Journal of Organometallic Chemistry, 178 (1979) 227—247
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ORGANOCOBALT CLUSTER COMPLEXES

XXIX *. NOVEL SILICON COMPOUNDS CONTAINING THE NONACARBONYL TRICOBALTCARBON SUBSTITUENT **

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(Received March 12th, 1979)

Summary

The reaction of bromomethylidynetricobalt nonacarbonyl or, more effectively, of methylidynetricobalt nonacarbonyl with diverse silicon hydrides (R_3SiH, Ph_3SiH, $Me_2(EtO)SiH$, $R_nCl_{3-n}SiH$ (n = 0—2), etc.) results in formation of silylmethylidynetricobalt nonacarbonyl complexes. Silicon-functional interconversions such as Si—Cl → SiOH, Si—Cl → Si—OMe, Si—OH → Si—F, and Si—OH → Si—OSiMe$_3$, have provided still other substituted silylmethylidynetricobalt nonacarbonyl complexes, generally in high yield. The compounds Me(HO)$_2$SiCCo$_3$(CO)$_9$ and (HO)$_3$SiCCo$_3$(CO)$_9$ have been incorporated into methylsilicone polymers by H_2SO_4-induced reactions with cyclo-(Me_2SiO)$_3$.

Introduction

The direct reaction of organic tri- and di-halides with dicobalt octacarbonyl or the tetracarbonylcobaltate(—I) anion has been used to effect the synthesis of a number of carbon-functional alkylidynetricobalt nonacarbonyl complexes (eq. 1). Examples are known where Z = hydrogen, halogen, alkyl, aryl, alkenyl,

$$YCX_3 + Co_2(CO)_8 \rightarrow YCCo_3(CO)_9 + CoX_2 + CO + \ldots \quad (1)$$

acyl, carboalkoxy, amido, dialkyl phosphonyl, etc. [2,3]. Such complexes have the structure shown in Fig. 1, but as triply-bridging carbyne complexes, they may be better represented as I [4]. Also prepared by this route have been silyl derivatives, $Me_3SiCCo_3(CO)_9$ and $Me_2PhSiCCo_3(CO)_9$ [3], as well as others, $R_3SiCCo_3(CO)_9$ where R was not specified [5]. The required (trichloromethyl)-

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* For part XXVIII see ref. 1.

** Dedicated to Professor Eugene G. Rochow on the occasion of his seventh birthday.

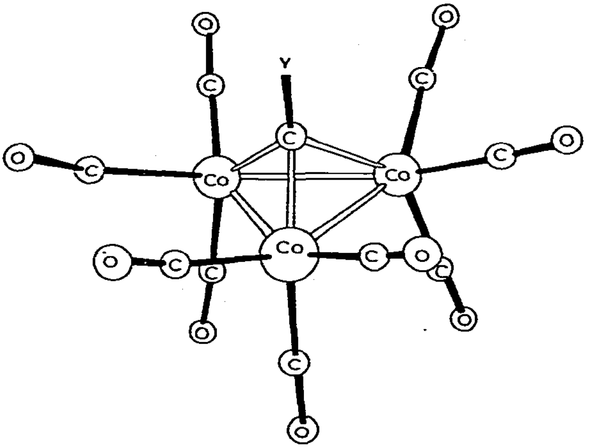
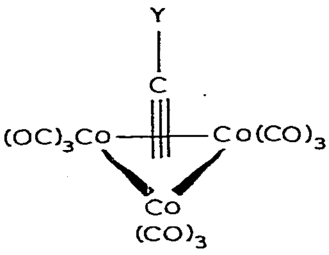


Fig. 1. Structure of alkylidynetricobalt nonacarbonyl complexes, $YCCo_3(CO)_9$.

silanes, R_3SiCCl_3, for this synthesis can in some cases be prepared by chlorination of methylsilicon compounds [5], more generally, by the reaction of trichloromethyllithium [6] or a trichloromethyl Grignard reagent [7] with appropriate triorganochlorosilanes.

The initial objective of our research on $(OC)_9Co_3C$-substituted silicon compounds was the synthesis of $(OC)_9Co_3C$-stabilized siliconium ions. Our previous work had shown that the $(OC)_9Co_3C$ cluster substituent stabilizes an adjacent carbonium ion center to a marked extent [1,8]. Thus in species such as II,



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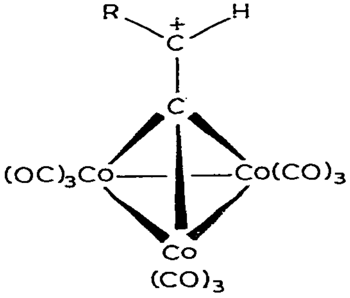

(II)

according to ^1H and ^{13}C NMR and IR spectroscopic evidence, the positive charge is transferred to a large extent from the carbon atom α to the $(OC)_9$-Co_3C cluster to the cobalt atoms. Although the structure of ions of type II and the exact nature of their bonding remains unclear *, the stabilization of a sili-

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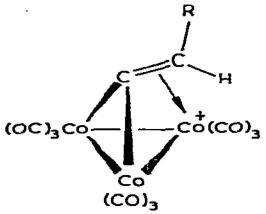
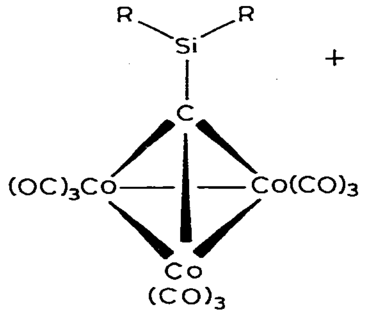
* Theoretical studies by Schilling and Hoffmann [9] have been published recently which supported a fluxional species with a "tipped" carbon structure, A.



(A)

conium ion by the $(OC)_9Co_3C$ cluster seemed an intriguing possibility. If the high electrophilic character of silicon which seems to prevail in siliconium species * were to be sufficiently diminished by transfer of electron density to silicon from the cluster, then a cation such as III might be sufficiently stable to allow isolation of its salts.



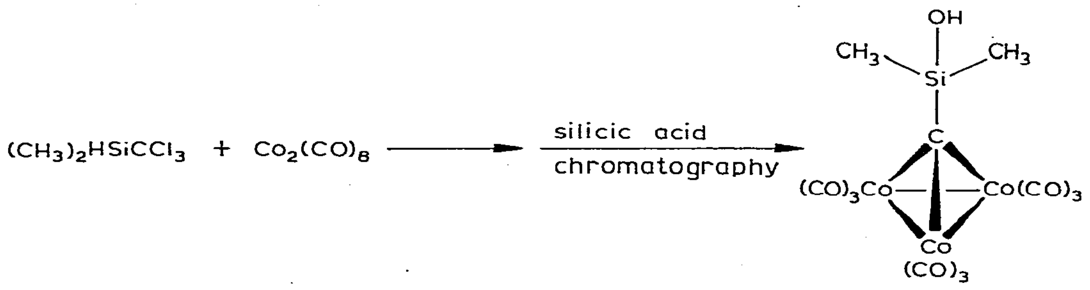
(III)

We report here concerning studies which consider this question. During the course of this work we have developed new, quite general and high yield routes for the preparation of $(OC)_9Co_3C$-substituted silicon compounds of type $R_nY_{3-n}SiCCo_3(CO)_9$, in which the organic substituent R and the inorganic substituent Y are capable of wide variation **.

Results and discussion

(1) Preparation of nonacarbonyl tricobaltcarbon-substituted silicon compounds

A cobalt cluster derivative suitable for our exploration of the possible stabilization of an α-siliconium ion by the $(OC)_9Co_3C$ cluster, IV, was obtained by the reaction of $(CH_3)_2HSiCCl_3$ with dicobalt octacarbonyl (eq. 2). The isolation of silanol IV rather than $(CH_3)_2HSiCCo_3(CO)_9$ was unexpected, and we do not know at what stage of reaction or work-up this conversion to the silanol took



(IV)

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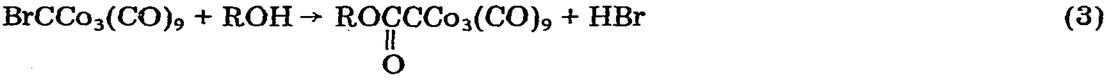
* It is this high electrophilic character which appears to have defeated all previous attempts to isolate a siliconium ion salt. R_3Si^+ species normally combine with ClO_4^- to form covalent silyl perchlorates and they abstract F^- from PF_6^- anf BF_4^- to form covalent silyl fluorides [10].

