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LETTER

The dynamics of ring rotation in 2,2',5,5'-tetra-tert-butyl-1,1'- diazametallocene compounds*

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The interest in cyclopentadienyl complexes of the transition metals remains high. Recently the conformations and structural dynamics of heteroferrocenes and ferrocenes with bulky substituents have become a topic of active interest in several groups [2–7] and various studies of the barrier to rotation of cyclopentadienyl groups in sandwich complexes, particularly using NMR, have been carried out for Cp rings having bulky substituents.

We report here the results of a ^{13}C NMR study which allows the accuracy of predictions of the barrier to ring rotation in 2,2',5,5'-tetra-tert-butyl-1,1'-diazferrocene (**1**), 2,2',5,5'-tetra-tert-butyl-1,1'-diazacobaltocinium tetrafluoroborate (**2**) and 1,1',3,3'-tetra-tert-butylferrocene (**3**) to be assessed. These theoretical studies employing extended Hückel calculations and molecular modelling are to be reported elsewhere [8]. ^{13}C NMR is particularly suitable for studying these systems because the exchange is a simple one between two sites of equal population and with no coupling between the exchanging nuclei. Four sets of signals with various separations (including those from the unprotonated carbon atoms) can be monitored, allowing

*Part XVII of a series on heterocycles as ligands. For Part XVI see ref. 1.

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a check of the results and extending the temperature range over which measurements can be carried out.

Experimental

2,2',5,5'-Tetra-tert-butyl-1,1'-diazferrocene (**1**) [9], 2,2',5,5'-tetra-tert-butyl-1,1'-diazacobaltocinium tetrafluoroborate (**2**) [10] and 1,1',3,3'-tetra-tert-butylferrocene (**3**) [11] were prepared by published procedures. The ^{13}C NMR measurements were carried out on Bruker WM-300 (**1** and **3**) and AMX-400 (**2**) NMR spectrometers. Chemical shifts were determined relative to solvent signals and converted to the TMS scale (D_8 -toluene: CD_3 , $\delta_{\text{C}} \equiv 20.43$ at -30°C and 20.51 at -50°C ; CD_2Cl_2 : $\delta_{\text{C}} \equiv 53.8$). The exchange rate was determined from the ^{13}C NMR spectra by lineshape analysis.

Results and discussion

At -80°C the 75.5 MHz ^{13}C NMR spectrum of 2,2',5,5'-tetra-tert-butyl-1,1'-diazferrocene (**1**) [9] consists of four pairs of signals, one each for the substituted and unsubstituted ring carbon atoms and for the quaternary and methyl carbons of the tert-butyl groups (see Table 1), consistent with the rotamer found by X-ray crystallography in which the rings are rotated by approximately 90° to each other. At higher temperature the pairs of signals coalesce and above *c.* -50°C just four signals are observed, indicating rapid rotation of the η^5 -rings in the NMR time scale. Thus the resonances of the substituted ring carbon atoms are observed at 119.1 and 112.5 ppm at -80°C , they coalesce at *c.* -50°C and at -10°C they give an averaged signal for C-2 and C-5 at 116.4 ppm with a linewidth at half

TABLE 1. ^{13}C chemical shift data for **1**, **2** and **3**

Metal	Temp. (°C)	δ_{C} ring C-H	δ_{C} ring C-H	δ_{C} quaternary ring C	δ_{C} t-butyl (quat. C)	δ_{C} t-butyl (methyl)
1^a Fe	-10		66.2	116.4	32.0	31.1
	-80		67.3	119.1	32.02	31.52
			65.9	112.5	31.99	30.61
2^b Co	10		82.1	broad	33.5	30.1
	-80		82.1	140.2	32.8	29.5
			80.8	131.9	32.5	28.9
3^a Fe	91	63.5	64.7	101.0	32.5	21.2
	40	63.3	64.5	broad	32.3	31.0
	-80	63.6	65.3	101.2	32.5	31.2
		63.8	97.7	31.7	30.7	

^aSolvent: D_8 -toluene. ^bSolvent: CD_2Cl_2 .

height of 8 Hz. The temperature ranges in which the corresponding changes in the spectra of 2,2',5,5'-tetra-tert-butyl-1,1'-diazacobaltocenium tetrafluoroborate (**2**) and 1,1',3,3'-tetra-tert-butylferrocene (**3**) [11, 12] occur are significantly higher: in the ^{13}C NMR spectrum of **3**, for example, the coalescence temperatures at 75.5 MHz of all ^{13}C resonances except the methyl signals lie above -10°C . At low temperature only one rotamer was observed. As in other investigations, no broadening of the tert-butyl methyl signals was observed at low temperature, so that there is no evidence of restricted rotation of the tert-butyl groups about the ring C to quaternary C bond.

