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Molybdocalixarene Structure Control via Rim Deprotonation. Synthesis, Characterization, and Crystal Structures of Calix[4]arene Mo(VI) Monooxo Complexes and Calix[4]arene Alkali Metal/Mo(VI) Dioxo Complexes

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We report a series of calix[4]arene Mo(VI) dioxo complexes M_2**RC4**MoO_2 (M = alkali metal, R = H or Bu^t) that were fully characterized by NMR, X-ray, IR, UV/vis, and elemental analysis. Molybdocalix[4]arene structures can be controlled via lower rim deprotonation, groups at para positions of calix[4]arene, and alkali metal counterions. Mono deprotonation at the lower rim leads to calix[4]arene Mo(VI) monooxo complexes **RC4**MoO (R = H, Bu^t, or allyl), and full deprotonation gives rise to calix[4]arene Mo(VI) dioxo complexes. Structural studies indicate that **HC4** Mo(VI) dioxo complexes easily form polymeric structures via cation–π interaction and coordination between different calixarene units. However, **Bu**^{t}C4 Mo(VI) dioxo complexes tend to form dimers or tetramers due to steric hindrance of the *tert*-butyl groups at para positions in calixarene. The structures of the reduced side products **A** and **C** were determined by X-ray diffraction studies. The mechanism of **RC4**MoO formation from the reaction of calixarene monoanions with MoO_2Cl_2 appears to include the addition of a calixarene –OH group across a Mo=O bond.

Introduction

Metallocalixarene chemistry has flourished over the past decade. Floriani et al., as well as many others, have established the utility of calixarenes as ligands for metals throughout the periodic table, leading to novel and interesting reactivity patterns.[1−3]

The most common precursors for metallocalixarenes are either the parent or the fully deprotonated calix[4]arenes and their methyl ethers. Floriani et al. reported the synthesis and characterization of the deprotonated *tert*-butyl-calix[4]arenes, stating that the partially deprotonated versions are unsuitable as metallocalixarene precursors.[4] We, on the other hand, described the synthesis and characterization of a large series of mono- and dianionic calixarene alkali metal salts[5,6] and have already demonstrated their utility as an entry into one metallocalixarene (the first reported antimony calixarene) that was inaccessible using the traditional parent calixarene as precursor.[7] Petrella et al. also productively utilized partially deprotonated calixarenes as precursors for new titanium/alkali metal calixarene complexes.[8] The present report demonstrates the importance of the level of calixarene deprotonation in the synthesis of new oxomolybdenum calixarene complexes.

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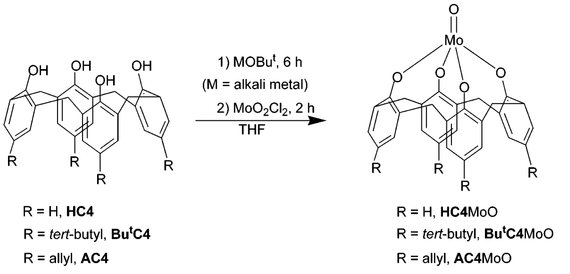
The scarcity of oxomolybdenum(VI) calixarene complexes has been noted, despite the fact that they "are of interest as models of heterogeneous metal-oxide catalyst surfaces, centers capable of supporting organometallic transformations, and as building blocks for supramolecular structures."[9,10] One dioxomolybdenum(VI) dimethylcalixarene has been reported,[11] as well as some monooxomolybdenum(VI) calixarenes,[12−14] one of which is virtually insoluble in organic solvents and therefore intractable.[12]

Herein we will describe the synthesis and characterization of tractable monooxocalix[4]arenes that are otherwise analogous to Floriani et al.'s insoluble material,[12] accessible only using the monodeprotonated calixanion as precursor, as well as a series of alkali metal dioxomolybdocalixarene dianions, potential precursors into heterobimetallic calix[4]arenes,[15] and more highly functionalized molecules. We will discuss the synthetic and structural trends encountered upon changing the nature of the cation, the probable mechanism of formation of the monooxomolybdenum complex, and some oligomeric side products encountered in the formation of these compounds.

Results and Discussion

1. Synthesis. 1.1. Monooxo Complexes. The reactions of calix[4]arene monoanions with MoO_2Cl_2 in THF provide the calix[4]arene Mo monooxo complexes (eq 1). In general, the reaction gives a mixture of Mo monooxo complexes and starting material (calix[4]arenes). Complex **HC4**MoO can be separated (in 38% yield) from the mixture by recrystallization, but the other two complexes are difficult to isolate. The groups at the para position have a strong effect on the solubility of Mo monooxo complexes. Complexes **HC4**MoO and **AC4**MoO are very soluble in organic solvents, but **Bu^{t}C4**MoO is totally insoluble in most organic solvents. These three complexes are relatively air-stable, but slowly release calix[4]arenes over one month in air.

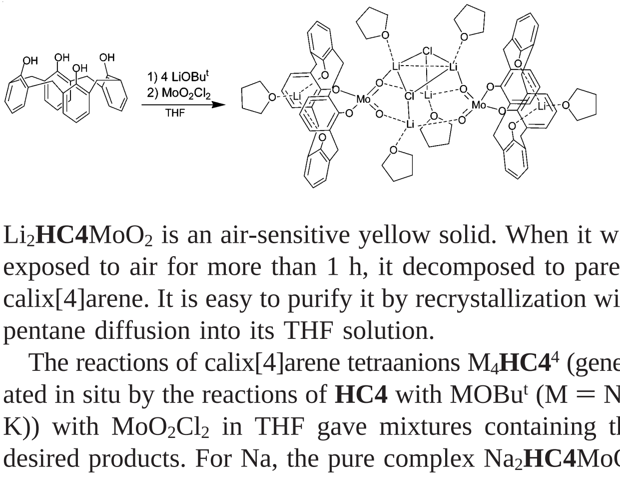


(1)

Complex **Bu^{t}C4**MoO was reported by Floriani et al.[12] as the product of the reaction of $MoOCl_4$ with 2 equiv of **Bu^{t}C4** in hexane. Floriani et al.'s strategy, however, was not successful for making **HC4**MoO. Chisholm et al.[16] later oxidized $(H_2NMe_2)_2$[$Mo_2(\mu,\eta^2,\eta^2$-**Bu^{t}C4**$)_2$] and $Mo_2(\eta^4$-H**Bu^{t}C4**$)_2$ using excess O_2 to give a complex with identical IR data to **Bu^{t}C4**MoO, reported herein.

1.2. Diooxo Complexes. A mixture of calix[4]arene Mo monooxo complex, calix[4]arene Mo dioxo complex, and parent calix[4]arene was obtained upon treatment of calix[4]arene with 2 or 3 equiv of strong bases and MoO_2Cl_2. However, Mo dioxo complex was primarily formed when 4 equiv of strong bases were used. Most Mo dioxo complexes are air-sensitive, but Cs_2**Bu^{t}C4**MoO_2 and M_2**HC4**MoO_2 (M = Rb, Cs) are only moderately air-sensitive (no decomposition was observed after exposure to air for 1 day). The structures of these Mo dioxo complexes depend on the alkali metal cations and the groups at the para positions of calix[4]arene, as will be discussed in a later section.

1.2.1. *p*-H-Calix[4]arene Complexes. Complex Li_2**HC4**MoO_2 was prepared in high purity and good yield (58%) by the reaction of calix[4]arene tetraanion Li_4**HC4**[4] (generated in situ by the reaction of **HC4** with LiOBu^t) with MoO_2Cl_2 in THF at room temperature (eq 2). Complex Li_2**HC4**MoO_2 is an air-sensitive yellow solid. When it was exposed to air for more than 1 h, it decomposed to parent calix[4]arene. It is easy to purify it by recrystallization with pentane diffusion into its THF solution.



