Journal of Organometallic Chemistry, 405 (1991) 365–373
Elsevier Sequoia S.A., Lausanne
JOM 21393

NMR studies on the metal complexes of metallocene-containing cryptands

C. Dennis Hall * and Nelson W. Sharpe
Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS (UK)

(Received August 28th, 1990)

Abstract

NMR spectroscopy has been employed to study the structural conformations of metallocene-containing cryptands and their magnesium complexes in acetonitrile solution. The complexes of both the ruthenocene- and ferrocene-containing cryptands are shown to be broadly isostructural, and complexation of the metal cation primarily involves coordination by the amide carbonyl functions of the host macrocycle. For both 1:1 and 2:1 host-guest complexes, a *cis* conformation of the carbonyl groups is adopted in order to achieve coordination with the metal cation.

Introduction

Cryptands incorporating the metallocene unit are attractive as potential redox-active and chromogenic host-guest sensors [1,2]. Structural data on three macrocycles of this type have been obtained recently by X-ray crystallography [3–5] and NMR studies have confirmed that the structures in the solid state persist in solution [6]. The latter studies were also used to evaluate the thermodynamic parameters associated with molecular fluxionality. Metallocene-containing cryptands form complexes with metal cations [2], but no crystallographic studies on these cryptates have been reported, since they are hygroscopic and difficult to crystallize. Thus, NMR data offer information on the structural configuration within metallocene-containing cryptates which is useful in the development of molecular design. An earlier report noted that metal cation coordination by ferrocene-containing cryptands gave host-guest complexes of either 2:1 or 1:1 stoicheiometry which were in equilibrium, and that these equilibria were temperature and concentration dependent [7]. In this paper we report our NMR studies on the magnesium complexes of cryptands containing either the ferrocene or ruthenocene unit, **1** and **2** respectively (Fig. 1). Two-dimensional NMR techniques have been used in order to characterise many of the structural features of these complexes in solution.

Experimental

The metallocene-containing cryptands **1** and **2** were synthesised by condensation of the appropriate 1,1′-di(chlorocarbonyl)metallocene with 4,13-diaza-18-crown-6

0022-328X/91/$03.50

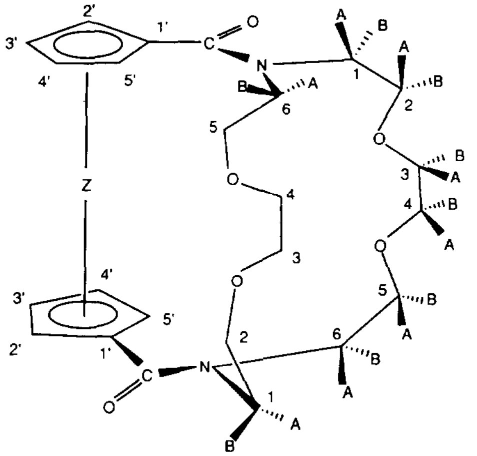

Fig. 1. Schematic structure of the metallocene-containing hosts 1,1'-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)metallocene, **1** (Z = Fe) and **2** (Z = Ru). This stereochemical representation includes the atom identification nomenclature used in the text for uncomplexed host molecules.

under high dilution conditions. The compounds were isolated by column chromatography and characterised by mass spectrometry, elemental analysis and multinuclear NMR. Magnesium perchlorate (Aldrich, A.C.S. reagent) was dried at 120 °C (1 mmHg, 3 h). High resolution ^{1}H and ^{13}C NMR data were obtained on a Bruker AM360 MHz instrument using the CD_3CN lines at 1.93 ppm for ^{1}H NMR and at 1.3 ppm for ^{13}C NMR as reference signals.

