

(Ethynylhydrosilane)cobalt Carbonyl Complexes. Reactivity of the Silicon-Hydrogen Bond

Robert J. P. Corriu,* Joël J. E. Moreau,* and Hervé Praet

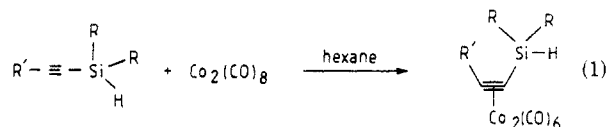
CNRS, Unité Associée 1097, Institut de Chimie Fine, Université des Sciences et Techniques du Languedoc, 34095 Montpellier Cedex 5, France

Received January 5, 1990

The reactivity of the silicon-hydrogen bond in (ethynylhydrosilane)cobalt carbonyl complexes has been studied. Halogenation of the Si-H bond was achieved under ionic or radical reaction conditions. A spontaneous dehydrogenative coupling reaction was observed with proton donors (methanol, water, benzoic acid, aniline). Hydrosilylation reactions of benzaldehyde, furfural, and phenylacetylene was found to take place without added catalyst. Whereas catalysis by cobalt cannot be excluded in the reaction with proton donors, it seems that the Si-H bond exhibits higher reactivity in the complex than in the parent silane. Di- and tricomplexed propynylsilanes have been formed upon selective complexation of two or three triple bonds. Although of lower thermal stability, complexes with a reactive Si-H bond were obtained.

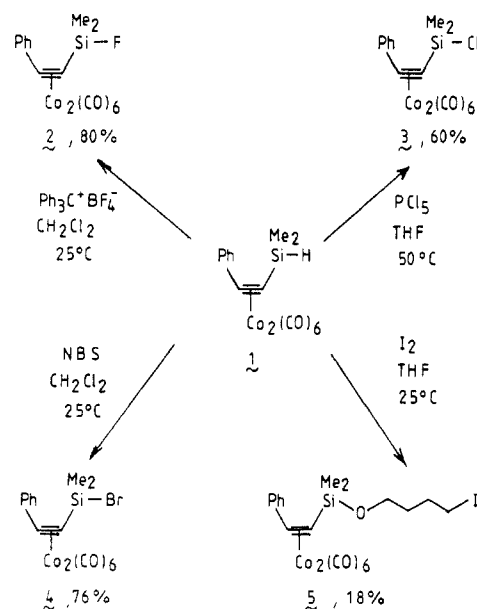
Introduction

We previously reported the preparation of cobalt carbonyl complexes of ethynylsilanes and examined some aspects of the reactivity at the silicon center.¹ Complexes with various functional groups attached to the silicon atom were obtained, and the $\text{Co}_2(\text{CO})_6$ unit was shown to withstand attack by a variety of reagents. Ethynylhydrosilanes reacted selectively at the carbon-carbon triple bond with $\text{Co}_2(\text{CO})_8$.^{1,2} It provided a straightforward route to cobalt carbonyl complexes with a silicon-hydrogen bond (eq 1).



As part of our study of organopolymetallic compounds and polymers we were interested in examining the reactivity of (ethynylhydrosilane)cobalt carbonyl complexes. The Si-H bond is reactive, and such complexes are of interest in organometallic synthesis. Moreover, whereas it is well established that the reactivity at a carbon atom adjacent to an organometallic moiety is affected by the latter, stabilizing for example a carbenium ion,³ few studies have dealt with reactivity at a silicon atom in such a position. Silicon hydrides in a position β to a (η^5 -cyclopentadienyl)iron dicarbonyl unit exhibited an enhanced reactivity toward methanol.⁴ Evidence for a very reactive exo Si-H bond was also found in (η^4 -silacyclopentadiene)iron tricarbonyl complexes.^{5,6} We report here some aspects of the reactivity of the silicon-hydrogen bond in

Scheme I. Halogenation Reactions of Complex 1



cobalt carbonyl complexes of mono, di-, or triethynylsilanes. A portion of this work has been communicated.⁷

Results and Discussion

(Monoethynylsilane)cobalt Carbonyl Complexes.

We first examined the reactivity of the silicon-hydrogen bond in (monoethynylsilane)cobalt carbonyl complexes. These were obtained by selective complexation of the triple bond in ethynylhydrosilane¹ according to eq 1.

Halogenation Reactions. Some reactions of the (dimethyl(phenylethynyl)silane)cobalt carbonyl complex 1 are presented in Scheme I. The hydrosilane 1 was converted to various halo derivatives in good yield. The fluorosilane 2 and the chlorosilane 3 were obtained under mild reaction conditions.⁸ The reaction of 1 with NBS in CCl_4 as solvent gave 4 in low yield (12%), together with some decomposition of the starting complex, whereas the use of CH_2Cl_2 allowed isolation of 4 in 76% yield. The cobalt carbonyl unit was not affected under such radical reaction conditions. The iodo derivative of 1 could not be isolated. Extensive decomposition occurred upon treat-

(1) Corriu, R. J. P.; Moreau, J. J. E.; Praet, H. *Organometallics* 1989, 8, 2779.

(2) Kotani, S.; Matsumoto, T.; Yamaguchi, H.; Shiina, K.; Sonogashira, K. *Chem. Lett.* 1989, 293.

(3) (a) Pettit, R.; Haynes, L. W. In *Carbenium Ions*; Olah, G. A., Schleyer, P. V. R., Eds.; Wiley-Interscience: New York, 1976; Vol. 5, p 2263, and references therein. (b) Seyferth, D. *Adv. Organomet. Chem.* 1976, 14, 97. (c) Nicholas, K. M.; Nestle, M. O.; Seyferth, D. In *Transition Metal Organometallics*; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, p 1, and references therein. (d) Seyferth, D.; Williams, G. H.; Eschbach, C. S.; Nestle, M. O.; Merola, J. S.; Hallgren, J. E. *J. Am. Chem. Soc.* 1979, 101, 4867.

(4) Bulkowsky, J. E.; Miro, N. D.; Sepelak, D.; Van Dyke, C. H. *J. Organomet. Chem.* 1975, 101, 267.

(5) Sakurai, H.; Hayashi, J.; Kobayashi, T. *J. Organomet. Chem.* 1976, 110, 303.

(6) (a) Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong, Chi Man, W. W. C. *J. Organomet. Chem.* 1987, 320, C1. (b) Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* 1987, 320, C7. (c) Carré, F. M.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wong Chi Man, W. W. C. *Organometallics* 1989, 8, 313. (d) Wong Chi Man, W. W. C. Thesis, Université Montpellier, Montpellier, France, 1987.

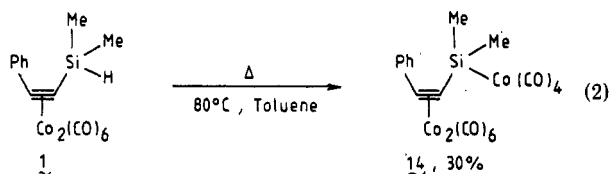
(7) Corriu, R. J. P.; Moreau, J. J. E.; Praet, H. *J. Organomet. Chem.* 1989, 376, C39.

(8) Bulkowski, J. E.; Stacy, R.; Van Dyke, C. H. *J. Organomet. Chem.* 1975, 87, 137.

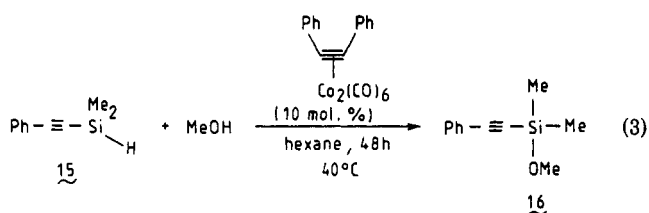
ment of a toluene solution of 1 with iodine even at low temperature. The reaction performed in THF allowed isolation in a moderate yield of the (δ -iodobutoxy)silane 5, derived from a ring-opening reaction⁹ of the THF solvent by the initially formed iodosilane.

