isomer was established by its visible and uv spectra, which agreed with that recorded by Basolo for this compound[14] and was almost identical with the spectrum for the *trans*-$[Co(NO_2)_2(en)_2]^+$ ion. A solution of the material recovered from a chromatogram was used as M_4.

Conclusion

This study does not destroy any of Werner's actual work but merely moderates the interpretation he placed on some of this work. We conclude that all such synthetic procedures should be viewed with a great deal of caution and should be monitored, wherever possible, by chromatographic processes.

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[14] F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Organometallic Compounds with Metal–Metal Bonds. XV. Synthesis and Infrared Spectra of Mono(tetracarbonylcobalt) Derivatives of Tin, Tetrakis(tetracarbonylcobalt)tin(IV), and Related Compounds[1]

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The syntheses and infrared spectra of a series of mono(tetracarbonylcobalt)tin(IV) derivatives of the general formula $R_nX_{3-n}SnCo(CO)_4$ [$R = C_6H_5$; X = Cl, Br, I; n = 0, 1, 2] are reported. Several triphenylphosphine complexes are also described. Assignments are suggested for the carbonyl stretching bands. Cobalt carbonyl reacts with tin(II) fluoride to form $FSn[Co(CO)_4]_3$ and with tin(II) acetate to yield $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $(CH_3CO_2)Sn[Co(CO)_4]_3$. The preparation of $Sn[Co(CO)_4]_4$ is also reported.

Introduction

In an earlier paper of this series,[2] we described the synthesis of an extensive series of derivatives of the type $R_nX_{3-n}GeCo(CO)_4$ [$R = C_6H_5, CH_3$; X = Cl, Br, I; n = 0, 1, 2, 3]. The infrared spectra of these germanium compounds in the carbonyl stretching region were also discussed.

We now report on an extension of this work to tin and describe the synthesis and infrared spectra of the series $R_nX_{3-n}SnCo(CO)_4$. The preparation of $Sn[Co(CO)_4]_4$, also described in this paper, completes a very extensive series of tin–cobalt compounds which may be represented by the general formula $R_nX_{m-n}Sn[Co(CO)_4]_{4-m}$ (m = 0, 1,[3] 2,[2,4] 3; $n \le m$).

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. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded on a Texas Instruments Servo-Riter with calibration as described previously.[5] Microanalyses were performed by Alfred Berhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Mass spectra were measured with an AEI MS-9 spectrometer with direct introduction of solid samples.

Tribromo(tetracarbonylcobalt)germanium(IV), $Br_3GeCo(CO)_4$.—A solution of 1.3 g (3.8 mmoles) of $Co_2(CO)_8$ in THF was added to 2.0 g (5.1 mmoles) of $GeBr_4$ in the same solvent and the mixture was stirred at room temperature. The solution became dark green and CO was rapidly evolved. THF was removed at reduced pressure when CO evolution had ceased, and the residue was extracted with n-pentane. Concentration and cooling of the extract to −20° afforded yellow crystals of product. Recrystallization from n-pentane gave 0.4 g of product. **Triiodo(tetracarbonylcobalt)germanium(IV), $I_3GeCo(CO)_4$,** was prepared in the same way from 2.9 g (5.0 mmoles) of GeI_4 and 1.3 g (3.8 mmoles) of $Co_2(CO)_8$ in THF (yield 1.4 g).

Trichloro(tetracarbonylcobalt)tin(IV), $Cl_3SnCo(CO)_4$.—A solution of 10 g (29 mmoles) of $Co_2(CO)_8$ in 200 ml of benzene was added dropwise over the course of 1 hr to 25 g (96 mmoles) of $SnCl_4$ in 100 ml of benzene stirred at room temperature. Carbon monoxide was evolved and a pale blue gelatinous precipitate formed. When CO evolution had ceased, the solution was filtered and evaporated to dryness *in vacuo*. The residue was extracted with n-pentane and the solution was concentrated and cooled to −20°, affording yellow crystals. Recrystallization from n-pentane yielded 1.1 g.

Tribromo(tetracarbonylcobalt)tin(IV), $Br_3SnCo(CO)_4$.—A solution of 5.2 g (16.4 mmoles) of $Co_2(CO)_8$ in 150 ml of benzene was added dropwise over the course of 30 min to a room-temperature solution of 13.0 g (29.7 mmoles) of $SnBr_4$ in 70 ml of benzene. When CO evolution had ceased, the solution was filtered free of precipitated cobalt bromide and evaporated to dryness under vacuum. The residue was dissolved in ~150 ml of n-pentane and the solution was cooled to −20°. A mixture of red and orange

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[1] Part XIV of this series: R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 523 (1968).

[2] D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967), where references to earlier literature are also given.

[3] D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 2222 (1966).

[4] D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966).

[5] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966).

crystals was deposited. Two recrystallizations from *n*-pentane afforded 5 g of pure product. The mother liquor from the initial pentane extraction was evaporated to 30 ml and cooled to −20° to give crude $Br_3Sn[Co(CO)_4]_2$ (0.6 g).

