Silicon–Transition-metal Compounds. Part I. Silyltetracarbonylcobalt and Related Compounds

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Iodosilane and di-iodosilane react with $NaCo(CO)_4$ in ether at low temperatures to give silyltetracarbonylcobalt, $SiH_3Co(CO)_4$, and silylenebis(tetracarbonylcobalt), $SiH_2[Co(CO)_4]_2$, respectively. Physical properties of both compounds are reported, together with i.r., mass, and n.m.r. spectra of $SiH_3Co(CO)_4$. Pyrolysis of gaseous $SiH_3Co(CO)_4$ at 120° yields H_2, CO, SiH_4, and a dark-coloured inert solid; some $HCo(CO)_4$ is also present in the early stages. The stoicheiometry and probable cross-linked polymeric nature of the solid product are inferred, and its metal coating properties are outlined. The Si–Co bond in $SiH_3Co(CO)_4$ is broken by HX (X = F, Cl, O/2) to give SiH_3X and $HCo(CO)_4$, also by HgX_2 (X = Cl, I) to give SiH_3X and $Hg[Co(CO)_4]_2$. $SiH_2[Co(CO)_4]_2$ behaves similarly. No insertion of CO into the Si–Co bond has been achieved; PPh_3 reacts slowly with $SiH_3Co(CO)_4$ to displace CO and probably yields *trans*-$SiH_3Co(CO)_3(PPh_3)$. Evidence for d_π–d_π interaction in the silicon–metal bond is discussed.

THE initial reports of a number of $SiR_3Co(CO)_4$ derivatives[1] and the unsubstituted compound $SiH_3Co(CO)_4$[2] showed how they could be prepared by reactions (1) and (2) respectively. Subsequent work demonstrated that reaction (3) also leads to Si–Co compounds[3,4] and that reaction (1) proceeds with retention of configuration about silicon when R_3SiH is optically active.[5]

$$R_3SiH + Co_2(CO)_8 \longrightarrow SiR_3Co(CO)_4 + HCo(CO)_4 \qquad (1)$$

$$SiH_3I + Co(CO)_4^- \longrightarrow SiH_3Co(CO)_4 + I^- \qquad (2)$$

$$R_3SiH + HCo(CO)_4 \longrightarrow SiR_3Co(CO)_4 + H_2 \qquad (3)$$

Interest in this area has grown rapidly. I.r.[6-10] and mass spectral[11] studies, also *X*-ray[12] and electron diffraction[13] experiments on various $SiR_3Co(CO)_4$ compounds have been reported recently; three preliminary communications dealing with the chemistry of $SiMe_3Co(CO)_4$[4] and $SiH_3Co(CO)_4$[14,15] have also appeared. We now present a full account of our work on the physical and chemical properties of silyltetracarbonylcobalt and silylenebistetracarbonylcobalt.

EXPERIMENTAL

Techniques.—Compounds were handled either in a mercury-free high-vacuum system or in a nitrogen-filled dry-box. I.r. spectra were recorded with Perkin-Elmer model 137 and 337 (low resolution) and 521 (high resolution) instruments; in the last case, the spectrometer was calibrated with DCl, NH_3, and indene. U.v. spectra in the gas phase were obtained with a Unicam SP700 spectrometer, n.m.r. spectra with a Varian HA-100 instrument, and mass spectra with a modified A.E.I. MS10 spectrometer.

Materials.—Iodosilane and di-iodosilane were prepared by a literature method.[16] Solvents, *etc.*, were dried by the following reagents, then fractionated under reduced pressure: diethyl and dimethyl ether, n-hexane, ammonia (Na); tetrahydrofuran (CaH_2); bromine (H_2SO_4). Silane was prepared from $SiCl_4$ and $LiAlH_4$ in ether.

Silyltetracarbonylcobalt.—*Preparation.* $Hg[Co(CO)_4]_2$ was first prepared from $Co_2(CO)_8$ by Dighe and Orchin's method;[17] it was sensitive to photolysis, especially in solution, and was stored and used in subdued light. Reduction of the crystallised product with 1% sodium amalgam[17] in dimethyl or diethyl ether was carried out in an all-glass reaction vessel consisting of two bulbs connected by a sintered-glass filter; capillary openers and sealing-off points were also attached. The colourless solution of $NaCo(CO)_4$ was filtered into one bulb, and the other bulb and filter were removed with a hand torch.

In a typical preparation, $NaCo(CO)_4$ was derived from 1·5696 g. of $Hg[Co(CO)_4]_2$ (2·89 mmole) in 90 ml. of diethyl ether. Iodosilane (0·8368 g., 5·27 mmole) was then distilled in and allowed to react at −23° for 15 min.; a white precipitate and a pink solution were obtained. Volatile products were then pumped from the bulb held at −46°: apart from ether, disiloxane (*ca.* 1 mg.) and a trace of $HCo(CO)_4$ were present. All remaining volatile compounds were now pumped off at room temperature, yielding, after extensive fractionation, more ether (passed through −64°) and *silyltetracarbonylcobalt* [silyltetracarbonylcobaltate(−I)] as a pale yellow liquid (55%, based on iodosilane). The involatile residue was treated with nitric acid (to destroy any remaining Co–CO compounds), and iodide (5·3 mmole) was determined titrimetrically. This confirmed that all the iodosilane had reacted.

In later experiments, it was found that yields of over 70% could be obtained with dimethyl ether as reaction medium. Less could be used [$NaCo(CO)_4$ is considerable

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[2] B. J. Aylett and J. M. Campbell, *Chem. Comm.*, 1965, 217.

