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Group 6 Metallocalixarenes Bearing "Hydrazido(2-)" Groups

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Introduction

In recent years, there has been considerable and growing interest in the metal coordination chemistry of calixarenes, partly owing to their ability to act as organic supports for reactive metal fragments.[1] To date, metallocalix[4]arenes bearing a variety of metal-bound substituents have been reported, including organoimido (NR, R = Bu^t; M = Mo, W; NAr, Ar = Ph, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,6-$^iPr_2C_6H_3$,$C_6H_4CH_2CH_2C_6H_4$-NH_2-2′; M = Nb, Mo, W),[2−4] oxo ([O], M = W, Mo, V, Nb, Cr),[5−9,16] chloride (M = W, Nb, Ta, Zr, Ti, Cr),[2−5,7,9−13,16−18] pyridine (M = V, Cr),[8,9] hydrazone ($NNCPh_2$; M = V),[8] cyclopentadienyl/pentamethylcyclopentadienyl (Cp/Cp*; M = Ta, Nb, Cr),[9,14] alkoxide/phenoxide (OR, R = Ph, C_6H_8O-2; M = Nb, Ta, W),[11,15,16] alkyl (Me, Et, Ph, p-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, CH_2Ph, CH_2SiMe_3; M = Cr, Zr, Zn),[9,12,17,19,20] alkylidene (≡CR, R = ^nPr, Ph, $SiMe_3$; M = W),[21] η_2-acyl/η_2-iminoacyl (OCR_2/Bu$tNCR_2$, R = Me, $PhCH_2$, p-MeC_6H_4; M = Ta, Zr),[12,17,19] ammonia (NH_3; M = Fe)[22] as well as metal−metal bonds (M−M, M = M, M≡M; M = Nb, Mo, W).[2,13,23−25] Transition metal complexes of a calix[4]arene tetraamide (5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diethylcarbamoylmethoxy)calix[4]arene) have also been reported (M = Fe, Ni, Cu, Zn, and Pb).[26]

By contrast, transition metal compounds containing the larger ring systems are still quite rare, presently being restricted to organoimido/amido (calix[5], M = W; calix[8], M = Mo),[3a,27] diphosphite (calix[6], M = Pd, Pt, Re),[28] chloride (calix[6], M = Ti),[29] and alkoxide (calix[8], M = Ti, Zr, V, Sn).[30]

We have recently developed a new approach to metal arylimido (M═NAr, Ar = aryl) calixarene chemistry, involving either displacement of *tert*-butoxide ligands (−Bu^tOH) or loss of HCl with concomitant loss of aniline (H_2Ar) in nonaqueous media.[3] This has allowed us to structurally characterize a number of novel complexes.

We now extend this chemistry to the NNR_2 moiety and describe the syntheses and crystal structures of two calix[4]arene (L) complexes, namely, [W(NCMe)($NNPh_2$)L] and [Mo($NNPh_2$)L]$_2$, a calix[6]arene (L^1) complex [Mo($NNPh_2$)]$_2$(μ-O)L^1] and a calix[8]arene (L^2) complex {[W($NNPh_2$)]L^2} (see Chart 1). Formally related to the alkylimido (NR) moiety (where the substituent R is a dialkylamino group), the "hydrazido(2-)" group may be regarded as binding to a metal center with a similar combination of 1σ and 2π interactions, affording a metal−nitrogen pseudo-triple-bond. There is still some ambiguity with regard to the extent of M−N and N−N multiple bond character and, as a consequence, the overall charge associated with NNR_2 groups.[31] Here, the term hydrazido(2-) is adopted, giving the metal an overall oxidation state of +VI. As far as we are aware, there are no reports of metallocalixarene complexes bearing the "hydrazido(2-)" functionality.

Experimental Section

General. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a

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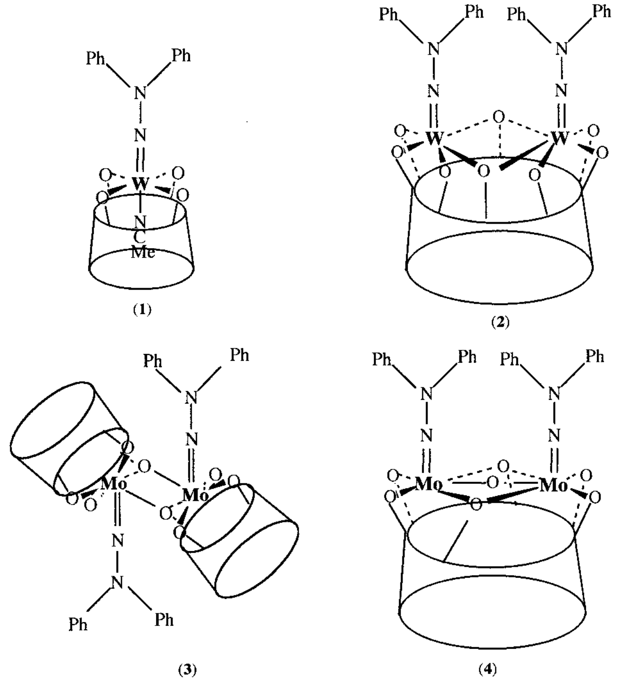
Chart 1



conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College and Medac Ltd. ^{1}H NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz and at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (Nujol mulls, CsI windows, Perkin-Elmer 577 and 457 grating spectrophotometers) of [W(NNPh$_2$)Cl$_4$], [Mo(NNPh$_2$)Cl$_3$], and [Mo(NNPh$_2$)$_2$Cl$_2$(dme)] were prepared according to literature methods.[32,33]All other chemicals were obtained commercially and used as received unless stated otherwise.

Synthesis of [W(NCMe)(NNPh$_2$)-*tert*-butylcalix[4]arene] (1). A mixture of [W(NNPh$_2$)(OBu^t)$_4$] [made in situ from W(NNPh$_2$)Cl$_4$ (2.3 g, 4.53 mmol) and KOBu^t (2.13 g, 18.98 mmol) in thf (30 cm^3)] and *tert*-butylcalix[4]areneH$_4$ (0.94 g, 1.59 mmol) were refluxed in toluene (ca. 20 cm^3) for 12 h. The volatiles were removed under reduced pressure and the residue taken up in hot MeCN (ca. 30 cm^3). Red-orange prisms of the product were deposited on cooling to room temperature. Yield: 3.6 g, 73%. Found (%): C, 66.0; H, 6.3; N, 4.8. WN$_3$O$_4$C$_{58}$H$_{65}$·MeCN requires the following (%): C, 65.9; H, 6.3; N, 5.1. IR (cm^{-1}): 2369w, 1587w, 1322m, 1262s, 1221s, 1153m, 1130s, 1105s, 1020s, 982m, 932w, 901w, 882w, 827s, 752s, 730m, 691w, 630w, 608w, 578m. 537w, 455w. ^{1}H NMR (CD$_3$CN): δ 7.84−7.24 (several m, 18H, aromatics), 4.38 (d, 4H, $^2J_{\mathrm{HH}} = 12.0$ Hz, endo-CH$_2$), 3.28 (d, 4H, $^2J_{\mathrm{HH}} = 12.0$ Hz, exo-CH$_2$), 2.19 (br s, 3H, MeCN), 1.20 (s, 36H, (CH$_3$)$_3$C), −0.15 (br s, 1.5H, 0.5MeCN).

Synthesis of {[W(NNPh$_2$)]$_2$-*tert*-butylcalix[8]arene} (2). A mixture of [W(NNPh$_2$)(OBu^t)$_4$] [made in situ from W(NNPh$_2$)Cl$_4$ (1.0 g, 1.97 mmol) and KOBu^t (0.89 g, 7.93 mmol) in thf (30 cm^3)] and *tert*-butylcalix[8]areneH$_8$ (1.27 g, 0.98 mmol) were refluxed in toluene (ca. 20 cm^3) for 12 h. The volatiles were removed under reduced pressure and the residue taken up in hot MeCN (ca. 30 cm^3). Removal of solvent afforded an orange solid; red-orange needles of the product were deposited from CH$_2$Cl$_2$ on cooling to −20 °C (1−2 days). Yield: 1.1 g, 51%. Found (%): C, 63.8; H, 6.1; N, 3.8. W$_2$N$_4$O$_8$C$_{112}$H$_{124}$·2MeCN·CH$_2$Cl$_2$ requires the following (%): C, 64.2; H, 6.1; N, 3.8. IR (cm^{-1}): 1594w, 1366m, 1261s, 1097vs, 1021s, 902w, 870w, 800w, 746w, 722w, 690w, 613w, 536w, 495w. ^{1}H NMR (C$_6$D$_6$): δ 7.33−6.23 (several m, 36H, aromatics), 5.72 (d, 2H, $^2J_{\mathrm{HH}} = 13.1$ Hz, endo-CH$_2$), 5.35 (d, partially obscured, 2H, endo-CH$_2$), 5.34 (s, 2H, CH$_2$Cl$_2$), 5.27 (d, 2H, $^2J_{\mathrm{HH}} = 14.7$ Hz, endo-CH$_2$), 5.01 (d, 2H, $^2J_{\mathrm{HH}} = 12.2$ Hz, endo-CH$_2$), 3.59 (d, 2H, $^2J_{\mathrm{HH}} = 11.9$ Hz, exo-CH$_2$), 3.41 (d, 2H, $^2J_{\mathrm{HH}} = 13.2$ Hz, exo-CH$_2$), 3.29 (d, 2H, $^2J_{\mathrm{HH}} = 12.4$ Hz, exo-CH$_2$), 3.22 (d, 2H, $^2J_{\mathrm{HH}} = 15.0$ Hz, exo-CH$_2$), 1.33 (s, 18H, 2 × C(CH_3)$_3$), 1.31 (s, 18H, 2 × C(CH_3)$_3$), 1.24 (s, 18H, 2 × C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.19 (s, 9H, C(CH_3)$_3$), 0.58 (s, 9H, 3CH$_3$CN).

