

## FLUXIONAL CRYPTANDS CONTAINING METALLOCENE UNITS

PHILIP J. HAMMOND, PAUL D. BEER\*, CLARE DUDMAN,  
IAN P. DANKS, C. DENNIS HALL\*

*Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS (Great Britain)*

JOHN KNYCHALA and MARTIN C. GROSSEL

*Department of Chemistry, Bedford College, University of London (Great Britain)*

(Received October 30th, 1985)

### Summary

A combination of dynamic  $^1\text{H}$  and  $^{13}\text{C}$  NMR has been used to study the fluxional behaviour of cryptands (**3**) containing ferrocene units. The coalescence phenomena associated with these molecules are due to restricted rotation about the Fe-CO-N bond system and activation parameters are reported for this rotational process. These are compared with activation parameters for rotation about the amide bond of 1,1'-metallocene-bis-amides.

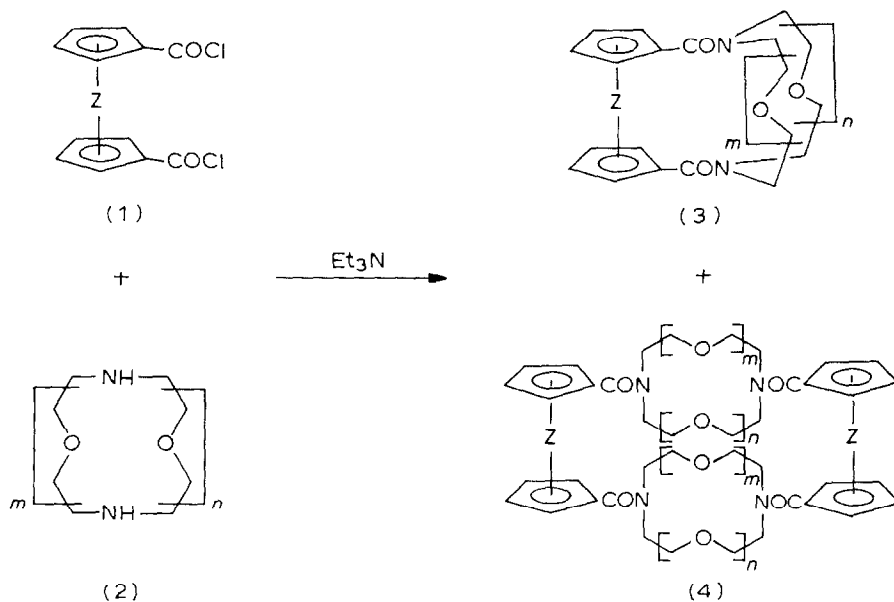
---

In recent publications [1,2,3] we reported the synthesis of a range of cryptands **3** and **4** ( $Z = \text{Fe}$  or  $\text{Ru}$ ,  $m = n = 1, 2$  or  $3$ ) and a determination of their structures by a combination of conventional  $^1\text{H}$  and  $^{13}\text{C}$  NMR, polarisation transfer techniques (INEPT and DEPT), [4]) and where appropriate,  $J$ -resolved 2-D NMR [5] of the  $^{13}\text{C}$  spectra. Some of the monomeric cryptands, **3**, with  $Z = \text{Fe}$  or  $\text{Ru}$  and  $m = n = 1$  or  $2$  were rigid on the NMR time scale over a temperature range from  $-60$  to  $+100^\circ\text{C}$ . For  $Z = \text{Fe}$  and  $m = 2, n = 1$ ;  $m = 3, n = 2$ , and  $m = n = 3$  however, coalescence phenomena were observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra over the same temperature range and we now report the details of these experiments.

All the cryptands were prepared by the standard condensation reaction (see Scheme 1 and refs. 2 and 6) and gave satisfactory elemental analysis and molecular masses by mass spectrometry (Table 1). The  $^{13}\text{C}$  NMR spectra of **3** (with  $m = 2$  and  $n = 1$ ) at 254 and 354 K in toluene- $d_8$  are recorded in Table 2 along with the corresponding assignments; Fig. 1 illustrates the spectra at the same two temperatures. It is obvious that the molecule is displaying fluxional behaviour on the NMR

---

\* Present addresses: Department of Chemistry, The University of Birmingham, Birmingham B15 2TT (Great Britain).



