observed spectroscopically at ca. 2 atm of the gases. The entropy effect could not be responsible for this difference.

For the diphosphine system $[Mn(CO)(R_2PC_2H_4PR_2)_2]^+$, direct competition studies show that H_2 binds stronger than N_2. However the thermodynamic difference is not as dramatic as for **2** since the complex with R = Et binds N_2 (1 atm) completely at room temperature, while the less electron-rich R = Ph analogue still coordinates to a 37% extent.[1a,d] Since **2** is more electrophilic than the latter, the obvious trend is that *H_2 becomes an increasingly better ligand than N_2 as the electrophilicity of the metal increases and back-donation decreases.* Conversely, for the most electron-rich system considered in this paper, $Mo(CO)(dppe)_2$, N_2 clearly binds more strongly than H_2.[2,6g] This disparity in relative coordinating abilities results from N_2 being a very poor σ-donor[16] and a good π-acceptor, though slightly weaker than H_2,[16b,d] as shown both theoretically and experimentally (mainly by Mossbauer studies). The data in Table 4 demonstrate that N_2 is clearly a poorer σ-donor than the very weak bases Et_2O and dichloromethane, both of which form fairly robust complexes with the highly electrophilic $[Re(CO)_4(PR_3)]^+$ and $[PtH(PR_3)_2]^+$ fragments.[1b,c] Theoretical calculations that include charge decomposition analysis of $W(CO)_5L$ show that for L = H_2 the contribution from σ-donation is 0.349e versus only 0.027e for N_2, while back-donation is 0.107e for N_2 versus 0.129e for H_2.[16d] It is apparent that N_2 can only be stabilized on a metal center by π-back-donation, even in *actinide* complexes[17] such as $[\{(NN'_3)U\}_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, for which DFT calculations show that back-donation to side-on-bound N_2 is the *only* significant U−N_2−U interaction.[16e] Therefore, cationic organometallic electrophiles may simply not provide enough π-back-donation to stabilize N_2 binding relative to neutral electrophiles, and N_2 cannot compensate for this loss by increasing its σ-donation as effectively as H_2 can. For the much more electron-rich $Mo(CO)(dppe)_2$ fragment on the other hand, back-donation to H_2 accounted for roughly two-thirds of the bond strength (versus two-thirds σ-donation for $Mo(CO)_5$),[18] showing how easily H_2 reverses its bonding capability. *Thus nonclassically bound H_2 is a more versatile ligand than N_2 and indeed many other classically coordinated ligands in its ability to adjust to a larger range of electronic situations.*

An exception to the general observation that N_2 tends to be a slightly better ligand than H_2 on neutral complexes is shown in eq 5.[19]



(5)

In cyclohexane solution, the H_2 binding is measured to be 1.24 kcal/mol more favorable than N_2 binding, possibly because of the slightly better back-bonding ability of H_2 versus N_2 to the electron-rich Rh center here. Surprisingly, N_2 binding is more favorable than ethylene binding by 1.57 kcal/mol, but this is no doubt a result of the steric demands of the bulky phosphines. Not surprisingly, CO_2 is the weakest ligand here, and very few transition metal fragments that bind H_2 also coordinate CO_2. Dioxygen is also rarely found on the same fragment as H_2,[20] although the reason is that O_2 usually oxidizes the low-valent fragments that favor H_2 binding.

Comparisons of the H_2 ligand to other types of ligands, including pure σ-donors, further support the versatility of the H_2 ligand. For example, $[Re(CO)_4(PR_3)]^+$ binds Et_2O and CH_2Cl_2 moderately strongly to give isolatable complexes that are more stable than the H_2 complex.[1c] However, H_2 gains the bonding advantage over such weak σ-donors on more electron-rich neutral systems such as $M(CO)_3(PCy_3)_2$, $Mo(CO)(R_2PC_2H_4PR_2)_2$, and most other group 6−10 fragments which do not bind ethers or CH_2Cl_2 in stable fashion. In these cases, the increased back-donation strengthens H_2 binding considerably but pure σ-bases cannot receive this. Thus H_2 is the perfect ligand because it is effectively *amphoteric*, i.e., essentially both a Lewis acid and a Lewis base like SO_2, with which there is an excellent parallel. *Just as SO_2 is the most versatile coordinating agent toward both transition metal and main-group compounds,[15] H_2 is perhaps the most adaptable "weak" ligand.* Virtually

