ciation in the two compounds are virtually the same with the methylcyclopentadienyl derivative perhaps being slightly faster. The enthalpy of activation of the methylcyclopentadienyl complex also borders on being significantly lower than that for the cyclopentadienyl compound.

In an attempt to compare the relative labilities of CO and olefins when bonded to the $C_5H_5Mn(CO)_2$ moiety, the rate of CO replacement in $C_5H_5Mn(CO)_3$ was studied. In the nonpolar solvent, decalin, its reaction with $P(C_6H_5)_3$ was immeasurably slow even at temperatures as high as 140°. This unreactivity of $C_5H_5Mn(CO)_3$ is not due to its relatively high stability compared to $C_5H_5Mn(CO)_2P(C_6H_5)_3$ since the latter compound can be readily prepared by ultraviolet irradiation of a solution of $C_5H_5Mn(CO)_3$ and $P(C_6H_5)_3$. It therefore appears that CO is far more inert than any olefin in this system.

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Infrared Spectra and Structure of Silicon Cobalt Tetracarbonyls

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The high-resolution gas-phase infrared spectra of $Cl_3SiCo(CO)_4$ and of the new compounds $F_3SiCo(CO)_4$, $(CH_3)_3SiCo(CO)_4$, and $H_3CSiH_2Co(CO)_4$ have been examined in the CO stretching region. The spectra are consistent with trigonal-bipyramidal type molecular structures in which the silicon substituent occupies an axial position. The data obtained suggest that there may be significant (d → d)-π double-bond character in the silicon–cobalt bond in silicon cobalt tetracarbonyls.

A number of silicon cobalt tetracarbonyls of general formula $R_3SiCo(CO)_4$ (R = H, Cl, C_2H_5, H_3CO) have recently been reported in the literature.[3,4] The present investigation was carried out in order to gain further information concerning the structure of and the nature of bonding in substituted silyl cobalt tetracarbonyls. For this purpose the new compounds $F_3SiCo(CO)_4$, $H_3CSiH_2Co(CO)_4$, and $(H_3C)_3SiCo(CO)_4$ were synthesized.[5] It was considered particularly desirable to examine $F_3SiCo(CO)_4$ since, apart from the recently reported $H_3SiCo(CO)_4$,[4] it is the only silyl cobalt carbonyl for which there is an analogous carbon cobalt carbonyl, *viz.*, $F_3CCo(CO)_4$, whose structure has been examined by infrared techniques.

Experimental Section

The silyl derivatives were prepared from the corresponding silane and $Co_2(CO)_8$, according to the method of Chalk and Harrod.[3] High-resolution infrared spectra were obtained with a double-beam Perkin-Elmer 521 spectrophotometer (spectral slit width of approximately 1 cm^{-1} in the carbonyl stretching region, near 2000 cm^{-1}).

The samples were contained in gas cells having a 10-cm path length fitted with NaCl or KBr windows. In the high-resolution spectra in the carbonyl stretching region gas pressures ($\leqslant$ 1 mm) were adjusted so that the maximum absorption had a transmittance of approximately 20–30%. Absorption maxima were located with a reproducibility of 1 cm^{-1}.

Results

The infrared CO stretching vibrations observed in this investigation for $F_3SiCo(CO)_4$, $(CH_3)_3SiCo(CO)_4$, $H_3CSiH_2Co(CO)_4$, and $Cl_3SiCo(CO)_4$ are listed in Table I together with the previously reported values for $Cl_3SiCo(CO)_4$ (heptane solution) and $H_3CCo(CO)_4$. Not unexpectedly, some variation between the solution and gas-phase spectra of $Cl_3SiCo(CO)_4$ are observed. Values for compounds such as $F_3CCo(CO)_4$[6] which have not been examined in the gas phase are not included.

The ^{13}CO stretching vibrations were assigned on the basis of their relative intensities and their separation from the strongest, [E], band, in accordance with the Teller–Redlich rule and the natural abundance of the isotopes.[7] Using values of ^{12}CO and ^{13}CO vibrations given in the literature[8] for a number of transition metal carbonyl derivatives, a value of 0.9811 was calculated for the $\nu_{^{13}CO}/\nu_{^{12}CO}$ ratio. The $\nu_{^{13}CO}$ values given in Table I for the compounds studied in this investigation do not differ by more than 2 cm^{-1} from the values calculated using this ratio.

The infrared spectra of $Cl_3SiCo(CO)_4$, $F_3SiCo(CO)_4$, and $(CH_3)_3SiCo(CO)_4$ showed the presence of three ^{12}CO stretching bands in the carbonyl region. A spectrum of $Cl_3SiCo(CO)_4$, which is typical, is given in

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[2] This research was sponsored by AFOSR(SRC)-OAR, USAF Contract No. AF 49(638)-1519.