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[11] F. E. Saalfield, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *Inorg. Chem.*, 1968, **7**, 1465.

[12] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 1208.

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[14] B. J. Aylett and J. M. Campbell, *Chem. Comm.*, 1967, 159.

[15] B. J. Aylett and J. M. Campbell, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 137.

[16] B. J. Aylett and I. A. Ellis, *J. Chem. Soc.*, 1960, 3415.

[17] S. V. Dighe and M. Orchin, *Inorg. Chem.*, 1962, **1**, 965.

more soluble in Me_2O than in Et_2O *] and its greater volatility facilitated separation.

Analysis.—Alkaline hydrolysis yielded hydrogen (Toepler) and silicate without displacement of CO. The resulting solution was kept for 1 week in a sealed Polythene tube in presence of air to ensure that all Co–CO compounds were oxidised; silicon was then determined colorimetrically.[18]

Preliminary experiments with $Hg[Co(CO)_4]_2$ showed that CO groups were rapidly and quantitatively displaced by bromine at room temperature, although *ca.* 40% of CO appeared not as such but as $COBr_2$. In the final procedure adopted, $SiH_3Co(CO)_4$ was allowed to warm slowly from −196° to room temperature with an excess of bromine †, and CO evolved at this stage was measured. The other volatile products were fractionated, giving a quantitative amount of HBr [equation (4)]. The remaining bromine, $COBr_2$, and $SiBr_4$ were sealed in a tube with degreased strips of tin foil and, after all the bromine had reacted, the tube was heated at 250° for 3 hr., liberating further CO.[19] Cobalt in the original residue was estimated electrolytically [20] [Found: Si, 13·8; H (alkaline hydrolysis), 1·44; H (bromine method), 1·50; Co, 29·0; CO, 55·1%; *M*, 202·3. $SiH_3Co(CO)_4$ requires Si, 13·9; H, 1·49; Co, 29·2; CO, 55·4%; *M*, 202·0].

$$2SiH_3Co(CO)_4 + 9Br_2 \longrightarrow 2SiBr_4 + 6HBr + 2CoBr_2 + 8CO \qquad (4)$$

$$CO + Br_2 \rightleftharpoons COBr_2 \qquad (5)$$

Vapour pressure. The following pressures (in mm.) were recorded in all-glass tensimeters; in parentheses are values calculated from the equation below: −10°, 4·1(4·2); 1·0°, 7·9(8·3); 7·5°, 11·7(12·3); 15·0°, 18·0(18·6); 22·3°, 28(27·5); 34·8°, 51(51·5); 45·5°, 85(84·5); 54·1°, 123(122·5); 63·6°, 183(181); 74·7°, 279(279); 84·4°, 442(398). At 89°, the liquid suddenly became brown and the pressure rapidly rose. These values determine the equation: $\log p = -1975/T + 8{\cdot}124$, whence the extrapolated b.p. is 102°, ΔH_{vap} is 9·04 kcal. mole^{-1} and ΔS_{vap} is 23·9 cal. deg.$^{-1}$ mole^{-1}.

Mass spectrum. With an ionising potential of 70 v, the following *m/e* values (and relative intensities) were recorded: 202(0·1), 174(0·5), 171(0·3), 146(0·5), 143(1), 118(2), 116(2), 115(4), 90(3), 89(1), 88(4), 87(10), 79(1), 78(3), 77(12), 76(5), 75(9), 74(3), 73(5), 72(3), 60(1), 59(20), 45(2), 44(2), 31(12), 30(7), 29(17), 28(100), 16(4), 12(30), and 2(60).

U.v. spectrum. In the gas phase, an exceedingly strong, broad absorption ($\lambda_{\text{max.}}$, 220 mμ) was observed. Even at high pressures (20 mm.), there were no peaks at higher wavelengths.

N.m.r. spectrum. We are grateful to Professor E. A. V. Ebsworth and Mr. A. G. Lee for these observations, made at the University Chemical Laboratory, Cambridge. The ^1H spectrum of neat $SiH_3Co(CO)_4$ with $SiMe_4$ as internal standard showed a singlet at τ 5·96 ± 0·01; J (^{29}Si-H) = 211·7 ± 0·2Hz.

Reaction with hydrogen fluoride. $SiH_3Co(CO)_4$ (0·38 mmole) was mixed in the gas phase with an excess of HF in an i.r. gas-cell, and the spectrum was monitored at intervals. After 3 hr., there were no further changes in the spectra. After a further 12 hr., the volatile products were removed, leaving no residue. Apart from a little incondensable gas (1·2 ml. at S.T.P.), $HCo(CO)_4$ and SiH_3F (0·38 mmole, determined by alkaline hydrolysis) were present.

Reaction with hydrogen chloride. $SiH_3Co(CO)_4$ (0·334 mmole) reacted with HCl (0·335 mmole) for 1 min. at 20°. The products were SiH_3Cl (0·046 mmole), unchanged $SiH_3Co(CO)_4$ (0·280 mmole) and HCl, and $HCo(CO)_4$ (*ca.* 0·04 mmole).

