

### Preliminary communication

---

## POTASSIUM SELECTIVE METALLOCENE CRYPTAND MOLECULES

PAUL D. BEER\*, CHRISTOPHER G. CRANE, ANTHONY D. KEEFE  
and ANDREW R. WHYMAN

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

(Received July 2nd, 1986)

### Summary

Novel metallocene cryptand molecules have been synthesised exhibiting selective complexation of  $K^+$  to the exclusion of either  $Li^+$ ,  $Na^+$  or  $Cs^+$ . This was demonstrated by fast atom bombardment mass spectrometry.

---

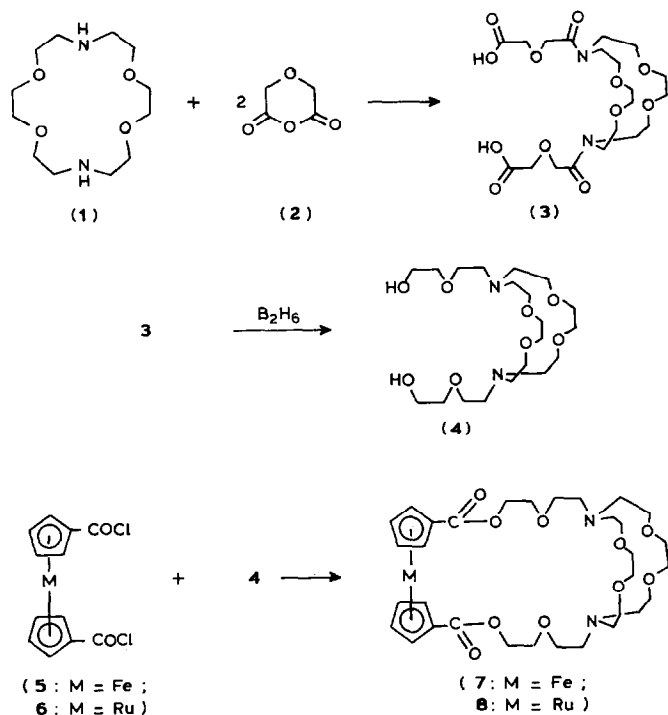
The synthesis of novel redox-active macrocyclic molecules designed to be selective and redox-responsive to the host binding of metal guest cations is of considerable current interest in the chemical literature [1–3]. We have recently reported the preparation of a number of metallocene bis(crown ethers) [4,5] and shown some of these ligands to be selective towards potassium guest cations [6].

This communication reports the synthesis of two new novel metallocene cryptand molecules **7** and **8** and their complexing behaviour towards alkali metal cations using fast atom bombardment (f.a.b.) mass spectrometry.

The functionalisation of the secondary nitrogen sites in the parent diaza-18-crown-6 macrocycle (**1**) permitted the respective attachment of the metallocene redox centres ferrocene and ruthenocene. The reaction of **1** with 3-oxoglutaric anhydride (**2**) gave **3** (95% yield), which was then reduced to **4** using diborane (92% yield). Condensation of the 1,1'-bis(chlorocarbonyl)metallocenes (**5** and **6**) with **4** in the presence of triethylamine under high dilution conditions in dry toluene gave, after column chromatography, (alumina 99%  $CH_2Cl_2$ , 1% MeOH) the ferrocene cryptand (**7**) (50% yield) and the ruthenocene analogue **8** (45% yield), Scheme 1.

