

Figure 1.—The crystal structure of  $\text{Ho}_2\text{S}_3$  projected down the crystal  $b$  axis. Full circles represent atoms in the plane  $y = 1/4$ ; dashed circles, those in the plane  $y = 3/4$ .

others are fourfold coordinated by Ho atoms. A consequence of the peculiar coordination is the occurrence of large empty channels running through the crystal in the  $y$  direction. The bond angles show considerable distortion. Of the three octahedrally coordinated Ho atoms Ho(3) has a maximum deviation of  $8.0^\circ$  and an average deviation of  $4.2^\circ$  from  $90^\circ$  bond angles. The least distorted S-centered tetrahedron has one angle almost  $20^\circ$  greater than the regular tetrahedron angle. The average Ho-S bond distance is 2.76 Å.

The most remarkable feature of the  $\text{Ho}_2\text{S}_3$  structure is the odd-numbered coordination of half the Ho atoms and one-third of the S atoms. In Table IV the aver-

TABLE IV  
AVERAGE COORDINATION NUMBERS IN  
LANTHANIDE SESQUISULFIDES

Structure type	Av coordn no. of metal	Av coordn no. of S
$\text{Ce}_2\text{S}_3$ (defect $\text{Th}_3\text{P}_4$ )	8	$5\frac{1}{3}$
$\text{Ho}_2\text{S}_3$	$6\frac{1}{2}$	$4\frac{1}{3}$
$\text{Yb}_2\text{S}_3$ ( $\alpha$ - $\text{Al}_2\text{O}_3$ )	6	4
$\text{Sc}_2\text{S}_3$	6	4

age coordination numbers are given for the four principal structure types of the rare earth sesquisulfides. For the  $\text{Ce}_2\text{S}_3$  group the S atoms are ideally in sixfold coordination positions but one-ninth of the metal atoms are randomly missing. The coordination numbers of the  $\text{Ho}_2\text{S}_3$  group are intermediate between those of the  $\text{Ce}_2\text{S}_3$  group with larger metal radii and those of the  $\text{Yb}_2\text{S}_3$  group with smaller metal radii. In a very recent abstract<sup>10</sup> it has been found that in the  $\alpha$  form of  $\text{Gd}_2\text{S}_3$  half of the Gd atoms are seven-coordinated and the other half, eight-coordinated. The coordination in this crystal is thus intermediate between that of the  $\text{Ho}_2\text{S}_3$  structure and that in the defect  $\text{Th}_3\text{P}_4$  structure.

It is intended to carry out more sophisticated analyses, using counter-measured intensity data, on crystals of the end members of the series,  $\text{Y}_2\text{S}_3$  and  $\text{Tm}_2\text{S}_3$ , in the hope that a detailed comparison of the bonding and the thermal vibrations may shed light on why the  $\text{Ho}_2\text{S}_3$  structure becomes unstable with respect to the  $\text{Ce}_2\text{S}_3$  and  $\text{Yb}_2\text{S}_3$  structures.

(10) C. A. Prewitt and A. W. Sleight, American Crystallographic Association Winter Meeting, Atlanta, Ga., Jan 1967.

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## Organometallic Compounds with Metal-Metal Bonds. IX. Pentafluorophenyltin Derivatives of Manganese Carbonyl<sup>1</sup>

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Compounds of the series  $(\text{C}_6\text{H}_5)_n(\text{C}_6\text{F}_5)_{3-n}\text{SnMn}(\text{CO})_5$  ( $n = 0, 1, 2$ ) have been prepared by reactions of  $\text{C}_6\text{F}_5\text{Li}$  or  $\text{C}_6\text{F}_5\text{MgBr}$  with  $(\text{C}_6\text{H}_5)_n\text{Cl}_{3-n}\text{SnMn}(\text{CO})_5$ . Carbonyl stretching frequencies are assigned and approximate force constants given. A linear relation between carbonyl stretching frequency and electronegativity of substituents on tin suggests a Pauling electronegativity of about 2.4 for the  $\text{C}_6\text{F}_5$  group. The compounds  $(\text{C}_6\text{F}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$  and  $(\text{OC})_5\text{Mn}(\text{C}_6\text{H}_5)_2\text{Sn-Sn}(\text{C}_6\text{H}_5)_2\text{Mn}(\text{CO})_5$  have also been prepared, the latter containing a four-metal chain. In both of the bis-pentacarbonylmanganese compounds, the number of strong carbonyl bands is greater than five, suggesting that a substantial coupling of  $\text{Mn}(\text{CO})_5$  groups takes place across the intervening tin atoms.

