stretching frequencies lie at 503 and 520 cm^{-1}, respectively. These values fall near the straight lines drawn by Brown and Morgan[23] relating Sn–C stretching frequencies to $J(^{119}Sn–CH_3)$. Indeed, there is a striking similarity of the coupling constants and Sn–C stretching frequencies for $(CH_3)_3Sn–Sn(CH_3)_3$ and $(CH_3)_3Sn–Mn(CO)_5$.[24]

Acknowledgment.—We are indebted to Professor F. W. Birss and to Mrs. Kathleen Simpson, who prepared computer programs for the force constant calculations. We thank Mr. R. S. Gay and Mrs. H. R. H. Patil for assistance. This work was supported in part by the National Research Council of Canada.

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(23) T. L. Brown and G. L. Morgan, *Inorg. Chem.*, **2**, 736 (1963).

(24) NOTE ADDED IN PROOF.—Since the submission of this paper, the compound $(CH_3)_3Sn–Mn(CO)_5$ has been reported by H. C. Clark and J. H. Tsai, *ibid.*, **5**, 1407 (1966). In a private communication, Professor Clark has agreed that the 1960-cm^{-1} band observed in the spectrum of his compound is a ^{13}C satellite of the E mode; under improved resolution, he observes at 1996 cm^{-1} the band which we have assigned as $A_1^{(1)}$.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Organometallic Compounds with Metal–Metal Bonds. V. An Investigation of Tris(tetracarbonylcobalt)tin(IV) Derivatives[1]

BY D. J. PATMORE AND W. A. G. GRAHAM

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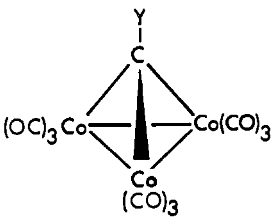
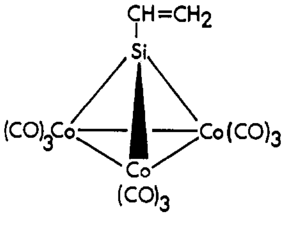
The preparation and infrared spectra of $RSn[Co(CO)_4]_3$ ($R = C_6H_5, CH_3, CH_2{=}CH, n\text{-}C_4H_9$) and $XSn[Co(CO)_4]_3$ ($X = Cl$, Br, I) are described. Their mass spectra are reported, and from this evidence their formulation as *tetra*carbonylcobalt derivatives (III) is conclusively established. Their structures thus differ from the carbon and silicon compounds (I and II) which possess a pyramidal CCo_3 or $SiCo_3$ skeleton with cobalt–cobalt bonds.

Introduction

The reaction of dicobalt octacarbonyl with various trihalogenomethyl compounds X_3CY ($Y = CH_3$, Cl, F, C_6H_5, COOH, etc.) is reported[2] to give rise to tris(tricarbonylcobalt) derivatives to which the structure I was assigned, largely on the basis of infrared studies.[3]



I



II

The compounds I are intensely purple in color and of high stability. A rational mechanism for their formation, as King[4] has pointed out, would involve successive displacements of the three halogens by tetracarbonylcobalt anion, followed by loss of carbon monoxide by the unstable tris(tetracarbonylcobalt) intermediate; concomitant formation of cobalt–cobalt bonds (two per cobalt atom) would preserve the inert gas configuration for the metal atoms. It is of interest that the CCo_3 nucleus characteristic of I arises also when binuclear acetylene complexes $Co_2(CO)_6(RC{\equiv}CH)$ are treated with acid.[5]

The thermal stability and chemical inertness of these CCo_3 clusters are surprising, since very low stability is a characteristic of the isolated cobalt–carbon σ bond.[6] On the other hand, a much greater stability is exhibited by compounds in which cobalt is covalently bonded to such main group metals as gallium,[7] indium,[7] silicon,[8] germanium,[9] tin,[9] and lead.[10] Thus it appeared that an examination of compounds containing the MCo_3 unit, in which M is a fourth-group element heavier than carbon, would be of interest.

