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Synthesis and Properties of Manganese Hydrides Having a Functional Silicon

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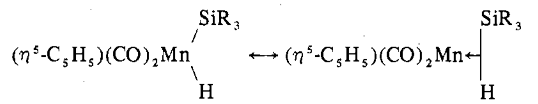
Received May 31, 1978

Complexes of the type $(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(H)SiR_1R_2X$ where R_1 = phenyl, R_2 = 1-naphthyl, and X = hydrogen, chlorine, fluorine, or methoxy have been prepared, and their chemical behavior has been studied. The different types of reactions they undergo are the following: (i) deinsertion reactions with formation of $R_1R_2Si(H)X$, (ii) cleavage of the Mn–Si bond with water or methanol, (iii) substitution reactions at silicon without cleavage of the Mn–Si bond, (iv) formation of salts by abstraction of H^+, and (v) reaction with $LiAlH_4$, which leads first to reduction of the function X and then to formation of the anion $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2MnSiR_1R_2H]^-$.

Introduction

Recently we described the synthesis and the chemical behavior of optically active (−)-hydrido(1-naphthylphenylmethylsilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese.[1] Cleavage reactions occur in three ways (see Scheme I).

The ease of deinsertion could be explained by taking into account the Si–H distance in the complex. This distance (1.76 Å) is shorter then the sum of the van der Waals radii (3.1 Å), showing a bonding interaction between both atoms.[2] This fact was represented by Graham and Hart-Davis as a resonance hybrid.[3]



$$(\eta^5\text{-}C_5H_5)(CO)_2Mn\begin{matrix}SiR_3\\ \\ H\end{matrix} \longleftrightarrow (\eta^5\text{-}C_5H_5)(CO)_2Mn\leftarrow\begin{matrix}SiR_3\\ | \\ H\end{matrix}$$

Substitution at silicon modifies the chemical behavior of the complexes. For instance, the triphenylsilyl complex is inert toward triethylamine, but the trichlorosilyl analogue behaves as an acid and easily leads to the corresponding anion.[4]

$$(\eta^5\text{-}C_5H_5)(CO)_2Mn(H)SiCl_3 \xrightarrow{(C_2H_5)_3N} [(\eta^5\text{-}C_5H_5)(CO)_2MnSiCl_3]^-(C_2H_5)_3NH^+$$

In this paper we describe the preparation and the chemical properties of complexes having a monofunctional silicon atom.

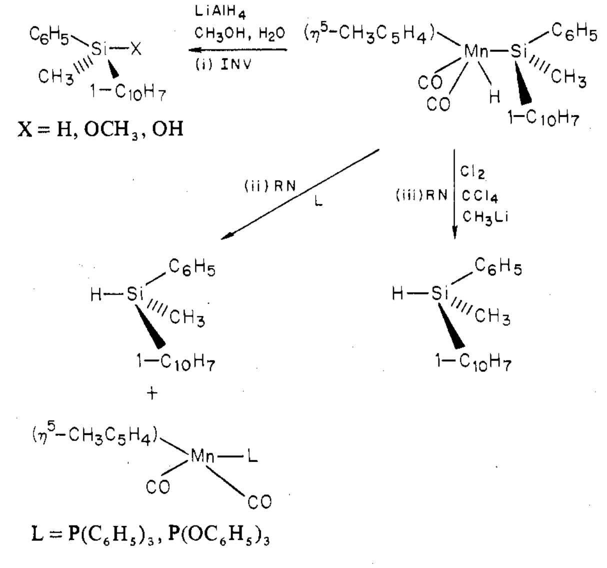
Experimental Section

All reactions were carried out under nitrogen, using a vacuum line, in Schlenk tubes. Photochemical reactions were performed in a Pyrex reaction vessel equipped with a water-cooled quartz finger. A 450 W UV lamp (Hanovia, high-pressure mercury) was placed inside the quartz finger.

Solvents were dried, distilled, and deoxygenated.

Melting points were taken under vacuum in a Dr. Tottoli's apparatus and are uncorrected. IR spectra were recorded in a Perkin-Elmer 257 spectrophotometer.

Scheme I[a]



[a] RN = retention of configuration; INV = inversion of configuration.

Satisfactory elemental analyses and mass spectra were obtained for all new compounds (Table V).

Starting material, $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, was purchased from Strem Chemicals Inc. Literature methods were used for the synthesis of $(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(H)Si(C_6H_5)_3$,[5] organosilicon compounds,[6] and $[(C_6H_5)_3P]_2NCl$.[7] All known compounds were compared with authentic samples.