### Introduction

Numerous pentafluorophenyl organometallic compounds of both main and transition group metals have been reported in recent years. Convenient synthetic methods are available, and the compounds are normally

more stable than their hydrocarbon analogs.<sup>2</sup> A recent communication from this laboratory suggested that a combination of coupling constant and chemical shift

(1) Part VIII: J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1365 (1967).

(2) For reviews, cf. P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964); F. G. A. Stone, *Endeavour*, **25**, 33 (1966). For recent leading references, cf. F. J. Hopton, A. H. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc., Sect. A*, 1326 (1966); C. Tamborski, E. J. Soloski, and S. M. Dec, *J. Organometal. Chem.* (Amsterdam), **4**, 446 (1965).

TABLE I  
 PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Mp, °C	Color	Analyses, %					
			Calcd			Found		
			C	H	F	C	H	F
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> SnMn(CO) <sub>5</sub>	94–95	White	43.5	1.6	...	43.8	1.8	...
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> SnMn(CO) <sub>5</sub> <sup>b</sup>	100–102	White	38.1	0.7	26.2	37.3	0.5	25.6
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> SnMn(CO) <sub>5</sub>	151–154	Yellow-white	33.9	0.0	35.0	34.7	0.0	34.7
(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Sn[Mn(CO) <sub>5</sub> ] <sub>2</sub>	151–152	Pale yellow	31.4	0.0	22.5	31.4	0.3	22.7
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SnMn(CO) <sub>5</sub> ] <sub>2</sub> <sup>c</sup>	158–161 dec	White	34.6	2.2	...	43.7	2.1	...

<sup>a</sup> All melting points determined using Kofler hot stage. <sup>b</sup> *Anal.* Calcd for (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>SnMn(CO)<sub>5</sub>: Mn, 7.6; exact mass (MS-9) of molecular ion [<sup>12</sup>C<sub>23</sub><sup>1</sup>H<sub>5</sub><sup>11</sup>F<sub>10</sub><sup>19</sup>O<sub>5</sub><sup>56</sup>Mn<sup>120</sup>Sn]<sup>+</sup>, 725.8379. Found: Mn, 7.0; mass of ion, 725.8395. <sup>c</sup> *Anal.* Calcd for [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnMn(CO)<sub>5</sub>]<sub>2</sub>: O, 17.1; Mn, 11.7; Sn, 25.4; mol wt, 936. Found: O, 17.1; Mn, 12.4; Sn, 24.8; mol wt (osmometric in benzene), 882.

data from the <sup>19</sup>F nmr spectra of pentafluorophenyl derivatives provided a means of assessing π-electronic interactions.<sup>3</sup> The possibility of using this technique to study metal–metal π bonding has led to the present work on manganese–tin bonding, with pentafluorophenyl groups on tin. We report here the preparation and infrared spectra of these compounds.

### Experimental Section

Infrared spectra in the carbonyl stretching region were recorded in cyclohexane solution using a Perkin-Elmer 337 spectrometer, with CO–DBr calibration and expansion as previously described.<sup>4</sup> Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, and by the microanalytical laboratory of this department, with results as given in Table I. All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride.

Phenylchloro(pentacarbonylmanganese)tin(IV), trichloro(pentacarbonylmanganese)tin(IV), and dichlorobis(pentacarbonylmanganese)tin(IV) were prepared as described by Gorsich.<sup>5</sup>

Diphenylchloro(pentacarbonylmanganese)tin(IV) was prepared by slow addition of a filtered THF solution of NaMn(CO)<sub>5</sub> (~20 mmoles) to a THF solution of diphenyltin dichloride (6.88 g, 20 mmoles) at –5°. The reaction mixture was stirred for 20 hr at room temperature. Removal of solvent at reduced pressure left a green oil, which was taken up in hexane and filtered to remove NaCl. The hexane filtrate was cooled affording white needles; after recrystallization from benzene, the melting point was 102–103.5° (Kofler hot stage; lit.,<sup>5</sup> 97–98°). It was found, as in the case of the methyl analog,<sup>4</sup> that if the reaction mixture was worked up immediately after addition, only diphenylbis(pentacarbonylmanganese)tin(IV) was obtained.

