Homogeneous Catalysis. IV. Some Reactions of Silicon Hydrides in the Presence of Cobalt Carbonyls

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Abstract: The catalysis of silicon hydride addition to 1-olefins, catalyzed by dicobalt octacarbonyl, was investigated for triethyl-, triethoxy-, and phenyldichlorosilane. In all three cases the rate of olefin isomerization exceeded that of olefin hydrosilation. Evidence for the mechanism of the reaction was obtained by examining the reaction of silicon hydrides with dicobalt octacarbonyl. Cobalt hydrocarbonyl and silylcobalt carbonyls were identified as the initial products. The cobalt hydrocarbonyl then decomposes to hydrogen and dicobalt octacarbonyl or reacts with silicon hydride to form a silylcobalt carbonyl and hydrogen depending on the concentration and nature of the silicon hydride. In the presence of olefin it is proposed that alkylcobalt carbonyls are formed from the cobalt hydrocarbonyl, and further reaction with silicon hydrides yields alkylsilanes and regenerates cobalt hydrocarbonyl. No evidence for the participation of silylcobalt carbonyls in the catalytic reaction was found, except for the exchange reaction: $R_3SiH + R'_3SiCo(CO)_4 \rightleftharpoons R_3SiCo(CO)_4 + R'_3SiH$. Isomerization of deuterium-labeled terminal olefins was found to involve intermolecular exchange of deuterium with both $C_3 \rightarrow C_2$ and $C_2 \rightarrow C_1$ shifts of deuterium. These results are similar to those found earlier for the rhodium chloride trihydrate catalyzed isomerization of olefins and are consistent with the rapid reversible addition of a hydrogen atom or ion to coordinated olefin. Carbon monoxide was found to participate in the reaction of triethylsilane and ethylene to produce unsaturated alkoxysilanes.

In previous communications[1,2] we reported the use of dicobalt octacarbonyl as a catalyst for the hydrosilation of olefins and the preparation of silylcobalt tetracarbonyls by direct reaction of silicon hydrides with dicobalt octacarbonyl. Since our original communication, the existence of compounds of the type $R_3Si \cdot Co(CO)_4$ has received independent confirmation with the synthesis of the parent compound $H_3Si \cdot Co(CO)_4$[3] and other silylcobalt carbonyls.[4]

In this paper we present in detail the preparation and properties of a series of silylcobalt carbonyls and our studies of their role in the cobalt carbonyl catalyzed hydrosilation of olefins, both in the presence and absence of carbon monoxide.

Experimental Section

Materials. Dicobalt octacarbonyl was obtained from Alpha Inorganics as a crystalline solid and as a solution in toluene or heptane. Solutions were analyzed by the method of Sternberg, *et al.*[5]

The other reagents were purified before use, unless otherwise indicated; the silanes were purified by distillation on a vacuum line, rejecting the first and last quarter of the distillate; olefins were treated by passage through an alumina column to give a product which no longer gave a positive test for hydroperoxide.[6]

Triethylsilane, diphenylsilane, triphenylsilane, trimethylsilane, and trihexylsilane were obtained from Peninsular Chem Research, Inc. Trichlorosilane, phenyldichlorosilane, triethoxysilane, and 1,3,5,7-tetramethylcyclotetrasiloxane were obtained from General Electric Silicone Products Department. Olefins (99% purity) were obtained from Phillips Petroleum Co. Cobalt hydrocarbonyl solutions in hydrocarbon solvents were prepared as described by Karapinka and Orchin.[7]

Preparation of Silylcobalt Carbonyls. Tetracarbonyl(trichlorosilyl)cobalt(I). An excess of trichlorosilane was distilled onto dicobalt octacarbonyl (0.96×10^{-3} mole) on a vacuum transfer line. The reaction mixture on being warmed from liquid nitrogen to room temperature turned from deep amber to pale yellow and evolved 1.3×10^{-3} mole of gas (Cl_3SiH, 20%; H_2, 78%; CO, 2%). Volatile material was distilled off at 25° and collected. The residue was a gray solid (I) weighing 60% more than the original dicobalt octacarbonyl. *Anal.* Calcd for $Cl_3SiCo(CO)_4$: C, 15.7; H, 0; Si, 9.2; Cl, 34.9; Co, 19.3. Found: C, 15.5; H, 0.3; Si, 9.1; Cl, 34.9; Co, 19.2. Both the residue and distillate were examined by infrared.

The experiment was repeated and the residue was purified by sublimation *in vacuo* to give a white crystalline solid, mp 44°, soluble in hydrocarbon solvents: mol wt (Mechrolab osmometer, cyclohexane solution), 463 ± 23 ($Cl_3SiCo(CO)_4$ = 306). *Anal.* Found: Co (micro), 18; Si (micro), 8.3; C, 15.5; H, 0; Cl, 34.2.

Tetracarbonyl(phenyldichlorosilyl)cobalt(I). Dicobalt octacarbonyl (10 ml, 0.12 *M* in toluene) was treated with an excess of phenyldichlorosilane on a vacuum transfer line; 1×10^{-3} mole of gas was evolved (H_2, 93.0%; CO, 3.0%).

The reaction was also followed by gas evolution using a gas buret. In this experiment 7.1×10^{-3} mole of phenyldichlorosilane was treated with an excess (5×10^{-3} mole) of 0.1 *M* dicobalt octacarbonyl in heptane. After 3 hr, 2×10^{-3} mole of gas had been evolved and the rate of gas evolution had diminished considerably. The product was subsequently recovered by fractional crystallization, cooling the solution in a slurry of solid carbon dioxide in acetone, filtering off the excess cobalt carbonyls, concentrating the solution on a rotary evaporator, and recooling. The resulting off-white crystals were sublimed under vacuum. A white crystalline solid resulted, which melted to a clear liquid at 34–35° and evolved gas at 150° and above; mol wt (in cyclohexane), 357 ± 18 ($C_6H_5SiCl_2Co(CO)_4$ = 347). *Anal.* Calcd for $C_6H_5SiCl_2Co(CO)_4$: Co, 17.0; C, 34.6; H, 1.4; Si, 8.1; Cl, 20.5. Found: Co, 17.3; C, 34.7; H, 1.4; Si, 8.1; Cl, 19.8.

Tetracarbonyl(triethylsilyl)cobalt(I). An excess of triethylsilane was distilled onto dicobalt octacarbonyl (0.93×10^{-3} mole); 1.5×10^{-3} mole of gas was collected (H_2, 79%; CO, 9%). The excess silane was distilled off below 50° and collected. The residue and distillate were examined by infrared spectroscopy. The residue, a liquid at room temperature, was further purified by distillation *in vacuo*. *Anal.* Calcd for $(C_2H_5)_3SiCo(CO)_4$: C, 42.0; H, 5.2; Si, 9.8. Found: C, 42.0; H, 5.3; Si (micro), 6.5.

A nonroutine method was used for silicon because of the presence of cobalt. Silicon could have been lost in the analysis so that the figure cited is a minimal value.

Tetracarbonyl(triphenylsilyl)cobalt(I). This derivative was synthesized in heptane solution by the same method as the phenyldichlorosilyl derivative. The rate of gas evolution was similar to that found for $C_6H_5SiCl_2H$ using similar concentrations. The

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(1) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(2) J. A. Chalk and J. F. Harrod, *ibid.*, **87**, 1133 (1965).