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(20) Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Inorg. Chem.* **1994**, *33*, 3515.

every known unsaturated transition metal fragment either molecularly binds or oxidatively adds H_2. The primary difference between H_2 (and other nonclassical ligands) and classical ligands such as SO_2 is that electron donation originates from a *bonding* electron pair to give a three-center interaction. SO_2 is a stronger π-acceptor, but H_2 is not too far behind, closely followed by ethylene, then N_2.[6m]

The main rival to H_2 is ethylene and other olefins which generally coordinate somewhat stronger to the same fragments as H_2 and bind to metals in the classic Dewar−Chatt−Duncanson π-bonding model, which is quite analogous to metal−H_2 bonding. However, from ^{31}P NMR evidence, ethylene does not coordinate to **2** even at −70 °C, and disproportionation to *trans*-$[Mn(CO)_4(PCy_3)_2][A]$ occurs instead (CO is a strong "sixth ligand" here). It is very likely that ethylene cannot bind in the electronically preferred geometry (parallel to the P−Mn−P axis as in the W analogue[6m]) for steric reasons (smaller first-row metal coordination sphere). Perhaps the tetracarbonyl results from rapid decomposition of an unstable adduct with an off-axis geometry. All of the group 6 and 7 $M(CO)_3(PR_3)_2$ species are indeed prone to slow disproportionation in solution, which conceivably may be promoted by equilibrium displacement of the agostic interaction by weak ligands or solvent. However, for reactions of **2** with N_2, silanes, and SO_2, much less $[Mn(CO)_4(PCy_3)_2]^+$ was formed.

Like H_2, silanes form σ-complexes with a wide range of fragments, although the Si−H bond is a slightly better acceptor than H−H and oxidatively adds more readily.[6h,i,m] Also, silane coordination to first-row octahedral group 6 and 7 metals appears to be much weaker than to second- and third-row metals, and $PhSiH_3$ does not form a stable complex with **2** down to −75 °C from ^1H and ^{31}P NMR evidence. Similarly, silane coordination was unobserved to $[Mn(CO)(dppe)_2]^+$ and even neutral $Cr(CO)_3(PR_3)_2$,[1d,6m] but silanes were found to coordinate to $[Re(CO)_4(PR_3)]^+$[1c] and even oxidatively add to $W(CO)_3(PR_3)_2$.[6m] Thus silane binding and activation is much more variable than that for H_2, which coordinates in a more predictable fashion throughout first- to third-row metals. This is mainly a result of the increased complexity of the R_3Si-H ligand where substituents are present on Si that can influence activation both electronically and sterically (important for smaller first-row metals), and reversal of trends can even occur depending on electrophilicity of the metal fragment.[6o] Silanes and also N_2 and SO_2 coordinate as well or better than H_2 to $CpMn(CO)_2$, which is both less sterically crowded and less electrophilic than **2**.

