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Oxidative Addition of Silanes to Cyclopentadienylbis(phosphine)carbonylmanganese. Fluxional Behavior of Manganese Silyl Hydride Complexes

Jiemin Sun,* Roy S. Lu, Robert Bau, and Gilbert K. Yang

*Department of Chemistry, University of Southern California,
Los Angeles, California 90089-0744*

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Photolysis of hydrocarbon solutions of $CpMn(CO)(P_2)$ (P_2 = DMPE, DMPP, DMPM, $(PMe_3)_2$, respectively, **1**, **3**, **5**, **7**) in the presence of $SiPh_nH_{4-n}$ yields the corresponding new manganese silyl hydrides $CpMn(P_2)(H)(SiPh_nH_{3-n})$ (**2a–c**, **4a–c**, **6**, **8**) in good to excellent yield. Complex **2b** crystallizes in space group $P2_1/n$ (No. 14) and its structure was refined to a final R factor of 7.41%. The molecular structure of **2b** is a distorted three-legged piano-stool geometry with an apparent vacant coordination site presumably occupied by the hydride ligand. All of these complexes undergo net exchange of the relative hydrido and silyl positions with $\Delta G^{\ddagger}_{ex} \approx 9.6$–11.9 kcal/mol. The magnitude of $\Delta G^{\ddagger}_{ex}$ appears to depend upon the size (or lack) of the chelate ring. A deuterium labeling experiment shows that neither intermolecular exchange nor intramolecular "windshield wiper" exchange of the bound vs unbound Si–H bonds is observed in these systems. These results are most consistent with a pseudorotation of a seven coordinate Mn center resulting in mutual exchange of the silyl and hydride sites. The mechanism of formation of **2**, **4**, **6**, and **8** appears to involve initial phosphine dissociation followed by silane addition. Loss of CO occurs from the formally Mn(III) center followed by ring closure to give the product.

Coordination of silanes to the CpMnLL′ moiety (L = CO, L′ = CO or PR_3) has been studied in detail to evaluate the relative roles of three-center two-electron bonding *vs* two-center two-electron bonding in metal silyl hydride complexes. In this context manganese complexes displaying a broad range of Si–H bond cleavage have been prepared and characterized.[1–14] In conjunction with photoelectron spectroscopy experiments[1–4] these studies have shown that placement of electron withdrawing groups on the silane or replacing one of the CO ligands by a phosphine facilitates cleavage of the Si–H bond. Even greater electron density can be imparted to the metal center by replacing both CO ligands with phosphines with potentially interesting results. In this paper we report the first examples of the synthesis and characterization of bis(phosphino)silane complexes of the cyclopentadienylmanganese moiety.

Results and Discussion

Synthesis of CpMn(PP)(H)(SiRR′). When NMR tubes containing benzene-d_6 solutions of DMPE complex **1** and excess hydrosilane are photolyzed with a medium pressure mercury lamp for several minutes, a number of new resonances appear in the ^1H NMR spectrum. Most noticeable is the growth of a single hydride resonance at *ca.* −14 ppm. On a larger scale with prolonged photolysis times (>∼50 h) in hexanes solution, excellent yields of the new silyl hydride complexes **2** are obtained (Scheme 1). These complexes are only slightly air-sensitive and are quite thermally robust.

Analogous photolysis of the bis(phosphine) carbonyl complexes **3** and **5** derived from DMPP and DMPM proceeded to yield the respective silyl hydrides **4** and **6** (Schemes 2 and 3). Photolysis of the bis(phosphine) carbonyl complex **7** was performed in hexane solutions of silane and excess trimethylphosphine (Scheme 4).

Molecular Structure of CpMn(DMPE)(H)(SiPh₂H). The diphenylsilyl hydride complex **2b** crystallized as yellow needles from pentane solution. The molecular structure of **2b** was determined by X-ray diffraction analysis. A summary of data collection and refinement results appears in Table 1, and the final atomic coordinates appear in Table 2. Tables of selected bond distances and bond angles are given in Tables 3 and 4.

The molecular geometry of the predominant form is shown in Figure 1. When one looks down the silicon–manganese axis, the phenyl groups on the silyl group are roughly eclipsing the cyclopentadienyl ring and the DMPE ligand. The Mn–Si bond length in **2b** is 2.319(4) Å and falls in the range 2.461–2.254 Å for Mn–Si bonds in similar manganese silyl complexes.[5] In **2b**, the Mn–Si bond length is comparable to the Mn–Si bond lengths of 2.327(1) and 2.310(2) Å found in $MeCpMn(CO)(PMe_3)(H)(SiHPh_2)$ and $CpMn(CO)_2(H)(SiPhCl_2)$, respectively. It is slightly longer

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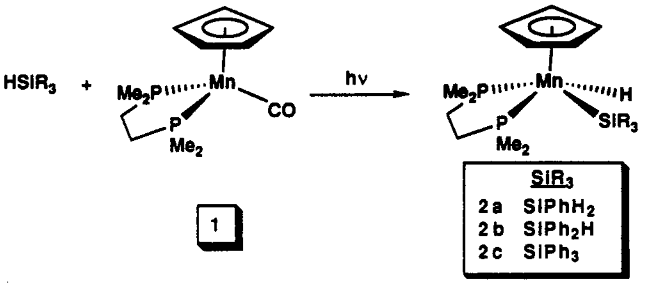
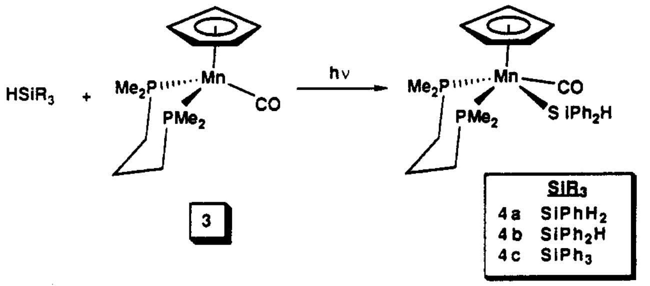
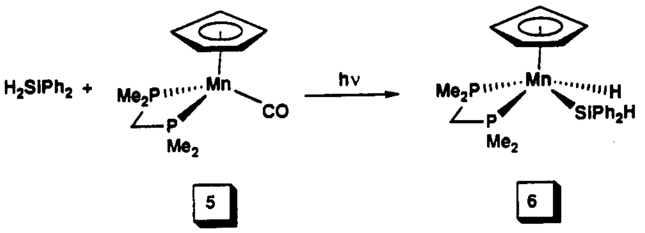
Scheme 1



Scheme 2



Scheme 3



Scheme 4

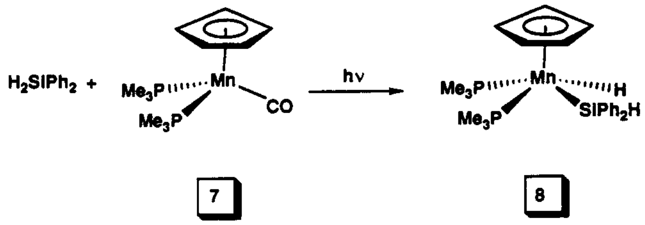


Table 1. Summary of Crystal Data and Refinement Results for 2b

mol wt	454.49
space group	$P2_1/n$ (No. 14)
molecules per unit cell	4
a (Å)	9.255(9)
b (Å)	16.514(15)
c (Å)	15.876(14)
α (deg)	90.0
β (deg)	97.70(8)
γ(deg)	90.0
V(Å^3)	2404.6
cryst dimens (mm)	0.2 × 0.3 × 0.6
calcd dens (g cm^{-3})	1.26
wavelength (Å) used for data collection	1.26
$(\sin\theta)/\lambda$ limit (Å^{-1})	0.5947
total no. of reflns measd	2368
no. of reflns used in structural analysis $I > 3\sigma(I)$	1824
no. of variable params	272
final agreement factor	$R(F) = 0.0741$

