Can alkali-metal ions influence the coordination and reactivity of calix[4]arenes at transition-metal centres?†

Vernon C. Gibson,*[a] Carl Redshaw,[a] William Clegg[b] and Mark R. J. Elsegood[b]

[a] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*
[b] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*

Novel chromium and molybdenum calix[4]arene complexes are described in which the calixarene coordination is constrained by alkali-metal ion interactions with the phenoxide units; in the chromium example, an unprecedented calixarene C–H bond activation is found.

There is currently much interest in the synthesis and characterisation of new metallocalixarenes.[1–6] The simplest of the calixarenes, the calix[4]arene system, usually binds in tetradentate fashion and retains its cone-like appearance.[1–9] In recent examples, however, it has been found that the calix[4]arene is capable of adopting alternative conformations in binding at metal centres, for example a partially flattened cone arrangement identified in aluminium[10] and zinc compounds[11] and an alkali-metal-constrained elliptical conformation in which the calixarene oxygens occupy mutually *cis* and *trans* sites in an octahedral geometry.[2] There has also been a report of an elliptical calixarene arrangement in the absence of alkali-metal ions;[8] it is thus unclear whether it is the transition metal or the alkali-metal ions that exert the more substantial influence on calix[4]arene conformation. Here, we describe two unusual structures that contain alkali-metal ions within elliptical calixarene ligands; in one case an unprecedented C–H bond activation of the calixarene ligand results, providing the first indication that highly reactive metal centres may arise from these constrained geometry ligand–metal environments.

Treatment of [Mo(NAr)(CHCMe$_2$Ph)(O$_3$SCF$_3$)$_2$(dme)] (Ar = C$_6$H$_3$Me$_2$-2,6) with 1 equiv. of K$_4$L (H$_4$L = *p-tert*-butylcalix[4]arene) in tetrahydrofuran (thf) affords, after work-up, orange prisms of [Mo(NAr)(L)K$_2$(NCMe)$_3$O]$_2$ **1**‡ in 70% yield. Crystals of **1** suitable for an X-ray determination§ were grown from acetonitrile at room temp. The asymmetric unit comprises one half of a dimeric molecule and two non-coordinated molecules of acetonitrile. The molecular structure is shown in Fig. 1 and selected bond lengths are given in the caption. The molecule is a centrosymmetric dimer in which each molybdenum atom possesses a pseudo-octahedral geometry. The calixarene 'cones' are distorted in such a way that two opposing phenoxide rings are drawn together by π interactions with potassium atom K(1) which is also bonded to the oxygens of the remaining two phenoxide units. One of the latter two rings is also involved in a π interaction with a bridging potassium atom, K(2), which forms part of a ladder motif. The Mo–O(5) bond distance within this motif, at 1.752(2) Å, is consistent with substantial multiple bond character.[12] The origin of the ladder oxygen atoms is most likely the thf solvent since the reaction and subsequent work-up were conducted under rigorous air- and moisture-free conditions.

In extending our investigations to chromium, [Cr(NBu^t)$_2$Cl$_2$] was reacted with 2 equiv. of LiOBu^t in thf to generate [Cr(NBu^t)$_2$(OBu^t)$_2$] which was then treated *in situ* with 2 equiv. of H$_4$L. This led after work-up to the formation of large green needles of **2** in 60% yield. Crystals suitable for an X-ray determination§ were grown from acetonitrile solution at room temp.; they incorporate four uncoordinated molecules of acetonitrile per molecule of the complex. The molecular structure is shown in Fig. 2; selected bond lengths and angles are given in the caption. All of the *tert*-butylimido and *tert*-butoxide ligands of the starting chromium species are sacrificed, as *tert*-butylamine and *tert*-butyl alcohol, respectively, and two calix[4]arene units are coordinated to the chromium centre. One possesses a similar coordination geometry to that observed in **1** with the exception that the smaller lithium ion interacts with just one of the arene rings and the interaction is strongest with the *ipso* and *ortho* ring carbons [Li···C(*ipso*) 2.599(10) Å, Li···C(*ortho*) 2.716(10), 2.797(10) Å]. A remarkable feature of the complex is the joining of this calixarene to a second calixarene unit *via* an ether [O(1)] linkage. This formally arises from the activation of a bridging methylene C–H bond of the second calixarene, to our knowledge the first time such reactivity has been observed in a metallocalixarene complex. The resultant ether oxygen atom is then bonded to an axial coordination site in the chromium complex.

