Nature of the Bonding between Silicon and the Cobalt Tetracarbonyl Group in Silyl Cobalt Tetracarbonyls[1]

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Abstract: Molecular structure data from X-ray and electron diffraction studies, mass spectral data, and molecular orbital calculations are presented for selected compounds of the type R–Co(CO)$_4$ (R = silyl or substituted silyl group). These data are shown to be consistent with the presence of (i) partial [Co(3d,4p) $\rightarrow$ Si(3d)]π and [Co(3d) $\rightarrow$ Si(3p)]π double-bond character between the cobalt and the silicon and (ii) an intramolecular interaction between the equatorial carbonyl groups and the silicon, which could be responsible, at least in part, for the raising of the equatorial carbonyl groups out of the molecular plane towards the silyl group. It is postulated that analogous types of interactions might exist in a variety of other transition metal carbonyls and their derivatives.

A series of silicon cobalt tetracarbonyls of general formula R$_3$Si–Co(CO)$_4$ (R = H, F, Cl, organic groups) have been reported during recent years.[2–4] Infrared,[5,6] Raman,[7] electron diffraction,[8] and X-ray studies[9,10] on certain of these compounds show that they have trigonal bipyramidal configurations about the cobalt with the R$_3$Si group in an axial position. In this respect, they are similar to the analogous alkyl[11] and perfluoroalkyl cobalt tetracarbonyls, R–Co(CO)$_4$,[12–15] and to the parent compound, HCo(CO)$_4$.[16]

Several infrared studies of the carbonyl stretching region in silicon cobalt tetracarbonyls have led to the conclusion that there may be some partial (d$\rightarrow$d)π double-bond character in the silicon–cobalt bond due to overlap of filled 3d$_{zz}$ and 3d$_{yz}$ cobalt orbitals with empty 3d$_{zz}$ and 3d$_{yz}$ orbitals on the silicon.[5,11] Conclusions as to the extent of this interaction vary.[11,17] Infrared studies on other transition metal carbonyls containing group IV elements, such as silicon, germanium, or tin, have also suggested the possible presence of an analogous (d$\rightarrow$d)π partial double bond between the group IV element and the transition element.[10,18,19] Dipole moment[11] and nuclear quadrupole resonance[20] studies have also been carried out on some of these compounds and are not inconsistent with the bonding concepts described in the present paper.

In a previous publication,[5] we had interpreted the apparently short Si–Co bond length in Cl$_3$Si–Co(CO)$_4$, determined by X-ray methods, as indicating the possible presence of some (d$\rightarrow$d)π double-bond character in this linkage. Since then, structural data on new compounds have become available and we believe that these, together with older data, are consistent with the (d$\rightarrow$d)π bonding concept. Another intriguing structural feature in this series of molecules is the displacement of the equatorial carbonyl groups toward the silicon substituent. Data from X-ray, electron diffraction, mass spectra, and molecular orbital calculations are examined in this study in an attempt to understand the factors which contribute to the bonding between silicon and the –Co(CO)$_4$ group in cobalt tetracarbonyls.

Results and Discussion

I. Multiple Bonding in the Si–Transition Metal Bond.

In determining whether a given group IV element–transition element bond is shorter than that expected for a single bond, as would be the case if significant (d$\rightarrow$d)π bonding were present in the linkage, an estimate of the hypothetical single bond length must first be made.

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Table I. Experimental and Calculated Group IV Element–Transition Element Bond Lengths

Compound	Exptl length, Å	Calcd length,[m] Å	Contraction,[m] Å
trans-HCF$_2$CF$_2$Co(CO)$_3$P(C$_6$H$_5$)$_3$[a]	1.95	2.10	0.15
H$_3$Si–Co(CO)$_4$[b]	2.38	2.49	0.11
F$_3$Si–Co(CO)$_4$[c]	2.23	2.48	0.25
Cl$_3$Si–Co(CO)$_4$[d]	2.25	2.48	0.23
(*cis*-CFH=CF)–Mn(CO)$_5$[e]	1.95	2.10[k] (2.19)	0.15 (0.24)
(CH$_3$)$_3$Si–Mn(CO)$_5$[f]	2.50	2.54 (2.63)	0.04 (0.13)
(C$_6$H$_5$)$_3$Ge–Mn(CO)$_5$[g]	2.53	2.57[l] (2.66)	0.04 (0.13)
(CH$_3$)$_3$Sn–Mn(CO)$_5$[h]	2.67	2.76 (2.85)	0.09 (0.18)
(C$_6$H$_5$)$_3$Sn–Mn(CO)$_5$[i]	2.67	2.76 (2.85)	0.09 (0.18)
trans-(C$_6$H$_5$)$_3$Sn–Mn(CO)$_4$P(C$_6$H$_5$)$_3$[j]	2.63	2.76 (2.85)	0.13 (0.22)