(3) B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 217 (1965).

(4) A. G. McDiarmid, *Inorg. Chem.*, in press.

(5) H. W. Sternberg, I. Wender, and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

(6) J. A. C. Yule and C. P. Wilson, Jr., *Ind. Eng. Chem.*, **23**, 1254 (1931).

(7) G. L. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

product was recovered by fractional crystallization to give off-white crystals, mp 135–140°; mol wt (in benzene), 370 ± 19 (($(C_6H_5)_3SiCo(CO)_4$ = 430). *Anal.* Calcd for $(C_6H_5)_3SiCo(CO)_4$: Co, 13.7; Si, 6.5; C, 61.4; H, 3.5. Found: Co, 12.9; Si (micro), 6.2; C, 60.8; H, 3.9.

Tetracarbonyl(diphenylhydridosilyl)cobalt(I). The reaction was studied in heptane solution, using a silicon hydride:dicobalt octacarbonyl ratio of 2:1 and 1:1. The same product was recovered in both cases by fractional crystallization. *Anal.* Calcd for $(C_6H_5)_2SiHCo(CO)_4$: C, 54.3; H, 3.1. Found: C, 54.0; H, 3.1.

Other Preparations. Silylcobalt carbonyls were also prepared from triethoxysilane and from 1,3,5,7-tetramethylcyclotetrasiloxane, but the compounds were not characterized by chemical analysis or molecular weight determination.

All of the compounds cited were also prepared in heptane solution by reaction of silicon hydride with dicobalt octacarbonyl in a molar ratio of 2:1. In these preparations the disappearance of silicon hydride and dicobalt octacarbonyl and the appearance of silyl cobalt carbonyl were monitored by infrared analysis of ν_{Si-H} and $\nu_{C=O}$. The products were isolated by low-temperature fractional crystallization.

Identification and Isolation of Cobalt Hydrocarbonyl. A series of silicon hydrides was treated with dicobalt octacarbonyl on a vacuum transfer line. Volatile products were distilled into cold traps containing (a) pyridine and (b) dodecane, and the presence of (a) pyridinium tetracarbonyl cobaltate and (b) cobalt hydrocarbonyl was determined by infrared examination of the solutions.

In one case, using triethylsilane, the reaction was carried out in benzene under 1 atm of carbon monoxide in an apparatus similar to that used for the preparation of cobalt hydrocarbonyl. By sweeping carbon monoxide through the apparatus at a flow rate of approximately 100 ml/min, some cobalt hydrocarbonyl was trapped in a flask containing magnetically stirred hexane cooled with Dry Ice and acetone.

The Reaction of Silicon Hydrides with Cobalt Hydrocarbonyl. Solutions of cobalt hydrocarbonyl (10 ml, 0.08 *M*) in *n*-hexane were treated with a variety of silicon hydrides under nitrogen. The rates and extents of gas evolution were measured with a gas buret and were compared with the values found in the absence of silanes.

Thermal Decomposition of Silylcobalt Carbonyls. The thermal decomposition of several derivatives was studied. We describe the decomposition of the triphenylsilyl derivative as a typical example.

A sample of $(C_6H_5)_3SiCo(CO)_4$ (1.7×10^{-4} mole) was heated under vacuum. It began to lose gas at 155°. After 30 min at 200° 5.6×10^{-4} mole of gas had been evolved, but some of the material had sublimed to the cooler parts of the tube. The sublimate was examined by infrared. Carbonyl absorptions showed the presence of some undecomposed starting material. Weak Si–H bands indicated some triphenylsilane and the remainder of the spectrum was consistent with some hexaphenyldisilane. The black residue was extracted with benzene and evaporated to give an off-yellow solid. After extraction with petroleum ether, this solid gave a spectrum identical with that of hexaphenyldisilane. It melted at approximately 330° (lit.[8a] hexaphenyldisilane, mp 352°; hexaphenyldisiloxane, mp 222°).

Reaction of Tetracarbonyl(triethylsilyl)cobalt(I) with Trihexylsilane. An excess of triethylsilane (5 ml) was distilled onto a sample of dicobalt octacarbonyl (1.9 g) on a vacuum transfer line. The reaction was allowed to go to completion at room temperature (18 hr), the evolved hydrogen was pumped off, and the excess silane was distilled away. To the resulting sample of triethylsilylcobalt carbonyl was added 5 ml of trihexylsilane under nitrogen. After stirring magnetically for 65 hr, a volatile liquid was distilled off by warming under vacuum to 60°. It was identified by infrared as triethylsilane containing a trace of triethylsilylcobalt carbonyl; yield based on triethylsilylcobalt carbonyl, 57%.

Hydrosilation and Isomerization of Olefins in the Presence of Cobalt Carbonyls. The simultaneous isomerization and hydrosilation of several 1-olefins was followed by infrared and gpc analysis, using triethylsilane, phenyldichlorosilane, and triethoxysilane as representative of a fairly wide variety of silicon hydrides. Reactions were carried out under nitrogen. For the infrared analysis, concentrations were determined by using the Si–H stretching frequency around 2100 to 2200 cm^{-1} and the C=C stretching frequency at 1650 cm^{-1}. Gpc samples of the products were also isolated for comparison with similar samples prepared using the more conventional catalyst, chloroplatinic acid. Isomerizations were followed by gpc as previously described.[8b]

An example of a typical hydrosilation follows. Triethylsilane (0.05 mole) was treated with 1-octene (0.15 mole) in the presence of dicobalt octacarbonyl (1.5×10^{-3} *M*). After 65 hr at 25° no triethylsilane was detectable by infrared. The reaction was repeated using chloroplatinic acid. Gpc analysis revealed the identical formation of triethyloctylsilane in quantitative yield. Samples isolated by gpc had identical infrared spectra and agreed well (for gpc samples) with the expected refractive index, $n^{20}D$ 1.44; lit.[9] 1.444.

Isomerization of 1-Heptene-3-*d*$_2$. The experimental techniques and preparation of substrate have been described previously.[10] In a typical experiment, the nmr sample tube was charged with 1-heptene-3-*d*$_2$ (0.5 ml), $Co_2(CO)_8$ (0.05 ml; 0.1 *M* in heptane), and triethoxysilane (0.05 ml). The disappearance of the various protons was followed using a Varian HR-60 spectrometer. The sample was also periodically removed by syringe and injected into an infrared cell to measure the disappearance of 1-heptene by checking $\nu_{C=C}$ against a calibration curve.

An intermolecular deuterium-exchange experiment was performed using the same recipe as above, except that 1-pentene (0.5 ml) was added to the mixture. The separation and analysis procedures were the same as previously described.[10]

Reaction of Triethylsilane, Ethylene, and Carbon Monoxide. Dicobalt octacarbonyl (0.5 g) and triethylsilane (31 ml) were placed in a 300-ml steel bomb under nitrogen. The bomb was flushed with carbon monoxide and charged with 400 psi of ethylene. The temperature was then maintained at 200° for 24 hr, during which time the pressure fell from approximately 1050 to 685 psi.