Triiodo(tetracarbonylcobalt)tin(IV), $I_3SnCo(CO)_4$.—Tin(IV) iodide (3.1 g, 4.8 mmoles) was treated in the same way as above with 1.3 g (3.8 mmoles) of $Co_2(CO)_8$ in benzene. Benzene was removed after 2 hr at room temperature and the residue was extracted wih *n*-pentane. Evaporation and cooling to −20° afforded red crystals of product which were recrystallized twice from *n*-pentane affording 2.0 g (78% yield) of product.

Butyldichloro(tetracarbonylcobalt)tin(IV), $Cl_2(C_4H_9)SnCo(CO)_4$.—A solution of 5.0 g (14.6 mmoles) of $Co_2(CO)_8$ in THF was slowly added dropwise to 5.6 g (14.8 mmoles) of $C_4H_9SnCl_3$ in THF with stirring at room temperature. After stirring for 3 hr, THF was evaporated *in vacuo* and the residue was extracted with *n*-pentane. The solution was cooled to −80° after evaporation to 20 ml affording yellow crystals of impure product and black crystals of $Co_4(CO)_{12}$. Several recrystallizations from *n*-pentane at −80° gave a white crystalline solid. This was an oil at room temperature and was freed from *n*-pentane under high vacuum (yield 5.0 g).

Phenyldichloro(tetracarbonylcobalt)tin(IV), $Cl_2(C_6H_5)SnCo(CO)_4$.—A THF solution of $Co_2(CO)_8$ (2.0 g, 5.85 mmoles) was slowly added to a stirred room-temperature solution of 3.5 g (11.6 mmoles) of $C_6H_5SnCl_3$ in THF. Evaporation and extraction by *n*-pentane after 2 hr stirring followed by cooling to −20° afforded 0.7 g of pure product after two recrystallizations.

Phenyldibromo(tetracarbonylcobalt)tin(IV), $Br_2(C_6H_5)SnCo(CO)_4$.—This compound was prepared as above from 4.0 g (9.2 mmoles) of $C_6H_5SnBr_3$ and 2.0 g (5.85 mmoles) of $Co_2(CO)_8$. Two recrystallizations from *n*-pentane afforded 2.6 g of pure yellow needles of product.

Phenyldiiodo- and Diphenyliodo(tetracarbonylcobalt)tin(IV), $I_2(C_6H_5)SnCo(CO)_4$ and $I(C_6H_5)_2SnCo(CO)_4$.—These were prepared by treating 1 mmole of $Cl_2(C_6H_5)SnCo(CO)_4$ or 2 mmoles of $Cl(C_6H_5)_2SnCo(CO)_4$ in acetone solution with 2 mmoles of NaI in the same solvent. Removal of precipitated NaCl by filtration followed by removal of acetone and several recrystallizations of the residue from *n*-pentane afforded yellow crystals of the pure products.

Diphenylchloro(tetracarbonylcobalt)tin(IV), $Cl(C_6H_5)_2SnCo(CO)_4$.—A THF solution of 2.5 g (7.3 mmoles) of $Co_2(CO)_8$ was added dropwise over the course of 30 min to a THF solution of 3.4 g (9.9 mmoles) of $(C_6H_5)_2SnCl_2$ stirred at room temperature. After complete addition of $Co_2(CO)_8$, the solution was stirred until CO evolution had ceased. Evaporation of THF was followed by *n*-pentane extraction. Concentration of this extract to 8 ml followed by cooling to −20° afforded 3.4 g of white crystals, which upon recrystallization from pentane gave 2.5 g of pure product.

Dimethylchloro(tetracarbonylcobalt)tin(IV), $Cl(CH_3)_2SnCo(CO)_4$.—This compound was prepared as above from 5.0 g (16.6 mmoles) of $Co_2(CO)_8$ and 4.5 g (20.5 mmoles) of $(CH_3)_2SnCl_2$. Extraction with *n*-pentane followed by evaporation to 50 ml and cooling to −20° gave 5.8 g of pale yellow crystals. Several recrystallizations from *n*-pentane afforded 4.0 g of white crystalline product.

Diphenylbromo(tetracarbonylcobalt)tin(IV), $Br(C_6H_5)_2SnCo(CO)_4$.—This compound was prepared similarly to the above from 1.0 g (2.9 mmoles) of $Co_2(CO)_8$ and 1.7 g (3.9 mmoles) of $(C_6H_5)_2SnBr_2$; yield, 1.0 g after two *n*-pentane recrystallizations.

Tribromo(triphenylphosphinetricarbonylcobalt)tin(IV), $Br_3SnCo(CO)_3P(C_6H_5)_3$.—Triphenylphosphine (0.6 g, 2.3 mmoles) was added to 1.0 g (1.9 mmoles) of $Br_3SnCo(CO)_4$ dissolved in benzene. Vigorous CO evolution ensued and the solution became warm. Precipitation of solid occurred and this was completed by addition of *n*-pentane. The solid was extracted with 50 ml of benzene leaving an insoluble residue. After evaporation of the benzene extract to 10 ml, *n*-pentane was slowly added, the initially formed greenish impure deposit was rejected, and the solution was cooled to −20° after a total of 80 ml of *n*-pentane had been added. This afforded 0.25 g of glistening orange crystals which were recrystallized from benzene and *n*-pentane.

