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Synthesis and Characterization of Monomeric Oxo Dichloro 1,3-Dialkyl *p-tert*-Butylcalix[4]arene Complexes of Molybdenum(VI,V) and Tungsten(VI,V)

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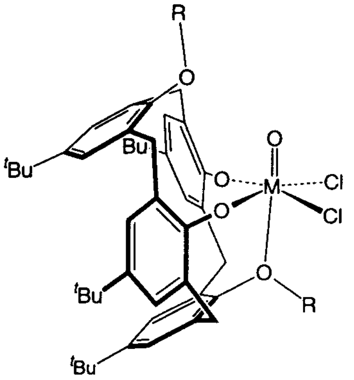
Introduction

There is considerable interest in the chemistry of oxophilic early transition metals and polydentate, oxygen-donor calix[*n*]arene ligands.[1] This interest is piqued by the ability of metal−calixarene complexes to serve as models for metal−oxide surfaces and to function as building blocks for supramolecular, host−guest and/or advanced materials. Our interest in calixarene chemistry stems from the potential of these ligands, and their thia analogues, to form high-valent, monomeric oxo− and/or thio−Mo and −W complexes with biomimetic or catalytic properties.[2,3]

Currently, the calixarene chemistry of Mo and W is dominated by chloro,[4] phenoxo,[4] imido,[5] organometallic,[4e,6] and metal−metal bonded[4d,4e,7] species. Despite the prevalence of oxo species in the chemistry of these elements,[8] oxo complexes containing calixarene coligands are extremely rare.[4a,9,10] Indeed, only one monomeric Mo calixarene complex, viz., $MoO(cal)(H_2O)\cdot(calH_4)\cdot PhNO_2$ ($calH_4$ = *p-tert*-butylcalix[4]arene), has been structurally characterized. It is composed of discrete $MoO(cal)(H_2O)$ and $calH_4$ molecules arranged to resemble a Fabergé egg, which encapsulates a nitrobenzene molecule.[10] A full description of this intriguing compound has yet to appear. Oxo−W calix[4]arene complexes of the type $WO(cal)\cdot n$(solvent) and $WO(cal)L'$ ($L' = H_2O, CH_3CO_2H$) have been reported by Floriani[4a] and Swager[9] and co-workers (here, cal signifies a number of *p*-substituted calix[4]arenes). Structurally characterized examples possess six-coordinate, octahedral structures, with an axial W═O unit and weakly coordinated trans ligand, e.g., $WO(cal)(CH_3CO_2H)$.[4a] The dichloro complex, *cis*-WCl_2(cal), is also known. Access to these oxo− and chloro−W complexes, particularly *cis*-WCl_2(cal), has enhanced the development of W−calixarene chemistry relative to Mo−calixarene chemistry, where oxo and/or chloro starting materials are limited or nonexistent. For example, reaction of *cis*-WCl_2(cal) with a range of alkylating agents generates methyl, mixed chloro/methyl, or alkylidyne derivatives, $[W(\equiv CR)(cal)]^-$, which can be protonated or metalated to form alkylidene complexes.[6a,c−e] Sodium reduction of *cis*-WCl_2(cal) in the presence of alkenes produces alkene complexes which undergo alkene coupling reactions and conversion to alkylidynes and alkylidenes.[6b,e] Finally, the complex undergoes metathesis reactions and serves as an entry into metal−metal bonded and supramolecular W−calixarene systems.[4b−e] Expansion of the coordination and organometallic chemistry of Mo− and W−calixarene complexes depends critically on access to versatile oxo and/or halo starting materials such as those reported herein.



M = Mo; R = Me (1), R = Et (2)
M = W; R = Me (3), R = Et (4)

This paper describes the synthesis and characterization of monomeric oxo dichloro Mo(VI) and W(VI) complexes of the

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type $(R_2cal)MOCl_2$ (**1**−**4**), formed in the reactions of $MOCl_4$ with 1,3-dialkyl *p-tert*-butylcalix[4]arenes (R_2calH_2) in hexane. The X-ray crystal structures of **2**·$CHCl_3$ and **3**·$CHCl_3$ confirm the monomeric nature of the complexes and reveal a novel tridentate calixarene moiety, wherein steric interactions between the M═O and uncoordinated −OR groups force a *tert*-butyl group to occupy the "bowl cavity" normally associated with calixarenes. We refer to the structure as "collapsed" (or "prolapsed"), the arene unit and its substituent having slipped from their more usual position into the ligand cavity. The structure of **2**·$CHCl_3$ is the first reported for a six-coordinate Mo(VI) complex of the type $(L_n)MOX_2$ (X = halogen) and a rare example of a monomeric, six-coordinate, monooxo−Mo(VI) species.[8] The structure of **3**·$CHCl_3$ is only the second reported for an oxo dichloro W(VI) complex.[11] Chemical and electrochemical reduction of the complexes produces stable, EPR-active, oxo−Mo(V) and −W(V) species. These $[(R_2cal)MOCl_2]^-$ complexes represent a new class of monomeric M(V) complex.[8,12] It is expected that these new calixarene complexes will be amenable to chemical modification, leading to progress in Mo− and W−calixarene coordination and organometallic chemistry.