The product was examined by gpc which revealed a complex mixture of substances with boiling points ranging from 90 to 300°. It was separated by means of a spinning-band column equivalent to 30 theoretical plates, and 33 fractions were further examined by gpc and infrared and ultraviolet spectroscopy. Elemental analyses were also carried out on both gpc samples and distillation cuts; *e.g.*, for distillation cut 10, bp 180° (*Anal.* Calcd for $C_3H_5OSi(C_2H_5)_3$: C, 63.8; H, 11.6; Si, 16.3. Found: C, 63.3; H, 11.7; Si, 15.6), and distillation cut 24, bp 295° (*Anal.* Calcd for $(C_2H_5)_3SiOC_4H_6OSi(C_2H_5)_3$: C, 60.8; H, 11.4; Si, 17.7. Found: C, 63.2; H, 11.9; Si, 17.8). A gpc sample of the main component of cut 25 gave C, 61.1%; H, 11.8%.

Results

Formation of Silylcobalt Carbonyls. Dicobalt octacarbonyl was found to react rapidly with silanes at room temperature. The principal products were hydrogen and a silylcobalt carbonyl produced in the stoichiometry of eq 1. Yields were in general high. It seems likely

$$2R_3SiH + Co_2(CO)_8 \longrightarrow 2R_3SiCo(CO)_4 + H_2 \qquad (1)$$

that the only side reaction is that due to the decomposition of dicobalt octacarbonyl to tetracobalt dodecacarbonyl. The latter was an impurity in the starting material and accumulates slowly with time.

When the reaction was performed with a 1:1 molar ratio of silane to dicobalt octacarbonyl, both silylcobalt carbonyl and cobalt hydrocarbonyl were isolated from the reaction product, suggesting the reaction

$$R_2SiH + Co_2(CO)_8 \longrightarrow R_3Si\cdot Co(CO)_4 + HCo(CO)_4 \qquad (2)$$

Diphenylsilane, with two active hydrogens, showed no tendency to react with a second cobalt carbonyl after having formed tetracarbonyl(diphenylsilyl)cobalt(I).

The reaction of dicobalt octacarbonyl with each of the silanes was accompanied by the disappearance of the bands due to the Si–H stretching and bending modes and the disappearance of the bands associated with the

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(8) (a) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1951, pp 173, 186; (b) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **86**, 1776 (1964).

(9) F. C. Whitmore, L. H. Sommer, P. A. Digiorgio, W. A. Strong, R. E. VanStrien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *ibid.*, **68**, 475 (1946).

(10) J. F. Harrod and A. J. Chalk, *ibid.*, **88**, 3491 (1966).

Table I. Infrared Absorptions of Silylcobalt Carbonyls and Parent Silanes

Parent silane	Si–H stretch, cm^{-1}	Carbonyl absorptions of silylcobalt carbonyls[a,b] in the ν_{CO} region, cm^{-1}					
Cl_3SiH	2250	2120 (s)	2070 (sh)	2070 (s)	2040 (vs, sh)	2030 (vs)	2000 (m, sh)
$C_6H_5SiCl_2H$	2220	2120 (s)	2070 (sh)	2060 (s)	2040 (vs)	2030 (vs)	1990 (sh)
$(C_2H_5O)_3SiH$	2200	2105 (s)	2060 (sh)	2040 (vs)	2025 (vs)	2010 (vs, sh)	
$(CH_3(H)SiO)_4$	2180	2105 (s)		2040 (s)	2020 (vs)	2010 (vs, sh)	
$(C_6H_5)_2SiH_2$	2150	2100 (s)	2055 (s)	2040 (vs)	2020 (vs)	2010 (vs, sh)	1965 (w)
$(C_6H_5)_3SiH$	2130	2100 (s)		2040 (s)	2015 (vs)	2010 (s, sh)	1975 (w, sh)
$(C_2H_5)_3SiH$	2100	2090 (s)		2030 (s)	2000 (vs)	1995 (vs, sh)	1960 (w, sh)

[a] Cobalt hydrocarbonyl shows the following absorptions: 2119 (m), 2070 (sh), 2053 (vs), 2030 (vs), 1996 (m), 1957 (sh), 1934 (sh). [b] Spectra measured in heptane solution.

Table II. Infrared Absorptions of Silylcobalt Carbonyls[a] and Parent Silanes

Compound	ν, cm^{-1}									
$Cl_3SiCo(CO)_4$[b]	1130 (m)	1050[d] (m)	825 (m)	570 (vs)	540 (s, sh)					
Cl_3SiH[a]	1110 (s)	1050[d] (sh)	975 (m)	800 (vs)	600 (vs)					
$C_6H_5SiCl_2Co(CO)_4$[c]	1580 (w)	1480 (w)	1425 (m)	1330 (w)	1300 (w)	1098 (m)	995 (w)	735 (m)	700 (m, sh)	
	690 (m)	545 (vs)	520 (s, sh)	475 (s, sh)	410 (m)					
$C_6H_5SiCl_2H$	1590 (m)	1480 (w)	1430 (s)	1330 (w)	1300 (w)	1120 (vs)	996 (m)	800 (vs)	730 (vs)	
	700 (s, sh)	690 (vs)								
$(C_6H_5)_3SiCo(CO)_4$[c]	1580 (w)	1480 (m)	1425 (s)	1320 (w)	1300 (w)	1260 (w)	1190 (w)	1155 (w)	1120 (m, sh)	
	1100 (m)	1090 (m, sh)	995 (m)	740 (m)	700 (s)	550 (s)	520 (s)	485 (s)	390 (m)	
$(C_6H_5)_3SiH$[c]	1580 (w)	1480 (w)	1425 (s)	1330 (w)	1305 (w)	1265 (w)	1185 (w)	1160 (w)	1110 (s)	995 (w)
	820 (s)	800 (s)	735 (s)	725 (s)	695 (s)					
$(C_2H_5)_3SiCo(CO)_4$[b]	1230 (m)	1075[d] (m)	1025 (s)	1005 (s)	980 (m)	970 (m)	860 (w)	730 (vs)	720 (vs)	680 (s)
$(C_2H_5)_3SiH$[9]	1240 (m)	1010 (s)	970 (m)	810 (vs)	700 (s)					
$(C_6H_5)_2SiHCo(CO)_4$[c]	1430 (s)	1100 (s, sh)	1095 (s)	1030 (s)	1010 (vs)	995 (s)	740 (w, sh)	730 (m)	700 (s)	
	690 (s)	550 (vs)	520 (s)	480 (s)	400 (s)					
$(C_2H_5)_2SiH_2$	1430 (s)	1120 (vs)	1105 (s, sh)	935 (vs)	845 (vs)	720 (s, sh)	695 (vs)	590 (vs)		

[a] Cobalt hydrocarbonyl shows the following absorptions:[11] 700 (m, sh), 578 (vw), 546 (s), 532 (sh). [b] In heptane. [c] In KBr. [d] Probably due to some hydrolysis (Si–O).

bridging CO of dicobalt octacarbonyl (*e.g.*, 1860 cm^{-1}). Tetracobalt dodecacarbonyl, present as an impurity, also reacted, but more slowly (decrease in the band at 1873 cm^{-1}).

