

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA**Organometallic Compounds with Metal-Metal Bonds. VIII.
Bis- and Tris-Pentacarbonylmanganese and -rhenium Derivatives of Tin¹**

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The preparation and properties are described of a number of compounds of two general types, $R_2Sn[M'(CO)_5]_2$ and $RSn[M'(CO)_5]_3$, in which $M' = Mn$ or Re , and $R = C_6H_5$, $CH_2=CH$, $n-C_4H_9$, CH_3 , Cl , or I . The sulfur heterocycles SCH_2CH_2 - $SSn[M'(CO)_5]_2$ are also reported. Carbonyl stretching frequencies in cyclohexane solution are given for all of the compounds. The mass spectrum of one compound of each type is summarized, and nmr spectra of methyl derivatives are reported.

Introduction

The first examples of tin-manganese bonds were reported in 1962 by Gorsich² and provided a striking example of the stability of this particular metal-metal bond. Thus, reaction of $(C_6H_5)_3SnMn(CO)_5$ in carbon tetrachloride with chlorine at 25° or with bromine at reflux did not cleave the tin-manganese bond, yielding instead the trihalogenotin derivatives of manganese carbonyl.² More recent studies of the tin-manganese bond include the reaction of $(CH_3)_3SnMn(CO)_5$ with fluoroolefins,³ nmr and infrared spectroscopic investigations of the bonding in compounds of this type,⁴ and the preparation of compounds having three-metal sequences such as $Mn-Sn-Mo$.^{5,6} In addition, the molecular structures of $(C_6H_5)_2Sn[Mn(CO)_5]_2$, $(C_6H_5)_3SnMn(CO)_5$, and *trans*- $(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$ have been determined by X-ray diffraction,⁷⁻⁹ confirming the geometry and supplying vital information about lengths and angles.

Several previous papers of this series have reported our investigations of bonding between main group and transition group metals. As an extension of our work⁴ on compounds of the type $R_3M-M'(CO)_5$ ($R =$ halogen or organic group; $M = Si, Ge, Sn, Pb$; $M' = Mn$ or Re), we now present the results of a detailed study of a number of bis- and tris-carbonyl derivatives of the types $R_2Sn[M'(CO)_5]_2$ and $RSn[M'(CO)_5]_3$.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was purified by distillation from lithium

aluminum hydride and stored over sodium wire. Manganese¹⁰ and rhenium¹¹ carbonyls were prepared by standard methods. Methyltin trichloride¹² and vinyltin trichloride¹³ were prepared by reported methods, while other organotin chemicals were generously provided by M and T Chemicals, Inc., Rahway, N. J. Other reagents were commercially available.

Microanalyses (Table I) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, and molecular weights were determined in the microanalytical laboratory of this department using a Mechrolab osmometer and dibromomethane as solvent. Melting points were taken with a Kofler hot-stage microscope.

Infrared spectra (Tables II and III) were obtained using a Perkin-Elmer 337 grating spectrometer. Bands in the metal carbonyl region were measured in expanded form on an external recorder and calibrated by interpolation between bands of CO and DBr imposed on each spectrum, as previously described.⁴

Proton magnetic resonance spectra were measured using Varian A-60 and HA-100 instruments. Mass spectra were observed using an AEI MS-9 double-focusing mass spectrometer, the sample being introduced by direct evaporation.

Diphenylbis(pentacarbonylrhenium)tin(IV), $(C_6H_5)_2Sn[Re(CO)_5]_2$.—Rhenium carbonyl (7.5 g, 1.15 mmoles) in 100 ml of THF was stirred over 20 ml of 1% sodium amalgam for 1 hr. After removal of the amalgam, $(C_6H_5)_2SnCl_2$ (3.0 g, 1.1 mmoles) was added and the mixture was stirred at room temperature for 20 min. The solution was concentrated to about 60 ml on a rotary evaporator and poured into ice water. The white, crystalline precipitate was filtered, washed twice with water, and dried under vacuum. Recrystallization from *n*-hexane afforded white plates (5.3 g).

Dimethylbis(pentacarbonylrhenium)tin(IV), $(CH_3)_2Sn[Re(CO)_5]_2$.—This was prepared by a similar procedure, although in this case the THF was entirely removed at reduced pressure, and the product was extracted with hot *n*-hexane.