Experimental Section

General. All reactions were performed under an atmosphere of dinitrogen using dried, distilled, and deoxygenated solvents. Samples of $MoOCl_4$ and $WOCl_4$ were prepared by the method of Nielson.[13] The 1,3-dialkyl *p-tert*-butylcalix[4]arenes were prepared by the method of Casrati et al.[14] Infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer as pressed KBr disks. ^1H and ^{13}C NMR spectra were obtained using Varian FT Unity 300 and Unity+400 spectrometers and were referenced to internal TMS (δ 0). UV−visible spectra were recorded on a Hitachi 150-20 double-beam spectrophotometer. Electrochemical measurements were performed on a Cypress Electrochemical System II, using a 3 mm glassy carbon working electrode and platinum auxiliary and reference electrodes. Cyclic voltammograms were recorded on solutions of the complexes (5−10 mM) in dichloromethane/0.1 M $NBu^n{}_4PF_6$ and employed ferrocene as internal reference. Potentials are reported relative to the saturated calomel electrode (SCE). Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Finnigan MAT model LCQ quadrupole ion trap mass spectrometer. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses. $(Me_2cal)MoOCl_2$ (1). A mixture of $MoOCl_4$ (1.98 g, 7.80 mmol) and 1,3-dimethyl *p-tert*-butylcalix[4]arene (6.01 g, 8.88 mmol) in hexane (30 mL) was stirred for 24−48 h, whereupon the solvent was removed by evaporation in vacuo. The residue was then dissolved in dichloromethane and filtered through a short column of silica. Column chromatography of the partially evaporated filtrate on silica using 3/2 CH_2Cl_2/petroleum spirits as eluent yielded one major purple band, which was collected and reduced to give purple crystals of **1**. Yield: 6.02 g, 90%.

Anal. Calcd for $C_{46}H_{58}Cl_2MoO_5$: C, 64.41; H, 6.82; Cl, 8.27. Found: C, 64.87; H, 6.87; Cl, 8.24%. IR (KBr): 2962 s, 2870 m, 1588 s, 1481 s, 1460 m, 1428 m, 1363 m, 1284 w, 1262 w, 1203 s, 1108 w, 1105 m, 1023 m, ν(Mo═O) 986 s, 937 w, 874 m, 858 s, 809 m, 732 m, 714 w, 688 w, 554 m, 447 w cm^{-1}. ^1H NMR ($CDCl_3$): 0.60 (s, 9H, ^{t}Bu), 1.13 (s, 9H, ^{t}Bu), 1.38 (s, 18H, 2 ^{t}Bu), 3.22 (d, 2H, *J* 13.5 Hz, CH_2), 3.45 (d, 2H, *J* 14.7 Hz, CH_2), 3.66 (s, 3H, OCH_3), 4.07 (s, 3H, OCH_3), 4.68 (d, 2H, *J* 13.5 Hz, CH_2), 5.08 (d, 2H, *J* 14.7 Hz, CH_2), 6.03 (s, 2H, 2 Ar−H), 6.84 (s, 2H, 2 Ar−H), 7.10 (d, 2H, *J* 2.4 Hz, 2 Ar−H), 7.20 (d, 2H, *J* 2.4 Hz, 2 Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.1, 31.4 ($C(CH_3)_3$), 32.1, 34.1 (CH_2), 33.5, 34.4, 34.8 ($C(CH_3)_3$), 61.8, 66.8 (OCH_3), 124.5, 125.3, 125.8, 127.4, 132.5, 134.2, 134.7, 139.1, 144.9, 148.7, 151.0, 153.3, 156.6, 165.6 (Ar−*C*). UV−visible (CH_2Cl_2): 833 (9800), 495 (6800), 354 nm (ϵ 5000 M^{-1} cm^{-1}). Electrochemistry: $E_{1/2}$ 0.112 V, ΔE_{pp} 73 mV, I_{pa}/I_{pc} 0.99.