The infrared spectra of the silylcobalt carbonyls were similar to that of cobalt hydrocarbonyl in the CO region 2200–1800 cm^{-1} (Table I). The remaining absorptions of the infrared spectra were similar to those of the parent silanes except for the disappearance of absorptions at 2200 and 800 cm^{-1} associated with Si–H stretching and bending and the appearance of other bands associated with the $Co(CO)_4$ group (Table II).

For both the trichlorosilane and triethylsilane derivatives, some absorptions occurred in the Si–O region which could indicate that some hydrolysis of the Si–Cl and Si–Co bonds had occurred. Such absorptions were absent in the other cases.

The analyses were generally in good agreement with the formula $R_3SiCo(CO)_4$. The decomposition of the triphenylsilane derivative to hexaphenyldisilane also supports this formulation. On heating the triethylsilane derivative, gas evolution did not occur until a somewhat higher temperature (190°), and hexaethyldisiloxane was identified as the main product. It seems likely in this case that some oxygen was removed from the carbonyl group since carbon was also formed in this pyrolysis.

The Reaction of Silicon Hydrides with Cobalt Hydrocarbonyl. At room temperature cobalt hydrocarbonyl undergoes a spontaneous decomposition, largely according to eq 3. In the presence of certain silanes the liberation of hydrogen was greatly accelerated. Some results of a quantitative study of the effect of silanes on the rate of hydrogen evolution are shown in Table III.

$$2HCo(CO)_4 \longrightarrow Co_2(CO)_8 + H_2 \quad (3)$$

Table III. Reaction of Silanes with Cobalt Hydrocarbonyl

Silicon hydride	Moles of silicon hydride/ mole of cobalt hydrocarbonyl	Initial rate of gas evolution rel to spontaneous decompn
None		1
$(C_6H_5)_3SiH$	1	1
$(C_6H_5)_3SiH$	5	1.2
$(C_2H_5)_3SiH$	1	1
$(C_2H_5)_3SiH$	5	5
$(CH_3(H)SiO)_4$	1	10

The reactions were followed to completion only in the last two cases. Here the volumes of hydrogen corresponded to 0.62 and 0.75 mole per mole of cobalt hydrocarbonyl, respectively. In the case of triphenylsilane, the reaction was also followed qualitatively by infrared which revealed the disappearance of cobalt hydrocarbonyl, a small decrease in the silane concentration, and the formation of dicobalt octacarbonyl and some triphenylsilyl cobalt carbonyl.

Hydrosilation and Isomerization Reactions. Dicobalt octacarbonyl was found to catalyze the hydrosilation of normal α-olefins at a useful rate when present in concentrations of *ca.* 0.001 to 0.01 *M* in the undiluted reactants. High yields were obtained at room tem-

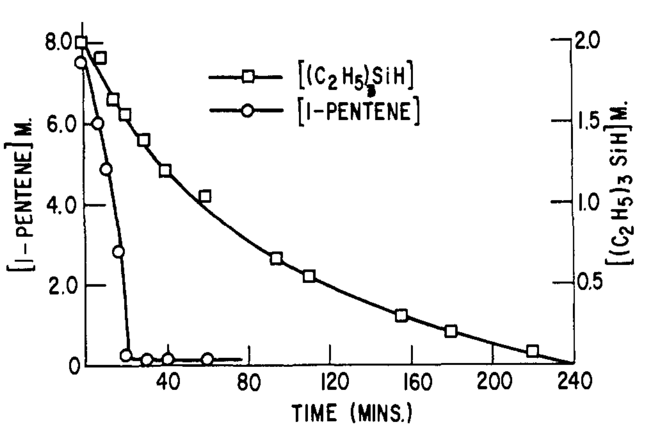

Figure 1. Relative rates of isomerization and hydrosilation for $(C_2H_5)_3SiH$: 30°, $[Co_2(CO)_8] = 0.02$ *M*.

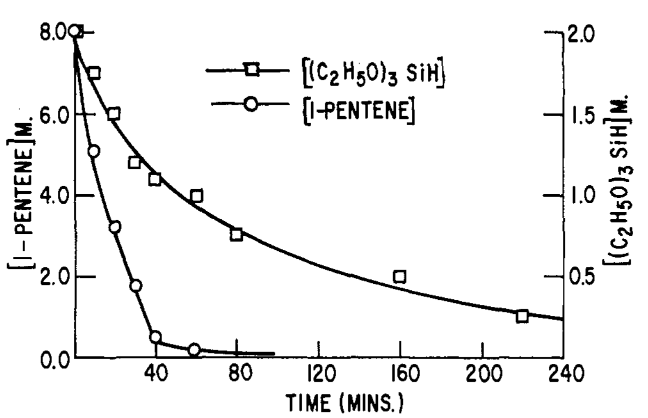

Figure 2. Relative rates of isomerization and hydrosilation for $(C_2H_5O)_3SiH$: 30°, $[Co_2(CO)_8] = 0.002$ *M*.

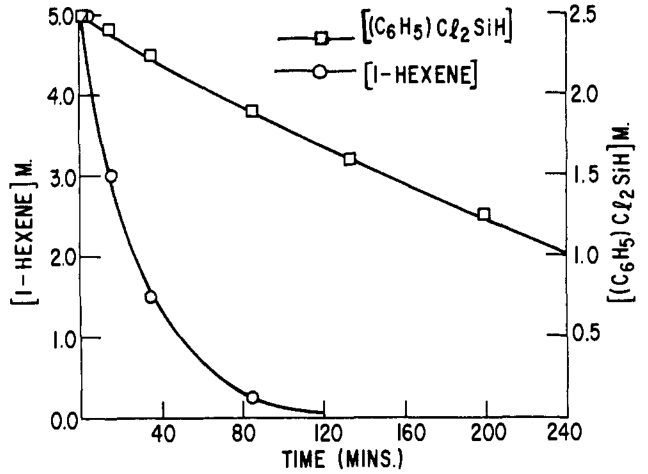

Figure 3. Relative rates of isomerization and hydrosilation for $(C_6H_5)Cl_2SiH$: 40°, $[Co_2(CO)_8] = 0.006$ *M*.

perature with a wide variety of silicon hydrides and several *n*-olefins. At higher temperatures (60°), yields were found to diminish owing to catalyst deactivation. Catalyst deactivation was less severe in reactions where the olefin was present in severalfold excess over that required for complete consumption of silane. Avoidance of exotherms due to too high a catalyst concentration was also found to be desirable for achieving high yields. No catalytic activity was observed when the catalyst was added to the pure silane, followed by addition of the olefin.

Although the reactions were always performed with 1-olefins, a rapid isomerization was observed in the early stages of reaction, which led to equilibration long before the completion of hydrosilation. The course of a hydrosilation of 1-pentene with triethylsilane is illustrated in Figure 1. It is clear, in this reaction, that isomerization is occurring at about 20 times the rate of hydrosilation. In Figure 2 the rate of silane consumption is compared to the rate of isomerization for the reaction of triethoxysilane with 1-pentene. Although the over-all rate in the latter reactions appears to be considerably higher (note difference in catalyst concentration), the relative rates of hydrosilation to isomerization are very comparable. It should be emphasized that absolute rates in these reactions are poorly reproducible, and no kinetic conclusions should be inferred from Figures 1-3. Figure 3 shows the relative rates of disappearance for a reaction of phenyldichlorosilane with 1-hexene.