Phenylbis(pentafluorophenyl)(pentacarbonylmanganese)tin(IV), C<sub>6</sub>F<sub>5</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnMn(CO)<sub>5</sub>.—Solid C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>SnMn(CO)<sub>5</sub> (4.6 g, 10 mmoles) was added directly to an ether solution of C<sub>6</sub>F<sub>5</sub>MgBr<sup>6</sup> (from 15 mmoles of C<sub>6</sub>F<sub>5</sub>Br). After stirring for 4.5 hr at room temperature, the mixture was hydrolyzed with about 15 ml of dilute hydrochloric acid. The ether layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed at reduced pressure to give a dark oil. This oil was dissolved in petroleum ether (bp 30–60°), treated with activated charcoal, filtered, and concentrated. Upon cooling to –20°, an oil separated which gradually crystallized. Recrystallization from 95% ethanol afforded fine white needles of the product.

Reaction of C<sub>6</sub>F<sub>5</sub>Li with (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub>.—A solution of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub> (5.0 g, 10 mmoles) in 40 ml of ether was added dropwise to a –78° solution of C<sub>6</sub>F<sub>5</sub>Li prepared from C<sub>6</sub>F<sub>5</sub>Br (2.72 g, 11 mmoles) in 15 ml of ether and *n*-butyllithium (11 mmoles, 6.9 ml of hexane solution, the commercial product

of Foote Mineral Co.). The –78° bath was then replaced by one at 0°. As the mixture warmed, it became bright yellow and a fine white precipitate appeared. Magnetic stirring was continued for 30 min at 0° and 1 additional hr at room temp. The white solid was filtered off and the yellow filtrate was evaporated at reduced pressure to give an oil; addition of petroleum ether gave white crystals of [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnMn(CO)<sub>5</sub>]<sub>2</sub>, which were recrystallized from hexane. Infrared bands (cyclohexane, with relative heights on linear transmittance scale) were observed at 2103 (2.9), 2098 (3.9), 2094 (2.6), 2044 (1.0), 2033 (1.4), 2016 (8.4), 2009 (10), 2004 (9.8), and 1999 (7.5, sh) cm<sup>-1</sup>. The petroleum ether solution was concentrated and cooled to –78°, affording white crystalline (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>F<sub>5</sub>SnMn(CO)<sub>5</sub>, which was recrystallized from petroleum ether.

Tris(pentafluorophenyl)(pentacarbonylmanganese)tin(IV), (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>SnMn(CO)<sub>5</sub>.—A suspension of Cl<sub>3</sub>SnMn(CO)<sub>5</sub> (2.1 g, 5 mmoles) in 25 ml of ether was added dropwise to a –78° solution of C<sub>6</sub>F<sub>5</sub>Li (17 mmoles) in 55 ml of ether, and the mixture was stirred for 2.5 hr at –78°, after which an essentially clear yellow solution was observed. A fine white suspension of LiCl formed as the solution warmed to room temperature. After filtration, solvent was removed at reduced pressure leaving a yellow oil, insoluble in petroleum ether. After addition of a small amount of ether, the solution was again filtered to remove LiCl, concentrated, and cooled to give pale yellow crystals of the product.

Bis(pentafluorophenyl)bis(pentacarbonylmanganese)tin(IV), (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Sn[Mn(CO)<sub>5</sub>]<sub>2</sub>.—Solid Cl<sub>2</sub>Sn[Mn(CO)<sub>5</sub>]<sub>2</sub> (2.8 g, 5 mmoles) was added directly to a magnetically stirred solution of C<sub>6</sub>F<sub>5</sub>Li (11 mmoles) in 70 ml of ether at –78°, and stirring was continued at –78° for 2 hr. The mixture was brought to room temperature and filtered, and solvent was removed at reduced pressure leaving an oil which was insoluble in petroleum ether. Addition of a few milliliters of ether induced crystallization. Recrystallization from benzene–hexane afforded white prisms of the product (yield, 1.3 g). Infrared bands in a cyclohexane solution, with relative heights on a linear transmittance scale, are 2113 (2.4), 2090 (8.1), 2043 (3.4), 2026 (10), 2024 (9.9), 2020 (8.8), 2008 (2.4), and 2000 (7.8) cm<sup>-1</sup>.

