Synthesis, N.m.r. Spectra, and Structure of Macrocyclic Compounds containing the Ferrocene Unit

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The condensation of 1,1'-bis(chlorocarbonyl)ferrocene with diaza-18-crown-6 gives 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diyldicarbonyl)ferrocene (5) together with its dimer 1,1'': 1',1'''-bis-(1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane-7,16-diyldicarbonyl)bisferrocene (6) and the separation and isolation of these compounds are described. High resolution ^1H and ^{13}C n.m.r. spectra using homo- and hetero-nuclear decoupling techniques allow a complete assignment of the spectral data for (5) and (6) and lead to a proposal of a structure for (5) involving a *trans*-disposition of the amide carbonyl groups. Variable-temperature n.m.r. data on (6) reveal two distinct dynamic processes within the molecule involving rotation about the ferrocene-carbonyl bond ($\Delta G^\ddagger = 50$ kJ mol^{-1}, $T_c = -10$ °C) and rotation about the N$-$CO bond ($\Delta G^\ddagger = 67$ kJ mol^{-1}, $T_c = +60$ °C). The preparation, ^1H and ^{13}C n.m.r. data of monocyclic compounds containing the ferrocene unit (13a—c), (14) and (15) are also described and the details of the synthesis of an ^{15}N-labelled analogue of (13c), the macrocycle (16), are reported.

A large number of macrocyclic compounds containing oxygen, sulphur, and nitrogen as the electron donor heteroatoms are now known.[1,2] Many of these compounds are capable of forming complexes with a wide variety of metallic and organic cations, with a high degree of specificity for particular cations dependent upon ring size and the nature of the heteroatoms.[1-3] In consequence macrocyclic compounds have found applications in areas such as phase-transfer catalysis,[1c,4] selective ion transport,[5,6] resolution of chiral molecules,[7] and to some extent in the study of electron transport.[2d]

One area of recent interest has been that of dinuclear cryptates in which two metal ions are complexed to the same cryptand.[8,9] Lehn has demonstrated viable synthetic routes to homonuclear complexes (1) and heteronuclear complexes (2) the latter involving co-ordination with two different metal ions.[9] Interest in dinuclear cryptates has been stimulated by the recognition that these compounds can facilitate the study of cation-cation interactions at short distances leading to electron transfer and may also act as simple models for many enzymes which have two metal ions held in close proximity at their active sites.[10]

The present work considered a novel approach to the synthesis of molecules analogous to dinuclear cryptates by the design of a series of macrocycles with a metal atom locked in the σ/π-bond framework of the macrocycle itself.[11] The metallocenyl moiety was assessed as being particularly suitable for this approach because of its stability and it was decided to condense a ferrocenyl unit with a selection of bidentate and macrocyclic ligands, all having the ability to complex a second metal ion. The results of these syntheses, together with details of the n.m.r. spectra of the products, are reported below.

Results and Discussion

Condensation of 1,1'-bis(chlorocarbonyl)ferrocene (3) with diaza-18-crown-6 (4) under conditions of high dilution, gave the cryptand (5) as the major product together with its dimeric analogue (6). The products were separated by column chromatography on alumina and both elemental analyses and mass spectra were consistent with the proposed molecular formulae. The ^{13}C and ^1H n.m.r. spectra of (5) and (6) are quite different (*vide infra*) but, nevertheless, consistent with the proposed monomeric and dimeric structures. Compound (5) has also been reported by Vögtle[12] but no detailed n.m.r. data was published and there was no mention of (6) as a co-product.
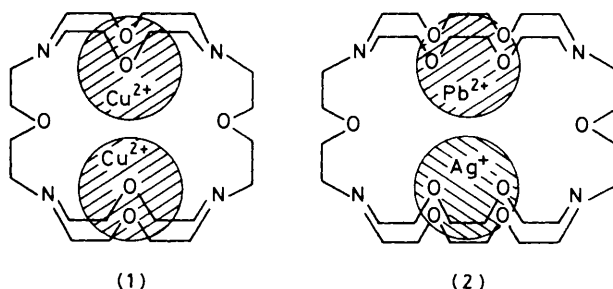

(1)　　　　　　　(2)

Table 1. ^{13}C and ^1H (δ values) N.m.r. data of (5) in CDCl$_3$

δ ^{13}C (p.p.m.)	m [a]	Assignment [b]	δ (^1H) [c]
50.1	t	C-1	2.92, 4.27
51.5	t	C-6	3.25, 4.15
69.4	t	C-2	3.51, 4.12
70.1	t	C-5	3.81, 4.06
70.5	t	C-3/C-4	3.70
71.0	d	C-5'	4.57
71.5	d	C-4'/C-3'	4.47/4.48 [d]
72.9	t	C-4/C-3	3.70
72.9	d	C-3'/C-4'	4.47/4.48 [d]
73.3	d	C-2'	4.80
78.5	s	C-1'	
170.7	s	C=O	

[a] m = Multiplicity in off-resonance decoupled spectrum. [b] Numbered as in (11). [c] Chemical shifts of attached protons. [d] Chemical shifts of protons too close to allow distinction.

The monomeric cryptand (5) has an extremely complex ^1H n.m.r. spectrum. It is primarily first-order however, when recorded at 250 or 400 MHz and with the aid of homonuclear and heteronuclear decoupling experiments a complete assignment has been made (*vide infra*, Tables 1 and 2).