Dichlorobis(pentacarbonylrhenium)tin(IV), $Cl_2Sn[Re(CO)_5]_2$.—Anhydrous HCl was bubbled through a solution of $(C_6H_5)_2Sn[Re(CO)_5]_2$ (2.0 g) in dichloromethane (40 ml) at room temperature for 15 min, during which the solution became yellow. After stirring for an additional 30 min, solvent was removed at reduced pressure. Recrystallization of the residue from dichloromethane-petroleum ether (bp 30–60°) afforded 1.02 g of white needles.

2,2-Bis(pentacarbonylrhenium)-2-stanna-1,3-dithiacyclopentane, $SCH_2CH_2SSn[Re(CO)_5]_2$.—To a suspension of $Cl_2Sn[Re$

(1) Presented in part at the Symposium on the Metal-Metal Bond in Inorganic Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; Abstracts, paper H70. Part VII: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

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(5) H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965).

(6) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1122 (1965); *Chem. Abstr.*, **63**, 8393 (1965); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1094 (1965).

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(13) D. Seyferth and F. G. A. Stone, *ibid.*, **79**, 595 (1957); we thank Mrs. H. R. H. Patil for preparing the compound.

TABLE I
ANALYTICAL DATA, COLOR, AND MELTING POINT

Compound	Mp, ^a °C	Color	Anal, %					
			Found			Calcd		
			C	H	O	C	H	O
(C ₆ H ₅) ₂ Sn[Re(CO) ₅] ₂	135–138 ^b	White	28.3	1.3	...	28.5	1.1	...
(CH ₃) ₂ Sn[Re(CO) ₅] ₂ ^c	119–121	Pale yellow	19.3	1.0	19.8	18.0	0.8	20.0
Cl ₂ Sn[Re(CO) ₅] ₂ ^d	171–172	White	14.9	0.3	...	14.3	0	...
$\overline{\text{S}(\text{CH}_2)_2\text{SSn}[\text{Re}(\text{CO})_5]_2}$ ^e	150–152	Bright yellow	17.5	0.7	18.4	16.7	0.5	18.5
$\overline{\text{S}(\text{CH}_2)_2\text{SSn}[\text{Mn}(\text{CO})_5]_2}$ ^f	141–142	Bright yellow	24.6	1.3	...	24.0	0.7	...
C ₆ H ₅ Sn[Mn(CO) ₅] ₃ ^g	130–140 dec	Orange-yellow	32.2	0.9	28.3	32.3	0.6	30.7
<i>n</i> -C ₄ H ₉ Sn[Mn(CO) ₅] ₃ ^h	143–145	Yellow	29.9	1.2	29.0	30.0	1.2	31.6
CH ₃ Sn[Mn(CO) ₅] ₃	120–155 dec	Yellow	28.3	0.3	30.5	26.7	0.4	33.4
CH ₂ =CHSn[Mn(CO) ₅] ₃ ⁱ	120–140 dec	Yellow	28.6	0.4	30.0	28.0	0.4	32.9
ClSn[Mn(CO) ₅] ₃ ^j	175–176 dec	Orange	24.8	0.0	31.1	24.4	0.0	32.5
ISn[Mn(CO) ₅] ₃ ^k	178 dec	Red	22.9	0.0	28.3	21.7	0.0	28.9
C ₆ H ₅ Sn[Re(CO) ₅] ₃ ^l	>195 dec	Yellow	22.1	0.5	20.5	21.5	0.4	20.4
<i>n</i> -C ₄ H ₉ Sn[Re(CO) ₅] ₃	165–166	Yellow	20.4	0.9	21.2	19.8	0.8	20.8
CH ₂ =CHSn[Re(CO) ₅] ₃	175–200 dec	Yellow	18.6	0.2	21.2	18.3	0.3	21.5
CH ₃ Sn[Re(CO) ₅] ₃	160–165 dec	Yellow	17.7	0.1	21.4	17.3	0.3	21.6
ClSn[Re(CO) ₅] ₃ ^m	193–196 dec	Yellow	16.9	0.4	21.0	15.9	0.0	21.2

