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Preparation and Properties of Some Mixed Metal Carbonyl Compounds. I. Compounds Containing a Group IV Metal and Manganese or Iron

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A number of mixed metal compounds of the type $R_{4-n}M[Mn(CO)_5]_n$ where R is alkyl or aryl, M is a group IV metal and n is 1 or 2 were prepared. Syntheses of compounds of the type $R_{3-n}X_nSnMn(CO)_5$, where R is aryl, X is bromine or chlorine and n is 1, 2 or 3 were achieved by either halogen cleavage reactions or by redistribution reactions. The preparation and properties of the triphenylphosphine and tetraphenylcyclopentadienone adducts of $(C_6H_5)_3SnMn(CO)_5$ are described. The compound $C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ was prepared for comparison with some tin–manganese compounds.

Covalent compounds containing two Group IV metals have been studied extensively. Little is known, however, about the chemical properties of covalent bimetallic compounds containing a transition metal and a group IV metal, although a number of these compounds have been synthesized. The preparation of a non-ionic organometallic compound containing a transition metal and a Group IV metal was first reported by Hein, *et al.*,[1] who obtained compounds of the type $[R_2PbFe(CO)_4]_2$ (R is an open chain aliphatic) and $(R_3Pb)_2Fe(CO)_4$ (R is phenyl or cyclohexyl) by treating an appropriate R_3PbOH compound with $Ca[HFe(CO)_4]_2$. Subsequently other mixed metal carbonyl compounds containing a Group IV metal and a transition metal were prepared by related procedures. These included compounds of the type $R_2Sn[Co(CO)_4]_2$ (R is alkyl),[2] $(C_6H_5)_3PbCo(CO)_4$[3] and $C_5H_5Fe(CO)_2Si(CH_3)_3$.[4,4a] Tin compounds of the type $[R_2SnFe(CO)_4]_2$ (R is alkyl) have recently been prepared by a novel reaction between iron pentacarbonyl and tetraorganotin compounds.[5] In the present study a number of bimetallic compounds having tin–manganese, lead–manganese and tin–iron bonds were synthesized for the purpose of investigating certain of their physical and chemical properties. Most of the chemical studies were made with compounds containing tin and manganese.

Synthesis.—The organic bimetallic compounds prepared in this work are listed in Table I. These mixed metal carbonyl compounds were obtained by treating the sodium salt of a metal carbonyl or a cyclopentadienylmetal carbonyl compound with a Group IV organometallic halide. Thus, bimetallic compounds of manganese and tin were prepared by treating a R_2SnCl_2 or a R_3SnCl compound with an equivalent amount of $NaMn(CO)_5$ (I) in tetrahydrofuran (THF). The reactions proceeded smoothly in THF to give compounds of the type $R_3SnMn(CO)_5$ or $R_2Sn[Mn(CO)_5]_2$ in yields ranging from 81 to 86%.

$$R_{4-n}SnCl_n + n\ NaMn(CO)_5 \longrightarrow R_{4-n}Sn[Mn(CO)_5]_n + n\ NaCl \quad (n = 1,2)$$

Triphenyltinmanganese pentacarbonyl (II), a typical example, was prepared in 86% yield by this method.

Lead–manganese compounds were conveniently synthesized by the same procedure. For example, $(C_2H_5)_3PbMn(CO)_5$ was formed in 76% yield from a 1:1 molar ratio of triethyllead chloride and compound I in THF. Other lead–manganese compounds of the type $R_3PbMn(CO)_5$ (R = CH_3, C_6H_5) and $R_2Pb[Mn(CO)_5]_2$ (R = CH_3, C_2H_5) were prepared with equal facility. All of the organolead and organotin halides, with the exception of trimethyllead chloride, afforded a single reaction product when treated with compound I. Trimethyllead chloride, prepared according to the method of Heap and Summers,[6] gave both $(CH_3)_3PbMn(CO)_5$ (III) and $(CH_3)_2Pb[Mn(CO)_5]_2$ (IV) in yields of 46% and 22%, respectively, when treated with compound I in THF in a 1:1 molar ratio. Initially, it was suspected that compound IV was formed because the trimethyllead chloride contained a significant amount of dimethyllead dichloride. Analysis of the monohalide indicated that it contained very little, if any, dihalide. Another plausible explanation was that compound III redistributed during the reaction or during work-up. This possible mode of reaction was disproved after heating compound III at 85° and in refluxing THF without forming compound IV.

A compound containing a silicon–manganese bond, $(C_6H_5)_3SiMn(CO)_5$, was obtained from the reaction of chlorotriphenylsilane with compound I in THF. The scarlet crystals oxidized in air to give manganese carbonyl, hexaphenyldisiloxane and a small amount of triphenylsilanol. The silicon–manganese bond is less oxidatively stable than analogous tin–manganese and lead–manganese bonds. This decreased stability of the silicon–manganese bond is not too surprising since the only other compound containing a transition metal bonded to silicon, $C_5H_5Fe(CO)_2Si(CH_3)_3$, also is quite air-sensitive.[4]

In addition to the compounds with tin–manganese bonds, a bimetallic compound with tin bonded to iron, $C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ (V), was prepared for comparison with some of the tin–manganese organometallic compounds. This carbonyl compound was readily obtained by treating triphenyltin chloride with $C_5H_5Fe(CO)_2Na$ in THF.