(3) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(4) B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 217 (1965).

(5) A. P. Hagen, S. K. Gondal, Y. L. Baay, and A. G. MacDiarmid, unpublished observations, 1965.

(6) W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch.*, **16b**, 229 (1961).

(7) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, p 164.

(8) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

TABLE I

GAS-PHASE CARBONYL STRETCHING VIBRATIONS FOR SELECTED SILICON AND CARBON COBALT TETRACARBONYLS

	$\nu^{12}CO$, cm^{-1}			$\nu^{13}CO$, cm^{-1}
Compound	A_1 (equatorial)	A_1 (axial)	E (equatorial)	E (equatorial)
$F_3SiCo(CO)_4$[a]	2128 (1.3)	2073 (3.4)	2049 (10)	2011 (0.5)
$Cl_3SiCo(CO)_4$[a]	2125 (2.1)	2071 (3.4)	2049 (10)	2011 (0.3)
$Cl_3SiCo(CO)_4$[b]	2120 s	2070 s	2044 vs, sh, 2030 vs	2000 wsh
$H_3CCo(CO)_4$[c]	2111 w	2045.9 m	2031.2 s	. . .
$H_3CSiH_2Co(CO)_4$[a]	2102 (3.9)	2043 (5.0)	2021 (10), 2015 (10)	1981 (0.6)
$(CH_3)_3SiCo(CO)_4$[a]	2100 (3.2)	2041 (5.0)	2009 (10)	1973 (0.9)

[a] Figures in parentheses following wavenumbers of certain peaks refer to the relative transmittance of peaks, assuming that the most intense peak in the carbonyl region has a transmittance of 10. [b] Reference 3. [c] L. Markó, G. Bor, G. Almaśy, and P. Szabo, *Brennstoff-Chem.*, **44,** 184 (1963).

Figure 1. The spectrum of $H_3CSiH_2Co(CO)_4$ was similar except that the E band appeared as a doublet. Considerable difficulty was experienced in obtaining $(CH_3)_3SiCo(CO)_4$ and $H_3CSiH_2Co(CO)_4$ completely free from traces of decomposition products. Peaks due to decomposition products were identified by permitting the sample to decompose slightly in the infrared cell. This process was hastened by occasionally freezing the sample in a portion of the cell and then allowing it to melt and evaporate.[5]

The infrared spectra of the three new compounds synthesized in this investigation were obtained down to 350 cm^{-1} and were found to be consistent with their molecular composition. Although a number of bands were observed in the 350–650-cm^{-1} region, it was not possible to assign these unambiguously to specific cobalt–carbon stretching and/or deformation modes.

Discussion

It is well known that many silyl compounds have different structures from their carbon analogs and/or exhibit unexpectedly large bond angles at certain atoms in the molecule;[9] for example, the heavy-atom skeleton of $(SiH_3)_3N$ is planar whereas that of $(CH_3)_3N$ is pyramidal.[9] These differences in structure have been ascribed to the possible presence of $(p \rightarrow d)-\pi$ bonding in the silyl compounds,[9] between lone-pair electrons on an atom attached to silicon and the empty 3d orbitals of silicon. It has been suggested that a somewhat analogous $(d \rightarrow d)-\pi$ bonding might be present in the Si–Co bond in the silicon cobalt tetracarbonyls.[3,4] The prime purpose of this investigation, therefore, was to gain information concerning the structure of silicon cobalt carbonyls since, if extensive $(d \rightarrow d)-\pi$ bonding were present in the Si–Co linkage, it might be suspected that this could cause silicon cobalt tetracarbonyls to exhibit a different structure from the analogous carbon compounds.

For $H_3CCo(CO)_4$[10] (gas phase, see Table I, and hexane solution) and for $F_3CCo(CO)_4$[6] (cyclohexane solution) the infrared evidence is consistent with C_{3v} symmetry for the $Co(CO)_4$ group for which three infrared-active ^{12}CO stretching modes ($A_1 + A_1 + E$) are observed. As can be seen from Table I, the infrared data