Isomerization of 1-Heptene-3-d_2. In the presence of small amounts of silicon hydrides, dicobalt octacarbonyl is a very effective catalyst for the isomerization of olefins. Some results of a study of the proton distributions in heptene-d_2 during isomerization by a dicobalt octacarbonyl–triethoxysilane catalyst are shown in Table IV. The change in the number of nonterminal vinyl protons (—CH=) is very similar to that observed with a rhodium chloride catalyst,[10] suggesting a similar type of mechanism for the isomerization.

Table IV. Distribution of Vinyl and Allyl Protons in Heptene-d_2 during Isomerization[a]

Time, min	Number of protons by nmr (±0.1) =CH₂	—CH=	—CH₂C=	Mole % 1-heptene-3-d_2[b]
0	2	1	0	100
12	0.7	0.65	1.00	40
24	0.32	0.43	1.46	25

[a] The number of protons for each sample appears to decrease with time. This is due to the fact that the allylic methyl protons of the product 2-heptene are not included. The total number of protons measured remained constant, within experimental error, throughout the reaction. [b] By infrared analysis.

An infrared analysis of the pentene fraction, after coisomerization of 1-pentene with 1-heptene-3-d_2 with a dicobalt octacarbonyl–triethoxysilane catalyst, showed that extensive intermolecular exchange of deuterium had occurred. The infrared spectrum of the pentene in the C–D stretching region contained bands due to deuterium on all of the carbon atoms of the allylic system. This result was also identical with that obtained with a rhodium chloride catalyst.

Infrared Spectra of Cobalt Carbonyl Species during Hydrosilation. The high extinction coefficients for $\nu_{C=O}$ in cobalt carbonyls allows the easy observation of infrared spectra of such species, even when they are present only in catalytic amounts. The spectrum of dicobalt octacarbonyl was measured in both *n*-hexane and 1-hexene. The spectrum was found to be the same in both solvents and agreed with published spectra for this compound.[11] The spectrum of cobalt hydrocar-

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[11] I. Wender, H. W. Sternberg, R. A. Friedel, S. J. Metlin, and R. E. Markby, *U. S. Bur. Mines Bull.*, **600,** 9 (1962).

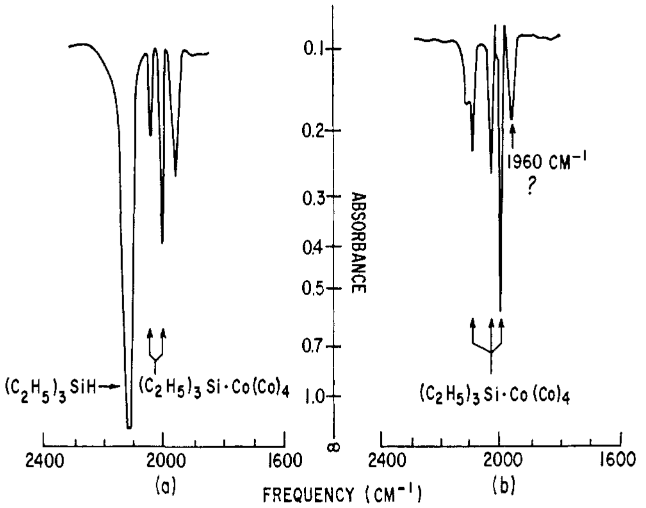


Figure 4. Infrared spectra of carbonyl species during $Co_2(CO)_8$-catalyzed hydrosilation of 1-pentene with $(C_2H_5)_3SiH$: (a) immediately after mixing reactants, (b) after near completion of reaction.

bonyl was also measured in *n*-hexane and 1-hexene. The spectrum in *n*-hexane was the same as that reported in the literature,[11] but in 1-hexene a much more complicated spectrum was observed. This spectrum contained bands due to $Co_2(CO)_8$ and $HCo(CO)_4$, in addition to several unassigned bands. The strongest of the latter, comparable in intensity to the strongest band in the spectrum, occurred at *ca.* 2010 cm^{-1}. The most important fact concerning the spectra discussed so far is that none of them contained bands due to linear carbonyl below 2000 cm^{-1}.

Figure 4a shows the initial spectrum obtained in the carbonyl region for a dicobalt octacarbonyl catalyzed reaction of triethylsilane with 1-pentene. Of the three intense carbonyl bands, the two at higher frequency (2000 and 2030 cm^{-1}) may be assigned to tetracarbonyl(triethylsilyl)cobalt(I). The lower frequency band (1960 cm^{-1}) belongs to some unidentified species which must account for a major fraction of the remaining cobalt. As the reaction progressed, the silyl cobalt carbonyl bands increased progressively in intensity, while the 1960-cm^{-1} band decreased. Figure 4b shows the spectrum obtained as the reaction approached completion. The disappearance of the ν_{Si-H} absorption allows observation of the 2090-cm^{-1} band of the tetracarbonyl(triethylsilyl)cobalt(I) in the latter spectrum.

Similar experiments, using triethoxysilane instead of triethylsilane, showed the presence of tetracarbonyl(triethoxysilyl)cobalt(I) and an unidentified species with a strong band at 1990 cm^{-1}.

Reactions of Silicon Hydrides with Olefins in the Presence of Carbon Monoxide. It was first established that no direct carbonylation of silicon hydrides occurs for temperatures up to 300° and carbon monoxide pressures up to 1700 psi in the presence or absence of dicobalt octacarbonyl. The catalyst was usually recovered in the form of the silylcobalt carbonyl.

In the presence of olefins, reaction products were so complex that it was difficult to establish the course of the reaction. In the case of triethylsilane, ethylene, and carbon monoxide, the lower boiling products appeared to be saturated and unsaturated aldehydes such as propionaldehyde. Propionaldehyde is the expected "oxo" product from ethylene, carbon monoxide, and hydrogen.

The higher boiling products of the reaction were found to contain silicon but also gave tests for aldehydes (Tollen's reagent and 2,4-dinitrophenylhydrazine). However, infrared absorptions around 1650 and 3040 cm^{-1} suggested C=C rather than C=O, and this was supported by the ultraviolet spectra which showed no carbonyl. This anomaly was satisfactorily resolved by the discovery that these fractions hydrolyzed in the presence of moderately strong acids to produce aldehydes. Thus a fraction, bp 180°, was hydrolyzed to propionaldehyde (identified by its 2,4-dinitrophenylhydrazone) and hexaethyldisiloxane. Chemical analysis of the original fraction gave $C_9H_{20}SiO$ which would be expected to contain the group $(C_2H_5)_3Si$ and to have an Si–O–C group from infrared absorptions found in the 1100–1200-cm^{-1} region. It therefore appears that this fraction contains unsaturated alkoxysilanes of formula $C_3H_5OSi(C_2H_5)_3$. A higher boiling fraction similarly contained unsaturated alkoxysilanes, $(C_2H_5)_3SiOC_4H_6OSi(C_2H_5)_3$. However, besides the unsaturated isomers there appeared to be some similar saturated products, the hydrogen resulting from the conversion of about 10% of the triethylsilane to hexaethyldisiloxane.

