

Preliminary communication

THE STRUCTURE OF NOVEL CRYPTANDS CONTAINING METALLOCENE UNITS BY POLARISATION TRANSFER SEQUENCES AND 2-D NMR

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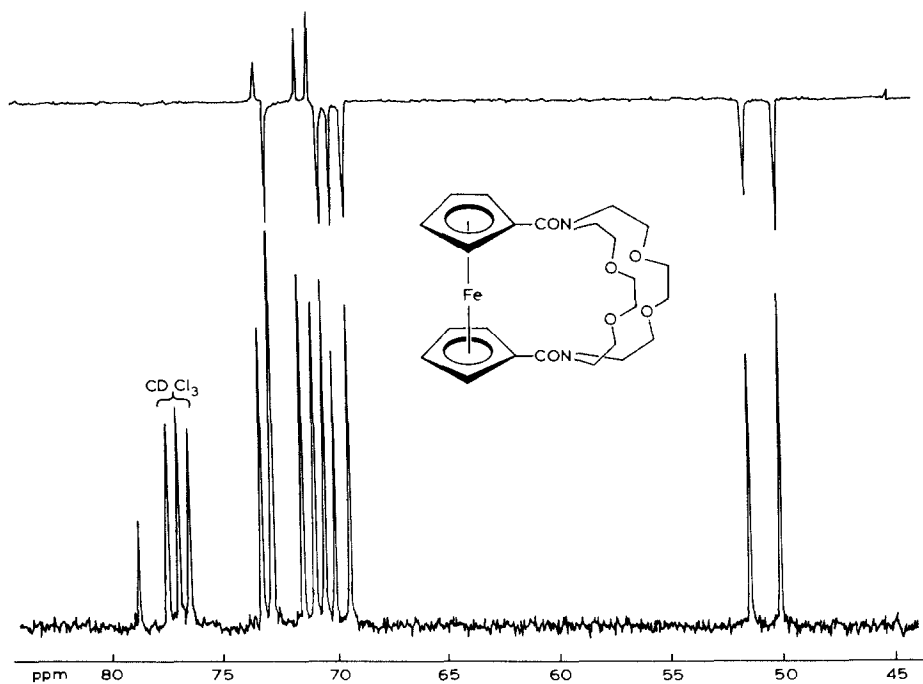
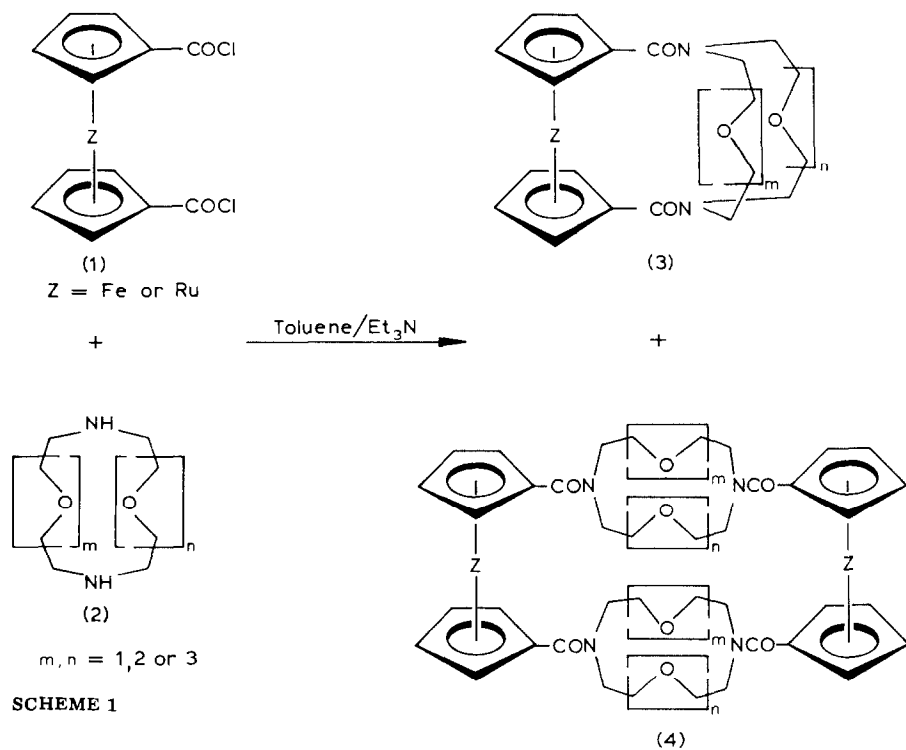
Summary