Reaction with mercuric iodide. $SiH_3Co(CO)_4$ vapour (0·318 mmole) was twice streamed over mercuric iodide (4 g.). Fractionation yielded disiloxane (1 mg.), $HCo(CO)_4$ (3 mg.), SiH_3I (0·280 mmole, determined as I^- after alkaline hydrolysis), and unchanged $SiH_3Co(CO)_4$ (0·02 mmole). Extraction of the mercury-containing residues with chloroform gave a yellow solution with i.r. absorptions at 2080 and 2020 cm.$^{-1}$ (appropriate for $Hg[Co(CO)_4]_2$) and 2105 cm.$^{-1}$. Separate experiments showed that when stoicheiometric amounts of HgI_2 and $Hg[Co(CO)_4]_2$ were mixed in chloroform, a yellow solution was obtained. This yielded dark yellow crystals on evaporation, and gave i.r. absorptions at 2105m and 2020s cm.$^{-1}$ in the carbonyl region.

Reaction with carbon monoxide. $SiH_3Co(CO)_4$ (110 mg.) was condensed into a heavy-walled reaction tube, and sufficient CO was introduced to give a pressure of 20 atmos. at room temperature. The tube was sealed and heated at 70° for 15 min.; apart from traces of $HCo(CO)_4$ and $(SiH_3)_2O$, only starting materials were recovered.

Thermal decomposition. (i) Preliminary experiments showed that after 2 weeks in the gas phase at 25°, hydrogen, carbon monoxide, and silane were produced, together with a brown solid containing $Co_2(CO)_8$ (i.r.). After 2 weeks in the liquid phase, another sample turned dark red and cloudy; it yielded a complex mixture of products amongst which $(SiH_3)_2O$, $HCo(CO)_4$, $SiH_3Co(CO)_4$, and $SiH_2[Co(CO)_4]_2$ were identified (i.r.).

(ii) $SiH_3Co(CO)_4$ (86·2 mg., 0·426 mmole) was heated in the gas phase at 120° for 15 min.; the whole bulb ‡ became coated with a dark-brown mirror. The volatile products were: hydrogen (0·083 mmole), CO (0·031 mmole), $HCo(CO)_4$ (0·058 mmole), SiH_4 (0·03 mmole), and $SiH_3Co(CO)_4$ (0·250 mmole). The brown residue was almost insoluble in $CHCl_3$; it dissolved in alkali with effervescence, and subsequent addition of acid liberated $HCo(CO)_4$. It also dissolved in concentrated nitric acid, and appeared unaffected when heated to redness.

(iii) $SiH_3Co(CO)_4$ (102·6 mg., 0·507 mmole) heated in the gas phase at 120° for 1 hr. produced a black mirror-like coating and the following volatiles: H_2 (0·47 mmole), CO (1·09 mmole), SiH_4 (0·02 mmole), and 1 mg. of an unidentified metal carbonyl compound. On alkaline hydrolysis, the black solid gave 0·57 mmole of hydrogen.

(iv) Further experiments were carried out in which $SiH_3Co(CO)_4$ was pyrolysed in either a static or a flow system at 160—280° in the presence of degreased strips of various metals. Zinc, brass, mild steel, and polished stainless-steel could all be coated with an apparently coherent, shiny dark film. In some cases, the film remained

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* When more than about 2% of $NaCo(CO)_4$ (by weight) was mixed with Et_2O, two liquid layers formed, believed to be (*a*) a liquid complex of $NaCo(CO)_4$ and ether and (*b*) a saturated solution of the complex in ether.

† $SiH_3Co(CO)_4$ reacted very violently with chlorine at low temperatures, and on one occasion exploded. Reaction with iodine was sluggish.

‡ Reaction vessels were pre-treated with SiH_3I vapour at 50° to remove sorbed water.

[18] J. D. H. Strickland, *Chem. and Ind.*, 1950, 393.

[19] S. Lenher and H.-J. Schumacher, *Z. phys. Chem.*, 1928, **135**, 85.

[20] A. I. Vogel, 'Quantitative Inorganic Analysis,' Longmans, London, 3rd edn., 1962, p. 614.

intact after being heated to 800° in air, but other specimens blistered or cracked. The film was resistant to attack by hot concentrated nitric acid HNO_3 or cold alkali, but was dissolved upon immersion first in boiling alkali then in concentrated nitric acid. I.r. spectra (KBr disc) of the film material, stripped from glass, showed diffuse ν(CO) absorption, but mull and ATR techniques were unsuccessful. *X*-Ray powder photographs * gave evidence of considerable disorder in a number of samples: CoSi and Co_2Si appeared to be absent.

Reaction of silane with pyrolysed $SiH_3Co(CO)_4$. A reaction vessel fitted with a number of capillary openers and containing $SiH_3Co(CO)_4$ (0·41 mmole) was heated at 150° for 1 hr.: a dense, black coating resulted. Volatile products were removed; silane (0·64 mmole) was then introduced into the vessel, and the whole was heated at 140° for 1½ hr. Fractionation of volatile products yielded only silane (0·65 mmole (Found: *M*, 31·8. Calc. for 32·1).

Reaction with air. (i) $SiH_3Co(CO)_4$ (15 mg.) was held at room temperature in a 10-cm. i.r. gas-cell and air was passed in at 20-cm. pressure. Traces of $(SiH_3)_2O$ and $HCo(CO)_4$ were observed, but there was no rapid oxidation. (ii) A tube containing gaseous $SiH_3Co(CO)_4$ was smashed: a yellow flash and mild explosion were noted.