Dehydrogenative Coupling. The reactions of silicon hydrides with proton donors usually require a nucleophilic or a transition-metal catalyst.¹⁰

Some reactions performed with ethynylhydrosilane complexes 1 and 6 are presented in Scheme II. The dehydrogenative coupling reactions needed no added catalyst. The methanolysis of complexes 1 and 6 were performed at 35 °C to give the methoxysilanes 7 and 8, respectively. A spontaneous reaction was observed also with water in acetone at room temperature to yield the silanol 9. *p*-Methoxyphenol also reacted with hydrosilane complexes 1 and 6 to give the corresponding phenoxy derivatives 10 and 11. Only moderate yields of pure material were obtained upon chromatographic purification. Benzoic acid and aniline also underwent the coupling reaction to give 12 and 13, respectively. It appears that ethynylhydrosilanes coordinated to cobalt spontaneously react with proton donors, whereas the uncomplexed molecule does not react in the absence of a catalyst. Dicobalt octacarbonyl itself is a known catalyst for such reactions of alcohols and amines with hydrosilanes.^{11,13} (Ethynylsilane)cobalt carbonyl complexes proved to be thermally unstable. The thermolysis of 1 gave 14, containing a silicon-cobalt bond (eq 2), together with small



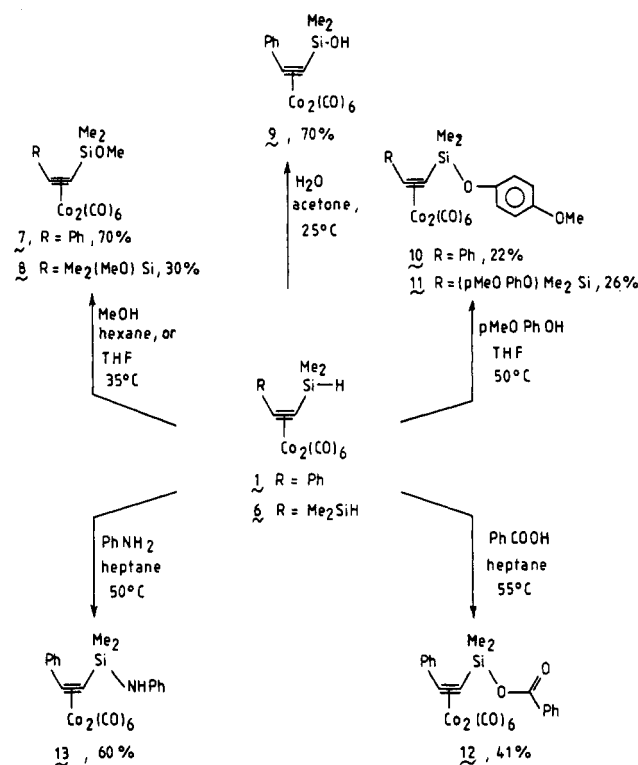
amounts of $\text{Co}_4(\text{CO})_{12}$. Therefore, traces of cobalt carbonyl arising from the decomposition of complex 1 could act as a catalyst for the observed reactions of proton donors. We also found that methanolysis of the uncomplexed ethynylhydrosilane 15 did take place in the presence of 10 mol % of a (diphenylacetylene)cobalt carbonyl complex (eq 3).



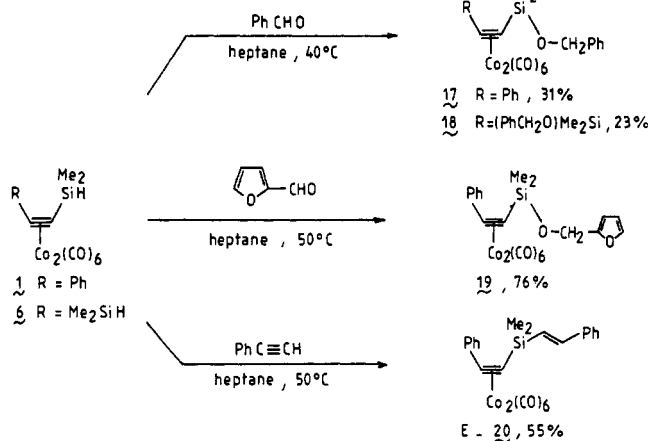
It is thus not clear whether the silicon-hydrogen bond in ethynylsilane becomes more reactive upon complexation, as was observed for (silole)iron carbonyl^{5,6} and (silyl-methyl)(η^5 -cyclopentadienyl)iron carbonyl complexes,³ or whether there is a cobalt catalysis.

Hydrosilylation Reactions. We studied the reactivity of complexed ethynylhydrosilanes under hydrosilylation reactions (cf. Scheme III). Complexes 1 and 6 underwent

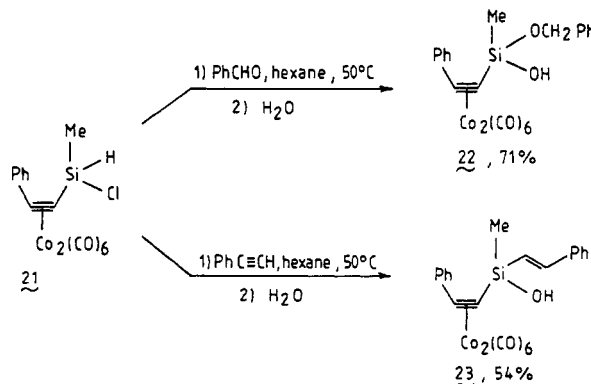
Scheme II. Dehydrogenative Coupling Reactions



Scheme III. Hydrosilylation Reactions



Scheme IV. Reactions of the Difunctional Ethynylsilane Complex 21



(9) (a) Voronkov, M. G.; Dubinskaya, E. I.; Komarov, V. G.; Pavlov, S. F. *Zh. Obshch. Khim.* 1976, 46, 1908. (b) Ho, T. L.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 774.

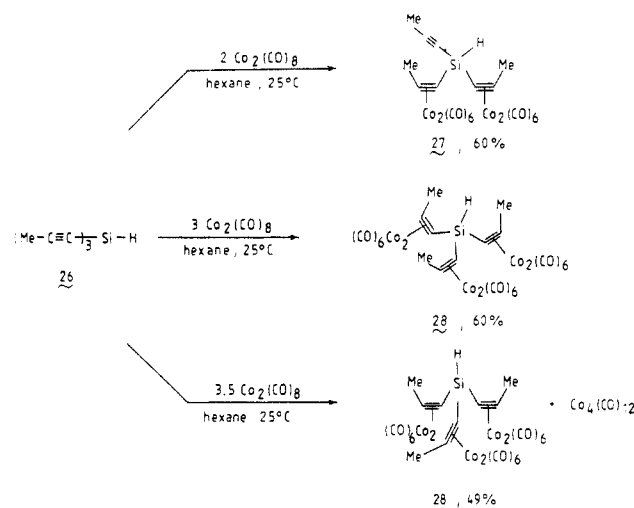
(10) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* 1984, 15, 43 and references therein.

(11) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* 1965, 87, 1133. (b) Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* 1969, 91, 7051. (c) Colomer, E.; Corriu, R. J. P. *Top. Curr. Chem.* 1981, 96, 79.

(12) Chalk, A. J. *J. Chem. Soc. D* 1970, 847.