$(Et_2cal)MoOCl_2$ (2). A mixture of $MoOCl_4$ (0.25 g, 0.99 mmol) and 1,3-diethyl *p-tert*-butylcalix[4]arene (0.71 g, 1.02 mmol) in hexane (10 mL) was stirred for 4 h, whereupon the solvent was removed by evaporation in vacuo. The residue was treated as described above for $(Me_2cal)MoOCl_2$. Following chromatography, dark red crystals of **2** were precipitated from dichloromethane by trituration with hexane. The crystals were isolated by filtration, washed with hexane, and vacuum-dried. Yield: 0.45 g, 51%.

Anal. Calcd for $C_{48}H_{62}Cl_2MoO_5$: C, 65.08; H, 7.05; Cl, 8.00. Found: C, 65.24; H, 7.11; Cl, 7.95%. IR (KBr): 2963 s, 2864 m, 1586 s, 1479 s, 1463 m, 1444 m, 1430 m, 1387 m, 1364 m, 1282 w, 1232 m, 1201 s, 1174 m, 1105 m, 1096 m, 1038 w, 1011 m, ν(Mo═O) 988 s, 937 w, 874 m, 858 s, 852 s, 825 w, 790 w, 768 w, 705 w, 633 m, 553 m, 450 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.62 (s, 9H, ^{t}Bu), 1.12 (s, 9H, ^{t}Bu), 1.22 (overlapping t, 6H, *J* 6.9 Hz, OCH_2CH_3), 1.38 (s, 18H, 2 ^{t}Bu), 3.18 (d, 2H, *J* 13.5 Hz, CH_2), 3.41 (d, 2H, *J* 14.7 Hz, CH_2), 3.79 (q, 2H, *J* 6.9 Hz, OCH_2), 4.66 (q, 2H, *J* 6.9 Hz, OCH_2), 4.78 (d, 2H, *J* 13.5 Hz, CH_2), 5.12 (d, 2H, *J* 14.7 Hz, CH_2), 6.03 (s, 2H, 2 Ar−H), 6.82 (s, 2H, 2 Ar−H), 7.09 (d, 2H, *J* 2.1 Hz, 2 Ar−H), 7.17 (d, 2H, *J* 2.1 Hz, 2 Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7, 15.4 (OCH_2CH_3), 31.1, 31.2, 31.4 ($C(CH_3)_3$), 32.3, 34.5 (CH_2), 33.5, 34.3, 34.7 ($C(CH_3)_3$), 70.2, 75.7 (OCH_2CH_3), 124.3, 125.0, 125.5, 127.3, 133.8, 134.7, 135.3, 139.1, 144.7, 148.3, 149.8, 150.9, 155.1, 165.6 (Ar−*C*). UV−visible (CH_2Cl_2): 830 (11000), 495 (8000), 355 nm (ϵ 5800 M^{-1} cm^{-1}). Electrochemistry: $E_{1/2}$ 0.104 V, ΔE_{pp} 84 mV, I_{pa}/I_{pc} 0.99.

$(Me_2cal)WOCl_2$ (3). The compound was prepared by the method described for **1** using $WOCl_4$ (0.72 g, 2.11 mmol) and 1,3-dimethyl *p-tert*-butylcalix[4]arene (1.51 g, 2.21 mmol) in hexane (30 mL). The yield of purple product was 130 mg, 7%.

Anal. Calcd for $C_{46}H_{58}Cl_2O_5W$: C, 58.42; H, 6.18; Cl, 7.50. Found: C, 59.65; H, 6.48; Cl, 7.05%. IR (KBr): 2962 s, 2870 m, 1596 m, 1481 s, 1461 m, 1394 w, 1364 m, 1301 w, 1243 m, 1195 s, 1120 m, ν(W═O) 1006 m, 986 m, 941 m, 876 s, 865 s, 811 w, 794 m, 734 m, 714 w, 557 m, 456 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.59 (s, 9H, ^{t}Bu), 1.12 (s, 9H, ^{t}Bu), 1.39 (s, 18H, 2 ^{t}Bu), 3.29 (d, 2H, *J* 13.5 Hz, CH_2), 3.49 (d, 2H, *J* 14.7 Hz, CH_2), 3.67 (s, 3H, OCH_3), 4.16 (s, 3H, OCH_3), 4.57 (d, 2H, *J* 13.5 Hz, CH_2), 4.99 (d, 2H, *J* 14.7 Hz, CH_2), 5.99 (s, 2H, 2 Ar−H), 6.86 (s, 2H, 2 Ar−H), 7.15 (unresolved d, 2H, 2 Ar−H), 7.25 (unresolved d, 2H, 2 Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.1, 31.1, 31.6 ($C(CH_3)_3$), 31.5, 33.8 (CH_2), 31.6, 33.4, 34.4 ($C(CH_3)_3$), 61.8, 67.6 (OCH_3), 124.2, 125.0, 125.9, 127.2, 131.8, 132.5, 132.8, 137.2, 144.6, 149.0, 149.4, 152.2, 156.7, 159.7 (Ar−*C*). UV−visible (CH_2Cl_2): 540 (1650), 405 nm (ϵ 1300 M^{-1} cm^{-1}). Electrochemistry: $E_{1/2}$ −0.484 V, ΔE_{pp} 86 mV, I_{pa}/I_{pc} 0.94.

