Synthesis of Novel Metallocene Bis(Crown Ethers). Potassium Selective Intramolecular Sandwich-type Complexation observed by Fast Atom Bombardment Mass Spectrometry

Paul D. Beer

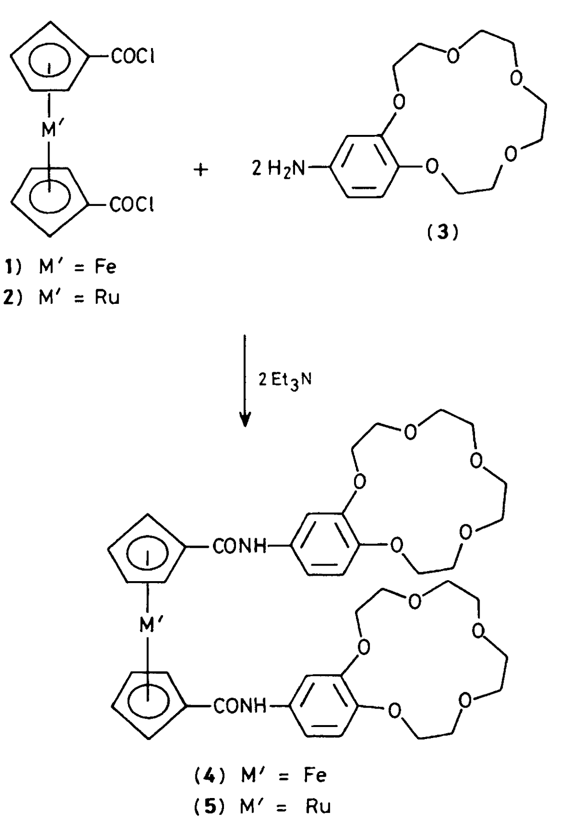
Department of Inorganic Chemistry, The University of Birmingham, Birmingham B15 2TT, U.K.

Two new novel metallocene bis(crown ethers) have been prepared exhibiting exclusive K^+ selective intramolecular sandwich-type complexation over either Na^+ or Cs^+; this has been observed by fast atom bombardment (f.a.b.) mass spectrometry.

The design and synthesis of macrocyclic compounds containing the ferrocene moiety as an integral part of the macrocyclic skeleton have recently received considerable attention in the chemical literature.[1—6] Interest in these molecules stems from the idea of binding guest metal cations in close proximity to the metallocene metal atom and to study subsequently any interactions between the two metal centres.

This communication reports the preparation of two new novel metallocene bis(crown ethers) (**4**) and (**5**) and their complexing behaviour towards alkali metal cations using fast atom bombardment (f.a.b.) mass spectrometry.

Condensation of respective 1,1′-bis(chlorocarbonyl)-metallocenes (**1**) and (**2**)[7] with two moles of 4-aminobenzo-15-crown-5 (**3**)[8] in the presence of triethylamine gave after column chromatography (alumina, 99% CH_2Cl_2, 1% MeOH) the ferrocene bis(crown ether) (**4**) (80% yield, m.p. 198—



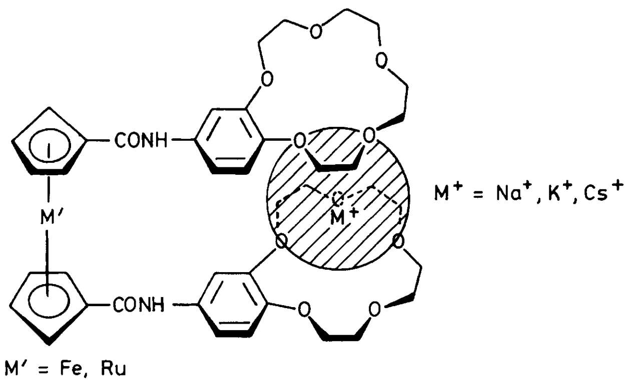


Figure 1

199 °C, orange crystals) and the ruthenocene analogue (**5**) (75% yield, m.p. 206—207 °C, pale yellow crystals).

The structures of both new air-stable metallocene bis(crown ethers) were verified by elemental analysis, mass spectrometry, and ^1H and ^{13}C n.m.r. spectroscopy.