Table 2. Final Atomic Coordinates for 2b

atom	x	y	z
Mn1	0.0232(2)	0.2419(1)	0.1030(1)
Si2	0.0688(3)	0.3781(2)	0.1308(2)
P3	0.1287(4)	0.2601(2)	0.0117(2)
P4	0.2089(4)	0.1600(2)	−0.1356(2)
C5	0.3262(11)	0.2501(8)	0.0133(7)
C6	0.3661(12)	0.1860(8)	0.0793(8)
C7	0.0825(13)	0.1849(8)	−0.0978(8)
C8	0.1140(12)	0.3516(7)	−0.0785(7)
C9	0.2885(12)	0.1514(8)	0.2490(8)
C10	0.1801(13)	0.0516(7)	0.1108(9)
C11	0.0098(9)	0.4130(6)	0.2353(6)
C12	0.0543(11)	0.3740(7)	0.3134(7)
C13	0.0137(12)	0.4031(8)	0.3893(8)
C14	−0.0734(11)	0.4703(9)	0.3887(8)
C15	−0.1198(11)	0.5115(8)	0.3123(9)
C16	−0.0775(10)	0.4821(6)	0.2356(7)
C17	0.2564(10)	0.4256(6)	0.1349(6)
C18	0.2731(10)	0.4940(6)	0.0836(6)
C19	0.4125(12)	0.5322(8)	0.0864(7)
C20	0.5263(12)	0.5039(9)	0.1433(8)
C21	0.5125(11)	0.4370(8)	0.1942(8)
C22	0.3775(10)	0.3981(7)	0.1909(7)
C23	−0.1504(11)	0.2310(8)	0.1794(9)
C24	−0.1962(12)	0.2821(9)	0.1064(10)
C25	−0.1138(13)	0.1524(8)	0.1510(10)
C26	−0.1882(13)	0.2355(9)	0.0315(9)
C27	−0.1407(12)	0.1549(8)	0.0550(10)
Mn1	0.1295(16)	0.2519(12)	0.0737(12)
P3′	−0.0896(19)	0.2489(17)	0.0756(16)
P4′	0.1283(19)	0.1585(16)	0.1739(16)

Table 3. Selected Bond Lengths (Å) for 2b

Mn1–Si2	2.319(4)	Si2–C17	1.900(12)
Mn1–P3	2.195(5)	P3–C5	1.829(13)
Mn1–P4	2.196(4)	P4–C6	1.867(14)
Mn1–C23	2.161(14)	C5–C6	1.494(20)
Mn1–C24	2.142(15)	C23–C24	1.448(21)
Mn1–C25	2.114(15)	C23–C27	1.436(21)
Mn1–C26	2.146(15)	C24–C25	1.397(22)
Mn1–C27	2.161(15)	C25–C26	1.434(21)
Si2–C11	1.903(13)	C26–C27	1.516(23)

Table 4. Selected Bond Angles (deg) for 2b

Si2–Mn1–P3	86.4(1)	Mn1–P4–C9	118.3(5)
Si2–Mn1–P4	115.8(2)	C6–P4–C9	104.6(7)
P3–Mn1–P4	82.0(2)	Mn1–P4–C10	117.5(5)
		C6–P4–C10	102.7(8)
C11–Si2–C17	102.2(5)	C9–P4–C10	99.5(8)
Mn1–Si2–C11	113.3(4)	P3–C5–C6	111.2(10)
Mn1–Si2–C17	123.4(4)	P4–C6–C5	111.5(9)
Mn1–P3–C5	110.6(5)		
Mn1–P3–C7	116.0(6)		
C5–P3–C7	102.7(7)		
Mn1–P3–C8	125.7(5)		
C5–P3–C8	101.1(7)		
C7–P3–C8	97.6(7)		
Mn1–P4–C6	112.1(5)		

than the Mn–Si bond length of 2.254(1) Å found in $MeCpMn(CO)_2(H)(SiCl_3)$.[5] The two phosphorus atoms and the silicon atom appear to form the base of a three-legged piano stool (Figures 2 and 3). The relative geometry of the three basal atoms is apparent from comparing the two Si–Mn–P angles. The Si2–Mn1–P3 angle is 86.4°, while the Si2–Mn1–P4 angle is 115.8°. The asymmetric placement of the phosphorus and silicon atoms around the metal center suggests that the hydride ligand occupies a fourth basal position *cis* to the silicon atom (Figure 3). The relatively poor quality of the data obtained from this crystal precluded location of the hydride ligand; however, in the molecular structures of similar manganese–silane complexes where the hydride can be located, it is found to occupy such a fourth coordination site in what is typically described as a four-legged piano-stool geometry.

Mechanism of Formation of Silyl Hydrides 2. The mechanism of formation of 2 does not appear to involve straightforward loss of CO followed by oxidative addition of silane. The strong d–π^* back-bonding seen in 1 (ν_{CO} = 1827 cm^{-1})[6] is expected to make the Mn–CO bond difficult

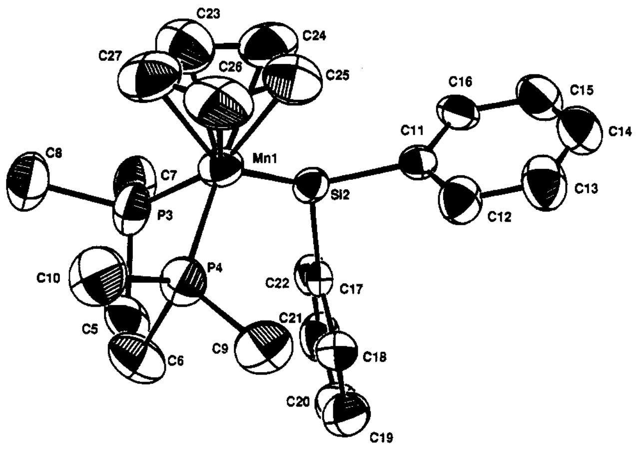


Figure 1.

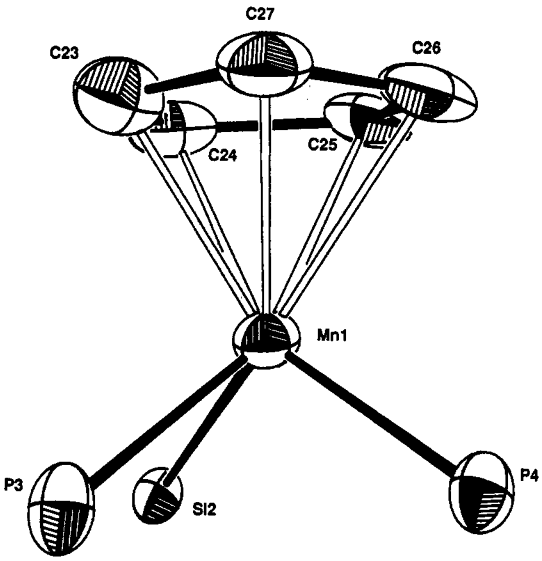


Figure 2.

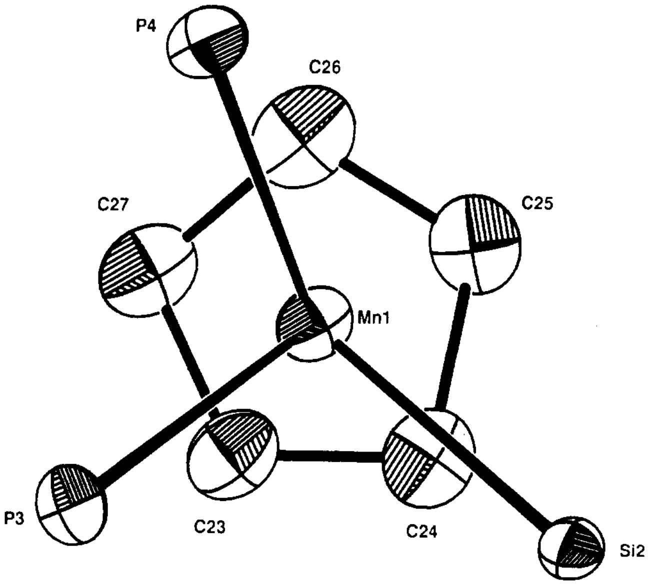


Figure 3.

to break. In accord with this hypothesis, when benzene-d_6 solutions of carbonyl complex **1** are photolyzed under vacuum in the absence of hydrosilane, no reaction of any kind is observed. Studies of the quantum yield for photochemical ligand substitution in the related complex CpMn(CO)(PPh$_3$)$_2$ have shown that CO dissociation is not a primary photochemical step;[7] instead, efficient dissociation of a phosphine ligand occurs. Thus, opening of the DMPE chelate ring to form the η^1-DMPE complex **9** is the reasonable primary photochemical step (Scheme 5). Without hydrosilane present, the chelate ring closes to yield carbonyl **1** with no net reaction. When hydrosilane is present, oxidative addition occurs to form the carbonyl silyl hydride **10**. Dissociation of CO from the formally Mn(III) metal center is now viable in a second photochemically driven step to yield intermediate **11**. Rapid chelation of the η^1-DMPE ligand leads to the final silyl hydride product **2**.

In support of the intermediacy of **10**, ^{31}P NMR spectra of partially photolyzed mixtures of hydrosilanes and carbonyl complex **1** in hexanes solution show a very small but visible new doublet in *ca.* −47 ppm. This resonance appears in a region consistent with a free dimethylphosphino moiety coupled to the coordinated phosphine.[6] This resonance disappears as nearly quantitative formation of product occurs.

