Organosilicon Chemistry. Part 26.[1a] Silyl Derivatives of Substituted Cobalt Carbonyls, of the Type $[Co(SiR_3)(CO)_nL_{4-n}]$

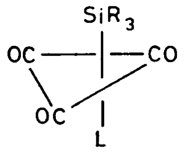
By **Robert N. Haszeldine, Adrian P. Mather,** and **R. V. (Dick) Parish,*** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The series of cobalt(I) silyl complexes $[Co(SiR_3)(CO)_nL_{4-n}]$ (R = F, n = 1—3; R = Ph or OEt, n = 2 or 3; L = tertiary phosphine or arsine) has been prepared, and the reaction of $[Co(SiR_3)(CO)_4]$ with PPh_3 has been studied. For R = Ph, substitution of CO occurs rapidly to give the unstable *cis*-$[Co(SiPh_3)(CO)_3(PPh_3)]$, which isomerises slowly to the stable *trans* form. For R = Et, however, decomposition occurs to give Si_2Et_6 and $[\{Co(CO)_3(PPh_3)\}_2]$. Three distinct geometric isomers of $[Co(SiR_3)(CO)_2L_2]$ have been obtained by different preparative routes.

COBALT forms a wide variety of complexes of the type $[Co(MR_3)(CO)_4]$ (M = Si, Ge, Sn, or Pb), but those in which the CO groups have been partially replaced by another neutral ligand are relatively uncommon. For the heavier members of Group 4, the reaction of MR_3X with $[Co(CO)_4]^-$ is a satisfactory and convenient preparative method, but with silicon derivatives success is much less certain.[2,3] A better route to cobalt–silyl complexes appears to be the oxidative addition of a tertiary silane, SiR_3H, to cobalt carbonyl, which is known to proceed in part by hydrogen elimination between the silane and $[CoH(CO)_4]$.[4] The hydrogen-elimination route appeared to be a promising method of obtaining substituted derivatives, although we have previously found that $[CoH(N_2)(PPh_3)_3]$ and $[CoH_3(PPh_3)_3]$ react with silanes to give cobalt(III) silyl complexes.[1b] We now present an examination of the reaction of tertiary silanes with $[\{Co(CO)_3L\}_2]$ and with $[CoH(CO)_nL_{4-n}]$ (L = tertiary phosphine or arsine) and of $[Co(SiR_3)(CO)_4]$ with neutral ligands.

RESULTS

Reactions of Tertiary Silanes with Cobalt Carbonyls.—(*i*) *With* $[\{Co(CO)_3L\}_2]$. The triphenylphosphine derivative $[\{Co(CO)_3(PPh_3)\}_2]$ was unreactive towards SiF_3H, $SiCl_3H$, $SiH(OEt)_3$, or $SiEt_3H$ in benzene, toluene, tetrahydrofuran (thf), or nitromethane, at temperatures up to 70 °C. The complex does not dissolve in any of the solvents under these conditions, which probably explains the lack of reaction since the anticipated products were obtained by other routes.



(1)

The complexes $[\{Co(CO)_3L\}_2]$ (L = PMe_2Ph, PEt_3, PBu^n_3, or $AsMe_2Ph$) were more soluble and more reactive. All reacted readily with SiF_3H to give extremely air-sensitive oils which were difficult to characterise. For L = PMe_2Ph, a solid was obtained the analysis of which was consistent with the formulation $[Co(SiF_3)(CO)_3(PMe_2Ph)]$. The i.r. spectra of these complexes and of the product of reaction between $[\{Co(CO)_3(PMePh_2)\}_2]$ and $SiH(OEt)_3$ (also an oil) showed two C–O stretching bands at *ca.* 1 970 and *ca.* 1 910 cm^{-1}. The spectrum of solid $[Co(SiF_3)(CO)_3(PMe_2Ph)]$ also showed a band at 324 cm^{-1} attributed to Co–Si stretching.[1b, 5–7] These complexes are expected to have trigonal-bipyramidal structures (1), as in the related germyl and stannyl derivatives [7,8] and the isoelectronic $[Fe(CO)_3L_2]$; [9] the i.r. spectra are consistent with this structure.[10]

When these reactions were attempted with chlorosilanes, $SiClR_2H$ (R = Cl or Me), or in chlorinated solvents, decomposition occurred to give residues of the green $[CoCl(PPh_3)_3]$ or blue $[CoCl_2(PPh_3)_2]$.