Somewhat similar reactions were found with other olefins such as pentene-1 and cyclohexene and other silanes such as phenyldimethylsilane and trimethylsilane. These reactions were all very complicated.

Discussion

Reaction of Dicobalt Octacarbonyl with Silicon Hydrides. Silicon hydrides react with dicobalt octacarbonyl liberating 1 mole of hydrogen per mole of carbonyl, according to eq 1. Also consistent with eq 1 was the disappearance during the reaction of the infrared absorptions corresponding to Si–H and the bridging carbonyl group of dicobalt octacarbonyl. The products isolated gave analyses in good agreement with the general formula $R_3SiCo(CO)_4$.

The volatility and ready solubility of the silylcobalt carbonyls is in agreement with the finding that the solutions contain monomeric species. Only with the trichlorosilyl derivative was the molecular weight somewhat high. This could result from some association or possibly some condensation resulting from hydrolysis (*e.g.*, giving $[(CO)_4CoSiCl_2]_2O$).

The occurrence of reaction 2 was confirmed by the isolation of cobalt hydrocarbonyl. Indirect evidence for reaction 3 was first obtained when it was found that, for some silanes, the rate of hydrogen evolution in reaction 1 was independent of the nature of the silane (triphenylsilane, phenyldichlorosilane). This would be readily explained if reaction 3 was the rate-controlling step. Reaction 3 was then confirmed by measuring the rate of decomposition of cobalt hydrocarbonyl in the presence of silicon hydrides. An increased rate of hydrogen evolution was only noted as either the concentration or the reactivity of the silane was increased, thus pointing to reaction 4. In these cases the amount of hydrogen produced was intermediate between that required by reaction 3 (0.5 mole per mole of $HCo(CO)_4$) and reaction 4 (1.0 mole per mole of $HCo(CO)_4$).

The experimental results, therefore, confirm that the over-all reaction (1) is the result of several reactions. The initial reaction (2) is the cleavage of silicon hydride to yield silylcobalt carbonyl and cobalt hydrocarbonyl. The cobalt hydrocarbonyl may spontaneously decompose to hydrogen and dicobalt octacarbonyl, according to reaction 3, or it may react with silicon hydride to yield hydrogen and silylcobalt carbonyl, according to

$$HCo(CO)_4 + R_3SiH \longrightarrow R_3SiCo(CO)_4 + H_2 \qquad (4)$$

The dicobalt octacarbonyl produced by (3) will be ultimately converted to silylcobalt carbonyl by recycling through reaction 2.

The silylcobalt carbonyls are analogous to the well-known alkylcobalt carbonyls.[12] In contrast to the alkyl derivatives all of the silyl complexes show a considerable degree of stability and react only very slowly with air or moisture. The greater stability of the silicon-to-metal bond is ascribed to π bonding between d orbitals, similar to that found with the isoelectronic phosphine complexes.[12a]

The infrared spectra of the silylcobalt carbonyls are very similar to that of cobalt hydrocarbonyl. It can be readily seen that ν_{C-O} is very sensitive to the electronegativity of the groups on silicon, which affect the charge on the metal. A similar effect was noted for the iridium silyl derivatives reported earlier.[13] The trichlorosilyl derivative has approximately the same ν_{C-O} as the hydrocarbonyl, signifying the similar electronegativity of H– and Cl_3Si–. This is consistent with the low polarity of the Si–H bond in trichlorosilane.[14] As less electronegative groups are substituted on the silicon, ν_{C-O} moves to progressively lower frequencies. This weakening of the C–O bonding is expected, since decreasing positive charge on the metal tends to increase donation by the metal into the antibonding π orbital of the carbonyl group.

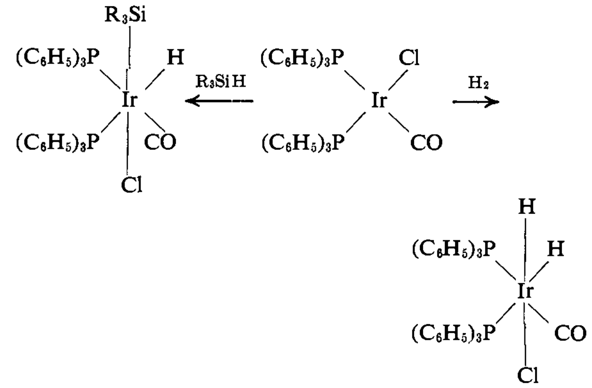
Catalysis of Isomerization and Hydrosilation by Cobalt Carbonyls. The role of group VIII metal complexes as hydrosilation catalysts has previously been discussed in terms of analogies between the reactions of such complexes with silicon hydrides and with hydrogen.[13] The pursuit of such analogies led also to the results described in the present paper.

It has been known for some time that dicobalt octacarbonyl may react directly with molecular hydrogen to produce cobalt hydrocarbonyl,[15] thus

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4 \qquad (5)$$

The demonstration of a similar cleavage of silicon hydrides by dicobalt octacarbonyl (eq 2) has completed the set of analogies which illustrate the three basic types of reaction between transition metal ions and hydrogen or silicon hydrides (eq 6–8).

$$HCo(CO)_4 + R_3SiCo(CO)_4 \xleftarrow{R_3SiH} Co_2(CO)_8 \xrightarrow{H_2} 2HCo(CO)_4 \qquad (6)$$

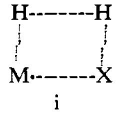

(7)

$$(R_3P)_2PtClH + R_3SiCl \xleftarrow{R_3SiH} (R_3P)_2PtCl_2 \xrightarrow{H_2} (R_3P)_2PtClH + HCl \qquad (8)$$

The reaction of dicobalt octacarbonyl illustrates a reaction in which a covalent bond is cleaved by two metal atoms, each metal atom accepting a fragment of the cleaved molecule. If we adopt the arbitrary convention that the acquired ligands are anionic, the metal atoms in this type of process increase their oxidation number by unity. Although both metal atoms are initially in the same molecule with dicobalt octacarbonyl, the reaction of hydrogen with two metal ions in a termolecular rate-determining step has also been documented.[16]

Reactions 7 illustrate two special cases of a rather general type of reaction.[17] In this reaction a single metal ion captures both fragments of the cleaved molecule, while undergoing an increase of two in both its oxidation and coordination numbers.

Reactions 8 illustrate the heterolytic cleavage of a covalent molecule, leading to ligand substitution, but no change in oxidation or coordination number of the metal ion. Although there is good kinetic evidence that several metal ions activate hydrogen in aqueous solution by a true heterolytic cleavage through a four-center transition state such as i,[16] it is entirely possible


M = metal ion
X = nucleophilic ligand

i

that reactions 8 proceed *via* unstable intermediates analogous to the products of reactions 7.