The remainder of the second calixarene unit is bonded to the metal centre through two phenoxide linkages whose oxygen atoms are hydrogen bonded to atoms O(5) and O(6), which in turn are coordinated to a lithium atom bound to O(3). The net result is the encapsulation of an octahedral chromium(III) centre by two fused calix[4]arene rings. While it is not possible to establish with any degree of certainty the mechanism of C–H bond activation in **2**, it is possible that it may be a consequence of the constrained calixarene coordination geometry which leads to severe bending at the axial oxygens O(1) and O(3) [120.0(3), 112.6(3)°, respectively]. Future studies will be directed towards probing the influence of the constrained

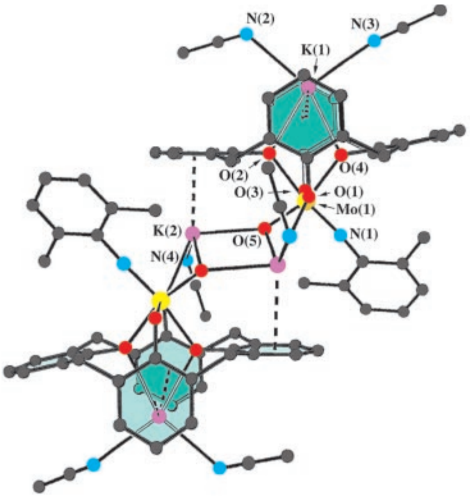

Fig. 1 The molecular structure of **1** with H atoms and Bu^t groups omitted. Selected distances (Å) and angles (°): Mo(1)–O(1) 2.059(2), Mo(1)–O(2) 2.108(2), Mo(1)–O(3) 2.037(2), Mo(1)–O(4) 2.053(2), Mo(1)–O(5) 1.752(2), Mo(1)–N(1) 1.768(3), K(1)–O(2) 2.639(2), K(1)–O(4) 2.607(2), K(1)–N(2) 2.832(4), K(1)–N(3) 2.819(4), K(1)–ring centroids 3.129(3), 3.164(3), K(2)–O(5) 2.632(2), K(2)–O(5A) 2.832(2), K(2)–O(1A) 2.642(2), K(2)–N(4) 2.741(4), K(2)–ring centroid 2.862(3); Mo(1)–O(1)–C(9) 119.6(2), Mo(1)–O(2)–C(20) 126.7(2), Mo(1)–O(3)–C(31) 119.8(2), Mo(1)–O(4)–C(42) 137.2(2).

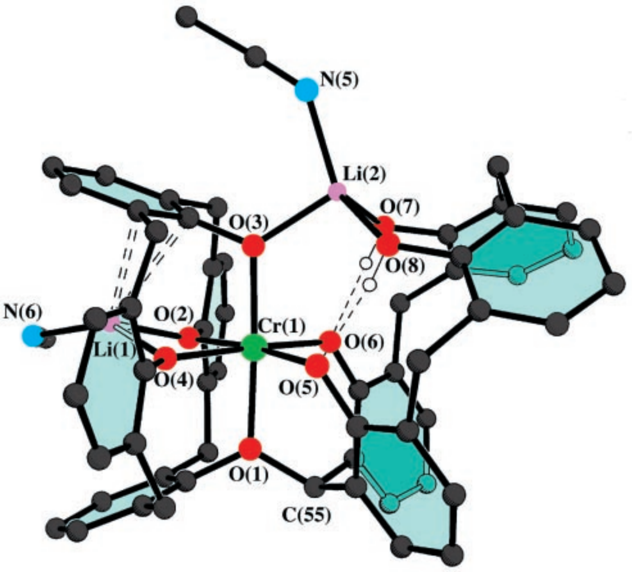

Fig. 2 Molecular structure of **2** with Bu^t groups and most H atoms omitted; OH groups are shown. Selected distances (Å) and angles (°): Cr–O(1) 1.995(3), Cr–O(2) 1.935(3), Cr–O(3) 1.972(3), Cr–O(4) 1.924(3), Cr–O(5) 1.959(3), Cr–O(6) 1.945(3), Li(1)–O(2) 1.857(9), Li(1)–O(4) 1.896(10), Li(1)–N(6) 2.000(11), shortest Li(1)–C 2.599(10), Li(2)–O(3) 1.920(8), Li(2)–O(7) 1.917(9), Li(2)–O(8) 1.922(9), Li(2)–N(5) 2.018(10); Cr–O(1)–C(1) 120.0(3), Cr–O(2)–C(12) 128.0(3), Cr–O(3)–C(23) 112.6(3), Cr–O(4)–C(34) 134.5(3), Cr–O(1)–C(55) 117.8(2), Cr–O(5)–C(45) 127.5(3), Cr–O(6)–C(56) 129.3(3).

calixarene coordination geometry on the reactivity of calixarene-complexed metal centres.

The Engineering and Physical Sciences Research Council is thanked for financial support. Dr P. Mountford (University of Nottingham) is thanked for sharing results prior to publication.