** A preliminary communication describing some of this work has been published [11].

place. However, this reaction is repeatable, and since it gave a product better suited for our study than the expected hydride derivative, we did not pursue this matter further.

While the yields of (trichloromethyl)silicon compounds obtained by the organolithium procedure are fairly satisfactory ($Me_2HSiCCl_3$ was obtained in 66% yield), the reactions involving CCl_3Li must be carried out at around —100°C and thus are unwieldy and tedious to effect. Furthermore, the reactive lithium reagent is incompatible with diverse reactive functionally on silicon as well as on carbon. Accordingly, a different route to $(OC)_9Co_3C$-C-substituted silicon compounds, one which did not require the prior preparation of (trichloromethyl)silanes, was desirable.

Prior research in these laboratories had shown that bromomethylidynetricobalt nonacarbonyl reacts readily with alcohols, phenols, primary and secondary amines and alkyl mercaptans to give functionally substituted cobalt cluster complexes [12,13]. In most cases products in which a carbon monoxide ligand had migrated to the apical carbon atom were obtained (eq. 3), and when alcohols, phenols and mercaptans were the reactants, triethylamine was found to



$$\mathrm{BrCCo_3(CO)_9 + ROH \rightarrow RO\underset{\underset{\displaystyle O}{\|}}{C}CCo_3(CO)_9 + HBr} \qquad (3)$$

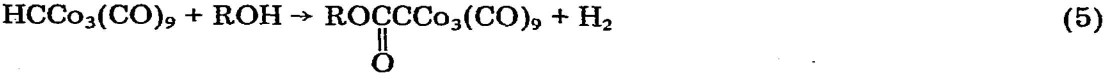
accelerate the reactions. In the case of arenethiols, however, such CO migration to the apical carbon atom did not take place (eq. 4) [13,14]. This led us to

$$\mathrm{BrCCo_3(CO)_9 + ArSH + Et_3N \rightarrow ArSCCo_3(CO)_9 + Et_3NH^+\,Br^-} \qquad (4)$$

investigate possible reactions of silicon hydrides with bromomethylidynetricobalt nonacarbonyl.

Triethylsilane did not react with bromomethylidynetricobalt nonacarbonyl in benzene solution at room temperature, but a reaction at 80°C for 16 h under an atmosphere of carbon monoxide gave $Et_3SiCCo_3(CO)_9$ in 46% yield. Other silicon hydrides were found to react with bromomethylidynetricobalt nonacarbonyl under these conditions to give the respective silylmethylidynetricobalt nonacarbonyls in modest yields (Table 1). The products derived from chlorosilicon hydrides were not isolated as such but were converted to the silanol or methoxysilane by treatment of the reaction mixture with water or methanol. Presumably, hydrogen bromide is formed in these reactions. Bubbling HBr through a solution of bromoethylidynetricobalt nonacarbonyl in benzene at 80°C results in instantaneous decomposition, so it is not surprising that the silylmethylidynetricobalt nonacarbonyl yields were not high. When a triethylsilane/bromomethylidynetricobalt nonacarbonyl reaction was carried out in the presence of an equimolar quantity of 1,8-bis(dimethylamino)naphthalene ("proton sponge") at 80°C, the yield of $Et_3SiCCo_3(CO)_9$ was only 44%.

We had found earlier [13] that methylidynetricobalt nonacarbonyl also reacts with alcohols to give products of type $ROC(O)CCo_3(CO)_9$, presumably



$$\mathrm{HCCo_3(CO)_9 + ROH \rightarrow RO\underset{\underset{\displaystyle O}{\|}}{C}CCo_3(CO)_9 + H_2} \qquad (5)$$

via eq. 5. Although the yields of cluster ester were lower than in comparable

TABLE 1

REACTIONS OF SILICON HYDRIDES WITH BROMOMETHYLIDYNETRICOBALT NONACARBONYL

mmol of $BrCCo_3(CO)_9$	Silicon hydride (mmol)	ml of benzene	Reaction temperature (°C)	Reaction time (h)	Product $RCCo_3(CO)_9$	
					R	Yield (%) [a]
1.9	Et_3SiH (32)	40	80	20	Et_3Si	29
1.9	Et_3SiH (6.3)	40	78	4	Et_3Si	46
1.9	$n\text{-}Pr_3SiH$ (4.8)	40	78	16	$n\text{-}Pr_3Si$	33
2.2	Me_2PhSiH (2.0)	40	78	16	Me_2PhSi	40
2.5	$Me_2\text{-}i\text{-}PrSiH$ (2.9)	40	78	16	$Me_2\text{-}i\text{-}PrSi$	37
1.9	$Me_2(EtO)SiH$ (7.3)	40	78	16	$Me_2(EtO)Si$	15
1.9	$Me_2(CH_2Cl)SiH$ (10)	40	78	16	$Me_2(CH_2Cl)Si$	48
1.9	Me_2ClSiH (9.0)	40	80	17	$Me_2(HO)Si$	36 [b]
1.9	Me_2ClSiH	40	80	17	$Me_2(MeO)Si$	32 [c]
2.9	$MeCl_2SiH$	60	75	36	$Me(HO)_2Si$	28 [b]
2.9	$MeCl_2SiH$	60	75	36	$Me(MeO)_2Si$	29 [c]
2.9	Cl_3SiH	60	75	72	$(HO)_3Si$	16 [b]
3.8	Cl_3SiH	60	75	72	$(MeO)_3Si$	23 [c]

[a] Yields based on $BrCCo_3(CO)_9$. [b] Crude reaction residue treated with water in 40 ml of benzene at 80°C for 30 min. [c] Crude reaction residue treated with methanol in 40 ml of benzene at 80°C for 30 min.

reactions of $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$, it seemed worthwhile to investigate reactions of silicon hydrides with $HCCo_3(CO)_9$.

The silicon hydride/$HCCo_3(CO)_9$ reaction (in refluxing toluene solution (105°C) for 30 min, under an atmosphere of CO) was found to be an excellent means of preparing silylmethylidynetricobalt nonacarbonyl complexes. Thus a reaction of triethylsilane (twofold excess) with $HCCo_3(CO)_9$ under these conditions gave $Et_3SiCCo_3(CO)_9$ in 76% yield. In benzene solution at reflux for 16 h, this reaction gave this product in 84% yield. Table 2 presents the results of our

TABLE 2

REACTIONS OF SILICON HYDRIDES WITH METHYLIDYNETRICOBALT NONACARBONYL [a]

mmol of $HCCo_3(CO)_9$	Silicon hydride (mmol)	Product $RCCo_3(CO)_9$	
		R	Yield (%) [b]
2.3	Et_3SiH (6.3)	Et_3Si	76
2.3	$n\text{-}Pr_3SiH$ (4.8)	$n\text{-}Pr_3Si$	81
2.3	$n\text{-}Bu_3SiH$ (5.0)	$n\text{-}Bu_3Si$	69
3.4	Ph_3Si (2.0)	Ph_3Si	39 [c]
3.4	Ph_3Ge (2.0)	Ph_3Ge	30 [c]
2.3	$Me_2\text{-}i\text{-}PrSiH$ (12)	$Me_2\text{-}i\text{-}PrSi$	70
2.3	Me_2PhSiH (6.5)	Me_2PhSi	91
2.3	$MePh_2SiH$ (2.5)	$MePh_2Si$	60
2.3	$Me_2(EtO)SiH$ (7.3)	$Me_2(EtO)Si$	48
2.3	Me_2ClSiH (9.0)	Me_2ClSi	90
2.3	$MeCl_2SiH$ (9.6)	$MeCl_2Si$	90
2.3	Cl_3Si (10)	Cl_3Si	92
5.9	$(HMe_2Si)_2O$ (2.9)	$HOMe_2SiOSiMe_2$	20
2.3	$N[CH_2CH(CH_3)O]_3SiH$ (2.3)	$N[CH_2CH(CH_3)O]_3Si$	32

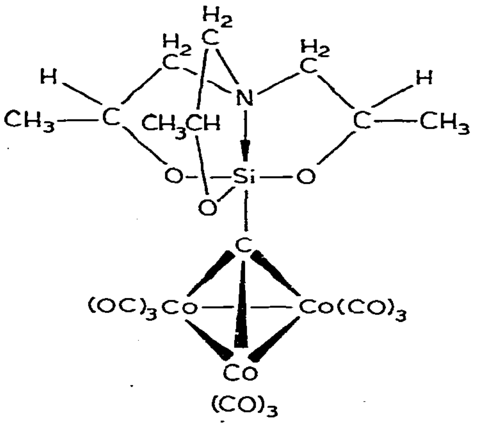
[a] All reactions in 40 ml of dry toluene for 30 min at reflux (~105°C). [b] yields based on $HCCo_3(CO)_9$. [c] Yield based on hydride.