The ^{13}C n.m.r. spectrum of (5) shows 12 different signals comprised of 5 ferrocenyl carbons, 1 carbonyl carbon, 4 different carbons attached to oxygen, and 2 different carbons attached to nitrogen. Each signal represents 2 equivalent carbon atoms and the implications of this spectrum are twofold. Firstly, there must be a degree of rigidity within the molecule since freedom of rotation about the 2 carbonyl groups, as observed in the non-bridged acyl ferrocenes,[13]
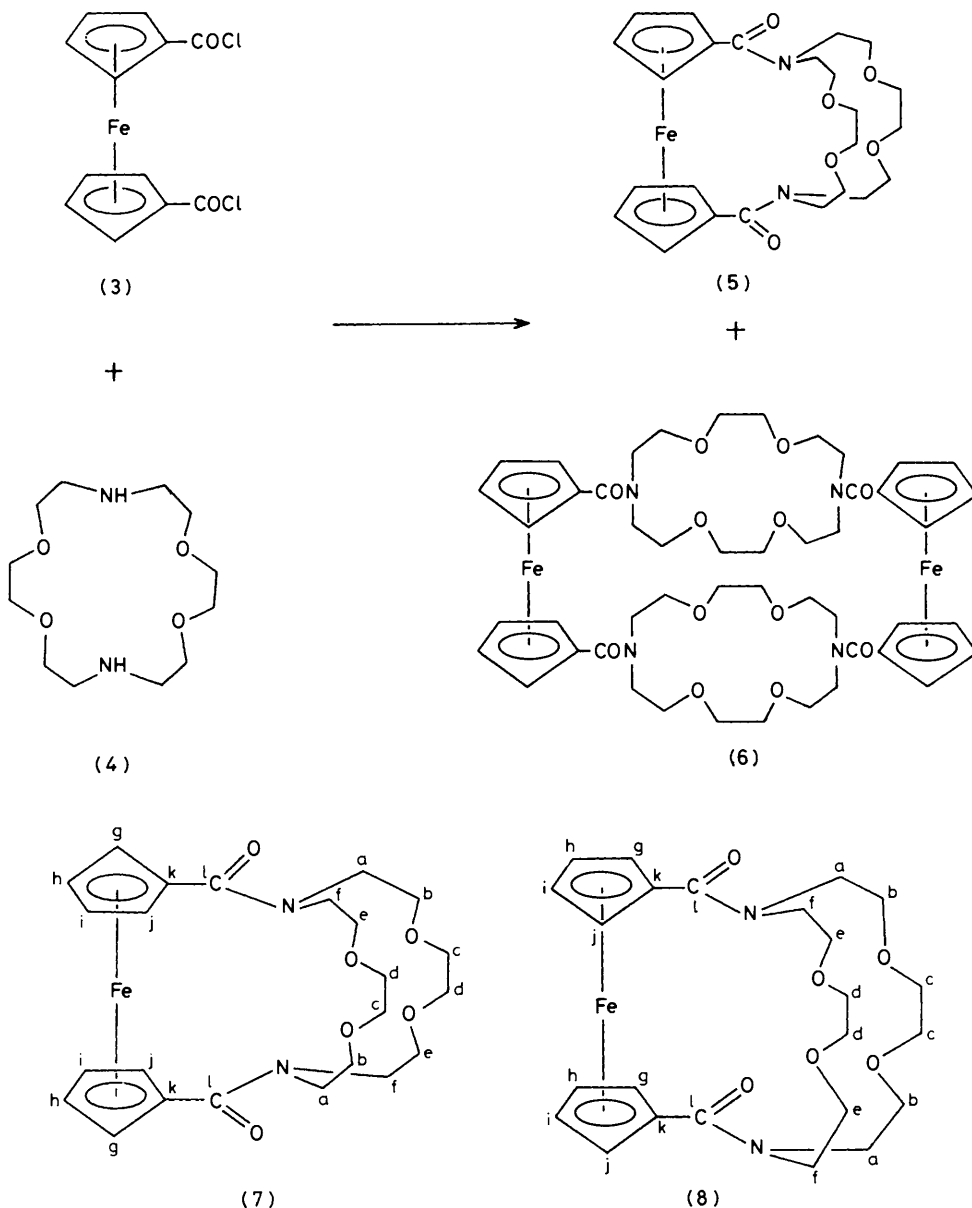
(3)

+

(5)

+

(4)

(6)

(7)

(8)

Table 2. ^{1}H N.m.r. data of (5) in CDCl$_3$

δ	Integ.	Assignment	J (Hz)
2.92	2	1A	1B, 14.1; 2A, 2.9; 2B, 10.3
3.25	2	6A	6B, 14.7; 5A, 5.0; 5B, 8.2
3.51	2	2A	2B, 10.0; 1B, 3.2
3.70	8	3A, B; 4A, B	
3.81	2	5A	5B, 9.7; 6B, 8.2
4.06	2	5B	6B, 6.5
4.12	2	2B	1A, 10.3
4.15	2	6B	
4.27	2	1B	
4.47	2	4'	2', 1.3; 3', 2.6; 5', 2.6
4.48	2	3'	2', 2.6; 5', 1.3
4.57	2	5'	2', 1.3
4.80	2	2'	

would mean fewer than 12 non-equivalent carbons. Secondly, there must be an element of symmetry within the molecule since total asymmetry would lead to 24 non-equivalent carbons.

One can envisage two possible configurations of (5) [labelled (7) and (8)] which are consistent with the n.m.r. data and in which the 12 pairs of equivalent carbons are designated (a)—(l).

Both (7) and (8) have the carbonyl groups co-planar with the ferrocene rings since this conformation allows maximum conjugation but in (7) the 2 carbonyl groups are *trans* to each other whereas in (8) they are *cis*. Furthermore, in (7) the 2 bridges of the diaza-crown ether unit each contain the same 6, non-equivalent carbons and, as shown in (9), the C_2 symmetry and hence the carbon and proton equivalencies are retained whatever the angle of twist (θ) between the two rings. In (8) however, the ^{13}C and ^{1}H n.m.r. data are only satisfied when the ferrocene rings and amide groups are eclipsed since then each ferrocene ring contains the same 5, non-equivalent carbons and each bridge of the crown contains 3 different pairs of equivalent carbons. The eclipsed conformation is however, energetically unfavourable due to the parallel dipoles of the carbonyl groups. This interaction can be alleviated by twisting the ferrocene rings, as in (10), but the plane of symmetry through the molecule is then lost; (a) is no longer

(9)　　　　(10)

(11)
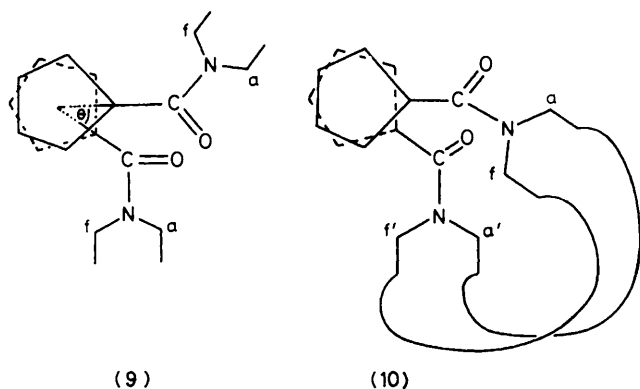
equivalent to (a'), and the carbon and proton equivalences of the eclipsed conformer are removed. This would give rise to n.m.r. spectra of greater complexity than those observed for (5). It should be noted that the variable-temperature n.m.r. (between −80 °C and +50 °C in CDCl₃) gave no indication of any time-averaged oscillation between the cyclopentadiene rings which might have produced the equivalence of (a) and (a') within (10). Thus, although the n.m.r. evidence does not preclude the possibility of (5) having *cis*-carbonyl groups specifically in an eclipsed conformation, the generalized configuration (7) with *trans* carbonyl groups and an indeterminate angle of twist (θ) offers a much more reasonable explanation.* Since theoretical calculations [14] and other studies [15] of acylferrocenes have also shown that the *trans* configuration of the carbonyl groups is preferred it seems safe to conclude that (7) represents the true configuration of (5). Hence a complete assignment of the ¹³C n.m.r. spectrum of (5) is reported in Table 1 using the notation shown in (11).