Butyldichloro(triphenylphosphinetricarbonylcobalt)tin(IV), $Cl_2(C_4H_9)SnCo(CO)_3P(C_6H_5)_3$.—A mixture of 1.0 g (2.4 mmoles) of $Cl_2(C_4H_9)SnCo(CO)_4$ and 0.7 g (2.7 mmoles) of $P(C_6H_5)_3$ was heated to 125°. Evolution of CO ceased after 1 hr and the mixture was then extracted with *n*-pentane to remove unreacted starting materials. The resulting crystalline mass was then extracted with 200 ml of hexane and the extract was evaporated to give greenish yellow crystals. The impure product was recrystallized by dissolving in acetone and slowly adding water to afford 0.6 g of yellow crystalline product.

Phenyldichloro(triphenylphosphinetricarbonylcobalt)tin(IV), $Cl_2(C_6H_5)SnCo(CO)_3P(C_6H_5)_3$.—Triphenylphosphine (0.3 g) was mixed with 0.45 g (1.05 mmoles) of $Cl_2(C_6H_5)SnCo(CO)_4$ and heated *in vacuo* to 100° for 10 min, when CO was rapidly evolved. The mixture was then extracted with *n*-pentane to remove unreacted starting material. The crude product was then crystallized from 6 ml of benzene with slow addition of pentane, the initial impure deposit being discarded. A further 50 ml of pentane was added, and the solution was cooled to 0° giving fine yellow needles. These were recrystallized from acetone by addition of water (yield 0.25 g).

Tetrakis(tetracarbonylcobalt)tin(IV), $Sn[Co(CO)_4]_4$.—(i) A solution of 12.0 g (35.1 mmoles) of $Co_2(CO)_8$ in 50 ml of THF was added to a solution of 2.6 g (10.0 mmoles) of $SnCl_4$ in 50 ml of the same solvent. The solution slowly evolved CO while being stirred at room temperature. After 4 hr the reaction mixture was filtered resulting in 1.8 g of dark crystals of crude product. The filtrate was evaporated to one-fourth of its original volume and stirred for 24 hr at room temperature. Filtration gave a further crop of 1.6 g of product. The combined crude products were extracted with 250 ml of acetone, which was evaporated to about 5 ml affording 1.0 g of very dark red glistening crystals of pure product. The compound could also be recrystallized in a similar way from *n*-pentane.

(ii) A solution of 2.6 g (3.9 mmoles) of $ClSn[Co(CO)_4]_3$ and 1.3 g (3.8 mmoles) of $Co_2(CO)_8$ in 40 ml of THF was stirred at room temperature with CO evolution. After about 3 hr the solution was filtered from precipitated product (0.6 g). The filtrate was stirred for a further 12 hr and refiltered, affording a further 2.0 g of crude product. The combined crude product was crystallized by evaporation of an *n*-pentane solution to small volume (yield 1.5 g).

Molecular weight calculated for $Sn[Co(CO)_4]_4$, 802.6; found, 880 ± 100 (osmometer, with argon atmosphere, 1.36 g/l. of cyclohexane).

Fluorotris(tetracarbonylcobalt)tin(IV), $FSn[Co(CO)_4]_3$.—Finely divided SnF_2 (4.0 g, 26.6 mmoles) was suspended in a solution of 7.2 g (21.0 mmoles) of $Co_2(CO)_8$ in THF and stirred at room temperature for 5 hr. After decanting the solution from excess SnF_2, solvent was removed *in vacuo* and the residue was extracted with 150 ml of *n*-pentane, which on cooling to −20° gave 4.0 g of very dark red crystals. Two recrystallizations from *n*-pentane afforded 3.4 g of pure product.

Bis(tetracarbonylcobalt)tin(IV) Diacetate, $(CH_3CO_2)_2Sn[Co(CO)_4]_2$, and Tris(tetracarbonylcobalt)tin(IV) Acetate, $CH_3CO_2Sn[Co(CO)_4]_3$.—Tin(II) acetate (9.0 g, 38 mmoles) was treated with 6.6 g (19.3 mmoles) of $Co_2(CO)_8$ in THF with stirring at room temperature. After 15 min the THF was removed at reduced pressure and the residue was extracted with 500 ml of *n*-pentane leaving 6.0 g of a red insoluble residue. The pentane extract was evaporated to 50 ml and cooled to −20° resulting in orange needles; two further recrystallizations from *n*-pentane afforded 0.4 g of pure $(CH_3CO_2)_2Sn[Co(CO)_4]_2$. The *n*-pentane mother liquor from the initial extraction was evaporated to 5 ml and cooled to −20° yielding dark red crystals. Recrystallization from *n*-pentane afforded 0.4 g of pure $CH_3CO_2Sn[Co(CO)_4]_3$.