SCHEME 1

time scale and by recording a series of spectra between these temperatures, coalescence temperatures ( $T_c$ ) and chemical shift differences ( $\Delta\nu$ ) were obtained for several  $^{13}\text{C}$  signals (Table 3). The Gutowsky equation then allowed calculation of the rate coefficients at each coalescence temperature (Table 3) from which an Arrhenius plot was derived (Fig. 2) which gave an  $E_A$  value of  $12.4 \text{ kcal mol}^{-1}$ .

A variable temperature study of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for the 3:2 monomer **3** ( $m = 3$ ,  $n = 2$ ) in toluene- $d_8$  gave a similar set of data (Table 4) from which an  $E_A$  value of  $11.0 \text{ kcal mol}^{-1}$  was calculated. Analogous data for the 3:3 monomer **3** ( $m = n = 3$ ) are shown in Table 5 and the corresponding Arrhenius plot gave an  $E_a$

TABLE 1

MELTING POINTS, RELATIVE MOLECULAR MASSES (RMM) AND ELEMENTAL ANALYSIS OF CRYPTANDS **3** WITH  $Z = \text{Fe}$  OR  $\text{Ru}$

Z	Cryptand <b>3</b>		M.p. (°C)	RMM (Found)	Elemental analysis (Found (calcd.) (%))		
	m	n			C	H	N
Fe	1	1	102–104	412	57.8 (58.3)	5.88 (5.86)	6.70 (6.79)
Fe	2	1	192–193	456	57.7 (57.9)	6.11 (6.18)	6.07 (6.14)
Fe	2	2	183–184	500	See ref. 2		
Fe	3	2	205 (dec.)	544	56.8 (57.4)	6.90 (6.66)	4.54 (5.14)
Fe	3	3	136–139	588	56.8 (57.1)	6.86 (6.85)	4.62 (4.76)
Ru	2	2	208–210	545	52.6 (52.8)	5.91 (5.91)	5.13 (5.11)

TABLE 2

$^{13}\text{C}$  NMR DATA OF CRYPTAND 3 ( $Z = \text{Fe}$ ,  $m = 2$ ,  $n = 1$ ) FROM BROAD BAND DECOUPLED (BBD) AND DEPT SPECTRA AT 62.9 MHz IN TOLUENE- $d_8$  AT 354 AND 254 K

Temperature (K)	Assignments and $\delta$ ( $^{13}\text{C}$ ) in ppm relative to TMS <sup>a</sup>				
	C=O	<i>ipso</i> -C	Metallocene-C (+) <sup>b</sup>	OCH <sub>2</sub> (-) <sup>b</sup>	NCH <sub>2</sub> (-) <sup>b</sup>
354	171.7 (2)	80.2	76.4 (2, br)	70.3 (2)	51.5 (2)
			73.9 (2)	70.1 (2)	48.5 (2, br)
			71.9 (2)	69.8 (2)	
			70.7 (2)		
254	172.6 170.4	79.9 79.6	78.2	69.8 (3)	51.7
			73.9	69.2	50.9 (2)
			73.7	68.1	45.1
			73.0	67.7	
			72.3		
			71.0		
			70.6		
			70.4		

<sup>a</sup> Figures in brackets denote number of carbon atoms at this chemical shift if greater than one; br = broad. <sup>b</sup> Signs in brackets denote positive or negative signals in the DEPT experiment.

value of  $8.5 \text{ kcal mol}^{-1}$ . Finally, the complete set of activation parameters corresponding to the fluxional processes are shown in Table 6.