It is reasonable that the mechanisms of formation of the other silyl hydrides **4** and **6** are analogous to that depicted in Scheme 2. The formation of bis(trimethylphosphine) complex **8** differs only by the lack of a chelating phosphine ligand. Our results have shown that while **8** cannot be prepared in the absence of excess phosphine, the presence of excess PMe$_3$ allows facile preparation of **8**. Apparently, lack of the intramolecular phosphine ligand can be overcome by providing a sufficiently high concentration of free PMe$_3$.

Dynamic NMR Spectra. The NMR spectra of these complexes are similar to one another and are consistent with the existence of silyl and hydride ligands in the metal coordination sphere. Most notably, each complex displays a triplet resonance ($J_{\text{H-P}} = {\sim}32$ Hz) in the hydride region consistent with equal coupling to two equivalent phosphorus nuclei. In diphenylsilyl complex **2b** coupling of the hydride to the silane hydrogen with a coupling constant of 10.4 Hz further splits the hydride resonance so that it appears as a triplet of doublets. In phenylsilyl complex **2a** the coupling of the silyl hydrogens to the hydride ligand is not resolved and the hydride resonance appears as a broad triplet. The cyclopentadienyl protons are weakly coupled to the phosphorus atoms ($J_{\text{H-P}} = 1.5$ Hz) and appear as triplets at a relatively high field just below 4 ppm. The DMPE ligand exhibits two sets of methyl resonances between 1 and 1.5 ppm, and a broad methylene resonance near 1 ppm. A single resonance in the ^{31}P NMR spectrum is observed in ~93 ppm.

From comparison to the NMR spectra of similar manganese silyl hydride complexes with four-legged piano-stool geometries, it is reasonable that the ligands in **2**, **4**, **6**, and **8** are similarly arranged in four-legged piano-stool geometries around the metal center.[5,8–20] Of course this geometry is consistent with that observed in the molecular structure of **2b**. However, the symmetrical couplings of

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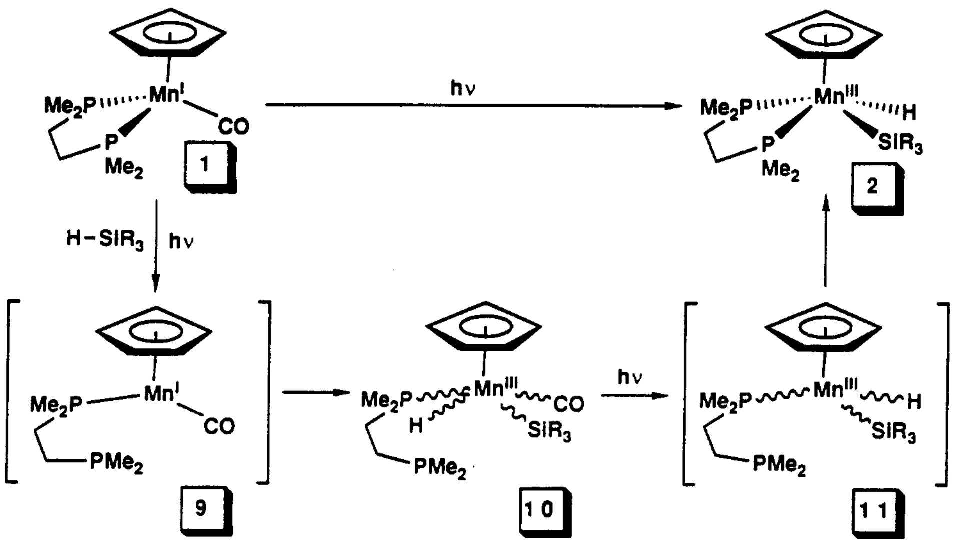
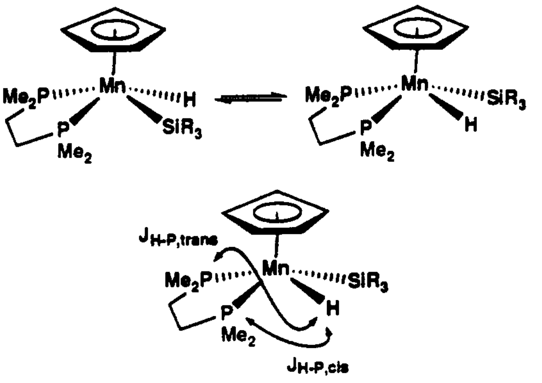
Scheme 5



the hydride ligands to the phosphorus ligands suggest either that the couplings are fortuitously identical or that the silyl and hydride ligands rapidly exchange positions on the NMR time scale via an intramolecular process.



A detailed discussion of the results obtained for the VT NMR spectrum of diphenylsilyl complex **2b** is illustrative of the generally observed spectral behavior. The VT NMR spectra of **2b** from 220 to 280 K exhibit the interesting dynamic behavior seen in these complexes. Similar behavior is seen for all the complexes **2**, **4**, **6**, and **8**. In the hydride region (Figure 4) at 220 K a large coupling to phosphorus (J_{H-P} = 59.6 Hz) and a smaller three bond coupling to the silyl hydrogen (J_{H-H} = 10.5 Hz) gave rise to an AMX doublet of doublets. As the temperature of the sample is raised, a broad new feature appears at the center of this resonance which gradually sharpens to a doublet at 280 K. This new feature gives the resonance in this region the overall appearance of an AMX_2 pattern. The peak positions of the outer doublet of doublet pattern is unchanged throughout this process with the separation between the outermost peaks remaining constant. The relative intensity of this outer doublet of doublets decreases to half its original intensity. The dynamic behavior in the hydride region is accompanied by the coalescence of peaks attributed to two different phenyl rings into one set of phenyl resonances and collapse of four different methyl resonances into two new methyl resonances.

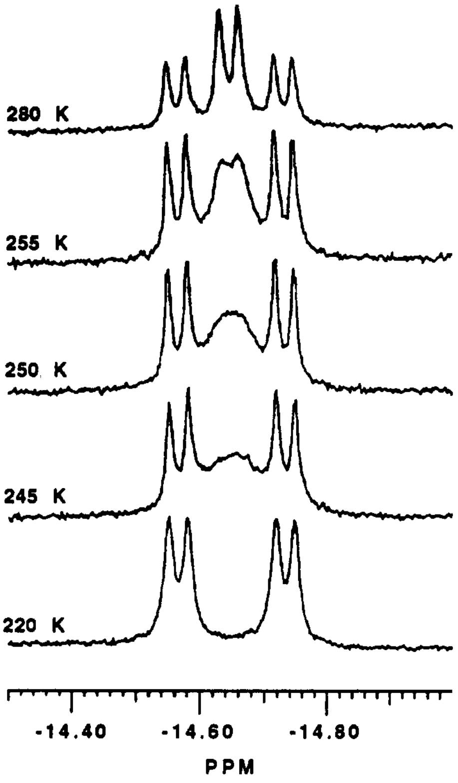


Figure 4. Variable temperature 360-MHz ^1H NMR spectrum of **2b** in CD_2Cl_2 solution. Only the hydride region is shown.

Schubert has shown that in phosphine silyl hydrides with four-legged piano-stool geometries, the *trans* phosphorus hydride coupling is small ($J_{H-P,trans}$ < 15 Hz)[5,15] while the *cis* phosphorus hydride coupling is large ($J_{H-P,cis}$ > 60 Hz).[5,16] Thus, the pattern seen in the slow exchange limit for **2b** can be described as an AMX pattern due to hydride coupling to the *cis* phosphine and to the silyl hydrogen. The coupling constant to the *trans* phosphine is close to zero and is not observed ($J_{H-P,trans} \approx 0$ Hz). The ^1H coupled ^{31}P NMR spectrum at 220 K confirms that hydride coupling to only one of the two inequivalent phosphorus nuclei is observed. At the fast exchange limit, rapid interchange of the relative silyl and hydride positions results in an AMX_2 spin system with equal coupling to both phosphorus nuclei. The phosphorus hydride coupling constant, J_{H-P}, is equal to the average of the *cis* and *trans* coupling constants, i.e., $J_{H-P} = (J_{H-P,trans} + J_{H-P,cis})/2$. The outer doublet of doublets remains invariant throughout this process since the sum of the phosphorus to hydrogen coupling remains constant with $J_{H-P,total} = J_{H-P,trans} +$

Table 5. Free Energy of Activation for Isomerization of Manganese Silyl Hydrides

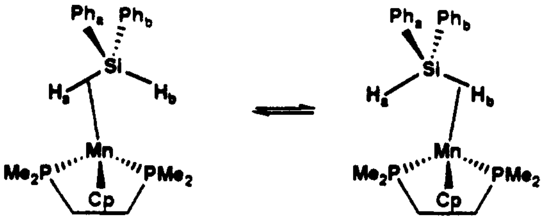
complex	phosphine	silyl ligand	$\Delta G^{\ddagger}_{ex}$ (kcal/mol)
2a	DMPE	SiH_2Ph	11.3
2b	DMPE	$SiHPh_2$	11.9
2c	DMPE	$SiPh_3$	9.6
4b	DMPP	$SiHPh_2$	10.9
6	DMPM	$SiHPh_2$	12.3
8	PMe_3	$SiHPh_2$	9.8

$J_{\mathrm{H-P},cis}$. In **2b** this isomerization process renders the phenyl rings on the silyl ligand equivalent and the DMPE protons appear as two sets of methyl and methylene resonances, one set *syn* to the Cp ring and one set *anti* to the Cp ring.