^a Kofler hot stage. ^b Lit. 139°: A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Proc. Acad. Sci. USSR, Chem. Sect.*, **156**, 502 (1964). ^c Mol wt: calcd, 490; found, 449. ^d Mol wt: calcd, 842; found, 807. Cl: calcd, 8.4; found, 8.5, 8.3. ^e Mol wt: calcd, 863; found, 861. ^f Mol wt: calcd, 601; found, 588. ^g Mol wt: calcd, 781; found, 786. ^h Mol wt: calcd, 761; found, 777. ⁱ Mol wt: calcd, 731; found, 729. ^j Cl: calcd, 4.8; found, 3.9. ^k Exact mass: calcd for ¹²⁷Tl¹³⁰Sn⁵⁵Mn₃ fragment, 411.6209; found, 411.6209. ^l Lit. mp 189°; see footnote *b*. ^m Cl: calcd, 3.1; found, 4.1.

TABLE II
CARBONYL STRETCHING FREQUENCIES OF BIS(MANGANESE OR RHENIUM)TIN COMPOUNDS^a

Compound	$\nu(\text{CO}), \text{cm}^{-1}$, with relative intensity ^b							
(CH ₃) ₂ Sn[Mn(CO) ₅] ₂ ^c	2099 (1.4)	2074 (5.3)	2019 (1.1)	2004 (10)	2002 ^e (9.2)	1984 (4.8)	1961 ^f (0.6)	...
(CH ₃) ₂ Sn[Re(CO) ₅] ₂	2114 (1.4)	2092 (6.5)	2070 (1.1)	2044 (0.5)	2010 ^e (2.9)	2009 (10)	1998 (9.0)	1987 (9.6)
(C ₆ H ₅) ₂ Sn[Mn(CO) ₅] ₂ ^c	2100 (3.4)	2078 (8.9)	2029 (4.9)	2009 (10)	2006 ^e (8.9)	2002 (8.7)	1986 (9.0)	1961 ^f (1.0)
(C ₆ H ₅) ₂ Sn[Re(CO) ₅] ₂	2118 (0.9)	2099 (5.1)	2039 (2.1)	2016 ^e (9.7)	2015 (10)	2001 (5.4)	1995 ^e (2.8)	1987 (8.9)
Cl ₂ Sn[Mn(CO) ₅] ₂ ^d	2119 (0.4)	2093 (5.9)	2056 (2.0)	2030 (10)	2024 (4.0)	2011 (1.3)	2002 (3.9)	
Cl ₂ Sn[Re(CO) ₅] ₂	2125 (0.3)	2116 (5.4)	2065 (2.5)	2034 (10)	2020 (6.1)	2015 (3.8)	2002 (7.3)	
$\overline{\text{S}(\text{CH}_2)_2\text{SSn}[\text{Mn}(\text{CO})_5]_2}$	2108 (9.6)	2081 (5.7)	2037 (1.7)	2018 (10)	2013 ^e (4.9)	1993 (4.5)		
$\overline{\text{S}(\text{CH}_2)_2\text{SSn}[\text{Re}(\text{CO})_5]_2}$	2125 (0.8)	2103 (5.6)	2048 (2.1)	2024 ^e (9.7)	2022 (10)	2010 (4.1)	1994 (8.1)	1963 ^f (0.6)

^a All measurements in cyclohexane. ^b Relative intensities are given in parentheses and refer to relative heights of the bands on a linear transmittance scale, with the most intense band taken as 10. ^c Prepared by Mrs. H. R. H. Patil using the method of R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962). ^d Prepared by the procedure of R. D. Gorsich in footnote *c*. ^e Shoulder. ^f Assigned as ¹³C satellite.