Results and conclusions

The ^{1}H and ^{13}C NMR spectra of **1** and **2** have been reported in detail for toluene as solvent [6]. Table 1 gives these data for MeCN-d_3 as solvent, in which only minor differences are noted. The crystal structures of **1** and **2** are known [3,5] and are very similar except that the metallocene inter-ring dimension is larger for the ruthenocene analogue. Figure 1 depicts the stereochemical structure of the uncomplexed host cryptands both in the solid state and in solution. The carbonyl groups are *trans*, with the substituents at the cyclopentadienyl (Cp) rings staggered by a little over 72° which results in the Cp rings being non-eclipsed. Molecular fluxionality results in a C_2 axis of rotation on the NMR timescale at room temperature. For **1** and **2** the Cp ^{1}H spectra are similar, since the magnetic environments of the ring protons are determined by their through-space disposition with respect to the carbonyls. However, the magnetic environments of the ring ^{13}C nuclei are determined in part by metal–carbon bonding interactions. For **1** these involve metal-centered $3d$ orbital interactions, whereas for **2** these involve the more spatially diffuse $4d$ orbitals of ruthenium. For metallocene ring symmetry lower than the eclipsed (local D_{5h}) conformation, e_2' molecular orbital degeneracy is lifted. This results in significant dissimilarities in the Cp ^{13}C spectra of **1** and **2**, which have been discussed previously [6].

The ^{13}C chemical shift data for equimolar solutions of **1** and **2** with magnesium perchlorate at room temperature in MeCN-d_3 as solvent are given in Table 2. These

Table 1

Chemical shift data (ppm) for **1** and **2** in MeCN-d_3. ^1H values refer to multiplet centroids.

^{13}C	**1**	**2**	^1H	**1**	**2**
C1	50.00	48.86	H1A	2.91	2.96
			H1B	4.14	4.14
C6	52.13	52.31	H6A	3.34	3.53 [a]
			H6B	3.94 [a]	4.05
C2	70.53	71.40	H2A	3.50	3.51 [a]
			H2B	4.00	3.76 [a]
C3			H3A		
	70.93	71.53	H3B	3.58	3.56
	73.16	71.97		3.65 [a]	3.63 [a]
C4			H4A	3.67 [a]	3.63 [a]
			H4B	3.67 [a]	3.63 [a]
C5	71.24	71.04	H5A	3.70	3.66 [a]
			H5B	3.94 [a]	3.72 [a]
C1′	80.75	85.73			
C2′	73.67	76.31	H2′	4.66	5.03
C3′	72.64	72.22	H3′	4.36	4.67
C4′	73.05	73.92	H4′	4.45	4.76
C5′	71.72	75.22	H5′	4.53	4.84
C=O	170.89	169.48			

[a] Overlapping multiplets.

data are best interpreted for host-guest complexes of 1 : 1 stoicheiometry. Previous equilibria data indicate that the carbonyl functions are necessary for coordination of metal cations, whereas the presence of oxygen atoms within the heterocyclic bridges

Table 2

^{13}C and ^1H chemical shift data for the complexes of Mg^{2+} with **1** and with **2**. MeCN-d_3 as solvent, at 0.05 ± 0.01 *M* and 22° C. Proton shifts refer to multiplet centroids.

^{13}C	Mg^{2+} : **1**	Mg^{2+} : **2**	^1H	Mg^{2+} : **1**	Mg^{2+} : **2**
C11	52.21	52.50	H11A	3.14	3.20
			H11B	4.26	4.23
C21	50.20	50.03	H21A	3.34	3.42
			H21B	4.01 [a]	3.87
C12	67.25	66.85	H12A	3.65 [a]	3.60 [a]
			H12B	3.65 [a]	3.60 [a]
C22	73.38	73.61	H22A	4.01 [a]	4.00 [a]
			H22B	4.01 [a]	4.00 [a]
C13			H13A	3.58	3.50
	70.77	70.83	H13B	3.73	3.67
	71.28	71.44			
C23			H23A	3.87	3.85
			H23B	4.03 [a]	4.04
C11′	82.09	86.21			
C12′	73.09	76.60	H12′	5.15	5.37
C13′	72.27	74.99	H13′	4.49	4.81
C14′	71.17	73.46	H14′	4.48	4.80
C15′	75.56	76.61	H15′	5.00	5.26
C=O	175.63	175.06			

[a] Overlapping multiplets.