[a] Reference 43. [b] Reference 8. [c] Reference 10. [d] Reference 9. [e] Reference 61. [f] R. S. Hamilton and E. R. Corey, Abstracts of the Inorganic Division of the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. 025. [g] Reference 53. [h] R. F. Bryan, *J. Chem. Soc.*, *A*, 696 (1968). [i] H. P. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966). [j] R. F. Bryan, *J. Chem. Soc.*, *A*, 172 (1967). [k] A radius of 0.73 Å for sp^2-hybridized carbon was used: H. A. Bent, *J. Chem. Educ.*, **37**, 616 (1960). [l] A value of 1.20 Å for the covalent radius of germanium was obtained from the Ge–Ge bond length in Ge$_2$H$_6$: L. Pauling, A. W. Laubengayer, and J. L. Hoard, *J. Amer. Chem. Soc.*, **60**, 1605 (1938). [m] Values in parentheses were calculated using a manganese radius of 1.46 Å. Adjacent values not in parentheses were calculated using a 1.37-Å radius for manganese.

It appears likely that the single bond covalent radius of cobalt in R$_3$Si–Co(CO)$_4$ is not less than 1.22 Å. A cobalt radius of 1.243 Å has been reported in CoH[21] while 1.32 Å has been found for cobalt in the pentacoordinate cobalt compound Co[(CH$_3$)$_2$N(CH$_2$)$_2$NCH$_3$-(CH$_2$)$_2$N(CH$_3$)$_2$]Cl$_2$,[22] when the usual value for the covalent radius of chlorine (0.99 Å)[21] is subtracted from the experimental Co–Cl bond distance. An X-ray study gives a value of 1.66 Å for the H–Co bond in the trigonal bipyramidal molecule, HCo[P(C$_6$H$_5$)$_3$]$_3$N$_2$.[23] Using 0.32 Å for the radius of hydrogen, 1.34 Å is obtained for the radius of cobalt. Values of the cobalt radius ranging from 1.22 to 1.32 Å have been found in 16 assorted cobalt carbonyl complexes.[24,25] In addition, values of 1.331 and 1.335 Å for the cobalt radius have been obtained from the Co–Co distance in [Co(CO)$_3$P(*n*-C$_4$H$_9$)$_3$]$_2$.[26,27] From studies on [Co(CNCH$_3$)$_5$]$^+$ and [Co(CNCH$_3$)$_5$]$_2$$^{4+}$, Cotton, *et al.*,[28] state that the cobalt radius is expected to be approximately 1.38 Å and certainly not less than 1.23 Å. It therefore seems likely that the radius which should be assigned to cobalt in compounds of the type R–Co(CO)$_4$ is probably close to the 1.33-Å value which is used for estimating the Si–Co single bond length in Table I.

Although the use of 1.46 Å for the single-bond covalent radius of manganese in compounds such as R$_3$Si–Mn(CO)$_5$ has been recommended by Doedens and Dahl,[29] the 1.31-[30] and 1.38-Å[31] radii for manganese obtained from neutron diffraction studies on H–Mn(CO)$_5$ and X-ray studies on Cl–Mn(CO)$_5$, respectively, suggest a smaller value. A preliminary C–Mn distance of 2.13 Å in H$_3$C–Mn(CO)$_5$ suggests a manganese radius of 1.36 Å; however, the structure is disordered and has not

allowed an accurate determination of this bond length.[32] It is difficult to decide on an appropriate radius to use for manganese in calculating bond lengths in compounds of this type; hence, values of 1.46 and also 1.37 Å are used for the calculations in Table I.

