Organosilicon Chemistry. Part 23.[1] Some Silylcobalt(III) Complexes and the Homogeneous Catalysis of Deuteriation, Hydrosilylation, and *O*-Silylation Reactions ‡

By **Nicholas J. Archer, Robert N. Haszeldine,* and R. V. (Dick) Parish,*** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The complexes [CoH(X_2)L_3] (X = H or N; L = PPh_3) react with silanes, SiR_3H, to give the new silylcobalt(III) complexes [$CoH_2(SiR_3)L_3$] [R_3 = F_3, MeF_2, or $(OEt)_3$]. The characterisation of these complexes and their reactions with N_2, H_2, HCl, CCl_4, and CO are described. With CO the new cobalt(I) silyl [Co(SiF_3)$(CO)_2L_2$] is formed. The stability of the silyls to loss of SiR_3H decreases as the electronegativity of R decreases, which allows the less-stable complexes to participate in catalytic processes. The reactions of SiR_3H with D_2 (R = F, OEt, Et, or Me), of $SiH(OEt)_3$ or $Me_3Si[OSi(H)Me]_nOSiMe_3$ with EtOH, and of $SiH(OEt)_3$ with hex-1-ene are catalysed by [CoH(X_2)L_3] or by [$CoH_2\{Si(OEt)_3\}L_3$]. The deuteriation reactions provide an easy route to deuteriosilanes, SiR_3D.

KNOWN silyl complexes of the 3*d* metals usually involve cyclopentadienyl and/or carbonyl ligands with the metal in a low oxidation state, *e.g.* [Co(SiR_3)$(CO)_4$] [2] or [Fe(SiR_3)(η-C_5H_5)$(CO)_2$],[3] although Jetz and Graham [4] have described the formal cobalt(III) and iron(IV) complexes [CoH($SiCl_3$)(η-C_5H_5)(CO)] and [FeH$(SiCl_3)_2$(η-C_5H_5)(CO)]. The only silyl complex which does not contain such ligands appears to be [Ni$(SiCl_3)_2$(bipy)] (bipy = 2,2′-bipyridine).[5] However, with the 4*d* and 5*d* metals, non-carbonyl-containing silyl complexes are well known for rhodium,[6,7] ruthenium,[8] iridium,[9] and platinum.[10-14] Many of these complexes are obtained by oxidative addition of tertiary silanes to complexes containing a metal in a low oxidation state, and we have now examined the reactions between cobalt(I) complexes and tertiary silanes. The chelated complex [CoH$(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) does not yield silyl complexes,[15] but the dinitrogen complex [CoH(N_2)L_3] † is more reactive. A preliminary report of this work has been given.[16]

RESULTS AND DISCUSSION

Synthesis and Characterisation.—A hexane suspension of the complex [CoH(N_2)L_3] reacts with tertiary silanes SiR_3H [R_3 = F_3, MeF_2, or $(OEt)_3$] to give yellow air-sensitive solids analysing as the cobalt(III) silyl complexes [$CoH_2(SiR_3)L_3$] [equation (1)]. The characteristic N–N stretching band of the starting material was not present in the i.r. spectrum of the products, but bands at *ca.* 1 945 and 330 cm^{-1} were observed in addition to those due to triphenylphosphine. Identical products were obtained starting from [CoH_3L_3] [equation (2)]. The high-energy i.r. bands were broad and weak and are assigned to Co–H stretching modes. The lower-energy band is similar to that observed in other silyl complexes,[17,18] and corresponds to a Co–Si stretching vibration.

$$[CoH(N_2)L_3] + SiR_3H \longrightarrow [CoH_2(SiR_3)L_3] + N_2 \quad (1)$$

$$[CoH_3L_3] + SiR_3H \longrightarrow [CoH_2(SiR_3)L_3] + H_2 \quad (2)$$

The presence of the hydride ligands was confirmed by the observation of ^1H n.m.r. signals at *ca.* τ 25. The signals are very broad (30—50 Hz) and show no fine structure, in contrast to the resolved spectra of [CoH(N_2)L_3] and [CoH_3L_3],[19] suggesting an exchange or relaxation process of intermediate rate. Unfortunately, the low solubility of the complexes did not allow spectra to be run at lower temperatures and the complexes decomposed when the solutions were warmed. The low solubility also prevented the recording of ^{19}F spectra. The possibility of exchange by phosphine dissociation seems unlikely since the line shape was unaffected by the addition of an excess of PPh_3. Dissociation of the silane is a possibility which would be consistent with some of the reactions described below or, alternatively, the complexes may be fluxional like [CoH_3L_3] [19] and [$FeH_2\{P(OPh)_3\}_4$].[20]

TABLE 1

Spectroscopic data for silyl-cobalt complexes

	I.r. (cm^{-1}) [a]			N.m.r.,[b]
Complex	ν(Co–H)	ν(Si–F)	ν(Co–Si)	τ(Co–H)
[$CoH_2(SiF_3)L_3$]	1 945w	790, 815, 825	330	24.9 (40)
[$CoH_2(SiMeF_2)L_3$]	2 040w, 1 960w	790, 810, 850	330	25.7 (30)
[$CoH_2(SiMeF_2)L_2$]	1 990w, 1 850w	800b		
[$CoH_2\{Si(OEt)_3\}L_3$]	1 945	*c*		25.0 (50)
[$CoH_2(SiF_3)(CO)L_2$]	1 945w, 2 000 (sh) [d,e]	800, 870 [d]		22.6

[a] Nujol mulls. [b] In benzene solution; the half-width (in Hz) is given in parentheses. [c] Si–O–C band at 1 075 cm^{-1}. [d] In benzene. [e] ν(C–O) at 1 935 cm^{-1}.

On heating *in vacuo* the complexes decompose without melting with liberation of the silane; other products could not be identified. The decomposition temperatures decrease in the order SiR_3 = SiF_3 (150—155 °C) > $SiMeF_2$ (130—135 °C) > $Si(OEt)_3$ (90—95 °C). Although many factors are involved in the decomposition reactions, the observed order is a rough guide to the stability of the complexes to dissociation, and parallels

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‡ No reprints available.

