N, 7.21; H, 4.60; Cu, 16.01; ClO_4, 16.22. Calcd for $C_{54}N_6H_{58}Cu_3Cl_2O_{12}$ (*n*-BuL′): C, 52.05; N, 6.75; H, 4.66; Cu, 15.32; ClO_4, 16.06. Found: C, 52.32; N, 6.33; H, 4.51; Cu, 15.09; ClO_4, 16.53. The above procedure when applied to $[Cu_3O_q(OH)_{1-q}(RL)_3](ClO_4)_{2-q}$ gave back the original product.

Magnetic moments (μ_{eff} in Bohr magnetons per copper) of the complexes at room temperature are as follows: EtL′, 1.09; *n*-PrL′, 1.08; *n*-BuL′, 1.09. Λ_M (in Ω^{-1} cm^2 mol^{-1}) data in acetonitrile solution ($\sim 10^{-3}$ M) are as follows: EtL′, 221; *n*-PrL′, 262; *n*-BuL′, 250.

Conversion of $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ to $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$. A 800-mg sample of $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ was dissolved in 40 mL of acetonitrile. To the bright green solution was added dropwise with constant stirring 2 mL of distilled triethylamine. Immediately a grayish green compound started precipitating. After 15 min, the compound was filtered off, washed thoroughly with acetonitrile, and dried in vacuo over P_4O_{10}; yield 600 mg.

Conversion of $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$ to $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$. To 270 mg of $[Cu_3O(PL)_3]ClO_4 \cdot H_2O$ taken in 30 mL of acetonitrile was added dropwise with constant stirring 5 mL < of 0.11 N $HClO_4$ in DMF. The mixture was filtered after stirring for 0.5 h. The filtrate was left in air. When the volume decreased to 2 mL, the green crystalline compound $[Cu_3OH(PL)_3](ClO_4)_2 \cdot H_2O$ was filtered off, washed with 5 mL of cold water, and dried in vacuo over P_4O_{10}; yield 150 mg.

Conversion of $[Cu_3OH(n\text{-}BuL')_3](ClO_4)_2$ to $[Cu_3O(n\text{-}BuL')_3]ClO_4$. A 200-mg sample of $[Cu_3OH(n\text{-}BuL')_3](ClO_4)_2$ was dissolved in 50 mL of methanol, and 2 mL of NEt_3 was added dropwise with stirring. Within 5 min, the crystalline compound started precipitating. The compound was filtered, washed with methanol, and dried in vacuo over P_4O_{10}; yield 120 mg.

Conversion of $[Cu_3O(n\text{-}BuL')_3]ClO_4$ to $[Cu_3OH(n\text{-}BuL')_3](ClO_4)_2$. Starting with $[Cu_3O(n\text{-}BuL')_3]ClO_4$, a procedure identical with that for preparing pure $[Cu_3OH(RL')_3](ClO_4)_2$ (vide supra) was followed to obtain the desired complex in 90% yield.

The interconversions of Cu_3O and Cu_3OH species derived from PhL and other RL′ ligands were achieved by similar procedures.

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Registry No. **5a**·ClO_4 (RL = PhL), 79682-14-7; **5a**·ClO_4 (RL′ = *n*-BuL′), 76986-47-5; **5a**·ClO_4 (RL′ = *n*-PrL′), 76986-49-7; **5a**·ClO_4 (RL′ = EtL′), 76986-51-1; **5a**·ClO_4 (RL = *n*-BuL), 73689-14-2; **5a**·ClO_4 (RL = *n*-PrL), 73668-62-9; **5a**·ClO_4 (RL = EtL), 53598-80-4; **6a**·2ClO_4 (RL = PhL), 73689-16-4; **6a**·2ClO_4 (RL′ = *n*-BuL′), 76998-84-0; **6a**·2ClO_4 (RL′ = *n*-PrL′), 76986-56-6; **6a**·2ClO_4 (RL′ = EtL′), 76986-58-8; **6a**·2ClO_4 (RL = *n*-BuL), 76986-60-2; **6a**·2ClO_4 (RL = *n*-PrL), 76986-62-4; **6a**·2ClO_4 (RL = EtL), 76986-64-6; **7a**·ClO_4, 79703-96-1; **8a**·2ClO_4, 79703-98-3; HPL, 873-69-8.

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Study of the Insertion Products of Manganese in the Silicon–Hydrogen Bond. Nature of the Bond and Proton Exchange in the H-Mn-Si-H System

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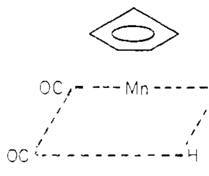
NMR studies (^{29}Si, ^{13}C, and ^1H) on silicon manganese hydrides show the possibility of a bond interaction between silicon and hydrogen. Evidence is given for a slow intramolecular equilibrium (on the NMR time scale) between the silicon manganese hydride and the deinserted complex (silicon hydride and manganese moiety). In the latter, however, both moieties are associated and a strong ligand is needed to displace the silicon hydride. Chemical reactions show that protonation of the anion $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2SiPh_3]^-$ leads only to the lateral hydride independent of its mode of generation. When the anion is alkylated, only the diagonal isomer is formed, showing that sterically crowded complexes prefer this geometry; thus the short distance observed between silicon and hydrogen does not seen to arise solely from steric hindrance.