Reaction of tetravinylsilane with dicobalt octacarbonyl has been reported[11] to produce the silicon analog, II, so formulated on the basis of analysis and infrared spectrum. It would be reasonable to expect that the heavier congeners of carbon and silicon would follow a similar pattern in forming $RM[Co(CO)_3]_3$ derivatives having cobalt–cobalt bonds.[12] We find, however, that tin gives rise to a different structural type, $RSn[Co(CO)_4]_3$, which does not possess cobalt–cobalt

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(1) Presented in part at the 49th Canadian Chemical Conference, Saskatoon, Saskatchewan, Canada, June 5–9, 1966. For Part IV, see W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(2) W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 169 (1961); G. Bor, L. Marko, and B. Marko, *Chem. Ber.*, **95**, 333 (1962).

(3) This structure has now been confirmed by X-ray methods: P. W. Sutton and L. F. Dahl, private communication, May 1966.

(4) R. B. King, *Advan. Organometal. Chem.*, **2**, 244 (1964).

(5) U. Krüerke and W. Hübel, *Chem. Ind.* (London), 1264 (1960).

(6) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **13b**, 122 (1958); the much more stable σ-bonded fluorocarbon derivatives are an exception: P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

(7) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).

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

(9) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

(10) F. Hein and W. Jehn, *Ann.*, **684**, 4 (1965).

(11) S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, 82 (1962).

(12) Although the compound $n\text{-}C_4H_9Sn[Co(CO)_3]_3$ has been claimed (S. D. Ibekwe and M. J. Newlands, *Chem. Commun.*, 114 (1965)), we have not been able to substantiate this finding.

bonds. This paper describes the preparation of these interesting new compounds and their infrared and mass spectra.

Experimental Section

All reactions were carried out under nitrogen, and products were recrystallized with minimum exposure to air. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride. Solutions of $NaCo(CO)_4$ were prepared by reduction of a THF solution of dicobalt octacarbonyl with excess 1% sodium amalgam. Methyltin trichloride was prepared from methyl chloride and molten tin(II) chloride[13] and purified by sublimation. Vinyltin trichloride was prepared according to Seyferth and Stone.[14] Other starting materials were obtained from commercial sources.

Infrared spectra were measured in 0.5-mm cells in cyclohexane solution using a Perkin-Elmer 337 grating spectrometer. Calibration with carbon monoxide and deuterium bromide and the use of an external recorder, as previously described,[1] result in an accuracy of ±1 cm^{-1} for the carbonyl stretching frequencies reported in Table I.

TABLE I

INFRARED SPECTRA[a]

Compound	ν(CO), cm^{-1}
$ClSn[Co(CO)_4]_3$	2110 vw, 2088 s, 2049 mw, 2043 mw, sh, 2028 s, 2001 w
$BrSn[Co(CO)_4]_3$	2108 vw, 2086 s, 2048 m, 2042 mw, 2026 s, 2000 m
$ISn[Co(CO)_4]_3$	2108 w, 2085 s, 2047 m, 2041 mw, 2026 s, 2000 m
$CH_3Sn[Co(CO)_4]_3$	2101 w, 2079 s, 2040 w, 2028 w, sh, 2020 s, 2010 s, 1992 w, sh, 1961 vw[b]
n-$C_4H_9Sn[Co(CO)_4]_3$	2100 mw, 2078 s, 2040 w, sh, 2029 m, sh, 2019 s, 2008 s, 1988 m, 1962 vw[b]
$CH_2{=}CHSn[Co(CO)_4]_3$	2102 w, 2080 s, 2037 w, sh, 2029 m, sh, 2022 s, 2012 s, 1997 m, 1965 vw[b]
$C_6H_5Sn[Co(CO)_4]_3$	2102 mw, 2079 s, 2037 mw, sh, 2023 s, 2010 s, 2000 m, 1965 vw[b]

[a] Cyclohexane solution. [b] Probably ^{13}C satellites.

Mass spectra were obtained with an AEI MS9 double-focusing mass spectrometer. Solid samples were introduced by direct evaporation; their volatility made it desirable to cool the ion source by turning off the electron beam until immediately before the spectrum was determined. Tin-containing fragments were readily identified by the characteristic pattern of the 11 stable tin isotopes. For simplicity, the masses and relative abundances quoted here refer to the most abundant isotope, ^{120}Sn.

