Trimethyl- and Trichlorosilylcobalt Tetracarbonyls and the Hydrosilation of Ethylene[1,2]

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The new compound $(CH_3)_3SiCo(CO)_4$ was synthesized by the reaction of $(CH_3)_3SiH$ with either $Co_2(CO)_8$ or $HCo(CO)_4$. The interaction of Cl_3SiH or CH_3SiH_3 with $HCo(CO)_4$ yielded $Cl_3SiCo(CO)_4$ and $CH_3SiH_2Co(CO)_4$, respectively. The new compound $[(CH_3)_2AsCo(CO)_3]_x$ was synthesized from $(CH_3)_2AsH$ and $HCo(CO)_4$ in an analogous manner. The thermal stability of the compounds $R_3SiCo(CO)_4$ ($R = CH_3$, Cl) was examined. The silicon–cobalt bond in $(CH_3)_3$-$SiCo(CO)_4$ was cleaved by water, methanol, dimethylamine, germanium tetrafluoride, and dimethylchloroarsine but not by phosphorus trifluoride, phosphorus pentafluoride, boron trifluoride, or acetyl chloride. The silicon–cobalt bond in $Cl_3SiCo(CO)_4$ was cleaved by iodine but not by phosphorus pentafluoride or ethyl iodide. Trimethylsilane, $(CH_3)_3SiH$, was found to add rapidly to ethylene at room temperature in the presence of catalytic quantities of $HCo(CO)_4$ to give high yields of $(CH_3)_3SiC_2H_5$. Hydrosilation did not occur in the gas phase or when $(CH_3)_3SiH$ was added to the products of the reaction of $HCo(CO)_4$ with ethylene. The mechanism of the hydrosilation reaction is discussed. Neither $(CH_3)_2AsH$ nor AsH_3 added to ethylene in the presence of $HCo(CO)_4$ when the reactants were treated in the manner necessary for hydrosilation of ethylene.

The synthesis of the parent silylcobalt tetracarbonyl, $H_3SiCo(CO)_4$, has recently been reported in the literature[3] and some of its physical and chemical properties have been examined.[3–5] The trigonal-bipyramidal structure of silylcobalt tetracarbonyls, in which the silicon substituent occupies an axial position, has been demonstrated from infrared,[6,7] X-ray,[8] and electron diffraction[9] studies.

The chief purpose of the present investigation, preliminary results of which have been reported previously,[10] was to study selected chemical properties of the completely methylated and chlorinated derivatives $(CH_3)_3SiCo(CO)_4$ and $Cl_3SiCo(CO)_4$ in order to obtain information concerning the nature of the silicon–cobalt bond. This linkage has so far been investigated to only a very small extent.[3–5,11–13] A secondary purpose was to study the closely related chemistry dealing with the role of dicobalt octacarbonyl, $Co_2(CO)_8$, as a catalyst in the hydrosilation of olefins.

Results and Discussion

(I) Synthesis of Trimethylsilylcobalt Tetracarbonyl

and Related Compounds.—Chalk and Harrod[11] have reported the synthesis of a number of compounds of general formula $R_3SiCo(CO)_4$ (R = a variety of different organic and inorganic groups) by the reaction of R_3SiH with dicobalt octacarbonyl, $Co_2(CO)_8$. The new compound, $(CH_3)_3SiCo(CO)_4$, was prepared in the present investigation by this method in high yield by a rapid, room-temperature reaction, *viz.*

$$2(CH_3)_3SiH + Co_2(CO)_8 \longrightarrow 2(CH_3)_3SiCo(CO)_4 + H_2 \quad (1)$$
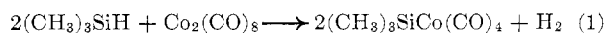
It was suggested by Chalk and Harrod[11] that the reaction between silanes and dicobalt octacarbonyl, as exemplified by eq 1, might occur *via* the intermediate formation of $HCo(CO)_4$ as given by

$$(CH_3)_3SiH + Co_2(CO)_8 \longrightarrow (CH_3)_3SiCo(CO)_4 + HCo(CO)_4 \quad (2)$$

$$(CH_3)_3SiH + HCo(CO)_4 \longrightarrow (CH_3)_3SiCo(CO)_4 + H_2 \quad (3)$$

Both they[12] and we[10] have subsequently shown that $HCo(CO)_4$ is indeed formed when dicobalt octacarbonyl is treated with a deficit of R_3SiH and that a reaction of the type given by eq 3 also occurs readily. Thus the present study shows that 100% yields of $(CH_3)_3SiCo(CO)_4$ are obtained in a rapid reaction according to eq 3 when liquid phase is present; no interaction occurs if only gas phase is present. Although the complete absence of reaction in the gas phase may be caused by the smaller concentrations present at the gas pressures used, it seems more likely that reaction proceeds *via* the formation of ionic or highly polar species which can only exist when stabilized by solvation in the presence of liquid phase. Trichlorosilane, Cl_3SiH, and also methylsilane, CH_3SiH_3, underwent analogous reactions with $HCo(CO)_4$ to give high yields of $Cl_3SiCo(CO)_4$ and $CH_3SiH_2Co(CO)_4$, respectively. Both of these compounds had previously been synthesized from the silane and $Co_2(CO)_8$.[11,14] However, silane, SiH_4, did not react appreciably under similar

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(2) This research was supported in part by fellowships from the National Institute of Health and from the University of Pennsylvania. It was also supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

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

(4) B. J. Aylett and J. M. Campbell, *ibid.*, 159 (1967).

(5) B. J. Aylett and J. M. Campbell, *Inorg. Nucl. Chem. Letters*, **3**, 137 (1967).

(6) A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 686, 1941 (1967).

(7) O. Kahn and M. Bigorgne, *Compt. Rend.*, **266C**, 792 (1968).

(8) W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

(9) A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. M. Campbell, *J. Organometal. Chem.* (Amsterdam), **14**, 279 (1968).

(10) Y. L. Baay and A. G. MacDiarmid, *Inorg. Nucl. Chem. Letters*, **3**, 159 (1967), see also A. G. MacDiarmid, *J. Pure Appl. Chem.*, in press.

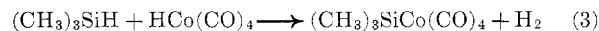(11) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(12) A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1640 (1967).

(13) L. H. Sommer and J. E. Lyons, *ibid.*, **90**, 4197 (1968).

(14) S. K. Gondal, Ph.D. Dissertation, University of Pennsylvania, 1968.

experimental conditions and the presence of at least one substituent on the silicon therefore appears to be essential if a reaction of the type given by eq 3 is to occur. The over-all reaction of a silane with $HCo(CO)_4$ is undoubtedly complex, particularly since reaction 3 may proceed, at least in the case of some silanes, as pointed out by Chalk and Harrod,[12] *via* a preliminary decomposition of the $HCo(CO)_4$ to hydrogen and $Co_2(CO)_8$, the latter species then reacting with the silane as given by eq 1.

It is of interest to note that the reaction of $HCo(CO)_4$ with metalloid–hydrogen bonds is not restricted to silicon–hydrogen bonds. Thus when dimethylarsine, $(CH_3)_2AsH$, was held with a deficit of $HCo(CO)_4$ at room temperature for 10 min, a 100% yield of the presumably polymeric new compound $[(CH_3)_2AsCo(CO)_3]_x$ was obtained, *viz.*

$$x(CH_3)_2AsH + xHCo(CO)_4 \longrightarrow$$
$$[(CH_3)_2AsCo(CO)_3]_x + xH_2 + xCO \quad (4)$$
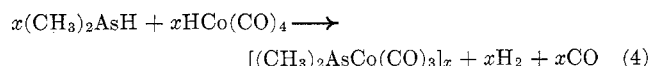
It appears possible that $(CH_3)_2AsCo(CO)_4$ might first be formed and that the lone pair of electrons on the arsenic then displaces a carbon monoxide from an adjacent molecule to give the products.

(II) Thermal Stability of Trimethylsilylcobalt Tetracarbonyl and Trichlorosilylcobalt Tetracarbonyl.—Although gaseous samples of $(CH_3)_3SiCo(CO)_4$ are fairly stable for several hours at room temperature, samples of $(CH_3)_3SiCo(CO)_4$ often liberate small quantities of $[(CH_3)_3Si]_2O$ after approximately 1 hr at room temperature *in vacuo* and become pale pink or red; however, after 3 months *in vacuo* at room temperature 87% of a sample was recovered unchanged. Hexamethyldisiloxane, $[(CH_3)_3Si]_2O$ was evolved when the compound was heated to approximately 150°; when evolution ceased, the composition of the residue corresponded closely to $RC\equiv Co_3(CO)_9$, where $R = (CH_3)_3Si$, *viz.*

$$3(CH_3)_3SiCo(CO)_4 \longrightarrow (CH_3)_3SiC\equiv Co_3(CO)_9 +$$
$$[(CH_3)_3Si]_2O + 2CO \quad (5)$$
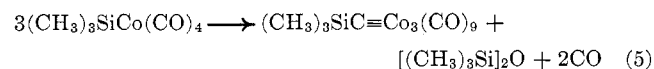
which is analogous to the known compounds where $R = CH_2=CHSi\equiv$[15] and $H_3CC\equiv$.[16]

Proton nuclear magnetic resonance studies show that solutions of $(CH_3)_3SiCo(CO)_4$ in cyclohexane are stable for long periods of time at room temperature and even after heating at 60° for several days.