Polarisation transfer sequences (INEPT and DEPT) in conjunction with 2-D NMR have been used to assign resonance signals in the ^{13}C NMR spectra of novel cryptands (**3**) containing ferrocene and ruthenocene units. The data are consistent with a *trans* disposition of the carbonyl groups in all examples of **3**.

In recent publications [1,2] we reported the synthesis of cryptands **3** and **4**, [$\text{Z} = \text{Fe}$, $m = n = 2$] and a determination of their structures by a combination of conventional ^1H and ^{13}C NMR. Subsequent work has shown that the ratio of monomer **3** to dimer **4** may be controlled by variation of the temperature of the condensation reaction [3] over the whole range of cryptands. We now report that the resonance signals in the ^{13}C NMR spectra of the monomers may be assigned using the polarisation transfer techniques (INEPT and DEPT)* [4] and when the ^{13}C signals of the oxymethylene and ferrocene carbons are coincident, the spectra may be resolved by 2-D NMR [5].

All the cryptands were prepared by the standard condensation reaction (see Scheme 1) and gave satisfactory elemental analyses and molecular weights by mass spectrometry. The ^{13}C spectrum of the 2/2 monomer (**3**, $\text{Z} = \text{Fe}$, $m = n = 2$) had already been assigned by a combination of broadband-decoupled and off-resonance ^{13}C NMR [2] and this was therefore used as a basis to establish the validity of polarisation transfer technique and the parameters to be used. When compared with the conventional ^{13}C broadband decoupled spectrum (Fig. 1) the DEPT spectrum shows positive signals for the ferrocene carbons, negative

*INEPT = insensitive nuclear enhancement by polarisation transfer, DEPT = distortionless enhancement by polarisation transfer.



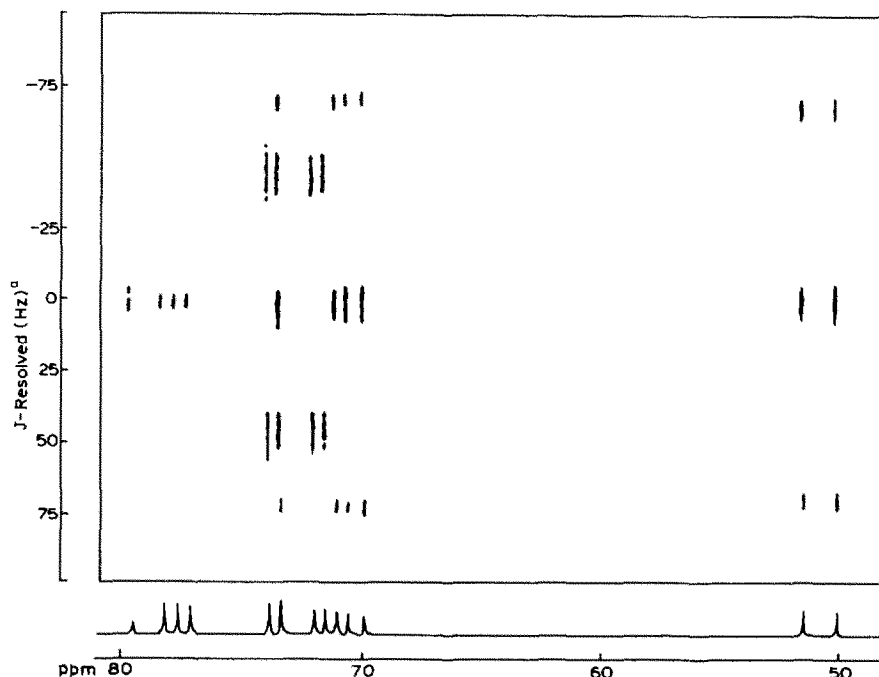


Fig. 2. Heteronuclear J -resolved (gated-decoupling) ^{13}C 2-D NMR of **3** ($m = n = 2$) in CDCl_3 (ref. TMS). (2-D parameters: F2: 2K for ^{13}C , SW 2100 Hz, Hz/Pt = 2.0, Gaussian window function, 16 transients, 10% solution; F1: the J dimension, 64 data points, (zero-filled to 128), SW 200 Hz, Hz/Pt = 3.125). (a) F1 transform gives all J -couplings at $1/2$ their actual value.