† Throughout this paper: L = PPh_3; 1 mmHg ≈ 13.6 × 9.8 Pa.

that observed for the corresponding rhodium complexes [RhH(Cl)(SiR_3)L_2].[6,21]

When the dinitrogen complex was suspended in diethyl ether, rather than hexane, and treated with $SiMeF_2H$ a very reactive yellow product was obtained, analysing as the bis(phosphine) complex [CoH_2($SiMeF_2$)L_2]. This product decomposed rapidly when dissolved in benzene and it was not possible to obtain molecular-weight or n.m.r. data. On reaction with 1 mol equivalent of PPh_3 a complex with properties identical to those described above was formed, and a similar material could be obtained by conducting the reaction of the dinitrogen complex in the presence of an excess of the ligand. Other unidentate ligands did not appear to react with [CoH_2($SiMeF_2$)L_2], but the chelating ligand dppe gave [CoH_2($SiMeF_2$)(dppe)L]. When an excess of dppe was present over a long period the final product was [CoH$(dppe)_2$].

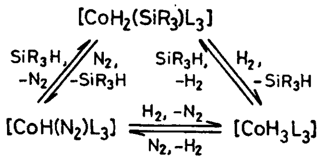
The dinitrogen complex did not react with $SiMe_3H$, $SiEt_3H$, or $SiPh_3H$ (but see deuteriation studies described below). With $SiCl_3H$ the known[22] cobalt(I) complex [$CoClL_3$] and $SiCl_2H_2$ were formed.

Attempts were made to prepare other dinitrogen complexes, [CoH(N_2)L'_3] [L = P(C_6H_4Me-*p*)$_3$ or P(n-C_8H_{17})$_3$][23] but only oils were isolated. These materials reacted with SiF_3H or SiH$(OEt)_3$; the i.r. spectra of the solutions showed the loss of the sharp band at *ca.* 2 000 cm^{-1} due to the N_2 ligand, while new weak bands appeared at 1 900—2 000 cm^{-1}, assigned as Co–H stretching modes. These products could not be isolated nor could n.m.r. spectra be obtained (the solutions appeared to contain paramagnetic species as impurities), but chromatography showed that only one major product had been formed in each case.

When $PEtPh_2$ was employed, only [CoH$(PEtPh_2)_4$] could be obtained. This complex and other complexes of the type [CoHL'_4] [L' = P$(OEt)_3$ or P$(OPh)_3$][24] did not react with SiF_3H or SiH$(OEt)_3$. The complex [$CoClL_3$] was similarly unreactive towards SiF_3H, $SiCl_3H$, or SiH$(OEt)_3$.

The complex [CoH(CO)L_3],[25] in benzene solution, reacts with SiF_3H, as shown by loss of the characteristic i.r. and n.m.r. patterns of the starting complex. The i.r. spectrum of the solution showed a strong band at 1 935 cm^{-1} [ν(C–O)], medium bands at 800 and 870 cm^{-1} [ν(Si–F)], and a weak band at 1 995 cm^{-1} with a shoulder at 2 000 cm^{-1}. The last two bands could be Co–H stretching modes, and the presence of hydride ligands was confirmed by the observation of a broad ^1H n.m.r. signal centred on τ 22.6. No dihydrogen was liberated during the reaction. All attempts to isolate this very air-sensitive product were unsuccessful, but it is tentatively formulated as [CoH_2(SiF_3)(CO)L_2].

Reactions of [CoH_2(SiR_3)L_3].—(*i*) *With dinitrogen or dihydrogen.* The SiF_3 and $SiMeF_2$ complexes are stable under dinitrogen, dihydrogen, or argon and *in vacuo*. The Si$(OEt)_3$ complex is stable in argon or *in vacuo* but reacts with dinitrogen or with dihydrogen with liberation of SiH$(OEt)_3$ and formation of [CoH(N_2)L_3] or [CoH_3L_3]. The same reactions occur in solution and are reversed by the addition of an excess of SiH$(OEt)_3$. The three complexes are thus readily interconverted *via* the equilibrium system shown in Scheme 1, which is related to the utility of these complexes as deuteriation and *O*-silylation catalysts (see below).



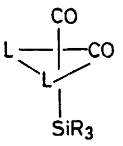
SCHEME 1 R = OEt

(*ii*) *With carbon monoxide.* Suspensions or solutions of the Si$(OEt)_3$ or $SiMeF_2$ complexes react rapidly with carbon monoxide with liberation of SiH$(OEt)_3$ or $SiMeF_2H$ and formation of [CoH(CO)L_3] which is readily identified by its i.r. and n.m.r. spectra.[25] With the triethoxysilyl complex, small quantities of the very insoluble [{Co$(CO)_3$L}$_2$] were also formed, but when [CoH_2($SiMeF_2$)L_2] was used this dimer was the major product.

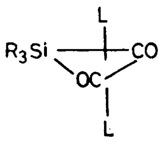
The complex [CoH_2(SiF_3)L_3] reacts very differently. When a benzene solution of the complex was treated with carbon monoxide the resulting pressure decrease corresponded to the uptake of 1 mol equivalent of gas and the atmosphere above the solution was shown to contain dihydrogen. When the carbon monoxide was admitted in small portions, the pressure changes corresponded to the uptake of half the aliquot until 2 mol equivalents had been added, after which there was no further uptake of gas. The complex appeared to be reacting by evolving 1 mol of dihydrogen for every 2 mol of carbon monoxide absorbed [equation (3)]. Addition of hexane to the solution immediately after absorption of gas was complete gave a yellow solid analysing as

$$[CoH_2(SiF_3)L_3] + 2CO \longrightarrow [Co(SiF_3)(CO)_2L_2] + H_2 + L \quad (3)$$

[Co(SiF_3)$(CO)_2L_2$] and which, on reaction with iodine in pyridine, yielded 2 mol equivalents of carbon monoxide. The complex did not react with carbon tetrachloride, which is consistent with the absence of hydride ligands. The i.r. spectrum showed, in addition to bands due to PPh_3 and SiF_3, two strong C–O stretching bands at 2 000 and 1 935 cm^{-1}. The relative intensity of these bands suggest that the CO groups are not mutually *trans*, and steric effects would presumably favour either equatorial (I) or axial (II) positions for the phosphine ligands.