Trichlorosilylcobalt tetracarbonyl is even more thermally stable than $(CH_3)_3SiCo(CO)_4$ and after heating at 150° for 5 days approximately 68% of the compound was recovered unchanged. A small amount of silicon tetrachloride but no $[Cl_3Si]_2O$, analogous to the $[(CH_3)_3Si]_2O$ or $[(C_2H_5)_3Si]_2O$ formed during the thermal decomposition of $(CH_3)_3SiCo(CO)_4$ or $(C_2H_5)_3SiCo(CO)_4$,[12] respectively, was obtained, nor was any Si_2Cl_6, analogous to the $Si_2(C_6H_5)_6$ formed during the thermal decomposition of $(C_6H_5)_3SiCo(CO)_4$,[12] isolated. Thus it appears that the thermal stability and particularly the nature of the silicon-containing thermal decomposition

product changes significantly according to the substituent on the silicon.

(III) Cleavage of the Silicon–Cobalt Bond by Protonic Reagents.—It has been reported[3] that the silicon–cobalt bond in $H_3SiCo(CO)_4$ is hydrolyzed rapidly to give disiloxane, $(H_3Si)_2O$, and $HCo(CO)_4$. The hydrolytic stability of the bond is not increased to any marked extent when the hydrogen atoms on the silicon are replaced by methyl groups. Thus, at room temperature in the presence of a slight excess of water, 58% yields of $[(CH_3)_3Si]_2O$ were obtained according to

$$2(CH_3)_3SiCo(CO)_4 + H_2O \longrightarrow [(CH_3)_3Si]_2O + 2HCo(CO)_4 \quad (6)$$

but hydrolysis proceeded quantitatively in the presence of a deficit of water during 2 hr. Hydrolysis might well be more rapid in a homogeneous reaction medium.

Quantitative cleavage of the silicon–cobalt bond in $(CH_3)_3SiCo(CO)_4$ occurred according to eq 7 when it was mixed with a slight deficit of methanol

$$(CH_3)_3SiCo(CO)_4 + CH_3OH \longrightarrow$$
$$(CH_3)_3SiOCH_3 + HCo(CO)_4 \quad (7)$$
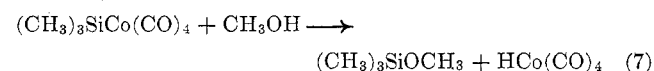
From studies of the reaction of ammonia with $H_3SiCo(CO)_4$ and $H_3SiMn(CO)_5$ it appears that the *primary* reaction which occurs may be represented by the general equation[5]

$$2H_3SiM(CO)_x + NH_3 \longrightarrow (H_3Si)_2NH + 2HM(CO)_x \quad (8)$$
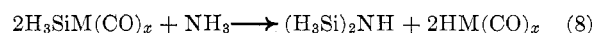
When $(CH_3)_3SiCo(CO)_4$ was treated with a slight deficit of dimethylamine a 19% yield of $(CH_3)_3SiN(CH_3)_2$, based on the dimethylamine employed, was obtained

$$(CH_3)_3SiCo(CO)_4 + (CH_3)_2NH \longrightarrow$$
$$(CH_3)_3SiN(CH_3)_2 + HCo(CO)_4 \quad (9)$$
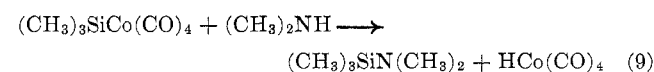
An unidentified, nonvolatile white solid was also formed. It is presumed that the solid consisted of $(CH_3)_2NH \cdot HCo(CO)_4$ and (since $H_3SiCo(CO)_4$ forms the adduct $H_3SiCo(CO)_4 \cdot 2N(CH_3)_3$ with trimethylamine[4]) an adduct of composition $(CH_3)_3SiCo(CO)_4 \cdot x(CH_3)_2NH$.

(IV) Cleavage of the Silicon–Cobalt Bond by Covalent Halides.—The silicon–cobalt bond in $(CH_3)_3SiCo(CO)_4$ was cleaved rapidly by germanium tetrafluoride to give essentially quantitative yields of the new compound trifluorogermylcobalt tetracarbonyl, $F_3GeCo(CO)_4$, *viz.*

$$(CH_3)_3SiCo(CO)_4 + GeF_4 \longrightarrow F_3GeCo(CO)_4 + (CH_3)_3SiF \quad (10)$$
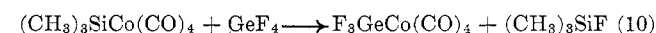
An analogous reaction appeared to take place with dimethylchloroarsine, $(CH_3)_2AsCl$, at low temperatures, *viz.*

$$(CH_3)_3SiCo(CO)_4 + (CH_3)_2AsCl \longrightarrow$$
$$(CH_3)_2AsCo(CO)_4 + (CH_3)_3SiCl \quad (11)$$
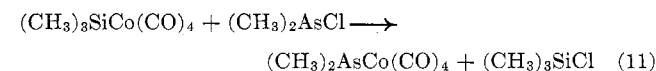
although the postulated product, $(CH_3)_2AsCo(CO)_4$, was not isolated since it apparently decomposed on warming to room temperature with the loss of carbon monoxide to give quantitative yields of the new, presumably polymeric compound $[(CH_3)_2AsCo(CO)_3]_x$, *viz.*

$$x(CH_3)_2AsCo(CO)_4 \longrightarrow [(CH_3)_2AsCo(CO)_3]_x + xCO \quad (12)$$

(15) S. F. A. Kettle and J. A. Khan, *Proc. Chem. Soc.*, 82 (1962).
(16) P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967).

Inorganic Chemistry

No significant cleavage of the silicon–cobalt bond or substitution of carbon monoxide on the cobalt appeared to take place even when $(CH_3)_3SiCo(CO)_4$ was heated to 100° with phosphorus trifluoride. Little or no reaction occurred between $(CH_3)_3SiCo(CO)_4$ and phosphorus pentafluoride, boron trifluoride, or acetyl chloride at room temperature. No reaction took place between $Cl_3SiCo(CO)_4$ and phosphorus pentafluoride or ethyl iodide at room temperature.

It is interesting to note that certain labile covalent halides cleaved the silicon–cobalt bond readily while others did not, even under more vigorous reaction conditions. Whether the absence of reaction in these latter cases is due to thermodynamic or kinetic factors, is, of course, not known although it seems likely that kinetic factors may be very important. However, the absence of reaction with boron trifluoride may be due to unfavorable thermodynamics since the boron–fluorine bond energy is greater than the silicon–fluorine bond energy.[17]

If the rate-controlling step in the cleavage reactions is nucleophilic attack upon silicon, then the expected increase in ease of attack of the silicon in $Cl_3SiCo(CO)_4$ as compared to $(CH_3)_3SiCo(CO)_4$ is certainly not apparent from the experimental results. Since both GeF_4 and $(CH_3)_2AsCl$, the covalent halides which readily cleaved the silicon–cobalt bond, tend to form cationic species, it is possible that the rate-controlling step may involve electrophilic attack upon the cobalt.
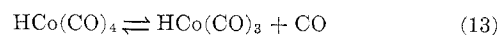
(V) Cleavage of the Silicon–Cobalt Bond by Iodine.—It has been reported that iodine does not react with $Cl_3SiCo(CO)_4$ at room temperature;[18] however, it was noted in this study that iodine cleaved the silicon–cobalt bond in $Cl_3SiCo(CO)_4$ on warming to 48° to give 80% yields of Cl_3SiI based on the $Cl_3SiCo(CO)_4$ which underwent reaction. Approximately half of the $Cl_3SiCo(CO)_4$ was recovered unchanged.

From information presently available, it is not yet possible to predict with any degree of accuracy the reagents or reaction conditions necessary to bring about cleavage of the silicon–cobalt bond in silicon cobalt tetracarbonyls.

(VI) Hydrosilation of Ethylene.—It has been shown by Chalk and Harrod[11] that dicobalt octacarbonyl, $Co_2(CO)_8$, acts as an efficient catalyst for the addition of a variety of trisubstituted silanes to olefins. Both they[12] and we[10] have subsequently shown that $HCo(CO)_4$ will also act as a catalyst for this addition. Since $HCo(CO)_4$ is formed in the reaction of a silane with $Co_2(CO)_8$,[10,12] as exemplified by eq 2, and since the catalytic activity of the $Co_2(CO)_8$ is not due to the $R_3SiCo(CO)_4$ formed in reaction 1,[12] it is therefore likely that $HCo(CO)_4$ is responsible for the observed catalytic activity of the $Co_2(CO)_8$.

