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Heterobimetallic Bismuth(III)/Molybdenum(VI) and Antimony(III)/Molybdenum(VI) Calix[5]arene Complexes. Progress toward Modeling the SOHIO Catalyst

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The treatment of the monometallic bismuth or antimony complexes $[\mathrm{M}\{{}^{t}\mathbf{BuC5(H)_2}\}]$ (M = Bi, Sb) with 1.5 equiv of $\mathrm{MoO_2(O^tBu)_2}$ in 1,2-dimethoxyethane (DME) produced soluble $\mathrm{Bi^{III}/Mo^{VI}}$ and $\mathrm{Sb^{III}/Mo^{VI}}$ heterometallic calix[5]arene complexes $[\mathrm{Bi_2Mo_4O_{11}}\{{}^{t}\mathbf{BuC5(H)}\}_2]$ **1** and $[\mathrm{Sb_2Mo_4O_{11}}\{{}^{t}\mathbf{BuC5(H)}\}_2]$ **2** in 55 and 45% yields, respectively. In solution the ^{1}H NMR patterns for **1** and **2** are characteristic of a C_s symmetry with three pairs of doublets for the methylene protons and three singlets in a 1:2:2 ratio for the *tert*-butyl groups. Complex **1** crystallizes in the $P\bar{1}$ space group and consists of a dimeric heterometallic Bi/Mo (1:2 ratio) complex featuring an overall $\mathrm{Mo_4Bi_2O_{21}}$ oxo cluster. The remarkable oxo-rich core structure of **1** contains Bi(μ-O)Mo, Mo(μ-O)Mo, Mo═O···Mo, and Bi—O—Bi interactions that resemble aspects of the proposed SOHIO catalyst active site and the crystal structure of the $\mathrm{Bi_2Mo_2O_9}$ oxide phase.

Introduction

The SOHIO process is the predominant methodology for the selective oxidation and ammoxidation of propene to produce acrolein and acrylonitrile, used in large scale in industry.[1,2] Commercial interest in replacing the substrate with propane has increased the need for the improvement of the bismuth molybdate catalyst.[3−7] Although the SOHIO process has been used for more than 4 decades, the mechanistic details of the ammoxidation and oxidation by the multicomponent $n\mathrm{MoO_3/Bi_2O_3}$ catalyst remain controversial.[1,2] The proposal that Bi(μ-O)Mo linkages are the active oxo transfer sites in propene oxidation[8] has provided incentive for the preparation of soluble Bi/Mo model compounds, ideally with pure oxo environments around the metals. However, to date only a few Bi/Mo heterobimetallic complexes are available and none of them has fulfilled the requirements above.

Limberg et al. synthesized and structurally characterized a series of $\mathrm{Mo^{II/IV}/Bi^{III}}$ heterobimetallic complexes bridged by alkoxide groups[9−11] and complexes with covalent $\mathrm{Mo^{VI}{-}O{-}Bi^{III/V}}$ linkages.[12,13] Most of their compounds have good solubility but the metal centers are stabilized by organic ligands such as cyclopentadienyl or allylic anions. The heteropolyanions $[\mathrm{Bi^{III}\{Mo_5O_{13}(OMe)_4(NO)\}_2}]^{3-}$,[14] $[\mathrm{Bi^{III}Mo_6O_{21}(O_2C(CH_2)_2NH_3)_3}]^{3-}$, $[\mathrm{Bi^{III}Mo_6O_{21}\{O_2C(CH_2)_3NH_3\}_3}]^{3-}$, and $[\mathrm{Bi^{III}Mo_6O_{21}\{\text{L-}O_2CCH[(CH_2)_4NH_2]NH_3\}_3}]^{3-}$[15] contain multiple Bi(μ-O)Mo linkages. These anions feature metallic cores in pure oxo environments, but their limited solubility in organic solvents and the unavailability of the bismuth atom (buried inside the oxo cage) are undesirable qualities.