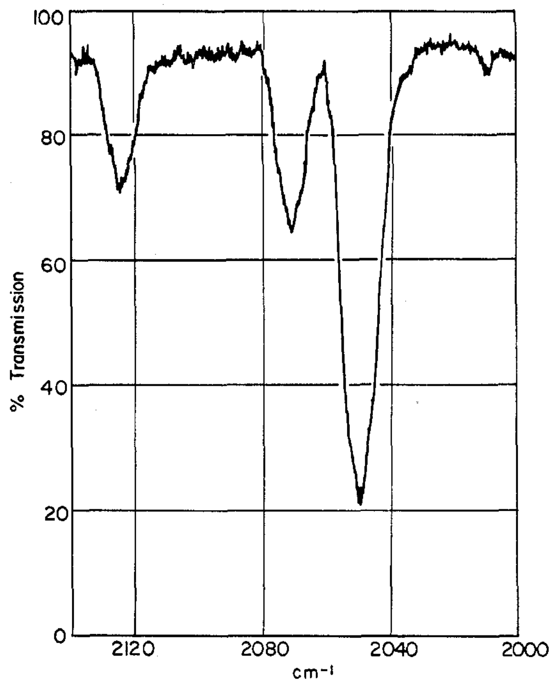

Figure 1.—Gas-phase infrared spectrum of trichlorosilyl cobalt tetracarbonyl.

listed for $Cl_3SiCo(CO)_4$, $F_3SiCo(CO)_4$, and $(CH_3)_3SiCo(CO)_4$ are also consistent with C_{3v} symmetry of the $Co(CO)_4$ groups in these compounds.[11] In the case of $H_3CSiH_2Co(CO)_4$ the degeneracy of the E band has been removed, presumably because of the unsymmetrical nature of the H_3CSiH_2 group.

If indeed $(d \rightarrow d)-\pi$ bonding is present in the Si–Co linkages in silicon cobalt tetracarbonyls, it apparently does not cause the symmetry of the $Co(CO)_4$ groups in analogous carbon and silicon cobalt tetracarbonyls to differ. It should be noted that if $(d \rightarrow d)-\pi$ bonding were present in the Si–Co bond, this would not cause hindered rotation at the Si–Co bond since the silicon 3d orbitals which are symmetrical about the bond can, in effect, form an infinite number of linear combinations. It can be seen (Figure 2A) that all of the CO groups are *cis* to each other in both the carbon and silicon cobalt carbonyls. It is possible that an alternative (C_{2v}) structure such as that shown in Figure

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(9) E. A. V. Ebsworth, *Intern. Ser. Monographs Inorg. Chem.*, **4,** 101 (1963); E. A. V. Ebsworth, *Chem. Commun.*, 530 (1966).

(10) L. Markó, G. Bor, G. Almaśy, and P. Szabo, *Brennstoff-Chem.*, **44,** 184 (1963).

(11) The ^{12}CO stretching bands for $H_3SiCo(CO)_4$ and their relative frequencies and intensities are similar to those observed for $Cl_3SiCo(CO)_4$, $F_3SiCo(CO)_4$, and $(CH_3)_3SiCo(CO)_4$: B. J. Aylett, private communication, April 1966.

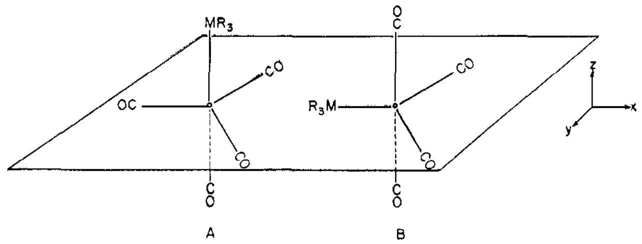

Figure 2.—*cis* and *trans* structures of $R_3MCo(CO)_4$ [M = C, Si].

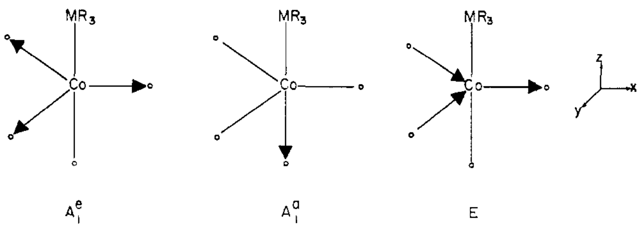

Figure 3.—The carbonyl stretching modes of $R_3MCo(CO)_4$ [M = C, Si]. Only one component of the E mode is shown.

2B is less energetically favorable owing to the fact that the two (strongly π-bonding) *trans*-CO groups are both competing for the same electrons in the cobalt d_{xz} and d_{yz} orbitals with which they have equally good overlap.

The assignment of the three observed ^{12}CO stretching vibrations was carried out using the method of oscillating dipoles.[12,13] Although all of the CO stretching vibrations must involve all four CO groups, the vibrations can be satisfactorily represented[12-14] by the motions depicted in Figure 3.