(2)

The reactions of calix[4]arene tetraanions M_4**HC4**[4] (generated in situ by the reactions of **HC4** with MOBu^t (M = Na, K)) with MoO_2Cl_2 in THF gave mixtures containing the desired products. For Na, the pure complex Na_2**HC4**MoO_2 was obtained in low yield (about 30%) by repeated recrystallization with THF−CH_3CN at −35 °C. If Na_4**HC4** was generated in situ by the reaction of **HC4** with Na metal, a single product was obtained, Na_2**HC4**MoO_2, which can be purified by washing with cold CH_3CN.

However, it is very difficult to get pure K_2**HC4**MoO_2. If K_4**HC4** was generated in situ by the reaction of **HC4** with KOBu^t and then reacted with MoO_2Cl_2, a very complex mixture was obtained. If K_4**HC4** is generated in situ by the reaction of **HC4** with K and then with MoO_2Cl_2 in THF, a mixture of K_2**HC4**MoO_2 and one side product (**A**) is obtained (eq 3). The mixture was washed with cold CH_3CN to give yellow solid (K_2**HC4**MoO_2) (63% yield) and a dark red solution. The dark red solution was kept in the freezer (−35 °C) for a week, and dark crystals **A** were obtained. The dark red crystals of **A** were characterized by X-ray crystallography

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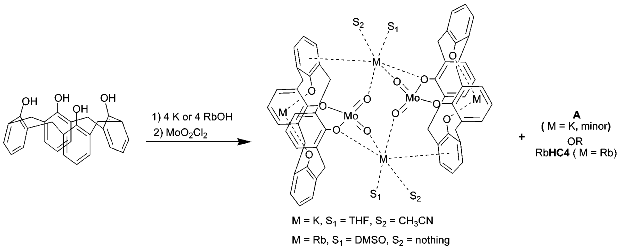
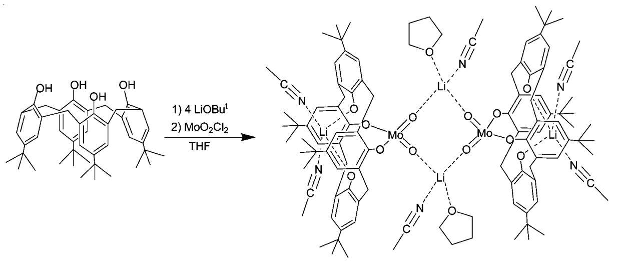


(3)

and ^{1}H NMR spectroscopy (four kinds of aromatic protons and two pairs of doublets for methylene groups). **A** is a calix[4]arene monooxo-μ-oxo molybdenum tetramer (see structural discussion).

The reactions of **HC4** with the heavier alkali metals (M = Rb, Cs) then MoO_2Cl_2 were carried out. A mixture of at least three compounds was obtained, again difficult to separate in each case. In this case, solvation and separation problems can be avoided by use of alkali metal hydroxide as base. The complexes M_2**HC4**MoO_2 (M = Rb, Cs) were made by reacting **HC4** with MOH·H_2O in toluene under reflux with a Dean–Stark condenser and then with MoO_2Cl_2 in a mixture of THF and toluene (eq 3). These reactions gave mixtures of M_2**HC4**MoO_2 and M**HC4** (3:2).[5] Complex Rb_2**HC4**MoO_2 was separated by recrystallization with DMSO–THF–toluene (1:8:8). It is very hard to separate Cs_2**HC4**MoO_2 from Cs**HC4**, though, due to their very similar solubility.

1.2.2. *p-tert*-Butylcalix[4]arene Complexes. It is necessary to stir **Bu^{t}C4** and LiOBu^t for at least 1.5 h before adding MoO_2Cl_2 to get clean Li_2**Bu^{t}C4**MoO_2 in good yield (eq 4).

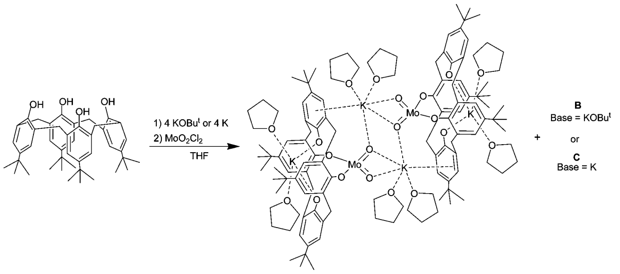


(4)

Complex Li_2**Bu^{t}C4**MoO_2 is somewhat air sensitive; it decomposed to parent calix[4]arene when it was exposed to air for 1 day (monitored by ^{1}H NMR spectroscopy).

Complexes Na_2**Bu^{t}C4**MoO_2 can be made by two methods. One is the reaction of **Bu^{t}C4** with 4 equiv of NaOBu^t then MoO_2Cl_2 in THF; the other is to react **Bu^{t}C4** with 4 equiv of Na then MoO_2Cl_2 in THF. The two methods gave the same results, forming the single product Na_2**Bu^{t}C4**MoO_2.

Complex K_2**Bu^{t}C4**MoO_2 can also be made by the above two methods (eq 5). The two methods gave the same major product (K_2**Bu^{t}C4**MoO_2) but different side products. When KOBu^t was used, the side product was a dark red powder (**B**) that is very soluble in organic solvents. The spectral characteristics of **B** are very similar to those of **A**. When K metal was used, the side product was a brownish yellow powder (**C**) that is also very soluble in organic solvents. Crystals of **C** were obtained from a concentrated hexane solution, and it was characterized by X-ray crystallography.



(5)

We could not make Rb_2**Bu^{t}C4**MoO_2 using RbOH·H_2O as strong base. However, it is possible to make Rb_2**Bu^{t}C4**MoO_2 in high yield (83%) using the reaction of **Bu^{t}C4** with 4 equiv of Rb metal then with MoO_2Cl_2 in THF. Complex Rb_2**Bu^{t}C4**MoO_2 is a light yellow powder with very limited solubility in organic solvents except DMSO.

The cesium complex Cs_2**Bu^{t}C4**MoO_2 was made in high purity and 60% yield by the reaction of **Bu^{t}C4** with CsOH·H_2O in refluxing toluene then with MoO_2Cl_2 in mixed toluene and THF (9:1). It has unexpected solubility behavior. It is very soluble in benzene and toluene, but it has very limited solubility in THF, $CHCl_3$, and DMSO, so it is very easy to purify Cs_2**Bu^{t}C4**MoO_2 by washing with THF. In contrast, the other calix[4]arene Mo dioxo complexes are very soluble in THF, $CHCl_3$, and DMSO. Complex Cs_2**Bu^{t}C4**MoO_2 can also be made by the procedure used for Rb_2**Bu^{t}C4**MoO_2.

2. Spectroscopic Characterization. All calix[4]arene Mo monooxo complexes exhibit a well-defined pair of doublets for methylene groups in their ^{1}H NMR spectra, indicating that they adopt the standard cone conformation. Complexes **HC4**MoO, **AC4**MoO, and **Bu^{t}C4**MoO have very strong Mo═O IR stretches at 956, 965, and 968 cm^{-1}, respectively, that are comparable with that of $MoO(OAr)_4$ (954 cm^{-1})[17]and smaller than that of Me_2**Bu^{t}C4**$MoOCl_2$ (986 cm^{-1}).[13] The color of Mo monooxo complexes depends on the groups at the para position in calixarenes and usually is dark brown or dark blue. Electronic spectra of the monooxo complexes display two intense bands in the 327–328 nm region and the 278–281 nm region in benzene.