Molecular weight calculated for $(CH_3CO_2)_2Sn[Co(CO)_4]_2$, 578.2; found, 755 ± 20 (8.02 g/l.), 765 ± 50 (22.9 g/l.) (osmometer, cyclohexane, argon atmosphere).

TABLE I

ANALYTICAL DATA, MELTING POINT, AND COLOR

	Mp,[a] °C	Color	% calcd				% found			
			C	H	O	X	C	H	O	X
$Br_3GeCo(CO)_4$	102 dec	Yellow	9.9	0.0	. . .	49.5	9.9	0.0	. . .	45.3
$I_3GeCo(CO)_4$	110 dec	Orange	7.7	0.0	. . .	61.0	9.1	0.0	. . .	62.9
$Cl_3SnCo(CO)_4$	79–80 dec	Yellow	12.1	0.0	16.1	26.8	13.2	0.0	15.8	26.4
$Br_3SnCo(CO)_4$	90–95 dec	Orange	9.2	0.0	12.1	45.3	9.3	0.0	12.1	40.6
$I_3SnCo(CO)_4$	92 dec	Red	7.2	0.0	9.5	56.8	7.4	0.0	9.6	61.8
$Cl_2(C_4H_9)SnCo(CO)_4$	. . .[b]	Orange	23.0	2.2	15.3	17.0	22.9	2.1	15.3	16.8
$Cl_2(C_6H_5)SnCo(CO)_4$	63–65	Yellow	27.7	1.1	14.6	16.2	27.0	1.1	14.9	13.5
$Br_2(C_6H_5)SnCo(CO)_4$	73.5–75	Yellow	22.8	0.9	12.1	30.3	23.1	0.8	12.1	30.3
$Cl(C_6H_5)_2SnCo(CO)_4$	66–68	Yellow	40.5	2.1	13.4	7.4	40.8	2.3	12.8	5.6
$Cl(CH_3)_2SnCo(CO)_4$	70–73	White	20.3	1.7	18.0	10.0	20.1	1.7	17.9	9.9
$Br(C_6H_5)_2SnCo(CO)_4$	55.5–57	Yellow	36.8	1.9	12.2	15.3	37.1	2.2	12.3	15.6
$I(C_6H_5)_2SnCo(CO)_4$	69–70	Yellow	33.7	1.8	11.2	22.2	33.6	1.8	11.2	22.5
$Br_3SnCo(CO)_3P(C_6H_5)_3$	135 dec	Orange	33.1	2.0	. . .	31.4	34.9	2.4	. . .	30.4
$Cl_2(C_4H_9)SnCo(CO)_3P(C_6H_5)_3$[c]	161–164 dec	Yellow	46.1	3.7	. . .	10.9	45.9	3.8	. . .	12.5
$Cl_2(C_6H_5)SnCo(CO)_3P(C_6H_5)_3$	158–162 dec	Yellow	51.2	3.0	. . .	10.5	47.9	3.1	. . .	10.3
$(CH_3CO_2)_2Sn[Co(CO)_4]_2$[d]	90 dec	Orange	24.4	1.0	33.2	. . .	24.7	1.4	32.6	. . .
$CH_3CO_2Sn[Co(CO)_4]_3$	87 dec	Dark red	24.4	0.4	32.4	. . .	24.2	0.8	31.0	. . .
$FSn[Co(CO)_4]_3$	84–87	Dark red	22.1	0.0	29.5	2.9	21.9	0.1	29.8	3.8
$Sn[Co(CO)_4]_4$[e]	140 dec	Very dark red	24.0	0.0	31.9	. . .	24.5	0.0	32.7	. . .

[a] In an evacuated tube, uncorrected. [b] Liquid at room temperature. [c] P: calcd, 4.7; found, 3.4. [d] Sn: calcd, 20.6; found, 20.7. [e] Sn: calcd, 14.8; found, 14.6. Co: calcd, 29.3; found, 27.7.

Results and Discussion

Cobalt carbonyl was found to react readily with organotin halides and tin tetrahalides to produce the mono(tetracarbonylcobalt) derivative, provided that the tin halide was kept always in excess by adding a solution of cobalt carbonyl to a solution of the tin halide

$$4R_nSnX_{4-n} + 3Co_2(CO)_8 \longrightarrow 4R_nSnX_{3-n}Co(CO)_4 + 2CoX_2 + 8CO \quad (n = 0, 1, 2;\ X = Cl, Br)$$

This reaction is analogous to the one previously used with germanium halides.[2] For the reaction of the organometallic halides, tetrahydrofuran was used as solvent. Benzene was used for the tetrahalide reactions, as tetrahydrofuran produced considerable disubstitution in this case. In the preparation of the trichlorotin derivative, it was necessary to use a considerable excess of $SnCl_4$ over that required by the equation in order to avoid extensive disubstitution. The corresponding iodo derivatives were prepared metathetically by treating the chlorotin compounds with sodium iodide in acetone.