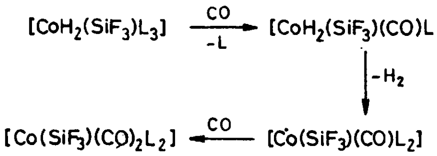


(I)



(II)

The reaction of [CoH_2(SiF_3)L_3] with carbon monoxide is inhibited in the presence of PPh_3. The most likely reaction mechanism is therefore that of Scheme 2 in which a phosphine is replaced by CO; the resulting monocarbonyl complex loses dihydrogen by reductive elimination to give a 16-electron cobalt(I) complex



SCHEME 2

which takes up a second mol of CO. These stages are not separable; the CO-uptake experiment showed clearly that long-lived monocarbonyl complexes were not formed.

(*iii*) *With hydrogen chloride*. The silyl complexes react with an excess of hydrogen chloride to give $[CoClL_3]$ and $SiClF_3$, $SiMeF_2H$, or $SiH(OEt)_3$ [equations (4) and (5)]. The differences in silicon-containing products, Si–Cl *vs.* Si–H formation, represents a difference in the mode of reaction; since SiF_3H does not react with hydrogen chloride, the $SiClF_3$ must be a primary product.

$$[CoH_2(SiF_3)L_3] + HCl \longrightarrow [CoClL_3] + SiClF_3 + H_2 \quad (4)$$

$$[CoH_2(SiR_3)L_3] + HCl \longrightarrow [CoClL_3] + SiR_3H + H_2 \; [R_3 = (OEt)_3, MeF_2] \quad (5)$$

$$[CoH_2(SiR_3)L_3] \xrightarrow{-SiR_3H} [CoHL_3] \xrightarrow{HCl} [CoClL_3] + H_2 \quad (6)$$

Three mechanistic paths can be envisaged for these reactions. For the SiF_3 complex, attack by hydrogen chloride could take place at the co-ordinated silicon atom, leading to the elimination of $SiClF_3$ and the formation of $[CoH_3L_3]$ which is known to react with HCl to give $[CoClL_3]$ and dihydrogen.[22] The other two silyl complexes are much less stable to dissociation, and it seems likely that in these cases reaction occurs by elimination of the silane to give the 16-electron intermediate $[CoHL_3]$ which would react rapidly with HCl to give the observed products [equation (6)]. This intermediate is also thought to play a role in the other reactions described below. However, it is also possible that all the silyl complexes react *via* a common intermediate, $[CoH(Cl)(SiR_3)L_3]$, which could eliminate either SiR_3Cl or SiR_3H depending on the nature of R [equation (7)].

$$[CoH_2(SiR_3)L_3] \xrightarrow[-H_2]{HCl} [CoH(Cl)(SiR_3)L_3] - \left[\begin{array}{l} \longrightarrow SiR_3Cl + [CoHL_3] \\ \longrightarrow SiR_3H + [CoClL_3] \end{array}\right. \quad (7)$$

With dichlorine, all the silyl complexes reacted to give SiR_3Cl, $[CoClL_3]$ and, eventually, $[CoCl_2L_2]$.

(*iv*) *With carbon tetrachloride and chloroform*. The silyl complexes all react with carbon tetrachloride to give, initially, $[CoClL_3]$, and ultimately, $[CoCl_2L_2]$, together with the silane, tetrachloroethylene, and a little chloroform. The reaction could be stopped at the first stage by cooling to −13 °C, when tetrachloroethylene was the minor product and appreciable quantities of chloroform were produced [equation (8)]. It was demonstrated separately that $[CoClL_3]$ reacts much more rapidly with chloroform [equation (9)] than with carbon tetrachloride [equation (10)], so that the conversion of chloroform into tetrachloroethylene proceeds essentially to completion in the second stage, despite the presence of an excess of carbon tetrachloride. The complex $[CoH(N_2)L_3]$ is known to react similarly with carbon tetrachloride to give dinitrogen, $[CoClL_3]$, and chloroform;[26] the last two products then react further as in equation (9).

The silyl complexes react similarly with chloroform to give the same two cobalt complexes. These reactions confirm further the presence of the hydride ligands in the silyl complexes. It is not known whether these reactions proceed *via* a chloro(silyl) complex, $[CoH(Cl)(SiR_3)L_3]$, which would eliminate the silane, or by initial dissociation of the silane and reaction of the intermediate $[CoHL_3]$ with chloroform. In view of the other reactions of the complexes which are thought to involve $[CoHL_3]$, the second alternative is not implausible and would allow the chlorocarbons to react by the usual oxidative-addition mechanisms.

(*v*) *With ethanol*. The SiF_3 and $SiMeF_2$ complexes were unreactive towards ethanol over several days, but the $Si(OEt)_3$ complex reacted during a few hours to give $Si(OEt)_4$ and $[CoH_3L_3]$. This reaction parallels that of $[Co(SiMe_3)(CO)_4]$[22] and its utility in a catalytic cycle is discussed below.

