The facile preparation of macrocyclic ethers is achieved using $S_NAr$ reactions of (dichlorobenzene)$\text{Cr}^{III}$ complexes with various dinucleophiles, followed by photolytic demetallation; X-ray crystallography gives unequivocal structural proof for one of these macrocycles.

Cyclic polyethers are important synthetic targets owing to their selective complexation and chiral recognition.$^{1-3}$ Interest in these materials originates from the size and nature of their cavity, which dictates whether or not such materials are capable of binding with other compounds.$^{2}$ Although a great deal of attention has been directed toward the encapsulation abilities of supramolecules, there is a growing interest in the synthesis of cyclic aryl ethers.$^{1-3}$ These compounds are appealing since the rigidity and stability of their structures greatly reduces conformational freedom which may allow chiral recognition or catalysis at high temperature or in hostile environments.$^{4,4}$ Mullins et al. reported that cyclic aryl ethers may be subjected to ring-opening polymerization to produce linear polyethers without the release of side-products.$^{4,4}$ Here, we report the synthesis of four new cyclic aryl ethers, and the crystal structure of 8 utilizing temporary complexation to the cyclopentadienyl-iron (CpFe$^+$) moiety.

The molecular design and controlled synthesis of aromatic polyethers with pendant CpFe$^+$ moieties has been a focus of our recent research. The complexation of chloroarenes to the CpFe$^+$ moiety has allowed nucleophilic aromatic substitution ($S_NAr$) reactions to take place with a large number of dinucleophiles.$^6$ This methodology has enabled us to prepare a number of oligomeric ethers, thioethers and amines under very mild experimental conditions. Owing to the paucity of existing methods for the preparation of cyclic aryl ethers, we have been exploring new routes for the synthesis of such materials. A drawback of the existing methods is the need for electron withdrawing substituents on the haloarene ring to promote the substitution reactions.$^5$ The ease of complexation and demetallation of the CpFe$^+$ to the arene systems shows the advantages of our methodology. The stepwise displacement of both chloro groups in [(η$^6$-1,2-dichlorobenzene)(η$^5$-cyclopentadienyl)]iron(II) hexafluorophosphate 10 or [(η$^6$-1,3-dichlorobenzene)(η$^5$-cyclopentadienyl)]iron(II) hexafluorophosphate 1 with a variety of dinucleophiles has allowed for the facile preparation of macrocycles 8, 9, 17, and 18. To our knowledge there are few reports which outline the preparation of macrocyclic materials using $S_NAr$ reactions of substituted chlorobenzenes activated by temporary complexation to a metal moiety.$^7$ The preparation of dibenzo crown ethers was achieved via the $S_NAr$ reactions of (o-dichlorobenzene)-Cr(CO)$_3$ with diethylene glycol and bis(2-mercaptopethyl) ether.$^{7,7}$ A disadvantage of this particular synthetic method is the implementation of harsh reaction conditions in order to obtain the desired products in rather modest yields.

Scheme 1 outlines the reaction sequence employed for the preparation of cyclic aryl ethers 8 and 9. The initial reaction of complex 1 and dinucleophile 2 or 3 in a 2:1 molar ratio was carried out in order to obtain the bimetallic complex (4 or 5) in high yield. The reaction of 4 or 5 with 2 in an equimolar ratio led to the formation of complexed cyclic aryl ethers 6 and 7 in yields of 86 and 89%, respectively. The rigid nature of these complexed macrocycles introduces both cis- and trans-orientations of the CpFe$^+$ moieties attached to the arene ring.$^8$ The presence of two different cyclopentadienyl (Cp) resonances as well as a complex aromatic region in the $^1$H NMR spectra indicated that there was a mixture of both cis and trans products present. Based on the integration of the respective Cp resonances, it was determined that for complex 6 the ratio was 3:1 while it was 1:1 for complex 7. The major structure was predicted to be trans based on previous findings.$^8$

Photolytic demetallation was implemented to allow for the recovery of the free organic macrocycles 8 or 9 in yields of 64 and 58%, respectively, which may be attributed to the poor solubility of these macrocyclic materials in most organic solvents.

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solvents. The $^1$H NMR spectra indicated the symmetric nature of these materials. It was noted that a triplet was present at a diagonal distance of 5.2 Å while the diagonal distance of oxygen atoms was found to be 10.9 Å.

Scheme 2 illustrates that an analogous sequence of reactions may be employed with the (o-dichlorobenzene)CoFe$^+$ complex (10) and dinucleophiles containing both aliphatic and aromatic bridges. In this fashion, macrocyclic compounds 17 and 18 with both oxygen and sulfur bridges were prepared. Once again NMR spectroscopy and elemental analyses were used to confirm the structure of all new materials. Unlike the rigid macrocycles prepared in Scheme 1, these structures have no inner ring protons and as a result no high field chemical shifts were observed.

This is the first example of iron cyclopentadienyl mediated cyclic aryl ether synthesis. The presented methodology will enable us to prepare a variety of these cyclic compounds under mild experimental conditions and in very high yields. An additional benefit of this process is the ability to isolate the intermediate bimetallic complex prior to ring closure. It has been demonstrated that it is possible to prepare both symmetric and asymmetric cyclic aryl ethers depending on the nucleophile used to close the macrocycle. Further investigations aimed at increasing the cavity size and varying the nature of the substituents are in progress and will be reported in due course.

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Footnotes and References
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† Crystal data for 8. Colourless crystals from CHCl$_3$, crystal dimensions 0.40 x 0.20 x 0.20 mm, monoclinic, space group $P2_1/c$, $a = 6.0546(16)$, $b = 16.093(2)$, $c = 13.514(4)$, $\alpha = 90$, $\beta = 90$, $\gamma = 90$, $R = 0.058$, $wR = 0.050$. CCDC 182696.