Chalk and Harrod have suggested[11] that the catalytic role of $HCo(CO)_4$ in the hydrosilation of olefins is as

(17) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth & Co. Ltd., London, 1958.
(18) M. Pankowski and M. Bigorgne, *Compt. Rend.*, **264**, 1382 (1967).

follows. The $HCo(CO)_4$ or possibly $HCo(CO)_3$ which might be present because of the equilibrium

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (13)$$

first adds to the olefin to give an alkylcobalt carbonyl, *viz.*

$$HCo(CO)_n + R'CH{=}CH_2 \rightleftharpoons R'CH_2CH_2Co(CO)_n \qquad (14)$$
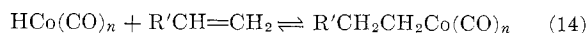
where $n = 3$ or 4. Cleavage of the carbon–cobalt bond by a silicon–hydrogen bond to give the desired compound with regeneration of the cobalt tetracarbonyl hydride catalyst is then postulated, *viz.*

$$R'CH_2CH_2Co(CO)_n + R_3SiH \longrightarrow$$
$$R'CH_2CH_2SiR_3 + HCo(CO)_n \qquad (15)$$
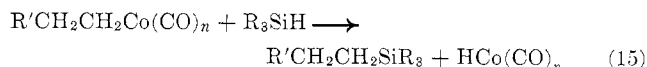
This portion of the investigation was carried out in order to ascertain whether experimental evidence consistent with a mechanism proceeding *via* reactions 14 and 15 could be obtained.

It was found that when excess ethylene, $(CH_3)_3SiH$, and $HCo(CO)_4$ were condensed separately in a trap at liquid nitrogen temperature and then held at room temperature for approximately 10 min, an 81% yield of $(CH_3)_3SiC_2H_5$, based on the quantity of $(CH_3)_3SiH$ employed, was obtained, *viz.*

$$(CH_3)_3SiH + CH_2{=}CH_2 \longrightarrow (CH_3)_3SiCH_2CH_3 \qquad (16)$$
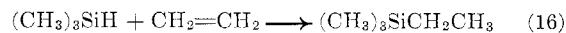
Some of the $(CH_3)_3SiH$ underwent reaction to give $(CH_3)_3SiCo(CO)_4$, according to eq 3. The role of the $HCo(CO)_4$ can certainly be regarded as "catalytic" since 0.120 mmol of $HCo(CO)_4$ caused the formation of 1.050 mmol of $(CH_3)_3SiC_2H_5$.

In contrast, when a *gaseous* mixture of ethylene and $(CH_3)_3SiH$, containing excess ethylene, was mixed with *gaseous* $HCo(CO)_4$ at room temperature, no $(CH_3)_3SiC_2H_5$ could be identified in the mixture of the products obtained after 3 hr at room temperature in the gas phase. Essentially all of the $HCo(CO)_4$ was consumed.

In order to gain information concerning the nature of the reaction between $HCo(CO)_4$ and ethylene (eq 14), gaseous $HCo(CO)_4$ was mixed with excess gaseous ethylene. An infrared examination of the gaseous mixture after approximately 5 min at room temperature showed that all of the $HCo(CO)_4$ had been consumed. The disappearance of the $HCo(CO)_4$ was consistent with the postulated reaction given by eq 14 but the formation of a $C_2H_5Co(CO)_n$ species could be neither confirmed nor disproved. Gaseous $(CH_3)_3SiH$ was then added to this gaseous mixture and an infrared examination after 30 min at room temperature showed that no $(CH_3)_3SiC_2H_5$ had been formed. These observations do not, therefore, support the reaction sequence given by eq 14 and 15. However, this result might have been expected in view of the observation that no catalytic hydrosilation of ethylene occurred when all reactants were present in the gaseous phase.

After liquid $HCo(CO)_4$ and ethylene had been held at room temperature for 85 sec an infrared spectrum of the material showed that essentially all of the $HCo(CO)_4$ had been consumed. The liquid products were

then shaken with $(CH_3)_3SiH$ for 1 min at 0°. An infrared and proton nuclear magnetic resonance spectral examination of the resulting mixture of unidentified compounds showed that no $(CH_3)_3SiC_2H_5$ had been formed.

Hence, although catalytic hydrosilation of ethylene in the presence of $HCo(CO)_4$ readily occurs in the presence of liquid phase, no evidence has been obtained in this investigation to support the hypothesis that hydrosilation occurs by addition of $HCo(CO)_4$ to the olefin to give an alkylcobalt carbonyl (eq 14), followed by cleavage of the carbon–cobalt bond by a silicon–hydrogen bond (eq 15) to give the addition product. It might be that the postulated reaction scheme is valid but that the $C_2H_5Co(CO)_n$ decomposed completely during the 85 sec it was held at room temperature. The fact that reaction *does* occur when ethylene, $(CH_3)_3SiH$, and $HCo(CO)_4$ are mixed in the gas phase, but *not* to give the expected hydrosilation product, suggests that the necessary transition complex for *hydrosilation* is either ionic or highly polar and that it is stabilized by solvation in the presence of liquid phase, under which conditions hydrosilation readily occurs to give high yields of $(CH_3)_3SiC_2H_5$. The active species insofar as hydrosilation is concerned might well be the transitory $HCo(CO)_n$–olefin π complex.[19,20]

In view of the fact that both $(CH_3)_2AsH$ and $(CH_3)_3SiH$ apparently undergo analogous types of reactions with $HCo(CO)_4$ (see eq 1 and 4), an attempt was made to add $(CH_3)_2AsH$ and also arsine, AsH_3, to ethylene in the presence of $HCo(CO)_4$ catalyst. However, in the case of $(CH_3)_2AsH$ essentially quantitative conversion of the $HCo(CO)_4$ to $[(CH_3)_2AsCo(CO)_3]_x$ took place. With AsH_3 no addition could be observed. In the case of $(CH_3)_2AsH$ the absence of a reaction analogous to hydrosilation under the experimental conditions employed may be due to the fact that reaction 4 occurred very much more rapidly than the addition reaction, and hence the $HCo(CO)_4$ catalyst was rapidly consumed.

Experimental Section

Apparatus.—All work was carried out in a borosilicate (Pyrex) glass vacuum system. All apparatus and techniques employed were identical with those previously described[21] with the exception of the reaction vessels which were constructed from thick-walled Pyrex tubing to which a Teflon stopcock was attached.

Materials.—The following commercial reagents were used without further purification: BF_3 (mol wt: calcd, 67.8; found, 68.1; confirmed by infrared spectrum[22]), $(CH_3)_2NH$ (anhydrous; mol wt: calcd, 45.1; found, 44.9; confirmed by infrared spec-

trum[23]), CH_3SiH_3 (mol wt: calcd, 46.1; found, 46.4; confirmed by infrared spectrum[24]), PF_5 (mol wt: calcd, 126.0; found, 125.0; confirmed by infrared spectrum[25]), SiH_4 (mol wt: calcd, 32.1; found, 32.3; confirmed by infrared spectrum[26]), $(CH_3)_3SiH$ (mol wt: calcd, 74.2; found, 74.2; confirmed by infrared spectrum[24]), C_2H_5I (mol wt: calcd, 157.0; found, 156.1; confirmed by infrared spectrum[27]), C_2H_4 (mol wt: calcd, 28.0; found, 28.0; confirmed by infrared spectrum[23]), and iodine. CH_3COCl (mol wt: calcd, 78.5; found, 79.0; confirmed by infrared spectrum[28]) and CH_3OH (mol wt: calcd, 32.0; found, 32.2; confirmed by infrared spectrum[23]) were dried with P_2O_5. $Co_2(CO)_8$ was resublimed and Cl_3SiH (mol wt: calcd, 135.4; found, 136.4; confirmed by infrared spectrum[29]) was purified by distillation through a trap held at −78° and another at −123° in which it condensed. $(CH_3)_2AsCl$ (mol wt: calcd, 140.4; found, 141.1; confirmed by infrared spectrum[30]) was prepared from $(CH_3)_2AsOOH$, PCl_3, and HCl.[31] GeF_4 (mol wt: calcd, 148.6; found, 147.9; confirmed by infrared spectrum[32]) was prepared from $BaGeF_6$.[33] $HCo(CO)_4$ (mp −30°; lit. mp[34] −33°; confirmed by infrared spectrum[35]) was prepared from $Co_2(CO)_8$, pyridine, and H_2SO_4.[36] $(CH_3)_2AsH$ (mol wt: calcd, 106.0; found, 106.8; confirmed by infrared spectrum[30]) was prepared from $(CH_3)_2AsOOH$, Zn, and HCl.[31] PF_3 (mol wt: calcd, 88.0; found, 89.0; confirmed by infrared spectrum[37]) was prepared by fluorinating PCl_3 with SbF_5 and was purified by passage through a trap held at −131°. $Cl_3SiCo(CO)_4$ (mp 45°; lit. mp[11] 44°; confirmed by infrared spectrum[12]) was prepared from Cl_3SiH and $Co_2(CO)_8$.[11] AsH_3 (mol wt: calcd, 77.9; found, 76.3; confirmed by infrared spectrum[38]) was prepared from As_2O_3 and $LiAlH_4$.[39]

Synthesis of $(CH_3)_3SiCo(CO)_4$. (A) By the Reaction of $(CH_3)_3SiH$ with $Co_2(CO)_8$. $(CH_3)_3SiH$ (231.2 mg, 3.116 mmol) was distilled into a 12-ml tube containing $Co_2(CO)_8$ (*ca.* 140 mg, *ca.* 0.4 mmol) and was warmed to room temperature with constant shaking. Liquid phase was present. Bubbling of the contents occurred for approximately 5 min. After 5 min at −196° noncondensable material (presumably H_2) was removed and all volatile materials were removed by distillation from the reaction vessel at room temperature. A black solid residue (2.9 mg) remained. Distillation of the volatile materials through traps held at −45 and −96° resulted in the condensation of pure $(CH_3)_3SiCo(CO)_4$ (196.0 mg, 0.8029 mmol, 92.9% yield based on the quantity of $(CH_3)_3SiH$ consumed; mp 51–53° with some decomposition; vapor pressure at room temperature <8.0 Torr) in the −45° trap. The material which passed through the −95° trap consisted primarily of unreacted $(CH_3)_3SiH$ (mol wt: calcd, 74.2; found, 74.3; confirmed by infrared spectrum;[24] 167.1 mg, 2.252 mmol) and the substance which condensed in the −96° trap consisted of a trace of $[(CH_3)_3Si]_2O$ and $HCo(CO)_4$ (2.1 mg; identified by infrared spectra[35,40]).