(13) Magomedov, G. K. I.; Shkol'nik, O. V.; Syrkina, V. G.; Sigachev, S. A. *Zh. Obshch. Khim.* 1979, 2050.

addition to aldehydes without added catalyst. Whereas hydrosilylation of benzaldehyde occurred in moderate yields, a high yield was obtained with furfural. However, no spontaneous reaction occurred with ketones such as

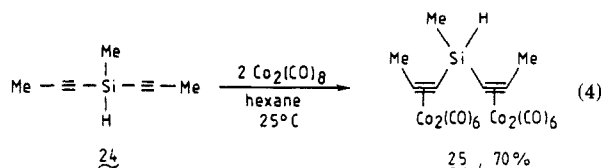
Scheme V. Reactions of Tripropynylsilane (26) with $\text{Co}_2(\text{CO})_8$ 

benzophenone up to 50 °C. A higher temperature caused decomposition of the (ethynylsilane)cobalt carbonyl complex. Hydrosilylation of the $\text{C}\equiv\text{C}$ triple bond in phenylacetylene without added catalyst led to the (*E*)-vinylsilane 20. No reaction was noted in the case of olefins such as styrene or hex-1-ene.

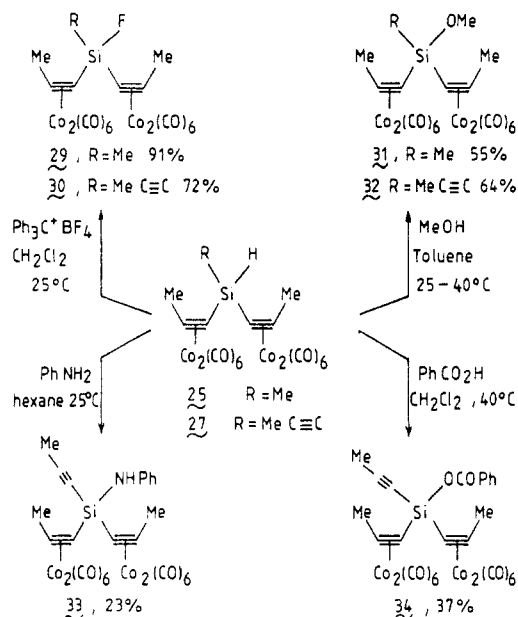
The addition reactions to benzaldehyde and phenylacetylene were also observed under mild conditions in the case of the difunctional ethynylsilane 21 as shown in Scheme IV. Isolation of the pure addition products was achieved by use of column chromatography, which caused hydrolysis of the unreacted Si-Cl bond. Interestingly the silanol derivatives 22 and 23 were isolated.

The hydrosilylation reaction proceeded under mild conditions. The silicon-hydrogen bond in the (ethynylsilane)cobalt carbonyl complex shows enhanced reactivity. In this case, no evidence for cobalt catalysis was obtained. Blank experiments conducted in the presence of 10 and 15 mol % of (diphenylacetylene)cobalt carbonyl did not reveal addition of ethynylhydrosilane 15 to benzaldehyde at 40 or 50 °C. Reactions performed in the presence of larger amounts of cobalt complexes or at higher temperatures resulted in the formation of several cobalt carbonyl species together with unreacted benzaldehyde and triphenylbenzene, respectively. The latter is derived from cobalt-catalyzed cyclotrimerization of phenylacetylene.

(Polyethynylsilane)cobalt Carbonyl Complexes. We also studied the complexation of di- and tripropynylsilanes. The reaction of 2 mol of $\text{Co}_2(\text{CO})_8$ with methyldipropynylsilane (24) in hexane at 25 °C gave the (dipropynylsilane)cobalt complex 25 in 70% yield (eq 4). No reaction of $\text{Co}_2(\text{CO})_8$ with the silicon-hydrogen bond was observed.



Whereas the reaction of 1 mol equiv of $\text{Co}_2(\text{CO})_8$ with tripropynylsilane (26) was not selective and led to a mixture of mono- and dicomplexed molecules, the reaction of 2 mol led selectively to the complexation of two propynyl groups (Scheme V). This was easily established by NMR analysis. Upon complexation of the propynyl group the methyl substituent appears 1.1 ppm downfield with respect

Scheme VI. Reactions of Dicomplexed Ethynylsilanes 25 and 27

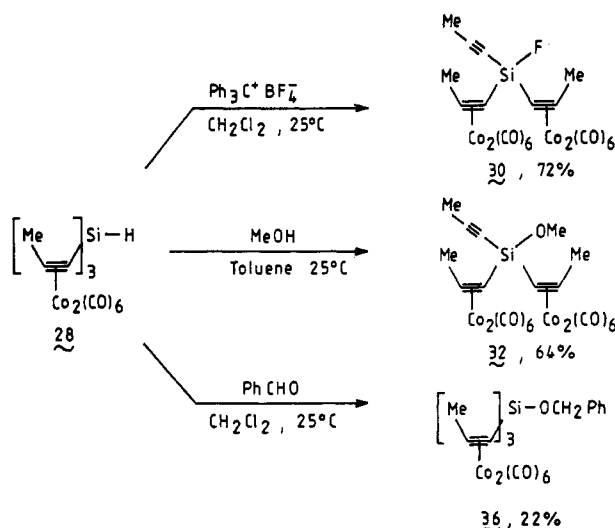
to the parent uncomplexed molecule. This observation allowed an unambiguous determination of the number of complexed triple bonds. Similarly the reaction of 3 mol of $\text{Co}_2(\text{CO})_8$ resulted in the complexation of the three $\text{C}\equiv\text{C}$ bonds in 26 to give complex 28 in 60% yield. The hindered silane 28 does not undergo oxidative addition to cobalt carbonyl. The reaction of 26 with 3.5 mol of $\text{Co}_2(\text{CO})_8$ led to the same tricomplexed molecule 28 together with some $\text{Co}_4(\text{CO})_{12}$. The latter is probably derived from some decomplexation reaction of complex 28. We observed that a hexane solution of 28 slowly decomposed at 30 °C. Whereas complex 1 with one complexed $\text{C}\equiv\text{C}$ bond was stable up to 60 °C, the thermal stability of the (ethynylsilane)cobalt carbonyl complex in solution decreases with the increasing number of $\text{Co}_2(\text{CO})_6$ units.

The reactivity of 25 and 27 is presented in Scheme VI. As observed previously, $\text{Ph}_3\text{C}^+\text{BF}_4^-$ behaved as a mild fluorinating agent and led to high yields of fluoro complexes 29 and 30. The reaction of proton donors such as methanol, aniline, and benzoic acid also proceeded smoothly at 25 or 40 °C to give substitution at the silicon atom. Complexes with Si-O and Si-N bonds, 31–34, were isolated. It is noteworthy that complexes 25 and 27, containing two $[(\text{C}\equiv\text{C})\text{Co}_2(\text{CO})_6]$ units, were found to react as readily as the less hindered complexes 1 and 6. The complex 27 also reacted with benzaldehyde. NMR analysis of the crude reaction mixture showed that some hydrosilylation had occurred but no pure adduct was isolated. The hydrosilylation product could also not be isolated in the reaction of phenylacetylene. Cyclotrimerization of the starting alkyne was observed.

The tricomplexed propynylsilane 28 was found to be a more fragile molecule. As shown in Scheme VII, the reaction of 28 with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ resulted in the expected fluorination at silicon, but complex 30, corresponding to the loss of one $\text{Co}_2(\text{CO})_6$ unit, was obtained. Similarly reaction of methanol led to the dicomplexed methoxysilane 32 in 64% yield. A substantial steric hindrance in complex 27 is probably responsible for the lability of one $\text{Co}_2(\text{CO})_6$ unit. Nevertheless, a reaction without decomplexation was observed with benzaldehyde. However, the hydrosilylation product 36 was isolated in moderate yield.