The ¹H n.m.r. spectrum of (5) shows 4 multiplets for the ferrocene protons, 4 eight-line patterns for the hydrogens of the methylene groups α to nitrogen (on C-1 and C-6), 4 eight-line patterns for the hydrogens of the methylene groups β to nitrogen, and 2 overlapping second-order patterns for the 8 protons of the remaining 2 glycolic linkages. Assignments of the various protons could not be made on the basis of chemical shift alone but were established using ¹³C, [¹H] heteronuclear decoupling and homonuclear decoupling techniques. The chemical shifts and coupling constants of all the protons are reported in Table 2 again using the notation depicted in (11). The fact that the 8 ferrocenyl protons, the 8 protons α to nitrogen and the 8 protons β to nitrogen are each found as 4 *pairs of equivalent protons* provides strong evidence for a *trans* configuration of the 2 carbonyl groups for the reasons given in the earlier discussion of the ¹³C n.m.r. spectra.

Among the 4 pairs of methylene protons adjacent to nitrogen decoupling experiments established which protons were geminal. The absorptions at δ 2.92 and 4.27 form one set of geminal protons (1A and 1B) and those at δ 3.25 and δ 4.15 form the other set (6A/6B). Selective heteronuclear decoupling at either δ 2.92 or 4.27 causes collapse of the ¹³C n.m.r. spectrum at δ 50.1 p.p.m. from a triplet to a doublet thus identifying a geminal pair and its associated carbon atom. The other geminal pairs of N–CH₂ protons are attached to the two carbons which resonate at δ 51.5 p.p.m. The differences in chemical shifts between these two sets of geminal protons are
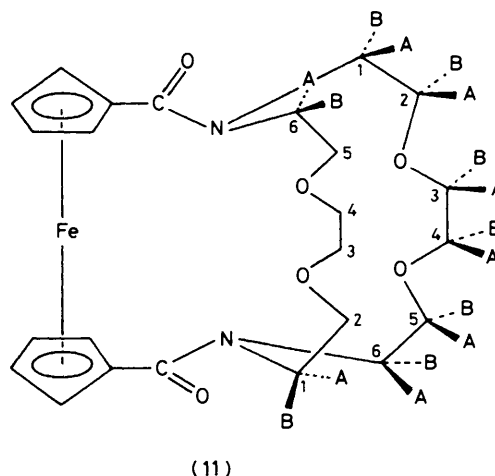
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* We hope to resolve this problem in the near future by an *X*-ray analysis of the molecule. It should be noted however, that the ¹³C n.m.r. of the unsymmetrical 2,1-cryptand analogue of (5) shows 22 carbons at ambient temperature which implies a *trans*-configuration or a *non-equilibrating, non-eclipsed cis*-isomer.

Table 3. ¹H N.m.r. data of (6) at 250 MHz in CDCl₃

Assignment	δ (−80 °C) *	δ (23 °C)	δ (50 °C)
O–CH	3.3—4.2br	3.4—4.0br	3.68
N–CH			3.75br
3'/4'-H	4.21	4.35br	4.36
4'/3'-H	4.49		
5'-H	4.30	4.63br	4.64
2'-H	4.90		

* CD₂Cl₂–CFCl₃.

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attributable to their differing disposition with respect to the carbonyl group. It is not however, immediately clear from inspection of the chemical shifts which of the pairs (at C-1 or C-6) is *cis* to the carbonyl group and which is *trans*. Difference n.O.e. spectroscopy [16] failed to establish whether or not any of the α-methylene protons were in close proximity to 5'-H but in view of the fact that these experiments required low-power irradiation of eight-line patterns this was not surprising. Only by reference to earlier reports on dialkylamides [17] and, in particular, to a recent, extensive ¹³C and ¹H n.m.r. study of di-isopropylamides [18] was an assignment possible. It then became clear that in (11) the methylene carbon *cis* to the carbonyl group has the *higher* field ¹³C n.m.r. absorption (*i.e.* C-1, δ 50.1 p.p.m.) and the greater disparity between the shifts of the geminal protons (1A, δ 2.92 and 1B, δ 4.27). Thus C-6 is *trans* to the carbonyl group at δ 51.5 p.p.m. with the two attached protons at δ 3.25 (6A) and δ 4.15 (6B) respectively.

Given the conical anisotropic shielding of the carbonyl group it is anticipated that the most deshielded proton of each geminal pair will be that which lies closest to the plane of the carbonyl group. The observation of a four-bond coupling between the two *lowest field* methylene protons in the diaza-12-crown-4 analogue of (11) supports this concept.[19] The so-called ' W-coupling ' is facilitated by a co-planar arrangement of the four bonds through which it is transmitted. Models show that such a co-planar arrangement can only be satisfied by the two protons (*e.g.* 1B and 6B) which lie close to the plane of the carbonyl group.

