trans isomers have been observed. An attempt will be made to rationalize these observations.

For X being a free-valence electron pair, the preference for the trans isomer can be explained by the fact the two free-valence electron pairs seek high s character,[27] i.e., form a linear sp hybrid. This results in strong contributions from semiionic three center-four electron bonds[28-30] to the $AF_4$ part. Since the 3c–4e bonds involve a single p orbital of the central atom for the bonding of two F ligands, the resulting F–A–F group must possess an approximately linear configuration. Since a linear X–A–X and two linear F–A–F groups are possible only for the trans isomer, this should be the preferred configuration.

The trans configuration of $H_2PF_4^-$ can be rationalized by both the 3c–4e bond model and intramolecular attractive forces between the H and the F ligands. The latter rationale is based on the assumption that the negatively polarized fluorine ligands are attracted by the positively polarized hydrogen ligands. In the trans isomer, each H possesses four closest F neighbors, and each F has two closest H neighbors. In the cis isomer, however, each H possesses only three closest F neighbors, and two of the fluorines possess only one closest H neighbor. Therefore, the trans isomer is expected to be energetically favored over the cis isomer.

If X is oxygen, the more electronegative fluorine ligands tend to polarize the X–O bonds. This results in an increased bond order of the X–O bonds according to

$$^{-}\!:\underset{..}{\ddot{O}}-X-F \leftrightarrow \,\dot{:}\!O=X\ F^{-}$$

and

$$\dot{:}\!O=X-F \leftrightarrow {}^{+}\!:O\equiv X\ F^{-}$$

and allows the shifting of a formal negative charge from the less electronegative oxygen ligand to the more electronegative fluorine ligand. Molecular orbital following arguments favor this kind of resonance for linear F–A–O groups. However, these are only possible for the cis isomer.

For singly bonded ligands of intermediate electronegativity, such as OH, $OCH_3$, Cl, Br, etc., both cis and trans isomers have been observed.[9,11-14] This indicates that other factors, such as steric effects or the nature of the formation reaction mechanism, become more important. Consequently, predictions of the expected stereoisomer will be considerably more difficult for these ligands.

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**Registry No.** KF, 7789-23-3; CsF, 13400-13-0; $H_2PF_3$, 13659-65-9; $KH_2PF_4$, 58188-50-4; $CsH_2PF_4$, 58188-51-5.

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# Silylphosphonium Compounds. Synthesis and Structure

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Trimethylsilylcobalt tetracarbonyl, $Me_3SiCo(CO)_4$, has been found to react instantly with $Me_3P$, $Me_2PSiMe_3$, and $MeP(SiMe_3)_2$ to give the solid silylphosphonium compounds $[Me_3SiPMe_3]^+[Co(CO)_4]^-$, $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$, and $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$, respectively, each of which contain at least one Si–P bond. No reaction occurs with $(Me_3Si)_3P$. The infrared and Raman spectra of the compounds are completely consistent with the phosphonium salt formulation. A single-crystal x-ray study of $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ shows that the bonding at both the phosphorus and cobalt atoms is almost exactly tetrahedral. A concentration- and temperature-dependent NMR study shows that the compounds dissociate in solution to $Me_3SiCo(CO)_4$ and the phosphine and that the dissociation increases with (i) the number of $Me_3Si$ groups in the cation, (ii) increasing temperature, and (iii) decreasing concentration.

## Introduction

In a preliminary study[1,2] we had reported a new type of reaction between a transition metal carbonyl and a phosphine. It was found that $Me_3P$ did not react with $Me_3SiCo(CO)_4$ in the expected manner to form $Me_3SiCo(CO)_3PMe_3$. Instead, an instantaneous reaction occurred to give quantitative yields of the solid silylphosphonium compound $[Me_3SiPMe_3]^+$-$[Co(CO)_4]^-$, the first reported example of a phosphonium compound containing an Si–P bond. Detailed studies of the

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products formed by the reaction of $Me_3SiCo(CO)_4$ with $PMe_3$, $Me_3SiPMe_2$, $(Me_3Si)_2PMe$, $(Me_3Si)_3P$, $H_3SiPMe_2$, $HPMe_2$, and $H_2PMe$ and preliminary studies of the reaction between $H_3SiCo(CO)_4$ and $PMe_3$ are reported in this communication.

## Experimental Section

**Apparatus.** All synthetic work was carried out using standard vacuum system techniques. The preparation of Nujol mulls for infrared studies and the handling of the pure phosphonium salts was performed in an inert-atmosphere box using argon which was constantly being recirculated and purified.

Infrared spectra were recorded with a Perkin-Elmer 521 double-beam grating spectrophotometer and Raman spectra were obtained with a Spex Ramalog instrument using an Ar–Kr coherent radiation ion laser with 6471 Å for excitation. NMR spectra were recorded with Varian Associates HA-100 and A-60 spectrometers.

**Reagents.** With the exception of $PMe_3$ which was purchased (Strem Chemical Co.), all reagents were synthesized according to methods given in the literature, sometimes with a slight modification in procedure: $Me_3SiCo(CO)_4$,[3] $Me_3SiPMe_2$,[4] $(Me_3Si)_3P$,[5] $(Me_3Si)_2PMe$,[6] $H_3SiPMe_2$,[4] $HPMe_2$[7] [from $(Me_2PS)_2$ and $LiAlH_4$ in $(n\text{-}C_4H_9)_2O$ at 80 °C with a water-cooled reflux condenser]; $H_2PMe$[8] [from $CH_3PO(OCH_3)_2$ and $LiAlH_4$ in diglyme at 20–50 Torr with a water-cooled condenser]; $H_3SiCo(CO)_4$.[9]

The purity of all substances was confirmed by NMR and/or infrared spectra and/or Dumas molecular weight measurements.

**Reactions. $Me_3SiCo(CO)_4$ and $PMe_3$.** A 1.48-g (6.06-mmol) sample of $Me_3SiCo(CO)_4$ was dissolved in approximately 10 ml of $CH_2Cl_2$, the mixture was cooled to −196 °C, and 0.460 g (6.06 mmol) of $Me_3P$ was distilled in. A pale brown solution was obtained when the mixture was warmed to room temperature with shaking and a small amount of CO was liberated. The solution was cooled to 0 °C and the $CH_2Cl_2$ was slowly removed by distillation. The resulting yellow to brownish powder was washed with $C_6H_{12}$ at room temperature and the $C_6H_{12}$ was removed by filtration in vacuo. Almost colorless $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ was obtained by subliming off the remainder of the $C_6H_{12}$ at 0 °C in vacuo. Its infrared spectrum was identical with that reported earlier for the compound.[1] The material can be sublimed at room temperature into a trap held at −196 °C with constant pumping. Partial separation into $Me_3SiCo(CO)_4$ and $PMe_3$ occurs during this process and the compounds appear as separate layers in the trap at −196 °C. A small amount of dark brown oily residue remains upon each sublimation. It should be noted that the solid slowly decomposes in a complex manner on standing at room temperature to give a brown material.

**$Me_3SiCo(CO)_4$ and $Me_3SiPMe_2$.** A 2.668-g (10.92-mmol) sample of $Me_3SiCo(CO)_4$ was dissolved in approximately 10 ml of $CH_2Cl_2$, and after cooling of the mixture to −196 °C, 1.466 g (10.92 mmol) of $Me_3SiPMe_2$ was distilled into the mixture. A pale brown solution resulted on warming to room temperature with shaking. The solution was slowly cooled in a stepwise fashion, in order to promote formation of large crystals, to −78 °C, at which temperature it was filtered in vacuo and the crystalline material was washed twice with $CH_2Cl_2$ at −78 °C on the filter. Final traces of solvent were removed by pumping at room temperature. Yields in excess of 90% of pure, yellow crystalline $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ could readily be obtained. Anal.[10] Calcd for $C_{12}H_{24}PSi_2CoO_4$: C, 38.1; H, 6.35; P, 8.20; Co, 15.6. Found: C, 37.8; H, 6.47; P, 7.96; Co, 15.5. The compound can be sublimed in vacuo at 60 °C and above without noticeable decomposition. It is thermally more stable at room temperature than $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ and it shows no visible sign of decomposition even after standing for several weeks at room temperature in vacuo or under argon.

**$Me_3SiCo(CO)_4$ and $(Me_3Si)_2PMe$.** A 0.921-g (3.78 mmol) amount of $Me_3SiCo(CO)_4$, 0.845 g (4.40 mmol) of $(Me_3Si)_2PMe$, and approximately 8 ml of $CH_2Cl_2$ were condensed in a vessel at −196 °C and warmed to room temperature with shaking. The resulting pale brown solution was cooled to −23 °C, at which temperature the $CH_2Cl_2$ was distilled off and the pale yellow solid was washed on the filter with approximately 10 ml of toluene at −78 °C in vacuo. In order to obtain high yields it is desirable to carry out the toluene filtration at −78°, since, although the solubility of the product is less in toluene than in $CH_2Cl_2$, it is still appreciable except at low temperature. Yields of 70–90% of the pale yellow solid, $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$, could readily be obtained. It can be sublimed at room temperature in vacuo without noticeable decomposition, and it appears to be stable at room temperature during several days.

