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Catalytic Thermal C–H Activation with Manganese Complexes: Evidence for η^2-H_2 Coordination in a Neutral Manganese Complex and Its Role in C–H Activation

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The reactivity of $MnH_3(dmpe)_2$ has been examined for its ability to activate C–H bonds. The complex loses H_2 readily and is characterized as having an η^2-H_2 ligand on the basis of NMR spectroscopic and electrochemical studies. Reaction of $MnH_3(dmpe)_2$ with added ligands gives $MnH(L)(dmpe)_2$ (L = CO, N_2, C_2H_4, CNR; R = *t*-Bu, CH_2CMe_3, 2,6-xylyl). The complex activates aromatic and benzylic C–H bonds under both thermal and photochemical conditions as determined by catalytic H/D exchange with C_6D_6 or D_2. Selectivity studies were also carried out by employing catalytic H/D exchange. A mechanism is proposed, and the neighboring group participation effect is discussed for explaining C–H activation selectivity. The complex MnH(CN-2,6-xylyl)$(dmpe)_2$ crystallizes in orthorhombic space group *Cmcm*, with *a* = 12.129 (5) Å, *b* = 13.136 (3) Å, *c* = 16.80 (3) Å, and *Z* = 4, and was found to have a trans geometry. The complex $MnH(N_2)(dmpe)_2$ crystallizes in orthorhombic space group $Pna2_1$, with *a* = 17.648 (4) Å, *b* = 9.191 (3) Å, *c* = 12.303 (2) Å, and *Z* = 4. The analogous hydride $MnH_3(depe)_2$ shows two distinct types of hydrogen ligands at low temperature, the larger of which has an extremely short T_1.

Introduction

The use of chemically unreactive alkanes as a chemical feedstock is a challenging problem. Toward this goal, C–H activation with metal complexes has attracted much interest in recent years.[1] While a substantial body of work has been put together over the past decade for C–H activation using second- and third-row transition metal complexes, little is known about comparable reactions of the first-row transition metal complexes. Only recently have C–H activation[2] and functionalization[3] been reported with iron complexes. The study of other first-row transition metal complexes is necessary in order to systematically study and formulate a comprehensive view of C–H activation. It has been reported that manganese complexes can adopt an agostic C–H interaction,[4] which is believed to be on the pathway to C–H activation.[5] Consequently, it should be possible to tune the manganese toward C–H activation by changing the electron density on the metal, which is the purpose of the study of $MnH_3(dmpe)_2$ reported here.

Results

Synthesis and Properties. The compound $MnH_3(dmpe)_2$ has been isolated previously from the hydrolysis of a well-characterized AlH_4-bridged dimer and was prepared by a modification of the literature method.[6] Reaction of manganese(II) dibromide with 2.5 equiv of 1,2-bis(dimethylphosphino)ethane (dmpe) in dry THF produces a white paramagnetic powder ($MnBr_2(dmpe)_2$), which was then dissolved in dry toluene and reacted with $LiAlH_4$. Hydrolysis and solvent removal yielded $MnH_3(dmpe)_2$, **1**, as a yellow powder.

Compound **1** is extremely air sensitive and thermally stable at room temperature for short periods. The ^1H NMR spectrum in C_6D_6 shows a quintet at δ −12.610 (J_{P-H} = 27.7 Hz, 3 H), a doublet at 1.442 (J_{P-H} = 14.8 Hz, 8 H), and a singlet at 1.328 (24 H) at room temperature. The $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 shows a broad singlet ($\nu_{1/2}$ = 400 Hz) at δ 82.73 ppm relative to external standard H_3PO_4/D_2O. The mass spectrum shows peaks at *m/e* = 356, 206, and 151 for $MnH(dmpe)_2^+$, $Mn(dmpe)^+$, and $dmpeH^+$, respectively.

Compound **1** loses dihydrogen very easily. Sublimation of a solid sample of **1** under high vacuum results in substantial decomposition and formation of a gray powder, suggesting the possible formulation of **1** as a labile dihydrogen compound (vide infra). Although a single crystal X-ray study of **1** has not been successful so far, the isoelectronic iron complexes $FeH(H_2)(L\text{-}L)_2^+$ have been isolated and identified as dihydrogen complexes.[7] The complexes $[OsH_3(dppe)_2]^+$ and $[OsH_3(depe)_2]^+$ are also characterized as containing η^2-H_2 ligands.[8] Compound **1** is consequently formulated as the fluxional dihydrogen complex $MnH(H_2)(dmpe)_2$, in which the hydride and H_2 hydrogens rapidly interchange.

Ligand Substitution. $MnH_3(dmpe)_2$ loses dihydrogen thermally or photochemically, and the intermediate formed can be trapped quantitatively by a variety of other ligands,

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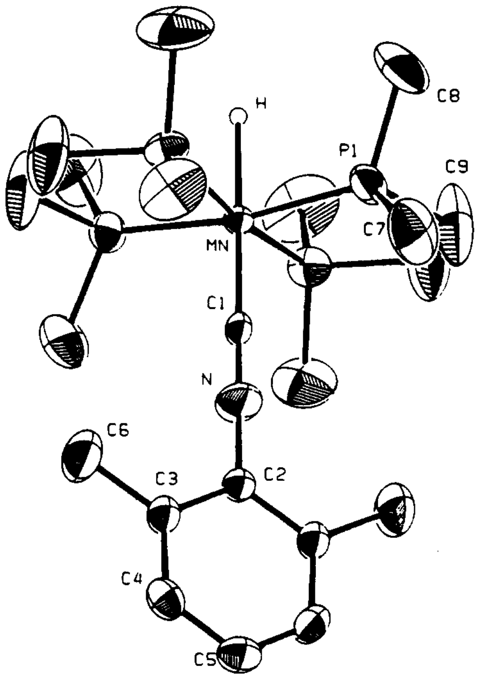

Figure 1. ORTEP drawing of $MnH(CN\text{-}2,6\text{-xylyl})(dmpe)_2$. Ellipsoids are shown at the 30% level, and hydrogen atoms attached to carbon have been omitted for clarity. The molecule lies along a 2-fold axis with the isonitrile lying in a mirror plane that bisects each dmpe ligand.

including CO, N_2, C_2H_4, 1-pentene, CN-*i*-Pr, CN-*t*-Bu, CN-2,6-xylyl, and $CNCH_2CMe_3$ (eq 1). In the presence

$$\underset{\mathbf{1}}{MnH_3(dmpe)_2} + L \xrightarrow{\Delta} MnH(L)(dmpe)_2 + H_2 \quad (1)$$

$$L = CO,\ C_2H_4,\ CNR,\ N_2$$

of an excess of the ligand, no products which correspond to phosphine loss or "dangling" (η^1) phosphine were observed, implying that dihydrogen loss is the only pathway operating under the reaction conditions. When reactions were carried out in C_6D_6 solvent, deuterium incorporation into the hydride resonance of the products was seen, indicating that the intermediate is very reactive toward benzene activation. In the case of L = C_2H_4, the major product is monodeuteride, indicating that the intermediate reacts reversibly with C_6D_6 very rapidly and that the rate is faster than the rate of back-reaction with H_2 (formed during the reaction) or C_2H_4 coordination. There is no deuterium incorporated into the ethylene (eq 2).

$$MnH_3(dmpe)_2 + C_2H_4 \xrightarrow[C_6D_6]{\Delta} MnD(C_2H_4)(dmpe)_2 + H_2 \quad (2)$$

Structure of $MnH(CN\text{-}2,6\text{-xylyl})(dmpe)_2$. A single-crystal X-ray study of the structure of $MnH(CN\text{-}2,6\text{-xylyl})(dmpe)_2$ was undertaken in order to examine the geometry of the CNR ligand. The molecule was found to crystallize with $Z = 4$ in the orthorhombic space group *Cmcm*, which has 16 general positions. This required that the molecule sit on a site with 4-fold degeneracy. Patterson map solution of the structure showed the complex to have a trans geometry, lying along a $2/m$ axis, as shown in Figure 1. The hydride ligand was located on a difference Fourier map and was included but not refined in the final cycle. The isocyanide was found to be perfectly linear, lying in a mirror plane and aligned along the 2-fold axis. This was somewhat surprising, as other low-valent electron-rich metal isocyanide complexes have shown significant bending of the C–N–R linkage.[9] Residual electron density peaks in the final difference Fourier map did not suggest a disordered bent structure for this ligand.