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In another experiment small portions of $(CH_3)_3SiH$ (21.9 mg, 0.392 mmol; 19.4 mg, 0.261 mmol; 24.5 mg, 0.330 mmol; 23.8 mg, 0.321 mmol; 15.6 mg, 0.210 mmol) were distilled into a 4.5-ml reaction vessel which contained $Co_2(CO)_8$ (507.0 mg, 1.483 mmol). After each addition of $(CH_3)_3SiH$, the reaction vessel remained at room temperature for 5–10 min before quenching it at $-196°$ and removing the noncondensable material formed (presumably CO and/or H_2), and all material volatile at room temperature was removed by distillation. These volatile fractions obtained after each addition of $(CH_3)_3SiH$ were combined and were separated by passing them through a trap held at $-95°$. The material passing through this trap was $(CH_3)_3SiH$ (mol wt: calcd, 74.2; found, 74.0; confirmed by infrared spectrum;[24] 27.0 mg, 0.364 mmol, 32.4% recovery). The $-95°$ condensate consisted of an inseparable mixture of $HCo(CO)_4$ and $[(CH_3)_3Si]_2O$ (identified by infrared spectra,[35,40] total quantity, 0.0467 mmol); from relative peak heights in the infrared spectrum the mixture contained 16.6% $[(CH_3)_3Si]_2O$ (1.3 mg) and 83.4% $HCo(CO)_4$ (6.7 mg, 0.039 mmol). From the quantity of $(CH_3)_3SiH$ consumed, the yield of $HCo(CO)_4$ was 5.1%, based on eq 2. The small yield is undoubtedly due to the fact that some of the $HCo(CO)_4$ formed initially would have undergone further reaction with $(CH_3)_3SiH$ according to eq 3, and some of it would have decomposed thermally in the liquid phase at room temperature. The presence of $[(CH_3)_3Si]_2O$ was not unexpected since small quantities of this compound are formed by the room-temperature thermal decomposition of $(CH_3)_3SiCo(CO)_4$.

(B) By the Reaction of $HCo(CO)_4$ with $(CH_3)_3SiH$.—$HCo(CO)_4$ (75.4 mg, 0.436 mmol) and $(CH_3)_3SiH$ (196.3 mg, 2.646 mmol) were gently shaken in a 2.5-ml reaction vessel at room temperature for 15 min, during which time the contents bubbled moderately. The light brown solution was held at $-196°$ for 5 min before removing the large quantity of noncondensable material (presumably H_2). After removal of all volatile material at room temperature a small brown residue (presumably $Co_2(CO)_8$ from some decomposition of $HCo(CO)_4$) remained. Unreacted $(CH_3)_3SiH$ (164.1 mg, 2.212 mmol; mol wt: calcd, 74.2; found, 75.1; confirmed by infrared spectrum[24]) was recovered from the product by distillation through a trap held at $-23°$. The condensate in the $-23°$ trap was $(CH_3)_3SiCo(CO)_4$ (106.6 mg, 0.437 mmol; infrared spectrum identical with that of the material prepared in (A) above; 100.6% yield based on the quantity of $HCo(CO)_4$ employed). The ratio in which $(CH_3)_3SiH$ and $HCo(CO)_4$ underwent reaction was 1.00 : 1.03.

When a gaseous mixture of $(CH_3)_3SiH$ and $HCo(CO)_4$ in the approximate molar ratio 2 : 1 and at a total pressure of approximately 26 Torr were held in an infrared cell for 21 hr at room temperature, the spectrum remained essentially unchanged. Hence reaction did not occur under these conditions.

Anal.[41] Calcd for $(CH_3)_3SiCo(CO)_4$ $(C_7H_9CoO_4Si)$: C, 34.43; H, 3.71; Co, 24.12; Si, 11.50. Found: C, 34.52; H, 3.81; Co, 24.92; Si, 11.01.

Reaction of $HCo(CO)_4$ with Cl_3SiH.—$HCo(CO)_4$ (33.6 mg, 0.195 mmol) and Cl_3SiH (275.0 mg, 2.030 mmol) were held in a 2.5-ml reaction vessel at room temperature for 35 min during which time it was twice cooled to $-196°$ to ensure mixing. A gas (presumably H_2) was evolved during this time and some solid phase was formed. Unreacted Cl_3SiH (255.9 mg, 1.889 mmol; mol wt: calcd, 135.4; found, 135.1; confirmed by infrared spectrum[29]) was recovered as the volatile material which passed through a trap held at $-23°$. The condensate was $Cl_3SiCo(CO)_4$ (51.6 mg, 0.168 mmol; identified by infrared spectrum;[11] 86.2% yield based on the quantity of $HCo(CO)_4$ employed).

Reaction of $HCo(CO)_4$ with CH_3SiH_3.—$HCo(CO)_4$ (41.0 mg, 0.238 mmol) and CH_3SiH_3 (133.4 mg, 2.890 mmol) were held in a 2.5-ml reaction vessel at room temperature for 1.5 hr. During the first 40 min the solution became dark red and it was cooled twice to $-196°$ to promote mixing. The reaction vessel was

held at $-196°$ for 5 min before removing the noncondensable material formed. After warming to room temperature and cooling again to $-196°$ for 5 min more noncondensable material was removed. This procedure was repeated until no more noncondensable material was formed. When all volatile material had been distilled from the reaction vessel at room temperature, a black residue (3.1 mg) remained. Unreacted CH_3SiH_3 (121.4 mg, 2.633 mmol; mol wt: calcd, 46.1; found, 44.8; confirmed by infrared spectrum[24]) was recovered from the volatile material by distillation through a $-126°$ bath, which it passed. The condensate remaining in the $-126°$ trap was further separated by a trap held at $-45°$, which allowed a mixture of unreacted CH_3SiH_3 and $[CH_3SiH_2]_2O$ (11.2 mg; identified by infrared spectra[24,42]) to pass. The latter compound is a known decomposition product of $CH_3SiH_2Co(CO)_4$.[14] The condensate remaining in the $-45°$ trap was $CH_3SiH_2Co(CO)_4$ (34.5 mg, 0.160 mmol; identified by infrared spectrum;[14] 67.2% yield based on the $HCo(CO)_4$ employed).

Reaction of $HCo(CO)_4$ with SiH_4.—$HCo(CO)_4$ (40.6 mg, 0.236 mmol) was treated with excess SiH_4 (77.3 mg, 2.41 mmol) in a 2.5-ml vessel during 25 min at room temperature with occasional cooling to $-196°$ to promote mixing, but 96% of the SiH_4 was recovered unchanged. Liquid phase was present at all times.

Reaction of $HCo(CO)_4$ with $(CH_3)_2AsH$.—$HCo(CO)_4$ (52.7 mg, 0.306 mmol) and $(CH_3)_2AsH$ (49.6 mg, 0.468 mmol) were distilled into a 2.5-ml reaction vessel which was then raised to room temperature for 10 min. During warming to room temperature the solution changed successively from colorless to yellow-orange to dark red. At room temperature bubbling was observed and the solution was blood red. The reaction vessel was then cooled to $-196°$ for 5 min before removing a large quantity of noncondensable material (assumed to be H_2 and CO). This cooling and warming process was repeated until no more noncondensable material was formed. When all volatile material had been distilled from the reaction vessel at room temperature a blood-red resinous material, $[(CH_3)_2AsCo(CO)_3]_x$, remained (77.9 mg, 0.314 mmol; 102.5% yield based on the quantity of $HCo(CO)_4$ employed). The volatile material was $(CH_3)_2AsH$ (13.6 mg, 0.0788 mmol; identified by infrared spectrum[30]; mol wt: calcd, 106.0; found, 95.0 (error probably due to small amount of sample)).

Anal.[43] Calcd for $[(CH_3)_2AsCo(CO)_3]_x$ $(C_5H_6AsCoO_3)$: C, 24.22; H, 2.44; As, 30.21. Found: C, 24.47; H, 2.53; As, 30.40.

Thermal Stability of $(CH_3)_3SiCo(CO)_4$.—Vessels used in studying $(CH_3)_3SiCo(CO)_4$ were pretreated with a sample of the compound at room temperature.

(A) Gas Phase.—No change was observed in the infrared spectrum of gaseous $(CH_3)_3SiCo(CO)_4$ after 5 hr in a gas infrared cell at room temperature.