Since the silylcobalt carbonyls are not catalysts for the hydrosilation of olefins, cobalt hydrocarbonyl is the most likely initial catalytic intermediate. In the presence of olefin, cobalt hydrocarbonyl is expected to produce alkylcobalt carbonyl,[21] thus

$$HCo(CO)_n + R'CH{=}CH_2 \rightleftharpoons R'CH_2CH_2Co(CO)_n \qquad (9)$$

Two possibilities, (10) and (11), were considered for closing the catalytic cycle to produce hydrosilated product and to regenerate catalyst. Unfortunately, alkylcobalt carbonyls rapidly rearrange to acylcobalt

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(12) D. S. Breslow and R. F. Heck, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

(12a) Note Added in Proof. In $Cl_3SiCo(CO)_4$ the Si–Co distance is 2.25 A, 0.09 A shorter than the sum of single bond covalent radii (W. T. Robinson and J. A. Ibers, American Crystallographic Association Meeting, Atlanta, Ga., 1967, paper 16).

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

(14) C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, p 199.

(15) M. Orchin, L. Kirch, and I. Goldfarb, *J. Am. Chem. Soc.*, **78**, 5450 (1956); I. Wender, H. W. Sternberg, and M. Orchin, *ibid.*, **75**, 3041 (1953); M. Orchin, *Advan. Catalysis*, **5**, 385 (1953).

(16) J. Halpern, *ibid.*, **11**, 301 (1959).

(17) We discussed this type of reaction previously,[13] using illustrations from the work of Chatt and Shaw[18] and of Vaska and DiLuzio.[19] More recently Collman[20] and co-workers have obtained further evidence for the generality of such reactions with d^8 transition metal complexes.

(18) J. Chatt, *J. Chem. Soc.*, 2301 (1950); J. Chatt and B. L. Shaw, *ibid.*, 4020 (1959).

(19) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(20) J. P. Collman and W. R. Roper, *ibid.*, **87**, 4008 (1965).

(21) R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4023 (1961).

$$R_3SiCo(CO)_n + R'CH_2CH_2Co(CO)_n \longrightarrow R_3SiCH_2CH_2R' + Co_2(CO)_{4+n} \qquad (10)$$

$$R'CH_2CH_2Co(CO)_n + R_3SiH \longrightarrow R'CH_2CH_2SiR_3 + HCo(CO)_n \qquad (11)$$

carbonyls[21] so they must be formed *in situ* by a reaction such as the addition of cobalt hydrocarbonyl to olefin. Since cobalt hydrocarbonyl was found to be a catalyst for the hydrosilation of olefins, eq 11 is known to proceed if olefin and cobalt hydrocarbonyl are substituted for alkylcobalt carbonyl.

Equation 10 is more susceptible to investigation, and here no hydrosilation products were found on adding silylcobalt carbonyls to solutions of cobalt hydrocarbonyl in olefin. An alternative test of eq 10 was to carry out a hydrosilation with one silicon hydride ($R_3'SiH$) in the presence of the silylcobalt carbonyl of a different silicon hydride ($R_3''SiCo(CO)_4$). Experiments such as these gave mixed products (both $RSiR_3'$ and $RSiR_3''$) suggesting the occurrence of reaction 10. However, this was then shown to be accounted for by the equilibration

$$R_3'SiH + R''SiCo(CO)_4 \rightleftharpoons R_3''SiH + R_3'SiCo(CO)_4 \qquad (12)$$

It seems, therefore, that reaction 11 rather than reaction 10 is the most likely final step in the catalysis.

In Figure 5, we show a diagram of the chemistry thus far encountered in the cobalt-catalyzed hydrosilation reaction. The fact that isomerization is very much faster than hydrosilation indicates that the final step (reaction 11) is the rate-controlling step. In the reaction of cobalt hydrocarbonyl with silicon hydrides, the dependence of rate on silane concentration explains the catalyst deactivation found for high silane:olefin ratios in the hydrosilation reaction.

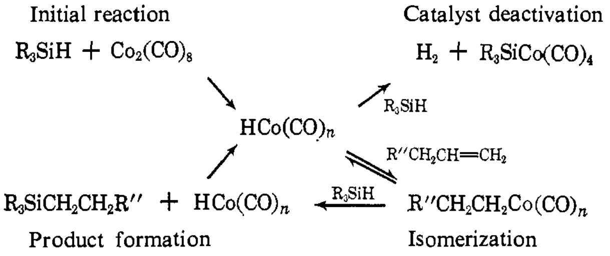
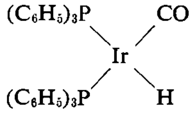


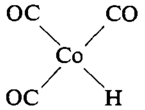
Figure 5. Cobalt carbonyl catalyzed hydrosilation.

Although the scheme of Figure 5 is sufficient to explain the observed behavior of cobalt carbonyls as hydrosilation catalysts, the failure of this scheme to satisfactorily explain the unidentified cobalt carbonyl bands in the infrared spectra of catalyzed reaction mixtures is a clear indication of its oversimplicity. The dependence of these bands on the nature of the silicon hydride necessitates the postulation of a catalytic intermediate containing silicon, cobalt, and carbon monoxide, which is quite different from the stable, isolable tetracarbonyl(silyl)cobalt(I) complexes.

A reconsideration of the process illustrated by eq 6, previously invoked to explain the catalysis of hydrosilation by Pt(II) and Rh(I), presents a plausible and unifying possibility for explaining the above observations. If the hydride, or alkyl, ligand of a hydrido, or alkyl, cobalt carbonyl is considered to be an anionic ligand, such complexes are formally analogous to the d^8 complexes which undergo expansion of their coordination sphere by cleavage of covalent molecules.[17,22] The analogy is particularly clear if one compares, for example, the known complex bis(triphenylphosphine)carbonylhydridoiridium(I) (ii)[22] with the hypothetical complex tricarbonylhydridocobalt(I) (iii)

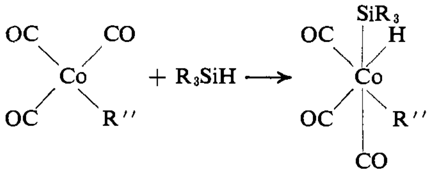


ii



iii

If complex iii can similarly expand its coordination sphere by cleaving a silicon hydride[23] iv is formed.



(13)

iv

This species (formally a Co(III) complex) may revert to the cobalt(I) hydrocarbonyl by elimination of R_3SiR''. A similar process may explain the observed silicon exchange between silicon hydrides and tetracarbonylsilylcobalt(I) complexes. In such a case, R'' in (13) would be a silyl residue and the reaction would be reversible.

The obvious relevance of this type of process to some more general problems of homogeneous catalysis necessitates the experimental substantiation of what, at the moment, is only a speculative possibility. If the unassigned cobalt carbonyl bands in the spectra of the reaction mixtures are in fact due to species similar to iv, there is some hope for their isolation at low temperature, even though they obviously decompose spontaneously and rapidly at room temperature. We are currently pursuing such a possibility.

Our studies on the isomerization of deuterioolefins indicate that isomerization occurs during hydrosilation through a rapid reversible addition of a hydrogen atom, or ion, to coordinated olefin. The results obtained were qualitatively the same as those obtained by us in studies of rhodium-catalyzed isomerization.[9] Whether the addition and removal of hydrogen occurs with a change in oxidation state of the cobalt, as suggested by Cramer[24] for the rhodium-catalyzed reaction (this again would necessitate the invocation of species such as iv), cannot be decided on the basis of presently available evidence.