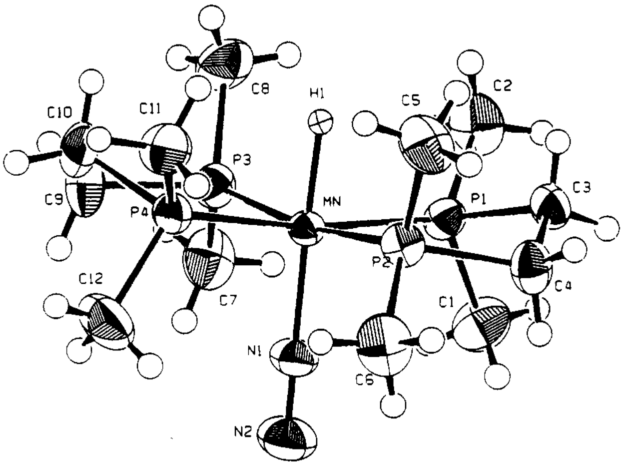

Figure 2. ORTEP drawing of $MnH(N_2)(dmpe)_2$. Ellipsoids are shown at the 50% level.

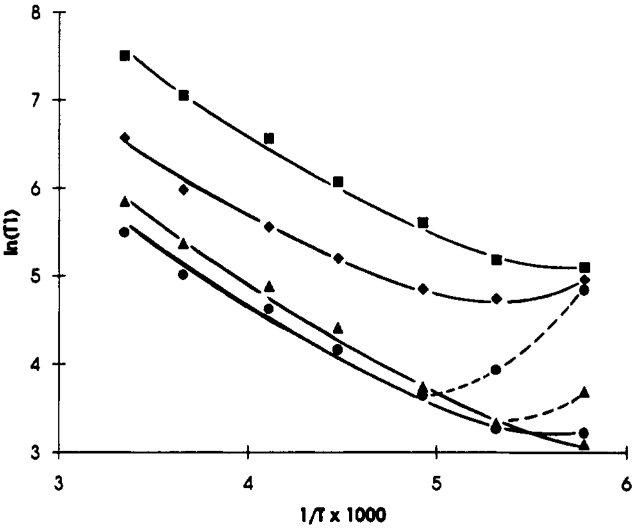

Figure 3. Plot of ln (T_1) vs $1/T$ for (a) $MnH_3(dmpe)_2$, ▲, (b) $MnH(N_2)(dmpe)_2$, ■, (c) $MnH_3(depe)_2$, ●, and (d) $MnH(N_2)(depe)_2$, ◆. Values were measured at 400 MHz.

Structure of $MnH(N_2)(dmpe)_2$. A single-crystal X-ray study of the structure of $MnH(N_2)(dmpe)_2$ was also undertaken. The molecule crystallizes from hexane in the orthorhombic space group $Pna2_1$ with $Z = 4$, a general position. Routine solution of the structure showed the molecule to have a trans geometry, consistent with the NMR data. The N–N distance is 1.127 (7) Å. The hydride ligand was located and refined isotropically, with a Mn–H distance of 1.51 (6) Å. Figure 2 shows an ORTEP drawing of the complex, with the four phosphorus atoms bending slightly toward the hydride ligand.

T_1 Measurements. As mentioned above, **1** is formulated as an η^2-H_2 complex. T_1 measurements were made to further examine this possibility.[10] At room temperature the T_1 value for the hydride quintet ($J_{\mathrm{P-H}}$ = 27 Hz) is 346 ms (400 MHz). As the temperature is decreased, the hydride resonance broadens slightly while maintaining the quintet structure (probably due to a T_2 effect[6]). At room temperature T_2 for the hydrides is 320 ms. The T_1 of the

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[9] See: Jones, W. D.; Foster, G. P.; Putinas, J. M. *Inorg. Chem.* **1987**, *26*, 2120–2127 and references therein.

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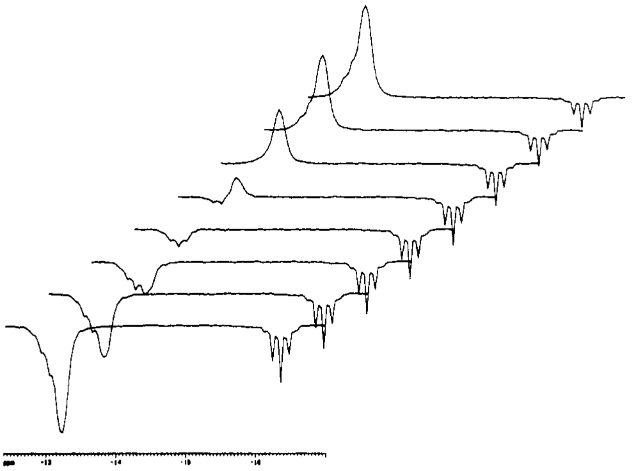

Figure 4. Inversion–recovery measurement of T_1 of the hydride resonances of $MnH_3(dmpe)_2$ at −100 °C. The sharp high-field quintet is from $MnH(N_2)(dmpe)_2$.

Table I. Temperature Dependence of T_1 (ms) of Manganese Complexes[a]

temp (°C)	MnH_3-$(dmpe)_2$	$MnH(N_2)$-$(dmpe)_2$	MnH_3-$(depe)_2$	$MnH(N_2)$-$(depe)_2$
23	346	1800	243	714
0	215	1150	148	395
−30	132	705	101	261
−50	82	432	64	181
−70	42	273	38	128
−85	28	178	26 (H_2) ~50 (H)	115
−100	22	164	25 (H_2) 126 (H)	143

[a] Measured by inversion recovery at 400 MHz in THF-d_8.

hydride resonance was found to decrease as the temperature decreased, and the minimum for T_1 was not observed over the temperature range examined in a plot of ln (T_1) vs $1/T$ (Figure 3a). At −100 °C in THF-d_8, the hydrides appear as a broad resonance ($\nu_{1/2}$ = 120 Hz) with a shoulder on the downfield side of the peak. The T_1 value for the broad resonance is 22 ms, within the range commonly claimed for dihydrogen complexes.[6] The downfield shoulder appears to have a longer T_1, suggesting the presence of two overlapping resonances (Figure 4).

In order to determine the magnitude of metal hydride dipole–dipole relaxation and other relaxation effects, T_1 of the N_2 complex $MnH(N_2)(dmpe)_2$ was also examined. T_1 for the hydride quintet (J_{P-H} = 42 Hz) drops from 1.8 s at 23 °C to a minimum of only 164 ms at −100 °C, indicating that Mn–H dipole–dipole relaxation is not responsible for the short T_1 observed in 1 (Figures 3b and 4).

