Letter

A novel ligand family based on bulky metallocalix[4 and 8]arene substituents†

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Condensation reactions of metallocalix[4 and 8]arene complexes containing pendant amino groups readily afford new bulky imine complexes; the X-ray crystal structures of three complexes, of which two were determined using synchrotron radiation, are reported.

In recent years, there has been considerable and growing interest in new metallocalixarenes and the coordination chemistry thereof.[1] Recent advances by Floriani and co-workers[2] have utilised the simplest of the calixarenes, the calix[4]arene system (L^1H_4), particularly for its ability to act as a quasi-oxo support. The majority of these metallocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the ligand. On the other hand, knowledge about the structure and reactivity of metal compounds containing the larger ring systems is comparatively scant.[3] In particular, clear methodologies for studying the coordination chemistry of these larger ring systems remain in the early stages of development. The first organoimido metal calixarenes [Mo(NAr)L^1(NCMe)]and [{Mo(NAr)(NCMe)}$_2L^2$] (Ar = $C_6H_3Pr^i_2$-2,6; L^2 = calix[8]arene or *p*-*tert*-butylcalix[8]arene), both of which were formed readily *via* alkoxide and imide displacement reactions, have been reported.[3f] This methodology was extended to include the related *ansa*-bis(imido) derivative {Mo(OBu^t)$_2$[(2-NC_6H_4)$_2CH_2CH_2$]}[4] which may be ring-opened on reaction with L^1H_4[5] to release a pendant amino group (see **1**). Such reactivity provided an opportunity to develop an entry into a new family of ligands bearing bulkymetallocalixarene substituents, the first example of which are described here. These include the ready synthesis of bulky imino-metallocalix[4]arene complex [Mo(NAr^1)L^1] (**2**) (Ar^1 = 2-$C_6H_4CH_2CH_2C_6H_4N$-2′-CHC_5H_5N). For the larger ring systems, we describe the preparation and structure of the dimetallocalix[8]arene complex {[Mo(NAr^2)]$_2L^2$}·6MeCN (**3**) (L^2 = *p*-*tert*-butylcalix[8]arene; Ar^2 = 2-$C_6H_4CH_2CH_2C_6H_4NH_2$-2′), containing two pendant amino groups, and its reactivity towards 3,5-di-*tert*-butylsalicylaldehyde at elevated temperatures to afford the bis(salicylaldiminato) complex {[Mo(NAr^3)]$_2L^2$}·5MeCN (**4**) (Ar^3 = 2-$C_6H_4CH_2CH_2C_6H_4N$-2′-CHC_6H_2-2″-(OH)-3″,5″-Bu^t_2), see Scheme 1. Furthermore, these Mo=N–R–NH_2 systems (R = Ar^1, Ar^3, *etc.*) have potential for the synthesis of unusual amines *via* cleavage of the remaining Mo=N bond (*i.e.* Mo–calixarene-mediated amine synthesis). Interestingly, novel salen-type calix[4]arene ligands (upper-rim) have recently been reported and their potential as rhenium-based radiopharmaceuticals has been demonstrated.[6]

The reaction of **1** with 2-pyridinecarboxaldehyde in refluxing ethanol affords, after work-up, the pyridyl-imino complex [Mo(NAr^1)L^1] (**2**) in good yield. The room temperature solution ^{1}H NMR spectrum is consistent with the C_{4v}-symmetric cone conformation. Crystals obtained from a saturated solution of acetonitrile at ambient temperature were too weakly diffracting to give reasonable structural details using a conventional sealed-tube X-ray source, but a data set was readily obtained using synchrotron radiation.[7] The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in the caption. There are 2 uncoordinated molecules of solvent (MeCN) per molecule of the complex. The molybdenum centre possesses a pseudo-octahedral geometrysimilar to that found in the amino analogue **1**, with the molybdenum atom displaced from the O_4 mean plane towards the imido nitrogen N(1) by 0.245 Å.