The radii used for M (M = group IV element) in R$_3$M–Co(CO)$_4$ were obtained, where possible, by halving the M–M distance in appropriate species. Values obtained in this manner were (Å): 1.16 ± 0.01 (H$_3$Si–);[33] 1.15 ± 0.05 (Cl$_3$Si–);[34] 1.17 ± 0.10 [(CH$_3$)$_3$-Si–].[35] No Si–Si bond length data are available for Si$_2$F$_6$; however, in view of the relative insensitivity of the radius of silicon to changes in the substituent on silicon, as evidenced from the Si$_2$H$_6$, Si$_2$Cl$_6$, and Si$_2$(CH$_3$)$_6$ data, it would seem that the radius of silicon in Si$_2$F$_6$ is not far removed from 1.15 Å. The radius for tin (1.39 Å) was taken as half the tin–tin distance in [(C$_6$H$_5$)$_2$Sn]$_6$.[36]

Experimental C–Co, Si–Co, C–Mn, Si–Mn, Ge–Mn, and Sn–Mn bond lengths, together with the values estimated for a single covalent bond, and corresponding contractions, are given in Table I. All experimental values are based on single crystal X-ray studies, except that for H$_3$Si–Co(CO)$_4$, which was determined on a gaseous sample (electron diffraction).[9] It might be noted that the contractions are of approximately the same magnitude as that (~0.2 Å) observed between the single-bond and double-bond length in H$_3$C–CH$_3$ and H$_2$C=CH$_2$, respectively; however, in the hydrocarbon case, the contraction is approximately 13%, whereas with the longer bonds in the transition metal species the contraction is never greater than 10%.

It is difficult to ascertain the extent to which these contractions are caused by the amount of ionic character in the bonds or by d-orbital contraction in the cobalt, at least in the case where the substituent has a relatively high electronegativity.[37] Allred and Rochow electronegativities[38] for the elements (Si = 1.74, Sn = 1.72,

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Co = 1.70, Mn = 1.60) suggest that the ionic character is probably small. The increase in contractions in the series $R_3Si-Co(CO)_4$ on proceeding from R = H to R = Cl to R = F is qualitatively consistent with an increase in ionic character in the Si–Co bond as well as with an increase in π bond character in this linkage due to lowering of the energy of the silicon 3d orbitals by the electronegative halogen atoms. However, as pointed out by Robiette, et al.,[8] the contraction in bond lengths of this type is more likely to be due to π-bonding effects in view of the relative insensitivity of Si–H and C–H bond lengths to change in electronegativity of other substituents on the carbon or silicon.[39] Furthermore, the Cl_3Si- and F_3Si- groups would be expected to have significantly different electronegativities, and yet the contractions in the Si–Co bond in these two compounds (see Table I) are almost identical (0.23 and 0.25 Å, respectively). Mass spectral appearance potential studies for $R_3Si-Co(CO)_4$ (R = F, Cl) have been interpreted as indicating relatively strong Si–Co bonding. These results are consistent with the presence of Co–Si multiple bonding.

It has been suggested[40-42] that in certain perfluoroalkyl derivatives of the transition metal carbonyls, there may be some double-bond character in the carbon-transition metal bond due to a partial overlap of filled d orbitals of appropriate symmetry on the transition metal with the lowest energy antibonding orbitals on the carbon. Evidence for this partial double-bond character has resulted in part from X-ray data, where the experimental bond length has been found to be shorter than the calculated value. For example, the experimental C–Co bond length in $trans$-$HCF_2CF_2-Co(CO)_3P(C_6H_5)_3$ (1.95 Å) is 0.15 Å shorter than the calculated value of 2.10 Å, using 1.33 Å as the radius for Co.[43] It is unfortunate that structural data on simple alkyl[32] transition metal carbonyls, analogous to that reported for the compounds discussed here, are not available; this is probably due, in many cases, to the smaller thermal stability of the carbon compounds.

The data in Table I suggest that similar interactions may be present in the manganese pentacarbonyl derivatives, although uncertainty in assigning a reliable value to the single-bond radius for manganese reduces the significance of the conclusions.

Molecular orbital calculations have been carried out on $F_3Si-Co(CO)_4$ and $Cl_3Si-Co(CO)_4$ in order to examine in part the types of interactions that can contribute to the Co–Si bonding. The extended Hückel theory (EHT) calculations were accomplished using the Hoffman program[44] modified for charge iterative adjustment of orbital energies and Slater exponents[45-48]

(Table II). The results of these calculations and a description of the procedure are found in Tables II, III, and IV.[49] Table III is particularly important in examining the Co–Si bonding, for it contains the calculated overlap energies for all overlapping orbital pairs on cobalt and silicon. The overlap energy can be thought of as the molecular energy term associated with bonding. The results in Table III show that this MO procedure predicts that σ bonding accounts for about 84% of the Co–Si bonding in $F_3Si-Co(CO)_4$, and that interactions using the silicon 3s and $3p_z$ orbitals are responsible for approximately 95% of the σ bonding energy, while the $3d_{z^2}$ contributes only approximately 5%. The two principal Co–Si π interactions are cobalt $3d_{xz,yz}$, silicon $3d_{xz,yz}(d\rightarrow d)\pi$, and cobalt $3d_{xz,yz}$, silicon $3p_{x,y}(d\rightarrow\sigma^*)\pi$, which respectively account for about 8 and 6% of the total Co–Si bonding. This calculational procedure thus predicts relatively small yet significant Co–Si π bonding.

