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Reactivity of $Fe(CO)_4(H)MPh_3$ (M = Si, Ge) and Mechanism of Substitution by Two-Electron-Donor Ligands: Implications for the Mechanism of Hydrosilylation of Olefins Catalyzed by $Fe(CO)_5$

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cis-$Fe(CO)_4(H)MPh_3$ (M = Si, Ge) complexes undergo carbonyl displacement with nucleophilic ligands (phosphines, phosphites) to give $Fe(CO)_3(H)(L)MPh_3$. With M = Si the geometry of these complexes depends on the nature of the solvent; in nucleophilic solvents the *mer*-*OC*-6-43 isomer is formed, while in nonnucleophilic solvents the *mer*-*OC*-6-23 isomer is obtained (the cis positions of H and Si are retained). These two isomers undergo concerted reductive elimination of silane with PPh_3. The *mer*-*OC*-6-43 isomer reacts 183 ± 19 times faster than the *mer*-*OC*-6-23 isomer in toluene at 26.0 °C, giving the same 16-electron intermediate; the calculated equilibrium constant for the interconversion of *OC*-6-43 and *OC*-6-23 is 823 ± 192 at 26.0 °C in toluene. Owing to the strong acidity of $Fe(CO)_4(H)MPh_3$ (pK_a estimated as <6 in CH_3CN) and of $Fe(CO)_3(H)(PPh_3)MPh_3$ (pK_a estimated as ≤8.94 in CH_3CN), reaction with basic two-electron-donor ligands [$P(alkyl)_3$, $P(cycloalkyl)_3$, NR_3] leads to the formation of the anionic trigonal-bipyramidal complexes $[Fe(CO)_4MPh_3]^-$ and $[Fe(CO)_3(L)MPh_3]^-$. *cis*-$Fe(CO)_4(H)SiPh_3$ reacts with isoprene to give $[Fe(CO)_4SiPh_3]_2$; this reaction is not observed with $Fe(CO)_3(H)(L)SiPh_3$. The versatile reactivity of these complexes sheds some light on the mechanism of hydrosilylation of olefins and conjugated dienes. Under thermal conditions previous coordination of the olefin to the metal in this reaction seems to be excluded.

Introduction

Hydrosilylation reactions are of great interest in organosilicon chemistry.[2] Iron pentacarbonyl and other iron complexes are efficient photochemical catalysts for these reactions.[3] The role of light is clear in the formation of the first active species, $Fe(CO)_4(H)SiR_3$,[4] but obscure for the successive steps. A recent study of the photochemical behavior of $Fe(CO)_4(H)SiR_3$[5] suggests that substitution of a carbonyl ligand by the olefin is the next step in the hydrosilylation reaction. Such a mechanism, however, may not apply to other transition metal catalysts.[2,6]

However, a radical mechanism has been proposed for the hydrosilylation of dienes catalyzed by $Fe(CO)_4(H)SiCl_3$.[7] This species is highly unstable,[4] and the study of its reactivity is difficult. Since the related complex $Fe(CO)_4(H)SiPh_3$ is more stable, a study of its reactivity with nucleophiles should give suitable information about the different reaction pathways which can occur during the hydrosilylation reaction.

Preliminary results on the reactivity of $Fe(CO)_4(H)SiPh_3$ with nucleophiles have already been reported.[8,9] We describe here additional reaction details and a mechanistic and kinetic study that allow a better understanding of the reaction processes.

Experimental Section

All reactions were carried out under nitrogen by using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. The following starting materials were prepared by literature methods: $Fe(CO)_4(H)SiPh_3$ (**1**),[4] (*OC*-6-43)-$Fe(CO)_3(H)(PPh_3)SiPh_3$,[8] $[Fe(CO)_4GePh_3]Et_4N$ (**14**).[10] Melting points were taken by using an oil circulating apparatus, in vacuo, and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 or 983 spectrophotometer, NMR spectra with a Varian EM 360 or EM 390 instrument or a Bruker WM 360 WB spectrometer (chemical shifts, δ, are relative to TMS, internal, or H_3PO_4, external). The physical properties of the complexes are given in Tables I–III.

Table I. IR Data for the Compounds Studied in This Work

compd no.	ν_{CO} absorptions in CH_2Cl_2, cm^{-1}	ref
1	2100 (m), 2045 (s), 2035 (sh), 2025 (s)	4, 9
2	2045 (w), 1980 (m), 1970 (s)	5
3[a]	2065 (s), 2000 (s), 1975 (sh)	8
3a[b]	2060 (s), 2036 (s), 1990 (sh)	
3b[b]	2053 (s), 2028 (s), 1983 (sh)	
4	2060 (w), 1990 (s)	
5	2060 (w), 1990 (s)	
6	2039 (vw), 1983 (s), 1971 (vs)	
7[c]	1992 (s), 1947 (s)	8
8[c]	2097 (m), 2036 (m), 2025 (s), 2022 (s)	11
9[b]	2050 (w), 1970 (s)	
10	2050 (w), 1990 (vs)	
11	1995 (m), 1907 (m), 1879 (vs)	19
12	1824 (s), 1818 (s)	
13	1855 (s), 1841 (s)	
14	1955 (m), 1907 (m), 1879 (s)	11
15	superimposable on that of **11**	
16	2000 (s, br)	

[a] In ether. [b] In toluene. [c] In hexane.

Table II. Selected NMR Data for the Compounds Studied in This Work (in CD_2Cl_2)

compd no.	δ_{Fe-H}	$^2J_{H,P}$, Hz	δ_{Si}	$^2J_{Si,H}$, Hz	$^2J_{Si,P}$, Hz	δ_P	$^2J_{P,P}$, Hz
1	−9.6		22.65 (d)	9.9			
2	−9.0 (d)	25		10[a]			
3[b]	−9.0 (d)	47					
4	−10.5 (d)	33					
5	−9.6 (d)	35					
6	−9.5 (d)	29	28 (q)	11	7.8		
7[c]	−9.3 (t)	32				93	
7[d]						94.7, 89.3	9

[a] Observed with ^1H resonance. [b] In ether. [c] In $CDCl_3$. [d] At 193 K.

Syntheses of the $Fe(CO)_3(H)(L)MPh_3$ Complexes 2, 4, 5, 9 and 10. These compounds are prepared by reaction of $Fe(CO)_4(H)MPh_3$ with the corresponding phosphorus ligands, in hexane, at room temperature. The synthesis of (*OC*-6-23)-tricarbonylhydrido(triphenylphosphine)(triphenylsilyl)iron (**2**) is given as an example. A solution of 4.26 g (10 mmol) of **1** and 2.60 g (10 mmol) of PPh_3 in 100 mL of hexane was

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(1) (a) Università di Perugia. (b) Université des Sciences et Techniques du Languedoc.

(2) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(3) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1978**, *128*, 345.

(4) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

(5) (a) Liu, D. K.; Brinkley, C. G.; Wrighton, M. S. *Organometallics* **1984**, *3*, 1449. (b) Knorr, M.; Schubert, U. *Transition Met. Chem. (Weinheim, Ger.)* **1986**, *11*, 268.

(6) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

(7) Connolly, J. W.; Hoff, C. D. *J. Organomet. Chem.* **1978**, *160*, 467. Connolly, J. W. *Organometallics* **1984**, *3*, 1333.