**$Me_3SiCo(CO)_4$ and $(Me_3Si)_3P$.** Equimolar quantities of $Me_3SiCo(CO)_4$ (1.140 g; 4.67 mmol) and $(Me_3Si)_3P$ (1.168 g; 4.67 mmol) were mixed with 8 ml of $CH_2Cl_2$ and warmed from −196 °C to room temperature with shaking. On cooling of the mixture to −60 °C, crystals of $Me_3SiCo(CO)_4$ precipitated, as evidenced by the fact that the $Me_3SiCo(CO)_4$ NMR signal decreased while that of $(Me_3Si)_3P$ remained unchanged. Methylene chloride was removed at −23 °C and on warming to room temperature only a liquid phase, presumably a solution of $Me_3SiCo(CO)_4$ in $(Me_3Si)_3P$, was obtained. Portions of this liquid were dissolved in $CH_2Cl_2$ and also in toluene, and $^1H$ NMR spectra were recorded at temperatures from +40 to −60 °C. In both solutions the spectra showed the presence of only free $Me_3SiCo(CO)_4$ and $(Me_3Si)_3P$. All coupling constants were present and had the same values as the pure starting materials in $CH_2Cl_2$ or toluene. When solutions in toluene were cooled, crystals of what appeared to be $Me_3SiCo(CO)_4$ precipitated. No evidence of any type for the formation of a phosphonium compound could be found.

**$Me_3SiCo(CO)_4$ and $HPMe_2$.** Equimolar quantities of $Me_3SiCo(CO)_4$ (0.756 g; 3.10 mmol) and $HPMe_2$ (0.192 g; 3.1 mmol) were warmed with approximately 10 ml of $CH_2Cl_2$ from −196 °C to room temperature with shaking. The initially pale brown solution slowly darkened on standing at room temperature for 30 min. During this time, a noncondensable gas, presumably CO, was evolved. The solution was then cooled to −23 °C and the $CH_2Cl_2$ was distilled off. A dark brown solid remained, from which colorless, crystalline $Me_3SiCo(CO)_4$ (identified by its infrared and NMR spectra) could be sublimed at room temperature in vacuo. The $^1H$ NMR spectrum of a solution of the reactants in $CH_2Cl_2$ at room temperature showed that much of the $Me_3SiCo(CO)_4$ remained unchanged. Its characteristic signal slowly decreased during a period of several hours at room temperature while at the same time the characteristic spectrum of the $[(Me_3Si)_2PMe_2]^+$ ion appeared and increased in intensity, together with numerous partially broadened, unidentified signals, which also increased in intensity with time.

The reaction was repeated in $C_6H_{12}$, using first a 1:1 molar ratio of reactants and then a 2:1 ratio. Thus 1.935 g (7.93 mmol) of $Me_3SiCo(CO)_4$ and 0.269 g (4.34 mmol) of $HPMe_2$ in approximately 8–10 ml of $C_6H_{12}$ were cooled to −196 °C and warmed to room temperature with shaking. A pale brown solution was obtained. After 10 min at room temperature bubbling was observed and the solution became at first lighter in color and then turbid. As vigorous CO evolution continued at room temperature the solution became progressively darker and at the same time a yellow-brown precipitate began to form. After a total of 45 min at room temperature, when the amount of precipitate did not increase further, the solution was cooled to −196 °C and a Dumas molecular weight of the noncondensable gas (mol wt: found, 28.8; calcd for CO, 28.0) showed it consisted primarily of CO.

As the solution was slowly warmed to room temperature, approximately 2 ml of material was removed by distillation. The mixture was filtered at room temperature in vacuo and washed twice with the recondensed solvent. The yield of crude $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ was 570 mg (1.51 mmol). Purification by recrystallization from $CH_2Cl_2$ at −78 °C gave a material whose infrared and NMR spectra were identical with those for the pure compound prepared as described previously.

**$Me_3SiCo(CO)_4$ and $H_2PMe$.** Equimolar quantities of $Me_3SiCo(CO)_4$ (0.391 g; 1.60 mmol) and $H_2PMe$ (0.077 g; 1.6 mmol) were warmed with approximately 6 ml of $C_6H_{12}$ from −196 °C to room temperature with shaking. During a period of several days at room temperature the initially pale brown solution became darker and dark brown-black oily droplets formed on the bottom of the reaction vessel. Carbon monoxide was slowly evolved during this period. After 3 days the $C_6H_{12}$ was distilled off and the dark residue was dissolved in $CH_2Cl_2$. The $^1H$ NMR spectrum of this solution at room temperature showed the presence of large amounts of unreacted $Me_3SiCo(CO)_4$. None of the other very broad signals could be ascribed to any known or expected compound.

The reaction was repeated in $CH_2Cl_2$ and essentially identical results were obtained except that the reaction proceeded very much more rapidly and appeared, after only 3 h, to be similar to the reaction in $C_6H_{12}$ after approximately 3 days at room temperature. This suggested that the reaction might proceed via a rate-controlling step involving an ionic or polar intermediate or transition state.

**$Me_3SiCo(CO)_4$ and $H_3SiPMe_2$.** Equimolar quantities of $Me_3SiCo(CO)_4$ (1.53 g; 6.28 mmol) and $H_3SiPMe_2$ (0.577 g; 6.28 mmol) were condensed in a vessel at −196 °C with approximately 10 ml of $CH_2Cl_2$ and the mixture was warmed to room temperature with shaking. The pressure over the pale brown solution slowly increased at room temperature, apparently due to the formation of CO and $SiH_4$. The $^1H$ NMR spectrum of the solution showed only small amounts of $Me_3SiCo(CO)_4$, but considerable quantities of $SiH_4$. Several temperature-dependent doublets ($J_{H-C-P}$ = 7–11 Hz), due to methyl groups attached to four-coordinate phosphorus, were clearly evident. After 3 days at room temperature 4.1 mmol of $SiH_4$ was isolated from the mixture by fractionation in the vacuum system. The $^1H$ NMR spectrum of the remainder showed the same temperature-dependent doublets in different relative intensities, together with some partially broadened signals in the $Me_3Si$ region, indicating the formation of at least five different compounds. None of these were isolated.

**$H_3SiCo(CO)_4$ and $Me_3P$.** Equimolar quantities of $H_3SiCo(CO)_4$ (0.425 g; 2.10 mmol) and $Me_3P$ (0.16 g; 2.1 mmol) were mixed with approximately 10 ml of $CH_2Cl_2$ in a vessel at −196 °C and warmed to −78 °C with shaking. A white precipitate was present. The vessel was removed from the −78 °C bath for a few seconds and shaken to dissolve all of the precipitate. Part of the resulting solution was transferred at −78 °C to an NMR tube attached as a side arm, both tubes were cooled to −196 °C (at the same time), and the NMR tube was sealed in vacuo. The proton NMR spectra at −70 °C showed a very broad peak ($\tau$ 8.68) with no sign of splitting in the $H_3C$–P (four-coordinate) region and a sharp peak ($\tau$ 5.56) was found in the Si–H region. Two small additional doublet signals were present in the $H_3C$–P region at a slightly lower field. On warming to −20 °C the broad peak at $\tau$ 8.68 became a sharp doublet with a coupling constant of approximately 10 Hz, characteristic for $J_{H-C-P}$ in a four-coordinate phosphorus atom. The sharp peak in the Si–H region did not change, but the small additional doublets slowly increased in intensity, indicating a slow decomposition of the originally formed compound.

The frozen solution which had not been transferred to the NMR tube was warmed a little above −78 °C until a clear yellow solution was obtained. When this solution was held again at −78 °C for 2 h, large white crystals were formed. The material remaining after removing the $CH_2Cl_2$ at −78 °C during several hours consisted of large white crystals mixed with a small amount of yellow solid. The white crystals could be sublimed in vacuo at 0 °C to another vessel held at −196 °C, leaving a considerable amount of yellow, nonvolatile residue which slowly turned reddish at room temperature with the evolution of some noncondensable gas. Most of the sublimed material could be resublimed at 0 °C, but again, a considerable amount of a yellow nonvolatile residue remained and decomposed slowly at room temperature, indicating that the sublimable white material partly decomposes at 0 °C. If the white sublimable material is warmed to room temperature, it turns yellow and partially melts, and some bubbling is observed. The pressure constantly increases, forming some noncondensable gas (presumably CO) and $SiH_4$.

**Collection of X-Ray Data.**[11] A crystal of $[(Si(CH_3)_3)_2P(CH_3)_2]^+[Co(CO)_4]^-$ measuring 0.3 × 0.4 × 0.7 mm was mounted in a thin glass capillary measuring 0.7 mm in diameter. Preliminary examination of the crystal and data collection were performed on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator. The crystal was found to be monoclinic and the space group was determined as $P2_1/n$. Cell constants (23 °C) obtained from a least-squares refinement of the setting angles for 15 strong reflections are $a$ = 14.713 (5) Å, $b$ = 9.877 (3) Å, $c$ = 15.537 (4) Å, $\beta$ = 115.36 (2)°, and $V$ = 2040.2 (9) Å$^3$. The width at half-height for $\omega$ scans of several strong reflections was 0.15°.

