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Synthesis of Transition Metal Derivatives of Arsenic, Antimony, and Bismuth with M-E σ Bonds

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The group V trihalides EX_3 (E = As, Sb, Bi) react with metal carbonyl anions and/or metal carbonyls with metal–metal bonds, to give complexes containing the cations $[X_2E(Fe(CO)_2Cp)_2]^+$ (X = Cl, Br; E = As, Sb), $[XSb(Fe(CO)_2Cp)_3]^+$ (X = Cl, Br), $[Sb(Fe(CO)_2(NO)PPh_3)_4]^+$, and $[Sb(Co(CO)_3PPh_3)_4]^+$. These are associated with a variety of anions which include FeX_4^{2-}, FeX_4^-, $SbBr_4^-$, $Sb_2Cl_7^-$, and possibly CoX_4^{2-}. Neutral species are also obtained from arsenic and antimony halides. Bismuth halides yield only uncharged compounds. Those characterized are as follows: $X_2AsFe(CO)_2Cp$ (X = Cl, Br), $Cl_2AsFe(CO)_2(NO)PPh_3$, $I_2SbFe(CO)_2Cp$, $Cl_2BiFe(CO)_2Cp$, $Cl_2BiFe(CO)_2(NO)PPh_3$, $Bi(Fe(CO)_3(NO))_3$, $Bi(Fe(CO)_2(NO)PPh_3)_3$, and $Bi(Co(CO)_3PPh_3)_3$. The reaction of $XFe(CO)_2Cp$ with SbX_3 yields $SbX_3(Fe(CO)_2CpX)_2$ while $SbCl_5$ and $(Fe(CO)_2Cp)_2$ afford $[(Fe(CO)_2Cp)_2Cl][SbCl_6]$.

Introduction

Although compounds involving metal–metal bonds between group III or IV elements and transition metals are many and varied, very few such derivatives involving group V elements are known (excluding cases where the group V element acts as a two-electron donor or three-electron bridge). Previously reported compounds include $As_2Fe_3(CO)_{11}$,[1] $SbFe_2(CO)_8$,[1] $SbFe(CO)_4$,[1] $Bi_2Fe_5(CO)_{20}$,[1] $(CF_3)_2AsMo(CO)_3\pi\text{-}C_5H_5$,[2] $(CF_3)_2AsFe(CO)_2(\pi\text{-}C_5H_5)$,[2] $Ph_2BiRe(CO)_5$,[3] $Ph_2BiCo(DMG)_2Py$,[4,5] $Me_2AsCo(CO)_4$,[6] $(C_6F_5)_2AsFe(CO)_2Cp$; $(C_6F_5)_2AsMo(CO)_3Cp$,[7] $Sb_4Co_4(CO)_{12}$,[8] $As_3Co(CO)_3$,[9] $As_2Co_2(CO)_6$,[10] $As_2Co_2(CO)_5PPh_3$,[10] $[ClSb(Fe(CO)_2(\pi\text{-}C_5H_5))_3]_2[FeCl_4]$,[11] $Cl_2SbCo(CO)_4$, and $Bi(Co(CO)_4)_3$.[12]

The purpose of the present investigation is to study the preparation of derivatives of this sort on a semisystematic basis with the object of discovering which transition metals can be σ bonded to arsenic, antimony, or bismuth. Because antimony is a Mossbauer nucleus, it is also hoped to study the bonding in any new compound using this technique. The preparative work is described in this paper.

A preliminary investigation of the reaction of ECl_3 (E = As, Sb, Bi) with $(Fe(CO)_2Cp)_2$ has already been published.[13]

Experimental Section

Unless otherwise specified, all reactions and manipulations were carried out in a nitrogen atmosphere, and a conventional vacuum system was used to manipulate volatile reagents. Evaporation of solvent was carried out on a rotary evaporator under reduced pressure. Iodobis(trifluoromethyl)stibine and the mercury derivatives $Hg[Fe(CO)_3NO]_2$ and $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ were prepared as described in the literature with one important modification. The yield of $Hg[Fe(CO)_3NO]_2$ was considerably increased by the use of stoichiometric amounts of $HgCl_2$ in place of $Hg(CN)_2$. All other reagents were obtained from commercial sources and used without further purification, with the exception of dichloromethane and *n*-pentane which were dried over $CaCl_2$. Microanalyses (Table I) were performed by Mr. Peter Borda of this department and Drs. F. and E. Pascher, Mikroanalytisches Laboratorium, Bonn, West Germany. The infrared spectra listed in Table I were recorded on a Perkin-Elmer 457 spectrophotometer calibrated with DCl gas and H_2O vapor.

Dichlorobis(dicarbonylcyclopentadienyliron)antimony(V) Heptachlorodiantimonate(III), $(Cl_2Sb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(Sb_2Cl_7)$. A solution containing 3.4 g (14.9 mmol) of $SbCl_3$ and 1.7 g (4.8 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 80 ml of dichloromethane was left at 20° for 8 hr. At the end of this period, 2.9 g of product (orange-brown plates) had precipitated. The compound can be recrystallized by dissolving in hot CH_2Cl_2 and cooling to 0° giving orange cubes of product. The same product was obtained using a 6:1 mole ratio of $SbCl_3$ to $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$.

Dichlorobis(dicarbonylcyclopentadienyliron)antimony(V) Hexafluorophosphate(V), $(Cl_2Sb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(PF_6)$. A solution of 0.5 g (3.0 mmol) of $NaPF_6$ in 5 ml of acetone was added to 1.0 g (0.97 mmol) of $(Cl_2Sb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(Sb_2Cl_7)$ in 80 ml of CH_2Cl_2. The solution was filtered and evaporated to about 5 ml giving orange crystals of product. These were recrystallized from CH_2Cl_2 and dried *in vacuo*.

The corresponding orange tetrathiocyanatodiamminechromate(III) salt, $(Cl_2Sb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(Cr(SCN)_4(NH_3)_2)$, was prepared similarly using 0.5 g (1.4 mmol) of Reinecke salt $(NH_4[Cr(SCN)_4(NH_3)_2]\cdot H_2O)$ in 10 ml of methanol, in place of the $NaPF_6$ solution.

Dibromo(dicarbonylcyclopentadienyliron)antimony(V) Tetrabromoantimonate(III), $(Br_2Sb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(SbBr_4)$. A mixture of 1.3 g (5.7 mmol) of $SbBr_3$ and 1.25 g (3.5 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 10 ml of CH_2Cl_2 was left for 16 hr at 20° affording orange needles of product. This was purified by recrystallization from acetone–ether.

Bis(trifluoromethyl)bis(dicarbonylcyclopentadienyliron)antimony(V) Diiodobis(trifluoromethyl)antimonate(III), $([CF_3]_2Sb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)([CF_3]_2SbI_2)$. A mixture of 1.0 g (2.6 mmol) of $(CF_3)_2SbI$ and 0.5 g (1.4 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ was allowed to react in an evacuated tube at 20° for 12 hr. The reaction mixture was then washed with *n*-pentane and the yellow solid remaining was recrystallized from CH_2Cl_2–*n*-pentane affording 0.5 g of yellow crystals of product.