(8) Bellachioma, G.; Cardaci, G. *Inorg. Chem.* **1982**, *21*, 3232.

(9) Vioux, A. Thèse d'Etat, Montpellier, 1981.

(10) Carré, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1982**, *229*, 257.

Table III. Melting Points, Colors, Yields, and Elemental Analyses for the New Compounds

compd			yield,	anal. found (calcd), %					
no.	mp, °C	color	%	C	H	Fe	P	N	Si
2	185–187	yellow	41	70.15 (70.69)	4.61 (4.68)				
4	132–133	white	76	65.60 (65.92)	4.37 (4.37)		4.5 (4.37)		
5	128 dec	white	55	56.94 (56.96)	4.78 (4.77)		5.5 (5.91)		
6	113–116	white	80	60.30 (60.51)	5.15 (5.29)				
9	190 dec	yellow	30	66.60 (66.23)	4.53 (4.39)				
10	80–100 dec	white	58	62.36 (62.04)	4.22 (4.14)				
13	211–212	white	92	66.98 (67.22)	5.98 (5.96)	6.68 (6.67)		1.72 (1.67)	
15	149–150	white	81	67.79 (67.80)	7.14 (6.92)	4.20 (4.38)			4.16 (3.95)
16	144 dec	yellow	70	61.62 (61.84)	3.48 (3.54)				

stirred in the dark for 4 days. A yellow solid formed; it was filtered and recrystallized from 1/1 CH_2Cl_2/hexane. Complex **2** was obtained as a yellow microcrystalline solid, yield 2.7 g (41%). An analytical sample was obtained after several recrystallizations under the same conditions.

Reactions with phosphites are faster and the yields are higher.

Complex **8** was prepared by acidification of **14** and was used without purification due to high instability.[11] Complex **9** is also unstable in solution; a suitable ^{1}H NMR spectrum could not be recorded due to the presence of paramagnetic impurities.

(*OC*-6-23)-Tricarbonylhydrido(trimethylphosphine)(triphenylsilyl)iron (6). UV irradiation for 12 h (Hanovia mercury lamp, 100 W) of a solution of 1 g (4.1 mmol) of $Fe(CO)_4PMe_3$[12] and 1 g (3.8 mmol) of Ph_3SiH in 50 mL of hexane gave a tan precipitate, which was recrystallized from 1/3 CH_2Cl_2/hexane to give 1.44 g (80%) of **6**.

Tricyclohexylphosphonium Tetracarbonyl(triphenylsilyl)ferrate (15). A solution of tricyclohexylphosphine (1 g, 3.6 mmol) in 70 mL of hexane was added slowly to a solution of **1** (1.5 g, 3.5 mmol) in 30 mL of hexane at room temperature. A thick white precipitate formed immediately. The solid was filtered and crystallized from 1/1 CH_2Cl_2/hexane. White crystals of **15** (2 g, 81%) were obtained. Its IR spectrum was identical with that of **11** in the carbonyl absorption region. ^{31}P NMR (DMSO): δ 29 (a value close to that of $HP(C_6H_{11})_3$ in fluorosulfonic acid, δ 32.7).[13] ^{13}C NMR (DMSO): δ 219 (CO), 145, 135, 127, 126 (aromatic), 27.7, 27, 25.8, 24.8 (cyclohexyl).

Reaction of 2 with PPh_3. A solution of **2** (660 mg, 1 mmol) and PPh_3 (260 mg, 1 mmol) in 30 mL of toluene was stirred at room temperature for 1 week. The mixture was concentrated in vacuo and the residue chromatographed on acid alumina; Ph_3SiH (260 mg, 100%) (9/1 hexane/benzene) and *trans*-$Fe(CO)_3(PPh_3)_2$[14] (660 mg, 100%) (CH_2Cl_2) were isolated and compared to authentic samples.

Synthesis of *trans*-[$Fe(CO)_3(PPh_3)SiPh_3$]Et_4N (12) and *trans*-[$Fe(CO)_3[P(OPh)_3]SiPh_3$]Et_4N (13). A solution of **4** (1.07 g, 1.55 mmol) in 40 mL of THF was added to a suspension of 100 mg (excess) of NaH in 10 mL of THF at room temperature. After 30 min, solvent was removed in vacuo and the residue taken up in CH_2Cl_2 (~50 mL) and treated with a solution of Et_4NCl (300 mg) in 20 mL of CH_2Cl_2; a white solid formed. Solvent was removed in vacuo, and the residue was washed with water and dissolved in CH_2Cl_2. After the solution was dried over $MgSO_4$, hexane was added carefully in order to obtain two layers. Crystallization at −20 °C gave 1.2 g (92%) of white crystals of **13**.

Complex **12** could be obtained only in solution and was characterized by comparison of its IR spectrum with that of **13**. Attempts at crystallization produced only *trans*-$Fe(CO)_3(PPh_3)_2$[14] in moderate yield (55%).

The same procedure was used with other bases: Et_3N, $LiAlH_4$, CH_3MgX, or CH_3Li.

Protonation of 12 and 13 with HCl. A suspension of **13** (420 mg, 0.5 mmol) in 60 mL of ether was treated at room temperature with 5 mL of a 0.13 N solution of HCl in ether. The reaction was monitored by IR spectroscopy, and after disappearance of the ν_{CO} absorptions due to the anion, the solution was concentrated and hexane was added. Crystallization at −20 °C afforded 300 mg (98%) of **4**.

Treatment of a solution of **12** in CH_2Cl_2 under the same conditions gave complex **2**.

Reaction of Complex 1 with Isoprene. To a solution of **1** (856 mg, 2 mmol) in 30 mL of hexane was added 3 mL (excess) of isoprene at room temperature. A yellow precipitate formed, and after 3 h, it was filtered and crystallized from toluene/pentane at −20 °C to afford complex **16** (1.2 g, 70%).

Cleavage Reactions on Complex 1. H_2O. To a stirred solution of 428 mg (1 mmol) of **1** in 20 mL of ether was added 10 mL of H_2O at room temperature. The reaction was monitored by IR spectroscopy, and after 2 h the ν_{CO} absorptions due to **1** had disappeared. The organic layer was decanted and dried. Crystallization from hexane gave 220 mg (80%) of Ph_3SiOH (compared to an authentic sample[15].

MeOH. To a solution of 856 mg (2 mmol) of **1** in 30 mL of hexane was added 1 mL of methanol at room temperature. After a few minutes a red color developed. Solvent was removed in vacuo, and the residue was dissolved in pentane, filtered, and left at −20 °C overnight. Ph_3SiOMe was obtained (450 mg, 80%) and compared to an authentic sample.[15]

Cl_2. A solution of 428 mg (1 mmol) of **1** in 20 mL of benzene was stirred for 12 h at room temperature after addition of 2 mL of a 0.5 M solution of Cl_2 in benzene. The IR spectrum showed the absence of both ν_{CO} and ν_{SiH} bands. Solvent was removed in vacuo and the residue extracted with pentane and filtered. The pentane was removed in vacuo, and the residue was reduced with $LiAlH_4$ in ether. Ph_3SiH (250 mg, 96%) was obtained after chromatography on silica gel (80/20 hexane/benzene) and was compared to an authentic sample.[15]

CCl_4. Complex **1** (428 mg, 1 mmol) was dissolved in 3 mL of CCl_4. The solution darkened and became black in the course of a few hours. The reaction mixture was monitored by IR spectroscopy; after 1 week at room temperature it showed the disappearance of **1**. The solvent was removed in vacuo, and the residue was treated with $LiAlH_4$ as above. Ph_3SiH (260 mg, 100%) was obtained.