$(Et_2cal)WOCl_2$ (4). The compound was prepared by the method described for **2** using $WOCl_4$ (0.36 g, 1.05 mmol) and 1,3-diethyl *p-tert*-butylcalix[4]arene (0.95, 1.34 mmol) in hexane (10 mL). The yield of purple product was 275 mg, 27%.

Anal. Calcd for $C_{48}H_{62}Cl_2O_5W$: C, 59.20; H, 6.42; Cl, 7.28. Found: C, 59.46; H, 6.50; Cl, 7.35%). IR (KBr): 2963 s, 2906 m, 2868 m, 1595 m, 1480 m, 1459 m, 1416 w, 1392 w, 1363 m, 1301 w, 1287 w, 1241 m, 1192 s, 1114 m, 1097 w, 1041 w, 1010 m, ν(W═O) 999 s, 940 m, 876 s, 864 s, 855 m, 794 m, 746 w, 704 w, 554 m, 457 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.57 (s, 9H, ^{t}Bu), 1.12 (s, 9H, ^{t}Bu), 1.22 (overlapping t, 6H, *J* 6.9 Hz, OCH_2CH_3), 1.38 (s, 18H, 2 ^{t}Bu), 3.24 (d, 2H, *J* 13.5 Hz, CH_2), 3.44 (d, 2H, *J* 14.7 Hz, CH_2), 3.82 (q, 2H, *J* 6.9 Hz, OCH_2), 4.75 (q, 2H, *J* 6.9 Hz, OCH_2), 4.66 (d, 2H, *J* 13.5 Hz, CH_2), 5.03 (d, 2H, *J* 14.7 Hz, CH_2), 5.99 (s, 2H, 2 Ar−H), 6.84 (s, 2H, 2 Ar−H), 7.13 (d, 2H, *J* 2.1 Hz, 2 Ar−H), 7.23 (d, 2H, *J* 2.1 Hz, 2 Ar−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.6, 15.4, (OCH_2CH_3), 31.0,

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Table 1. Crystallographic Data

	2·$CHCl_3$	3·$CHCl_3$
formula	$C_{49}H_{63}Cl_5MoO_5$	$C_{47}H_{59}Cl_5O_5W$
fw	1005.18	1065.04
temp, K	293(2)	293(2)
wavelength, Å	0.71069	0.71069
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	13.230(3)	10.242(2)
b, Å	14.950(3)	15.710(2)
c, Å	15.799(4)	16.236(5)
α, deg	95.87(2)	88.64(3)
β, deg	112.00(2)	79.91(3)
γ, deg	112.090(10)	78.67(2)
V, Å^3	2574.9(10)	2521.7(10)
Z	2	2
D_{calc}, g cm^{-3}	1.296	1.403
μ(Mo Kα), mm^{-1}	0.556	2.596
F(000)	1048	1080
GOF on F^2	1.012	1.067
R indices $[I > 2\sigma(I)]^a$	*R* 0.0478, R_w 0.1214	*R* 0.0301, R_w 0.0862
R indices (all data)^a	*R* 0.0651, R_w 0.1327	*R* 0.0349, R_w 0.0894

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2)]^{1/2}$.

31.1, 31.6 ($C(CH_3)_3$), 31.9, 34.2 (CH_2), 33.4, 34.3, 34.3 (CH_2 and $C(CH_3)_3$), 70.0, 77.2 (OCH_2CH_3), 124.0, 124.7, 125.6, 127.2, 133.0, 133.2, 133.4, 137.1, 144.4, 148.6, 148.9, 149.0, 155.3, 159.7 (Ar−*C*). UV−visible (CH_2Cl_2): 538 (2400), 406 nm (ϵ 2000 M^{-1} cm^{-1}). Electrochemistry: $E_{1/2}$ −0.500 V, ΔE_{pp} 82 mV, I_{pa}/I_{pc} 0.88.