Intensity data were collected at 23 °C with Mo K$\alpha$ radiation using the $\theta$–$2\theta$ scan technique and a variable scan rate of 4.0–24.0°/min, depending on the intensity of the reflection. A symmetrical scan range of $2\theta$(Mo K$\alpha_1$) − 0.8° to $2\theta$(Mo K$\alpha_2$) + 0.8° was used to measure 2637 unique reflections up to a maximum $2\theta$ of 45°. Stationary-crystal stationary-counter background counts were taken at each end of the $2\theta$ scan range; the total background counting time is equal to the scan time. Three standard reflections were measured after every 100 reflections to check on crystal and electronic stability. No trends in the standards were observed. In the refinement of the structure 1644 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. Here $\sigma(F_o^2)$ is the standard deviation for the observed intensity of a reflection and is calculated from the following formula: $\sigma(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]^{1/2}$ where $S$ is the scan rate, $C$ is the total integrated peak count, $R$ is the ratio of scan time to background counting time, and $B$ is the total background count. The parameter $p$ used in the calculation of standard deviations was set equal to 0.07.

Table I. Atomic Positional and Isotropic Temperature Factors for $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$

| Atom | $x$ | $y$ | $z$ | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| Co | 0.7421 (1) | 0.2400 (2) | 0.0111 (1) | 5.2 (1) |
| P | 0.4980 (2) | 0.3065 (3) | 0.2086 (3) | 4.2 (1) |
| Si(1) | 0.5630 (3) | 0.0922 (3) | 0.2468 (2) | 4.5 (1) |
| Si(2) | 0.4253 (3) | 0.3879 (4) | 0.3021 (3) | 5.3 (1) |
| O(1) | 0.532 (1) | 0.317 (1) | −0.063 (1) | 8.7 (3) |
| O(2) | 0.827 (1) | 0.245 (1) | 0.217 (1) | 7.7 (2) |
| O(3) | 0.757 (1) | −0.028 (1) | −0.055 (1) | 10.4 (3) |
| O(4) | 0.848 (1) | 0.441 (1) | −0.051 (1) | 10.0 (3) |
| C(1) | 0.617 (1) | 0.286 (1) | −0.034 (1) | 6.6 (3) |
| C(2) | 0.796 (1) | 0.243 (1) | 0.135 (1) | 6.0 (3) |
| C(3) | 0.749 (1) | 0.082 (2) | −0.027 (1) | 7.4 (4) |
| C(4) | 0.806 (1) | 0.355 (2) | −0.026 (1) | 7.5 (4) |
| C(5) | 0.600 (1) | 0.419 (1) | 0.216 (1) | 5.4 (3) |
| C(6) | 0.402 (1) | 0.313 (1) | 0.084 (1) | 6.1 (3) |
| C(7) | 0.571 (1) | 0.027 (1) | 0.137 (1) | 5.8 (3) |
| C(8) | 0.473 (1) | −0.010 (1) | 0.276 (1) | 5.5 (3) |
| C(9) | 0.689 (1) | 0.120 (1) | 0.349 (1) | 5.8 (3) |
| C(10) | 0.503 (1) | 0.331 (1) | 0.427 (1) | 6.8 (3) |
| C(11) | 0.295 (1) | 0.313 (1) | 0.249 (1) | 6.8 (3) |
| C(12) | 0.428 (1) | 0.578 (1) | 0.295 (1) | 7.1 (3) |

**Refinement of the Structure.**[11] Normalized structure factors were generated using the computer program FAME. An initial phase set showing good figures of merit was generated by the program MULTAN. An $E$ map revealed the four heavier atoms and a subsequent least-squares cycle and difference Fourier map produced the remaining 16 nonhydrogen atoms. The structure was refined isotropically to convergence by three full-matrix least-squares cycles to give the following discrepancy indices: $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.087$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_c|^2]^{1/2} = 0.126$. The terms $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes, and $w$ is the weighting factor, $4F_o^2/\sigma^2$, where $\sigma$ is the esd of $F_o^2$. No unusual trends were found in the data as a function of $\lambda^{-1} \sin\theta$, $|F_o|$, Miller indices, or reflection number.[12]

The values for $R_1$ and $R_2$ are reasonable for the isotropic refinement stage when one considers that the large isotropic temperature factors probably indicate large anisotropic movement of atoms. A final difference Fourier map was found to be featureless, indicating that all of the structure has been determined. The atomic positional and thermal parameters for $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ are given in Table I.

## Results

The results obtained for various silylcobalt carbonyl and phosphine systems are summarized below.

**$Me_3SiCo(CO)_4$–$PMe_3$.** An instantaneous reaction occurred between equimolar quantities of $Me_3SiCo(CO)_4$ and $PMe_3$ when the mixture was warmed to room temperature in the presence of $CH_2Cl_2$, viz.

$$Me_3SiCo(CO)_4 + PMe_3 \rightleftarrows [Me_3SiPMe_3]^+[Co(CO)_4]^- \quad (1)$$

Solid $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ could be isolated by evaporation of the $CH_2Cl_2$. Only traces of CO were evolved. The compound could be sublimed in vacuo at room temperature, presumably via a process involving reversible dissociation of the phosphonium salt, since a partial separation into $Me_3P$ and $Me_3SiCo(CO)_4$ occurred on subliming the compound into a trap held at −196 °C. The compound decomposes instantly in the presence of traces of air.

As shown in Table II, the Raman and ir spectra of the solid were consistent with its proposed phosphonium salt structure; in particular, the characteristic CO stretching and bending (Raman) vibrations of the $Co(CO)_4^-$ ion were clearly evident. The very small amount of $Me_3SiCo(CO)_4$ observed in the ir spectrum of a Nujol mull is believed to be due to some partial

**Table II.** Infrared[a] and Raman[b] Absorption Maxima (cm$^{-1}$)

| $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ | $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ | $[Me_3Si)_3PMe]^+[Co(CO)_4]^-$ | Assignment[c] |
|---|---|---|---|
| | Raman Spectral Data | | |
| | 3009 w | | |
| 2990 w | 2993 m | 2985 w | $\nu_{as}(CH_3)$ |
| | 2971 m | 2970 w | |
| 2920 m | 2925 m | 2910 m | $\nu_s(CH_3)$ |
| | 2909 m | | |
| | 2792 w | 2792 w | Unassigned |
| | 1910 m | | |
| 1905 m | 1900 m | 1888 m | $\nu_{CO}$ ($\nu_5$) |
| 1885 s | 1880 s | | |
| | 1430 sh, vw | | |
| 1415 w | 1417 w | 1420 vw | $\delta_{as}(CH_3)$ |
| | 1399 sh, vw | | |
| | 1267 vw | | $\delta_s(CH_3)$ |
| | 860 vw | | $\rho_{as}(CH_3)$ |
| | 828 vw | | |
| 771 m | 756 m | 767 w | $\nu_s(PC)$ |
| 715 m | 710 m | 705 m | $\delta$(Co–C–O) ($2\nu_9$) |
| 678 s | 695 m | | $\nu_{as}(SiC_3)$ |
| 622 s | 625 s | 635 s | $\nu_s(SiC_3)$ |
| | 555 m | | $\nu$(Co–(CO)) ($\nu_6$) |
| 530 s | 530 s | 534 m | $\delta$(Co–C–O) ($\nu_7$) |
| 440 vs | 439 vs | 438 s | $\nu$(Co–(CO)) ($\nu_2$) |
| 417 m | 379 s | 353 m | $\nu_s(SiP)$ |
| 277 m | 267 m | | $\delta$(PC) |
| 240 m | 244 s | | $\delta_s(SiC_3)$ |
| 210 s | 198 vs | 191 s | $\delta_{as}(SiC_3)$ |
| 160 w | 160 m | | $\rho(SiC_3)$ |
| 97 vvs | 92 vvs | 91 vvs | $\delta$((OC)–Co–(CO)) ($\nu_4$) |
| | 80 sh | | |
| | Infrared Spectral Data[d] | | |
| 1885 vs, vb | 1885 vs, vb | 1880 s, b | $\nu_{CO}[Co(CO)_4^-]$ |
| 2000 sh | 1995 vs, sp | 1995 vs, sp | |
| | 2030 m, sp | 2030 m, sp | $\nu_{CO}[Me_3SiCo(CO)_4]$[e] |
| 2095 vw | 2095 m, sp | 2095 m, sp | |

[a] Infrared spectra recorded as Nujol mulls. [b] Raman spectra recorded as the pure solids. [c] Assignments of $Me_3Si$ vibrations based on data for $Me_3SiPH_2$, $(Me_3Si)_2PH$, and $(Me_3Si)_3P$ given by H. Bürger, U. Goetze, and W. Sawodny, *Spectrochim. Acta, Part A*, **26**, 671 (1970). Infrared and Raman assignments for the $Co(CO)_4^-$ ion based on data given by W. F. Edgell et al., *J. Chem. Phys.*, **52**, 4329 (1970). [d] Only the CO stretching region is given. The remainder of the spectrum is consistent with the phosphonium compound listed and with the presence of free $Me_3SiCo(CO)_4$ and phosphine together with Nujol peaks. [e] J. F. Bald, Jr., Ph.D. Thesis, University of Pennsylvania, 1971.

dissociation of the compound promoted by the solvent effect of the Nujol.

The proton and $^{31}$P NMR spectra parameters of $Me_3SiCo(CO)_4$, $PMe_3$, and $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ in $CH_2Cl_2$ solutions are given in Table III.

The NMR data are consistent with the compound existing in $CH_2Cl_2$ solutions at concentrations ranging from 0.45 to 9 mol % and temperatures ranging from +40 to −30 °C, as $[Me_3PSiMe_3]^+[Co(CO)_4]^-$ in equilibrium with variable amounts of $Me_3SiCo(CO)_4$ and $Me_3P$ as given by eq 1.