Reaction of Complex 1 with CO, $SbPh_3$, and $AsPh_3$. The reaction of $Fe(CO)_4(H)SiPh_3$ (**1**) with poor nucleophilic ligands (L = CO, $SbPh_3$, $AsPh_3$) in toluene results in the formation of the monosubstituted derivatives $Fe(CO)_4L$. A kinetic study was attempted but the results were irreproducible owing to the high reactivity of **1** toward oxygen. For a large excess of $SbPh_3$ (10/1 with respect to complex **1**) the rate is independent of the concentration of the ligand and, at 35 °C, the first-order rate constants are $(\sim 5\text{–}7) \times 10^{-5}\ s^{-1}$. The reaction with CO shows a rate of the same magnitude. These results suggest that the reductive elimination of Ph_3SiH is the rate-determining step. At higher concentrations of $SbPh_3$ (also with $AsPh_3$) the formation of an intermediate having the geometry *OC*-6-43 was observed from the ν_{CO} absorption band in the IR spectrum (Table I). The concomitant formation of the disubstituted derivatives, $Fe(CO)_3L_2$, as final products was observed.

Stability and Isomerization Equilibrium of Complex 2. Complex **2** (31.55 mg) was dissolved in 10 mL of toluene ($c = 4.76 \times 10^{-3}$ M) and to 5 mL of this solution was added 143.7 mg of Ph_3SiH ($c = 11.04 \times 10^{-2}$ M). The remaining 5 mL were allowed to react without Ph_3SiH. Both solutions were left at 30.0 °C, and the reaction mixtures were monitored by IR spectroscopy. The solution without Ph_3SiH showed decomposition with formation of $Fe(CO)_3(PPh_3)_2$. The solution with Ph_3SiH was stable for 94 h. During this time no isomerization to complex **3** could be detected.

Kinetic Measurements. The kinetic runs on isomer **2** with PPh_3 were carried out in toluene. A thermostated vessel (±0.1 °C) fitted with a rubber cap, from which aliquots were syringed at chosen intervals, was used.

Complex **3** was prepared in situ by reaction of **1** with PPh_3 at −20 °C in toluene, and complete reaction was achieved by bubbling nitrogen through the reaction mixture.[8] Owing to the high rate, reaction of **3** with PPh_3 was followed in a thermostated IR cell equipped with a flexible connection for filling. Examples of the IR spectra of the solution are given in Figure 1.

All the kinetic runs were carried out in the presence of a large excess of PPh_3 and Ph_3SiH in order to obtain pseudo-first-order conditions. The pseudo-first-order rate constants (k_{obs}) were obtained by monitoring both

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(11) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *85*, 237.

(12) Strohmeier, W.; Muller, F. J. *Chem. Ber.* **1969**, *102*, 3613.

(13) Olah, G. A.; McFarland, C. W. *J. Org. Chem.* **1969**, *34*, 1832.

(14) Lewis, J.; Nyholm, R. S.; Sandhu, S. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1964**, 2825. Clifford, A. F.; Mukherjee, A. K. *Inorg. Synth.* **1966**, *8*, 185.

(15) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Organosilicon Compounds*; Academic Press: New York, 1975.

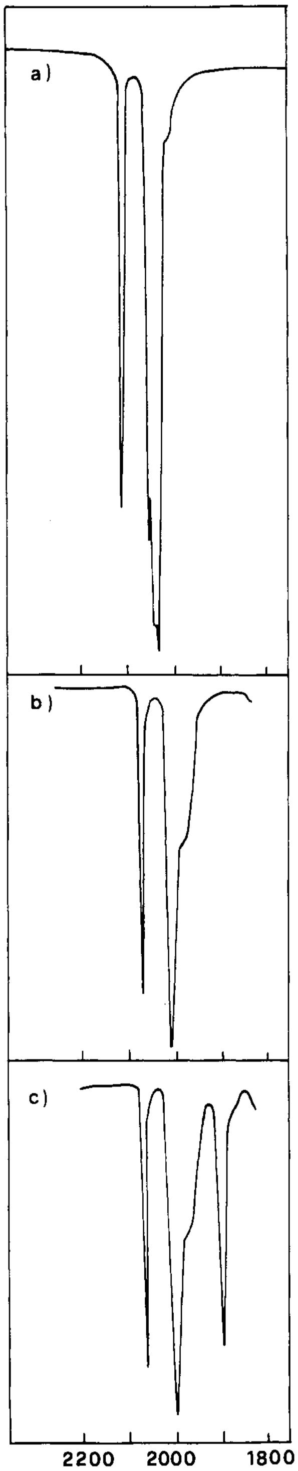


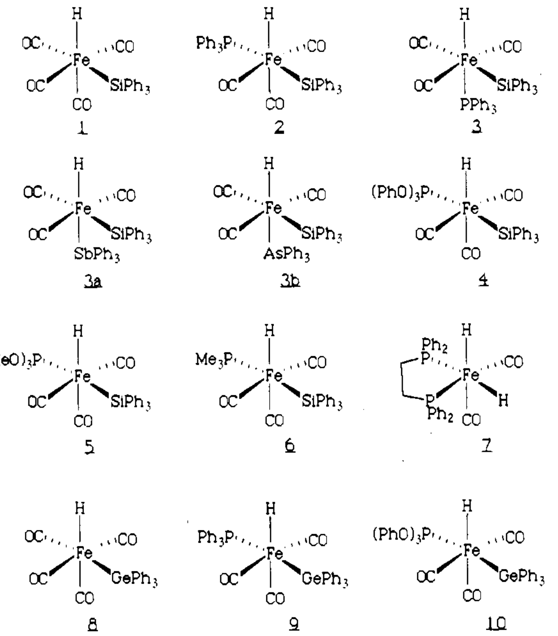
Figure 1. Inrared spectra at various times of the reaction between $Fe(CO)_4(H)SiPh_3$ and PPh_3 in toluene: (a) initial spectrum of $Fe(CO)_4(H)SiPh_3$; (b) spectrum after its conversion into complex **3**; (c) spectrum after partial conversion of complex **3** into $Fe(CO)_4(PPh_3)_2$.

the disappearance of complex **2** (or **3**) (plotting ln (D_0/D_t) vs t, where D_0 and D_t are the initial absorbance and that at time t of the reagent) and the appearance of $Fe(CO)_3(PPh_3)_2$ (plotting ln $D_\infty/(D_\infty - D_t)$ vs t, in which D_∞ and D_t are the absorbances at the end of the reaction and at time t, respectively).

Results

Chart I shows the formulas and the structures of the compounds studied in this work.