It is evident that the free energy of activation for the fluxional process is the same for each of the monomers and is very similar to the free energy of activation

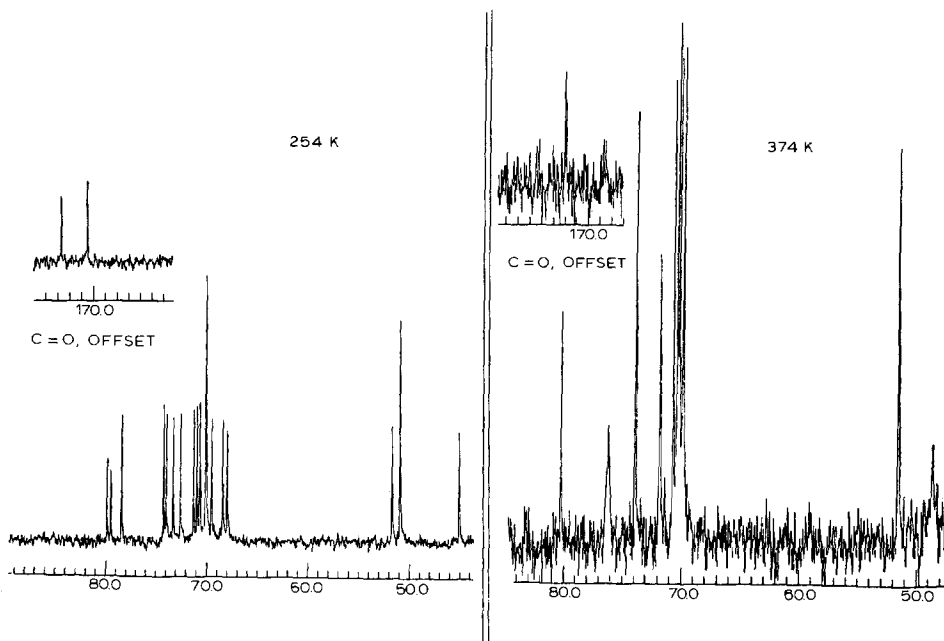


Fig. 1.  $^{13}\text{C}$  NMR spectra of 3 ( $m = 2$ ,  $n = 1$ ) in  $\text{C}_7\text{D}_8$  at 254 and 374 K relative to TMS.

TABLE 3

COALESCENCE TEMPERATURES ( $T_c$ ), CHEMICAL SHIFT DIFFERENCES ( $\Delta\nu$ ) AND RATE COEFFICIENTS AT COALESCENCE ( $k_c$ ) FROM THE  $^{13}\text{C}$  NMR SPECTRA OF **3** ( $Z = \text{Fe}$ ,  $m = 2$ ,  $n = 1$ ) IN TOLUENE- $d_8$

Carbon atom	$T_c$ (K)	$\Delta\nu$ (Hz)	$k_c$ ( $\text{s}^{-1}$ )
<i>ipso</i> -C	295	21.2	47.1
N- $\text{CH}_2$	309	51.3	114
C=O	320	138	307
Ferro-C(2',5')	334	268	594
N- $\text{CH}_2$	344	368	817

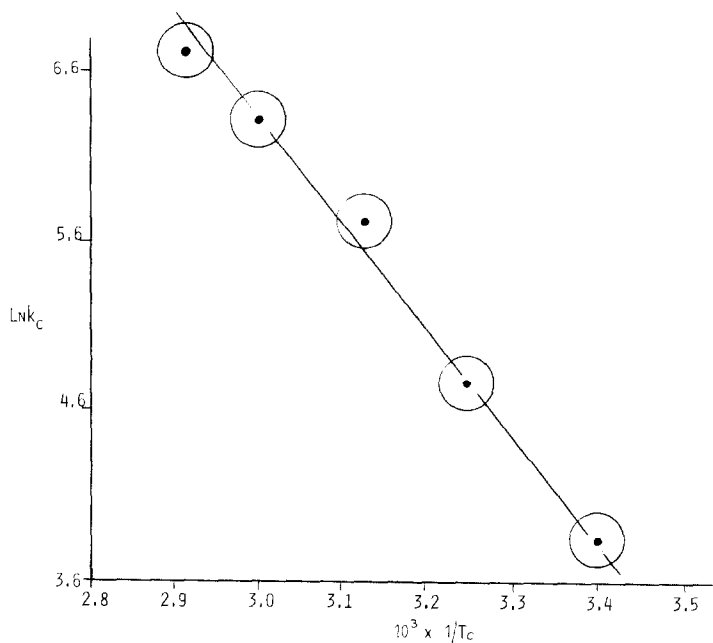


Fig. 2. Arrhenius plot of  $\log k_c$  versus  $1/T_c$  for five  $^{13}\text{C}$  NMR signals of **3** ( $m = 2$ ,  $n = 1$ ); see Table 3.