Table II. Atom–Atom Net Overlap Populations[49] from EHT Calculations[a-c]

	$H-Co(CO)_4^{d,e}$ (R = H)	$F_3Si-Co(CO)_4^d$ (R = Si)	$Cl_3Si-Co(CO)_4^d$ (R = Si)
R–Co	0.353	0.293	0.187
$3(R-C_{eq})$	0.128	0.303	0.254
$3(R-O_{eq})$	−0.014	−0.023	−0.028
$Co-C_{eq}$	0.495	0.488	0.496
$Co-O_{eq}$	−0.129	−0.127	−0.132
$Co-C_{ax}$	0.434	0.441	0.431
$Co-O_{ax}$	−0.124	−0.124	−0.130
$3(C_{ax}-C_{eq})$	0.085	0.092	0.097
$3(O_{ax}-O_{eq})$	0.000	0.000	0.000
$3(C_{ax}-O_{eq})$	−0.006	−0.006	−0.007
$3(C_{eq}-O_{ax})$	−0.006	−0.007	−0.007
$C_{ax}-O_{ax}$	1.391	1.391	1.388
$C_{eq}-O_{eq}$	1.363	1.354	1.350

[a] Positive overlap populations are bonding; negative values are antibonding. [b] All input VSIP were taken from ref 46 except cobalt 4s = −7.75, 4p = −4.60, 3d = −9.50, and silicon 3d = −2.50 eV. All input orbital exponents were taken from ref 47 except silicon 3d (ϵ 1.302, ref 48) and cobalt 4s (ϵ 1.400), 4p (ϵ 1.250), and 3d (ϵ 3.250). The VSIP were varied with charge by the procedure VSIP = $VSIP^0$ − 0.15B(charge), where the definition and values for B are given in ref 46. The Slater exponents are varied with charge by the procedure $\epsilon = \epsilon^0 + 0.35/n$(charge). Off-diagonal elements are approximated using the Wolfsberg–Helmholz approximation. [c] The coordinate system is shown in Figure 1 with the R–Co bond lying along the z axis. [d] The coordinates for the $Co(CO)_4$ fragment have been held constant for the three molecules and correspond to the observed structure in $Cl_3Si-Co(CO)_4$ (ref 10) (ref 9) which differs only slightly from that in $F_3Si-Co(CO)_4$ (ref 10) and is probably close to that in $H-Co(CO)_4$ (ref 9). The $SiCl_3$ and SiF_3 structural parameters are from ref 9 and 10. [e] The H–Co distance is taken as 1.60 Å.

Analogous calculations for $Cl_3Si-Co(CO)_4$ show significantly less π interaction in the Si–Co bond, σ bonding accounting for about 97% of the bonding. Again, most of the σ bonding involves interactions using the silicon 3s and $3p_z$ orbitals. The π bonding involving the silicon $3d_{xz,yz}$ and cobalt $3d_{xz,yz}$ orbitals is comparable to that in $F_3Si-Co(CO)_4$; the very much smaller total π bonding in $Cl_3Si-Co(CO)_4$ is caused by a strong antibonding interaction between the silicon $3p_{x,y}$ and the cobalt $4p_{x,y}$ orbitals.

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Table III. Overlap Energies[49] for the Si-Co Interaction in X₃Si-Co(CO)₄[a] from EHT Calculations

