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The Reactions of Stannic Halides with Some Triphenylphosphine, -arsine and -stibine-substituted Iron Carbonyls

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The reactions of stannic chloride and bromide with triphenylphosphine, -arsine and -stibine tetracarbonyl iron(0) undergo oxidative-elimination reactions to afford new binuclear organometallic compounds in good yields; $Fe(CO)_4EPh_3+SnX_4 \rightarrow Fe(CO)_3EPh_3SnX_4+CO$ (E=P, As, Sb; X=Cl, Br; $Ph=C_6H_5$), where one molecule of carbon monoxide is discharged. The complexes are characterized by elemental analysis, by infrared and Mössbauer spectroscopies, and by conductivity measurements; these data are used to predict their possible formulation as nonionic, hexa-co-ordinate iron derivatives of the $Fe(CO)_3(X)(EPh_3)(SnX_3)$ type containing a tin-to-iron metal-metal bond.

A number of Lewis acid-base adducts containing hetero metal-metal bonds have previously been prepared by treating zerovalent transition-metal carbonyl complexes with main-group metal halides.[1],[2] These reaction may, for convenience, be devided into two classes: (a) oxidative-addition reactions and (b) oxidative-elimination reactions, according to whether or not the elimination of carbon monoxide occurs during the reaction.[3] Examples of Reaction (a) are found among numerous mercury-to-transition-metal-bonded compounds.[4–6] By Reaction (b) Graham and Kummer have synthesized a series of tin-molybdenum- and tin-tungsten-bonded compounds.[7] It is also hoped that, with a good choice of ligands, iron carbonyl derivatives will undergo a reaction of either the (a) or (b) type with appropriate main-group halides to yield new hetero binuclear compounds.

In this paper syntheses of tin-iron-bonded compounds will be described, and the structure and the nature of the isolated products will be discussed on the basis of the spectroscopic data.

Experimental

All the preparative procedures were carried out under nitrogen, and the solvents available were purified by distillation prior to use. The stannic chloride and stannic bromide were commercially obtained. The substituted-iron carbonyls were prepared according to the methods in the literature, and their purities were checked by both elemental analysis and by studying their infrared spectra.[8–10]

Preparation of $Fe(CO)_3PPh_3SnCl_4$. A solution of stannic chloride (10 mM) dissolved in 50 ml of dichloromethane was stirred, by drop, into triphenylphosphine tetracarbonyliron (10 mM) in the same solvent. As the reaction proceeded, the solution gradually changed from yellow into red; at the same time a vigorous evolution of carbon monoxide was observed. After the solution had been stirred for an hour, the solvent was removed under reduced pressure. The red residue was then extracted in 20 ml of nitromethane; the solution was subsequently allowed to stand in a refrigerator until yellow crystals separated.

Procedures similar to this were used to prepare other tin-iron-bonded compounds.

The molecular weights were measured osmometrically in methyl ethyl ketone. The magnetic susceptibilities were determined by the Gouy method at room temperature. The electric conductivities in nitromethane solutions were determined at 25°C using a Radiometer type CDM 2d-Conductivitymeter. The infrared spectra were obtained as Nujol mull on a Hitachi EPI-G2 Grating Spectrometer. The Mössbauer spectra were recorded with a Hitachi 505 Mössbauer Spectrometer equipped with a cryostat maintaining a γ-ray emitter (^{57}Co diffused onto platinum foil) and an absorber at the temperature of liquid nitrogen.

Results and Discussion

Results of the elemental analyses and the physical properties for the isolated Sn-Fe complexes are summarized in Tables 1 and 2 respectively. These products can be described by the general formula $Fe(CO)_3EPh_3SnX_4$, where E is P, As, or Sb, where X is Cl or Br, and where Ph is C_6H_5. They are diamagnetic, yellow-to-orange crystals and are sufficiently stable in air for various physicochemical experiments. They are readily soluble in chloroform, benzene, nitromethane, alcohols, and many other polar organic solvents. The obtained molecular weights correspond to a monomer structure. The electric conductivities in nitromethane and the infrared frequencies in the carbonyl stretching region are given in Table 3. The conductivities of the products suggest their essentially nonionic character, in spite of the observed small conductance, which is presumably due to partial dissociation in nitromethane. The observed low molecular weights in methyl ethyl ketone reflect it.