Further substantiation of the assignment of 1 as an η^2-H_2 complex comes from examination of the analog $MnH_3(depe)_2$, 2. The hydride quintet resonance separates into two distinct resonances at −100 °C (δ −10.88, 1 H; δ −11.41, 2 H). Examination of the temperature dependence of the T_1 values for these resonances shows values similar to those of 1 down to −70 °C. Below this temperature, the two new resonances display distinct T_1 values of 25 and 126 ms for the area 2 H and area 1 H resonances, respectively, at −100 °C (Figures 3c and 5; Table I). T_1 of the analogous N_2 complex was also determined. The T_1 value drops from 714 ms at 23 °C to a minimum of 115 ms at −85 °C, before increasing to 143 ms at −100 °C (Figure 3d).

Electrochemistry. The cyclic voltammetric properties of complex 1 are very similar to those of other closely related Mn(I) complexes.[11] A single-scan CV of complex 1 in 0.2 M $(TBA)PF_6$–THF is shown in Figure 6b. A single reversible oxidation is seen as fast scan rates (>200 mV/s). For comparison, cyclic voltammograms of $MnH(C_2H_4)(dmpe)_2$, $MnH(CO)(dmpe)_2$, MnH(CN-*t*-Bu)$(dmpe)_2$, MnH(CN-2,6-xylyl)$(dmpe)_2$, and $MnH(CNCH_2CMe_3)$ were recorded. These also show a single reversible wave (Table II). There are no reduction processes observed for any of the complexes in the range down to −3.0 V (vs NHE). Attempts to make closely related Mn(III) complexes were unsuccessful.[12] The observation that 1 is easier to oxidize than most of the other Mn(I) complexes provides support for the formulation of 1 as a

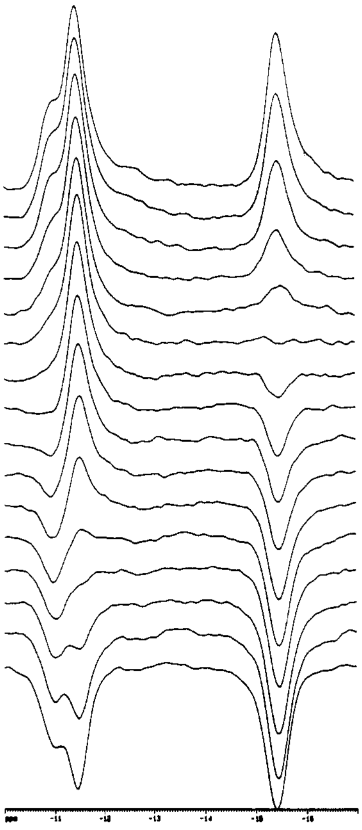

Figure 5. Inversion–recovery measurement of the T_1 of the hydride resonances of $MnH_3(depe)_2$ at −100 °C. The broad upfield resonance at δ −15.4 is from $MnH(N_2)(depe)_2$.

Table II. Reversible Oxidation Potentials of MnH(L)$(dmpe)_2$ Complexes in THF/$(TBA)PF_6$[a]

cmpd	$E_{1/2}$ (V)	chem shift (δ)
$MnH(C_2H_4)(dmpe)_2$	−1.10	−11.857
$MnH_3(dmpe)_2$	−0.85	−12.610
MnH(CN-*t*-Bu)$(dmpe)_2$	−0.72	−11.813
$MnH(CNCH_2CMe_3)(dmpe)_2$	−0.63	−11.344
MnH(CN-2,6-xylyl)$(dmpe)_2$	−0.46	−10.937
$MnH(CO)(dmpe)_2$	−0.29	−10.788

[a] Potentials are vs NHE, using internal Cp_2Fe/Cp_2Fe^+ calibration.

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(11) The electrochemical behavior of "high" oxidation state transition metal polydrides have been reported. See: Costello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563–2564.

(12) The closely related Mn(III) complexes $MnX_3(dmpe)_2$ have not been synthesized. $Mn^{II}(CNR)_6^{2+}$ complexes have been synthesized, but oxidized Mn(III) products are not stable. (a) Treichel, P. M.; Mueh, H. J. *Inorg. Chem.* **1977**, *16*, 1167–1169. (b) Rao, J. M.; Hughes, M. C.; Macero, D. *J. Inorg. Chim. Acta* **1976**, *18*, 127–131. (c) Hughes, M. C.; Macero, D. J.; Rao, J. M. *Inorg. Chim. Acta* **1981**, *49*, 241–245. (d) Treichel, P. M.; Dirreen, G. E. *J. Organomet. Chem.* **1972**, *39*, C20–C22. (e) Treichel, P. M.; Dirreen, G. E.; Mueh, H. J. *J. Organomet. Chem.* **1972**, *44*, 339–352.

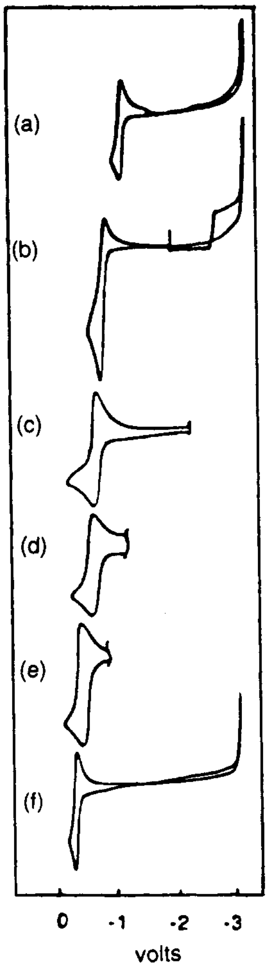

Figure 6. Cyclic voltammograms of $MnH_3(dmpe)_2$ and derivatives vs NHE: (a) $MnH(C_2H_4)(dmpe)_2$; (b) $MnH_3(dmpe)_2$; (c) $MnH(CNt\text{-}Bu)(dmpe)_2$; (d) $MnH(CNCH_2CMe_3)(dmpe)_2$; (e) $MnH(CN\text{-}2,6\text{-}xylyl)(dmpe)_2$; (f) $MnH(CO)(dmpe)_2$.

Mn(I) dihydrogen complex. It is also worth noting the trend in the chemical shift of the hydride ligand in this series of compounds. The chemical shift correlates with the ease of oxidation of the complex, with 1 having the largest downfield shift of all, consistent with its formulation as an electron-rich Mn(I) species.

C–H Activation Studies. (a) H/D Exchange between C_6D_6 and Hydride. As mentioned above, $MnH_3(dmpe)_2$ can exchange the hydrides for deuterides when the ligand-exchange reactions are carried out in C_6D_6. In a typical experiment, $MnH_3(dmpe)_2$ was dissolved in C_6D_6 in a resealable NMR tube. At 86 °C (or upon irradiation, $\lambda > 300$ nm), the hydride resonance was observed to decrease with time and eventually disappear as the residual benzene C_6D_5H resonance increased. H/D exchange was also confirmed by mass spectroscopy,[13] showing $MnH_2D(dmpe)_2$ as a major product after 15 min of irradiation. Consequently, there must be a rapid H/D exchange process with the deuterium coming from the C_6D_6 solvent. Similarly, when the reaction was carried out in the presence of hydrogen (500 mm), free HD was detected by ^1H NMR spectroscopy after 12 h along with a large increase in the C_6D_5H signal.