Reaction of (CH<sub>3</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub> with Pentafluorophenyllithium.—A solution of (CH<sub>3</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub> (3.8 g, 10 mmoles) in 60 ml of ether was added slowly at –78° to a stirred solution of C<sub>6</sub>F<sub>5</sub>Li (11 mmoles) in 20 ml of ether. An intense yellow coloration developed, and a white precipitate appeared. The mixture was warmed to room temperature, stirred 1 hr, and filtered, and solvent was removed affording an oil. Slow addition of petroleum ether gave white crystals, recrystallized from petroleum ether, mp 104–105°; the melting point<sup>7</sup> and infrared spectrum<sup>1</sup> of this material showed that it was (CH<sub>3</sub>)<sub>2</sub>Sn[Mn(CO)<sub>5</sub>]<sub>2</sub>. Solvent was removed from the mother liquor leaving an oil which consisted mainly of (CH<sub>3</sub>)<sub>2</sub>Sn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, as shown by the nmr spectrum (main peak at τ 9.1 and characteristic methyltin satellites with *J*(<sup>119</sup>Sn–CH<sub>3</sub>) = 65 cps).<sup>7</sup>

Reaction of (CH<sub>3</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub> with C<sub>6</sub>F<sub>5</sub>MgBr.—Solid (CH<sub>3</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub> (2.5 g, 6.6 mmoles) was added to 7 mmoles

(3) M. G. Hogben, R. S. Gay, and W. A. G. Graham, *J. Am. Chem. Soc.*, **88**, 3457 (1966).

(4) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(5) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

(6) E. Nield, T. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

(7) A. G. Massey, E. W. Randall, and D. Shaw, *Chem. Ind. (London)*, 1244 (1963).

TABLE II  
 INFRARED ASSIGNMENTS AND FORCE CONSTANTS<sup>a</sup>

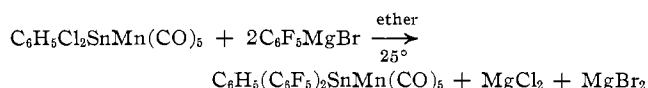
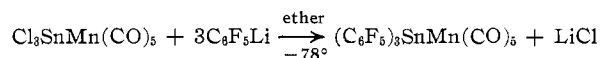
Compound	Freq, cm <sup>-1</sup>			Force constants, mdynes/A			Freq, cm <sup>-1</sup>	
	A <sub>1</sub> ( <sup>2</sup> )	E	A <sub>1</sub> ( <sup>1</sup> )	k <sub>1</sub>	k <sub>2</sub>	k <sub>i</sub>	B <sub>1</sub> (calcd)	B <sub>1</sub> (found)
C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> SnMn(CO) <sub>5</sub>	2113	2031	2023	16.65	17.07	0.208	2056	2058
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ClSnMn(CO) <sub>5</sub>	2103	2018	2018	16.59	16.87	0.212	2044	2044
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> F <sub>5</sub> SnMn(CO) <sub>5</sub>	2101	2012	2016	16.57	16.79	0.221	2039	2038
C <sub>6</sub> H <sub>5</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> SnMn(CO) <sub>5</sub>	2108	2020	2020	16.62	16.92	0.220	2047	2047
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> SnMn(CO) <sub>5</sub> <sup>b</sup>	2116	2029	2034	16.86	17.06	0.217	2055	2059
	2116	2034	2029	16.75	17.12	0.207	2059	2059

<sup>a</sup> For cyclohexane solutions; force constants as defined and calculated by the method of F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962). <sup>b</sup> The first assignment is slightly preferable on the basis of intensities; *cf.* discussion in text.

of C<sub>6</sub>F<sub>5</sub>MgBr in 50 ml of ether. After stirring 4 hr at room temperature the mixture was hydrolyzed with water, and the ether layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the ether left a dark residue which was dissolved in petroleum ether, treated with activated charcoal, filtered, concentrated, and cooled to afford white crystals (600 mg), shown by melting point and infrared spectrum to be (CH<sub>3</sub>)<sub>2</sub>Sn[Mn(CO)<sub>5</sub>]<sub>2</sub>. The mother liquor again contained (CH<sub>3</sub>)<sub>2</sub>Sn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>.