Interestingly, it was not possible to control the reactions of tin tetrachloride or phenyltin trichloride with $Co(CO)_4^-$ to obtain only monosubstituted products. The displacement reaction with the cobalt carbonyl anion invariably resulted in the formation of bis and even tris derivatives. Thus reaction of $C_6H_5SnCl_3$ with $Co(CO)_4^-$ in a 2:1 molar ratio in methanol solution produced only $C_6H_5ClSn[Co(CO)_4]_2$, while treatment of excess $SnCl_4$ in tetrahydrofuran with $NaCo(CO)_4$ resulted in a mixture of $Cl_2Sn[Co(CO)_4]_2$ and $ClSn[Co(CO)_4]_3$.

All of the mono(tetracarbonylcobalt) compounds (Table I) occur as yellow-to-orange crystals which are stable in air for several days without apparent change. The stability is thus considerably greater than that of the trialkyl derivatives.

The infrared spectra in the carbonyl stretching region are similar to those already reported for the corresponding germanium derivatives,[2] and band assignments can be made is analogous fashions as is done in Table II. Derivatives with C_{3v} symmetry exhibit the expected three infrared-active bands ($2\ A_1 + E$). The degenerate E mode is split in compounds of C_s symmetry, where four bands are expected and seen ($3\ A' + A''$). In both cases, the band at highest frequency, designated $A_1^{(2)}$ or $A'^{(2)}$, is assigned to the symmetric stretching mode of the three equatorial carbonyl groups, and the second highest band ($A_1^{(1)}$ or $A'^{(1)}$), to the axial carbonyl stretching mode. As noted earlier,[2] the equatorial and axial A modes are doubtless coupled. Other workers have reached the same conclusion as to assignments in related compounds[6–8] and it is hoped that detailed force constant calculations currently in progress will provide confirmation.[9]

It was found for the germanium analogs that a plot of the frequency of the two A_1 bands (or the corresponding A' bands) against the sum of the Pauling electronegativities of the halogen substituents on germanium gave two straight lines.[2] A similar plot for the tin derivatives is now found to give three closely spaced straight lines for each of the two A_1 (or A') bands, compounds of one particular halogen lying on the same line, while all three lines converge to the $(C_6H_5)_3SnCo(CO)_4$ point. The slope of the lines decreases from chlorine to bromine to iodine. This

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(7) M. Bigorgne and A. Quintin, *Compt. Rend.*, **264**, 2055 (1967).

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(9) Research in progress by Mr. R. S. Gay.

TABLE II

INFRARED CARBONYL STRETCHING BANDS[a]

C_{3v} symmetry	$A_1^{(2)}$	$A_1^{(1)}$	E	
$Cl_3SnCo(CO)_4$	2120 (8.0)	2068 (6.8)	2048 (10)	
$Br_3SnCo(CO)_4$	2116 (8.1)	2063 (6.3)	2043 (10)	
$I_3SnCo(CO)_4$	2109 (8.0)	2058 (4.6)	2037 (10)	
$Br_3SnCo(CO)_3P(C_6H_5)_3$	2056 (0.3)	. . .	1999 (10)	
C_s symmetry	$A'^{(2)}$	$A'^{(1)}$	$A' + A''$	
$Cl_2(C_4H_9)SnCo(CO)_4$	2106 (9.1)	2052 (8.7)	2032 (9.1)	2016 (10)
$Cl_2(C_6H_5)SnCo(CO)_4$	2108 (9.4)	2054 (8.6)	2033 (9.9)	2021 (10)
$Br_2(C_6H_5)SnCo(CO)_4$	2106 (9.4)	2052 (7.7)	2032 (9.9)	2020 (10)
$I_2(C_6H_5)SnCo(CO)_4$	2102 (8.7)	2048 (6.1)	2028 (10)	2018 (10)
$Cl(C_6H_5)_2SnCo(CO)_4$	2097 (8.8)	2040 (7.7)	2019 (10)	2004 (8.7)
$Cl(CH_3)_2SnCo(CO)_4$	2095 (9.0)	2037 (7.8)	2013 (10)	1998 (9.9)
$Br(C_6H_5)_2SnCo(CO)_4$	2096 (9.0)	2040 (7.6)	2019 (10)	2004 (8.8)
$I(C_6H_5)_2SnCo(CO)_4$	2094 (9.5)	2038 (8.1)	2017 (10)	2003 (9.5)
$Cl_2(C_4H_9)SnCo(CO)_3P(C_6H_5)_3$	2046 (1.0)	. . .	1988 (9.0)	1972 (10)
$Cl_2(C_6H_5)SnCo(CO)_3P(C_6H_5)_3$	2048 (1.0)	. . .	1990 (9.9)	1978 (10)
Miscellaneous compounds	ν(CO)			
$(CH_3CO_2)_2Sn[Co(CO)_4]_2$	2112 (1.6), 2106 (0.4), 2093 (9.0), 2088 sh (7.3), 2066 (10), 2044 (9.0), 2030 sh (9.0), 2024 (10), 2019 sh (8.7)			
$(CH_3CO)_2Sn[Co(CO)_4]_3$	2110 (0.8), 2086 sh (8.9), 2084 (9.7), 2049 (2.7), 2040 (4.0), 2025 (10), 2021 sh (9.7), 2008 (3.2), 1998 (2.5)			
$FSn[Co(CO)_4]_3$	2087 (10), 2049 (5.2), 2041 (1.5), 2026 (10), 2006 sh (0.5), 2001 (3.9)			
$Sn[Co(CO)_4]_4$	2079 (9.8), 2032 (3.0), 2018 (10), 1999 sh (0.5), 1994 (2.3)			