For several years now, we have sought to prepare soluble complexes featuring $\mathrm{Bi^{III}}(\mu\text{-O})\mathrm{Mo^{VI}}$ interactions in pure oxo environments that resemble the proposed SOHIO catalyst active site. We have been interested in calixarene ligands because of their potential to mimic features of heterogeneous catalyst surfaces and their ability to hold several metals simultaneously. In particular, calix[5]arene has proved to be excellent for the insertion of more than one metal in the lower rim.[16] We recently reported the synthesis of monometallic $[\mathrm{M}\{{}^{t}\mathbf{BuC5(H)_2}\}]$ (M = Bi, Sb) complexes,[16] prepared by the metathesis reaction of the $3\mathrm{M'}\cdot{}^{t}\mathbf{BuC5(H)_3}$[17]

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precursors (M′ = Li, Na, K) with MCl_3. The [M{**^{t}BuC5(H)$_2$**}] complexes contain two unreacted OH groups that permit the formation of bimetallic complexes of the type [M_2O{**^{t}BuC5(H)**}],[16] upon treatment with M(O^{t}Bu)$_3$. These bimetallic complexes display M(μ-O)M interactions and pure oxo environments that are key features for our heterometallic model. With this successful background, we decided to treat the [Bi{**^{t}BuC5(H)$_2$**}] and [Sb{**^{t}BuC5(H)$_2$**}] complexes with molybdenum precursors in the hope of obtaining analogous complexes of the type [BiOMo{**^{t}BuC5(H)**}].

Herein we report the synthesis, structure, and full characterization of the first examples of soluble M^{III}/Mo^{VI} (M = Bi, Sb) complexes with both metals surrounded by oxygen environments, utilizing the *p-tert*-butylcalix[5]arene [**^{t}BuC5(H)$_5$**] ligand as an oxygen-rich platform. This work also provides the first rational synthesis of metallocalixarene complexes containing Group 15 and transition metals in the lower rim, aiming to model the SOHIO catalyst.

Experimental Section

General Considerations. All manipulations were carried out in a nitrogen filled glovebox. Complexes [Bi{**^{t}BuC5(H)$_2$**}],[16] [Sb{**^{t}BuC5(H)$_2$**}],[16] and MoO_2(O^{t}Bu)$_2$[18] were obtained by the literature procedures. Tetrahydrofuran was freshly distilled from Na/benzophenone; other anhydrous solvents were purchased from Aldrich and stored over molecular sieves under nitrogen before using. Dimethyl sulfoxide was dried over CaH_2. The melting points were taken in capillary tubes on a Mel-temp apparatus (Laboratory devices, Cambridge, MA) using a 500 °C thermometer. ^{1}H NMR and ^{13}C spectra were recorded on a Varian XL-300 spectrometer at 300 and 75 MHz, respectively. Analytical samples were dried under vacuum for at least 72 h. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. IR and UV/vis spectra were obtained with an Infinity Gold FTIR spectrometer and Agilent 8453 spectrophotometer, respectively. Filtrations used a medium sintered glass filter. X-ray diffraction of complex **1** was performed in a Bruker SMART 1000 CCD detector at 213(2) K using Mo Kα radiation.