Silylenebis(tetracarbonylcobalt).—Preparation. Di-iodosilane (1·94 mmole) reacted with $NaCo(CO)_4$ (6·08 mmole) in diethyl ether (80 ml.) at −23° for 15 min. After most of the solvent had been removed at −46°, remaining volatile products were pumped out (3 hr.) and fractionated, yielding a trace of $HCo(CO)_4$ and *silylenebis(tetracarbonylcobalt)* as a yellow liquid, m.p. 15°, (held at −23°) (Found: H, 0·54; Co, 31·5, 31·8; CO, 59·6, 60·8%. $SiH_2[Co(CO)_4]_2$ requires H, 0·54; Co, 31·7; CO, 60·3%). Estimation of iodine in the solids remaining in the reaction vessel showed that 98% of the added SiH_2I_2 had reacted, thus confirming the absence of $SiH_2I[Co(CO)_4]$ as a volatile product.

Vapour pressure. The following pressures (in mm.) were recorded, with calculated values in parentheses: 23·5°, 1·0(4·2); 41°, 8·2(10·0); 47°, 13·6(13·2); 52°, 16·5(16·5); 55°, 17·9(18·8); 62°, 26·0(25·2); 69·5°, 40·2(34·1); 75·5°, 63(43·3). In the range 23·5—62°, these values determine the equation: $\log p = -2020/T + 7{\cdot}429$, whence ΔH_{vap} is 9·25 kcal. mole⁻¹, the b.p. (by a long extrapolation) is *ca.* 171°, and ΔS_{vap} is 20·8 cal. deg.⁻¹ mole⁻¹. At *ca.* 70°, decomposition was indicated by a slow continuous rise in pressure. Heating was continued to 95°, at which point a brown or black solid covered the tensimeter walls. On opening to the vacuum system, the volatile products included H_2, CO, SiH_4, and $HCo(CO)_4$.

I.r. spectrum. The vapour pressure was too low to obtain a gas-phase spectrum at room temperature, so a film of the compound was deposited on the inside surface of a cooled gas cell window. The following peaks were noted (in cm.⁻¹): 2105s, 2085sh, 2060vs, 2010vs, 1990sh, 965w, 940w, and 812m.

Attempted Preparations of Silyltriphenylphosphinetricarbonylcobalt.—(i) Direct reaction of $SiH_3Co(CO)_4$ with an excess of triphenylphosphine in hexane or ether proceeded very slowly. In one experiment, after 3 hr. at 60° and a further 4 days at 25°, 85% of the CO required by equation (11) had been evolved, leaving a yellow solution. Removal of solvent and unchanged $SiH_3Co(CO)_4$ gave a yellow solid, presumably containing unchanged PPh_3. I.r. peaks (apart from those due to PPh_3) were at: 2150sh, 2125m, 2050w, 2030w, 1960vs, 1895sh, 945m, 890s, 710m, cm.⁻¹ (KBr disc; nujol mull very similar). Attempts to sublime the product *in vacuo* led to decomposition.

(ii) $Na[Co(CO)_3PPh_3]$ was prepared from $Hg[Co(CO)_3PPh_3]_2$ [21] and allowed to react with SiH_3I at −55° for 2 hr. in tetrahydrofuran solution. Most of the solvent was removed at −46° (18 hr.). All remaining volatiles were then pumped off at room temperature; some silane was evolved at this stage. The remaining yellow solid was soluble in ether but almost insoluble in light petroleum. In the dry-box it decomposed rapidly, giving a red-brown solid, almost insoluble in ether, with a i.r. spectrum similar to that of $[Co(CO)_3PPh_3]_2$.[22]

RESULTS AND DISCUSSION

Silyl tetracarbonylcobalt, $SiH_3Co(CO)_4$, and silylenebis(tetracarbonylcobalt), $SiH_2[Co(CO)_4]_2$, were prepared in good yield as volatile liquids according to equation (6). Diethyl or dimethyl ether were suitable solvents: the latter was easier to remove but tended to promote disproportionation of the silicon hydride derivatives. A similar reaction seemed to occur with SiH_3I and $Na[Co(CO)_3PPh_3]$, but the involatile silyl product decomposed during separation. This is perhaps attributable to tetrahydrofuran, used as solvent †, which is known to react with silyl compounds.[23]

$$SiH_{4-x}I_x + x\,NaCo(CO)_4 \xrightarrow{-23^\circ} SiH_{4-x}[Co(CO)_4]_x + x\,NaI \quad (x = 1, 2) \qquad (6)$$

Attempts to prepare these compounds from iodosilanes and mercury bis[tetracarbonyl cobaltate(−I)] under a variety of conditions led only to traces of silicon-metal compounds. The reason for this became clear when it was found that reaction (7) proceeded rapidly and almost completely from left to right at room temperature. Mercuric chloride behaved similarly. This implies that $-Co(CO)_4$ lies to the left of ·I in the usual conversion series; [24] insofar as the series is an order of increasing electronegativity, this suggests a low effective electronegativity for $Co(CO)_4$ when linked to SiH_3.

$$2SiH_3Co(CO)_4 + HgI_2 \rightleftharpoons 2SiH_3I + Hg[Co(CO)_4]_2 \qquad (7)$$

When the solid products from reaction (7) (containing unchanged HgI_2) were extracted with chloroform, the resulting yellow solution showed i.r. absorptions appropriate for $Hg[Co(CO)_4]_2$ together with a band at 2105 cm.⁻¹. It was suspected that this was due to the half-substituted derivative $IHg[Co(CO)_4]$, and subsequent

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* Kindly provided by Dr. J. D. Donaldson, Chelsea College of Science and Technology, London.

† $Na[Co(CO)_3PPh_3]$ is very sparingly soluble in ether.

[21] W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

[22] O. Vohler, *Chem. Ber.*, 1958, **91**, 1235.

[23] B. J. Aylett, *J. Inorg. Nuclear Chem.*, 1960, **15**, 87.