study of this general reaction (eq. 6).

$$\geqslant Si{-}H + HCCo_3(CO)_9 \rightarrow \geqslant Si{-}CCo_3(CO)_9 + H_2 \tag{6}$$

Inspection of Table 2 shows that a wide variety of substitution on silicon in the silicon hydride is possible in this reaction. Trialkylsilanes posed no problems. Triphenylsilane could not be used in excess in its reaction with $HCCo_3(CO)_9$ since the unconverted Ph_3SiH was converted to triphenylsilanol during work-up. Separation of the latter from $Ph_3SiCCo_3(CO)_9$ was not possible. Chlorine-substituted silicon hydrides reacted with $HCCo_3(CO)_9$ to give the highest product yields. The chlorosilylmethylidynetricobalt nonacarbonyls could not be purified by column chromatography and even attempts at recrystallization introduced Si—OH-containing impurities. However, it was found that if the reaction mixture was evaporated at reduced pressure and the residue was washed with hexane and dried thoroughly in vacuo, analytically pure products, $Me_nCl_{3-n}SiCCo_3(CO)_9$ (n = 0—2) resulted.

An alkoxysilicon hydride, $Me_2(EtO)SiH$, reacted readily with $HCCo_3(CO)_9$. The reaction of 3,7,10-trimethylsilatrane with methylidynetricobalt nonacarbonyl gave the novel silatrane derivative V. A silicon dihydride, diphenylsilane, Ph_2SiH_2, on the other hand reacted with $HCCo_3(CO)_9$ to give complete decomposition. Tetramethyldisiloxane, when used as the limiting reagent, resulted in the formation of a cobalt cluster with a disiloxane mono-ol substituent, $(OC)_9Co_3CSiMe_2OSiMe_2OH$, after silica gel chromatographic work-up.



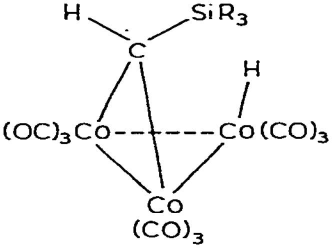
(V)

Since the silicon hydride/methylidynetricobalt nonacarbonyl reaction proved to be such a useful preparative procedure for silyl-substituted methylidynetricobalt nonacarbonyl complexes, a study of its mechanism was of some interest. According to the postulated eq. 6, molecular hydrogen was the other product of this reaction. In an attempt to confirm this, a mixture of one part of $HCCo_3(CO)_9$ and three of triethylsilane in toluene was sealed under vacuum in a thick-walled Pyrex tube and heated at 100° C for 20 min. The tube was cooled to —196° C and the gaseous components of the reaction mixture were collected and examined by mass spectroscopy. The major products were carbon monoxide and methane; only a trace of hydrogen was present. The presence of methane is indicative of the hydrogenolysis of $HCCo_3(CO)_9$, and it is noteworthy that Geoffrey and Epstein [15] have reported that the photolysis of $HCCo_3(CO)_9$ in the presence of molecular hydrogen produces methane and $Co_4(CO)_{12}$. Thus the formation of methane in our experiment provides indirect conformation that molecular hydrogen is formed in the $Et_3SiH/HCCo_3(CO)_9$ reaction.

Several plausible mechanisms were considered as possibilities for the silicon hydride/$HCCo_3(CO)_9$ reaction. A C—H bond polarity, $(OC)_9Co_3C^{\delta-}—H^{\delta+}$, has been discussed for methylidynetricobalt nonacarbonyl, and thus a polar reaction with silicon hydrides, $R_3Si^{\delta+}—H^{\delta-}$, could be envisaged. This possibility could be tested experimentally. As chlorine substituents accumulate on a silicon hydride, $R_nCl_{3-n}SiH$, the $Si^{\delta+}—H^{\delta-}$ polarity diminishes and finally is reversed. Thus $HSiCl_3$ is a useful source of the Cl_3Si^- anion [16]. If the $Si^{\delta+}—H^{\delta-}$ polarity were the dominating factor, then $PhMe_2SiH$ should be more reactive towards $HCCo_3(CO)_9$ than $PhCl_2SiH$. The opposite was found to be the case. In a competition experiment between these silanes, both of which reacted individually with $HCCo_3(CO)_9$ to give excellent product yields, for a deficiency of $HCCo_3(CO)_9$ the products were $PhCl_2SiCCo_3(CO)_9$ (isolated as its hydrolysis product, $Ph(HO)_2SiCCo_3(CO)_9$) in 71% yield and $PhMe_2SiCCo_3(CO)_9$ in 2% yield.

Silicon hydrides also undergo radical reactions, as in their peroxide- or UV-initiated additions to olefins. Electronegative groups on silicon facilitate such radical processes, and the reactivity order $Cl_3SiH > MeCl_2SiH > Et_3SiH$ has been observed [17]. Thus our observed relative reactivities $PhCl_2SiH > PhMe_2SiH$ do not speak against a radical pathway. However, previous work has shown that radical addition of $HCCo_3(CO)_9$ to olefins requires a large amount of initiator (azobisisobutyronitrile) and long reaction times [18]. This stands in marked contrast to the facility with which the silicon hydride/$HCCo_3(CO)_9$ reactions occur, so we consider a radical mechanism to be less likely.

Oxidative addition of silicon hydrides to low valent transition metal complexes is a well-known process [19]. For example, hydrosilylation of olefins catalyzed by dicobalt octacarbonyl involves the initial formation of $R_3SiCo(CO)_4$ and $HCo(CO)_n$, the chain carrier. Thus in the $R_3SiH/HCCo_3(CO)_9$ reaction one may consider an oxidative addition of R_3SiH to the $HCCo_3(CO)_9$ cluster to give a more open intermediate, VI, with subsequent elimination of molecular hydrogen to form the product cluster, $R_3SiCCo_3(CO)_9$.



(VI)

Of these three possibilities, we favor the third (or some variation of this oxidative addition/reductive elimination) process. However, since there is no experimental evidence in its favor, this proposed mechanism remains speculative.

A limited investigation was made of the possible applicability of the hydride/$HCCo_3(CO)_9$ reaction, which worked so well with silicon, to the preparation of methylidynetricobalt nonacarbonyl complexes with substituents containing other metals and metalloids. Triphenylgermane was found to react with $HCCo_3(CO)_9$ to give $Ph_3GeCCo_3(CO)_9$ in 30% yield. However, reactions of $HCCo_3(CO)_9$ with tri-n-butyltin hydride and di-η^5-cyclopentadienylzirconium chlorohydride proved to be far more complex and the expected products were not isolated.

(2) *Reactions of nonacarbonyl tricobaltcarbon-substituted silicon compounds*

As expected, the chlorosilylmethylidynetricobalt nonacarbonyl complexes underwent hydrolysis and alcoholysis. Reactions with water and with methanol in benzene medium at 80° C served to convert them to the respective silanol and methoxysilane, respectively. Table 3 lists the products formed in experiments in which various chlorosilicon hydrides were allowed to react with $HCCo_3(CO)_9$ under the conditions specified in the previous section and the products formed were treated with water or methanol without prior isolation. The most remarkable of the silylmethylidynetricobalt nonacarbonyl complexes listed in Table 3 is the silanetriol, $(HO)_3SiCCo_3(CO)_9$, which was isolated as a stable, crystalline solid. It was characterized by combustion analysis, molecular weight determination by vapor pressure osmometry in acetone solution and NMR integration of protons with respect to $CH_3OC(O)CCo_3(CO)_9$, which has the same number of protons. All indications are that the complex exists as

TABLE 3

REACTIONS OF CHLOROSILICON HYDRIDES WITH METHYLIDYNETRICOBALT NONACARBONYL, FOLLOWED BY HYDROLYSIS OR METHANOLYSIS OF THE PRODUCTS