Synthesis of Complex [$Bi_2Mo_4O_{11}${^{t}BuC5(H)}$_2$] (1). A solution of MoO_2(O^{t}Bu)$_2$ (0.0103 g, 0.0376 mmol) in dimethoxyethane (DME, 3 mL) and a yellow suspension of [Bi{**^{t}BuC5(H)$_2$**}] (0.0254 g, 0.0250 mmol) in DME (5 mL) were placed together in a solvent bomb. The resulting dark brown suspension was placed in an isotemp bath at 75 °C and allowed to heat for 20 h. Some red crystals were obtained on the bottom and side walls of the flask. The crystals were removed from the mixture by centrifugation (or filtration), washed with DME (2 mL), and dried under vacuum to yield 0.0030 g of [$Bi_2Mo_4O_{11}${**^{t}BuC5(H)**}$_2$] (**1**). The remaining dark solution was centrifuged (or filtered) to remove the small amount of solid remaining, and then dried under vacuum. The dark brown solid was dissolved in diethyl ether (Et_2O, 3 mL) and centrifuged to remove any insoluble material. The final dark solution was allowed to stand for 14 h at room temperature (rt) yielding red single crystals. The supernatant was removed by pipet, and the crystals were washed three times with 2 mL portions of Et_2O to yield 0.0103 g of pure [$Bi_2Mo_4O_{11}${**^{t}BuC5(H)**}$_2$] (**1**). Total yield 55% (0.0133 g, 0.00513 mmol). mp 338−340 °C; ^{1}H NMR (300 MHz, in DMSO-d$_6$): δ 1.00 (s, 18H, C(C*H*$_3$)$_3$), 1.16 (s, 18H, C(C*H*$_3$)$_3$), 1.21 (s, 9H, C(C*H*$_3$)$_3$), 3.03 (d, *J* = 12.9 Hz, 2H, ArC*H*$_2$Ar), 3.05 (d, *J* = 12.3 Hz, 1H, ArC*H*$_2$Ar), 3.15 (d, *J* = 12.9 Hz, 2H, ArC*H*$_2$Ar), 5.12 (two doublets overlapping, 3H, ArC*H*$_2$Ar), 5.37 (d, *J* = 12.9 Hz, 2H, ArC*H*$_2$Ar), 6.99 (s, 2H, Ar*H*), 7.03 (s, 2*H*, Ar*H*), 7.07 (s, 2H, Ar*H*), 7.20 (s, 2H, Ar*H*), 7.26 (s, 2H, Ar*H*), no OH peaks were observed at rt; ^{13}C NMR (DMSO-d$_6$, TMS): δ 25.8, 29.9 (Ar*C*H$_2$Ar), 31.3, 32.2, 32.6 (C(*C*H$_3$)$_3$), 33.8 (ArCH$_2$Ar), 34.0, 34.1, 36.3 (*C*(CH$_3$)$_3$), 124.4, 124.5, 131.5, 132.9, 133.5, 134.2, 134.8, 135.0, 138.1, 140.3, 141.1, 142.5, 152.3, 154.7, 158.0, 162.6 ppm (aromatic carbons). IR (KBr): ν = 3438w (OH), 2959vs, 2910m, 2870m, 1598w, 1574w, 1459vs, 1393w, 1362m, 1290m, 1250s, 1198vs, 1125s, 1079w, 938m, 906m, 870s, 824s, 802m, 771m, 664m; UV/vis (DMSO) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 217 (5.62×10^4), 279 (1.20×10^4), 489 (8.13×10^2). C, H analysis calcd (%) for $C_{110}H_{132}Bi_2Mo_4O_{21}$: C 50.97, H 5.13; Found C 51.18, H 5.36.

Synthesis of Complex [$Sb_2Mo_4O_{11}${^{t}BuC5(H)}$_2$] (2). A solution of MoO_2(O^{t}Bu)$_2$ (0.0103 g, 0.0376 mmol) in DME (2 mL) and a white suspension of [Sb{**^{t}BuC5(H)$_2$**}] (0.0232 g, 0.0250 mmol) in DME (3 mL) were placed together in a solvent bomb. The resulting yellowish suspension was placed in an isotemp bath at 95 °C and allowed to heat for 36 h yielding a light yellow solution and a red solid. The solution was removed by pipet, the red solid was dissolved with tetrahydrofuran (THF, 7 mL), and the THF solution was centrifuged to remove any insoluble material. The red THF solution was dried under vacuum to give the crude product as a red solid. This solid was dissolved with Et_2O (or DME) (3 mL), centrifuged to remove any insoluble material, and then placed in the freezer at −35 °C to yield pure [$Sb_2Mo_4O_{11}${**^{t}BuC5(H)**}$_2$] (**2**) in 45% yield (0.0102 g, 0.00422 mmol) as red needle crystals. mp 242−244 °C; ^{1}H NMR (300 MHz, in DMSO-d$_6$): δ 0.74 (s, 18H, C(C*H*$_3$)$_3$), 1.22 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (s, 9H, C(C*H*$_3$)$_3$), 3.06 (d, *J* = 13.8 Hz, 2H, ArC*H*$_2$Ar), 3.15 (two doublets overlapping, 3H, ArC*H*$_2$Ar), 4.72 (d, *J* = 12.3 Hz, 1H, ArC*H*$_2$Ar), 4.98 (d, *J* = 13.5 Hz, 2H, ArC*H*$_2$Ar), 5.32 (d, *J* = 13.8 Hz, 2H, ArC*H*$_2$Ar), 6.62 (s, 2H, Ar*H*), 6.73 (s, 2*H*, Ar*H*), 7.08 (s, 2H, Ar*H*), 7.22 (s, 2H, Ar*H*), 7.29 (s, 2H, Ar*H*), no OH peaks were observed at rt; No ^{13}C NMR was obtained because of limited solubility in DMSO. IR (KBr): ν = 3306w (OH), 2960vs, 2906m, 2869m, 1602w, 1478vs, 1459vs, 1393w, 1362m, 1293m, 1251m, 1198vs, 1124s, 1045w, 947m, 910m, 890m, 874m, 822m, 800m, 771m, 751m, 675m. UV/vis (DMSO) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 218 (6.31×10^4), 278 (1.15×10^4), 486 (7.34×10^2). C, H analysis calcd (%) for $C_{110}H_{132}Sb_2Mo_4O_{21}$: C 54.65, H 5.50; Found C 54.93, H 5.76.