Chart I. List of the Compounds Studied in This Work

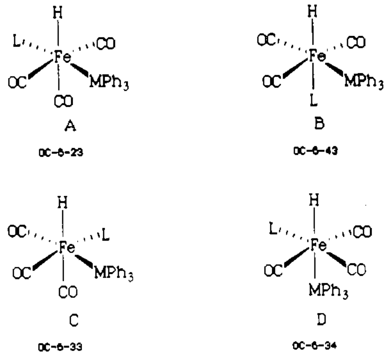


$[Fe(CO)_4SiPh_3]Et_4N$ **11** $[Fe(CO)_3(PPh_3)SiPh_3]Et_4N$ **12**

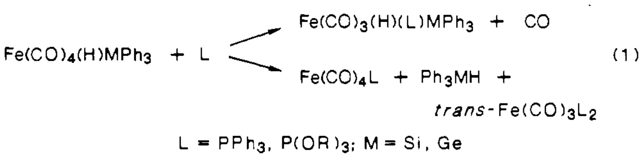
$[Fe(CO)_3P(OPh)_3SiPh_3]Et_4N$ **13** $[Fe(CO)_4GePh_3]Et_4N$ **14**

$[Fe(CO)_4SiPh_3](C_6H_{11})PH$ **15** trans-$Fe(CO)_4SiPh_3{}_2$ **16**

Chart II. Possible Isomers of $Fe(CO)_3(H)(L)MPh_3$



(a) Synthesis and Structure of $Fe(CO)_3(H)(L)MPh_3$ Complexes (L = Phosphines, Phosphites; M = Si, Ge). Reaction of $Fe(CO)_4(H)SiPh_3$ (**1**),[4] in hexane solution with a stoichiometric amount of triphenylphosphine at room temperature gives a fine precipitate of $Fe(CO)_3(H)(PPh_3)SiPh_3$ (**2**) contaminated with some *trans*-$Fe(CO)_3(PPh_3)_2$ (eq 1) (other products formed are



$$Fe(CO)_4(H)MPh_3 + L \begin{cases} \nearrow Fe(CO)_3(H)(L)MPh_3 + CO \\ \searrow Fe(CO)_4L + Ph_3MH + trans\text{-}Fe(CO)_3L_2 \end{cases} \quad (1)$$

$L = PPh_3, P(OR)_3; M = Si, Ge$

$Fe(CO)_4PPh_3$ and Ph_3SiH). This demonstrates the competition between carbon monoxide and triphenylsilane elimination.[4,16] According to the spectral data for the purified compounds (Tables I and II) the structure is assigned to *OC*-6-23,[17] isomer A (Chart II). This isomer is also obtained by photochemical reaction of $Fe(CO)_4PPh_3$ with Ph_3SiH at room temperature.[5,18] This observation is in contrast to that reported previously,[8] since, in ether or toluene solution at −18 °C, only isomer B (complex **3** for L = PPh_3 and M = Si) having the structure *OC*-6-43 was formed.

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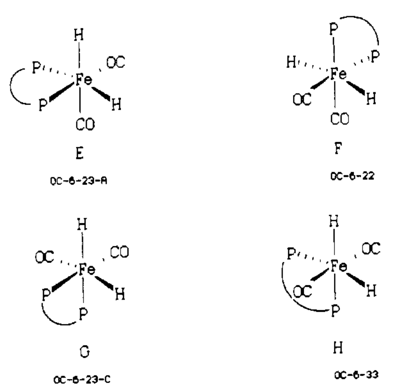
(16) Parish, R. V.; Riley, B. F. *J. Chem. Soc., Dalton Trans.* **1979**, 482.

(17) IUPAC Rule. *Pure Appl. Chem.* **1971**, *28*, 55. Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1273.

(18) Brinkley, C. G.; Dewan, J. C.; Wrighton, M. S. *Inorg. Chim. Acta* **1986**, *121*, 119.

Chart III. Possible Isomers of 7



The latter was not isolated and was characterized spectroscopically in solution.

Similar treatment of $Fe(CO)_4(H)SiPh_3$ (**1**) or $Fe(CO)_4(H)GePh_3$ (**8**) with other phosphorus ligands provides the corresponding complexes having the *OC*-6-23 geometry. A strong limitation, is, however, observed, since carbon monoxide replacement takes place only with less basic ligands (triphenylphosphine, phosphites). Protonation at phosphorus occurs with the more basic trialkylphosphines[8] (eq 2). Therefore, the tri-

$$\mathrm{Fe(CO)_4(H)SiPh_3 + R_3P \rightarrow [Fe(CO)_4SiPh_3]^-R_3PH^+} \quad (2)$$

$$\mathrm{R = alkyl}$$

methylphosphine derivative **6** was prepared by UV irradiation of $Fe(CO)_4PMe_3$ in the presence of triphenylsilane[5] (eq 3).

$$\mathrm{Fe(CO)_4PMe_3 + Ph_3SiH \xrightarrow{h\nu} Fe(CO)_3(H)(PMe_3)SiPh_3 + CO} \quad (3)$$

The reaction of **1** with 1,2-bis(diphenylphosphino)ethane (diphos) leads to the chelate complex **7** (Tables I and II), the structure of which was erroneously given in ref 8 as dicarbonyl[1,2-bis(diphenylphosphino)ethane](hydrido)(triphenylsilyl)iron. For this compound four isomers are possible (Chart III). The ^{31}P NMR spectrum at 300 K shows a single resonance with coalescence at 253 K. At 193 K two doublets are observed ($^2J_{P,P}$ = 9 Hz). The Fe–H signal is a triplet ($^2J_{H,P}$ = 32 Hz), implying that the two cis couplings are in the same range; this eliminates structure H, which should possess one cis and one trans coupling. Structures F and H are incompatible with the observation of two different ^{31}P resonances at low temperature. Thus, the only compatible isomers are the enantiomeric pair E and G, with *OC*-6-23 geometry (and with A and C configurations, respectively). This result is in agreement with the observations of Schubert and Knorr.[46]

(b) Synthesis and Structure of $[Fe(CO)_3(L)MPh_3]^-$ Complexes (L = CO, Phosphine, Phosphite; M = Si, Ge). The acidity of $Fe(CO)_3(H)(L)MPh_3$ is comparable to that of HCl, since the latter is displaced when treating the hydridoiron complexes with Et_4NCl (eq 4) as already observed for complex **1**.[19] A method

$$\mathrm{Fe(CO)_3(H)(L)MPh_3 + Et_4NCl \rightarrow [Fe(CO)_3(L)MPh_3]Et_4N + HCl} \quad (4)$$

$$\mathrm{L = CO,\ phosphine,\ phosphite;\ M = Si,\ Ge}$$

to obtain the anionic derivatives is the reaction with basic ligands [$L = NR_3$, PR_3 (R = alkyl)].[8,19]

The most convenient route to the tetraethylammonium salt is, however, proton abstraction with NaH[9,20] followed by cation exchange (eq 5). Contrary to reactions of other metal carbonyl