Footnotes and References

* E-mail: v.gibson@ic.ac.uk

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc/cccenha.htm

‡ Satisfactory elemental analyses have been obtained. *Selected spectroscopic data* for **1**: ^{1}H NMR (CDCl$_3$, 500 MHz, 298 K) δ 7.00 $-$6.65 (overlapping m, 22 H, aryl), 4.42 (d, 4 H, $^3J_{HH}$ 13.8 Hz, CH$_2$), 4.31 (d, 4 H, $^3J_{HH}$ 14.3 Hz, CH$_2$), 3.27 (d, 4 H, $^3J_{HH}$ 14.5 Hz, CH$_2$), 3.07 (d, 4 H, $^3J_{HH}$ 14.0 Hz, CH$_2$), 2.37 (s, 12 H, CH$_3$Ar), 1.31 (m, 18 H, MeCN), 1.19 $-$ 1.11 (overlapping m, 72 H, [(CH$_3$)$_3$C]). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.6 MHz, 298 K) δ 165.5, 164.2, 162.7, 154.1 (4 $\times$ s, *ipso*-aryl), 140.2, 138.7, 138.2, 134.8, 134.3, 134.1, 133.8, 132.2, 131.1, 130.9, 130.6, 128.2, 127.2, 124.1, 123.8, 123.6, 123.1, 122.9, 122.8, 122.5, 36.2 (Ar*C*H$_2$Ar), 35.4 (Ar*C*H$_2$Ar), 32.0 [C(*C*H$_3$)$_3$], 31.9 [C(*C*H$_3$)$_3$], 31.8 [C(*C*H$_3$)$_3$], 31.7 [C(*C*H$_3$)$_3$], 28.0, 22.5, 18.5 (C$_6$H$_3$*Me*$_2$-2,6) [quaternary (CH$_3$)$_3$*C* not observed]. ^{1}H NMR spectra of **2** are broad and uninformative; the X-band EPR spectrum (solid, 298 K) is complex comprising broad low-field features centred at g = 3.35 and several weaker features out to g = 1.19.

§ *Crystal data*: **1**·4MeCN: C$_{116}$H$_{140}$K$_4$Mo$_2$N$_8$O$_{10}$·4CH$_3$CN, M = 2318.9, monoclinic, space group $P2_1/n$, a = 20.2461(12), b = 12.0202(7), c = 27.1727(15) Å, β = 110.700(2)°, U = 6185.9(6) Å^3, Z = 2, D_c = 1.245 g cm^{-3}, μ = 0.40 mm^{-1} (Mo-Kα, λ = 0.71073 Å), T = 160 K. 37557 reflections were measured on a Siemens SMART CCD area-detector diffractometer and corrected semiempirically for absorption (transmission 0.761–0.917), yielding 13952 unique data ($2\theta_{max}$ = 55.0°, R_{int} = 0.0479). The structure was determined by direct methods and refined by F^2 for all data, with anisotropic displacement parameters, and riding isotropic H atoms. Final $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1135 for all data, conventional R = 0.0571 on F values of 11481 reflections with $F_o^2 > 2\sigma(F_o^2)$; goodness of fit = 1.232 on F^2 values for 715 refined parameters. All final difference map features were within ± 0.5 e Å^{-3}.

2·4MeCN: C$_{92}$H$_{111}$CrLi$_2$N$_2$O$_8$·4CH$_3$CN, M = 1602.9, monoclinic, space group $P2_1/c$, a = 17.5630(7), b = 46.3196(18), c = 13.0311(5) Å, β = 108.796(2)°, U = 10035.6(7) Å^3, Z = 4, D_c = 1.061 g cm^{-3}, μ = 0.17 mm^{-1} (Mo-Kα, λ = 0.71073 Å), T = 160 K. Experimental and computational methods were as for **1**, with 47608 measured data, transmission 0.448–0.962, 13090 unique data ($2\theta_{max}$ = 45.0°, R_{int} = 0.0681), disorder in some Bu^t groups modelled with restraints, R_w = 0.2646 for all data, R = 0.0873 for 9667 data having $F_o^2 > 2\sigma(F_o^2)$; goodness of fit = 1.067 for 1136 refined parameters and 306 restraints, extremes of difference map +1.29 and $-$0.39 e Å^{-3}. The hydroxyl hydrogens were located in a difference map and freely refined. Programs: Siemens SMART (control), SAINT (integration) and SHELXTL, and local programs. CCDC 182/537.

1 L. Giannini, E. Solari, A. Zanotti-Gerosa, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2825; B. Castellano, A. Zanotti-Gerosa, E. Solari and C. Floriani, *Angew. Chem., Int. Ed. Engl.*, 1996, **15**, 4894.
2 A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizoli, *Chem. Commun.*, 1997, 183.
3 J. A. Acho, L. H. Doerrer and S. J. Lippard, *Inorg. Chem.*, 1995, **34**, 2542.
4 V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 2371.
5 J. A. Acho and S. J. Lippard, *Inorg. Chim. Acta*, 1995, **229**, 5.
6 A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Chem. Commun.*, 1996, 119.
7 F. Corazza, C. Florianni, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 640.
8 F. Corazza, C. Florianni, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1991, **30**, 4465.
9 F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 1083.
10 J. L. Atwood, M. G. Gardiner, C. Jones, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2487.
11 M. G. Gardiner, S. M. Lawrence, C. L. Raston, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2491.
12 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley Interscience, New York, 1988.

Received in Basel, Switzerland, 3rd April 1997; 7/02272G