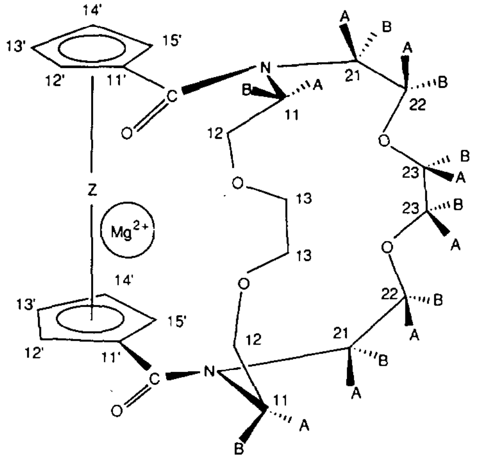

Fig. 2. Stereochemical representation together with atom identification nomenclature for the structures of the complexes of Mg^{2+} with **1** and **2**.

is not [2]. In order to accommodate coordination in this manner, model studies suggest that the carbonyls may adopt a *cis* configuration with the Cp rings becoming eclipsed, which results in the cryptates of both **1** and **2** having a plane of

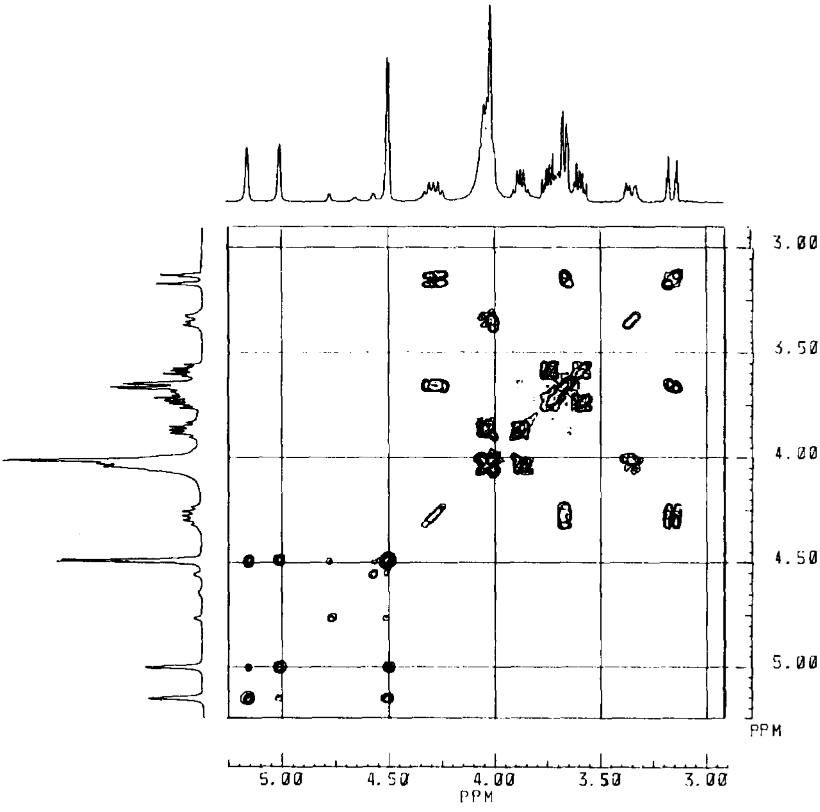

Fig. 3. 2D-COSY spectrum of the complex of Mg^{2+} with **1**.

