Preparation of Ferrocenium Phosphorus, Arsenic, Antimony, and Bismuth Halides. The Structure of Ferrocenium Tetrachlorobismuthate

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Summary Eleven ferrocenium halogenopentelides (P, As, Sb, or Bi) have been prepared by the reaction of a group 5 element halide with ferrocene in an organic solvent; the structure of one of the products, $[Fe(\eta^5\text{-}C_5H_5)_2][BiCl_4]$, determined by *X*-ray crystallography, reveals an extended, one-dimensional anion of irregular, edge-sharing $BiCl_6^{3-}$ octahedra.

Although it has been known since its discovery that ferrocene could be readily oxidized to the ferrocenium cation,[1] $(\eta^5\text{-}C_5H_5)_2Fe^+$, only a small number of crystalline ferrocenium salts have been isolated, and no detailed *X*-ray structural studies have been reported.[2] We now report that the combination of a wide variety of group 5 halides, *e.g.*, PCl_3, $AsCl_3$, AsI_3, $SbCl_3$, $BiCl_3$ $MePCl_2$, $PhPCl_2$, $MeAsCl_2$, $MeAsI_2$, $PhAsCl_2$, Me_2AsCl, or $MeSbCl_2$ with ferrocene in benzene or other inert organic solvent produces at room temperature in a few days high yields of blue, crystalline ferrocenium halogenopentelides. Reaction times can be significantly shortened by irradiation with Pyrex-filtered sunlight.[3] As confirmed by Mössbauer spectroscopy, the cation in all cases is the ferrocenium ion, but the composition of the anion varies depending upon the group 5 halide.

The structure of the salt obtained from a 1:1 molar ratio of ferrocene and $BiCl_3$ in acetone, $[Fe(\eta^5-C_5H_5)_2][BiCl_4]$, has been characterized by *X*-ray crystallography. *Crystal data:* monoclinic, space group $P2_1/c$, $a = 10·998$, $b = 17·449$, $c = 7·569$ Å, $\beta = 98·46°$, $Z = 4$. A set of 1374 reflections was refined to $R_1 = 0·03$ and $R_2 = 0·037$ excluding hydrogen atom parameters. The structure (Figure) reveals that the Bi atoms are surrounded by six Cl atoms in an irregular octahedral array; adjacent Bi atoms are connected by halogen bridges such that the overall structure is an infinite chain of edge-sharing octahedra extending along the *c* axis. Each of the six Bi–Cl bond distances is unique: bonds to the four bridging chlorine atoms are long, av. 2·88 Å, while the two non-bridging Bi–Cl bond distances are short, av. 2·51 Å. Related 'polymeric' anion structures have been reported for two quaternary organonitrogen salts.[4] The ferrocenium ions occupy the spaces between the $(BiCl_4)_x$ chains and differ from ferrocene primarily by an eclipsed rather than staggered relationship of the cyclopentadienyl rings. In contrast to previous indications from i.r. data,[5] no deviation from coplanarity of the rings is observed. The Fe–C ring distance (1·70 Å) is somewhat longer than that found in ferrocene (1·66 Å).[6]

