Novel Metal Imido Calixarene Complexes

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Treatment of [Mo(NR)₂(OBuᵗ)₂] (R = C₆H₃Prⁱ₂-2,6) with calix-4-arene (H₄L¹) and calix-8-arene (H₈L²) affords novel mono- and di-metallocalixarene complexes; the crystal structures of [Mo(NR) L¹ (NCMe)] 1 and [{Mo(NR)(NCMe)}₂ L²] 2, both incorporating additional acetonitrile solvent of crystallisation, are reported.

The coordination chemistry of calixarenes is a field of investigation that is attracting growing interest,[1,2] partly owing to the ability of calixarenes to transport ions through hydrophobic membranes,[3] and also because of their potential for mediating shape-selective transformations.[4] We were additionally attracted to calixarenes as organic supports for reactive metal fragments of potential catalytic utility. Here we describe novel metal imido calixarene complexes derived from calix-4-arene (H₄L¹) and calix-8-arene (H₈L²) ring systems which provide further valuable insight into the coordination environment imposed by these cyclic polyphenoxide ligands. The metallocalixarene compounds‡ are accessed *via* alkoxide and imido ligand displacement reactions according to Scheme 1.

Treatment of [Mo(NR)₂(OBuᵗ)₂] (R = 2,6-diisopropylphenyl) with 1 equivalent of H₄L¹ in diethyl ether affords, after work-up, the monoimido complex [Mo(NR) L¹ (NCMe)] 1 (Scheme 1). Complex 1 is presumed to form *via* initial displacement of two *tert*-butoxide ligands in an analogous fashion to reactions of [Mo(NR)₂(OBuᵗ)₂] with diols,§ followed by transfer of two protons to one of the imido ligands to release 2,6-diisopropylaniline. The intermediate bis(imido) species, [Mo(NR)₂(H₂L¹)], is not observed. Crystals of 1 suitable for an X-ray determination were grown from acetonitrile at room temperature. The asymmetric unit comprises two independent molecules of the metal complex and one molecule of acetonitrile; the two molecules of the metal complex are very similar.

The molecular structure¶ of one of the molecules is shown in Fig. 1 and selected bond lengths and angles are given in the caption.

The molybdenum possesses a pseudo-octahedral geometry with the four calixarene oxygens defining an equatorial plane from which the Mo(1) is displaced towards the imido nitrogen N(1) by 0.252 Å. The spherical cone section of the ligand closely resembles that found for the related oxo complex [WO-L¹ (MeCO₂H)],[2a] with similar coordination of a molecule of acetic acid within the calixarene cavity and *trans* to the multiply bonded arylimido ligand.