The methylene groups β- to nitrogen show similar trends in their ¹³C and ¹H n.m.r. spectra to those of the α-methylene groups. The carbon which is *cis* to the carbonyl (C-2) resonates upfield of C-5 and proton 2B resonates downfield of 5B whereas 2A resonates upfield of 5A. Although no definite assignments of C-3 and C-4 can be made it seems likely that a similar trend will be followed so that the resonance at δ 70.5

Table 4. [13]C N.m.r. data of (6) at 62.5 MHz in $CDCl_3$

Assignment	δ (−50 °C)	δ (0 °C)	δ (23 °C)	δ (55 °C)
N–C	46.8	47.0	47.3br ⎫	
N–C	48.5	49.1	49.3br ⎬ ·············· ·ca. 48br	
O–C	65.8	67.0	67.7br ⎫	
Ferrocene–C (3'/4')	69.1 ⎫			
O–C	69.3 ⎬	69.9		
O–C	69.7 ⎬ ······················ ·70.3br	70.0	70.4br ⎬ ·············· ·70.6br	
Ferrocene–C (3'/4')	72.0 ⎭			
O–C	72.1	72.1	72.0 ⎭	
Ferrocene–C (2'/5')	72.2 ⎫			
Ferrocene–C (2'/5')	75.5 ⎭ ················ ·73.9br		73.9br	73.3br
Ferrocene–C (ipso)	78.0	79.1	79.6	80.0sh *
C=O	169.7	170.0	170.1	170.0sh

* sh = Sharp.
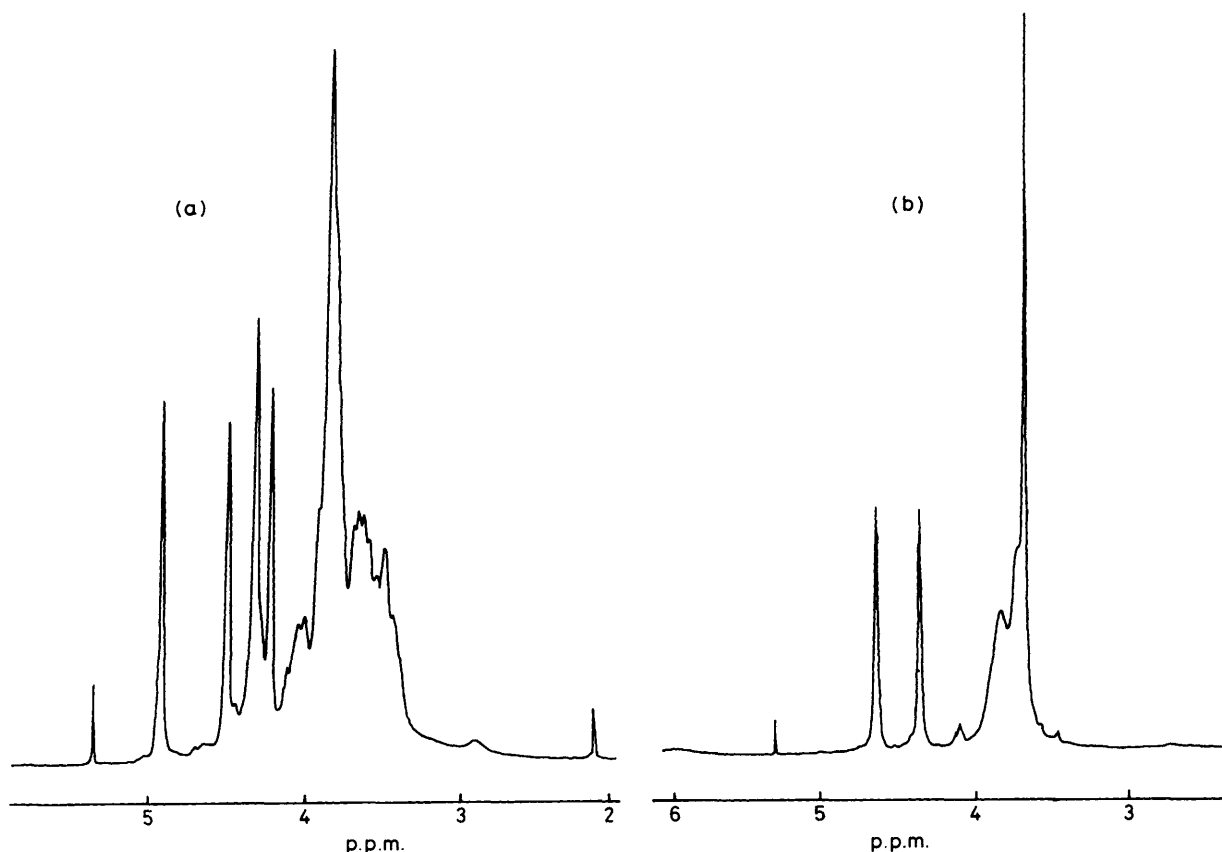
Figure 1. (a) [1]H N.m.r. spectrum of (6) at −80 °C in CD_2Cl_2–$CFCl_3$; (b) [1]H N.m.r. spectrum of (6) at +50 °C in $CDCl_3$

is that of C-3 (cis to the carbonyl) with C-4 appearing at δ 72.9 p.p.m.

Of the four ferrocenyl protons, 2' and 5' are known to be deshielded in acylferrocenes [20] with respect to 3' and 4'. In (11) [where the configuration of the carbonyl group with respect to the ferrocene ring is fixed], one may expect 2'-H to resonate at lower field than 5'-H due to the closer spacial proximity of the carbonyl group.[21] Selective irradiation of 2'-H collapses 4'-H to a triplet and 3'-H to a doublet of doublets and hence allows assignment of 3'-H and 4'-H.

The ^{1}H and [13]C n.m.r. of the dimer (6) were recorded at various temperatures and the details of the spectra are reported in Tables 3 and 4. The [1]H n.m.r. spectrum at ambient tem-

perature (23 °C) shows two broad absorptions at δ 4.35 and 4.63 each representing 4 protons and a very broad absorption between 3.4 and 4.0 p.p.m. representing 24 protons. As the temperature is reduced the signals at 4.35 and 4.63 p.p.m. broaden and then separate into two pairs of resonance signals. At −80 °C there is a range of unresolved signals between 3.3 and 4.2 p.p.m. and two pairs of well-resolved absorptions with one pair at δ 4.21 and 4.49 and the other at δ 4.30 and 4.90 (Figure 1a). The coalescence temperature is −20 °C. At 50 °C the two signals at 4.35 and 4.63 p.p.m. become sharper but the other absorption although sharper, remains unresolved (Figure 1b).