The NMR spectra at low temperature are consistent with the most stable conformation being that in which the tert-butyl groups take up their greatest possible mutual separations. The rotation of one ring relative to the other could take place clockwise or counterclockwise (see Fig. 1). These pathways are not equivalent: in one case (II) the molecule passes through the e_2 rotamer, in which both pairs of substituents become eclipsed and strong interannular repulsions between the tert-butyl groups should be present. However, when rotation takes place in the opposite sense (I), then at any one time no more than one pair of tert-butyl groups is eclipsed (e_1 rotamers). The barrier to rotation via e_2 should therefore be significantly higher than for rotation in the opposite sense.

The barriers have been calculated from the exchange rate data assuming that rotation I occurs much faster than rotation II, so that the overall rate of exchange at any given temperature is due to process I alone. (If both exchange processes had been equivalent, then the rate for each would be only half the overall rate.) The postulated ring motion is thus essentially a back-and-forth movement between the conformers (A and B) of lowest energy. This model has been published by Abel *et al.* [6], who discuss in detail the various rotamers involved.

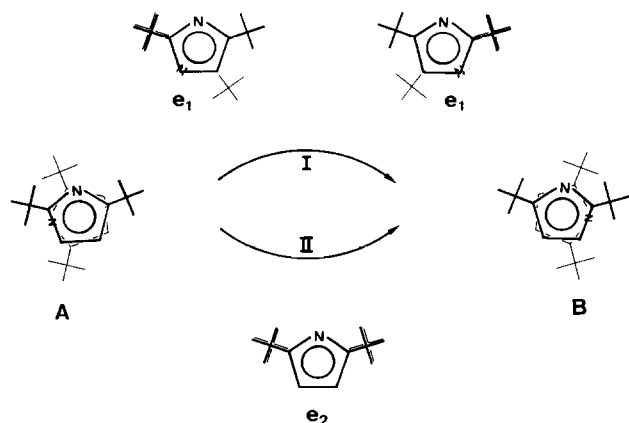


Fig. 1. The rotamers are labelled according to refs. 4a and 6.

TABLE 2. Barriers to ring rotation ΔG^\ddagger in heterometallobenes with bulky substituents

	ΔG^\ddagger (kJ/mol)	Ref.
2,2',5,5'-Tetra-tert-butyl-1,1'-diazaferrrocene (1)	41.4	a
2,2',5,5'-Tetra-tert-butyl-1,1'-diazacobaltocenium tetrafluoroborate (2)	45.7	a
1,1',3,3'-Tetra-tert-butylferrocene (3)	55.3	a
	55.6	6
	54.8	2
1,1',3,3'-Tetra-tert-butyl-cobaltocenium hexafluorophosphate	53.1	5

^aThis work (**1**, **2**: -50°C , **3**: -10°C).

The barrier to rotation in **3** has previously been determined by Luke and Streitwieser [2] from the coalescence temperature of the tert-butyl signals in the ^1H NMR spectrum and more recently by Abel *et al.* using ^1H and ^{13}C lineshape analyses [6]. Our result for **3** is consistent with both literature values (Table 2).

The experiments reported here show that the barrier to rotation of the η^5 -rings in the diheteroferrocene **1** is considerably lower than in the corresponding ferrocene **3**. We also find that the barrier in 2,2',5,5'-tetra-tert-butyl-1,1'-diazacobaltocenium tetrafluoroborate (**2**) is larger than in its isoelectronic iron analogue **1**. Interestingly, whereas the presence of nitrogen in the ring reduces the barrier in both the iron and the cobalt complexes (compare **2** with 1,1',3,3'-tetra-tert-butyl-cobaltocenium hexafluorophosphate in D_6 -acetone (53.1 kJ/mol) [5]), replacement of N by Sb enhances the rotational barrier in the diheterometallobene derivatives markedly [13].

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