Synthesis of [Mo(NNPh$_2$)(*tert*-butylcalix[4]arene)]$_2$ (3). A mixture of [Mo(NNPh$_2$)$_2$Cl$_2$(dme)] (1.0 g, 1.61 mmol) and *tert*-butylcalix[4]areneH$_4$ (1.04 g, 1.61 mmol) were refluxed for 12 h in toluene (30 cm^3). Removal of volatiles under reduced pressure and extraction of the product with CH$_2$Cl$_2$ (25 cm^3) afforded a brown-purple solution. Removal of volatiles and extraction into acetone gave on standing (evaporation) under air (2−3 days) purple prisms of **3** (0.45 g, 27%). Found (%): C, 68.9; H, 7.1; N, 2.1. Mo$_2$O$_8$N$_4$C$_{112}$H$_{130}$·4(acetone)·CH$_2$Cl$_2$ requires the following (%): C, 69.3; H, 7.0; N, 2.3. IR (cm^{-1}): 1599w, 1589w, 1563m, 1303s, 1261s, 1240m, 1195s, 1165m, 1159m, 1126m, 1108m, 1092m, 1022m, 958w, 914w, 880w, 870w, 824m, 799m, 764w, 750m, 748m, 723w, 694w, 635w, 555w, 523w. ^{1}H NMR (CDCl$_3$): δ 7.28−6.57 (several m, 36H, aromatics), 5.53 (d, 4H, $^2J_{\mathrm{HH}} = 11.6$ Hz, endo-CH$_2$), 3.98 (d, 4H, $^2J_{\mathrm{HH}} = 13.6$ Hz, endo-CH$_2$), 2.67 (d, 4H, $^2J_{\mathrm{HH}} = 12.0$ Hz, exo-CH$_2$), 2.08 (d, 4H, $^2J_{\mathrm{HH}} = 14.0$ Hz, exo-CH$_2$), 1.21 (s, 18H, C(CH_3)$_3$), 1.13 (s, 54H, C(CH_3)$_3$).

Synthesis of [Mo(NNPh$_2$)]$_2$(μ-O)(*tert*-butylcalix[6]arene)] (4). [Mo(NNPh$_2$)Cl$_3$] (1.0 g, 2.6 mmol) and KOBu^t (0.88 g, 7.84 mmol) were combined in thf (30 cm^3) and stirred for 12 h. After removal of volatiles under vacuum, *tert*-butylcalix[6]areneH$_6$ (1.26 g, 1.29 mmol) and toluene (30 cm^3) were added and the system was refluxed for 12 h. Volatiles were again removed in vacuo, the residue was extracted into warm MeCN (2 × 30 cm^3). On standing (1−2 days) large brown prisms formed. Yield: 1.3 g, 62%. Found (%): C, 69.7; H, 6.4; N, 5.6. Mo$_2$O$_7$N$_4$C$_{90}$H$_{98}$·2MeCN requires the following (%): C, 69.9; H, 6.5; N, 5.2. IR (cm^{-1}): 1593w, 1304m, 1301m, 1261s, 1198m, 1161m, 1091s, 1020s, 918w, 868w, 862w, 801s, 752w, 722m, 693w. ^{1}H NMR (CDCl$_3$): δ 7.28−6.61 (several m, 32H, aromatics), 4.33 (d, 2H, $^2J_{\mathrm{HH}} = 12.9$ Hz, endo-CH$_2$), 4.31(d, 2H, $^2J_{\mathrm{HH}} = 12.3$ Hz, endo-CH$_2$), 4.10 (d, 2H, $^2J_{\mathrm{HH}} = 13.8$ Hz, endo-CH$_2$), 2.97 (d, 2H, $^2J_{\mathrm{HH}} = 12.4$ Hz, exo-CH$_2$), 2.85 (d, 2H, $^2J_{\mathrm{HH}} = 14.0$ Hz, exo-CH$_2$), 2.49 (d, 2H, $^2J_{\mathrm{HH}} = 13.1$ Hz, exo-CH$_2$), 1.36 (s, 18H, C(CH_3)$_3$), 1.13 (s, 18H, C(CH_3)$_3$), 1.02 (s, 18H, C(CH_3)$_3$).