General X-ray Structure Information. The crystallographic data and some details of the data collection and refinement of complex **1** are given in Table 1. Absorption corrections were applied by SADABS.[19] The X-ray structure of **1** was solved by direct methods and subsequent difference Fourier syntheses and refined by full matrix least-squares methods against F^2 (SHELX 97).[20] Disorder for some *tert*-butyl groups was due to a 2-fold axis and was modeled using partial occupancies (PART instruction)[20] and isotropic displacement parameters. The H atoms in structures were taken in calculated positions. In the crystal structure of complex **1** highly disordered Et_2O molecules were treated with the program SQUEEZE.[21] PLATON/SQUEEZE[21] estimated the solvent-accessible region void to occupy 1912.8 Å^3 and contain 231 electrons. The electron density was modeled as 6 diethyl ether (Et_2O) molecules (3 Et_2O per asymmetric unit) which accounts for 252 electrons. The 3 Et_2O molecules were added to the formula weight of the asymmetric unit. The two hydrogen atoms remaining in the calixarene ligands could not be located on the density map but they were added in the formula weight of the asymmetric unit.

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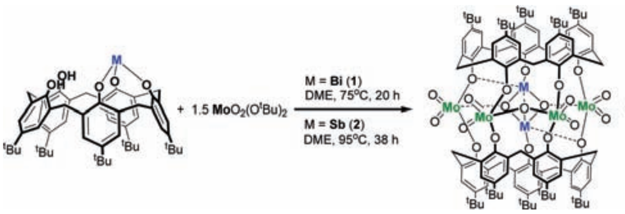
Table 1. Crystal Data and Structure Refinement for Complex $\mathbf{1}\cdot 3C_4H_{10}O$

	$\mathbf{1}\cdot 3C_4H_{10}O$
formula	$C_{122}H_{162}Bi_2Mo_4O_{24}$
Fw	2814.30
cryst syst	triclinic
space group	$P\bar{1}$
T, K	213(2)
a, Å	15.9705(13)
b, Å	18.4194(15)
c, Å	23.3498(18)
α, deg	97.864(2)
β, deg	101.8890(10)
γ, deg	96.2080(10)
V, A^3	6592.0(9)
Z	2
d_{calcd} $g \cdot cm^{-3}$	1.418
μ, mm^{-1}	3.083
refl collected	33803
T_{min}/T_{max}	0.889
N_{measd}	18756
$[R_{int}]$	[0.0615]
R [I > 2sigma(I)]	0.0435
R (all data)	0.0686
R_w [I > 2sigma(I)]	0.0993
R_w (all data)	0.1052
GOF	0.916

The programs ORTEP32[22] and POVRay[23] were used to generate the X-ray structural diagrams pictured in this article.