The [13]C n.m.r. of (6) at +55 °C shows 5 absorptions

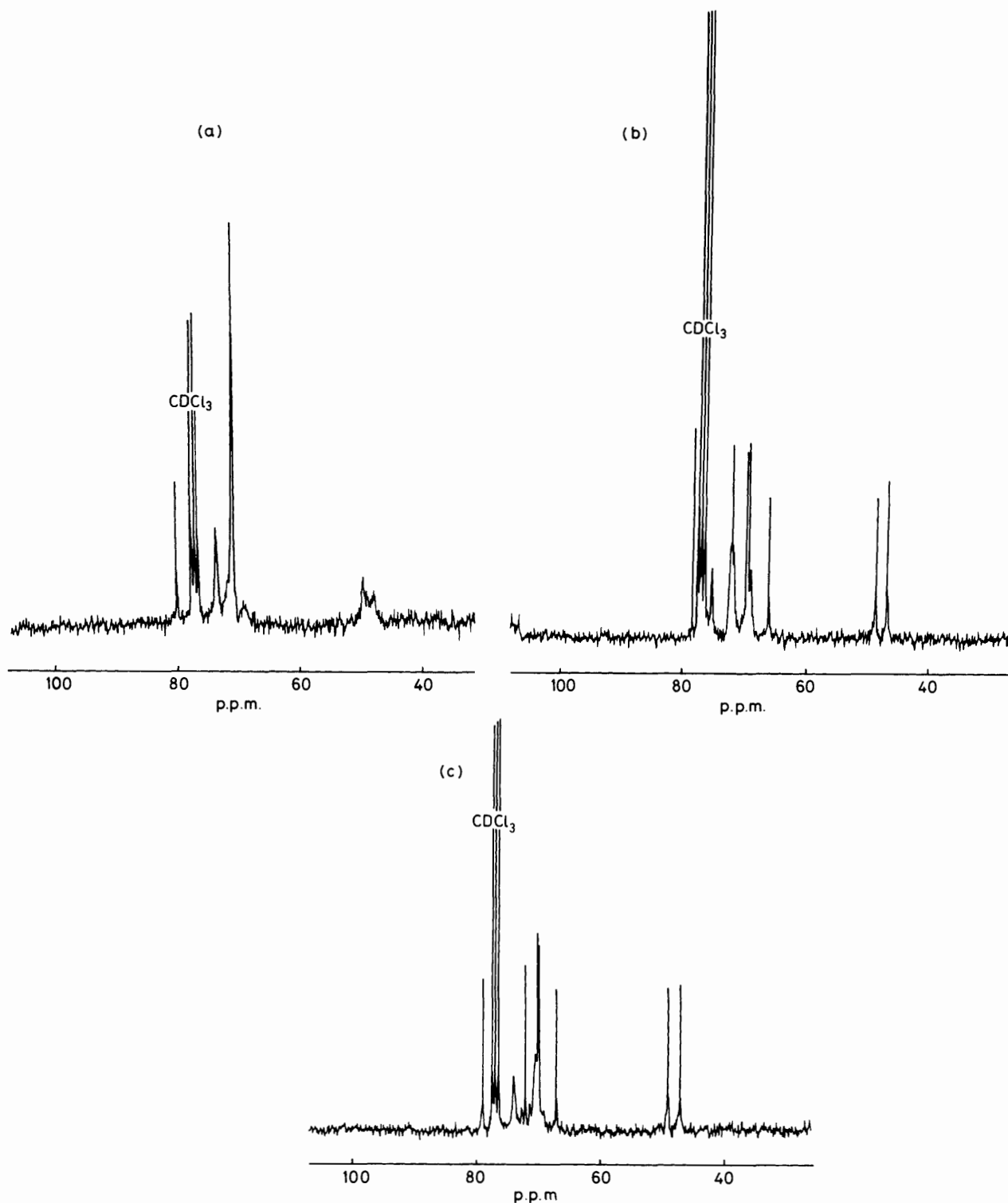**Figure 2.** (a) ^{13}C N.m.r. spectrum of (6) at $+55$ °C in CDCl$_3$; (b) ^{13}C n.m.r. spectrum of (6) at -50 °C in CDCl$_3$; (c) ^{13}C n.m.r. spectrum of (6) at 0 °C in CDCl$_3$

(Figure 2a) 2 of which at δ 170.0 (C=O) and δ 80.0 (*ipso* carbon on the ferrocene ring) are sharp whereas those at δ 49.4, 70.6, and 73.3 p.p.m. are broad. In contrast the spectrum at -50 °C (Figure 2b), which bears a marked resemblance to that of the monomer (5), has 12 absorptions including 1

carbonyl carbon (not shown), 5 ferrocenyl carbons, 4 carbons bound to oxygen and 2 carbons attached to nitrogen.

The clearest indication of the dynamic processes involved however, is found in the spectrum at 0 °C (Figure 2c) which has 8 sharp resonance signals (C=O, *ipso* C, 4 × C−O and 2 ×

Table 5. ^{13}C N.m.r. data of compounds (13a—c), (14), and (15) in CDCl$_3$ recorded at 22.6 MHz

Compound Assignment	(13a)	(13b)	(13c)	(15)	(14)
C-1'	77.6	78.1	77.8	87.7	77.4
C-2'/5'	74.1	74.2	73.6	68.1	71.3
C-3'/4'	69.5	68.7	69.4	67.1	70.3
C(1)-N	146.2	146.9	147.2	145.9	
C(2)-O	128.2	128.9	128.4	139.4	
C(3)-C(6)	123.4	123.5	123.7	122.7	
	122.1	122.4	121.9	116.8	
	119.7	119.9	120.7	113.3	
	111.1	112.8	112.2	111.2	
C=O	167.0	167.5	167.5		169.8
CH$_2$-O	66.8	68.0	68.0	68.1	69.8
CH$_2$-O		70.0	69.4		69.9
CH$_2$-O			70.2		
CH$_2$-N				42.6	39.3

Table 6. ^{1}H N.m.r. data of compounds (13a—c), (14) and (15) in CDCl$_3$ recorded at 90 MHz *

| Compound Assignment	(13a)	(13b)	(13c)	(15)	(14)
2'-, 5'-H	4.70	4.95	5.01	4.13	4.53
3'-, 4'-H	4.49	4.43	4.46	4.02	4.46
N-H	8.41	8.48	8.40	4.00	6.54
Ar-H(2)	8.54	8.38	8.24	6.65	
Ar-H(3), H(4), H(5)	7.04	7.01	6.94	6.65	
OC-H	4.51	4.03	3.79	4.31	3.71
		4.30	3.90		
			4.25		
NC-H				3.98	3.71

*All multiplicities and integrations consistent with proposed structures.