For a nonexchanging $[Me_3SiPMe_3]^+$ ion one would expect a high-field $Me_3Si$ doublet in the $^1$H NMR spectrum and a $Me_3P$ doublet at a lower field. In concentrated solutions only a single singlet $Me_3Si$ signal was observable. The $Me_3P$ doublet was present under all conditions. The absence of coupling with phosphorus in the $Me_3Si$ signal is undoubtedly due to rapid exchange of $Me_3Si$ groups. Comparison of the chemical shift and $J_{H-C-P}$ values for $Me_3P$, $[Me_4P]^+I^-$, and $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ given in Table III is consistent with the latter compound having the $Me_3Si$ and $Me_3P$ groups present in a phosphonium cation.

On lowering the temperature of concentrated solutions, the $Me_3Si$ signal began to broaden at approximately −55 °C and at approximately −60 °C doublet structure began to develop due to coupling between the $Me_3Si$ protons and the phosphorus, thus indicating a decrease in the exchange rate and the presence of an Si–P bond. In these concentrated solutions considerable precipitation of solute occurred and prevented studies at lower temperatures. As the temperature was lowered in these concentrated solutions, the chemical shifts and $J_{H-C-P}$ values changed only very slightly.

Upon dilution, a small low-field signal attributable to free $Me_3SiCo(CO)_4$ appeared and grew in intensity with increasing dilution; the chemical shifts of the $Me_3Si$ groups remained almost constant while the $Me_3P$ signal shifted to higher field. At the same time, $J_{H-C-P}$ decreased markedly. These observances all indicated a shift in the equilibrium to the left.

The appearance of free $Me_3SiCo(CO)_4$ showed that $Me_3SiCo(CO)_4$ was not involved in the phenomenon responsible for the absence of coupling between the $Me_3Si$ protons and the phosphorus but that this phenomenon was probably due to the exchange of $Me_3Si^+$ groups between four- and three-coordinate phosphorus atoms, i.e., between $[Me_3SiPMe_3]^+$ and $Me_3P$, viz.

$$[Me_3SiP'Me_3]^+ + PMe_3 \rightleftarrows [Me_3SiPMe_3]^+ + P'Me_3 \qquad (2)$$

It can be seen that exchange of $Me_3Si$ groups between cobalt and phosphorus either by reaction 1 or by reaction 3, viz.

$$Me_3Si'Co(CO)_4 + [Me_3SiPMe_3]^+ \rightleftarrows Me_3SiCo(CO)_4 + [Me_3Si'PMe_3]^+ \qquad (3)$$

is slow on the NMR time scale. This is reasonable, since a low-energy pathway is available in the case of exchange occurring by reaction 2, involving nucleophilic attack on the Si in a $[Me_3SiP'Me_3]$ ion by a free $PMe_3$.

The changes in chemical shift of the $Me_3P$ protons and in the value of $J_{H-C-P}$ upon dilution are consistent with the equilibrium given by eq 1 moving further toward the left on dilution. Since in the dilute solutions there are relatively more free $PMe_3$ groups to exchange with $Me_3P$ groups in the $[Me_3SiPMe_3]^+$ ion, the time-averaged $Me_3P$ signal will move closer to the chemical shift and $J_{H-C-P}$ values characteristic of free $Me_3P$. The chemical shift of the $Me_3Si$ protons is not expected to change as much as that of the $Me_3P$ protons on dilution because, as shown in Table III, the chemical shifts of the $Me_3Si$ protons in $Me_3SiCo(CO)_4$ and $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ are more similar in value than are the $Me_3P$ protons in $Me_3P$ and in $[Me_3SiPMe_3]^+[Co(CO)_4]^-$.

In the more dilute solutions, as the temperature was lowered, the intensity of the high-field $Me_3Si$ signal increased relative to that of the low-field $Me_3Si$ signal. The chemical shifts of the two peaks changed only slightly, while the chemical shift of the $Me_3P$ group moved to lower field with an increase in $J_{H-C-P}$. These changes are consistent with equilibrium 1, moving further to the right on lowering the temperature.

The extent to which the chemical shift of the P–C–H protons and the coupling constant, $J_{H-C-P}$, vary is illustrated by comparing the results of the measurement of two samples with different concentrations at two different temperatures: for +40 °C, at $c$ 9 mol %, $\tau$ 8.24, $J_{H-C-P} = 11.8$ Hz; at $c$ 0.45 mol %, $\tau$ 8.47, $J_{H-C-P} = 7.4$ Hz; for −20 °C at $c$ 9 mol %, $\tau$ 8.26, $J_{H-C-P} = 11.85$ Hz; at $c$ 0.45 mol %, $\tau$ 8.23, $J_{H-C-P} = 11.4$ Hz. The position of the chemical equilibrium in $CH_2Cl_2$ solution, given by eq 1, may be calculated from the NMR data by two different methods: (i) using the $J_{H-C-P}$ values of the free phosphine and that of the phosphonium ion with the relationship

$$X[J_{H-C-P}(\text{phosphonium ion})] + Y[J_{H-C-P}(\text{free phosphine})] = \text{measd } J_{H-C-P}$$

where $X$ and $Y$ ($X + Y = 1$) are the mole fractions of the

**Table III.** NMR Spectral Parameters of Selected Phosphines and Silylphosphonium Compounds

| | $\tau$(Me$_3$Si) | $\tau$(H$_3$-C-P) | $J_{H-C-P}$, Hz | $J_{H-C-Si-P}$, Hz | $J_{^{29}Si-C-H}$, Hz | $J_{^{13}C-H}$ (Me$_3$Si), Hz | $J_{^{13}C-H}$ (H$_3$C-P), Hz | $\delta$($^{31}$P),[i] ppm |
|---|---|---|---|---|---|---|---|---|
| Me$_3$SiCo(CO)$_4$[a] | 9.37 | | | | 6.7 ± 0.1 | 121 ± 1 | | |
| PMe$_3$[b] | | 9.025 | 2.0 ± 0.1 | | | | 127.5 ± 1 | +62[j] |
| [Me$_4$P]$^+$I$^-$ [c] | | 7.53 | 14.6 | | | | | −25.3 |
| [Me$_3$SiPMe$_3$]$^+$[Co(CO)$_4$]$^-$ [a,d] | 9.425 | 8.24 | 11.8 ± 0.1 | 6.0 ± 1[e] | 7.0 ± 0.1 | 121 ± 1 | 134 ± 1 | +25 |
| Me$_3$SiPMe$_2$[b] | 9.85 | 8.95 | 2.1 ± 0.1 | 4.3 ± 0.1 | 6.6 ± 0.1 | 120 ± 1 | 130 ± 1 | +132[k] |
| [(Me$_3$Si)$_2$PMe$_2$]$^+$[Co(CO)$_4$][a,d] | 9.45 | 8.42 | 10.3 ± 0.1 | 7 ± 0.5[f] | 6.9 ± 0.1 | 120 ± 1 | 134 ± 1 | +85 |
| (Me$_3$Si)$_2$PMe[b] | 9.80 | 9.01 | 1.25 ± 0.1 | 4.65 ± 0.1 | 6.8 ± 0.2 | 120 ± 1 | 131 ± 1 | +197[k] |
| [(Me$_3$Si)$_3$PMe]$^+$[Co(CO)$_4$]$^-$ [a,d] | 9.46 | 8.58 | 8.55 ± 0.1 | *g* | *h* | *h* | *h* | +149 |
| (Me$_3$Si)$_3$P[b] | 9.73 | | | 4.7 | 6.6 ± 0.2 | 120 ± 1 | | +251[k] |

[a] Approximately 5–10 mol % in CH$_2$Cl$_2$ at +40 °C. The chemical shifts were measured with respect to the CH$_2$Cl$_2$ solvent and were converted to $\tau$ values using $\tau$(CH$_2$Cl$_2$) 4.68. Concentrations were measured by comparison of the signal with the CH$_2$Cl$_2$ solvent signal. [b] Measured as described in footnote *a*. The data for the phosphines in CH$_2$Cl$_2$ solutions, especially $J_{H-C-P}$, differ significantly from those observed for the neat liquids. [c] In CDCl$_3$ solution: H. Schmidbauer, W. Buchner, and D. Scheutzow, *Chem. Ber.*, **106**, 1251 (1973). [d] The data for the phosphonium compounds are taken as being characteristic of the pure phosphonium ions. The values reported are those constant limiting values obtained which did not change further on either increasing the concentration or decreasing the temperature. These conditions are existent for all of the phosphonium ions at a concentration of approximately 5 mol % and at a temperature of −20 °C. [e] Observed as an incompletely resolved doublet at approximately −60 °C as the solid solute began to crystallize from solution. [f] Observed as a well-defined doublet at approximately −60 °C as solid solute was crystallizing from solution. [g] $J_{H-C-Si-P}$ could not be observed even at −60 °C. [h] Not observed because of broadening of all signals. [i] Chemical shifts are reported in ppm with respect to external H$_3$PO$_4$. Concentrations and temperatures for the phosphonium compounds are those given in footnote *d*. [j] $^{31}$P chemical shift of neat liquid: J. R. Van Wazer and J. H. Letcher, *Top. Phosphorus Chem.*, **5**, 75 (1970). [k] $^{31}$P chemical shift of neat liquid: G. Fritz and H. Schäfer, *Z. Anorg. Allg. Chem.*, **409**, 137 (1974).