All calix[4]arene Mo dioxo complexes exhibit a well-defined pair of doublets for methylene groups and two kinds of arene protons in their ^{1}H NMR spectra, which indicate that the calix[4]arene rings adopt a flattened cone conformation. They have two strong $Mo({=}O)_2$ IR stretches of about 890 and 860 cm^{-1}, which are significantly lower than those of noncalixarene Mo dioxo aryloxides.[17,18]

Electronic spectra of the complexes display two intense bands in different regions in different solvents (Table 1). All Mo dioxo complexes are yellow solids, and they all decompose before melting. The elemental analyses of Mo dioxo complexes are in accordance with calculated values.

The spectral characteristics of side products **A** through **C** are quite different from those of the mono- and dioxo

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Table 1. Comparison of Selected UV/Vis Data of Mo Monooxo and Dioxo Complexes

	solvent	$\lambda_{\max/(\mathrm{nm})}$	$\epsilon/(\mathrm{dm^3 mol^{-1} cm^{-1}})$	color
$MoO_2(OC_6H_3-2,4,6\text{-}t\text{-}Bu_3)_2$[19]	C_6H_6	277, 362	6.3×10^3, 7.8×10^3	orange-yellow
K_2**HC4**MoO_2	THF	276, 318	9.5×10^3, 3.2×10^3	yellow
Rb_2**HC4**MoO_2	DMSO	278, 316	6.7×10^3, 2.3×10^3	yellow
Cs_2**Bu^tC4**MoO_2	C_6H_6	279, 337	1.2×10^4, 4.0×10^3	yellow
HC4 MoO	C_6H_6	273, 342	1.8×10^3, 1.7×10^3	dark brown
$MoO(C_6H_3-2,6\text{-}^iPr_2)_4$[17]	C_6H_6	278, 315, 618	9.9×10^3, 4.4×10^3, 3.7×10^3	dark blue

complexes. Complexes **A** and **B** are quite similar to each other. The ^1H NMR spectrum of **B** shows two pairs of doublets for methylene groups at 5.26, 4.79, 3.46, and 3.40 ppm, four singlets for aromatic protons at 7.26, 7.23, 7.09, and 7.04 ppm, and three kinds of *tert*-butyl groups at 1.45, 1.40, and 0.89 ppm. For side product **C**, in contrast, the ^1H NMR spectrum shows three singlets for aromatic protons at 7.51, 7.10, and 7.07 ppm, three pairs of doublets for methylene groups at 4.60, 4.46, 4.34, 4.05, and 3.30−3.39 ppm, and three kinds of *tert*-butyl groups at 137, 1.15, and 0.94 ppm.

3. Crystal Structures of Mo Oxo Calixarenes. 3.1. HC4MoO. The crystal structure of compound **HC4**MoO·C_6H_6 is shown in Figure 1. The calixarene in **HC4**MoO has a cone conformation with symmetry close to C_{4v}. The coordination around Mo is *pseudo*-octahedral with a single oxo group (Mo−O(5) = 1.678(2) Å) and a weakly bonded water molecule (Mo−O(6) = 2.340(2) Å) in the axial positions. Four almost coplanar oxygen atoms define the equatorial coordination plane. The Mo−O bond distances (1.883(2)−1.915(2) Å) and O═Mo−O angles (88.74(7)−100.24(9)°) in **HC4**MoO are normal; however, the Mo−O−C (aryl) angles are constrained by the rigid structure and symmetry of calix[4]arene (Table 2).[20] The solvent benzene molecule faces the bottom of the calixarene cavity. The structure of **HC4**MoO is very similar to those of the calix[4]arene W(VI) monooxo,[21] calix[4]arene Mo(VI) imido,[22] and Bu^tcalix[4]arene Mo(VI) oxo[12] complexes (cone conformation, similar Mo−O−C (aryl) angles).

3.2. Dioxo Complexes. The structures of M_2**Bu^tC4**MoO_2 (M = Li, K, Cs), M_2**HC4**MoO_2 (M = Li, K, Rb), and Li_2**Br_2C4**MoO_2 were determined by X-ray crystallography.

3.3. Core Structures. The core structures of the dioxo complexes are very similar. As an example, the core structure of *K*$_2$**Bu^tC4**MoO_2 is shown in Figure 2. Each molybdenum atom possesses a distorted octahedral coordination geometry with two phenolate oxygens of flattened aromatic rings and two oxygens of the oxo groups defining an equatorial plane. Each molybdenum is coordinated to two terminal oxo ligands and a tetradentate **Bu^tC4**$^{4-}$ ligand.

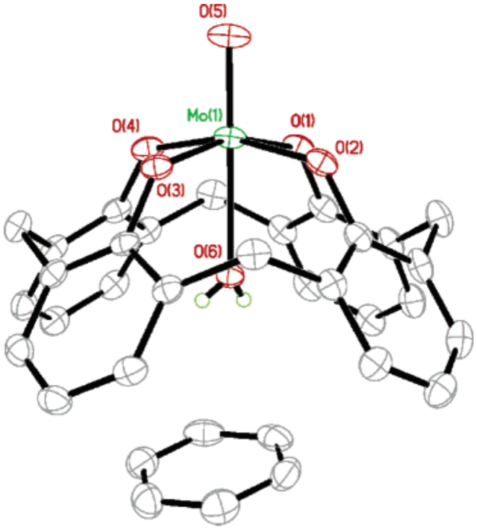

Figure 1. Crystal structure of Mo monooxo complex **HC4**MoO·C_6H_6. Thermal ellipsoids are shown at 50% probability; hydrogen atoms are omitted for clarity.

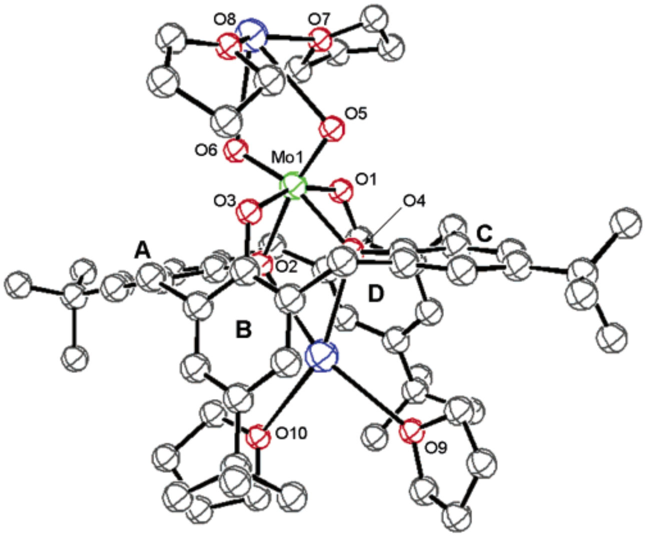

Figure 2. Asymmetric unit of $(K_2$**Bu^tC4**$MoO_2)_2$·8THF. The flattened rings are labeled A and C rings, and the cone rings are assigned as B and D in all X-ray crystal structures of all calixarene molybdenum dioxo complexes.