With continued heating, the resonance for free HD disappeared and (presumably) free D_2 gas was formed.

Table III. Intermolecular H/D Exchange Catalyzed by $MnH_3(dmpe)_2$[a]

substrate	turnovers aromatic[b]	turnovers aliphatic	tot. turnovers	selectivity[b] arom/aliphatic
toluene	70.0	11.9	81.9	5.9
m-xylene	24.7	29.8	54.5	0.8
mesitylene	0	48.0	48.0	0
anisole	8.0	3.0	11.0	2.6
THF			60.1[c]	

[a] Experiments were carried out at 86 °C for 20 h in C_6D_6. [b] From exchange with D_2 in neat substrate. [c] α position only.

Under photochemical conditions the same kind of reaction was observed but long irradiation times resulted in broadening of the NMR spectra consistent with decomposition to form paramagnetic species.

(b) H/D Exchange between C_6D_6 or D_2 and Chelating Phosphine Ligands. During the H/D exchange process between C_6D_6 and the hydride ligands of 1, another slower H/D exchange process was observed between the C_6D_6 solvent and the chelating phosphine ligands on the metal center. In a typical experiment, $MnH_3(dmpe)_2$ was dissolved in C_6D_6 in an NMR tube and heated to 86 °C. After 4 days, the dmpe ligands of the compound were deuterated as shown by ^1H and ^2H NMR spectroscopy.[14] The result was also confirmed by mass spectroscopy,[15] showing that $MnD_3[(CD_3)_2PCD_2CD_2P(CD_3)_2]_2$ was formed and 1-d_{23} was a major product. In all cases, the parent peaks could not be observed; instead peaks corresponding to H_2, HD, or D_2 loss were observed. The same H/D exchange results are obtained using *n*-pentane solvent under and 1 atm of D_2. The H/D exchange is a catalytic process, and eventually the complex is totally deuterated in the hydride and methyl positions, suggesting that 1 might be an efficient catalyst for other intermolecular H/D exchange reactions.

(c) Catalytic Intermolecular H/D Exchange. As shown above, $MnH_3(dmpe)_2$ can catalytically activate the C–H bonds of the coordinated phosphine competitively with those of an arene solvent. To further test the range of C–H activation reactions, an experiment was carried out in which 0.3 mL of C_6D_6 and 0.2 mL of C_6H_6 were reacted with 10 mg of $MnH_3(dmpe)_2$ in a sealed NMR tube under air-free conditions. GC/MS showed that deuterium was totally scrambled between the possible benzene-d_x isotopomers after 6 days at 86 °C, the biggest peak being observed at $m/e = 81$. The number of turnovers was calculated to be about 300.[16]

Complex 1 was found to be reactive toward C–H activation of other substrates under mild conditions. $MnH_3(dmpe)_2$ was found to activate the C–H bonds of toluene, *m*-xylene, mesitylene, THF, and anisole (both aromatic and methyl positions; see Table III), but it did not catalyze exchange in fluorobenzene, chlorobenzene, and bromobenzene. In the latter cases, the catalyst was deactivated by reaction with the halobenzene. A similar attempt to exchange deuterium into *n*-pentane showed no deuteration of the alkane.

While the total number of turnovers could be determined by integration of the ^2H NMR spectrum, the se-

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(13) The mass spectral data are shown below after irradiation at room temperature for 15 min: *m/e* 357, 356, 355, and 206 for $MnD(dmpe)_2$, $MnH(dmpe)_2$, $Mn(dmpe)_2$, and Mn(dmpe), respectively. The parent peaks could not be observed in all cases.

(14) In the ^2H NMR spectrum, four resonances are observed at δ 1.45, 1.35, 0.95, and 0.75 in C_6D_6, indicating that the chelating ligands are deuterated and the compound is decomposing to produce free dmpe during the reaction.

(15) After 4 days at 86 °C: *m/e* 381, 380, 379, 378, 219, 218, 217, 161, 160, 159, and 158. See ref 13.

(16) After 4 days at 86 °C, mass spectral data from the GC/MS: *m/e* = 84 (10%), 83 (44%), 82 (88%), 81 (100%), 80 (70%), 79 (33%), and 78 (12%).

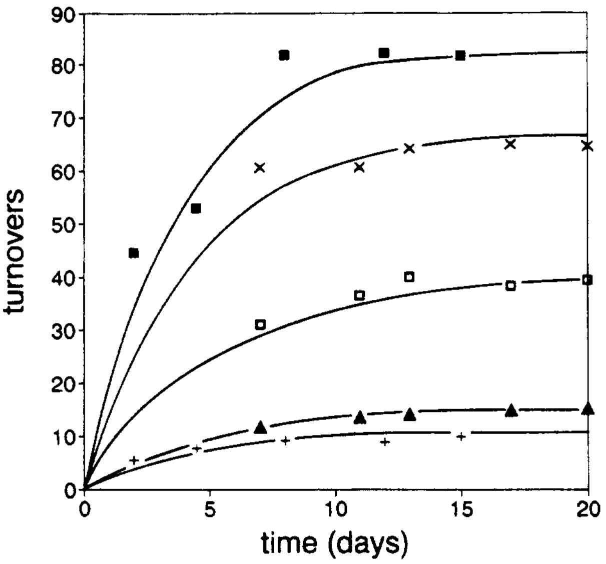


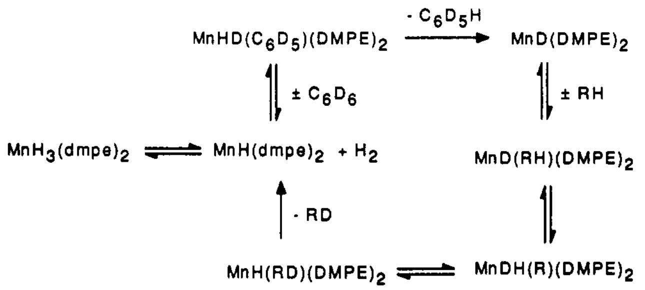
Figure 7. Catalytic H/D exchange by $MnH_3(dmpe)_2$ from C_6D_6 into various organic substrates at 86 °C: (+) mesitylene methyl; (▲) *m*-xylene methyl; (□) toluene methyl; (×) anisole methyl; (■) *α*-THF.

lectivity between different aromatic positions could not be determined since the aromatic resonances overlap with one another. Since the methyl group resonances of toluene, anisole, *m*-xylene, mesitylene, and the *α* position of THF are well separated, however, one can follow these H/D exchange rates and also monitor the lifetime of the catalyst. The relative H/D exchange data are shown in Figure 7 for the nonaromatic positions. A separate set of experiments was carried out in order to determine the selectivity for aromatic vs aliphatic positions using neat arene with D_2 gas as the deuterium source. During the intermolecular H/D exchange processes, the catalyst is gradually deactivated. Intermolecular and intramolecular C–H activation are two competing processes, and the catalyst was eventually deuterated.

(d) Catalytic H/D Exchange between C_6D_6 and $HSiMe_3$. $MnH_3(dmpe)_2$ can also catalyze H/D exchange between C_6D_6 solvent and $HSiMe_3$. When a solution of 1 and $HSiMe_3$ in C_6D_6 is heated to 86 °C (or upon irradiation $\lambda > 300$ nm) for 12 h, the resonance of Si–H decreases in the ^1H NMR spectrum. This result was confirmed by ^2H NMR spectroscopy. The exchange occurs only at the Si–H position; deuteration of the methyl groups was not observed.