In order to extend this approach to the larger *p*-*tert*-butylcalix[8]arene (L^2) ring system, {Mo(OBu^t)$_2$[(2-NC_6H_4)$_2$-CH_2CH_2]}[4] was treated with H_8L^2 (0.5 equiv.) in toluene affording, after work-up, the bis(imido) complex {[Mo(N-Ar′)]$_2L^2$} (**3**), in which each imido ligand contains a pendant amino group. The IR spectrum of **3** contains two broad (weak) stretches at *ca.* 3365 and 3180 cm^{-1} in the *v*(N–H) region, with the lower stretching constant associated with the H-bonded N(2) amino group. Complex **3** is presumedto form *via* loss of four *tert*-butanol ligands (two from each molybdenum) followed by proton transfer to each of the imido ligands, to release two pendant amino groups in an analogous fashion to that observed for [{Mo(NAr)(NCMe)}$_2$(calix[8]arene)].[3f] Crystals of **3** suitable for an X-ray analysis were grown from acetonitrile solution at room temperature in *ca.* 48% yield. The molecular structure is shown in Fig. 2, with selected bond lengths and angles given in the caption. Each molybdenum possesses a pseudo-octahedral geometry, resulting in what is best described as a central edge-shared bioctahedral arrangement, featuring asymmetric phenoxide bridges [Mo(2)–O(1) = 2.247(4) *cf.* Mo(2)–O(5) = 2.061(5) Å] which are coplanar with terminal organoimido ligands.

The conformation of the calixarene ring is such that each organoimido group is encapsulated by 3 calixarene-phenolate subunits—a double cup. The pendant $C_6H_4NH_2$ [N(4)] group of one of the imido groups shows some signs of disorder, though this could not be successfully modelled. In contrast, the N(2)-containing group of the other imido ligand shows no sign of disorder, due to the H-bonding locking in the pendant arm

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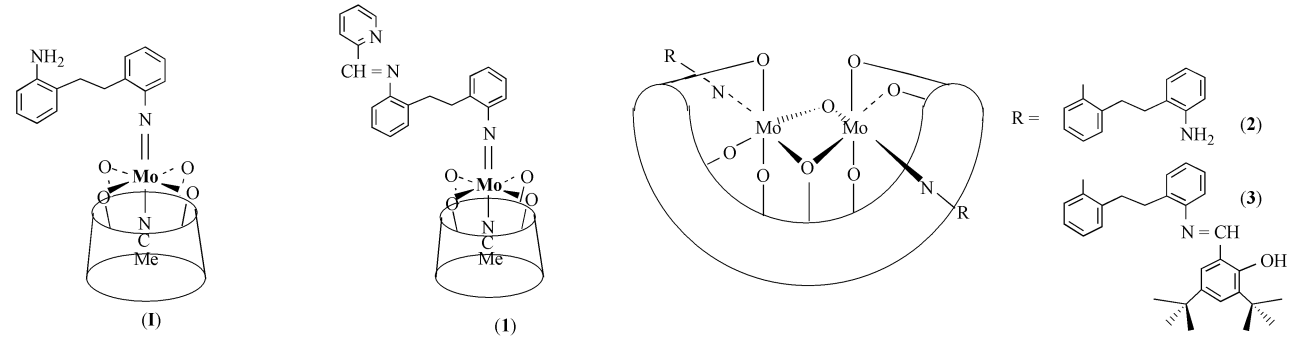