R in $RCCo_3(CO)_9$ intermediate	Reaction with	Product $R'CCo_3(CO)_9$	
		R'	Yield (%) [a]
Me_2ClSi	MeOH	$Me_2(MeO)Si$	78
Me_2ClSi	H_2O	$Me_2(HO)Si$	76
$MeCl_2Si$	MeOH	$Me(MeO)_2Si$	73
$MeCl_2Si$	H_2O	$Me(HO)_2Si$	81
Cl_3Si	MeOH	$(MeO)_3Si$	62
Cl_3Si	H_2O	$(HO)_3Si$	66
$PhCl_2Si$	MeOH	$Ph(MeO)_2Si$	62
$PhCl_2Si$	H_2O	$Ph(HO)_2Si$	71
PhMeClSi	MeOH	PhMe(MeO)Si	69

[a] Based on $HCCo_3(CO)_9$ used in the reaction sequence:

$$HCCo_3(CO)_9 + R_nCl_{3-n}SiH \rightarrow R_nCl_{3-n}SiCCo_3(CO)_9 \xrightarrow[R' = H \text{ or } Me]{R'OH} R_n(R'O)_{3-n}SiCCo_3(CCo_3(CO)_9$$

The chlorosilylmethylidynetricobalt nonacarbonyl intermediate was not isolated, rather the reaction solution was treated with water or methanol directly.

the stable monomer. The infrared spectrum (Nujol mull) of $(HO)_3SiCCo_3(CO)_9$ showed a weak band at 3650 and a broad band at 3390 cm^{-1} in the O—H stretching region, which is indicative of hydrogen bonding. Very few silanetriols have been reported [20] and those which are known are prone to undergo homocondensation to siloxanes. Silanol condensation is a bimolecular process and thus its rate is sensitive to steric factors [21]. We have stressed previously that the substituent attached to the apical carbon atom in the $CCo_3(CO)_9$ cluster is extremely hindered (note Fig. 1) [22] and it is the steric factors which result which serve to explain the stability of $(HO)_3SiCCo_3(CO)_9$, even in the presence of HCl, which is known to promote silanol condensation [23]. The silanol and the silanediols in Table 3 also were quite resistant to homocondensation. In fact, smooth homocondensation of these compounds could not be effected by reaction with concentration sulfuric acid in diethyl ether.

However, these reaction conditions did permit the cocondensation of $Me_2(HO)SiCCo_3(CO)_9$, $Me(HO)_2SiCCo_3(CO)_9$ and $(HO)_3SiCCo_3(CO)_9$ with hexamethyldisiloxane (eq. 7) *. Similarly, these cluster-silanols were found to react

$$\underset{(n = 0, 1, 2)}{Me_n(HO)_{3-n}SiCCo_3(CO)_9} + Me_3SiOSiMe_3 \xrightarrow[Et_2O]{\text{concd. } H_2SO_4} Me_n(Me_3SiO)_{3-n}SiCCo_3(CO)_9 \qquad (7)$$

with hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane to give simple 1/1 reaction products or higher molecular weight polysiloxanes containing the $CCo_3(CO)_9$ substituent, depending on the stoichiometry used. The mild conditions (2 h at room temperature) which were sufficient to allow the reaction of hexamethyldisiloxane with $Me_2(HO)SiCCo_3(CO)_9$ to proceed in good yield were not sufficient in the case of the silanediol and silanetriol. Under these conditions the products obtained were $Me(HO)(Me_3SiO)SiCCo_3(CO)_9$ and $(HO)(Me_3SiO)_2SiCCo_3(CO)_9$, respectively. Complete conversion to $Me(Me_3SiO)_2SiCCo_3(CO)_9$ and $(Me_3SiO)_3SiCCo_3(CO)_9$ was achieved in Et_2O/benzene medium at 50° C, using reaction times of 5 and 10 h, respectively. Both $(Me_2SiO)_3$ and $(Me_2SiO)_4$ reacted with $Me(HO)_2SiCCo_3(CO)_9$ in the presence of concentrated sulfuric acid in Et_2O/benzene at 45° C to give the respective cyclosiloxanes, VIIa and VIIb, respectively, in 1/1 reactions and purple silicone polymers when an excess of the cyclic trimer and tetramer was used. The reactions of the $(OC)_9Co_3C$-substituted silanols are summarized in Table 4.

The $(OC)_9Co_3C$-substituted silanols also reacted with boron trifluoride diethyl etherate in diethyl ether solution [25] to yield the corresponding fluorides, $Me_2FSiCCo_3(CO)_9$, $MeF_2SiCCo_3(CO)_9$ and $F_3SiCCo_3(CO)_9$, in good yield. The trifluorosilyl derivative could not be purified by chromatography since it adhered strongly to both silicic acid and alumina. The action of aqueous concentrated (49 *M*) hydrofluoric acid in diethyl ether on $(HO)_3SiCCo_3(CO)_9$ at room temperature did not give the trifluorosilyl derivative, rather it caused cleavage of the Si—C bond. The product of this reaction was $HCCo_3(CO)_9$, which was isolated in 95% yield.

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* Acid-catalyzed siloxane equilibrations of this type are well known and have been studied in some detail [24].

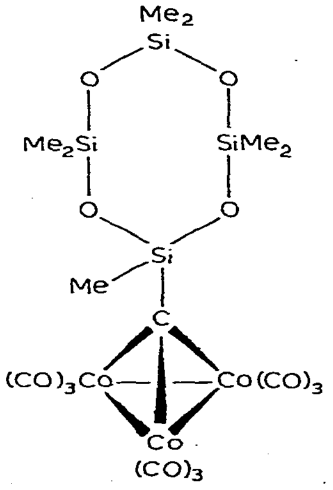
TABLE 4

REACTIONS OF NONACARBONYL TRICOBALTCARBON-SUBSTITUTED SILANOLS

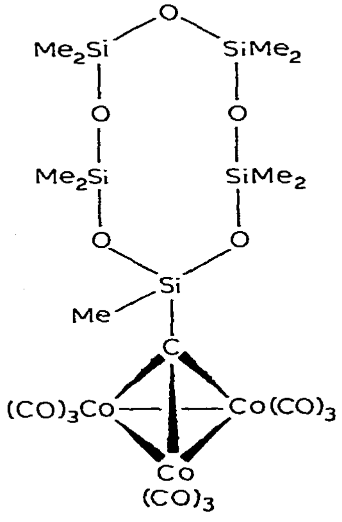
R in $RCCo_3(CO)_9$ starting material	Reaction with	Product $R'CCo_3(CO)_9$	
		R′	Yield (%) [a]
$Me_2(HO)Si$	$BF_3 \cdot OEt_2$	Me_2FSi	93
$Me(HO)_2Si$	$BF_3 \cdot OEt_2$	MeF_2Si	87
$(HO)_3Si$	$BF_3 \cdot OEt_2$	F_3Si	85
$Me_2(HO)Si$	$(Me_3Si)_2O$	$Me_3SiOSiMe_2$	68
$Me(HO)_2Si$	$(Me_3Si)_2O$ [b]	$Me_3SiOSi(OH)Me$	70
$Me(HO)_2Si$	$(Me_3Si)_2O$ [c]	$(Me_3SiO)_2MeSi$	74
$(HO)_3Si$	$(Me_3Si)_2O$ [b]	$(Me_3SiO)_2(HO)Si$	68
$(HO)_3Si$	$(Me_3Si)_2O$ [d]	$(Me_3SiO)_3Si$	79
$Me(HO)_2Si$	$(Me_2SiO)_3$ [e]	$(Me_2SiO)_3SiMe$ O	73
$Me(HO)_2Si$	$(Me_2SiO)_4$ [e]	$(Me_2SiO)_4SiMe$ O	75

[a] Yields based on cluster-substituted silanol. [b] Reaction at room temperature for 2 h in the presence of concentrated sulfuric acid. [c] Reaction at 45°C for 5 h in the presence of concentrated sulfuric acid. [d] Reaction at 50°C for 10 h in the presence of concentrated sulfuric acid. [e] Reaction at 45°C for 90 min in the presence of concentrated sulfuric acid.