**Table IV.** Bond Angles (deg)[a] in [(Me$_3$Si)$_2$PMe$_2$]$^+$[Co(CO)$_4$]$^-$

| | | | |
|---|---|---|---|
| Anion | | | |
| Co-C(1)-O(1) | 179.4 (13) | C(1)-Co-C(3) | 108.5 (7) |
| Co-C(2)-O(2) | 176.8 (13) | C(1)-Co-C(4) | 109.2 (7) |
| Co-C(3)-O(3) | 177.9 (15) | C(2)-Co-C(3) | 109.8 (7) |
| Co-C(4)-O(4) | 176.8 (15) | C(2)-Co-C(4) | 108.0 (7) |
| C(1)-Co-C(2) | 109.9 (7) | C(3)-Co-C(4) | 111.4 (7) |
| Cation | | | |
| Si(1)-P-Si(2) | 114.6 (2) | C(7)-Si(1)-C(8) | 111.4 (6) |
| Si(1)-P-C(5) | 107.8 (4) | C(7)-Si(1)-C(9) | 113.2 (6) |
| Si(1)-P-C(6) | 110.4 (5) | C(8)-Si(1)-C(9) | 114.7 (6) |
| Si(2)-P-C(5) | 109.8 (4) | P-Si(2)-C(10) | 107.8 (5) |
| Si(2)-P-C(6) | 107.5 (5) | P-Si(2)-C(11) | 104.1 (5) |
| C(5)-P-C(6) | 106.5 (6) | P-Si(2)-C(12) | 106.6 (5) |
| P-Si(1)-C(7) | 105.4 (4) | C(10)-Si(2)-C(11) | 113.3 (7) |
| P-Si(1)-C(8) | 107.6 (4) | C(10)-Si(2)-C(12) | 110.2 (6) |
| P-Si(1)-C(9) | 103.6 (4) | C(11)-Si(2)-C(12) | 114.1 (7) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

phosphonium cation and of the free phosphine in the equilibrium state under investigation and (ii) using the ratios of the intensity of the free Me$_3$Si–Co(CO)$_4$ $^1$H NMR signal and that of the exchanging Me$_3$Si groups with the relationship

$$Y/X = B/A$$

where $A$ and $B$ are the intensities of the exchanging Me$_3$Si groups and the free Me$_3$Si–Co(CO)$_4$, respectively. In all cases where appropriate data were available, the values of $X$ and $Y$ calculated by both methods are in good agreement.[13] This offers the most reliable proof that indeed, as stated before, Me$_3$Si–Co(CO)$_4$ does not participate in the exchange of Me$_3$Si groups according to eq 1 or 3.

**Me$_3$SiCo(CO)$_4$–Me$_3$SiPMe$_2$.** These compounds underwent reaction under experimental conditions similar to those of the Me$_3$SiCo(CO)$_4$–PMe$_3$ reaction and in an analogous manner to this reaction to produce the new silylphosphonium compound, [(Me$_3$Si)$_2$PMe$_2$]$^+$[Co(CO)$_4$]$^-$, viz.

$$\mathrm{Me_3SiCo(CO)_4 + Me_3SiPMe_2 \rightleftarrows [(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-} \quad (4)$$

Bis(trimethylsilyl)dimethylphosphonium tetracarbonylcobalt(I) can be sublimed in vacuo at temperatures higher than 60 °C, presumably by reversible dissociation into Me$_3$Si–Co(CO)$_4$ and Me$_3$SiPMe$_2$. It decomposes instantly in the presence of traces of air.

**Table V.** Bond Lengths (Å)[a] in [(Me$_3$Si)$_2$PMe$_2$]$^+$[Co(CO)$_4$]$^-$

| | | | | | |
|---|---|---|---|---|---|
| Co-C(1) | 1.73 (2) | P-C(5) | 1.83 (1) | Si(2)-C(11) | 1.88 (1) |
| Co-C(2) | 1.73 (1) | P-C(6) | 1.85 (1) | Si(2)-C(12) | 1.88 (1) |
| Co-C(3) | 1.69 (2) | Si(1)-C(7) | 1.87 (1) | C(1)-O(1) | 1.16 (2) |
| Co-C(4) | 1.73 (2) | Si(1)-C(8) | 1.87 (1) | C(2)-O(2) | 1.16 (2) |
| P-Si(1) | 2.294 (5) | Si(1)-C(9) | 1.87 (1) | C(3)-O(3) | 1.20 (2) |
| P-Si(2) | 2.288 (5) | Si(2)-C(10) | 1.86 (1) | C(4)-O(4) | 1.21 (2) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

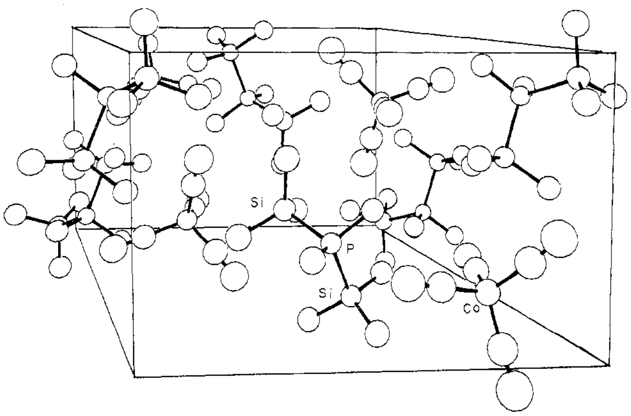

Figure 1. Unit cell of [(Me$_3$Si)$_2$PMe$_2$]$^+$[Co(CO)$_4$]$^-$.

A single-crystal x-ray study of the compound[11] confirmed its phosphonium salt structure, all bond angles about both the phosphorus and cobalt being very close to tetrahedral. Bond angle and bond length data are given in Tables IV and V, respectively, and a picture of the unit cell is given in Figure 1. The atoms corresponding to the numbers given in Tables IV and V are shown diagrammatically in Figure 2.

The Raman spectrum of the solid and the infrared spectrum in a Nujol mull (Table II) are both consistent with the postulated phosphonium salt structure and show strong CO stretching and bending (Raman) vibrations characteristic of the Co(CO)$_4^-$ ion. The ir spectrum shows the presence of a significant amount of free Me$_3$SiCo(CO)$_4$, larger than that observed for [Me$_3$SiPMe$_3$]$^+$[Co(CO)$_4$]$^-$. This also is presumably due to partial dissociation of that portion of the compound which dissolved in the Nujol.

The proton and $^{31}$P NMR spectral parameters of Me$_3$SiCo(CO)$_4$, Me$_3$SiPMe$_2$, and [(Me$_3$Si)$_2$PMe$_2$]$^+$[Co-

**Table VI.** Proton Chemical Shifts ($\tau$) of the $Me_3Si$ Group in $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$

| | +28 °C | | +20 °C | | 0 °C | | −20 °C | | −40 °C | | −60 °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concn[a] | A[b] | B[c] | A[b] | B[c] | A[b] | B[c] | A[b] | B[c] | A[b] | B[c] | A[b] | B[c] |
| 7 | 9.45 | *d* | 9.45 | *d* | 9.46 | *d* | 9.46 | *d* | *e* | *e* | *e* | *e* |
| 4.4 | 9.45 | 9.39[f] | 9.45 | 9.39[f] | 9.46 | 9.41[f] | 9.47 | 9.42[f] | 9.48 | *d* | *e* | *e* |
| 1.85 | 9.45 | 9.37[j] | 9.45 | 9.37[k] | 9.45 | 9.38[f] | 9.46 | 9.40[f] | 9.48 | 9.43[f] | 9.50 | *d* |
| 0.3 | 9.50 | 9.37[g] | 9.49 | 9.38[h] | 9.47 | 9.39[i] | 9.46 | 9.41[j] | 9.48 | 9.43[j] | 9.50 | 9.49[j] |

[a] Concentration as mole percent in $CH_2Cl_2$ solution. [b] $\tau$ of the exchanging $Me_3Si$ groups. [c] $\tau$ of the free $Me_3SiCo(CO)_4$. [d] Not observed. [e] Data not included; actual concentration significantly lower than stated because of crystallization of a large amount of the solute. [f] Approximately 2% of peak A. [g] Ratio $A/B = 4.5/1$. [h] Ratio $A/B = 6/1$. [i] Ratio $A/B = 8.2/1$. [j] Ratio $A/B = 15/1$. [k] Ratio $A/B = 19/1$.

**Table VII.** Proton Chemical Shifts ($\tau$) and $J_{H-C-P}$ Values of the $Me_2P$ Group in $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$

| | +28 °C | | +20 °C | | 0 °C | | −20 °C | | −40 °C | | −60 °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concn[a] | $\tau$ | J[b] | $\tau$ | J[b] | $\tau$ | J[b] | $\tau$ | J[b] | $\tau$ | J[b] | $\tau$ | J[b] |
| 7 | 8.42 | 9.85 | 8.42 | 9.9 | 8.42 | 10.1 | 8.43 | 10.1 | *c* | *c* | *c* | *c* |
| 4.4 | 8.42 | 9.75 | 8.42 | 9.9 | 8.42 | 10.0 | 8.43 | 10.2 | 8.43 | 10.3 | *c* | *c* |
| 1.85 | 8.45 | 8.9 | 8.45 | 9.1 | 8.43 | 9.75 | 8.42 | 10.05 | 8.43 | 10.2 | 8.46 | 10.2 |
| 0.3 | 8.59 | 6.1 | 8.56 | 6.95 | 8.48 | 8.8 | 8.45 | 9.8 | 8.45 | 10.2 | 8.46 | 10.2 |

[a] Concentration in mole percent in $CH_2Cl_2$ solution. [b] $J_{H-C-P}$ in hertz. [c] Data not included; actual concentration significantly lower than stated because of crystallization of a large amount of the solute.