It must be kept in mind that the CO ligand trans to L in the neutral and cationic $M(CO)_3(PR_3)_2(L)$ and $M(CO)(R_2PC_2H_4PR_2)_2(L)$ systems has a strong trans influence;[6m,9] that is, H_2, N_2, and other π-acceptors L must compete with CO for back-donation and are less activated. For example, H−H distances are usually <0.9 Å and J(HD) is >30 Hz for all complexes where CO is trans to H_2. However, for systems with trans ligands that are primarily electron donors such as chloride and phosphine, e.g., $[Re(CO)_2(triphos)]^+$, the above bonding trends still hold. Both H_2 and N_2 bind similarly to second-row $TcCl(dppe)_2$,[9] while H_2 binding is again favored over N_2 on the more electrophilic $[RuCl(dppe)_2]^+$ cationic congener.[11a] The π-donating chloride ligand generally has a low trans influence and is a weak field ligand, and $TcCl(dppe)_2(H_2)$ consequently has an elongated H−H bond, >1 Å. Another cationic system under intense study in regard to alkane activation is $[PtXL_2(L')]^+$ where X = H, Me, Ph; L = phosphine or amine; and L′ = labile ligand.[1b,21] The X ligands here also have a strong *trans-donor* effect. We have shown that the $[PtH(PPr^i_3)_2]^+$ fragment does not coordinate N_2, yet gives stable H_2 binding at −40 °C (H_2 dissociates on warming).[1b] Interestingly even SO_2 does not bind to this feebly back-bonding, highly electrophilic fragment, although weak bases readily give isolatable, air-stable $[PtX(PR_3)_2(L)]^+$ for L = Et_2O and CH_2Cl_2.

A last consideration is why N_2 and silanes are much poorer ligands toward *cationic* electrophiles than neutral electron-poor fragments such as $Cr(CO)_5$ which bind N_2, H_2, and silanes at either low temperatures or high pressures (130 atm) with very similar enthalpies of dissociation (16−17 kcal/mol).[22] For silanes, steric factors may prevail (the cations have bulky phosphines). However this should not be relevant for N_2, and the much lower propensity to coordinate to *positively charged* organometallic electrophiles could be related to polarizability effects, i.e., soft/hard ligand properties. However from guided ion-beam mass spectrometric evidence, both H_2 and N_2 interact equally well with very hard naked metal ions such as Fe^+ to form $[Fe(L)_n]^+$ species, where polarizability is a large factor.[23] Therefore, we are left with the conclusion that cationic organometallic electrophiles are weaker π-donors than $M(CO)_5$ fragments.

Clearly more theoretical guidance is needed for these cationic systems, as has been carried out recently for H_2, N_2, and CO on the neutral fragments $Fe(CO)_4$ and group 6 $M(CO)_{5-n}P_n$.[18,24] As pointed out by Hoffmann,[24a] the reason CO is such an excellent and ubiquitous ligand is the balance between its good donating and accepting capabilities and its innate molecular stability. It is clear that the H_2 ligand offers these same advantages, albeit on a lower scale energetically. Interestingly, theoretical calculations[24c] have recently shown that the first CO dissociation energy from $[M(CO)_6]^n$ (M = group 4−9 metal; n = −2 to +3) is unexpectedly *higher* for the cationic complexes because σ-donation from CO increases, just as H_2 greatly increases its σ-donation to cationic systems.

Conclusions

The electrophilic and sterically crowded cationic $[Mn(CO)_3(PCy_3)_2]^+$ fragment (**2**) has been found to bind H_2 but not N_2, ethylene, or silanes, even at −70 °C.

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Remarkably, the normally strong SO_2 ligand is bound only weakly in equilibrium with **2**, which attests to the poor back-bonding ability of **2**. The relatively strong internal agostic C−H interaction in **2** thus appears to be more resistant to displacement by external ligands than similar neutral and cationic fragments with agostic interactions. There is also a clear overall trend that electrophilic *cationic* systems highly favor H_2 binding over N_2 and even stronger ligands such as SO_2. Although H_2 is generally considered to be a "weak" ligand, the amphoteric nature of H_2 bonding to transition metals makes H_2 much more versatile than N_2, olefins, silanes, and virtually any other ligand. Dihydrogen is thus able to coordinate (or oxidatively add) to a wider array of transition metal fragments, particularly cationic species, than even most "strong" ligands. On the other hand, N_2 is an exceedingly poor electron donor, even toward strong electrophiles, where it is much more feeble than the weakest known ligands, e.g., CH_2Cl_2. The complete lack of binding to **2** and other electron-poor cationic complexes indicates that N_2 apparently can only be stabilized on a metal center by a high degree of π-back-donation, even in actinide complexes,[16e,17] offering indirect experimental evidence for the controversial existence of back-donation from f-elements. In light of this and computations that show η^2-N_2 is favored over η^1-N_2 in $Ni(PH_3)_2(N_2)$,[16f] it is surprising that η^2-N_2 is not more common and is virtually unknown in mononuclear complexes. These new viewpoints on the bonding of N_2 and other small molecule ligands discussed in this paper are quite relevant to their chemical and biochemical transformations (e.g., structure and function of enzymes such as nitrogenase and hydrogenase[25]) and an important topic for further study. The principles derived from H_2 coordination can be extended to other σ-ligands, particularly alkane binding which could be enhanced on cationic electrophilic centers such as Pt(II) species that are under current scrutiny in regard to Shilov activation of methane.[21]