(e) Complex Decomposition and Catalyst Deactivation Pathways. As shown in the plots in Figure 7, compound 1 was deactivated after about 1 week. In the ^1H NMR spectrum, new hydride resonances were detected. The deactivation process could be slowed by adding free hydrogen gas to the reaction system. The decomposition products have not been fully characterized, but independent experiments show that possibilities include $MnH(dmpe)_2(\eta^1\text{-dmpe})$ or μ-dmpe dimers.[17] The formation of a small amount of a paramagnetic species is also indicated on the basis of the observation of general line broadening. There is no $MnH_3(dmpe)_2$ catalyst left when the system is deactivated, suggesting that the deactivation is not due to inhibition by free dmpe or hydrogen formed during the decomposition process.

Scheme I



Discussion

The above results show that the high electron density in 1 plays an important role in the reactivity of the intermediate responsible for C–H bond activation. The activation of the THF *α* C–H bonds and anisole methyl C–H bonds is possibly due to heteroatom precoordination to the metal center. Arene η^2-coordination of the substrates can result in a lower activation energy for the C–H activation process[18] but does not account for the observation of facile exchange of benzylic hydrogens. Since both arene methyl groups and compounds containing heteroatoms undergo H/D exchange with C_6D_6, and since only the *α* position of THF is exchanged, neighboring group participation is strongly implicated. Other complexes are known to show similar NGP effects in H/D exchange reactions.[19] For alkanes such as *n*-pentane, no H/D exchange was observed, apparently due to its lack of precoordination ability.

The mechanism for the H/D exchange is proposed in Scheme I on the basis of the reactions mentioned above and is similar to that proposed for $ReH_3(dppe)_2$.[20] The intermediate $[MnH(dmpe)_2]$ can activate either the C–H bonds of the substrate or the C–H bonds of the ligands leading to catalytic H/D exchange. The initial complex formed, $MnD(RH)(dmpe)_2$, can involve either η^2 coordination of the arene (in the case of aromatic or benzylic exchange) or coordination of an oxygen (in the case of THF or anisole).

$MnH_3(dmpe)_2$ loses molecular hydrogen fairly easily to generate the reactive Mn(I) intermediate $[MnH(dmpe)_2]$, which rapidly leads to activation of C_6D_6 solvent or trapping by D_2. The product formed, $MnHD(C_6D_5)(dmpe)_2$ or $MnHD_2(dmpe)_2$, undergoes intramolecular hydride/deuteride positional interchange (which is also a fast process), and reductive elimination results in a metal deuteride intermediate $[MnD(dmpe)_2]$. Further oxidative addition, hydride/deuteride interchange, and reductive elimination leads to the net H/D exchange observed. In the reductive elimination step, either hydrogen or deuterium could be removed from the metal center, but only metal deuteride could lead to further H/D exchange. The rate of hydride/deuteride interchange therefore must be as fast or faster than the observed rate of H/D exchange.

$MnH_3(dmpe)_2$ is a very fluxional molecule in solution as the three hydrides (or η^2-dihydrogen and hydride) are still equivalent on the NMR time scale at −70 °C. The hydride interchange must therefore have a very low barrier.

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[17] ^1H NMR in C_6D_6 at room temperature: δ −15.76 (quint of d, J = 49.9, 11.2 Hz). Due to the formation of small amounts of paramagnetic material, the methyl and methylene groups overlap as a broad peak at δ 1–1.5. ^{31}P NMR in C_6D_6 at room temperature shows a broad peak at δ 77.16 relative to external standard H_3PO_4/D_2O.

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At −100 °C, however, a shoulder appears at lower field with a longer T_1 (~40 ms) than the broad resonance. In the depe complex 2, these two resonances are resolved and show similar T_1 behavior, with the smaller downfield resonance (area 1 H) having a longer T_1 than the larger (2 H) upfield resonance. In other $MH(\eta^2-H_2)$ complexes that have been characterized, the hydride ligand resonates upfield of the η^2-H_2 ligand. The short T_1's of the area 2 H resonances of 1 and 2 (22–25 ms) provides strong evidence for the assignment of these ligands as η^2-H_2.

The longer T_1 of the remaining hydride ligand in 2 (126 ms) is typical of that seen in other MnHL(dmpe)$_2$ and MnHL(depe)$_2$ complexes. The shorter T_1 of the downfield hydride resonance in 1 (~50 ms) is probably attributable to incomplete quenching of the exchange between the hydride and η^2-H_2 ligands. The contribution to relaxation effects in 1 from all other nuclei in the molecule can be calculated to be 4.7 s^{-1}, which is only a small portion of the observed relaxation rate of 45.5 s^{-1}.[21]

Equations 3 and 4 can be used to estimate the H–H distance in 1, depending on whether of not η^2-H_2 is freely rotating (ν = 400 MHz).[10] For 1, these values are 0.90 (2) and 1.13 (2) Å with and without rotation, respectively, and are well within the range expected for an η^2-H_2 complex.

$$r_{H_2} = 4.611(T_1(\mathrm{min})/\nu)^{1/6} \quad \text{with rotation} \qquad (3)$$

$$r_{H_2} = 5.815(T_1(\mathrm{min})/\nu)^{1/6} \quad \text{without rotation} \qquad (4)$$

A similar situation was observed in $[FeH_3(dmpe)_2]^+$ and $[FeH_3(dppe)_2]^+$, which are also fluxional at room temperature but unlike the present case are static at ~200 K.[7] The ability to easily freeze out two distinct types of Fe–H interaction in these complexes allowed a more thorough characterization of these species as η^2-H_2 complexes. In addition, single-crystal X-ray diffraction studies showed the complexes to possess a trans geometry, as proposed for 1. The isoelectronic complex $[FeH_3(dmpe)_2]^+$ has been found to be labile and has been used to generate CO, C_2H_4, and CNMe derivatives.[22] It is also worthwhile noting that the iron complex $FeH_2(dmpe)_2$, upon irradiation at low temperature in pentane, leads to alkane oxidative addition products.[2] The nature of the intermediates [Fe(dmpe)$_2$] and [MnH(dmpe)$_2$] will require further examination to explain the differences in their oxidative addition behavior.

A variety of indicators are now being used to characterize the presence of η^2-H_2 ligands. Direct observation of an M–H_2 stretch (2300–2700 cm^{-1}) is sometimes possible,[23] but no such band is seen in 1. A large H–D coupling constant is also indicative of an η^2-H_2 complex,[8,23] but the large width of the hydride resonance for 1 prevented the observation of any such coupling. The P–H coupling constants in other η^2-H_2 complexes are typically 1–5 Hz.[8] The larger values observed in 1 and 2 of 27 and 30 Hz argue for a classical trihydride structure. Averaging the P–H couplings of the H and η^2-H_2 ligands in these complexes would have predicted a value of only ~18 Hz.

The frequency of the N–N stretch in the isostructural N_2 adducts has been observed to fall in the range 2060–2150 cm^{-1} for other η^2-H_2 complexes.[24] The N–N stretch in the N_2 adducts of 1 and 2 falls below this range, at 1947 and 1946 cm^{-1}, respectively. Finally, oxidation potentials have been used to assign dihydrogen vs dihydride ligation.[11] Using the additive ligand approach developed by Lever,[24b,25] the oxidation potential of Mn(H)$_3$(dmpe)$_2$ is calculated to be −1.82 V, whereas that of Mn(H)(η^2-H_2)(dmpe)$_2$ is calculated to be −0.53 V, which compares favorably with the observed value of −0.85 V.