(*ii*) *With* $[CoH(CO)_3(PPh_3)]$. The complex $[CoH(CO)_3(PPh_3)]$ in pentane (prepared *in situ*) reacted with SiF_3H at −95 °C with evolution of a non-condensable gas and precipitation of a yellow solid. The i.r. spectrum of the solid was very similar to those of the complexes described above (Table 1), and on this basis and the (rather poor) analytical data the product is formulated as $[Co(SiF_3)(CO)_3(PPh_3)]$. On one occasion a product with an i.r. spectrum identical to that of $[Co(SiF_3)(CO)_2(PPh_3)_2]$ (see below) was obtained. As explained in the Experimental section, it is difficult to avoid an excess of PPh_3. When $SiH(OEt)_3$ was used a bis(phosphine) complex was again isolated. Since $[CoH(CO)_2(PPh_3)_2]$ was found not to react with $SiH(OEt)_3$ (see below), this product must arise by attack of PPh_3 on $[Co\{Si(OEt)_3\}(CO)_3(PPh_3)]$.

Triphenylsilane reacted with $[CoH(CO)_3(PPh_3)]$ at −78 °C to give a yellow-orange solid, but no gas evolution was observed. The i.r. spectrum of the solid was complex: the C–O stretching region showed bands at 1 880w, 1 922vs, 1 950s, 1 975s, and 2 000s cm^{-1}, indicating that the product was a mixture of at least two compounds. The solid was dissolved in benzene and treated with carbon monoxide for several hours, when a white solid was obtained which showed only a single strong i.r. band in the C–O stretching region, at 1 950 cm^{-1}, which agrees with the reported spectrum of $[Co(SiPh_3)(CO)_3(PPh_3)]$.[3] It seems likely that the initial orange solid contained this complex together with its presumed precursor, $[CoH_2(SiPh_3)(CO)_2(PPh_3)]$.

No reaction was found between $[CoH(CO)_3(PPh_3)]$ and either $SiEt_3H$ or $SiMe_3H$ at low temperatures; when warmed, the reaction mixtures rapidly deposited $[\{Co(CO)_3(PPh_3)\}_2]$.

(*iii*) *With* $[CoH(CO)_2(PPh_3)_2]$. The disubstituted hydride $[CoH(CO)_2(PPh_3)_2]$ did not react with $SiMe_3H$, $SiEt_3H$, SiF_2MeH, or $SiH(OEt)_3$. With SiF_3H a yellow solid was obtained, the i.r. spectrum of which showed two strong C–O stretching bands (1 920 and 1 965 cm^{-1}) and analysis confirmed the formulation [Co(SiF$_3$)(CO)$_2$(PPh$_3$)$_2$]. The spectrum of the Si(OEt)$_3$ derivative described above is very similar. A product of the same stoicheiometry was obtained earlier[1b] by reaction of [CoH$_2$(SiF$_3$)(PPh$_3$)$_3$] with carbon monoxide, but this showed strong C–O bands at 1 935 and 2 000 cm^{-1}; this reaction was repeated, and the same product was obtained. These two compounds must be the isomers (2) and (3), since structures like (4), with Ph$_3$P–Co–PPh$_3$ bond angles of *ca.* 90°, would be unfavourable on steric grounds, while (5), with a linear OC–Co–CO arrangement, would give only one strong C–O stretching band in the i.r. The highest C–O stretching frequency observed (2 000 cm^{-1}) is consistent with a CO group *trans* to the SiF$_3$ group, *i.e.* isomer (2); the isomer with the smaller difference between the two frequencies, that obtained here from SiF$_3$H and [CoH(CO)$_2$(PPh$_3$)$_2$], must be (3).