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(1) F. Hein, H. Pobloth and E. Heuser, *Z. Anorg. u. Allgem. Chem.*, **248**, 84 (1941); **249**, 293 (1942); **254**, 138 (1947); **255**, 125 (1948).

(2) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1270 (1957).

(3) F. Hein, P. Kleinert and W. Jehn, *Naturwisseschaften*, **44**, 34 (1957).

(4) T. S. Piper, O. Lemal and G. Wilkinson, *ibid.*, **43**, 129 (1956).

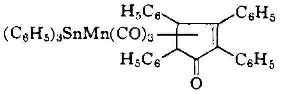
(4a) In a paper to be published shortly, Dr. Dietmar Seyferth and his co-workers describe the preparation of triphenylgermyl-π-cyclopentadienyliron dicarbonyl and triphenylgermylmanganese pentacarbonyl. Both of these compounds are significantly more air-stable than the silicon analogs.

(5) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 3833 (1960).

(6) R. Heap and B. C. Summers, *J. Chem. Soc.*, 2983 (1949).

TABLE I

MIXED METAL COMPOUNDS[a]

Formula[b]	Crystallization solvent	Yield, %	Melting point, °C.	Color	Analyses Calcd. C	Calcd. H	Found C	Found H
$(C_6H_5)_3SnMn(CO)_5$[c] (II)	*n*-Hexane	81	148–150	White	50.69	2.92	50.90	2.87
$(C_6H_5)_3Sn[Mn(CO)_5]_2$ (X)	*n*-Hexane	82	137–139	White	39.86	1.81	39.83	1.68
$Me_2Sn[Mn(CO)_5]_2$ (XII)	*n*-Hexane	86	102–104	Pale yellow	26.75	1.12	26.85	1.19
$(C_6H_5)_3PbMn(CO)_5$	*n*-Hexane	79	146–148	Yellow	43.60	2.39	44.25	2.59
$Et_2Pb[Mn(CO)_5]_2$	*n*-Hexane	66	77–79	Orange	25.66	1.54	25.81	1.61
$Et_3PbMn(CO)_5$	None	76	(B.p. 70–73, 0.1 mm.)	Yellow	27.00	3.09	27.40	3.18
$Me_3PbMn(CO)_5$[d] (III)	Pet. ether	47[e]	30–31	Yellow	21.48	2.03	21.35	1.97
$Me_2Pb[Mn(CO)_5]_2$[f] (IV)	Pet. ether	23[e]	108–110	Orange	22.98	0.96	23.03	0.99
$CpFe(CO)_2SnC_6H_5$ (V)	Ethanol	39	139–141	Orange				
$(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$[g] (VI)	Ethanol–benzene	94	228–230	White	61.65	3.88	61.85	3.88
$(C_6H_5)_3SnMn(CO)_4As(C_6H_5)_3$[h]	Ethanol–benzene	42	222–224	White	58.35	3.67	58.84	3.71
 (VIII)	CH_2Cl_2–hexane	30	205–207	Yellow	68.75	4.04	68.56	4.10

[a] All but three compounds were obtained by treating a Group IV alkyl- or arylmetal halide with the sodium derivative of a transition metal carbonyl in THF. Compounds VIII, VI and the arsenic analog of VI were obtained *via* carbonyl displacement reactions on II. [b] Cp = cyclopentadienyl; C_6H_5 = phenyl; Me = methyl; Et = ethyl. [c] Calcd.: Mn, 10.1; Sn, 21.78; mol. wt., 544. Found: Mn, 9.9; Sn, 21.88; mol. wt., 539. [d] Calcd.: Pb, 46.33. Found: Pb, 46.42. [e] Yield based on $NaMn(CO)_5$. [f] Calcd.: Pb, 33.04. Found: Pb, 33.10. [g] Calcd.: P, 4.0; mol. wt., 779. Found: P, 4.2; mol. wt., 726. [h] Calcd.: Mn, 6.67. Found: Mn, 6.96.

$$C_5H_5Fe(CO)_2Na + (C_6H_5)_3SnCl \longrightarrow \underset{\text{V}}{C_5H_5Fe(CO)_2Sn(C_6H_5)_3} + NaCl$$

Properties.—All of the mixed metal compounds in Table I, except $(C_2H_5)_3PbMn(CO)_5$, are solids at 25° and range in color from deep orange for the tin–iron compound V and some lead–manganese compounds to white for most of the compounds having tin–manganese bonds. The lead–manganese compound $(C_2H_5)_3PbMn(CO)_5$ is a yellow liquid which can be distilled only at reduced pressures. The tin–manganese compounds are thermally more stable than analogous lead–manganese compounds, particularly $(C_6H_5)_3SnMn(CO)_5$ (II), which only begins to evolve carbon monoxide at 195°. The solids were purified by crystallization from appropriate solvents while $(CH_3)_3PbMn(CO)_5$, a low melting solid, was purified by distillation at reduced pressures. The mixed metal compounds are readily soluble in polar solvents like methylene chloride, ether, acetone and THF; they are fairly soluble in ethanol, benzene and other aromatic solvents and are moderately to slightly soluble in aliphatic solvents like *n*-hexane.