In summary, some of these methods (ν_{N-N}, J_{P-H}) argue in favor of a classical trihydride structure, whereas others (T_1, oxidation potential) indicate a nonclassical structure. The strength of the direct evidence provided by the T_1 experiments supports the formulation of 1 as an η^2-H_2 complex. The other methods are more empirical and were based largely on metal complexes of groups 6, 8, and 9 rather than on group 7.

Experimental Section

General Comments. All manipulations were done under nitrogen, either in a glovebox or on a high-vacuum line. All solvents were distilled from benzophenone ketyl under nitrogen. NMR spectra were recorded on a Bruker AMX-400 spectrometer. T_1 measurements were made using the standard inversion–recovery program on the spectrometer. All materials were of reagent grade quality and were used without further purification. Electrochemical measurements were done under nitrogen using a Pt wire working electrode, a Pt counter electrode, and a Ag wire reference electrode. The supporting electrolyte ((TBA)PF$_6$) was recrystallized and dried under high vacuum. The cell was assembled in a glovebox, and measurements were made on a PAR Model 370 electrochemical apparatus.

Synthesis of MnH$_3$(dmpe)$_2$. This preparation is a modification of the literature method.[6] A 0.21-g amount (1 mmol) of $MnBr_2$ was stirred in 40 mL of THF for 30 min. To this suspension 0.3 g of dmpe (6.7 mmol) was added dropwise. The $MnBr_2$ dissolved, and the color of the mixture changed from colorless to pale yellow upon stirring. The solvent was removed under vacuum after 5 h. The white powder obtained was dissolved in 40 mL of toluene, and 0.4 g of $LiAlH_4$ was added slowly. The mixture was stirred at room temperature for 30 h and then filtered under reduced pressure, yielding an orange yellow solution. Distilled water was added dropwise with stirring until bubble formation stopped. The solution was then filtered under reduced pressure. The solvent was evaporated and the residue extracted with 60 mL of hexane, yielding a yellow powder after removal of solvent (yield 77.2%). MS (70 eV): *m/e* 356, 206, 151.

Reaction of MnH$_3$(dmpe)$_2$ with CO and N$_2$. A 5-mg amount (0.014 mmol) of MnH$_3$(dmpe)$_2$ was placed in a resealable NMR tube and the tube evacuated on a vacuum line. A 0.5-mL volume of C_6D_6 was distilled in under vacuum and the NMR tube sealed under 550 mm of CO. The sample was covered with aluminum foil to exclude light. Reaction occurred slowly at room temperature, showing 20% completion after 3 days. The sample was then placed in an 86 °C oil bath for 5 min. The reaction to produce MnH(CO)(dmpe)$_2$ was quantitative, and free hydrogen was seen by ^{1}H NMR spectroscopy. Pure complex was isolated by removing the solvent. MS (70 eV): *m/e* = 386, 385, 384, 357, 356, 355, 207, 206. Anal. Calcd (found) for $MnP_4OC_{13}H_{33}$: C, 40.64 (40.70); H, 8.66 (8.70). IR (KBr): 1795 cm^{-1}.

An identical procedure was used for the preparation of the N_2 analog, substituting N_2 gas for CO. Anal. Calcd for $MnP_4C_{12}H_{33}N_2$ (found): C, 37.51 (37.30); H, 8.66 (9.57); N, 7.29 (6.0). ν_{CO} (KBr) = 1947 cm^{-1}.

Thermal Reaction of MnH$_3$(dmpe)$_2$ with Isocyanides. A 10-mg amount (0.028 mmol) of MnH$_3$(dmpe)$_2$ was dissolved in 0.5 mL of benzene in a resealable NMR tube, and 10 equiv of CN-*t*-Bu was introduced. The reaction was found to be complete after heating for 10 min at 86 °C. The product was isolated by

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[21] The calculation was done using the same structure as MnH(N_2)(dmpe)$_2$, with η^2-H_2 replacing the N_2 ligand. The Mn–H distance used was 1.60 Å. See: Desrosiers, P. J.; Cai, L.; Lin, A.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184.

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Table IV. NMR Data (δ) for the Manganese Complexes in C_6D_6 (24 °C)

complex	^1H	^{31}P
$MnH_3(dmpe)_2$	−12.610 (quint, J_{PH} = 27.7 Hz, 3 H), 1.328 (s, 24 H), 1.442 (d, J = 14.8 Hz, 8 H)	82.73
$MnH(dmpe)_2$(CN-2,6-xylyl)	−10.937 (quint, J_{PH} = 46.2 Hz, 1 H), 0.804 (s, 4 H), 1.250 (s, 12 H), 1.287 (s, 12 H), 1.395 (s, 4 H), 2.384 (s, 6 H), 6.739 (t, J_{PH} = 7.4 Hz, 1 H), 6.947 (d, J_{PH} = 7.4 Hz, 2 H)	79.47
$MnH(dmpe)_2(CNCH_2CMe_3)$	−11.344 (quint, J_{PH} = 44.8 Hz, 1 H), 0.863 (s, 9 H), 1.273 (s, 12 H), 1.398 (s, 12 H), 1.465 (s, 8 H), 3.083 (s, 2 H)	81.53
$MnH(dmpe)_2$(CN-*t*-Bu)	−11.813 (quint, J_{PH} = 45.1 Hz, 1 H), 1.503 (d, J = 4.9 Hz, 8 H), 1.477 (s, 12 H), 1.312 (s, 12 H), 1.210 (s, 9 H)	79.77
$MnH(dmpe)_2$(CN-*i*-Pr)	−11.222 (quint, J_{PH} = 45.1 Hz, 1 H), 3.666 (sept, J = 6.8 Hz, 1 H), 1.456 (br s, 20 H), 1.297 (s, 12 H), 1.091 (d, J = 6.8 Hz, 6 H)	80.37
$MnH(dmpe)_2(CO)$	−10.788 (quint, J_{PH} = 43.6 Hz, 1 H), 1.201 (s, 12 H), 1.406 (s, 20 H)	79.29
$MnH(dmpe)_2(C_2H_4)$	−11.857 (quint, J_{PH} = 55.4 Hz, 1 H), 1.447 (s, 6 H), 1.295 (s, 6 H), 1.205 (s, 12 H), 1.015 (s, 12 H)	81.55
$MnH(dmpe)_2$(1-pentene)	−12.865 (m, 1 H), 0.798 (br s, 7 H), 1.078 (br s, 12 H), 1.330 (s, 8 H), 1.492 (s, 12 H), 1.775 (s, 2 H), 2.048 (s, 1 H)	79.39
$MnH(dmpe)_2(N_2)$	−16.1 (quint, J_{PH} = 42 Hz, 1 H), 1.37 (m, 20 H), 1.21 (s, 12 H)	77.84

removing the volatiles under vacuum and recrystallizing from hexane, giving isolated yields of 90–95%. Similar procedures were used to prepare the derivatives with CN-*i*-Pr, CN-*t*-Bu, $CNCH_2CMe_3$, and CN-2,6-xylyl. NMR data are given in Table IV. Anal. Calcd for $MnH(dmpe)_2$(CN-2,6-xylyl) (found): C, 51.75 (52.03); H, 8.69 (8.88). IR (KBr): 1842 cm^{-1}. Calcd for $MnH(dmpe)_2$(CNi-Pr) (found): C, 45.18 (44.46); H, 9.48 (9.40). Calcd for $MnH(dmpe)_2$(CNt-Bu) (found): C, 46.47 (46.77); H, 9.64 (9.73); N, 3.19 (3.25). IR (KBr): 1817 cm^{-1}. Calcd for $MnH(dmpe)_2(CNCH_2CMe_3)$ (found): C, 47.69 (47.39); H, 9.78 (10.02); N, 3.09 (2.89). IR (KBr): 1798 cm^{-1}.