Preparation of Reduced Species. Reduced M(V) species were produced in situ by treatment of solutions of the M(VI) complexes with either $NBu^n{}_4SH$ or cobaltocene. Reaction of **1** and **2** with an excess of reducing agent in dry toluene led to the formation of orange, EPR-active Mo(V) species, [**1**]$^-$ and [**2**]$^-$, with isotropic $\langle g\rangle$ and $\langle A_{Mo}\rangle$ values of 1.9239 (48.3 × 10^{-4} cm^{-1}) and 1.9229 (47.4 × 10^{-4} cm^{-1}), respectively. Frozen-glass EPR data were as follows: for [**1**]$^-$, g_1 1.9407, g_2 1.9266, g_3 1.9063; for [**2**]$^-$, g_1 1.9421, g_2 1.9275, g_3 1.9069. A_i values could not be unambiguously determined by inspection. ESI-MS experiments on the samples exhibited peak clusters at *m/z* 858 and 886 for [**1**]$^-$ and [**2**]$^-$, respectively. Addition of cobaltocene to a dry toluene solution containing either **3** or **4** resulted in formation of red/orange, EPR-active W(V) species, [**3**]$^-$ and [**4**]$^-$, with isotropic $\langle g\rangle$ values of 1.7273 and 1.7226, respectively. Spectra of the W complexes were observed only at low temperatures (<250 K), and ^{183}W hyperfine splitting was observed but not clearly resolved. Frozen, anisotropic data were as follows: for [**3**]$^-$, g_1 1.7641, g_2 1.7313, g_3 1.6723; for [**4**]$^-$, g_1 1.7706, g_2 1.7310, g_3 1.6663.

X-ray Crystallography. Crystals of **2**·$CHCl_3$ and **3**·$CHCl_3$ were grown by slow evaporation of chloroform solutions of the compounds. Crystallographic data for both compounds are collected in Table 1. Unit cell parameters and crystal orientations were obtained by a least-squares procedure from the angular settings of 25 reflections. Crystallographic data were collected on an Enraf Nonius CAD4f diffractometer using the ω:2θ scan method. Reflections were measured over the range 4° ≤ 2θ ≤ 50° at an operating temperature of 293(2) K using Mo Kα radiation with a wavelength of 0.71069 Å. Intensity statistics were consistent with the triclinic space group $P\bar{1}$ for both compounds. For **2**·$CHCl_3$, a total of 9132 reflections were measured, of which 8703 were unique ($R_{int} = 0.0151$) and 6943 were considered observed [$I \geq 2\sigma(I)$]. For **3**·$CHCl_3$, a total of 9203 reflections were measured, of which 8864 were unique ($R_{int} = 0.0223$) and 8078 had $I \geq 2\sigma(I)$. The structures were solved by direct methods (SHELXS-86[15]) and refined using full-matrix least-squares on F^2 (SHELXL-97[16]). The *tert*-butyl groups and the ethyl group attached to O(3) of **2** were disordered, and, where possible, disordered atoms were refined with split occupancies. Three of the *tert*-butyl groups of **3** were disordered and treated similarly. Hydrogen atoms were included in idealized positions with the exception of the disordered *tert*-butyl carbons, whereon they were not included. Absorption corrections were performed on **3** using analytical methods (maximum, mininum transmission 0.56, 0.41).[17] A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$, was adopted for both structures (for **2**, $A = 0.0725$, $B = 2.1545$; for **3**, $A = 0.0607$, $B = 2.0562$). The atomic scattering factors used were those incorporated in the SHELXL-97 program. The largest residual peaks in the final difference Fourier map were 0.556 and 0.862 e·Å^{-3} for **2**·$CHCl_3$ and **3**·$CHCl_3$, respectively. The molecular diagrams in Figure 1 were generated using the program ZORTEP.[18] Selected bond lengths and angles for both compounds are given in Table 2.