Silylmanganese Hydrides. Hydrido(1-naphthylphenylhydrosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese, **1**, hydrido(1-naphthylphenylchlorosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese, **2**, hydrido(1-naphthylphenylfluorosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese, **3**, and hydrido(1-naphthylphenylmethoxysilyl)(η^5-methylcyclopentadienyl)dicarbo-

Table I. Melting Points, Infrared Carbonyl Bands, and Yields of Functional Silylmanganese Hydrides, (η^5-$CH_3C_5H_4$)Mn$(CO)_2$(H)SiPh-1-NpX

compd	X	mp, °C	color	ν(CO), cm^{-1} (in CCl_4)	% yield
1	H	91–92	yellow	1978 (s), 1918 (s)	41
2	Cl	113–114	pale yellow	1990 (s), 1934 (s)	68
3	F	103–103.5	yellow	1988 (s), 1930 (s)	36
4	OCH_3	86–87	yellow	1972 (s), 1910 (s)	21

Table II

starting material	time, days	% yield	
		(1-$C_{10}H_7$)-(C_6H_5)-SiH_2	(η^5-$CH_3C_5H_4$)-Mn$(CO)_2$P-$(C_6H_5)_3$
1	10	87	67
2	7	83	36
3	8	67	33
4	3	86	45

Table III

starting material	time, h	final product (identified by IR)	(1-$C_{10}H_7$)-(C_6H_5)SiH_2 % yield
1	8	(1-$C_{10}H_7$)(C_6H_5)Si(H)OCH_3	70
2	90	(1-$C_{10}H_7$)(C_6H_5)Si$(OCH_3)_2$	80
3	76	(1-$C_{10}H_7$)(C_6H_5)Si(F)OCH_3	76
4	12	(1-$C_{10}H_7$)(C_6H_5)Si$(OCH_3)_2$	75

Table IV. Interconversion Reactions of Functional Silylmanganese Hydrides

starting material	reagent	solvent	final product	% yield
1	Cl_2	CCl_4	2	30
1	PCl_5	CCl_4 or THF	2	23
2	$LiAlH_4$	ether/THF	1	*a*
4	PCl_5	CCl_4	2	20
4	$(i\text{-}C_4H_9)_2AlH$	hexane	1	18
4	BF_3	ether	3	*b*
3	$(i\text{-}C_4H_9)_2AlH$	hexane	1	19
3	$LiAlH_4$	ether/THF	1	*a*

[a] These reactions will be discussed later. [b] 3 was identified by IR spectroscopy but could not be induced to crystallize.

nylmanganese, **4**, were prepared by UV irradiation of (η^5-methylcyclopentadienyl)tricarbonylmanganese in the presence of the corresponding silane in hexane solution, by use of the technique of Jetz and Graham.[5] Compounds were isolated and purified after several recrystallizations from toluene/hexane (1/2) or ether/hexane (1/1) at −18 °C.

In a typical experiment 9.2 g (34.3 mmol) of (1-$C_{10}H_7$)(C_6H_5)-SiHCl and 7.5 g (34.4 mmol) of η^5-$CH_3C_5H_4Mn(CO)_3$ in 250 mL of hexane were irradiated for 27 h. After filtration of the solution and recrystallization from toluene/hexane, 10.2 g of **2** was obtained (see Table I for properties of **1**–**4**).

Deinsertion Reactions. Compounds **1**–**4** (1 mmol) were treated with 262 mg (1 mmol) of $P(C_6H_5)_3$ in 5–6 mL of benzene. The reaction was followed by IR spectroscopy; when the ν(CO) absorptions of the starting material were replaced by those of (η^5-$CH_3C_5H_4$)-$Mn(CO)_2P(C_6H_5)_3$[8] (1928 and 1860 cm^{-1} in benzene), the solvent was pumped off and the residue dissolved in ether and treated with an excess of $LiAlH_4$. After hydrolysis of the reaction mixture, column chromatography on alumina afforded the silane (elution with hexane) and (η^5-$CH_3C_5H_4$)$Mn(CO)_2P(C_6H_5)_3$ (elution with benzene) (Table II).

External UV irradiation of **1** (1 mmol) in the presence of $P(C_6H_5)_3$ (1 mmol) in hexane (50 mL) in a quartz Schlenk tube for 2 h afforded the deinserted silane and (η^5-$CH_3C_5H_4$)$Mn(CO)_2P(C_6H_5)_3$. No replacement of carbonyl was observed.

Cleavage Reactions. Cleavage with Water. Compound **1** (103 mg, 0.24 mmol) was stirred in 10 mL of ether and 5 mL of water. After 24 h, the ether layer was separated and dried over Na_2SO_4. IR carbonyl absorptions of **1** had disappeared. The solution was evaporated and the residue dissolved in di-*n*-butyl ether and refluxed for 1 h over $LiAlH_4$. After hydrolysis of the reaction mixture, the solvent was pumped off and the residue chromatographed on silica gel. A 39 mg amount (yield 70%) of (1-$C_{10}H_7$)(C_6H_5)SiH_2 was obtained.

Cleavage with Methanol. Compounds **1**–**4** (0.5 mmol) were each stirred in 5 mL of benzene and 2 mL of methanol. IR spectra were used in identification of the obtained silanes and were compared to those of authentic samples. After total reaction, the solvent was pumped off and the residue dissolved in ether and reduced with an excess of $LiAlH_4$. The usual workup afforded (1-$C_{10}H_7$)(C_6H_5)SiH_2 (Table III). In both reactions the manganese moiety decomposed. (η^5-$CH_3C_5H_4$)$Mn(CO)_3$ was obtained in very low yield.