The cleavage of the silicon-hydrogen bond in di- and tricomplexed propynylsilanes by proton donors occurred

Scheme VII. Reactions of Tricoordinated Propynylsilane (28)



under mild reaction conditions without added catalyst. However, owing to the lower stability of these complexes, especially complex **28**, for which loss of one $\text{Co}_2(\text{CO})_6$ complexation was observed, cobalt catalysis may operate. The observed hydrosilylation of benzaldehyde, for which no evidence for cobalt catalysis was obtained, favors a higher reactivity of the Si-H bond in (ethynylhydrosilane) cobalt carbonyl complexes. This may be related to a weakening of the Si-H bond in the complex. Examination of the infrared spectra of ethynylhydrosilane complexes in the Si-H stretching frequency region shows a decrease of $20\text{--}30\text{ cm}^{-1}$ in wavenumber with respect to the $\nu(\text{Si-H})$ vibration in the parent uncomplexed molecule. A similar observation was reported in the case of the (silole)iron carbonyl complex.^{6c,d} The infrared absorption corresponding to the more reactive exo Si-H bond is 50 cm^{-1} lower than in the parent uncomplexed organosilane. On the other hand, that for the unreactive endo Si-H bond in the same complex is 25 cm^{-1} higher.

It seems that complexed silicon hydrides possess a Si-H bond which is more reactive than that in the parent uncomplexed silicon hydride. Whereas ethynylhydrosilanes are not reactive toward proton donors, aldehydes, or alkynes in the absence of a catalyst, we observed that complexed ethynylhydrosilanes underwent some spontaneous reactions. No evidence for catalysis by cobalt species was found in the hydrosilylation reaction; however, this cannot be excluded in the reactions with proton donors. Our observations are consistent with the chemical behavior of related silicon hydride iron complexes.⁴⁻⁶

Experimental Section

All reactions were carried out under nitrogen by use of a vacuum line and Schlenk tube techniques. Solvent were dried and distilled before use. Melting points were measured by using an oil-circulating apparatus under vacuum. The spectra were recorded with a Perkin-Elmer 298 spectrophotometer in the form indicated. ^1H NMR spectra were recorded on Varian EM 360 and EM 390 spectrometers, ^{13}C NMR spectra with a Bruker WP 80 spectrometer, and ^{29}Si NMR spectra on a Bruker WP 200 SY apparatus. Solvents and chemical shifts (δ relative to Me_4Si) are indicated. Mass spectra were measured on a JEOL JMS-D100 or JMS-DX 300 mass spectrometer (ionization energy 70 eV). Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique.

(Monoethynylhydrosilane)cobalt Carbonyl Complexes. Complex **1** was obtained upon reaction of dimethyl(phenylethynyl)silane with dicobalt octacarbonyl as previously described.¹

Complex **6** was similarly obtained upon selective complexation of bis(dimethylsilyl)ethyne¹⁴ with cobalt carbonyl. Complex **21** was obtained from chloromethyl(phenylethynyl)silane according to the same procedure.¹

Halogenation Reactions of Complex 1. With $\text{Ph}_3\text{C}^+\text{BF}_4^-$. To a solution of **1** (1.7 g, 3.8 mmol) in 5 mL of CH_2Cl_2 at -20°C was added a solution containing $\text{Ph}_3\text{C}^+\text{BF}_4^-$ (1.25 g, 3.8 mmol) in 5 mL of CH_2Cl_2 . The solution was then warmed to room temperature and stirred for 1 h. The solvent was pumped off and the black residue extracted with hexane. Filtering, concentrating, and cooling the resulting solution afforded 1.4 g (yield 80%) of black crystals of the fluorosilane **2**, mp $93\text{--}94^\circ\text{C}$, having characteristics similar to those previously reported.¹

With PCl_5 . A solution of PCl_5 (0.7 g, 3.4 mmol) in 5 mL of THF was added to **1** (1.5 g, 3.4 mmol) dissolved in 5 mL of THF. The mixture was stirred at 50°C for 1 h and then pumped to dryness. Extraction of the residue with the minimum quantity of hexane and crystallization at -20°C gave 0.98 g (yield 60%) of complex **3** as black crystals: mp $90\text{--}92^\circ\text{C}$; IR (CCl_4 , cm^{-1}) $\nu(\text{C}\equiv\text{O})$ 2093, 2060, 2030; ^1H NMR (CDCl_3 , δ) 0.75 (6 H, s), 7.4 (5 H, m); ^{13}C NMR (CDCl_3 , δ) 3.83, 128.39, 129.06, 130.07, 137.59. Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{O}_8\text{ClSiCo}_2$: C, 39.98; H, 2.30. Found: C, 39.73; H, 2.02.

With NBS. To a solution of **1** (1.5 g, 3.4 mmol) in 5 mL of CH_2Cl_2 at 0°C was added 0.6 g (3.4 mmol) of NBS in 5 mL of CH_2Cl_2 . The mixture was stirred at 25°C and pumped to dryness. The residue was extracted with hexane and crystallized at -20°C , to give 1.35 g (yield 76%) of complex **4** as black crystals exhibiting physical characteristics similar to those reported.¹

With Iodine. To a solution of **1** (2.0 g, 4.5 mmol) in 5 mL of THF was added a solution containing 1.14 g (4.5 mmol) of iodine in 5 mL of THF. The reaction mixture was then stirred at room temperature for 6 h and pumped to dryness. The crude product was chromatographed over a column of Florisil (60–100 mesh, Fluka). Upon elution first with pentane and then with a pentane/ Et_2O (95/5) mixture a black band was collected. After evaporation of the solvents 0.52 g (yield 18%) of complex **5** as a black oil was obtained: IR (CCl_4 , cm^{-1}) $\nu(\text{C}\equiv\text{O})$ 2087, 2049, 2019; ^1H NMR (C_6D_6 , δ) 0.33 (6 H, s), 1.46 (4 H, m), 2.73 (2 H, t), 7.20 (5 H, m); ^{13}C NMR (CDCl_3 , δ) 0.16, 6.50, 30.28, 33.62, 62.43, 128.42, 129.24, 130.00, 138.43. Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_8\text{I}_2\text{SiCo}_2$: C, 38.23; H, 3.04. Found: C, 38.08; H, 3.07.

Reactions of Complex 1 with Proton Donors. Methanol. A hexane solution of **1** (1.0 g, 2.2 mmol) with an excess of methanol (145 μL , 3.6 mmol) was stirred at 35°C for 24 h. The solvent was then evaporated under vacuum and the black residue extracted with the minimum quantity of hexane. Crystallization at -20°C gave 0.75 g (yield 70%) of the methoxy derivative **7** as black crystals with characteristics identical with the ones previously reported.¹

Water. A solution of **1** (0.89 g, 2 mmol) and water (140 μL , 2 mmol) in 3 mL of acetone was stirred at 25°C for 12 h. The above workup afforded 0.64 g (yield 70%) of black crystals of **9**: mp $64\text{--}67^\circ\text{C}$; IR (hexane, cm^{-1}) $\nu(\text{O-H})$ 3680, $\nu(\text{C}\equiv\text{O})$ 2088, 2055, 2023; ^1H NMR (C_6D_6 , δ) 0.33 (6 H, s), 1.50 (1 H, s), 7.36 (5 H, m); ^{13}C NMR (CDCl_3 , δ) -1.69, 128.31, 129.19, 130.22, 138.32, 200.00. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_7\text{SiCo}_2$: C, 41.57; H, 2.61. Found: C, 41.62; H, 2.73.

***p*-Methoxyphenol.** A solution containing 0.6 g (5 mmol) of *p*-methoxyphenol in 5 mL of THF was added to 2.2 g (5 mmol) of **1** in 5 mL of THF and the mixture stirred for 2 h at 50°C . The solvent was then evaporated and the residue passed over a column of Florisil (30–60 mesh, Fluka). Upon elution first with pentane and then with a 7/3 pentane/ Et_2O mixture, 0.62 g (yield 22%) of **5** identical with that previously reported¹ was collected.