TABLE III
CARBONYL STRETCHING FREQUENCIES OF TRIS(MANGANESE OR RHENIUM)TIN COMPOUNDS^a

Compound	$\nu(\text{CO}), \text{cm}^{-1}$, with relative intensity ^b							
CH ₃ Sn[Mn(CO) ₅] ₃	2105 (0.4)	2072 (8.8)	2014 (9.5)	2005 (6.4)	1994 (10)	1985 (3.3)	1973 ^d (0.5)	1963 ^d (0.6)
CH ₃ Sn[Re(CO) ₅] ₃	2118 (0.3)	2090 (7.9)	2044 (1.3)	2107 (10)	2007 (8.2)	1999 (4.6)	1993 (9.5)	1988 (9.5)
<i>n</i> -C ₄ H ₉ Sn[Mn(CO) ₅] ₃	2103 (1.2)	2083 (1.6)	2070 (9.5)	2037 (1.1)	2017 (6.6)	2012 (9.8)	2003 (9.0)	1954 ^d (1.0)
<i>n</i> -C ₄ H ₉ Sn[Re(CO) ₅] ₃	2119 (0.4)	2090 (8.1)	2026 ^e (2.7)	2016 (10)	2007 (7.9)	1999 (5.2)	1992 (9.3)	1988 (9.7)
CH ₂ =CHSn[Mn(CO) ₅] ₃	2107 (0.4)	2084 (0.9)	2073 (9.3)	2017 (9.9)	2006 (5.6)	1996 (10)	1987 (5.9)	1974 ^d (0.8)
CH ₂ =CHSn[Re(CO) ₅] ₃	2119 (0.2)	2092 (8.0)	2044 (0.8)	2030 (2.4)	2020 (10)	2008 (8.1)	1995 (8.3)	1962 ^d (0.6)
								1988 (9.8)
								1953 ^d (0.8)
C ₆ H ₅ Sn[Mn(CO) ₅] ₃	2106 (0.6)	2085 (6.4)	2039 ^e (2.0)	2023 ^e (5.5)	2015 (10)	2005 (6.8)	1995 (8.3)	1987 (5.6)
C ₆ H ₅ Sn[Re(CO) ₅] ₃	2121 (0.5)	2093 (8.1)	2044 (1.5)	2032 (3.5)	2020 (10)	2008 (7.6)	2000 ^e (5.3)	1996 (7.7)
								1988 (10)
ClSn[Mn(CO) ₅] ₃	2093 (0.4)	2080 (8.3)	2037 (5.8)	2030 ^e (3.0)	2020 (8.0)	2005 (10)	1989 (4.2)	
ClSn[Re(CO) ₅] ₃	2117 (0.4)	2101 (5.9)	2044 (4.5)	2034 (2.7)	2026 (10)	2013 (4.9)	2006 (7.7)	1992 (9.3)
ISn[Mn(CO) ₅] ₃	2093 (1.4)	2080 (7.8)	2044 (4.7)	2037 (5.9)	2029 (5.3)	2020 (8.6)	2005 (10)	1989 (5.1)

^a All measurements in cyclohexane solution. ^b Relative intensity given in parentheses refers to the relative band height on a linear transmittance scale, with the most intense band taken as 10. ^c Shoulder. ^d Assigned as ¹³C satellite.

(CO)₅)₂ (0.5 g, 0.6 mmole) in 15 ml of benzene-dichloromethane (2:1) was added ethanedithiol (0.05 g, 0.6 mmole). There was no visible change until (C₂H₅)₃N (0.16 ml, 1.2 mmoles) was added, when a bright yellow coloration appeared. Starting material dissolved and a light, crystalline precipitate (presumed to be (C₂H₅)₃NH⁺Cl⁻) appeared. After stirring an additional 30 min, the solution was filtered, and the filtrate was taken to dryness at reduced pressure affording yellow crystals (500 mg, 97%) which were recrystallized from benzene-hexane at -78°.

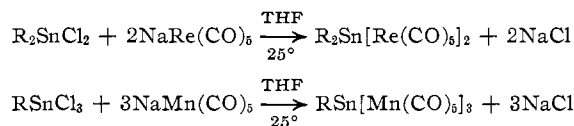
Preparation of RSn[M'(CO)₅]₃ (R = CH₃, n-C₄H₉, CH₂=CH, C₆H₅; M' = Mn, Re).—The same basic procedure was used for all eight compounds of this class. Typically, RSnCl₃ (3–5 mmoles) was added to a slight excess of NaMn(CO)₅ or NaRe(CO)₅ in THF (30–50 ml) at room temperature. After stirring for 30–60 min, the solution was filtered by suction in a sintered-glass funnel while a nitrogen stream was directed into the funnel. Solvent was stripped from the filtrate at reduced pressure leaving a solid or an oil. The manganese derivatives were more soluble and could be obtained pure by cooling a hot ligroin or ligroin-benzene extract of the residue. In the case of rhenium, the residue was dissolved in acetone, and the crystalline product was obtained by slow addition of water. Yields averaged about 50%.