Crystallography. Measurements for **1**·2MeCN, **3**·4Me$_2$CO, and **4**·4MeCN were made on a Bruker AXS SMART CCD area-detector diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data for **2**·3MeCN·(2$^1/_2$)CH$_2$Cl$_2$ were measured using a similar diffractometer on station 9.8 at Daresbury SRS using synchrotron radiation ($\lambda = 0.6875$ Å) for which full experimental procedures have been reported previously.[10] Narrow-frame exposures (0.3° in ω) were employed for all data sets. Data were collected at 160 K to $2\theta > 50°$. Cell parameters were refined from the observed ω angles of all strong reflections in each data set except for 2·3MeCN·(2$^1/_2$)CH$_2$Cl$_2$, where the unit cell parameters were refined from 551 reflections collected in a preliminary series of frames. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. No significant intensity decay was observed, but beam decay of ca. 15% was corrected for in the case of **2**·3MeCN·(2$^1/_2$)CH$_2$Cl$_2$. (The rather large features in the final difference map for **2**·3MeCN·(2$^1/_2$)CH$_2$Cl$_2$ were close to the W atoms and resulted in imperfect corrections for synchrotron beam decay and absorption by the needle-shaped crystal.) Structures **1**·2MeCN and **3**·4Me$_2$CO were solved by Patterson synthesis, the others by direct methods. Refinement was on F^2 values for all unique data by full-matrix least-squares. Table 2 gives further details. All non-hydrogen atoms were refined anisotropically. Disorder was modeled successfully with restraints on geometry and anisotropic displacement parameters for the methyl groups of one calixarene ^{t}Bu group in each structure (two in **3**·4Me$_2$CO) and for four carbon atoms in one of the hydrazide phenyl rings in **2**·3MeCN·(2$^1/_2$)CH$_2$Cl$_2$. Programs used were

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(31) We have preformed DFT calculations on a number of [M(NNR$_2$)L$_4$] (L = halide or alkoxide) derivatives as well as the complex [W(NNPh$_2$)$_2$Cl$_4$], the results of which will form the basis of a future publication.

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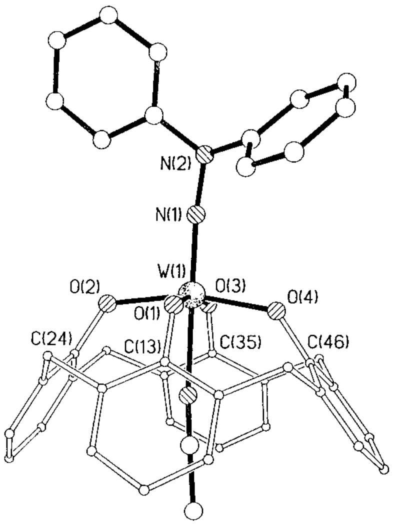

Figure 1. Molecular structure of **1** without ^{t}Bu groups and H atoms. In all figures, the calixarene ligands are shown with open bonds. Probability ellipsoids are at the 50% level.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

W(1)−N(1): 1.7523(19)	W(1)−O(4): 1.9336(16)
W(1)−O(2): 1.9338(15)	W(1)−O(3): 1.9657(15)
W(1)−O(1): 1.9758(15)	W(1)−N(3): 2.2610(18)
N(1)−N(2): 1.333(3)	
W(1)−N(1)−N(2): 170.4(2)	N(1)−W(1)−N(3): 176.98(8)
O(1)−W(1)−O(3): 167.16(6)	O(2)−W(1)−O(4): 163.57(6)
N(1)−W(1)−O(4): 97.40(8)	N(1)−W(1)−O(2): 99.02(8)
N(1)−W(1)−O(1): 93.95(8)	N(1)−W(1)−O(3): 98.85(8)
W(1)−O(1)−C(13): 125.98(13)	W(1)−O(2)−C(24): 129.29(13)
W(1)−O(3)−C(35): 127.00(13)	W(1)−O(4)−C(46): 133.22(14)

