lationship between the two sets of alkaline hydrolysis comes the important conclusion that an aromatic system bonded to a $Cr(CO)_3$ group shows a dependence of reactivity on structure very similar to that of an uncomplexed aromatic system. This further supports the view of a completely delocalized type of bonding between the metal and the aromatic ring, in agreement with a recent X-ray determination of $Cr(CO)_3C_6H_6$, in which no significant deviations from a D_{6h} symmetry of the hydrocarbon ligand were found to exist.[21]

Pettit and co-workers[10] have recently reported on the rates of solvolysis of (benzyl chloride)tricarbonylchromium. This appears to be an SN1 reaction with rate constants considerably higher than those of the corresponding uncomplexed compound. This was explained by an enhanced stability of the carbonium ion $Cr(CO)_3C_6H_5CH_2^+$ presumably formed in the rate-determining step; in turn the increased stability of the intermediate carbonium ion was attributed to backfeeding of electrons from the $Cr(CO)_3$ group into antibonding orbitals of the aromatic ligand.

Although the mechanism of benzoic ester–tricarbonylchromium hydrolysis is different from that of (benzyl chloride)tricarbonylchromium solvolysis, a similar stabilizing effect by the $Cr(CO)_3$ group on the incipient carbonium ion in I could be postulated in order to explain the observed increase of rate constants with respect to the uncomplexed compounds. That this explanation is incorrect in our case is shown by the fact that the ρ of the chromium tricarbonyl complexes is positive; *i.e.* the reaction is accelerated by electron-withdrawing groups in *meta* and *para* positions. Negative values of ρ would be observed if the stabilization of the incipient carbonium ion was the important factor.

We conclude by saying that the enhanced reactivity of complexed benzoic methyl esters can be best explained by a decreased electron density at the electrophilic center. Bond making appears to be the important factor in the alkaline hydrolysis of both the uncomplexed benzoic methyl esters and their chromium tricarbonyl complexes.

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Organometallic Compounds with Metal–Metal Bonds. VII. Preparation and a Study of the Infrared Spectra of Mono- and Bis(tetracarbonylcobalt) Derivatives of Germanium and Tin[1]

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Infrared spectra in the carbonyl stretching region are reported and discussed for a large number of mono- and bis(tetracarbonylcobalt) derivatives of germanium and tin, most of which are new compounds. The monocobalt derivatives are of the types $X_nR_{3-n}GeCo(CO)_4$ (X = Cl, Br, I; R = CH_3, C_6H_5), $X_3SnCo(CO)_4$ (X = Cl, I), $R_3SnCo(CO)_4$ (R = CH_3, C_6H_5), and $(C_6H_5)_3PbCo(CO)_4$. Assignments are proposed for the three or four terminal stretching bands; a linear increase in frequency of the A_1 modes with electronegativity of substituents on germanium or tin is noted. The biscobalt derivatives are of the type $X_nR_{2-n}M[Co(CO)_4]_2$ (M = Ge, Sn), and two of the seven or eight observed carbonyl bands are tentatively assigned. Nmr spectra are reported for the methyltin derivatives. The compounds are moderately stable in the absence of air, and most are prepared by reaction of $Co(CO)_4^-$ with halides or organometallic halides of germanium or tin.

Introduction

Compounds which would now be regarded as having tin–cobalt covalent bonds were first obtained in 1957.[2,3] Only analytical data were available for these compounds, and a satisfactory structural formulation was not then possible. It soon became evident that their general stability was much greater than that of simple organic derivatives such as $CH_3Co(CO)_4$, which decompose at temperatures above −35 to −20°.[4] There have been several more recent studies of compounds in which cobalt is bonded to tin,[5–8] as well as to silicon,[9–12] germanium,[6] and lead.[5]

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Table I

Analytical Data, Melting Points, and Colors

Compound	Mp,[a] °C	Color	Calcd %			Found %		
			C	H	X	C	H	X
$Cl_3GeCo(CO)_4$	71–73	Yellow	13.7	0.0	30.4	14.2	0.2	27.0
$Cl_2(C_6H_5)GeCo(CO)_4$[b]	59–61	Pale yellow	30.9	1.3	18.1	31.1	1.4	14.3
$I_2(CH_3)GeCo(CO)_4$	70–71.5	Yellow	11.7	0.6	49.5	11.8	0.8	51.4
$Cl(CH_3)_2GeCo(CO)_4$	51–54	Pale yellow	23.3	2.0	11.5	21.6	1.9	12.7
$Cl(C_6H_5)_2GeCo(CO)_4$	59–61	Pale yellow	44.2	2.3	8.2	44.2	2.3	7.0
$(C_6H_5)_3GeCo(CO)_4$	130	White	55.7	3.2	...	57.2	3.1	...
$Cl_2Ge[Co(CO)_4]_2$[c]	102–104	Red	19.8	0.0	14.6	20.0	0.0	14.5
$I(CH_3)Ge[Co(CO)_4]_2$[d]	66–68	Orange	19.4	0.5	22.8	20.9	0.2	25.2
$(CH_3)_2Ge[Co(CO)_4]_2$	39–41	Yellow	27.0	1.4	...	26.1	1.5	...
$(CH_3)_3SnCo(CO)_4$[e]	73–75	White	25.1	2.7	...	25.2	3.3	...
$(C_6H_5)_3SnCo(CO)_4$[f]	110–120 dec	White	50.6	2.9	0.0	49.8	2.1	0.0
$(CH_3)_2Sn[Co(CO)_4]_2$	35–37	Yellow	24.5	1.2	0.0	24.3	1.8	0.0
$(C_6H_5)_2Sn[Co(CO)_4]_2$	128–131 dec	Yellow	39.1	1.6	0.0	39.0	2.0	0.0
$Cl(CH_3)Sn[Co(CO)_4]_2$	...	Yellow-orange	21.1	0.6	6.9	20.7	0.8	7.0
$Cl(C_6H_5)Sn[Co(CO)_4]_2$[g]	71–73	Yellow-orange	29.4	0.9	6.2	28.9	2.0	6.7
$Cl(n\text{-}C_4H_9)Sn[Co(CO)_4]_2$[h]	29–30	Yellow-orange	26.1	1.6	6.4	25.9	1.5	5.4
$Cl(CH_2{=}CH)Sn[Co(CO)_4]_2$[i]	45–47	Yellow-orange	23.2	0.6	6.8	22.7	0.6	7.5
$(C_6H_5)_3PbCo(CO)_4$	100–102	Yellow	43.5	2.5	...	43.2	2.5	...

[a] Melting points measured in a sealed, evacuated capillary. Values are uncorrected. [b] O: calcd, 16.3; found, 16.0 [c] O: calcd, 26.5; found, 26.6. [d] O: calcd, 23.0; found, 22.2. [e] Co: calcd, 17.6; found, 15.6. [f] Co: calcd, 11.3; found, 10.8. [g] Co: calcd, 20.6; found, 22.4. [h] O: calcd, 23.2; found, 22.2. [i] O: calcd, 24.5; found, 23.9.