TABLE II

ANALYTICAL DATA, COLOR, AND MELTING POINTS

Compound	Mp,[a] °C	Color	Calcd, %					Found, %				
			C	H	O	X	Co	C	H	O	X	Co
$ClSn[Co(CO)_4]_3$	97.5–100	Dark red	21.6	0.0	28.8	5.3	26.5	21.1	1.5	24.4	5.2	28.7
$BrSn[Co(CO)_4]_3$	100–103	Dark red	20.2	0.0	27.0	11.2	24.8	20.3	0.0	27.1	10.0	27.6
$ISn[Co(CO)_4]_3$	110–117 dec	Dark red-purple	19.0	0.0	25.3	16.7	...	21.4	0.0	26.6	15.9	...
$CH_3Sn[Co(CO)_4]_3$	69–71	Red	24.2	0.5	29.7	...	...	23.4	0.4	27.0	...	...
n-$C_4H_9Sn[Co(CO)_4]_3$	60–62	Red	28.0	1.3	27.9	...	...	29.0	1.4	27.4	...	...
$CH_2{=}CHSn[Co(CO)_4]_3$	57–60	Red	25.5	0.5	29.2	0.0	...	25.9	0.5	30.1	0.0	...
$C_6H_5Sn[Co(CO)_4]_3$	89–91	Red	30.5	0.7	27.1	...	24.9	29.6	0.5	30.1	...	26.0

[a] In sealed, evacuated capillary tube, uncorrected.

Microanalyses (Table II) were carried out by Bernhardt Mikroanalytiches Laboratorium (Mülheim) and by Pascher Mikroanalytiches Laboratorium (Bonn).

Chlorotris(tetracarbonylcobalt)tin(IV), $ClSn[Co(CO)_4]_3$. Method A.—A solution of $SnCl_4$ (10.4 g, 40.0 mmoles) in THF was added at room temperature to a stirred solution of $Co_2(CO)_8$ (31.0 g, 90.6 mmoles) in the same solvent. After CO evolution had ceased, THF was removed at reduced pressure. Extraction of the residue with n-pentane left behind a green solid, presumably a THF adduct of $CoCl_2$. The pentane extract was concentrated at reduced pressure to 100 ml and cooled to −20°, affording the product as dark red needles (20.0 g, 75%) which were recrystallized from n-pentane.

Method B.—A solution of $Cl_2Sn[Co(CO)_4]_2$ was prepared[9] by reaction of $SnCl_2$ (0.9 g, 4.7 mmoles) with $Co_2(CO)_8$ (1.7 g, 5.0 mmoles) in THF for 5 min at room temperature. Thallium(I) acetylacetonate (2.0 g, 6.6 mmoles) in THF was added with stirring. After 10 min, THF was removed *in vacuo* and the residue extracted with n-pentane. The extract was cooled to −80°, affording 0.8 g of dark red needles; the yield (based on tin) was 20% after recrystallization.

Bromotris(tetracarbonylcobalt)tin(IV), $BrSn[Co(CO)_4]_3$. Method A.—To tin(IV) bromide (4.4 g, 9.8 mmoles) in 200 ml of THF was added $Co_2(CO)_8$ (7.7 g, 22.5 mmoles) in the same solvent. After stirring 10 min at room temperature, CO evolution ceased and THF was removed at reduced pressure. A pentane extract, after concentration and cooling to −20°, afforded long needles of the product in 64% yield; recrystallization was from n-pentane.

Method B.—To a THF solution of $Br_2Sn[Co(CO)_4]_2$ prepared[9] from $SnBr_2$ (1.4 g, 5.1 mmoles) and $Co_2(CO)_8$ (1.7 g, 5.0 mmoles), sodium metal in thin slices was added and stirring was continued for 30 min. Following removal of THF at reduced pressure, a pentane extract of the residue was concentrated to 20 ml and cooled to −20° affording 0.5 g of $BrSn[Co(CO)_4]_3$.