Introduction

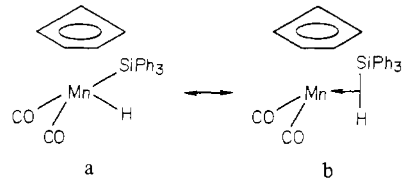
Insertion reactions of metals into the silicon–hydrogen bond are of current interest because of their implication in catalytic hydrosilylation reactions.[2]

In previous work carried out in our laboratory, we have studied the chemical and stereochemical behavior of complexes arising from the insertion of manganese into the Si–H bond.[3-5]



R = alkyl, aryl

Scheme I



Scheme II

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2(H)SiPh_3 + PPh_3 \underset{\text{determining}}{\overset{\text{rate}}{\rightleftharpoons}} (\eta^5\text{-}C_5H_5)Mn(CO)_2 + HSiPh_3 + PPh_3 \overset{\text{fast}}{\rightleftharpoons} (\eta^5\text{-}C_5H_5)Mn(CO)_2PPh_3 + HSiPh_3$$

18-electron complex

16-electron complex

This type of complex was first described by Jetz and Graham[6] (R = phenyl). An X-ray diffraction study[7] showed a bonding interaction between silicon and hydrogen.

The manganese–silicon bond length (2.42 Å) and the manganese–hydrogen length (1.55 Å) show normal values,

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(1) (a) Laboratoire des Organométalliques. (b) Laboratoire des Heterocycles Azotés.

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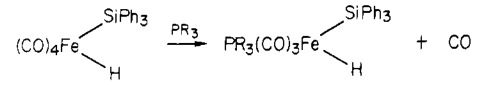
Scheme III



R = Ph, OPh

Scheme IV

$$(CO)_4Fe(H)SiPh_3 + Et_4NCl \rightarrow [(CO)_4FeSiPh_3]Et_4N + HCl^{14}$$

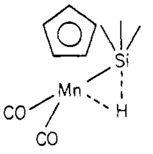
$$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(H)SiPh_3 \begin{cases} + Et_4NCl \rightarrow \text{no reaction}^{14} \\ + Et_3N \rightarrow \text{no reaction}^{14} \\ + NaH \rightarrow [(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2 \\ \quad SiPh_3]Na + H_2{}^{4} \end{cases}$$

whereas the silicon–hydrogen distance (1.76 Å), though longer than the normal Si–H bond distance (1.48 Å), is much shorter than the sum of the van der Waals radii for both elements (3.1 Å). This sum is generally considered to be the limit to which two nonbonded atoms would normally approach each other. Thus, approach to as close as 1.76 Å indicates bonding.

This structure has been represented by Graham and Hart-Davis as a resonance hybrid of two canonical forms[8] (Scheme I). Structure a is probably the major contributor because of the normal Mn–H bond length, while b is a complex similar to $(\eta^5\text{-}C_5H_5)Mn(CO)_2PPh_3$ except that the electrons donated by the ligand to the manganese atom happen to be a bonding pair in H–$SiPh_3$ instead of a nonbonding pair in the isoelectronic PPh_3.

A kinetic study of the reductive elimination of silane by triphenylphosphine shows the sequence given in Scheme II. Cowie and Bennett,[9] however, interpret the short distance between silicon and hydrogen as the result of steric crowding that forces the hydride ligand close to the silicon atom.

Kaesz et al.[10] propose that the situation is better expressed in terms of a structural tautomer such as c, which corresponds



c

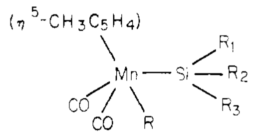
to an equilibrium position of the atoms arrested at some point along the reaction coordinate b to a representing the oxidative addition of an Si–H bond at a transition-metal center.

On the the other hand, the complex $(CO)_4Fe(H)SiPh_3$, arising from the insertion of iron in the SiH bond, undergoes carbon monoxide displacement with phosphorus ligands[11,12] (Scheme III). In this case the Si–H distance is 2.73 Å[13] and both ligands may be considered as independent.

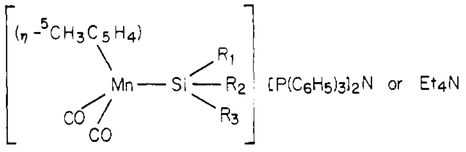
The difference in behavior between these two complexes is also reflected in their acidities (Scheme IV).