Previous papers of this series have described the preparation and spectra of compounds with bonds between main and subgroup metals. Trends in rather extensive series of related compounds were examined to gain an understanding of the metal–metal interaction. This approach is continued in the present paper, which emphasizes germanium–cobalt and tin–cobalt bonding. The compound types considered are $X_nR_{3-n}MCo(CO)_4$ and $X_nR_{2-n}M[Co(CO)_4]_2$, where X = halogen, R = organic radical, and M = Ge or Sn. In previous work, we have found that the study of series of related compounds is particularly informative.[13] We describe here the most extensive series of derivatives yet reported for a compound containing a specific metal–metal bond. We stress particularly the interpretation of the carbonyl stretching frequencies in the infrared spectrum, in which the effect of varying substituents is most clearly revealed.

Experimental Section

All reactions were carried out under a static nitrogen atmosphere, and solid products were handled with minimum exposure to air. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride. Solutions of sodium tetracarbonylcobaltate(–I) were prepared by stirring a THF solution of dicobalt octacarbonyl with excess 1% sodium amalgam. Methanol solutions of $Co(CO)_4^-$ were prepared by dissolving dicobalt octacarbonyl in methanol and heating to 50° with stirring until CO evolution had ceased. The quantity of $Co_2(CO)_8$ required was based on the equation[14]

$$3Co_2(CO)_8 + 2nCH_3OH \longrightarrow 2[Co(CH_3OH)_n][Co(CO)_4]_2 + 8CO$$

Typically, 1.0 g (3 mmoles) of $Co_2(CO)_8$ was dissolved in 25 ml of methanol to give 4 mmoles of $Co(CO)_4^-$. After filtration, the resultant rose-colored solution was treated with a methanol solution of the appropriate organometallic halide, and the mixture was stirred, usually at room temperature, for 5–15 min.

Phenylgermanium trichloride and diphenylgermanium dichloride were prepared by heating appropriate amounts of $GeCl_4$ and $(C_6H_5)_4Ge$ with $AlCl_3$ as catalyst in sealed tubes and were purified by distillation.[15] Methylgermanium triiodide was prepared[16] by heating GeI_2 and CH_3I in a sealed tube at 110° for 24 hr and was purified by recrystallization from *n*-pentane. Other reactants were obtained from commercial sources.

Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded on a Texas Instruments Servo-Riter with calibration as described previously.[13] Nmr measurements were made on Varian A-60 or HA-100 instruments.

Microanalyses (Table I) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

Triphenyl(tetracarbonylcobalt)germanium(IV), $(C_6H_5)_3GeCo(CO)_4$.—Methanolic $Co(CO)_4^-$ (9.1 mmoles) was treated with 4.5 g (9.5 mmoles) of triphenylgermanium bromide, dissolved in THF, at 40° for 10 min. Addition of water to the cooled solution precipitated a white crystalline solid; recrystallization from pentane afforded 1.2 g of pure product.

Trichloro(tetracarbonylcobalt)germanium(IV), $Cl_3GeCo(CO)_4$.—(i) A THF solution of 10 mmoles of $NaCo(CO)_4$ was added to 2.1 g of $GeCl_4$ (10.0 mmole) dissolved in the same solvent. After 5 min of stirring at room temperature the solution was evaporated *in vacuo*, and the residue was extracted with *n*-pentane. Cooling to –80° afforded a 57% yield of product as yellow crystals, which were purified by recrystallization from *n*-pentane.

(ii) A solution of 5.0 g (23.3 mmoles) of $GeCl_4$ in THF was added to a stirred THF solution of 5.9 g (18.9 mmole) of $Co_2(CO)_8$ at room temperature. After 15 min THF was removed *in vacuo*, and the residue was extracted with 25 ml of *n*-pentane. Cooling to –20° gave 4.0 g of product, which was recrystallized from *n*-pentane.

Phenyldichloro(tetracarbonylcobalt)germanium(IV), $(C_6H_5)Cl_2GeCo(CO)_4$.—A solution of 1.2 g (4.7 mmoles) of $C_6H_5GeCl_3$ in THF was added to 1.6 mmoles of $NaCo(CO)_4$ in THF. After stirring at room temperature for 2.5 hr, the solution was evaporated at reduced pressure and the residue was extracted with *n*-pentane. Cooling the extract to –80° yielded a solid which was recrystallized from *n*-pentane affording 0.7 g of pale yellow crystals.

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Dimethylchloro(tetracarbonylcobalt)germanium(IV), $(CH_3)_2ClGeCo(CO)_4$.—A THF solution of 7.6 mmoles of $NaCo(CO)_4$ was mixed with one of 0.8 g of $(CH_3)_2GeCl_2$ (4.6 mmoles) and the solution was stirred for 5 min. After removal of solvent at reduced pressure, the residue was extracted with *n*-pentane and the solution was concentrated and cooled to −20° affording crystals of product. Recrystallization from *n*-pentane afforded 0.4 g of pale yellow crystals.

Diphenylchloro(tetracarbonylcobalt)germanium(IV), $(C_6H_5)_2ClGeCo(CO)_4$.—A solution of $(C_6H_5)_2GeCl_2$ (3.0 g, 10.0 mmoles) in THF was treated with a THF solution of $NaCo(CO)_4$ (23.2 mmoles). After stirring for several hours, solvent was removed under reduced pressure and the residue was extracted with *n*-pentane. Concentration to a volume of a few milliliters, followed by cooling to −20°, gave pale yellow crystals, which were recrystallized from pentane to afford 1.6 g of product.

Methyldiiodo(tetracarbonylcobalt)germanium(IV), $(CH_3)I_2GeCo(CO)_4$.—Methylgermanium triiodide (1.7 g, 3.6 mmoles) in THF was treated with 3.6 mmoles of $NaCo(CO)_4$ in the same solvent. After 5 min at room temperature, solvent was removed at reduced pressure, and the residue was extracted with *n*-pentane. Concentration and cooling to −20° afforded yellow crystals of product (1.2 g after recrystallization from pentane).

Dichlorobis(tetracarbonylcobalt)germanium(IV), $Cl_2Ge[Co(CO)_4]_2$.—Germanium tetrachloride (0.5 g, 2.3 mmoles) in THF was added to 2.0 g (5.9 mmoles) of $Co_2(CO)_8$ in the same solvent. After stirring for 10 min, THF was removed *in vacuo* and the residue was extracted with *n*-pentane. Cooling to −80° gave 0.8 g of red crystals, which were recrystallized from *n*-pentane.