The availability of the silanol $Me_2(HO)SiCCo_3(CO)_9$ by two different syntheses allowed us to examine the question raised in the Introduction: can the $(OC)_9Co_3C$ moiety stabilize a siliconium ion (or the silicon analog of A, with Me_2Si replacing RCH, if the Schilling/Hoffmann structure is correct)? Cations of type I were prepared by treatment of the corresponding alcohols, RCH(OH)-$CCo_3(CO)_9$, with 65% aqueous hexafluorophosphoric acid in propionic anhy-



(VIIa)



(VIIb)

dride [1,8a]. An immediate precipitation of $[RCHCCo_3(CO)_9]^+ [PF_6]^-$ resulted. When $Me_2(HO)SiCCo_3(CO)_9$ was dissolved in propionic anhydride and hexafluorophosphoric acid was added, an exothermic reaction gave a dark precipitate. The latter was soluble in dichloromethane. Such a dichloromethane solution, after treatment with ethanol, on evaporation and crystallization of the residue from hexane, gave an almost quantitative yield of the fluorosilane, $Me_2FSiCCo_3(CO)_9$, even after it had been treated with ethanol and water. It appears that the incipient siliconium ion abstracts fluoride ion from the hexafluorophosphate anion immediately after its formation to give the observed fluorodimethylsilyl derivative. Alternatively, a siliconium species, even a transient one, need not be involved at all. A similar result was obtained when $Me_2(HO)SiCCo_3(CO)_9$ was treated with $BF_3 \cdot OEt_2$ in dichloromethane, as mentioned above. Interception of a possible siliconium ion intermediate with *N,N*-dimethylaniline was unsuccessful.

Aluminum chloride in dichloromethane was too harsh a reagent: thin layer chromatography indicated that it reacted immediately with $Me_2(HO)SiCCo_3(CO)_9$, but subsequent aqueous work-up gave the desilylated product, $HCCo_3(CO)_9$, in 86% yield.

$Me_2(HO)SiCCo_3(CO)_9$ was found to dissolve in cold, concentrated sulfuric acid. When such a solution was poured into cold methanol, the methoxysilyl derivative, $Me_2(MeO)SiCCo_3(CO)_9$, could be isolated in 91% yield. A similar reaction with ethanol gave $Me_2(EtO)SiCCo_3(CO)_9$. In view of the observation that silanols do not ionize in concentrated sulfuric acid [26] and exist in such solutions as the covalent bisulfates, this observed chemistry may be explained quite satisfactorily in terms of formation and subsequent alcoholysis of $(OC)_9Co_3CSiMe_2OSO_2OH$ or $[(OC)_9Co_3CSiMe_2]_2SO_4$.

These various experiments thus have given no evidence in favor of a stable $(OC)_9Co_3C$-stabilized siliconium ion, and siliconium ions remain as elusive as before. However, the present research has developed a useful, high-yield route to silyl derivatives of the $CCo_3(CO)_9$ cluster. A beginning has been made in the exploration of the chemistry of this interesting new class of organosilicon compounds, but, obviously, much more can be done in terms of their reaction chemistry at silicon. Our efforts in this area are continuing.

Experimental

General comments

Solid samples in general were purified by recrystallization or by sublimation (50°C at 0.1 mmHg). Infrared spectra were obtained using a Perkin—Elmer 475A double-beam grating infrared spectrophotometer. The stretching frequencies for the terminal CO ligands are much stronger than the rest of the spectrum; to record them accurately the sample was diluted after the initial spectrum had been recorded. In general, spectra were taken using 0.1 mm NaCl cavity cells and carbon tetrachloride as solvent. Proton NMR spectra were obtained using a Varian Associates T60 spectrometer. Tetramethylsilane and chloroform were used as internal standards. Melting points were taken using a Büchi circulating oil melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was not applicable in following the course of most of these reactions since starting materials and products usually had nearly the same R_f values. The chlorosilyl derivatives were an exception since they were converted to the respective silanols on TLC. These have low R_f values and may be easily distinguished from the high R_f $HCCo_3(CO)_9$.

Dicobalt octacarbonyl was purchased from Strem Chemical Co. Methylidyne- and bromomethylidyne-tricobalt nonacarbonyl were prepared as described in a previous paper of this series [3]. The silicon hydrides were purchased from Petrarch Systems Inc. and from Silar Laboratories and were used as received. Dr. C.L. Frye (Dow Corning Corp.) kindly donated a sample of 3,7,10-trimethylsilatrane. The siloxanes used in the equilibration studies were obtained from Petrarch Systems, Inc. All solvents were rigourously dried prior to use.

General procedures for the silylation of methylidyntricobalt nonacarbonyls

The standard apparatus consisted of a flame-dried (under a stream of nitrogen) 100 ml, three-necked, round-bottomed flask which was equipped with a reflux condenser, a thermometer, a gas inlet tube for the admission of carbon monoxide and a magnetic stir-bar. The apparatus was charged with 2—4 mmol of $HCCo_3(CO)_9$ or $BrCCo_3(CO)_9$ and 40 ml of the appropriate solvent (benzene with the latter, toluene with the former). The system then was purged with a stream of carbon monoxide and the mixture was heated to reflux (ca. 80° C with benzene, ca. 105° C with toluene) while being stirred under an atmosphere of carbon monoxide. A reflux time of about 16 h was required for reactions of $BrCCo_3(CO)_9$ with silicon hydrides. A reaction time of 30 min was sufficient in the case of $HCCo_3(CO)_9$. During this time the color of the reaction mixture changed from purple to reddish brown-purple, not a distinct color change.

Subsequently, the reaction mixture was cooled to room temperature and the solvent was removed in vacuo to leave a dry residue. Filtration chromatography, generally using hexane as eluent, through a pad of silicic acid was used to separate the desired product. In most cases the chlorosilylidynetricobalt nonacarbonyl complexes were converted to the corresponding silanol or methoxysilane prior to product separation. The flask (usually a 200 ml, one-necked, round-bottomed flask) containing the initial reaction residue was charged with 30 ml of benzene and equipped with a magnetic stir-bar and a reflux condenser topped with a carbon monoxide inlet tube. Water or methanol (5 ml) was added, and the mixture was heated to reflux and stirred under carbon monoxide for 30 min. Subsequently, the solvent was removed in vacuo. Filtration chromatography on sililic acid using benzene for the methoxysilanes and diethyl ether for the silanols yielded the products which were purified by sublimation or recrystallization.

If isolation of the chlorosilyl-substituted cluster complexes was desired, they could not be purified by chromatography because this procedure converted them to the respective silanols. In such cases the solvent was removed in vacuo from the reaction mixture and the residue was slurried in hexane and filtered to leave the chlorosilylmethylidynetricobalt nonacarbonyl, usually in good purity.

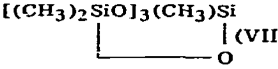
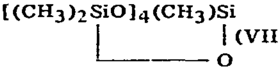
In Tables 1 and 2 we give details of the reactions carried out between various silicon hydrides and $BrCCo_3(CO)_9$ and $HCCo_3(CO)_9$, respectively. In addition, we describe selected reactions from these tables in more detail below. Table 5

TABLE 5

NEW $RCCo_3(CO)_9$ COMPLEXES: PROPERTIES AND ANALYSES

R in $RCCo_3(CO)_9$	Color	Behavior on being heated	Analysis Found (calcd.) (%)		
			C	H	Cl
$(C_2H_5)_3Si$	red-brown	softens above 80°C	34.69 (34.55)	2.79 (2.72)	
$(n\text{-}C_3H_7)_3Si$	red-brown	85—86°C	38.37 (38.14)	3.65 (3.55)	
$(n\text{-}C_4H_9)_3Si$	black	69—70°C	41.42 (41.26)	4.46 (4.26)	
$(C_6H_5)_3Si$	black	139—140°C	48.10 (48.02)	2.21 (2.16)	
$(C_6H_5)_3Ge$	black	114—115°C	45.43 (45.15)	2.13 (2.03)	
$(CH_3)_2CH(CH_3)_2Si$	red-brown	softens above 110°C	33.07 (33.23)	2.55 (2.42)	
$CH_3(C_6H_5)_2Si$	red-brown	84—85°C	43.22 (43.28)	2.13 (2.06)	
$(CH_3)_2(CH_2Cl)Si$	red-brown	dec. above 200°C	28.49 (28.46)	1.66 (1.47)	6.47 (6.46)
$(CH_3)_2(EtO)Si$		120—122°C	31.00 (30.90)	2.09 (2.04)	
$(CH_3)_2(MeO)Si$		dec. above 140°C	29.47 (29.45)	1.82 (1.71)	
$CH_3(MeO)_2Si$	red-brown	softens above 120°C	28.74 (28.59)	1.74 (1.66)	
$(MeO)_3Si$	red-brown	softens above 120°C	27.96 (27.78)	1.70 (1.62)	
$C_6H_5(MeO)_2Si$	purple	70—71°C	35.81 (35.55)	1.90 (1.83)	
$CH_3(C_6H_5)(MeO)Si$	purple	63—64°C	36.82 (36.51)	1.97 (1.88)	
$(CH_3)_2ClSi$	black	dec. above 150°C	26.53 (26.96)	1.36 (1.13)	7.07 (6.63)
CH_3Cl_2Si	black	dec. above 150°C	24.03 (23.81)	0.56 (0.55)	13.00 (12.78)
Cl_3Si	black	dec. above 170°C	20.78 (20.87)		18.34 (18.49)
$(CH_3)_2FSi$	black	205—206°C	27.85 (27.82)	1.32 (1.16)	
CH_3F_2Si	black	dec. above 170°C	25.55 (25.31)	0.75 (0.58)	
F_3Si	purple-black	dec. above 120°C	23.28 (22.83)		
$(CH_3)_2(HO)Si$	red-brown	dec. above 130°C	28.11 (27.93)	1.55 (1.37)	
$CH_3(HO)_2Si$	red-brown	dec. above 140°C	25.53 (25.50)	1.14 (0.97)	
$(HO)_3Si$	red-brown	dec. above 150°C	22.97 (23.10)	0.83 (0.58)	
$C_6H_5(HO)_2Si$	purple	111—112°C	33.46 (33.12)	1.39 (1.22)	
$N[CH_2CH(CH_3)O]_3Si$	purple	softens ~175°C, does not melt below 140°C	34.87 (34.72)	2.90 (2.77)	
$HO(CH_3)_2SiO(CH_3)_2Si$	red-brown	56—58°C	28.63 (28.49)	2.22 (2.22)	
$(CH_3)_3SiO(CH_3)_2Si$	red-brown	70—71°C	30.74 (30.62)	2.61 (2.58)	