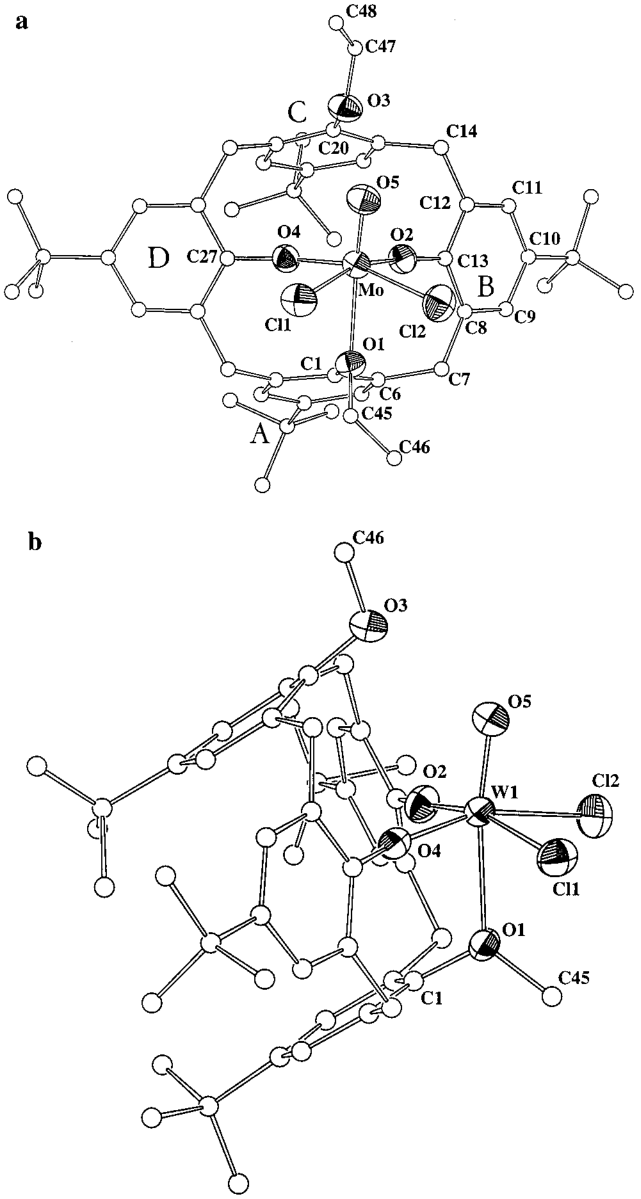

Figure 1. (a) View along the bisector of the O(2)−Mo−O(4) angle of **2** showing the octahedral coordination sphere. (b) View showing the tridentate, “collapsed” structure of the calixarene in **3** and the roughly parallel relationship of the phenyl rings bonded to O(1) (A) and O(3) (C). Anisotropic thermal ellipsoids are shown at the 30% probability level, but carbon atoms, numbered according to the scheme employed by Giannini et al.,[19] are represented as spheres of arbitrary size. Hydrogen atoms have been omitted for clarity.

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

	2	**3**
M−O(5)	1.650(3)	1.673(3)
M−O(1)	2.371(2)	2.339(3)
M−O(2)	1.865(2)	1.855(3)
M−O(3)	3.702(2)	3.739(3)
M−O(4)	1.877(2)	1.855(3)
M−Cl(1)	2.3927(13)	2.3780(14)
M−Cl(2)	2.3819(12)	2.3646(12)
O(1)−M−O(2)	83.76(10)	84.60(12)
O(1)−M−O(4)	83.76(10)	81.34(11)
O(1)−M−O(5)	169.91(12)	170.47(12)
O(1)−M−Cl(1)	80.29(7)	79.39(8)
O(1)−M−Cl(2)	79.03(7)	79.84(8)
O(2)−M−O(4)	94.38(11)	93.77(13)
O(2)−M−O(5)	102.55(13)	103.30(14)
O(2)−M−Cl(1)	163.93(8)	163.87(9)
O(2)−M−Cl(2)	88.07(8)	88.65(10)
O(4)−M−O(5)	103.38(13)	103.17(13)
O(4)−M−Cl(1)	85.80(8)	85.78(9)
O(4)−M−Cl(2)	162.25(8)	160.71(9)
O(5)−M−Cl(1)	93.00(11)	92.47(11)
O(5)−M−Cl(2)	93.20(11)	94.86(11)
Cl(1)−M−Cl(2)	87.05(5)	86.64(5)
M−O(2)−C(13)	168.9(2)	167.0(3)
M−O(1)−C(1)	115.52(18)	117.5(2)
M−O(4)−C(27)	160.5(2)	159.7(3)

[a] For **2**, M = Mo; for **3**, M = W.