TABLE 1

Infrared data (cm^{-1}) for cobalt–silyl complexes in Nujol mulls, except where indicated otherwise

Complex	ν(C–O)	ν(Si–F)	ν(Co–Si)
[Co(SiF$_3$)(CO)$_3$(PPh$_3$)]	1 980m, 1 936s	848m, 820s	328
[Co(SiF$_3$)(CO)$_3$(PMe$_2$Ph)]	1 962m, 1 905s	852m, 810s	324
[Co(SiF$_3$)(CO)$_3$(PEt$_3$)] [a]	1 965m, 1 910s	865m, 815s	
[Co(SiF$_3$)(CO)$_3$(PBu$_3$)] [a]	1 963m, 1 908s	860m, 812s	
[Co(SiF$_3$)(CO)$_3$(AsMe$_2$Ph)] [a]	1 970m, 1 917s	872m, 820s	
[Co{Si(OEt)$_3$}(CO)$_3$(PMe$_2$Ph)] [a]	1 968m, 1 919s		
[Co(SiPh$_3$)(CO)$_3$(PPh$_3$)]	1 950vs		350
[Co(SiPh$_3$)(CO)$_3$(PMePh$_2$)]	1 940vs		340
[Co(SiPh$_3$)(CO)$_3$(PEt$_3$)] [a]	1 940vs		
[Co(SiPh$_3$)(CO)$_3$(AsPh$_3$)]	1 945vs		340
[Co(SiPh$_3$)(CO)$_3$(SbPh$_3$)]	1 935vs		*b*
[Co(SiF$_3$)(CO)$_2$(PPh$_3$)$_2$] [c]	1 965s, 1 920s	870m, 825s	
[Co(SiF$_3$)(CO)$_2$(PPh$_3$)$_2$] [d]	2 000s, 1 935s	840m, 800s	
[Co{Si(OEt)$_3$}(CO)$_2$(PPh$_3$)$_2$] [c]	1 965s, 1 925s		
[Co(SiPh$_3$)(CO)$_2$(PMePh$_2$)$_2$] [e]	1 940m, 1 870vs		
[Co(SiPh$_3$)(CO)$_2$(dppe)] [e]	1 960m, 1 880vs		
[Co(SiF$_3$)(CO)(PPh$_3$)$_3$]	1 945s	875m, 805s	

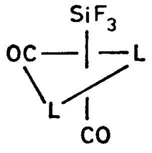
[a] In toluene. [b] Obscured. [c] Isomer (3), from [CoH(CO)$_2$(PPh$_3$)$_2$] + SiR$_3$H. [d] Isomer (2), from [CoH$_2$(SiF$_3$)(PPh$_3$)$_3$] + CO. [e] Isomer (4), from [Co(SiPh$_3$)(CO)$_4$] + 2PMePh$_2$ (or dppe).

(*iv*) *With* [CoH(CO)(PPh$_3$)$_3$]. The complex [CoH(CO)(PPh$_3$)$_3$] in benzene reacted with SiF$_3$H with evolution of hydrogen (identified by mass spectrometry) and precipitation of a yellow air-sensitive solid, the i.r. spectrum of which showed a single C–O stretching band at 1 945 cm^{-1}. A product obtained previously by this route showed i.r. absorption at 1 935 cm^{-1}, and its solution gave a broad ^{1}H n.m.r. signal at τ 22.6. No gas evolution was observed, and the product was tentatively formulated as [CoH$_2$(SiF$_3$)(CO)(PPh$_3$)$_2$]. The present product showed no high-field n.m.r. signal, which is consistent with the evolution of hydrogen and suggests that the dihydride has undergone reductive elimination to give [Co(SiF$_3$)(CO)(PPh$_3$)$_3$]. No other silanes were found to react with [CoH(CO)(PPh$_3$)$_3$] under a variety of conditions.

(*v*) *With* [CoHL$_4$]. The complexes [CoHL$_4$] [L = PMePh$_2$, P(OPh)$_3$, or P(OMe)$_3$] did not react with tertiary silanes, although long-term (4 months) exposure of [CoH(PMePh$_2$)$_4$] to SiF$_3$H gave a solid showing i.r. absorption at 808 and 862 cm^{-1} characteristic of SiF$_3$ groups. The complex [CoH(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) was unreactive to a variety of silanes. The only exceptions were silanes containing at least one Si–Cl bond; in agreement with our earlier report,[11] [CoCl(dppe)$_2$] is formed.