(B) Solid Phase.—After 3 months at room temperature in ordinary laboratory lighting, 87% of a sample of pure $(CH_3)_3SiCo(CO)_4$ was recovered unchanged. In a preliminary experiment it was noted that after 20 hr at approximately 150° only about 70% of the $(CH_3)_3Si$ groups initially present in a sample had been liberated as $[(CH_3)_3Si]_2O$.[44]

(C) Liquid Phase.—No change was observed in the nmr spectrum of a solution of approximately 25 mol % of $(CH_3)_3SiCo(CO)_4$ in cyclohexane after 50 days at room temperature in the dark. No change was observed even after this sample had been heated at 60° for 3 days.

Reaction of $(CH_3)_3SiCo(CO)_4$ with H_2O.—After $(CH_3)_3SiCo(CO)_4$ (281.7 mg, 1.154 mmol) and degassed, distilled H_2O (35.6 mg, 1.98 mmol) had been held in a 4.5-ml reaction vessel at room temperature for 15 min, unreacted $(CH_3)_3SiCo(CO)_4$ (*ca.* 0.20–0.40 mmol; identified by infrared spectrum) was re-

(41) Analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The sample was transported in liquid nitrogen.

(42) E. A. V. Ebsworth, M. Onyszchuk, and N. Sheppard, *J. Chem. Soc.*, 1453 (1958).

(43) Analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(44) A. G. MacDiarmid and W. G. Lawn, unpublished observations, 1966.

covered from the products by distillation through a trap held at
$-45°$ in which $(CH_3)_3SiCo(CO)_4$ condensed. Material passing
through the trap was $[(CH_3)_3Si]_2O$, $HCo(CO)_4$, and H_2O (identi-
fied by infrared spectra[35,40]).

$[(CH_3)_3Si]_2O$ (54.0 mg, 0.333 mmol; mol wt: calcd, 162.2;
found, 158.8; 57.7% yield based on the quantity of $(CH_3)_3SiCo$-
$(CO)_4$ employed) was obtained after drying over P_2O_5 followed
by complete thermal decomposition of the $HCo(CO)_4$ (ca. 16.5
mg, ca. 0.0959 mmol from relative peak heights in the infrared
spectrum; ca. 14.3% yield based on the quantity of $[(CH_3)_3Si]_2O$
formed) by heating for 1 hr at $50°$ in a 2.5-ml reaction vessel.

In another experiment $(CH_3)_3SiCo(CO)_4$ (209.4 mg, 0.8578
mmol) and water (6.0 mg, 0.33 mmol) were held in a 4.5-ml
reaction vessel at room temperature for 2 hr, during which time
the contents in the reaction vessel became dark brown. After
quenching at $-196°$ for 5 min, a large quantity of noncondensable
material (presumably H_2) was removed. Repeated distillation
of the remaining volatile material through traps held at -23 and
$-63°$ resulted in the condensation of unreacted $(CH_3)_3SiCo(CO)_4$
(identified by infrared spectrum) in the trap at $-23°$ and
$[(CH_3)_3Si]_2O$ (identified by infrared spectrum;[40] 43.8 mg, 0.270
mmol) which contained a trace of $HCo(CO)_4$ in the trap at $-63°$.
The material passing through the trap held at $-63°$ was identi-
fied by an infrared spectrum as a mixture of $[(CH_3)_3Si]_2O$ (ca.
0.067 mmol) and $HCo(CO)_4$ (ca. 0.024 mmol). A dark residue
(95.8 mg) remained in the reaction vessel—possibly $Co_2(CO)_8$
from thermal decomposition of some of the $HCo(CO)_4$.

Reaction of $(CH_3)_3SiCo(CO)_4$ with CH_3OH.—$(CH_3)_3SiCo$-
$(CO)_4$ (177.3 mg, 0.7263 mmol) and CH_3OH ($\sim$20 mg, $\sim$0.62
mmol) were held in a 2.5-ml reaction vessel at room temperature
for approximately 45 min during which time bubbles slowly
formed. A dark red solution formed. After cooling to $-196°$
and warming to room temperature on several occasions to pro-
mote mixing, noncondensable gas (presumably H_2 from decom-
position of $HCo(CO)_4$ which formed) was removed at $-196°$.
Unreacted $(CH_3)_3SiCo(CO)_4$ (8.8 mg, 0.036 mmol; identified by
infrared spectrum) was recovered from the products by first
removing the more volatile materials at $-18°$ and then distilling
the $(CH_3)_3SiCo(CO)_4$ from a solid residue (presumably Co_2-
$(CO)_8$) at room temperature. Pure $(CH_3)_3SiOCH_3$ (73.2 mg,
0.702 mmol; 101.5% yield based on the quantity of $(CH_3)_3SiCo$-
$(CO)_4$ consumed; mol wt: calcd, 104.2; found, 104.7; confirmed
by infrared spectrum[45]) was obtained from the more volatile
materials by decomposing the $HCo(CO)_4$ (identified by infrared
spectrum[35]) present into H_2 and $Co_2(CO)_8$ by heating for 2 hr
at $60°$.

Reaction of $(CH_3)_3SiCo(CO)_4$ with $(CH_3)_2NH$.—$(CH_3)_3SiCo$-
$(CO)_4$ (132.9 mg, 0.5444 mmol) and $(CH_3)_2NH$ (20.5 mg, 0.455
mmol) were held in a 12-ml reaction vessel at room temperature
for approximately 40 min during which time the reaction vessel
was repeatedly cooled to $-196°$ and warmed to room tempera-
ture to promote mixing. A mixture of unreacted $(CH_3)_3SiCo$-
$(CO)_4$ contaminated with $[(CH_3)_3Si]_2O$ (4.8-mg total weight;
identified by infrared spectrum[40]) was recovered from the products
by distillation through a trap held at $-23°$ in which it condensed.
The material passing through the trap was impure $(CH_3)_3SiN$-
$(CH_3)_2$ (10.0 mg, 0.0855 mmol; identified by infrared spectrum;[46]
19% yield based on the quantity of $(CH_3)_2NH$ employed). The
quantity of material obtained was insufficient for a reliable molec-
ular weight. A solid white residue (128.9 mg) remained in the
reaction vessel.

Reaction of $(CH_3)_3SiCo(CO)_4$ with GeF_4.—$(CH_3)_3SiCo(CO)_4$
(51.9 mg, 0.213 mmol) and GeF_4 (392.8 mg, 2.643 mmol) were
held in a 2.5-ml reaction vessel at room temperature for 15 min.
The heavy yellow precipitate which formed on standing dissolved
partly in the colorless liquid when shaken, to yield a brown solu-
tion. The material which distilled from the reaction vessel at
room temperature was an inseparable mixture of GeF_4 and

$(CH_3)_3SiF$ (identified by infrared spectra[32,47]). The molecular
weight found to be 145.3 indicated the presence of 366.1 mg
(2.464 mmol) of GeF_4 and 14.1 mg (0.153 mmol) of $(CH_3)_3SiF$.
This corresponds to a 71.7% yield of $(CH_3)_3SiF$ based on the
quantity of $(CH_3)_3SiCo(CO)_4$ employed. It might be noted
that a molecular weight of 144.04 would give a 100% yield of
$(CH_3)_3SiF$. The solid yellow residue remaining in the reaction
vessel was pure $F_3GeCo(CO)_4$ (62.3 mg, 0.207 mmol; 97.2%
yield based on the quantity of $(CH_3)_3SiCo(CO)_4$ employed;
mp ca. $75°$ dec).

Anal.[43] Calcd for $F_3GeCo(CO)_4$ $(C_4CoF_3GeO_4)$: C, 15.98;
H, 0.0; F, 18.96. Found: C, 15.86; H, 0.0; F, 18.73. Found
(in another preparation): C, 15.78; H, 0.12.

Thermal Stability of $F_3GeCo(CO)_4$.—The solid appeared to
be stable indefinitely at room temperature *in vacuo.* A series of
infrared spectra in CH_3NO_2 indicated slight decomposition during
approximately 2 hr.

Reaction of $(CH_3)_3SiCo(CO)_4$ with $(CH_3)_2AsCl$.—$(CH_3)_3SiCo$-
$(CO)_4$ (195.9 mg, 0.8025 mmol) and $(CH_3)_2AsCl$ (64.1 mg, 0.456
mmol) were held in a 100-ml reaction vessel at $-95°$ for 15 min
and then at $-63°$ for 20 min. No change was noted. After 20
min at $-45°$ the reactants had become bright yellow, and after
15 min at $-23°$, dark red. After an additional 15 min at $-23°$
the reaction vessel was held at room temperature for 30 min
during which time bubbling was observed and a large quantity of
noncondensable gas (presumably CO) was formed. The volatile
material which distilled from the reaction vessel at room tempera-
ture contained $(CH_3)_3SiCo(CO)_4$ (74.9 mg, 0.307 mmol), a
trace of $[(CH_3)_3Si]_2O$ (identified by infrared spectrum[40]), and
$(CH_3)_3SiCl$ (45.1 mg, 0.415 mmol; identified by infrared spec-
trum;[48] 91.1% yield based on the quantity of $(CH_3)_2AsCl$ em-
ployed). The former material was obtained as a condensate on
distillation of the products through a trap held at $-23°$ in which
the latter compound did not condense. The solid blood red
residue remaining was pure $[(CH_3)_2AsCo(CO)_3]_x$ (114.2 mg,
0.4605 mmol; 101.1% yield based on the quantity of $(CH_3)_2AsCl$
employed). This was soluble in $(CH_3)_2AsCl$ and in tetrahydro-
furan but not in other common organic solvents. The insolu-
bility of this material in nondonor solvents suggested it might be
polymeric.