Substitution at Silicon without Cleavage of the Mn–Si Bond. Compounds **1**–**4** (1 mmol) were each treated in the appropriate solvent by the equimolar amount of the reagent (Cl_2 was used as a solution in CCl_4, diisobutylaluminum hydride in hexane). The reactions, followed by IR spectroscopy, are almost instantaneous except for the reduction of **3** into **1** (6 days) (Table IV) and appear to be quantitative. The solvent was removed, the residue extracted with hexane, and the solution filtered and allowed to crystallize at −18 °C.

Reduction of Hydrido(1-naphthylphenylmenthoxysilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese. (η^5-Methylcyclopentadienyl)tricarbonylmanganese (3 g, 13.7 mmol) and 1-naphthylphenylmenthoxysilane (4.9 g, 12.6 mmol) ($|\alpha|^{25}{}_{D}$ − 65°) were irradiated for 24 h in 250 mL of hexane.

The product of this reaction (ν(CO): 1966 and 1910 cm^{-1} in ether) could not be induced to crystallize. The hexane solution was then treated overnight with an excess of $(i\text{-}C_4H_9)_2AlH$; the volume of the solution was reduced to ~40 mL and allowed to stand at −18 °C. Yellow crystals of racemic **1** were obtained (260 mg, overall yield 5%).

Tetraethylammonium (1-Naphthylphenylchlorosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, 7. A 1.01-g sample of **2** (2.2 mmol) in 40 mL of tetrahydrofuran was added to a suspension of 200 mg (excess) of sodium hydride in 10 mL of tetrahydrofuran at −78 °C. After complete addition, the reaction was allowed to warm at room temperature overnight (ν(CO) of the Na salt: 1878 and 1810 cm^{-1}). The solution was filtered and the solvent pumped off. The residue was dissolved in 20 mL of dichloromethane, and 365 mg of tetraethylammonium chloride (2.2 mmol) in 10 mL of dichloromethane was added. A fine precipitate of NaCl formed immediately; after a few minutes the solvent was pumped off and the residue extracted with 20 mL of tetrahydrofuran. The solution was filtered, 20 mL of hexane was added, and the solution was allowed to crystallize at −18 °C (647 mg).

Similar procedures were used for the other salts: μ-nitrido-bis(triphenylphosphorus) (1-naphthylphenylhydrosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **5**, μ-nitrido-bis(triphenylphosphorus) (1-naphthylphenylchlorosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **6**, tetraethylammonium (1-naphthylphenylchlorosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **7**, μ-nitrido-bis(triphenylphosphorus) (1-naphthylphenylfluorosilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **8**, μ-nitrido-bis(triphenylphosphorus) or tetraethylammonium (1-naphthylphenylmethoxysilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **9**, tetraethylammonium (1-naphthyldiphenylsilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **10**, μ-nitrido-bis(triphenylphosphorus) or tetraethylammonium (1-naphthylphenylmethylsilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **11**, and tetraethylammonium (triphenylsilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganate, **12**.

The reaction was slower for nonfunctional hydrides. In these cases the addition was done at room temperature.

All these salts were crystallized from pure tetrahydrofuran except **6**, **7**, and **10** which were crystallized from tetrahydrofuran/hexane (1/1) (Table VI).

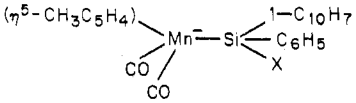
Reaction of Salts with Hydrogen Chloride. A 0.07-M solution of HCl in tetrahydrofuran was prepared by bubbling dry hydrogen chloride into the solvent.

Table V. Analytical Data for Silylmanganese Hydrides and Salts

	% calcd							% found						
compd	C	H	Mn	Si	Hal	N	P	C	H	Mn	Si[a]	Hal	N	P[b]
1	67.92	4.95	12.97	6.60				67.93	4.88	12.96	8.27			
2	62.81	4.59	11.98	6.11	7.74			62.23	4.62	11.99	5.97	8.16		
3	65.16	4.52	12.44					64.96	4.53	12.68				
4	66.08	5.07	12.11	6.17				65.62	4.94	12.31	6.46			
5	74.92	5.20				1.46		74.07	5.26				1.35	
6	72.33	4.92		2.81	3.57	1.41	6.23	71.92	4.95		3.02	3.93	1.27	6.56
7	65.34	6.64			6.04			64.88	7.05			6.07		
8	73.54	5.11			1.94	1.43	6.33	73.38	5.12			1.86	1.26	6.4
10	72.47	6.99	8.74			2.23		72.13	7.13	8.58			2.05	
12	70.97	7.25		4.84		2.41		70.52	7.27		4.99		2.57	

[a] Low precision due to the presence of manganese. [b] Low precision due to the presence of silicon.

Table VI. Melting Points, Color, and Infrared Carbonyl Bands of Silylmanganese Salts



salt	X	mp, °C	color	cation	ν(CO), cm^{-1} (CH_2Cl_2)	% yield
5	H	169-171	yellow	PPN	1854 (s), 1780 (s)	74
6	Cl	180-181	yellow	PPN	1870 (s), 1797 (s)	54
7	Cl	113-114	yellow	$(C_2H_5)_4N$	1868 (s), 1792 (s)	50
8	F	191-192	yellow	PPN	1860 (s), 1785 (s)	61
9	OCH_3	*a*	yellow in THF soln	PPN or $(C_2H_5)_4N$	1858 (s), 1775 (s) in THF	
10	C_6H_5	195-196	yellow	$(C_2H_5)_4N$	1850 (s), 1775 (s)	35
11	CH_3	*a*	yellow in THF soln	PPN or $(C_2H_5)_4N$	1890 (s), 1810 (s)	
12	*b*	181-182	yellow	$(C_2H_5)_4N$	1850 (s), 1773 (s)	40

[a] Not crystallized. [b] (Triphenylsilyl)manganese anion.