From the coalescence behavior seen in the hydride region, the free energies of activation ($\Delta G^{\ddagger}_{ex}$) for the isomerization reactions can be calculated and are given in Table 5. In DMPE complexes **2**, it is somewhat surprising that the more bulky triphenylsilyl complex **2c** exhibits the smallest barrier to isomerization. Perhaps the bulky nature of the triphenylsilyl group reduces the barrier for rotation by destabilizing the ground state.

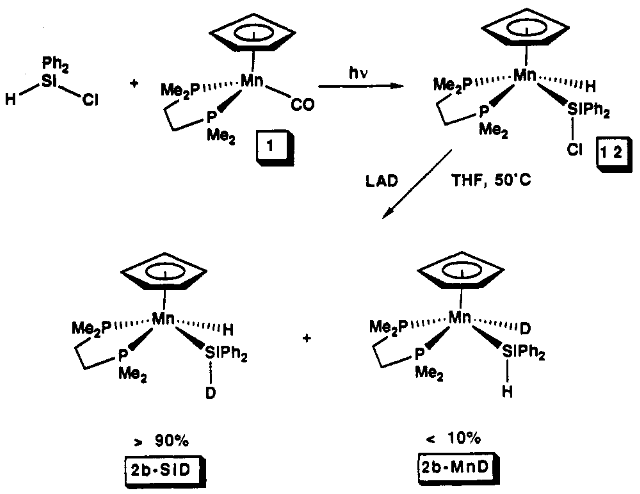
The clearest trend in $\Delta G^{\ddagger}_{ex}$ is seen upon comparing the series of diphenyl silyl hydrides prepared with different bidentate phosphines (**2b**, **4b**, and **6**) or trimethylphosphines (**8**). These values of $\Delta G^{\ddagger}_{ex}$ increase in the order **8**, **4b**, **2b**, and **6**. This ordering corresponds to the order in which the P–Mn–P angle becomes more constrained (vide infra).

Mechanism of Silyl/Hydride Ligand Interchange. At the fast exchange limit, exchange of the silyl and hydride ligand sites renders the two phosphorus ligands equivalent. One potential pathway resulting in exchange of the phosphorus ligands would involve a "windshield wiper" type of exchange between the "free" Si–H bond and the coordinated Si–H bond.

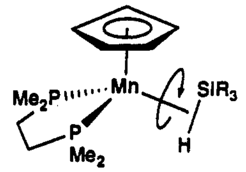


This isomerization would result in both phosphorus atoms residing in identical chemical environments. Such sliding of a metal center along a σ backbone has been proposed by Simon et al. in metal–alkane complexes.[21–24] This mechanism would also result in exchange of the silane and hydride environments for the hydrogen. Although the VT NMR spectra showed no evidence that the silane hydrogen was involved in any exchange processes, the wide separation (~15 ppm) between the silane and the hydride environments may have precluded facile observation of coalescence behavior. Deuterium labeling of the silane Si–H bond provided a straightforward method of examining whether the windshield wiper process is mechanistically significant.

Scheme 6



Scheme 7



Photolysis of DMPE carbonyl **1** in the presence of chlorodiphenylsilane yields chlorodiphenylsilyl hydride **12** (Scheme 6). Reduction of the Si–Cl moiety in **12** was easily accomplished with LAD in THF at 50 °C over a 0.5-h period. The deuterium labeled **2b** was obtained in high yield, and its isotopic purity was determined by ^{1}H NMR spectroscopy. Integration of the silane and the hydride resonances clearly showed that the deuterium label was found only in the silane position. A conservative estimate is that at most 10% of the label appeared in the hydride position (**2b-MnD**) while more than 90% of the label appeared in the silane position (**2b-SiD**).

This result rules out both (a) migration of the metal center around the σ bond framework of the silane even at elevated temperature and (b) an intermolecular component for hydride/silyl site exchange.[25] Both of these processes would result in a 50/50 statistical distribution of the deuterium label between the two possible sites. The similarity between $\nu_{\mathrm{Mn-H}}$ in **2b** and $\nu_{\mathrm{Si-H}}$ in silanes suggests that there would be only a small isotope effect on the position of the equilibrium between **2b-MnD** and **2b-SiD**. We can conclude that the exchange process must be intramolecular and cannot involve exchange between the silane hydrogen and the hydride ligands.

In addition, two independent observations support this conclusion. First, two sets of phenyl resonances are observed at low temperatures which coalesce into a well defined single set of phenyl resonances as the temperature is increased. Since the windshield wiper mechanism does not result in phenyl exchange, it is not able to account for this coalescence behavior. Second, the observation that phosphorus–hydride coupling in the silyl hydride complexes is observed at the fast exchange limit rules out an intermolecular exchange process. These results strongly suggest that it is exchange of the silyl and hydride ligands that results in the observed fluxionality.

Two other potential explanations for the silyl/hydride site exchange are mechanisms involving either rotation of

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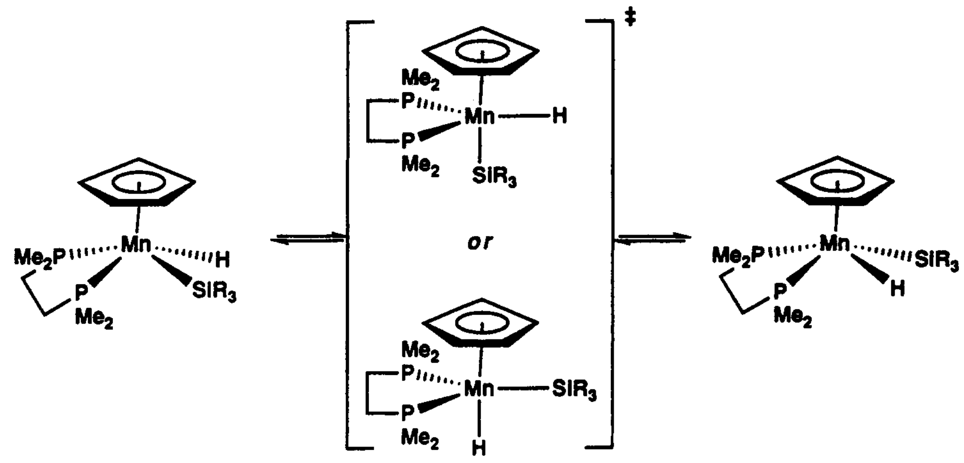
(25) Evidence that intermolecular silane exchange does not occur has been reported by Corriu et al.[20] The result reported herein is the first demonstration that intramolecular silane exchange does not occur under conditions where silyl/hydride site exchange does occur.

Scheme 8



a three-center two-electron metal Si–H system (Scheme 7) or rearrangement involving pseudorotation of the four-legged piano-stool moiety (Scheme 8). The stereochemical nonrigidity of four-legged piano-stool complexes has been studied in detail by Faller et al.[26] and by Flood et al.[27,28]

Effect of Chelate Ring Size on the Barrier for Silyl/Hydride Exchange. Examination of the trend in the magnitude of $\Delta G^{\ddagger}_{ex}$ for the series of diphenylsilyl hydrides as a function of the phosphine geometry is suggestive of the mechanism of isomerization.

The largest barrier for isomerization of 12.3 kcal/mol is found in DMPM silyl hydride **6** where the bidentate phosphine forms a four-membered ring. When the ring size is increased to five in DMPE complex **2b**, the barrier decreases to 11.9 kcal/mol. With the larger six-membered ring DMPP complex **4b**, the barrier for exchange is 10.9 kcal/mol. The smallest value of $\Delta G^{\ddagger}_{ex}$ is 9.8 kcal/mol found for the bis(trimethylphosphine) complex **8**.