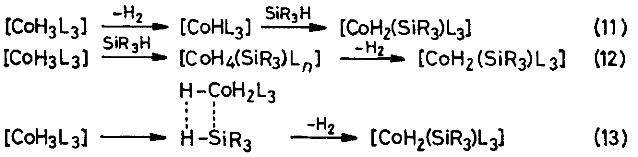
Deuteriation Studies.—The formation of the silyl complexes by reaction of $[CoH(N_2)L_3]$ with silanes presumably involves the intermediate $[CoHL_3]$ also thought to participate in several reactions of the silyl complexes. This 16-electron complex would readily undergo oxidative addition of the silane. When $[CoH_3L_3]$ is the starting complex, the same intermediate could be formed by the elimination of dihydrogen [equation (11)]. However, it is also possible that the reaction could proceed by an initial oxidative-addition reaction with the silane followed by elimination of dihydrogen [equation (12)]; in this case, temporary loss of one phosphine ligand would be likely, to allow the intermediate to be an 18-electron complex. A third

$$[CoH_2(SiR_3)L_3] + CCl_4 \longrightarrow [CoClL_3] + SiR_3H + CHCl_3 \quad (8)$$

$$2[CoClL_3] + 2CHCl_3 \longrightarrow 2[CoCl_2L_2] + 2L + H_2 + Cl_2C{=}CCl_2 \quad (9)$$

$$2[CoClL_3] + 2CCl_4 \longrightarrow 2[CoCl_2L_2] + L{\cdot}Cl_2 + Cl_2C{=}CCl_2 + L \quad (10)$$

possibility is the four-centre associative route in which the silane approaches the complex, possibly being held by Co→Si electron donation, with the elimination of dihydrogen between the silane and the complex [equation (13)]. These routes could, in principle, be distinguished if the initial complex were deuteriated, as described by Parshall *et al.*[27] and Wells and his co-workers.[28] If $[CoD_3L_3]$ were allowed to react with SiF_3H, the composition of the gaseous product would depend on the reaction path followed, *e.g.* dissociation of $[CoD_3L_3]$ [equation (11)] would lead to the elimination of pure D_2, and the four-centre mechanism [equation (13)] would give HD as the primary product. The oxidative route [equation (12)] should give a 1 : 1 mixture of HD and D_2, an average composition $H_{0.25}D_{0.75}$.



$$[CoH_3L_3] \xrightarrow{-H_2} [CoHL_3] \xrightarrow{SiR_3H} [CoH_2(SiR_3)L_3] \qquad (11)$$

$$[CoH_3L_3] \xrightarrow{SiR_3H} [CoH_4(SiR_3)L_n] \xrightarrow{-H_2} [CoH_2(SiR_3)L_3] \qquad (12)$$

$$[CoH_3L_3] \longrightarrow \begin{matrix} H\text{-}CoH_2L_3 \\ \vdots \quad \vdots \\ H\text{-}SiR_3 \end{matrix} \xrightarrow{-H_2} [CoH_2(SiR_3)L_3] \qquad (13)$$

The deuteriated complex was obtained by reaction of $[CoH(N_2)L_3]$ with an excess of D_2. Mass-spectrometric analysis of the gas phase showed that the reaction was essentially complete after 3 h, the final composition showing equilibration with one hydrogen ligand in the complex. No exchange with the *o*-hydrogen atoms of the phosphine ligand was found. The purity of the product was checked by its reaction with dinitrogen and analysis of the liberated dihydrogen, which was found to be 89% deuterium. Diethyl ether suspensions of $[CoD_3L_3]$ were then shaken for 15 min with various amounts of SiF_3H and the residual gas analysed by mass spectrometry. The results are shown in Table 2 together with the compositions expected for each of the mechanisms. The bulk of the deuterium is eliminated as D_2, and the quantity is clearly much more than is required for equations (12) or (13), or for random exchange. Rather less deuterium was obtained than was expected from equation (11). However, when the excess trifluorosilane from the last experiment was analysed, it was found to contain the balance (14%) of the deuterium, *i.e.*, in addition to the direct reaction, exchange of deuterium occurs between the gaseous silane and either $[CoD_3L_3]$ or the product $[CoH(D)(SiF_3)L_3]$. Slow exchange was observed between $[CoH_2(SiF_3)L_3]$ and D_2. These data are consistent with the formation of the silyl complexes by the mechanism of equation (11).

TABLE 2

Reaction of $[CoD_3L_3]$ with SiF_3H. The actual composition of the starting complex was $[CoD_{2.67}H_{0.33}L_3]$. Reaction time, 15 min

	% D in non-condensable gas				
		Calc. for:			
Mol ratio SiF_3H : $[CoD_3L_3]$	Found	Equation (11)	(12)	(13)	Random exchange
0.9	79	89	67	45	70
1.1	78	89	67	45	67
2.0	75	89	67	45	55

The observation of the above exchange reactions suggested that exchange might also occur between silanes and D_2, catalysed by the cobalt complexes. It was found that the dinitrogen complex was an effective catalyst at a low concentration, giving essentially complete reaction within a few hours as shown by mass-spectrometric analysis of the gas phase and the appearance of an Si–D stretching vibration in the i.r. spectrum of the silane (Table 3). Deuteriation of SiF_3H was relatively slow, paralleling the high stability of the SiF_3 complex. The reaction of $SiEt_3H$ and $SiMe_3H$ indicates that these silanes are able to interact with the cobalt complex even though stable silyl complexes could not be isolated.

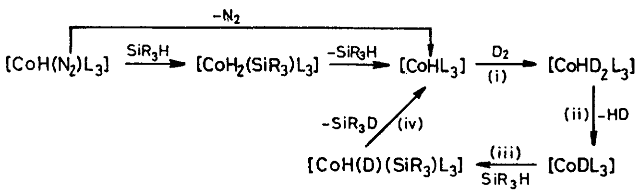
TABLE 3

Deuteriation of SiR_3H catalysed by $[CoH(N_2)L_3]$

R	Reaction time (t/h)	%D Found	%D Calc. for equilibrium	ν(Si–D) cm^{-1}
OEt	5	40	47	1 660
Et	5	62	55	1 530
Me	18	30	50	1 540
F	18	50	50	1 650

Presumably, complete deuteriation of the silane could be achieved by repeated exposures to fresh D_2 samples, providing a facile route to deuteriosilanes. Previously,[29] it has been necessary to prepare $SiCl_3D$ from DCl and silicon and to replace the chlorine atoms by the desired substituents, or to reduce chlorosilanes with $Li[AlD_4]$, which procedures are time-consuming and expensive. The new route provides a quick convenient method of deuteriating a range of silanes although, of course, chlorosilanes could not be used.