Photochemical Reaction of $MnH_3(dmpe)_2$ with 2,6-Xylyl Isocyanide. A 5-mg amount (0.014 mmol) of $MnH_3(dmpe)_2$ was dissolved in 0.5 mL of C_6D_6. A 5-equiv amount of 2,6-xylyl isocyanide was added and the sample irradiated with a 200-W Hg/Xe lamp. After 40 min of irradiation the reaction was found to be quantitative by ^1H NMR spectroscopy. The product was isolated by removing the solvent under vacuum and purified by washing with hexanes.

Reaction of $MnH_3(dmpe)_2$ with C_2H_4. A 5-mg amount (0.014 mmol) of $MnH_3(dmpe)_2$ was dissolved into 0.6 mL of C_6D_6 in a resealable NMR tube. A 0.29-mmol of amount C_2H_4 (20 mm, 273 mL, 298 K) was condensed into the tube and the tube then sealed. The reaction was complete after heating to 86 °C for 10 min, on the basis of ^1H NMR spectroscopy. The products were isolated by removing the volatiles under vacuum. NMR spectroscopy showed that the mixture contained 23% $MnH(C_2H_4)(dmpe)_2$ and 77% $MnD(C_2H_4)(dmpe)_2$. This complex has been isolated previously by the reaction of $MnBr_2(dmpe)_2$ with LiEt.[5]

Reaction of $MnH_3(dmpe)_2$ with 1-Pentene. A 10-mg amount (0.028 mmol) of $MnH_3(dmpe)_2$ was placed in a resealable NMR tube, and 0.2 mL of 1-pentene and 0.3 mL of n-pentane were added. The sample was irradiated for 30 min and the product isolated by removal of the solvent under vacuum. ^1H NMR data are given in Table IV. Anal. Calcd (found) for $MnP_4C_{17}H_{43}$: C, 47.89 (37.30); H, 10.17 (9.57); N, 0.00 (6.0). The sample was too unstable to permit analysis.

Preparation of $MnH_3(depe)_2$. A 0.15-g amount (0.7 mmol) of $MnBr_2$ was stirred for 1 h in 40 mL THF, and 0.32 g of depe was added dropwise to this suspension. The $MnBr_2$ dissolved to give a colorless solution upon stirring for 48 h. Removal of solvent under vacuum yielded a white powder, which was dissolved in 25 mL of toluene. A 0.25-g amount of $LiAlH_4$ (7 mmol, 10 equiv) was slowly added and the resulting dark gray suspension stirred for 48 h. The brown solution was filtered and then carefully treated dropwise with water until bubble formation stopped. The solvent was then removed under vacuum and the residue extracted with hexane (30 mL). Filtration and removal of solvent under vacuum yielded the yellow product. ^1H NMR (C_6D_6): δ 1.65 (t, J = 6.1 Hz, 8 H), 1.22 (q, J = 7.5 Hz, 16 H), 1.10 (t, J = 7.5 Hz, 24 H), −10.8 (quint, J = 30.0 Hz, 3 H). ^{31}P NMR (C_6D_6): δ 112.0.

Preparation of $MnH(N_2)(depe)_2$. A 10-mg amount (0.021 mmol) of $MnH_3(depe)_2$ was placed in a resealable NMR tube and evacuated on a vacuum line. A 0.5-mL volume of C_6D_6 was distilled into the tube and the tube sealed under 700 mmN_2. The sample was heated in an oil bath at 60 °C for 60 h. $MnH(N_2)(depe)_2$ was obtained quantitatively, and free H_2 could be seen in the ^1H NMR spectrum. Removal of solvent yielded a yellow crystalline solid. ^1H NMR (C_6D_6): δ −15.3 (quint, J = 44 Hz). ^{31}P NMR (C_6D_6): δ 96.08.

Reaction of $MnH_3(dmpe)_2$ with H_2 in C_6D_6. A 5-mg amount (0.014 mmol) of $MnH_3(dmpe)_2$ was placed into a resealable NMR tube, and 0.5 mL of C_6D_6 was distilled in under vacuum. The tube was sealed under 500 mmH_2. The reaction was carried out at 86 °C and followed by ^1H NMR spectroscopy. Free HD (δ 4.422, J = 43.5 Hz, 1:1:1 triplet) was detected after 10 h, and a significant increase in the intensity of the C_6D_5H resonance (473 turnovers) was observed after 1 week. The hydride sites were 50% deuterated, with a successive upfield isotopic perturbation of resonance observed upon deuteration. The widths of the components of the quintent resonance were too broad ($\nu_{1/2} \sim 10$ Hz) to observe any H–D coupling. Continuing the thermolysis led to the disappearance of the HD resonance.

H/D Exchange between D_2 and Chelating Phosphine Ligands. A 10-mg amount (0.28 mmol) of $MnH_3(dmpe)_2$ was placed into a resealable NMR tube and evacuated. A 0.4-mL volume of n-pentane was vacuum distilled in and the tube sealed under 620 mmD_2. The sample was heated at 86 °C for 3 days. ^2H NMR spectra before and after reaction showed the incorporation of deuterium into the dmpe ligand.

Catalytic H/D Exchange between C_6D_6 and $HSiMe_3$. A 5-mg amount (0.014 mmol) of $MnH_3(dmpe)_2$ was placed into a resealable NMR tube. A 0.5-mL volume of C_6D_6 was vacuum distilled into the tube, and about 5 equiv of $HSiMe_3$ was added. The sample was placed into an 86 °C oil bath, and the reaction was followed by ^1H and ^2H NMR spectroscopy as described in the text.

Catalytic Intermolecular H/D Exchange between Arenes and C_6D_6 Solvent. A 45-mg (0.13 mmol) of $MnH_3(dmpe)_2$ was dissolved into 5 mL of C_6D_6. This stock solution was filtered and kept in the dark until use. In each experiment, 0.4 mL of the stock solution was transferred by syringe into a resealable NMR tube and 0.4 mL of arene added subsequently. The sample was heated at 86 °C and monitored by ^2H NMR spectroscopy and GC/MS. Reactions with all substrates were carried out similarly, and H/D exchange rates were obtained on the basis of the integration of ^2H NMR data.

Selectivity Studies. To each of four resealable NMR tubes which contained pure anisole, toluene, *m*-xylene, or mesitylene was added 5 mg of $MnH_3(dmpe)_2$. After freeze–pump–thaw degassing, 700 mmD_2 gas was applied and each tube closed. The samples were placed in an 86 °C oil bath. After three cycles of providing fresh deuterium gas over each sample at 2-day intervals, ^2H NMR spectra were taken for each sample. On the basis of the integration, aromatic vs aliphatic selectivity was obtained (Table III).

