Cyclopentadienyldicarbonyliron Derivatives of Arsenic, Antimony and Bismuth with M–Fe σ-Bonds (M=As, Sb, Bi)

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Summary The reactions of MX_3(M = As, Sb; X = Cl, Br) with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in CH_2Cl_2 solution give ionic derivatives containing the $[X_2M\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2]^+$ cation as well as the neutral compounds $X_2AsFe(CO)_2(\pi\text{-}C_5H_5)$, while similar reactions of SbX_3 and BiX_3 (X = Cl, Br, I) in C_6H_6 or tetrahydrofuran yield $X_2MFe(CO)_2(\pi\text{-}C_5H_5)$ and $XSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$.

ALTHOUGH considerable effort has been devoted to the synthesis of compounds with main-group metals σ-bonded to transition metals, very little is known concerning similar derivatives of Group V elements.[1] Dahl and his co-workers have recently described the structures of cluster compounds such as $As_3Co(CO)_3$,[2] $As_2Co_2(CO)_6$,[3] and $Sb_4Co_4(CO)_{12}$[4] in which the Group V atom is formally tervalent. Simpler compounds in which the Group V element is believed to be similarly bonded include $(CF_3)_2AsFe(CO)_2(\pi\text{-}C_5H_5)$, $(CF_3)_2AsMo(CO)_3(\pi\text{-}C_5H_5)$,[5] $(C_6F_5)_2AsFe(CO)_2(\pi\text{-}C_5H_5)$, $(C_6F_5)_2AsMo(CO)_3(\pi\text{-}C_5H_5)$,[6] $Cl_2SbCo(CO)_4$, and $Bi(Co(CO)_4)_3$.[7]

TABLE

Reaction of Group V halides with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$

Halide	Mole ratio (halide : dimer)	Solvent	Products isolated
AsX_3 (X = Cl, Br)	2 : 1	CH_2Cl_2	$[X_2As\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2]AsX_4 + X_2AsFe(CO)_2(\pi\text{-}C_5H_5)$
SbX_3 (X = Cl, Br)	1 : 1	CH_2Cl_2	$[X_2Sb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2]A^a + X_3Sb[XFe(CO)_2(\pi\text{-}C_5H_5)]_2{}^b$
SbX_3 (X = Cl, Br, I)	1 : 1	C_6H_6	$X_2SbFe(CO)_2(\pi\text{-}C_5H_5) + XFe(CO)_2(\pi\text{-}C_5H_5)$
SbX_3 (X = Cl, Br, I)	2 : 1	THF	$XSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 + XFe(CO)_2(\pi\text{-}C_5H_5)$
BiX_3 (X = Cl, Br, I)	1 : 1	C_6H_6 or CH_2Cl_2	$X_2BiFe(CO)_2(\pi\text{-}C_5H_5) + XFe(CO)_2(\pi\text{-}C_5H_5)$

[a] A = $Sb_2Cl_7^-$ or $SbBr_4^-$. [b] Also isolated from $SbX_3 + XFe(CO)_2(\pi\text{-}C_5H_5)$.

One common method for the formation of M–M′ bonds involves the 'insertion' of a lower-valent metal halide such as $SnCl_2$ into the metal–metal bond of a transition-metal complex such as $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$.[8] An analogous reaction could in principle occur with the Group V trihalides and would involve formal oxidation to the pentavalent state.

The reaction of MX_3 (M = Sb, As; X = Cl, Br) with $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ in CH_2Cl_2 at room temperature gives rise to the ionic derivatives $[X_2M\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2][A]$ ($A = MX_4^-$ or $Sb_2Cl_7^-$) as well as the neutral arsenic species $X_2AsFe(CO)_2(\pi\text{-}C_5H_5)$ while in C_6H_6 or THF (tetrahydrofuran) SbX_3 (X = Cl, Br, I) reacts to give only the neutral derivatives $X_2SbFe(CO)_2(\pi\text{-}C_5H_5)$ and $XSb[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$.† Bismuth trihalides and SbI_3, however, give neutral species in both THF and CH_2Cl_2. A partial list of compounds produced is summarised in the Table.

These reactions could be described in terms of an initial insertion of MX_3 into the Fe–Fe bond as suggested above, followed by elimination from the M^V intermediate of either X^- to generate the ionic species, or $XFe(CO)_2(\pi\text{-}C_5H_5)$ to produce the neutral compounds. Alternately the reactions could involve ionisation of MX_3 to MX_2^+ and MX_4^- followed by insertion of MX_2^+ into the Fe–Fe bond with the formation of the ionic products.

The neutral species are poor conductors in acetone solution and are monomeric in benzene and THF. The ionic derivatives are better electrolytes in acetone, and some molar conductance values are: $[Br_2As\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2][AsBr_4]$, 110 mho cm^2 mol^{-1}; $[Br_2Sb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2][SbBr_4]$ 75 mho cm^2 mol^{-1}, and $[Cl_2Sb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2][Sb_2Cl_7]$ 46 mho cm^2 mol^{-1}. The low values for the antimony derivatives are possibly due to association *via* halogen bridges. They are probably best described as substitution products of $Fe(CO)_3(\pi\text{-}C_5H_5)^+$ where one CO is replaced by $X_2[Fe(CO)_2(\pi\text{-}C_5H_5)]M$.

The reaction of $AsCl_3$ is more complicated than indicated in the Table, the initial product using a mole ratio of 2 : 1 is a

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† All new compounds analyse well for at least C, H, and halogen.

crystalline product which gives analytical data consistent with the formulation $[Cl_2As\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2]_3[As_4Cl_{15}]$ On recrystallization from acetone–ether this is converted into $[Cl_2As\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2][AsCl_4]$.

Similar reactions involving substituted halides occur; *e.g.* $(CF_3)_2SbI$ gives $[(CF_3)_2Sb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_2][(CF_3)_2SbI_2]$ as a stable crystalline material.

The reaction with antimony trihalides under more forcing conditions yields ionic derivatives with more than two Sb–Fe bonds; thus $SbBr_3$ affords $[BrSb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_3][SbBr_6],Me_2CO$ which was also characterized at the Ph_4B^- salt.

This work is currently being extended to other transition metals.

We thank the National Research Council of Canada for financial support.

(*Received, May 24th*, 1971, *Com.* 843.)

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