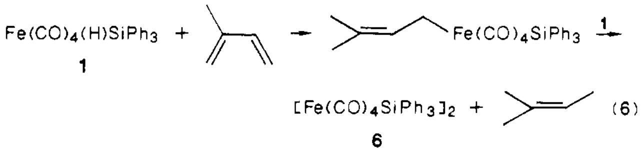
$$\mathrm{Fe(CO)_3(H)(L)MPh_3 + base \rightarrow [Fe(CO)_3(L)MPh_3]^-cation^+ \xrightarrow{Et_4NCl} [Fe(CO)_3(L)MPh_3]^-Et_4N^+ + cation^+Cl^-} \quad (5)$$

$$\mathrm{M = Si,\ Ge;\ L = phosphine,\ phosphite;\ base = Et_3N,\ NaH,\ LiAlH_4,\ MeMgBr,\ MeLi}$$

derivatives of silicon and germanium, nucleophiles such as $LiAlH_4$, CH_3MgX, and CH_3Li react only as bases, instead of attacking at a carbonyl[21,22] or cleaving the transition-metal–silicon bond.[23]

These anions can be protonated with HCl. In the case of the salt **12**, the reprotonation gives exclusively the hydride **2**, which possesses the *OC*-6-23 geometry, instead of the other possible isomer **3** (*OC*-6-43) even at low temperature. The structure of the anions **11**, **14**, and **15** can be assigned on the basis of the IR spectra, which show, as observed for similar complexes,[8,19,20,24] three stretching bands, assignable to the C_{3v} trigonal-bipyramidal structure, with the MPh_3 group occupying the apical position. Complexes **12** and **13** show two CO stretching bands in the IR spectra, assignable to the C_{3v} trigonal-bipyramidal structure with both L and MPh_3 ligands in trans positions.

(c) Reaction of 1 with Isoprene. Reaction of **1** with isoprene gives the dimer *trans*-$[Fe(CO)_4SiPh_3]_2$ (**16**), the formation of which may be rationalized as shown in eq 6 as an addition of the



acidic function to the conjugated diene, similar to the previously reported reactions of $Fe(CO)_4(H)SiCl_3$.[4,7] The second step of the reaction is the cleavage of the Fe–C σ-bond by another molecule of the acid **1**.[25] The phosphorus-substituted hydrides failed to react with dienes, probably due to their lower acidity.

(d) Kinetics and Mechanism of the Reductive Elimination of Hydrosilane. Hydrosilane elimination and carbonyl displacement are competitive reactions, as mentioned above. However, for complexes **1** and **8**, carbonyl replacement can be achieved in high yield, whereas for complexes containing phosphorus ligands, silane elimination is predominant (eq 7). In this reaction the products

$$\underset{\mathbf{2}}{\mathrm{Fe(CO)_3(H)(PPh_3)SiPh_3}} + \mathrm{PPh_3 \xrightarrow{room\ temp} Fe(CO)_3(PPh_3)_2 + Ph_3SiH} \quad (7)$$

can be isolated in quantitative yield.

The mechanism of the reductive elimination of silane in complexes **2** and **3** was studied kinetically, as described in the Experimental Section.

The kinetic results for the reaction of complex **3** with PPh_3 in toluene are given in Table IV. The reaction was monitored at different temperatures with excess PPh_3 and Ph_3SiH. Some of the kinetic runs were carried out at constant Ph_3SiH concentration while varying PPh_3 and others were carried out at constant PPh_3 concentration and varying Ph_3SiH, in order to distinguish the effects of the individual reagents. The variations of the pseudo-first-order rate constants (k_{obs}) with Ph_3SiH and PPh_3 concentrations are given in Figure 2. The values of $1/k_{obs}$ are plotted vs $1/[PPh_3]$ at a constant concentration of Ph_3SiH (Figure 2a) and vs $[Ph_3SiH]$ at a constant concentration of PPh_3 (Figure 2b).

The kinetic results for the reaction of complex **2** with PPh_3 are given in Table IV. The variations of k_{obs} are given in Figure 3.

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(19) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1647.

(20) Schubert, U.; Kunz, E.; Knorr, M.; Müller, J. *Chem. Ber.* **1987**, *120*, 1079.

(21) Carré, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Young, J. C.; Ricard, L.; Weiss, R. *J. Organomet. Chem.* **1979**, *179*, 215.

(22) Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1982**, *236*, 33.

(23) Colomer, E.; Corriu, R.; Vioux, A. *J. Chem. Res., Synop.* **1977**, 168. *J. Chem. Res., Miniprint* **1977**, 1939.

(24) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

(25) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

Table IV. Pseudo-First-Order Rate Constants (k_{obs}) for the Reaction of Complexes **2** and **3** with PPh_3 in Toluene

complex **3**			complex **2**		
$[HSiPh_3]$, M	$10[PPh_3]$, M	10^5k_{obs}, s^{-1}	$10^2[HSiPh_3]$, M	$10^2[PPh_3]$, M	10^6k_{obs}, s^{-1}
	1.031	26.4 ± 0.2[a]	5.58	4.25	2.66 ± 0.08[b]
	1.031	27.11 ± 0.08[a]	5.58	5.91	2.79 ± 0.05[b]
0.101	0.99	25.5 ± 0.1[a]	5.58	10.15	3.51 ± 0.04[b]
0.20	0.999	24.21 ± 0.07[a]	5.58	10.14	3.02 ± 0.09[b]
0.35	1.02	24.13 ± 0.08[a]	5.58	1.24	1.44 ± 0.03[b]
0.506	1.01	22.25 ± 0.05[a]	0.49	10.18	4.0 ± 0.1[b]
0.101	1.64	27.17 ± 0.02[a]	1.06	10.18	3.57 ± 0.09[b]
0.101	1.65	27.42 ± 0.08[a]	3.07	10.18	3.22 ± 0.05[b]
0.101	0.483	22.4 ± 0.1[a]	10.06	10.47	2.55 ± 0.07[b]
0.101	4.00	26.79 ± 0.04[a]	5.58	1.42	1.59 ± 0.03[b]
0.101	5.16	29.7 ± 0.2[a]	5.58	2.03	1.74 ± 0.05[b]
0.101	1.01	64.8 ± 0.3[b]	5.58	3.26	2.4 ± 0.1[b]
0.101	1.01	64.7 ± 0.2[b]			
0.101	5.13	71.1 ± 0.2[b]			
0.101	5.08	68.8 ± 0.2[b]			
0.101	1.01	236 ± 4[c]			
0.101	1.01	224 ± 4[c]			
0.101	5.04	225.3 ± 0.4[c]			
0.101	5.01	235.1 ± 0.6[c]			
0.101	1.01	224 ± 2[c]			

[a] 20.0 °C. [b] 26.0 °C. [c] 35.0 °C.