Preparation of ClSn[M'(CO)₅]₃ (M' = Mn, Re).—Addition of SnCl₄ (0.25 ml, 2.14 mmoles) to 15 ml of THF at 0° produced a white adduct. This was added as a slurry to a solution of NaM'(CO)₅ (from 4.6 mmoles of M'₂(CO)₁₀ and 4 ml of 1% sodium amalgam) in 30 ml of THF. The reaction mixture immediately became dark red, and stirring was continued for 2 hr at room temperature. The solution was filtered and solvent stripped from the filtrate to yield an orange solid. Recrystallization was from benzene-ligroin for the manganese derivative and from acetone-water for the rhenium compound. Reaction of ClSn[Mn(CO)₅]₃ with sodium iodide in THF afforded iodotriss(pentacarbonylmanganese)tin(IV), ISn[Mn(CO)₅]₃, which was recrystallized from pentane-dichloromethane.

Discussion

Several derivatives of the type R₂Sn[M'(CO)₅]₂ have been reported previously,^{2,6} and the compounds C₆H₅-Sn[Re(CO)₅]₃ and BrSn[Re(CO)₅]₃ have been described.¹⁴ This paper, however, represents the first comprehensive study of the preparation and spectra of these structural types. It complements previous investigations of compounds containing SnCo₂ and SnCo₃ units.^{1,15}

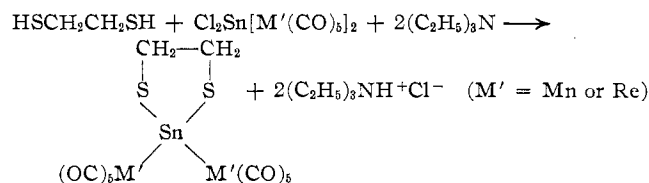
The alkyl- and aryltin derivatives reported here were all prepared by reaction of the appropriate organotin chloride with the sodium salts of manganese or rhenium carbonyls



Reactions proceeded well at room temperature in tetrahydrofuran, requiring about 1 hr for completion. However, yields of crude product rarely exceeded 60%, and considerable losses were encountered in many cases during recrystallization.

Bis-Pentacarbonylmanganese or -rhenium Derivatives.—In general, these crystalline compounds are stable to light and air but are slowly oxidized in solution. Rhenium derivatives are somewhat more stable

than their manganese analogs. As earlier observed for the manganese case,² (C₆H₅)₂Sn[Re(CO)₅]₂ is smoothly converted to Cl₂Sn[Re(CO)₅]₂ by anhydrous hydrogen chloride. Using the dichlorotin compounds, novel sulfur-containing heterocycles were prepared by the reaction



This reaction is similar to one used earlier for the preparation of dimethyl analogs of silicon, germanium, and tin.¹⁶ Combination of stoichiometric amounts of the dithiol and the colorless dichlorotin compound produced no visible change, but addition of the amine resulted in immediate formation of a bright yellow solution. The crystalline *yellow* product is air stable and melts without decomposition. The intense color produced by the S-Sn-M' system is an interesting phenomenon, since the component S-Sn and Sn-M' systems do not absorb in the visible region. There is evidence for tin-manganese multiple bonding,⁴ and there may be conjugation over the whole S-Sn-M' system in these compounds.

Tris-Pentacarbonylmanganese or -rhenium Derivatives.—These crystalline, air-stable compounds vary from yellow to red in color.¹⁷ They sublime readily and may be recrystallized from hydrocarbon solvents, in which they are moderately soluble. The organotin derivatives can advantageously be crystallized from acetone-water, a solvent system which greatly reduces decomposition during the procedure. In hydrocarbon solvents, insoluble decomposition products begin to form after a brief period.