The compounds listed in Table I are fairly air-stable. All of the compounds decompose at varying rates in organic solvents. Oxidation of the compounds, both in solution and in the crystalline state, seems to be accelerated by light. In general, oxidative stability of the metal–metal bond in compounds of the type $(C_6H_5)_3MMn(CO)_5$, where M is a Group IV metal, is Sn > Pb > Si. Also, as the number of $Mn(CO)_5$ groupings in the bimetallic compounds increases, *e.g.*, $(C_6H_5)_2Sn[Mn(CO)_5]_2$, the oxidative stability decreases.

The infrared spectra of metal carbonyl compounds having tin–manganese, lead–manganese or tin–iron bonds did not exhibit absorption bands characteristic of CO bridging.[7] The infrared spectrum of compound II as a KBr disk showed only terminal manganese–carbonyl stretching frequencies at 4.78 μ and 5.03 μ.[8] If indeed the carbonyl groups were involved in bridging, a pronounced shift of the manganese-carbonyl stretching frequency to a higher wave length certainly would have been expected.[9]

Chemical Reactions.—Although most known reactions of metal carbonyls involve substitution of the carbonyl grouping, three sites in the mixed metal carbonyl compounds are subject to attack by either electrophilic, nucleophilic or neutral chemical reagents. Thus, in compounds of the type $R_3MMn(CO)_5$ or $R_2M[Mn(CO)_5]_2$, the carbon–metal, metal–metal or metal–carbonyl linkages are potential points of chemical reaction.

Carbon monoxide can be displaced from metal carbonyls with varying ease by compounds such as triphenylphosphine either thermally or catalytically (ultraviolet).[10] When carbonyl compound II was heated with excess triphenylphosphine at about 195° in the absence of a solvent and under a nitrogen atmosphere, $(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$ (VI), was obtained in 94% yield.

$$(C_6H_5)_3SnMn(CO)_5 + P(C_6H_5)_3 \longrightarrow \underset{\text{VI}}{(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3} + CO$$

No other substitution product was isolated under these conditions. Compound VI is diamagnetic

(7) The suggestion has been made that carbonyl bridging exists in the compound $(C_4H_9)_2Sn[Co(CO)_3P(C_6H_5)_3]_2$; however, no structural evidence was given in support.[2]

(8) The CO stretching frequencies are very similar to those reported for $CH_3Mn(CO)_5$; 4.8 μ, 5.0 μ and 5.1 μ [R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957)] and for $ClMn(CO)_5$; 4.83 μ and 4.96 μ [E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959)].

(9) J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," Ed. by H. Zeiss, Reinhold Publishing Corp., New York, N. Y., 1960, p. 478.

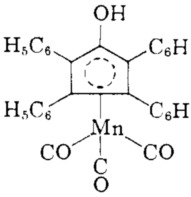
(10) A general discussion of this type of substitution reaction is given in ref. 9, p. 484.

and melts without carbon monoxide evolution. The corresponding arsine derivative, $(C_6H_5)_3SnMn(CO)_4As(C_6H_5)_3$, was prepared in a similar fashion. Compound VI was unambiguously synthesized by treating triphenyltin chloride with $NaMn(CO)_4P(C_6H_5)_3$.[11]

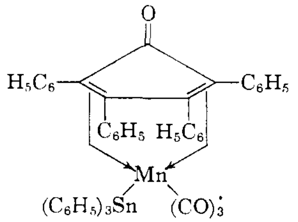
$$(C_6H_5)_3SnCl + NaMn(CO)_4P(C_6H_5)_3 \longrightarrow VI + NaCl$$

Until recently no manganese carbonyl derivative containing a π-bonded olefin or diene ligand in which the organic moiety effectively contributed an even number of electrons to the central metal atom was reported.[12] Weiss and Hübel[13] showed that treatment of $Mn_2(CO)_{10}$ with tetraphenylcyclopentadienone in an inert solvent afforded an unstable intermediate which, after hydrolysis, gave the cyclopentadienyl derivative, compound VII. Apparently an unstable intermediate is formed which is stabilized after hydrolysis by forming the well-known "sandwich" type of cyclopentadienyl derivative in which the cyclopentadienyl moiety effectively contributes five electrons to the central manganese atom. Since the tin–manganese bond in compound II is thermally stable, it should be possible to thermally displace carbon monoxide from compound II by a hydrocarbon ligand to give a derivative in which the π-bonded ligand contributes an even number of electrons to manganese. This type of π-bonded complex, compound VIII, was obtained in 31% yield by heating a mixture of compound II and tetraphenylcyclopentadienone (1:1 molar ratio) between 180 and 194° for 4 hr. in the absence of a solvent and under a nitrogen atmosphere.

Although crystals of compound VIII apparently are insensitive to air, a benzene solution of the material gradually turns deep red. Elemental analysis and a molecular weight measurement support the assigned structure for VIII. The infrared spectrum showed absorption bands characteristic of terminal manganese–carbonyl bonds. An absorption band characteristic of the carbonyl grouping in the organic moiety appeared at 6.25 μ.[14]



VII



VIII

Halogen Derivatives.—The reactions of bimetallic compounds, particularly those containing a tin–manganese bond, with electrophilic reagents such as halogen or hydrogen chloride can occur at either of two sites. The tin–manganese bond can be broken, or the organic moieties attached to tin can be totally or selectively cleaved. The point of attack in a tin–manganese compound by a specific electrophilic reagent is dependent on the type of organic radical attached to tin and on the number of $Mn(CO)_5$ groups in the bimetallic compound.