Bruker AXS SHELXTL[35] for structure solution, refinement, and molecular graphics, Bruker AXS SMART (control) and SAINT (integration), and local programs.[36]

Results and Discussion

Tungsten Complexes. Reaction of [W(NNPh$_2$)(OBu^t)$_4$] (generated in situ from W(NNPh$_2$)Cl$_4$ and KOBu^t in thf) with H$_4$L in refluxing toluene affords, following the removal of *tert*-butyl alcohol and recrystallization from MeCN, the hydrazido(2-) complex [W(NCMe)(NNPh$_2$)L] (**1**) as large solvent-dependent orange-red needles in good yield (70−80%). The room-temperature solution NMR (^{1}H) spectrum of a sample of **1** (dried in vacuo for 12 h) is of the C_{4v}-type, consistent with a cone conformation, and possesses broad resonances for MeCN consistent with fluxional behavior. The structure is shown in Figure 1; bond lengths and angles are given in Table 1 (crystallographic data are presented in Table 2). The mononuclear compound has tungsten in a pseudo-octahedral enviroment. As in the metal imido complexes,[3] the metal is displaced somewhat (0.248 Å) away from the equatorial plane defined by the four calixarene oxygens toward the nitrogen N(1) of the hydrazido group. For the latter, the short W(1)−N(1) distance [1.7523(19) Å], long N(1)−N(2) distance [1.333(3) Å], and almost linear W(1)−N(1)−N(2) angle [170.43(17)°] are consistent with those previously associated with (described as) the hydrazido(2-) ligand. The geometry at N(2) is best described as being slightly pyramidal (sum of the angles is 350.5°).

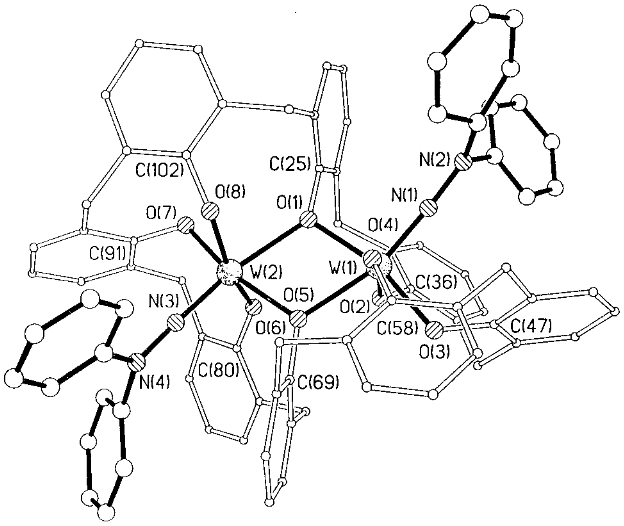

Figure 2. Molecular structure of **2** without ^{t}Bu groups and H atoms. Probability ellipsoids are at the 50% level.

The packing of **1**·2MeCN shows only a slight cup-to-cup interaction; we have previously observed calixarene "pockets" arising from such interactions.[3b] There are two noncoordinated molecules of MeCN in the crystal lattice. Interestingly, reaction of the tetrachlorotungsten complex [W(NNPh$_2$)Cl$_4$] with H$_4$L affords a bis(isodiazene) complex [W(NNPh$_2$)$_2$Cl$_4$].[31]

Similar treatment of H$_8$L^2 with 2 equiv of [W(NNPh$_2$)(OBu^t)$_4$] affords the dimetallocalix[8]arene complex {[W(NCMe)(NNPh$_2$)]$_2$L^2} (**2**) via a process that is presumed to be analogous to that operating in the formation of **1**, resulting in the elimination of eight molecules of Bu^{t}OH. Small needle-shaped crystals suitable for X-ray determination using synchrotron radiation were grown from dichloromethane at −20 °C; they incorporate three molecules of MeCN and approximately 2.5 molecules of CH$_2$Cl$_2$ per molecule of complex. The molecular structure is shown in Figure 2, and selected bond lengths and angles are given in Table 3 (crystallographic data are in Table 2). The calix[8]arene twists considerably to accommodate the bulky metal hydrazido fragments with each hydrazido fragment being capped by three linked phenoxide groups of the calixarene. Each tungsten exists in a local pseudo-octahedral enviroment similar to that found in **1** with the tungsten atoms displaced by an average 0.253 Å out of the plane of calixarene oxygens toward N$_\alpha$ of each hydrazide (2-) ligand. The W−O−W bridges are asymmetric with W(1)−O(1) and W(2)−O(5) [av 2.077(4) Å] trans to O, being rather shorter than W(1)−O(5) and W(2)−O(1) [av 2.198(4) Å] trans to the hydrazide N. The hydrazide ligands are linear [∼174°] with W−N bond distances of 1.744(4) Å and N−N distances of 1.321(6) Å. Here, the sum of the angles at N(2) [and N(4)] is ≥359° (planar).