Chlorotin derivatives, such as ClSn[Mn(CO)₅]₃ and its rhenium analog, were prepared by adding a tetrahydrofuran solution of 1 mole of SnCl₄ to 4 moles of the metal carbonyl anion in the same solvent. Use of 3 moles of anion produced a mixture of bis- and trisubstitution products. Under the conditions used, the 1:4 mole ratio gave no indication of a tetrakis derivative, which might have been expected.¹⁸ Displacement of the fourth chlorine group might well be difficult on steric grounds. A reaction of tin(IV) iodide with Mn(CO)₅⁻ did not yield useful amounts of ISn[Mn(CO)₅]₃; the compound may be obtained in moderate yield by reaction of ClSn[Mn(CO)₅]₃ with excess sodium iodide in tetrahydrofuran.

Infrared Spectra.—Typical spectra of the bis-pentacarbonylmanganese compounds are shown in Figures 1 and 2, with numerical values for all compounds of this

(16) M. Wieber and M. Schmidt, *Z. Naturforsch.*, **18b**, 846 (1963).

(17) This applies to both organo and halogeno groups on tin. In view of the color of ClSn[Mn(CO)₅]₃, ISn[Mn(CO)₅]₃, and ClSn[Re(CO)₅]₃ (Table I), it is surprising that BrSn[Re(CO)₅]₃ is reported to be colorless.¹⁴

(18) One compound in which tin carries four transition metals has been reported: S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, **87**, 1146 (1965). Very recently a compound which appears to be Sn[Co(CO)₄]₄ has been prepared in this laboratory by Mr. D. J. Patmore.

(14) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Dokl. Akad. Nauk SSSR*, **156**, 383 (1964); *Proc. Acad. Sci. USSR, Chem. Sect.*, **156**, 502 (1964).

(15) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 2222 (1966).

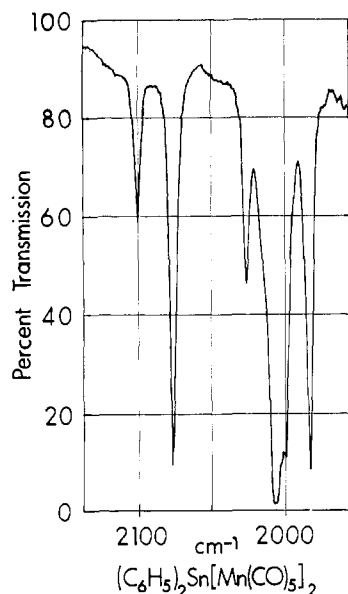


Figure 1.—Carbonyl stretching region of the infrared spectrum of $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$. About 1 mg/ml of cyclohexane; 0.5-mm cells.

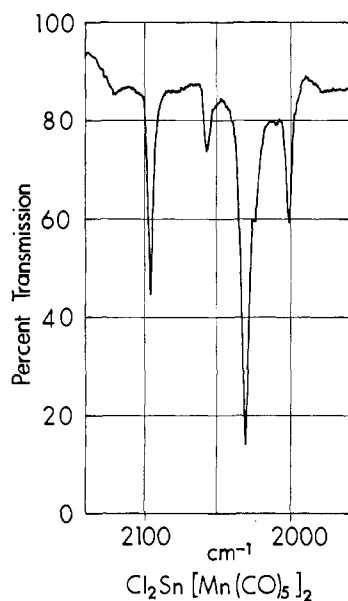


Figure 2.—Carbonyl stretching region of the infrared spectrum of $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$. About 1 mg/ml of cyclohexane; 0.5-mm cells.

type given in Table II. Only terminal carbonyl bands are observed for the compounds reported in this paper. The number of such bands to be expected in a molecule of the type $\text{X}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ depends on the conformation, and the minimum number of bands predicted for any of the possible conformations is 8, with a maximum of 10.¹⁹ Fewer bands are observed than the

(19) The minimum value occurs for one of the two conformations that belong to the C_{2v} point group, although that particular conformation is sterically least attractive for the molecule. Nonetheless, the molecule illustrates a curious situation. In the well-known case of $\text{Mn}_2(\text{CO})_{10}$, the two possible symmetric conformations (D_{4d} staggered and D_{3h} eclipsed) belong to different point groups but have the same number of infrared carbonyl bands. In contrast, two of the conformations of $\text{X}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ belong to the same point group but differ in the number of bands.

minimum prediction, which is not surprising, as some bands may be weak or accidentally degenerate.