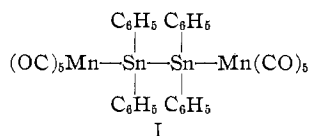
### Discussion

Preparation of the new pentafluorophenyltin compounds was carried out in a straightforward reaction of the appropriate halogenotin species with either C<sub>6</sub>F<sub>5</sub>Li or C<sub>6</sub>F<sub>5</sub>MgBr

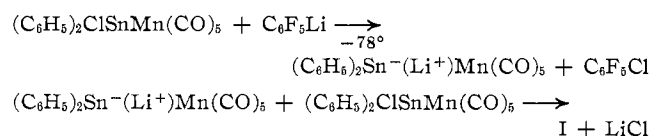


In view of the instability of C<sub>6</sub>F<sub>5</sub>Li, reactions involving this reagent were necessarily carried out at -78°. After addition of the organotin halide to the C<sub>6</sub>F<sub>5</sub>Li solution, a bright yellow color was observed, and lithium chloride did not begin to precipitate until temperatures above about -25° were reached. The yellow color may be attributed to formation of a lithiotin derivative in an exchange reaction, as the following observations suggest.

In the reaction of C<sub>6</sub>F<sub>5</sub>Li with (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub>, two products were formed in approximately equal amounts. One was the expected (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>F<sub>5</sub>SnMn(CO)<sub>5</sub>, while the other (easily separated because of lower solubility in petroleum ether) was shown by complete elemental analysis to be the novel compound I,



which possesses a *four-metal chain*. Only one similar compound has been reported previously, a compound formulated as [(OC)<sub>5</sub>Re]<sub>3</sub>Sn-Sn[Re(CO)<sub>5</sub>]<sub>3</sub>.<sup>8</sup> Formation of I can probably be attributed to the sequence of reactions



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

The pentafluorophenyltin product could be formed in the reaction of the lithiotin intermediate with C<sub>6</sub>F<sub>5</sub>Cl, or in a concurrent normal displacement of chloride by C<sub>6</sub>F<sub>5</sub>Li. Further work on possible preparative uses of such lithiotin intermediates is in progress.

Attempts to prepare (CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>F<sub>5</sub>SnMn(CO)<sub>5</sub> by the Grignard or lithium procedures failed, the products being (CH<sub>3</sub>)<sub>2</sub>Sn[Mn(CO)<sub>5</sub>]<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>Sn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>. It is assumed that the desired compound is formed initially but undergoes disproportionation.

The pentafluorophenyl compounds prepared in the course of this investigation are stable to light and air in the solid state over periods of several months. They melt without decomposition and are soluble in most organic solvents. Some difficulty was encountered in obtaining good crystals, presumably a result of the molecular asymmetry. Compound I was appreciably less stable, darkening over a period of 1 or 2 weeks if kept in the light.

**Infrared Spectra.**—Band positions and assignments for the compounds containing a single pentacarbonyl-manganese group are given in Table II. Although the phenyldichlorotin and diphenylchlorotin derivatives are not new,<sup>5</sup> their spectra have not previously been reported. With the usual approximation of C<sub>4v</sub> symmetry, three infrared-active bands are expected (2A<sub>1</sub> + E). A weaker band (B<sub>1</sub>) which would be infrared inactive in strict C<sub>4v</sub> symmetry is invariably observed, as well as weaker bands due to <sup>13</sup>CO vibrations.

The assignments follow the pattern established in related molecules,<sup>4</sup> but in several of the compounds here reported the proximity of the E band and the low-frequency A<sub>1</sub> band (designated A<sub>1</sub>(<sup>1</sup>) in the Cotton-Kraihanzel notation<sup>9</sup>) produces some uncertainty. The A<sub>1</sub>(<sup>1</sup>) band may lie at higher or lower frequencies, or be coincident with E, and examples of the three situations have been given.<sup>4</sup> In the previous work, the good separation of the two bands, and the large intensity difference, made the assignment of the weaker band as A<sub>1</sub>(<sup>1</sup>) fairly obvious. It should be pointed out, however, that the approximate force constant treatment previously applied<sup>4</sup> does not rule out an assignment in which the A<sub>1</sub>(<sup>1</sup>) and E values are interchanged. Thus, in the particular case of (CH<sub>3</sub>)<sub>2</sub>ClSnMn(CO)<sub>5</sub> (spectrum shown in Figure 3 of ref 4), the alternative assignment A<sub>1</sub>(<sup>2</sup>) at 2101, E at 2015, and A<sub>1</sub>(<sup>1</sup>) at 2006 cm<sup>-1</sup> yields

(9) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962). The force constants k<sub>1</sub>, k<sub>2</sub>, and k<sub>i</sub> are also defined here.

the acceptable force constants  $k_1 = 16.38$ ,  $k_2 = 16.83$ , and  $k_t = 0.217$  mdynes/A, with a calculated  $B_1$  position of  $2041\text{ cm}^{-1}$ . We emphasize that the alternative assignment made previously<sup>4</sup> was on the basis of intensities. The difference in approximate force constants for the two assignments is not great however.