Reactions of [Co(SiR$_3$)(CO)$_4$] *with Tertiary Phosphines*.—The complex [Co(SiPh$_3$)(CO)$_4$] reacted readily with PPh$_3$ with rapid evolution of 1 mol equivalent of carbon monoxide and formation of [Co(SiPh$_3$)(CO)$_3$(PPh$_3$)] identical to that isolated from the reaction of SiPh$_3$H with [CoH(CO)$_3$(PPh$_3$)]. Analogous products were obtained using PMePh$_2$, PEt$_3$, AsPh$_3$, and SbPh$_3$, but the PEt$_3$ derivative could not be isolated as a solid. The i.r. spectra of these products are similar to those of other complexes of this stoicheiometry.[2,3,10]

The progress of the reactions with PPh$_3$ and PMePh$_2$ were monitored by following the i.r. spectra, which are shown schematically in the Figure. The initial and final spectra are consistent with the presence of [Co(SiPh$_3$)(CO)$_4$] and [Co(SiPh$_3$)(CO)$_3$L] (L = PPh$_3$ or PMePh$_2$) respectively. In the early stages of the reactions (1—2 h) additional bands are seen at (L = PPh$_3$) 1 978s, 2 050m, and 2 095mw cm^{-1}, clearly due to intermediate complexes, and analogous changes are seen for L = PMePh$_2$. Evolution of carbon monoxide occurred only during the first few minutes of the reaction.



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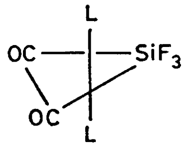

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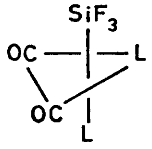

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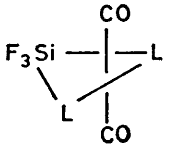
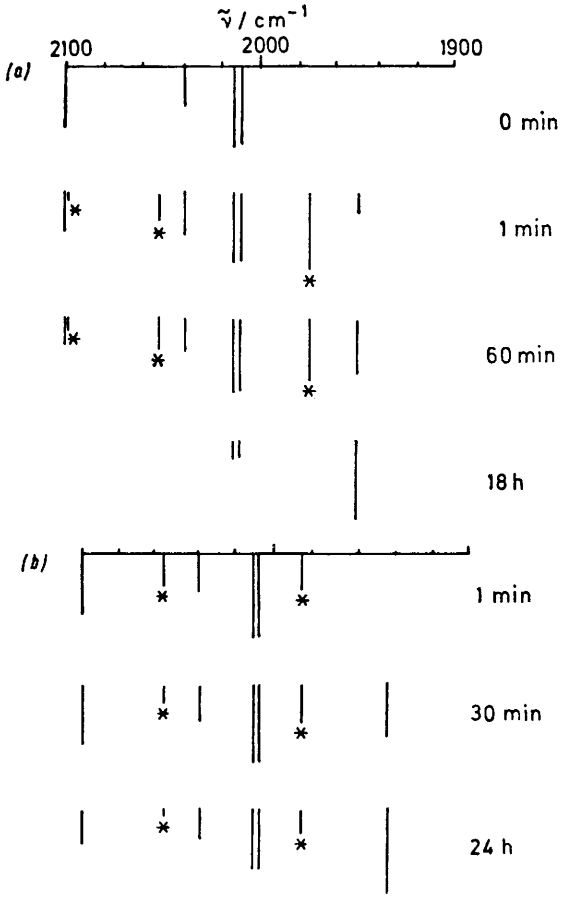


(5)

In the majority of cases only monosubstitution occurred, regardless of the amount of ligand added. However, with PMePh$_2$, further reaction occurred readily. With an excess of this phosphine, a bright yellow product with a complex i.r. spectrum was obtained but, with careful control of the stoicheiometry, 2 mol equivalents of carbon monoxide were evolved and [Co(SiPh$_3$)(CO)$_2$(PMePh$_2$)$_2$] was isolated. The i.r. spectrum of this product in the C–O stretching region was very different from those of the two forms of [Co(SiF$_3$)(CO)$_2$(PPh$_3$)$_2$] described above, consisting of two bands at lower frequencies and of unequal intensities (Table 1). When the reaction was repeated using 1 mol equivalent of dppe a product with a very similar spectrum was obtained, [Co(SiPh$_3$)(CO)$_2$(dppe)]. In this complex the phosphine groups must of necessity occupy adjacent positions, but the i.r. spectrum is clearly incompatible with structures analogous to (2) or (5), and it is unlikely that the bidentate ligand would span two equatorial positions. Structures of type (4) are likely for both these complexes.