Method C.—From the reaction in THF at room temperature of $Br_2Sn[Co(CO)_4]_2$ (2.4 mmoles, prepared as above) and $TlC_5H_7O_2$ (0.75 g, 2.5 mmoles) was isolated (pentane extraction and recrystallization) 0.2 g of pure $BrSn[Co(CO)_4]_3$.

Method D.—A solution of $NaCo(CO)_4$ (4.5 mmoles) in THF was added to $Br_2Sn[Co(CO)_4]_2$ (4.8 mmoles) in the same solvent with stirring at room temperature. Removal of THF followed by extraction and recrystallization at −80° with n-pentane afforded the pure product (0.2 g).

Iodotris(tetracarbonylcobalt)tin(IV), $ISn[Co(CO)_4]_3$.—Tin(IV) iodide (1.5 g, 4.9 mmoles) in THF was added to a stirred THF solution of 3.1 g of $Co_2(CO)_8$ (9.1 mmoles) at room temperature. After the initial rapid evolution of CO had ceased, solvent was removed *in vacuo*. Extraction with n-pentane, followed by cooling to −80°, afforded dark red-purple needles of the product (73% yield), which was recrystallized from n-pentane.

Methyltris(tetracarbonylcobalt)tin(IV), $CH_3Sn[Co(CO)_4]_3$.—Dicobalt octacarbonyl (4.0 g, 11.7 mmoles) was dissolved in methanol and heated to 50° until no more CO was evolved. The resulting rose-colored solution was treated with 1.4 g of CH_3SnCl_3 (5.8 mmoles) in THF with warming to 50°. The dark red solution was filtered and cooled to 0°. Slow dropwise addition of water to the stirred solution afforded red crystals. Recrystallization from n-pentane at −80° gave a 53% yield of pure product.

n-Butyltris(tetracarbonylcobalt)tin(IV), n-$C_4H_9Sn[Co(CO)_4]_3$.

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(13) A. C. Smith, Jr., and E. G. Rochow, *J. Am. Chem. Soc.*, **75**, 4105 (1953).

(14) D. Seyferth and F. G. A. Stone, *ibid.*, **79**, 515 (1957); we thank Mrs. H. R. H. Patil for preparing this compound.

Method A.—A solution of *n*-butyltin trichloride (1.4 g, 5.0 mmoles) in THF was added with stirring to 20.5 mmoles of $NaCo(CO)_4$ in the same solvent at room temperature. Solvent was removed *in vacuo* after 5 min, and the residue was extracted with *n*-pentane. The solution was evaporated to 50 ml and cooled to −80°. The red crystals so formed were purified by recrystallization from *n*-pentane affording a 60% yield of product.

Method B.—A solution of *n*-butyltin trichloride (0.5 g, 1.8 mmoles) in THF was added to one of dicobalt octacarbonyl (0.3 g, 3.8 mmoles) with stirring at room temperature. When CO evolution had ceased, THF was taken off under reduced pressure, and the residue was extracted with 25 ml of *n*-pentane. On cooling to −80°, excess $Co_2(CO)_8$ crystallized out. Evaporation of the mother liquor to 5 ml, followed by cooling to −80°, afforded 0.35 g of red crystals of product, characterized by infrared spectrum.

Vinyltris(tetracarbonylcobalt)tin(IV), $CH_2{=}CHSn[Co(CO)_4]_3$.—A THF solution of $NaCo(CO)_4$ (15.8 mmoles) was added to a stirred solution of 1.3 g of vinyltin trichloride (5.0 mmoles) at room temperature. Solvent was removed at reduced pressure, and the residue was extracted with *n*-pentane. The extract was evaporated to 20 ml and cooled to −80°. Individual red and yellow crystals were deposited. These were separated by hand and recrystallized from *n*-pentane affording 0.6 g of red crystals of product and 0.4 g of yellow crystals of **vinylchlorobis(tetracarbonylcobalt)tin(IV)**, characterized by analysis and infrared spectrum.[15]

Phenyltris(tetracarbonylcobalt)tin(IV), $C_6H_5Sn[Co(CO)_4]_3$.—A solution of 32 mmoles of $NaCo(CO)_4$ in THF was added to a stirred THF solution of 2.9 g of phenyltin trichloride (9.6 mmoles) at room temperature. Solvent was taken off under reduced pressure and the residue was extracted with *n*-pentane. After cooling to −80°, the red crystals so produced were recrystallized from *n*-pentane affording a 67% yield of product.