Methyliodobis(tetracarbonylcobalt)germanium(IV), $CH_3(I)Ge[Co(CO)_4]_2$.—Cobalt carbonyl (3.0 g, 8.8 mmoles) was reduced in THF solution with sodium amalgam and was added to 2.2 g (4.7 mmoles) of CH_3GeI_3 in THF. After stirring for 10 min, solvent was removed at reduced pressure. A pentane extract of the residue was cooled to −80° to afford 1.8 g of orange crystals of product. These were recrystallized from *n*-pentane.

Dimethylbis(tetracarbonylcobalt)germanium(IV), $(CH_3)_2Ge[Co(CO)_4]_2$.—A THF solution of 20 mmoles of $NaCo(CO)_4$ was added to 1.7 g (10 mmoles) of $(CH_3)_2GeCl_2$ in THF. After stirring for 10 min, THF was evaporated at reduced pressure. Extraction of the residue with *n*-pentane, followed by concentration and cooling to −80°, gave yellow crystals of product. This was purified by recrystallization from *n*-pentane.

Trimethyl(tetracarbonylcobalt)tin(IV), $(CH_3)_3SnCo(CO)_4$.[17]—Methanol solutions of 4 mmoles of $Co(CO)_4^-$ and trimethyltin chloride (0.8 g, 4.0 mmoles) were allowed to react with warming and stirring for 5 min. The solution was cooled in ice, and water was slowly added to precipitate a pale buff microcrystalline powder. This was sublimed under high vacuum to give 0.45 g of pure crystalline product.

Triphenyl(tetracarbonylcobalt)tin(IV), $(C_6H_5)_3SnCo(CO)_4$.—Triphenyltin chloride (1.92 g, 5 mmoles) in methanol was treated with 5 mmoles of $Co(CO)_4^-$ in methanol at room temperature for 10 min. Addition of water afforded an off-white microcrystalline solid which was purified by recrystallization from methanol.

Diphenylbis(tetracarbonylcobalt)tin(IV), $(C_6H_5)_2Sn[Co(CO)_4]_2$.[18]—Reaction of 0.86 g (2.5 mmoles) of diphenyltin dichloride and 5 mmoles of $Co(CO)_4^-$ in methanol at room temperature for 10 min, followed by addition of water, afforded a pale yellow crystalline solid. This was purified by recrystallization from methanol–water; yield, 0.86 g.

Chlorophenylbis(tetracarbonylcobalt)tin(IV), $C_6H_5(Cl)Sn[Co(CO)_4]_2$.—Phenyltin trichloride (0.75 g, 2.5 mmoles) and 5 mmoles of $Co(CO)_4^-$ were allowed to react in methanol at room temperature for 10 min. The product was precipitated by addition of water as a yellow crystalline solid and was purified by recrystallization from methanol–water; yield, 1.0 g.

Dimethylbis(tetracarbonylcobalt)tin(IV), $(CH_3)_2Sn[Co(CO)_4]_2$.[17]—Dimethyltin dichloride (0.38 g, 1.73 mmoles) was treated with methanolic $Co(CO)_4^-$ (3.4 mmoles) at room temperature for 10 min. Addition of water to the solution at 0° afforded a yellow crystalline solid which was purified by sublimation, or by recrystallization from methanol–water.

Methylchlorobis(tetracarbonylcobalt)tin(IV), $CH_3(Cl)Sn[Co(CO)_4]_2$.—Treatment of methyltin trichloride (0.96 g, 4 mmoles) with 8 mmoles of $Co(CO)_4^-$ in methanol solution at room temperature for 10 min followed by cooling in ice and addition of water produced orange crystals. Recrystallization from water–methanol afforded 1.2 g of pure product.

***n*-Butylchlorobis(tetracarbonylcobalt)tin(IV), $n\text{-}C_4H_9(Cl)Sn[Co(CO)_4]_2$.**—*n*-Butyltin trichloride (2.8 g, 10 mmoles) was added to 20 mmoles of $Co(CO)_4^-$ in methanol with stirring at room temperature. The solution was cooled to 0° after 10 min and water was slowly added. An oil was produced which was separated from the aqueous methanol layer and dissolved in *n*-pentane. After drying with Na_2SO_4, it was cooled to −80° affording yellow crystals. Recrystallization from *n*-pentane at −80° gave a 70% yield of product.

Triphenyl(tetracarbonylcobalt)lead(IV), $(C_6H_5)_3PbCo(CO)_4$.[19]—Reaction of 6 mmoles of $Co(CO)_4$ with 2.3 g (4.9 mmoles) of triphenyllead chloride in methanol at room temperature for 15 min, followed by addition of water, deposited yellow needlelike crystals, which afforded 1.9 g of pure product on recrystallization from pentane.

Discussion

The first reported germanium–cobalt bond was prepared by an "insertion" reaction of germanium(II) iodide with cobalt carbonyl.[6] Numerous new examples of this bond are described here, most of which have been prepared by the conventional halide displacement method, *e.g.*

$$C_6H_5GeCl_3 + Na^+Co(CO)_4^- \xrightarrow{THF} (C_6H_5)Cl_2Ge\text{-}Co(CO)_4 + NaCl$$

$$CH_3GeI_3 + 2Na^+Co(CO)_4^- \xrightarrow{THF} (CH_3)IGe[Co(CO)_4]_2 + 2NaI$$

Halogeno derivatives can also be prepared by a direct reaction of the germanium tetrahalide with cobalt carbonyl, in the correct ratio

$$4GeX_4 + 3Co_2(CO)_8 \xrightarrow{THF} 4X_3GeCo(CO)_4 + 2CoX_4 + 8CO$$

$$2GeCl_4 + 3Co_2(CO)_8 \xrightarrow{THF} 2Cl_2Ge[Co(CO)_4]_2 + 2CoX_2 + 8CO$$

Such reactions may involve cleavage of the Co–Co bond of cobalt carbonyl by the Ge–Cl bond, followed by decomposition of the unstable $ClCo(CO)_4$ product.

Similar procedures are applicable to the tin–cobalt derivatives. In this case, the displacement reaction can be carried out with a conveniently prepared methanol solution of $Co(CO)_4^-$; after the reaction, the product is precipitated in crystalline form by addition of water.

All of the compounds described are stable, crystalline materials which can be stored for long periods under nitrogen. All eventually oxidize on exposure to air, as indicated by change in color; this occurs in 15 min with $(CH_3)_2Sn[Co(CO)_4]_2$, but only after 1 day with $(C_6H_5)_2Sn[Co(CO)_4]_2$. The halogen-substituted derivatives are even more resistant to oxidation.