TABLE 4

COALESCENCE TEMPERATURES ( $T_c$ ), CHEMICAL SHIFT DIFFERENCES ( $\Delta\nu$ ) AND RATE COEFFICIENTS AT COALESCENCE ( $k_c$ ) FROM THE  $^1\text{H}$  AND  $^{13}\text{C}$  NMR SPECTRA OF **3** ( $Z = \text{Fe}$ ,  $m = 3$ ,  $n = 2$ ) IN TOLUENE- $d_8$

Nucleus	Group	$T_c$ (K)	$\Delta\nu$ (Hz)	$k_c$ ( $\text{s}^{-1}$ )
$^1\text{H}$	Ferrocene- <i>H</i>	296	25	56
$^1\text{H}$	Ferrocene- <i>H</i>	313	48	106
$^1\text{H}$	Ferrocene- <i>H</i>	313	55	122
$^1\text{H}$	Ferrocene- <i>H</i>	328	140	311
$^{13}\text{C}$	N- $\text{CH}_2$	333	184	409

TABLE 5

COALESCENCE TEMPERATURE ( $T_c$ ), CHEMICAL SHIFT DIFFERENCES ( $\Delta\nu$ ) AND RATE COEFFICIENTS AT COALESCENCE ( $k_c$ ) FROM THE  $^1\text{H}$  AND  $^{13}\text{C}$  NMR SPECTRA OF **3** ( $Z = \text{Fe}$ ,  $m = 3$ ,  $n = 2$ ) IN TOLUENE- $d_8$

Nucleus	Group	$T_c$ (K)	$\Delta\nu$ (Hz)	$k_c$ ( $\text{s}^{-1}$ )
$^1\text{H}$	Ferrocene- $H(3',4')$	300	21.8	48
$^1\text{H}$	Ferrocene- $H(2',5')$	300	32.0	71
$^{13}\text{C}$	N- $\text{CH}_2$	316	51.5	114
$^{13}\text{C}$	Ferrocene- $C(2',5')$	326	151	335
$^{13}\text{C}$	N- $\text{CH}_2$	373	440	977

TABLE 6

ACTIVATION PARAMETERS FOR THE COALESCENCE PHENOMENA OBSERVED IN THE  $^1\text{H}$  AND  $^{13}\text{C}$  NMR SPECTRA OF **3** IN TOLUENE- $d_8$

Compound	$k_c$ at 298 K ( $\text{s}^{-1}$ )	$\Delta G^*$ at 298 K ( $\text{kcal mol}^{-1}$ )	$E_A$ ( $\text{kcal mol}^{-1}$ )	$\Delta S^*$ (298 K) ( $\text{cal mol}^{-1}\text{K}^{-1}$ )
$m = 2$ , $n = 1$	62	15.1	12.4 ( $\pm 1.1$ )	-11 ( $\pm 2$ )
$m = 3$ , $n = 2$	57	15.1	11.0 ( $\pm 1.5$ )	-16 ( $\pm 3$ )
$m = 3$ , $n = 3$	55	15.0	8.5 ( $\pm 1.6$ )	-24 ( $\pm 3$ )