Experimental Section

General Procedures. All manipulations were performed either under a helium atmosphere in a Vacuum Atmospheres drybox or under an argon atmosphere using standard Schlenk techniques unless otherwise specified. Toluene and hexane were distilled from Na under Ar. CH_2Cl_2 was distilled under Ar from CaH_2. Anhydrous EtOH was stored over activated molecular sieves and was deoxygenated by bubbling Ar through the solvent prior to use. Solvents for preparation of the agostic complex were vacuum transferred from P_2O_5, CH_2Cl_2, or Na/K alloy, hexane prior to use. All gases except SO_2 (anhydrous grade) and ethylene were of UHP grade. Ethylene was polymerization grade, purified by passage through an Oxisorb-Glas column. $PhSiH_3$ was purchased from Aldrich Chemical Co. HD gas was acquired from Isotec. Na[A] was prepared according to literature methods.[26] All solids were weighed out in the drybox under a He atmosphere. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 550 spectrometer or a Varian Unity 300. ^1H chemical shifts were referenced to the residual solvent resonance relative to TMS; ^{31}P chemical shifts were referenced to external 85% H_3PO_4. Infrared spectra were recorded on a BioRad FTS-40 FT-IR spectrometer. Elemental analyses (C, H, and N) were performed by Oneida Research Services, Inc., or in house (complex **2**).

Preparation of $MnBr(CO)_3(PCy_3)_2]$, 1. In the drybox, $MnBr(CO)_5$ (1.065 g, 3.874 mmol) and PCy_3 (2.178 g, 7.766 mmol) were placed into a 200 mL Schlenk flask, and about 150 mL of toluene was added. This orange solution was transferred by cannula into a photochemical reactor and irradiated for 15 min with a medium-pressure Hg lamp through a water-jacketed quartz immersion well, cooled to 5 °C. During irradiation the solution was stirred, gas was seen to form, and the system was flushed with argon using an oil bubbler. The resulting yellow solution was removed from the reaction vessel, toluene solvent was removed in vacuo, and the resulting solid residue was taken up in 15 mL of CH_2Cl_2 and filtered. On addition of 15 mL of EtOH, a yellow precipitate formed. The volume was reduced to approximately 2 mL, and approximately 4−6 mL of CH_2Cl_2 was added to the flask. The yellow solid persisted. Precipitation was completed by the addition of 15 mL of EtOH. The yellow solid (0.678 g) was collected and washed with 30 mL of hexane. A second crop (0.347 g) was crystallized from CH_2Cl_2/EtOH to give a total yield of 0.975 g, 32%. The essentially analytically pure product gave excellent elemental analysis (% found(theory)): C, 59.85-(60.07); H, 8.46(8.53); N, 0.00(0.00). IR (cm^{-1}, KBr, ν_{CO}): 1885-(s), 1925(s), 2015(m). ^1H NMR (toluene, 25 °C): δ 2.46−1.25 (m, Cy). $^{31}P\{^1H\}$ NMR (toluene, 25 °C): δ 46.44(s). Suitable X-ray quality crystals were obtained from a CH_2Cl_2 solution by layering with ethanol.