The complex [Co(SiEt$_3$)(CO)$_4$] reacted very differently. With 1 mol equivalent of PPh$_3$ there was immediate vigorous evolution of gas and a colour change to deep red. On standing, [{Co(CO)$_3$(PPh$_3$)}$_2$] was precipitated. Fractional distillation and g.l.c. analysis of the supernatant liquid showed Si$_2$Et$_6$ to be present. Similar results were obtained using PMePh$_2$ or dppe. These reactions are in marked contrast to those reported by Kahn and Bigorne,[10] who obtained substituted complexes [Co(SiEt$_3$)(CO)$_3$(PEt$_3$)] by this reaction. Attempts were made to follow the i.r. spectra during the reaction, but resolution was poor owing to the continual precipitation of solid. With PMePh$_2$ an intermediate with strong C–O absorption at 1 984 cm^{-1} was observed, while with dppe a new band was found at 1 904 cm^{-1}.



Infrared spectra in the C–O stretching region of mixtures of [Co(SiPh$_3$)(CO)$_4$] with (*a*) PPh$_3$ and (*b*) PMePh$_2$ in toluene at various times. Bands marked with an asterisk correspond neither to the starting material nor to the product, [Co(SiPh$_3$)(CO)$_3$L]

DISCUSSION

The range of complexes [Co(SiR$_3$)(CO)$_n$L$_{4-n}$] is now known with the sole exception of the member with $n = 0$. All these derivatives are highly air-sensitive. Other workers have found that the salt-elimination route to compounds of this type is very restricted in its application to silyl derivatives,[3] although it is effective for the heavier members of Group 4.[7] The hydrogen-elimination route described here [equation (1)] works well with tertiary silanes, but some of the cobalt hydrides required are not convenient starting materials, being thermally unstable and air-sensitive.

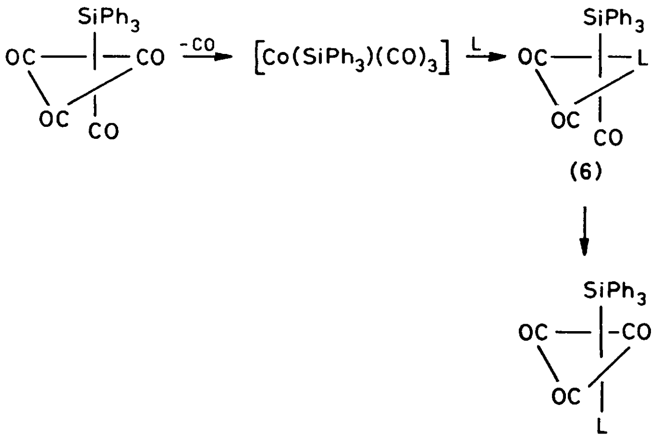
$$[\mathrm{CoH(CO)}_n\mathrm{L}_{4-n}] + \mathrm{SiR_3H} \longrightarrow [\mathrm{Co(SiR_3)(CO)}_n\mathrm{L}_{4-n}] + \mathrm{H_2} \quad (1)$$

The starting complexes [CoH(CO)$_n$L$_{4-n}$] become less reactive with increasing phosphine substitution, and the silanes become more reactive as the groups on the silicon increase in electronegativity. The latter observation (which is usual in oxidative addition of silanes [12]) is consistent with initiation of the reaction by nucleophilic attack on silicon by the cobalt complex. The nucleophilicity of the complexes would increase as the value of n decreases but, at the same time, steric interactions would increase markedly.

Other factors are undoubtedly involved in the stability of the cobalt–silyl complexes, however, since we find that [Co(SiEt$_3$)(CO)$_4$] decomposes on treatment with PPh$_3$ in toluene. Other workers have investigated the reactions of [Co(SiR$_3$)(CO)$_4$] (R = H, Et, or Me) with tertiary phosphines in non-polar solvents, with various results. Several groups find a CO-displacement reaction with formation of [Co(SiR$_3$)(CO)$_3$L] (L = PEt$_3$ or PPh$_3$),[10,13,14] but the heterolysis products [SiR$_3$L][Co(CO)$_4$] (R = Me or Et; L = PEt$_3$ or PMe$_3$) have also been reported.[13] Clearly the reaction is not straightforward, and it may depend critically on the conditions used.[13] The effect observed here is superficially similar to that of treating *cis*-[Fe(SiCl$_3$)$_2$(CO)$_4$] with PPh$_3$,[1a,15] since in both cases a disilane and a phosphine-substituted metal carbonyl are obtained. However, with the iron complex an intramolecular process is both feasible and likely, whereas in the cobalt system reaction must occur either intermolecularly or by a radical mechanism. Absi-Halabi and Brown [16] have studied the reaction of [Co(SnCl$_3$)(CO)$_4$] with ligands, which gives [Co(CO)$_3$L$_2$][SnCl$_3$] (L = PPh$_3$ or AsPh$_3$), and have found evidence for a radical reaction. Attack by the ligand on the tin atom is followed by homolysis of the Co–Sn bond. In the present case, attack on the silicon atom seems unlikely, since an Et$_3$Si group would not have high electrophilicity and would not be greatly different from a Ph$_3$Si group except, perhaps, in steric crowding. The Cl$_3$Si compounds, which would be stronger Lewis acids, react by simple CO displacement. The previous workers also found that the rate of reaction and the nature of the products were sensitive to the presence of light or oxygen.[16]