Excess chlorine in carbon tetrachloride at 25° ruptured the three phenyl-tin bonds in compound II to give $Cl_3SnMn(CO)_5$ (IX) and chlorobenzene

$$(C_6H_5)_3SnMn(CO)_5 + 3Cl_2 \longrightarrow \underset{IX}{Cl_3SnMn(CO)_5} + 3C_6H_5Cl$$

however, resistance of the tin–manganese bond in compound IX to further attack by chlorine was unexpected. Initially, it was thought that further reaction with chlorine did not occur because of the low solubility of compound IX in carbon tetrachloride. This was disproved by treating compound II with excess chlorine in methylene chloride, a solvent in which compound IX is soluble; again, compound IX was the only product isolated. Compound IX is a white solid which is sensitive to moisture and which decomposes sharply at 168° without melting. The bromo analog, $Br_3SnMn(CO)_5$, was obtained by treating compound II with excess bromine in carbon tetrachloride either at ambient temperature or at reflux temperature. Even at reflux temperature there was no indication of the tin–manganese bond being broken by bromine.

A halogen derivative related to compound IX, $Cl_3SnMn(CO)_4P(C_6H_5)_3$, was prepared in 64% yield from the non-halogen derivative (VI) and chlorine in methylene chloride.

$$\underset{VI}{(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3} + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_4P(C_6H_5)_3 + 3C_6H_5Cl$$

Compounds of the type $R_2Sn[Mn(CO)_5]_2$ gave different cleavage products with electrophilic reagents, depending on the electrophile. When $(C_6H_5)_2Sn[Mn(CO)_5]_2$ (X) was treated with hydrogen chloride, products were obtained that were different from those isolated when chlorine was used. Thus, chlorine attacked compound X to give compound IX, chlorobenzene and $ClMn(CO)_5$ recovered as $Cl_2Mn_2(CO)_8$. Hydrogen chloride was considerably more selective. In methylene chloride at 25°, hydrogen chloride cleaved only the phenyl–tin bonds of compound X to give 69% of $Cl_2Sn[Mn(CO)_5]_2$ (XI) and benzene.

$$(C_6H_5)_2Sn[Mn(CO)_5]_2 + 2HCl \longrightarrow \underset{XI}{Cl_2Sn[Mn(CO)_5]_2} + 2C_6H_6$$

In the cleavage of compound X by chlorine to give compound IX, the first step probably involves rupture of the phenyl–tin bonds as described by reaction 1. This is then followed by attack of

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[11] An elegant method for preparing $NaMn(CO)_4P(C_6H_5)_3$ was recently described by W. Hieber, G. Faulhaber and F. Theubert, *Z. Naturforsch.*, **15b**, 326 (1960).

[12] An ethylene complex of $C_5H_5Mn(CO)_3$, $C_5H_5Mn(CO)_2C_2H_4$, was prepared recently by a reaction between $C_5H_5Mn(CO)_3$ and ethylene which was catalyzed by ultraviolet light; H. P. Kögler and E. O. Fischer, *Z. Naturforsch.*, **15b**, 676 (1960). In addition, a π-allyl derivative of manganese, $C_3H_5Mn(CO)_4$, in which the organic moiety effectively contributes three electrons to the central atom has been prepared; H. D. Kaesz, R. B. King and F. G. A. Stone, *ibid.*, **15b**, 682 (1960). Also, see W. R. McClellean, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Hawk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

[13] E. Weiss and W. Hubel, *J. Inorg. and Nuclear Chem.*, **11**, 42 (1959).

[14] The infrared spectra of a number of tetraphenylcyclopentadienone derivatives of iron, cobalt and molybdenum carbonyls have a band characteristic of a ketonic C=O between 6.0 and 6.23 μ; see ref. 13.

TABLE II

HALOGENATED MIXED METAL COMPOUNDS

			Analyses					
			Calcd.			Found		
Formula[a]	Yield, %	Melting point, °C.	C	H	X	C	H	X
$Cl_3SnMn(CO)_5$[b] (IX)	61	168 (dec.)	14.30		25.32	14.29		25.71
$Br_3SnMn(CO)_5$[c]	86[d]	145–147	10.85		43.32	11.40		42.8
$C_6H_5Cl_2SnMn(CO)_5$	86	83–85	28.61	1.09	15.36	28.17	1.21	14.85
$C_6H_5Br_2SnMn(CO)_5$ (XIII)	85	96–98	23.99	0.92		23.86	0.94	
$(C_6H_5)_2ClSnMn(CO)_5$	86	97–98	40.56	2.00		40.85	2.06	
$(C_6H_5)_2BrSnMn(CO)_5$	71	95–97	37.27	1.84	14.59	37.37	1.90	14.69
$Cl_2Sn[Mn(CO)_5]_2$ (XI)	69	143–144	20.72			20.86		
$CpFe(CO)_2SnCl_3$[e] (XIV)	85	150 (dec.)	20.91	1.25		21.02	1.30	
$Cl_3SnMn(CO)_4P(C_6H_5)_3$	66	159 (dec.)	40.38	2.31	16.26	40.29	2.43	15.78