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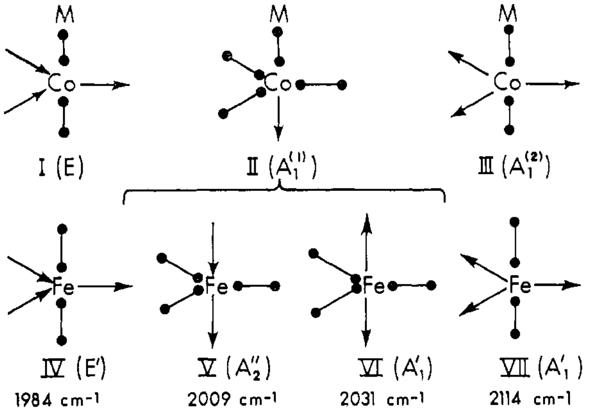
[17] These compounds were earlier prepared in this laboratory by Mrs. H. R. H. Patil, whose exploratory experiments we gratefully acknowledge. Mrs. Patil treated $Co_2(CO)_8$ with lithium or with pyridine to obtain the $Co(CO)_4^-$ anion. The method here reported is much more convenient.

[18] This compound has been prepared in alternative ways by Bonati.[7]

[19] This compound has been prepared by P. Kleinert, Dissertation, University of Jena, 1957. *Cf.* Hein and Jehn,[5] footnote 3.

Infrared Spectra of Mono(tetracarbonylcobalt) Derivatives.—In order to make assignments, a geometry must be assumed for the molecule; we assume a trigonal-bipyramidal structure, with the germanium or tin atom positioned on the threefold axis.[20] Under this assumption, compounds of the series $X_nR_{3-n}MCo(CO)_4$ would be expected to display three or four strong bands in the carbonyl stretching region depending on whether they have C_{3v} or C_s symmetry, respectively. This is in agreement with group theoretical predictions of three infrared-active bands for the C_{3v} structure ($2\ A_1 + E$) and four for C_s ($3\ A' + A''$), and examples of both types are shown in Figures 1 and 2. Numerical values and intensity data are given in Table II. We next proceed to assign the observed bands; this can be done with little ambiguity in the case of the E mode and rather tentatively for the others by comparison with related systems.

Using the principle that, in any vibrational mode, the intensity should be proportional to the square of the vector sum of the local dipoles,[21] one concludes that the E mode represented by I would be the most intense of the three modes. Of the remaining two, we expect $A_1^{(1)}$ (II) to have medium intensity, while $A_1^{(2)}$ (III) should have a very low or perhaps vanishing intensity.[22] Thus we assign the most intense band, which is also at lowest frequency (Figure 1, 2005 cm^{-1}) as E; this is confirmed by the obvious splitting (Figure 2) of the low-frequency band into A′ and A″ modes when the symmetry is reduced to C_s. Our crude intensity predictions for the A_1 bands have not been fulfilled, however, as they are almost equally strong. We shall discuss later the relative A_1 intensities but turn now to an alternative means of distinguishing the A_1 bands.



A consideration of the related vibrations of $Fe(CO)_5$ can be used to make this distinction, in the same way

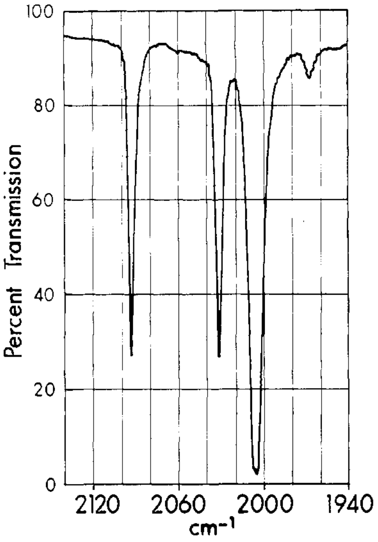


Figure 1.—Infrared spectrum of $(C_6H_5)_3GeCo(CO)_4$; *ca.* 1 mg/ml of cyclohexane.

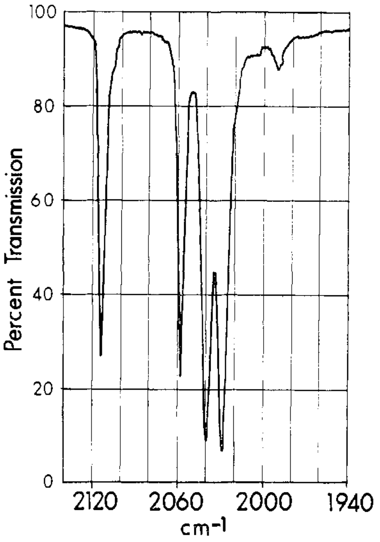


Figure 2.—Infrared spectrum of $(C_6H_5)Cl_2GeCo(CO)_4$; *ca.* 1 mg/ml of cyclohexane.

Table II

Infrared Spectra of Mono(tetracarbonylcobalt) Derivatives[a]

Compounds with point group C_{3v}	ν(CO), cm^{-1} $A_1^{(2)}$	$A_1^{(1)}$	E
$Cl_3GeCo(CO)_4$	2122 (6.4)	2069 (6.5)	2050 (10)
$Br_3GeCo(CO)_4$[b]	2118 (6.4)	2066 (5.8)	2048 (10)
$I_3GeCo(CO)_4$[b]	2113 (7.4)	2062 (5.2)	2042 (10)
$(C_6H_5)_3GeCo(CO)_4$	2091 (7.2)	2030 (7.2)	2006 (10)
$Cl_3SnCo(CO)_4$[b]	2120 (8.0)	2068 (6.8)	2048 (10)
$I_3SnCo(CO)_4$[b]	2109 (8.0)	2058 (4.6)	2037 (10)
$(CH_3)_3SnCo(CO)_4$	2082 (7.3)	2020 (6.9)	1988 (10)
$(C_6H_5)_3SnCo(CO)_4$	2087 (6.6)	2027 (5.1)	1999 (10)
$(C_6H_5)_3PbCo(CO)_4$	2081 (8.0)	2022 (4.9)	1997 (10)

Compounds with point group C_s	ν(CO), cm^{-1} $A'^{(2)}$	$A'^{(1)}$	A′ + A″	
$Cl_2(C_6H_5)GeCo(CO)_4$	2112 (7.8)	2056 (8.3)	2038 (9.7)	2027 (10)
$I_2(CH_3)GeCo(CO)_4$	2106 (8.7)	2053 (8.2)	2033 (9.8)	2022 (10)
$I_2(C_6H_5)GeCo(CO)_4$[b]	2106 (8.5)	2052 (6.7)	2033 (9.4)	2024 (10)
$Cl(CH_3)_2GeCo(CO)_4$	2100 (7.4)	2041 (8.3)	2021 (9.9)	2004 (10)
$Cl(C_6H_5)_2GeCo(CO)_4$	2101 (7.6)	2043 (7.9)	2026 (10)	2010 (9.2)
$I(C_6H_5)_2GeCo(CO)_4$[b]	2099 (7.9)	2042 (7.2)	2023 (10)	2010 (8.7)

[a] All spectra measured in cyclohexane; figures in parentheses are relative heights of bands measured on a linear transmittance scale. Assignments are in accordance with text. [b] Preparation and characterization of these compounds will be described in a later paper.