A useful development offered by this approach is its ready extension to multiple substitutions of larger calixarene rings. For example, treatment of H₈L² with 2 equivalents of [Mo(NR)₂(OBuᵗ)₂] affords the dimetallocalixarene complex [{Mo(NR)(NCMe)}₂ L²] 2 *via* a condensation process that is presumed to be analogous to that operating in the formation of
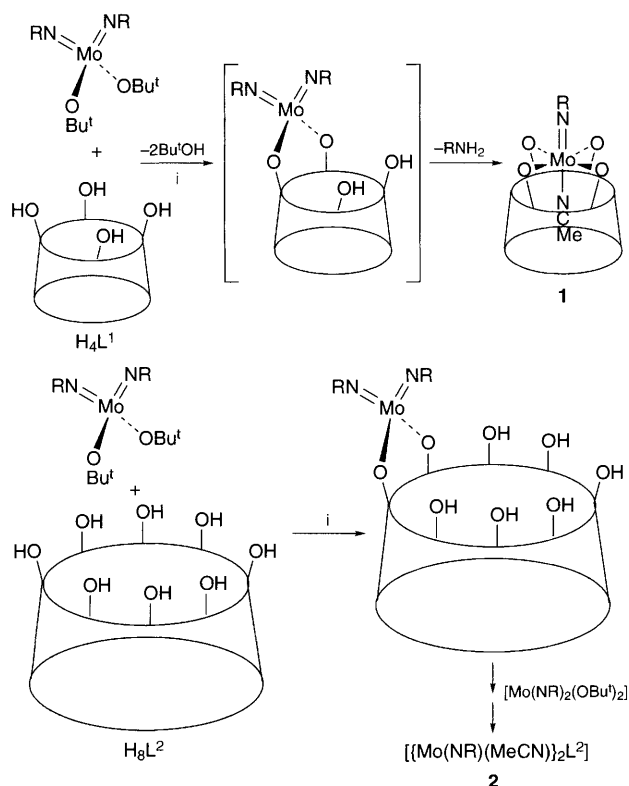
Scheme 1 *Reagents and conditions*: i, Et₂O, 25 °C, 1 h, followed by removal of Et₂O–BuᵗOH, then reflux in toluene for 12 h; recrystallisation from MeCN
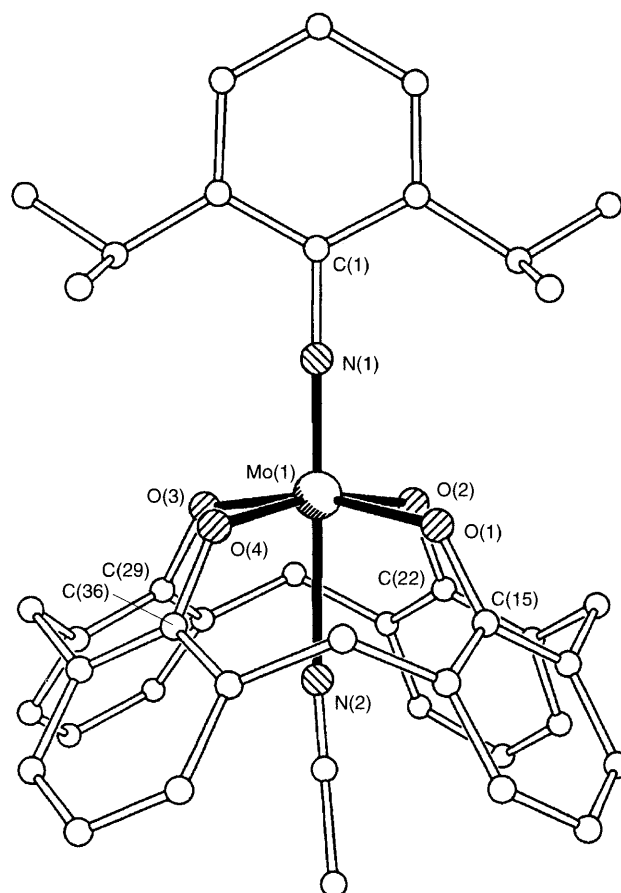
Fig. 1 Molecular structure of one of the two independent molecules in the structure of **1**, without H atoms and with key atoms labelled. Selected dimensions (Å and °, the other molecule is very similar): Mo(1)–N(1) 1.729(3), N(1)–C(1) 1.385(4), Mo–O(1) 1.939(2), Mo–O(2) 1.952(2), Mo(1)–O(3) 1.932(2), Mo(1)–O(4) 1.951(2), Mo(1)–N(2) 2.340(3); Mo(1)–N(1)–C(1) 179.2(2), Mo(1)–O(1)–C(15) 131.6(2), Mo(1)–O(2)–C(22) 126.1(2), Mo(1)–O(3)–C(29) 131.2(2), Mo(1)–O(4)–C(36) 130.5(2).
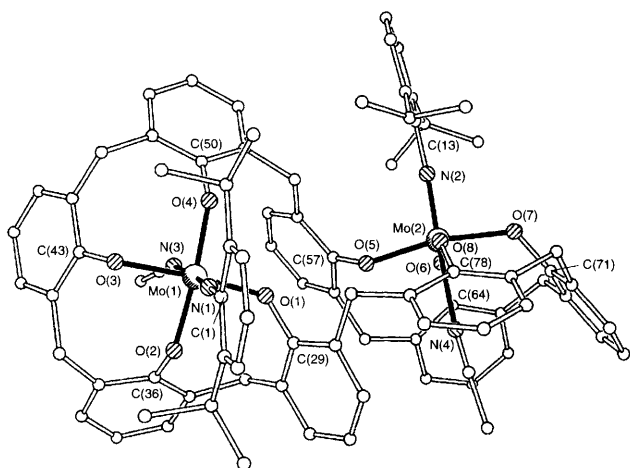
Fig. 2 Molecular structure of **2**, without H atoms and with key atoms labelled. Selected dimensions (Å and °): Mo(1)–N(1) 1.736(6), N(1)–C(1) 1.392(9), Mo(1)–O(1) 1.949(4), Mo(1)–O(2) 1.925(5), Mo(1)–O(3) 1.984(4), Mo(1)–O(4) 1.901(4), Mo(1)–N(3) 2.339(6), Mo(2)–N(2) 1.752(6), N(2)–C(13) 1.394(9), Mo(2)–O(5) 1.950(5), Mo(2)–O(6) 1.924(5), Mo(2)–O(7) 1.963(5), Mo(2)–O(8) 1.901(5), Mo(2)–N(4) 2.333(7); Mo(1)–N(1)–C(1) 179.5(5), Mo(2)–N(2)– C(13) 171.6(5), Mo(1)–O(1)–C(29) 127.1(4), Mo(1)–O(2)–C(36) 140.2(4), Mo(1)–O(3)–C(43) 125.2(4), Mo(1)–O(4)–C(50) 139.6(4), Mo(2)–O(5)–C(57) 128.2(4), Mo(2)–O(6)–C(64) 136.3(5), Mo(2)– O(7)–C(71) 125.2(5), Mo(2)–O(8)–C(78) 145.5(4).