Results and Discussion

Synthesis and Characterization. The synthesis of complexes $[Bi_2Mo_4O_{11}\{{}^t\mathbf{BuC5(H)}\}_2]$ **1** and $[Sb_2Mo_4O_{11}\{{}^t\mathbf{BuC5(H)}\}_2]$ **2** is depicted in eq 1. Our first attempt to introduce a molybdenum center in the calix[5]arene lower rim involved the treatment of the monometallic $[M\{{}^t\mathbf{BuC5(H)_2}\}]$ (M = Bi, Sb) precursors with 1 equiv of $MoO_2(O^tBu)_2$ in THF or DME at high temperatures. Unfortunately, under these reaction conditions, the resulting dark brown solutions showed complex mixtures of products by ^1H NMR spectroscopy. All our attempts to isolate a single compound failed because of fast decomposition of products to parent calixarene. However, if the ratio of $MoO_2(O^tBu)_2$ was increased to 1.5 equiv, complexes **1** and **2** were readily obtained as red solids in 55 and 45% yields, respectively (eq 1, each calixarene ring contains an OH group (not located)).



(1)

The high solubility of complexes **1** and **2** in $CHCl_3$, THF, and DMSO, and stability in the solid state (up to two months under inert conditions), facilitated their solution and solid state characterization. In solution the ^1H NMR patterns for **1** and **2** are characteristic of a C_s symmetry (Figure 1). There are three pairs of doublets for the methylene protons (geminal coupling due to nonequivalent methylene hydrogens), three singlets in a 1:2:2 ratio for the *tert*-butyl groups, and no OH groups were observed at room temperature.

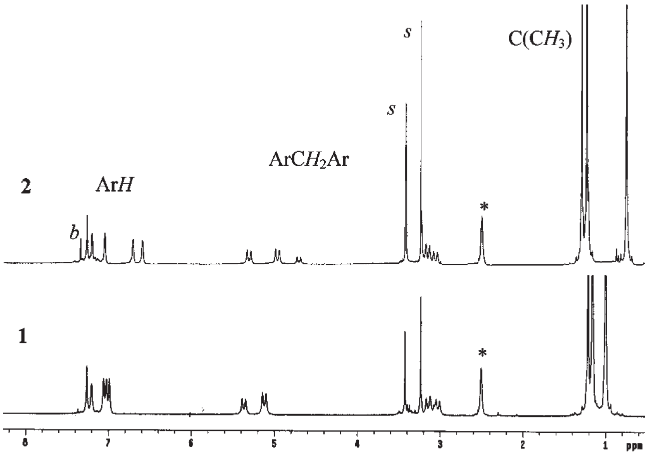


Figure 1. ^1H NMR spectrum of complexes **1** and **2** in *DMSO-d_6. Crystals obtained from DME (*s*). *b* = residual benzene.

The IR spectra of **1** and **2** (see Supporting Information, Figures S3 and S6) show the intense two-band pattern characteristic of the stretching vibrations of the MoO_2^{2+} group in the range of 822−870 cm^{-1}. There are several strong signals in the region of 3000−2800 cm^{-1} because of the ν(C−H) of the *tert*-butyl and methylene groups. A broad band around 3400 cm^{-1} suggests the presence of calixarene OH groups, consistent with our analogously prepared $[M_2O\{{}^t\mathbf{BuC5(H)}\}]$ (M = Bi, Sb) complexes that also contained an unreacted OH group.[16]

We obtained single crystals of complex **1** from a concentrated Et_2O solution at room temperature and single crystals of **2** from an Et_2O solution at −35 °C (poor quality). The crystal structure of complex **1** is depicted in Figures 2 and 3, and selected bond distances and angles are shown in Table 2. Complex **1** (Figure 2) crystallizes in the $P\bar{1}$ space group and consists of a dimeric heterometallic Bi/Mo unit (1:2 ratio). Complex **1** represents the first example of a calix[5]arene containing one heavy Group 15 element and two transition metals in the lower rim and one of the very rare examples of rationally designed bimetallocalixarenes.[24] The calixarene ligands adopt a distorted flattened-cone conformation where one of the rings tilts and its *tert*-butyl group blocks the cavity (Figure 2a).

The unexpected 1:2 Bi/Mo ratio observed in the core structure of **1** could explain why the reaction of $[M\{{}^t\mathbf{BuC5(H)_2}\}]$ and 1 equiv of $MoO_2(O^tBu)_2$ was unsuccessful. Attempts to increase the yield of the products by using two or more equivalents of $Mo(O^tBu)_2$ failed, producing intractable mixtures in all cases.