In each complex containing a bidentate phosphine ligand, the chelate ring places some geometrical constraints on the P–Mn–P angle. In typical DMPM, DMPE, and DMPP complexes of first row transition metals, the P–M–P angles are ~70–75, ~85, and ~91°, respectively.[29–41] The ground state L–Mn–L angles seen in **2b** (L = P) and in similar manganese silyl hydrides with nonchelating ligands (L = P or CO) are 80–90°.[5] As a consequence, the chelate rings are not significantly constraining the P–M–P angle in the manganese silyl hydride series of complexes.

In the pseudorotation mechanism, the transition state with the phosphine ligands occupying equitorial sites would account for silyl/hydride site exchange. In this geometry the ideal P–Mn–P angle would be 120°. Consequently, the chelate rings place severe constraints on the relative positions of the phosphine ligands, resulting in destabilized transition states. The smaller the chelate ring, the more destabilization is expected and a correspondingly larger barrier to rotation may be expected.

The variation in $\Delta G^{\ddagger}_{ex}$ values follows the trend predicted by this model. The largest barrier is found for the complex with the smallest ring, with the barrier decreasing as the ring size increases. The smallest barrier is found for bis(trimethylphosphine) complex **8** with a ring strain free transition state.

This evidence is supportive of the pseudorotation mechanism but is far from conclusive. However, since the silane rotation and the pseudorotation mechanisms result in the same net movement of atoms, distinguishing between these processes is problematic. The final word on this subject will undoubtedly entail more substantial studies specifically addressing this issue.

Experimental Section

General Procedures. All reactions and manipulations were performed on either a high-vacuum line or in a glovebox under an atmosphere of dry argon or prepurified nitrogen. The metal carbonyl complex $CpMn(CO)_3$ was purchased from Strem chemicals and used without further purification. Phosphine ligands DMPM, DMPE, DMPP, and PMe_3 were purchased from Organometallics, Inc., Aldrich, or Strem and stored over 4-Å molecular sieves. H_2SiPh_2 and H_3SiPh (Aldrich Chemical Co. or Petrarch Systems) were distilled and degassed on the vacuum line, and stored in vials in an argon atmosphere glovebox. $HSiClPh_2$ (Petrarch Systems) and $HSiPh_3$ (Aldrich Chemical Co.) were stored in a glovebox and were used as purchased. Hexane and diethyl ether were distilled under a nitrogen or argon atmosphere from $LiAlH_4$. Tetrahydrofuran was distilled under an argon atmosphere before use from sodium and benzophenone

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ketal. All solvents were degassed by three to five freeze–pump–thaw cycles prior to use. Methylene-d_2 chloride was dried over $\mathrm{CaH_2}$ overnight, distilled under vacuum and then stored under vacuum.

All photolysis reactions were performed with a 450-W medium pressure Hanovia mercury lamp. Reactions were carried out in a Pyrex tube (typically 50–300 mL) sealed with a Kontes vacuum valve. A side arm with a 14/20 joint enabled easy connection to a vacuum line. Microanalyses were performed by Galbraith Laboratories, Inc. Infrared spectra were recorded on either an IBM System 9000 FT-IR spectrometer or a Perkin-Elmer 281 infrared spectrophotometer. The samples were held in 0.2-mm path solution cells with KBr or NaCl windows, calibrated against polystyrene film. ^{1}H NMR spectra were measured on a Bruker AC250 or AM360. ^{13}C NMR spectra were obtained at 62.895 MHz on a Bruker AC250 or at 90.556 MHz on a Bruker AM360. ^{1}H and ^{13}C spectra were referenced to residual internal solvent signals. ^{31}P NMR spectra were obtained at 145.785 MHz on a Bruker AM360 spectrometer. ^{31}P spectra were referenced to external 85% $\mathrm{H_3PO_4}$.

$\mathrm{CpMn(CO)(PMe_3)_2}$, $\mathrm{CpMn(CO)(\eta^2\text{-}DMPM)}$, $\mathrm{CpMn(CO)(\eta^2\text{-}DMPE)}$, and $\mathrm{CpMn(CO)(\eta^2\text{-}DMPP)}$ were synthesized with use of known methodology.[6]

Variable-Temperature NMR Measurements. All variable-temperature experiments were run at 360-MHz on the above-described AM360-MHz instrument. The temperature was regulated by a chilled stream of nitrogen gas. NMR probe temperatures were calibrated by using a standard MeOH reference tube after each run. Temperatures were corrected by a calibration graph and are accurate to ±2 deg.

Preparation of CpMn(H)(SiH₂Ph)(DMPE) (2a). A solution of CpMn(CO)(DMPE) (0.26 g, 0.87 mmol) and $\mathrm{H_3SiPh}$ (3.2 g, 30 mmol) in 150 mL of hexane was photolyzed at 5 °C for 80 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPE) at 1825 cm^{-1}. When all of the CpMn(CO)(DMPE) had been consumed, the solvent and excess $\mathrm{H_3SiPh}$ were removed under vacuum. The crude yellow/green product was dissolved in THF (0.5 mL). Hexane (10 mL) was added, and this mixture was chilled to −30 °C. Filtering and washing with cold hexane yielded 0.19 g (58% yield) of green-yellow crystals of **2a**. IR (THF solution): ν(Si–H) 2005 cm^{-1}, ν(Mn–H) 1840 cm^{-1}. ^{1}H NMR (360 MHz, $\mathrm{CD_2Cl_2}$): δ −14.14 (d of d, br, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 32.3$ Hz, 1H, $\mathrm{Mn}H$), 1.28 (m, 2H, $\mathrm{C}H\mathrm{H'}$), 1.43 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 3.9$ Hz, 6H, $\mathrm{C}H_3$), 1.56 (m, 2H, $\mathrm{CH}H'$), 1.58 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 4.4$ Hz, 6H, $\mathrm{C}H'_3$), 3.79 (t, $J_{\mathrm{HP}} = 1.5$ Hz, 5H, $\mathrm{C_5H_5}$), 4.96 (m, 2H, $\mathrm{Si}H$), 7.22 (m, 3H, $\mathrm{C_6H_5}$), 7.69 (d of d, $J_{\mathrm{HH'}} = 7.4$ Hz, $J_{\mathrm{HH''}} = 1.8$ Hz, 2H, $\mathrm{C_6}H_5$). ^{31}P NMR (146 MHz, $\mathrm{CD_2Cl_2}$): δ 91.51 (s, br). ^{13}C (^{1}H-coupled) NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 147.35 (s, br, $C_6\mathrm{H_5}$), 135.42 (d of m, $J_{\mathrm{HC}} = 157.0$ Hz, $C_6\mathrm{H_5}$), 127.29 (d of d, $J_{\mathrm{HC}} = 156.1$ Hz, $^2J_{\mathrm{H'C}} = 6.5$ Hz, $C_6\mathrm{H_5}$), 127.17 (d of t, $J_{\mathrm{HC}} = 158.4$ Hz, $^2J_{\mathrm{H'C}} = 7.3$ Hz, $C_6\mathrm{H_5}$), 76.21 (d of quintet, $J_{\mathrm{HC}} = 174.6$ Hz, $^2J_{\mathrm{H'C}} = 6.7$ Hz, $C_5\mathrm{H_5}$), 30.63 (t of d of d, $J_{\mathrm{HC}} = 130.6$ Hz, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 22.4$ Hz, $C\mathrm{H_2}$), 22.78 (quartet of m, $J_{\mathrm{HC}} = 127.4$ Hz, $C\mathrm{H_3}$), 22.65 (br, $C'\mathrm{H_3}$, broad due to coalescence at room temperature). Anal. Calcd for $\mathrm{C_{17}H_{29}P_2MnSi}$: C, 53.96; H, 7.72. Found: C, 54.03; H, 7.64.