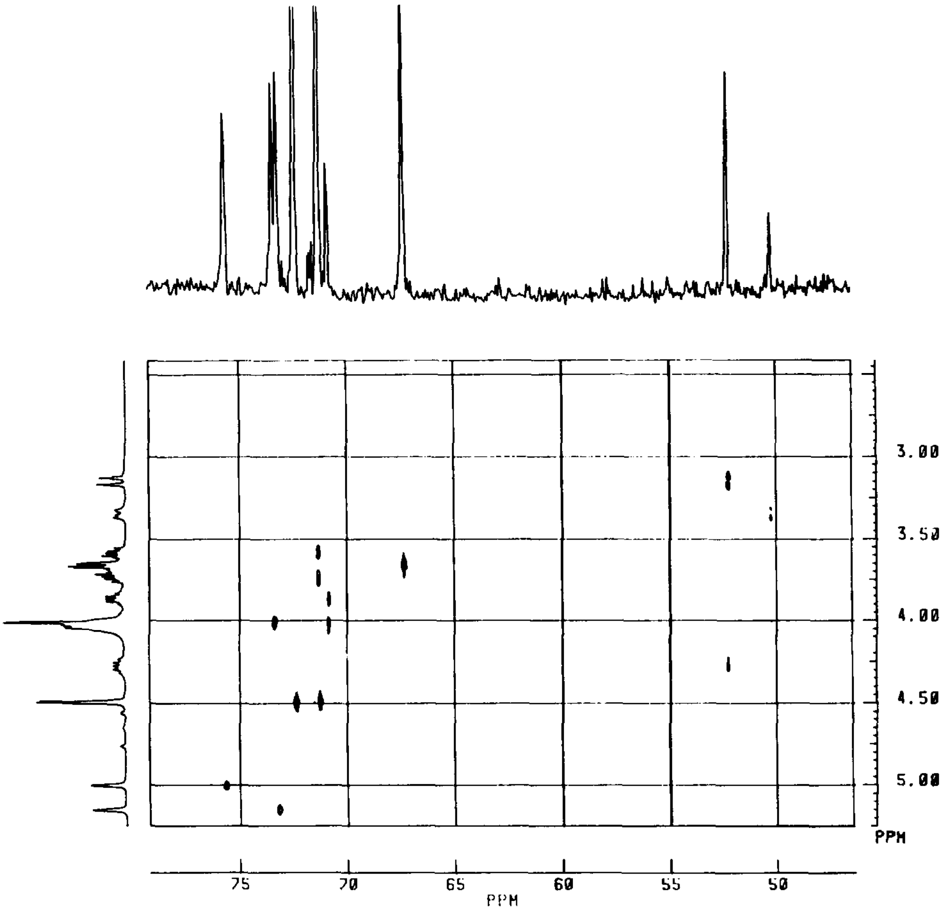

Fig. 4. ^{13}C–^{1}H shift correlation spectrum of the complex of Mg^{2+} with **1**.

symmetry as shown schematically in Fig. 2. Unless the carbonyls within the cryptate are *cis*, it seems unlikely that the host-guest complex can contain a symmetry element. The 2D COSY and ^{13}C–^{1}H shift correlation spectra for **1** and **2** are shown in Figs. 3–6.

Assignment of the resonance signals is thus possible if, for the CH class of protons the Cp ring proton H12′, and if, for the CH_2 class of protons the heterocyclic bridge proton H11B are those associated with the most downfield signal observed for their respective classes of proton. This assumption is reasonable since it is these nuclei which reside most in the conical anisotropic deshielding zone of the carbonyl functions. Detailed examination of the 2D COSY and ^{13}C–^{1}H shift correlation spectra then permit identification of the resonances associated with all other nuclei, in most cases unambiguously.

In general, the corresponding Cp ring nuclei of the complex with **2** are more deshielded than the complex with **1**. That these two complexes are broadly isostructural is evidenced by the similarity of their Cp ^{1}H spectra, which are primarily determined by through-space interaction with the carbonyls. The ordering of