Scheme 1

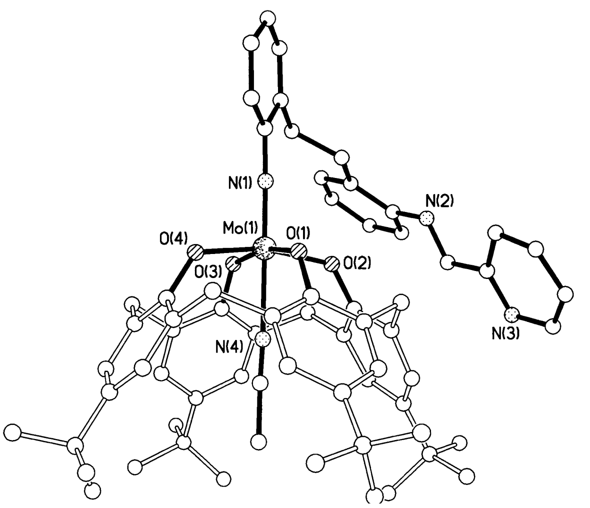


Fig. 1 The molecular structure of **2**. H-atoms, calix[4]arene *p*-Bu^t groups and 2 MeCN molecules of crystallisation omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 1.931(7), Mo(1)–O(2) 1.940(7), Mo(1)–O(3) 1.942(7), Mo(1)–O(4) 1.929(7), Mo(1)–N(1) 1.738(7), Mo(1)–N(4) 2.324(7), N(1)–C(45) 1.361(11); Mo(1)–N(1)–C(45) 171.9(7).

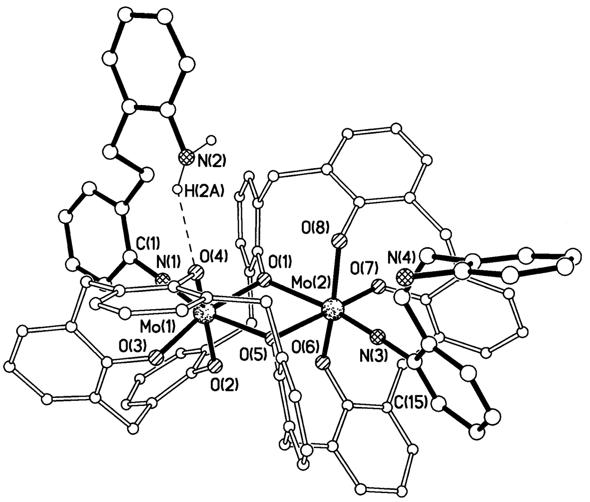


Fig. 2 The molecular structure of **3**. Most H-atoms, calix[8]arene *p*-Bu^t groups and 6 MeCN molecules of crystallisation omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 2.078(4), Mo(1)–O(2) 1.925(5), Mo(1)–O(3) 1.940(5), Mo(1)–O(4) 1.961(5), Mo(1)–O(5) 2.216(5), Mo(1)–N(1) 1.735(6), Mo(2)–O(1) 2.247(4), Mo(2)–O(5) 2.061(5), Mo(2)–O(6) 1.940(5), Mo(2)–O(7) 1.940(5), Mo(2)–O(8) 1.957(4), Mo(2)–N(3) 1.727(6),N(1)–C(1) 1.385(9), N(3)–C(15) 1.400(9); Mo(1)–N(1)–C(1) 178.1(5), Mo(2)–N(3)–C(15) 178.7(6).

[O(4)–H(2A) = 2.25 Å; O(4)–H(2A)–N(2) = 142°]. There are 6 MeCN solvent molecules in the asymmetric unit, one of which is very diffuse (or partially present). However, there is no solvent within the double cup calixarene cavities.

The ring opening reaction (see Scheme 2 for an example) described above gives a new dimension to the chemistry of imido-metallocalix[8]arenes and offers an entry point into complexes functionalised with a free reactive group. For example, reaction (condensation) of **3** with two equivalents of 3,5-di-*tert*-butylsalicylaldehyde in refluxing ethanol readily affords the bis(salicylaldimine) complex $\{[\mathrm{Mo(NAr''})]_2\mathrm{L}\}$ (**4**) (Ar″ = 2-$NC_6H_4CH_2CH_2C_6H_4N$-2-CHC_6H_2-2′-(OH)-3″,5″-$Bu^{t}{}_2$) in good yield (60–70%). As expected, the IR spectrum contains stretches in the *v*(OH) region (broad/weak)together with a strong band in the *v*(C=N) region. Small needle-shaped crystals of **4** suitable for an X-ray determination using synchrotron radiation[7] were grown from acetonitrile at 0 °C; they incorporate 5 molecules of solvent per molecule of the complex.