The overall $Mo_4Bi_2O_{21}$ core in complex **1** (Figure 3) contains two pentacoordinated Bi^{III} centers with primary bonds to one aryloxide [Bi(1)−O(2), 2.158(5) Å] and two bridging oxygens [Bi(1)−O(11) 2.189(5) and Bi(1)−O(12) 2.166(5) Å] and secondary bonds to one aryloxide and one μ_4-oxygen [Bi(1)−O(1) 2.407(5) and Bi(1)−O(19) 2.852(6) Å].[25]

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[25] Several mechanisms have been proposed for bismuth oxo formation in cluster systems, but in this case residual water is the most plausible source of the oxo groups, as previously observed in our $[M_2O\{{}^t\mathbf{BuC5(H)}\}]$ complexes (M = Bi, Sb).

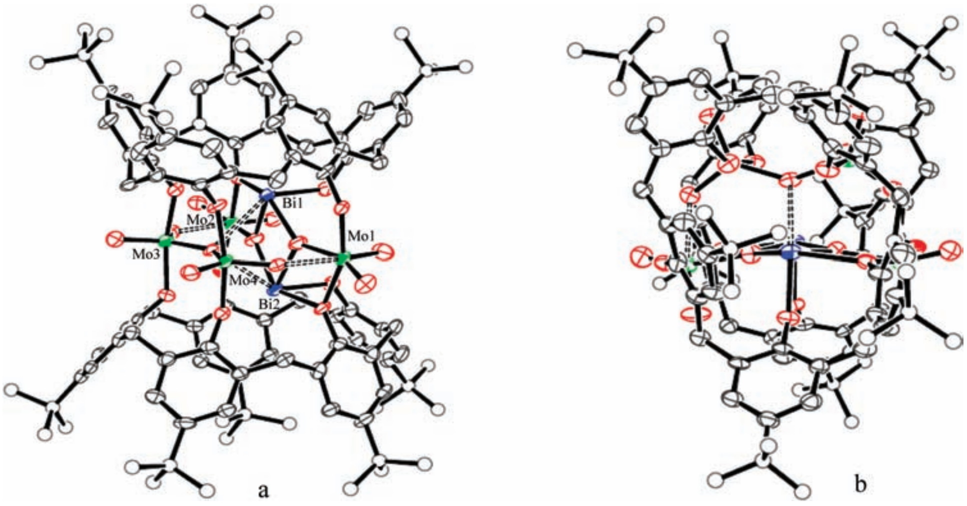

Figure 2. Crystal structure of complex **1**: (a) side view, (b) top view. Thermal ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity.

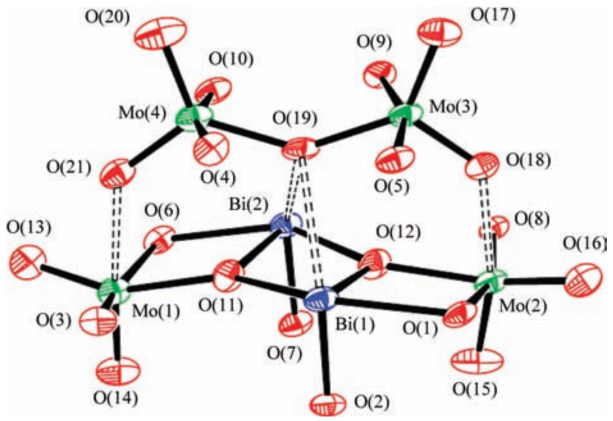

Figure 3. ORTEP drawing of the core structure of complex **1**. Thermal ellipsoids shown at 50% probability.