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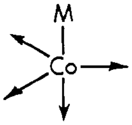
(20) A referee cautions that this *is* an assumption and that the structure may not be the same for all members of the series. Another possibility would involve equatorial placement of tin or germanium in the trigonal bipyramid, with resulting C_{2v} symmetry for the molecule. However, the fact that three carbonyl stretching bands become four when threefold symmetry of the tin or germanium group is eliminated (see following discussion) rather strongly suggests that there *is* a threefold molecular axis, with the tin or germanium group located on it.

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

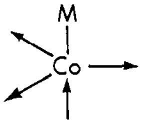
(22) (a) As Orgel[22b] has pointed out in the analogous C_{4v} case, $A_1^{(2)}$ is almost infrared-forbidden; it might gain intensity from a noncoplanarity of the equatorial carbonyl groups, from an accompanying electronic migration along the threefold axis, or, more importantly, from coupling with $A_1^{(1)}$. (b) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

that Orgel[22] has discussed the spectrum of $(C_6H_5)_3PMo(CO)_5$ in terms of that of $Mo(CO)_6$. From Raman and infrared studies,[23–25] the observed carbonyl stretching frequencies of $Fe(CO)_5$ have been assigned (in D_{3h} symmetry) to the modes IV–VII, which are shown below the corresponding modes of $R_3MCo(CO)_4$. On this basis we would assign the high-frequency band (Figure 1, at 2091 cm^{-1}) as $A_1^{(2)}$ (III) and the middle band (at 2030 cm^{-1}) as $A_1^{(1)}$ (II). It is reasonable that the simultaneous stretching of three geminal carbonyl groups should require more energy than the independent (see later discussion, however) stretching of a single carbonyl group; moreover, it is of interest that the ratio of the separations of the two A_1 bands from the E band, *i.e.*, (II − I):(III − I), is very similar in $(C_6H_5)_3GeCo(CO)_4$ and various $R_3PFe(CO)_4$ derivatives,[25,26] perhaps indicative of a general similarity in the two classes of compounds. The ratio in all these cases falls in the range 0.28–0.34, as it does in $Fe(CO)_5$ itself if one takes the mean of the symmetrical and unsymmetrical axial vibrations, V and VI, as the appropriate value for comparison with the single axial mode of the tetracarbonyl derivatives.

The relative intensities of the A_1 modes in this assignment can best be accounted for by assuming that the actual modes are not well represented by II and III. Rather, we assume a strong coupling to produce VIII and IX;[27] VIII would correspond to the high-frequency band, involving as it does the simultaneous stretching of four carbonyls. As El-Sayed has shown,[28] a resonance interaction of coinciding fundamental bands can lead to two bands of equal intensity in the special case where the intensity of one of the fundamentals is zero, due to cancellation of moments. The simple local dipole picture also leads one to expect equal intensities for VIII and IX.



VIII ($A_1^{(2)}$)
= II + III

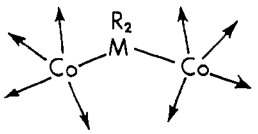


IX ($A_1^{(1)}$)
= III − II

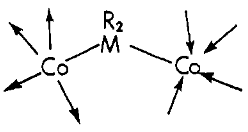
In Figure 1 and in the above discussion, we have taken the triphenylgermanium derivative as our example; the A_1 bands have essentially equal intensity here. An examination of the data in Table II for all of the compounds reveals that the high-frequency band becomes *more* intense with larger R_3M or X_3M groups. We suggest that this is a steric effect, with the bulkier groups displacing the equatorial groups downward so that the dipoles are additive in the higher energy mode VIII and somewhat opposed in IX, enhancing or diminishing the intensities of the respective modes. If it is correct, this interpretation would support the view[29] that the displacement of equatorial carbonyls *toward* the R_3M group observed in crystals of $R_3MCo(CO)_4$ and $R_3MMn(CO)_5$ compounds[29,30] is the result of intermolecular packing forces in the lattice and is not an intrinsic property of the free molecule.

Infrared Spectra of Bis(tetracarbonylcobalt) Derivatives.—The spectra of $(C_6H_5)_2Sn[Co(CO)_4]_2$, $Cl_2Sn[Co(CO)_4]_2$, and $C_6H_5(Cl)Sn[Co(CO)_4]_2$ are presented in Figures 3–5, and are representative of all of the compounds of Table III. It is at once apparent that there is appreciable coupling of the two $Co(CO)_4$ groups across the germanium or tin atom; if there were no coupling, one would expect only three or four infrared bands on the basis of the "local symmetry" of the equivalent $Co(CO)_4$ groups. The over-all molecular symmetry must be considered, however.[31] For $(C_6H_5)_2Sn[Co(CO)_4]_2$ the over-all symmetry is C_{2v}, whence group theory predicts seven infrared-active bands ($3\,A_1 + 3\,B_1 + B_2$). In Figure 3, we in fact observe a total of seven bands, including one shoulder. For $Cl_2Sn[Co(CO)_4]_2$, also of C_{2v} symmetry, the general intensity pattern (Figure 4) is rather different, although it is still possible to count seven bands if two poorly resolved shoulders are included. In Figure 5, eight bands are clearly resolved, in agreement with the number predicted for the C_s symmetry of $C_6H_5(Cl)Sn[Co(CO)_4]_2$ ($4\,A' + 4\,A''$).

Assignments in such a complex spectrum are difficult,[32] and we shall discuss only the pair of high-frequency bands present in all of the bis(tetracarbonylcobalt) derivatives and separated in all cases by 17 ± 2 cm^{-1}. We suggest that these bands arise from the symmetric and asymmetric combination of the $A_1^{(2)}$ modes (VIII) of the individual $Co(CO)_4$ groups, with phases and symmetry designations (in C_{2v}) as shown in X and XI. We assume that the higher frequency of the pair of bands corresponds to A_1 (X), it being more difficult to stretch all of the carbonyl groups at once than to stretch one set and compress the other.[33]



X (A_1)



XI (B_1)

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[23] L. H. Jones and R. S. McDowell, *Spectrochim. Acta*, **20**, 248 (1964). These authors made important revisions of earlier carbonyl stretching assignments.[24] The revised assignments have been substantiated by more recent studies of phosphite derivatives of $Fe(CO)_5$.[25]

[24] W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963).

[25] A. Reckziegel and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **3**, 341 (1965).

[26] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[27] Similarly, Edgell, Wilson, and Summitt[24] prefer to represent the axial and equatorial A'_1 modes of $Fe(CO)_5$ as coupled.

[28] M. A. El-Sayed, *J. Chem. Phys.*, **37**, 680 (1962).

[29] H. P. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966).

[30] B. T. Kilbourne, T. L. Blundell, and H. M. Powell, *ibid.*, 444 (1965).