TABLE 5 (continued)

R in $RCCo_3(CO)_9$	Color	Behavior on being heated	Analysis Found (calcd.) (%)		
			C	H	Cl
$(CH_3)_3SiO(HO)(CH_3)Si$	red-brown	77—78°C	28.79 (28.49)	2.30 (2.22)	
$[(CH_3)_3SiO]_2(CH_3)Si$	purple-black	53—54°C	30.95 (30.82)	3.25 (3.20)	
$[(CH_3)_3SiO]_2(HO)Si$	red-brown	51—52°C	29.07 (28.92)	2.98 (2.89)	
$[(CH_3)_3SiO]_3Si$	purple-black	139—140°C	31.21 (30.98)	3.83 (3.70)	
 $[(CH_3)_2SiO]_3(CH_3)Si$—O (VIIa)	purple		28.71 (28.26)	2.91 (2.94)	
 $[(CH_3)_2SiO]_4(CH_3)Si$—O (VIIb)	purple		28.81 (28.64)	3.19 (3.42)	

presents characterizing data and analytical results for the silyl-substituted methylidynetricobalt nonacarbonyl complexes.

Reactions of silicon hydrides with bromomethylidynetricobalt nonacarbonyl

(a) Triethylsilane. The standard apparatus was charged with 1.00 g (1.9 mmol) of the cobalt complex, 5 ml (31.5 mmol) of triethylsilane and 40 ml of benzene. The resulting solution was stirred and heated at reflux while carbon monoxide was bubbled through it for 20 h. Subsequently, the solvent and unreacted triethylsilane were removed at reduced pressure. The residue was taken up in a minimum volume of hexane and placed atop a silicic acid pad in a sintered glass funnel. Filtration chromatography using hexane as eluent gave 0.60 g of an oily red-brown solid. Upon sublimation in vacuo at 50°C, 0.31 g (29%) of $Et_3SiCCo_3(CO)_9$ was obtained.

The best yield of 46% was realized after a reaction time of 16 h at 80°C. No reaction occurred at room temperature. In a reaction in which equimolar amounts of $BrCCo_3(CO)_8$ and 1,8-bis(dimethylamino)naphthalene and an excess of Et_3SiH were used (16 h at 80°C) $Et_3SiCCo_3(CO)_9$ was obtained in 44% yield. In another experiment, a reaction of 1.9 mmol of $BrCCo_3(CO)_9$ and 6.3 mmol of triethylsilane in 40 ml of benzene was carried out at 78°C for 16 h in the presence of 1 ml of triethylamine. Triethylsilylmethylidynetricobalt nonacarbonyl was isolated in 27% yield. Obviously, HBr scavengers do not aid the reaction.

(b) Dimethyl(chloromethyl)silane. The standard apparatus was charged with 1.00 g (1.92 mmol) of $BrCCo_3(CO)_9$, 1.0 ml (10 mmol) of dimethyl(chloromethyl)silane, $Me_2(ClCH_2)SiH$ [27], and 40 ml of benzene. The mixture was stirred and heated at reflux while carbon monoxide was bubbled through it for 16 h at 80°C. Subsequent removal of volatiles at reduced pressure was followed by filtration chromatography of the residue (silicic acid/hexane). Recrystallization of the solid thus obtained from dichloromethane/hexane gave 0.5 g (48%) of $Me_2(ClCH_2)SiCCo_3(CO)_9$, a red-brown solid which decomposed above 200°C when it was heated.

Reactions of silicon hydrides with methylidynetricobalt nonacarbonyl

(a) Triethylsilane. The standard apparatus was charged with 1.00 g (2.3 mmol) of $HCCo_3(CO)_9$, 1.0 ml (6.3 mmol) of triethylsilane and 40 ml of toluene. The resulting solution was stirred and heated at reflux while carbon monoxide was bubbled through it for 30 min. Upon completion of the reaction the volatiles were evaporated at reduced pressure. Filtration chromatography (silici acid/benzene).of the residue and sublimation in vacuo at 50° C gave 0.95 g (76%) of $Et_3SiCCo_3(CO)_9$.

A similar reaction was carried out with the same quantities of starting materials in benzene solution. A reaction time of 16 h at reflux gave an 84% yield of $Et_3SiCCo_3(CO)_9$.

(b) Triphenylsilane. Following the general procedure, a reaction was carried out between $HCCo_3(CO)_9$ (1.5 g, 3.4 mmol) and triphenylsilane (0.52 g, 2.0 mmol). The cobalt complex was used in excess to ensure complete consumption of Ph_3SiH. If any of the latter remained, it was converted to triphenylsilanol on work-up, and this product cannot be separated easily from $Ph_3SiCCo_3(CO)_9$. Separation of the desired product was effected by filtration chromatography: hexane eluted unreacted $HCCo_3(CO)_9$ (0.52 g, 1.2 mmol), benzene the product, $Ph_3SiCCo_3(CO)_9$. Recrystallization of the latter from hexane gave 0.55 g (39%) of pure product (based on Ph_3SiH), black crystals which gave a greenish-black solution.

(c) Trichlorosilane. (i) Without hydrolysis. Following the general procedure, a reaction was carried out using 1.00 g (2.3 mmol) of $HCCo_3(CO)_9$ and 1.0 ml (10 mmol) of $HSiCl_3$ in 40 ml of toluene at reflux for 30 min. The reaction residue obtained after removal of volatiles could not be purified by filtration chromatography since the product is converted to the silanetriol by silicic acid. However, analytically pure product was obtained when the residue was washed with hexane and dried in vacuo at room temperature overnight. The black solid, $Cl_3SiCCo_3(CO)_9$, were isolated in 92% yield.

(ii) With hydrolysis. The reaction residue obtained in a similar reaction (2.3 mmol of $HCCo_3(CO)_9$, 10 mmol of $HSiCl_3$) and 30 ml of benzene and 5 ml of water was stirred and heated under carbon monoxide at reflux for 30 min. Filtration chromatography (silicic acid/diethyl ether) followed by recrystallization from acetone/hexane gave 0.77 g (66%) of red-brown solid $(HO)_3SiCCo_3(CO)_9$.

The ^1H NMR spectrum (acetone-d_6) of $(HO)_3SiCCo_3(CO)_9$ showed a singlet at δ 5.47 ppm, its ^{13}C NMR spectrum (saturated acetone solution) showed the apical carbon atom resonance at 297.3 ppm, the carbon monoxide ligand carbon atoms as a singlet at 205 ppm, and its ^{29}Si NMR spectrum (acetone) showed a singlet at 51.8 ppm upfield from internal tetramethylsilane. The molecular weight of $(HO)_3SiCCo_3(CO)_9$ in acetone (by vapor pressure osmometry) was 498 (calcd. 520). The number of protons in $(HO)_3SiCCo_3(CO)_9$ was established by proton NMR spectroscopy. An NMR spectrum was recorded of an equimolar mixture of $(HO)_3SiCCo_3(CO)_9$ and $CH_3OC(O)CCo_3(CO)_9$ and an integration of the number of protons was performed. In CCl_4 solution this mixture showed signals at δ 3.12 (s, OCH_3) and 4.85 ppm (s, $Si(OH)_3$).