[a] Cp = cyclopentadienyl; C_6H_5 = phenyl. [b] Calcd.: Mn, 13.1. Found: Mn, 13.2. [c] Calcd.: Mn, 9.93. Found: Mu, 10.0. [d] Reaction temperature was 25°. In another run in which compound II was refluxed with excess Br_2 in CCl_4, a 72% yield of $Br_3SnMn(CO)_5$ was obtained. [e] Calcd.: Sn, 29.5. Found: Sn, 30.2

the tin–manganese bond by chlorine as shown in reaction 2. Reaction 2 was independently carried

$$(C_6H_5)_2Sn[Mn(CO)_5]_2 + 2Cl_2 \longrightarrow Cl_2Sn[Mn(CO)_5]_2 + 2C_6H_5Cl \quad (1)$$

$$Cl_2Sn[Mn(CO)_5]_2 + Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + ClMn(CO)_5 \quad (2)$$

out and verified. Only a low yield of pure compound IX was isolated when compound XI was treated with chlorine because of difficulty in separating compound IX from $Cl_2Mn_2(CO)_8$, to which $ClMn(CO)_5$ was converted during the work-up procedure.

The cleavage of $(C_6H_5)_3SnMn(CO)_5$ (II) can be made more selective by altering either the reaction temperature, the stoichiometry or the nature of the electrophilic reagent. Treatment of compound II with excess hydrogen chloride at 0–5° gave mainly $(C_6H_5)Cl_2SnMn(CO)_5$ together with a small amount of compound IX. The bromo analog, $(C_6H_5)Br_2SnMn(CO)_5$ (XIII), was more conveniently prepared by treating one mole of compound II with two moles of bromine in carbon tetrachloride.

$$(C_6H_5)_3SnMn(CO)_5 + 2Br_2 \longrightarrow (C_6H_5)Br_2SnMn(CO)_5 + 2C_6H_5Br$$

An attempt to extend this procedure to the synthesis of $(C_6H_5)_2BrSnMn(CO)_5$ by treating compound II with bromine in a 1:1 molar ratio failed; instead only compound XIII and a mixture of products, which could not be separated, were isolated.

Halogen derivatives of compound II unobtainable by direct halogenation could be obtained by a redistribution reaction. Redistribution reactions between alkyl- or aryltin compounds and organotin halides are not uncommon[15]; however no mixed metal carbonyl compound ever has been reported to undergo this type of reaction. In this investigation the redistribution reaction proved to be an invaluable tool for preparing compounds of the type $(C_6H_5)_2XSnMn(CO)_5$. An 85% yield of $(C_6H_5)_2ClSnMn(CO)_5$ was obtained by heating compounds II and IX in a 2:1 molar ratio at 148° for 0.75 hr.

$$2(C_6H_5)_3SnMn(CO)_5 + Cl_3SnMn(CO)_5 \longrightarrow 3(C_6H_5)_2ClSnMn(CO)_5$$

The bromo analog was prepared by a similar procedure using equimolar quantities of compounds II and XIII.

$$(C_6H_5)_3SnMn(CO)_5 + (C_6H_5)Br_2SnMn(CO)_5 \longrightarrow 2(C_6H_5)_2BrSnMn(CO)_5$$

The redistribution reaction should prove to be a very versatile tool for synthesizing a variety of halogen derivatives of $R_3SnMn(CO)_5$ compounds. It should be particularly applicable for obtaining halogen derivatives of bimetallic compounds containing alkyl groups, since such derivatives are difficult to obtain by cleavage reactions using halogens or hydrogen halide.

Various halogen derivatives of mixed metal carbonyl compounds, together with appropriate physical data, are listed in Table II.

The behavior of bimetallic compounds other than those having a tin–manganese bond toward electrophilic reagents was studied in less detail. Hydrogen chloride readily attacked the lead–manganese bond in $(C_6H_5)_3PbMn(CO)_5$ at 25° to give $ClMn(CO)_5$, benzene or chlorobenzene, and unidentified lead species. Similarly, $(C_2H_5)_2Pb[Mn(CO)_5]_2$ was attacked by chlorine in carbon tetrachloride at 5° to give $ClMn(CO)_5$ and a solid containing both diethyl and triethyllead groupings.

The iron–tin bond in $C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ (V) was also easily cleaved by chlorine in carbon tetrachloride. In sharp contrast, hydrogen chloride attacked only the carbon–tin bonds. Thus treatment of V with excess hydrogen chloride in methylene chloride at 25° gave 85% of $C_5H_5Fe(CO)_2SnCl_3$ (XIV).

$$C_5H_5Fe(CO)_2Sn(C_6H_5)_3 + 3HCl \longrightarrow C_5H_5Fe(CO)_2SnCl_3 + 3C_6H_6$$

Compound XIV is a reddish-brown crystalline solid decomposing at 150°. The product decomposes slowly both in the crystalline state and in solution when exposed to air.

Infrared Data.—Compounds of type $R_{4-n}M[Mn(CO)_5]n$, where R is alkyl or aryl and M is lead or tin, showed terminal manganese–carbonyl stretching frequencies at 4.78–4.80 μ and 5.0–5.5 μ. In some cases a weak third band was resolved at 4.85 μ or 5.1 μ. The halogen derivative showed strong bands also at 4.70–4.78 μ and 4.93–5.0 μ. Metal carbonyl compounds containing a neutral ligand like triphenylphosphine or a π-bonded organic ligand exhibit a definite shift of the metal–

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[15] For a general discussion of redistribution reactions in organotin chemistry, see R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, **60**, 483 (1960).

carbonyl stretching frequencies toward higher wave lengths.[16] This shift was observed with the triphenylphosphine adduct of compound II (4.91 and 5.15 μ) and was even more pronounced with the diene complex VIII (5.0 and 5.25 μ).