Trichlorobis(chlorodicarbonylcyclopentadienyliron)antimony(III), $[ClFe(CO)_2(\pi\text{-}C_5H_5)]_2SbCl_3$. A mixture of 0.5 g (2.36 mmol) of $ClFe(CO)_2(\pi\text{-}C_5H_5)$ and 0.5 g (2.19 mmol) of $SbCl_3$ in 30 ml of ether was evaporated to small volume producing 0.6 g of red crystals of product. This was recrystallized from ether. The same product was obtained using 2.36 mmol of $ClFe(CO)_2(\pi\text{-}C_5H_5)$ and 4.4 mmol of $SbCl_3$. It was also found to be a by-product of the reaction of $SbCl_3$ with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$.

μ-Chloro-bis(dicarbonylcyclopentadienyliron) Hexachloroantimonate(V), $([Fe(CO)_2(\pi\text{-}C_5H_5)]_2Cl)(SbCl_6)$. Antimony pentachloride

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Table I. Analytical, Infrared, Conductance, and Magnetic Data for New Compounds

		% calcd						% found								
	Color	C	H	N	X	M	A[a]	C	H	N	X	M	A[a]	ν(CO), cm^{-1} (in CH_2Cl_2)	Λ,[b] Ω^{-1} mol^{-1} cm^2	μ_{eff},[c] BM
$Cl_2AsFe(CO)_2Cp$[d]	Orange	26.1	1.6		22.0			26.0	1.7		21.5				7	
$Br_2AsFe(CO)_2Cp$	Orange	20.4	1.2		38.9			20.2	1.3		38.8			2036 m, 1990 s		
$Cl_2AsFe(CO)_2NOPPh_3$[e]	Brown	43.7	2.7	2.6	12.9			43.1	2.5	2.3	13.2			2026 w, 1966 s		
$[Cl_2As(Fe(CO)_2Cp)_2][FeCl_4]$	Orange	24.1	1.6		30.6	24.0	10.7	24.1	1.4		30.7	24.3	13.0	2071 s, 2057 s, 2030 s	128	5.9
$[Br_2As(Fe(CO)_2Cp)_2][FeBr_4]$	Red	17.4	1.0		49.7	17.4		17.4	0.8		49.2	17.0		2069 s, 2054 s, 2028 s	106	6.2
$Br_3As(ClFe(CO)_2Cp)_3$	Dark red	23.2	1.4		44.1			22.9	1.5		44.2			2048 s, 2001 s		
$[Cl_2Sb(Fe(CO)_2Cp)_2][Sb_2Cl_7]$	Orange	16.2	1.0		30.8	10.8	35.5	16.1	1.0		30.5	11.0	34.5	2065 s, 2054 s, 2020 s	47	0
$[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$	Orange	24.3	1.6		10.2			24.3	1.6		10.2			2065 s, 2053 s, 2020 s	137	
$[Cl_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$	Orange	25.0	1.8	9.7	8.2			25.1	2.0	10.0	8.1			2073 vs, 2048 m, 2000 m[f]	99	
$[Br_2Sb(Fe(CO)_2Cp)_2][SbBr_4]$	Orange	15.6	0.9		44.5	10.4	22.3	15.8	1.0		44.4	10.1	22.3		71	
$[(CF_3)_2Sb(Fe(CO)_2Cp)_2][(CF_3)_2SbI_2]$	Yellow	19.2	0.9		22.5	10.0		19.1	0.9		22.2	10.1		2063 s, 2050 s, 2021 s	145	
$[ClSb(Fe(CO)_2Cp)_3][FeCl_4]$	Dark red	28.4	1.7		20.0	25.1	13.8	28.6	1.9		19.5	25.3	13.8	2043 m, 2027 s, 2018 m, sh, 1991 s, br	110	5.5
$[ClSb(Fe(CO)_2Cp)_3][PF_6]$	Dark red	30.3	1.8		4.3	20.0		30.0	1.8		4.5	19.7		2044 m, 2027 s, 2017 m, sh, 1990 s	128	0
$[ClSb(Fe(CO)_2Cp)_3][Cr(SCN)_4(NH_3)_2]\cdot{}^2/_3CH_2Cl_2$[g]	Dark red	29.0	2.2	7.9	7.8			29.1	2.8	7.7	8.9			2047 m, 2027 s, 2016 m, sh, 1990 s, 1984 s, sh	82	
$[ClSb(Fe(CO)_2Cp)_3][BPh_4]$	Dark red	53.7	3.5		3.6			53.5	3.4		3.5			2044 m, 2026 s, 2017 m, sh, 1990 s, 1982 s, sh	87	
$[BrSb(Fe(CO)_2Cp)_3]_2[FeBr_4]\cdot{}^1/_2(CH_3)_2CO$	Dark red	28.0	1.8		25.6	20.9	13.0	28.1	2.0		25.3	20.8	11.4	2045 m, 2026 s, 2018 m, sh, 1991 s, br	124	4.3
$[BrSb(Fe(CO)_2Cp)_3][Cr(SCN)_4(NH_3)_2]\cdot 3Me_2CO$[h]	Dark red	33.3	3.2	6.9	6.5			33.8	3.1	7.6	6.8			2045 m, 2026 s, 2018 m, sh, 1990 s, 1982 s	88	
$[BrSb(Fe(CO)_2Cp)_3][BPh_4]$	Dark red	50.9	3.3		7.5			50.7	3.3		7.4			2044 m, 2025 s, 2018 m, sh, 1992 s, 1983 s, sh	90	
$Cl_3Sb(ClFe(CO)_2Cp)_2$	Dark red	25.8	1.5		27.2			25.8	1.6		27.3			2054 s, 2008 s	2	
$Br_3Sb(BrFe(CO)_2Cp)_2$	Dark red	19.2	1.1		45.6			19.4	1.2		45.5			2048 s, 2001 s		
$[Cl(Fe(CO)_2Cp)_2][SbCl_6]$	Dark red	22.9	1.4		35.3	15.2	16.6	22.6	1.3		35.1	15.3	16.5			
$[Sb(Fe(CO)_2(NO)PPh_3)_4][FeCl_4]$[i]	Very dark red	49.7	3.1	2.9	7.3	14.4		50.0	3.1	3.3	4.3	13.2		2027 w, 2006 m, 1960 s, 1945 w, sh	116	4.3
$[Sb(Fe(CO)_2(NO)PPh_3)_4][FeBr_4]$[i]	Very dark red	45.5	2.8	2.6	15.1	13.2		45.2	3.2	2.6	15.0	12.8		2029 w, 2008 m, 1963 s, 1943 w, sh	110	4.9
$[Sb(Fe(CO)_2(NO)PPh_3)_4][Cr(SCN)_4(NH_3)_2]\cdot{}^1/_2CH_2Cl_2$[i-k]	Very dark red	48.4	3.2	6.7	1.7			48.9	3.2	6.5	1.7			2027 w, 1006 m, 1962 s	85	3.7
$[Sb(Fe(CO)_2(NO)PPh_3)_4][PF_6]$	Very dark red	51.1	3.2	3.0	0.0	11.8		51.2	3.5	3.2	0.0	10.9		2027 w, 2007 m, 1962	124	0
$[Sb(Co(CO)_3PPh_3)_4]_3[Sb_5Cl_{18}]$	Very dark red	46.8	2.8		9.9	10.9	15.1	47.0	2.8		7.7	11.1	15.4	2028 m, 1985 s, 1958 w	342	
$[Sb(Co(CO)_3PPh_3)_4]_3[Sb_2Cl_9]$	Very dark red	52.4	3.1		5.5	12.2	10.5	52.4	3.4		5.6	14.6	10.1	2027, 1984 s, 1960 v		
$[Sb(Co(CO)_3PPh_3)_4][PF_6]\cdot{}^1/_3CH_2Cl_2$[j]	Very dark red	52.8	3.2		1.2			52.6	3.4		1.1			2028 m, 1985 vs, 1958 w	140	
$[Sb(Co(CO)_3PPh_3)_4][Cr(SCN)_4(NH_3)_2]$[l]	Very dark red	51.3	3.2	4.1	0.0			51.1	3.2	3.9	0.0			2028 m, 1985 vs, 1958 w	82	
$[Sb(Co(CO)_3PPh_3)_4]_3[Sb_5Br_{18}]$	Very dark red	41.7	2.5		19.8	9.7	13.4	42.0	2.5		19.7	9.8	13.4	2027 m, 1986 vs, 1959 w	354	
$Cl_2BiFe(CO)_2Cp$	Dark red	18.4	1.1		15.5		45.8	18.7	1.1		15.3		45.0	2048 w, 2016 s, 1970 s[f]	4	
$Cl_2BiFe(CO)_2NOPPh_3$	Red	35.2	2.1	2.2	10.4			35.1	2.2	2.0	10.2			1996 m, 1945 s[f]		
$Bi(Fe(CO)_3NO)_3$[m]	Black	15.1	0.0	5.8				14.7	0.0	5.7						
$Bi(Fe(CO)_2NOPPh_3)_3$	Black	50.6	3.2	3.0	0.0			51.0	3.8	2.7	0.0			1988 w, 1968 m, 1928 s		
$Bi(Co(CO)_3PPh_3)_3$		53.1	3.2		0.0			53.2	3.1		0.0			2010 w, 1992 m, 1956 s, 1945 s, 1916 w, sh		