Anal.[43] Calcd for $[(CH_3)_2AsCo(CO)_3]_x$ $(C_5H_6AsCoO_3)$: C,
24.22; H, 2.44; As, 30.21. Found: C, 24.48; H, 2.46;
As, 30.13.

Thermal Stability of $[(CH_3)_2AsCo(CO)_3]_x$.—The compound
was stable indefinitely *in vacuo* at room temperature. It dark-
ened on heating and extensive decomposition appeared to have
taken place by $185°$.

Reaction of $(CH_3)_3SiCo(CO)_4$ with PF_5.—$(CH_3)_3SiCo(CO)_4$
(271.0 mg, 1.110 mmol) and PF_5 (ca. 1.0 g., ca.8 mmol; 20 atm
autogenous pressure) were held in a 12-ml reaction vessel at
room temperature for 2 hr. After this time the reaction vessel
was cooled to $-196°$ for 5 min before removing a small quantity
of noncondensable material (presumably CO). After removing
the volatile material from the reaction vessel a dark residue
(45.8 mg) remained. The volatile material was passed through
a trap held at $-63°$. A mixture of PF_5 and $(CH_3)_3SiF$ (identi-
fied by infrared spectra;[20,40] from relative peak heights the
$(CH_3)_3SiF$ constituted ca. 2% of the mixture) passed through
the trap held at $-63°$. The $-63°$ condensate was passed
through a trap held at $-45°$ in which $(CH_3)_3SiCo(CO)_4$ (identi-
fied by infrared spectrum) condensed. Small quantities of POF_3
and $HCo(CO)_4$ (identified by infrared spectra[35,37]) passed
through this trap.

Reaction of $(CH_3)_3SiCo(CO)_4$ with PF_3.—$(CH_3)_3SiCo(CO)_4$
(130.9 mg, 0.5362 mmol) and PF_3 (110.0 mg, 1.251 mmol) were
held in a 12-ml reaction vessel at $50°$ for 1 hr, during which time
the solid and liquid phases present in the reaction vessel became
dark brown. After cooling the reaction vessel to $-196°$ for
5 min a noncondensable material (presumably CO) was removed.

(45) R. Forneris and E. Funck, *Z. Elektrochem.*, **62**, 1130 (1958).
(46) J. Goubeau and J. Jiménez-Barberá, *Z. Anorg. Allgem. Chem.*, **303**, 217 (1960).

(47) H. Kriegsmann, *ibid.*, **294**, 113 (1958).
(48) A. L. Smith, *J. Chem. Phys.*, **21**, 1997 (1953).

Since an infrared spectrum of the more volatile contents of the reaction vessel indicated that little, if any, reaction had occurred, the complete mixture was held at approximately 100° for 75 min. After cooling the reaction vessel to −196° for 5 min, noncondensable material (presumably CO) was removed. PF_3 containing some $(CH_3)_3SiF$ and POF_3 (identified by infrared spectra[37,47]) was distilled from the reaction vessel at −63°. The material remaining consisted of unreacted $(CH_3)_3SiCo(CO)_4$ (identified by infrared spectrum) and some nonvolatile material (*ca.* 70 mg) which was probably formed by partial thermal decomposition of the $(CH_3)_3SiCo(CO)_4$. No $[(CH_3)_3Si]_2O$ was isolated, even though its formation, due to partial thermal decomposition of the $(CH_3)_3SiCo(CO)_4$ during the experiment, would be expected. It may have undergone some type of reaction with the PF_3 to give $(CH_3)_3SiF$ and POF_3.

Reaction of $(CH_3)_3SiCo(CO)_4$ with BF_3.—$(CH_3)_3SiCo(CO)_4$ (146.7 mg, 0.6010 mmol) and BF_3 (275.9 mg, 4.068 mmol) were held in a 12-ml reaction vessel for 30 min at room temperature except for a single quenching at −196° after 15 min to promote mixing. After cooling the reaction vessel at −131° for 5 min, BF_3 (mol wt: calcd, 67.8; found, 67.9; confirmed by infrared spectrum;[22] 272.1 mg, 4.012 mmol, 98.7% recovery) was distilled out. $(CH_3)_3SiCo(CO)_4$ (148.8 mg, 0.6060 mmol), containing a trace of $[(CH_3)_3Si]_2O$ (identified by infrared spectra[40]), remained. No noncondensable material was formed during the reaction.

Reaction of $(CH_3)_3SiCo(CO)_4$ with CH_3COCl.—$(CH_3)_3SiCo(CO)_4$ (116.0 mg, 0.4752 mmol) and CH_3COCl (26.6 mg, 0.339 mmol) were held at room temperature for 60 min. During the first 30-min period the reaction vessel was cooled to −196° intermittently to promote mixing of the reactants. Distillation of the volatile material from the reaction vessel at −18° yielded CH_3COCl and $(CH_3)_3SiCl$ (identified by infrared spectra;[28,48] mol wt: calcd for CH_3COCl 78.5; found, 80.9; wt, 28.2 mg; $(CH_3)_3SiCl$ wt, *ca.* 3 mg). $(CH_3)_3SiCo(CO)_4$ (114.4 mg, 0.4691 mmol; identified by infrared spectra;[28,40] 98.7% recovery of $(CH_3)_3SiCo(CO)_4$) remained.

Thermal Stability of $Cl_3SiCo(CO)_4$.—$Cl_3SiCo(CO)_4$ (193.3 mg, 0.6329 mmol) was held in a 4.5-ml reaction vessel at approximately 100° for 43 hr and at 70° for 78 hr before removing a small quantity of noncondensable material at −196°. At this time little of the $Cl_3SiCo(CO)_4$ appeared to have decomposed. The reaction vessel was then held at 150° for 120 hr after which time a small quantity of noncondensable material was removed at −196°. Shortly after heating was commenced, $Cl_3SiCo(CO)_4$ started to darken and a black nonvolatile deposit (65.0 mg) remained after all volatile material had been removed. The volatile material consisted of $Cl_3SiCo(CO)_4$ (132.2 mg, 0.4329 mmol, 68.5% recovery; identified by infrared spectrum[11]) together with a small quantity of $SiCl_4$ (identified by infrared spectrum[48]). The infrared spectrum gave no evidence for the presence of any $[Cl_3Si]_2O$ or Si_2Cl_6.

Reaction of $Cl_3SiCo(CO)_4$ with PF_5.—$Cl_3SiCo(CO)_4$ (198.6 mg, 0.6502 mmol) and PF_5 (*ca.* 1.0 g, *ca.* 8 mmol; 20 atm autogenous pressure) were held in a 12-ml reaction vessel at room temperature for 2 hr. The side of the tube was cooled at 15-min intervals to promote mixing of the PF_5 with the solid $Cl_3SiCo(CO)_4$. A very slight brown discoloration of some of the $Cl_3SiCo(CO)_4$ was noted. No noncondensable material was formed. PF_5 (mol wt: calcd, 126.0; found, 125.1) was distilled from the reaction vessel at 0° and passed through a trap held at −45°. $Cl_3SiCo(CO)_4$ (identified by infrared spectrum;[11] 192.0 mg, 0.6286 mmol; 96.7% recovery) was the −45° condensate. A light brown nonvolatile residue (1–2 mg) remained. A trace of SiF_4 was also produced.

Reaction of $Cl_3SiCo(CO)_4$ with C_2H_5I.—$Cl_3SiCo(CO)_4$ (224.8 mg, 0.7360 mmol) and C_2H_5I (73.6 mg, 0.469 mmol) were held in a 4.5-ml reaction vessel for 1.5 hr at room temperature. Most of the $Cl_3SiCo(CO)_4$ appeared to dissolve in the C_2H_5I to form a yellow solution. After cooling to −196° on three occasions to promote mixing it was held at −78° for 16 hr. No noncon-

densable material was formed. C_2H_5I (74.4 mg, 0.474 mmol; identified by infrared spectrum;[27] mol wt: calcd, 157.0; found, 152.0; 101% recovery; $Cl_3SiCo(CO)_4$ present as impurity) was distilled from the reaction vessel at approximately −45°. $Cl_3SiCo(CO)_4$ (223.8 mg, 0.7327 mmol; identified by infrared spectrum[11]; 99.6% recovery) remained in the reaction vessel.