^{13}C N.m.r. spectroscopy was used initially to investigate the complexation of (**4**) and (**5**) with alkali metal cations sodium, potassium, and caesium. The stepwise addition of an alkali metal nitrate salt to a methanol (65%)–acetone (35%) solution of (**4**) and methanol (65%)–dichloromethane (35%) solution of (**5**) led to considerable shifts of the OCH_2 carbons of the respective bis(crown molecules). In all cases the stoicheiometry of metallocene bis(crown ether) to guest alkali metal cation was found to be 1 : 1.† This result suggests that both (**4**) and (**5**) are adopting a conformation in which the amido-benzo-15-crown-5 units are lying cofacial to one another and are acting co-operatively, in concert, to form intramolecular sandwich complexes with the alkali metal cation guest species, Figure 1. In contrast to this observation a very recent publication[9] reports the 18-crown-6 units of a related ferrocene bis(crown ether) to be acting independently of one another and complexing two alkali metal guest ions.

Fast atom bombardment (f.a.b.) mass spectrometry, a new powerful semi-quantitative technique has been used to study the selectivity of *monocyclic* crown ethers for metal cations in competition experiments.[10] It seemed reasonable to apply this method for the first time to bis(crown ethers).

Individual f.a.b. mass spectrometric experiments of (**4**) (5×10^{-3} M; 0.5 ml 65% methanol–35% acetone) and (**5**) (5×10^{-3} M, 0.5 ml 65% methanol–35% dichloromethane) with the nitrates of sodium, potassium, and caesium (5×10^{-3} M, 0.5 ml water–1.0 ml glycerol) gave gas-phase [bis(crown ether) + metal]$^+$ ions at *m/z* values corresponding to the respective intramolecular sandwich complexes.‡ Analogous competition experiments of (**4**) and (**5**) with an aqueous solution of sodium, potassium, and caesium nitrates each at a concentration of 5×10^{-3} M gave the respective [(**4**) + potassium]$^+$ ion (*m/z* 843) and [(**5**) + potassium]$^+$ ion (*m/z* 889) *exclusively*.

The exclusive selectivity exhibited by both (**4**) and (**5**) towards potassium suggests that a well defined cavity exists between the cofacial amido-benzo-15-crown-5 units which provides an optimal spatial fit for the potassium guest cation.[11]

The author thanks the S.E.R.C. for use of the high field n.m.r. service at the University of Warwick.

Received, 9th May 1985; Com. 627

References

1 S. Akabori, Y. Habata, Y. Sakamoto, M. Sato, and S. Ebine, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 537.
2 M. Sato, M. Kubo, S. Ebine, and S. Akabori, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 421.
3 S. Akabori, S. Shibahara, Y. Habata, and M. Sato, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 63.
4 M. Sato, S. Tanaka, S. Ebine, and S. Akabori, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1929.
5 P. D. Beer, P. J. Hammond, and C. D. Hall, *J. Chem. Soc., Chem. Commun.*, 1983, 1161.
6 P. D. Beer, J. Elliot, P. J. Hammond, C. Dudman, and C. D. Hall, *J. Organomet. Chem.*, 1984, **263**, C37.
7 H. J. Lorkowski, R. Pannier, and A. Wende, *J. Prakt. Chem.*, 1967, **35**, 149.
8 R. Ungaro, B. El Haj, and J. Smid, *J. Am. Chem. Soc.*, 1977, **98**, 5198.
9 B. Czech, A. Czech, S. I. Kang, and R. A. Bartsch, *Chem. Lett.*, 1984, 37.
10 R. A. W. Johnstone and M. E. Rose, *J. Chem. Soc., Chem. Commun.*, 1983, 1268.
11 E. Weber and F. Vögtle, *Top. Curr. Chem.*, 1981, **98**, 1.
12 E. Amble and E. Amble, *Polyhedron*, 1983, **2**, 1063.

---

† Deduced from respective Δδ p.p.m. *vs.* [alkali metal salt]/[metallocene bis(crown ether)] titration curves, ref. 12.

‡ Positive ion f.a.b. mass spectrometry was performed using a primary atom beam of Kr (6 keV) on a Kratos MS80 RF mass spectrometer coupled to Kratos DS55 data system. At an accelerating voltage of 4 kV, the mass range *m/z* 800—950 was scanned in 10 s per decade (scan cycle time 25 s).