Benzoic Acid. A solution containing 0.41 g (3.4 mmol) of benzoic acid and 1.5 g (3.4 mmol) of **1** in 10 mL of heptane was stirred at 50°C for 7 h. After removal of the solvent under vacuum extraction of the residue with hexane, crystallization at -80°C afforded 0.8 g (yield 41%) of black crystals of **12**: mp $40\text{--}41^\circ\text{C}$; IR (CCl_4 , cm^{-1}) $\nu(\text{C}\equiv\text{O})$ 2093, 2057, 2027, $\nu(\text{C}=\text{O})$ 1690; ^1H NMR (toluene, δ) 0.0 (6 H, s), 6.23–7.33 (10 H, m); ^{13}C NMR (CDCl_3 ,

(14) (a) Seyferth, D.; White, D. L. *J. Organomet. Chem.* **1971**, *32*, 317. (b) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

δ) 0.62, 128.31, 128.37, 129.03, 130.20, 130.29, 130.95, 133.22, 137.86, 199.53. Anal. Calcd for $C_{23}H_{16}O_8SiCo_2$: C, 48.78; H, 2.84. Found: C, 48.30; H, 2.86.

Aniline. A solution of **1** (0.89 g, 2 mmol) and aniline (0.19 g, 2 mmol) in 6 mL of heptane was stirred for 3 h at 50 °C. The previous workup then allowed isolation of 0.64 g (yield 60%) of complex **13** as black crystals: mp 58–59 °C; IR (CCl_4 , cm^{-1}) $\nu(N-H)$ 3380, $\nu(C=O)$ 2081, 2050, 2020; 1H NMR (C_6D_6 , δ) 0.0 (6 H, s), 2.85 (1 H, s), 6.40 (10 H, m); ^{13}C NMR ($CDCl_3$, δ) 1.06, 116.96, 118.58, 128.04, 128.92, 129.25, 130.02, 138.03, 146.00; mass spectrum (relative intensity, assignment) m/e 397 (1, $M^+ - 5CO$) 369 (2, $M^+ - 6CO$), 310 (2, $M^+ - Co(CO)_6$), 251 (50, $M^+ - Co_2(CO)_6$), 236 (83, $M^+ - MeCo_2(CO)_6$). Anal. Calcd for $C_{22}H_{17}O_8SiCo_2$: C, 49.17; H, 3.18. Found: C, 48.92; H, 3.12.

Thermolysis of Complex 1. A solution of 1.0 g (2.2 mmol) of **1** in 5 mL of heptane was stirred for 48 h at 80 °C. The mixture was then pumped to dryness and the residue extracted with hexane. Filtering and cooling at -20 °C afforded 0.41 g (yield 30%) of black crystals of complex **14** exhibiting physical characteristics identical with those reported previously.¹

Methanolysis of Dimethyl(phenylethynyl)silane (15). A solution containing 0.8 g (5 mM) of dimethyl(phenylethynyl)silane, 0.3 g (10 mM) of methanol, and 0.23 g (5×10^{-4} M) of a (diphenylacetylene)cobalt carbonyl complex¹⁵ in 10 mL of hexane was heated at 40 °C. After 48 h, a total conversion of the starting hydrosilane was noted. Chromatography of the crude mixture over a column of Florisil (30–60 mesh, Fluka) allowed isolation of methoxydimethyl(phenylethynyl)silane (**16**): IR (CCl_4 , cm^{-1}) $\nu(C\equiv C)$ 2160; 1H NMR (δ) 0.0 (6 H, s), 3.2 (3 H, s), 7.1 (5 H, m). Anal. Calcd for $C_{11}H_{14}OSi$: C, 69.42; H, 7.41. Found: C, 69.30; H, 7.49.

Reactions of Complex 6. With Methanol. A solution containing 1.0 g (2.5 mmol) of the silyl complex **22** and 1 mL of methanol in 5 mL of THF was stirred for 6 h at 35 °C. The reaction mixture was then pumped to dryness and the residue extracted with pentane and crystallized at -20 °C to give 0.37 g (yield 30%) of black crystals having characteristics identical with those already reported for the dimethoxy complex **8**.¹

With *p*-Methoxyphenol. A solution containing 1.5 g (3.5 mmol) of **22** and 0.86 g (7 mmol) of *p*-methoxyphenol in 10 mL of heptane was stirred at 60 °C for 12 h. The above workup afforded complex **11** (0.6 g, yield 26%) as black crystals (at -80 °C) that melt to a black oil at room temperature: IR (neat, cm^{-1}) $\nu(C=O)$ 2093, 2055, 2033; 1H NMR (CCl_4 , δ) 0 (6 H, s), 3.1 (3 H, s), 6.1 (4 H, s). Anal. Calcd for $C_{26}H_{26}O_{10}Si_2Co_2$: C, 46.43; H, 3.89. Found: C, 46.64; H, 4.07.

Hydrosilylation Reactions of Complex 1. Benzaldehyde. A 0.36-g (3.4-mmol) amount of benzaldehyde in 5 mL of heptane was added to a solution of 1.5 g (3.4 mmol) of **1** also in 5 mL of heptane. The mixture was stirred 1 h at 60 °C and pumped to dryness. The black residue was chromatographed over a column of Florisil (30–60 mesh, Fluka). Elution first with pentane and then with a 7/3 pentane/ether mixture allowed recovery of 0.58 g (yield 31%) of **17** as a black oil: IR (CCl_4 , cm^{-1}) $\nu(C=O)$ 2090, 2056, 2026; 1H NMR ($CDCl_3$, δ) 0.50 (6 H, s), 4.76 (2 H, s), 7.33 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) 0.11, 65.44, 126.50, 127.26, 128.10, 128.32, 128.95, 130.16, 138.10, 140.50, 199.76; mass spectrum (relative intensity, assignment) m/e 412 (1, $M^+ - 5CO$), 384 (1, $M^+ - 6CO$), 266 (57, $M^+ - Co_2(CO)_6$). Anal. Calcd for $C_{23}H_{18}O_7SiCo_2$: C, 50.01; H, 3.28. Found: C, 49.87; H, 3.51.

Furfural. As above, the reaction of 0.48 g (5 mmol) of furfural and 2.2 g (5 mmol) of **1** in 10 mL of heptane for 1 h at 50 °C gave after chromatographic purification 2.0 g (yield 76%) of **19** as a black oil: IR (CCl_4 , cm^{-1}) $\nu(C=O)$ 2091, 2055, 2026; 1H NMR (C_6D_6 , δ) 0.40 (6 H, s), 4.56 (2 H, s), 5.83 (2 H, m), 7.10 (6 H, m), ^{13}C NMR ($CDCl_3$, δ) 0.05, 58.17, 107.92, 110.43, 117.56, 128.20, 129.08, 130.33, 138.26, 142.47, 153.73. Anal. Calcd for $C_{21}H_{16}O_8SiCo_2$: C, 46.51; H, 2.97. Found: C, 46.75; H, 3.28.

Phenylacetylene. The reaction of phenylacetylene (0.2 g, 2 mmol) in 5 mL of heptane was conducted at 50 °C for 7 h. The above workup led to isolation of 0.6 g of **20** as black crystals: mp 56–58 °C; IR (CCl_4 , cm^{-1}) $\nu(C=O)$ 2089, 2053, 2025; 1H NMR (CCl_4 , δ) 0.0 (6 H, s), 5.83 (1 H, d, $J_E = 20$ Hz), 6.33 (1 H, d, J_E

= 20 Hz), 7.1 (5 H, m). Anal. Calcd for $C_{24}H_{18}O_8SiCo_2$: C, 52.57; H, 3.30. Found: C, 52.30; H, 3.33.

Reactions of Dimethyl(phenylethynyl)silane. With Benzaldehyde. A solution containing 1.6 g (10 mmol) of dimethyl(phenylethynyl)silane, 1.1 g (10 mmol) of benzaldehyde, and 0.46 g (1 mmol) of a (diphenylacetylene)cobalt carbonyl complex¹⁵ in 20 mL of heptane was stirred at 60 °C for 12 h. No reaction was noted, and the starting silane was recovered upon chromatography of the crude mixture.

With Phenylacetylene. As above, the attempted reaction of dimethyl(phenylethynyl)silane (1.6 g, 10 mmol) and phenylacetylene (1.02 g, 10 mmol) in the presence of $(Ph_2C_2)Co_2(CO)_6$ at 65 °C for 18 h led to partial recovery of the starting material and formation of triphenylbenzene.

