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LETTER

The synthesis of new di(cyclopentadienyliron) complexes of polyaromatic ethers

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The most facile route known for the synthesis of η^6,η^6-arene-bis(η^5-cyclopentadienyliron) dications is the Lewis acid-catalyzed ligand exchange reactions [1, 2]. While the ligand exchange reaction is a successful route to the synthesis of some polyaromatic and heterocyclic aromatic complexes, this method suffers from poor yields, as well as the difficulty of introducing some functional groups [2]. In this letter, we would like to report a new and interesting synthesis of some dicationic complexes of polyaromatic ethers, along with a preliminary investigation of their electronic and structural properties. The prepared complexes will serve as models for more extensive multinuclear systems, and could possibly act as electron reservoirs [3].

Nucleophilic substitution reactions of chloroarene complexes with various carbon, nitrogen, oxygen and sulfur containing nucleophiles have been extensively investigated [4]. To the best of our knowledge, there has been no report of a one-step double nucleophilic substitution reaction leading to arene–di(cyclopentadienyliron) complexes. In the present work, we have carried out such reactions between the chlorobenzene complex (I) and dioxygen nucleophiles (**IIa–e**) in a THF/DMF solvent mixture under nitrogen atmosphere for 8 h at 65 °C. The reaction proceeded smoothly, resulting in the formation of di(cyclopentadienyliron) complexes of aromatic ethers, which were isolated in high yield (70–95%) as hexafluorophosphate salts (Scheme 1). The elemental analyses of all complexes (**IIIa–e**) were found to be satisfactory. Chemical shifts and splitting patterns of both proton and carbon signals observed in high-resolution ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were in full agreement with expectations (Table 1). The symmetry that these complexes possess, as well as their very flexible ether linkages, lead to simple and sharply defined NMR spectra. Low temperature ^{1}H and ^{13}C NMR of the complexes were also recorded, however the spectra remain unchanged even at temperatures as low as −90 °C. Similar results have been obtained for a chromium complex of 1,3,5-triphenylbenzene, in which a $Cr(CO)_3$ moiety is bound to each of the three outer rings [5]. Our results indicate that the barrier to rotation about the ether linkage is too low to observe any possible loss of degeneracy in nuclei that are equivalent at room temperature.

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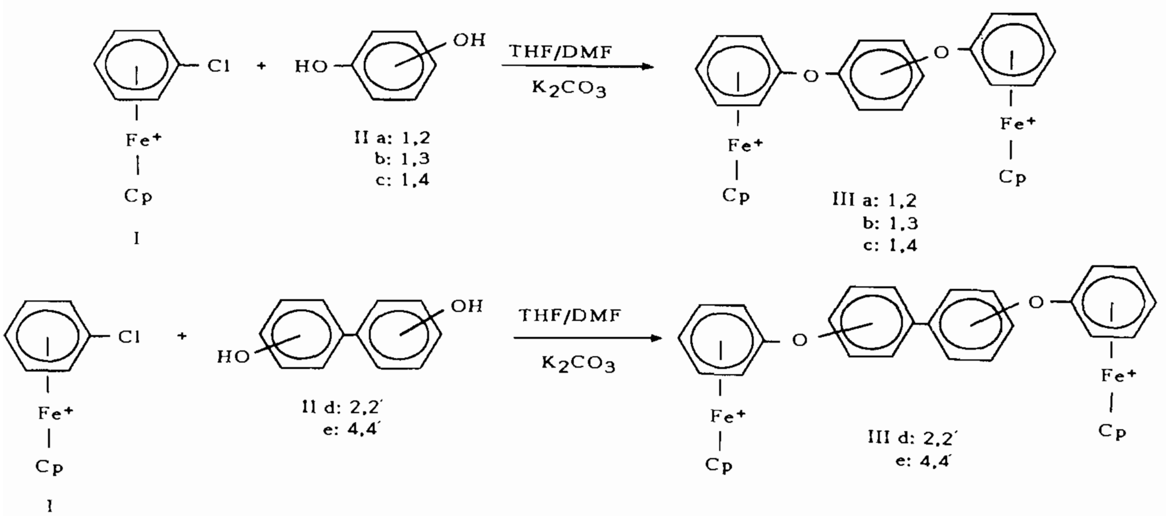

Scheme 1.

TABLE 1. ^1H and ^{13}C NMR chemical shift data (in ppm, referenced to $(CD_3)_2CO$) for the di(cyclopentadienyliron) complexes of polyaromatic ethers, at 20 °C