Si	Co	Overlap energy, eV F₃Si-Co(CO)₄	Cl₃Si-Co(CO)₄
3s	4s	-0.0516 ⎫	+0.0120 ⎫
	4p_z	-0.2839 ⎬ -0.5903	-0.0278 ⎬ -0.2065
	3d_z²	-0.2548 ⎭	-0.1907 ⎭
3p_z	4s	-0.2461 ⎫	-0.2302 ⎫
	4p_z	-0.5422 ⎬ -1.2003	-0.4722 ⎬ -1.0586
	3d_z²	-0.4120 ⎭	-0.3560 ⎭
3d_z²	4s	-0.0011 ⎫	+0.0059 ⎫
	4p_z	-0.0154 ⎬ -0.0900	-0.0105 ⎬ -0.0579
	3d_z²	-0.0735 ⎭	-0.0533 ⎭
Total σ overlap energies		-1.8806	-1.3230
3p_x,y	3d_zz,yz	-0.1326 ⎫	-0.0742 ⎫
	4p_x,y	-0.0035 ⎭ -0.1361	+0.1571 ⎭ +0.0829
3d_zz,yz	4p_x,y	-0.0502 ⎫	-0.0058 ⎫
	3d_zz,yz	-0.1732 ⎭ -0.2234	-0.1128 ⎭ -0.1186
Total π overlap energies		-0.3595	-0.0357

a A negative sign indicates a bonding interaction.

Table IV. Overlap Energies for Silicon-Equatorial Carbon Interactions from EHT Calculations

Si	C	F₃Si-Co(CO)₄	Cl₃Si-Co(CO)₄
3s	2s	-0.131 ⎫	-0.109 ⎫
	2p_z	-0.556 ⎬ -0.800	-0.492 ⎬ -0.681
	2p_x,y	-0.113 ⎭	-0.080 ⎭
3p_z	2s	-0.197 ⎫	-0.293 ⎫
	2p_z	-0.554 ⎬ -0.981	-0.547 ⎬ -1.133
	2p_x,y	-0.230 ⎭	-0.293 ⎭
3p_x,y	2s	-0.293 ⎫	-0.222 ⎫
	2p_z	-0.245 ⎬ -0.683	-0.224 ⎬ -0.526
	2p_x,y	-0.145 ⎭	-0.080 ⎭
3d_zz,yz	2s	-0.161 ⎫	+0.015 ⎫
	2p_z	-0.160 ⎬ -0.447	-0.102 ⎬ -0.120
	2p_xy	-0.126 ⎭	-0.033 ⎭
3d_xy,x²-y²	2s	-0.065 ⎫	-0.035 ⎫
	2p_z	-0.044 ⎬ -0.104	-0.023 ⎬ -0.049
	2p_xy	+0.005 ⎭	+0.009 ⎭
3d_z²	2s	+0.018 ⎫	+0.030 ⎫
	2p_z	-0.003 ⎬ +0.010	-0.002 ⎬ +0.030
	2p_xy	-0.005 ⎭	+0.002 ⎭

With respect to the (d→σ*)π interaction discussed in the previous paragraph, it is interesting to find that the Si-F stretching frequencies in F₃Si-Co(CO)₄[50] support this (d→σ*)π-type of interaction. Such an interaction, if present, would be expected to weaken the Si-F bond and hence to reduce its stretching frequencies. In F₃Si-Co(CO)₄, the E Si-F stretching band falls at 940 cm⁻¹ and the A₁ band at 825 cm⁻¹. The weighted average (2E + A₁)/3, 901 cm⁻¹, is approximately 50 cm⁻¹ less than that in SiF₃X (X = F, H, CH₃, (CH₃)₃SiO, (CH₃)₂N, etc.).[51] A similar, although somewhat greater reduction in C-F stretching frequencies in per-

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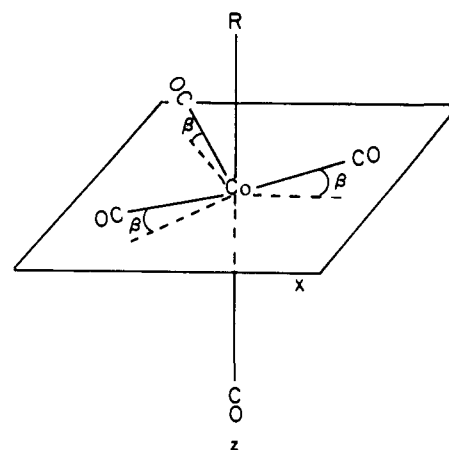
Figure 1. Diagrammatic representation of compounds of general formula R-Co(CO)₄.

fluoroalkyl transition metal carbonyl derivatives has been interpreted in terms of partial (d→σ*)π double-bond character in the C-metal bond.[42,52]