The Mo═O bond distances (1.718(3)−1.735(3) Å) in these calixarene dioxo molybdenum complexes are on the long side of the normal range (1.674(2)−1.742(4) Å) for dioxo molybdenum complexes $MoO_2(OAr)_2L_2$[9] and slightly longer than those of Me_2**Bu^tC4**MoO_2 (1.690(3), 1.694(3) Å).[11] Our dioxo compounds are bridged dimers, which may contribute to the differences. The O═Mo═O angles (101.31(15)−105.03(10)°) are in the normal range.[9]

The Mo−O(Ar) distances are 1.954(3)−2.105(2) Å, as compared to 1.916(3)-2.559(3) Å in Me_2**Bu^tC4**MoO_2[11] and 1.815(5)-2.568(2) Å in a typical $MoO_2(OAr)_2L_2$ molecule.[9] The Mo−O(Ar) interactions can be viewed as two covalent bonds (X ligands) and two negatively charged O donor atoms

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Table 2. Selected Bond Distances and Bond Angles of Mo Monooxo Complexes

	Mo═O/Å	Mo−O/Å	O═Mo−O/°	Mo−O−C/°	ref
$\mathbf{HC4}\mathrm{MoO}$	1.678(2)	1.8831(16), 1.9109(18), 1.9140(17), 1.9148(17), 2.3396(19) Mo−O (H_2O)	99.48(9), 100.24(9) 87.84(8), 88.74(7) O═Mo−O (H_2O) 179.05(9)	132.80(15), 132.37(14) 134.32(14), 133.09(15)	[a]
$\mathbf{Bu^tC4}\mathrm{MoO}\cdot\mathbf{Bu^tC4}\cdot\mathrm{PhNO_2}$	1.673(16)	1.901(5), Mo−O (H_2O) 2.408(5)	100.2(3) O = M−O (H_2O) 180.0(4)	134.06	12
$\mathrm{MoO(biphenolate)_2}$	1.672(4)	1.881(4), 1.895(3), 1.928(3), 1.937(4)	110.7(2), 97.3(2), 96.7(2)	126.7(3), 119.2(3), 126.2(3), 122.6(3)	23
$\mathrm{MoO(O\text{-}Me_2Ph)_4}$	1.681(4)	1.881(2)	104.75(7)	146.7(2)	17
$\mathbf{Bu^tC4}\mathrm{Me_2MoOCl_2}$	1.650(3)	1.865(2) 1.877(2) 2.371(2) (OCH_3)	83.76(10)	160.5(2), 168.9(2)	13

[a] This work.

Table 3. Selected Structural Parameters for $\mathrm{M_2}\mathbf{RC4}\mathrm{MoO_2}$ (M = alkali metal, R = H or Bu^t)

compound	M−O (phenolate)/Å	normal M−O range/Å [ref]	M−solvent interactions	M−C (phenolate)/Å π−cation interactions	normal M−C range/ Å [ref]
$\mathrm{Li_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$	1.871(6)−1.915(7)	1.923(11)−1.975(11)[5]	3 CH_3CN, 1 THF	−	−
$\mathrm{K_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$	2.600(2)−2.652(3)	2.553(7)−2.861(5) [5,6]	4 THF	3.313(3)−3.445(3)	3.168(6)−3.582(2)[4−6]
$\mathrm{Cs_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$	2.889(3)−2.927(3)	2.875(4)−3.074(17)[5,25,26]	3 THF	3.419(4)−3.671(4)	3.374(3)−3.961(3)[5,25,26]
$\mathrm{Li_2}\mathbf{HC4}\mathrm{MoO_2}$	1.860(11)−1.933(9)	1.923(11)−1.975(11)[27,28]	3 THF	−	−
$\mathrm{K_2}\mathbf{HC4}\mathrm{MoO_2}$	2.691(3)−2.816(3)	2.553(7)−2.861(5) [5,6]	THF, CH_3CN	3.142(4)−3.383(4)	3.168(6)−3.582(2)[5,6]
$\mathrm{Rb_2}\mathbf{HC4}\mathrm{MoO_2}$	2.8700(18)−2.8678(17)	2.734(3)−3.124(2)[5,25]	DMSO	3.271(3)−3.591(3)	2.973(2)−3.731(3)[5,25]
$\mathrm{Li_2}\mathbf{Br_2C4}\mathrm{MoO_2}$	1.842(6)−1.858(6)	1.923(11)−1.975(11)[5]	3 THF	−	−

for the "L" ligands. In $\mathrm{K_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$, there is a set of "short" bonds (2.001(2) and 2.006(2) Å) and a pair of "long" bonds (2.074(2) and 2.105(2) Å), but there is not always a clear distinction. For $\mathrm{Cs_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$, for example, the Mo−O(Ar) distances are 1.990(3), 2.026(3), 2.066(3), and 2.088(3) Å. One asymmetric calixarene was used, with para Br substituents on the 1,3 rings. In this case ($\mathrm{Li_2}\mathbf{Br_2C4}\mathrm{MoO_2}$), the "short" bonds (1.991(2) and 1.995(2) Å) are to the brominated rings (cone) and the "long" bonds (2.100(2) and 2.1068(19) Å) to the unsubstituted rings (flattened).

All calix[4]arene rings exhibit the flattened cone conformation. This conformation is quite typical for octahedral metal centers supported on calixarenes.[1] In general, the flattened rings (rings A and C of Figure 1) correspond to the longer Mo−O(Ar) bonds, consistent with behavior as L ligands. These are trans to the oxo groups, as expected. The Mo−O−C(Ar) angles are in the range 120.59(8)−135.01(7)°, the larger angles corresponding to the flattened rings. A normal range for the X ligands is 137.16(12)−166.5(2)°, while the normal range for the L ligands is 71.76(8)−101.55(10)°.[9]

One alkali metal cation is in each calixarene cavity, coordinated to the oxygens of the flattened calixarene rings, to solvent, and in some cases to the carbons of the inner arene rings through π−cation interactions (Table 3). For example, in $\mathrm{K_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$, the K(2) cations inside the cavities are coordinated to two phenolate oxygens of the flattened aromatic rings and two O atoms of THF molecules (Figure 1). It can be seen in Table 2 that these distances all lie in normal ranges. This type of included cation is very common in calixarene complexes, including the parent calixarene anions[5] and charged metallocalixarenes.[2,24] As we found with calixarene anions, the *p-tert*-butylcalixarenes have solvent "capping" cavity alkali metal ions, while the less sterically crowded *p*-H-calixarenes allow proximity of the other calixarene units to form polymeric structures in the solid state.[5,6]

Table 4. Dihedral Angles of Opposite Flattened Phenyl Rings of Calix[4]arene Mo Dioxo Complexes

	A/C[a]	B/D[a]
$\mathrm{Li_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$	172.14	47.65
$\mathrm{K_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$	172.71	43.60
$\mathrm{Cs_2}\mathbf{Bu^tC4}\mathrm{MoO_2}$	176.13	43.61
$\mathrm{Li_2}\mathbf{HC4}\mathrm{MoO_2}$	170.60	46.27
$\mathrm{K_2}\mathbf{HC4}\mathrm{MoO_2}$	175.90	42.27
$\mathrm{Rb_2}\mathbf{HC4}\mathrm{MoO_2}$	169.99	45.55
$\mathrm{Li_2}\mathbf{Br_2C4}\mathrm{MoO_2}$	173.53	46.00

[a] See Figure 2.

For K, Rb, and Cs, π−cation interactions are evident as well (Table 3). In all cases the cation is sandwiched between two rings and shows strong interaction with the π system. Indeed, the angles between the inner rings appear to vary according to the ability of the cation to interact with the π systems of the arene rings. The dihedral angles between rings B and D (Figure 2) are larger for the lithium complexes (46.00−47.65°), with no π interactions, compared to the rest of the compounds (42.27−45.55°). The dihedral angles between flattened phenyl rings, in contrast, show no discernible trend (Table 4).