Each complex exhibits three carbonyl stretching bands. It is interesting to note that the averaged stretching frequencies of each product undergo a high shift of about 100 cm^{-1} compared to the starting iron carbonyl complexes, $Fe(CO)_4EPh_3$.

Figure 1 shows the ^{57}Fe Mössbauer spectra of $Fe(CO)_4PPh_3$ and $Fe(CO)_3PPh_3SnCl_4$. The isomer shift and the quadrupole splitting values of the products are presented in Table 4, along with the values of the related iron carbonyl complexes. In triphenylarsine

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[1] J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev., A*, **4**, 479 (1969).

[2] D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970).

[3] J. Lewis and S. B. Wild, *J. Chem. Soc., A*, **1966**, 69.

[4] D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *ibid.*, **1968**, 1067.

[5] J. L. Dawes and R. D. W. Kemmitt, *ibid.*, **1968**, 1072.

[6] K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *ibid.*, **1968**, 2851.

[7] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968).

[8] J. Lewis, R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, **1964**, 2825.

[9] A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, **2**, 151 (1963).

[10] M. H. Stiddard, *J. Chem. Soc.*, **1962**, 4712.

TABLE 1. ELEMENTAL ANYLYSES

Compound	C	H	X	Fe	Mol. wt.
$C_{21}H_{11}O_3Cl_4SnPFe$	38.03(38.06)	2.24(2.28)	20.89(21.40)	7.1_3(8.43)	550(663)
$C_{21}H_{11}O_3Br_4SnPFe$	30.11(30.01)	1.73(1.80)	38.17(38.03)	5.1_3(6.64)	780(841)
$C_{21}H_{11}O_3Cl_4SnAsFe$	34.99(35.69)	2.03(2.14)	20.28(20.07)	7.6_9(7.90)	570(707)
$C_{21}H_{11}O_3Br_4SnAsFe$	28.80(28.52)	1.69(1.71)	36.41(36.14)	5.0_4(6.31)	810(884)
$C_{21}H_{11}O_3Cl_4SnSbFe$	33.26(33.48)	1.94(2.01)	18.92(18.82)	5.2_8(7.41)	690(753)
$C_{21}H_{11}O_3Br_4SnSbFe$	26.89(27.08)	1.46(1.62)	34.76(34.32)	4.7_5(6.00)	860(931)

TABLE 2. PHYSICAL PROPERTIES AND YIELDS

Compound	Melting point (°C)	Color	Yield %	Conductivity (μ cm^2 ohm^{-1} mol^{-1})
$Fe(CO)_3(Cl)PPh_3SnCl_3$	111—111.5 (dec)	Yellow	90	14.0
$Fe(CO)_3(Br)PPh_3SnBr_3$	120.5—121 (dec)	Orange yellow	93	22.1
$Fe(CO)_3(Cl)AsPh_3SnCl_3$	113—113.5 (dec)	Yellow	83	12.5
$Fe(CO)_3(Br)AsPh_3SnBr_3$	124 (dec)	Orange	91	35.2
$Fe(CO)_3(Cl)SbPh_3SnCl_3$	125—126 (dec)	Orange	75	20.0
$Fe(CO)_3(Br)SbPh_3SnBr_3$	124 (dec)	Orange yellow	78	28.3

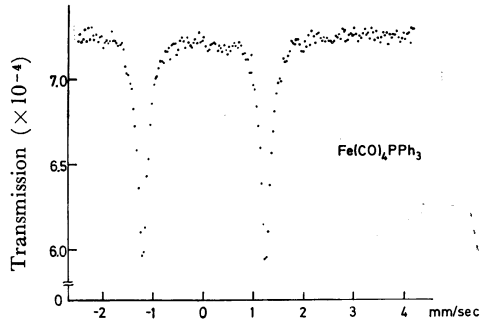
TABLE 3. INFRARED SPECTROSCOPIC DATA ($CHCl_3$ SOLUTION)