II. Direct Interaction between Si and the Equatorial CO Groups. The parent compound, HCo(CO)₄, for the series of compounds with general formula R-Co(CO)₄ has been shown by gas phase infrared studies to have a trigonal bipyramidal (C₃ᵥ) structure in which the equatorial carbonyl groups are displaced toward the hydrogen[16] (Figure 1). Similarly, the equatorial carbonyl groups in R₃Si-Co(CO)₄ (R = H[8], Cl[9], F[10]) are displaced toward the silicon. The displacement of the equatorial carbonyl groups toward the substituent also occurs with other cobalt tetracarbonyls such as (C₆H₅)₃-PAu-Co(CO)₄,[53] Hg[Co(CO)₄]₂,[54] Hg[Co(CO)₃P-(C₂H₅)₃]₂,[26] and [Co(CO)₃P(n-C₄H₉)₃]₂.[26,27] A compilation of the values for this equatorial carbonyl displacement in group IV element-transition metal carbonyls is given in Table V.

Table V. Out-of-Plane Displacements of Equatorial Carbonyl Groups in Group IV Element-Transition Metal Carbonyls

Compound	Average R-M-CO_eq bond angle, deg	Displacement, β° [a]
trans-HCF₂CF₂-Co(CO)₃P(C₆H₅)₃[b]	88.4	1.6
H₃Si-Co(CO)₄[c]	81.7	8.3
F₃Si-Co(CO)₄[d]	85.4	4.6
Cl₃Si-Co(CO)₄[e]	85.2	4.8
(cis-CFH=CF)-Mn(CO)₅[f]	86	4
(CH₃)₃Si-Mn(CO)₅[g]	84.5	5.5
(CH₃)₃Sn-Mn(CO)₅[h]	84.4	5.6
(C₆H₅)₃Sn-Mn(CO)₅[i]	86.7	3.3
trans-(C₆H₅)₃Sn-Mn(CO)₄P(C₆H₅)₃[j]	85.7	4.3

a β is the angle defined in Figures 1 and 2. b Reference 43. c Reference 8. d Reference 10. e Reference 9. f Reference 61. g R. S. Hamilton and E. R. Corey, Abstracts of the Inorganic Division of the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. 025. h R. F. Bryan, J. Chem. Soc., A, 696 (1968). i H. P. Weber and R. F. Bryan, Chem. Commun., 443 (1966). j R. F. Bryan, J. Chem. Soc., A, 172 (1967).

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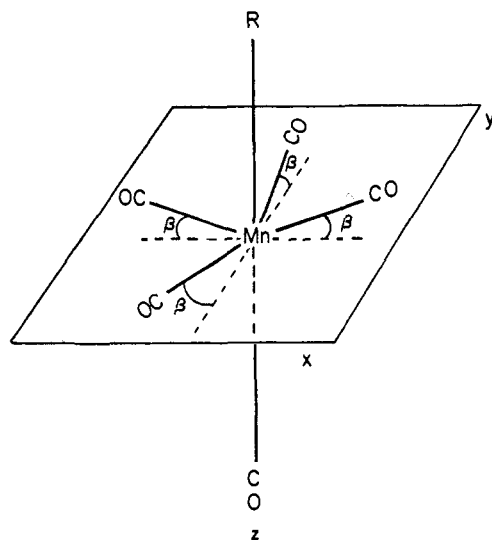Figure 2. Diagrammatic representation of compounds of general formula R–Mn(CO)₅.

Several factors which may contribute to this experimentally observed displacement are: (i) intermolecular interactions in the crystal, (ii) unequal steric requirements of the substituent and the axial carbonyl group, (iii) unequal π interactions of the cobalt with the substituent and with the axial carbonyl group, or (iv) a direct intermolecular bonding interaction between the axial substituent and the equatorial carbonyl groups.

i. The magnitude and general occurrence of these carbonyl displacements toward the substituent are ample evidence that they are *not* simply due to intermolecular interactions in the crystal (Table V). This viewpoint is supported by the presence of this structural feature in gas phase studies on H_3Si–Co(CO)₄.[8]

ii. The bending of the equatorial carbonyl groups toward the hydrogen in HCo(CO)₄ is qualitatively consistent with simple steric arguments, the axial carbonyl group having greater steric requirements than the hydrogen *trans* to it. However, in many other R–Co(CO)₄ species, it is difficult to determine whether R, the substituent, or the carbonyl group *trans* to it, has the greater steric requirement. The use of van der Waals radii to estimate steric requirements for these axial groups do not show definitely whether the equatorial carbonyl groups should be bent toward or away from the axial substituent. For the purpose of the present discussion, it will be assumed that steric effects alone will cause the cobalt and the equatorial carbonyl groups to be approximately coplanar. It should be noted that rough calculations based on van der Waals radii do show that the distortion of the equatorial carbonyl groups toward the substituent is definitely unfavorable.