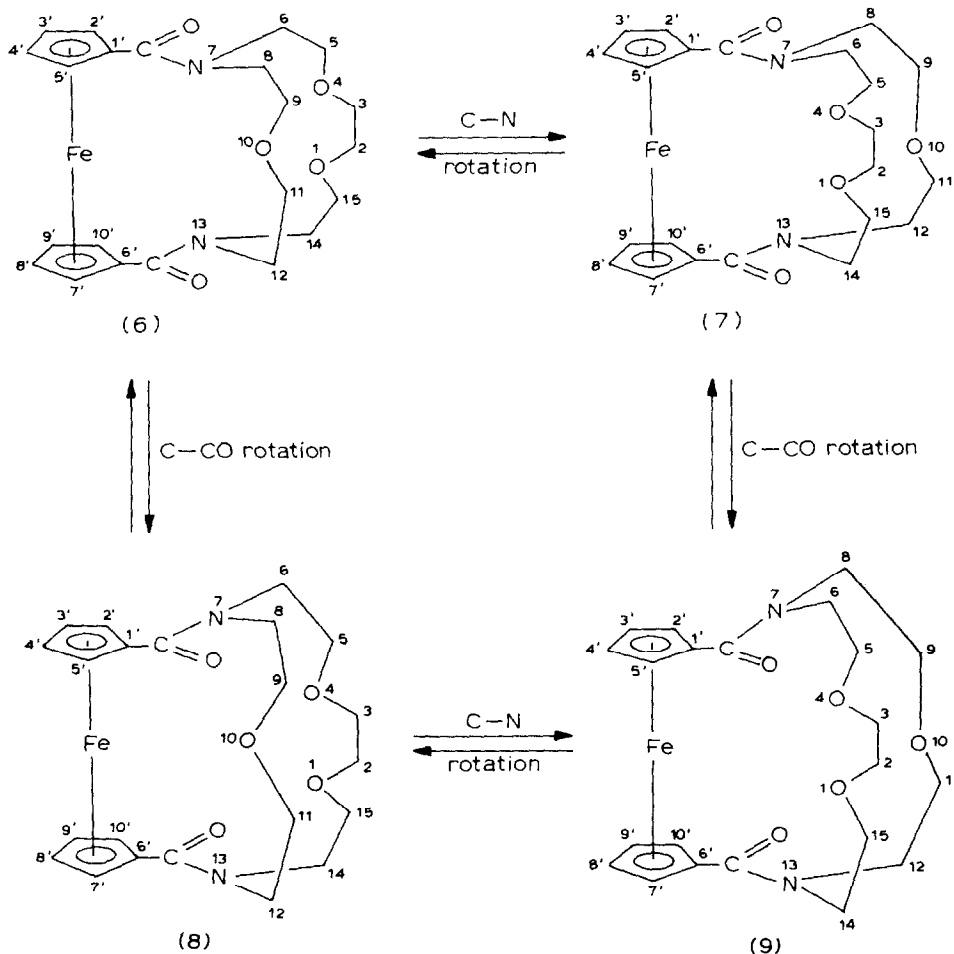
associated with the rotation about the amide bond of 1,1'-ferrocene-bis-amides (**5**) (Table 7). The latter results were obtained by a variable temperature study of the  $^1\text{H}$  NMR spectra of these molecules and the  $E_A$  values were derived by a computerised line-shape analysis for a two-site exchange [7]. It follows therefore that the fluxional process observed with the cryptands is due to restricted rotation about the Fe-CO-N bond system. The NMR spectra at low temperature indicate only one frozen configuration for each cryptand and by analogy with earlier work (cf. [2] and [3]) it seems reasonable to assume that this configuration is the one with the carbonyl groups *trans* to each other. For the 1:1-monomer **3** ( $m = n = 1$ ) and the 2:2-monomer **3** ( $m = n = 2$ ) the molecules are rigid on the NMR time scale over the same temperature range [2,3] and one must conclude that the fluxional behaviour is

TABLE 7

ACTIVATION PARAMETERS FOR THE ROTATION ABOUT THE AMIDE BOND OF 1,1'-METALLOCENE-BIS-AMIDES (**5**)<sup>a</sup>

R	NMR coalescence parameter	$T_c$ (K)	$k_c$ ( $\text{s}^{-1}$ )	$\Delta G^*$ at $T_c$ ( $\text{kcal mol}^{-1}$ )	$\Delta H^*$ ( $\text{kcal mol}^{-1}$ )	$\Delta S^*$ ( $\text{cal mol}^{-1}\text{K}^{-1}$ )
(i) $Z = \text{Fe}$						
Me	$^1\text{H}/\text{NMe}_2$	278	32	14.5	14.3	-0.6
Et	$^{13}\text{C}/\text{NCH}_2$	293	100	14.6	13.3	-5
Pr <sup>i</sup>	$^{13}\text{C}/\text{NCH}(\text{CH}_3)_2$	323	298	15.4	13.9	-5
- $\text{CH}_2(\text{CH}_2)_3\text{CH}_2$ -	$^{13}\text{C}/\text{NCH}_2$	288	231	13.8	13.6	-0.8
- $\text{C}_2\text{H}_4\text{OC}_2\text{H}_4$ -	$^{13}\text{C}/\text{NCH}_2$	280	249	13.4	-	-
(ii) $Z = \text{Ru}$						
Me	$^1\text{H}/\text{NMe}_2$	287	47	14.6	-	-

<sup>a</sup>  $\Delta H^*$  and  $\Delta S^*$  values where quoted were derived from total line shape analysis of the coalescing spectra.