Results and Discussion

Complexes **1**−**4** were formed in the reactions of $MOCl_4$ and 1,3-dialkyl *p*-*tert*-butylcalix[4]arenes in hexane at room temperature (eq 1). The HCl gas evolved was swept from the reaction mixtures by a flow of dinitrogen and produced a positive test for chloride when bubbled through silver nitrate solution.

$$MOCl_4 + R_2calH_2 \rightarrow (R_2cal)MOCl_2 + 2HCl \qquad (1)$$

Complexes **1** and **2** were isolated in good yields, but the yields of **3** and **4** were reduced by the formation of unidentified byproducts. The complexes were conveniently purified by column chromatography and are indefinitely stable as solids. They are highly soluble, and toluene, benzene, $CHCl_3$, and CH_2Cl_2 solutions are stable for days. Solutions of **1** and **2** in coordinating solvents such as methanol and acetonitrile rapidly decompose to reduced (blue) molybdates and *p*-*tert*-butylcalix[4]arene; the W complexes were more stable in these solvents. Reaction of complexes **1** and **2** with water in the presence of silica leads to decomplexation and the formation of R_2calH_2 and reduced molybdates. Reactions with NEt_3 in wet dichloromethane result in decomposition and the formation of free monoalkylated calix[4]arene, as observed by Giannini et al.[19] for $(Me_2cal)ZrCl_2$.

Analytical and spectroscopic data were totally consistent with the proposed formulations. Infrared spectra revealed bands characteristic of the calixarene ligand and a single strong band assignable to a ν(M═O) vibration, at ca. 990 cm^{-1} for **1** and **2** and ca. 1000 cm^{-1} for **3** and **4**. ^1H and ^{13}C NMR spectra were indicative of species with C_s symmetry. In the ^1H NMR spectrum of **1** the *tert*-butyl protons were revealed as a set of three singlets with an integrated ratio of 2:1:1 while two inequivalent methoxy proton resonances were observed at δ 3.66 and 4.07. However, the ^{13}C NMR spectrum of this complex exhibited two singlets of equal intensity for the methyl carbon atoms of the *tert*-butyl groups. Heteronuclear NMR studies revealed that the 1:1 proton signals at δ 0.60 and 1.13 both correlate with the ^{13}C resonance at δ 31.14. Thus, the simple appearance of the ^{13}C NMR spectrum of the complex can be attributed to coincidental overlap of two ^{13}C resonances. The ^{13}C NMR spectrum of **2**−**4** exhibited the expected 2:1:1 pattern for the methyl resonances of the *tert*-butyl groups. The ^1H NMR spectra of these complexes exhibited resonances due to inequivalent alkyl groups and a 2:1:1 pattern for the *tert*-butyl groups under C_s symmetry.

Cyclic voltammograms of **1**−**4** revealed electrochemically reversible, one-electron reduction processes at ca. +0.11 and −0.48 V vs SCE for the Mo and W complexes, respectively. The observed difference in the M(VI)/M(V) potential for the Mo and W complexes is in accord with expectations based on other studies.[20] Chemical reduction of **1** and **2** using $NBu^n{}_4SH$ or $CoCp_2$ in toluene resulted in the formation of orange, air-stable species. No reaction occurred between **3** or **4** and $NBu^n{}_4SH$, but these complexes were reduced by cobaltocene. The reduced species are formulated as monomeric M(V) anions, $[(R_2cal)MOCl_2]^-$, on the basis of EPR studies and ESI-MS results. The solution EPR spectra of [**1**]$^-$ and [**2**]$^-$ consisted of a strong central resonance due to Mo isotopomers with $I = 0$ (75%) flanked by six signals due to ^{95,97}Mo isotopomers ($I = {}^5/_2$, 25%); the isotropic $\langle g \rangle$ (and $\langle A_{Mo} \rangle$) values were 1.9239 (48.3×10^{-4} cm^{-1}) and 1.9229 (47.4×10^{-4} cm^{-1}) for [**1**]$^-$ and [**2**]$^-$, respectively. Rhombic frozen-glass EPR spectra were observed, but the anisotropy in the **g** tensor was small, as might be expected for these pseudoaxial molecules. ESI-MS of the anions generated in situ revealed peak clusters at *m*/*z* 858.1 and 886.1 for [**1**]$^-$ and [**2**]$^-$, respectively. At room temperature, EPR signals are not observed for the W(V) complexes. However, these appear and increase in intensity as the temperature is lowered. At 250 K, a broad signal with an isotropic $\langle g \rangle$ value of ca. 1.72 was observed but ^{183}W hyperfine splitting remained poorly resolved. Frozen-glass EPR spectra were rhombic but with only a small anisotropy.