The molecular structure is shown in Fig. 3 and reveals the way in which the macrocyclic ring twists to adopt an edge-shared bioctahedron about the molybdenum centres. This 'pinched' conformation is similar to that observed for Na{Bu^{t}calix[8]arene[Ti(OPr^i)]$_2$}.[3d] The highly functionalised 'organoimido' (salicylaldimine) ligands are clearly acting as four-electron donors [Mo(1)–N(1) = 1.723(3) Å; Mo(1)–N(1)–C(89) = 179.0(3)°]; the bridging phenoxides are asymmetric, with those *trans* to the 'organoimido' groups being substantially longer [Mo(1)–O(5) = 2.243(2) *cf.* Mo(1)–O(1) = 2.065(2) Å],as observed in complex **2**. Each salicylaldimine group exhibits some internal H-bonding.

Future studies will be directed towards the use of these bulky ligands in transition metal chemistry.

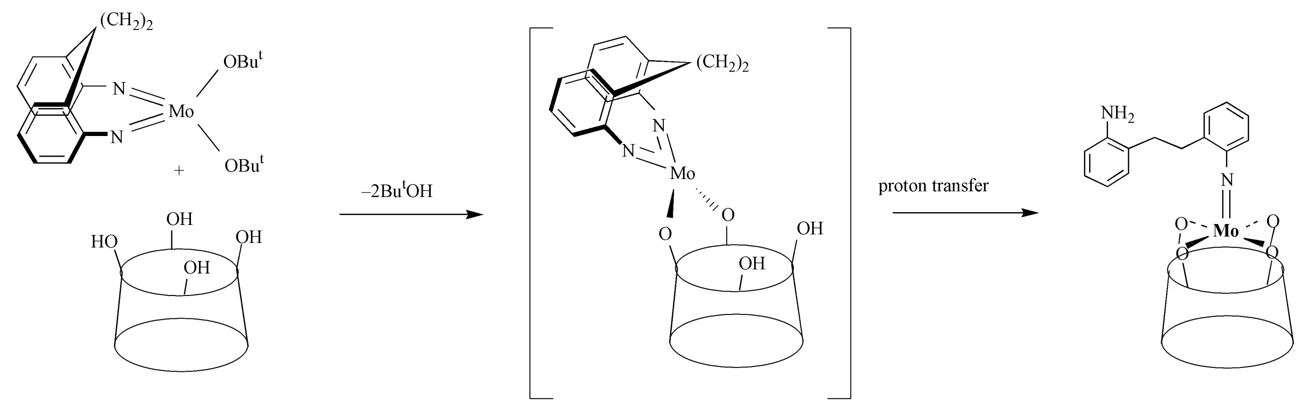
Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use.

Selected data for 2–4

Elemental analysis for **2**: calcd for $C_{66}H_{72}O_4N_4Mo\cdot 0.5MeCN$: C, 73.0; H, 6.7; N, 5.7; found: C, 73.3; H, 6.6; N, 5.9%. For **3**: calcd for $C_{116}H_{132}O_8N_4Mo_2\cdot 6C_2H_3N$: C, 71.5; H, 7.0; N, 6.5; found: C, 71.2; H, 6.9; N, 6.4%. For **4**: calcd for $C_{146}H_{172}O_{10}N_4Mo_2\cdot 5C_2H_3N$: C, 73.7; H, 7.4; N, 4.9; found: C, 73.5; H, 7.4; N, 4.6%.