The unrecrystallized solid in addition to the bands due to the product also showed infrared bands at 1943, 1900, and 1844 cm^{-1}. These bands were not observed in the pure recrystallized product.

Preparation of $[Mn(CO)_3(PCy_3)_2][A]$, 2. In a glovebox, Na[A] (0.114 g, 0.129 mmol) was added to a stirred solution of $MnBr(CO)_3(PCy_3)_2$ (0.100 g, 0.128 mmol) in CH_2Cl_2 (5 mL). After stirring for 10 min, the dark green reaction mixture was filtered through Celite to remove precipitated NaBr, and hexanes (5 mL) were added to the filtrate. Storage at room temperature for 1 h provided dark green crystals of **2** (0.159 g, 80% yield). Crystals of a mono-CH_2Cl_2 solvate suitable for X-ray diffraction studies were obtained by diffusion of hexanes into a CH_2Cl_2 solution of **2** at room temperature. Anal. Calcd for $C_{72}H_{80}Cl_2F_{24}O_3P_2BMn$: C, 52.48; H, 4.89; N, 0.00. Found: C, 52.56; H, 5.00; N, 0.01. FT-IR (Nujol), ν(CO): 2048(w), 1962(s), 1942(s), 1933(sh). ^1H NMR (CD_2Cl_2): δ 1.0−2.6 (m, 66H, Cy), 7.53 (s, 4H, A), 7.73 (s, 8H, A). $^{31}P\{H\}$ NMR (CD_2Cl_2): δ 51.6.

Reaction of 2 with SO_2. A sample of **2** (0.010 g) was transferred to a J-Young NMR tube and dissolved in 0.5 mL of CD_2Cl_2. The tube was placed on a vacuum line, frozen, pumped down, and back-filled to 0.8 atm of SO_2 (the ambient atmospheric pressure is near 600 Torr). The yellow-green solution was warmed to room temperature and the tube closed off. At room temperature the $^{31}P\{^1H\}$ NMR (CD_2Cl_2) showed a mixture of the agostic (51.6 ppm) and SO_2 (56.9 ppm) complexes present at a ratio of 1/0.7, respectively. When cooled to −40 °C, all was converted to the SO_2 complex. ^1H NMR (−40 °C, CD_2Cl_2): δ 7.73 (s, 8H, A), 7.55 (s, 4H, A), 1.0−2.7 (m, 66H, Cy). $^{31}P\{^1H\}$ NMR (−40 °C, CD_2Cl_2): δ 57.1. The reaction with SO_2 was completely reversible, and when the volatiles were removed from the NMR sample under vacuum and the green residue was dissolved in CD_2Cl_2, only the signal 51.7 ppm for the agostic complex was observed in the $^{31}P\{^1H\}$ NMR.

Reaction of 2 with C_2H_4, $PhSiH_3$, and $^{15}N_2$. In a similar fashion, approximately 1.5 equiv of ethylene was added to a frozen CD_2Cl_2 solution of **2**. The NMR tube was kept cold and inserted into a precooled probe at −70 °C. Proton and $^{31}P\{^1H\}$ NMR spectra were recorded at this temperature as well as −40, 0, and 20 °C, but only free ethylene was observed in

(25) Pavlov, M.; Siegbahn, P. E. M.; Blomberg, M. R. A.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 848,

(26) Brookhart, M.; Grant, R. G.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

the ^1H spectra. In the ^{31}P spectra, **2** plus *trans*-$[Mn(CO)_4(PCy_3)_2][A]$ (58.9 ppm) was seen at −70 °C. As the solution was warmed to room temperature, the reaction mixture turned colorless, and the ratio of the latter to **2** increased until it finally became 1/0.