To 170 mg of **8** (0.17 mmol) in 10 mL of tetrahydrofuran was added 2.5 mL of HCl solution. The turbid reaction mixture was cooled and filtered, and 10 mL of pentane was added. The solution was allowed to crystallize at room temperature. A total of 45 mg of **3** (yield 60%) was obtained.

Similar procedures were used for the other salts. The silylmanganese hydrides were obtained in all cases with yields varying from 50 to 80%.

Reaction of 3 with Phenyllithium. To an ether solution (30 mL) of **3** (507 mg, 1.15 mmol) was added 4 mL (2.4 mmol) of phenyllithium (0.6 M in ether) at −78 °C. The solution was allowed to warm at room temperature (3 h). The ether was pumped off, the residue was dissolved in dichloromethane, and 659 mg (1.15 mmol) of PPN chloride in 10 mL dichloromethane was added. The solvent was pumped off, the residue dissolved in hot tetrahydrofuran, and the solution filtered and allowed to crystallize at −18 °C. A total of 664 mg of **8** (yield 59%) was obtained.

Depending on the function X and the lithium compound, substitution at silicon may also occur. Thus phenyllithium substitutes silicon when X = H or Cl and methyllithium when X = H, Cl, or F. With fluorine a mixture of substituted and nonsubstituted salt is obtained. The workup was similar to the one described. Yields vary from 30 to 40%. When the salts could not be crystallized, the magnesium hydrides were generated by treatment with hydrogen chloride and isolated.

Reaction of 7 with Phenyllithium. To **7** (600 mg, 1.02 mmol) in 20 mL of tetrahydrofuran was added 3 mL of phenyllithium (0.4 M in ether) at room temperature. After the usual workup, 200 mg of **10** (yield 31%) was obtained.

Reaction of Salts with $LiAlH_4$. Compound **6** (450 mg, 0.45 mmol) in 20 mL of tetrahydrofuran was slowly added to a suspension of $LiAlH_4$ (excess) in tetrahydrofuran. The solvent was pumpepd off after 2 h, and the residue was dissolved in 20 mL dichloromethane and hydrolyzed with water. The dichloromethane solution was separated and dried over Na_2SO_4; the solution was filtered, and the solvent was pumped off. The residue was crystallized from tetrahydrofuran, affording 150 mg of **5** (yield 35%).

A similar procedure with **8** afforded **5** in 34% yield.

Reaction of 5 with Water or Methanol. A 170-mg sample of **5** (0.18 mmol) in 5 mL of tetrahydrofuran and 2 mL of methanol was stirred for 8 days. An IR spectrum showed the formation of $(1\text{-}C_{10}H_7)(C_6H_5)Si(H)OMe$. The solvent was pumped off, and the residue was extracted with ether and reduced with $LiAlH_4$. Column chromatography on silica gel afforded 25 mg of $(1\text{-}C_{10}H_7)(C_6H_5)SiH_2$ (yield 59%).

A similar procedure was used for the reaction with water, except for the $LiAlH_4$ reduction that was performed in refluxing di-*n*-butyl ether. $(1\text{-}C_{10}H_7)(C_6H_5)SiH_2$ was obtained in 62% yield.

Attempt of Reaction of 6 or 12 with $P(C_6H_5)_3$. UV irradiation of equimolar amounts of **6** or **12** and $P(C_6H_5)_3$ in tetrahydrofuran for 6 h did not give any reaction. Carbonyl absorptions remained unchanged.

Reaction of 2 or 3 with $LiAlH_4$. A 0.3-M solution of $LiAlH_4$ in ether was prepared and titrated by means of iodine and sodium thiosulfate.

To 609 mg of **2** (1.3 mmol) in 30 mL of tetrahydrofuran was added 5 mL (1.5 mmol) of $LiAlH_4$ solution at −78 °C. The reaction mixture was allowed to warm at room temperature. IR spectroscopy showed the disappearance of the ν(CO) bands of **2** that were replaced by those of **1**. The solvent was then pumped off, the residue dissolved in hexane, and the solution filtered and allowed to crystallize at −18 °C. Compound **1** (425 mg, yield 77%) was obtained.

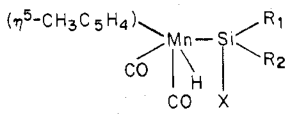
A similar procedure on **3** and further deinsertion with $P(C_6H_5)_3$ afforded $(1\text{-}C_{10}H_7)(C_6H_5)SiH_2$ (overall yield 55%).

An excess of $LiAlH_4$ led to salt formation.

Reaction of 1 with $LiAlH_4$. To 460 mg of **1** (1.08 mmol) in 20 mL of tetrahydroduran was added 5 mL of 0.3 M $LiAlH_4$ solution at −78 °C. The reaction mixture was left at room temperature. After one night, the IR spectrum showed a mixture of **1** and its parent lithium salt (ν(CO): 1861 and 1750 cm^{-1}). The usual workup afforded the PPN salt **5** (170 mg, yield 16%).