Table V. Kinetic Parameters at Various Temperatures for the Reaction of $Fe(CO)_3(H)(PPh_3)SiPh_3$ with PPh_3 in Toluene

	complex **3**				complex **2**	
T, °C	k_1, s^{-1}	k_{-1}/k_2	ΔH^*, kJ/mol	ΔS^*, J/(K·mol)	k'_1, s^{-1}	k'_{-1}/k_2
20.0	$(2.81 \pm 0.11) \times 10^{-4}$	0.118 ± 0.007	104.9 ± 5.0	63 ± 17		
26.0	$(7.14 \pm 0.31) \times 10^{-4}$	0.102 ± 0.006			$(3.90 \pm 0.24) \times 10^{-6}$	0.45 ± 0.03
35.0	$(2.29 \pm 0.10) \times 10^{-3}$					

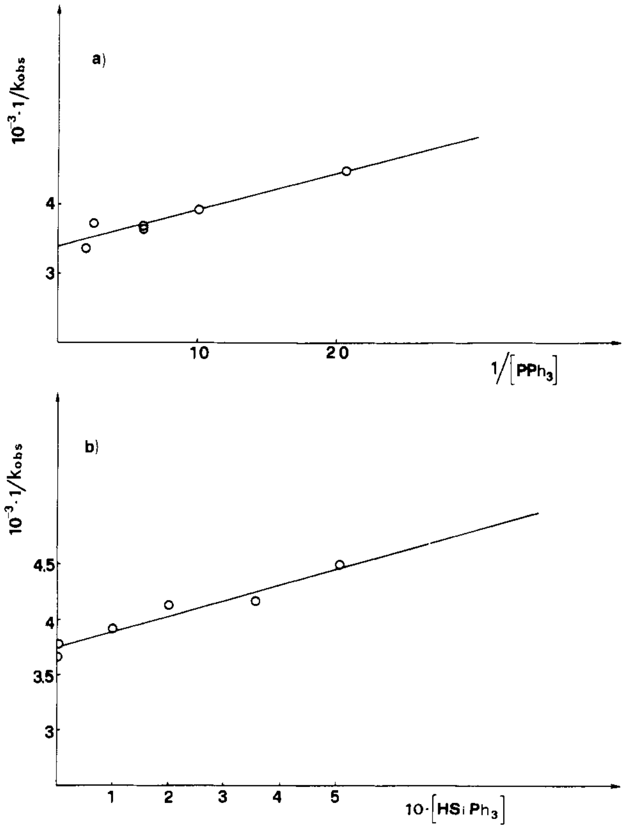


Figure 2. (a) $1/k_{obs}$ vs $1/[PPh_3]$ for the reaction of complex **3** with PPh_3 at 20.0 °C in toluene and with $[HSiPh_3] = 0.101$ M. (b) $1/k_{obs}$ vs $[HSiPh_3]$ for the reaction of complex **3** with PPh_3 at 20.0 °C in toluene and with $[PPh_3] = 10^{-1}$ M.

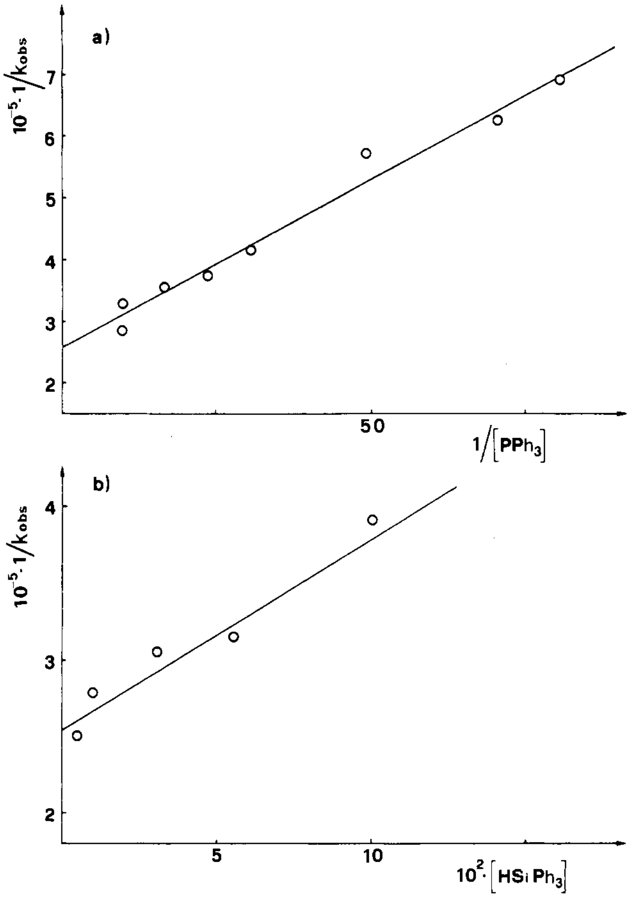


Figure 3. (a) $1/k_{obs}$ vs $1/[PPh_3]$ for the reaction of complex **2** with PPh_3 at 26.0 °C in toluene and with $[HSiPh_3] = 5.58 \times 10^{-2}$ M. (b) $1/k_{obs}$ vs $[HSiPh_3]$ for the reaction of complex **2** with PPh_3 at 26.0 °C in toluene and with $[PPh_3] = 10^{-1}$ M.

The values of $1/k_{obs}$ are plotted vs $1/[PPh_3]$ at constant Ph_3SiH concentration (Figure 3a) and vs $[Ph_3SiH]$ at constant PPh_3 concentration (Figure 3b).

The linear trend observed in Figures 2 and 3 can be explained on the basis of the concerted reductive elimination mechanism given in eq 8.

$$\begin{tikzcd}
\mathrm{Fe(CO)_3(H)(PPh_3)SiPh_3} \arrow[r, shift left, "k_1"] & \mathrm{Fe(CO)_3PPh_3 + Ph_3SiH} \arrow[l, shift left, "k_{-1}"] \arrow[d, "\mathrm{PPh_3}"', "k_2"] \\
 & \mathrm{Fe(CO)_3(PPh_3)_2}
\end{tikzcd} \qquad (8)$$

Assuming the steady-state approximation for the intermediate $Fe(CO)_3PPh_3$, a rate law (eq 9) is obtained, in which the meaning

$$v = \frac{k_1k_2[\mathrm{PPh_3}][\mathrm{c}]}{k_{-1}[\mathrm{Ph_3SiH}] + k_2[\mathrm{PPh_3}]} = k_{\mathrm{obs}}[\mathrm{c}] \qquad (9)$$

of the constants is given in eq 8 and [c] is the concentration of the complex.

From eq 9, the pseudo-first-order rate constant is

$$k_{\mathrm{obs}} = \frac{k_1k_2[\mathrm{PPh_3}]}{k_{-1}[\mathrm{Ph_3SiH}] + k_2[\mathrm{PPh_3}]} \qquad (10)$$

$$1/k_{\mathrm{obs}} = \frac{k_{-1}[\mathrm{Ph_3SiH}]}{k_1k_2[\mathrm{PPh_3}]} + \frac{1}{k_1} \qquad (11)$$

Plots of $1/k_{\mathrm{obs}}$ vs [Ph_3SiH] at a constant concentration of PPh_3 should be linear as observed in Figure 2b for complex **3** and in Figure 3b for complex **2**. Plots of $1/k_{\mathrm{obs}}$ vs 1/[PPh_3] at a constant concentration of Ph_3SiH should be linear as observed in Figure 2a for complex **3** and in Figure 3a for complex **2**. The intercept of the curves gives the k_1 values for the reductive elimination of Ph_3SiH. The slopes give the k_{-1}/k_2 values. In Table V, the values of k_1, k_{-1}/k_2, and activation parameters refer to complex **3** and the values of k'_1 and k'_{-1}/k_2 refer to complex **2**.

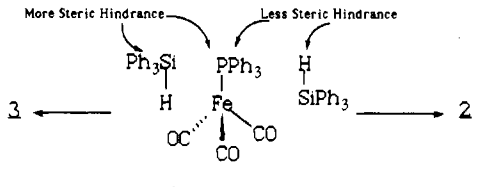
The mechanism shown in eq 8 is also supported by the activation parameters (Table V), which are very similar to the values observed in the literature[26,27] for the reductive elimination of Ph_3SiH.