3.4. Extended Structures. The most important determinants of extended structure appear to be the extent of alkali metal cation interaction with the π systems of the calixarene rings and steric bulk. This is entirely consistent with the

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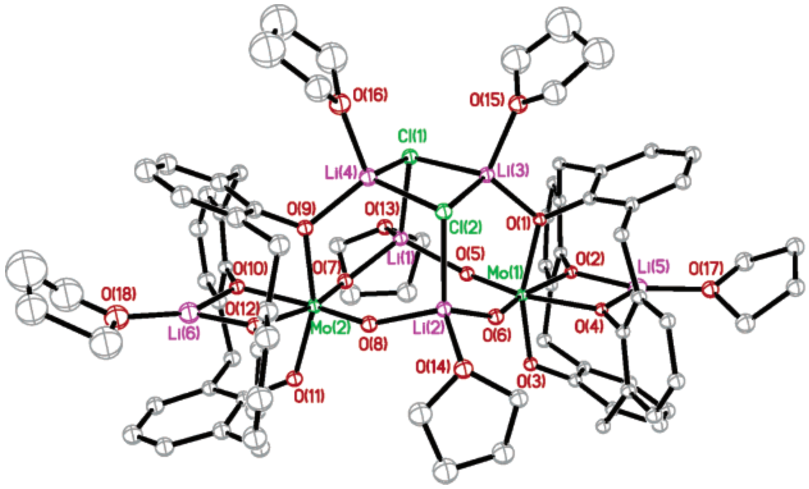

Figure 3. Crystal structure of Mo dioxo complex $(\mathrm{Li_2}\mathbf{HC4}\mathrm{MoO_2})_2\cdot 6\mathrm{THF}\cdot 2\mathrm{LiCl}$. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and noncoordinated solvent molecules are omitted for clarity.

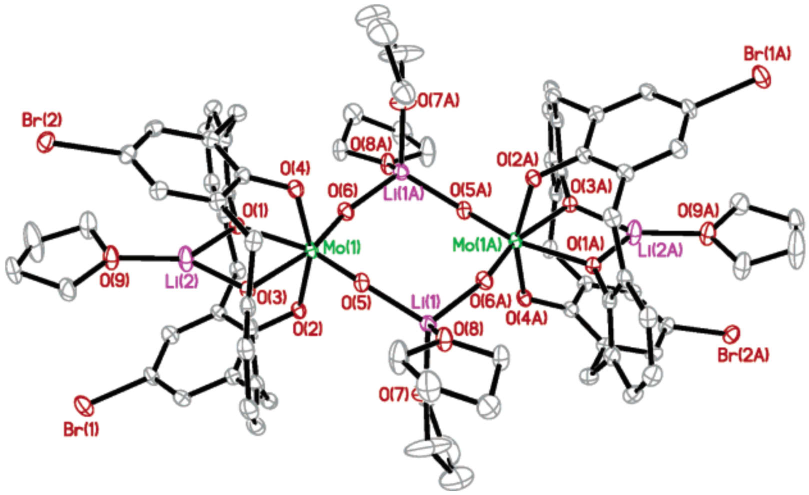

Figure 4. Crystal structure of Mo dioxo complex $(\mathrm{Li_2}\mathbf{Br_2C4}\mathrm{MoO_2})_2\cdot 6\mathrm{THF}\cdot 3\mathrm{CH_3CN}$. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent $\mathrm{CH_3CN}$ molecules are omitted for clarity.

extended structures of the alkali-metalated calixarene anions that we have reported previously.[5,6]

3.4.1. Discrete Dimeric Units. The overall structure of $(\mathrm{Li_2}\mathbf{HC4}\mathrm{MoO_2})_2\cdot 6\mathrm{THF}\cdot 2\mathrm{LiCl}$ can be viewed as a dimer (Figure 3) where the two monomeric dioxo complexes are bridged by two lithium cations and two molecules of LiCl. Additional Li(THF) groups are inside both cavities. The $\mathrm{Li^+}$ cations outside cavities are coordinated to one phenolate oxygen, one O atom from solvate THF, and two Cl atoms. The other two bridged $\mathrm{Li^+}$ cations are coordinated to two O atoms of oxo groups from each unit and one O atom of THF.

The structure of $(\mathrm{Li_2}\mathbf{Br_2C4}\mathrm{MoO_2})_2\cdot 6\mathrm{THF}\cdot 3\mathrm{CH_3CN}$ is shown in Figure 4. It is a centrosymmetrical complex connected by two lithium cations outside the calix[4]arene cavities without bridging lithium chloride as in $(\mathrm{Li_2}\mathbf{HC4}\mathrm{MoO_2})_2\cdot 6\mathrm{THF}\cdot 2\mathrm{LiCl}$. Again Li−THF groups are found in both calixarene cavities. The coordination number of the bridging $\mathrm{Li^+}$ atoms (4) is different from that of $\mathrm{Li^+}$ atoms inside the cavities (3). Each bridging $\mathrm{Li^+}$ is coordinated to two O atoms from oxo groups and two O atoms from THF molecules, and each cavity $\mathrm{Li^+}$ is coordinated to two phenolate oxygen atoms and one O atom from THF.

The structure of $(\mathrm{K_2}\mathbf{Bu^tC4}\mathrm{MoO_2})_2\cdot 12\mathrm{THF}$ is shown in Figure 5. This dimeric structure is somewhat different from that of $(\mathrm{Li_2}\mathbf{Br_2C4}\mathrm{MoO_2})_2\cdot 6\mathrm{THF}$. It is a centrosymmetrical complex connected by two potassium cations outside the calix[4]arene cavities. Each bridging $\mathrm{K^+}$ is coordinated to three O atoms from oxo groups and two O atoms from THF molecules and forms η^6 cation−π arene interactions. The interactions with neighboring calixarene rings force the dimer to skew so that the facing calixarenes no longer overlap completely. The $[\mathrm{Mo(1)O(2)O(4)O(5)O(6)K(1)}]_2$ core is planar.

3.4.2. Polymer of Dimers. Compound $(\mathrm{K_2}\mathbf{HC4}\mathrm{MoO_2})_3\cdot 3\mathrm{THF}\cdot 6\mathrm{CH_3CN}$ has a polymeric structure; in this complex, there are no coordinated THF molecules at the $\mathrm{K^+}$ atoms inside cavities as in $(\mathrm{K_2}\mathbf{Bu^tC4}\mathrm{MoO_2})_2\cdot 12\mathrm{THF}$. Instead, these atoms form additional interactions with the phenolate O atoms and THF molecules from another calix[4]arene (Figure 6). The bridging K(2) cation and its centrosymmetrical equivalent are each bonded to three O atoms of the $\mathbf{HC4}$−$\mathrm{MoO_2}^{2-}$ anions, the O and N atoms of the THF and $\mathrm{NCCH_3}$ groups, and η^6-bonded to the arene ring of the opposite calixarene, forming the main centrosymmetrical structural

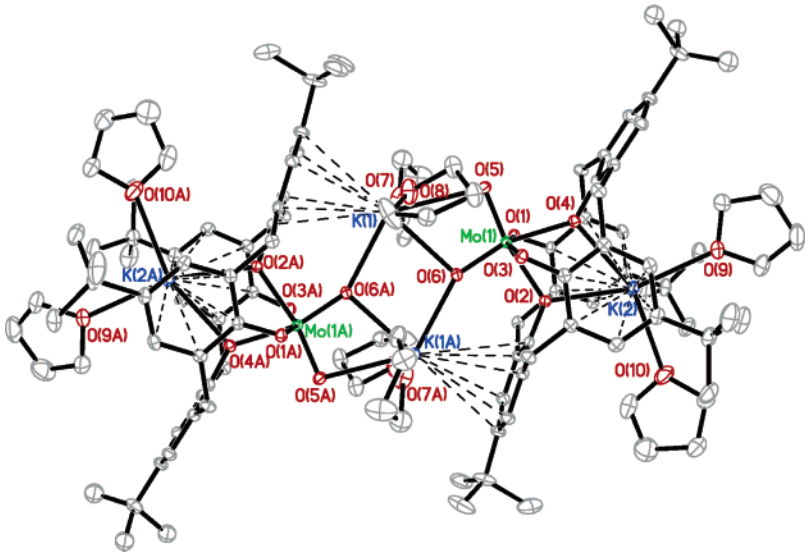

Figure 5. Crystal structure of the centrosymmetrical Mo dioxo complex $(K_2\mathbf{Bu^tC4}MoO_2)_2\cdot 12THF$. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent THF molecules not involved in coordination of the K atoms are omitted for clarity.

