

Molecular Design in Organometallic Chemistry: the First Example in the Synthesis of Poly(cyclopentadienyliron) Cations of Polyaromatic Ethers and Thioethers

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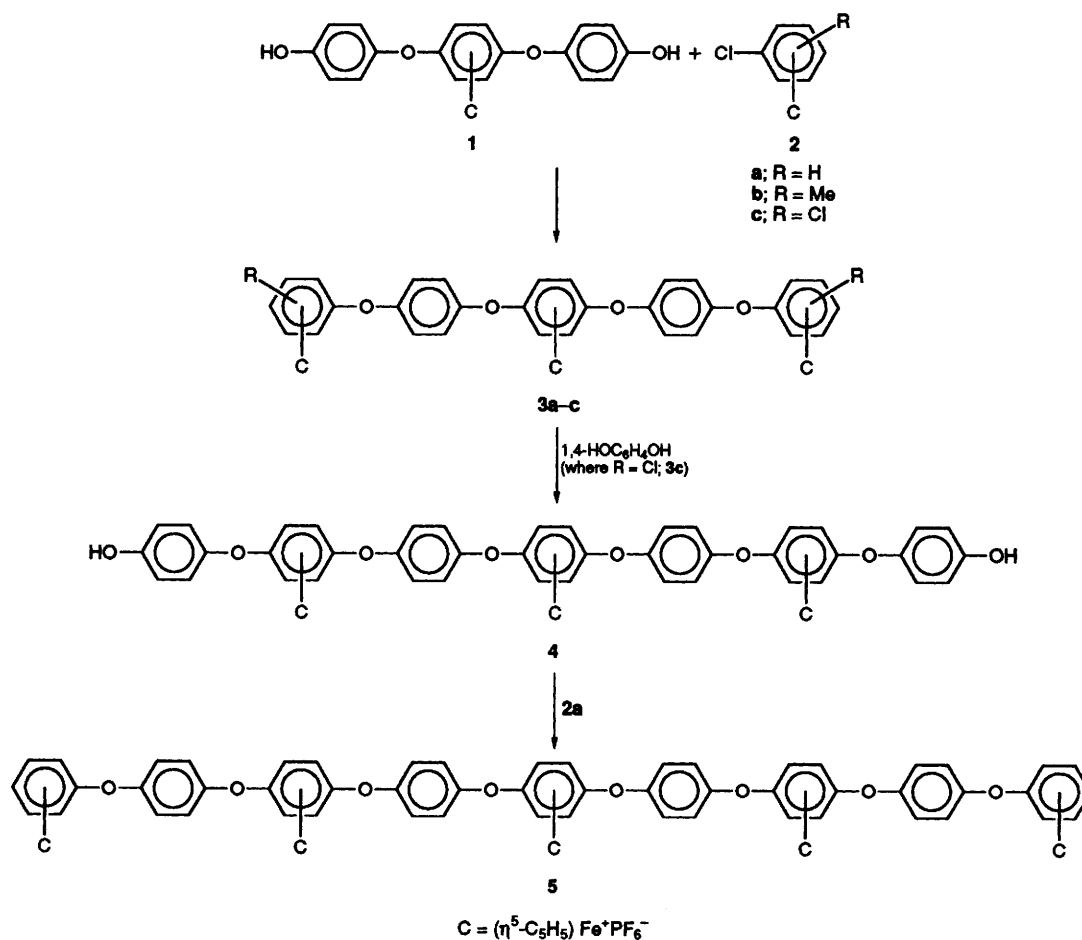
Polyaromatic ethers and thioethers with pendent cyclopentadienyliron moieties have been prepared in very high yield using a highly efficient and mild methodology.