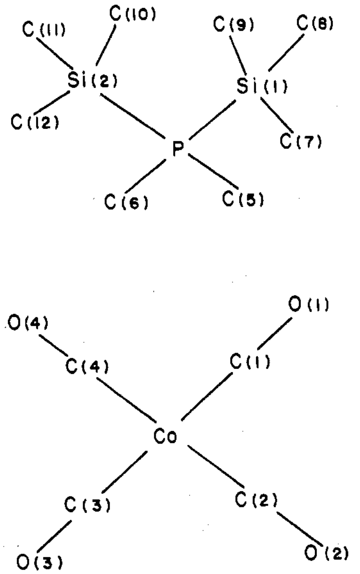

**Figure 2.** Designation of atoms in $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ for use in Tables I, IV, and V.

$(CO)_4]^-$ in $CH_2Cl_2$ solution are given in Table III. The changes in chemical shift of the $Me_3Si$ protons in $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ with change in concentration and with change in temperature are given in Table VI. The corresponding changes in chemical shift and $J_{H-C-P}$ of the $Me_2P$ protons are given in Table VII.

The NMR data for $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ and the change with changes of temperature and concentration are qualitatively identical with those previously discussed for $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ and differ from them primarily in that they show the compound begins to dissociate to an observable extent at higher concentrations and at lower temperatures than $[Me_3SiPMe_3]^+[Co(CO)_4]^-$. This observation is consistent with the infrared spectrum of the compound in a Nujol mull which indicates a larger amount of free $Me_3SiCo(CO)_4$ than in the case of $[Me_3SiPMe_3]^+[Co(CO)_4]^-$.

An obvious constitutional difference between this compound and $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ is that upon dissociation (eq 4), it will give two different compounds containing $Me_3Si$ groups, $Me_3SiCo(CO)_4$ and $Me_3SiPMe_2$, rather than $Me_3SiCo(CO)_4$ alone (eq 1). However, as can be seen from Tables VI and VII, signals for free $Me_3SiPMe_2$ could not be observed under those conditions where free $Me_3SiCo(CO)_4$ was present. This suggests that an exchange phenomenon analogous to that given by eq 2, i.e.

$$[(Me_3Si)_2P'Me_2]^+ + Me_3SiPMe_2 \rightleftarrows [(Me_3Si)_2PMe_2]^+ + Me_3SiP'Me_2 \qquad (5)$$

is responsible both for the absence of signals characteristic of free $Me_3SiPMe_2$ and for the absence of $J_{H-C-Si-P}$ coupling at the higher temperatures. The nonobservance of separate signals for free $Me_3SiPMe_2$ when $J_{H-C-Si-P}$ coupling was present is understandable, since such coupling could only be seen in the concentrated solution in $CH_2Cl_2$ and at low temperatures—conditions under which the equilibrium given by eq 4 lies very far to the right, the amount of free $Me_3SiPMe_2$ then present being negligible.

The $^1H$ NMR spectrum of a solution of the compound in toluene at 0 °C showed it was completely dissociated, but although $J_{H-C-P}$ was present and equal in magnitude to that found in free $Me_3SiPMe_2$, $J_{H-C-Si-P}$ was absent. This was consistent with the exchange process given in eq 5, but with the equilibrium lying so far to the left that none of the chemical shifts were noticeably altered from those of the pure starting materials.

It was not possible to examine the NMR spectrum of concentrated solutions at very low temperatures, since the concentration of species in solution was then reduced greatly because of precipitation of $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$. The same method of calculation used for the $[Me_3SiPMe_3]^+$-$[Co(CO)_4]^-$ system could be employed for determining the position of the equilibrium in $CH_2Cl_2$ solution according to eq 4. In this case the relationship

$$Y/(2X + Y) = B/A$$

is used for the intensities of the $Me_3Si$ groups, where $A$, $B$, $X$, and $Y$ refer to the same quantities as given previously. Again, both methods of calculation give results[14] that are in accord with the previously made statement that $Me_3Si-Co(CO)_4$ is not involved in the exchange process of the $Me_3Si$ groups in this system.

**$Me_3SiCo(CO)_4$–$(Me_3Si)_2PMe$.** $(Me_3Si)_2PMe$ underwent reaction with $Me_3SiCo(CO)_4$ under experimental conditions similar to those of the $PMe_3$–$Me_3SiPMe_2$ reaction and in an analogous manner to that reaction to produce the new silylphosphonium compound, $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$, viz.

$$Me_3SiCo(CO)_4 + (Me_3Si)_2PMe \rightleftarrows [(Me_3Si)_3PMe]^+[Co(CO)_4]^- \qquad (6)$$

Tris(trimethylsilyl)methylphosphonium tetracarbonylcobaltate(I) can be sublimed in vacuo at room temperature without noticeable decomposition. It decomposes instantly in the presence of traces of air. The Raman spectrum of the solid and the infrared spectrum in a Nujol mull (Table II) are both consistent with the postulated phosphonium salt structure and show strong CO stretching and bending (Raman) vibrations characteristics of the $Co(CO)_4^-$ ion. The infrared spectrum shows the presence of large amounts of free $Me_3SiCo(CO)_4$, larger than that observed for $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ and $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$. This is also presumably due to the dissociation of that portion of the compound which dissolved in Nujol.

The proton and $^{31}P$ NMR spectral parameters of $Me_3SiCo(CO)_4$, $(Me_3Si)_2PMe$, and $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$ are given in Table III.

The NMR data for $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$ and their change with changes of temperature and concentration are qualitatively identical with those previously discussed for $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ and $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ and differ from them primarily in that they show the compound begins to dissociate to an observable extent at higher concentrations and at lower temperatures. This is also consistent with the infrared spectrum of $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$ in Nujol, which indicates an even larger amount of free $Me_3SiCo(CO)_4$ than in the case of $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$.

As can be seen from eq 6, $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$, like $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$, will dissociate to produce two different species containing $Me_3Si$ groups—$Me_3SiCo(CO)_4$ and $(Me_3Si)_2PMe$. Experimentally, besides $Me_3SiCo(CO)_4$, only one $Me_3Si$ signal is observed and it is believed that the exchange process responsible is analogous to that given by eq 2 and 5, viz.

$$[(Me_3Si)_3P'Me]^+ + (Me_3Si)_2PMe \rightleftarrows [(Me_3Si)_3PMe]^+ + (Me_3Si)_2P'Me \qquad (7)$$

Unlike $[Me_3SiPMe_3]^+[Co(CO)_4]^-$ and $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$, no coupling between $Me_3Si$ protons and the phosphorus in the cation could be observed at low temperatures, due presumably to the lower stability of the compound. This is also consistent with the observation that the $^1H$ NMR spectrum of a solution of the compound in toluene at temperatures from +28 to −60 °C showed that it was completely dissociated into its constituents. Moreover, unlike $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$, the coupling between the $Me_3Si$ protons and the phosphorus in the $Me_3SiPMe_2$ formed on dissociation was present. Thus there is no sign whatsoever of an interaction between $Me_3SiCo(CO)_4$ and $(Me_3Si)_2PMe$ in toluene solution. On cooling, the ionic phosphonium salt precipitates; thus $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$ may be crystallized from the toluene solution. As with the two systems previously discussed, the two different methods of calculation of the position of the chemical equilibrium in $CH_2Cl_2$ solution, according to eq 6, show reasonable agreement.[15] The appropriate relationship for the intensities of the $Me_3Si$ groups is in this case

$$Y/(3X + 2Y) = B/A$$

where again $A$, $B$, $X$, and $Y$ refer to the same quantities described previously. This again proves that $Me_3Si{-}Co(CO)_4$ does not exchange with the silyl groups present in species such as those given in eq 7.

**$Me_3SiCo(CO)_4$–$(Me_3Si)_3P$.** No indication of an interaction between $Me_3SiCo(CO)_4$ and $(Me_3Si)_3P$ could be observed. Solutions in $CH_2Cl_2$ and toluene, even at −60 °C, showed no sign of an interaction between the compounds. On cooling, only $Me_3SiCo(CO)_4$ precipitates.