Results

The complexes studied are

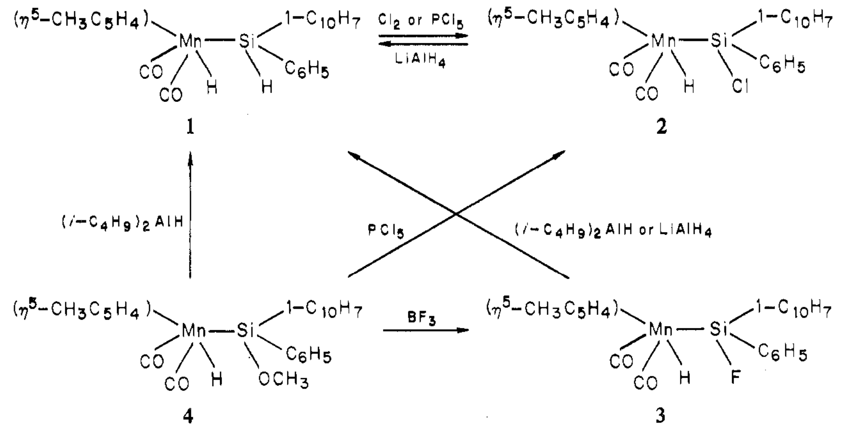


$R_1 = 1\text{-}C_{10}H_7$, $R_2 = C_6H_5$

1, X = H; **2**, X = Cl;

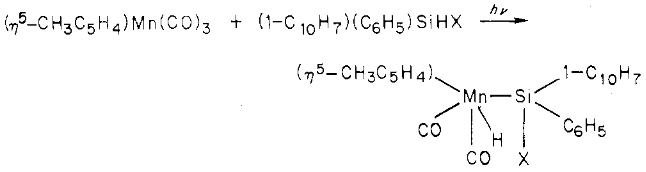
3, X = F; **4**, X = OCH_3

Scheme II. Substitutions at Silicon without Cleavage of the Mn-Si Bond



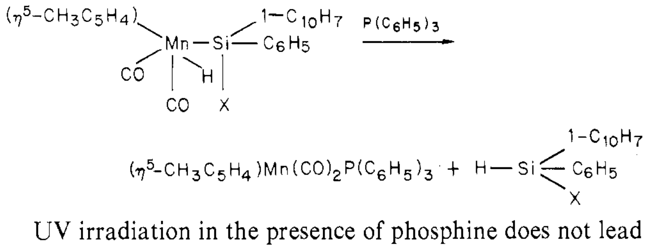
The different reactions they undergo are classified into five types: (i) deinsertion reactions, (ii) cleavage of the Mn–Si bond, (iii) reactions of substitution at silicon without cleavage of the Mn–Si bond, (iv) formation of salts by abstraction of H^+, and (v) reaction with lithium aluminum hydride.

(1) Synthesis of the Complexes. UV irradiation[5] of (η^5-$CH_3C_5H_4$)$Mn(CO)_3$ in the presence of functional hydrosilanes affords the new manganese–silicon compounds in which the silicon is functional:



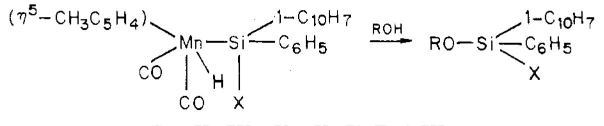
X = H, Cl, F, OCH_3

(2) Deinsertion Reactions. Compounds **1**–**4** undergo deinsertion of silane when treated with an excess of triphenylphosphine in a hydrocarbon solvent at room temperature. Reaction times for quantitative deinsertion are fairly longer (3–10 days) than for the nonfunctional complexes (only a few hours).



UV irradiation in the presence of phosphine does not lead to replacement of carbonyl but again to deinsertion of silane. This behavior has already been observed[1,3] for compounds in which silicon is not functional.

(3) Cleavage of the Mn–Si Bond. Treatment with nucleophiles such as water or methanol displaces the manganese moiety:



R = H, CH_3; X = H, Cl, F, OCH_3

When X = H, F, or OCH_3 the parent methoxysilanes are obtained, but when X = Cl, which is a good leaving group, further substitution at silicon takes place, and $(CH_3O)_2Si(1\text{-}C_{10}H_7)(C_6H_5)$ is obtained. The course of the reactions was followed by IR spectroscopy since the spectra of the products are different enough to allow their characterization. Nevertheless, substitution compounds were isolated and identified after $LiAlH_4$ reduction into 1-naphthylphenylsilane.

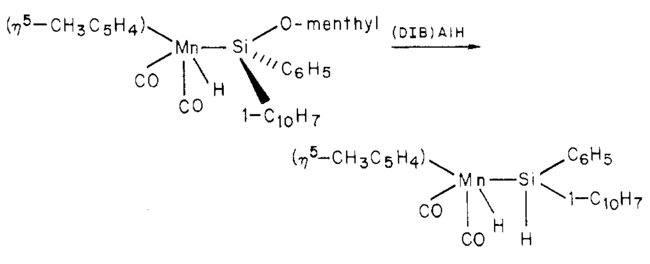
(4) Substitution at Silicon. In some cases it is possible to interconvert these compounds without cleavage of the silicon–manganese bond (Scheme II).