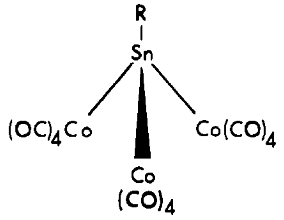
Effect of Heat on $CH_3Sn[Co(CO)_4]_3$.—(a) A sample of $CH_3Sn[Co(CO)_4]_3$ (0.3 g, 4.6 mmoles) was sealed in an evacuated tube and heated to 80–90° for 1 hr. The contents of the tube were then dissolved in *n*-pentane and cooled to −80° affording 0.3 g of starting material characterized by infrared spectrum. (b) A toluene solution of $CH_3Sn[Co(CO)_4]_3$ was refluxed for 5 hr. Complete decomposition to a metallic mirror and black insoluble material was observed.

Ultraviolet Irradiation of $CH_3Sn[Co(CO)_4]_3$.—A 0.2-g sample was dissolved in 25 ml of *n*-hexane and irradiated with ultraviolet light for 45 min. The solution became cloudy. The infrared spectrum of the filtered solution showed only starting material, $Co_4(CO)_{12}$, and $Co_2(CO)_8$ to be present.

Discussion

As an extension of our studies[9,15] of compounds involving bonds between elements of the fourth main group and cobalt, we now report the preparation of tris(tetracarbonylcobalt)tin(IV) derivatives and their mass and infrared spectra. With the exception of the compounds based on the CCo_3 and $SiCo_3$ nuclei mentioned in the Introduction, only a few tris(transition metal) derivatives of the group IV elements have been prepared. Nesmeyanov, *et al.*,[16] have reported $C_6H_5Sn[Re(CO)_5]_3$, $BrSn[Re(CO)_5]_3$, and the unusual compound $[(OC)_5Re]_3Sn–Sn[Re(CO)_5]_3$; very recently, a number of $RSn[Mn(CO)_5]_3$ derivatives have been prepared in this laboratory.[17] It should also be noted that in some circumstances, four transition metals can be grouped around a tin atom in a stable compound.[18]

The organotin tris(tetracarbonylcobalt) derivatives (III) were all prepared by treating the appropriate organotin trihalide with 3 moles of tetracarbonylcobalt anion



III

$$RSnCl_3 + 3NaCo(CO)_4 \xrightarrow{THF} RSn[Co(CO)_4]_3 + 3NaCl$$

In all cases except R = vinyl, the only product was the triscobalt derivative, but, with vinyltin trichloride, $CH_2{=}CH(Cl)Sn[Co(CO)_4]_2$ was isolated as well. The *n*-butyl derivative prepared by this method was found to be identical with that obtained by treating the trihalide with cobalt carbonyl

$$n\text{-}C_4H_9SnCl_3 + Co_2(CO)_8 \longrightarrow n\text{-}C_4H_9Sn[Co(CO)_4]_3$$

The latter reaction has previously been reported[12] to form a tris(tricarbonylcobalt)tin(IV) compound. All of the compounds prepared in this work analyzed as the tetracarbonyl derivatives, and mass spectral results (*vide infra*) establish this conclusively. They are moderately air-stable, red, crystalline substances not substantially decomposed thermally below 100°.

The halogeno derivatives (III, R = Cl, Br, I) could all be prepared in 60–75% yield by reaction of the tin(IV) halide with dicobalt octacarbonyl at room temperature according to the following idealized equation

$$4SnX_4 + 9Co_2(CO)_8 \xrightarrow{THF} 4XSn[Co(CO)_4]_3 + 6CoX_2 + 24CO$$

These derivatives were also produced, in relatively small yields, by two rather unexpected reactions: those of $X_2Sn[Co(CO)_4]_2$ with thallium(I) acetylacetonate and those with metallic sodium. In a more rational process, reaction of $Br_2Sn[Co(CO)_4]_2$ with $NaCo(CO)_4$ produced $BrSn[Co(CO)_4]_3$.