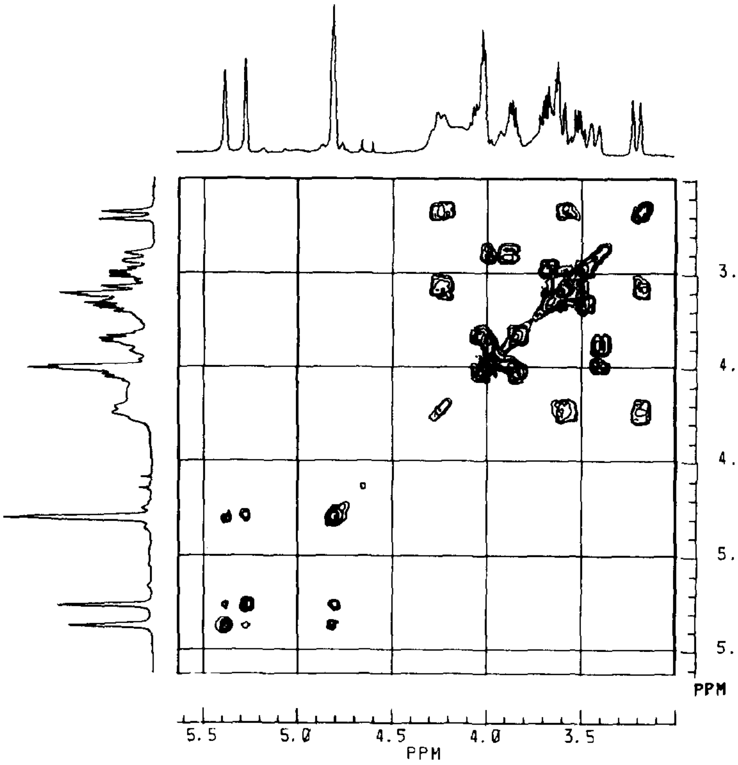

Fig. 5. 2D-COSY spectrum of the complex of Mg^{2+} with **2**.

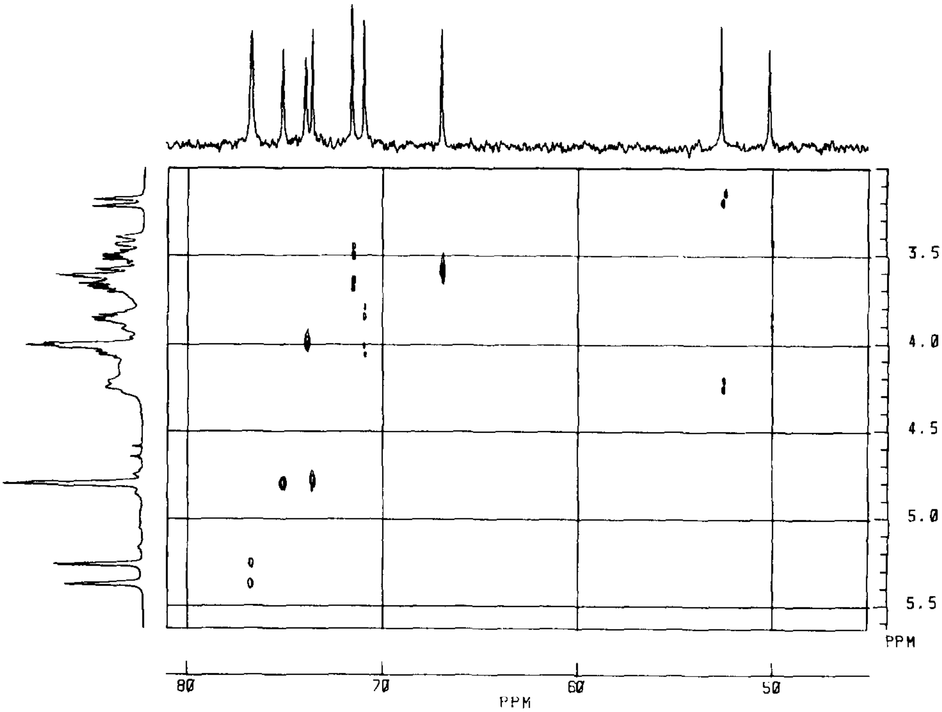

Fig. 6. ^{13}C–^{1}H shift correlation spectrum of the complex of Mg^{2+} with **2**.

deshielded Cp ^{1}H nuclei for both complexes is H12′ > H15′ > H13′ ⩾ H14′. Since the Cp rings become eclipsed upon complexation of the Mg^{2+} cation, the orbital degeneracy of e_2' is restored, and the ordering of deshielded Cp ^{13}C nuclei is the same for both complexes with C11′ > C15′ > C12′ > C13′ > C14′. For the eclipsed conformation of the metallocene moiety (local D_{5h} symmetry), both the in-plane metal-centered d_{xy} and $d_{x^2-y^2}$ orbitals (i.e. the doubly degenerate e_2' bonding molecular orbital) interact with the Cp ring orbitals to corresponding extents for both the ferrocene and ruthenocene analogues. Therefore, the extent of the shielding electron density afforded the Cp ring ^{13}C nuclei follow the same respective ordering both for when the bonding involves 3*d* or 4*d* metal-centered atomic orbitals. In general, the ^{13}C Cp ring nuclei in the ruthenium analogue are more deshielded (i.e. less shielded), since the metal–carbon bonding interaction involves the more diffuse 4*d* metal orbitals. By contrast, for the uncomplexed host macrocycles, in which the metallocene moieties are not eclipsed, the respective ordering of the chemical shifts of the Cp ring ^{13}C nuclei for the two analogues were observed to differ [6].