In the reaction of [Co(SiPh$_3$)(CO)$_4$] with tertiary phosphines, evolution of carbon monoxide occurs over a much shorter period than the changes in the i.r. spectrum. It is probable that there is rapid formation of a mono-substituted complex of configuration different from that of the final product, followed by a slow isomerisation (Scheme). Assuming the intermediate to have the usual trigonal-bipyramidal geometry,(6) is the only likely configuration and would be consistent with the observed i.r. spectrum, *viz.* the retention of the high-frequency C–O band corresponding to the axial CO group, and the presence of two other bands separated by *ca.* 50 cm^{-1} with an intensity pattern similar to that for the equatorial CO groups of isomer (4) of $[Co(SiPh_3)(CO)_2L_2]$.

Five-co-ordinate complexes usually undergo intramolecular exchange reactions very rapidly, and many have been shown to be fluxional on the n.m.r. time scale. However, it has recently been shown by ^{13}C n.m.r. spectroscopy that the molecules $[Co(MR_3)(CO)_4]$ undergo exchange at rates related to the bulk of the MR_3 group, showing that steric factors are important in the rearrangement.[17] If two bulky substituents were present, as in $[Co(SiPh_3)(CO)_3(PPh_3)]$, rearrangement would be considerably slowed, as we observed in the substitution reaction. This argument is also consistent with our finding three different isomers (2)—(4) of the type $[Co(SiR_3)(CO)_2L_2]$, from three different preparative routes. These isomers must be completely inhibited from rearranging by the presence of three bulky substituents.



SCHEME

The i.r. spectra of the isolable form of the monosubstituted species $[Co(SiR_3)(CO)_3L]$ are only consistent with structure (1), as deduced by other workers.[10] This structure has (at most) C_{3v} symmetry, for which two C–O stretching modes are i.r. active, A_1 and E. The E mode is observed for all the complexes, but the intensity of the A_1 mode is very sensitive to the nature of the substituents at silicon. When electronegative substituents are present (F, OEt), the A_1 mode is readily observed, but with *C*-bonded substituents it is very weak or absent. In the latter case the complexes behave as if the symmetry were higher. This difference presumably reflects a difference in the degree of coplanarity of the $Co(CO)_3$ group. If this group were closely planar, the A_1 mode would involve very little change in dipole moment, resulting in a minimal intensity for the formally allowed i.r. transition. This would be the case when the two substituents are similar electronically and sterically, *i.e.* there can be little difference in the electron distribution in the Co–$SiPh_3$ and Co–PPh_3 bonds. Such a configuration is observed for $[Co(GePh_3)(CO)_3(PPh_3)]$.[8] When the effective electronegativity of the silicon is increased, this equivalence no longer applies and the CO groups move out of the plane towards the silicon, as observed in several unsubstituted complexes $[Co(SiR_3)(CO)_4]$.[18-20]

Finally, the utility of fluorosilanes in these reactions should be noted. With chlorine-containing silanes no silyl complexes were obtained, but only $[CoCl(PPh_3)_3]$ or $[CoCl_2(PPh_3)_2]$ were obtained.[1b] With fluorosilanes, silyl complexes are readily formed.

EXPERIMENTAL

All solvents were rigorously dried and degassed immediately before use. Reactions were conducted under dry nitrogen or *in vacuo* in sealed tubes or Schlenk apparatus. The complexes $[CoH(N_2)(PPh_3)_3]$, $[Co(SiR_3)(CO)_4]$ (R = Et or Ph), $[CoH(CO)(PPh_3)_3]$, and $[\{Co(CO)_3L\}_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PBu_3, or $AsMe_2Ph$) were prepared by literature methods.[21-24] Analytical data for new compounds are displayed in Table 2.