In view of the way in which D_2 reacts with the silyl complexes, it seems likely that a similar mechanistic path could be involved in the catalytic process, *viz.* the reversible addition of the silane or of D_2 to the intermediate $[CoHL_3]$ (Scheme 3). Attempts were made to confirm this by studying the rate of reaction of $SiH(OEt)_3$ catalysed by the dinitrogen complex. The data (Table 4) show that the rate of appearance of H in the gas phase is roughly constant in the early stages of reaction, and is proportional to the product of the concentrations of the silane and the catalyst and independent of the amount of D_2 present. This is consistent with step (iii) or (iv) being the rate-controlling reaction.



SCHEME 3 R = OEt

The 16-electron intermediate is likely to react rapidly and step (iv), the dissociation of the silyl, is probably the slowest step. There are considerable differences in the rates of formation of H_2 and HD which roughly parallel the concentration of HD, as would be expected. The source of H_2 must be step (i) but with HD being taken up rather than D_2, giving $[CoH_2DL_3]$. There is also a strong correlation with the catalyst : D_2 ratio, production of H_2 being greater when this ratio is large. This may indicate that under these conditions the *o*-hydrogen atoms of the phenyl groups of the phosphine are participating in the reaction.

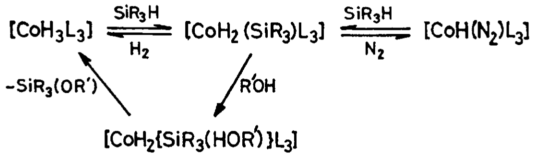
Catalysis of O-*Silylation.*—The observation that the $Si(OEt)_3$ complex reacts with ethanol to give $[CoH_3L_3]$, which is also known to react with the silane to form the original complex (Scheme 1), raises the possibility of a catalytic *O*-silylation reaction. Such reactions are of considerable commercial importance.

TABLE 4

Deuteriation of $SiH(OEt)_3$

	Amount/mmol						mmol of H formed as			
Run	$SiH(OEt)_3$	D_2	$[CoH(N_2)L_3]$	t/min	%H_2	%HD	H_2	HD	total	d[H]/dt / mmol min^{-1}
1	16.0	11.8	0.1035	0	0.73	9.0				
				10	4.3	16.4	0.85	0.87	1.72	
				20	6.1	19.0	1.27	1.18	2.45	
				30	8.8	25.1	1.91	1.90	3.81	0.086
				40	9.3	26.8	2.03	2.10	4.13	
				50	10.1	32.5	2.22	2.77	4.99	
2	26.6	4.36	0.0566	0	0.78	10.8				
				10	7.4	18.0	0.57	0.31	0.88	
				20	11.9	23.2	0.97	0.54	1.51	0.076
				30	14.7	30.2	1.21	0.85	2.06	
				40	26.0	34.2	2.20	1.02	3.22	
3	16.0	8.82	0.1315	1	1.7	14.0				
				6	4.3	14.7	0.46	0.06	0.52	
				16	10.1	18.5	1.48	0.40	1.88	
				31	14.1	23.1	2.19	0.80	2.99	0.114
				41	20.0	26.5	3.23	1.10	4.33	
				51	20.8	28.5	3.37	1.28	4.65	
4	16.0	7.43	0.0581	0	0.74	12.5				
				15	2.0	19.5	0.19	0.52	0.71	
				40	5.3	30.8	0.68	1.36	2.04	
				55	7.6	36.0	1.03	1.75	2.78	0.050
				90	9.2	40.0	1.26	2.04	3.30	
				170	14.0	53.6	1.98	3.05	5.03	
5	10.7	2.08	0.0496	1	1.5	14.1				
				11	7.1	17.2	0.23	0.06	0.29	
				21	11.0	20.4	0.40	0.13	0.53	0.024
				31	14.2	23.9	0.53	0.20	0.73	

The complex $[CoH(N_2)L_3]$ or $[CoH_3L_3]$ was found to be an effective catalyst for the reaction of $SiH(OEt)_3$ with MeOH or EtOH, reaction being complete in 8—10 h. No reaction was observed with Bu^{n}OH, and none of the alcohols reacted when $[CoH(CO)L_3]$ was used. The two active complexes gave similar rates of reaction, suggesting a common reaction path. Methanol reacted three times faster than ethanol; it is likely, therefore, that the rate-determining step involves attack by the alcohol, presumably on the cobalt-bound silyl group (Scheme 4). The reaction was inhibited by the dihydrogen which was generated; when the dihydrogen was displaced with argon, reaction resumed at the original rate. This inhibition reflects the equilibrium between $[CoH_3L_3]$ and $[CoH_2\{Si(OEt)_3\}L_3]$ observed earlier. For effective catalysis, therefore, the dihydrogen must be continuously removed. The reaction of the polysilane $Me_3Si[OSi(H)Me]_nOSiMe_3$ (*n* = *ca*. 50) with ethanol was also catalysed by $[CoH(N_2)L_3]$, but trialkylsilanes did not react.



SCHEME 4 R = OEt

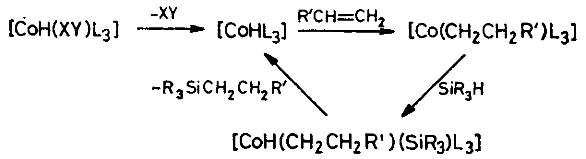
Catalysis of Hydrosilylation.—Several transition-metal complexes act as hydrosilylation catalysts, and mechanistic schemes involving hydrido(silyl)metal complexes have been proposed. Since the silyl cobalt complexes are of this type, preliminary experiments were carried out to test their catalytic activity. The precursors and several other complexes were also examined and the results are displayed in Table 5. It is clear that the critical property of the active catalysts is their ability to interact reversibly with $SiH(OEt)_3$. A likely mechanism would again involve the 16-electron $[CoHL_3]$

TABLE 5

Catalysis of the reaction $C_4H_9CH{=}CH_2 + SiH(OEt)_3 \longrightarrow C_6H_{13}Si(OEt)_3$

Catalysts		
Active	Inactive	
$[CoH(N_2)L_3]$	$[CoH_2(SiF_3)L_3]$	$[CoH(CO)L_3]$
$[CoH_3L_3]$	$[CoH(dppe)_2]$	$[CoH\{P(OPh)_3\}_4]$
$[CoH_2\{Si(OEt)_3\}L_3]$	$[CoClL_3]$	$[CoH\{P(OMe)_3\}_4]$

postulated in several of the other reactions discussed above (Scheme 5), although direct interaction of the olefin with $[CoH_2(SiR_3)L_3]$ cannot be ruled out. Such interaction would presumably require prior dissociation of a phosphine ligand, which would be consistent with the observed strong inhibition of the catalysis by added PPh_3. Alternatively, the cobalt(I) intermediate might be deactivated by conversion into $[CoHL_4]$.