Preparation of CpMn(H)(SiHPh₂)(DMPE) (2b). A solution of CpMn(CO)(DMPE) (0.14 g, 0.47 mmol) containing $\mathrm{H_2SiPh_2}$ (0.45 g, 2.4 mmol) in 50 mL of hexane was photolyzed at 5 °C for 80 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPE) at 1825 cm^{-1}. When all of the CpMn(CO)(DMPE) had been consumed, the solvent was removed under vacuum. A column with silica gel (230–400 mesh, THF/hexane = 1:40) was used to separate $\mathrm{H_2SiPh_2}$ from the product **2b**. The crude yellow–light green solid was dissolved in THF (1 mL), 5 mL hexane was added, and this mixture was chilled to −30 °C. Filtering and washing with cold hexane yielded 0.17 g (80% yield) of yellow–light green crystals of **2b**. IR (THF solution): ν(Si–H) 1979 cm^{-1}, ν(Mn–H) 1820 cm^{-1}. ^{1}H NMR (360 MHz, $\mathrm{CD_2Cl_2}$): δ − 14.42 (d of d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 30.2$ Hz, $J_{\mathrm{HH}} = 10.4$ Hz, 1H, $\mathrm{Mn}H$), 0.72 (m, 2H, $\mathrm{C}H\mathrm{H'}$), 1.38 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP}} = 3.6$ Hz, 6H, $\mathrm{C}H_3$), 1.42 (m, 2H, $\mathrm{CH}H'$), 1.76 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP}} = 4.3$ Hz, 6H, $\mathrm{C}H'_3$), 3.76 (t, $J_{\mathrm{HP}} = 1.6$ Hz, 5H, $\mathrm{C_5}H_5$), 6.24 (d of d of d, $J_{\mathrm{HH}} = 10.4$ Hz, $^2J_{\mathrm{HP}} \approx {}^2J_{\mathrm{HP'}} = 3.2$ Hz, 1H, $\mathrm{Si}H$), 7.13 (m, 6H, $\mathrm{C_5}H_5$), 7.66 (d of m, $J_{\mathrm{HH}} = 7.6$ Hz, 4H, $\mathrm{C_6}H_5$). ^{31}P NMR (146 MHz, $\mathrm{CD_2Cl_2}$): δ 94.64 (s, br). ^{13}C (^{1}H-coupled) NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 149.89 (m, $C_6\mathrm{H_5}$), 134.74 (d of m, $J_{\mathrm{HC}} = 162.7$ Hz, $C_6\mathrm{H_5}$), 127.31 (d of d, $J_{\mathrm{HC}} = 157.1$ Hz, $^2J_{\mathrm{H'C}} = 6.9$ Hz, $C_6\mathrm{H_5}$), 126.98 (d of t, $J_{\mathrm{HC}} = 158.7$ Hz, $^2J_{\mathrm{HC'}} = 7.6$ Hz, $C_6\mathrm{H_5}$), 76.89 (d of quintet, $J_{\mathrm{HC}} = 174.6$ Hz, $^2J_{\mathrm{H'C}} = 6.7$ Hz, $\mathrm{C_5H_5}$), 29.97 (t of d of d, $J_{\mathrm{HC}} = 130.0$ Hz, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 22.0$ Hz, $\mathrm{CH_2}$), 23.85 (br, $C\mathrm{H_3}$, broad due to partial coalescence at room temperature), 23.38 (d of q, $J_{\mathrm{HC}} = 125.7$ Hz, $^2J_{\mathrm{CP}} = 15.6$ Hz, $C'H_3$). Anal. Calcd for $\mathrm{C_{23}H_{33}P_2MnSi}$: C, 60.78; H, 7.32. Found: C, 60.49; H, 7.41.

Preparation of CpMn(H)(SiPh₃)(DMPE) (2c). A solution of CpMn(CO)(DMPE) (0.087 g, 0.29 mmol) and $\mathrm{HSiPh_3}$ (0.47 g, 1.8 mmol) in 60 mL of hexane was photolyzed for 60 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPE) at 1825 cm^{-1}. When all of the CpMn(CO)(DMPE) had been consumed, the solvent was removed under vacuum. A column with silica gel (230–400 mesh, THF/hexane = 1:20) was used to remove excess $\mathrm{HSiPh_3}$ from the product **2c**. The crude yellow–light green product was dissolved in THF (2 mL). Hexane (10 mL) was added, and this mixture was chilled to −30 °C. Filtering and washing with cold hexane yielded 0.090 g (62% yield) of yellow crystals of **2c**. IR (THF solution): ν(Mn–H) 1821 cm^{-1}. ^{1}H NMR (360 MHz, $\mathrm{CD_2Cl_2}$): δ −14.13 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 35.5$ Hz, 1H, $\mathrm{Mn}H$), 0.53 (m, 2H, $\mathrm{C}H\mathrm{H'}$), 1.32 (m, 2H, $\mathrm{CH}H'$), 1.39 (m, 6H, $\mathrm{C}H_3$), 1.47 (m, 6H, $\mathrm{C}H'_3$), 3.82 (t, $J_{\mathrm{HP}} = 1.5$ Hz, 5H, $\mathrm{C_5}H_5$), 7.19 (m, 9H, $\mathrm{C_6}H_5$), 7.59 (m, 6H, $\mathrm{C_6}H_5$). ^{31}P NMR (146 MHz, $\mathrm{CD_2Cl_2}$): δ 92.50 (s, br). ^{13}C {^{1}H} NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 148.98 (s, $C_6\mathrm{H_5}$), 136.77 (s, $C_6\mathrm{H_5}$), 126.76 (s, $C_6\mathrm{H_5}$), 126.65 (s, $C_6\mathrm{H_5}$), 76.73 (s, $C_5\mathrm{H_5}$), 30.42 (d of d, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 21.8$ Hz, $\mathrm{CH_2}$), 25.47 (d of d, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 14.6$ Hz, $C\mathrm{H_3}$), 23.32 (d of d, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 7.3$ Hz, $C'\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_{29}H_{37}P_2MnSi}$: C, 65.65; H, 7.03. Found: C, 65.42; H, 6.77.

Preparation of CpMn(H)(SiH₂Ph)(DMPP) (4a). A solution of CpMn(CO)(DMPP) (0.34 g, 1.1 mmol) and $\mathrm{H_3SiPh}$ (3.6 g, 33 mmol) in 150 mL of hexane was photolyzed at 5 °C for 80 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPE) at 1821 cm^{-1}. When all of the CpMn(CO)(DMPE) had been consumed, the solvent and excess $\mathrm{H_3SiPh}$ was removed under vacuum. The crude yellow–green product was dissolved in THF (0.5 mL). Hexane (10 mL) was added, and this mixture was chilled to −30 °C. Filtering and washing with cold hexane yielded 0.22 g (49% yield) of green-yellow crystals of **4a**. IR (THF solution): ν(Si–H) 2012 cm^{-1}, ν(Mn–H) 1823 cm^{-1}. ^{1}H NMR (360 MHz, $\mathrm{CD_2Cl_2}$): δ −14.58 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 31.9$ Hz, 1H, $\mathrm{Mn}H$), 1.26 (m, 2H, $\mathrm{C}H\mathrm{H'}$), 1.49 (d of d, $J_{\mathrm{HP}} \approx J_{\mathrm{HP'}} = 3.9$ Hz, 6H, $\mathrm{C}H_3$), 1.59 (m, 1H, $\mathrm{CH}H'$), 3.71 (t, $J_{\mathrm{HP}} = 1.7$ Hz, 5H, $\mathrm{C_5}H_5$), 4.96 (m, 2H, $\mathrm{Si}H$), 7.23 (m, 3H, $\mathrm{C_6}H_5$), 7.71 (m, 2H, $\mathrm{C_6}H_5$). ^{31}P NMR (146 MHz, $\mathrm{CD_2Cl_2}$): δ 49.00 (s, br). ^{13}C (^{1}H-coupled) NMR (90 MHz, $\mathrm{CD_2Cl_2}$): δ 147.41 (s, br, $C_6\mathrm{H_5}$), 135.56 (d of m, $J_{\mathrm{HC}} = 156.3$ Hz, $C_6\mathrm{H_5}$), 127.32 (d of d, $J_{\mathrm{HC}} = 150.5$ Hz, $^2J_{\mathrm{H'C}} = 6.6$ Hz, $C_6\mathrm{H_5}$), 127.18 (d of t, $J_{\mathrm{HC}} = 158.5$ Hz, $^2J_{\mathrm{H'C}} = 7.3$ Hz, $C_6\mathrm{H_5}$), 77.12 (d of quintet, $J_{\mathrm{HC}} = 167.7$ Hz, $C_5\mathrm{H_5}$), 32.15 (t of d of d, $J_{\mathrm{HC}} = 128.0$ Hz, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 16.1$ Hz, $C\mathrm{H_2}$), 24.95 (q of m, $J_{\mathrm{HC}} = 127.7$ Hz, $C\mathrm{H_3}$), 21.69 (q of d of d, $J_{\mathrm{HC}} = 157.1$ Hz, $J_{\mathrm{CP}} \approx J_{\mathrm{CP'}} = 7.2$ Hz, $C\mathrm{H_3}$), 20.42 (t, $J_{\mathrm{HC}} = 127.6$ Hz, $C'H_2$). Anal. Calcd for $\mathrm{C_{18}H_{29}P_2MnSi}$: C, 55.51; H, 7.96. Found: C, 55.08; H, 7.63.