[31] This has been pointed out for the compound $(n\text{-}C_4H_9)_2Sn[Co(CO)_4]_2$ by G. Bor, "Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, Sept 1964," Akadémiai Kiadó, Budapest, 1965, p 367. We thank Dr. Bor for drawing this work to our attention.

[32] A referee considers that analysis of isolated portions of spectra such as these is hazardous. Recognizing this, we feel nonetheless that a useful purpose is served when a simple, qualitative approach is tested by extending it as fully as possible. The problem of bis(tetracarbonylcobalt) derivatives invites a more rigorous analysis, but it may be some time before this is accomplished.

[33] (a) In accordance with earlier conclusions for $Mn(CO)_5$ derivatives,[13] we consider that interaction of $Co(CO)_4$ groups across the central metal atom results from a $d\pi$–$d\pi$–$d\pi$ effect. An argument similar to that detailed by Cotton and Wing[33b] for $(OC)_5MM(CO)_5$ systems then leads to the above assumption. (b) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965).

Table III

Infrared Spectra of Bis(tetracarbonylcobalt) Derivatives[a]

Compounds with point group C_{2v}	ν(CO), cm⁻¹ A₁	B₁	2 A₁ + 2 B₁ + B₂				
$Cl_2Ge[Co(CO)_4]_2$	2117 (0.1)	2100 (9.6)	2058 (6.7)	2054 (3.8)[d]	2044 (10)	2026 (4.4)	2016 (2.4)
$I_2Ge[Co(CO)_4]_2$[c]	2113 (4.1)	2096 (10)	2054 (7.5)	2051 (5.6)[d]	2042 (10)	2025 (5.4)	2013 (2.9)
$(CH_3)_2Ge[Co(CO)_4]_2$	2098 (3.5)	2081 (9.8)	2033 (3.5)[d]	2027 (7.4)	2019 (9.8)	2006 (10)	1997 (7.2)
$Cl_2Sn[Co(CO)_4]_2$[c]	2114 (0.1)	2097 (9.9)	2056 (6.6)	2052 (3.8)[d]	2040 (10)	2023 (5.2)	2016 (3.8)[d]
$Br_2Sn[Co(CO)_4]_2$[c]	2113 (0.1)	2096 (9.7)	2055 (4.5)	2050 (2.8)[d]	2040 (10)	2026 (3.3)	2016 (2.2)[d]
$I_2Sn[Co(CO)_4]_2$[c]	2110 (3.5)	2093 (9.6)	2053 (5.1)	2048 (3.6)[d]	2037 (10)	2021 (4.4)	2012 (2.6)[d]
$(CH_3)_2Sn[Co(CO)_4]_2$	2095 (3.7)	2078 (10)	2031 (1.9)[d]	2024 (5.4)	2013 (8.8)	2002 (9.5)	1992 (6.0)
$(C_6H_5)_2Sn[Co(CO)_4]_2$	2095 (5.1)	2080 (9.9)	2033 (4.0)[d]	2029 (7.4)	2018 (10)	2009 (9.7)	1995 (7.3)
$(CH_2{=}CH)_2Sn[Co(CO)_4]_2$[b]	2097 (4.6)	2080 (10)	2037 (3.7)[d]	2028 (6.8)	2018 (9.6)	2009 (9.7)	1998 (7.4)

Compounds with point group C_s	ν(CO), cm⁻¹ A′	A″	3 A′ + 3 A″					
$I(CH_3)Ge[Co(CO)_4]_2$	2106 (2.9)	2089 (10)	2046 (4.3)	2040 (4.4)	2030 (9.0)	2024 (9.2)	2014 (4.9)	2000 (2.9)
$Cl(CH_3)Sn[Co(CO)_4]_2$	2104 (3.0)	2088 (10)	2044 (3.7)	2038 (4.0)	2022 (8.7)	2017 (8.8)	2005 (5.5)	1996 (3.5)
$Cl(C_6H_5)Sn[Co(CO)_4]_2$	2105 (3.3)	2088 (10)	2045 (4.8)	2039 (4.5)	2030 (9.0)	2021 (8.7)	2014 (5.7)	1999 (2.9)
$Cl(n\text{-}C_4H_9)Sn[Co(CO)_4]_2$	2103 (3.3)	2086 (10)	2044 (4.4)	2037 (3.9)	2024 (8.4)	2018 (8.7)	2007 (5.4)	1996 (3.1)
$Cl(CH_2{=}CH)Sn[Co(CO)_4]_2$[e]	2106 (4.3)	2088 (10)	2046 (6.6)	2040 (6.1)	2029 (9.6)	2022 (9.7)	2012 (7.4)	2000 (4.6)

[a] Spectra measured in cyclohexane; assignments in accordance with text. Figures in parentheses are relative heights of bands measured on a linear transmittance scale. [b] Preparation and characterization to be described later. [c] Spectra reported previously in another solvent: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5,** 1405 (1966). [d] Shoulder. [e] Preparation described by D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5,** 2222 (1966).

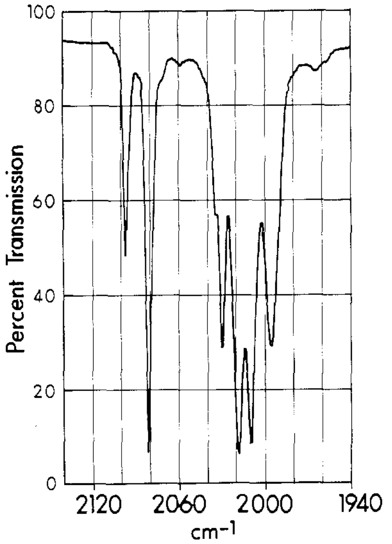

Figure 3.—Infrared spectrum of $(C_6H_5)_2Sn[Co(CO)_4]_2$; *ca.* 1 mg/ml of cyclohexane.

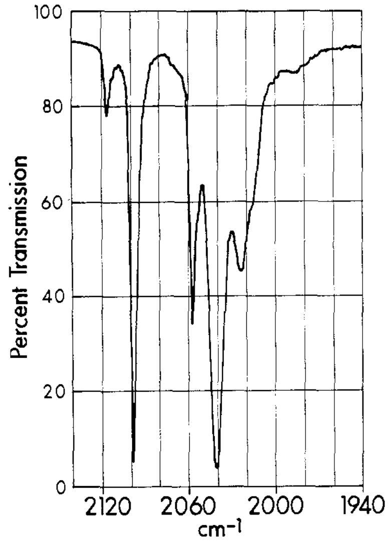

Figure 4.—Infrared spectrum of $Cl_2Sn[Co(CO)_4]_2$; *ca.* 1 mg/ml of cyclohexane.