[a] A = As, Sb, or Bi. [b] Measured in acetone solution, concentrations about 2 mmol l.$^{-1}$. [c] Measured using the Gouy method. [d] Cp = π-C_5H_5. [e] PPh_3 = $P(C_6H_5)_3$. [f] In acetone solution. [g] Approximate amount of solvent of crystallization remaining after evacuation for 4 hr; ν(SCN) 2069 (vs) cm^{-1}. [h] ν(SCN) 2068 (vs) cm^{-1}. [i] ν(NO) 1758 (s) cm^{-1}. [j] Sample heated to 60° *in vacuo*. [k] ν(SCN) 2069 (vs) cm^{-1}. [l] ν(SCN) 2068 (vs) cm^{-1}. [m] Unstable at room temperature.

(2 g) was slowly added to a solution of 1.0 g (2.8 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in CH_2Cl_2 cooled to 0°. After gas evolution had ceased, the solution was evaporated to a small volume. Addition of chloroform gave red crystals of product which was recrystallized from CH_2Cl_2; yield 0.3 g.

Chlorotris(dicarbonylcyclopentadienyliron)antimony(V) Tetrachloroferrate(III), $(ClSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)(FeCl_4)$. A mixture of 1.2 g (5.3 mmol) of $SbCl_3$ and 5.4 g (15.3 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 50 ml of 1,2-dichloroethane was refluxed for 20 hr. At the end of this period 4.0 g of fine dark red crystals had deposited. These were dissolved in 100 ml of acetone. The solution was filtered and evaporated to 20 ml. Addition of 80 ml of ether precipitated dark red crystals of a compound which has not been fully characterized. The mother liquor was evaporated to 20 ml and a further 80 ml of ether was slowly added affording red crystals of crude product. This was recrystallized from acetone–ether and dried *in vacuo*.

An acetone solution of 1.0 g of the crude product of this reaction was filtered, and to it was added a solution of 0.7 g of $NaB(C_6H_5)_4$ in 50 ml of methanol. Evaporation of the solution to a small volume precipitated dark glistening crystals of $(ClSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)(B(C_6H_5)_4)$, which were recrystallized from acetone–ether.

The corresponding hexafluorophosphate(V) salt, **$(ClSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)(PF_6)$**, and the tetrathiocyanatodiamminechromate(III) salt, **$(ClSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)(Cr(SCN)_4(NH_3)_2)$**, were prepared similarly using respectively 0.7 g of $NaPF_6$ and 0.5 g of Reinecke salt, in place of $NaB(C_6H_5)_4$. Recrystallization of these salts was from CH_2Cl_2. The latter product recrystallized with about $^2/_3$ mol of dichloromethane of crystallization which was not removed *in vacuo*.

Reaction of Antimony Tribromide with Tetracarbonyldicyclopentadienyldiiron. (i) A mixture of 1.0 g (2.73 mmol) of $SbBr_3$ and 2.0 g (5.65 mmol) of $[Fe(CO)_2(C_5H_5)]_2$ was heated to 120° under a CO pressure of 800 psi for 8 hr. The reaction mixture was extracted first with CH_2Cl_2 to remove unreacted starting material and then with about 200 ml of acetone. The latter extract was evaporated to 15 ml affording 1.2 g of dark red crystals. These were recrystallized from acetone–ether. Analytical data were consistent with the formula **$(BrSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)_2(FeBr_4)\cdot{}^1/_2(CH_3)_2CO$.**

(ii) A solution of 3.2 g (8.85 mmol) of $SbBr_3$ and 9.1 g (21.8 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 60 ml of methyl ethyl ketone was refluxed for 5 hr during which time CO was evolved and a red-brown crystalline solid was deposited (7.8 g). This was removed and extracted with 200 ml of acetone. Evaporation of this solution to a small volume gave dark red crystals of the above product.

To an ethanol solution of 0.3 g of the product obtained from this reaction was added a solution of 0.15 g of $NaB(C_6H_5)_4$ in 5 ml of ethanol, affording a red precipitate of $(BrSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)(B(C_6H_5)_4)$, which was washed with ethanol and ether and recrystallized twice from acetone; yield 0.2 g.