Complexation of the metal cation probably causes distortion throughout the π-bonded planar cyclopentadienyl-amido unit, with the coordinating carbonyl O-atoms bent inward toward the complexed Mg^{2+} cation. Model studies suggest that this is relayed through the π-bonded framework and results in a metallocene inter-ring tilt, with Cp rings distorted about an axis containing C13′ and some point intersecting the bond C15′–C11′. This places the Cp ring ^{13}C nuclei closer to the electron-rich plane containing the occupied bonding metal-centered d_{xy} and $d_{x^2-y^2}$ orbitals in the relative order C11′ > C12′ > C13′ > C14′ > C15′. The magnetic environment of these ^{13}C nuclei is strongly dependent on the bonding electron densities in their vicinity. For the more diffuse 4*d* orbitals in **2**, the shielding of the ^{13}C nuclei is less than for the 3*d* orbitals in **1**. For broadly isostructural complexes, the relative additional deshielding of corresponding Cp ring ^{13}C nuclei in **2** compared to **1** will reflect the extent to which the ^{13}C nuclei are less close to the electron-rich plane containing the metal-centered d_{xy} and $d_{x^2-y^2}$ orbitals. This is seen to be the case, with the additional deshielding of the Cp ^{13}C ring nuclei in **2** compared to **1** following the order C11′ > C12′ > C13′ > C14′ > C15′, and being (in ppm) +4.12, +3.51, +2.72, +2.29 and +1.05 respectively. The ^{13}C=O chemical shifts for both complexes are similar, but both are significantly deshielded with respect to the free host molecules. This reflects the electron withdrawing effect of the complexed positively charged cation.

The chemical shift data for the corresponding heterocyclic bridge nuclei for the complexes containing **1** and **2** are very similar, and indeed, the ^{13}C–^{1}H shift correlation spectra for the heterocyclic nuclei for the two complexes are almost super-imposable. This confirms the isostructural comparability of the two complexes, and suggests that only limited unpuckering of the heterocyclic bridges occurs in the complex with **2** in order to accommodate the greater metallocene inter-ring dimension in the case of the ruthenium analogue. For both complexes, the most and the least deshielded heterocyclic bridge ^{1}H nuclei are bonded to the carbon atom which is *cis* to the carbonyl, which is the more deshielded NCH_2 nucleus. This contrasts with the cases of the uncomplexed host molecules in which the most and least deshielded heterocyclic ^{1}H nuclei are similarly those bonded to the carbon which is *cis* to the carbonyl, but it is this ^{13}C nucleus which is the more shielded of the NCH_2 nuclei. In the free host cryptands the carbonyls are oriented *trans* with

Table 3

Chemical shifts (ppm) for the 2:1 complex of **1** with Mg^{2+} in MeCN-d_3 (see text for conditions). ^1H values refer to multiplet centroids. Nuclei are those *cis* or *trans* to the carbonyl, Cp ring numbering with H2′ *cis* to carbonyl.

^{13}C	δ	^1H	δ
NCH_2CH_2O (*cis*)	48.72	A	3.01
		B	4.15
NCH_2CH_2O (*trans*)	52.66	A	3.55 [a]
		B	3.90
NCH_2CH_2O (*cis*)	71.14	A	3.55 [a]
		B	3.80 [a]
NCH_2CH_2O (*trans*)	69.83	A	3.60 [a]
		B	3.75 [a]
OCH_2CH_2O (*cis*)	70.50	A	3.65 [a]
		B	3.65 [a]
OCH_2CH_2O (*trans*)	71.63	A	3.50 [a]
		B	3.60 [a]
Cp C1′	80.75		
Cp C2′	73.25	H1′	4.68
Cp C3′	70.88	H3′	4.45
Cp C4′	72.31	H4′	4.53 [a]
Cp C5′	73.78	H5′	4.53 [a]
C=O	171.85		

[a] Overlapping multiplets.

respect to each other, whereas in the complexes they are *cis*, and it is probably the conformational changes in molecular re-organisation upon complexation which gives rise to the switch in NCH_2 shielding patterns.