Complex number	Cp		Complexed aromatics		Uncomplexed aromatics	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
IIIa	5.21 (10H, s)	78.35 (10C)	6.49–6.41 (8H, m) 6.32 (2H, t, J=5.9 Hz)	78.00 (4C), 86.40 (2C), 87.94 (4C), 133.32^a (2C)	7.71–7.69 (2H, m) 7.61–7.59 (2H, m)	124.21 (2C), 129.39 (2C), 145.30^a (2C)
IIIb	5.25 (10H, s)	78.09 (10C)	6.51–6.43 (8H, m) 6.31 (2H, t, J=5.8 Hz)	78.22 (4C), 85.95 (2C), 87.71 (4C), 133.79^a (2C)	7.75 (1H, t, J=8.2 Hz) 7.44 (1H, br s) 7.38 (2H, d, J=8.2 Hz)	114.26 (1C), 119.29 (2C), 133.51 (1C), 155.69^a (2C)
IIIc	5.26 (10H, s)	78.21 (10C)	6.46 (8H, br s) 6.32 (2H, br s)	77.79 (4C), 85.93 (2C), 87.93 (4C), 134.73^a (2C)	7.59 (4H, s)	124.47 (4C), 151.91^a (2C)
IIId	5.00 (10H, s)	78.16 (10C)	6.37 (8H, br s) 6.23 (2H, m)	78.75 (4C), 86.07 (2C), 87.77 (4C), 133.54^a (2C)	7.63–7.41 (8H, m)	121.22 (2C), 127.42 (2C), 130.43^a (2C), 131.75 (2C), 133.30 (2C), 152.17^a (2C)
IIIe	5.28 (10H, s)	78.13 (10C)	6.52–6.45 (8H, m) 6.32 (2H, t, J=5.8 Hz)	78.19 (4C), 85.98 (2C), 87.92 (4C), 134.71^a (2C)	7.90 (4H, d, J=8.6 Hz) 7.47 (4H, d, J=8.6 Hz)	122.23 (4C), 130.11 (4C), 138.85^a (2C), 154.02^a (2C)

^{a}Quaternary carbon atoms.

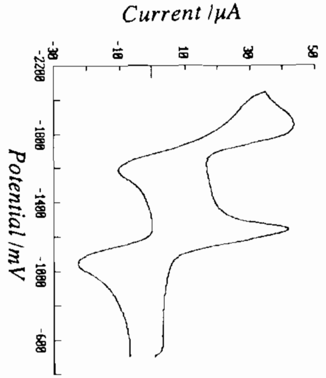

Fig. 1. Cyclic voltammogram at hanging mercury drop electrode of 0.1 mM complex **IIIa** in 0.1 M tetrabutylammonium perchlorate in DMF, ν=40 V/s. Pt wire and Ag/AgCl/KCl(sat.) served as the auxiliary and reference electrode, respectively.

The flexibility of the ether bridging ligands has further consequences for the electronic properties of these complexes. Cyclic voltammograms for all complexes have been obtained. The cyclic voltammetric experiments were performed using a conventional three electrode system. As an example, the voltammogram of complex **IIIa**, which was recorded at a sweep rate of 40 V/s, is provided (see Fig. 1). The voltammograms of all five complexes reveal two reduction steps, requiring sweep rates in excess of 10 V/s to observe the chemical reversibility of these steps. For all complexes, the $E_{1/2}$ values of the first reduction step range from −1.27 to −1.29 V, while the range for the second reduction step is −1.98 to −2.04 V. The cyclic voltammograms of these dications appear to be quite similar to those of related monocations we have studied previously [6]. However, it appears that both reduction steps consist of two unresolved one electron transfers, indicating an isolation of the redox centers. This phenomenon has been previously noted for the reduction of the η^6,η^6-terphenyl-bis(η^5-cyclopentadienyliron) dication as well [7]. Our results indicate that there is weak bridge mediated electron-exchange interaction, due to the minimal conjugation along the bridging ligand, and that the Fe–Fe distance would be too large to allow any direct electron exchange. More extensive electrochemical investigations are underway, including the determination of the kinetics of following chemical reactions, as well as the effects of solvent and temperature. X-ray structural analysis of selected complexes will also be communicated in due course.

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References

1 W. H. Morrison, Jr., E. Y. Ho and D. N. Hendrickson, *J. Am. Chem. Soc., 96* (1974) 3606.

2 R. G. Sutherland, M. Iqbal and A. Piorko, *J. Organomet. Chem., 302* (1986) 307.

3 (a) M. Lacoste, F. Varret, L. Toupet and D. Astruc, *J. Am. Chem. Soc., 109* (1987) 6504; (b) M. Lacoste, H. Rabaa, D. Astruc, N. Ardoin, F. Varret, J. Saillard and A. Le Beuze, *J. Am. Chem. Soc., 112* (1990) 9548.

4 (a) C. C. Lee, A. S. Abd-El-Aziz, R. L. Chowdhury, U. S. Gill, A. Piorko and R. G. Sutherland, *J. Organomet. Chem., 315* (1986) 79; (b) C. C. Lee, A. S. Abd-El-Aziz, R. L. Chowdhury, A. Piorko and R. G. Sutherland, *Synth. React. Inorg. Met.-Org. Chem., 16* (1986) 541; (c) A. S. Abd-El-Aziz, C. C. Lee, A. Piorko and R. G. Sutherland, *J. Organomet. Chem., 348* (1988) 95.

5 B. Mailvaganam, B. E. McCarry, B. G. Sayer, R. E. Perrier, R. Faggiani and M. J. McGlinchey, *J. Organomet. Chem., 335* (1987) 213.

6 (a) A. S. Abd-El-Aziz, A. S. Baranski, A. Piorko and R. G. Sutherland, *Inorg. Chim. Acta, 147* (1988) 77; (b) A. S. Abd-El-Aziz, K. Winkler and A. S. Baranski, *Inorg. Chim. Acta, 194* (1992) 207.

7 W. H. Morrison, Jr., E. Y. Ho and D. N. Hendrickson, *Inorg. Chem., 14* (1975) 500.