Although we will attempt no band assignments here, it is of interest that the general pattern of Figures 1 and 2 resembles that found in $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.¹ A pair of bands at higher frequency is observed, separated from a group at lower frequency. The change in relative intensity of the upper pair in going from the diphenyl to the dichloro derivative strongly resembles the trend observed in the cobalt series,¹ and a similar explanation in terms of bond angles may be possible.

A spectrum typical of the tris-pentacarbonyl derivatives is shown in Figure 3, with complete values for all such compounds given in Table III. The minimum number of infrared bands predicted for any conformation is 8,²⁰ and again in some cases the observed number falls short of this value. It is worth noting, however, that in both bis- and tris-pentacarbonyl derivatives, the number of bands far exceeds the "local symmetry" values,²¹ which would be 5 at most.

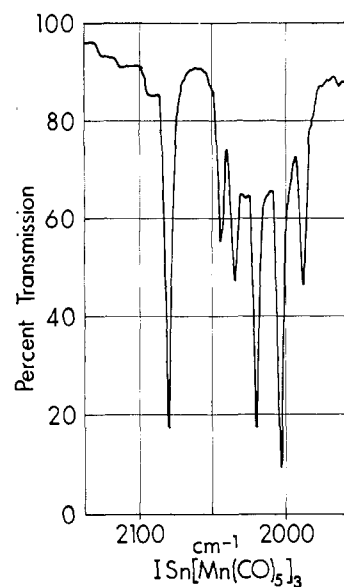


Figure 3.—Carbonyl stretching region of the infrared spectrum of $\text{ISn}[\text{Mn}(\text{CO})_5]_3$. About 1 mg/ml of cyclohexane; 0.5-mm cells.

Mass Spectra.—Mass spectra have been recorded for a number of the compounds reported here, with occasional verification of peak identity by exact mass determination. We summarize in Table IV the principal fragments observed for two representative compounds. As is normally observed in such spectra, several series of fragments differing in mass by a single CO unit occur. In contrast to the situation in tris-

(20) For two conformations of the C_{3v} point group, eight and nine bands are predicted. For a much more sterically reasonable model assignable to C_s , ten bands are predicted.

(21) In the method of local symmetry (F. A. Cotton, A. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956)), it is assumed that selected portions of a complex molecule may be treated as isolated units—in this case, the $\text{Mn}(\text{CO})_5$ groups. The failure of this assumption in this and related cases¹ implies that one cannot ignore interactions between or among the individual $\text{Mn}(\text{CO})_5$ groups. Coupling of vibrational modes across the tin atom must take place, and the conditions under which such interaction takes place across heteroatoms is being further studied in this laboratory.

TABLE IV^a
 MASS SPECTRAL DATA FOR (CH₃)₂Sn[Mn(CO)₅]₂ AND ClSn[Mn(CO)₅]₃

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(CH ₃) ₂ Sn[Mn(CO) ₅] ₂ ^b																
(CH ₃) ₂ SnMn ₂ (CO) _z ⁺	m	w ^c	w ^c	w ^c	w	w	w					
CH ₃ SnMn ₂ (CO) _z ⁺	w	w	w	w	w	w	w	w	w	w	w					
(CH ₃) ₂ SnMn(CO) _z ⁺	w	w ^c	w ^c	s ^d										
CH ₃ SnMn(CO) _z ⁺	w										
ClSn[Mn(CO) ₅] ₃ ^e																
ClSnMn ₃ (CO) _z ⁺	s	m	m	w	w	...	m ^c	w	w	w	w
ClSnMn ₂ (CO) _z ⁺	m	w	...	w ^c	w	s ^{c,d}					
SnMn(CO) _z ⁺	m	s										

^a Entries in table are approximate relative peak intensities: w, weak; m, medium; s, strong. Dots indicate absence of a particular peak. ^b Other fragments observed are SnMn⁺, SnMn²⁺, SnMn(CO)₅⁺, CH₃Sn⁺, and (CH₃)₂Sn⁺. ^c Assignment not certain owing to overlap with fragments of other series. ^d Most abundant ion for this compound. ^e Other fragments observed are SnMn⁺, ClSnMn⁺, SnMn₂⁺, ClSnMn₂⁺, ClSnMn₃⁺, and SnMn₃(CO)₁₆⁺.

tetracarbonylcobalt derivatives of tin,¹⁵ a weak but definite parent peak is observed in all the trimanganese and -rhenium derivatives examined.