In order to elucidate the particular nature of the bond formed by insertion of manganese in the Si–H bond, we have studied the NMR behavior of ^{29}Si, ^{13}C, and ^1H nuclei to see whether this Si–H interaction was reflected by it. Furthermore, we have studied the hydrogen exchange between Mn–H and Si–H bonds in $(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(H)Si(1\text{-}C_{10}H_7)PhH$ and compared the stereochemistry of protonation and alkylation of the anion $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2SiPh_3]^-$.

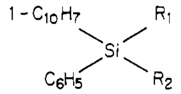
Chart I



1a, R = H, $R_1 = R_2 = R_3 = C_6H_5$
b, R = H, $R_1 = C_6H_5$, $R_2 = 1\text{-}C_{10}H_7$, $R_3 = H$
c, R = H, $R_1 = C_6H_5$, $R_2 = 1\text{-}C_{10}H_7$, $R_3 = F$
d, R = H, $R_1 = C_6H_5$, $R_2 = 1\text{-}C_{10}H_7$, $R_3 = Cl$
e, R = H, $R_1 = C_6H_5$, $R_2 = 1\text{-}C_{10}H_7$, $R_3 = CH_3$
f, R = H, $R_1 = C_6H_5$, $R_2 = 1\text{-}C_{10}H_7$, $R_3 = OCH_3$
g, $R = CH_3$, $R_1 = R_2 = R_3 = C_6H_5$



2



3a, $R_1 = R_2 = H$
b, $R_1 = H$, $R_2 = F$
c, $R_1 = H$, $R_2 = Cl$
d, $R_1 = H$, $R_2 = OCH_3$
e, $R_1 = R_2 = F$

Experimental Section

All experiments were carried out under nitrogen, with use of a vacuum line. For ^{29}Si and ^{13}C NMR spectra, samples were prepared in sealed tubes as described.[15] For ^1H NMR spectra, samples were prepared under nitrogen immediately prior to the recording.

^{29}Si NMR spectra were carried out with a Bruker WH 90 spectrometer operating at 17.87 MHz, equipped with a Nicolet NBC 12 (4K and 8K storage) computer (standard resolution 0.7 Hz). In order to avoid the negative NOE, the spectra were recorded in the gated pulse modulated interrupted proton band decoupling mode.[16] Pulses of 9×10^{-6} s with an angle of 45° were used with a repetition time of 20 s. ^{13}C NMR spectra were obtained with a Bruker WP 80 DS spectrometer operating at 20.115 MHz (standard resolution 0.9 Hz). ^1H NMR spectra were recorded on Varian EM 390 or EM 360 spectrometers. All chemical shifts (δ) are relative to Me_4Si.

Complexes **1a–g** and **2a–d** (see Chart I) were prepared according to the literature.[3-6] Other silicon compounds were commercially available or prepared as described.[17] Complex **1b(DD)** is prepared as **1b**[4] starting with $(1\text{-}C_{10}H_7)(C_6H_5)SiD_2$ (obtained by reduction of $(1\text{-}C_{10}H_7)(C_6H_5)Si(OCH_3)_2$ with $LiAlD_4$); the acidification of the anion was also described.

Attempt To React 1b(DD) with 1-Naphthylphenylsilane. A solution of 426 mg (1 mmol) of **1b(DD)** and 234 mg (1 mmol) of the silane was stirred at room temperature in 10 mL of benzene for 18 h. After this time solvent was pumped off and the residue crystallized from toluene/hexane at −20 °C. The ^1H NMR spectrum in CD_2Cl_2 showed no MnH or SiH signals.

Protonation of 2a Formed from 1g. To 466 mg (1 mmol) of **1g** in 20 mL of THF (ν(CO) 1970 and 1910 cm^{-1}) was added 2 mL of a 0.7 M solution of *n*-butyllithium at room temperature. After 12 h the reaction was complete, and only the anion **2a** was present (ν(CO) 1855 and 1740 cm^{-1}). At this moment a THF solution of HCl was added until the IR absorptions due to the anion disappeared (~2 mL of a 1 M solution). The solvent was then pumped off, the residue was dissolved in hexane, and the solution was filtered and left at −20 °C. Yellow crystals of **1a** were obtained (380 mg, yield 84%), which