The tetrathiocyanatodiamminechromate(III) salt was prepared in aqueous solution using 0.15 g of Reinecke salt rather than $NaB(C_6H_5)_4$. The red precipitate so obtained was recrystallized from a small volume of acetone by addition of ether to yield dark red needles of **$(BrSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_3)(Cr(SCN)_4(NH_3)_2)\cdot 3(CH_3)_2CO$.**

Bis(bromodicarbonylcyclopentadienyliron)tribromoantimony(III), $Br_3Sb[BrFe(CO)_2(\pi\text{-}C_5H_5)]_2$. An ether solution of 2.0 g (5.5 mmol) of $SbBr_3$ and 1.0 g (2.8 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ was allowed to stand at 20° for 3 days. The orange precipitate was removed and the solution was evaporated to dryness. The residue was extracted with ether and the extract was evaporated to small volume and cooled to −80° giving red crystals of product. These were recrystallized from ether; yield 0.2 g.

Diiodo(dicarbonylcyclopentadienyliron)antimony(III), $I_2SbFe(CO)_2(\pi\text{-}C_5H_5)$. A suspension of 2.5 g (5.0 mmol) of finely ground SbI_3 was stirred for 4 days at 20° with 1.7 g (4.8 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 50 ml of CH_2Cl_2. The solution was filtered and evaporated to 20 ml. Addition of 10 ml of pentane afforded red crystals of product which was recrystallized from CH_2Cl_2–pentane; yield 1.1 g.

Reaction of $AsCl_3$ with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$. A solution containing 2.2 g (12.2 mmol) of $AsCl_3$ and 1.7 g (4.8 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 10 ml of CH_2Cl_2 was allowed to stand at 20° for 7 days. At the end of this time 0.85 g of large dark brown cubes of A had deposited. These were removed and the solution allowed to stand for another 7 days affording a further 0.4 g of A. The orange mother liquor was evaporated to a small volume and *n*-pentane added giving brown crystals of B. The mother liquor from this stage was then evaporated to a very small volume affording yellow crystals which were characterized as **$Cl_2AsFe(CO)_2(\pi\text{-}C_5H_5)$** after recrystallization from CH_2Cl_2–*n*-pentane.

A and B have not yet been fully characterized; however recrystallization from acetone–ether gave orange-brown needles of **$(Cl_2As[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(FeCl_4)$.**

Reaction of $AsBr_3$ with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$. A solution of 2.1 g (6.7 mmol) of $AsBr_3$ and 1.2 g (3.4 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 10 ml of CH_2Cl_2 was allowed to stand at 20° for 1 week. Pentane was then slowly added to the solution to precipitate red crystals which were then recrystallized three times from CH_2Cl_2–*n*-pentane giving 0.3 g of **$(Br_2As[Fe(CO)_2(\pi\text{-}C_5H_5)]_2)(FeBr_4)$.**

The mother liquor from the deposition of this compound was treated with more *n*-pentane and evaporated to a small volume to afford brown crystals. These were recrystallized from CH_2Cl_2–*n*-pentane to give 0.2 g of **$Br_2AsFe(CO)_2(\pi\text{-}C_5H_5)$.** The mother liquor from this step was evaporated leaving an oil which gave a dark purple solid on washing with *n*-pentane. The solid was recrystallized from CH_2Cl_2–*n*-pentane to give a compound whose analysis was consistent with the formula **$Br_3As[BrFe(CO)_2(\pi\text{-}C_5H_5)]_3$.**

Dichloro(dicarbonylcyclopentadienyliron)bismuth(III), $Cl_2BiFe(CO)_2(\pi\text{-}C_5H_5)$. A suspension of 6.3 g (20.0 mmol) of finely pulverized $BiCl_3$ was stirred at room temperature with 3.6 g (10.2 mmol) of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in 40 ml of CH_2Cl_2. The $BiCl_3$ dissolved while a bright red solid was deposited (6.4 g). It was recrystallized from 400 ml of acetone by evaporation to a small volume giving dark red sparkling crystals of product.

Reaction of $NaCo(CO)_3P(C_6H_5)_3$ and $(Co(CO)_3P(C_6H_5)_3)_2$ with SbX_3. (i) A solution of 4.93 mmol of $NaCo(CO)_3P(C_6H_5)_3$ prepared by sodium amalgam reduction of 2.0 g (2.47 mmol) of $[Co(CO)_3P(C_6H_5)_3]_2$ in THF was treated with 1.2 g (5.25 mmol) of $SbCl_3$ at 20° for 1 hr. The deep red solution was then evaporated and extracted with CH_2Cl_2. Addition of *n*-pentane to this solution gave dark red crystals of product which were purified by recrystallization from CH_2Cl_2 and pentane. A similar reaction occurred using a ratio of 10 mmol of the sodium salt to 6 mmol of $SbCl_3$; in this case, however, the product was recrystallized once from THF and twice from CH_2Cl_2–*n*-pentane giving a deep red crystalline material whose analysis was consistent with **$(Sb[Co(CO)_3P(C_6H_5)_3]_4)_3(Sb_2Cl_9)$.**

(ii) A suspension of 1.6 g (2.0 mmol) of $[Co(CO)_3P(C_6H_5)_3]_2$ in 30 ml of 1,2-dichloroethane was refluxed with 0.45 g (1.47 mmol) of $SbCl_3$ for 4 hr. The deep purple solution so produced was filtered and evaporated to a small volume. Addition of 15 ml of CH_2Cl_2 followed by slow addition of *n*-pentane gave 0.9 g of dark red crystals which were recrystallized from CH_2Cl_2. This compound has the same infrared spectrum in the ν(CO) region as the product of (i). It was used to prepare the salts **$(Sb[Co(CO)_3P(C_6H_5)_3]_4)(PF_6)$** and **$(Sb[Co(CO)_3P(C_6H_5)_3]_4)(Cr(SCN)_4(NH_3)_2)$** by treating acetone solutions with $NaPF_6$ and Reinecke salt in methanol using methods similar to those described above for the preparation of other such salts.

The corresponding bromo derivative $(Sb[Co(CO)_3P(C_6H_5)_3]_4)_3(Sb_5Br_{18})$ was prepared from 5 mmol of $NaCo(CO)_3P(C_6H_5)_3$ and 1 mmol of $SbBr_3$ by a procedure similar to (i) above. The salt $(Sb[Co(CO)_3P(C_6H_5)_3]_4)(B(C_6H_5)_4)$ was prepared from an acetone solution of this derivative using $NaB(C_6H_5)_4$ in methanol.

Tris(tricarbonyltriphenylphosphinecobalt)bismuth(III), $Bi[Co(CO)_3P(C_6H_5)_3]_3$. Bismuth trichloride (0.7 g, 2.2 mmol) in 10 ml of THF was treated with 5 mmol of $NaCo(CO)_3P(C_6H_5)_3$ in THF. The deep red solution was stirred at 20° for 0.5 hr and evaporated to dryness. The residue was extracted with 80 ml of CH_2Cl_2 and the solution was evaporated to about 5 ml affording dark crystals of product which were recrystallized from CH_2Cl_2.