(d) Phenyldichlorosilane, with methanolysis. Following the general procedure, a reaction was carried out between 1.00 g (2.3 mmol) of $HCCo_3(CO)_9$ and

	$(HO)_3SiCCo_3(CO)_9$ (A) g(mmol)	$CH_3OC(O)CCo_3(CO)_9$ (B) g(mmol)	Integration, A/B
Run 1	0.0467 (0.0898)	0.0449 (0.0898)	1.00/1.21
Run 2	0.0468 (0.0898)	0.0448 (0.0898)	1.00/1.17
Run 3	0.0467 (0.0898)	0.0449 (0.0898)	1.00/1.24

1.00 ml (6.9 mmol) of $PhSiHCl_2$ in 40 ml of toluene under carbon monoxide at reflux. The volatiles were removed at reduced pressure and the residue was treated with 2.0 ml of methanol and 30 ml of benzene under carbon monoxide at reflux for 60 min. Triethylamine (0.2 ml, 1.4 mmol) was added to remove the hydrochloric acid which was formed. Separation of the desired product was effected by filtration chromatography (silicic acid/dichloromethane). Subsequent sublimation in vacuo at 50°C gave 0.87 g (62%) of $Ph(MeO)_2SiCCo_3(CO)_9$ as a purple crystalline solid.

(e) sym-Tetramethyldisiloxane. A reaction was carried out between 2.60 g (5.9 mmol) of $HCCo_3(CO)_9$ and 0.5 ml (2.9 mmol) of $HMe_2SiOSiMe_2H$, following the usual procedure, in 40 ml of toluene under carbon monoxide at reflux for 1 h. Separation of the products was carried out by filtration chromatography. Elution with hexane yielded 0.25 g of a mixture of $HCCo_3(CO)_9$ and another compound which was believed to be $[(OC)_9Co_3CSiMe_2]_2O$ (IR and NMR). Elution with dichloromethane and subsequent recrystallization from hexane gave 0.34 g (20%) of $HOMe_2SiOSiMe_2CCo_3(CO)_9$ as a red-brown powder.

Competition reaction of phenyldichlorosilane and phenyldimethylsilane for methylidynetricobalt nonacarbonyl

The standard reaction apparatus was charged with 2.00 g (4.5 mmol) of $HCCo_3(CO)_9$, 0.95 ml (6.5 mmol) of $PhSiHCl_2$, 1.00 ml (6.6 mmol) of $Ph(CH_3)_2SiH$ and 80 ml of toluene. The mixture was stirred and heated at reflux under carbon monoxide for 30 min. The volatiles were removed at reduced pressure and the residue was treated with 5.0 ml of water in 30 ml of benzene at reflux under carbon monoxide for 30 min. The products were separated by filtration chromatography. Elution with 4/1 hexane/dichloromethane gave 0.05 g (2%) of $Ph(CH_3)_2SiCCo_3(CO)_9$, while elution with diethyl ether and subsequent recrystallization from dichloromethane/hexane gave 1.85 g (71%) of $Ph(HO)_2SiCCo_3(CO)_9$.

Reactions of nonacarbonyl tricobaltcarbon-substituted silanols

(a) Conversion to fluorosilanes. (i) $MeF_2SiCo_3(CO)_9$. A flame-dried, 100 ml one-necked, round-bottomed flask equipped with a magnetic stir-bar and a nitrogen inlet tube was charged with 0.55 g (1.1 mmol) of $Me(HO)_2SiCCo_3(CO)_9$, 5.0 ml of boron trifluoride diethyl etherate and 30 ml of diethyl ether. The mixture was stirred under nitrogen at room temperature for 2 h. The progress of the reaction was monitored by TLC: the product has a high R_f when hexane is used as eluent, while the starting material does not move. After the volatiles had been removed at reduced pressure the residue was taken up in hexane. Filtration chromatography (silicic acid/hexane) and subsequent sublimation in vacuo at 50° C gave 0.48 g (87%) of $MeF_2SiCCo_3(CO)_9$, a black, crystalline solid.

(ii) $F_3SiCCo_3(CO)_9$. A similar procedure was used in the reaction of 0.80 g (1.5 mmol) of $(HO)_3SiCCo_3(CO)_9$ and 5.0 ml of $BF_3 \cdot OEt_2$ in 30 ml of diethyl ether at room temperature. In this case, TLC indicated that the product adhered to both silicic acid and alumina, rendering separation by chromatography impossible. After the volatiles had been removed at reduced pressure, the residue was recrystallized from dichloromethane/hexane to give purple-black crystals (0.69 g, 85%) of $F_3SiCCo_3(CO)_9$.

(b) Reactions with hexamethyldisiloxane in the presence of sulfuric acid. Such reactions of $(HO)_3SiCCo_3(CO)_9$ are described to illustrate the procedure used.

A flame-dried, 100 ml one-necked, round-bottomed flask equipped with a magnetic stir-bar and a nitrogen inlet tube was charged with 0.80 (1.5 mmol) of $(HO)_3SiCCo_3(CO)_9$, 1.0 ml (4.7 mmol) of hexamethyldisiloxane and 30 ml of diethyl ether. One ml of concentrated sulfuric acid was added dropwise to this solution. The resulting mixture was stirred under nitrogen at room temperature for 2 h. The progress of the reaction could be followed by TLC; using dichloromethane/hexane as eluent, the products have a high R_f, while the starting material has $R_f = 0$. After 2 h, the reaction mixture was extracted with 100 ml of water and neutralized with sodium bicarbonate solution. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure and the residue was purified by filtration chromatography (silicic acid). Hexane eluted a small amount of purple solid, while dichloromethane eluted $(Me_3SiO)_2(HO)SiCCo_3(CO)_9$ (0.69 g, 68%, after sublimation in vacuo at 50° C).

In another reaction, a solution of 1.5 mmol of $(HO)_3SiCCo_3(CO)_9$, 3.0 ml of hexamethyldisiloxane, 30 ml of diethyl ether and 10 ml of benzene was treated dropwise with 2.0 ml of concentrated sulfuric acid. Subsequently, the resulting mixture was stirred and heated at reflux (~50°) under nitrogen for 10 h. At the end of this time, TLC showed the presence of a single product with a high R_f in hexane. The mixture then was extracted with 100 ml of water, neutralized with sodium bicarbonate solution, and the organic layer was dried and evaporated at reduced pressure. Filtration chromatography (silicic acid/hexane) and subsequent sublimation in vacuo at 50° C gave 0.90 g (79%) of purple-black crystals of $(Me_3SiO)_3SiCCo_3(CO)_9$.

(c) Reactions with cyclosiloxanes.

(i) 1/1 reactions. The apparatus used in (b) was charged with 1.80 g (3.5 mmol) of $Me(HO)_2SiCCo_3(CO)_9$, 0.78 g (3.5 mmol) of hexamethylcyclotrisiloxane, 30 ml of diethyl ether and 10 ml of benzene, Concentrated sulfuric acid (3.0 ml) was added to this solution, dropwise with stirring. The resulting mixture was stirred and heated at 45° C for 90 min. Subsequently, it was shaken with water and aqueous sodium bicarbonate. The organic layer was dried and evaporated at reduced pressure. Filtration chromatography (silicic acid/hexane) of the residual oil gave 1.83 g (73%) of a purple semi-solid. The latter was dissolved in hexane, filtered and evaporated at reduced pressure; the residue was evacuated overnight. The purple solid thus obtained had a molecular weight of 749 in acetone solution (by vapor pressure osmometry); calculated for VIIa: 723.

A similar reaction of $Me(HO)SiCCo_3(CO)_9$ (1.0 mmol) was carried out with octamethylcyclotetrasiloxane (1.7 mmol) to give 0.58 g (75%) of a purple semi-solid. This product was purified as described for VIIa above to give VIIb.

(ii) Excess of cyclosiloxane. A 50 ml, one-necked, round-bottomed flask containing 4.28 g (19.3 mmol) of hexamethylcyclotrisiloxane was heated to 65°C to melt the contents and solid $Me(HO)_2SiCCo_3(CO)_9$ (1.00 g, 1.9 mmol) was added, followed by dropwise addition of 0.5 ml of concentrated sulfuric acid. An exotherm was observed and the mixture solidified into an unstirrable mass within 10 min. After the mixture had cooled to room temperature, the rubbery mass was treated with hexane to soften it and then was removed from the flask, washed with sodium bicarbonate solution and with hexane. Subsequently, it was dried in vacuo to leave a purple rubber. (Found: C, 27.69; H, 6.30%).