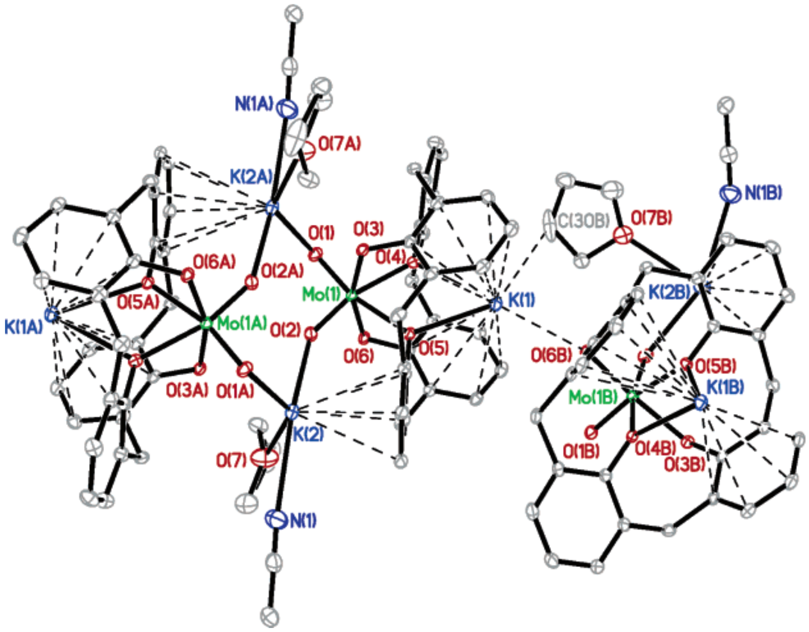

Figure 6. Crystal structure of Mo dioxo complex $(K_2\mathbf{HC4}MoO_2)_3\cdot 3THF\cdot 6CH_3CN$. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent CH_3CN molecules are omitted for clarity.

unit of $K_2\mathbf{HC4}MoO_2$. In this case, the Mo/K/O core is strongly puckered, rather than planar.

Compound $(Rb_2\mathbf{HC4}MoO_2)_4\cdot 4DMSO$ (Figure 7) forms a polymeric structure in the same fashion as $(K_2\mathbf{HC4}MoO_2)_3\cdot 3THF\cdot 6CH_3CN$. It is a centrosymmetrical complex connected by two Rb^+ cations outside the calix[4]arene cavities. Each bridging Rb^+ forms one η^6 cation$-\pi$ arene interaction with the flattened ring of one calixarene, and is coordinated to one O atom from the opposite calixarene phenolate group, two O atoms from oxo groups, and one O atom from a DMSO molecule.

Complex $(Li_2\mathbf{Bu^tC4}MoO_2)_2\cdot 2THF\cdot 6CH_3CN$ (Figure 8) is a centrosymmetrical complex in which two $Li\mathbf{Bu^tC4}MoO_2\cdot 2CH_3CN$ units are connected by two lithium cations outside the calix[4]arene cavities. Each bridging Li^+ is coordinated to two O atoms from oxo groups, one O atom from a THF molecule, and one N atom from an acetonitrile molecule.

The X-ray data indicate that the crystal structure of $(Li_2\mathbf{Bu^tC4}MoO_2)_2\cdot 2THF\cdot 6CH_3CN$ consists of two types of dimeric structural units: the first one with two CH_3CN solvent molecules coordinated to the Li^+ atoms inside cavities via their N atoms (as shown in Figure 8); the second one with only one CH_3CN solvent molecule coordinated to the Li^+ atoms inside cavities. It can be predicted that the latter coordination of the Li^+ atoms inside cavities will be unstable. In this crystal structure, these two types of dimeric units are associated by forming additional interactions between the Li^+ atoms inside cavities of the second dimer type (with one CH_3CN solvent molecule at the Li atom) and Me groups of the CH_3CN solvent molecules in another dimeric units (with

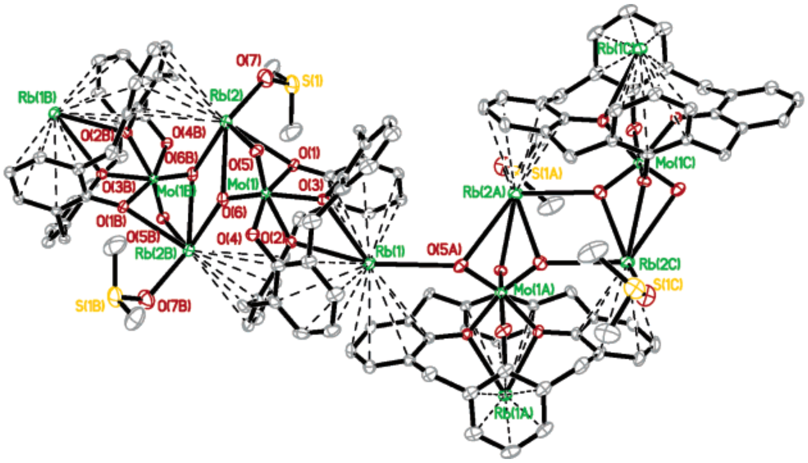

Figure 7. Crystal structure of Mo dioxo complex (Rb$_2$**HC4**MoO$_2$)$_4$·4DMSO. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent molecules are omitted for clarity.

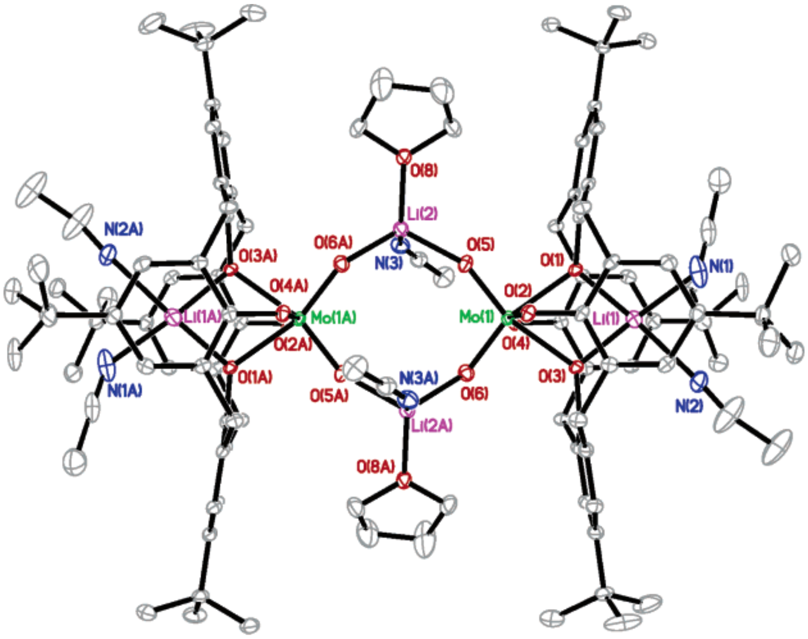

Figure 8. Crystal structure of Mo dioxo complex (Li$_2$**Bu^{t}C4**MoO$_2$)$_2$·2THF·6CH$_3$CN. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent molecules are omitted for clarity.

two CH$_3$CN solvent molecules). Thus, one CH$_3$CN solvent molecule is bridged and coordinated by the N atoms to one Li$^+$ atom and by the Me group to another Li$^+$ atom. As a result, the bridging CH$_3$CN solvent molecules in the crystal structure of (Li$_2$**Bu^{t}C4**MoO$_2$)$_2$·2THF·6CH$_3$CN are disordered around a center of symmetry.