The effect of the structure of the isomer (i.e. **2** or **3**) on the values of the rate constants of elimination of silane is surprising. Indeed, isomer **3** reacts 183 ± 19 times faster than **2** at 26.0 °C (Table V); this strong effect can be explained by the steric effect of PPh_3 in both structures.[28] In fact, in complex **3**, the cis arrangement of the bulky PPh_3 and $SiPh_3$ ligands deforms the octahedral structure, thus forcing a close contact between the H and $SiPh_3$ ligands and rendering the reductive elimination of silane easier. In complex **2**, the trans position of the bulkier ligands does not cause the same deformation and the elimination is more difficult.[29] This suggests three-center-two-electron bonding in complex **3**,[30-32] a good evidence for which would be the value of $J_{\mathrm{H,Si}}$; unfortunately, it could not be observed either by ^1H or ^{29}Si NMR (decomposition of **3** occurred partially during accumulation of the proton spectrum, and no signal was observed for silicon in this case). The steric effect is also observed in the values of k_{-1}/k_2 and k'_{-1}/k_2, which give the relative reactivity of the intermediate $Fe(CO)_3PPh_3$ with Ph_3SiH and PPh_3. The intermediate, $Fe(CO)_3PPh_3$, was observed in the photochemical reaction of $Fe(CO)_4PPh_3$[5a] and exhibits a C_s symmetry. Since this intermediate is the same for both **2** and **3** (eq 12), the k_2 values are the same

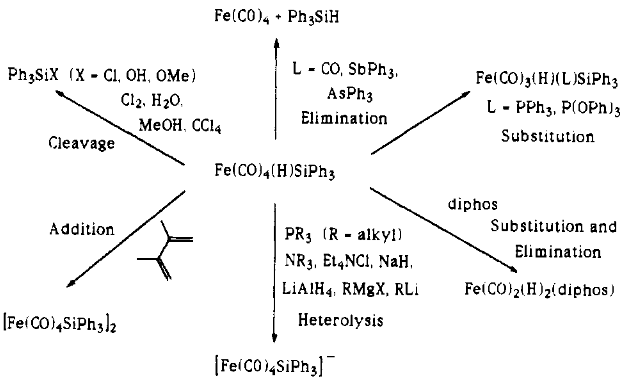
$$\mathbf{3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(CO)_3PPh_3 + Ph_3SiH} \underset{k'_1}{\overset{k'_{-1}}{\rightleftharpoons}} \mathbf{2} \qquad (12)$$

and the ratio of the relative rates is k'_{-1}/k_{-1}. This value for both reactions at 26.0 °C is 4.5 ± 0.6 and gives the relative rate for the oxidative addition of silane to $Fe(CO)_3PPh_3$, which leads to isomers **2** and **3**. The formation of isomer **2** is easier[33] because Ph_3SiH approaches the 16-electron complex with its less crowded substituent, i.e. the hydride, close to PPh_3, instead of the bulky phenyl groups (Scheme I). The effect of steric hindrance on oxidative addition (k'_{-1}/k_{-1} = 4.5 ± 0.6) is lower than that on reductive elimination k_1/k'_1 = 183 ± 19); this can be rationalized in terms of the high reactivity of the intermediate, the energy of which is close to that of the activated complex; therefore, the ability to discriminate the steric effect is reduced.

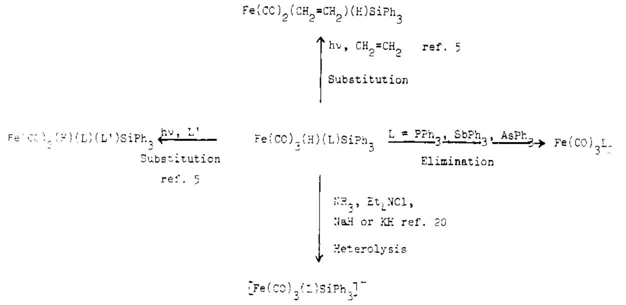
Scheme I. Formation of **2** from the 16-Electron Complex



Scheme II. Reactivity of $Fe(CO)_4(H)SiPh_3$



Scheme III. Reactivity of $Fe(CO)_3(H)(L)SiPh_3$



The isomerization equilibrium constant (K_e) between complexes **2** and **3** cannot be measured experimentally, but on the basis of eq 9, it can be calculated by using the rate constants of Table V, $K_e = k_1k'_{-1}/k_{-1}k'_1$ = 823 ± 192 at 26.0 C. This high value explains why isomerization of isomer **2** is not observed experimentally.

The less stable isomer, **3**, is formed in solvents having a nucleophilic character[8] (ether, benzene, toluene). Its formation is due to the strong trans-labilizing effect of the hydride ligand[34] in complex **1** with respect to Ph_3Si.[35] The trans effect of the hydride dissociates the trans CO, and the square-pyramidal structure obtained is stabilized by the solvent (via agostic hydrogen interaction).[36] Subsequently, complex **3** is obtained by reaction with PPh_3. In absence of the stabilizing effect of the nucleophilic solvent (for instance, in hexane), isomerization to other stable

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(26) Hart-Davis, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* **1971**, *93*, 4388.

(27) Harrod, J. F.; Smith, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2699.

(28) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(29) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

(30) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368.

(31) Carré, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 1272.

(32) Schubert, U.; Scholz, G.; Müller, J.; Ackermann, K.; Wörle, B.; Stansfield, R. F. D. *J. Organomet. Chem.* **1986**, *306*, 303.

(33) Brady, R.; De Camp, W. H.; Flynn, B. R.; Schneider, M. L.; Scott, J. D.; Vaska, L.; Werneke, M. F. *Inorg. Chem.* **1975**, *14*, 2669. Cardaci, G.; Bellachioma, G.; Zanazzi, P. F. *Organometallics*, in press. Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881.

(34) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1966; pp 24-29.

(35) On the contrary, the trans-labilizing effect of Cl_3Si is higher than that of the hydride; cf.: Pomeroy, R. K.; Xiang-Hu. *Can. J. Chem.* **1982**, *60*, 1279.