[24] E. A. V. Ebsworth, 'Volatile Silicon Compounds,' Pergamon, Oxford, 1963.

experiments showed that reaction (8) proceeds very readily in chloroform. The i.r. spectrum of the pro-

$$\mathrm{HgI_2 + Hg[Co(CO)_4]_2 \longrightarrow 2IHg[Co(CO)_4]} \qquad (8)$$

duct was consistent with those recently reported for the chloro-[25] and bromo-[26] analogues.

Physical properties of the new compounds are summarised in the Table. In their analysis, hydrogen and silicon could be determined in the usual way by alkaline hydrolysis; no carbon monoxide was evolved, in agreement with Hieber's findings with $Co_2(CO)_8$ itself.[27] The dark blue hydrolysate was strongly reducing, and had to be oxidised (*e.g.* by air) to form cobalt(II) before determination of silicon as silicomolybdate. Bromine caused complete decomposition, as shown in equation (4), under mild conditions. Recovery of HBr gave another measure of hydrogen in the silyl compound. This method is of general applicability to silicon–transition-metal compounds.[14,28]

	$SiH_3Co(CO)_4$	$SiH_2[Co(CO)_4]_2$
M.p.	−53·5°	15°
B.p. (extrap.)	102°	171°
ΔH_{vap} (kcal. mole^{-1})	9·04	9·25
ΔS_{vap} (cal. deg.$^{-1}$ mole^{-1})	23·9	20·8
d (g. ml.$^{-1}$)	1·27/20°	—

The mass spectrum of $SiH_3Co(CO)_4$ under low resolution showed a very weak molecular ion (*m/e* 202). Because of the similar masses of Si and CO, peaks at *m/e* values of 171, 143, 115, and 87 could be due to either $SiCo(CO)_n^+$ or $Co(CO)_{n+1}^+$ ($n = 3, 2, 1, 0$). Attribution of peaks at *m/e* 174, 146, 118, and 90 to $SiH_3Co(CO)_n^+$ ($n = 3, 2, 1, 0$) seems unambiguous, but there is uncertainty regarding $HCo(CO)_{n+1}^+$ or $SiHCo(CO)_n^+$ ($n = 1, 0$) at *m/e* 116 and 88. From the relative intensities of peaks at *m/e* 89 (SiH_2Co^+) and 88, it seems likely that the latter is almost entirely due to $HCo(CO)^+$. The presence of these peaks that could be derived from $HCo(CO)_4$ and also a range of peaks between *m/e* 78 and 72 (attributed to $Si_2OH_n^+$, where $n = 6$ to 0) might suggest that hydrolysis of the sample had occurred. However, the spectrometer had been rigorously flushed with $SiH_3Co(CO)_4$ before all runs, and the spectra were reproducible over periods of at least 30 min. Furthermore, no strong peak was observed at *m/e* 144, found by Saalfield *et al.*[29] to be the fifth most intense peak in the mass spectrum of $HCo(CO)_4$. At present we favour the hypothesis that ions such as $(SiH_3)_2O^+$ and $HCo(CO)^+$ arise from the decomposition of $SiH_3Co(CO)_4$; in support of this, $Me_3SiCo(CO)_4$ is reported[4] to give $(Me_3Si)_2O$ slowly at room temperature, while $(SiH_3)_2O$ and $HCo(CO)_4$ were observed, albeit as minor products, in our own studies on pyrolysis of $SiH_3Co(CO)_4$ (*vide infra*). Other simultaneous decomposition routes seem to be loss of CO groups (as found, *e.g.*, with $Ph_3SnMn(CO)_5$[30]) and cleavage of Si–H bonds. It is hoped to resolve these uncertainties by a high-resolution study shortly.

I.r. Spectra.—High-resolution spectra of $SiH_3Co(CO)_4$ in the gas phase at pressures between 1 and 15 mm. showed the absorptions listed in Table 1. Frequencies are considered to be accurate to ±1 cm.$^{-1}$ over the whole range. Although band structure of *PQR* type is marked (Figure 1), the spectra are generally comparable in the carbonyl stretching region with those found for a range of $SiR_3Co(CO)_4$ derivatives in the gas phase[9] and in solution.[3,6,8]

TABLE 1

I.r. absorption of $SiH_3Co(CO)_4$ (gas phase, cm.$^{-1}$)

Absorption	Proposed assignment	Absorption	Proposed assignment
2164sh	ν(SiH)	950sh	$\delta(SiH_3)$
2160s		946m	
2154s		942m	
2111s	$\nu(CO)A_1$	909s	$\delta(SiH_3)$
2105s		905s	
2101sh		901sh	
2068vw	$\nu(^{13}CO)$	600s	(SiH_3) rock
2055sh	$\nu(CO)A_1$	559s	δ(MCO) ?
2050vs		545s	
2043s		484m	ν(MC) ?
2030sh	$\nu(CO)E$	413w	
2025vvs		374w	
2019sh		310m	ν(SiCo)
1988w	$\nu(^{13}CO)$	303sh	