Nmr Spectra.—Considerable attention has been directed recently to tin-proton spin-spin coupling in methyltin compounds. The methyl-tin coupling constant, *J*,²² is sensitive, among other things, to the coordination number of the tin atom, rising from 59.7 cps in trimethyltin chloride to 67.0 cps in its pyridine adduct.²³ In four-coordinate methyltin derivatives, *J* varies with the electronegativity of the substituents in a way consistent with Bent's rule.²⁴ Previous papers of this series have reported *J* for tin attached to one or two pentacarbonylmanganese or -rhenium groups, and in Table V, *J* values are given for a methyltin group carry-

ing three manganese or rhenium atoms. Thus values of *J* (in cps) for a complete series of seven compounds can now be examined:²⁵ CH₃SnCl₃, 100.0; (CH₃)₂SnCl₂, 71.0; (CH₃)₂SnCl, 59.7; (CH₃)₄Sn, 54.0; (CH₃)₃SnMn(CO)₅, 48.3; (CH₃)₂Sn[Mn(CO)₅]₂, 36.7; CH₃Sn[Mn(CO)₅]₃, 24.

Values for Re(CO)₅ analogs do not differ appreciably, but the difference is significant for corresponding Co(CO)₄ compounds:¹ (CH₃)₂SnCo(CO)₄, 52.6 cps; (CH₃)₂Sn[Co(CO)₄]₂, 45.7 cps; CH₃Sn[Co(CO)₄]₃, 33 cps. If the electronegativity is that over-all property of a substituent that governs *J*, one may conclude that the Co(CO)₄ group is more electronegative than Mn(CO)₅ in these compounds. This is in harmony with the facts that HCo(CO)₄ is a stronger acid than HMn(CO)₅²⁶ and that Co(CO)₄⁻ is a weaker nucleophile than Mn(CO)₅⁻.²⁷

To achieve sufficient solubility for nmr studies of the CH₃Sn[(Mn or Re)(CO)₅]₃ compounds, pyridine was used as the solvent; previous studies were done in chloroform. This raised the possibility that pyridine would influence *J* by coordination to tin. We therefore determined *J* values in pyridine for (CH₃)₃SnRe(CO)₅ and (CH₃)₂Sn[Re(CO)₅]₂; the results agree with earlier values measured in CDCl₃ and enable one to conclude that tin has no appreciable acceptor properties in these compounds.

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 TABLE V
 NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS

Compound	Solvent	τ ^a (CH ₃)	Coupling constants, cps	
			<i>J</i> ^(117Sn-CH₃)	<i>J</i> ^(119Sn-CH₃)
(CH ₃) ₃ SnRe(CO) ₅	CDCl ₃	9.58	44.7	46.7
	Pyridine	9.29	44.3	46.3
(CH ₃) ₂ Sn[Re(CO) ₅] ₂	CDCl ₃	9.14	34.9	36.7
	Pyridine	9.13	34.8	36.3
CH ₃ Sn[Re(CO) ₅] ₃	Pyridine	8.43		24.7 ^b
CH ₃ Sn[Mn(CO) ₅] ₃	Pyridine ^c	8.62		~24 ^d

^a Chemical shift in ppm relative to tetramethylsilane. ^b ¹¹⁷Sn and ¹¹⁹Sn couplings not resolved. Low solubility necessitated use of Varian time-averaging computer and several scans. ^c Measured at 55° for increased solubility. ^d Average value; ¹¹⁷Sn and ¹¹⁹Sn satellites not resolved.

(22) For brevity we shall refer only to *J*^(119Sn-CH₃), designated simply as *J*.

(23) M. L. Maddox, N. Flitcroft, and H. D. Kaesz, *J. Organometal. Chem.* (Amsterdam), **4**, 50 (1965).

(24) N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

(25) *J* values for methyltin chlorides taken from M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

(26) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 150 (1965).

(27) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 361 (1964); R. E. Dessy, R. L. Pohl, and R. B. King, *ibid.*, **86**, 5121 (1966).