[a] All spectra measured in cyclohexane. Figures in parentheses are relative heights of bands measured on a linear transmittance scale; sh = shoulder. Assignments in accordance with text and as detailed by D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

separation according to halogen was noted to a lesser extent for the $A_1^{(1)}$ (or $A'^{(1)}$) frequencies of the germanium analogs but was totally absent for the $A_1^{(2)}$ (or $A'^{(2)}$) bands in the germanium case. The general trend to higher frequencies with increasingly electronegative substituents on tin is readily understood in terms of enhanced cobalt to tin π bonding and changes in the inductive effect operating *via* the tin–cobalt σ bond.[10]

Another interesting trend in the series $(C_6H_5)_3MCo(CO)_4$ [M = Si, Ge, Sn, Pb] is the monotonic decrease of the carbonyl stretching frequencies along the series Si > Ge > Sn > Pb, as has already been noted by Bigorgne[6] (Table III). This trend may indicate a decrease in Co→M π bonding from silicon to lead, due perhaps to increased size and energy of the vacant d orbitals of the group IV element. A similar though much less marked trend has been found in the corresponding series of manganese pentacarbonyl derivatives; in that case, however, a comparison of force constants suggests that there is little difference among the $(C_6H_5)_3M$ groups as ligands.[5,11]

Several triphenylphosphine derivatives of these tetracarbonylcobalt compounds were prepared (Tables I and II). The infrared spectrum of $Br_3SnCo(CO)_3P(C_6H_5)_3$ shows one very strong band and one very weak band at higher frequency (Figure 1a); the spectrum of a more concentrated solution of the compound in chloroform confirmed that the 2056-cm^{-1} band was genuine, although slightly shifted in that solvent. Two infrared bands (A_1 and E) are expected for the *trans* derivative of C_3 symmetry, and the usual intensity arguments[12,13] strongly suggest that the very weak high-frequency band is due to the A_1 totally symmetric equatorial stretching mode, while the intense lower frequency band is due to the E mode. This assignment is borne out in the C_s compounds $Cl_2(n\text{-}C_4H_9)SnCo(CO)_3P(C_6H_5)_3$ and $Cl_2(C_6H_5)SnCo(CO)_3P(C_6H_5)_3$ by the splitting of the low-frequency band (Figure 1b).

TABLE III

	$A_1^{(2)}$	$A_1^{(1)}$	E
$(C_6H_5)_3SiCo(CO)_4$[a]	2093	2032	2003
$(C_6H_5)_3GeCo(CO)_4$[2]	2091	2030	2006
$(C_6H_5)_3SnCo(CO)_4$[2]	2087	2027	1999
$(C_6H_5)_3PbCo(CO)_4$[2]	2081	2022	1997

[a] This compound was originally prepared by A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965); the frequencies given here are those measured in this laboratory by Dr. S. K. Hall for a cyclohexane solution.

Although three infrared-active bands would be expected for both *cis* and *trans* forms of the latter compounds, the observed weak–strong–strong intensity pattern favors the *trans* form. For a *cis* isomer, the highest frequency band would be expected to be of comparable intensity to the lower bands.

The higher frequency equatorial A_1 band is much weaker relative to the E band in the triphenylphosphine derivatives than it is in the tetracarbonyl cases. This phenomenon may be explained on the basis that the anticipated weak equatorial A_1 mode gains intensity in the tetracarbonyl through coupling with the axial A_1

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[10] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

[11] W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).

[12] L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

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

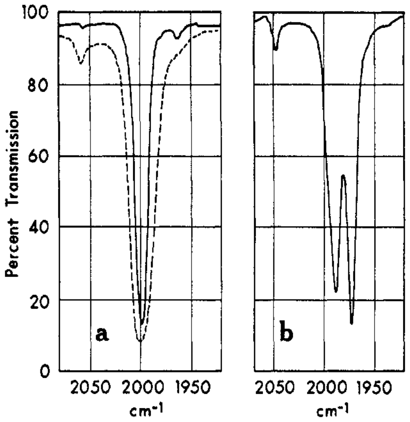

Figure 1.—Carbonyl stretching region of the infrared spectrum. (a) Upper solid curve, $Br_3SnCo(CO)_3P(C_6H_5)_3$, saturated solution in cyclohexane, 0.5-mm cells; lower dashed curve, the same compound in chloroform, ~1 mg/ml, 0.5-mm cells. (b) Cl_2-(n-C_4H_9)$SnCo(CO)_3P(C_6H_5)_3$ in cyclohexane, ~1 mg/ml.