Similar experiments in which hexamethyldisiloxane was added to such systems as an end-blocking agent (1 $Me(HO)_2SiCCo_3(CO)_9$/5 $(Me_2SiO)_3$/1 $Me_3SiOSiMe_3$ and 1 $Me(HO)_2SiCCo_3(CO)_9$/2 $(Me_2SiO)_3$/1 $Me_3SiOSiMe_3$) gave purple oils.

A similar experiment in which 1.6 mmol of $(HO)_3SiCCo_3(CO)_9$ and 16.3 mmol of $(Me_2SiO)_3$ were allowed to react in the presence of 0.5 ml of concentrated sulfuric acid gave a purple viscous oil whose IR spectrum showed no O—H stretch; only cluster C=O bands, $SiCH_3$ and Si—O absorptions were observed. (Found: C, 30.66; H, 6.63%.)

Reaction of dimethyl(trichloromethyl)silane with dicobalt octacarbonyl

A one-liter three-necked, round-bottomed flask equipped with a no-air septum, a nitrogen inlet and a solids transfer tube was purged with nitrogen and charged with 82.9 g (0.242 mol) of dicobalt octacarbonyl. The solids transfer tube was replaced with an overhead stirrer. Tetrahydrofuran (500 ml) was added, the mixture stirred to effect solution, and 23.8 g (0.134 mol) of $(CH_3)_2HSiCCl_3$ * was added. Some immediate gas evolution was observed. The mixture was heated to 50°C. After 4 h at this temperature, gas evolution had ceased and the reaction mixture was red. It then was poured into 500 ml of 10% aqueous HCl. The organic layer was washed with water until the washings were clear and the aqueous layer was extracted with pentane. The combined organic phase was dried and evaporated at reduced pressure. The residue was purified by column chromatography (silicic acid/(1/1 hexane/dichloromethane)) and subsequent recrystallization from hexane to give 16.5 g (24%) of $(CH_3)_2(HO)SiCCo_3(CO)_9$.

A similar reaction was carried out in which the initial reaction mixture was evaporated at reduced pressure and the residue was extracted with pentane. Evaporation of the pentane extracts was followed by recrystallization of the residue from hexane. The product which was isolated was $Me_2(HO)SiCCo_3(CO)_9$ (27%), not the expected $Me_2HSiCCo_3(CO)_9$.

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[*] Prepared in 66% yield by the reaction of CCl_3Li with Me_2HSiCl, in THF/Et_2O/hexane at —110°C (in situ procedure); b.p. 134—138°C. ^1H NMR: δ 0.48 (d, J 4 Hz, 6 H, Me_2Si) and 4.31 ppm (heptet, J 4 Hz, 1 H, Si—H).

Reaction of dimethyl(nonacarbonyl tricobalt carbon)silanol with sulfuric acid, followed by methanol

A 100 ml three-necked, round-bottomed flask equipped with a nitrogen inlet tube and a magnetic stir-bar and containing 1.03 g (2.0 mmol) of $Me_2(HO)SiCCo_3(CO)_9$ was cooled in an ice-bath and 50 ml of concentrated sulfuric acid was added. The resulting brown solution was stirred for 1 h at 0°C and then was poured into 500 ml of ice-cold absolute methanol. The resulting purple solution was extracted twice with 200 ml portions of pentane. The combined extracts were washed with water, dried over $MgSO_4$ and evaporated at reduced pressure. The residue was recrystallized from hexane to give 0.96 g (91%) of $Me_2(MeO)SiCCo_3(CO)_9$.

Reaction of dimethyl(nonacarbonyl tricobaltcarbon)silanol with hexafluorophosphoric acid

The standard carbonium ion formation apparatus [1,22] was purged with nitrogen, flame-dried and charged with 1.03 g (2.0 mmol) of $Me_2(HO)SiCCo_3(CO)_9$ and 6 ml of freshly distilled propionic anhydride. The mixture was stirred to effect solution and 0.6 g (2.6 mmol, ca. 0.5 ml) of 65% aqueous hexfluorophosphoric axid was added. An exothermic reaction resulted in the formation of a dark precipitate. The mixture was stirred for 5 min and then was filtered under nitrogen. The filtered solid dissolved in 5 ml of dichloromethane; an additional 10 ml of solvent was added. The resulting solution was treated with 5 ml of anhydrous ethanol. Subsequently, this mixture was poured into 100 ml of water. The organic layer was washed with water, dried and evaporated at reduced pressure. The residue was recrystallized from hexane to give 0.95 g (92%) of $Me_2FSiCCo_3(CO)_9$.

Cleavage of silanol substituents from the $CCo_3C(O)_9$ cluster

Cleavage to give $HCCo_3(CO)_9$ in high yield was observed in the following cases: (a) Treatment of $Me_2(HO)SiCCo_3(CO)_9$ with $H_2SO_4/H_2O/THF$ at room temperature after 24 h gave $HCCo_3(CO)_9$ in 89% yield.

(b) Treatment of $Me_2(HO)SiCCo_3(CO)_9$ with $AlCl_3$ (excess) in dichloromethane (immediate brown color), followed by addition of ethanol and then water, gave $HCCo_3(CO)_9$ in 86% yield.

(c) Treatment of $(HO)_3SiCCo_3(CO)_9$ with 49 *M* HF in diethyl ether, followed by addition of water, gave $HCCo_3(CO)_9$ in 95% yield.

Spectroscopy of silyl-substituted methylidynetricobalt nonacarbonyl complexes

Characteristic of the $CCo_3(CO)_9$ cluster unit are four bands in the infrared spectrum in the terminal carbonyl region: ~2100 m, 2045—2060 s to vs, 2035—2040 s hs vs, and 2015—2020 w. These frequencies are not significantly shifted as the organic substituent R in $RCCo_3(CO)_9$ is changed, and therefore there is little purpose to tabulating the IR spectra of individual compounds. All cluster complexes prepared during the course of this study showed this characteristic band pattern. The infrared spectra of all new compounds are tabulated in the Ph.D. theses of C.N. Rudie (M.I.T., 1977) and M.O. Nestle (M.I.T., 1977).

The proton NMR spectra of the compounds prepared in this study are simple and straightforward since simple substituents on silicon are involved in all cases. They are recorded in the Ph.D. theses mentioned above.

Some ^{13}C NMR spectra were measured: $(HO)_3SiCCo_3(CO)_9$: $\delta(C)$ 297.3 (broad, apical carbon atom); 205.1 (s, CO ligand carbon) ppm (in acetone). $(Me_3SiO)_2MeSiCCo_3(CO)_9$: $\delta(C)$ 301.3 (broad, apical carbon atom); 197.9 (s, CO ligand carbon); —0.6 (q, SiMe, J(C—H) 120 Hz); —1.3 ppm (q, $OSiMe_3$, J(C—H) 120 Hz) ppm (neat, at 56° C).

In previous studies, the apical-carbon atom resonances of various $RCCo_3(CO)_9$ complexes were observed in the range 257—306 ppm, the CO ligand carbon atom resonances in the range 195—201 ppm [1,28].

^{29}Si NMR spectra also were recorded: $Et_3SiCCo_3(CO)_9$: $\delta(Si)$ 16.9 ppm (in CCl_4). $(HO)_3SiCCo_3(CO)_9$: $\delta(Si)$ —51.8 ppm (in acetone). $(Me_3SiO)_2MeSiCCo_3(CO)_9$: $\delta(Si)$ 9.7 ($OSiMe_3$); —38.5 ppm (α-Si) ppm (neat, 56°).

NMR spectra of two of the fluorosilanes also were measured: $Me_2FSiCCo_3(CO)_9$: ^{19}F NMR: 146.8 ppm (heptet, J 6 Hz) upfield from $CFCl_3$. ^1H: 0.57 (d, J(H—F) 7 Hz). $MeF_2SiCCo_3(CO)_9$: ^1H: 0.60 (t, J(H—F) 5.5 Hz).

^{13}C and ^{29}Si NMR spectra were obtained in the Fourier transform mode utilizing a modified Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR data system and are accurate to ±0.2 ppm. For further details of measurement, see ref. 1.

Acknowledgements

The authors are grateful to the National Science Foundation for support of this work (NSF CHE76-2917 and CHE79-0007) and to Dr. Cecil L. Frye for a sample of 3,7,10-trimethylsilatrane.

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