Reaction of Complex 6 with Benzaldehyde. A solution containing 1.5 g (3.5 mmol) of **6** and 0.75 g (7 mmol) of benzaldehyde in 10 mL of heptane was stirred at 40 °C for 4 h. The solvent was then evaporated and the crude product dissolved in pentane. Cooling at -80 °C gave black crystals, which melted upon warming to room temperature. A 0.5-g amount of **18** (yield 23%) was collected: IR (neat, cm^{-1}) $\nu(C=O)$ 2092, 2053, 2023; 1H NMR (CCl_4 , δ) 0.0 (6 H, s), 4.23 (2 H, s), 6.66 (5 H, m). Anal. Calcd for $C_{26}H_{26}O_8SiCo_2$: C, 48.76; H, 4.09. Found: C, 48.60; H, 3.89.

Reactions of Complex 21. With Benzaldehyde. A solution containing 0.53 g (5 mmol) of benzaldehyde and 2.2 g (5 mmol) of **21** in 5 mL of hexane was stirred at 50 °C for 9 h. The reaction mixture was then pumped to dryness and the residue chromatographed over a Florisil column (30–60 mesh, Fluka). Elution first with pentane then with CH_2Cl_2 allowed isolation of a black band. A 1.96-g amount of **22**, as a black oil, was isolated: IR (neat, cm^{-1}) $\nu(O-H)$ 3380, $\nu(C=O)$ 2093, 2054, 2023; 1H NMR ($CDCl_3$, δ) 0.4 (3 H, s), 2.6 (1 H, s), 4.85 (2 H, s), 7.33 (10 H, m); ^{13}C NMR ($CDCl_3$, δ) -1.80, 65.35, 126.89, 127.60, 128.37, 128.58, 129.13, 130.44, 138.15, 140.39, 200.00; mass spectrum (relative intensity, assignment) m/e 470 (1, $M^+ - 3CO$), 442 (1, $M^+ - 4CO$), 414 (1, $M^+ - 5CO$), 386 (7, $M^+ - 6CO$), 327 (3, $M^+ - Co(CO)_6$), 268 (63, $M^+ - Co_2(CO)_6$). Anal. Calcd for $C_{22}H_{16}O_8SiCo_2$: C, 47.67; H, 2.90. Found: C, 48.00; H, 2.75.

With Phenylacetylene. The reaction of 2.3 g (5 mmol) of **21** with 0.5 g (5 mmol) of phenylacetylene was performed in 5 mL of hexane at 50 °C for 20 h. The above workup allowed isolation of **23** as a black oil: 1.57 g (yield 54%); IR (neat, cm^{-1}) $\nu(O-H)$ 3380, $\nu(C=O)$ 2097, 2053, 2023; 1H NMR ($CDCl_3$, δ) 0.51 (3 H, s), 2.25 (1 H, s), 6.45 (1 H, d, $J_E = 20$ Hz), 6.85 (1 H, d, $J_E = 20$ Hz), 7.40 (10 H, m); ^{13}C NMR ($CDCl_3$, δ) 0.27, 125.09, 126.94, 128.09, 128.31, 128.80, 128.97, 129.13, 130.11, 130.33, 147.34, 200.00; mass spectrum (relative intensity, m/e) 494 (1, $M^+ - 2CO$), 466 (1, $M^+ - 3CO$), 438 (1, $M^+ - 4CO$), 3.82 (1, $M^+ - 5CO$), 323 (5, $M^+ - Co(CO)_6$), 264 (30, $M^+ - Co_2(CO)_6$), 249 (40, $M^+ - CH_3Co_2(CO)_6$). Anal. Calcd for $C_{23}H_{16}O_7SiCo_2$: C, 50.19; H, 2.93. Found: C, 50.47; H, 3.11.

Methyldipropynylsilane (24). An excess of propyne (3 L, 0.13 mol) was bubbled through a THF solution containing 0.1 mol of $EtMgBr$ at 0 °C. The mixture was then stirred for 4 h at room temperature and cooled again to 0 °C. Methyldichlorosilane (5.2 mL, 0.05 mol) in 50 mL of THF was then added dropwise and the solution stirred for 12 h at room temperature. The mixture was then poured onto a cold 2 N aqueous HCl solution, extracted with ether, and dried over Na_2SO_4 . Evaporation of the solvents and distillation of the residue afforded 3.84 g of methyldipropynylsilane: bp (760 mmHg) 110 °C; IR (neat, cm^{-1}) $\nu(C\equiv C)$ 2195, $\nu(Si-H)$ 2158; 1H NMR (C_6D_6 , δ) 0.26 (3 H, d, $J = 4$ Hz), 1.40 (6 H, d, $J = 2$ Hz), 4.33 (1 H, m); ^{13}C NMR ($CDCl_3$, δ) -2.46, 4.69, 78.10, 105.10.

Reaction of Methyldipropynylsilane (24) with $Co_2(CO)_8$. To a solution of **24** (1.83 g, 15 mmol) in 150 mL of hexane at 25 °C was added slowly 300 mL of a hexane solution containing 10.26 g (30 mmol) of $Co_2(CO)_8$. After addition the mixture was stirred for an additional 12 h and then pumped to dryness. Extraction of the residue with the minimum quantity of hexane and crystallization at -20 °C afforded 7.28 g of black crystals of **25**: mp 88–90 °C; IR (hexane, cm^{-1}) $\nu(Si-H)$ 2140, $\nu(C=O)$ 2088, 2055, 2030, 2020; 1H NMR (C_6D_6 , δ) 0.61 (3 H, d, $J = 4$ Hz), 2.53 (6 H, s), 5.30 (1 H, q, $J = 4$ Hz); ^{13}C NMR ($CDCl_3$, δ) -0.03, 21.78, 200.00. Anal. Calcd for $C_{19}H_{10}O_{12}SiCo_4$: C, 32.87; H, 1.43. Found: C, 32.89; H, 1.47.

Tripropynylsilane (26). A solution of propynylmagnesium bromide was prepared as above from 1.12 L (50 mmol) of propyne and 50 mL of a 1 M THF solution of EtMgBr. To this solution at $-20\text{ }^{\circ}\text{C}$ was then added 1.76 mL (17 mmol) of trichlorosilane dissolved in 20 mL of THF. Hydrolysis, extraction, and drying was carried out as for the preparation of silane 24. The crude product was dissolved in the minimum quantity of pentane and cooled at $-20\text{ }^{\circ}\text{C}$. A 1.51-g amount (yield 61%) of colorless crystals was collected: mp $98\text{--}99\text{ }^{\circ}\text{C}$; IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{Si-H, C}\equiv\text{C})$ 2177; $^1\text{H NMR}$ (CDCl_3 , δ) 1.91 (9 H, br s), 4.41 (1 H, m); $^{13}\text{C NMR}$ (CDCl_3 , δ) 4.47, 76.51, 105.90; $^{29}\text{Si NMR}$ (INEPT, CDCl_3 , δ) -90.17 (d, $^1J_{\text{Si-H}} = 244\text{ Hz}$); mass spectrum (relative intensity, assignment) m/e 146 (60, M^+), 145 (97, $\text{M}^+ - \text{H}$), 131 (30, $\text{M}^+ - \text{CH}_3$).

