Synthesis of Macrocyclic Compounds containing the Ferrocene Unit

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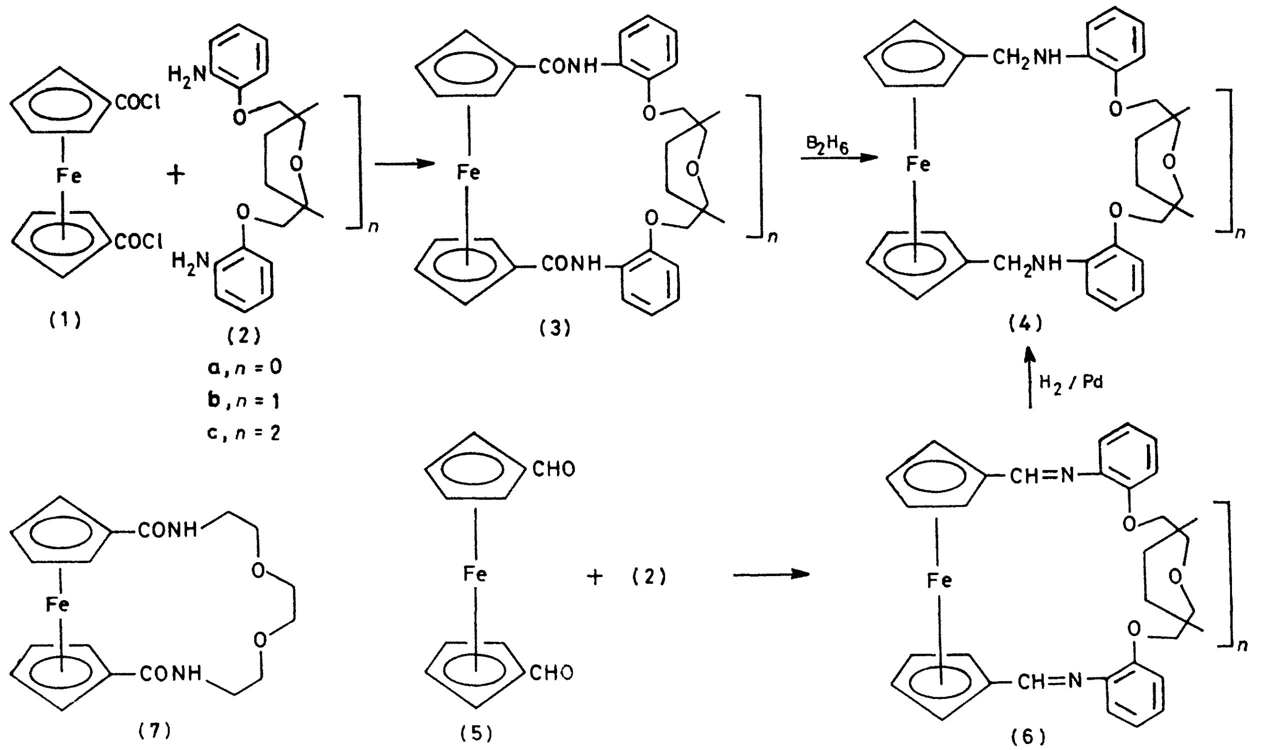
Summary The synthesis and n.m.r. spectra (^{1}H and ^{13}C) of macrocyclic compounds containing the ferrocene unit as an integral part of the macrocyclic skeleton are reported.

A LARGE number of macrocyclic compounds containing oxygen, sulphur, and nitrogen as the common electron donor heteroatoms are now known.[1–5] These compounds are capable of complexing a wide variety of metallic and organic cations, often with a high degree of specificity[1–4] and this property has been utilised in phase-transfer catalysis,[6] selective ion transport,[2b] resolution of chiral molecules[7] and to some extent, electron transport studies.[5b]

We set out to synthesise compounds with a metal atom incorporated in a macrocyclic skeleton with a view to studying the effect of such a metal atom on the complexing ability of the macrocycle. This communication