SCHEME 5 R = OEt; R′ = Bu^n; XY = H_2 or N_2

An approximate comparison of the activity of the various catalysts was made by studying the rate of self-heating of a 2 : 1 mixture of hex-1-ene and $SiH(OEt)_3$ in the presence of a standard amount of the catalyst. Reactants were mixed at 20 °C and the temperature rise caused by the exothermic reaction was monitored. The results are displayed in the Figure, from which it is seen that the new catalysts are highly effective, being of comparable activity to $[Co_2(CO)_8]$. The rapid reactions did not go to completion, probably because of the decomposition of the catalysts at 70—80 °C; distinct colour changes were observed in the reaction mixtures as the temperature increased. The residual hexene was found to consist mostly of *cis*- and *trans*-hex-2-ene; isomerisation of hex-1-ene in the presence of $[CoH(N_2)L_3]$ has been reported previously.[30] Small amounts (*ca.* 10%) of a low-boiling product were also obtained; this appeared to be hexane, the identification of which led to a search for a hydrogen-deficient product. G.l.c. analysis of the high-boiling product [mainly $C_6H_{13}Si(OEt)_3$], showed the presence of a minor component thought to be $C_4H_9CH{=}CHSi(OEt)_3$, which has been observed previously in high-temperature hydrosilylation reactions.[31] These products could arise by a second mode of dissociation of the intermediate postulated in Scheme 5 [equations (14) and (15)].

$$[CoH(C_6H_{13})(SiR_3)L_3] \longrightarrow [Co(SiR_3)L_3] + C_6H_{14} \qquad (14)$$

$$[Co(SiR_3)L_3] + 1\text{-}C_6H_{12} \longrightarrow [CoHL_3] + C_6H_{11}SiR_3 \qquad (15)$$

No catalysis was observed for the attempted reactions of hex-1-ene with SiF_3H, $SiCl_3H$, or $SiEt_3H$. With the first two silanes, $[CoH_2(SiF_3)L_3]$ or $[CoClL_3]$ were formed, neither of which was an active catalyst at temperatures up to 70 °C. With $SiEt_3H$ no reaction at all was observed. The deuteriation experiments indicate that this silane is able to add to $[CoHL_3]$, and it must be assumed either that the lifetime of the adduct is too short to allow interaction with the olefin or that $SiEt_3H$ cannot add to $[Co(C_6H_{13})L_3]$.

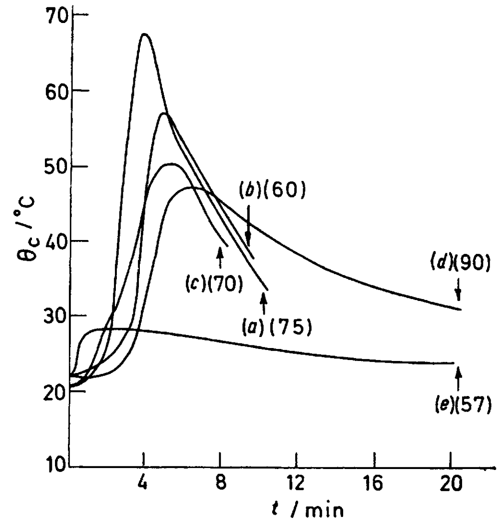
Conclusions.—Silylcobalt(III) complexes, $[CoH_2(SiR_3)L_3]$, have been obtained by oxidative-elimination reactions of silanes with $[CoH(N_2)L_3]$. These new silyl derivatives are 18-electron species in which the presence of hydride ligands is apparently essential, since their replacement by chloride leads to decomposition, and the complex $[CoClL_3]$ is unreactive towards silanes. This is in marked contrast to the rhodium system, where the 16-electron silyl complexes $[RhH(Cl)(SiR_3)L_2]$ are readily formed by oxidative elimination from $[RhClL_3]$.[6,7] An essential prerequisite for the formation of the cobalt complexes seems to be the ability of the 18-electron cobalt(I) complex to dissociate to a 16-electron species, $[CoHL_3]$ [equation (16)] since the complexes $[CoH(dppe)_2]$ and $[CoHL'_4]$ [L′ = $P(OMe)_3$ or $P(OPh)_3$], which do not dissociate readily, were unreactive.

$$[CoH(N_2)L_3] \longrightarrow [CoHL_3] + N_2 \qquad (16)$$

$$[CoH_3L_3] \rightleftharpoons [CoHL_3] + H_2 \qquad (17)$$

$$[CoH_2(SiR_3)L_3] \rightleftharpoons [CoHL_3] + SiR_3H \qquad (18)$$

The 16-electron intermediate can presumably[27] also be formed from $[CoH_3L_3]$ [equation (17)], which is also a useful starting material in the synthesis, and it appears to be important in many of the reactions of the silyl complexes, *e.g.* with hydrogen chloride and chlorocarbons, and in the catalysis of deuteriation and hydrosilylation. In the absence of other reagents, equilibria (17) and (18) presumably lie far to the left, since they cannot be detected by conventional methods, but the rapid consumption of the product, $[CoHL_3]$, in another reaction would allow complete reaction of the starting material.