Reaction of Tripropynylsilane (26). With 2 Equiv of $\text{Co}_2(\text{CO})_8$. To a solution of tripropynylsilane (26; 0.59 g, 4.1 mmol) in 40 mL of hexane was added slowly 2.8 g (8.2 mmol) of $\text{Co}_2(\text{CO})_8$ dissolved in 100 mL of hexane. The mixture was then stirred for 14 h and pumped to dryness. Dissolution of the residue in hexane and crystallization at $-20\text{ }^{\circ}\text{C}$ afforded 1.76 g (yield 60%) of 27 as black crystals: mp $59\text{--}60\text{ }^{\circ}\text{C}$; IR (toluene, cm^{-1}) $\nu(\text{C}\equiv\text{C})$ 2188, $\nu(\text{Si-H})$ 2150, $\nu(\text{C}=\text{O})$ 2088, 2056, 2028; $^1\text{H NMR}$ (CDCl_3 , δ) 1.92 (3 H, s), 2.75 (6 H, s), 5.36 (1 H, s); $^{13}\text{C NMR}$ (CDCl_3 , δ) 4.26, 21.32, 71.70, 106.40, 200.00; $^{29}\text{Si NMR}$ (INEPT, CDCl_3 , δ) 48.02 (d, $^1J_{\text{Si-H}} = 239\text{ Hz}$); mass spectrum (relative intensity, assignment) m/e 545 (5, $\text{M}^+ - 3\text{CO}$), 578 (7, $\text{M}^+ - 5\text{CO}$), 522 (12, $\text{M}^+ - 7\text{CO}$), 494 (12, $\text{M}^+ - 8\text{CO}$), 466 (12, $\text{M}^+ - 9\text{CO}$), 438 (14, $\text{M}^+ - 10\text{CO}$), 410 (12, $\text{M}^+ - 11\text{CO}$), 382 (12, $\text{M}^+ - 12\text{CO}$), 264 (23, $\text{M}^+ - \text{Co}_2(\text{CO})_{12}$). Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{O}_{12}\text{SiCo}_4$: C, 35.16; H, 1.40. Found: C, 35.15; H, 1.32.

With 3 Equiv of $\text{Co}_2(\text{CO})_8$. The reaction was carried out as above by using 5.13 g of $\text{Co}_2(\text{CO})_8$ and 0.73 g (5 mmol) of 26. Crystallization gave 3.01 g of black crystals of 28: mp $107\text{--}110\text{ }^{\circ}\text{C}$; IR (toluene, cm^{-1}) $\nu(\text{C}=\text{O})$ 2087, 2059, 2022; $^1\text{H NMR}$ (CDCl_3 , δ) 2.92 (9 H, s), 5.92 (1 H, s); $^{13}\text{C NMR}$ (CDCl_3 , δ) 23.39, 107.37, 200.00; $^{29}\text{Si NMR}$ (INEPT, CDCl_3 , δ) -24.44 (d, $^1J_{\text{Si-H}} = 233\text{ Hz}$); mass spectrum (relative intensity assignment) m/e 976 (1, $\text{M}^+ - \text{CO}$), 500 (4, $\text{M}^+ - 18\text{CO}$). Anal. Calcd for $\text{C}_{27}\text{H}_{10}\text{O}_{18}\text{SiCo}_6$: C, 32.29; H, 1.00. Found: C, 32.54; H, 1.12.

With 3.5 Equiv of $\text{Co}_2(\text{CO})_8$. A solution containing 0.36 g (2.5 mmol) of 26 and 2.99 g (8.7 mmol) of $\text{Co}_2(\text{CO})_8$ in 50 mL of hexane was stirred first for 4 h at $25\text{ }^{\circ}\text{C}$ and then for 5 h at $50\text{ }^{\circ}\text{C}$. Crystallization at $-20\text{ }^{\circ}\text{C}$ afforded 1.22 g of black crystals of 28 having characteristics identical with those of the above sample.

Reactions of Complex 25. With $\text{Ph}_3\text{C}^+\text{BF}_4^-$. To a solution of 3.47 g (5 mmol) of 25 in 10 mL of CH_2Cl_2 at $0\text{ }^{\circ}\text{C}$ was added 1.65 g (5 mmol) of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ in 10 mL of CH_2Cl_2 . The mixture was then stirred at $25\text{ }^{\circ}\text{C}$ for 18 h and pumped to dryness. Extraction with hexane and crystallization gave black crystals (3.23 g) of 29 (yield 91%): mp $93\text{--}95\text{ }^{\circ}\text{C}$; IR (C_6D_6 , cm^{-1}) $\nu(\text{C}=\text{O})$ 2090, 2059, 2031; $^1\text{H NMR}$ (C_6D_6 , δ) 0.71 (3 H, d, $J = 6\text{ Hz}$), 2.53 (6 H, s); $^{13}\text{C NMR}$ (CDCl_3 , δ) 1.5 (d, $J = 20\text{ Hz}$), 21.78, 200.00; $^{19}\text{F NMR}$ (reference CFCl_3 , δ) +140. Anal. Calcd for $\text{C}_{19}\text{H}_9\text{O}_{12}\text{FSiCo}_4$: C, 32.04; H, 1.27. Found: C, 32.33; H, 1.23.

With Methanol. A solution containing 0.06 g (1.8 mmol) of methanol and 1.25 g (1.8 mmol) of 25 in 2 mL of toluene was stirred for 30 h at $45\text{ }^{\circ}\text{C}$. The usual extraction and crystallization in hexane gave 0.71 g (yield 55%) of black crystals of 31: mp $103\text{--}104\text{ }^{\circ}\text{C}$; IR (toluene, cm^{-1}) $\nu(\text{C}=\text{O})$ 2086, 2054, 2025; $^1\text{H NMR}$ (CDCl_3 , δ) 0.66 (3 H, s), 2.96 (6 H, s), 3.8 (3 H, s); $^{13}\text{C NMR}$ (CDCl_3 , δ) 0.95, 21.94, 51.68, 200.00. Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{O}_{13}\text{SiCo}_4$: C, 33.17; H, 1.67. Found: C, 33.31; H, 1.73.

Reactions of Complex 27. With $\text{Ph}_3\text{C}^+\text{BF}_4^-$. The reaction was performed as for 25 by using 0.66 g (2 mmol) of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ and 1.43 g (2 mmol) of 27. Crystallization gave 0.91 g of 30 as black crystals (yield 62%): mp $65\text{--}66\text{ }^{\circ}\text{C}$; IR (hexane, cm^{-1}) $\nu(\text{C}=\text{O})$ 2091, 2060, 2036; $^1\text{H NMR}$ (CDCl_3 , δ) 1.84 (3 H, s), 2.76 (6 H, s); mass spectrum (relative intensity, assignment) m/e 736 (1, M^+), 708 (8, $\text{M}^+ - \text{CO}$), 680 (4, $\text{M}^+ - 2\text{CO}$), 652 (16, $\text{M}^+ - 3\text{CO}$),

624 (4, $\text{M}^+ - 4\text{CO}$), 596 (8, $\text{M}^+ - 5\text{CO}$), 568 (5, $\text{M}^+ - 6\text{CO}$), 540 (30, $\text{M}^+ - 7\text{CO}$), 512 (30, $\text{M}^+ - 8\text{CO}$), 484 (15, $\text{M}^+ - 9\text{CO}$), 456 (15, $\text{M}^+ - 10\text{CO}$), 428 (15, $\text{M}^+ - 11\text{CO}$), 400 (21, $\text{M}^+ - 12\text{CO}$), 341 (3, $\text{M}^+ - \text{Co}(\text{CO})_{12}$), 282 ($\text{M}^+ - \text{Co}_2(\text{CO})_{12}$). Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{O}_{12}\text{FSiCo}_4$: C, 34.26; H, 1.23. Found: C, 34.28; H, 1.21.

With Methanol. As in the case of the reaction of 25, 0.04 g (1.25 mmol) of methanol and 0.89 g (1.25 mmol) of 27 in 2 mL of toluene were stirred at $25\text{ }^{\circ}\text{C}$ for 48 h. Crystallization from hexane gave 0.67 g of 32 as black crystals (yield 72%): mp $72\text{ }^{\circ}\text{C}$; IR (toluene, cm^{-1}) $\nu(\text{C}\equiv\text{C})$ 2188, $\nu(\text{C}=\text{O})$ 2087, 2054, 2027; $^1\text{H NMR}$ (CDCl_3 , δ) 1.91 (3 H, s), 2.83 (6 H, s), 3.76 (3 H, s); mass spectrum (relative intensity, assignment) m/e 294 (1, $\text{M}^+ - \text{Co}_2(\text{CO})_{12}$), 235 (2, $\text{M}^+ - \text{Co}_3(\text{CO})_{12}$), 176 (5, $\text{M}^+ - \text{Co}_4(\text{CO})_{12}$). Anal. Calcd for $\text{C}_{22}\text{H}_{12}\text{H}_{13}\text{SiCo}_4$: C, 35.31; H, 1.61. Found: C, 35.59; H, 1.60.