In the compounds reported here, the two bands in question vary from almost coincident (a single asymmetric band) to a separation of 4 or 5  $\text{cm}^{-1}$ , as shown in Figure 1. In Figure 1c, intensity considerations suggest the lower frequency band should be assigned  $A_1^{(1)}$ , and this is the choice made in Table II. While the lower band of Figure 1d is slightly more intense and broader, the choice is certainly not clear; both assignments result in acceptable Cotton-Kraihanzel force constants, as shown in Table II. The very small intensity difference in Figure 1d raises the possibility that the doublet may result from a splitting of the doubly degenerate E mode by the bulky pentafluorophenyltin ligands; this phenomenon has been observed in other cases of highly asymmetric ligands.<sup>10</sup>

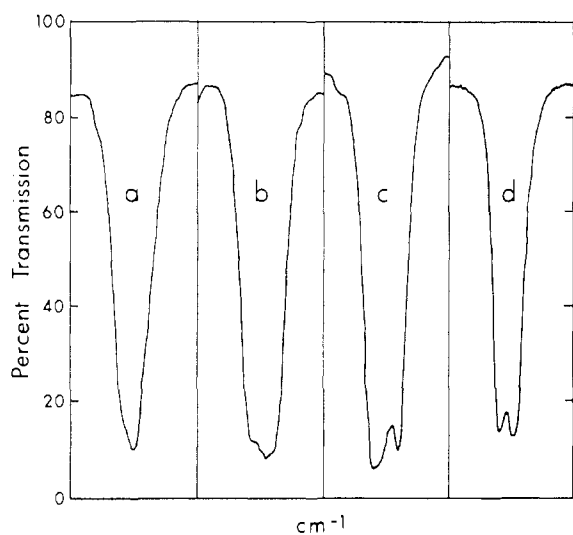


Figure 1.—Detail of E and  $A_1^{(1)}$  bands in certain compounds (cyclohexane solution). A  $45\text{-cm}^{-1}$  segment of each spectrum is shown: (a)  $\text{C}_6\text{H}_5(\text{C}_6\text{F}_5)_2\text{SnMn}(\text{CO})_5$ ; (b)  $(\text{C}_6\text{H}_5)_2\text{C}_6\text{F}_5\text{SnMn}(\text{CO})_5$ ; (c)  $\text{C}_6\text{H}_5\text{Cl}_2\text{SnMn}(\text{CO})_5$ ; (d)  $(\text{C}_6\text{F}_5)_3\text{SnMn}(\text{CO})_5$ .

We have previously used the force constant of the *trans* CO group ( $k_1$ ) as a measure of the  $\pi$ -acceptor properties of the ligand.<sup>4</sup> The  $k_1$  values in Table II suggest that the pentafluorophenyltin groups have  $\pi$ -acceptor ability intermediate between those of the triphenyltin and trichlorotin derivatives.

Previous workers have noted a regular increase of CO stretching frequencies with the electronegativity of substituents, as in the series  $\text{XMn}(\text{CO})_5$ .<sup>11</sup> More recently, a strikingly linear relation was found in an extensive series of compounds of the type  $\text{R}_{3-n}\text{X}_n\text{GeCo}(\text{CO})_4$  when  $\nu(\text{CO})$  was plotted against the sum

(10) J. B. Wilford and F. G. A. Stone, *J. Organometal. Chem.* (Amsterdam), **2**, 371 (1964); *Inorg. Chem.*, **4**, 380 (1965).