Molybdenum Complexes. By contrast, the reaction of [Mo(NNPh$_2$)$_2$Cl$_2$(dme)][32] with H$_4$L after workup afforded the air-stable complex [Mo(NNPh$_2$)(L)]$_2$ **(3)**. Complex **3** is presumed to form via formal loss of diphenylhydrazine hydrachloride (Ph$_2$NNH$_2$·HCl) and an HCl molecule. X-ray quality crystals of **3**·4Me$_2$CO were grown by slow evaporation of an acetone solution in air. The molecular structure is shown in Figure 3 with selected bond lengths and angles given in Table 4 (crystallographic data are in Table 2). The binuclear complex **3** adopts a centrosymmetric distorted edge-shared bioctahedral geometry; the asymmetric phenoxide bridges are derived one from each calixarene ligand. The longer Mo−O bridging bond (2.285(3) vs 2.075(3) Å for the nonbridging Mo−O) is found trans to the near-linear hydrazido(2-) ligand (Mo(1)−N(1)−N(2) = 175.7(3)°); the bond

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(34) Smith, J. M.; Bott, S. G. *Chem. Commun.* **1996**, 377.

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Table 2. Summary of Crystal Data and Structure Determination for Compounds **1**·2MeCN, **2**·3MeCN·(2$^1/_2$)CH_2Cl_2, **3**·4Me_2CO, and **4**·4MeCN

compound	**1**·2MeCN[a]	**2**·3MeCN·(2$^1/_2$)CH_2Cl_2[b]	**3**·4Me_2CO[c]	**4**·4MeCN[d]
fw	1134.1	2357.3	2078.3	1703.8
space group	$P\bar{1}$ [No.2]	$P\bar{1}$ [No.2]	$P2_1/n$ [No.14]	$P2_1/n$ [No.14]
a, Å	10.7852(6)	16.7386(14)	16.0888(11)	20.3075(12)
b, Å	14.7376(8)	18.809(2)	17.7004(12)	17.8252(11)
c, Å	18.2479(9)	20.0969(17)	19.4921(14)	26.0735(14)
α, deg	94.057(2)	94.791(6)		
β, deg	91.513(2)	108.422(5)	91.078(2)	112.312(2)
γ, deg	108.029(2)	99.972(8)		
V, $Å^3$	2747(3)	5847.4(9)	5549.9(7)	8731.6(9)
Z	2	2	2	4
$D_{calcd,}$ g cm^{-3}	1.371	1.339	1.244	1.296
μ, mm^{-1}	2.154	2.136	0.288	0.347
R^e	0.0227	0.0554	0.0595	0.0627
$R_w{}^f$	0.0576	0.1511	0.1520	0.01243
max, min in diff map, e $Å^{-3}$	0.85, −1.05	4.49, −4.10	0.83, −0.91	0.64, −0.68

[a] Molecular formula: $C_{58}H_{65}N_3O_4W·2CH_3CN$. [b] Molecular formula: $C_{112}H_{127}N_4O_8W_2·3CH_3CN·(2^1/_2)CH_2Cl_2$. [c] Molecular formula: $C_{112}H_{124}Mo_2N_4O_8·4OC(CH_3)_2$. [d] Molecular formula: $C_{90}H_{98}Mo_2N_4O_7·4CH_3CN$. [e] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for "observed" reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$. [f] $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$ for all data.

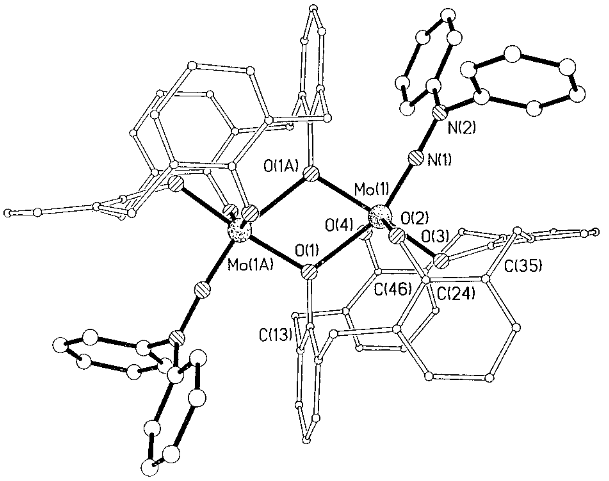

Figure 3. Molecular structure of **3** without ^{t}Bu groups and H atoms. Probability ellipsoids are at the 50% level.