The R–C_{eq} and C_{ax}–C_{eq} distances are both less than the sum of the van der Waals radii of the atoms concerned. Hence an interaction—either bonding or antibonding—might be expected. It may be of significance to note that EHT MO calculations suggest that the net interaction between the axial and the equatorial carbonyl groups is actually bonding (attractive) rather than antibonding (repulsive). The EHT model is not the best MO model for examining interligand repulsions, for it does not explicitly contain electronic re-

pulsion integrals. Instead, positive and negative overlap populations function respectively as the bonding (attractive) and antibonding (repulsion) contributions. The MO calculation result is that there is a net positive (bonding) overlap population between the axial and the equatorial carbons of the carbonyl groups (Table II).

iii. It has been suggested from symmetry arguments[55] that the out-of-plane displacements of the equatorial carbonyl groups could be caused by a difference in π acceptor capacity of the substituent as compared to the axial carbonyl groups, the equatorial carbonyl groups being bent toward the weaker π acceptor.

iv. Although the interaction described in part iii may account, at least in part, for the displacement of the equatorial carbonyl groups in certain compounds, we believe that an intramolecular bonding interaction between the substituent and the equatorial carbonyl groups may be very important in many cases. Orbital overlap considerations[56–59] have suggested that an interaction of this type occurs in HCo(CO)₄, the parent compound of these species. The results of our molecular orbital calculations on HCo(CO)₄ are consistent with the presence of a significant bonding interaction between the hydrogen and the equatorial carbonyl groups (Table II). The question now arises as to whether similar interactions can be expected for other axial substituents. The average Si–C_{eq} intramolecular distances in H_3Si–Co(CO)₄, Cl_3Si–Co(CO)₄, and F_3Si–Co(CO)₄ are 2.77, 2.75, and 2.74 Å, respectively. These values are less than the sum of the van der Waals radii of silicon and carbon (3.54 Å), but are greater than the sum of the covalent radii of these atoms (1.94 Å). These data, although consistent with a direct Si–C interaction, cannot be regarded as supporting evidence for such an interaction, since atoms which are attached to the same central element in *cis* positions approach closer to each other than the sum of their van der Waals radii. Even though the experimental Si–Co bond lengths vary from 2.23 to 2.38 Å in the above compounds, the average Si–C_{eq} intramolecular distances of 2.77, 2.75, and 2.74 Å are remarkably constant; this is also consistent with a direct Si–C_{eq} interaction.[60]

It should be noted that a similar argument could be formulated for perfluoroalkyl transition metal carbonyls, namely, that the empty σ^* orbitals of appropriate symmetry on the perfluoroalkyl group could interact with the equatorial carbonyl groups. The distortion of the equatorial groups in $HFC=CF$—Mn(CO)₅[61] (Table V) might indeed be due, at least in part, to this effect. Although structural data are available for *trans*-HCF₂CF₂–Co(CO)₃P(C₆H₅)₃ (Tables I and V), no clear interpretation of these data is possible at the present time in view of the difficulty in assessing the extent of interaction, if any, between the (equatorial) carbonyl groups and the phosphorus.

Overlap population and overlap energy analysis have been applied to the results of EHT molecular orbital

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Table VI. Ratios of $Co(CO)_x{}^+/R_3SiCo(CO)_{x-1}{}^+$ Ion Currents[a]

Compound	HCo-(CO)₄	F₃SiCo-(CO)₄	Cl₃SiCo-(CO)₄
Co(CO)₄⁺/RCo(CO)₃⁺	0	0	0
Co(CO)₃⁺/RCo(CO)₂⁺	0.59	0	0
Co(CO)₂⁺/RCo(CO)⁺	9.75	4.30	0.76
Co(CO)⁺/RCo⁺	20.0	1.51	0.86

[a] Calculated from 70-V spectra expressed in terms of per cent total ion current.

calculations on $R_3Si-Co(CO)_4$ (R = F, Cl) in order to determine whether this MO model could yield information on the possible direct $Si-C_{eq}$ interaction (Tables II and III). One of the most prominent results of these EHT calculations is the prediction of a large bonding interaction between the axial silicon group and the carbon of the equatorial carbonyl groups. This Si-C bonding interaction is reflected in both the large positive (bonding) $Si-C_{eq}$ overlap population (Table II) and the large overlap energy (Table IV).