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Table I. ^{29}Si Chemical Shifts in Ppm, Relative to Me_4Si, and Coupling Constants in Hz for Compounds 1–3

compd	solvent	δ(Si)	*J*(Si–H)	*J*(Si–F)
1a	C_6D_6	18.5	64.7	
1b	C_6D_6	7.5	208 69	
1c	CD_2Cl_2	57.3		348
1d	CD_2Cl_2	58.3		
1g	CD_2Cl_2	38.7		
2a[a]	CD_2Cl_2	57		
2b[b]	CD_2Cl_2	42.6		
2c[b]	CD_2Cl_2	98.9		287.5
2d[b]	CD_2Cl_2	80.6		
3a	C_6D_6	−35.4	198.3 6.2	
	CD_2Cl_2	−35.5	198.0 6.0	
3b	C_6D_6	−1.5	229.4 6.2	287.5
3c	C_6D_6	−5.1	238.5 6.0	
3d	C_6D_6	−7.5	212.2	
3e	C_6D_6	−26.1		292.7
$(C_6H_5)_3SiH$		−21.1[20]	198[21]	
$(C_6H_5)_2SiH_2$		−33.9[22]	200[18]	
$(C_6H_5)_3SiF$		−4.7[23]		292[24]
$(C_6H_5)_2SiF_2$		−29.5[22]		290[24]
$(CH_3)_3SiH$		−17.5[22]		
$(CH_3)_2SiH_2$		−40.5[22]		
$(CH_3)_3SiF$		34.4[25]		
$(CH_3)_2SiF_2$		5.3[22]		
$(CH_3)_3SiCl$		30.2[26]		
$(CH_3)_3SiOCH_3$		17.2[27]		

[a] $(C_2H_5)_4N$ cation. [b] $[P(C_6H_5)_3]_2N$ cation.

were shown to be identical with the compound arising from UV irradiation of $(C_6H_5)_3SiH$ and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$[6] by comparison of their IR (ν(CO) 1983 and 1926 cm^{-1} in hexane) and NMR spectra (δ(Mn–H) −11.44 in C_6D_6) and by mixture melting point (95–96 °C).

Reaction of 1g with Ph_3GeLi. To 466 mg (1 mmol) of **1g** in 15 mL of ether was added 1 mmol of Ph_3GeLi (from 304 mg of Ph_3GeH in 15 mL of ether and 1.5 mL of a 0.84 M solution of *n*-butyllithium in ether). The mixture was stirred at room temperature for 1 h. After this time the solvent was pumped off and the residue taken up in CH_2Cl_2. To the solution was added 200 mg (excess) of Et_4NCl in CH_2Cl_2; after 10 min the solution was filtered, the solvent was pumped off, and the residue was dissolved in THF. This solution was filtered in order to eliminate the excess of Et_4NCl, and standing at −20 °C afforded 380 mg (yield 66%) of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2SiPh_3]Et_4N$, which was compared to an authentic sample.[4] The mother liquor was evaporated and the residue chromatographed on silica gel (plc) with elution with hexane/benzene (9/1); 300 mg of Ph_3GeCH_3 (94%) was isolated.

Results

^{29}Si NMR Spectra. The difficulties in observing the ^{29}Si isotope have already been pointed out.[18] More complications are awaited if the ^{29}Si nuclei are directly bonded to transition metals: such types of compounds have recently been studied with use of the selective population transfer (SPT) technique.[19]

We report here the direct NMR observation of ^{29}Si nuclei bonded to Mn in compounds of type **1** and **2** (Chart I). The ^{29}Si chemical shifts and ^{29}Si–H and ^{29}Si–F coupling constants are assembled in Table I, together with those observed in parent silanes **3**.

We have verified that for selected compounds of type **1** and **3**, the solvent used (C_6D_6 or CD_2Cl_2) has a very weak influence on the chemical shifts and coupling constants.

a. Substituent Effects. We have compared the effect of the substitution of H in complexes **1–3** (Table II). It is obvious that such effects are not uniform and depend on the electronic environment. This behavior has already been pointed out[22] and prevents any ^{29}Si chemical shift prediction. The only trend is that substituent effects on ^{29}Si shifts are more important when silicon is bonded to manganese. In comparison to compounds of series **3**, the ^{29}Si signals owing to manganese hydrides **1** are strongly shifted downfield (Table III). It can be noticed that the effect of a given substituent depends on the other substituents at silicon.

The only Si–Mn derivative previously studied by ^{29}Si NMR spectroscopy, $(CH_3)_3SiMn(CO)_5$,[19] has a chemical shift of +17.9 ppm. The authors conclude that, from a change in the transition metal, all the parameters contributing to ^{29}Si chemical shifts make their prediction difficult to rationalize.

In the case of Hg–Si complexes,[28] the authors assign the paramagnetic effect observed in such compounds to the interactions between these two nuclei, which are separated by a distance considerably shorter than the sum of the covalent radii. It seems, thus, likely that for compounds in which silicon is bonded to a transition metal (as is the case for analogous tin compounds[29]) the paramagnetic effect observed on Si is due to (d → d) π overlap between Si and the transition metal. The downfield effect observed on the Si–Mn derivatives we report may also arise in part from the carbonyl groups attached to manganese.