The vectorial sums of the oscillating dipoles for the $A_1^{\text{equatorial}}$, A_1^{axial} (hereafter denoted as A_1^e and A_1^a, respectively), and E modes in a C_{3v} model in which a central atom is joined to and is coplanar with three equatorial CO groups are 0.0, 1.0, and 2.0. These vectorial sums give relative energies of 0.0, 1.0, and 2.0 (the 0.0 band being the highest energy band in the series, the other bands falling 1.0 and 2.0 units, respectively, below the 0.0 band). The relative intensities of these bands are 0.0, 1.0, and 4.0, respectively. The assignments given in Table I are based on the observation that the relative energies and intensities of the ^{12}CO stretching modes observed agree, to a first approximation, with the calculated values. The fact that the A_1^e mode does not have zero intensity may be due to coupling between the two A_1 modes or to nonplanarity of the cobalt atom and the equatorial carbonyl groups. From steric factors alone, it seems highly likely that the latter effect will be important since the difference in size between the R_3Si group and the CO group *trans* to it would be expected to lead to significant distortion from planarity.

In view of the fact that the CO stretching vibration in metal carbonyls is very sensitive to changes in the extent of π overlap within the CO group,[15] it is of particular interest to examine the frequency of the A_1^a CO stretching mode relative to the frequencies of the A_1^e and E modes. Although all CO stretching modes would probably be affected by any π interaction between the R_3M group and the cobalt, it is the A_1^a mode which would be affected to the greatest extent because of the direct competition between the (axial) R_3M group and the axial CO for the electrons in the cobalt d_{xz} and d_{yz} orbitals. One convenient way of expressing the energy of the A_1^a mode relative to the energies of the A_1^e and E modes is by means of the quantity $(k_e - k_a)$, where k_e and k_a are the force constants for the equatorial and axial carbonyl groups, respectively. Using the symmetry coordinates as shown in Figure 3, the following secular equations are obtained if mixing of modes of the same symmetry is neglected.[16]

$$\lambda_{A_1^e} = (k_e + 2k_i)/\mu \tag{1}$$

$$\lambda_{A_1^a} = k_a/\mu \tag{2}$$

$$\lambda_E = (k_e - 2k_i)/\mu \tag{3}$$

In these relationships $\lambda = 0.588851 \times 10^{-6}\nu^2$ (ν in cm^{-1}), μ is the reduced mass of the carbonyl group in atomic weight units, and k_e, k_a, and k_i are expressed in mdynes/A.[17] The interaction constant, k_i, indicates the effect of the equatorial carbonyl groups upon each other during a vibration. The relationships $k_e = \mu(\lambda_{A_1^e} + \lambda_E)/2$ and $k_a = \mu\lambda_{A_1^a}$ result from eq 1–3.

Mixing of the A_1^e and A_1^a modes has been neglected, at least in the first instance, on the assumption that it will not differ greatly from compound to compound throughout the series. It can be seen from Table II that the $(k_e - k_a)$ values obtained for the silicon cobalt carbonyls are significantly smaller than the corresponding values for the carbon compounds. However, if such mixing is taken into consideration, then the magnitudes of the $(k_e - k_a)$ values for the silicon compounds relative to those of the carbon compounds would be even smaller. This is because the mixing contribution would actually be somewhat greater in the silicon compounds than in the carbon compounds since the A_1^e and A_1^a modes in the silicon compounds are closer in energy than the A_1^e and A_1^a modes in the carbon compounds.[18] Thus, if mixing of the A_1^e and A_1^a modes occurs, the $(k_e - k_a)$ values for all compounds given in Table II will be reduced in magnitude, but it is apparent that the differing extents of mixing of the A_1^e and A_1^a modes in the silicon and carbon compounds should bring about a larger reduction in the $(k_e - k_a)$ values for the silicon compounds. Hence the difference in magnitudes of the $(k_e - k_a)$ values for the carbon compounds as a group and the silicon compounds as a group will be enhanced. It can be seen from those compounds, the spectra of which were measured both in the gas phase and in solution ($H_3CCo(CO)_4$ and $HCo(CO)_4$), that the $(k_e - k_a)$ values are relatively insensitive to the phase in which the spectra are measured.

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(12) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

(13) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).

(14) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(15) S. F. A. Kettle, *Spectrochim. Acta*, **22**, 1388 (1966).

(16) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 59.

(18) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 216.