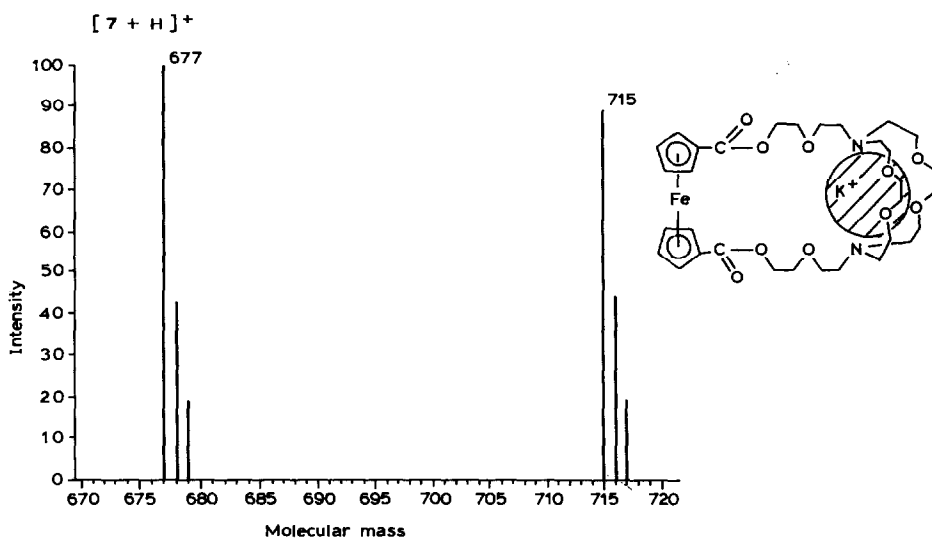
The structures of both new air stable metallocene cryptands were verified by elemental analysis, mass spectrometry and  $^1H$  and  $^{13}C$  NMR spectroscopy.

Fast atom bombardment (f.a.b.) mass spectrometry was used to study the selectivity of these metallocene cryptand molecules towards the Group 1A alkali metals [6,7]  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $Cs^+$ . Individual f.a.b. mass spectrometric experiments of **7** and **8** ( $5 \times 10^{-3} M$ , 0.5 ml methanol) with the alkali metal nitrates ( $5 \times 10^{-3} M$ , 0.5 ml water/1.0 ml glycerol) gave gas-phase [metallocene cryptand + metal] $^+$  ions at  $m/z$  values corresponding to the respective complexes. Analogous



SCHEME 1

competition experiments of **7** and **8** with an aqueous solution of lithium, sodium, potassium and caesium nitrates each at a concentration of  $5 \times 10^{-3} M$  were undertaken. Both **7** and **8** showed exclusive selectivity for potassium, [**7** +

Fig. 1. F.a.b. mass spectrum of **7** and [**7** + potassium]<sup>+</sup>.

potassium]<sup>+</sup> ion (*m/z* 715) and [8 + potassium]<sup>+</sup> ion (*m/z* 761), suggesting that the respective host's cavity provides an optimal spatial fit for the potassium guest cation [8], Fig. 1.

**Acknowledgements.** Part of this work was carried out at Institut Le Bel, Université Louis Pasteur, Strasbourg, France under a N.A.T.O. exchange scheme. We thank N.A.T.O., the SERC for an 'earmarked' studentship to A.D.K. and The Research Corporation Trust for financial support. P.D.B. is grateful to Professor J.M. Lehn (Institut Le Bel, Université Louis Pasteur, Strasbourg) for helpful discussions.

## References

- 1 T. Saji, *Chem. Lett.*, (1986) 275.
- 2 R.E. Wolf Jr. and S.R. Cooper, *J. Am. Chem. Soc.*, 106 (1984) 4646.
- 3 S. Akabori, Y. Habata, Y. Sakamoto, M. Sato and S. Ebine, *Bull. Chem. Soc. Jpn.*, 56 (1983) 537.
- 4 P.D. Beer, *J. Organomet. Chem.*, 297 (1985) 313.
- 5 P.D. Beer and A.D. Keefe, *J. Organomet. Chem.*, 306 (1986) C10.
- 6 P.D. Beer, *J. Chem. Soc. Chem. Commun.*, (1985) 1115.
- 7 R.A.W. Johnstone and M.E. Rose, *J. Chem. Soc. Chem. Commun.*, (1983) 1268.
- 8 E. Weber and F. Vögtle, *Topics in Current Chemistry*, 98 (1981) 1.