SCHEME 2

dependent not only upon the size of the diazacrown macrocycle but also upon an unsymmetrical structure.

Taking the 2:1-monomer as an example, the equivalence of four pairs of ferrocene carbons, one pair of *ipso* carbons, one pair of carbonyl carbons, two pairs of N-CH<sub>2</sub> carbons and three pairs of OCH<sub>2</sub> carbons can be achieved in one of two ways. Rotation about the N-CO link converts **6** to **7** (Scheme 2) which on rotation through a C<sub>2v</sub> axis produces a molecule with C(6)≡C(14) and C(8)≡C(12) (i.e. two NCH<sub>2</sub> carbons), C(5)≡C(15), C(2)≡C(3), and C(9)≡C(11) (i.e. three OCH<sub>2</sub> carbons), 1' = 6' (i.e. one *ipso* carbon), equivalent carbonyl carbons, and C(2')≡C(7)'; C(3')≡C(8)', C(4')≡C(9)' and C(5')≡C(10)' (i.e. four ferrocene CH carbons). But such a motion requires one side of the macrocyclic ring to pass above or below the other side in the transition state and although molecular models suggest that such a motion is possible, it seems extremely unlikely in view of the resultant severe crowding of carbon and hydrogen atoms in the transition state. The alternative motion is a rotation of the carbonyl groups relative to the ferrocene ring system, i.e. **6** to **8**. The resultant molecule, **8**, on rotation through a second C<sub>2v</sub> axis is a mirror

image of **6** again rendering C(6)≡C(14), C(8)≡C(12) etc. in which the  $^{13}\text{C}$  spectrum would show half the original number of peaks. If both processes were to occur however, the ferrocene carbons would degenerate to two, with C(2)′≡C(5)′≡C(7)′≡C(10)′ and C(3)′≡C(4)′≡C(8)′≡C(9)′. We suggest therefore that rotation about the ferrocene-CO bond is responsible for the coalescence phenomena. Such a rotation requires the  $\pi$ -orbitals of the carbonyl group and the lone-pair of the N atom to become orthogonal in the transition state and this would show the typical activation parameters associated with rotation about the amide link. Furthermore, such a rotation would require a specific orientation of the cyclopentadiene rings and more critically, a specific orientation of the macrocyclic ring in the transition state in order to minimise steric repulsion and this would account for the negative values of  $\Delta S^\ddagger$ .

Finally it only remains to explain why the 1:1- and 2:2-monomers are rigid on the NMR time scale whereas the unsymmetrical 2:1- and 3:2-monomers and the 3:3-monomer show fluxional behaviour. Inspection of models reveals that in the 1:1- and 2:2-monomers with the carbonyl groups *trans* to one another, the molecules have no difficulty in achieving co-planarity between the  $\pi$ -orbitals of the carbonyl group and the lone pair on nitrogen. With the unsymmetrical 2:1- and 3:3-cryptands such coplanarity is not so easily accomplished and there appears to be a considerable dihedral angle between at least one of the  $\pi$ -orbitals of the carbonyl group and the nitrogen lone pair which would obviously raise the ground state energy of these molecules. The same argument is not applicable to the 3:3-monomer but the size of the macrocyclic ring makes the system inherently more flexible.

### Experimental

All melting points are uncorrected. NMR spectra were obtained on a Bruker WH250 FT machine fitted with a variable temperature probe and operating at 250 MHz for  $^1\text{H}$  NMR and 62.9 MHz for  $^{13}\text{C}$  NMR using either broad band decoupling or the DEPT programme [4] to give CH carbons as positive signals (+) and the OCH<sub>2</sub> and NCH<sub>2</sub> carbons as negative signals (-).