Experimental

A nitrogen atmosphere was used in all reactions involving air- and moisture-sensitive compounds. An inert atmosphere was also employed while carrying out carbon monoxide displacement reactions. All glassware was dried at 125° and flushed with nitrogen before use in such operations. Tetrahydrofuran (THF) was refluxed over calcium hydride overnight. Before distilling THF for use, sufficient lithium aluminum hydride was added to remove the last trace of water. Melting points were determined in capillary tubes heated by an oil bath and are uncorrected. Boiling points are also uncorrected. Infrared spectra were produced on a Perkin-Elmer Model 21 recording double beam spectrometer with a sodium chloride prism.

The preparations described below are representative of the procedures indicated in Table I and II.

$(C_6H_5)_3SnMn(CO)_5$ (II).—A tetrahydrofuran (THF) solution of $NaMn(CO)_5$[17] was prepared from 19.5 g. (0.05 mole) of $Mn_2(CO)_{10}$ and sodium amalgam (5 g. of Na and 500 g. of Hg) in about 300 ml. of THF. The reaction mixture was stirred at room temperature for 30 min. after which the mercury was separated. Subsequently, 38.0 g. (0.096 mole) of triphenyltin chloride was added and the reaction mixture was stirred at room temperature for 20 min. Then the mixture was reduced to about one-half volume by distillation. The mixture was poured into ice-water and the solid was filtered off. The solid was dried and extracted several times with refluxing *n*-hexane. The combined extracts were concentrated to about 70 ml. On cooling, white crystals were filtered off and dried at room temperature under reduced pressure to give 44.7 g. of compound II.

$(CH_3)_3PbMn(CO)_5$ (III) and $(CH_3)_2Pb[Mn(CO)_5]_2$ (IV).—To about 300 ml. of THF containing 0.1 mole of $NaMn(CO)_5$ was added, in small portions, 28.8 g. (0.1 mole) of trimethyllead chloride.[18] The reaction mixture was stirred at room temperature for 3 hr. after which the THF was distilled under reduced pressure at about 55°. The residue was extracted several times with petroleum ether. Concentration and chilling of the extracts resulted in the deposition of orange crystals which were filtered off and dried to give 7.23 g. of compound IV.

The solvent was evaporated from the filtrate and the residual oil was distilled at 3 mm. to give 20.8 g. of compound III, b.p. 60–62°. The distillate was recrystallized from cold petroleum ether to give yellow platelets of compound III.

When compound III was heated at 85° for 2.5 hr. in the absence of a solvent and in a sealed ampoule, no compound IV could be obtained after an attempted crystallization of the product from petroleum ether. When compound III was refluxed in THF, some decomposition occurred; however, no compound IV could be found after refluxing was stopped.

$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ (V).—A THF solution of $C_5H_5Fe(CO)_2Na$ was prepared[4] from 10.6 g. (0.03 mole) of $[C_5H_5Fe(CO)_2]_2$ and sodium amalgam (3.0 g. of Na and 300 g. of Hg) in about 250 ml. of THF. The mixture was stirred at room temperature overnight. After separating the mercury, 20 g. (0.0519 mole) of triphenyltin chloride was added to the reaction mixture which was then stirred at room temperature for 2 hr. The solvent was evaporated and the residue was extracted with methylene chloride. The solvent was removed and the product was crystallized from *n*-hexane to give 10.7 g. of compound V. The product was further purified by recrystallization from ethanol.

$(C_6H_5)_3SiMn(CO)_5$.—A THF solution containing 0.04 mole of $NaMn(CO)_5$ was treated with 20.7 g. (0.07 mole) of chlorotriphenylsilane. A methylene chloride extract of the crude mixture was concentrated and chilled, leaving scarlet crystals, presumably $(C_6H_5)_3SiMn(CO)_5$, that were readily oxidized during the work-up procedure. From a portion of the oxidized product there was sublimed 0.65 g. of $Mn_2(CO)_{10}$. Recrystallization of the residue from toluene gave 1.3 g. of hexaphenyldisiloxane, m.p. 223–225°, identified by infrared analysis. Work-up of the filtrate yielded 0.25 g. of triphenylsilanol, m.p. 148–150°, identified by infrared analysis.

$(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$ (VI). (A) **From II and $P(C_6H_5)_3$.**—A mixture of 4.0 g. (0.0073 mole) of compound II and 1.92 g. (0.0074 mole) of triphenylphosphine was heated at about 200° for 2 hr. The resulting crystalline solid, 5.4 g., was crystallized from a mixture of benzene and ethanol. Recrystallization was effected from the same mixture of solvents.