**$Me_3SiCo(CO)_4$–$Me_2PH$.** When a mixture of $Me_3SiCo(CO)_4$ and $Me_2PH$ in the presence of either $CH_2Cl_2$ or cyclohexane was warmed from liquid nitrogen temperature to room temperature, a slow complex reaction took place with evolution of CO. The NMR spectrum of the mixture showed that the reactants were only slowly consumed even at room temperature and that $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ was formed. When $Me_3SiCo(CO)_4$ and $Me_2PH$ were allowed to react in a 2:1 molar ratio in $C_6H_{12}$ at room temperature, an approximately 30% yield of $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$ was obtained according to

$$2Me_3SiCo(CO)_4 + Me_2PH \rightarrow [(Me_3Si)_2PMe_2]^+[Co(CO)_4]^- + HCo(CO)_4 \qquad (8)$$

**$Me_3SiCo(CO)_4$–$MePH_2$.** Equimolar quantities of $Me_3SiCo(CO)_4$ and $MePH_2$ underwent a slow complex reaction in cyclohexane solution during several days at room temperature with slow evolution of CO. After 3 days at room temperature large quantities of unreacted $Me_3SiCo(CO)_4$ were identified. Reaction took place very much faster in $CH_2Cl_2$ solution. None of the new and very broad signals in the $^1H$ NMR spectra of the mixture of products could be ascribed to any known compound or expected product.

**$Me_3SiCo(CO)_4$–$H_3SiPMe_2$.** On warming equimolar quantities of $Me_3SiCo(CO)_4$ and $H_3SiPMe_2$ in $CH_2Cl_2$ from liquid nitrogen to room temperature, a complex reaction occurred with low evolution of $SiH_4$ and CO, and after 3 days at room temperature 87% of the Si–H hydrogen and 65% of the $H_3Si$ silicon were recovered as $SiH_4$. The NMR signal of $Me_3SiCo(CO)_4$ disappeared rapidly while the system was still at low temperatures.

**$H_3SiCo(CO)_4$–$Me_3P$.** Equimolar quantities of $H_3SiCo(CO)_4$ and $Me_3P$ were mixed with $CH_2Cl_2$ at liquid nitrogen temperatures and then warmed with shaking to −78 °C. The $^1$NMR spectrum in the −60 to −20 °C temperature range was consistent with the presence of a four-coordinate phosphorus compound, although some unexplained low-field signals were also present. Removal of $CH_2Cl_2$ at −78 °C from the reaction mixture gave well-defined white crystals which could be sublimed at 0 °C, but only with considerable decomposition.

**Spectral Data for the Phosphonium Compounds.** The infrared and Raman spectra of the compounds are consistent with the phosphonium salt formulation. The symmetric Si–P stretching vibrations may be compared with those found in $Me_3SiPH_2$ (423 $cm^{-1}$), $(Me_3Si)_2PH$ (403 $cm^{-1}$), and $(Me_3Si)_3P$ (380 $cm^{-1}$) (Table II, footnote *c*.) It can be seen on comparing these values with the symmetric Si–P stretching vibrations in Table II that the values for the phosphonium cation are, in each case, somewhat lower than for the parent phosphine having the same number of attached $Me_3Si$ groups. It may be noted that each of the phosphonium compounds shows all of the strong Raman lines characteristic of the $Co(CO)_4^-$ ion. The splitting of the band at approximately 1880 $cm^{-1}$ is presumably due to the removal of the degeneracy of CO stretching vibrations because of the slight distortion of the $Co(CO)_4^-$ tetrahedron.

The $^{31}P$ NMR data of the phosphonium cations and the phosphine containing one less methyl group from which they may be regarded as being derived are also consistent with the phosphonium salt formulation. As can be seen from Table III, the phosphorus is considerably more deshielded in the phosphonium compounds to the extent of 90–110 ppm. It might also be noted that $J_{H-C-P}$ decreases with increasing $Me_3Si$ substitution at phosphorus. Both $J_{H-C-P}$ and $J_{P-Si-C-H}$ are much larger in the phosphonium cation than in the parent phosphine, as would be expected from the increased s-orbital participation in the tetracovalent phosphorus atom.

## Discussion

Transition metal carbonyls and phosphines generally react according to either

$$\mathrm{R{-}M(CO)}_x + \mathrm{PR'}_3 \rightarrow \mathrm{R{-}M(CO)}_{x-1}(\mathrm{PR'}_3) + \mathrm{CO} \qquad (9)$$

or

$$\mathrm{R{-}M(CO)}_x + \mathrm{PR'}_3 \rightarrow \mathrm{R{-}(CO){-}M(CO)}_{x-1}(\mathrm{PR'}_3) \qquad (10)$$

where R and R' are the same or different organic groups and M is a transition metal. The results of this investigation show that a third type of reaction is also possible when R is an electron-releasing group and the $\mathrm{M(CO)}_x^-$ ion is a good leaving group, viz.

$$\mathrm{R{-}M(CO)}_x + \mathrm{PR'}_3 \rightarrow [\mathrm{RPR'}_3]^+[\mathrm{M(CO)}_x]^- \qquad (11)$$

Thus $\mathrm{Me_3SiCo(CO)_4}$ and $\mathrm{Me_3P}$, $\mathrm{Me_3SiPMe_2}$, and $\mathrm{(Me_3Si)_2PMe}$ react rapidly below room temperature according to eq 11 to give the corresponding silylphosphonium compounds $[\mathrm{Me_3SiPMe_3}]^+[\mathrm{Co(CO)_4}]^-$, $[\mathrm{(Me_3Si)_2PMe_2}]^+[\mathrm{Co(CO)_4}]^-$, and $[\mathrm{(Me_3Si)_3PMe}]^+[\mathrm{Co(CO)_4}]^-$ as solid crystalline materials. Traces of CO were evolved in each of these reactions. No reaction occurred between $\mathrm{Me_3SiCo(CO)_4}$ and $\mathrm{(Me_3Si)_3P}$.

In all cases it was found that in $\mathrm{CH_2Cl_2}$ solution the phosphonium salts underwent reversible dissociation according to the equation

$$\mathrm{Me_3SiCo(CO)_4} + \mathrm{PR'R''R'''} \rightleftarrows [\mathrm{Me_3SiPR'R''R'''}]^+[\mathrm{Co(CO)_4}]^- \qquad (12)$$

and that at low temperatures and at higher concentrations the equilibrium lay essentially completely to the right. On either raising the temperature or diluting the solution, the equilibrium shifted to the left, as might be expected. As the basicity of the phosphine was decreased by adding the $\mathrm{Me_3Si}$ groups, the phosphonium salt became progressively more dissociated under comparable temperatures and concentration conditions. It was therefore not surprising to find that no sign of any phosphonium salt could be observed on mixing $\mathrm{Me_3SiCo(CO)_4}$ with $\mathrm{(Me_3Si)_3P}$. From steric considerations the existence of a $[\mathrm{(Me_3Si)_4P}]^+$ ion is significantly less favorable than for the other phosphonium compounds. The steric requirements of the $\mathrm{Me_3Si}$ group are indicated by the Si–P–Si bond angle of 114.6° in $[\mathrm{(Me_3Si)_2PMe_2}]^+[\mathrm{Co(CO)_4}]^-$ (see Table IV).

It should be stressed that constant limiting values for the $^1$H NMR data for all the isolable phosphonium compounds could be obtained in $\mathrm{CH_2Cl_2}$ solution such that an increase in concentration or a decrease in temperature brought about no further change in their values. This showed that under these conditions, which were existent for all the compounds at −20 °C and ion concentrations higher than 5 mol %, the phosphonium cations were not dissociated to any experimentally observable extent.

It appears that lattice energies in the solid compounds and solvation energies in the case of solutions of the compounds are significant factors in determining their stability to reversible dissociation. For example, the $^1$H NMR spectra of solutions of $[\mathrm{(Me_3Si)_2PMe_2}]^+[\mathrm{Co(CO)_4}]^-$ and $[\mathrm{(Me_3Si)_3PMe}]^+[\mathrm{Co(CO)_4}]^-$ in toluene showed they were completely dissociated under conditions where, with the more polar $\mathrm{CH_2Cl_2}$ solvent, most of the undissociated phosphonium cation would be present. This is also consistent with the qualitative observation that the infrared spectra of Nujol mulls of the compounds, in which the phosphonium compounds might be expected to have a slight solubility, showed the presence of increasing amounts of free $\mathrm{Me_3SiCo(CO)_4}$ as the number of $\mathrm{Me_3Si}$ groups on the phosphorus increased, even though Raman spectra of the solid compounds in sealed capillaries showed that free $\mathrm{Me_3SiCo(CO)_4}$ was absent.