The Bi(1) and Bi(2) centers are covalently linked through O(11) and O(12) to form a central $Bi_2(\mu\text{-}O)_2$ four-membered ring similar to those found in bismuth calixarene complexes.[16,26−28] All the Bi-OAr and Bi−Bi bond distances, and O−Bi−O and Bi−O−Bi angles, fall in the normal ranges for Bi^{III} calixarene complexes.[16,26−28]

There are two types of Mo^{VI} centers within the core structure of **1**. The Mo(1) and Mo(2) centers are hexacoordinated with distorted octahedral geometries. Each molybdenum is bonded to two aryloxides, two dioxo groups, one bridging oxygen, and one dioxo group of a vicinal Mo center. The apical positions are defined by the aryloxide groups, and the Mo(1)−O(6) [2.063(5) Å] and Mo(2)−O(1) [2.045(5) Å] bond distances are longer than the Mo(1)−O(3) [1.925(5) Å] and Mo(2)−O(8) [1.904(5) Å] distances because of their bridging interactions with the Bi(2) and Bi(1) atoms, respectively. The Mo(3) and Mo(4) centers, on the other hand, are coordinated to two aryloxides, two dioxo groups, and one bridging oxygen O(19) in a distorted trigonal bipyramidal geometry. The apical positions in Mo(3) and Mo(4) are occupied again by aryloxide groups with ArO−Mo−OAr angles around 160°, close to the expected 180°. The Mo(3) and Mo(4) atoms are covalently linked through O(19)[25] with bond distances of 1.960(5) and 1.947(5) Å, respectively.

Each calixarene ring in complex **1** contains an OH proton that could not be located on the crystal structure density map. Using bond valence sum calculations,[29,30] we found that the Mo−O and Mo═O bonds should have distances of approximately 1.907 and 1.605 Å, respectively. In complex **1**, we observed that the Mo(1)−O(3) [1.925(5) Å] and Mo(2)−O(8) [1.904(5) Å] distances are close to the calculated Mo−O values. However, the Mo(3)−O(5) [1.972(5) Å], Mo(3)−O(9) [1.963(5) Å], Mo(4)−O(10) [1.972(5) Å], and Mo(4)−O(4) [1.958(5) Å] distances are larger than the calculated Mo−O values. These bond distance elongations suggest that the two remaining hydrogen atoms are delocalized between the O(5)−Mo(3)−O(9) and the O(4)−Mo(4)−O(10) bonds.

The dioxo groups in all the Mo^{VI} centers are *cis* to each other, as usually observed in MoO_2^{2+} centers, and have bond distances comparable to those observed in Mo^{VI} calixarene complexes.[31] The Mo(3)═O(18) [1.734(5) Å] and Mo(4)═O(21) [1.730(5) Å] bond distances display slight elongations because of their bridging interactions with Mo(2) and Mo(1), respectively.

A key feature of complex **1** is the formation of several Bi(μ-O)Mo interactions as a result of the Lewis acidity of the bismuth atoms and the proximity of the metal centers provided by the calixarene template. Bi(1) is singly bridged to Mo(1) by O(11), doubly bridged to Mo(2) by O(1) and O(12) and bridged to Mo(3) and Mo(4) by O(19). Likewise, Bi(2) is oxo bridged to Mo(2) by O(12), doubly bridged to Mo(1) by O(6) and O(11), and

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex **1**

	1		
Bi(1)−O(1)	2.407(5)	Bi(2)−O(6)−Mo(1)	106.98(18)
Bi(1)−O(12)	2.166(5)	Bi(1)−O(12)−Mo(2)	115.1(2)
Bi(2)−O(7)	2.151(5)	Mo(4)−O(19)−Mo(3)	142.1(3)
Bi(2)−O(11)	2.155(5)	Bi(2)−O(11)−Bi(1)	104.7(2)
Bi(2)−O(12)	2.230(5)	Bi(2)−O(11)−Mo(1)	114.2(2)
Bi(2)−O(6)	2.417(5)	Bi(2)−O(12)−Bi(1)	102.9(2)
Mo(1)−O(14)	1.691(5)	Bi(1)−O(1)−Mo(2)	107.98(19)
Mo(1)−O(13)	1.697(5)	Mo(3)−O(18)−Mo(2)	131.0(2)
Mo(1)−O(3)	1.925(5)	Mo(4)−O(21)−Mo(1)	132.8(3)
Mo(2)−O(12)	2.109(5)	Mo(2)−O(12)−Bi(2)	141.9(2)
Mo(2)−O(15)	1.677(5)	Mo(1)−O(11)−Bi(1)	141.1(3)
Mo(4)−O(19)	1.947(5)	O(6)−Mo(1)−O(11)	72.78(18)
Mo(3)−O(19)	1.960(5)	O(6)−Bi(2)−O(11)	65.83(16)
Mo(4)−O(21)	1.730(5)	O(1)−Mo(2)−O(12)	72.30(18)
Mo(3)−O(18)	1.734(5)	O(1)−Bi(1)−O(12)	64.57(17)