(B) **From $(C_6H_5)_3SnCl$ and $NaMn(CO)_4P(C_6H_5)_3$.**—The $NaMn(CO)_4P(C_6H_5)_3$ was prepared[11] from 9.0 g. (0.021 mole) of $Mn(CO)_4P(C_6H_5)_3$ and sodium amalgam (2.0 g. Na and 200 g. Hg) in 100 ml. of purified THF. After stirring the mixture at ambient temperature for 25 min., excess amalgam was drawn off and 7.7 g. (0.02 mole) of triphenyltin chloride was added in small portions during 20 min. Excess solvent was evaporated and the residue was crystallized from a mixture of benzene and ethanol (2B) to give 11.5 g. (74%) of product, m.p. 232–234°, which was demonstrated to be identical with that from method A by comparison of infrared spectra and non-depression of the melting point when the two were admixed.

$(C_6H_5)_3SnMn(CO)_3C_5(C_6H_5)_4O$ (VIII).—A mixture of 5.0 g. (0.009 mole) of compound II and 3.5 g. (0.009 mole) of tetraphenylcyclopentadienone was heated between 180 and 194° for 4 hr. while maintaining a nitrogen atmosphere. Subsequently, the reaction mass was extracted several times with refluxing *n*-hexane. The combined extracts were concentrated until yellow crystals began to separate. The mixture was cooled to room temperature and the diene adduct VIII, 2.43 g., was filtered off. Further purification was achieved by recrystallization from methylene chloride and *n*-hexane. Benzene is also a good solvent for recrystallization. From the original filtrate was recovered 0.8 g. of unchanged compound II, which did not depress the melting point of an authentic sample.

$Cl_3SnMn(CO)_5$ (IX).—Chlorine was bubbled through a carbon tetrachloride solution containing 10.0 g. (0.0183 mole) of compound II at a moderate rate for 25 min. A white solid precipitated. Excess chlorine was removed under reduced pressure. The resulting solution was heated to reflux and filtered while hot. The filtrate was concentrated until white needles began to settle out. The needles were filtered off and dried to give 4.68 g. of compound IX. The product was slightly to moderately soluble in acetone, methanol and benzene and very soluble in methylene chloride.

In another run chlorine was passed into 25 ml. of methylene chloride containing 1.0 g. (0.0018 mole) of compound II for 20 min. Excess chlorine and solvent were distilled off, and the residue was crystallized from carbon tetrachloride to give 0.52 g. (67%) of compound IX.

Hydrolysis of compound IX by water in acetone left a white solid which was insoluble in water but very soluble in acetone. The product decomposed at 152°.

$(C_6H_5)Cl_2SnMn(CO)_5$.—Anhydrous hydrogen chloride was bubbled through a solution of 2.0 g. (0.0037 mole) of compound II in about 125 ml. of carbon tetrachloride for 45 min. while keeping the reaction temperature at 0–5°. Subsequently the solvent was evaporated at 10–15° under reduced pressure. The white residue was extracted with refluxing *n*-hexane and filtered hot. The yield of white crystals of $(C_6H_5)Cl_2SnMn(CO)_5$ was 1.45 g. A small amount of compound IX was extracted by hot carbon tetrachloride from the hexane-insoluble product.

$(C_6H_5)Br_2SnMn(CO)_5$ (XIII).—A solution of 2.96 g. (0.0184 mole) of bromine in about 20 ml. of carbon tetrachloride was added, during 1 hr., to a stirred solution of 5.0 g. (0.009 mole) of compound II in 80 ml. of carbon tetrachloride. The end-point of the reaction could be detected by a change in color from yellow to orange. The residue, after evaporation of the solvent, was crystallized from *n*-hexane to give 4.28 g. of XIII.

$(C_6H_5)_2BrSnMn(CO)_5$.—A mixture of 1.5 g. (0.00283 mole) of the bromo compound XIII and 1.55 g. (0.00283

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[16] See ref. 9, p. 479.

[17] See R. D. Closson, *et al.*, in ref. 8.

[18] This was prepared by the method given in ref. 6. *Anal.* Calcd. for C_3H_9ClPb: C, 12.52; H, 3.12; Cl, 12.32; Pb, 72.1. Found: C, 12.65; H, 3.21; Cl, 12.52; Pb, 73.5. The lead was determined as trimethyllead by the dithizone method of S. R. Henderson and L. J. Snyder, *Anal. Chem.*, **33**, 1172 (1961). No dimethyllead species was detected in the sample.

mole) of compound II was heated at about 150° for 5 hr. The crude product was crystallized from hexane to give 2.2 g. of the redistribution product.

$(C_6H_5)_2ClSnMn(CO)_5$.—A mixture of 4.2 g. (0.01 mole) of the chloro derivative IX and 11.0 g. (0.02 mole) of compound II was heated at about 150° for 0.75 hr. The crude product was crystallized from *n*-hexane to give 13.0 g. of $(C_6H_5)_2ClSnMn(CO)_5$.

$Cl_2Sn[Mn(CO)_5]_2$ (XI).—Anhydrous hydrogen chloride was passed through a solution of 2.0 g. (0.003 mole) of $(C_6H_5)_2Sn[Mn(CO)_5]_2$ in about 75 ml. of methylene chloride for 0.5 hr. The solvent was evaporated and the residue was recrystallized from ethanol to give 1.2 g. of white needles identified as XI by elemental analysis.

