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Preliminary communication

THE SYNTHESIS OF FLUXIONAL RUTHENOCENE BIS-CROWN ETHERS

PAUL D. BEER* and A.D. KEEFE

Department of Chemistry, The University of Birmingham, Birmingham B15 2TT (Great Britain)

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Summary

The synthesis of novel ruthenocene bis-crown ethers is reported. Dynamic ^{13}C NMR studies reveal a common intramolecular fluxional phenomenon resulting from rotation about the N—CO bond system.

The design and synthesis of macropolycyclic molecules containing a redox-active centre in close proximity to a coordination site has been the subject of many recent publications [1—4]. Interest in these molecules stems from the idea of studying any interactions between the redox-active centre and a closely bound metal cation guest species.

The metallocene redox centre ferrocene has been successfully appended to a variety of crown ethers and their coordination and redox chemistries are currently under investigation [5, 6]. This communication reports the synthesis of novel ruthenocene bis-crown ethers and of a ruthenocene bis-morpholine amide derivative.

All the compounds were prepared by the standard condensation reaction (Scheme 1) and gave satisfactory elemental analysis, ^1H NMR and molecular masses by mass spectrometry.

The ^{13}C NMR of **4**, **5** and **6** were recorded at various temperatures and all three were found to display fluxional behaviour on the NMR timescale. At 223 K the ^{13}C NMR reveals two absorptions for the respective NCH_2 carbons of **4**, **5** and **6**. On warming these individual signals broaden and eventually coalesce. Also the respective OCH_2 carbon absorptions collapse to give simplified broadened peaks.

These observations suggest that at the coalescence temperatures and above the aza-crown ether rings of **4** and **5**, and the morpholine rings of **6** are no longer fixed relative to the respective carbonyl groups and rotation about the amide N—CO bond system if fast on the NMR timescale. This dynamic phen-

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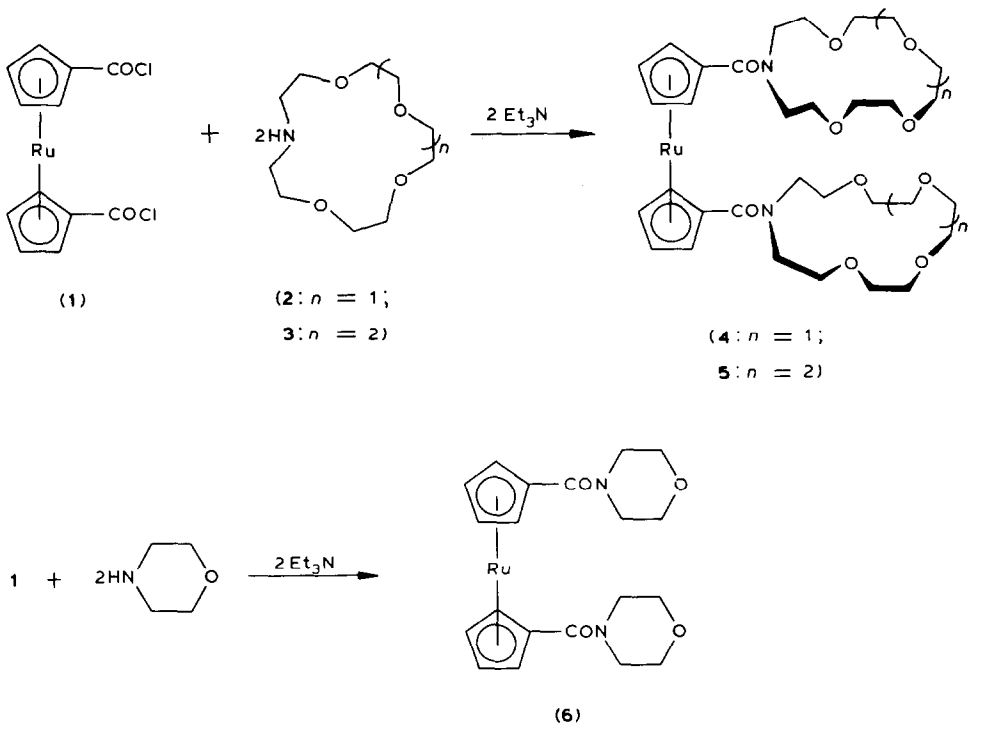

SCHEME 1

TABLE 1

COALESCENCE TEMPERATURES (T_c), CHEMICAL SHIFT DIFFERENCES ($\Delta\nu$) AND $\Delta G^{\ddagger}$[a] VALUES OF 4, 5 AND 6

Compound	T_c (±5 K)	$\Delta\nu$ at 223 K (Hz)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
4	320	68.1	64.1
5	323	238.0	61.4
6	298	1178	54.5

[a] $\Delta G^{\ddagger}$ values calculated from the Gutowsky [7] and Eyring [8] equations.

omenon is also displayed by related ferrocene bis-crown ether molecules [6].

The respective coalescence temperatures (T_c), chemical shift differences ($\Delta\nu$) and $\Delta G^{\ddagger}$ values for this dynamic process are reported in Table 1. It is evident that the $\Delta G^{\ddagger}$ values for 4 and 5 are very similar and are found to be in good agreement with $\Delta G^{\ddagger}$ values obtained for the analogous ferrocene bis-crown ethers [6].

The coordination chemistry of these ruthenocene bis-crown ethers and other metallocene crown and cryptand molecules will be described in the full paper.

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