C-N) and 2 broad signals at 70.4 and 73.9 p.p.m. which represent the ferrocenyl carbons. This situation is analogous to simple acyl ferrocenes where free rotation of the acyl group renders C-2' equivalent to C-5' and C-3' equivalent to C-4'.[12] The absorption at δ 70.4 is therefore assigned to C-3'/4' and that at 73.9 p.p.m. to C-2'/5'. At −80 °C the rotation of the macrocyclic amide group about the *ferrocene-carbonyl carbon bond* in (6) becomes slow on the n.m.r. time scale and 4, non-equivalent ferrocenyl carbons are observed. The value of $\Delta G^{\ddagger}$ for this process, calculated using the Gutowsky equation, is 50 kJ mol^{-1} (12 kcal mol^{-1}) at the coalescence temperature of −10 °C. This rotation also explains the variable temperature ^{1}H n.m.r. data. At ambient temperature the two absorptions at δ 4.63 and δ 4.35 represent 2'-/5'-H and 3'-/4'-H respectively. At − 80 °C the rotation about the ferrocene-carbonyl carbon bond is slow on the n.m.r. time scale and separate absorptions are observed for all 4, non-equivalent protons from which a $\Delta G^{\ddagger}$ value of 50 kJ mol^{-1} is calculated at T_c = −20 °C a value which is in good agreement with that from the ^{13}C n.m.r. spectra.

At temperatures below 0 °C the observation of two non-equivalent carbons α to nitrogen and 4 non-equivalent carbons attached to oxygen indicates that, on the n.m.r. time scale, the macrocyclic ring is in a non-fluxional, probably co-planar environment relative to the carbonyl group. At ambient temperature there is a slight broadening of these 6 absorptions and at 55 °C there is a coalescence of each of the 3 pairs of previously non-equivalent carbons (Table 4 and Figure 2a—c). The implication is that at this temperature the macrocyclic ring is no longer fixed relative to the carbonyl group. Together with the rotation about the ferrocenyl-carbonyl linkage already identified, there is now rotation about the amide bond itself. At the coalescence temperature of 60 °C (N-C signals), $\Delta G^{\ddagger}$ for rotation *about the amide bond* in (6) is 67 kJ mol^{-1} (16 kcal mol^{-1}) which is in good agreement with the barriers to rotation about conventional amide links.[22]

There can be no doubt that two dynamic processes are involved. The free energies of activation differ by 17 kJ mol^{-1} which is well outside experimental error and if a single rotation were responsible for the various spectroscopic changes, then the carbons α to nitrogen having Δv = 100 Hz should coalesce at a lower temperature than the ferrocenyl carbons which have greater frequency differences (Δv 2',5' = 210 Hz and Δv 3',4' = 180 Hz). This is contrary to observation and the results are, therefore, best explained in terms of two dynamic processes.

Another series of macrocycles (13) was synthesized by

condensation of 1,1'-bis(chlorocarbonyl)ferrocene (3) with a number of α, ω-aromatic diamines (12). Likewise, reaction of (3) with 1,8-diamino-3,6-dioxaoctane gave (14). In one instance (13a; n = 0) reduction with diborane gave the diamine (15) but this compound failed to condense with bis-acid chlorides to give analogues of (5). All three types of compound (13)—(15) analysed correctly and had ^{13}C (Table 5) and ^{1}H (Table 6) n.m.r. spectra consistent with their assigned structures. Some dimer formation in the condensation reactions cannot be excluded but such compounds were not isolated at the time and were not detected by mass spectrometry in the purified products.

The macrocycle (16), an ^{15}N-labelled analogue of (13c), was synthesized from p-cresol with a view to assessing the potential value of ^{15}N n.m.r. in detecting and analysing complex formation in these molecules. The extent of co-ordination with various alkali and alkaline earth metal cations was then estimated *qualitatively* by variations in the ^{15}N n.m.r. chemical shift of the macrocycle. The results of this work together with the n.m.r. parameters are reported in full elsewhere.[23] In summary it was found that the complexes with both calcium and lithium ions had ^{15}N n.m.r. chemical shifts significantly different from that of the parent macrocycle whereas the chemical shift in the presence of potassium ion was the same as that of the free macrocycle. The sequence of metal-ion complexing ability (Ca^{2+} ≈ Li$^+$ ≫ K$^+$) is similar to that found with (5) and the results suggest that ^{15}N n.m.r. is sufficiently sensitive not only to detect complex formation but also to discriminate between different metal ions according to their co-ordinating ability.

It is clear from the spectral data that each of the macrocyclic amides (13a—c) and (14) and the amine (15) permit a flexibility of the bridging moiety that is not found in (5). This is evident since, in contrast to (5), only two sets of non-equivalent protons are found in the ferrocene rings. The fact that 2'-H is equivalent to 5'-H and 3'-H equivalent to 4'-H eliminates the possibility of each carbonyl group having a fixed configuration co-planar with the adjacent ferrocene ring. A perpendicular configuration of the carbonyl groups cannot be ruled out but the size of the bridging groups (at least 12 carbon atoms) which would allow extended π-conjugation in (13a—c) and (14) makes this unlikely. It appears therefore, that whereas in (5) the crown ether bridge locks the configuration of the carbonyl group, in the five singly bridged compounds each carbonyl group is able to rotate with respect to the ferrocene ring.

The cation binding ability of the ferrocenyl macrocycles together with the n.m.r. data of the resulting complexes and cryptates will be reported in detail in a future publication.

(3)

(12) a; $n = 0$
b; $n = 1$
c; $n = 2$

(13a–c)

(14)

(15)