The halogeno compounds crystallize in long, dark red needles, and the bromo and chloro members resemble the organotin derivatives in general stability. The iodo compound, however, decomposed partially on heating in cyclohexane, forming $Co_4(CO)_{12}$ (by infrared). This lower stability was also apparent in the mass spectrum, in which peaks due to $Co_4(CO)_{12}$ were superimposed on those from $ISn[Co(CO)_4]_3$; presumably heat from the ion source caused some decomposition of the solid or gaseous sample.

The infrared spectra shown in Figures 1 and 2 are typical of the organo and halogeno derivatives, respectively. The molecules can reasonably be taken as having C_{3v} symmetry, regarding the organic groups higher

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(15) This compound and other mono- and bis(tetracarbonylcobalt) derivatives of tin and germanium have been studied in this laboratory in some detail and will form the subject of a future paper of this series.

(16) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Proc. Acad. Sci. USSR, Chem. Sect.*, **156**, 502 (1964).

(17) J. A. J. Thompson, unpublished work.

(18) S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, **87**, 1146 (1965).

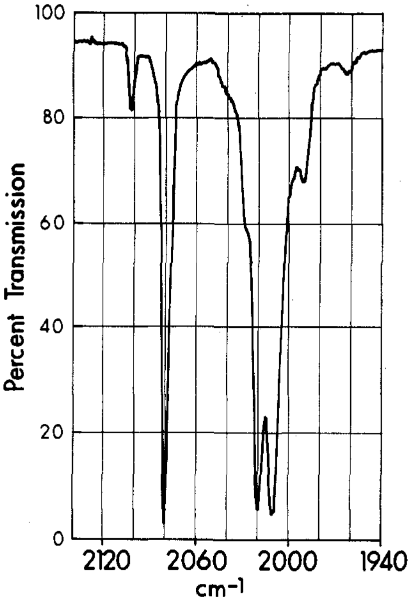


Figure 1.—Carbonyl stretching region of the infrared spectrum of $CH_3Sn[Co(CO)_4]_3$. Cyclohexane; 0.5-mm cells.

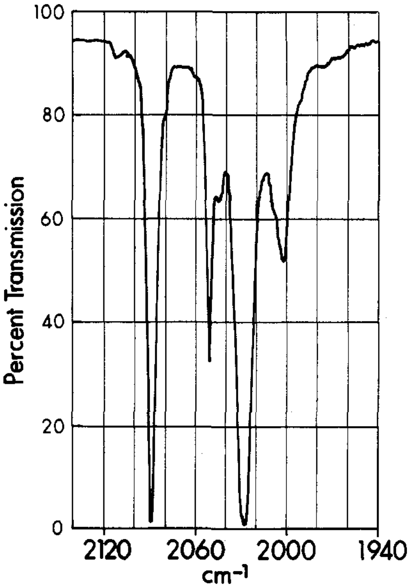


Figure 2.—Carbonyl stretching region of the infrared spectrum of $ClSn[Co(CO)_4]_3$. Cyclohexane; 0.5-mm cells.

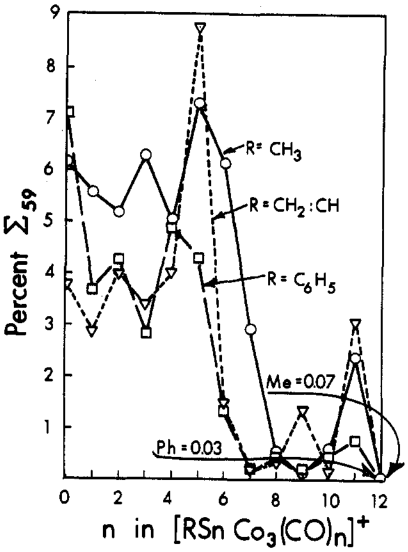


Figure 3.—Abundance of $RSnCo_3(CO)_x{}^+$ fragments observed in the mass spectra of $RSn[Co(CO)_4]_3$ as a function of the number of CO molecules in the fragment. $\%\Sigma_{59}$ is the abundance of a particular fragment expressed as a percentage of the sum of all of the ^{120}Sn- and ^{59}Co-containing fragments observed: ○, CH_3; ▽, $CH_2{=}CH$; □, C_6H_5.