Dichloro(dicarbonyltriphenylphosphinenitrosyliron)arsenic(III), $Cl_2AsFe(CO)_2(NO)P(C_6H_5)_3$. A suspension of 2.0 g (2.0 mmol) of $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ in 15 ml of benzene was treated with 1.0 g (5.35 mmol) of $AsCl_3$ and stirred at 20° for 1 day. The dirty yellow suspension was then filtered and the brown solution was evaporated to dryness giving 1.0 g of crude product. This was purified by recrystallization from CH_2Cl_2–*n*-pentane.

Tetrakis(dicarbonyltriphenylphosphinenitrosyliron)antimony(V) Tetrabromoferrate(III), $(Sb[Fe(CO)_2(NO)P(C_6H_5)_3]_4)(FeBr_4)$. A solution of 5.0 mmol of $NaFe(CO)_2(NO)P(C_6H_5)_3$ in THF was treated with 0.9 g (2.5 mmol) of $SbBr_3$. The deep purple solution so formed was stirred at 20° for 0.5 hr and then evaporated to dryness. The residue was extracted with 30 ml of CH_2Cl_2 and filtered. Slow addition of *n*-pentane to the filtrate gave 1.5 g of very dark red crystals of product which was recrystallized from CH_2Cl_2–*n*-pentane.

The tetrachloroferrate(III) derivative, **$(Sb[Fe(CO)_2(NO)P(C_6H_5)_3]_4)(FeCl_4)$**, was prepared in a similar fashion from 5.3 mmol of $SbCl_3$ and 11.9 mmol of $NaFe(CO)_2(NO)P(C_6H_5)_3$ in THF. Dichloromethane solutions of this salt were used to prepare the salts $(Sb[Fe(CO)_2(NO)P(C_6H_5)_3]_4)(PF)_6$ and $(Sb[Fe(CO)_2(NO)P$-

$(C_6H_5)_3]_4)(Cr(SCN)_4(NH_3)_2)$ by addition of methanol solutions of $NaPF_6$ and Reinecke salt and were recrystallized from CH_2Cl_2-*n*-pentane.

Dichloro(dicarbonyltriphenylphosphinenitrosyliron)bismuth(III), $Cl_2BiFe(CO)_2(NO)P(C_6H_5)_3$. A THF solution of 6.0 mmole of $NaFe(CO)_2(NO)P(C_6H_5)_3$ was added to 1.9 g (6.0 mmol) of $BiCl_3$ in the same solvent and the mixture was stirred at 20° for 0.25 hr. After removal of the THF the solid residue was extracted with acetone (~300 ml) and the solution was filtered and evaporated to about 10 ml giving 1.8 g of red crystals. The product was recrystallized from acetone and dried *in vacuo*.

Tris(dicarbonyltriphenylphosphinenitrosyliron)bismuth(III), $Bi[Fe(CO)_2(NO)P(C_6H_5)_3]_3$. Bismuth trichloride (0.6 g, 1.9 mmol) in THF was treated with 6.0 mmol of $NaFe(CO)_2(NO)P(C_6H_5)_3$ and the mixture was stirred at 20° for 1 hr. The solution was evaporated and the residue was extracted with 70 ml of CH_2Cl_2. The extract was filtered and evaporated to 20 ml and *n*-pentane added affording 2.4 g of crude product. This was recrystallized from CH_2Cl_2.

Tris(tricarbonylnitrosyliron)bismuth(III), $Bi(Fe(CO)_3NO)_3$. A solution of 3.0 g (5.55 mmol) of $Hg(Fe(CO)_3NO)_2$ in THF was reduced with sodium amalgam and added to 1.1 g (3.5 mmol) of $BiCl_3$. After 0.25 hr at 20° the solvent was removed and the residue was extracted with *n*-pentane. After filtration the extract was evaporated to a small volume giving 0.6 g of glistening black crystals which were recrystallized from *n*-pentane. The product was unstable at room temperature.

Discussion

The present work represents a preliminary survey of two synthetic methods which can be used for the preparation of group V derivatives of transition metal carbonyls where the group V element acts as a one-electron donor. So far $Fe(CO)_2Cp$, $Co(CO)_3PPh_3$, and $Fe(CO)_2(NO)L$ derivatives have been isolated from reactions involving EX_3 with Na or Hg derivatives of metal carbonyl anions or EX_3 with metal carbonyl species containing metal-metal bonds. Analytical and other pertinent data for new compounds are listed in Table I.

$Fe(CO)_2Cp$ Derivatives. As reported previously[13] the products of the reaction of $SbCl_3$ and $SbBr_3$ with $(Fe(CO)_2Cp)_2$ were found to depend on the solvent in which the reaction was carried out. In dichloromethane solution the ionic derivatives $[Cl_2Sb(Fe(CO)_2Cp)_2]^+[Sb_2Cl_7]^-$ and $[Br_2Sb(Fe(CO)_2Cp)_2]^+[SbBr_4]^-$ were formed. They were found to have molar conductivities of 47 and 71 Ω^{-1} mol^{-1} cm^2, respectively. These rather low values could be due to association *via* halogen bridging in solution. The existence of a positive charge on the cation is consistent with the higher carbonyl stretching frequencies (see Table I) compared with those of the neutral isoelectronic $X_2Sn(Fe(CO)_2Cp)_2$[14,15] species (X = Cl, ν(CO) 2040 (sh), 2025 (vs), 1993 (vs) cm^{-1} (Nujol mull); X = Br, ν(CO) 2027 (s), 2002 (s), 1973 (s), 1959 (m, sh) cm^{-1} ($CHCl_3$ solution). Recently the crystal structure of the chloro derivative has been determined by Einstein and Jones[16] confirming the proposed formula. The structure involves discrete $Cl_2Sb(Fe(CO)_2Cp)_2{}^+$ groups and double chains of $SbCl_3$ and $SbCl_4{}^-$ groups linked by chlorine bridges. The repeating anion unit in the solid appears to be $Sb_4Cl_{14}{}^{2-}$. If the anion survives as a polymer in solution this may explain the low conductivity. The large size of the anion would result in decreased mobility and hence decreased conductivity. The reduction in the number of charge carriers would have the same effect. This interpretation is strengthened by the higher conductivities of the $Cr(SCN)_4(NH_3)_2{}^-$ and $PF_6{}^-$ salts where anion association is very unlikely.

The formal oxidation number of antimony in these derivatives can be regarded as either V where the $[X_2Sb(Fe(CO)_2Cp)_2]^+$ ion is considered as a derivative of $SbCl_4{}^+$ (produced by removal of X^- from Sb^VX_5) or as III where $X_2(Fe(CO)_2Cp)Sb$: acts as a two-electron donor toward the other iron giving a derivative of the known $Fe(CO)_3Cp^+$ ion. The latter case would be analogous to the $Ph_3SbFe(CO)_2Cp^+$ ion.[17] The true state of affairs probably lies between these two extremes.