(16)
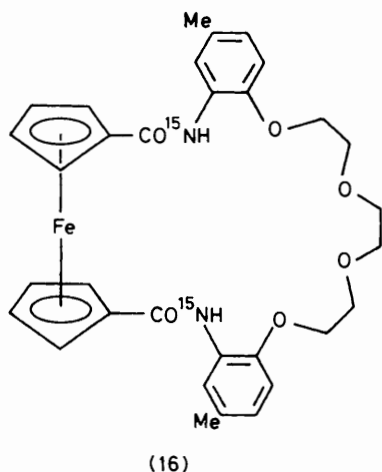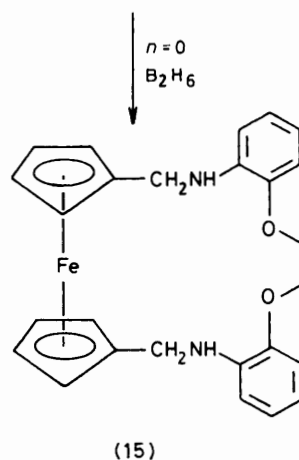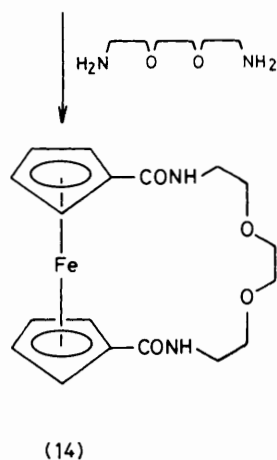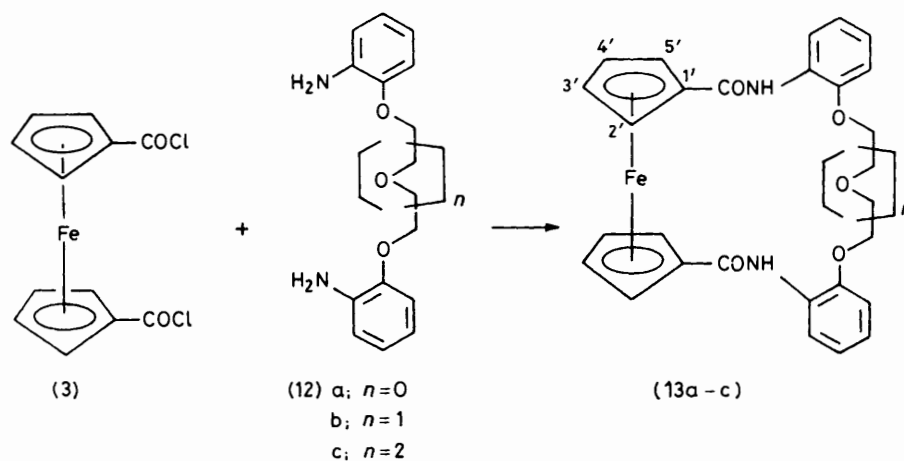
Experimental

[1]H N.m.r. spectra were recorded at 90, 250, and 400 MHz using Bruker WH 90, WM 250, and WH 400 instruments respectively. [13]C N.m.r. spectra were recorded using the same instruments at 22.6, 62.9, and 100 MHz respectively.

Diaza-18-crown-6 was obtained commercially from Merck-Schuchardt.

1,1'-Bis(chlorocarbonyl)ferrocene was prepared by lithiation of ferrocene [24] followed by carboxylation using CO_2 to give the dilithio-salt of ferrocenedicarboxylic acid. This was then chlorinated using oxalyl chloride.[25]

Ethylene glycol bis(aminophenyl)ethers were prepared from the corresponding glycols by bromination, then reaction with sodium o-nitrophenate and subsequent reduction with hydrogen using Pd on charcoal as catalyst.

Benzene was dried by distillation from lithium aluminium hydride.

Preparation and Separation of 1,1'-(1,4,10,13-*Tetraoxa*-7,16-*diazacyclo-octadecane*-7,16-*diyldicarbonyl)ferrocene* (5) *and* 1,1" : 1',1'''-*Bis*(1,4,10,13-*tetraoxa*-7,16-*diazacyclo-octadecane*-7,16-*diyldicarbonyl)bisferrocene* (6).—A 1-l 3-necked, creased flask equipped with a mechanical stirrer, was flushed with nitrogen and then charged with dry benzene (100 ml). A solution of 1,1'-bis(chlorocarbonyl)ferrocene (0.726 g, 2.3 × 10^{-3} mol) dissolved in benzene (100 ml) was placed in a pressure-equalised dropping funnel. In a second, similar dropping funnel were placed 1,4,10,13-tetraoxa-7,16-diaza-cyclo-octadecane (diaza-18-crown-6) (0.613 g, 2.3 × 10^{-3} mol) and triethylamine (0.5 g, 5 × 10^{-3} mol) in benzene (100 ml). The two solutions were added dropwise, simultaneously during 3 h to the vigorously stirred benzene at ambient temperature. The mixture became orange and deposited a fine precipitate of triethylamine hydrochloride. When addition was complete the mixture was stirred for a further 2.5 h and allowed to stand overnight. The solids were separated by filtration and the solvent was then removed to leave an oily orange residue which crystallised on standing. This material was chromatographed on a column of alumina using methylene chloride–0.5% methanol. An orange band was collected and shown by [1]H n.m.r. to be the monomeric cryptand (5). After solvents were removed, recrystallisation from CH_2Cl_2–pentane gave (5) (0.465 g, 40%) as orange

crystals, m.p. 183—184 °C (Found: C, 57.35; H, 6.5; N, 5.55%; M, 500. Calc. for $C_{24}H_{32}FeN_2O_6$: C, 57.61; H, 6.44; N, 5.60%; M, 500) ^{13}C and ^1H n.m.r. data of (5) are given in Tables 1 and 2.

Further elution of the column using CH_2Cl_2-2% MeOH produced a second orange band. After removal of solvents and recrystallisation from CH_2Cl_2-pentane this fraction gave (6) (0.15 g, 26%) as orange crystals m.p. 243.5—245 °C (Found: C, 57.05; H, 6.5; N, 5.45%; M, 1 000. $C_{48}H_{64}Fe_2$-N_4O_{12} requires C, 57.61; H, 6.44; N, 5.60%; M, 1 000). The ^{13}C and ^1H n.m.r. data of (6) at various temperatures are shown in Tables 3 and 4.

Preparation of 1,1'-[Ethane-1,2-diylbis(oxy-o-phenylene-iminocarbonyl)]ferrocene (13a).—The procedure for the preparation of (13a) followed that described for (5). A solution of 1,1'-bis(chlorocarbonyl)ferrocene (0.5 g, 1.6 mmol) in benzene (100 ml) and a solution of the diamine (12a) (0.43 g, 1.6 mmol) in benzene (30 ml) containing triethylamine (0.35 g, 3.5 mmol) were added dropwise and simultaneously to vigorously stirred benzene (100 ml). When addition was completed stirring was continued for 1 h and the solution was then filtered. After removal of solvents the crude solid product was dissolved in $CHCl_3$ and washed through a column of silica to remove polymeric products. Recrystallisation from toluene gave (13a) (0.54 g, 70%) as orange-brown cubic crystals, m.p. 274 °C (Found: C, 66.4; H, 4.55; N, 5.7%; M, 482. $C_{26}H_{22}FeN_2O_4$ requires C, 64.75; H, 4.60, N, 5.81%; M, 482). The ^{13}C and ^1H n.m.r. data for (13a) are reported in Tables 5 and 6.

