Multilayered iron complexes of [2.2]paracyclophane

(cyclophanes/transition metal complexes/photochemical and Lewis acid-catalyzed arene-metal exchanges)

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ABSTRACT Recent syntheses of ruthenium complexes of [2.2]paracyclophane provided a highly interesting class of compounds, the multilayered transition metal complexes of cyclophanes. The present study discloses that arene-metal exchange procedures with ferrocene derivatives, effected either photochemically or by Lewis acid catalysis, are convenient methods for preparing the analogous multilayered iron complexes of [2.2]paracyclophane.

The era of cyclophane chemistry was opened by Cram's syntheses of paracyclophanes (1), and in his first paper he noted that the electronic spectra of [2.2]- and [3.3]paracyclophane differed from those of higher members of the series as well as acyclic analogs. However, an appreciation for the fact that cyclophanes with benzene decks held in close face-to-face proximity, as is true of all cyclophanes with two-carbon bridges, behave as one π-electron system came out of later ESR (2) and photoelectron (3-5) spectral studies. Because all of the symmetrical [2]cyclophanes are now known (6), an important question to answer was whether such cyclophanes are capable of forming transition metal complexes at each face of the cyclophane. If such complexes could be formed, then polymers (1) of the type shown below for [2.2]paracyclophane would be possible in which the whole of the polymer molecule might behave as one delocalized π-electron system.

Past attempts to prepare multilayered chromium complexes of cyclophanes, using the standard procedures with chromium hexacarbonyl (7-10) or chromium metal atoms (11) had not been useful for this purpose. However, recently we were able to show that the Bennett procedure for making bis(arene)-ruthenium(II) complexes from bis(arene)dichloro-di-μ-chloro-diruthenium(II) (12, 13) proceeds smoothly in good yield with [2.2]paracyclophane to give the double- and triple-layered ruthenium(II) complexes 2 and 3 (14).

One of the most studied examples of electron delocalization in a transition metal complex is that of the bis(fulvalene)diiron mixed-valence compound (4), for which Mossbauer spectroscopy has shown the two iron atoms to be equivalent (15). Similar studies of mixed-valence compounds derived from multilayered iron complexes of cyclophanes would be highly desirable.

Thus, we undertook experiments to prepare such iron complexes, both to have examples of complexes with a different metal than ruthenium and also to obtain transition metal complexes of cyclophanes suitable for Mossbauer spectral studies. Both Nesmeyanov et al. (16) and Sutherland and coworkers (17) have reported that ferrocene undergoes ligand exchange with arenes when treated with aluminum chloride and aluminum metal at elevated temperatures. When these conditions were investigated with [2.2]paracyclophane, we found that conversion to the corresponding triple-layered iron complex (5) occurred smoothly and the complex could be isolated as the corrsponding hexafluorophosphate derivative in 63% yield.

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More recently Gill and Mann (18) have shown that irradiation of \((\eta^5\text{-p-xylene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}\) hexafluorophosphate in methylene chloride with sunlight in the presence of arenes leads to arene exchange. Applying this method to [2.2]paracyclophane led to the isolation of the double-layered iron complex 6 in good yield. Although the formation of 5 was not observed in this case, repetition of the experiment using a higher ratio of \((\eta^5\text{-p-xylene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}\) hexafluorophosphate to [2.2]paracyclophane led to the isolation of 5 by this method as well.

In view of the ease with which multilayered iron complexes of [2.2]paracyclophane are formed, the preparation of iron complexes with various other \([2n]\)cyclophanes, as well as their oligomers and polymers, should be rewarding to investigate.

**EXPERIMENTAL**

\((\eta^5\text{-}[2.2]\text{Paracyclophane})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}\) Hexafluorophosphate, 6. A nitrogen-deaerated solution of \((\eta^5\text{-p-xylene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}\) hexafluorophosphate (320 mg, 0.860 mmol) and [2.2]paracyclophane (896 mg, 4.30 mmol) in dry methylene chloride was irradiated with visible light (General Electric reflector flood lamp, 150 W) for 3 hr and 50 min. The reaction mixture was filtered through glass wool before the solvent was removed under reduced pressure. The resulting solid was washed repeatedly with hot heptane to remove all traces of excess [2.2]paracyclophane. This gave 546 mg (85%) of a pure orange solid. Recrystallization of a sample from ethanol gave orange crystals; mp 258–260°C with decomposition; \(^1\text{H}\) NMR (in deuterated acetone), \(\delta\) (in ppm relative to tetramethylsilane) 2.94–3.30 (8H, multiplet, –CH\(_2\)–), 4.82 [5H, singlet, ArH (cyclopentadiene)], 5.76 (4H, singlet, ArH), and 6.70 (4H, singlet, ArH).

**Analysis.** Calculated for C\(_{21}\)H\(_{18}\)F\(_6\)FeF: C, 53.19; H, 4.46. Found: C, 53.38; H, 4.19.

When the above experiment was repeated using a 4:1 molar ratio of \((\eta^5\text{-p-xylene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)}\) hexafluorophosphate to [2.2]paracyclophane, the triple-layered complex 5 was isolated in poor yield. Optimal conditions for forming 5 by the irradiation procedure have not been explored.

\[(\eta^5\text{-}[2.2]\text{Paracyclophane}):(\eta^5\text{-cyclopentadienyl})\text{iron(II)}\]

Bis(hexafluorophosphate), 5. A mixture of ferrocene (2.35 g, 12.6 mmol), aluminum chloride (4.65 g, 34.9 mmol), aluminum powder (0.075 g, 2.75 mmol), and [2.2]paracyclophane (503 mg, 2.41 mmol) in dry decalin (20 ml, passed through alumina, activity 1) was heated at 160°C for 4 hr under a nitrogen atmosphere. The reaction mixture was cooled in an ice bath before dropwise addition of 20 ml of distilled water. The resulting mixture was washed from the reaction vessel with 50 ml of water followed by 50 ml of diethyl ether. The aqueous layer was filtered and the filtrate was washed with two 100-ml portions of ether. The aqueous layer was then filtered again and a solution of 10 g of ammonium hexafluorophosphate in 15 ml of water was added to the filtrate. The solid that precipitated was collected by filtration and dried overnight at 40°C under reduced pressure. The resulting product was dissolved in nitromethane and reprecipitated by addition of anhydrous ether. After collection of the precipitate by filtration and drying, there was isolated 1.13 g (63%) of a tan powder; mp, decomposed above 225°C; \(^1\text{H}\) NMR (in deuterated acetone), \(\delta\) 3.25 (8H, singlet, –CH\(_2\)–), 4.92 [10H, singlet, ArH (cyclopentadiene)], and 5.96 (8H, singlet, ArH); \(^13\text{C}\) NMR (in deuterated dimethyl sulfoxide) \(\delta\) (in ppm relative to tetramethylsilane) 116.8 (cyclopentadiene-CH), 82.61 (Ar-C), 73.36 (Ar-CH), and 29.03 (–CH\(_2\)–).

**Analysis.** Calculated for C\(_{26}\)H\(_{26}\)F\(_2\)Fe\(_2\)P\(_2\): C, 42.20; H, 3.54. Found: C, 43.44; H, 3.74.

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