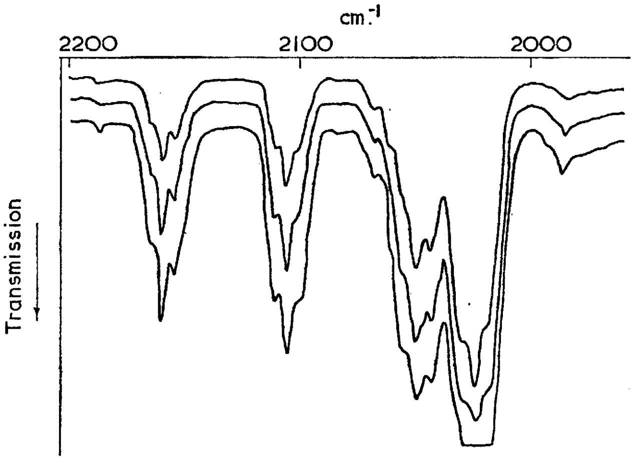

FIGURE 1 High-resolution i.r. spectrum of gaseous $SiH_3Co(CO)_4$ (2200—1970 cm.$^{-1}$)

Structural studies of solid $SiCl_3Co(CO)_4$[12] and gaseous $SiH_3Co(CO)_4$[13] indicate a trigonal bipyramidal structure of C_{3v} symmetry for both molecules. On this basis, the three strong bands at 2105, 2050, and 2025 cm.$^{-1}$ are assigned to $A_1(1)$, $A_1(2)$, and E ν(CO) modes respectively. The weak bands at 2068 and 1988 cm.$^{-1}$ are probably the corresponding $\nu(^{13}CO)$ vibrations of the first and

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third types; their shifts of 37 cm.$^{-1}$ to lower frequencies are consistent with observations on other metal carbonyl systems[31] and with the Teller-Redlich Product Rule.[32]

Two recent publications have dealt with calculations of non-rigorous carbonyl stretching force-constants in $SiR_3Co(CO)_4$ species. Hagen and MacDiarmid[9] apply a modification of Cotton and Kraihanzel's method[33] to determine the axial and radial force constants k_1 and k_2 (see Figure 2), and suggest that $(k_2 - k_1)$ is related to the extent of L–Co π-bonding in $LCo(CO)_4$, but not to σ-inductive effects. By using more complete calculations Stone and his co-workers[10] infer that inductive effects chiefly determine k_1, and k_2, although it is accepted that π-interaction may occur. A difficulty common to both treatments is that σ- and π-effects are, in principle, not even approximately separable[33] in trigonal pyramidal systems. Also overlaps between different metal d_π-orbitals and CO groups may be altered by distortions from ideal geometry.[34]

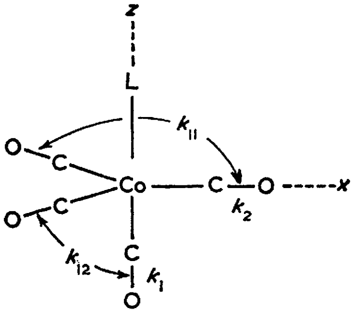

FIGURE 2 Labelling of force constants in $LCo(CO)_4$

As shown clearly by Bor's graphical treatment,[35] absolute and relative value of k_1 and k_2 depend on the value of k_{12} (Figure 2). When (as in ref. 9) k_{12} is set equal to zero, k_1 and k_2 will be in error, but it may still be valid to make comparisons between force constants of similar compounds. Table 2 shows values of k_1 and k_2 thus calculated for gaseous species. These approximate force constants show a general increase with increasing inductive power of X in $SiX_3Co(CO)_4$, although the order of $SiMe_3Co(CO)_4$ and $SiH_3Co(CO)_4$ seems anomalous; an inductive effect alone cannot explain the change in passing from $SiH_3Co(CO)_4$ to $CH_3Co(CO)_4$. On the other hand, the near-zero bond dipole of Si–H in Cl_3SiH[38] implies that, on inductive grounds alone, force constants for $SiCl_3Co(CO)_4$ and $HCo(CO)_4$ should be similar; this is seen to be only approximately true (*cf.* ref. 3). The evidence from force constants is thus ambiguous.

TABLE 2

Approximate ν(CO) force constants (mdyne Å^{-1})

Compound	k_1	k_2
$SiMe_3Co(CO)_4$ (g) [a]	16·82	16·80
$SiH_3Co(CO)_4$ (g) [b]	16·97	17·01
$SiCl_3Co(CO)_4$ (g) [a]	17·32	17·38
$SiF_3Co(CO)_4$ (g) [a]	17·35	17·40
$CH_3Co(CO)_4$ (g) [c,d]	16·90	17·10
$HCo(CO)_4$ (g) [c]	17·17	17·29

[a] Frequencies from ref. 9. [b] This work. [c] Frequencies from ref. 36. [d] Frequencies from ref. 37.

The weighted mean ν(CO) frequency of gaseous $SiH_3Co(CO)_4$ is 2051 cm.$^{-1}$; experience with $SiH_3Mn(CO)_5$[39] suggests a decrease of *ca.* 10 cm.$^{-1}$ in solution. On the basis of Kahn and Bigorgne's relationship,[7] the SiH_3 group in $SiH_3Co(CO)_4$ is then slightly electron-releasing, *i.e.* with a bond dipole in the sense $Si^{\delta+}–Co^{\delta-}$.

Absorptions assigned to Si–H stretching and SiH_3 deformation occur in the normal regions at 2160 and *ca.* 925 cm.$^{-1}$ respectively. The Si–H stretching frequency in SiH_3X molecules generally decreases with decreasing electronegativity of X;[40] the present value is amongst the lowest recorded.* Below 900 cm.$^{-1}$, bearing in mind the probable occurrence of mixing, the band at 600 cm.$^{-1}$ is probably associated with a SiH_3 rocking mode. By analogy with the generally comparable spectra of $CH_3Co(CO)_4$, $SiCl_3Co(CO)_4$, and $SiMe_3Co(CO)_4$ (Table 3), the band at 310 cm.$^{-1}$ is tentatively assigned to Si–Co stretching. Carbonyl deformation and metal–carbon stretching vibrations also occur between 600 and 300 cm.$^{-1}$; chiefly on the ground of intensity, the bands at 559 and 545 cm.$^{-1}$ may be associated with the former, and that at 484 cm.$^{-1}$ with the latter.

