New, Improved Syntheses of Bisbenzeneiron(II) Hexafluorophosphate and Related Compounds

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Summary Bisbenzeneiron(II) hexafluorophosphate is made in excellent yield by the reaction of $FeCl_3$, $AlCl_3$, and benzene followed by solvolysis and treatment with aqueous ammonium hexafluorophosphate.

BISARENEIRON(II) salts were first prepared by Fischer and his co-workers[1,2] and Zeiss and Tsutui described their stability trends.[3] We recently reported a greatly improved preparative procedure for such salts based upon the reaction of an arene, $FeCl_2$, and $AlCl_3$ in cyclohexane.[4,5] While the complexation of arenes with $FeCl_2$ regularly gives 55—75% yields of hexafluorophosphate salts when 2–6 methyl groups are present on each hydrocarbon ring, the yields are much lower for the benzene (3%) and toluene (28%) derivatives.[6] Presumably the reduced yields reflect the reduced π electron donor ability of rings with fewer substituents and the reduced hydrolytic stability of the products. Fischer and Böttcher failed to isolate a bisbenzeneiron(II) salt and Zeiss and Tsutsui's mention of the ion is unsupported by preparative details, physical constants, or analytical data.

We now report a new synthetic route to bisareneiron(II) salts based on a long-known reaction, the chlorination of arenes by $FeCl_3$.[7] In such reactions $FeCl_2$ is a by-product. Presumably, it is in a much more highly activated state than $FeCl_2$ prepared externally and complexes rapidly and selectively with the excess of the arene used as solvent. In the case of benzene reactions (1)—(3) occur.

$$C_6H_6 + FeCl_3 \rightarrow C_6H_5Cl + FeCl_2 + HCl \qquad (1)$$

$$2C_6H_6 + FeCl_2 + 2AlCl_3 \rightarrow [(C_6H_6)_2Fe](AlCl_4)_2 \qquad (2)$$

$$[(C_6H_6)_2Fe](AlCl_4)_2 \xrightarrow{H_2O,\ NH_4PF_6} [(C_6H_6)_2Fe](PF_6)_2 \qquad (3)$$

Iron(III) chloride and aluminium chloride are refluxed overnight in an excess of benzene. After cooling to −50°, the mixture is solvolysed by addition of cold aqueous methanol. The orange aqueous layer is then treated with aqueous NH_4PF_6 to give bisbenzeneiron(II) hexafluorophosphate, m.p. 145—152° (decomp.) as a pale orange solid in yields as high as 79%.

The highest mass peak in the mass spectrum was that of benzene (*m/e* 78) indicating the absence of co-ordinated chlorobenzene. This was supported by a negative Lassaigne test for chlorine. The n.m.r. spectrum (CH_3CN; Varian A60) showed a sharp singlet at τ 3·00. The i.r. spectrum (KBr) showed absorptions at 3116s, 1627m, and 1456s cm^{-1}.

Similarly a 65% yield of the toluene analogue was obtained. The yield of bismesityleneiron(II) hexafluorophosphate was raised from 65% in the case of the $FeCl_2$ reaction to 86% by use of $FeCl_3$.

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