X-ray Structure of MnH(CN-2,6-xylyl)$(dmpe)_2$. A single crystal of the complex was mounted, and cell constants were

Table V. Summary of Crystallographic Data for $MnH(CN\text{-}2,6\text{-}xylyl)(dmpe)_2$ and $MnH(N_2)(dmpe)_2$

	$MnH(CN\text{-}2,6\text{-}xyl)(dmpe)_2$	$MnH(N_2)\text{-}(dmpe)_2$
formula	$MnP_4NC_{21}H_{42}$	$MnP_4N_2C_{12}H_{33}$
mol wt	487.4	384.2
space group (No.)	*Cmcm* (No. 63)	$Pna2_1$ (No. 33)
a (Å)	12.129 (5)	17.648 (4)
b (Å)	13.136 (3)	9.191 (3)
c (Å)	16.797 (29)	12.303 (2)
V (Å^3)	2676 (6)	1996 (1)
ρ_{calc} (g cm^{-3})	1.21	1.28
Z	4	4
temp (°C)	25	−20
radiation (graphite monochr) [λ (Å)]	Mo [0.71073]	Mo [0.71073]
μ (cm^{-1})	7.62	9.44
range of trans factors	0.74–1.40	0.91–1.08
$R(F_o)$	0.0468	0.0303
$R_w(F_o)$	0.0683	0.0327
goodness of fit	2.16	1.17
largest resid peak in diff map	0.28	0.26

Table VI. Positional Parameters and B_{eq} Values for $MnH(CN\text{-}xylyl)(dmpe)_2$

atom	x	y	z	B_{eq} (Å^2)
Mn	1.0000	0.18900 (6)	$^1/_4$	2.93 (4)
P(1)	1.11293 (8)	0.17267 (7)	0.34671 (7)	5.18 (5)
N	1.0000	0.4355 (5)	$^1/_4$	7.1 (4)
C(1)	1.0000	0.3363 (4)	$^1/_4$	3.3 (3)
C(2)	1.0000	0.5473 (5)	$^1/_4$	3.7 (3)
C(3)	1.0000	0.6050 (4)	0.1781 (3)	4.3 (2)
C(4)	1.0000	0.7186 (4)	0.1801 (3)	5.1 (2)
C(5)	1.0000	0.7767 (6)	$^1/_4$	5.6 (4)
C(6)	1.0000	0.5442 (5)	0.1004 (4)	8.2 (4)
C(7)	1.2070 (5)	0.2783 (5)	0.3650 (4)	10.5 (4)
C(8)	1.1922 (6)	0.0517 (5)	0.3584 (4)	12.8 (5)
C(9)	1.0484 (5)	0.1716 (5)	0.4443 (3)	13.1 (5)
H	1.0000	0.0486	$^1/_4$	6.0

Table VII. Selected Distances (Å) and Angles (deg) for $MnH(CN\text{-}xylyl)(dmpe)_2$

	Distances		
Mn–P(1)	2.136 (2)	N–C(1)	1.303 (8)
Mn–C(1)	1.935 (6)	N–C(2)	1.468 (8)
	Angles		
P(1)–Mn–P(1)	99.0 (1)	C(1)–N–C(2)	180.00
P(1)–Mn–P(1)	79.8 (1)	Mn–C(1)–N	180.00
P(1)–Mn–P(1)	168.47 (6)	N–C(2)–C(3)	122.2 (3)
P(1)–Mn–C(1)	95.76 (3)		

Table VIII. Positional Parameters and B_{eq} Values for $MnH(N_2)(dmpe)_2$

atom	x	y	z	B_{eq} (Å^2)
Mn	0.11084 (5)	0.10819 (9)	0	2.17 (3)
P(1)	0.0235 (1)	0.2702 (2)	0.0442 (1)	2.73 (7)
P(2)	0.0258 (1)	−0.0547 (2)	0.0535 (2)	2.78 (7)
P(3)	0.1857 (1)	0.2697 (2)	−0.0796 (2)	3.03 (8)
P(4)	0.1891 (1)	−0.0550 (2)	−0.0694 (2)	3.07 (8)
N(1)	0.1566 (3)	0.1141 (6)	0.1322 (4)	3.2 (2)
N(2)	0.1843 (3)	0.1152 (7)	0.2147 (5)	5.2 (3)
C(1)	0.0369 (4)	0.3711 (7)	0.1709 (6)	4.6 (4)
C(2)	−0.0098 (4)	0.4183 (7)	−0.0436 (6)	4.7 (4)
C(3)	−0.0679 (3)	0.1787 (7)	0.0705 (5)	3.3 (3)
C(4)	−0.0525 (3)	0.0345 (7)	0.1266 (6)	3.7 (3)
C(5)	−0.0299 (4)	−0.1575 (8)	−0.0459 (6)	4.6 (4)
C(6)	0.0516 (4)	−0.1983 (8)	0.1515 (6)	5.0 (4)
C(7)	0.2264 (4)	0.4208 (8)	−0.0025 (7)	4.6 (4)
C(8)	0.1549 (4)	0.3627 (8)	−0.2031 (6)	4.8 (4)
C(9)	0.2717 (4)	0.1799 (8)	−0.1307 (6)	4.5 (4)
C(10)	0.2502 (4)	0.0307 (8)	−0.1721 (6)	4.5 (4)
C(11)	0.1587 (4)	−0.2184 (7)	−0.1417 (6)	4.2 (4)
C(12)	0.2593 (4)	−0.1367 (8)	0.0203 (7)	5.9 (4)
H(1)	0.070 (3)	0.104 (5)	−0.108 (5)	4 (1)

Table IX. Selected Distances (Å) and Angles (deg) for $MnH(N_2)(dmpe)_2$

	Distances		
Mn–P(1)	2.211 (2)	Mn–P(4)	2.211 (2)
Mn–P(2)	2.220 (2)	Mn–N(1)	1.817 (5)
Mn–P(3)	2.216 (2)	N(1)–N(2)	1.127 (7)
	Angles		
P(1)–Mn–P(2)	84.84 (7)	P(2)–Mn–N(1)	93.2 (2)
P(1)–Mn–P(3)	94.20 (7)	P(3)–Mn–P(4)	84.92 (7)
P(1)–Mn–P(4)	170.97 (7)	P(3)–Mn–N(1)	96.3 (2)
P(1)–Mn–N(1)	94.0 (2)	P(4)–Mn–N(1)	95.1 (2)
P(2)–Mn–P(3)	170.50 (7)	Mn–N(1)–N(2)	178.6 (6)
P(2)–Mn–P(4)	94.54 (7)		

obtained from 25 centered reflections with values of χ between 0 and 70°. Routine data collection of one octant of data was undertaken on the orthorhombic *C*-centered cell. The Molecular Structure Corp. TEXSAN analysis software package was used for data reduction and solution.[26] Standard Patterson map solution of the structure to locate the manganese, followed by expansion of the structure with the program DIRDIF, revealed all non-hydrogen atoms. After isotropic refinement, an absorption correction was applied using the program DIFABS. Full-matrix least-squares anisotropic refinement of the non-hydrogen atoms with hydrogens attached to carbon in idealized positions was carried out to convergence. The final difference Fourier map showed the largest peak (0.5 e/Å^3) in the position expected for the hydride ligand. This ligand was included in the final structure factor calculation but was not refined. Crystal data are given in Table V, fractional coordinates in Table VI, and distances and angles in Table VII.

X-ray Structural Determination of $MnH(N_2)(dmpe)_2$. Collection of one quadrant of data on a crystal mounted on a glass fiber in a stream of cold nitrogen followed by structure solution and refinement proceeded as described above. The hydride ligand could be located in a difference Fourier map and was refined isotropically in the final model. Coordinates are given in Table VIII, and distances and angles are given in Table IX.

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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(26) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.