Substituent effects on the coupling constant $J(^{119}Sn\text{-}CH_3)$ are not additive, as demonstrated in the series $(CH_3)_3SnCH_3$, $(CH_3)_3Sn\text{–}Mo(CO)_3C_5H_5$, $(CH_3)_3SnCl$, and $Cl(CH_3)_2Sn\text{–}Mo(CO)_3C_5H_5$. The values are 54.0, 49.0, 59.7, and 47.7 cps, respectively. The chlorine and molybdenum substituents do not offset one another in their effect on $J(^{119}SnCH_3)$ in the last compound.

The ultraviolet absorption data of Table II are reported for the sake of completeness. There is little that can be said by way of interpretation at this stage of development, but it is hoped that correlations will become possible as more data accumulate.

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Organometallic Compounds with Metal–Metal Bonds. II. The Insertion of Tin(II) and Germanium(II) Halides into Metal–Metal Bonds[1]

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

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New examples of insertion reactions into metal–metal bonds are described. Tin(II) chloride reacts smoothly with dicobalt octacarbonyl, $[(C_6H_5)_3PCo(CO)_3]_2$, or dimeric π-cyclopentadienylnickel carbonyl to form $(OC)_4Co\text{–}SnCl_2\text{–}Co(CO)_4$, $(C_6H_5)_3P(OC)_3Co\text{–}SnCl_2\text{–}Co(CO)_3P(C_6H_5)_3$, or $\pi\text{-}C_5H_5(OC)Ni\text{–}SnCl_2\text{–}Ni(CO)\text{-}\pi\text{-}C_5H_5$, respectively. Germanium(II) iodide and tin(II) bromide and iodide undergo similar reactions with dicobalt octacarbonyl. Infrared spectra of the new compounds are reported.

Introduction

The term "insertion reaction" has been applied to several processes in metal carbonyl chemistry and is best regarded as descriptive of the over-all process, without mechanistic implications. The original[2] and best understood[3] case involves the conversion of methyl- to acetylmanganese pentacarbonyl. More recently, Dighe and Orchin have reported examples of the insertion of mercury into metal–metal bonds,[4] while the reaction of π-cyclopentadienyliron dicarbonyl dimer with tin(II) chloride[5] or germanium(II) iodide[6] affords $[\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ or $[\pi\text{-}C_5H_5Fe(CO)_2]_2GeI_2$, respectively. The similarity of mercury, tin(II) chloride, and germanium(II) iodide in these reactions is noteworthy and is based on the ability of these reagents to increase their covalency by two units and on the fact that both mercury and tin form strong covalent bonds with transition metals. Our interest in metal–metal bonding has prompted us to explore more fully the scope of the insertion reaction.

Experimental Section

All reactions were carried out in a nitrogen atmosphere. Infrared spectra were determined using a Perkin-Elmer Model 421 spectrometer with double-grating interchange. Carbonyl bands were run on an expanded scale with deuterium chloride calibration on each spectrum.[1] Values are given in cm^{-1}. Color, melting points, and analytical data are given in Table I. Infrared data are given in Table II.

Dichlorobis(tetracarbonylcobalt)tin(IV).—Dicobalt octacarbonyl (10.3 g, 30 mmoles) and anhydrous tin(II) chloride (5.7 g, 30 mmoles) were stirred at room temperature for 15 min in 250 ml of tetrahydrofuran. Solvent was removed at reduced pressure from the deep orange solution, and the residue was dissolved in the minimum amount of dichloromethane. After filtration, slow addition of *n*-pentane to the solution cooled in ice gave orange-red, air-stable, prismatic crystals. Recrystallization from dichloromethane–pentane gave the product in 50% yield. **Dibromobis(tetracarbonylcobalt)tin(IV)** and **diiodobis(tetracarbonylcobalt)tin(IV)** were similarly prepared from the anhydrous halides, *n*-pentane only being used for extraction and recrystallization.

Triphenylphosphinetricarbonylcobalt Dimer.—$[(C_6H_5)_3PCo(CO)_3]_2$ was most conveniently prepared from $Co_4(CO)_{12}$.[7] Triphenylphosphine (4.0 g, 15.3 mmoles) and tetracobalt dodecacarbonyl (2.0 g, 3.5 mmoles) were stirred in 50 ml of *p*-xylene for 1.5 hr. The dark brown product was filtered off and washed with ether to remove unreacted triphenylphosphine; yield 3.6 g.