bridged to Mo(3) and Mo(4) by O(19). In the Bi(1)Bi(2)-Mo(1)Mo(2) ladder the Bi-OMo bond distances range from 2.155(5) to 2.417(5) Å, while Mo-OBi distances range from 2.045(5)−2.140(5) Å. All of these oxo bridging distances lie in the normal ranges found in alkoxide bridged Bi/Mo complexes,[9−11] and they are similar to Bi−OMo distances observed in the crystal structure of the heterogeneous $Bi_2Mo_2O_9$ catalyst.[32] The four-coordinate O(19)[25] weakly bridges Bi(1) and Bi(2) with Mo(2) and Mo(4). The Bi−O bond distances of 2.812(8) and 2.852(6) Å are longer than the Bi···O=Mo interactions observed in the $[Bi\{Mo_5O_{13}(OMe)(NO)_2\}]^{3-}$ anion [2.42(1)−2.519(9) Å],[14] but noticeably shorter than the sum of the van der Waals radii (3.67 Å).

We have pointed out that a trademark “ladder” motif appears in many bismuth oxo complexes.[1,16,26,28] In the core structure of **1**, the Bi(μ-O)Mo interactions between Bi(1), Bi(2), Mo(1), and Mo(2) build up a ladder system that contains a central $Bi_2(\mu\text{-}O)_2$ and two terminal $Bi(\mu\text{-}O)_2Mo$ rings. The three four-membered rings display individual planarity (torsion angles range from 1.71 to 10.47°), and they are coplanar with each other, similar to Uchiyama’s bismuth-oxo ladder complex.[33] The ladder system resembles a fragment of the Graselli’s proposed SOHIO active catalyst site, with alternate $Bi^{III}(\mu\text{-}O)Mo^{VI}$ arrangements, and the Mo^{VI} centers containing two terminal dioxo groups.[34] Likewise, the ladder system contains $Bi(\mu\text{-}O)_2Bi$, and several Mo(μ-O)Bi(μ-O)Mo moieties similar to those found in the crystal structure of $Bi_2Mo_2O_9$ (the best oxidation catalyst among bismuth molybdates).[32] The Bi···Mo distances in the $Bi(\mu\text{-}O)_2Mo$ rings are close to 3.61 Å, and the Bi−O−Mo angles range from 106.98(18) to 115.1(2)°. These angles are comparable to those observed in Limberg’s $Bi(\mu\text{-}OR)_2Mo$ and $Bi(\mu\text{-}OR)_3Mo$ alkoxide bridged complexes [93.88(11)−115.2(3)°].[9−11] No metal-arene π-interactions were observed.

Conclusion

We have synthesized and characterized the first calixarene M(III)/Mo(VI) (M = Bi, Sb) heterometallic complexes $[Bi_2Mo_4O_{11}\{^{t}\mathbf{BuC5(H)}\}_2]$ **1** and $[Sb_2Mo_4O_{11}\{^{t}\mathbf{BuC5(H)}\}_2]$ **2** by the reaction of monometallic $[M\{^{t}\mathbf{BuC5(H)_2}\}]$ (M = Bi, Sb) precursors with $MoO_2(O^tBu)_2$. Complexes **1** and **2** have good solubility in organic solvents such as THF, Et_2O, and DMSO, and display all-oxygen environments around the metal centers. The remarkable oxo-rich core structure of **1** contains Bi(μ-O)Mo, Mo(μ-O)Mo, Mo=O···Mo, and Bi−O−Bi interactions that are promising features for catalytic and mechanistic studies related to the SOHIO process.

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Supporting Information Available: Sample ^1H NMR and IR spectra. Full list of bond distances and angles, and CIF file for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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