Temperature profiles for the reaction of $SiH(OEt)_3$ with hex-1-ene catalysed by (*a*) $[CoH(N_2)L_3]$, (*b*) $[Co_2(CO)_8]$, (*c*) $[CoH_3L_3]$, (*d*) *trans*-$[PtCl_2(SEt_2)_2]$, or (*e*) H_2PtCl_6. Figures in parentheses represent the final extents of reaction (%) at the times indicated by the positions of the arrows

The dissociation equilibrium (18) may also explain the broadening of the ^1H n.m.r. spectra of the silyl complexes or, alternatively, the molecules may be fluxional. The hydride signals show no resolvable coupling with the phosphorus nuclei, in contrast to those of $[CoH(N_2)L_3]$, $[CoH_3L_3]$, or $[CoH(CO)L_3]$. The trihydride shows equal coupling to all three phosphorus nuclei, demonstrating that this species is a rapid fluxional molecule.[19] In the deuteriation experiments no evidence was found for non-equivalence of the two hydride ligands in $[CoH_2(SiF_3)L_3]$, and it is likely that these complexes would be pseudo-tetrahedral fluxional molecules like $[FeH_2\{P(OEt)_3\}_4]$.

The reactivity of the silyl complexes follows the order of thermal stability, and accords with other studies in which silanes with electronegative substituents are the most resistant to elimination. Thus, the SiF_3 group often remains bound to the cobalt under conditions in which the $SiMeF_2$ and $Si(OEt)_3$ groups are displaced. There is indirect evidence from the deuteriation studies that $SiEt_3H$ can interact with $[CoHL_3]$, but the lifetime of any $SiEt_3$ complex is insufficient to allow its isolation, its spectroscopic detection, or even its participation in the hydrosilylation or *O*-silylation reactions.

The stability of the silylcobalt(III) complexes also depends critically on the other ligands present. Thus, chloro-complexes are unstable to loss of the silane, as shown by the lack of reactivity of $[CoClL_3]$ and its formation in reactions of the silyls with other chloro-compounds. Similarly, the presence of a carbonyl ligand encourages the formation of cobalt(I) complexes, *e.g.* $[CoH_2(SiR_3)L_3]$ reacts with carbon monoxide either by loss of the silane and formation of the unreactive $[CoH(CO)L_3]$, or by loss of dihydrogen to give $[Co(SiR_3)(CO)_2L_2]$; significantly, the latter reaction occurs only for R = F, the less-stable complexes undergoing dissociative loss of the silane. This reaction may involve the unstable intermediate $[CoH_2(SiF_3)(CO)L_2]$, indicaations of which were found in the reaction of $[CoH(CO)L_3]$ with SiF_3H. The dicarbonylcobalt(I) complex $[Co(SiF_3)(CO)_2L_2]$ is a new member of the series $[Co(SiR_3)(CO)_nL_{4-n}]$, the known members being those with $n = 3$ or 4.

The triethoxysilyl complex, or its precursors, shows some catalytic activity in hydrosilylation or *O*-silylation reactions but is rather selective, in that the silanes which can be employed must have appropriate substituents, neither too electronegative nor too electropositive, as in $SiH(OEt)_3$ or $Me_3Si[OSi(H)Me]_nOSiMe_3$. Neither SiF_3H nor $SiEt_3H$ is reactive, although for different reasons. The utility of the cobalt complexes as deuteriation catalysts for a wide range of silanes is, however, extremely beneficial, and the ready availability of $SiDF_3$ by this route has already found application.[17]

EXPERIMENTAL

The complexes $[CoH(N_2)L_3]$, $[CoH_3L_3]$, and $[CoH(CO)L_3]$ were prepared by literature methods.[32,33] A method was developed for the preparation of $[CoClL_3]$ which was very similar to that later described by Sacco and his co-workers.[22] Trifluorosilane was obtained by repeated passage of $SiCl_3H$ over SbF_3 at 0 °C, and purified by distillation from a toluene slush bath at −95 °C. Infrared spectra were recorded with Perkin-Elmer 137, 257, or 621 spectrometers, ^1H n.m.r. spectra with Varian HA100 or Perkin-Elmer R20 spectrometers, and mass spectra with an A.E.I. MS10 spectrometer. Microanalytical determinations were made in this Department. Molecular-weight determinations were carried out by the method of Shriver.[34] All reactions were carried out *in vacuo* or in an atmosphere of dry nitrogen or argon, in sealed tubes or Schlenk apparatus.

Silylcobalt(III) *Complexes*.—Great care was necessary to exclude all traces of chlorine-containing compounds. The complex $[CoH(N_2)L_3]$ (0.44 g, 0.50 mmol) and the solvent were placed in a tube and the silane (1.0 mmol) added by syringe or by condensation. The tube was sealed and shaken until the red colour of the starting complex had disappeared. The times required are shown in Table 6. The yellow *product* was filtered off, washed with a little solvent, and dried *in vacuo*. Analytical data are given in Table 7. Similar results were obtained starting from $[CoH_3L_3]$. In all cases except the $SiMeF_2H$–$[CoH(N_2)L_3]$–OEt_2 reaction the product was $[CoH_2(SiR_3)L_3]$. In the reaction of $SiH(OEt)_3$ with $[CoH(N_2)L_3]$, mass spectrometry showed that dinitrogen was evolved.

TABLE 6

Reactions of silanes with $[CoH(N_2)L_3]$

Silanes	Solvent	Time for complete reaction (*t*/min)
SiF_3H	OEt_2	10
	C_6H_6–n-C_6H_{14}	20
	n-C_6H_{14}	360
	thf *	60
$SiMeF_2H$	C_6H_6–n-C_6H_{14}	15
	OEt_2 (20 cm^3)	15
	OEt_2 (5 cm^3) + PPh_3 (2.5 mmol)	15
$SiH(OEt)_3$	none	360
	OEt_2	60
	C_6H_6–n-C_6H_{14}	60

* thf = Tetrahydrofuran.