If the reaction of SbX_3 with $(Fe(CO)_2Cp)_2$ is carried out in benzene or THF, Newlands and coworkers[13] found that only the neutral species $X_2SbFe(CO)_2Cp$ and $XSb(Fe(CO)_2Cp)_2$ together with $XFe(CO)_2Cp$ were formed

$$SbX_3 + (Fe(CO)_2Cp)_2 \rightarrow X_2SbFe(CO)_2Cp + XSb(Fe(CO)_2Cp)_2$$

These reactions can be described in terms of an initial insertion of SbX_3 into the Fe–Fe bond (oxidative addition to the antimony) followed by elimination from the intermediate $[X_3Sb(Fe(CO)_2Cp)_2]$ of either $XFe(CO)_2Cp$ or X^- with formation of the neutral or ionic species, respectively

$$[CpFe(CO)_2]_2 + SbX_3 \rightarrow [Cp(CO)_2FeSbX_3Fe(CO)_2Cp]$$

$$[Cp(CO)_2FeSbX_3Fe(CO)_2Cp] \begin{array}{l} \nearrow Cp(CO)_2FeX + SbX_2Fe(CO)_2Cp \\ \searrow X^- + [X_2Sb(Fe(CO)_2Cp)_2]^+ \end{array}$$

Alternatively since molten $SbCl_3$ is believed to ionize to some extent to $SbCl_2{}^+$ and $SbCl_4{}^-$ [18] and if a similar ionization were to occur in CH_2Cl_2 solution, insertion of $SbCl_2{}^+$ into the Fe–Fe bond could occur giving $[Cl_2Sb(Fe(CO)_2Cp)_2]^+[SbCl_4]^-$ directly. This would be analogous to the well-known insertion reactions of tin and germanium dihalides[14,15]

$$(CpFe(CO)_2)_2 + [SbX_2]^+ \rightarrow [(Cp(CO)_2Fe)_2SbX_2]^+$$

However we find that the measured conductivity of $SbCl_3$ in CH_2Cl_2 is very low (about 0.012 Ω^{-1} mol^{-1} cm^2 at 32 mmol/l.) and 0.030 at 6 mmol/l.) so that the extent of such ionization can only be very small.

As minor by-products in the reaction of $SbCl_3$ with $(Fe(CO)_2Cp)_2$ in CH_2Cl_2, red crystalline products of formula $(SbX_3)(XFe(CO)_2Cp)_2$ were isolated. The chloride could also be prepared simply by mixing $SbCl_3$ with $ClFe(CO)_2Cp$ in ether. The crystal structure of the latter compound has been determined by Einstein and McGregor[19] and is found to be dimeric as shown in Figure 1. The molecule has a center of symmetry: the bridging chlorine atoms of the $Cp(CO)_2FeCl$ moieties are noteworthy.

Bigorgne and coworkers[20] have described infrared evidence for interactions between metal carbonyl halides and potential Lewis acids such as $FeCl_3$, $AlBr_3$, and $SbCl_5$ but the adducts were not characterized.

The trifluoromethylantimony derivative $(CF_3)_2SbI$ reacted in a similar fashion to SbX_3 with $(Fe(CO)_2Cp)_2$ resulting in the formation of $[(CF_3)_2Sb(Fe(CO)_2Cp)_2]^+[(CF_3)_2SbI_2]^-$. The pseudohalogen character of fluorocarbon groups[21,22] is seen in this reaction. Very few anions containing only CF_3, E, and halogen are known[23] and cations containing a group V element bonded to a fluorocarbon group were previously

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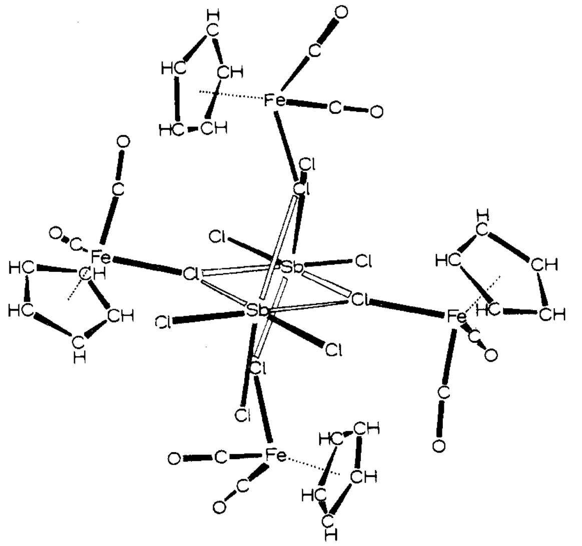

Figure 1. The structure of $[SbCl_3(Fe(CO)_2CpCl)_2]_2$.

unknown, although ions such as $[(CF_3)_3PCl]^+$ and $[(CF_3)_3PCl_3]^-$ have been postulated to account for the conductivity of $(CF_3)_3PCl_2$ in acetonitrile.[24]

The reactions of $(CF_3)_2EX$ (E = P, As) with metal carbonyls usually afford $(CF_3)_2E$ bridged species.[25] The reaction of $(CF_3)_4Sb_2$ with $(Fe(CO)_2Cp)_2$ gave what is believed to be $(CF_3)_2SbFe(CO)_2Cp$ but the material was not stable enough for a microanalysis. It would be analogous to the known arsenic derivative.[2]

$$(CpFe(CO)_2)_2 + (CF_3)_2E\text{-}E(CF_3)_2 \rightarrow CpFe(CO)_2E(CF_3)_2$$
$$E = As, Sb$$

The reactions of $SbCl_3$ and $SbBr_3$ with $(CpFe(CO)_2)_2$ under more forcing conditions gave $XSb(Fe(CO)_2Cp)_3^+$ salts. Thus $SbCl_3$ in refluxing 1,2-dichloroethane gave a crystalline material which on recrystallization from acetone–ether gave two crystalline fractions, one only slightly soluble in acetone and the other much more so. The former has not yet been characterized, but the latter appears to be $[ClSb(Fe(CO)_2Cp)_3][FeCl_4]$, on the basis of analytical and magnetic data ($\mu_{eff} = 5.5$ BM). The identity of the cation was confirmed by the characterization of the BPh_4^-, PF_6^-, and $Cr(SCN)_4(NH_3)_2^-$ salts. This same cation was isolated as the $FeCl_4^{2-}$ salt from a reaction involving the interaction of $[Fe(CO)_2Cp]^-$ with $SbCl_3$.[11] The structure of the compound which was eventually isolated, $[ClSb(Fe(CO)_2Cp)_3]_2[FeCl_4]\cdot CH_2Cl_2$, was confirmed by an X-ray study.[11]

$$(CpFe(CO)_2)_2 + SbX_3 \rightarrow [(Cp(CO)_2Fe)_3SbX]^+{}_n[FeX_4]^{n-}$$
$$X = Cl,\ n = 1;\ X = Br,\ n = 2$$