A notable difference between cobalt carbonyls and platinum complexes as hydrosilation catalysts is that a wide variation in the relative rates of isomerization and hydrosilation occurs with the latter catalysts, depending on the nature of the silicon hydride. With cobalt carbonyl catalysts, comparatively little variation in the relative rates was observed.

Reactions of Silicon Hydrides with Olefins in the Presence of Carbon Monoxide. These reactions were

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(22) L. Malatesta, M. Angoletta, and G. Caglio, *Proc. Intern. Conf. Coordination Chem., 8th Vienna, 1964,* 210 (1965).

(23) R. F. Heck, *Advan. Organometal. Chem.*, in press, has proposed similar reactions of cobalt tricarbonyls in a recent review.

(24) R. Cramer, *J. Am. Chem. Soc.*, **88**, 2278 (1966).

very complex, but it was established that, among the reactions occurring between ethylene, triethylsilane, and carbon monoxide, eq 14 and 15 took place. The products of both reactions are unsaturated alkoxysilanes, a number of isomers being possible.

$$C_2H_4 + (C_2H_5)_3SiH + CO \longrightarrow (C_2H_5)_3SiOC_3H_5 \qquad (14)$$

$$C_2H_4 + 2(C_2H_5)_3SiH + 2CO \longrightarrow (C_2H_5)_3SiOC_4H_6OSi(C_2H_5)_3 \qquad (15)$$

A discussion of all the possible reaction paths would be largely speculative so that only two points will be made. (i) Since no reaction occurred in the absence of olefin, no facile carbon monoxide insertion occurs for silylcobalt carbonyls, unlike the corresponding alkylcobalt carbonyls. (ii) In view of the above, it seems most probable that the reaction in the presence of olefins occurs by carbon monoxide insertion in an alkylcobalt carbonyl as in the hydroformylation reaction. Reactions 14 and 15 would then be analogous to the hydrosilation reaction but with an additional carbonyl insertion step. The resulting products would then rearrange from α-silyl ketones to unsaturated alkoxysilanes, *e.g.*

$$(C_2H_5)_3SiCOC_2H_5 \xrightarrow[\bigcirc]{} (C_2H_5)SiOC_3H_5$$

The product of reaction 15 could then be formed from further reaction of this olefin.

Formation of 1,3-Dianions of Acetanilide and Related Amides by Means of *n*-Butyllithium. Condensations with Electrophilic Compounds[1]

Robert L. Gay and Charles R. Hauser

Contribution from the Department of Chemistry, Duke University, Durham, North Carolina. *Received October 28, 1966*

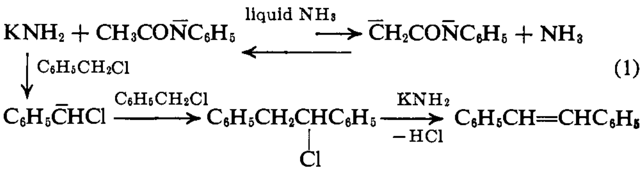
Abstract: The 1,3-dianion of acetanilide, which could not be prepared satisfactorily with potassium amide in liquid ammonia, was made by means of *n*-butyllithium in an inert solvent and condensed at its α-carbon with various electrophilic compounds. Similarly, several other secondary amides were converted to their 1,3-dianions, which were condensed at their α-carbon with benzophenone. The method appears to be quite general and useful for the synthesis of a number of α-substituted secondary amides.

Many unsymmetrical 1,3-dianions have previously been prepared from appropriate active hydrogen compounds by means of 2 molar equiv of an alkali amide in liquid ammonia and alkylated to form derivatives that are isomeric with the alkyl derivatives of the intermediate monoanions. For example, 1,3-dianions **1** and **2** have been made by this method from acetylacetone[2] and phenylacetamide[3] and benzylated at the terminal position[2b] and at the α-carbon,[3] respectively. Also, other types of condensations at these positions have been realized.[2a,4,5]

$$CH_3CO\bar{C}HCO\bar{C}H_2 \qquad\qquad C_6H_5\bar{C}HCO\bar{N}H$$

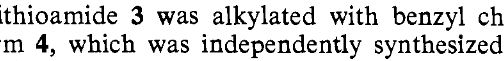
1 **2**

The 1,3-dianion of acetanilide, however, could not be formed satisfactorily by this method even though this amide is isomeric with phenylacetamide which is readily converted to dianion **2**. Thus, treatment of acetanilide with 2 molar equiv of potassium amide in liquid ammonia followed by 1 molar equiv of benzyl chloride has afforded stilbene instead of α-benzylacetanilide.[6] This result may be rationalized by eq 1, since benzyl chloride is known to be converted by this reagent to stilbene.[7]



$$\begin{array}{l} KNH_2 + CH_3CO\bar{N}C_6H_5 \overset{\text{liquid } NH_3}{\underset{\longleftarrow}{\longrightarrow}} \bar{C}H_2CO\bar{N}C_6H_5 + NH_3 \\ \big\downarrow C_6H_5CH_2Cl \qquad\qquad\qquad\qquad\qquad\qquad (1) \\ C_6H_5\bar{C}HCl \xrightarrow{C_6H_5CH_2Cl} C_6H_5CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HC_6H_5 \xrightarrow[-HCl]{KNH_2} C_6H_5CH{=}CHC_6H_5 \end{array}$$

We have now found that the 1,3-dianion of acetanilide (**3**) can be prepared satisfactorily by means of 2 molar equiv of *n*-butyllithium in ether–hexane or tetrahydrofuran (THF)–hexane (eq 2), as evidenced by condensations at the α-carbon of **3** with various electrophilic compounds (Table I).



$$CH_3CONHC_6H_5 \xrightarrow[\text{ether–hexane or THF–hexane}]{2LiC_4H_9} LiCH_2CO\overset{Li}{N}C_6H_5 \qquad (2)$$

3

Dilithioamide **3** was alkylated with benzyl chloride to form **4**, which was independently synthesized from hydrocinnamoyl chloride and aniline (eq 3).

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[1] (a) Supported by the Petroleum Research Fund administered by the American Chemical Society and by the Public Health Service, Research Grant No. CA-04455 from the National Cancer Institute. (b) For a preliminary communication on part of this work, see R. L. Gay, S. Boatman, and C. R. Hauser, *Chem. Ind.* (London), 1789 (1965).

[2] (a) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958); (b) K. G. Hampton, T. M. Harris and C. R. Hauser, *J. Org. Chem.*, **30**, 61 (1965).

[3] R. B. Meyer and C. R. Hauser, *ibid.*, **26**, 3696 (1961).

[4] R. J. Light and C. R. Hauser, *ibid.*, **25**, 538 (1960); R. J. Light and C. R. Hauser, *ibid.*, **26**, 1716 (1961).

[5] E. M. Kaiser and C. R. Hauser, *ibid.*, **31**, 3317 (1966).

[6] D. R. Bryant, Ph.D. Thesis, Duke University, 1962; stilbene and its dimer were obtained in yields of 54 and 22%, respectively, and 68% of the starting acetanilide was recovered.

[7] See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956); D. R. Bryant, S. D. Work, and C. R. Hauser, *J. Org. Chem.*, **29**, 236 (1964).