Reaction of $Cl_3SiCo(CO)_4$ with Iodine.—$Cl_3SiCo(CO)_4$ (133.4 mg, 0.4367 mmol) was distilled into a 4.5-ml reaction vessel containing I_2 (115.2 mg, 0.4539 mmol). After 135 min at room temperature (except for a single quenching at −196° after 60 min to promote mixing) a small quantity of noncondensable material (presumably CO) was removed at −196°. A 48° bath was then placed around the reaction vessel for 2.5 hr in order to melt the $Cl_3SiCo(CO)_4$ (mp 44°).[11] After 2.5 hr the bottom of reaction vessel was black and opaque. After an additional 16 hr at room temperature and 5 min at −196° a large quantity of noncondensable material (presumably CO) was removed. Distillation of the volatile material through a trap held at 0° yielded unreacted $Cl_3SiCo(CO)_4$ (69.9 mg, 0.229 mmol; 52.5% recovery; identified by infrared spectrum[11]) as a condensate. The more volatile material was Cl_3SiI (43.1 mg, 0.165 mmol; 79.3% yield based on the $Cl_3SiCo(CO)_4$ consumed; identified by infrared spectrum;[49] mol wt: calcd, 261.4; found, 234.6) which contained a small amount of $[Cl_3Si]_2O$ (identified by infrared spectrum[50]). The small amount of Cl_3SiI remaining after attempted purification did not permit the measurement of a more accurate molecular weight. Of the Cl_3Si groups originally introduced as $Cl_3SiCo(CO)_4$, 90.2% were recovered as unreacted $Cl_3SiCo(CO)_4$ or as Cl_3SiI. A black nonvolatile residue remained in the reaction vessel.

Infrared Absorption Spectra of $(CH_3)_3SiCo(CO)_4$.—Spectra were recorded with a Perkin-Elmer Model 521 double-beam, grating spectrophotometer. Volatile materials were confined in a 10-cm cell fitted with KBr windows cemented with Glyptal resin. The 400–4000-cm^{-1} spectrum of $(CH_3)_3SiCo(CO)_4$ and the high-resolution spectrum in the CO stretching region were measured at pressures of approximately 0.1 and approximately 1.5 Torr, respectively. The absorption maxima are listed in Table I.

Nuclear Magnetic Resonance Spectrum of $(CH_3)_3SiCo(CO)_4$ —Proton magnetic resonance spectra were recorded by means of an HA-60 Varian Associates spectrometer at 60 Mc/sec at the ambient temperature of the probe. The spectrum of a cyclohexane solution of $(CH_3)_3SiCo(CO)_4$ (approximately 26 mol %) consisted of a sharp singlet 0.83 ppm upfield from cyclohexane. Two small satellite resonances separated by 7.2 Hz could be observed owing to ^{29}Si–C–H coupling.

Mass Spectrum of $(CH_3)_3SiCo(CO)_4$.—Mass spectra were obtained by means of a Consolidated Electrodynamics Model 21-130 mass spectrometer. An ionizing voltage of 76.0 V and an ionizing current of 20 μA were used. A pressure increase was noted in the micromanometer when the sample was admitted. This suggested some immediate thermal decomposition of the compound in the heated inlet system. Possible assignments for the major fragments excluding those which could have arisen from $[(CH_3)_3Si]_2O$, a known thermal decomposition product, are Si^+ or CO^+ (100%), $(CH_3)_3Si^+$ (27.2%), Co^+ (15.3%), H_2C_3-$SiCoC^+$ (10.2%), $C_2SiCo(CO)^+$ (9.8%), CH_3Si^+ (9.1%), and $H_2C_3Si^+$ (4.5%).

Reaction of $(CH_3)_3SiH$ with Ethylene in the Presence of $HCo(CO)_4$. (A) Gas Phase.—$HCo(CO)_4$ (*ca.* 10 Torr) and C_2H_4 (*ca.* 60 Torr) were mixed in the gas phase in an infrared cell. After approximately 5 min at room temperature no $HCo(CO)_4$ remained although CO stretching peaks were present in the 2000–2070-cm^{-1} region in addition to other bands belonging to unidentified species. Then gaseous $(CH_3)_3SiH$ (*ca.* 25 Torr) was introduced into the infrared cell. After 30 min an infrared

(49) J. Stokr and D. Schneider, *Chem. Listy*, **52**, 985 (1958).

(50) A. N. Lazarev, M. G. Voronkov, and T. F. Tenisheva, *Opt. i Spektroskopiya*, **5**, 365 (1958).

TABLE I
INFRARED ABSORPTION MAXIMA FOR $(CH_3)_3SiCo(CO)_4$

Assignment	Absorption, cm⁻¹	Intens[a]	Ref
C=O str			7
Axial A_1	2100	vs (ms)	
Equatorial A_1	2041	vs (s)	
Equatorial E	2009	vs (vs)	
Impurity[b]	2044	vvw	
^{13}C=O str	1973	m	7
C—H str			40, 47
Asym	2957	w	
Sym	2895	vw	
C—Si str			40, 47
Asym	686	vs	
Sym	618	w	
CH_3 def			42
Asym	1404	w	
Sym	1252	s	
CH_3 rock			40, 46
Asym	839	vs	
Sym	751	m	
Co—CO vib	548	vs	d
	513	m	
Si—O—Si str[c]	1068	vw	40
Unassigned	1952	vw (sh)	
	1302	vvw	
	1021	vvw	

[a] Intensities given in parentheses taken from a high-resolution spectrum in the carbonyl stretching region. [b] $HCo(CO)_4$ impurity (variable intensity in different spectra). The most intense peak reported for $HCo(CO)_4$ is at 2043 cm⁻¹: L. Markó, G. Bor, G. Almásy, and P. Szabó, *Brennstoff-Chem*, **44**, 184 (1963). [c] $[(CH_3)_3Si]_2O$ impurity.[40] [d] W. Beck and R. E. Nitzschmann, *Chem. Ber.*, **97**, 2098 (1964); D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, **4**, 166 (1965).

spectrum showed that a little $HCo(CO)_4$ (*ca.* 1 Torr) had been re-formed and that some $[(CH_3)_3Si]_2O$ (*ca.* 5 Torr) and $(CH_3)_3$-$SiCo(CO)_4$ (*ca.* 0.5 Torr) were now present. The walls of the infrared cell were pale red.

In another experiment a gaseous mixture of C_2H_4 (*ca.* 100 Torr) and $(CH_3)_3SiH$ (*ca.* 25 Torr) were added to $HCo(CO)_4$ (*ca.* 10 Torr) in an infrared cell. An infrared spectrum of the gaseous mixture after 3 hr at room temperature showed that little if any $HCo(CO)_4$ remained. Some $[(CH_3)_3Si]_2O$ (*ca.* 4 Torr) and $(CH_3)_3SiCo(CO)_4$ (*ca.* 0.5 Torr) were present. The walls of the infrared cell were yellow-brown.

In both experiments a number of bands belonging to unidentified species were present in the infrared spectra at the conclusion of each experiment. In neither case were bands characteristic of $(CH_3)_3SiC_2H_5$ observed.

(B) Liquid Phase.—$(CH_3)_3SiH$ (96.0 mg, 1.29 mmol), C_2H_4 (86.0 mg, 3.06 mmol), and $HCo(CO)_4$ (20.7 mg, 0.120 mmol) were condensed in a 4.5-ml reaction vessel and were then slowly warmed from $-196°$; vigorous bubbling and a darkening of the liquid phase were observed as the contents approached room temperature. The bubbling ceased after 10 min at room temperature. A dark brown liquid was present. After cooling the reaction vessel to $-196°$ and warming it to room temperature on five successive occasions, it was held at $-196°$ for 5 min before removing the small quantity of noncondensable material (presumably H_2). Unreacted C_2H_4 (53.9 mg, 1.92 mmol; mol wt: calcd, 28.0; found, 28.1; confirmed by infrared spectrum[23]) was recovered as the volatile fraction which passed through a

trap held at $-131°$. The $-131°$ condensate was subsequently passed through traps held at -63 and $-45°$. The $-45°$ condensate was $(CH_3)_3SiCo(CO)_4$ (24.0 mg, 0.102 mmol; identified by infrared spectrum); the $-63°$ condensate was an unknown species (5.3 mg). The material distilling through the trap held at $-63°$ was $(CH_3)_3SiC_2H_5$ (107.4 mg, 1.050 mmol; mol wt: calcd, 102.2; found, 102.0; confirmed by infrared[51] and nmr[52] spectra; 81.1% yield based on the quantity of $(CH_3)_3SiH$ employed). A black residue (5.2 mg, possibly mainly $Co_2(CO)_8$) remained in the reaction vessel.

Reaction of $HCo(CO)_4$ with Ethylene. (A) Gas Phase.—Gaseous $HCo(CO)_4$ (*ca.* 8 Torr) and C_2H_4 (*ca.* 30 Torr) were mixed *in situ* in a gas infrared cell and were held for approximately 18 hr at room temperature. An infrared spectrum recorded after approximately 3.5 min showed that most of the $HCo(CO)_4$ had reacted. The new bands which had appeared both in the carbonyl stretching region (high resolution) and elsewhere after 18 hr could not definitely be assigned to any known species, such as $C_2H_5Co(CO)_4$ or $C_2H_5COCo(CO)_4$.[53]

(B) Liquid Phase.—C_2H_4 (*ca.* 73 mg,, *ca.* 2.6 mmol) and $HCo(CO)_4$ (*ca.* 100 mg, *ca.* 0.6 mmol) were held at room temperature in a 2.5-ml reaction vessel for 85 sec during which time the liquid and gaseous phases were mixed by gentle shaking. The light brown solution bubbled fairly vigorously. It was held at $-196°$ for 5 min before removing the noncondensable material. Unreacted C_2H_4 (identified by infrared spectrum[23]) was recovered as the more volatile fraction passing through a trap held at $-95°$. A gas-phase infrared examination of the $-95°$ condensate showed that little if any $HCo(CO)_4$ remained. In the C–H stretching region bands were observed at 2730, 2810, and 2980 cm⁻¹; in the carbonyl stretching region bands were at 2025 and 2120 cm⁻¹ (relative intensities 1 and 7, respectively); and in the acyl carbonyl stretching region they were at 1760 cm⁻¹. Constant decomposition of the liquid phase occurred during distillation in the vacuum system and a dark residue remained after each distillation.