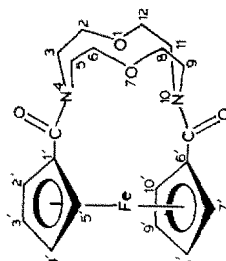
signals for OCH_2 and NCH_2 carbons, and no signal for the *ipso*-carbons of the ferrocene ring. It is immediately apparent that one OCH_2 carbon coincides with one ferrocene carbon at 72.9 ppm and this is confirmed by the 2-D spectrum (Fig. 2) which, in the J -resolved axis, reveals a doublet ($\text{Fe}-\text{C}$) superimposed upon a triplet (OCH_2). Details of the spectral parameters are reported in the Figure captions.

The DEPT technique was then applied to a range of monomeric cryptands and the resultant assignments appear in Table 1. It is clear that the method promises to be invaluable in the assignment of signals within these complex spectra, and in addition the data allow certain structural deductions to be made.

In the case of the symmetrical cryptands **3** ($n = m$) the carbonyl groups could, in principle, be *cis* or *trans* to each other in the rigid structure. Tentative arguments, based on variable temperature ^1H and ^{13}C NMR spectra, have been advanced [2] to suggest that the structures are in fact *trans*. However, the observation of four $\text{N}-\text{CH}_2$ signals and eight ferrocene-C signals for the unsymmetrical monomer **3** ($m = 2, n = 1$) and a similar complexity in the other unsymmetrical monomer **3** ($m = 3, n = 2$) strongly implies the *trans* configuration since the *cis* isomers would contain a plane of symmetry through the metal atom parallel to the plane of the cyclopentadiene rings. The inference therefore, is that all the monomeric structures have a *trans* disposition of the carbonyl groups.

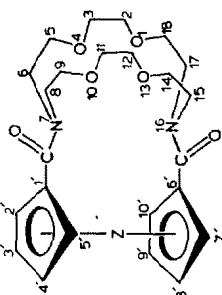
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TABLE 1
 THE ^{13}C NMR DATA OF CRYPTANDS **3** FROM BROAD BAND DECOUPLED (BBD) AND DEPT/INEPT SPECTRA (solvent: CDCl_3 ; reference TMS)

Cryptand	$\delta(^{13}\text{C})$ (ppm) ex BBD at 62.9 MHz		$\delta(^{13}\text{C})$ (ppm) ex DEPT ^a /INEPT ^b	NCH_2 (-)	
	C=O	ipso-C			
 (3 , $m = n = 1$)	172.0	77.3 (C(1')/6')	70.8 (C(4'/9')) 71.5 (C(3'/8')) 74.2 (C(5'/10')) 78.3 (C(2'/7'))	68.8 (C(2/8)) 69.1 (C(6/12))	44.2 (C(3/9)) 50.5 (C(5/11))
	171.3 173.7	78.9 (C(1')/6')	70.4 (C(3')) 70.6 (C(9')) 71.0 (C(8')) 72.2 (C(4')) 72.8 (C(10')) 73.5 (C(2')) 73.8 (C(7')) 78.1 (C(5'))	68.1 (C(5)) 68.9 (C(2/3/9/11)) 69.5 (C(15)) 69.8 } 70.1 } (C(2/3/9/11)) 70.2 }	45.3 (C(12)) 50.9 (C(6)) 51.3 (C(8)) 52.3 (C(14))

(**3**, $m = 2$, $n = 1$)

170.7 78.5 (C(1'/6'))
50.1 (C(6/15))
51.5 (C(8/17))