1, resulting in the elimination of four molecules of Bu^{t}OH and two of diisopropylaniline. Crystals suitable for an X-ray structure determination were grown from acetonitrile at room temperature; they incorporate approximately 1.75 molecules of solvent per molecule of complex. The molecular structure‖ is shown in Fig. 2 and reveals the way in which the calix-8-arene ring twists to accommodate the two bulky metal imido fragments. This conformation contrasts with the 'pinched' conformation observed in the anionic titanium complex described by Pedersen and co-workers.[2b] Each molybdenum exists in a local pseudo-octahedral environment similar to that found in **1** with the molybdenum atoms displaced by an average distance of 0.254 Å out of the plane of calixarene oxygens towards the imido nitrogen atoms. A molecule of acetonitrile is again bound to each molybdenum within the calixarene cone and lying *trans* to the linear arylimido ligand.

The compounds described herein provide useful insight into the coordination environments afforded by small and medium-sized calixarene supports. In particular, **2** represents a rare example of a calixarene ring coordinating more than one metal fragment and illustrates the scope for generating yet more highly functionalised metallocalixarenes including the potential for synthesising mixed-metal derivatives. The interplay of such calixarene-supported metal fragments will be of considerable interest.

(d, 4 H, $^2J_{HH}$ 12.4 Hz, CH$_2$), 1.52 [d, 12 H, $^3J_{HH}$ 6.8 Hz, (CH_3)$_2$CH], 0.05 (br s, 3 H, MeCN). For **2**: ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K) δ 7.18 (dd, 2 H, $^3J_{HH}$ 6.0, $^4J_{HH}$ 1.2 Hz), 7.06 (t, 6 H, $^3J_{HH}$ 6.4 Hz), 7.02 (t, 4 H, $^3J_{HH}$ 7.4 Hz), 6.93 (dd, 2 H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.4 Hz), 6.80 (d, 2 H, $^3J_{HH}$ 7.2 Hz), 6.72 (t, 4 H, $^3J_{HH}$ 7.4 Hz), 6.52 (td, 4 H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 2.2 Hz), 6.39 (t, 4 H, $^3J_{HH}$ 8.2 Hz), 6.18 (t, 2 H, $^3J_{HH}$ 7.4 Hz), all aromatic hydrogens; 4.98 (d, 2 H, $^2J_{HH}$ 16.0 Hz, CH$_2$), 4.47 (d, 2 H, $^2J_{HH}$ 12.8 Hz, CH$_2$), 4.45 [spt, 2 H, CH(CH$_3$)$_2$, partially obscured], 4.25 (d, 2 H, $^2J_{HH}$ 12.0 Hz, CH$_2$), 3.33 (d, 2 H, $^2J_{HH}$ 16.0 Hz, CH$_2$), 3.24 (d, 2 H, $^2J_{HH}$ 12.8 Hz, CH$_2$), 3.15 [spt, 2 H, $^3J_{HH}$ 6.8 Hz, CH(CH$_3$)$_2$], 3.06 (d, 2 H, $^2J_{HH}$ 12.4 Hz, CH$_2$), 2.62 (AB q, 4 H, CH$_2$), 1.93 (br s, 3 H, MeCN), 1.34 [d, 6 H, $^3J_{HH}$ 6.8 Hz, CH(CH_3)$_2$], 1.24 [d, 6 H, $^3J_{HH}$ 6.8 Hz, CH(CH_3)$_2$], 1.05 [d, 6 H, $^3J_{HH}$ 6.8 Hz, CH(CH_3)$_2$], 0.64 [d, 6 H, $^3J_{HH}$ 6.4 Hz, CH(CH_3)$_2$], 0.44 (br s, 3 H, MeCN).