Low temperature spectra have been recorded for solutions of these complexes, in which 2:1 host-guest complexation stoicheiometries are observed. Table 3 gives the chemical shift data for a solution of **1** with Mg^{2+} at ca. 0.05 *M* and −10 °C. At temperatures between +22 and −10 °C this solution gives rise to the super-position of the spectra of the 1:1 host-guest complex (see Table 2) and the 2:1 complex reported in Table 3. Lowering the temperature gradually shifts the equilibrium in favour of the 2:1 complex whose spectrum grows in intensity as the spectrum of the 1:1 complex decreases. At −10 °C this solution consists almost entirely of the 2:1 complex. The spectrum consists of the same number of signals as that for the 1:1 complex, and therefore the solution structure of the 2:1 host-guest complex must possess elements of symmetry. The most deshielded CH_2 signal and the most deshielded CH signal are assigned to those protons *cis* to the carbonyl. Detailed examination of the 2D-COSY and ^{13}C–^1H shift correlation spectra permit the assignments given in Table 3. The data is best interpreted by a structure in which the central Mg^{2+} cation is four coordinate, with two donor carbonyl O-atoms from each of the two molecules of **1** forming the 2:1 host-guest complex. For retention of symmetry, the carbonyls within each coordinating cryptand are oriented *cis*. The chemical shift of the carbonyl ^{13}C nucleus at 171.85 ppm is less than that for the 1:1 complex. This is attributed to charge dispersion amongst the four coordinating carbonyls in the 2:1 complex. When this solution is warmed the spectrum of the 1:1 complex is seen to grow in intensity at the expense of the spectrum of the 2:1 complex.

Low temperature studies on the corresponding solution of **2** with Mg^{2+} were hampered by problems in data collection, probably associated with solubility problems on cooling. However, the spectrum of the 2 : 1 host-guest complex of **2** with Mg^{2+} was seen to develop on cooling. The spectrum of this 2 : 1 complex displays pronounced similarities with its ferrocene analogue, the most characteristic signals seen to develop on cooling being the corresponding $N\mathit{C}H_2CH_2O$ (*cis*) and $N\mathit{C}H_2CH_2O$ (*trans*) species at 48.2 and 53.4 ppm respectively.

For complexes of both **1** and **2** with Mg^{2+}, the addition of D_2O to the solutions appears to cause decomplexation as evidenced by the regeneration of the spectra of the free hosts in MeCN-d_3/D_2O as solvent.

Acknowledgements

We thank Mrs. Fran Gallwey for collection of the NMR data and RTZ Chemicals Ltd./Rhone Poulenc Chemicals for financial support (N.W.S.)

References

1 C.D. Hall, N.W. Sharpe, I.P. Danks and Y.P. Sang, J. Chem. Soc., Chem. Commun., (1989) 419.
2 C.D. Hall, I.P. Danks and N.W. Sharpe, J. Organomet. Chem., 390 (1990) 227.
3 P.D. Beer, C.D. Bush and T.A. Hamor, J. Organomet. Chem., 339 (1988) 133.
4 C.D. Hall, I.P. Danks, S.C. Nyburg, A.W. Parkins and N.W. Sharpe, Organometallics, 9 (1990) 1602.
5 C.D. Hall, A.W. Parkins, S.C. Nyburg and N.W. Sharpe, J. Organomet. Chem., 407 (1991) 107.
6 C.D. Hall and N.W. Sharpe, Organometallics, 9 (1990) 952.
7 C.D. Hall, I.P. Danks, M.C. Lubienski and N.W. Sharpe, J. Organomet. Chem., 384 (1990) 139.