All the functions (Cl, F, OCH_3) may be reduced either by $LiAlH_4$ (Cl and F) or by diisobutylaluminum hydride (F and OCH_3). The halogenation of SiH is possible either by chlorine or phosphorus pentachloride. The Si–OCH_3 bond may be converted into Si–Cl by phosphorus pentachloride or into Si–F by boron trifluoride.

This type of reaction is rather uncommon with silicon bonded to transition metals. There are only a few reports of substitution at silicon bonded to metals,[9] although substitution reactions at functional germanium, tin, or lead bonded to several transition metals are well-known.[10]

Conversions are followed very easily by IR spectroscopy and appear to be almost quantitative. Chemical yields in isolated complexes are low because of several crystallizations needed to free them from byproducts.

Reaction of (–)-1-naphthylphenylmenthoxysilane with (η^5-$CH_3C_5H_4$)$Mn(CO)_3$ probably yields the optically active silicon–manganese hydride. This compound cannot be isolated but is reacted "in situ" with diisobutylaluminum hydride ((DIB)AlH) giving racemic **1**.

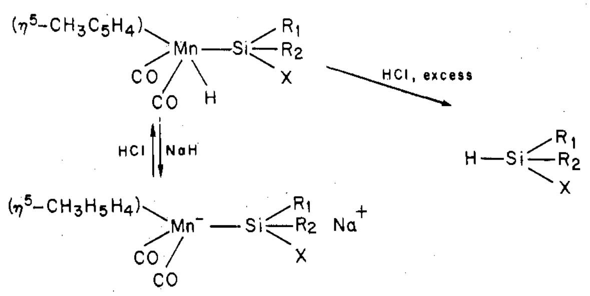


racemic **1**

(5) Abstraction of Hydrogen. Reaction of compounds **1**–**4** with a strong base such as sodium hydride leads to abstraction of hydrogen and formation of the corresponding anion. The same reaction takes place with the triphenylsilyl and the methyl-1-naphthylphenylsilyl derivatives. As opposed to the case of the reaction of trichlorosilylmanganese hydride, the triphenyl analogue did not react with weak bases such as triethylamine.[4] Most of the anions can be isolated as tetraethylammonium or μ-nitrido-bis(triphenylphosphorus) (PPN) salts which are crystalline, yellow solids (Scheme III).

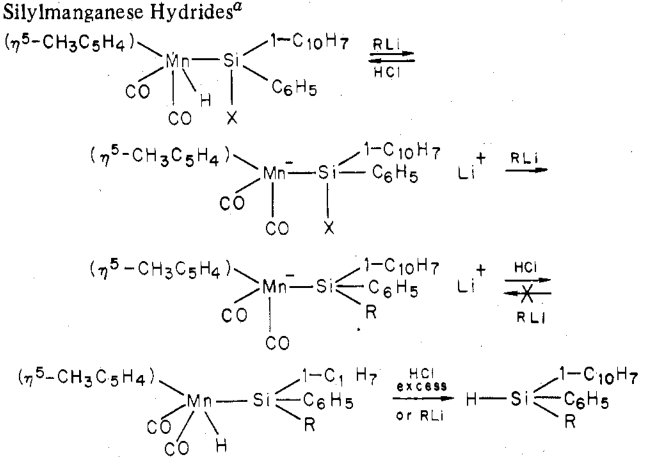
The structure of these salts is determined by generating the manganese hydride with the stoichiometric amount of hydrogen chloride.

Scheme III. Reaction with Sodium Hydride



5, $R_1 = 1\text{-}C_{10}H_7$, $R_2 = C_6H_5$, $X = H$
6 and **7**, $R_1 = 1\text{-}C_{10}H_7$, $R_2 = C_6H_5$, $X = Cl$
8, $R_1 = 1\text{-}C_{10}H_7$, $R_2 = C_6H_5$, $X = F$
9, $R_1 = 1\text{-}C_{10}H_7$, $R_2 = C_6H_5$, $X = OCH_3$
10, $R_1 = 1\text{-}C_{10}H_7$, $R_2 = X = C_6H_5$
11, $R_1 = 1\text{-}C_{10}H_7$, $R_2 = C_6H_5$, $X = CH_3$
12, $R_1 = R_2 = X = C_6H_5$

Scheme IV. Reactions of Organolithiums with Silylmanganese Hydrides[a]



[a] $R = CH_3, C_6H_5$; $X = H, Cl, F, OCH_3$.

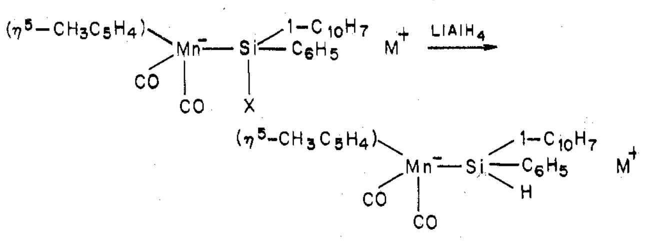
An excess of hydrogen chloride cleaves the silicon–manganese bond affording the silane. The manganese moiety decomposes.