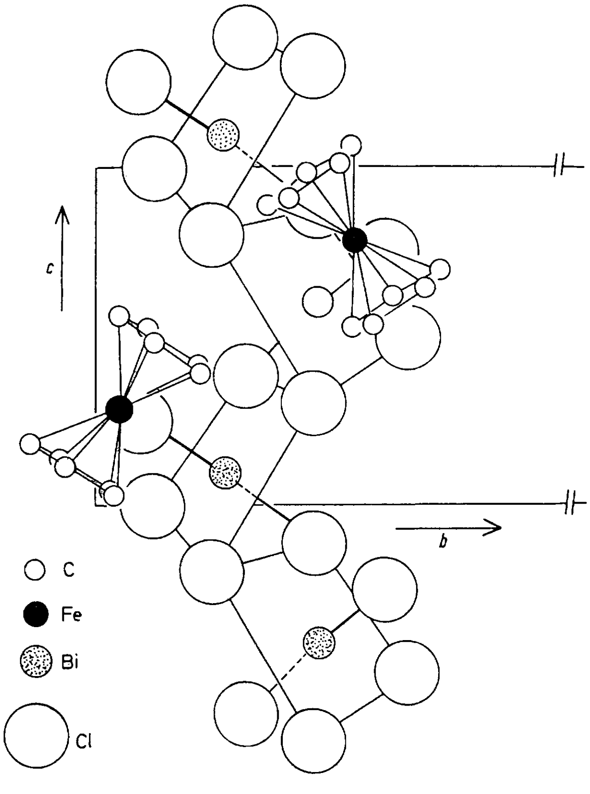

FIGURE. Structural view of $[Fe(\eta^5-C_5H_5)_2]$ $[BiCl_4]$ along the *a* axis.

Empirical formulae analogous to $[Fe(\eta^5-C_5H_5)_2][BiCl_4]$ have been obtained for the products from AsI_3 and $SbCl_3$.[7] Several of the group 5 halides produce products of differing composition dependent upon the initial molar ratio of halide to ferrocene. *E.g.*, when $AsCl_3$ is in large excess $[Fe(\eta^5-C_5H_5)_2Fe][As_2Cl_7]$ is obtained; from an equimolar mixture the product has the empirical formula, $[Fe(\eta^5-C_5H_5)_2]_2$ $[As_3Cl_{10}]$. The degree of complexity is unknown.

These reactions do not occur if oxygen is rigorously excluded. Molecular oxygen is the apparent electron acceptor. Various group 5 oxide halides are also recovered from the reactions. If water is also present, complex oxide and hydroxide halide mixtures result. In the specific case of the alkylphosphorus and arsenic halides, alkylphosphonic and arsonic acids are obtained in 'wet' reactions. If stronger electron acceptors such as hydrogen peroxide are used, regardless of the group 5 halide, only the ferrocenium tetrahalogenoferrate, $[Fe(\eta^5-C_5H_5)][FeX_4]$ is obtained. Also dissolution of many of the ferrocenium salts in ethanol or water is accompanied by a slow conversion into the tetrahalogenoferrate salt as determined by its characteristic e.s.r. spectrum.[8]

In the temperature range 250–575 K, the single crystals of $[Fe(\eta^5-C_5H_5)_2][BiCl_4]$ are semiconductors with an activation energy for conduction of *ca.* 1·1 eV. The d.c. conductivity of the crystals is highly anisotropic; in the direction of the extended structure (along the *c* axis), the conductivity (*ca.* 10^{-8} Ω^{-1} at 300 K) is two orders of magnitude greater than along the other two axes. In this temperature range, a plot of log σ *vs.* T^{-1} is non-linear suggesting a mixture of intrinsic and extrinsic conductivity modes.

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[1] E. G. Perevalova and T. V. Nikitina, *Organometallic Reactions*, 1972, **4**, 353.

[2] The structure of the tri-iodide salt has been reported, but extreme disorder prevented a determination of the cation structure (T. Bernstein and F. H. Herbstein, *Acta Cryst.*, 1968, **B24**, 1640). The structure of 1,1-dimethylferrocenium tri-iodide has been determined (J. W. Bats, J. J. De Boer, and D. Bright, *Inorg. Chim. Acta*, 1971, **5**, 605).

[3] Y. Hoshi, T. Akiyama, and A. Sugimori, *Tetrahedron Letters*, 1970, 1485.

[4] B. K. Robertson, W. G. McPherson, and E. A. Meyers, *J. Phys. Chem.*, 1967, **71**, 3531.

[5] P. Sohar and J. Kuszmann, *J. Mol. Structure*, 1969, **3**, 359.

[6] J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 1959, **12**, 28.

[7] An ammonium hexachloroantimonate salt with ferrocene gives a compound of the same empirical formula [G. W. Cowell, A. Ledwith, A. C. White, and H. J. Woods, *J. Chem. Soc.* (*B*), 1970, 227].

[8] I. J. Spilners, *J. Organometallic Chem.*, 1968, **11**, 381; R. M. Golding and L. E. Orgel, *J. Chem. Soc.*, 1962, **363**.