In complexes **2** the ^{29}Si signals are greatly shifted downfield compared to those of the corresponding hydrides **1** (Table III). The effect is very important (+20 to +40 ppm) if compared to the downfield effect observed for carbon atoms α to negative charges[30] in ^{13}C NMR spectroscopy.

b. Si–H and Si–F Coupling Constants. i. ^1J(Si–H) Direct Coupling. ^1J(Si–H) coupling constants for compounds **1b** and **3a–d** are comparable to those of other silanes (Table I).

ii. ^1J(Si–F) Direct Coupling. The value of this coupling is greatly increased in compound **1c** if compared to those in **3b** or **3e**. This same increase is observed in ^{13}C NMR when carbon is bonded to transition metals[31] and when comparison is made between the ^1J(Si–F) in $C_6H_5SiF_3$ (J = 266 Hz[24]) and in $(CO)_4CoSiF_3$ (J = 370 Hz[25]).

In the anion **2c** the decrease of this ^1J(Si–F) coupling compared to that in the hydride **1c** may be explained by the proximity of the negative charge as is the case for ^1J(C–H) coupling constants.[32]

iii. ^2J(Si–H) Coupling. This geminal coupling is observed between the silicon atom and the proton attached to manganese. Values for H–C–Si couplings have been found in the range 6.6–7.2 Hz.[33]

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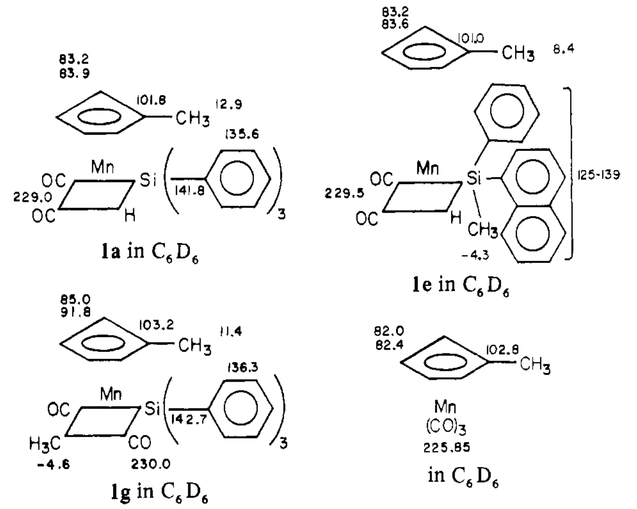
Table II. Substituent Effects on ^{29}Si NMR Spectroscopy (Shifts Relative to the Parent Compound in Which X = H)

X	1	2	3	$(CH_3)_3SiX$	$(C_6H_5)_3SiX$	$(CH_3)_2SiX_2$	$(C_6H_5)_2SiX_2$
F	+49.8	+56.3	+33.8	+51.9	+16.4		
Cl	+50.8	+38.0	+30.3	+47.7			
OCH_3			+27.9	+34.7			
2F			+9.2			+45.8	+4.4

Table III. Shifts of Silymanganese Species Relative to Their Parent Silanes

compared compds	shift, ppm	compared compds	shift, ppm
	Hydrides		
1a-$(C_6H_5)_3SiH$	+39.6	1d-3c	+63.4
1b-3a	+42.9	$(CH_3)_3SiMn(CO)_5$-$(CH_3)_3SiH$	+35.4
1c-3b	+58.8		
	Anions		
2a-$(C_6H_5)_3SiH$	+78.1	2d-3c	+85.7
2b-3a	+78.0	2c-3b	+100.4

Chart II[a]



[a] All values shown are the ^{13}C chemical shifts in ppm.

In compounds **1a** and **1b** the H-Mn-Si coupling constants reach values of 65 and 69 Hz. Geminal coupling constants across metal atoms have not been extensively studied; however, they seem to have higher values than H-C-Si ones, for instance, for diagonal $(Cl_3Si)_2Fe(H)(CO)(\eta^5\text{-}C_5H_5)$ in which hydrogen is cis to both silicon atoms, a coupling constant $J = 20$ Hz[34] has been reported. Although geminal coupling constants depend on the nature of the atom through which the coupling occurs, they are mainly sensitive to the geometry of the system and to the nature and orientation of the α substituents. For square-pyramidal complexes $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(PR_3)H]^+$[35] and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PR_3)H$,[36] ^2J(P-H) is 21-29 Hz for the diagonal isomers and 64-73 Hz for the lateral ones. ^2J(H-M-P) couplings are also higher than ^2J(H-C-P) ones.[37]

The high ^2J(H-Mn-Si) coupling (65 and 69 Hz) measured for **1a** and **1b** compared to ^2J(H-Fe-Si) (20 Hz) reported above could arise from the bonding interaction between H and Si. This could result in an increase of J(H-Mn-Si) making it intermediate between ^2J(H-Si) and ^1J(H-Si).