Compounds **1**–**4** react with organolithiums affording the anions. The first step is an abstraction of hydrogen, but in some cases there is a subsequent reaction of the lithium compound at silicon. Phenyllithium displaces hydrogen in **1** and chlorine in **2**, and methyllithium displaces hydrogen in **1**, chlorine in **2**, and fluorine in **3** (Scheme IV). In fact, **3** leads to a mixture of the substituted and nonsubstituted anions.

This sequence is determined by treatment of the functional salts (prepared by hydrogen abstraction with sodium hydride) with the appropriate lithium compounds. Furthermore, reaction of methyl or phenyllithium gives deinsertion of silane on nonfunctional silylmanganese hydrides.

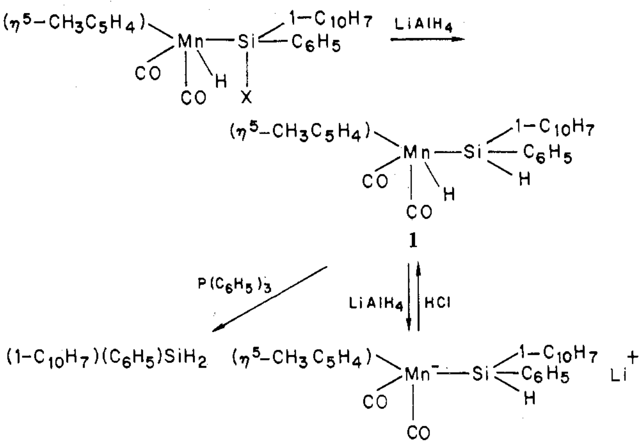
The new substituted salts are identified by treatment with hydrogen chloride and comparison of the parent hydrides with authentic samples.

Other reactions at silicon on anions are possible. Thus, salts **6** and **8** react with lithium aluminum hydride:

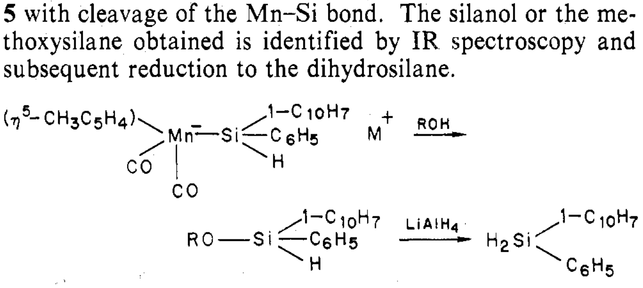


$X = Cl, F$; $M^+ = (CH_3CH_2)_4N^+, PPN^+$

Scheme V. Reactions of Silylmanganese Hydrides with $LiAlH_4$



Water or methanol reacts slowly with the functional salt **5** with cleavage of the Mn–Si bond. The silanol or the methoxysilane obtained is identified by IR spectroscopy and subsequent reduction to the dihydrosilane.



$R = H, CH_3$; $M^+ = PPN^+$

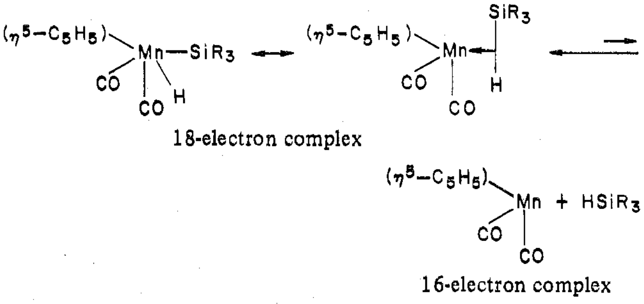
Triphenylphosphine does not react with salts even under UV irradiation.

(6) Reactions with Lithium Aluminum Hydride. Lithium aluminum hydride exhibits a reverse reactivity compared to organolithiums. When **2** or **3** is treated with an ethereal solution of $LiAlH_4$, first **1** is formed.

This first step corresponds to the reduction of the Si–X bond. At this point, deinsertion of the silane by means of triphenylphosphine affords in good yield 1-naphthylphenylsilane. When excess $LiAlH_4$ is added, the anion was then formed, and the salt **5** could be isolated (Scheme V). The evolution of these reactions was followed by IR spectroscopy.

Discussion

It is of interest to know whether the substitution reactions take place on the complex itself or on the deinserted form. Graham[3] suggested from kinetic studies that the replacement of the silane by triphenylphosphine took place on the 16-electron complex

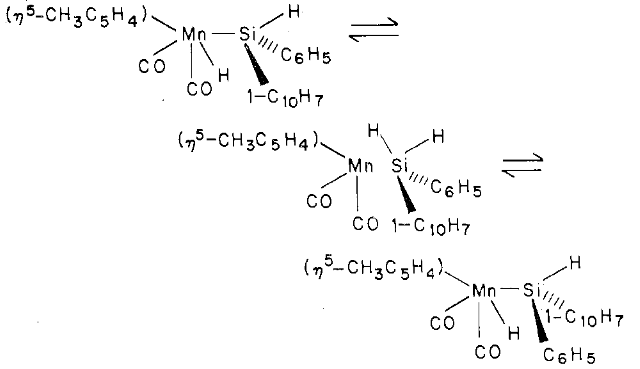


We could expect the reactions at silicon to take place on the latter. Nevertheless, 1-naphthylphenylsilane undergoes chlorination with phosphorus pentachloride much slower than the complex **1**, even in the presence of a catalytic amount of **1**.