mode, resulting in two A_1 bands of similar intensity.[2] When the axial carbonyl group is replaced by a triphenylphosphine group, the equatorial A_1 mode no longer has another mode of similar frequency and the same symmetry with which to couple, and it is thus weaker.[14]

Tetrakis(tetracarbonylcobalt)tin(IV).—When a tetrahydrofuran solution of $SnCl_4$ or $ClSn[Co(CO)_4]_3$ was stirred at room temperature with cobalt carbonyl, small, very dark red (almost black) glistening crystals were slowly deposited over the course of 1 day. The crystals have been characterized as $Sn[Co(CO)_4]_4$, a compound to which brief reference was previously made.[15] A complete elemental analysis is in agreement with this formulation, as is the molecular weight in cyclohexane. The mass spectrum shows no fragments higher than m/e 776, which corresponds to $SnCo_4(CO)_{15}^+$, the parent ion less one carbonyl group. Other instances are known of cobalt carbonyl derivatives in the mass spectra of which the heaviest ion observed is one carbonyl group less than the molecular ion, the compounds $RSn[Co(CO)_4]_3$ being among them.[3] All fragments due to consecutive loss of CO, from $SnCo_4(CO)_{15}^+$ to $SnCo_4^+$, as well as series such as $SnCo_3(CO)_x^+$ [x = 0–12], were observed.

Tetrakis(tetracarbonylcobalt)tin(IV) is only slightly soluble in n-pentane and hexane (about 1 g/l.) and is not much more soluble in acetone and tetrahydrofuran but it can be recrystallized by evaporation of pentane or acetone solutions to small volume. However, some decomposition invariably occurs during this process and it is very difficult to obtain a really pure product. It decomposes readily on heating above 70° *in vacuo* leaving behind an apparently crystalline magnetic metallic powder, presumably an alloy of tin and cobalt. After the completion of this work, we learned that the same compound had been prepared by Bigorgne and Quintin, by the reaction of tin(II) chloride with excess cobalt carbonyl in tetrahydrofuran solution;[7] this reaction would undoubtedly involve the initial insertion of $SnCl_2$ to form $Cl_2Sn[Co(CO)_4]_2$,[4] which would then react further with cobalt carbonyl.

The carbonyl stretching region of the infrared spectrum of $Sn[Co(CO)_4]_4$ in cyclohexane solution is shown in Figure 2. It consists of two strong bands (2079 and 2018 cm^{-1}) and two or threee weak bands at 2032, 1999, and 1994 cm^{-1}, after allowance is made for peaks due to decomposition products near 2040 cm^{-1}, the intensities of which increase rapidly with time. Bigorgne and Quintin[7] reported only three bands for cetane solutions (2079, 2018, and 1994 cm^{-1}) but apparently did not observe the weaker bands at 2032 and 1999 cm^{-1} which we find quite reproducible. While the 1999-cm^{-1} band is a very weak shoulder, the 2032-cm^{-1} band seems too strong to result from a ^{13}C isotope shift.

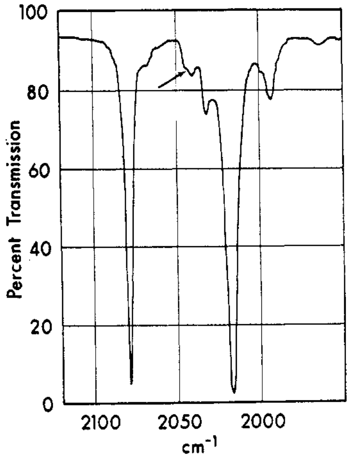

Figure 2.—Carbonyl stretching region of the infrared spectrum of $Sn[Co(CO)_4]_4$ in cyclohexane solution. Arrow marks bands that increase in intensity with time and are attributed to decomposition products.

The question at issue is whether the molecule in solution has true T_d symmetry, in which case only three infrared-active carbonyl stretching modes are possible (3 T_2). Of the two possible T_d conformations of the molecule, one can be considered sterically reasonable; but that T_d conformation is converted by rotation of a single $Co(CO)_4$ group through 60° to an even more sterically attractive C_{3v} conformation. It is of interest that the general appearance of the spectrum of the tetrakis(tetracarbonylcobalt) compound is similar, except for intensity differences, to that of $ClSn[Co(CO)_4]_3$, which would have C_{3v} symmetry at most.[3]

Fluorotris(tetracarbonylcobalt)tin(IV).—Reaction of cobalt carbonyl with tin(II) fluoride in tetrahydrofuran solution afforded $FSn[Co(CO)_4]_3$, characterized by analysis and mass spectrum. Fragments with m/e values corresponding to $FSnCo_3(CO)_x^+$ [x = 0–12] were all observed, including the molecular ion at m/e 652.

That the tris derivative was obtained rather than the

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[14] In the case of the *trans* isomers of C_s symmetry, the A′ equatorial mode could couple with an A′ mode derived from the E mode of the C_{3v} molecule. It may thus be significant that the relative intensity of the higher band is somewhat greater in the less symmetrical molecule (compare Figures 1a and b).