In the drybox, a large excess of $PhSiH_3$ (0.1 mL) was added to a CD_2Cl_2 solution of **2** (10 mg) in an NMR tube, and the olive green color of the reaction mixture persisted. ^1H NMR experiments showed no peaks attributable to σ-bound Si−H or the oxidative addition product at room temperature or at −70 °C, and the $^{31}P\{^1H\}$ NMR spectra showed only a sharp peak for unreacted **2**.

For reaction of **2** with 0.8 atm of $^{15}N_2$ as above for ethylene, no signals indicative of coordination were seen at −58 °C in the ^{15}N NMR. Only the signal for free $^{15}N_2$ was observed.

Formation of $[Mn(CO)_3(PCy_3)_2(H_2)][A]$. Reactions of **2** with H_2 (0.8 atm) were run as above, and the color of the solution turned immediately from green to pale yellow. The sample was characterized by ^1H and ^{31}P NMR at −78 °C and also 25 °C, at which temperature the H_2 complex existed in equilibrium with **2**. ^1H NMR (CD_2Cl_2, 25 °C): δ −8.43 (br, 2H), 2.50−0.17 (m, Cy), 4.59 (br, free H_2), 7.57 (s, 4H), 7.73 (s, 8H). ^1H NMR (−78 °C): δ −8.56 (br, 2H, 277 Hz), 1.95−0.07 (m, 66H), 5.21 (br, free H_2), 7.53 (s, 4H), 7.72 (s, 8H). ^{31}P NMR (25 °C): δ 63.47 (s, H_2 complex), 51.25 (s, **2**). ^{31}P NMR (−78 °C): δ 63.29 (s, H_2 complex).

Formation of $[Mn(CO)_3(PCy_3)_2(HD)][A]$. Analogous to the formation of $[Mn(CO)_3(PCy_3)_2(H_2)][A]$, HD gas was used instead of H_2 gas. At 300 K, ^1H NMR (CD_2Cl_2): δ 7.72, (8H, s, ortho-Ar′]); 7.56, (4H, s, para-Ar′]); 2.51−1.13, (66H, m, PCy_3); −8.46 (1H, t (J = 33 Hz, Mn−HD). $^{31}P\{H\}$ NMR (CD_2Cl_2): δ 58.9.

X-ray Structure Determination of 1. A yellow parallelepiped was mounted on a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, was immediately placed under a liquid N_2 stream on a Siemens P4/PC diffractometer. The radiation used was graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. Reflections were collected using ω scans with a 0.86° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections, and structure solution and graphics were performed using SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELX 93 software.[27] The data were corrected for absorption using the ellipsoid option in the XEMP facility of SHELXTL PC. Data collection parameters are given in Table 1.

The structure was solved in space group $P\bar{1}$ using direct methods. The manganese, bromine, and phosphorus atoms were identified from the direct methods solution. Subsequent Fourier synthesis revealed all remaining atoms. Due to the inversion symmetry of the molecule, two trans sites were modeled as one-half occupancy bromine and one-half occupancy carbonyl. The secondary and tertiary carbon hydrogen atoms were fixed in positions of ideal geometry, with C−H distances of 0.97 and 0.98 Å, respectively. All hydrogen atoms were refined using the riding model in the HFIX facility in SHELXL 93 and had their isotropic temperature factors fixed at 1.2 times the equivalent isotropic U of the carbon atom they were bonded to. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1 = 0.0466 and wR2 = 0.0953.[28]

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Supporting Information Available: X-ray data for **1** and **2** (23 pages). See any current masthead page for ordering information and Internet access instructions.

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(27) XSCANS and SHELXTL PC are products of Siemens Analytical X-ray Instruments, Inc., 6300 Enterprise Lane, Madison, WI 53719. SHELX-93 is a program for crystal structure refinement written by G. M. Sheldrick, University of Göttingen, Germany, 1993.

(28) $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.1733P]$.

(29) *SMART*, Version 4.210; Bruker Analytical X-ray Systems, Inc.: 6300 Enterprise Lane, Madison, WI 53719, 1996.