The structures of the chloroform solvates of **2** and **3** were determined by X-ray crystallography. The six-coordinate, mononuclear complexes exhibit a distorted octahedral coordination geometry, as shown in Figure 1. The central metal is coordinated by a terminal oxo ligand, two chloro ligands, and a tridentate R_2cal^{2-} ligand. The oxo and chloro ligands are mutually cis, and the oxygen donor atoms of the calixarene adopt a *facial* arrangement. Selected bond distances and angles are given in Table 2. In **2**, the Mo−O(5) distance of 1.650(3) Å and the Mo−Cl(1) and Mo−Cl(2) distances (average 2.387 Å) are in accord with expectations for six-coordinate oxo−Mo(VI) complexes.[21] In **3**, the W−O(5) distance of 1.673(3) Å is slightly shorter than terminal W═O distances typical of oxo−W(VI) complexes (1.70 Å[21]). In both complexes, the tridentate calixarene ligand is coordinated to the metal by two deprotonated phenolate oxygen atoms and one alkyloxy oxygen atom. The

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phenolate oxygens, which are trans to the chloro ligands, are characterized by average M−O(2/4) distances of 1.871 Å for **2** and 1.855 Å for **3**. The coordinated alkyloxy group is trans to the oxo ligand, and the M−O(1) distances are 2.371(2) and 2.339(3) Å for **2** and **3**, respectively. The uncoordinated alkyloxy group resides near the terminal oxo ligand, the O(3)···O(5) separations being 2.630(4) Å for **2** and 2.638(3) Å for **3**. Tridentate coordination of a calix[4]arene has been demonstrated for $[Fe(NH_3)(Me_3Sical)]_2 \cdot 3C_6H_{14}$[22] but has also been suggested for $(Mecal)ZrCl(pyridine)_2$.[19]

The phenolic oxygen atoms and the chlorine atoms of both complexes define a plane, with the metals lying 0.30 Å (**2**) or 0.33 Å (**3**) out of this plane toward the oxo ligand. The calixarene ligand adopts a very uncommon structure due to its tridentate binding mode and the steric clash of the M═O and −O(3)R groups (Figure 1b). Three of the *tert*-butylphenyl groups are arranged in a familiar fashion, each being splayed away from the vector bisecting the O(2)−M−O(4) unit to form part of an elliptical bowl, as is typical of calixarenes. In **2**, for example, phenyl ring A (see Figure 1a) is inclined at approximately 30° with respect to this bisector, with an M−O(1)−C(1) angle of 115.52(18)°. Phenyl rings B and D are inclined at approximately 60° with respect to the bisector with Mo−O−C units approaching linearity (160.5(2)° and 168.9(2)°, respectively). Phenyl ring C adopts an unusual conformation, being pivoted through ca. 60° from its nominal (bowl or calix) position to lie roughly parallel to phenyl ring A; in **2** the two rings are related by a separation of ca. 5.1 Å and a dihedral angle of only 5.2°. The *tert*-butyl group on ring C has collapsed into the cavity region of the calixarene to effectively block any approach to the metal from within the calixarene framework. Phenyl rings B and D are splayed away from each other (vide supra) to accommodate the collapsed *tert*-butyl group. This calix[4]arene conformation has been observed in three polynuclear compounds, viz., $[Fe(NH_3)(\mu\text{-}Me_3Sical)]_2 \cdot 3C_6H_{14}$,[22] $Nb_4O_2Cl_8(\mu\text{-cal})_2$,[23] and $[Li_4(\mu\text{-cal})(hmpa)_2]_2$ (hmpa = hexamethylphosphoramide);[24] in all cases, a bridging role by one (or more) of the calixarene oxygen atoms induces the unusual conformation. The calixarene structure observed in **1**−**4** is unique in mononuclear complexes. As is common in structures of *tert*-butylcalixarenes, the *tert*-butyl groups display a degree of positional disorder[4−7,9,10] and there is considerable thermal motion associated with the uncoordinated ethoxy group in **2**. In both **2** and **3**, a chloroform molecule is present in the lattice but is prevented from entering the calixarene framework as a result of the collapsed *tert*-butylphenyl moiety. Overall, the two complexes reveal remarkably uniform structures.

This paper describes the synthesis and characterization of Mo and W complexes with the potential to facilitate progress in oxo−Mo and −W calixarene chemistry and its applications. Chloride exchange reactions and the chemical and catalytic attributes of these and related complexes are currently under investigation.

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Supporting Information Available: Two X-ray crystallographic files in CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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