The cryptands **3** were prepared by the general procedure outlined in Scheme 1 as described in refs. 2, 3, and 6. The general procedure for the preparation of metallocene-bis-amides **5** is as follows for Z = Fe and R = Me.

#### *1,1'-Bis-N,N-dimethylamidoferrocene*

A mixture of dimethylamine (0.29 g,  $6.4 \times 10^{-3}$  mol) and triethylamine (0.7 g,  $7 \times 10^{-3}$  mol) in toluene (10 ml) was added with stirring to a solution of **1** (1.0 g,  $3.2 \times 10^{-3}$  mol) in toluene (100 ml) at 0°C. After stirring for 10 minutes the mixture was filtered to remove the precipitated triethylamine hydrochloride and the filtrate was evaporated to dryness. The residue was chromatographed on alumina (Grade 1) using CH<sub>2</sub>Cl<sub>2</sub> (500 ml) as initial eluant followed by 1% methanol in CH<sub>2</sub>Cl<sub>2</sub> when the product eluted from the column as an orange band. Evaporation of the solvent and recrystallisation of the residue from chloroform/ether yielded (95%) of product, m.p. 130°C. The melting points and relative molecular masses of the bis-amide products, which all gave satisfactory elemental analyses, are recorded in Table 8 and the principle features of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (above coalescence) are shown in Table 9.

TABLE 8  
MELTING POINTS AND RELATIVE MOLECULAR MASSES OF METALLOCENE-BIS-AMIDES

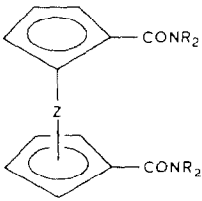
Metallocene-bis-amide		M.p. (°C)	RMM (Found calcd.)	
Z	R			
Fe	Me	130–31	328 (328)	 <p>(5)</p>
Fe	Et	159–160	384 (384)	
Fe	Pr <sup>i</sup>	127–128	440 (440)	
Fe	–CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> –	165–166	408 (408)	
Fe	–C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> –	180–181	412 (412)	
Ru	Me	149–150	373 (373)	

TABLE 9  
<sup>1</sup>H AND <sup>13</sup>C NMR SPECTRA OF METALLOCENE-BIS-AMIDES IN CDCl<sub>3</sub> RELATIVE TO TMS

Nucleus	Assignment	R (Z = Fe unless shown otherwise)					
		Me T 40°C	Me (Z = Ru) T 30°C	Et T 30°C	Pr <sup>i</sup> T 30°C	C <sub>5</sub> H <sub>10</sub> T 30°C	C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> T 30°C
<sup>1</sup> H	H(2',5'γ)	4.19 (t)	5.0 (t)	4.64 (t)	4.60 (t)	4.58 (t)	4.60 (t)
	H(3',4'γ)	3.95 (t)	4.7 (t)	4.36 (t)	4.40 (t)	4.38 (t)	4.40 (t)
	N–CH	2.77	3.02	3.45 (q)	3.9 (sep)	3.65	3.66 (br. 16H)
	C–CH	–	–	1.20 (t)	1.30 (d)	1.62	–
<sup>13</sup> C	C=O	170.1	168.5	169.1	168.9	168.5	167.1
	<i>ipso</i> -C	80.6	83.6	81.3	83.1	81.4	80.7
	C(2),C(5)	72.3	74.3	71.5	71.3	71.7	72.2
	C(3),C(4)	71.3	73.2	71.4	70.9	71.1	71.3
	N–C	37.7	37.8	41.8	49.8 } 46.2 }	46.1	45.7
	C	–	–	13.9	21.1	26.3 24.8	67.1

### Acknowledgment

We are indebted to the SERC for financial support to P.J.H., P.D.B., C.D., I.P.D., and J.K.

### 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, J. Elliot, P.J. Hammond, C. Dudman and C.D. Hall, *J. Organomet. Chem.*, 263 (1984) C37.
- 4 (a) G.A. Morris and R. Freeman, *J. Am. 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. Kummer and 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, *J. Chem. Soc., Chem. Commun.*, (1983) 1161.
- 7 G. Binsch and A. Kessler, *Angew. Chem. Intern. Edit.*, 19 (1980) 411.