With Benzoic Acid. A solution containing 0.48 g (4 mmol) of benzoic acid and 2.87 g (4 mmol) of 27 in 4 mL of CH_2Cl_2 was stirred at $35\text{ }^{\circ}\text{C}$ for 4 h. The mixture was then pumped to dryness and the residue chromatographed with Florisil. Elution first with pentane and then with a 1/1 pentane/ CH_2Cl_2 mixture gave, as a black oil, 1.24 g (yield 37%) of 34: IR (neat, cm^{-1}) $\nu(\text{C}\equiv\text{C})$ 2198, $\nu(\text{C}=\text{O})$ 2088, 2050, 2018, $\nu(\text{C}=\text{O})$ 1705; $^1\text{H NMR}$ (CDCl_3 , δ) 1.87 (3 H, s), 2.81 (6 H, s), 7.75 (5 H, s); $^{13}\text{C NMR}$ (CDCl_3 , δ) 4.64, 22.03, 69.59, 95.01, 106.82, 130.55, 130.72, 131.32, 141.83, 166.27, 200.00; mass spectrum (relative intensity, assignment) m/e 782 (10, $\text{M}^+ - 2\text{CO}$), 754 (3, $\text{M}^+ - 3\text{CO}$), 726 (10, $\text{M}^+ - 4\text{CO}$), 698 (11, $\text{M}^+ - 5\text{CO}$), 670 (8, $\text{M}^+ - 6\text{CO}$), 642 (19, $\text{M}^+ - 7\text{CO}$), 614 (27, $\text{M}^+ - 8\text{CO}$), 586 (18, $\text{M}^+ - 9\text{CO}$), 558 (10, $\text{M}^+ - 10\text{CO}$), 530 (26, $\text{M}^+ - 11\text{CO}$), 502 (22, $\text{M}^+ - 12\text{CO}$), 266 (9, $\text{M}^+ - \text{Co}_4(\text{CO})_{12}$). Anal. Calcd for $\text{C}_{28}\text{H}_{14}\text{O}_{14}\text{SiCo}_4$: C, 40.12; H, 1.68. Found: C, 40.32; H, 1.79.

With Aniline. Aniline (0.37 g, 4 mmol) and 27 (2.87 g, 4 mmol) in 4 mL of hexane were stirred 5 days at $25\text{ }^{\circ}\text{C}$. As above, chromatographic purification with Florisil gave 0.62 g (yield 23%) of 33 as a black oil: IR (neat, cm^{-1}) $\nu(\text{N-H})$ 3410, $\nu(\text{C}\equiv\text{C})$ 2195, $\nu(\text{C}=\text{O})$ 2086, 2049, 2016; $^1\text{H NMR}$ (CDCl_3 , δ) 1.9 (3 H, s), 2.86 (6 H, s), 4.10 (1 H, s), 7.06 (5 H, m); mass spectrum (relative intensity, assignment) m/e 809 (1, M^+), 781 (1, $\text{M}^+ - \text{CO}$), 753 (1, $\text{M}^+ - 2\text{CO}$), 725 (4, $\text{M}^+ - 3\text{CO}$), 697 (1, $\text{M}^+ - 4\text{CO}$), 669 (1, $\text{M}^+ - 5\text{CO}$), 641 (4, $\text{M}^+ - 6\text{CO}$), 613 (1, $\text{M}^+ - 7\text{CO}$), 585 (4, $\text{M}^+ - 8\text{CO}$), 557 (9, $\text{M}^+ - 9\text{CO}$), 529 (3, $\text{M}^+ - 10\text{CO}$), 501 (3, $\text{M}^+ - 11\text{CO}$), 473 (45, $\text{M}^+ - 12\text{CO}$), 237 (45, $\text{M}^+ - \text{Co}_4(\text{CO})_{12}$). Anal. Calcd for $\text{C}_{27}\text{H}_{15}\text{O}_{12}\text{NSiCo}_4$: C, 40.07; H, 1.87. Found: C, 40.27; H, 1.95.

Reactions of Complex 28. With $\text{Ph}_3\text{C}^+\text{BF}_4^-$. A solution containing 28 (3.01 g, 3 mmol) and $\text{Ph}_3\text{C}^+\text{BF}_4^-$ (0.99 g, 3 mmol) in 10 mL of CH_2Cl_2 was stirred for 24 h at room temperature. Complex 30 (1.58 g, yield 72%) was crystallized from the reaction mixture and exhibited physical characteristics identical with those of the sample prepared from 27.

With Methanol. As previously described, the reaction of 3.0 g (3 mmol) of complex 28 with methanol in toluene for 36 h at room temperature led to a sample of 32 (yield 64%) identical with the one isolated from the methanolysis of 27.

With Benzaldehyde. 28 (2.0 g, 2 mmol) and benzaldehyde (0.21 g, 2 mmol) in 4 mL of CH_2Cl_2 were reacted for 12 h at $50\text{ }^{\circ}\text{C}$. Purification of the residue by chromatography over Florisil gave 0.48 g (yield 22%) of 36: IR (hexane, cm^{-1}) $\nu(\text{C}=\text{O})$ 2090, 2060, 2032; $^1\text{H NMR}$ (CDCl_3 , δ) 2.76 (9 H, s), 5.67 (2 H, s), 7.29 (5 H, m); $^{13}\text{C NMR}$ (CDCl_3 , δ) 22.14, 82.11, 127.98, 128.37, 139.30, 200.00; mass spectrum (relative intensity, assignment) m/e 970 (1, $\text{M}^+ - 5\text{CO}$), 942 (1, $\text{M}^+ - 6\text{CO}$), 824 (2, $\text{M}^+ - \text{Co}_2(\text{CO})_6$), 796 (2, $\text{M}^+ - \text{Co}_2(\text{CO})_7$), 768 (71, $\text{M}^+ - \text{Co}_2(\text{CO})_8$), 740 (12, $\text{M}^+ - \text{Co}_2(\text{CO})_9$), 712 (3, $\text{M}^+ - \text{Co}_2(\text{CO})_{10}$), 684 (50, $\text{M}^+ - \text{Co}_2(\text{CO})_{11}$), 656 (31, $\text{M}^+ - \text{Co}_2(\text{CO})_{12}$), 597 (51, $\text{M}^+ - \text{Co}_3(\text{CO})_{12}$), 538 (5, $\text{M}^+ - \text{Co}_4(\text{CO})_{12}$), 520 (3, $\text{M}^+ - \text{Co}_4(\text{CO})_{13}$), 482 (17, $\text{M}^+ - \text{Co}_4(\text{CO})_{14}$), 454 (5, $\text{M}^+ - \text{Co}_4(\text{CO})_{15}$), 426 (24, $\text{M}^+ - \text{Co}_4(\text{CO})_{16}$), 398 (96, $\text{M}^+ - \text{Co}_4(\text{CO})_{17}$), 370 (14, $\text{M}^+ - \text{Co}_4(\text{CO})_{18}$), 311 (2, $\text{M}^+ - \text{Co}_5(\text{CO})_{18}$), 252 (2, $\text{M}^+ - \text{Co}_6(\text{CO})_{18}$). Anal. Calcd for $\text{C}_{34}\text{H}_{16}\text{O}_{19}\text{SiCo}_6$: C, 36.78; H, 1.45. Found: C, 37.18; H, 1.56.