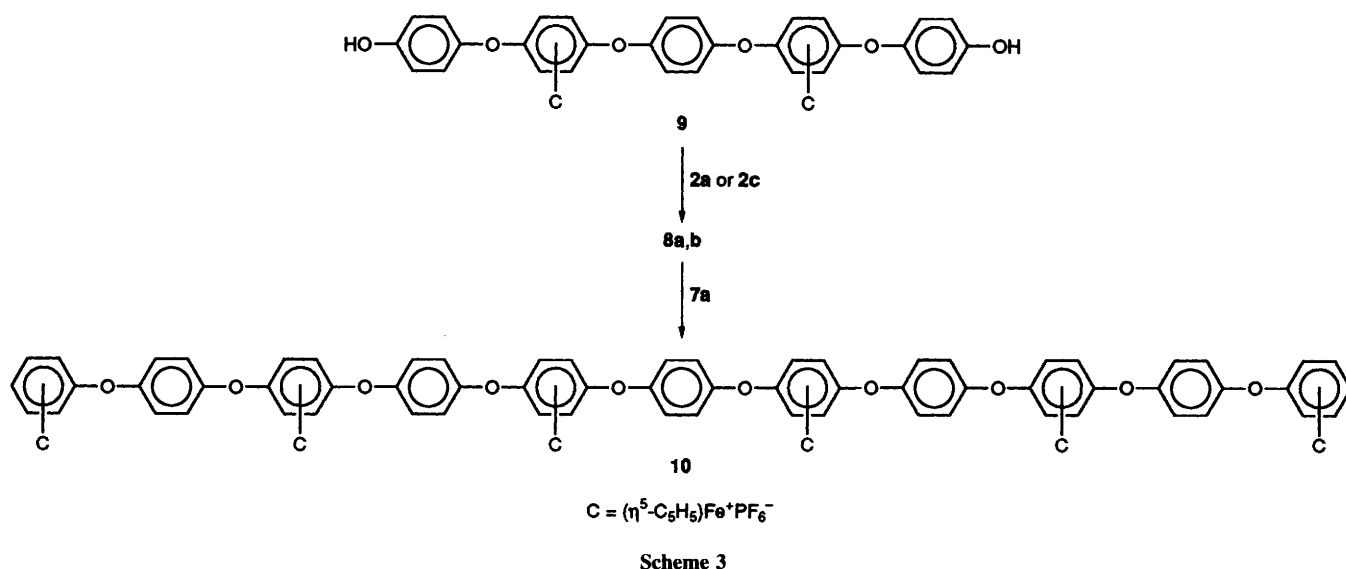
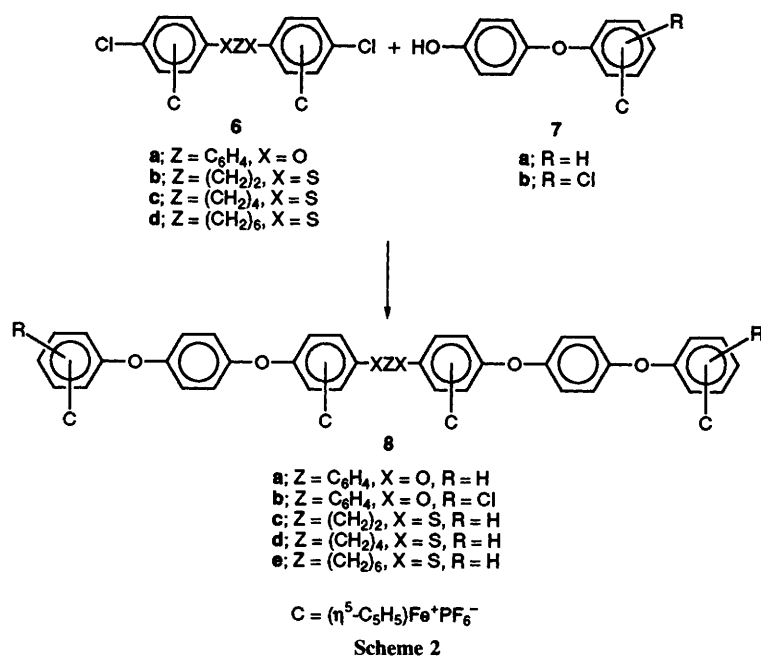
Although the field of organometallic polymers is relatively new, recent discoveries indicate the tremendous potential of these polymers in material science. Considerable attention is being given to their thermal and electrical properties. These polymers are being applied to the development of rechargeable batteries, the modification of the redox properties of certain electrodes, electrocatalysis, medicinal chemistry and many other fields.¹⁻⁵ One important subclass of organometallic polymers is the pendent-type, in which the metal moiety is attached to the polymer backbone.⁶⁻⁹ To date, there are few reports where the rutheniumcyclopentadienyl moiety was pendent to the backbone of a polymer.^{10,11} Here, we report the first example of the synthesis of poly(cyclopentadienyliron) arene complexes with oxygen and sulfur linkages.