Selected spectroscopic data for **2**: IR *v*(C=N) 1616 cm^{-1}. ^{1}H NMR (C_6D_6 , 300 MHz, 298 K) δ: 8.64 (s, 1H, CH=N), 5.17 (d, 4H, $^2J_{HH}$ 12.2 Hz, *endo*-CH$_2$), 4.33 (t, 2H, $^2J_{HH}$ 6.4 Hz, NCH$_2$), 4.17 (t, 2H, $^2J_{HH}$ 7.1 Hz, NCH$_2$), 3.55 (d, 4H, $^2J_{HH}$



Scheme 2

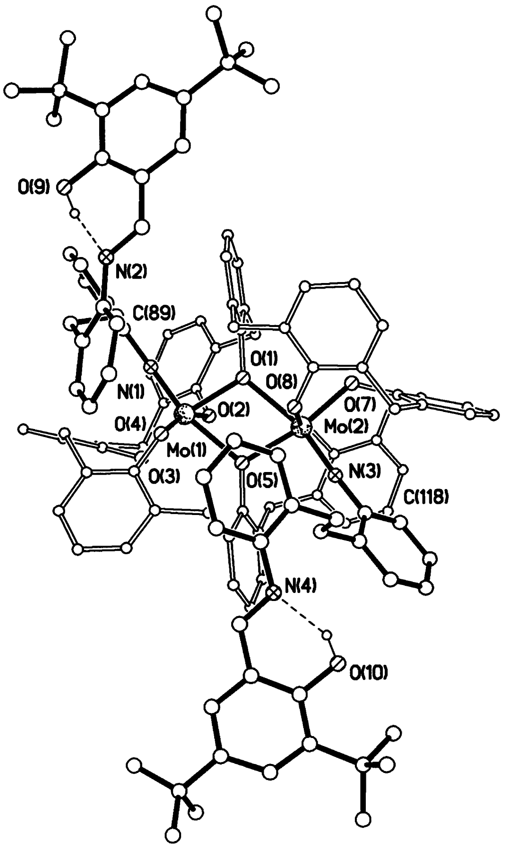


Fig. 3 The molecular structure of **4**. Most H-atoms, calix[8]arene *p*-Bu^t groups and 5 MeCN molecules of crystallisation omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 2.065(2), Mo(1)–O(2) 1.919(2), Mo(1)–O(3) 1.931(2), Mo(1)–O(4) 1.931(3), Mo(1)–O(5) 2.243(2), Mo(1)–N(1) 1.723(3), Mo(2)–O(1) 2.241(2), Mo(2)–O(5) 2.045(2), Mo(2)–O(6) 1.916(2) [note that O(6) is *trans* to O(8), but masked by Mo(2) in the diagram], Mo(2)–O(7)1.937(2), Mo(2)–O(8) 1.948(2), Mo(2)–N(3) 1.722(3), N(1)–C(89) 1.393(5), N(3)–C(118) 1.398(5); Mo(1)–N(1)–C(1) 179.0(3), Mo(2)–N(3)–C(15) 176.5(2).

12.1 Hz, *exo*-CH$_2$). For **3**: IR: ν(NH$_2$) 3365, 3181 cm^{-1}; ν(C–N) 1263 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298K) δ: 5.42 (d, 2H, $^2J_{HH}$ 12.1 Hz, *endo*-CH$_2$), 4.78 (d, 2H, $^2J_{HH}$ 13.9 Hz, *endo*-CH$_2$), 4.54 (d, 2H, $^2J_{HH}$ 14.0 Hz, *endo*-CH$_2$), 4.42 (d, 2H, $^2J_{HH}$ 13.9 Hz, *endo*-CH$_2$), 3.25 (d, 2H, $^2J_{HH}$ 12.8 Hz, *exo*-CH$_2$), 2.85 (d, 2H, $^2J_{HH}$ 12.7 Hz, *exo*-CH$_2$) (2 × *exo*-CH$_2$ obscured by overlap with ArCH$_2$). For **4**: IR ν(OH) 3370 cm^{-1}, ν(C=N) 1616 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K) δ: 14.10 (s, 2H, OH), 8.82 (s,2H, CH=N), 5.58 (d, 2H, $^2J_{HH}$ 12.2, *endo*-CH$_2$), 5.25 (d, 2H, $^2J_{HH}$ 14.1, *endo*-CH$_2$), 4.84 (d, 2H, $^2J_{HH}$ 11.8, *endo*-CH$_2$), 4.30 (overlapping d + t, 4H, ArCH$_2$ + *endo*-CH$_2$), 3.95 (t, 2H, $^2J_{HH}$ 7.7 Hz, ArCH$_2$), 3.73–3.27 (overlapping m, 12H, *exo*-CH$_2$ + NH$_2$).