Preparation of CpMn(H)(SiHPh₂)(DMPP) (4b). A solution of CpMn(CO)(DMPP) (0.25 g, 0.80 mmol) and $\mathrm{H_2SiPh_2}$ (0.85 g, 4.6 mmol) in 120 mL of hexane was photolyzed for 60 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPP) at 1821 cm^{-1}. When all of the CpMn(CO)(DMPP) had been consumed, the solvent was removed under vacuum. The solvent was removed in vacuo to produce a yellow solid which was then dissolved in 1 mL of THF. Hexane (10 mL) was added and this mixture was chilled to 30 °C. Filtering and washing with cold hexane, yielded 0.30 g (80% yield) of yellow-orange crystals of **4b**. IR (THF solution): ν(Si–H) 1987 cm^{-1}, ν(Mn–H) 1817 cm^{-1}. ^{1}H NMR (360 MHz, CD_2Cl_2): δ −14.47 (d of d of d, $J_{HP} \approx J_{HP'} = 29.6$ Hz, $J_{HH'} = 10.2$ Hz, 1H, $\mathrm{Mn}H$), 0.64 (m, 2H, $\mathrm{C}H_2$), 1.41 (m, 4H, $\mathrm{C}H'_2$), 1.47 (d of d, $J_{HP} \approx J_{HP'} = 3.1$ Hz, 6H, $\mathrm{C}H_3$), 1.68 (d of d, $J_{HP} \approx J_{HP'} = 3.7$ Hz, 6H, $\mathrm{C}H'_3$), 3.67 (s, 5H, $\mathrm{C_5}H_5$), 6.37 (d of d of d, $J_{HP'} = 10.4$ Hz, $J_{HP} \approx J_{HP'} = 2.5$ Hz, 6H, $\mathrm{Si}H'$), 7.18 (m, 6H, $\mathrm{C_6}H_5$), 7.74 (d, 4H, $\mathrm{C_6}H'_5$). ^{31}P NMR (145.8 MHz, CD_2Cl_2): δ 47.76 (s, br). ^{13}C (^{1}H-coupled) NMR (90.6 MHz, CD_2Cl_2): δ 149.98 (br, $C_6\mathrm{H}_5$), 135.03 (d of m, $J_{HC} = 160.0$ Hz, $C_6\mathrm{H}_5$), 127.46 (d of d, $J_{HC} = 157.0$ Hz, $^2J_{H'C} = 6.8$ Hz, $C_6\mathrm{H}_5$), 127.07 (d of t, $J_{HC} = 158.7$ Hz, $^2J_{H'C} = 7.6$ Hz, $C_6\mathrm{H}_5$), 77.54 (d of quintet, $J_{HC} = 174.1$ Hz, $^2J_{H'C} = 6.6$ Hz, $C_5\mathrm{H}_5$), 31.57 (t of d of d, $J_{HC} = 125.1$ Hz, $J_{CP} \approx J_{CP'} = 15.8$ Hz, $C\mathrm{H}_2$), 25.74 (q of m, $J_{HC} = 128.7$ Hz, $C\mathrm{H}_3$), 21.62 (q of d of d, $J_{HC} = 123.7$ Hz, $J_{CP} \approx J_{CP'} = 7.3$ Hz, $C'\mathrm{H}_3$), 20.19 (t, $J_{HC} = 126.3$ Hz, $C'\mathrm{H}_2$). Anal. Calcd for $C_{24}H_{35}P_2MnSi$: C, 62.18; H, 7.40. Found: C, 61.53; H, 7.53.

Preparation of CpMn(H)(SiPh$_3$)(DMPP) (4c). A solution of CpMn(CO)(DMPP) (0.22 g, 0.74 mmol) and $HSiPh_3$ (0.95 g, 3.65 mmol) in 60 mL of hexane was photolyzed for 60 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPP) at 1821 cm^{-1}. When all of the CpMn(CO)(DMPP) had been consumed, the solvent was removed under vacuum. A column with silica gel (230–400 mesh, THF/hexane = 1:20) was used to remove unreacted $HSiPh_3$ from the product **4c**. The crude orange–yellow product was dissolved in THF (3 mL). Hexane (15 mL) was added and this mixture was chilled to −30 °C. Filtering and washing with cold hexane, yielded 0.27 g (67% yield) of orange crystals of **4c**. IR: ν(Mn–H) 1823 cm^{-1}. ^{1}H NMR (360 MHz, CD_2Cl_2, 270 K): δ −14.41 (d of d, $J_{HP} \approx J_{HP'} = 36.1$ Hz, 1H, $\mathrm{Mn}H$), 0.46 (m, 4H, $\mathrm{C}H_2$), 1.25 (m, 2H, $\mathrm{C}H'_2$), 1.43 (m, 12H, $\mathrm{C}H_3$), 3.76 (s, 5H, $\mathrm{C_5}H_5$), 7.20 (m, 9H, $C_6\mathrm{H}_5$), 7.62 (m, 6H, $C_6\mathrm{H}_5$). ^{31}P NMR (146 MHz, CD_2Cl_2, 270 K): δ 45.04 (s, br). ^{13}C{^{1}H} NMR (90.6 MHz, CD_2Cl_2, 270 K): δ 149.29 (s, $C_6\mathrm{H}_5$), 137.05 (s, $C_6\mathrm{H}_5$), 126.68 (s, $C_6\mathrm{H}_5$), 126.63 (s, C_6H_5), 76.94 (s, $C_5\mathrm{H}_5$), 31.59 (d of d, $J_{CP} \approx J_{CP} = 15.5$ Hz, $C\mathrm{H}_2$), 27.90 (d of d, $J_{CP} \approx J_{CP'} = 15.9$ Hz, $C\mathrm{H}_3$), 21.77 (d of d, $J_{CP} \approx J_{CP} = 7.6$ Hz, $C'\mathrm{H}_3$), 19.82 (s, $C'\mathrm{H}_2$). Anal. Calcd for $C_{30}H_{39}P_2MnSi$: C, 66.16; H, 7.22. Found: C, 65.49; H, 6.62.

Preparation of CpMn(H)(SiHPh$_2$)(DMPM) (6). A solution of CpMn(CO)(DMPM) (0.13 g, 0.45 mmol) containing H_2SiPh_2 (0.96 g, 5.4 mmol) in 80 mL of hexane was photolyzed at 5 °C for 60 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPM) at 1823 cm^{-1}. When most of the CpMn(CO)(DMPE) had been consumed, the solvent was removed under vacuum. A column with silica gel (230–400 mesh, THF/hexane = 1:50) was used to isolate the product **6**. The crude yellow–light green solid was dissolved in THF (1 mL), and 5 mL of hexane was added. This mixture was chilled to −30 °C. Filtering and washing with cold hexane yielded 0.04 g (20% yield) yellow–light green crystals of **6**. IR (THF solution): ν(Si–H) 2002 cm^{-1}, ν(Mn–H) 1817 cm^{-1}. ^{1}H NMR (360 MHz, CD_2Cl_2): δ −9.59 (d of d of d, $J_{HP} \approx J_{HP'} = 30.9$ Hz, $J_{HH} = 6.2$ Hz, 1H, $\mathrm{Mn}H$), 1.35 (m, 6H, $\mathrm{C}H_3$), 1.65 (d of d, $J_{HP} \approx J_{HP} = 5.8$ Hz, 6H, $\mathrm{C}H'_3$), 2.42 (m, 2H, $\mathrm{C}H\mathrm{H}'$), 3.35 (m, 2H, $\mathrm{CH}H'$), 3.78 (t, $J_{HP} = 1.6$ Hz, 5H, $\mathrm{C_5}H_5$), 6.15 (m, 1H, $\mathrm{Si}H$), 7.18 (m, 6H, $\mathrm{C_5}H_5$), 7.76 (d of m, $J_{HH} = 9.7$ Hz, 4H, $\mathrm{C_6}H_5$). ^{31}P NMR (146 MHz, CD_2Cl_2): δ 33.20 (s, br). ^{13}C {^{1}H} NMR (90 MHz, CD_2Cl_2): δ 150.65 (s, $C_6\mathrm{H}_5$), 135.27 (s, $C_6\mathrm{H}_5$), 127.36 (s, $C_6\mathrm{H}_5$), 126.88 (s, $C_6\mathrm{H}_5$), 76.10 (s, $C_5\mathrm{H}_5$), 54.72 (d of d, $J_{CP} \approx J_{CP'} = 16.3$ Hz, $C\mathrm{H}_2$), 22.44 (m, br, $C\mathrm{H}_3$, $C'\mathrm{H}_3$).