Our research has been focused on the synthesis, functionalization and applications of bis(cyclopentadienyliron) arene complexes containing oxygen, sulfur and nitrogen bridges.¹²⁻¹⁴ We are now investigating the synthesis of poly(cyclopentadienyliron) complexes and have discovered that there are few feasible routes which lead to the formation of these materials. It should be noted, however, that there are two routes that we have exploited to date. The first involves

the reaction of a dihydroxyaromatic nucleophile with a cyclopentadienyliron complex of *p*-dichlorobenzene to produce the monoiron species with terminal phenolic groups. These then act as dinucleophiles in the reaction with substituted chlorobenzene complexes to give polyaromatic ether complexes with an odd number of cyclopentadienyliron moieties. As a model experiment, 4,4'-di-(4-hydroxyphenoxy) benzene complex, **1**, was treated with the chlorotoluene complex, **2b**, in a molar ratio of 1:2, in the presence of an excess of potassium carbonate in DMF, at room temp. for 16 h. The resulting triiron complex, **3b**, was isolated by filtration into 10% HCl, followed by the addition of a concentrated aqueous solution of ammonium hexafluorophosphate to yield a yellow solid in 96%.[†] Using the same methodology, we have also carried out the reaction with chlorobenzene and isomeric dichlorobenzenes (Scheme 1). The yields of these reactions varied from 83–96%. It was possible to increase the number of pendent metal moieties to five by further reaction of the triiron complex as illustrated in Scheme 1.

The second route which allows for the synthesis of even numbered metallic moieties involves the reaction of a diiron complex with a monoiron containing nucleophile in a 1:2





molar ratio to produce the tetrametallic species, which could then be modified to give the hexametallal species (Scheme 2 and 3). To further explore the flexibility of our synthetic strategy we carried out similar reactions with sulfur containing bimetallic complexes as our starting material. As an example, complex **6d** was treated with **7a** in a 1:2 molar ratio using the above-described reaction conditions, to produce the tetrairon ether–thioether mixed system, **8e**, in a 86% yield (Scheme 2).[†] The change in the methylene chain length of the dithiol bridge from 2–6 resulted in a decrease in the reaction yield. In a similar manner, we were able to prepare the tetrairon species where complex **8a** or **b** could be prepared *via* the reaction of complex **9** with **2a** or **2c**. Following this reaction, the hexairon species was synthesized as shown in Scheme 3.

The efficiency of this methodological approach, which was implemented to make these types of new building blocks for polymeric materials, enabled us to control the size and nature of the backbone linkage of these polymeric materials.

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Footnotes

[†] Satisfactory analytical data were obtained for all synthesized complexes. Selected data for new complexes. **3b**: ¹H NMR (200 MHz, CD₃COCD₃): δ 2.52 (s, 6 H, CH₃), 5.22 (s, 5 H, Cp), 5.34 (s, 10 H, 2 Cp), 6.30–6.41 (m, 12 H, complexed ArH), 7.58 (s, 8 H, uncomplexed ArH); ¹³C NMR (50.3 MHz, CD₃COCD₃): 19.92 (CH₃), 75.45 (4 C, complexed ArC), 76.74 (4 C, complexed ArC), 78.51 (10 C, 2 Cp), 78.96 (5 C, Cp), 87.80 (4 C, complexed ArC), 101.54 (2 C, quaternary complexed ArC), 124.33 (4 C, uncomplexed ArC), 124.43 (4 C, uncomplexed ArC), 132.24 (2 C, quaternary complexed ArC), 133.67 (2 C, quaternary complexed ArC), 151.92 (2 C, quaternary uncomplexed ArC), 152.08 (2 C, quaternary uncomplexed ArC).

[‡] NMR data for **8e**: ¹H NMR (CD₃COCD₃): 1.59 (m, 4 H, CH₂), 1.81 (m, 4 H, CH₂), 3.25 (t, *J* 7.3 Hz, CH₂), 5.22 (s, 10 H, Cp), 5.26 (s,

10 H. Cp), 6.31–6.52 (m, 18 H, complexed ArH), 7.58 (s, 8 H, uncomplexed ArH); ^{13}C NMR (CD_3COCD_3): 28.78 (2 C, CH_2), 29.04 (2 C, CH_2), 32.95 (2 C, CH_2), 76.61 (4 C, complexed ArC), 77.58 (10 C, Cp), 78.11 (4 C, complexed ArC), 79.66 (10 C, Cp), 83.95 (4 C, complexed ArC), 85.85 (2 C, complexed ArC), 87.81 (4 C, complexed ArC), 107.34 (2 C, quaternary complexed ArC), 124.34 (4 C, uncomplexed ArC), 124.46 (4 C, uncomplexed ArC), 133.18 (2 C, quaternary complexed ArC), 134.69 (2 C, quaternary complexed ArC), 151.79 (2 C, quaternary complexed ArC), 151.95 (2 C, quaternary uncomplexed ArC).

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