(36) Ziegler, T.; Versluis, L.; Tschinke, T. *J. Am. Chem. Soc.* **1986**, *108*, 612. Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572.

pyramidal structures is possible and formation of the more stable isomer **2** is observed.[5a]

Conclusion

Scheme II summarizes the reactivity of complex **1**. With poor nucleophilic ligands (L = CO, $SbPh_3$, $AsPh_3$) reductive elimination of silane is observed. The approximate first-order rate constant [(~5–7) × 10^{-5} s^{-1}] at 35 °C is independent of the nature of the entering ligand. This fact and the qualitative mass effect[8] support a concerted reductive elimination of Ph_3SiH. With increasing nucleophilicity of the ligand (L = PPh_3, $P(OPh)_3$], substitution of CO becomes predominant and formation of $Fe(CO)_3(H)(L)SiPh_3$ is observed. The structure of the complex depends on the experimental conditions. A further increase of the basicity of L [PEt_3, $P(C_6H_{11})_3$, amine] activates the heterolysis of the Fe–H bond with formation of the anionic species $[Fe(CO)_4SiPh_3]^-$. This process is a result of the acidic character of the Fe–H bond, already observed[19] and recently supported by theoretical calculations.[37] The displacement of HCl in the reaction with Et_4NCl suggests that **1** is at least as acidic as HCl in organic solvents, as already observed for other metal carbonyl hydrides.[38] The pK_a value for HCl in CH_3CN is 8.94,[39] a value close to that of $HCo(CO)_4$ in the same solvent (pK_a = 8.3).[40]

The reactivity of $Fe(CO)_3(H)(L)SiPh_3$ is given in Scheme III in which are added the results of the photochemical study of Wrighton and co-workers.[5a] With phosphorus ligands elimination of Ph_3SiH and formation of $Fe(CO)_3L_2$ is observed. Only under photochemical conditions was further substitution giving $Fe(CO)_2(H)(L)_2SiPh_3$ observed. With NR_3, Et_4NCl, and alkali-metal hydrides, formation of the anions $[Fe(CO)_3(L)SiPh_3]^-$ is observed. The displacement of HCl with Et_4NCl again shows the high acidity of the corresponding hydrides. Since phosphine ligands decrease the acidic character of hydrido carbonyl complexes and this effect is at least 3 pK_a units both in organic solvents[40] and in water,[41] it is possible to predict a pK_a value for **1** of, at least, 6 in CH_3CN. Thus **1** is a stronger acid than $HCo(CO)_4$. This strong acidity can be responsible for a heterolytic cleavage in the hydrosilylation of a diene with complex **1**. The absence of reaction of the complex $Fe(CO)_3(H)(L)SiPh_3$ (L = PPh_3) with isoprene can be explained by the less acidic character of this complex with respect to **1**.

However, since the trend of thermal stability is generally opposite to that of the acid character,[42] a mechanism involving a homolytic cleavage of the Fe–H bond cannot be excluded. Such cleavage is observed for the reaction of $Fe(CO)_4(H)SiCl_3$ with conjugated dienes[7] and in several reactions with $HCo(CO)_4$.[43]

Light is not necessary for the isomerization process, as previously proposed,[8] but it can activate the substitution of CO by poorly nucleophilic ligands such as olefins.[5]

The versatile reactivity of **1** and $Fe(CO)_3(H)SiPh_3$ suggests that the mechanism for hydrosilylation of olefins can follow different pathways as a function of the experimental conditions and the nature of the olefin. Under photochemical conditions the activation of the substitution of carbonyl ligands supports the classical mechanism involving insertion of the coordinated olefin in the Fe–H[41,44] or the Fe–Si bonds.[45] Under thermal conditions, however, a direct addition of the Fe–H group (by a radical or an ionic process) can occur as observed in the reaction of $Fe(CO)_4(H)SiCl_3$ with dienes[7] and in the reaction of **1** with isoprene.

Registry No. **1**, 30351-80-5; **2**, 90458-37-0; **3**, 81802-57-5; **3a**, 81802-60-0; **3b**, 81802-59-7; **4**, 117939-43-2; **5**, 117939-44-3; **6**, 117939-45-4; **7**, 81802-58-6; **8**, 118014-52-1; **9**, 117939-46-5; **10**, 117939-47-6; **11**, 33361-64-7; **12**, 117939-49-8; **13**, 117958-59-5; **14**, 82696-51-3; **15**, 117939-50-1; **16**, 86885-21-4; $Fe(CO)_4PMe_3$, 18475-02-0; Ph_3SiH, 789-25-3; *trans*-$Fe(CO)_3(PPh_3)_2$, 21255-52-7; Ph_3SiOH, 791-31-1; MeOH, 67-56-1; Ph_3SiOMe, 1829-41-0; Cl_2, 7782-50-5; CCl_4, 56-23-5; $Fe(CO)_5$, 13463-40-6; isoprene, 78-79-5.

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(37) Rabaâ, H.; Saillard, J. Y.; Schubert, U. Private communication.

(38) Hieber, W. *Angew. Chem.* **1952**, *64*, 400.

(39) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 3927.

(40) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(41) Hieber, W.; Hübel, W. *Z. Elektrochem.* **1953**, *57*, 235. Hieber, W.; Lindner, E. *Chem. Ber.* **1961**, *94*, 1417.

(42) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(43) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.

(44) Sanner, R. D.; Austin, R. G.; Wrighton, M. S.; Honnick, W. D.; Pittman, C. U., Jr. *Inorg. Chem.* **1979**, *18*, 928.

(45) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

(46) Schubert, U.; Knorr, M. Submitted for publication in *Inorg. Chem.*

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Rate Law and Product Distribution for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ Revisited

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Product distributions have been accurately determined or redetermined for the nitrosation reaction of $(NH_3)_5CoN_3^{2+}$ in acidic aqueous media at 25 °C, μ = 1.0 M. In Cl^--containing media, $(NH_3)_5CoCl^{2+}$ is formed along with $(NH_3)_5CoOH_2^{3+}$, and the product ratio $(NH_3)_5CoCl^{2+}$:$(NH_3)_5CoOH_2^{3+}$ is accurately linear in [Cl^-], even when the coanion is the strongly ion-pairing SO_4^{2-} ion. Indeed, the competition for a wide range of competitors Cl^-, Br^-, NO_3^-, HSO_4^-, and HSO_4^-/SO_4^{2-} at the 0.5 and 1.0 M concentration levels has been determined, with a similar result. Moreover, the results are independent of whether the supporting electrolyte contains largely Na^+ or H^+. For the mixed-anion systems, the anion competition has been measured for various binary combinations (0.5 M/0.5 M) of the above anions and for $CF_3SO_3^-$ and the more familiar ClO_4^-. The striking result is that competition for one anion is totally independent of competition by the other anion: Y = Cl^-, R = 0.217 ± 0.008 (17 determinations); Br^-, R = 0.215 ± 0.012 (15); NO_3^-, R = 0.460 ± 0.007 (15); HSO_4^-, R = 0.249 ± 0.011 (22). [For HSO_4^-/SO_4^{2-} (1:1), R = 0.416 ± 0.039 (12), and here R varies slightly and systematically with total sulfate concentration, consistent with some dissociation of HSO_4^- on dilution.] The general result refutes an earlier work which suggested that the R values were dependent on the nature of the coanion and were rationalized by an ion-pairing model. In the light of the fact that the rate law for the nitrosation reaction contains anion-independent and anion-dependent terms, the relative contributions of which depend on both the nature and concentration of the particular anions, the present work strongly suggests that the product distribution and the nitrosation rate law are independent; i.e., the products arise by a process subsequent to the rate-determining step, and an intermediate is involved. The detailed mechanism and in particular the implications of ion pairing for the intermediate are discussed.

Introduction

The detailed mechanism for the induced aquation reaction

$$(NH_3)_5CoN_3^{2+} + HNO_2 + H^+ + Y \rightarrow (NH_3)_5CoOH_2^{3+} + (NH_3)_5CoY + N_2 + N_2O$$

has received attention on at least four occasions.[1-4] The central issues have been (i) the question of a reactive $(NH_3)_5Co^{3+}$ in-

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(1) Haim, A.; Taube, H. *Inorg. Chem.* **1963**, *2*, 1199.