Preparation of CpMn(H)(SiHPh$_2$)(PMe$_3$)$_2$ (8). A solution of $CpMn(CO)(PMe_3)_2$ (0.22 g, 0.73 mmol), PMe_3 (0.4 mL, 3.9 mmol), and H_2SiPh_2 (1.0 g, 5.4 mmol) in 40 mL of hexane solution was photolyzed for 200 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPE) at 1820 cm^{-1}. When most of the $CpMn(CO)(PMe_3)_2$ had been consumed, the solvent and excess PMe_3 was removed under vacuum. A silica gel column (230–400 mesh, THF/hexane = 1:50) was used to isolate the product 8. The orange–red product was dissolved in THF (0.5 mL). Hexane (10 mL) was added, and this mixture was chilled to −30 °C. Filtering and washing with cold hexane gave 0.16 g (48% yield) of orange–red crystals of 8. IR (THF solution): ν(Si–H) 1979 cm^{-1}, ν(Si–H) 1824 cm^{-1}. ^{1}H NMR (360 MHz, CD_2Cl_2): δ −14.23 (d of d of d, $J_{HP} \approx J_{HP'} = 31.9$ Hz, $J_{HH'} = 8.6$ Hz, 1H, $\mathrm{Mn}H$), 1.32 (s, br, 18H, $\mathrm{C}H_3$), 3.66 (s, br, 5H, $\mathrm{C_5}H_5$), 6.35 (s, br, 1H, $\mathrm{Si}H$), 7.17 (m, $\mathrm{C_6}H_5$, 6H), 7.71 (m, $\mathrm{C_6}H_5$, 4H). ^{31}P NMR (145.8 MHz, CD_2Cl_2): δ 44.94 (s, br). ^{13}C (^{1}H-coupled) NMR (90.6 MHz, CD_2Cl_2): δ 150.11 (s, br, $C_6\mathrm{H}_5$), 134.89 (d of m, $J_{HC} = 154.3$ Hz, $C_6\mathrm{H}_5$), 127.42 (d of d, $J_{HC} = 157.2$ Hz, $^2J_{H'C} = 7.1$ Hz, $C_6\mathrm{H}_5$), 127.01 (d of t, $J_{HC} = 157.2$ Hz, $^2J_{H'C} = 7.6$ Hz, $C_6\mathrm{H}_5$), 77.63 (d of quintet, $J_{HC} = 174.4$ Hz, $^2J_{H'C} = 6.7$ Hz, $C_5\mathrm{H}_5$), 25.30 (q of d of d, $J_{HC} = 127.1$ Hz, $J_{CP} \approx J_{CP'} = 12.2$ Hz, $C\mathrm{H}_3$). Anal. Calcd for $C_{23}H_{35}P_2MnSi$: C, 60.06; H, 7.51. Found: C, 60.52; H, 7.73.

Preparation of CpMn(H)(SiPh$_2$Cl)(DMPE) (12). A solution of CpMn(CO)(DMPE) (0.192 g, 0.644 mmol) containing $HSiClPh_2$ (0.65 g, 3.0 mmol) in 100 mL of hexane was photolyzed at 5 °C for 25 h with a medium pressure mercury lamp. The reaction vessel was periodically evacuated to remove any CO that evolved during the reaction. The reaction was monitored by the decrease in the infrared carbonyl stretching band of CpMn(CO)(DMPE) at 1825 cm^{-1}. When all of the CpMn(CO)(DMPE) had been consumed, the solvent was removed under vacuum. The crude yellow solid was dissolved in Et_2O and filtered to remove residue. This solution was concentrated to 5 mL. Hexane (10 mL) was added, and the mixture was chilled to −30 °C. Filtering and washing with cold hexane yielded 0.24 g (76% yield) of yellow crystals of 12. IR (THF solution): ν(Mn–H) 1819 cm^{-1}. ^{1}H NMR (360 MHz, C_6D_6): δ −14.54 (d of d, $J_{HP} \approx J_{HP'} = 33.8$ Hz, 1H, $\mathrm{Mn}H$), 0.80 (d of d, $J_{HP} \approx J_{HP'} = 5.2$ Hz, 6H, $\mathrm{C}H_3$), 0.89 (m, 4H, $\mathrm{C}H_2$), 1.44 (d of d, $J_{HP} \approx J_{HP'} = 6.2$ Hz, 6H, $\mathrm{C}H'_3$), 3.85 (br, 5H, $\mathrm{C_5}H_5$), 7.08 (t, $J_{HH'} = 10.4$ Hz, 2H, $\mathrm{C_6}H_5$), 7.22 (t, $J_{HH'} = 10.5$ Hz, 4H, $\mathrm{C_6}H'_5$), 8.11 (d, $J_{HH'} = 10.2$ Hz, 4H, $\mathrm{C_6}H''_5$). ^{31}P NMR (146 MHz, C_6D_6): δ 91.18 (s, br). ^{13}C {^{1}H} NMR (63 MHz, C_6D_6): δ 150.02 (s, $C_6\mathrm{H}_5$), 134.37 (s, $C_6\mathrm{H}_5$), 127.46 (s, $C_6\mathrm{H}_5$), 127.28 (s, $C_5\mathrm{H}_5$), 77.93 (s, $C_5\mathrm{H}_5$), 30.35 (d of d, $J_{CP} \approx J_{CP'} = 21.97$ Hz, $C\mathrm{H}_2$), 24.44 (m, $C\mathrm{H}_3$), 22.38 (m, $C'\mathrm{H}_3$). Anal. Calcd for $C_{23}H_{32}ClP_2MnSi$: C, 56.50; H, 6.60. Found: C, 56.72; H, 6.55.

Preparation of CpMn(H)(SiPh$_2$D)(DMPE) (2b-SiD). To 0.075 g of $CpMn(H)(SiPh_2Cl)(DMPE)$ (0.15 mmol) in 10 mL of THF solution was added 0.01 g (0.2 mmol) of $LiAlD_4$. The reaction mixture was heated and stirred in a 50 °C water bath for 1 h. The solvent was pumped off, the residue was dissolved in hexanes, and the solution was filtered and concentrated to 5 mL. Recrystallization at −30 °C from THF/hexane gave 0.06 g (86% yield) of yellow crystals of **2b-SiD**, $CpMn(H)(SiPh_2D)(DMPE)$. IR (THF solution): ν(Mn–H) 1821 cm^{-1}. ^{1}H NMR (360 MHz, CD_2Cl_2): δ −14.42 (d of d, br, $J_{HP} \approx J_{HP'} = 30.2$ Hz, 1H, $\mathrm{Mn}H$), 0.72 (m, 2H, $\mathrm{C}H\mathrm{H}'$), 1.38 (d of d, $J_{HP} \approx J_{HP} = 3.6$ Hz, 6H, $\mathrm{C}H_3$), 1.42 (m, 2H, $\mathrm{CH}H'$), 1.76 (d of d, $J_{HP} \approx J_{HP} = 4.3$ Hz, 6H, $\mathrm{C}H'_3$), 3.76 (t, $J_{HP} = 1.6$ Hz, 5H, $\mathrm{C_5}H_5$), 7.13 (m, 6H, $\mathrm{C_5}H_5$), 7.66 (d of m, $J_{HH} = 7.6$ Hz, 4H, $\mathrm{C_6}H_5$).

Molecular Structure of CpMn(DMPE)(H)(SiPh$_2$H) (2b). The diphenylsilyl hydride complex **2b** crystallized from pentane solution as yellow needles in space group $P2_1/n$ (No. 14). A suitable crystal was mounted in a thin-walled glass capillary and was used for data collection on a Siemens $P2_1$ X-ray diffractometer. The structure was solved by conventional Patterson and difference-Fourier techniques. Least-squares refinement initially led to a structure with a poor *R* factor of 0.010. At this point it was noticed that three regions of residual electron density remained in chemically unreasonable positions. It was recognized that a packing disorder existed in the crystal, whereby the DMPE ligand and the MnCp moiety were effectively interchanged in about 8% of the molecules. The three main residual electron-density peaks could be identified as partially-occupied manganese and phosphorus atoms by virtue of their peak heights and their positions relative to the nondisordered silicon atom. Occupancy refinement resulted in population factors of 92% and 8% for the major (Mn_1, P_3, P_4) and minor (Mn_1', P_3', P_4') positions. This disordering would also involve the cyclopentadienyl carbons (on Mn) as well as the methyl groups (on P), but at an occupancy level of 8% these carbons would not be expected to be detectable in an electron-density map. When this disordered model was incorporated into the least-squares refinement, the *R* factor converged to a more satisfactory final value of 0.074. In these last cycles of refinement, the molecular geometry of the minor disordered component was constrained to be equal to that of the major component.

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Supplementary Material Available: Tables of crystal data and refinement results, final atomic coordinates, temperature factors, bond distances, and bond angles for **2b** (5 pages). Ordering information is given on any current masthead page.

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