3.4.3. Discrete Tetrameric Units. Complex (Cs$_2$**Bu^{t}C4**MoO$_2$)$_4$·10THF has a tetrameric structure with symmetry $\bar{4}$ formed by four **Bu^{t}C4**MoO$_2$Cs(1)(THF)$_2$ structural units, four Cs(2) cations, and THF solvent. The four Cs(2) cations are joined via μ_2-, μ_3-, and μ_4-bridging oxygen atoms and asymmetric η^6 cation−π arene interactions of the Cs(2) atoms with arene rings of calix[4]arene ligands (Figure 9).

The inorganic core of (Cs$_2$**Bu^{t}C4**MoO$_2$)$_4$·10THF is shown in Figure 10. The Cs(2) atoms are additionally coordinated by solvent THF molecules that are disordered over two positions (in a 1:1 ratio) since there is not enough empty space for coordination of all the Cs(2) atoms at the same time. In complex (Cs$_2$**Bu^{t}C4**MoO$_2$)$_4$·10THF, the Cs(1) atoms are coordinated to two THF solvent molecules, which protect the tetrameric units from forming a polymeric structure.

3.4.4. Side Products A and C. The structure of side product **A** was determined by X-ray crystallography (Figures 11 and 12). In the solid state, **A** is a dimeric Mo monooxo calix[4]arene with Mo−O−Mo bridges.

The calixarene units are similar to those observed in the dioxo complexes; each is in the flattened cone conformation with a K$^+$ cation in the cavity. The cavity K$^+$ cations are capped with two acetonitrile molecules. As in K$_2$**HC4**MoO$_2$, there is significant π−cation interaction inside the cavity; the range of K−C bond distances is 3.12(1)−3.42(1) Å, and the dihedral angles of rings B and D are 36−38°.

Each molybdenum is coordinated to six oxygens; four from the calixarene, and two from the “dioxo” portion. Here, however, rather than a Mo dioxo structure, the structure includes one μ-O bridge between two Mo centers and one

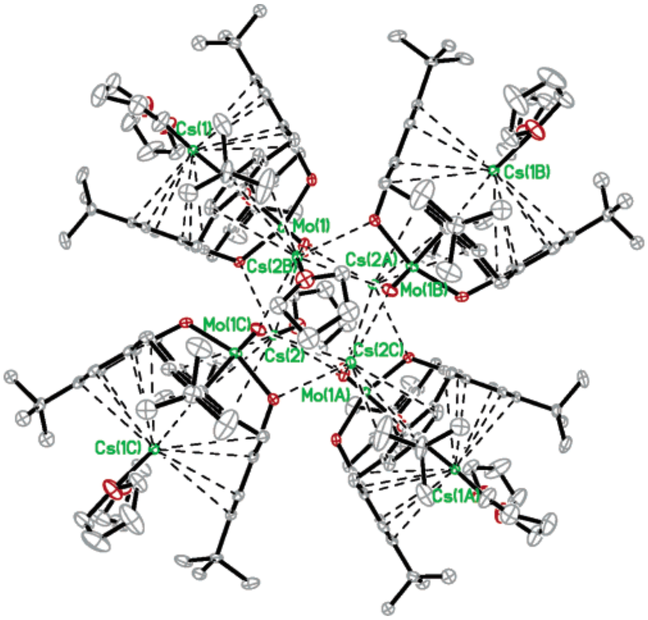

Figure 9. Crystal structure of Mo dioxo complex (Cs$_2$**Bu^{t}C4**MoO$_2$)$_4$·14THF. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent molecules are omitted for clarity.

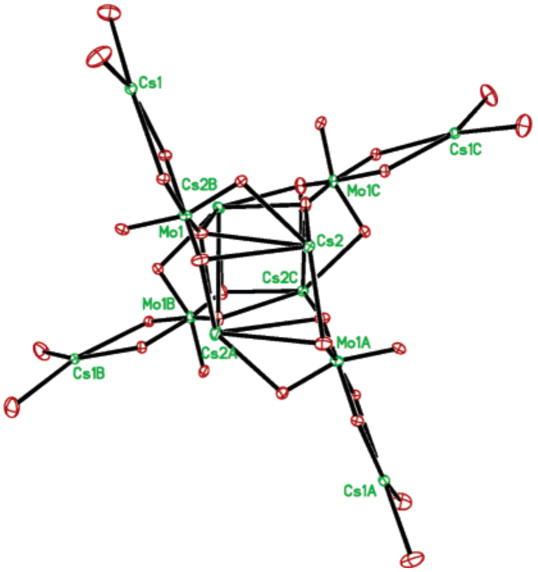

Figure 10. Core structure of Mo dioxo complex (Cs$_2$**Bu^{t}C4**MoO$_2$)$_4$·14THF.

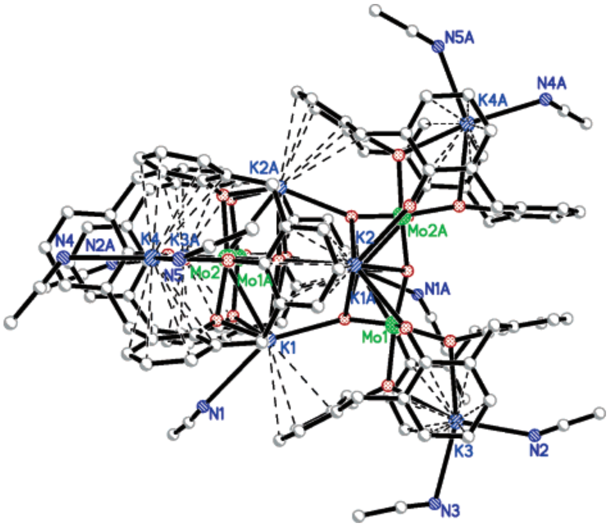

Figure 11. Crystal structure of side product **A**. Hydrogen atoms and solvent molecules are omitted for clarity.

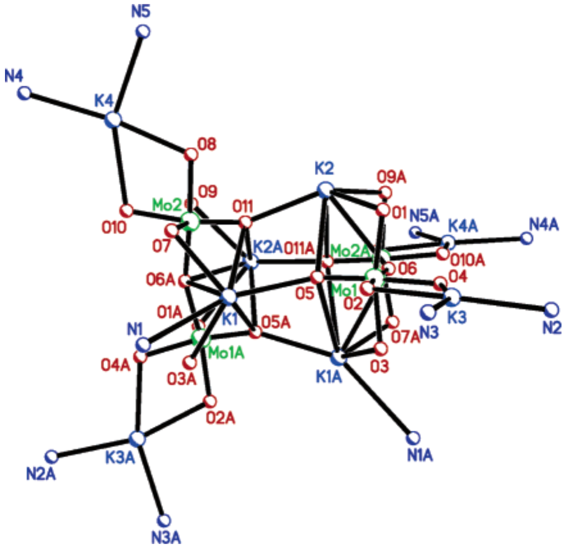

Figure 12. Core structure of side product **A**.