Compound	C-O Stretching frequencies (cm^{-1})		
$Fe(CO)_3(Cl)PPh_3SnCl_3$	2110(w)	2062(s)	2044(s)
$Fe(CO)_3(Br)PPh_3SnBr_3$	2102(w)	2053(s)	2044(s)
$Fe(CO)_3(Cl)AsPh_3SnCl_3$	2111(w)	2063(s)	2043(s)
$Fe(CO)_3(Br)AsPh_3SnBr_3$	2104(w)	2056(s)	2042(s)
$Fe(CO)_3(Cl)SbPh_3SnCl_3$	2102(w)	2055(s)	2036(s)
$Fe(CO)_3(Br)SbPh_3SnBr_3$	2100(w)	2052(s)	2037(s)

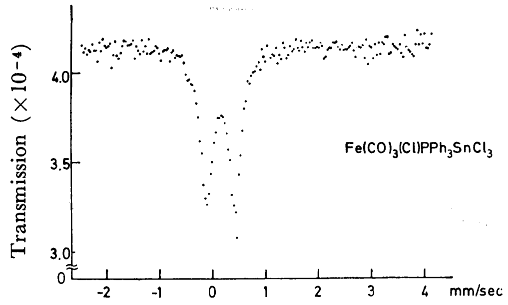
TABLE 4. ^{57}Fe MÖSSBAUER DATA (78 K)

Compound	I. S.	Q. S.
$Fe(CO)_3(Cl)PPh_3SnCl_4$	0.19	0.64
$Fe(CO)_3(Cl)SbPh_3SnCl_4$	0.14	0.48
$Fe(CO)_4SbPh_3$	−0.11	3.22
$Fe(CO)_4PPh_3$	−0.04	2.92
$Fe(CO)_3(PPh_3)_2$	−0.03	3.12
$Fe(CO)_5$	0.05	2.52

I. S. Isomer shift *vs.* $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (mm/sec).
Q. S. Quadrupole splitting (mm/sec).



a) Doppler velocity *vs.* $Na_2[Fe(CN)_5NO]\cdot 2H_2O$

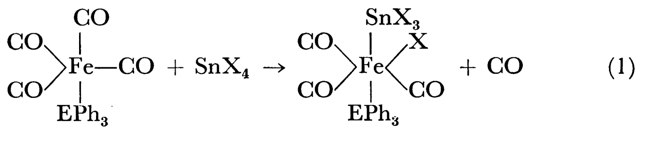


b) Doppler velocity *vs.* $Na_2[Fe(CN)_5NO]\cdot 2H_2O$

Fig. 1. The Mössbauer specra of a) $Fe(CO)_4PPh_3$ and b) $Fe(CO)_3(Cl)PPh_3SnCl_3$.

derivatives, the Mössbauer effect could not be measured because of the large non-reasonant absorption of arsenic nuclides. It can readily be seen that each product shows a more positive isomer shift and quadrupole splitting smaller than the starting iron carbonyl complex. The small quadrupole splitting suggests that the products have a more symmetrical environment around the iron atom, probably a hexaco-ordinate octahedral structure containing a tin-iron metal-metal bond. The determination of the precise structure of $Fe(CO)_3AsSnBr_4$ by single-crystal X-ray analysis is currently in progress in this laboratory.

It can be concluded that the iron derivatives obtained here should be formulated as $Fe(CO)_3(X)EPh_3(SnX_3)$ and that an ionic formulation such as $[Fe(CO_3)EPh_3SnX_3]X$ or $[Fe(CO)_3EPh_3X]SnX_3$ should be ruled out. The above reactions may proceed as follows:



$$Fe(CO)_4EPh_3 + SnX_4 \rightarrow Fe(CO)_3(X)(SnX_3)EPh_3 + CO \quad (1)$$

The elimination of one molecule of carbon monoixide was confirmed by gas-burette measurements. Thus, the reaction may reasonably be classified as an oxidative-elimination reaction and the products may be regarded as Lewis acid-base adducts.

Under the same preparative conditions as in the above experiments, no reaction occurred between iron carbonyl derivatives, $Fe(CO)_4EPh_3$, $Fe(CO)_3(EPh_3)_2$, and tetramethyltin, trimethyltin chloride, dimethyltin dibromide, and tin tetraiodide. Probably these failures are due to the low Lewis acidity of the metal-halide reactants.