TABLE 2

Analytical data (%) for cobalt–silyl complexes, with calculated values in parentheses

Complex	C	H
$[Co(SiF_3)(CO)_3(PPh_3)]$	53.2 (51.3)	3.6 (3.1)
$[Co(SiF_3)(CO)_2(PPh_3)_2]$	62.5 (62.9)	4.4 (4.1)
$[Co(SiF_3)(CO)(PPh_3)_3]$	69.3 (68.8)	5.0 (4.7)
$[Co(SiF_3)(CO)_3(PMe_2Ph)]$	35.8 (36.3)	2.7 (3.0)
$[Co\{Si(OEt)_3\}(CO)_3(PPh_3)]$	66.1 (65.6)	4.8 (5.6)
$[Co(SiPh_3)(CO)_3(PPh_3)]$	71.3 (70.4)	4.9 (4.5)
$[Co(SiPh_3)(CO)_3(PMePh_2)]$	67.1 (67.6)	4.9 (4.7)
$[Co(SiPh_3)(CO)_2(PMePh_2)_2]$	75.7 (71.2)	5.5 (5.3)
$[Co(SiPh_3)(CO)_3(AsPh_3)]$	66.0 (65.8)	4.2 (4.1)
$[Co(SiPh_3)(CO)_3(SbPh_3)]$	60.4 (62.0)	4.6 (4.0)
$[Co(SiPh_3)(CO)_2(dppe)]$	73.7 (72.7)	5.0 (5.0)

Tricarbonylhydrido(triphenylphosphine)cobalt(I).— The hydride $[CoH(CO)_3(PPh_3)]$ is very unstable, decomposing above −50 °C to $[\{Co(CO)_3(PPh_3)\}_2]$. It is therefore best prepared *in situ* from $[CoH(CO)_4]$ and PPh_3. Unfortunately, $[CoH(CO)_4]$ is itself thermally unstable, and could not be obtained in quantitative yield, and the $[CoH(CO)_3(PPh_3)]$ solution was often contaminated with PPh_3, $[CoH(CO)_2(PPh_3)_2]$, or $[\{Co(CO)_3(PPh_3)\}_2]$; on occasions these were the major products.

Dicobalt octacarbonyl was dissolved in an excess of pyridine, 30% sulphuric acid was added at 0 °C, and $[CoH(CO)_4]$ swept out of the reaction vessel with a stream of nitrogen, through a column of P_2O_5, and collected in pentane at −95 °C. This solution was added to a pentane solution of a stoicheiometric amount of PPh_3 at −95 °C. The temperature was raised briefly to −25 °C, when a pale yellow colour developed and a gas was evolved. On cooling to −80 °C yellow crystals were formed, which were collected and stored at low temperature. Owing to the difficulty of controlling the stoicheiometry and the pronounced air-sensitivity and thermal instability of the product, yields were typically *ca.* 20%.

Dicarbonylhydridobis(triphenylphosphine)cobalt(I) was obtained similarly using an excess of PPh_3 at 0 °C. The product was filtered off and washed with pentane. Yield 60% (Found: C, 71.2; H, 5.0. Calc. for $C_{38}H_{16}CoO_2P_2$: C, 71.2; H, 4.9%).

Tricarbonyl(dimethylphenylphosphine)trifluorosilylcobalt(I).

—(*i*) *From* [{$Co(CO)_3(PMe_2Ph)$}$_2$]. The dimeric complex (0.5 g) and solvent (9% v/v hexane in benzene, 5 cm^3) were placed in a tube and an excess of SiF_3H was condensed in. The tube was sealed and shaken at room temperature for several hours. The resulting yellow *solid* was filtered off and washed with hexane. With ligands other than PMe_2Ph, products could be obtained only as oils.

(*ii*) *From* [$CoH(CO)_3(PPh_3)$]. A pentane solution of [$CoH(CO)_3(PPh_3)$] at −78 °C was transferred to a tube, cooled to −195 °C, and SiF_3H was condensed in. The tube was sealed, warmed to 0 °C, and the mixture stirred for several hours. The resulting yellow solid was filtered off at low temperature. Reactions of [$CoH(CO)_2(PPh_3)_2$] and [$CoH(CO)(PPh_3)_3$] were carried out similarly.

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