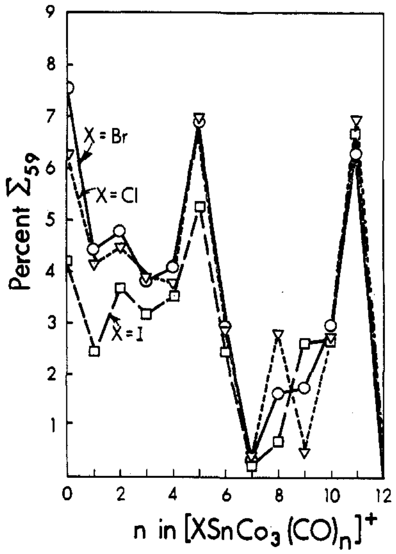
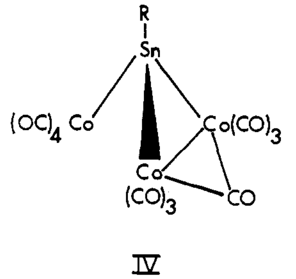


Figure 4.—Abundance of $XSnCo_3(CO)_x{}^+$ fragments observed in the mass spectra of $XSn[Co(CO)_4]_3$ as a function of the number of CO molecules in the fragment. $\%\Sigma_{59}$ is the abundance of a particular fragment expressed as a percentage of the sum of all the ^{120}Sn- and ^{59}Co-containing fragments observed: ○, Br; ▽, Cl; □, I.

than methyl as spherical or cylindrical. Group theory then predicts seven infrared-active carbonyl stretching modes ($3\,A_1 + 4\,E$). We count six or seven bonds, including shoulders, in each figure, in reasonable agreement with expectation. The general band pattern differs slightly in the two compound types.

Mass Spectra.—The predominating fragments observed in the mass spectra of both the halogeno and organo derivatives belong to the series $RSnCo_3(CO)_x{}^+$ produced by consecutive loss of CO from the parent ion $RSnCo_3(CO)_{12}{}^+$. Only in the case of the methyl and phenyl derivatives, however, was this parent ion actually observed. In all cases the ion $RSnCo_3(CO)_{11}{}^+$ was present in moderate to high abundance compared to the other fragments, as shown in Figures 3 and 4. To account for the high stability of the $RSnCo_3(CO)_{11}{}^+$ ion, a structure such as IV could be postulated involving a Co–Co bond supported by a bridging CO. Further evidence for such a structure is given by the mass



IV

spectrum of $Cl_2Sn[Co(CO)_4]_2$,[19] which has strong peaks due to $Cl_2SnCo_2^+$ up to $Cl_2SnCo_2(CO)_7^+$, but no parent peak. Here a structure similar to IV could be postulated with the $Co(CO)_4$ group replaced by chlorine. Such structures are reasonable considering that the neutral species from which they are derived obey the effective atomic number rule. Also the mass spectra of compounds such as $(CH_3)_3SnCo(CO)_4$, possessing only one $Co(CO)_4$ group and thus not capable of forming a bridged ion, display parent ion peaks which have intensities of the same order as other fragments produced by loss of CO.[19] The presence of a cobalt–cobalt bond in IV might also account for the occurrence of Co_2^+ in the mass spectra.

The mass spectrum of the *n*-butyl derivative was complicated by loss of hydrogen from the organic group, but the fragments $C_4H_8SnCo_3(CO)_{12}^+$ and $C_4H_8SnCo_3(CO)_{11}^+$ were identified.

The next most abundant fragments in nearly all cases were produced by loss of $Co(CO)_4$ groups from the parent ion giving rise to the $RSnCo_2(CO)_x^+$ series. In most cases the whole series (x = 0–8) could not be observed owing to overlapping with other more abundant fragments. Also identified in every case were fragments such as Co^+, $SnCo(CO)_x^+$, $RSnCo(CO)_x^+$, $Co(CO)_x^+$, and Co_2^+. The mass spectrum of $CH_3Sn[Co(CO)_4]_3$ is reported in Table III as being representative of the whole series, and in Table IV a summary of all the spectra is given.