Antimony tribromide underwent a similar reaction with $(Fe(CO)_2Cp)_2$ on heating to 120° under 800 psi pressure of CO as well as on refluxing together in methyl ethyl ketone. The product is believed to be a solvated $FeBr_4^{2-}$ salt $[BrSb(Fe(CO)_2Cp)_3]_2[FeBr_4]\cdot{}^1/_2(CH_3)_2CO$ analogous to the $FeCl_4^{2-}$ derivative mentioned above. The presence of acetone was confirmed by a band at 1700 cm^{-1} in the infrared spectrum, which vanished on heating *in vacuo*. The presence of the $FeBr_4^{2-}$ ion was supported by magnetic measurements ($\mu_{eff} = 4.3$ BM). Again the identity of the cation was confirmed by conversion to the BPh_4^- and $Cr(SCN)_4(NH_3)_2^-$ salts. Conductivity measurements of all of the above compounds were consistent with 1:1 electrolytes (or 2:1 in the case of the $FeBr_4^{2-}$ salt).

Antimony pentachloride reacted with $(Fe(CO)_2Cp)_2$ with CO evolution and formation of $[Cl(Fe(CO)_2Cp)_2][SbCl_6]$. The PF_6^- and BF_4^- salts have previously been described.[26] In our case the $SbCl_5$ is acting as a chlorinating agent.

$$(Fe(CO)_2Cp)_2 + SbCl_5 \rightarrow [Fe(CO)_2ClFe(CO)_2Cp]^+SbCl_6^-$$

Arsenic trihalides were also found to react with $(Fe(CO)_2Cp)_2$ in CH_2Cl_2 solution although in this case both the neutral $X_2AsFe(CO)_2Cp$ species and the ionic $[X_2As(Fe(CO)_2Cp)_2][FeX_4]$ derivatives were formed

$$(Fe(CO)_2Cp)_2 + AsX_3 \rightarrow X_2AsFe(CO)_2Cp + [X_2As(Fe(CO)_2)_2]^+[FeX_4]^-$$

Reaction paths similar to those proposed for the SbX_3 reactions are possible. In the $AsCl_3$ case other, as yet incompletely characterized, products were obtained. Thus with an $AsCl_3$:$(Fe(CO)_2Cp)_2$ ratio of 1:1 brown crystals were gradually deposited during the course of 1 week. These were tentatively formulated as $[Cl_2As(Fe(CO)_2Cp)_2]_2[FeCl_4]$ on the basis of an elemental microanalysis. *Anal.* Calcd: C, 28.45; H, 1.67; Cl, 23.7. Found: C, 28.60; H, 1.53; Cl, 23.15. However with a ratio of 2.5:1 the deposit of brown cubic crystals has different C:Cl ratio, possibly due to replacement of $FeCl_4^{2-}$ by $FeCl_4^-$. *Anal.* Calcd for $[Cl_2As(Fe(CO)_2Cp)_2]_3[FeCl_4]_2$: C, 26.6; H, 1.58; Cl, 26.2; Fe, 23.6. Found: C, 26.3; H, 1.63; Cl, 24.9; Fe, 23.2. In fact when the latter compound was recrystallized from acetone–ether pure $[Cl_2As(Fe(CO)_2Cp)_2][FeCl_4]$ was produced. This was characterized by an elemental analysis and conductivity and magnetic measurements (Table I). Also the ν(CO) bands in the infrared spectrum were very similar in position and intensity to those of the analogous $[X_2Sb(Fe(CO)_2Cp)_2]^+$ ion. The neutral $Cl_2AsFe(CO)_2Cp$ species was isolated from the mother liquor after separation of the above $[Cl_2As(Fe(CO)_2Cp)_2]^+$ salts.

The reaction of $AsBr_3$ with $(Fe(CO)_2Cp)_2$ was more straightforward in that the only major products were $[Br_2As(Fe(CO)_2Cp)_2][FeBr_4]$ and $Br_2AsFe(CO)_2Cp$, although red crystals of $(Br_3As)(BrFe(CO)_2Cp)_3$ were isolated as a by-product. The latter compound is presumably similar to the previously mentioned $(Cl_3Sb)(ClFe(CO)_2Cp)_2$ (Figure 1).

Bismuth derivatives were also prepared by the reaction of BiX_3 on $(Fe(CO)_2Cp)_2$. Bismuth trichloride reacted in CH_2Cl_2 solution with formation of red crystals of $Cl_2BiFe(CO)_2Cp$. Newlands and coworkers found that a similar reaction occurred with $BiBr_3$ and BiI_3 in benzene solution, the other product being $XFe(CO)_2Cp$. The absence of cations containing bismuth is not unexpected in view of the usual instability of Bi^V derivatives.

$$BiX_3 + (Fe(CO)_2Cp)_2 \rightarrow X_2BiFe(CO)_2Cp$$

$Co(CO)_3PPh_3$ Derivatives. Antimony trichloride and BiI_3 had previously been found to react with $Co_2(CO)_8$ to produce $Cl_2SbCo(CO)_4$ and $Bi(Co(CO)_4)_3$, respectively.[12] On attempting to extend this work to SbX_3 and $(Co(CO)_3PPh_3)_2$ it has been found that the expected $Cl_2SbCo(CO)_3PPh_3$ was not formed, although the compound could be prepared from the tetracarbonyl and PPh_3.[12] Instead, a very deep red, almost black, crystalline material was obtained on refluxing $SbCl_3$ or $SbBr_3$ with $(Co(CO)_3PPh_3)_2$ in 1,2-dichloroethane. Although these compounds themselves have not yet been fully characterized, magnetic measurements show that they

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are paramagnetic and probably contain CoX_4^{2-}. They were shown to be salts of the $Sb(Co(CO)_3PPh_3)_4^+$ cation by conversion to the PF_6^- and $Cr(SCN)_4(NH_3)_2^-$ salts. The same cation was formed by the reaction of SbX_3 with $Co(CO)_3PPh_3^-$ in THF; in this case the products which were diamagnetic were tentatively characterized as the $Sb_5X_{18}^{3-}$ $((SbX_4^-)_3(SbX_3)_2)$ salts; this however is supported only by total elemental analyses and so should be accepted with reservations. On recrystallization of the chloro derivative from THF and ether, followed by CH_2Cl_2 and pentane, the microanalytical data indicated that it had been converted to the $Sb_2Cl_9^{3-}$ salt through loss of $SbCl_3$ (possibly due to formation of a stable THF complex of $SbCl_3$). The infrared carbonyl stretching bands (Table I) of all of the above $Sb(Co(CO)_3PPh_3)_4^+$ salts were identical within the limits of experimental error. The conductivities were consistent with the proposed formulas.