TABLE 7

Analytical data

Complex	Analysis (%) [a] C	Analysis (%) [a] H
$[CoH_2(SiF_3)L_3]$	68.8 (69.4)	5.1 (5.1)
$[CoH_2(SiMeF_2)L_3]$	71.0 (71.2)	5.3 (5.4)
$[CoH_2\{Si(OEt)_3\}L_3]$	69.9 (70.5)	5.3 (6.1)
$[CoH_2(SiMeF_2)L_2]$	66.7 (66.6)	5.3 (5.2)
$[CoH_2(SiMeF_2)L(dppe)]$ [b]	65.8 (66.8)	5.9 (5.5)
$[Co(SiF_3)(CO)_2L_2]$ [c]	58.4 (62.9)	4.2 (4.1)

[a] Calculated values are given in parentheses. [b] *M* 780 ± 50 (802). [c] F, 8.9 (7.9)%; *M* 692 ± 50 (724).

Reaction of the Silyl Complexes with Carbon Monoxide.—The complex $[CoH_2(SiF_3)L_3]$ (1.0 g, 1.1 mmol) was suspended in benzene (20 cm^3). Carbon monoxide was admitted and the mixture stirred while the decrease in pressure was monitored. Reaction was complete in *ca.* 20 min, and corresponded to the uptake of 1.04 ± 0.1 mol equivalents of gas (average from four experiments). Mass spectrometry showed the residual gas to contain dihydrogen. The experiment was repeated adding the CO in small aliquots, each of which was allowed to react completely before the next was added. The pressure changes corresponded to the apparent absorption of half of each aliquot until 2 mol equivalents had been added, after which no further decrease in pressure occurred. In a further experiment, the CO was replaced by argon after absorption was complete, and a yellow *solid* was obtained by the addition of hexane. The solid appeared to be [Co(SiF_3)(CO)$_2$L$_2$] since, when samples were treated with an excess of I_2–C_5H_5N, 2.00 ± 0.05 mol equivalents of CO were evolved.

Deuteriation Experiments.—Dideuterium was obtained by the reaction of lithium metal with deuterium oxide; the product contained 97% D. The complex [CoH_3L_3] (0.87 g, 1.0 mmol) was suspended in benzene (20 cm^3) under nitrogen in a flask (500 cm^3). The nitrogen was pumped out and replaced by deuterium to a pressure of 500 mmHg, and the suspension was stirred vigorously. Samples (*ca.* 3 cm^3) of gas were removed periodically and analysed by mass spectrometry. Reaction was effectively complete after 3 h, when the flask was evacuated, filled with argon, and transferred to an argon-filled glove-box. The product was analysed by allowing a sample to react with nitrogen; the liberated gas contained 9.9% H.

The deuteriated complex [CoD_3L_3] (0.13 g, 0.15 mmol) and benzene (4 cm^3) were placed in a tube (20 cm^3 capacity) fitted with a Rotaflo tap. The tube was evacuated and SiF_3H (0.16 mmol) was condensed in. The tube was shaken at room temperature for 15 min and the non-condensable gas analysed by mass spectrometry. The experiment was repeated with other ratios of SiF_3H:[CoD_3L_3], and the results are given in Table 2.

Catalysed exchange reactions were carried out by one of two methods, depending on the volatility of the silane. (*i*) The silane $SiEt_3H$ or SiH(OEt)$_3$ (3.0 cm^3) was added to a flask (500 cm^3) containing benzene (15 cm^3) under argon. The catalyst, [CoH(N_2)L$_3$] (0.05 g, 0.057 mmol), was added and the argon was pumped out and replaced by D_2 (400 mmHg, 11 mmol) and the solution was stirred vigorously. Samples of gas (*ca.* 3 cm^3) were removed periodically and analysed by mass spectrometry. At the completion of the experiment the liquid was distilled and the i.r. spectrum of the silane-containing fraction was recorded. (*ii*) The silane SiF_3H or $SiMe_3H$ (3 mmol) was condensed into a tube (250 cm^3) fitted with a Rotaflo tap, containing benzene (15 cm^3) and [CoH(N_2)L$_3$] (0.050 g, 0.057 mmol). Dideuterium (400 mmHg, 5.5 mmol) was admitted, and the tube was sealed, allowed to warm to room temperature, and shaken for 18 h. After cooling to −179 °C, a sample of the gas was removed for mass-spectrometric analysis, and the i.r. spectrum of the gaseous silane was obtained. The results of these experiments are displayed in Tables 3 and 4.

O-*Silylation Reactions*.—A flask (100 cm^3) with a side-arm tip-tube and a magnetic stirrer was connected to a gas burette and the whole was flushed with argon. The alcohol (12 mmol) and SiH(OEt)$_3$ (12 mmol) were injected through a serum cap and thoroughly mixed. The catalyst, [CoH(X_2)L$_3$] (0.012 mmol; X = H or N), was added and the rate of gas evolution measured. Similar rates were obtained with the two catalysts: 3.0×10^2 mol H_2 per mol SiH(OEt)$_3$ per min for MeOH, and 1.0×10^2 mol per mol per min for EtOH. No reaction was observed with Bu^{n}OH.

Hydrosilylation Reactions.—Triethoxysilane (1.0 cm^3, 5.0 mmol) was injected through a serum cap into a flask flushed with argon. The catalyst (0.001 mmol) was added and stirred with the silane for 1 min after which hex-1-ene (1.3 cm^3, 10 mmol) was injected. The temperature of the mixture was monitored, and the results obtained are displayed in the Figure and Table 5. The extent of reaction was determined by quantitative measurement of the i.r. peak at 2 190 cm^{-1} due to the H–Si stretching mode of the silane. The volatile components were shown by g.l.c. (Ag[NO_3], glycol) to be: n-hexane, 12.5%; hex-1-ene, trace amount; *cis*-hex-2-ene, 35.9%; *trans*-hex-2-ene, 51.6%; hex-3-ene, trace amount.

We thank Mr. C. Evans and Dr. R. D. Sedgwick for the n.m.r. and mass spectra.

[8/924 *Received*, 17*th May*, 1978]

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