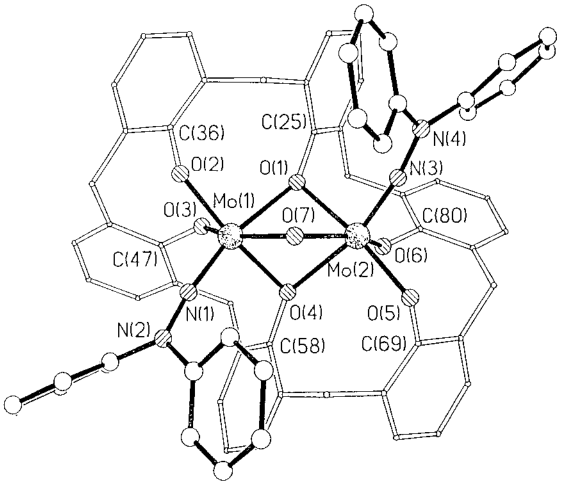

Figure 4. Molecular structure of **4** without ^{t}Bu groups and H atoms. Probability ellipsoids are at the 50% level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**

W(1)−N(1): 1.744(4)	W(1)−O(1): 2.078(4)
W(1)−O(2): 1.883(4)	W(1)−O(3): 1.959(4)
W(1)−O(4): 1.951(4)	N(1)−N(2): 1.321(6)
W(1)−N(1)−N(2): 175.0(4)	N(1)−W(1)−O(1): 94.90(18)
O(1)−W(1)−O(3): 163.55(15)	O(2)−W(1)−O(4): 160.41(16)
N(1)−W(1)−O(4): 96.26(18)	N(1)−W(1)−O(2): 100.43(18)
N(1)−W(1)−O(1): 94.90(18)	N(1)−W(1)−O(3): 99.61(18)
W(1)−O(1)−C(25): 131.7(3)	W(1)−O(2)−C(36): 135.3(3)
W(1)−O(3)−C(47): 122.4(3)	W(1)−O(4)−C(58): 129.4(3)
W(1)−O(5)−C(69): 119.3(3)	W(1)−O(1)−W(2): 109.33(15)
W(1)−O(5)−W(2): 109.31(15)	

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **3**

Mo(1)−N(1): 1.750(4)	Mo(1)−O(1): 2.285(3)
Mo(1)−O(2): 1.928(3)	Mo(1)−O(3): 1.964(3)
Mo(1)−O(4): 1.948(3)	Mo(1)−O(1′): 2.075(3)
N(1)−N(2): 1.320(5)	
Mo(1)−N(1)−N(2): 175.7(3)	N(1)−Mo(1)−O(1′): 91.31(14)
O(4)−Mo(1)−O(3): 82.88(12)	O(2)−Mo(1)−O(1′): 96.31(11)
N(1)−Mo(1)−O(4): 98.76(14)	N(1)−Mo(1)−O(2): 103.27(14)
N(1)−Mo(1)−O(1): 159.79(13)	N(1)−Mo(1)−O(3): 93.10(14)
O(1)−Mo−O(1′): 68.60(12)	Mo(1′)−O(1)−Mo(1): 111.40(12)
Mo(1)−O(1)−C(13): 122.5(2)	Mo(1)−O(2)−C(24): 132.2(2)
Mo(1)−O(3)−C(35): 128.3(3)	Mo(1)−O(4)−C(46): 130.5 (2)

lengths associated with the latter, [Mo(1)−N(1) = 1.750(4) Å and N(1)−N(2) = 1.321(5) Å] are similar to those found in **1**. Again, as in **1** and **2**, the sum of the angles at N(2) [359.1°] are consistent with planarity. The calixarene(O)−Mo bonds occupy four adjacent Mo coordination sites, and to maintain octahedral coordination, it is necessary for one of the phenoxy rings to bend out, affording a "down, down, down, out" configuration for the calixarene (consistent with a non-C_{4v} NMR spectrum; see Experimental Section). The bulky diphenylhydrazido(2-) ligands are too large to fit into the calixarene cavities. Interestingly, there is no coordination of solvent (acetone) presumably because the metal already has attained the favored octahedral enviroment via the bridging coordination of the calix[4]arene ligand and doubtless also because of the poorer ligating properties of acetone (cf. MeCN).