$$SbX_3 + (Co(CO)_3PPh_3)_2 \rightarrow [Sb(Co(CO)_3PPh_3)_4]^+A^-$$

Again bismuth behaved differently from antimony in forming the neutral $Bi(Co(CO)_3PPh_3)_3$ derivative when $BiCl_3$ was treated with $Co(CO)_3PPh_3^-$

$$BiCl_3 + [Co(CO)_3PPh_3]^- \rightarrow Bi(Co(CO)_3PPh_3)_3$$

$Fe(CO)_2(NO)PPh_3^-$ Derivatives. The synthesis of various tin derivatives of $Fe(CO)_2(NO)PPh_3$ by the reaction of SnX_4 and $RSnX_3$ with $Hg(Fe(CO)_2(NO)PPh_3)_2$ was recently reported.[27] Attempts to extend this particular method to the synthesis of analogous group V derivatives have so far only been successful with $AsCl_3$, reaction of which with $Hg(Fe(CO)_2(NO)PPh_3)_2$ afforded $Cl_2AsFe(CO)_2(NO)PPh_3$. Since we had found that $Co(CO)_3PPh_3^-$ reacts with SbX_3 giving the $Sb(Co(CO)_3PPh_3)_4^+$ cation, the analogous reaction of $Fe(CO)_2(NO)PPh_3^-$ (from the sodium amalgam reduction of the mercury salt) with SbX_3 was attempted and indeed gave the isoelectronic $Sb(Fe(CO)_2(NO)PPh_3)_4^+$ cation

$$[Fe(CO)_2(NO)PPh_3]^- + SbX_3 \rightarrow [Sb(Fe(CO)_2(NO)PPh_3)_4][FeX_4]$$

In this case the anion appeared to be FeX_4^- on the basis of microanalytical data and magnetic susceptibility measurements. Again the cation was characterized by conversion to the PF_6^- and $Cr(SCN)_4(NH_3)_2^-$ salts.

Neutral bismuth derivatives only were isolated from reaction of $Fe(CO)_2(NO)PPh_3^-$ and $Fe(CO)_3(NO)^-$ with $BiCl_3$, namely, $Cl_2BiFe(CO)_2(NO)PPh_3$, $Bi(Fe(CO)_3NO)_3$, and $Bi(Fe(CO)_2(NO)PPh_3)_3$.

Conclusions

The reactions of $(CpFe(CO)_2)_2$, $(Co(CO)_3PPh_3)_2$, and metal carbonyl anions with group V trihalides EX_3 produce a wide range of ionic and neutral compounds, containing M–E σ bonds. In the neutral species bismuth can form bonds with up to three metal atoms as in $Bi(Co(CO)_3PPh_3)_3$. Antimony can form two as in $XSb(Fe(CO)_2Cp)_2$, and arsenic only one as in $Cl_2AsFe(CO)_2(NO)PPh_3$. In the cationic species arsenic is bonded to two iron atoms in $[Cl_2As(Fe(CO)_2Cp)_2]^+$ yet the same metal group will form three bonds to antimony as in $[ClSb(Fe(CO)_2Cp)_3]^+$. Four M–E bonds are formed by antimony in the ions $[Sb(Fe(CO)_2(NO)PPh_3)_4]^+$ and $[Sb(Co(CO)_3PPh_3)_4]^+$. The reactions are not simple as is evidenced by the isolation of salts of FeX_4^{2-} and FeX_4^-. The tendency of antimony halides in particular to form polyhalo anions is a further complicating factor. Nevertheless the results indicate that there is a rich chemistry to be discovered in these previously neglected derivatives.

Registry No. $Cl_2AsFe(CO)_2Cp$, 34823-23-9; $Br_2AsFe(CO)_2Cp$, 34823-24-0; $Cl_2AsFe(CO)_2NOPPh_3$, 38415-50-8; $[Cl_2As(Fe(CO)_2Cp)_2][FeCl_4]$, 37279-44-0; $[Br_2As(Fe(CO)_2Cp)_2][FeBr_4]$, 38386-58-2; $Br_3As(ClFe(CO)_2Cp)_3$, 37260-91-6; $[Cl_2Sb(Fe(CO)_2Cp)_2][Sb_2Cl_7]$, 11082-37-4; $[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$, 38386-59-3; $[Cl_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$, 37279-45-1; $[Br_2Sb(Fe(CO)_2Cp)_2][SbBr_4]$, 38386-60-6; $[(CF_3)_2Sb(Fe(CO)_2Cp)_2][(CF_3)_2SbI_2]$, 37270-75-0; $[ClSb(Fe(CO)_2Cp)_3][FeCl_4]$, 37260-95-0; $[ClSb(Fe(CO)_2Cp)_3][PF_6]$, 37260-96-1; $[ClSb(Fe(CO)_2Cp)_3][Cr(SCN)_4(NH_3)_2]$, 37260-94-9; $[ClSb(Fe(CO)_2Cp)_3][BPh_4]$, 37260-99-4; $[BrSb(Fe(CO)_2Cp)_3][FeBr_4]$, 37260-92-7; $[BrSb(Fe(CO)_2Cp)_3][Cr(SCN)_4(NH_3)_2]$, 37260-93-8; $[BrSb(Fe(CO)_2Cp)_3][BPh_4]$, 37260-98-3; $Cl_3Sb(ClFe(CO)_2Cp)_2$, 37261-02-2; $Br_3Sb(BrFe(CO)_2Cp)_2$, 37261-01-1; $[Cl(Fe(CO)_2Cp)_2][SbCl_6]$, 38386-61-7; $[Sb(Fe(CO)_2(NO)PPh_3)_4][FeCl_4]$, 38415-51-9; $[Sb(Fe(CO)_2(NO)PPh_3)_4][FeBr_4]$, 38498-44-1; $[Sb(Fe(CO)_2(NO)PPh_3)_4][Cr(SCN)_4(NH_3)_2]$, 38415-52-0; $[Sb(Fe(CO)_2(NO)PPh_3)_4][PF_6]$, 38415-53-1; $[Sb(Co(CO)_3PPh_3)_4]_3[Sb_5Cl_{18}]$, 37261-05-5; $[Sb(Co(CO)_3PPh_3)_4]_3[Sb_2Cl_9]$, 37261-04-4; $[Sb(Co(CO)_3PPh_3)_4][PF_6]$, 38415-54-2; $[Sb(Co(CO)_3PPh_3)_4][Cr(SCN)_4(NH_3)_2]$, 38531-35-0; $[Sb(Co(CO)_3PPh_3)_4]_3[Sb_5Br_{18}]$, 37261-03-3; $Cl_2BiFe(CO)_2Cp$, 38386-62-8; $Cl_2BiFe(CO)_2NOPPh_3$, 38415-55-3; $Bi(Fe(CO)_3NO)_3$, 38498-45-2; $Bi(Fe(CO)_2NOPPh_3)_3$, 38566-00-6; $Bi(Co(CO)_3PPh_3)_3$, 38402-91-4.

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