TABLE II

VALUES OF $(k_e - k_a)^a$ IN $RCo(CO)_4$

R	$10^2(k_e - k_a)$	R	$10^2(k_e - k_a)$
HCF_2CF_2[b]	48	C_6F_5[b]	35
$F_3C(CF_2)_5CF_2$[c]	46	$(H_3CO)_3Si$[h]	35
H_3C[d]	43	H_3CSiH_2[i]	30
H_3C[e]	43	F_3Si[i]	27
F_3C[f]	42	Cl_3Si[i]	27
F_3CCF_2[g]	42	$(C_6H_5)_3Si$[h]	27
H[d]	36	$(C_2H_5)_3Si$[h]	24
H[e]	36	$(CH_3)_3Si$[i]	24

[a] $(k_e - k_a)$ in mdynes/A. [b] Cyclohexane solution: J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 6519 (1965). [c] Nujol mull: W. Hieber and E. Lindner, *Chem. Ber.*, **95,** 2042 (1962). [d] Gas phase: ref 10. [e] Hexane solution: ref 10. [f] Cyclohexane solution: ref 6. [g] Carbon tetrachloride solution: reference in footnote *b*. [h] Heptane solution: ref 3. [i] Gas phase.

In those cases where the attached R_3M group has the potential capability of withdrawing electrons from the cobalt into its bonding orbitals by a π interaction (Figure 4A), the $A_1{}^a$ mode would be expected to fall at a relatively higher frequency [smaller $(k_e - k_a)$] than those cases where such an interaction does not occur (Figure 4B). The fact that the $(k_e - k_a)$ values for silicon compounds are indeed smaller than those for the carbon compounds (Table II) therefore strongly suggests that significant (d → d)–π bonding may be present in the silicon–cobalt linkage in all of the silicon cobalt carbonyls with the possible exception of $(CH_3O)_3SiCo(CO)_4$. In this particular compound strong (p → d)–π bonding between the oxygen of the CH_3O group and the silicon might decrease the π-acceptor properties of the silicon toward the cobalt electrons. In this respect it should be noted that no conclusive information is available regarding the relative magnitudes of (p → d)–π bonding between silicon and oxygen, fluorine, or chlorine, respectively,[9] although the above information would suggest that it may be greatest with oxygen.

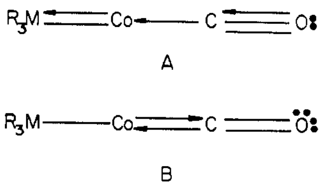
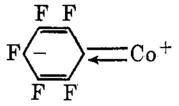


Figure 4.—Schematic representation of possible extreme forms of bonding in the $R_3MCo(CO)$ bond system. (For convenience only one CO group is shown as attached to the cobalt.)

The small value for $HCo(CO)_4$ could well be related to the fact that there may be a significant interaction between the hydrogen atom and the CO groups in this molecule.[19] The smaller value for $C_6F_5Co(CO)_4$ might be accounted for in terms of resonance contributions to the molecular structure of forms such as



which would tend to give higher $A_1{}^a$ CO stretching vibrations (see Figure 4) and hence a smaller $(k_e - k_a)$ value.[20]

Acknowledgment.—The authors are particularly indebted to Dr. Herbert D. Kaesz and also to Drs. Julian H. R. Clarke and Andrew Wojcicki for many helpful comments and suggestions concerning certain aspects of this investigation and to Mr. George M. J. Slusarczuk for obtaining the high-resolution spectra.

(19) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

(20) NOTE ADDED IN PROOF.—The authors are greatly indebted to Professor James A. Ibers and Dr. Ward T. Robinson, who have given them, since this paper was accepted for publication, a copy of their manuscript (presented at the American Crystallographic Association Annual Meeting, Atlanta, Ga., Jan 1967) on the X-ray crystal structure of $Cl_3SiCo(CO)_4$. This study shows that the $-Co(CO)_4$ group (and indeed the whole molecule) has essentially C_{3v} symmetry. The infrared and X-ray studies are, therefore, in agreement. Moreover, a Si–Co bond length of 2.254 A has been determined. In view of the uncertainty in assigning a reliable value for the covalent radius of cobalt in a compound such as this, it is difficult to state definitely whether or not the above Si–Co bond length suggests double-bond character in the linkage. However, it appears likely that the covalent radius of cobalt is not less than 1.22 A in view of the 1.243 A covalent radius for cobalt in CoH (L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 257) and the range of values 1.22 to 1.32 A for this radius found in fifteen assorted cobalt carbonyls [see P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967)]. If the radius for silicon of 1.15 A from Si_2Cl_6 [Y. Morino and E. Hirota, *J. Chem. Phys.*, **28**, 185 (1958)] is taken, this then gives a minimum calculated value for a single Si–Co bond of 2.37 A. The fact that this value is significantly more than the experimental Si–Co bond length could be interpreted as indicating some double-bond character in this linkage, as suggested by the infrared studies described in this paper.