Table III

Partial Mass Spectrum of $CH_3Sn[Co(CO)_4]_3$

Mass no.[a]	% Σ_{59}[b]	Ion	Mass no.[a]	% Σ_{59}[b]	Ion
648	0.07	$CH_3SnCo_3(CO)_{12}^+$	266	0.33	$SnCo_2CO^+$
. . .[c]	. . .	. . .	238	5.45	$SnCo_2^+$
312	6.13	$CH_3SnCo_3^+$			
			222	0.19	$CH_3SnCoCO^+$
633	0.07	$SnCo_3(CO)_{12}^+$			
. . .	. . .	. . .	179	2.72	$SnCo^+$
297	5.14	$SnCo_3^+$			
			171	0.17	$Co(CO)_4^+$
477	1.67	$CH_3SnCo_2(CO)_8^+$	. . .	. . .	. . .
393	4.77	$CH_3SnCo_2(CO)_5^+$	59	3.95	Co^+
. . .	. . .	. . .			
253	2.01	$CH_3SnCo_2^+$	118	2.25	Co_2^+

[a] In the case of tin-containing ions, the mass number refers to the ^{120}Sn fragment. [b] This is the abundance expressed as a percentage of the sum of all the tin-120- and cobalt-containing fragments observed. [c] Dots indicate observation of all intermediate ions caused by consecutive loss of CO.

Table IV

Summary of Mass Spectral Results[a]

	R in $RSnCo_3(CO)_{12}$					
Fragment	CH_3	$CH_2{=}CH$	C_6H_5	Cl	Br	I
$RSnCo_3(CO)_x^+$	0–12	0–11	0–12	0–11	0–11	0–11
$RSnCo_2(CO)_x^+$	0–5, 8	0–5, 7, 8	0–5, 8	0–6, 8	0–8	0–6
$RSnCo(CO)_x^+$	1, 2	0, 2	0, 1	0	0, 1	
$SnCo_3(CO)_x^+$	0–12	0	0, 12			
$SnCo_2(CO)_x^+$	0, 1	2, 3	3, 5	0	0	
$SnCo(CO)_x^+$	0	0, 2–4	0	0	0	
$Co(CO)_x^+$	0–4	0–4	0–4	0–4	0–4	
Co_2^+	*b*	*b*	*b*	*b*	*b*	

[a] Entries in the table refer to values of x, the number of CO groups, for which fragments of each of the series given in the first column were observed. The notation *m–n* signifies that fragments appeared for all integral values of x from m to n, inclusive; the notation m, n implies that peaks corresponding to intermediate numbers of CO groups, although they may be present, could not be unambiguously assigned owing to superposition of other more abundant fragments. [b] Fragment observed.

The mass spectra thus provide conclusive evidence for the formation of $RSn[Co(CO)_4]_3$. It would not be reasonable to regard fragments of mass higher than $RSnCo_3(CO)_9^+$ as being due to recombination owing to the low pressure employed in the mass spectrometer. Indeed the mass spectrum of $CH_3C[Co(CO)_3]_3$ showed no sign of fragments of mass higher than $CH_3CCo_3(CO)_9^+$.[19,20] There is also a considerable abundance of species caused by tin–cobalt bond breakage, which is not observed to such an extent in the case of $CH_3C[Co(CO)_3]_3$, which possesses the very stable pyramidal CCo_3 skeleton involving cobalt–cobalt bonds. Thus in the mass spectrum of $CH_3C[Co(CO)_3]_3$, ions of the series $CH_3CCo_3(CO)_x^+$ (x = 0–9) account for 75% of the total fragments, while for $RSnCo_3(CO)_{12}$ the series $RSnCo_3(CO)_x^+$ (x = 0–12) accounts for only 30–48% of the total ions.[19]

The absence of an especially intense peak due to $RSnCo_3(CO)_9^+$ would possibly indicate that a condensed system involving cobalt–cobalt bonds, analogous to I and II, is not especially stable. Indeed it was not found possible to prepare $CH_3Sn[Co(CO)_3]_3$ by the action of heat or ultraviolet light on $CH_3Sn[Co(CO)_4]_3$.

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