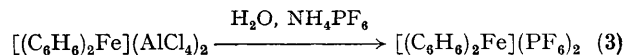
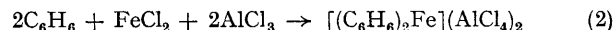


New, Improved Syntheses of Bisbenzeneiron(II) Hexafluorophosphate and Related Compounds

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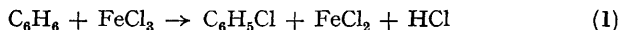
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Summary Bisbenzeneiron(II) hexafluorophosphate is made in excellent yield by the reaction of FeCl₃, AlCl₃, and benzene followed by solvolysis and treatment with aqueous ammonium hexafluorophosphate.



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, FeCl₂, and AlCl₃ in cyclohexane.^{4,5} While the complexation of arenes with FeCl₂ 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 Tsutui'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 FeCl₃.⁷ In such reactions FeCl₂ is a by-product. Presumably, it is in a much more highly activated state than FeCl₂ 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.



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 NH₄PF₆ 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 (CH₃CN; 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 FeCl₂ reaction to 86% by use of FeCl₃.

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¹ E. O. Fischer and R. Böttcher, *Chem. Ber.*, 1956, **89**, 2397.

² E. O. Fischer and R. Röhrscheid, *Z. Naturforsch.*, 1962, **17b**, 483.

³ M. Tsutui and H. Zeiss, *Naturwiss.*, 1957, **44**, 420.

⁴ J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 7207.

⁵ J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 7209.

⁶ J. F. Helling and S. L. Rice, unpublished data.

⁷ E.g. P. Kovacic and N. O. Brace, *J. Amer. Chem. Soc.*, 1954, **76**, 5491.