Preparation of 1,1'-[Oxybis(ethane-1,2-diyloxy-o-phenylene-iminocarbonyl)]ferrocene (13b).—The procedure for the preparation of (13b) followed that described for (5). A solution of 1,1'-bis(chlorocarbonyl)ferrocene (0.92 g, 2.96 mmol) in benzene (100 ml) and a solution of the diamine (12b) (0.85 g, 2.96 mmol) in benzene (100 ml) containing triethylamine (0.6 g, 6 mmol) were added dropwise and simultaneously to benzene (100 ml). When addition was complete stirring was continued for 1 h and the solution was filtered. After removal of solvents the crude solid product was dissolved in $CHCl_3$ and washed through a column of silica. Recrystallisation from ethanol gave (13b) (1.02 g, 67%) as orange-brown crystals, m.p. 174 °C (Found: C, 63.6; H, 4.95; N, 5.25%; M, 526. $C_{28}H_{26}FeN_2O_5$ requires C, 63.87; H, 4.98; N, 5.32%; M, 526). Full ^{13}C and ^1H n.m.r. data for (13b) are reported in Tables 5 and 6.

Preparation of 1,1'-[Ethane-1,2-diylbis(oxyethane-1,2-diyl-oxy-o-phenyleneiminocarbonyl)]ferrocene (13c).—The procedure for the preparation of (13c) followed that described for (5). A solution of (3) (1.0 g, 3.2 mmol) in benzene (100 ml) and a solution of the diamine (12c) (1.07 g, 3.2 mmol) in benzene (100 ml) containing triethylamine (0.7 g, 7.0 mmol) were added dropwise and simultaneously to benzene (100 ml). When addition was complete stirring was continued for 1 h and the solution then filtered. After removal of solvents the crude solid product was dissolved in CH_2Cl_2 and washed through a column of alumina using ethyl acetate. Recrystallisation from toluene gave (13c) (0.94 g, 58%) as orange-brown crystals (decomp. 230 °C) (Found: C, 62.55; H, 5.35; N, 4.75%; M, 570. $C_{30}H_{30}FeN_2O_6$ requires C, 63.15; H, 5.30; N, 4.91%; M, 570). The ^{13}C and ^1H n.m.r. data for (13c) are reported in Tables 5 and 6.

Preparation of 1,1'-[Ethane-1,2-diylbis(oxyethane-1,2-diyl-iminocarbonyl]ferrocene (14).—The procedure for the preparation of (14) followed that described for (5). A solution of (3) (1.0 g, 3.2 mmol) in benzene (50 ml) and a solution of 1,8-diamino-3,6-dioxaoctane (0.45 g, 3.2 mmol) in ethanol (0.73 g) and benzene (50 ml) containing triethylamine (0.7 g, 7 mmol) were allowed to react by simultaneous dropwise addition to benzene (100 ml). When addition was complete, the solution was filtered. After removal of solvents the crude solid product was dissolved in chloroform and washed through a column of alumina. Recrystallisation from toluene gave (14) (0.4 g, 33%) as orange-brown crystals, m.p. 210 °C (Found: C, 56.6; H, 5.8; N, 7.05%. Calc. for $C_{18}H_{22}FeN_2O_4$. C, 55.96; H, 5.74; N, 7.26%). The ^{13}C and ^1H n.m.r. data for (14) are reported in Tables 5 and 6.

Preparation of 1,1'-[Ethane-1,2-diylbis(oxy-o-phenylene-iminomethylene)]ferrocene (15).—To a solution of (13a) (0.57 g, 1.2 mmol) in dry tetrahydrofuran (30 ml) was added, under N_2, a solution of diborane (excess) in tetrahydrofuran. The solution was stirred at ambient temperature for 3 d. Hydrochloric acid (1M; 25 ml) was then added and the mixture stirred under nitrogen until the evolution of gas had ceased. The mixture was then extracted with CH_2Cl_2 (4 × 25 ml). The organic extract was dried over $MgSO_4$, concentrated, and then chromatographed on silica gel using CH_2Cl_2 as eluant to give (15) (0.43 g, 80%) as an orange-yellow oil (Found: M, 454. $C_{26}H_{26}FeN_2O_2$ requires M, 454). The ^{13}C and ^1H n.m.r. data which are consistent with the assigned structure are reported in Tables 5 and 6.

Preparation of ^{15}N-Labelled 1,1-[Ethane-1,2-diylbis[oxy-ethane-1,2-diyl(4-methyl-1,2-phenylene)iminocarbonyl]] ferrocene (16).—*para*-Cresol (2.55 g) in benzene (5.85 g) was added dropwise to $H^{15}NO_3$ (11.8 ml; 17% HNO_3, w/v) and the temperature of the mixture was maintained at 30 °C by careful heating and control of the addition rate. After addition was complete the mixture was stirred at 30 °C for 1 h. The organic layer was separated, washed with a saturated solution of NaCl (2 × 10 ml) and then with water (1 × 10 ml). After drying over sodium sulphate, the solvent was removed to yield ^{15}N-labelled 2-nitro-4-methylphenol (3.37 g, 92%).

The nitrophenol (3.37 g, 2.2 mmol) was converted into its sodium salt and was then condensed with 1,8-dibromo-3,6-dioxaoctane (3.0 g, 1.1 mmol) in DMF at 100 °C to give 1,8-di-2-nitro-4-methylphenoxy-3,6-dioxaoctane (5.3 g, 10 mmol, 90%) which, in turn, was reduced with hydrogen over Pd/C to give ^{15}N-labelled-1,8-di-2-amino-4-methylphenoxy-3,6-dioxaoctane (4.4 g, 9.3 mmol, 93%). Condensation of the bis-amine (2.4 g, 5 mmol) with (3) (1.56 g, 5.0 mmol) gave (16) (1.9 g, 55%) as orange crystals, m.p. 220 °C (Found: C, 63.55; H, 5.75; N, 5.0%; M, 600. $C_{32}H_{34}Fe^{15}N_2O_6$ requires C, 64.00; H, 5.67; N, 5.00%; M, 600). The ^1H, ^{13}C, and ^{15}N n.m.r. data of this compound are reported elsewhere.[22]

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