iv. ^3J(Si-H) Coupling Constants. Such couplings have been measured between Si and the aromatic protons in compounds **3a-c** and have a value of ~6 Hz. No coupling has been observed between Si and the C-H protons of the cyclopentadienyl ring via manganese, in contrast to coupling through iron.[38]

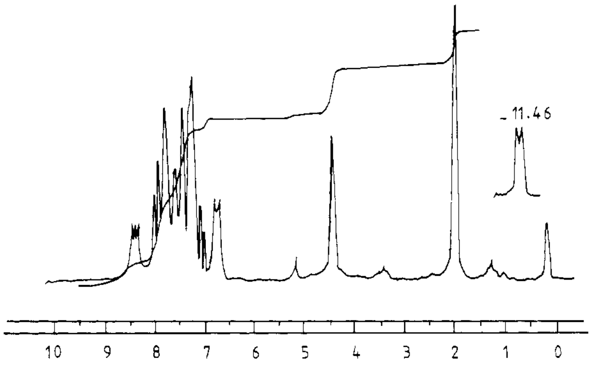


Figure 1. NMR spectrum of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(H)Si(1\text{-}C_{10}H_7)(C_6H_5)H$.

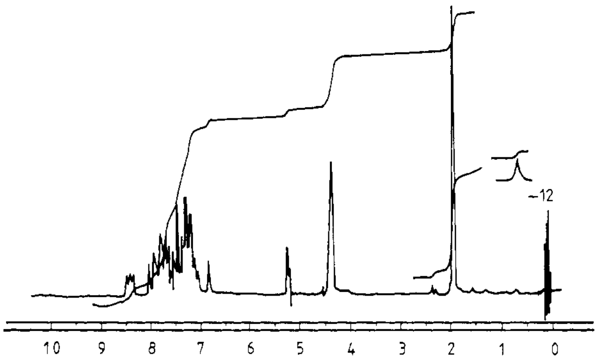
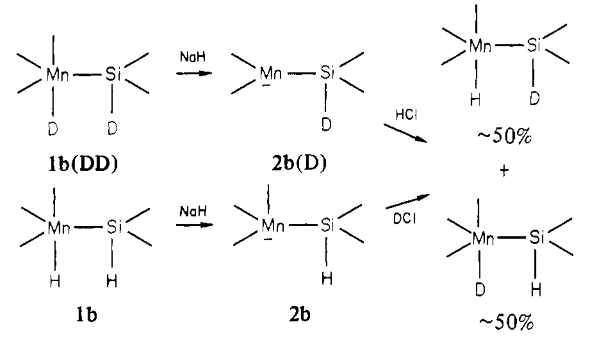


Figure 2. NMR spectrum of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(H)Si(1\text{-}C_{10}H_7)(C_6H_5)D$ and of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(D)Si(1\text{-}C_{10}H_7)(C_6H_5)H$.

Scheme V



^{13}C NMR Spectra. In Chart II are assembled the ^{13}C chemical shifts for **1a,e,g** and methylcymantrene. In square-pyramidal molybdenum complexes[39] the observation of the CO signals allows determination of the lateral and diagonal isomers. However, only one signal is observed in any complex, even for **1e** where the carbonyls are diastereotopic, irrespective of the structure, due to asymmetry at silicon.

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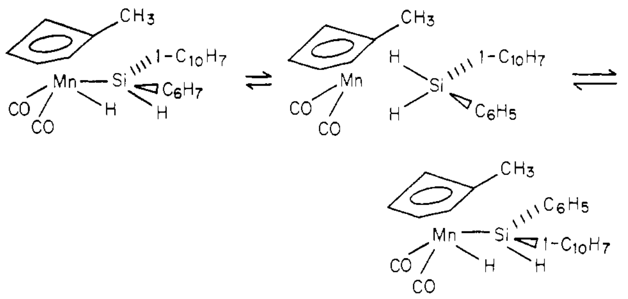
Table IV. ^{1}H NMR Spectra (Ppm) of Compounds **1a-g**, **2a**, and **2b**

compd	solvent	MnR	R_1, R_2, R_3	C_5H_4	CH_3Cp
1a	C_6D_6	−11.44	7.14–7.66	3.92	1.42
	CS_2	−11.80	7.16–7.36	4.15 4.25	1.79
1b	C_6D_6	−11.23 (J = 4.5 Hz)	masked (R_3)	3.85	1.50
	CD_2Cl_2	−11.46 (J = 4.5 Hz)	6.73 (J = 4.5 Hz) (R_3)	4.21	1.83
1b(DD)	CD_2Cl_2			4.35	1.94
1b(D)	CD_2Cl_2	−11.40 sharp	6.84 sharp (R_3)	4.35	1.91
1c	C_6D_6	−11.70 (J(HF) = 11.5 Hz)		3.95	1.43
1d	C_6D_6	−10.68		3.95	1.41
1e	C_6D_6	−11.97	1.21 (R_3)	3.79	1.42
	$(CD_3)_2CO$	−12.00[a]	1.26 (R_3)	4.49	1.84
1f	C_6D_6	−12.03	3.42 (R_3)	4.01	1.40
1g	C_6D_6	0.97	7.20–7.84	3.74 4.10	1.34
2a	CD_2Cl_2		7.10–7.34	3.80 4.04	1.81
2b	CD_2Cl_2		5.90 (R_3)	3.92 4.11	1.79
2b(D)	CD_2Cl_2			complex	1.75