TABLE 3

I.r. absorptions of cobalt carbonyl derivatives below 600 cm.$^{-1}$ *

$SiH_3Co(CO)_4$ [a]		$CH_3Co(CO)_4$ [b]		$SiMe_3Co(CO)_4$ [c]		$SiCl_3Co(CO)_4$ [c]	
		565sh	δ(MCO)			573	ν(SiCl)
559s	δ(MCO)	551vs	δ(MCO)	550vs	δ(MCO)	548vs	δ(MCO)
545s	δ(MCO)	485s	δ(MCO)	518s	δ(MCO)	504vs	δ(MCO)
484m	ν(MC)			496m	ν(MC)	480m	ν(MC)
						470m	ν(SiCl)
				459w	ν(MC)	436w	ν(MC)
413w				418w	ν(MC)	408w	ν(MC)
374w		381m	ν(CCo)	377w	δ(MCO)	371w	δ(MCO)
				346vw	δ(MCO)	334vw	δ(MCO)
				331m	δ($SiMe_3$)		
310m	ν(SiCo)			295s	ν(SiCo)	303m	ν(SiCo)
303sh							

* Assignments are those proposed by the cited authors in each case.
[a] This work. [b] Ref. 37. [c] Ref. 8.

The spectrum of $SiH_2[Co(CO)_4]_2$ as a solid film showed bands appropriate for Si–H stretching, C–O stretching,

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* There may however be some interaction between modes formally designated as ν(Si–H) and ν(CO).

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[38] C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 199.

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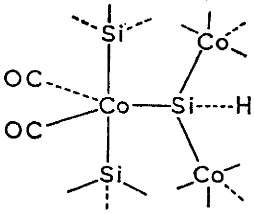
and SiH_2 deformation vibrations, including a band at 812 cm.$^{-1}$ assigned to SiH_2 wag.

Thermal Decomposition.—The temperature at which decomposition began, as evidenced by formation of a dark mirror-like coating on the vessel, was rather variable, but always below 100°. In the gas phase at *ca.* 2 cm. pressure, some 40% had decomposed after 15 min. at 120°, yielding H_2, SiH_4, CO, and $HCo(CO)_4$ as volatile products. The composition of the dark brown solid was inferred to be $SiH_{1\cdot24}Co_{0\cdot82}(CO)_{1\cdot10}$ (I). After 1 hr. under the same conditions, all starting material had decomposed and no $HCo(CO)_4$ was present, while the involatile solid had the composition $SiH_{1\cdot05}Co_{1\cdot06}(CO)_{1\cdot93}$ (II). On alkaline hydrolysis, the second solid gave 0·57 mmole of hydrogen; the calculated amount from (II), assuming that it contains no Si–Si bonds but that all hydrogen is attached to silicon, is 0·53 mmole. It thus appears that (II) is not simply a mixture of $[Co(CO)_x]_n$ and $(SiH_x)_n$ polymers (which would yield further hydrogen from hydrolysis of Si–Si bonds) but contains Si–Co links. Formula (III) represents a portion of an idealised structure of composition $SiHCo(CO)_2$ with five-co-ordinate cobalt that is consistent with these facts.



(III)

It seemed possible that silane, often formed in the pyrolysis of silyl compounds but here recovered only in small amounts, might suffer catalysed decomposition on the mirror-like solid surface. Control experiments showed, however, that silane was unaffected after 1 hr. in contact with the surface at 150°. This implies that if silane is a reaction intermediate it must all be consumed in the early stages of the reaction [for example by reaction with $HCo(CO)_4$].

The solid products (I) and (II) were remarkably resistant to attack, especially after further heating. It was found that coherent films could be deposited on a range of metal substrates and, in some cases, these resisted abrasion and heating to red heat. Presumably the end product of pyrolysis of compound (III) would be CoSi, the structure of which is known.[41] The solids obtained in the present study were all essentially amorphous to *X*-rays, however, and could not be identified in this way.

In the liquid phase at room temperature, $SiH_3Co(CO)_4$ apparently disproportionates slowly to give SiH_4 and $SiH_2[Co(CO)_4]_2$. Other modes of decomposition proceed at the same time, since $(SiH_3)_2O$, $HCo(CO)_4$, and a dark solid are also formed. Although $SiH_2[Co(CO)_4]_2$ was not observed to decompose at room temperature, above 70° it rapidly yielded the same volatile products as gaseous $SiH_3Co(CO)_4$, together with a brownish black solid.

The decomposition of $SiH_3Co(CO)_4$ clearly proceeds very differently from that of $CH_3Co(CO)_4$. The latter compound is reported[42] to decompose above −35°; when in the gas phase, the products include acetone and $Co_4(CO)_{12}$,[37,42] but in solution carbonyl insertion occurs to give $CH_3COCo(CO)_4$.[43] With $SiH_3Co(CO)_4$, higher temperatures are required, and no insertion products (*vide infra*) or disilyl ketone * are formed. Perhaps insertion provides an easy reaction route in the methyl case that is not available to the silyl compound. It has been briefly reported that solid $SiMe_3Co(CO)_4$ very slowly decomposes at room temperature to give $(SiMe_3)_2O$,[4] while $SiPh_3Co(CO)_4$ decomposes on heating to yield Si_2Ph_6 and a trace of Ph_3SiH.[3] Here, too, different routes seem to be followed.