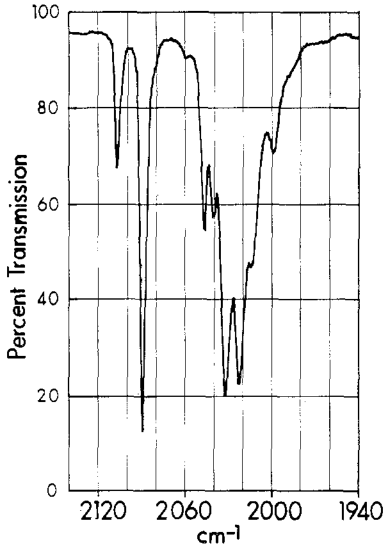

Figure 5.—Infrared spectrum of $C_6H_5(Cl)Sn[Co(CO)_4]_2$; *ca.* 1 mg/ml of cyclohexane.

These tentative assignments for the pair of high-frequency modes are consistent with the observed relative intensities. The higher frequency member of the pair is always weaker, and, in the A_1 (X) mode, the resultant dipoles on the individual $Co(CO)_4$ groups tend to oppose one another for Co–M–Co angles greater than 90°. In the stronger B_1 (XI) mode, the dipoles of the two parts of the molecule tend to reinforce one another.[34] It is clear from X and XI, within the limits of the local dipole approximation, that the A_1 (X) mode should approach zero intensity as the Co–M–Co angle approaches 180°, while for a 90° bond angle, the two modes should have equal intensities. If the dipoles on the cobalt atoms are taken to be collinear with the M–Co bond, one can derive a simple geometrical relation

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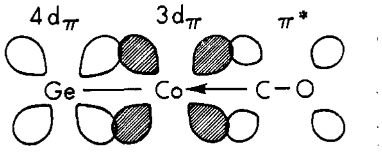
(34) It is assumed throughout, as mentioned earlier, that the intensity of a mode is proportional to the square of vector sum of the local dipoles.[21]

$$\frac{A_{A_1}}{A_{B_1}} = \cot^2\left(\frac{\theta}{2}\right)$$

in which A is the absorbance of the indicated band and θ the Co–M–Co angle. From the observed absorbance ratio,[35] the following θ values are obtained: 155° in $Cl_2Sn[Co(CO)_4]_2$, 131° in $C_6H_5(Cl)Sn[Co(CO)_4]_2$, and 126° in $(C_6H_5)_2Sn[Co(CO)_4]_2$. We do not suggest that these "bond angles" are to be taken literally, but consider it interesting that the trend is as would be expected on the basis of Bent's rule[36] that electronegative substituents tend to free the s character of the tin atom for use in the metal–metal bonds, with increase in the metal–metal–metal bond angle.

Electronegativity Effects.—An examination of the infrared spectra of the $X_nR_{3-n}GeCo(CO)_4$ series (n = 0–3) showed a regular shift of the CO stretching frequency, ν(CO), to higher frequencies as the number of halogen atoms on the germanium was increased. In particular it was found that by plotting the frequency of the $A_1^{(1)}$ or $A'^{(1)}$ band against the sum of the Pauling electronegativities of the halogens on germanium a remarkably good straight line was obtained, as illustrated in Figure 6.[37] In a similar graph using the $A_1^{(2)}$ or $A'^{(2)}$ band, the points lie on two straight lines (Figure 6), all the chloro derivatives falling on one line and the iodo derivatives on the other, with the single bromo derivative in between.

These trends can be explained in terms of substituent effects on π bonding in the molecule. In line with previous evidence,[13] we can schematically represent the π interactions as in XII. The two ligands compete



XII

for electron density in the filled cobalt $3d_\pi$ orbitals. An increase in π bonding to germanium must occur at the expense of π bonding to carbon monoxide and accordingly must be reflected in higher CO bond order and stretching frequency. The inductive effect of halogen substituents will increase the electron affinity of the empty germanium d_π orbitals,[39] producing just this effect.

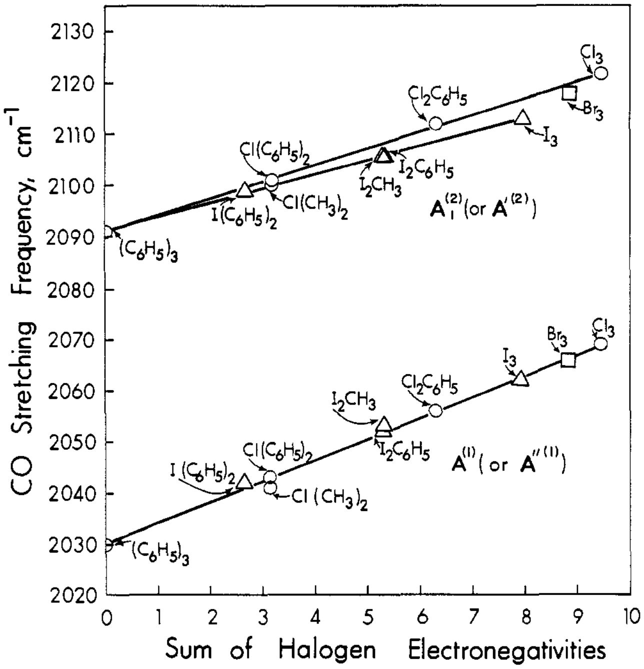


Figure 6.—Effect of halogen substituents on carbonyl stretching frequencies in $X_nR_{3-n}GeCo(CO)_4$ compounds. Upper series assigned as $A_1^{(2)}$ and lower series as $A_1^{(1)}$. Points labeled by substituents on the germanium atom: ○, chlorine series; △, iodine series; □, bromine compound.

It is surprising that the $A_1^{(1)}$ mode should give a single straight line, with most points within 1 cm^{-1} and all within 2 cm^{-1} of that line, while the $A_1^{(2)}$ mode gives two distinctly separated straight lines, one for iodo and one for chloro derivatives. The reason for the difference is not clear. The linearity is all the more remarkable in view of the fact that no account is taken of the electron-withdrawing tendency of phenyl or methyl groups on germanium. It should also be noted that ν(CO) values for the E mode do not give rise to a straight line, although the trend is as expected.

Nmr Results.—Chemical shifts and proton–tin coupling constants, $J(^{117}Sn\text{-}CH_3)$ and $J(^{119}Sn\text{-}CH_3)$, for methyltin derivatives are given in Table IV. We discuss the trends in coupling constants using an interpretation put forward by Kaesz, *et al.*, to explain changes in $J(Sn\text{-}CH_3)$ in methyltin hydrides and chlorides.[40] Coupling of the spins of adjacent nuclei by

TABLE IV

NMR SPECTRA[a]

Compound	τ	$J(^{117}Sn\text{-}CH_3)$	$J(^{119}Sn\text{-}CH_3)$
$(CH_3)_3SnCo(CO)_4$	9.37	50.6	52.6
$(CH_3)_2Sn[Co(CO)_4]_2$	8.88	43.6	45.7
$Cl(CH_3)Sn[Co(CO)_4]_2$	8.48	42.2[b]	...
$CH_3Sn[Co(CO)_4]_3$[c]	8.98	33.0[b]	...