[a] Signal shifted to −11.7 ppm at −40 °C and became sharper from a temperature effect on the ^{55}Mn quadrupolar relaxation.

Scheme VI



The only interesting feature is the difference in chemical shift for the cyclopentadienyl carbon atoms (83.2 and 83.9 ppm for **1a** and 85.0 and 91.8 ppm for **1g**). This change of structure is also reflected in the ^{29}Si shift (+20.2 ppm), which cannot be explained only by replacing H by CH_3.

^{1}H NMR Spectra. ^{1}H chemical shift and coupling constants are gathered in Table IV. Because of the use of careful experimental conditions we have obtained sharp signals, unlike those previously described for similar derivatives.[6] A vicinal coupling of 4.5 Hz is observed between MnH and SiH in **1b**. This value corresponds to those found for H–C–Si–H couplings (3.30–4.68 Hz[40]) (Figure 1).

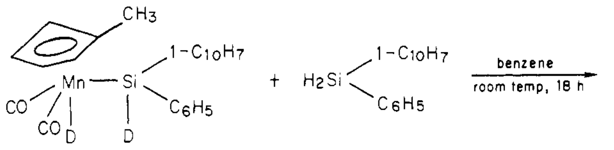
Prototropy of MnHSiH in 1b. In order to show the occurrence of a prototropy between protons bonded to manganese and silicon, we have carried out the experiments reported in Scheme V and Figure 2. Whatever the starting compound, **1b** or **1b(DD)**, the same NMR spectrum is obtained with two uncoupled signals of equal intensity (the integration of which is 0.5 proton each) at δ −11.40 and 6.73. This shows clearly proton exchange between silicon and manganese. No ^3J(H-H) coupling is observed; this is due to the fact that no MnH–SiH (and hence MnD–SiD) is formed.

This prototropy gives a satisfactory explanation to the lack of success in obtaining optically active $(\eta^5\text{-}CH_3C_5H_4)(CO_2)\text{-}HMnSi^*H(1\text{-}C_{10}H_7)(C_6H_5)$[4] (Scheme VI).

Attempts at Intermolecular Exchange. Since we evidenced the intramolecular exchange, we tried to exchange the silyl ligand by another silicon hydride (Scheme VII). No exchange is observed in ^{1}H NMR spectroscopy when a silane is added to **1b**.

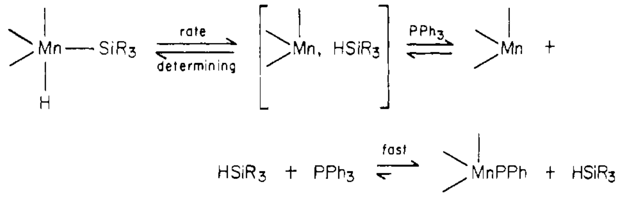
These results are in full agreement with Graham's kinetic observations (Scheme II). Indeed, a fast equilibrium on the NMR time scale between the 18-electron complex and the deinserted form would not allow observation of two distinct signals for both protons, bonded to manganese and silicon. The failure in exchanging the silane shows that the 16-electron complex and the silane are not independent but associated. Their dissociation needs the presence of strong ligand such as a phosphine. We can therefore propose the sequence shown in Scheme VIII.

Scheme VII

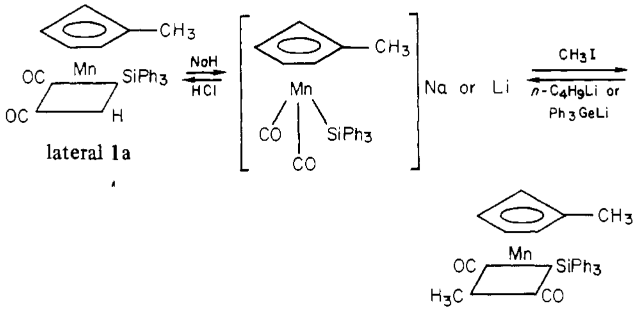


1b(DD)

Scheme VIII



Scheme IX



lateral **1a**

diagonal **1g**

Stereochemical Study. The lateral hydride **1a** is obtained by insertion of the manganese atom between silicon and hydrogen. However, one could expect to obtain the diagonal isomer by other ways, and we have tried to prepare such a compound.