A number of dinuclear complexes containing bridging ligands derived from calixarenes have been structurally characterized, for example, the titanium(IV) and iron(III) compounds {$Ti_2(\mu$-$L)_2$} and {$[Fe(NH_3)]_2(\mu$-$LOSiMe_3)_2$} and the recently reported vanadium(IV) complex [$V_2(\mu$-$L)_2$] in which each metal is bound only to three of the calixarene oxygens.[8,22]

Reaction of the mixture generated (in thf) from [$Mo(NNPh_2)Cl_3$] and $KOBu^t$ (3 equiv) with the ring system H_6L^1 (0.5 equiv) in refluxing toluene reproducibly affords, after workup, brown prisms of the dimetallocalixarene {$[Mo(NNPh_2)]_2(\mu$-$O)L^1$} (**4**) in good yield (ca. 60%). X-ray quality crystals were grown from MeCN. The molecular structure is shown in Figure 4; selected bond lengths and angles are given in Table 5 (crystallographic data are in Table 2). The calix[6]arene framework adopts a unique conformation in which two opposite bridging phenolic

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

Mo(1)−N(1):	1.749(4)	Mo(1)−O(1):	2.241(3)
Mo(1)−O(2):	1.933(3)	Mo(1)−O(3):	1.886(3)
Mo(1)−O(4):	2.111(3)	Mo(1)−O(7):	1.921(3)
N(1)−N(2):	1.311(5)	Mo(2)−N(3):	1.737(4)
Mo(2)−O(1):	2.130(3)	Mo(2)−O(4):	2.305(3)
Mo(2)−O(5):	1.962(3)	Mo(2)−O(6):	1.881(3)
Mo(2)−O(7):	1.908(3)	N(3)−N(4):	1.311(5)
Mo(1)−N(1)−N(2):	171.9(3)	N(1)−Mo(1)−O(1):	167.01(14)
O(4)−Mo(1)−O(3):	85.97(11)	O(2)−Mo(1)−O(1):	97.49(11)
N(1)−Mo(1)−O(4):	94.50(14)	N(1)−Mo(1)−O(2):	94.67(14)
N(1)−Mo(1)−O(7):	98.37(14)	N(1)−Mo(1)−O(3):	105.56(15)
Mo(1)−O(4)−Mo(2):	84.48(10)	Mo(2)−O(1)−Mo(1):	85.64(10)
Mo(2)−O(7)−Mo(1):	101.84(13)	Mo(1)−O(1)−C(25):	149.3(2)
Mo(1)−O(2)−C(36):	123.1(2)	Mo(1)−O(3)−C(47):	139.5(3)
Mo(1)−O(4)−C(58):	119.1 (2)	N(3)−Mo(2)−O(1):	93.90(14)
N(3)−Mo(2)−O(6):	105.35(15)	N(3)−Mo(2)−O(5):	95.65(14)
N(3)−Mo(2)−O(7):	98.89(15)	N(3)−Mo(2)−O(4):	164.98(14)
O(1)−Mo(2)−O(6):	85.20(11)	O(4)−Mo(2)−O(5):	98.75(11)

rings support a central core comprising of a distorted confacial bioctahedral structure (similar to that observed in **2**); the third bridging atom is the oxygen atom O(7) through which a noncrystallographic C_2 axis passes. This oxo group is believed to arise by abstraction from the ether solvent. The two bulky hydrazido(2-) groups [Mo(1)−N(1) = 1.749(4) Å, Mo(2)−N(3) = 1.737(4) Å, N(1)−N(2) = 1.311(5) Å, N(3)−N(4) = 1.311(5) Å] and μ_2-O(7) [Mo(1)−O(7) = 1.921(3) Å, Mo(2)−O(7) = 1.908(3) Å] (N(2) and N(4) are again planar) form the top surface above the calixarene ring whose conformation contrasts with the up, up, out conformation observed recently for the calix[6]arene-derived diphosphite $[\mathrm{L^1P_2PdCl_2}]$[28] and that observed for the pentaaluminum complex $[\mathrm{L^1(AlMe_3)(AlMe_2\text{-}thf)(AlMe_2)(AlMe)_2}]$ recently reported by Bott.[34] The ring in **4**·4MeCN is best described as adopting an enlarged cup conformation; interestingly, as in **2** and **3** there is no incorporation of metal-bound solvent.

Concluding Remarks

In summary, the use of established methodology[3] provides a simple route into new metallocalixarenes bearing the $\mathrm{NNR_2}$ moiety. In particular, complexes **2** and **4** represent rare examples of structurally characterized dimetallocalix[6] and [8]arenes. The M−N and N−N distances found in these complexes together with the near-linear M−N−N angles are consistent with multiple bond character and the "hydrazide(2-)" description. The simultaneous coordination of other functionalities is now under investigation.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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