[a] Measured in $CDCl_3$. Coupling constants J in cps. [b] Average of ^{117}Sn and ^{119}Sn values; bands not resolved in this case. [c] D. J. Patmore and W. A. G. Graham, *Inorg. Nucl. Letters*, **2,** 179 (1966); *Inorg. Chem.*, **5,** 2222 (1966). Measured in benzene.

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(35) This is not, of course, the same value as one would obtain by taking the ratio of the *transmittance* values given in Table III. We approximate the area of each band as the product of its absorbance and its width at 50% absorbance, determined on an expanded-scale spectrum. Uncertainties in the ratio (due in particular to the choice of base line) lead to variations of at least ±5° in θ.

(36) H. A. Bent, *Chem. Rev.*, **61,** 290 (1961). The rule, which was formulated for first-row elements, states: "Atomic s character concentrates in orbitals directed toward electropositive substituents."

(37) This general trend has been observed in other, less extensive series of compounds. A classic case is the series $[Cl_n(C_6H_5)_{3-n}P]_3Mo(CO)_3$, in which ν(CO) rises as n increases;[38] $\Delta\nu$(CO) per chlorine atom is roughly constant, indicating that *some* additive property of chlorine is operative. The present work shows that electronegativity is *the* principal property involved, since it correlates the influence of three *different* halogens on ν(CO). A similar linear correlation is found to hold in the series $X_nR_{3-n}SnMn(CO)_5$ described previously.[13]

(38) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

(39) L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p 144.

(40) N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85,** 1377 (1963); J. R. Holms and H. D. Kaesz, *ibid.*, **83,** 3903 (1961).

means of bonding electrons is expected to be proportional to the densities of the bonding electrons at the respective nuclei; thus, the coupling of the nuclei will be greater the larger the s character of the overlapping hybrid atomic orbitals that form the bond between them. Similar principles apply to tin–proton coupling in methyltin compounds in which the interaction takes place across two bonds. Assuming that the hybridization of carbon remains constant,[41] changes in J can be attributed to variation in the amount of s character in the s–p hybrid orbitals of tin directed to the methyl group.

Taking tetramethyltin (with $J(^{119}Sn–CH_3) = 54$ cps) as the basis for comparison, the decreasing coupling constants observed in $(CH_3)_3SnCo(CO)_4$, $(CH_3)_2Sn[Co(CO)_4]_2$, and $CH_3Sn[Co(CO)_4]_3$ suggest that the tin orbitals bonding to carbon in these compounds possess *less* than the 25% s character expected in the four equivalent orbitals of tetramethyltin. This implies that the tin orbitals bonding to cobalt are enriched in s character, in accordance with Bent's rule.[36] While undoubtedly oversimplified, this appears to provide a useful interim viewpoint from which metal–metal bonds of this type may be regarded.

Acknowledgment.—We thank the National Research Council of Canada for support of this work.

[41] An assumption supported by the small variation of $J(^{13}CH_3)$ in related compounds. In $(CH_3)_3SnMn(CO)_5$, $J(^{13}CH_3) = 129.2$ cps,[13] differing only slightly from the value of 128 cps reported for tetramethyltin.[40]

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Kinetic Studies of Group VI Metal Carbonyl Complexes. IV. Substitution Reactions of *o*-Phenanthroline Complexes of Chromium Hexacarbonyl[1]

By ROBERT J. ANGELICI and JAMES R. GRAHAM

Received December 17, 1966

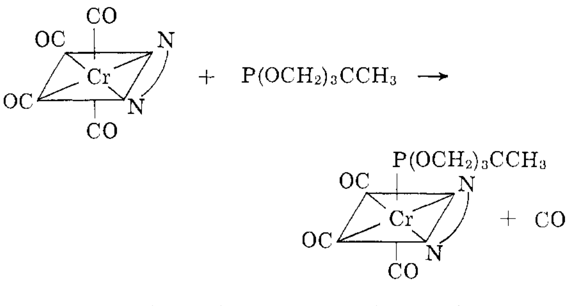
$Cr(CO)_4$(X-*o*-phen) reacts with $P(OCH_2)_3CCH_3$, L, at a rate which is independent of the concentration of L to form *cis*-$Cr(CO)_3$(L)(X-*o*-phen) as the only reaction product. The rate of reaction of $Cr(CO)_4$(X-*o*-phen) is however dependent on the basicity of the X-*o*-phen chelate in a manner which is predictable from a linear free energy expression. The reaction rate dependence on the pK_a of X-*o*-phen is contrary to what would be predicted from current π-bonding theories since the reaction rate was found to increase with increasing pK_a of the chelate. The C–O stretching frequencies of the $Cr(CO)_4$(X-*o*-phen) complexes decrease with increasing basicity of X-*o*-phen. This would be predicted from π-bonding theory but does not explain the observed rate trend. The increases in reaction rates with increasing chelate pK_a are discussed in terms of a stabilized transition state and in terms of labilizing and nonlabilizing ligands.

Introduction

The complexes, $M(CO)_4$(dipy), where M = Cr, Mo, or W, have been found to undergo substitution reactions with phosphites, L, to form $M(CO)_3$(L)(dipy).[2,3] These reactions were observed to proceed under unusually mild conditions and occurred even faster for the analogous 4,4′-dimethyl-2,2′-dipyridyl complexes. This result indicated that the more basic dipyridyl ligand significantly labilized the CO groups. Since a number of substituted *o*-phenanthrolines, X-*o*-phen, were available to us, the present study was undertaken in an attempt to examine the relationship between the rate of CO replacement in $M(CO)_4$(X-*o*-phen) and the basicity of the *o*-phenanthroline.

The unsubstituted *o*-phenanthroline complexes, $M(CO)_4$(*o*-phen),[4] and their products of reaction with phosphines, L, and phosphites, $M(CO)_3$(L)(*o*-phen),[4,5] have already been prepared. Analogous complexes of the substituted *o*-phenanthrolines have been prepared and their reaction products with phosphines and phosphites identified. For comparison, the $M(CO)_4$(1,2-diamino-2-methylpropane) complexes were synthesized and their reactions with phosphites examined.

All of the $M(CO)_4$(N–N) complexes, where N–N is an *o*-phenanthroline or 1,2-diamino-2-methylpropane, have been found to react with phosphines and phosphites according to eq 1. The kinetics of these reactions



(1)

have been investigated for the molybdenum and tungsten as well as the chromium complexes. The current paper reports the kinetic results for the $Cr(CO)_4$(X-*o*-phen) reaction. A subsequent paper will

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[1] Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30, 1965.

[2] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965).

[3] J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).

[4] G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

[5] L. W. Houk and G. R. Dobson, *J. Chem. Soc., Sect. A*, 317 (1966).