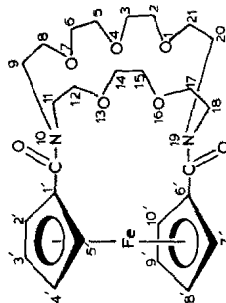
(3, Z = Fe, m = n = 2)
(3, Z = Ru, m = n = 2)

71.0 (C(2'/7'))
71.5 (C(3'/4'/8'/9'))
72.9 (C(3'/4'/8'/9'))
73.3 (C(5'/10'))
69.4 (C(5/14))
70.1 (C(9/18))
70.5 (C(2/3/11/12))
72.9 (C(2/3/11/12))

169.4 83.8 (C(1'/6'))
48.8 (C(6/15))
51.4 (C(8/17))

71.7 (C(2'/7'))
73.6 (C(3'/4'/8'/9'))
74.8 (C(3'/4'/8'/9'))
74.9 (C(5'/10'))
70.0 (C(5/14))
70.5 (C(9/18))
70.7 (C(2/3/11/12))
71.5 (C(2/3/11/12))

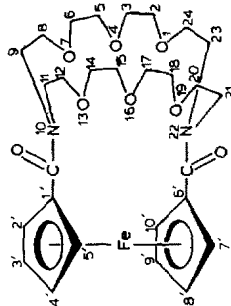
169.8 77.4 (C(1'/6'))
170.5 83.5 (C(1'/6'))
46.9 (C(18))
48.2 (C(9))
49.5 (C(11))
51.3 (C(20))



(3, m = 3, n = 2)

68.8 (C(3'/9'))
70.9 (C(8'))
71.0 (C(4'))
71.9 (C(10'))
72.7 (C(2'))
72.8 (C(7'))
75.5 (C(5'))
68.2 (C(17))
68.4 (C(14/15))
69.6 (C(12))
69.9 (C(14/15))
70.15 (2)
70.2 } C(2/3/5/6/8/21)
70.5 (2)
71.6

174.3 82.3 (C(1'/6'))
54.2 (C(9/21))
55.0 (C(11/23))



(3, m = n = 3)^c

76.3 (C(2'/7'))
76.6 (C(3'/4'/8'/9'))
79.0 (C(3'/4'/8'/9'))
81.3 (C(5'/10'))
75.4 (8)^d
75.8 (C(8/12/20/24))
76.0 (C(8/12/20/24))

^a DEPT parameters: $\theta = \frac{3\pi}{4}$, $t_{90}(\text{H})$ 32 μs , $t_{90}(\text{C})$ 15.5 μs , 300 transients, 10% solution. ^b INEPT parameters: $1/\omega_1$, 1.67 msec, refocusing delay 2.5 msec, $t_{90}(\text{H})$ 32 μs , $t_{90}(\text{C})$ 15.5 μs , 300 transients, 10% solution. ^c Spectra run in toluene- d_6 at -50°C ; cryptand exhibits dynamic phenomenon to be discussed in a future publication [6]. ^d 4 Carbons C(2/3/5/6), C(14/15/17/18).

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References

- 1 A.P. Bell and C.D. Hall, *J. Chem. Soc., Chem. Commun.*, (1980) 163.
- 2 P.J. Hammond, A.P. Bell and C.D. Hall, *J. Chem. Soc., Perkin Trans I*, (1983) 707.
- 3 P.D. Beer, P.J. Hammond and C.D. Hall, *J. Chem. Soc., Chem. Commun.*, (1983) 1161.
- 4 (a) G.A. Morris and R. Freeman, *J. Amer. Chem. Soc.*, 101 (1979) 760; (b) D.M. Doddrell, D.T. Pegg and M.R. Bendall, *J. Magn. Reson.*, 48 (1982) 323; (c) D.T. Pegg, D.M. Doddrell and M.R. Bendall, *J. Chem. Phys.*, 72 (1982) 2745.
- 5 (a) L. Muller, A. Kumar, R.R. Ernst, *J. Chem. Phys.*, 63 (1975) 5490; (b) G. Bodenhausen, R. Freeman, and D.L. Turner, *J. Chem. Phys.*, 65 (1976) 839.
- 6 P.D. Beer, P.J. Hammond and C.D. Hall, unpublished results.