Reaction of $[(C_6H_5)_3PCo(CO)_3]_2$ with $SnCl_2$.—Anhydrous tin(II) chloride (0.24 g, 1.27 mmoles) and $[(C_6H_5)_3PCo(CO)_3]_2$ (1.0 g, 1.23 mmoles) were refluxed for 3 hr in 50 ml of tetrahydrofuran. Solvent was removed at reduced pressure and the residue extracted with dichloromethane. Addition of *n*-pentane to the extract followed by cooling in Dry Ice gave red crystals. Several recrystallizations from dichloromethane–pentane gave the pure product.

Reaction of $Cl_2Sn[Co(CO)_4]_2$ with $(C_6H_5)_3P$.—Triphenylphosphine (0.55 g, 2.1 mmoles) and $Cl_2Sn[Co(CO)_4]_2$ (0.53 g, 1.0 mmole) were stirred in refluxing tetrahydrofuran for 2 hr. Removal of tetrahydrofuran and extraction with methylene chloride gave a red solution, from which orange crystals were

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[1] Presented in part at the 48th Canadian Chemical Conference, Montreal, June 1965. For Part I of this series, see H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

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TABLE I

ANALYTICAL DATA, MELTING POINTS, COLORS

Compd	Mp,[a] °C	Color	Calcd, %			Found, %		
			C	H	X	C	H	X
$Cl_2Sn[Co(CO)_4]_2$	106 dec	Orange-red	18.1	0.0	13.3	19.2	0.5	13.3
$Br_2Sn[Co(CO)_4]_2$	75–85 dec	Orange	15.4	0.0	25.3	15.4	0.4	26.5
$I_2Sn[Co(CO)_4]_2$	70–75 dec	Purple	13.5	0.0	35.5	14.6	0.3	32.6
$Cl_2Sn[(C_6H_5)_3PCo(CO)_3]_2$[b]	220 dec	Orange-yellow	50.9	3.0	7.2	49.0	3.0	7.9
$I_2Ge[Co(CO)_4]_2$	95 dec	Red	14.4	0.0	38.0	14.2	0.0	38.0
$Br_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$	168–171	Orange	26.6	1.6	25.1	27.2	1.4	26.3
$I_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$[c]		Dark orange	23.1	1.4	35.0	23.0	1.5	31.1
$Cl_2Sn[\pi\text{-}C_5H_5NiCO]_2$	90 dec	Dark green	29.2	2.0	14.4	29.2	2.0	14.3
$[(C_6H_5)_3PCo(CO)_3]_2$[d]		Dark brown	62.2	3.7		61.6	3.7	

[a] dec = decomposition at melting point. [b] Calcd: P, 6.2; Co, 11.8. Found: P, 4.9; Co, 9.1. [c] Decomposes at 180°, no melting. [d] Decomposes at 200°, no melting.

TABLE II

INFRARED SPECTRA (cm^{-1})