[15] J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1365 (1967).

bis (which results in the case of the other tin(II) halides[4]) may be due to the insolubility of SnF_2 in tetrahydrofuran, so that $Co_2(CO)_8$ is always in large excess, and the $F_2Sn[Co(CO)_4]_2$ which presumably forms in an initial insertion reaction will react further to produce $FSn[Co(CO)_4]_3$.

The product occurs as dark red needles which are moderately air stable. It is moderately soluble in *n*-pentane and readily soluble in polar solvents, differing very strikingly in this respect from organotin fluorides, which as a rule are very low in solubility in organic solvents.[16] The ^{19}F nmr shows a singlet at 122.9 ppm in chloroform and at 117.7 ppm in C_6H_6, both values relative to $CFCl_3$. No peaks due to tin–fluorine spin–spin coupling were observed within 1500 cps of the main peak.

Tin(II) Acetate Derivatives.—Reaction of tin(II) acetate with cobalt carbonyl in tetrahydrofuran solution afforded a fairly low yield of a mixture of orange needles and dark red crystals. These were characterized by analysis as $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $CH_3CO_2Sn[Co(CO)_4]_3$. The mass spectrum of the diacetate has no fragments higher than *m/e* 524, which can be assigned to either $(CH_3CO_2)_2SnCo_2(CO)_6^+$ or $(CH_3O)_2SnCo_2(CO)_8^+$; fragments due to consecutive loss of CO from this were also observed, as well as $SnCH_3CO_2^+$ and $Sn(CH_3CO_2)_2^+$.

The molecular weight of the diacetate in cyclohexane indicated a considerable degree of association: observed values were in the 750–800 range, with 578 the calculated value for $(CH_3CO_2)_2Sn[Co(CO)_4]_2$. Such association is well known in organotin carboxylates,[17] and might account for the somewhat different carbonyl stretching pattern compared with that usually observed for bis(tetracarbonylcobalt) derivatives.[2,4] The pattern of carbonyl stretching bands for $CH_3CO_2Sn[Co(CO)_4]_3$ is somewhat different from that of $ClSn[Co(CO)_4]_3$, in that the two very strong bands observed in the latter[3] both possess strong shoulders in the former. This may possibly be due to a reduction in symmetry from C_{3v} to C_s by the asymmetric nature of the acetate group.

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[16] G. E. Coates, "Organo-Metallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 183 ff.

[17] P. B. Simons and W. A. G. Graham, *J. Organometal. Chem.* (Amsterdam), **8**, 479 (1967), and references cited there.

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Comparative Stereochemical Populations and Thermodynamics of Structural Interconversion of Planar and Tetrahedral Cobalt(II) and Nickel(II) Complexes

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A series of new bis(β-ketoamino)cobalt(II) and -nickel(II) complexes of general formulation $M(R{-}R_\gamma R_\beta R_\alpha)_2$ have been prepared in which R is the donor nitrogen substituent and R_γ, R_β, R_α are the chelate ring carbon atom substituents. It has been demonstrated from spectral, magnetic, and nmr measurements that cobalt complexes with R = H and nickel complexes with R = CH_3 undergo the planar $\rightleftharpoons$ tetrahedral configurational equilibrium in chloroform solution and that cobalt (R = CH_3) and nickel (R = H) complexes exist exclusively in solution as the tetrahedral and planar stereoisomers, respectively. A series of equilibrium pairs comprised of $Ni(CH_3{-}R_\gamma R_\beta R_\alpha)_2$ and $Co(H{-}R_\gamma R_\beta R_\alpha)_2$ complexes, which possess the minimal ligand structural differences possible for direct measurement and comparison of the configurational equilibria, were examined in chloroform solution. Thermodynamic quantities characterizing the configurational changes were obtained from measurement of the temperature dependence of the contact shifts (nickel) and magnetic susceptibilities (cobalt). Stereochemical populations for the pairs were found usually to parallel one another. The relative equilibrium positions of the members of each pair are controlled principally by enthalpy effects. The stability differences between tetrahedral and planar Ni(II) (R = CH_3) were found to be ~2–4 kcal/mole greater than those between tetrahedral and planar Co(II) (R = H). These differences were concluded to arise mainly from differences in the crystal field stabilization energies and metal–ligand bond energies of Ni(II) and Co(II) in their two stereoisomeric configurations. Stability differences corrected for CFSE effects could not be obtained because of the lack of information required to estimate CFSE values for the planar configurations of each metal.

Introduction

In formulating the structural systematics of complexes of the divalent transition metal ions having their most common coordination numbers as six and four, there are two problems of special general significance. The first of these involves determination of the relative stabilities of six- and four-coordinate complexes as the metal ion is varied in the sequence Mn(II)–Zn(II). Solution investigations are the most feasible and the existing data from equilibrium and thermodynamic studies[3,4] indicate that the actual

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[3] S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 3284 (1965).

[4] (a) W. Libús and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966); (b) A. B. Blake and F. A. Cotton, *ibid.*, **3**, 5 (1964).