Reaction of $(CH_3)_3SiH$ with the Products of the $HCo(CO)_4$–Ethylene Reaction.—The products obtained from the liquid-phase reaction of C_2H_4 and $HCo(CO)_4$ (as described in section B) and $(CH_3)_3SiH$ were shaken for 1 min in a 2.5-ml reaction vessel at $0°$. Unreacted $(CH_3)_3SiH$ (identified by infrared spectrum[24]) was recovered as the more volatile fraction which passed through a trap held at $-95°$. The largest portion of the $-95°$ condensate passed through a trap held at $-45°$ and condensed in a trap held at $-78°$. The $-78°$ condensate showed metal–carbonyl stretching vibrations in its infrared spectrum. These disappeared when the sample was heated at $60°$ for 30 min. An infrared and proton nmr examination of the material remaining after the heating did not show the presence of any identifiable material such as $(CH_3)_3SiC_2H_5$[51,52] or $(CH_3)_3SiOC_2$-H_5.[54] The infrared spectrum was completely different from that of the starting material and it showed a very strong band at 1260 cm⁻¹ which is characteristic of the $(CH_3)_3Si$ group.

Attempted Addition of Arsines to Ethylene. (A) Dimethylarsine.—$(CH_3)_2AsH$ (150.2 mg, 1.417 mmol), C_2H_4 (21.1 mg, 3.25 mmol), and $HCo(CO)_4$ (23.2 mg, 0.135 mmol) were held in a 4.5-ml reaction vessel for 40 min at room temperature. The solution became yellow and some bubbling was observed. At room temperature two liquid phases were present; on shaking a white precipitate was formed in an orange solution which later became dark red and opaque. The reaction vessel was held at $-196°$ for 5 min before removing the noncondensable material (presumably H_2 and CO). Unreacted C_2H_4 (91.4 mg, 3.26 mmol; mol wt: calcd, 28.0; found, 28.3; confirmed by infrared spectrum[23]) was the more volatile fraction passing through a

(51) H. Westermark, *Acta Chem. Scand.*, **9**, 947 (1955).

(52) A. G. MacDiarmid and F. Rabel, unpublished observations, 1966.

(53) L. Markó, G. Bor, G. Almásy, and P. Szabó, *Brennstoff-Chem.*, **44**, 184 (1963).

(54) T. Ostdick and P. A. McCusker, *Inorg. Chem.*, **6**, 98 (1967).

trap held at −131°. The −131° condensate was unreacted $(CH_3)_2AsH$ (134.6 mg, 1.270 mmol; mol wt: calcd, 106.0; found, 105.3; confirmed by infrared spectrum[30]). From the stoichiometry of the reaction, the dark red residue remaining in the reaction vessel was $[(CH_3)_2AsCo(CO)_3]_x$ (33.6 mg, 0.136 mmol; 100% yield based on the quantity of $HCo(CO)_4$ employed).

(B) Arsine.—AsH_3 (126.9 mg, 1.628 mmol), C_2H_4 (78.8 mg 2.81 mmol), and $HCo(CO)_4$ (82.6 mg, 0.480 mmol) were condensed into a 4.5-ml reaction vessel. A yellow solution was observed after holding the contents at −45° for 15 min, and a black

solution was observed after 25 min at −35°. After 15 min at −23°, 30 min at −15°, and 15 min at room temperature it was held at −196° for 5 min before removing a large quantity of non-condensable material (possibly CO and/or H_2).

A mixture of unreacted C_2H_4 and AsH_3 (identified by infrared spectra;[23,38] from mol wt, 78.8 mg (2.81 mmol) of C_2H_4 and 87.4 mg (1.12 mmol) of AsH_3) was recovered as the more volatile fraction passing through a trap held at −131°. The −131° condensate was impure $HCo(CO)_4$ (10.7 mg, 0.0622 mmol; identified by infrared spectrum[35]). A solid residue remaining in the reaction vessel weighed 97.0 mg.

Notes

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The Preparation of Gallium(I) β-Alumina

BY R. H. RADZILOWSKI

Monovalent gallium compounds have been reported in the literature since 1930,[1,2] but only in recent years have structural studies[3,4] confirmed the existence of the Ga^+ ion in crystalline materials. This paper reports the preparation of a crystalline Ga(I) compound by an ion-exchange method in which silver in silver-substituted β-alumina is replaced mole for mole by gallium.

Beevers and Ross[5] have determined the crystal structure of sodium β-alumina and found that for the ideal, fixed occupation of all atomic sites in the crystal lattice the formula $Na_2O \cdot 11Al_2O_3$ is required. Sodium analyses of clear, single crystals have shown that the chemical formula varies between $Na_2O \cdot 9Al_2O_3$ and $Na_2O \cdot 10.5Al_2O_3$. Nevertheless, Yao and Kummer[6] have reported that sodium β-alumina exchanges all of its Na^+ ions for other cations (*e.g.*, Ag^+, K^+, Rb^+, Li^+, Tl^+, NH_4^+) in molten salts without altering the basic β-alumina structure, and the exchange is reversible giving back the original sodium β-alumina. In all cases, the resulting compounds are isomorphous with $Na_2O \cdot 11Al_2O_3$. From the known properties of sodium β-alumina and experiments described below, it is most probable that the gallium species in gallium(I) β-alumina is the Ga^+ ion.

(1) J. C. Hutter, "Nouveau Traite de Chimie Minerale," Vol. VII, Masson et Cie, Editeurs, Paris, 1961.

(2) N. N. Greenwood, *Advan. Inorg. Chem. Radiochem.*, **5**, 91 (1963).

(3) G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

(4) F. M. Brewer, J. R. Chadwick, and G. Garton, *ibid.*, **23**, 45 (1961).

(5) C. A. Beevers and M. A. S. Ross, *Z. Krist*, **97**, 59 (1937); the X-ray powder pattern data are listed and indexed in ASTM X-Ray Powder Data File 1-1300.

(6) Y. F. Yu Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.*, **29**, 2453 (1967).

Experimental Section

Single crystals of gallium(I) β-alumina were prepared by exchanging Ag^+ ions in silver(I) β-alumina[7] with Ga^+ ions in a melt containing metallic gallium and gallium iodide. Pure gallium metal and solid iodine were mixed in the mole ratio of 5:1 with single crystals of silver(I) β-alumina in a quartz tube which was evacuated, sealed, and heated at 285° for 16 hr. The melt to crystal volume ratio was 10:1. The melt was dissolved in dilute hydrochloric acid leaving a pool of gallium–silver metal and the gallium(I) β-alumina crystals which were transparent and reddish brown. The average thickness and diameter of the single crystals were 0.15 mm and 1 mm, respectively. After one exchange 99.6% of the Ag^+ ions were replaced by Ga^+ ions. A second exchange in a freshly prepared melt removed the remaining detectable silver leaving at most 0.02 wt % Ag. The gallium content of completely exchanged samples ranged from 11.96 to 12.91 ± 0.03 wt % Ga with ≤0.02 wt % Ag. The chemical analyses were obtained by atomic absorption spectroscopy using a Techtron AA (Cary Instruments, Inc., Monrovia, Calif.). X-Ray powder diffraction data were obtained with a Debye–Scherrer 114.59-mm camera. The samples were ground to 60-μ size and packed in 0.3-mm glass capillaries. Samples were exposed to Ni-filtered Cu Kα radiation for 5 hr on a Norelco X-ray generator. Intensities of reflections were measured on a double-beam recording microdensitometer (Joyce, Loebl and Co., Ltd., Gateshead, England). The thermogravimetric analyses were made on the R. G. automatic electrobalance (Cahn Instrument Co., Paramount, Calif.).

Discussion

Gallium(I) β-alumina is isomorphous with the hexagonal layer structure of $Na_2O \cdot 11Al_2O_3$[5] which has the space group P6/mmc, with one molecule per unit cell. The lattice constants of gallium(I) β-alumina, $Ga_2O \cdot 11Al_2O_3$, containing 12.9 wt % Ga are $a_0 = 5.600$ and $c_0 = 22.718$ Å determined from a Debye–Scherrer powder pattern and refined by a least-squares method. The diffraction pattern for gallium(I) β-alumina is given in Table I.

The variation of gallium in gallium(I) β-alumina

(7) The β-alumina used was obtained from fused cast bricks (Monofrax H) made by the Harbison Carborundum Co., Falconer, N. Y. This material when placed in $AgNO_3$ melt for 2 hr produced silver β-alumina by ion exchange. A chemical analysis showed complete exchange of Na^+ ions for Ag^+ ions.