$Cl_3SnMn(CO)_4P(C_6H_5)_3$.—Chlorine was passed through a solution of 2.0 g. (0.0013 mole) of compound VI in 90 ml. of methylene chloride at a moderate rate for 10 min. Evaporation of the solvent left a solid that was redissolved in methylene chloride and filtered. Hot hexane was added, and methylene chloride was distilled until white needles began to crystallize. The product, m.p. 159° (dec.), was shown to be $Cl_3SnMn(CO)_4P(C_6H_5)_3$ by elemental analysis. The yield was 1.1 g. The infrared spectrum showed bands only at 6.75 and 6.97 μ characteristic of a phenyl–phosphorus bond. Compound VI showed a weak doublet at 6.97 and a singlet at 7.03 μ, the latter characteristic of a phenyl–tin stretching frequency.

$C_5H_5Fe(CO)_2SnCl_3$ (XIV).—Two grams (0.0038 mole) of compound V was dissolved in about 90 ml. of methylene chloride. Anhydrous hydrogen chloride was passed through the solution for 10 min. at room temperature after which time the solvent was evaporated. The product, 1.43 g., was recrystallized from a mixture of methylene chloride and carbon tetrachloride to give 1.3 g. of reddish-brown needles which were identified as compound XIV by elemental analysis.

When compound V was treated with excess chlorine in carbon tetrachloride between 0 and 10°, the tin–iron bond was broken to give a black solid which was insoluble in common organic solvents.

Chlorine and XI.—Chlorine was bubbled through 25 ml. of methylene chloride containing 0.3 g. (0.0005 mole) of compound XI for 10 min. The cloudy mixture was filtered and the solvent distilled. The residue was fractionally crystallized from carbon tetrachloride to give 0.1 g. (35%) of compound IX, m.p. 168° (dec.) having an infrared spectrum identical with that of an authentic specimen. The remainder of the product consisted of a mixture of compound IX and $Cl_2Mn_2(CO)_8$, the latter being identified by infrared analysis.

Chlorine and X.—Two grams (0.003 mole) of $(C_6H_5)_2Sn[Mn(CO)_5]_2$ in 25 ml. of methylene chloride was treated with chlorine for 10 min. Evaporation of the solvent gave a yellow solid consisting of a mixture of compound IX and $ClMn(CO)_5$. The products were partially separated with difficulty by first extracting the yellow solid four times with ether. The solid from the extract was refluxed in carbon tetrachloride to convert $ClMn(CO)_5$ to $Cl_2Mn_2(CO)_8$. Fractional crystallization from carbon tetrachloride gave 0.15 g. of compound IX, m.p. 168° (dec.), identified by elemental analysis, and 0.08 g. of $Cl_2Mn_2(CO)_8$. The infrared spectrum of the latter showed terminal metal–carbonyl stretching frequencies very similar to those described previously. The ether-insoluble material was refluxed in carbon tetrachloride to give 0.7 g. of a product which was shown by its infrared spectrum to consist of a mixture of $Cl_2Mn_2(CO)_8$ and compound IX.

Hydrogen Chloride and $(C_6H_5)_3PbMn(CO)_5$.—Anhydrous hydrogen chloride was passed through a methylene chloride solution containing 2.0 g. (0.0032 mole) of $(C_6H_5)_3PbMn(CO)_5$ for 20 min. A white unidentified inorganic lead compound, 0.8 g., was filtered off. From the filtrate was obtained a solid which was recrystallized from carbon tetrachloride to give 0.6 g. (93%) of $Cl_2Mn_2(CO)_8$, m.p. 165° (dec.), identified by infrared analysis.

Chlorine and $(C_2H_5)_2Pb[Mn(CO)_5]_2$.—Two grams (0.0031 mole) of $(C_2H_5)_2Pb[Mn(CO)_5]_2$ in 60 ml. of carbon tetrachloride was treated with chlorine for four minutes. Excess chlorine was removed and the product was refluxed in carbon tetrachloride. The solvent was distilled under reduced pressure. The residue, 1.87 g., was washed with water, leaving $Cl_2Mn_2(CO)_8$, m.p. 165° (dec.). Evaporation of the water left a white solid. The infrared spectrum showed this solid to contain both diethyl and triethyllead groupings.

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The Amminehydroxocopper(II)-diolate Chelation Reaction[1,2]

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Potentiometric methods have led to the finding of approximate constants ($k_1 = 250$, $k_2 = 49$) for the stepwise addition of two hydroxide ions to amminecopper(II) in ammonia solutions of unit activity. This finding has facilitated a further study of the amminecopper-diol chelation reaction and evidence is presented which indicates that the reactive species are amminemonohydroxocopper(II) and the singly charged diolate anion. Chelation constants were calculated for three cyclic diols, methyl α-D-glucopyranoside, D-mannosan and lactate.

In the conformational analysis of carbohydrate derivatives with the ultimate objective of relating molecular shape to chemical properties, or to factors such as enzyme specificity, emphasis must be placed upon methods which cast light on the shapes of these molecules in aqueous solution. The amminecopper-diolate chelation reaction has received attention in such studies because it proceeds to a stable equilibrium accompanied by the liberation of protons, by extensive changes in ultraviolet absorbancy, and—with certain substances—by dramatic changes in optical activity. Although the reaction has been known for a century, *e.g.*, in the solubilization of cellulose, only recently has the one-to-one combining ratio between copper and diol been firmly established, and a singly charged diolate anion implicated as one of the reacting

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[2] The derivation of equations and data for the calculation of one of the chelation constants has been deposited as Document number 7101 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

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