Compd	Metal carbonyl bands	Other bands
$Cl_2Sn[Co(CO)_4]_2$[a]	2115 w, 2098 s, 2057 m, 2038 s, 2023 m	
$Br_2Sn[Co(CO)_4]_2$[a]	2112 m, 2095 s, 2054 m, 2036 m, 2020 m, 2014 w sh, 1992 vw	
$I_2Sn[Co(CO)_4]_2$[a]	2110 m, 2093 s, 2053 m, 2048 m sh, 2037 s, 2021 ms, 2012 w sh	
$Cl_2Sn[(C_6H_5)_3PCo(CO)_3]_2$[b]	2048 s, 2038 m, 2010 m sh, 1981 s, 1969 s sh	3050 mult, 2400 w, 1810 w, 1600 w, 1570 w, 1520 w, 1480 m, 1435 m, 1330 w, 1310 w, 1280 w, 1270 w, 1240 w, 1230 w, 1184 w, 1160 w, 1120 s, 1100 m, 1073 w, 1030 w, 1002 w, 934 w, 925 w, 880–720 w b, 660 w, 625 w, 560 m
$I_2Ge[Co(CO)_4]_2$[a]	2112 m, 2096 s, 2054 m, 2039 s, 2025 m sh, 2012 w sh, 1994 vw	760 m vb
$Br_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$[b]	2027 s, 2002 s, 1973 s, 1959 m sh	3108 vw, 3075 w, 3030 s, 3020 s, 1430 vw, 1415 vw, 1225 m, 1215 m sh, 1220 m sh, 852 m, 820 w sh, 785 m, 750 m, 630 m, 580 m
$I_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$[b]	2026 s, 2002 s, 1974 s	3040 w, 3000 s, 2995 s, 1210 m, 920 w, 840 w, 805 w, 775 s, 760 s, 735 s
$Cl_2Sn[\pi\text{-}C_5H_5NiCO]_2$[d]	2086 w, 2043 s, 2019 s	3115 w sh, 3110 m, 1860 m, 1755 m, 1670 m, 1645 m, 1580 m, 1545 m, 1390 m, 1350 m, 1010 s, 840 m, 812 ms, 780 vs
$[(C_6H_5)_3PCo(CO)_3]_2$[c,e]	2018 w, 2003 w, 1964 m sh, 1941 s, 1894 w	3060 w, 1485 m, 1438 ms, 1190 w, 1160 w, 1100 m, 1030 w, 1005 w, 750 m, 730 w, 712 m, 698 ms

[a] CCl_4 solution. [b] $CHCl_3$ solution. [c] Halo oil–Nujol mull. [d] Cyclohexane. [e] Compare Vohler.[8]

precipitated by adding pentane and cooling. By analysis and by comparison of infrared spectra, the product was identical with $Cl_2Sn[Co(CO)_3P(C_6H_5)_3]_2$ prepared above.

An attempt was made to prepare the mono(triphenylphosphine)-substituted compound by using only 1 mole of $(C_6H_5)_3P$/mole of $Cl_2Sn[Co(CO)_4]_2$; only disubstituted product, in addition to unreacted starting material, was recovered.

Diiodobis(tetracarbonylcobalt)germanium(IV).—Dicobalt octacarbonyl (3.4 g, 10 mmoles) and anhydrous germanium(II) iodide (3.26 g, 10 mmoles) were stirred in tetrahydrofuran at room temperature for 10 min. Solvent was removed at reduced pressure. A pentane extract of the residue, upon concentrating and cooling to 0°, gave red needles. After two crystallizations from pentane, the pure product (2.0 g) was obtained.

Dibromobis(π-cyclopentadienyldicarbonyliron)tin(IV).—Anhydrous tin(II) bromide (2.8 g, 10 mmoles) and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (3.54 g, 10 mmoles) were refluxed in tetrahydrofuran (200 ml) for 18 hr. Solvent was removed, and the residue was washed with pentane to remove unreacted iron dimer and crystallized from boiling methanol; recrystallization from toluene–*n*-pentane gave the pure product. The **diiodo derivative** was prepared in a similar fashion, with recrystallization from dichloromethane–*n*-pentane.

Dichlorobis(π-cyclopentadienylcarbonylnickel)tin(IV).—Anhydrous tin(II) chloride (0.8 g, 4.2 mmoles) and $[(\pi\text{-}C_5H_5)NiCO]_2$ (1.0 g, 3.3 mmoles) were refluxed in 50 ml of tetrahydrofuran for 2 hr. After removing tetrahydrofuran at reduced pressure, the residue was extracted with *n*-hexane. The hexane extract was filtered and cooled to give very dark green, air-stable, needlelike crystals. These were purified by dissolving in the minimum quantity of tetrahydrofuran, adding *n*-hexane, and cooling.