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(40) Reference 33, p 300.

Scheme X

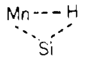
$$S(-)\text{-}(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(H)SiMePh(1\text{-}C_{10}H_7) \xrightarrow[\substack{n\text{-BuLi, } Cl_2,\ CCl_4, \\ PR_3, \text{ or } P(OR)_3}]{\text{retention}} R(+)\text{-}HSiMePh(1\text{-}C_{10}H_7)$$

When **1a** is treated with NaH, the corresponding sodium salt is obtained.[4] This salt can be alkylated to form the diagonal alkyl derivative[5] **1g** or protonated to re-form **1a** (Scheme IX). The lithium salt can also be formed by treatment of **1g** with butyllithium. Reaction of **1g** with Ph_3GeLi leads to the formation of Ph_3GeCH_3 and the lithium salt of the manganese complex, corresponding to the attack of Ph_3Ge^- at the methyl group of the diagonal complex **1g**.

Complex **1a** arising from the protonation of the anion is not, in any case, the diagonal isomer but the lateral one. It is interesting to notice that the steric crowding of the methyl group leads to the formation of the diagonal isomer exclusively.

Discussion

The peculiar bond between manganese, silicon, and hydrogen proposed by Graham (Scheme I) could be also represented as a structural tautomer,[10] which is, in fact, a three-centered bond:



This problem has already been pointed out for $[HW_2(CO)_{10}]^-$,[41] and the authors view this anion as a donor–acceptor complex in which the electrons of the W–H bond of $[HW(CO)_5]^-$ (an 18-electron species) are donated to the empty orbital of an electron-deficient $W(CO)_5$ moiety.

The chemical and the stereochemical behavior of the manganese hydride is not in agreement with that of independent silyl and hydrido ligands. Indeed, we observe that many different reagents give a very easy deinsertion,[8] which takes place with absolute retention of configuration at silicon[3] (Scheme X).

Furthermore, the low acidity of this hydride (only the very basic NaH is able to abstract the Mn–H proton[4]) contrasts with the very high acidity of the silyliron hydride $(CO)_4Fe(H)SiPh_3$ in which the ligands may be considered as independent.

Moreover, the cleavage of the Si–Mn bond in the optically active **1e** by $LiAlH_4$, H_2O, or MeOH takes place with inversion of configuration at silicon corresponding to a nucleophilic cleavage at Si[3] while the parent compound $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMePh(1\text{-}C_{10}H_7)$ is cleaved with retention of configuration.[42]

The most significative comments are the following:

(i) None of these results give evidence against the silicon–hydrogen bond interaction.

(ii) Some observations are satisfactorily explained by such an interaction, e.g., the high ^2J(Si–H) coupling constant and the absence of diastereoisomers in complex **1e**.[3] (Indeed, in a lateral structure the Mn atom should be chiral and two diastereoisomers should be observed.)

(iii) The prototropy observed between Mn–H and Si–H in **1b** as well as the lack of success in exchanging a silicon ligand in **1b** are in full agreement with the mechanism given for the reductive elimination of silane by phosphines. Indeed, the first equilibrium is slow on the NMR scale, and this allows the observation of two different signals for both protons and of their ^3J(H–H) coupling. Lack of success in exchanging the silicon hydride shows also the existence of an association between the 16-electron complex and the silane; only strong σ-donor ligands (e.g., phosphines and phosphites) can displace it.

(iv) It does not seem that the short distance between Si and H is a result of steric hindrance since the anion corresponding to **1a** gives diagonal **1g** with CH_3I but again lateral **1a** with HCl, independent of whether the anion has been generated from **1a** or **1g**. If there were steric hindrance in **1a**, the protonation of the anion would lead to the diagonal hydride in which the steric crowding would be greatly disminished. Moreover, we recall that the anion formed from diagonal **1g** gives also lateral **1a** by protonation.

All these features indicate clearly that there is an affinity between silicon and hydrogen that favors the cis geometry and causes the short distance between both atoms.

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Registry No. **1a**, 34664-13-6; **1b**, 79681-56-4; **1b(DD)**, 79681-57-5; **1b(D)**, isomer 1, 79681-58-6; **1b(D)**, isomer 2, 79681-59-7; **1c**, 79681-60-0; **1d**, 79681-61-1; **1e**, 79681-62-2; **1f**, 79681-63-3; **1g**, 79681-64-4; **2a**, 79681-66-6; **2b**, 79703-90-5; **2b(D)**, 79681-68-8; **2c**, 79681-70-2; **2d**, 79681-72-4; **3a**, 21701-61-1; **3b**, 63322-14-5; **3c**, 41422-91-7; **3d**, 7427-12-5; **3e**, 63322-24-7.

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