Reactions at silicon bonded to manganese are possible, as proved by displacement of X by lithium compounds and

$LiAlH_4$ on the salts. This shows that reactions at silicon do not need the tautomeric equilibrium which, in the case of the anions, is obviously nonexistent.

The racemization observed for the reduction of hydrido(1-naphthylphenylmenthoxysilyl)(η^5-methylcyclopentadienyl)dicarbonylmanganese may be explained by the equilibrium with the deinserted form:



The comparison of the reactivities of the functional and nonfunctional silylmanganese hydrides toward nucleophiles is interesting. Both types of compounds undergo deinsertion with phosphines, and no carbonyl replacement is possible.

Functional silylmanganese hydrides easily gave the corresponding anions when treated with NaH, $LiAlH_4$, or organolithiums. Nonfunctional hydrides underwent H^+ abstraction with difficulty by means of NaH, whereas $LiAlH_4$ gave nucleophilic displacement of the manganese moiety at silicon and organolithiums led to deinsertion of silane.[1]

In none of the cases is attack by organolithiums at a carbonyl ligand observed. This type of reaction was found in other complexes with transition-metal–group 4B metal bonds.[11-13]

Lack of success in reacting triphenylphosphine with these salts in order to replace a carbonyl is not very surprising. Indeed, the increased electron density naturally increases the tendency of the metal atom to donate electrons back to carbon monoxide, and this donation makes the carbon monoxide ligands in metal carbonyl anions inert to substitution.[14]

The reactions reported here show the importance of the Si–H interaction in silylmanganese hydrides and the drastic changes of reactivity due to the functions at silicon. Nevertheless, we have described the possibility of substitution without cleavage of the Mn–Si bond.

Registry No. **1**, 68833-26-1; **2**, 68833-27-2; **3**, 68833-28-3; **4**, 68833-29-4; **5**·PPN, 68833-31-8; **6**·PPN, 68833-33-0; **7**·$(C_2H_5)_4N$, 68833-34-1; **8**·PPN, 68833-36-3; **9**·PPN, 68833-38-5; **9**·$(C_2H_5)_4N$, 68833-39-6; **10**·$(C_2H_5)_4N$, 68833-41-0; **11**·PPN, 68833-43-2; **11**·$(C_2H_5)_4N$, 68833-44-3; **12**·$(C_2H_5)_4N$, 68844-76-8; $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, 12108-13-3; $(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(H)Si(C_6H_5)_3$, 68833-45-4; $(1\text{-}C_{10}H_7)(C_6H_5)SiH_2$, 21701-61-1; $(1\text{-}C_{10}H_7)(C_6H_5)Si(H)OCH_3$, 41114-86-7; $(1\text{-}C_{10}H_7)(C_6H_5)Si(OCH_3)_2$, 36147-17-8; $(1\text{-}C_{10}H_7)(C_6H_5)Si(F)OCH_3$, 68813-34-3; 1-naphthylphenylmenthoxysilane, 33632-85-8; H_2O, 7732-18-5; CH_3OH, 67-56-1.

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Reactivity of Tricarbonyl(arene)manganese(I) and -rhenium(I) Cations. Nucleophilic Addition of Tributylphosphine to the Arene and Nucleophilic Displacement of the Arene by Acetonitrile

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Received August 14, 1978

The complexes $[(\text{arene})M(CO)_3]^+$, M = Mn or Re, readily react with tri-*n*-butylphosphine to yield the corresponding cyclohexadienylphosphonium ring adducts $[(\text{arene}\cdot PBu_3)M(CO)_3]^+$:

$$[(\text{arene})M(CO)_3]^+ + PBu_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\text{arene}\cdot PBu_3)M(CO)_3]^+$$

The equilibrium constant for the addition reaction (k_1/k_{-1}) is slightly greater for M = Re. The kinetics with M = Mn were studied in detail and activation parameters obtained for k_1 and k_{-1}. Limited kinetic data for M = Re suggest a similar rate. The manganese adducts in the absence of oxygen are photochemically converted to $[(\text{arene})Mn(CO)_2PBu_3]^+$, while the rhenium analogues fail to undergo this reaction. The $[(\text{arene})M(CO)_3]^+$ complexes react with CH_3CN by an associative mechanism to yield $[(CH_3CN)_3M(CO)_3]^+$ and activation parameters for both metals were obtained. In contrast to addition at the arene ring, the ring displacement with CH_3CN is about 2×10^4 times faster for rhenium.

Introduction

The reactivity of π-organic molecules such as olefins and arenes is often drastically altered upon coordination to a transition metal. In particular, cyclic π-hydrocarbons when coordinated to neutral or cationic organometallic fragments frequently undergo facile nucleophilic addition reactions. Such reactions are of considerable interest since they provide simple and sometimes unique routes to new organic molecules.[1-4]

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0020-1669/79/1318-0700$01.00/0