Reactions of $SiH_3Co(CO)_4$.—The Si–Co bond was cleaved by a variety of protic reagents [equation (9)].

$$SiH_3Co(CO)_4 + HX \longrightarrow SiH_3X + HCo(CO)_4 \quad (9)$$
$$X = F,\ Cl,\ O/2$$

In accordance with its greater acid strength, HCl reacted more rapidly than HF. Similar reactions occurred with $SiH_2[Co(CO)_4]_2$; with water, solid $(SiH_2O)_x$ polymers resulted. These reactions are all consistent with a bond polarity in the sense $Si^{\delta+}–Co^{\delta-}$, thus agreeing with the conclusion reached from i.r. spectra that SiH_3 is slightly electron-releasing in $SiH_3Co(CO)_4$. Similar Si–Co bond cleavage occurs in $SiMe_3Co(CO)_4$.[4]

Attempts to induce carbonyl insertion into the Si–Co bond by direct reaction with CO at *ca.* 25 atmos. pressure at 70° were unsuccessful. Other Si–Co,[3] Si–Mn,[15] and Si–Rh[45] compounds are similarly reluctant, but the corresponding reaction with $CH_3Co(CO)_4$ is very easy.[43] Further, reaction (10) with PPh_3 leads chiefly to the substituted acetyl product.[46] With $SiH_3Co(CO)_4$, however, displacement of CO occurred. Reaction was very slow at room temperature, in hexane or ether solution, and attempts to speed it by heating led to decomposition. A yellow solid, involatile at room temperature, was isolated, which gave one strong i.r. absorption bond in the carbonyl region at 1960 cm.$^{-1}$, together with a weak doublet centred on 2040 cm.$^{-1}$. A molecule $XM(CO)_3Y$

$$CH_3Co(CO)_4 + PPh_3 \longrightarrow CH_3COCo(CO)_3PPh_3 \quad (10)$$

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* The organosilyl analogue $(SiPh_3)_2CO$ is thermally rather unstable,[44] and $(SiH_3)_2CO$ is unknown.

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of C_{3v} symmetry is expected[47] to give rise to one strong absorption at lower frequency and a weak band at higher frequency, corresponding to E and A_1 modes respectively. No absorptions in the range expected for ketonic CO groups were present, while the decrease in ν(CO) was typical of that associated[48] with direct replacement of CO by PPh_3. It therefore seems likely that reaction (11) is occuring, although the silyl product has not been completely characterised.

$$SiH_3Co(CO)_4 + PPh_3 \longrightarrow trans\text{-}SiH_3Co(CO)_3PPh_3 + CO \quad (11)$$

It was hoped that less reactive and more easily handled products could be obtained by phosphine substitution; there is a marked increase in thermal stability in the series: $MeCo(CO)_4$ (decomp. −35°),[42] $MeCo(CO)_3PPh_3$ (decomp. 20°),[48] and $MeCo(CO)_2(PPh_3)_2$ (decomp. 120°).[49] Present evidence suggests, however, that the phosphine-substituted compound described above has similar thermal and hydrolytic stability to $SiH_3Co(CO)_4$ itself.

The Question of Silicon–Metal π-Bonding.—Silicon–cobalt d_π–d_π bonding in $SiH_3Co(CO)_4$ might reasonably be expected to lead to: (*a*) a 'short' Si–Co bond, *i.e.* significantly less than the sum of covalent radii, (*b*) low effective electronegativity for $Co(CO)_4$, (*c*) high effective electronegativity for SiH_3, and (*d*) a diminution in metal–CO π-bonding, resulting (perhaps selectively) in higher carbonyl stretching frequencies and related force constants.

Taking these in turn, a recent electron diffraction study[13] has shown that *d*(Si–Co) in $SiH_3Co(CO)_4$ is 2·381 ± 0·007 Å, while Robinson and Ibers[12] estimate the single bond length as *ca.* 2·33 Å and find that *d*(Si–Co) in solid $SiCl_3Co(CO)_4$ is 2·254 ± 0·003 Å. On this basis, π-bonding is minimal in the first compound and possibly significant in the second.

The second and third criteria are somewhat subjective, and depend on comparisons with other SiH_3X and $YCo(CO)_4$ compounds in which Si–X and Y–Co bonds are supposed to have negligible π-character. Kahn and Bigorgne[7] have suggested that the $Co(CO)_4$ group is normally about as electronegative as bromine: evidence given earlier in this paper from Conversion Series reactions and ν(SiH) frequencies indicates that $Co(CO)_4$ in $SiH_3Co(CO)_4$ is apparently less electronegative than iodine. Also, by using a proposed correlation between SiH_3 rocking frequencies and electronegativities of attached groups,[50] the value for $SiH_3Co(CO)_4$ (600 cm.$^{-1}$) is close to that for SiH_3I (592 cm.$^{-1}$). There is thus some case for criterion (*b*). The close similarity in carbonyl stretching frequencies between $SiH_3Co(CO)_4$ and $CH_3Co(CO)_4$ could imply that SiH_3 is almost as electronegative as CH_3, which is certainly at variance with conventional scales, and possibly supports (*c*) and (*d*). As regards more detailed discussion of force constants, we feel that these do not provide unequivocal evidence for (*d*), and are of limited value at present because of the unknown role of σ-inductive effects.

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