(11) A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 5343 (1965).

of the Pauling electronegativities of the halogens on the germanium atom.<sup>12</sup>

From the data of Table II it is evident that there is a regular increase in the  $A_1^{(2)}$  frequency of  $7\text{--}9\text{ cm}^{-1}$  as phenyl groups are replaced by pentafluorophenyl groups. As shown in Figure 2, the points for the series  $(\text{C}_6\text{H}_5)_{3-n}\text{Cl}_n\text{SnMn}(\text{CO})_5$  ( $n = 0\text{--}3$ ), as well as  $\text{Br}_3\text{SnMn}(\text{CO})_5$ , fall on a straight line when  $\nu(\text{CO})$  for the  $A_1^{(2)}$  band is plotted against the sum of the Pauling electronegativity values<sup>13</sup> of the halogens on tin. Using this line, values of  $\nu(\text{CO})$  for the pentafluorophenyltin derivatives can be used to estimate a value for the electronegativity of the pentafluorophenyl group in this situation. The average value is 2.4, slightly lower than that for iodine (2.66). Previous estimates are somewhat higher, a Mössbauer study<sup>14</sup> yielding a value very close to that of bromine, while proton nmr results on pentafluorophenyltin derivatives suggested a value intermediate between those for chlorine and bromine.<sup>7</sup> Naturally the effective electronegativity of the  $\text{C}_6\text{F}_5$  group will depend on the way it can interact with the rest of the molecule. For example, application of the frequency-electronegativity relation to the series  $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$ ,  $\text{ClMn}(\text{CO})_5$ ,  $\text{BrMn}(\text{CO})_5$ , and  $\text{IMn}(\text{CO})_5$  would place the  $\text{C}_6\text{F}_5$  group between Br and I.<sup>15</sup>

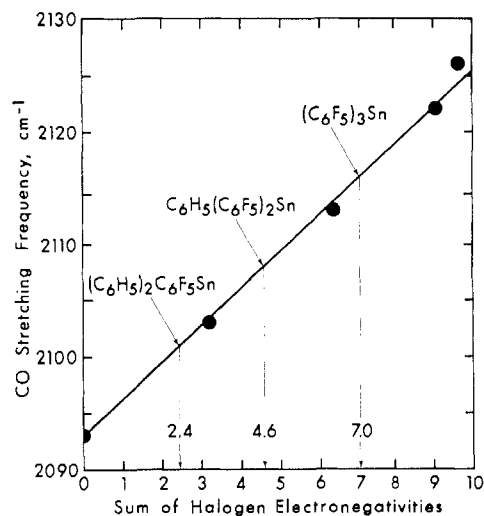


Figure 2.—Stretching frequency of  $A_1^{(2)}$  bands vs. the sum of Pauling electronegativities of halogens on tin. Circled points generating the line are, from left to right,  $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ ,  $(\text{C}_6\text{H}_5)_2\text{ClSnMn}(\text{CO})_5$ ,  $\text{C}_6\text{H}_5\text{Cl}_2\text{SnMn}(\text{CO})_5$ ,  $\text{Br}_3\text{SnMn}(\text{CO})_5$ , and  $\text{Cl}_3\text{SnMn}(\text{CO})_5$ .

The most striking feature of the infrared spectra of  $(\text{C}_6\text{F}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$  and  $(\text{OC})_5\text{MnSn}(\text{C}_6\text{H}_5)_2\text{--Sn}(\text{C}_6\text{H}_5)_2\text{Mn}(\text{CO})_5$  is that both show more strong carbonyl bands than the maximum of five predicted by "local symmetry," *i.e.*, for the two equivalent, isolated  $\text{Mn}(\text{CO})_5$  groups. This phenomenon has been observed

(12) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

(13) As given by A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961), and quoted by F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966, p 103.

(14) M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 2306 (1964).

(15) The  $A_1^{(2)}$  frequencies for these compounds, respectively, are 2130,<sup>10</sup> 2138,<sup>16</sup> 2133,<sup>16</sup> and 2125<sup>16</sup>  $\text{cm}^{-1}$ .