Attempted Reaction of $Mn_2(CO)_{10}$ with $SnCl_2$.—Equimolar amounts of these compounds were refluxed in tetrahydrofuran for periods up to 3 weeks; only starting materials were recovered. This confirms the earlier report that tin(II) chloride did not insert into manganese carbonyl.[5]

Discussion

Tin(II) halides have been found to undergo facile insertion into the metal–metal bonds of $Co_2(CO)_8$ and $[\pi\text{-}C_5H_5NiCO]_2$, while germanium(II) iodide forms a stable insertion product with $Co_2(CO)_8$. These compounds, as well as $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (for which this reaction was first reported[5,6]), possess metal–metal

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(8) O. Vohler, *Chem. Ber.*, **91**, 1325 (1957).

bonds supported by bridging carbonyl groups. On the other hand, in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and $Mn_2(CO)_{10}$, bridging carbonyl groups are absent, and tin(II) chloride does not insert.[5]

It appeared that the importance of carbonyl bridges might be clarified by examining the behavior of the substituted cobalt carbonyl, $[(C_6H_5)_3PCo(CO)_3]_2$; this compound does *not* have bridging carbonyl groups[8] but presumably has an unsupported cobalt–cobalt covalent bond. Contrary to our expectation, the insertion product was formed, but only at higher temperatures and longer reaction times than sufficed for dicobalt octacarbonyl itself. However, this result cannot be taken as proof that tin(II) chloride can insert into a cobalt–cobalt bond unsupported by carbonyl bridges. A nonbridged form of $Co_2(CO)_8$ has been shown to exist in equilibrium with the bridged form in solution;[9] it is possible that a bridged form of the triphenylphosphine substitution product may also exist in solution, and the reaction could proceed *via* this form.

While one cannot conclude that carbonyl bridges are required for tin(II) halide and germanium(II) iodide insertion, the evidence suggests that reaction proceeds more readily when this is the case. The point of attack may well be the electron pair in the bent metal–metal bond generally assumed in the carbonyl-bridged derivatives. In this connection, it is interesting to note that the insertion of GeH_2 into $Mn_2(CO)_{10}$ has been suggested as a possible step in the reaction of germane with manganese pentacarbonyl hydride.[10]

Among the compounds described here are several with metal–metal bonds which do not appear to have been reported previously. Discussion of the infrared spectra will be deferred until completion of a detailed analysis and comparison with other related compounds.

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The Reactivity of Metal–Metal Bonds. II. The Tin–Manganese Bond[1]

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The reactions of trimethyltinpentacarbonylmanganese with tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, and ethylene are described. Only with tetrafluoroethylene is an adduct, namely, $(CH_3)_3SnCF_2CF_2Mn(CO)_5$, obtained, although trimethyltin fluoride and fluorocarbon–carbonylmanganese products are also formed. With trifluoroethylene and chlorotrifluoroethylene, trimethyltin halides and fluorovinylpentacarbonylmanganese compounds are produced, although in the latter case perfluoroacryloylpentacarbonylmanganese, $CF_2{=}CFCOMn(CO)_5$, is a major product. Ethylene does not cleave the Sn–Mn bond, but rather displaces carbon monoxide to form $(CH_3)_3SnMn(CO)_4(\pi\text{-}C_2H_4)$. The spectroscopic properties of the new compounds are discussed.

Introduction

In the previous paper,[3] we discussed the behavior of hexamethylditin and polymeric diorganotin species with a series of fluoroolefins, whereby the considerable reactivity of the Sn–Sn bond toward homolytic fission under suitable free-radical conditions was revealed. We now consider the analogous behavior of the Sn–Mn bond as the first step in some studies of the reactivities of the bonds formed between group IV-A elements (Si, Ge, Sn, and Pb) and transition metals. Many factors will influence these reactivities, including the electron configuration of the transition metal, the bond polarity, and the nature of the other substituents on the two metal atoms. The importance of each of these factors has yet to be determined, since most studies of these metal–metal bonded compounds have been synthetic in nature, as illustrated by the work of Gorsich,[4,5] Graham *et al.*,[6] and Dighe and Orchin.[7] The reactions of trimethyltinpentacarbonylmanganese, $(CH_3)_3SnMn(CO)_5$, with some olefins are described here, and similar reactions of other metal–metal bonded compounds will be described later.

Triphenyltinpentacarbonylmanganese has been investigated to some extent by Gorsich,[4,5] who established the general synthetic route

$$R_{4-n}SnCl_n + nNaMn(CO)_5 \longrightarrow R_{4-n}Sn[Mn(CO)_5]_n + nNaCl$$

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