When $\mathrm{CH_2Cl_2}$ solutions of the phosphonium salts of any concentration were held at room temperature for several days, a slow reaction took place, CO was evolved, and brown soluble compounds were formed in each case. It is believed that under these conditions a reaction between the free $\mathrm{Me_3SiCo(CO)_4}$ and phosphines analogous to that given by eq 9 was slowly taking place. These reactions occurred much faster in solutions of lower concentrations where the equilibrium given by eq 12 lay appreciably to the left. Evidence for the formation of the substitution products, according to eq 9, could be obtained from the NMR spectra, but the reaction was complicated by partial rearrangement or decomposition of the $\mathrm{Me_3Si{-}Co(CO)_3PR_3}$ compounds to $\mathrm{Me_3Si{-}O}$ derivatives. Rearrangements of this type have been observed previously.[16]

It was interesting to find that $\mathrm{Me_3SiCo(CO)_4}$ and $\mathrm{Me_2PH}$ did not react to give $[\mathrm{Me_3Si(H)PMe_2}]^+[\mathrm{Co(CO)_4}]^-$ but that $[\mathrm{(Me_3Si)_2PMe_2}]^+[\mathrm{Co(CO)_4}]^-$ was formed according to the overall reaction given by eq 8. It is well known[3] that the Si–Co bond in $\mathrm{Me_3SiCo(CO)_4}$ is readily cleaved even by very weak protonic acids and it seems likely, therefore, that the first reaction to occur involved the weakly protonic P–H hydrogen, viz.

$$\mathrm{Me_3SiCo(CO)_4} + \mathrm{Me_2PH} \rightarrow \mathrm{Me_3SiPMe_2} + \mathrm{HCo(CO)_4} \qquad (13)$$

It seems not unlikely that this reaction proceeded via $[\mathrm{Me_3Si(H)PMe_2}]^+[\mathrm{Co(CO)_4}]^-$, since it occurred very much more rapidly in $\mathrm{CH_2Cl_2}$, which we have shown facilitates phosphonium salt formation, than in nonpolar $\mathrm{C_6H_{12}}$ solution. This reaction is analogous to that between $\mathrm{Me_3SiCo(CO)_4}$ and $\mathrm{Me_2NH}$,[3,17] from which appreciable quantities of $\mathrm{Me_3SiNMe_2}$ can be isolated under appropriate conditions. The $\mathrm{Me_3SiPMe_2}$ formed according to eq 13 then presumably reacts with more $\mathrm{Me_3SiCo(CO)_4}$, according to eq 4, to give $[\mathrm{(Me_3Si)_2PMe_2}]^+[\mathrm{Co(CO)_4}]^-$. When $\mathrm{Me_3SiCo(CO)_4}$ was treated with $\mathrm{MePH_2}$, a slow, complex reaction took place and no products could be isolated or identified.

The reaction between $\mathrm{Me_3SiCo(CO)_4}$ and $\mathrm{H_3SiPMe_2}$ was also slow and complex and appeared to result ultimately in the randomization reaction

$$4\mathrm{H_3SiPMe_2} \rightarrow 3\mathrm{SiH_4} + \mathrm{Si(PMe_2)_4} \qquad (14)$$

with $\mathrm{Si(PMe_2)_4}$ and the intermediate disproportionation products reacting according to eq 9 to yield a complex mixture of substitution products. The rapid disappearance of the $\mathrm{Me_3SiCo(CO)_4}$ signal at low temperatures is consistent with the initial rapid formation of the corresponding phosphonium compound which then decomposed.

A preliminary experiment between $\mathrm{H_3SiCo(CO)_4}$ and $\mathrm{Me_3P}$ which was not studied in detail suggested that these compounds may have reacted to give $[\mathrm{H_3SiPMe_3}]^+[\mathrm{Co(CO)_4}]^-$, which appeared to decompose between 0 °C and room temperature yielding a complex mixture of volatile and nonvolatile decomposition products.

The bond angles and bond lengths resulting from the single-crystal x-ray study of $[\mathrm{(Me_3Si)_2PMe_2}]^+[\mathrm{Co(CO)_4}]^-$ are given in Tables IV and V, respectively. A diagrammatic representation of the structure for use in conjunction with Tables I, IV, and V is given in Figure 2 and the unit cell is shown in Figure 1. The C–Co–C bond angles in the $\mathrm{Co(CO)_4}^-$ ion are very close to tetrahedral and the Co–C–O bond angles are close to 180°. The Co–C bond lengths are slightly shorter than those in the $\mathrm{Co(CO)_4}^-$ ion in $\mathrm{Tl}^+[\mathrm{Co(CO)_4}]^-$ [18] and in the $C_{3v}$ molecule $\mathrm{Cl_3Si{-}Co(CO)_4}$.[19] The cobalt carbonyl anion and the phosphonium cation are so loosely packed that no interaction between the silicon atoms and the oxygen atoms can be present, nor is there any other interaction observed between atoms of different ions.

The bond angles about the phosphorus are approximately tetrahedral, as would be expected for a phosphonium cation. The fact that the Si–P–Si bond angle (114.6°) is somewhat greater than tetrahedral is consistent with some steric repulsion between the two bulky $\mathrm{Me_3Si}$ groups, as is also the observation that the $\mathrm{(H_3)C{-}P{-}C(H_3)}$ angle (106.5°) is less than tetrahedral. It is interesting to note that all the C–Si bond angles in both $\mathrm{Me_3Si}$ groups are significantly and consistently greater than tetrahedral by 2–5° and the C–P–Si angles are less than tetrahedral.

The Si–P bond length is of particular interest in view of the possible presence of (p → d)π bonding between lone-pair phosphorus electrons and silicon in silylphosphines. Since such bonding is impossible in silylphosphonium compounds, the Si–P bond length in silylphosphines should be less than that in silylphosphonium compounds if indeed silicon–phosphorus (p → d)π bonding is present in silylphosphines. Unfortunately, no x-ray structural data are available for any silylphosphines, although vapor-phase electron diffraction studies[20,21] of $(SiH_3)_3P$, $SiH_3PH_2$, $SiH_3PHMe$, and $SiH_3PMe_2$ show that the Si–P bond lengths do not vary significantly in the series and are close to 2.25 Å. The length of the silicon–phosphorus bonds found in this study, 2.291 Å, is slightly, although significantly, longer than those in the silylphosphines by approximately 0.05 Å; however, it cannot be used in conclusive (p → d)π bonding discussions, since it is not clear to what extent it will vary according to whether it is present in a neutral molecule or in a cation. There is no simple way to estimate the influence of the different hybridization states of the three- and four-bonding phosphorus atoms nor is the effect of the methyl substitution at the silicon atom completely understood. Also, it is not clear to what extent the differences in bond lengths may be caused by the different phases in which the electron diffractions and x-ray measurements were performed and by the different techniques employed.

It should be stressed that the reaction of phosphines with silylcobalt tetracarbonyls to give silylphosphonium compounds is not a general reaction of all phosphines or of all silylcobalt tetracarbonyls. The formation of a silylphosphonium compound appears to take place only if the resulting phosphonium ion would contain no electronegative group either on the phosphorus or on the silicon. Thus no phosphonium cation[2] is formed from $Me_3SiCo(CO)_4$ with $PX_3$ (X = F, Cl, $C_6H_5$) or from $Cl_3SiCo(CO)_4$ and $PX'_3$ (X' = F, $CH_3$). This is reasonable, since the presence of an electronegative group in the cation, either on the silicon or phosphorus, would tend to make electron loss to form a positive ion less favorable. In this respect it might be noted that a phenyl group, although not strongly electronegative, is more electronegative than a methyl group. In those cases where no phosphonium compound is formed, the expected type of reaction

$$R_3SiCo(CO)_4 + R'_3P \rightarrow R_3SiCo(CO)_3PR'_3 + CO \qquad (15)$$

occurs, often under somewhat more vigorous conditions than that required for phosphonium salt formation. Thus the following compounds may be isolated by the reaction of the appropriate carbonyl and phosphine: *trans*-$Cl_3SiCo(CO)_3PMe_3$,[1,2] *trans*-$Cl_3SiCo(CO)_3PEt_3$,[2,22] $Cl_3SiCo(CO)_3PF_3$,[2,23] and $Me_3SiCo(CO)_3(PPh_3)$.[1,2]

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**Registry No.** $[Me_3SiPMe_3]^+[Co(CO)_4]^-$, 28774-35-8; $[(Me_3Si)_2PMe_2]^+[Co(CO)_4]^-$, 57652-79-6; $[(Me_3Si)_3PMe]^+[Co(CO)_4]^-$, 57652-81-0; $Me_3SiCo(CO)_4$, 15693-82-0; $PMe_3$, 594-09-2; $Me_3SiPMe_2$, 26464-99-3; $(Me_3Si)_2PMe$, 18339-98-5; $HPMe_2$, 676-59-5; $H_2PMe$, 593-54-4; $H_3SiPMe_2$, 23685-81-6; $H_3SiCo(CO)_4$, 14652-62-1.

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(10) Analyses performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.
(11) The x-ray crystal structure analysis was carried out by the Molecular Structure Corp., College Station, Tex. 77840.
(12) Atomic scattering factors were taken from the "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.
(13) For example, at 20 °C (0.45 mol %), from (i) $J_{P-C-H}$, $X = 0.765$ and $Y = 0.235$, and from (ii) $Me_3Si$ ratio, $X = 0.80$ and $Y = 0.20$; at 0 °C (0.45 mol %), from (i) $J_{P-C-H}$, $X = 0.89$ and $Y = 0.11$, and, from (ii) $Me_3Si$ ratio, $X = 0.88$ and $Y = 0.12$.
(14) For example, at 20 °C (1.85 mol %), from (i) $J_{P-C-H}$, $X = 0.85$ and $Y = 0.15$, and, from (ii) $Me_3Si$ ratio, $X = 0.90$ and $Y = 0.10$; at 0° (0.3 mol %), from (i) $J_{P-C-H}$, $X = 0.82$ and $Y = 0.18$, and, from (ii) $Me_3Si$ ratio, $X = 0.78$ and $Y = 0.22$.
(15) For example, at 20 °C (3.5 mol %), from (i) $J_{P-C-H}$, $X = 0.62$ and $Y = 0.38$, and, from (ii) $Me_3Si$ ratio, $X = 0.68$ and $Y = 0.32$; at 0 °C (3.5 mol %), from (i) $J_{P-C-H}$, $X = 0.88$ and $Y = 0.12$, and, from (ii) $Me_3Si$ ratio, $X = 0.81$ and $Y = 0.19$.
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