X-Ray crystallography for 2·2MeCN, 3·6MeCN, and 4·5MeCN

Intensity data were collected using Bruker SMART 1K CCD diffractometers. Sealed-tube Mo-Kα radiation (λ = 0.71073 Å) was used for **3**·6MeCN, otherwise, synchrotron radiation (λ = 0.6923 Å for **2**·2MeCN, λ = 0.6878 Å for **4**·5MeCN) at Daresbury SRS Station 9.8, as described previously.[7] Two-fold positional disorder was modelled with restraints for some calixarene *p*-^{t}Bu groups in **3**·6MeCN and **4**·5MeCN. Programs used: SHELXTL[8] for structure solution and refinement and molecular graphics, Bruker AXS SMART (control), and SAINT (integration) and localprograms.[9]

Crystal data for **2**·2MeCN: C$_{66}$H$_{72}$MoN$_4$O$_4$·2C$_2$H$_3$N, M = 1163.32, monoclinic, space group $P2_1/n$, a = 14.142(2), b = 21.946(3), c = 20.008(3) Å, β = 90.146(3)°, V= 6209.5(16) Å^3, T= 160 K, Z = 4, μ = 0.264 mm^{-1}, 29388 data measured, of which 10529 were unique, R_{int} = 0.189, all unique data used in refinement against F^2 values to give final wR = 0.2341 (for all data), R = 0.0926 [for 5448 data with $F^2 > 4\sigma(F^2)$]. The structure suffered from *ca.*58 : 42(2) twinning with the b and c axes interchanged. For **3**·6MeCN: C$_{116}$H$_{132}$Mo$_2$N$_4$O$_8$·6C$_2$H$_3$N, M = 2148.46, trigonal, space group $P3_2$, a = 16.7686(15), c = 34.515(3) Å, V= 8404.9(13) Å^3, T= 160 K, Z = 3, μ (Mo-Kα) = 0.286 mm^{-1}, 44602 data measured, of which 19554 were unique, R_{int} = 0.093, all unique data used in refinement against F^2 values to give final wR = 0.1429 (on F^2 for all data), R = 0.0718 [for 13334 data with $F^2 > 4\sigma(F^2)$], absolutestructure parameter x = – 0.01(3). For **4**·5MeCN: C$_{146}$H$_{172}$Mo$_2$N$_4$O$_{10}$.5C$_2$H$_3$N, M = 2540.03, monoclinic, space group $P2_1/c$, a = 23.3956(17), b = 31.216(2), c = 21.2594(15) Å, β = 107.908(2)°, V= 14773.7(18) Å^3, T= 160 K, Z = 4, μ = 0.228 mm^{-1}, 83968 data measured of which 31474 were unique, R_{int} = 0.079, all unique data used in refinement against F^2 values to give final wR = 0.1869 (on F^2 for all data), R = 0.0670 [for 18014 data with $F^2 > 4\sigma(F^2)$].

CCDC reference numbers 173184–173186. See http://www.rsc.org/suppdata/nj/b1/b108088c/ for crystallographic data in CIF or other electronic format.

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