§ Treatment of [Mo(NR)$_2$(OBu^t)$_2$] with diols results in displacement of the two *tert*-butoxide ligands to give bis(imido)molybdenumdiolato complexes; details will be reported at a future date.

¶ *Crystal data* for **1**: C$_{42}$H$_{40}$MoN$_2$O$_4$·0.5 CH$_3$CN, M = 753.23, monoclinic, space group $P2_1/c$, a = 12.951(4), b = 18.905(5), c = 29.310(8) Å, β = 95.34(3)°, U = 7145(4) Å^3, Z = 4, D_c = 1.400 g cm^{-3}, $F(000)$ = 3128. 16810 reflections were measured on a Stoe-Siemens diffractometer at 160 K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 5 < 2θ < 46°, μ = 0.414 mm^{-1}) with ω scans and on-line profile fitting. Structure solution was by Patterson synthesis, refinement by full-matrix least-squares analysis on F^2 for all 9923 independent reflections (R_{int} = 0.0215). R_w = {Σ[$w(F_o^2 - F_c^2)^2$]/Σ[$w(F_o^2)^2$]}$^{1/2}$ = 0.0883 for all data, conventional R [on F values of 8348 reflections with F_o^2 > 2σ(F_o^2)] = 0.0330, goodness of fit S = 1.030 on F^2 for 938 refined parameters. All non-H atoms were refined with anisotropic displacement parameters, H-atoms were constrained. Disorder was modelled in one of the isopropyl groups. Programs: Siemens SHELXTL (G. M. Sheldrick, University of Göttingen) and local programs.

‖ *Crystal data* for **2**: C$_{84}$H$_{80}$Mo$_2$N$_4$O$_8$·1.75 CH$_3$CN, M = 1537.24, monoclinic, space group $P2_1/n$, a = 13.4451(8), b = 29.235(2), c = 19.4289(12) Å, β = 100.952(2)°, U = 7497 8(8) Å^3, Z = 4, D_c = 1.362 g cm^{-3}, $F(000)$ = 3194. 65655 reflections were measured on a Siemens SMART CCD area detector diffractometer at 160 K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2.8 < 2θ < 51.4°, μ = 0.396 mm^{-1}) with ω scan narrow frames (0.3°), and three-dimensional profile fitting. Structure solution was by direct methods, refinement by full-matrix least-squares analysis on F^2 for all 13066 independent reflections (R_{int} = 0.0879). R_w = 0.1880 for all data, conventional R = 0.0943 (for 12358 observed data), goodness of fit = 1.298 on F^2 for 959 refined parameters. All non-H atoms were refined anisotropically, H-atoms were constrained. One of the acetonitrile molecules had a refined occupancy of *ca.* 75%. This value was constrained at exactly 75% in the final cycles of refinement. Programs: Siemens SHELXTL; SMART and SAINT software for data collection and reduction, and local programs. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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