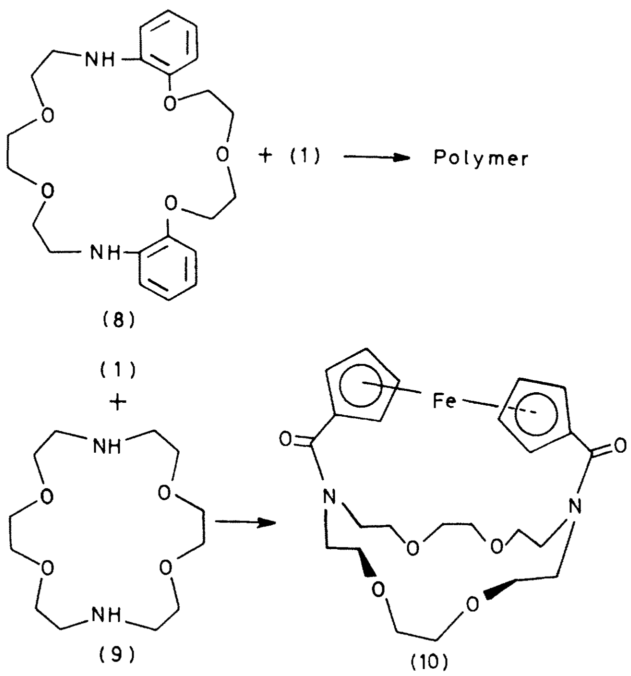
SCHEME 1

reports the synthesis of macrocycles and cryptands containing the ferrocene unit.

Compounds of types (**3**) and (**4**) were prepared by either of the routes shown in Scheme 1[5,8] with overall yields based on (**2**), of *ca.* 60%.† In addition, macrocycles with entirely aliphatic polyether substructures [*e.g.* (**7**)] were synthesised by the ferrocene bis-acid chloride route. At present the route *via* the amides (**3**) is preferred since, in our hands, the literature method[9] to the ferrocene bis-aldehyde (**5**) gave poor yields.‡ However, the reduction of (**3**) to the amine (**4**) using diborane requires several days at room temperature and other reducing agents are not successful.

The ^{1}H and ^{13}C n.m.r. data for (**3**), (**4a**), and (**7**) are consistent with the proposed structures. It is noticeable that for the amides, the phenyl proton *ortho* to the acylamido group is downfield of the rest and the 2,5 (and 2′,5′) protons of the cyclopentadiene rings lie in the deshielding cone of the carbonyl group. It seems likely, therefore, that the cyclopentadiene and phenyl rings are co-planar and model studies indicate that this is a very reasonable, unstrained geometry. As expected, none of the phenyl or cyclopentadiene protons of the amine (**4**) show any deshielding but the NCH_2 carbon of (**4**) appears at 42·6 p.p.m. thus confirming the reduction of the carbonyl group which resonates at *ca.* 167 p.p.m. in the ^{13}C n.m.r. spectra of (**3**).

As shown by attempts to extract metal picrates from aqueous solution into methylene chloride solutions of the macrocycles,[10] the amides showed only weak, if any, complexing capacity for Li^+, Na^+, or K^+ ions. Likewise, the only amine isolated in any quantity (n = 0) also failed to extract significant amounts of picrates. This unexpected result is probably due to the rigidity of the molecule and the small size of the cavity although it is known that lack of symmetry within macrocycles reduces the ion-binding capacity considerably.[4]



SCHEME 2

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† All the compounds gave the correct elemental analyses for C, H, and N and had i.r. spectra consistent with the proposed structures.

‡ We have since developed a method using a modified Vilsmeier proceedure which gives yields of (**5**) of *ca.* 60%.

In consequence, attempts were made to prepare cryptands containing the ferrocene unit Condensation of macrocycles of type (**8**) with (**1**) led only to polymeric amide (Scheme 2) Presumably the rigidity of the dibenzo-macrocyclic amines prevents efficient cyclisation but the observation that these polymers complexed metal ions encouraged further attempts to synthesise the cryptands Success was achieved using diaza-18-crown-6 (**9**)[11] and (**1**) when (**10**) was obtained in 30% yield (*cf* refs 11b and 12 for a similar synthetic approach) The mass spectrum of this material exhibits a parent peak at *m/e* 500 and the ^{1}H and ^{13}C n m r spectra are consistent with the proposed structure although it is impossible to decide whether the carbonyls are *cis* or *trans* to each other and further work will be necessary to confirm the assignments of the ferrocenyl and methylene carbons in the region from 73·4 to 69·5 p p m

Preliminary studies indicate that this cryptand extracts metal picrates from aqueous solution into methylene chloride with a remarkable degree of specificity which follows the order, $Ca^{2+} >> Li^{+} > Mg^{2+} \simeq Na^{+} >> K^{+}$ Work is in progress to establish the effect of variations of the macrocyclic structure on the oxidation potential of the bound iron(II) ion and the redox potential of any guest cations

We thank the S R C for financial assistance

(*Received*, 13*th November* 1979, *Com* 1184)

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