(16) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

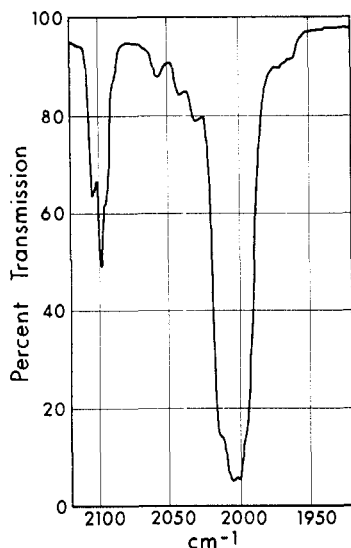


Figure 3.—Carbonyl stretching region of the infrared spectrum of  $(\text{OC})_3\text{MnSn}(\text{C}_6\text{H}_5)_2\text{-Sn}(\text{C}_6\text{H}_5)_2\text{Mn}(\text{CO})_3$ . Cyclohexane solution, about 1 mg/ml in 0.05-mm cells.

before in other bis-pentacarbonylmanganese and bis-tetracarbonylcobalt derivatives where the metal carbonyl moieties are separated by a single germanium or

tin atom.<sup>1,12</sup> It has been attributed to a coupling of vibrations on the individual  $\text{M}(\text{CO})_n$  groups across the intervening heteroatom, which is considered to occur by means of overlapping d orbitals on the three metal atoms.<sup>12</sup> The infrared spectrum of the  $\text{MnSnSnMn}$  compound is shown in Figure 3, and although the bands are not well resolved, it is possible to count at least seven medium or strong bands and shoulders.

If this is the result of coupling, as seems probable, then it would mark the first time coupling has been observed across *two* intervening metal atoms. Again, it would seem likely that an interaction over such a large distance takes place *via*  $\pi$  electrons of the metal-metal bonds. As a note of caution in attributing these extra bands to coupling, it should be remembered that an alternative explanation based on the presence of more than one conformational isomer of the molecule cannot be excluded; a conformational effect on metal carbonyl bands has recently been discovered.<sup>17</sup>

**Acknowledgment.**—We thank the National Research Council of Canada for financial assistance and for a Studentship to J. A. J. T.

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

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## Organometallic Compounds with Metal-Metal Bonds. XI. Some Cobalt Carbonyl Derivatives of Six-Coordinate Tin<sup>1</sup>

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Reaction of bis(2,4-pentanedionato)dichlorotin(IV) with tetracarbonylcobaltate(−I) anion yields under specified conditions the compounds  $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$ ,  $(\text{C}_5\text{H}_7\text{O}_2)\text{Sn}[\text{Co}(\text{CO})_4]_2$ , and  $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}(\text{Cl})\text{Co}(\text{CO})_4$ . The first has a bridging carbonyl group, and the suggested structure involves an  $\text{SnCo}_2$  triangular cluster. The other two have only terminal carbonyl bands and are considered to be *trans*-octahedral derivatives. These are the first examples to be reported of metal-metal bonding by six-coordinate tin.

### Introduction

Many tetracarbonylcobalt derivatives of tin(IV) have been reported in which tin is four-coordinate and presumably tetrahedral; examples are  $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$ ,<sup>2</sup>  $\text{I}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ ,<sup>3</sup> and  $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ .<sup>4</sup> In a preliminary communication<sup>5</sup> we recently described the first metal-metal bonded derivative of six-coordinate tin,  $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$ ,<sup>6</sup> to which structure I was assigned. We now report full details of the preparation and properties of I and of the related compounds  $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$  and  $(\text{acac})_2\text{Sn}(\text{Cl})\text{Co}(\text{CO})_4$ .

- (1) Part X: R. Kummer and W. A. G. Graham, *Inorg. Chem.*, in press.
- (2) Part IX: J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1875 (1967).
- (3) D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967).
- (4) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966).
- (5) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 2222 (1966).
- (6) D. J. Patmore and W. A. G. Graham, *Chem. Commun.*, **7** (1967).
- (7) We abbreviate the 2,4-pentanedionato ligand  $(\text{C}_5\text{H}_7\text{O}_2)$  as acac.

### Experimental Section

All reactions and crystallizations were carried out under an atmosphere of purified nitrogen. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride. Microanalyses were carried out by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany. Molecular weights were determined using a Mechrolab osmometer at 37° in cyclohexane solution with benzil calibration. To prevent oxidation of these sensitive compounds, argon saturated with cyclohexane was passed into the chamber at  $9 \text{ cm}^3 \text{ min}^{-1}$ ; under these conditions, the calibration curve was very nearly linear. Each reported value is the mean of determinations on six drops, with standard deviation as shown.

Infrared spectra were measured for cyclohexane solutions in 0.5-mm cells, using a Perkin-Elmer Model 337 grating spectrometer. Scale expansion and calibration were carried out as previously described.<sup>7</sup> Mass spectra were obtained using an AEI

- (7) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).