Overlap energy analysis shows that in this MO calculational model, the largest $Si-C_{eq}$ interaction involves the silicon 3s and $3p_z$ orbitals overlapping with the equatorial carbon $2p_z$ orbitals, which is analogous to $HCo(CO)_4$ where the hydrogen orbital interacts primarily with the $2p_z$ orbitals of equatorial carbons. Because the axial substituent's 2s and $2p_z$ orbitals dominate this binding interaction with the equatorial carbonyls, it may be expected to be a general phenomenon for any axial substituent. In fact, the results of this MO calculation indicate a small, but significant, binding interaction between the carbons of the axial and equatorial carbon monoxide groups, thus producing a weak cage bonding network.

The silicon d orbitals are also involved in the $Si-C_{eq}$ bonding and account for about 20% of the total calculated $Si-C_{eq}$ overlap energy. The quantitative results from EHT calculations given in Tables II, III, and IV are moderately sensitive to the orbital exponent and orbital energy parameterizations and charge adjustment routine; however, the principal results and general conclusions drawn from these calculations, such as the large $Si-C_{eq}$ bonding interaction, are unchanged by large variations in parameters such as the exponents of the silicon and cobalt 3d orbitals and the ionization potentials of the silicon 3d and cobalt 3d, 4s, and 4p orbitals. The conclusions also remain unchanged by the inclussion of an interatomic Madelung correction.

The fragmentation patterns of $R-Co(CO)_4$ (R = H,[62] F₃Si,[63] Cl₃Si[64]) and other cobalt carbonyl hydride derivatives[62] suggest that when four or three carbonyl groups are attached to the cobalt the R group is then held more firmly to the cobalt. This is illustrated by the ratios $Co(CO)_x{}^+/RCo(CO)_{x-1}{}^+$, given in Table VI,

where $Co(CO)_x{}^+$ and $RCo(CO)_{x-1}{}^+$ refer to the respective ion currents of these fragments. The smaller the ratio, the more strongly R is held to the $Co(CO)_x$ group. The data are consistent with significant strengthening of the overall $R-Co(CO)_x$ interaction when x = 4 or 3, which is, in turn, consistent with a $R-C_{eq}$ interaction with the (three) "equatorial" carbonyl groups.[64]

It should be pointed out that intramolecular bonding between the equatorial carbonyl groups and a substituent group may account, either in whole or in part, for many of the experimental observations previously attributed to $(d{\rightarrow}d)\pi$ or $(d{\rightarrow}\sigma^*)\pi$ bonding. This type of interaction could also be expected to contribute to the observed reduction in the Si-Co bond length. It is difficult at the present time to ascertain how these two effects could be clearly distinguished experimentally. It is possible that this type of interaction could affect the carbonyl stretching vibrations.

The interaction of hydrogen and silicon with the equatorial carbonyl group, as here suggested for $H-Co(CO)_4$ and its derivatives, may well be a somewhat general type of interaction. These types of interactions might well contribute to the observed displacements in $R-Mn(CO)_5$ compounds[65] and other hydride, metalloid, or metal derivatives of transition metal carbonyls, where low-energy molecular orbitals on a substituent interact with equatorial carbonyl groups attached to the adjacent transition metal atom. Thus, in a species such as $Mn_2(CO)_{10}$, for example, where the equatorial groups are staggered, one possible type of interaction might involve molecular orbitals formed from the interaction of the 4s orbitals of manganese with the $2p_z$ orbitals of the equatorial carbonyl groups on the adjacent manganese atom. This would represent, in effect, incipient bridge carbonyl bonding. Such interaction might be important, for example, in causing the equatorial ligands in compounds such as $[Co(CO)_3-P(n-C_4H_9)_3]_2$,[26,27] $Mn_2(CO)_{10}$,[66] $Tc_2(CO)_{10}$,[67] $[Mn(CO)_4-P(C_2H_5)_3]_2$,[68] $\pi-C_5H_5Fe(CO)_5-Mn(CO)_5$,[69] $[Co(CN-CH_3)_5]_2{}^{4+}$,[28] etc., to be bent toward the adjacent metal. The effects of this incipient bridge carbonyl bonding may be very important in determining many chemical reactions of carbonyls such as methyl migrations, which result in carbonyl insertion reactions, and ligand or ^{13}CO carbonyl replacement reactions.[70]

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