terminal oxo. Among many structures of Mo(V) complexes containing the O═Mo−O−Mo═O unit, there are only a few examples with oxygen-donating ligands.[29,30] The terminal oxo atoms in their structures are in the trans configuration. To our knowledge, side product **A** is the first dimeric dinuclear oxomolybdate complex containing two nearly linear O−Mo−O−Mo−O moieties (O(8)−Mo(2)−O(6A)−Mo(1A)−O(2A) and O(2)−Mo(1)−O(6)−Mo(2A)−O(8A)) in which the terminal oxo atoms are cis to each other. The Mo−O bond distances and K−O bond distances are consistent with those of K$_2$**Bu^{t}C4**MoO$_2$ and K$_2$**HC4**MoO$_2$. Selected bond distances and angles with comparison to those in the literature are shown in Table 5. The Mo−O$_\mu$ bond distance (1.886(7) Å) is consistent with that in the literature.[29−31] The Mo−O−Mo angle (160.2(4)°) is very similar to that reported for one conformer of Arzoumanian et al.'s complex.[31]

The extended structure is somewhat complex. A dimeric unit is formed by a μ-O bridge between two Mo centers; in Figure 11, this is between Mo(1) and Mo(2A). The bridging K$^+$ atoms K(2) and K(1A) are also coordinated to the μ-O group. The overall structure is a tetramer, composed of the two facing dimers at a 90° rotation relative to each other. Potassium atoms bridge between the pair of dimers via the Mo−O groups (e.g., Mo(1)−O(5)−K(1) in Figures 11 and 12) and also by π−cation interactions between a K$^+$ cation and a neighboring calixarene ring. This is very similar to the bridging π−cation interaction we observe in K$_2$**Bu^{t}C4**MoO$_2$.

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Table 5. Comparison of Selected Bond Distances and Angles

	Mo═O/Å	Mo−O (aryloxy)/Å	Mo−O_μ/Å	K−O (aryl)/Å	K−C (arene)/Å	Mo−O−Mo/°
A	1.709(7)	1.989(7), 2.074(6), 2.081(7), 2.086(6)	1.886(7)	2.591(6)−2.841(6)	3.12(1)−3.42(1)	160.2(4)
K_2**Bu^{t}C4**MoO_2	1.720(2) 1.733(2)	2.001(2), 2.006(2), 2.074(2), 2.105(2)	−	2.600(2)−2.652(2)	3.313(3)−3.445(3)	−
K_2**HC4**MoO_2	1.718(3) 1.723(3)	2.023(3), 2.033(2), 2.079(3), 2.090(2)	−	2.691(3)−2.816(3)	3.142(4)−3.383(4)	−
$Mo_2O_3Cl_4(DME)_2$[29]	1.655(3)	−	1.851(1)	−	−	180
$Mo_2O_3L_2 \cdot 2H_2O$[30] L = tetradentate Schiff base	1.705(5)	2.087(5), 2.031(4)	1.8816(7)	−	−	180
$Mo_2O_5(SCN)_2L_2$(meso)[31] L = bipyridine	1.694(2) 1.701(2)		1.876(1)	−	−	179.99(1)
$Mo_2O_5(SCN)_2L_2$(d,l)[31] L = bipyridine	1.696(2) 1.690(2) 1.700(2) 1.703(2)		1.892(2) 1.895(2)	−	−	155.7(1)

The solid structure of side product **C** was revealed in an X-ray diffraction study. An ORTEP diagram of side product **C** is shown in Figure 13.

Side product **C** appears to be the result of reduction by the K metal to form a Mo−Mo-bound dimer. The central dimer consists of two Mo/calix[4]arene moieties bridged by two μ-oxo groups, a short Mo−Mo bond, and four bridging potassium cations. There is additionally one potassium cation in each cavity. The range of Mo−O distances (2.000(3)−2.023(3) Å) falls into normal values of dimolybdenum calix[4]arene complexes.[16,32,33]

Two calixarene monoanions[6] are involved in the coordination to the Mo_2^{8+} core structure of **C** from both sides of the plane defined by the Mo core and two μ-oxo atoms. The bridging potassium cations K(2) and K(2A) are bound to the additional calixarene unit by two oxygens and to water and THF molecules (note that the calixarene dianion[34] would not be expected to be stable in the presence of water molecules). The K(2)−O(6) and K(2)−O(7) bond distances (2.760(3) and 2.870(3) Å) are consistent with those of calix[4]arene monopotassium salts.[6]

The hexa coordination of the metal Mo and the inclusion of the potassium cation remove the planarity of calixarene oxygens; again, we see a flattened cone conformation. However, the Mo−Mo core is entirely planar, with two bridging μ-oxo groups. The K(1) and K(1A) atoms are tightly bonded to μ-oxo atoms (K−O, 2.569(3) Å) and have two η^6 cation−π arene interactions with the flattened rings of two calixarenes from the Mo_2^{8+} core.

The Mo−Mo distance of 2.3973(3) Å and the eclipsed geometry of the Mo_2O_{10} moiety are indicative of a double bond. Our Mo−Mo bond length is in the range of reported Mo−Mo double bond distances, 2.3048(4)−2.534(1) Å.[35,36] The Mo−O_μ bond distances (2.000(3) and 2.007(3) Å) are slightly longer than those of $Mo_2(DXylF^{2,6})_2(O_2CCH_3)_2(\mu_2-O)_2$, and the O_μ−Mo−O_μ angle (106.52(9)°) is consistent with that of $Mo_2(DXylF^{2,6})_2(O_2CCH_3)_2(\mu_2\text{-}O)_2$.[36]

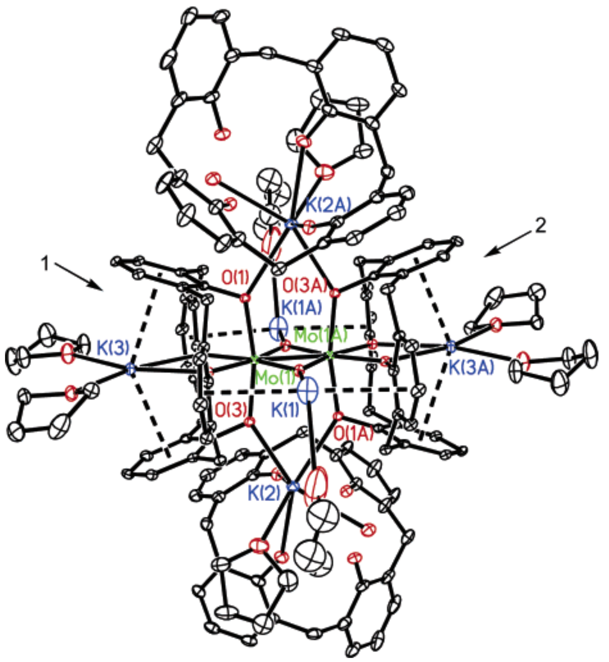

Figure 13. Crystal structure of side product **C**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent pentane molecules are omitted for clarity.

There are three types of potassium atoms in the structure. Each Mo/calixarene cavity has a potassium cation (K(3)) bound to two calixarene oxygens (O(2) and O(4)) and π-bridging between opposite arene rings, similar to the cations in the cavity of the Mo dioxo calixarenes. A second potassium pair (K(1) and K(1A)) bridges the two calixarenes by π-cation interaction with one flattened ring in each side (e.g., K(1) bridges ring C of calixarene 1 and ring C of calixarene 2). These potassium atoms are also coordinated to the μ-oxo atoms (O(5) and O(5A)) that bridge the two Mo atoms and one THF molecule. These bridges are also similar to those found in our dioxo complexes. Finally, the third pair of potassium cations (K(2) and K(2A)) bridge the calixarene oxygen atoms (O(1), O(3), O(6), and O(7)), with no cation−π interaction. This type of bridging has been observed in Floriani W/calixarene dimers.[1,37] Although each of these types of potassium bridge is well-precedented, this

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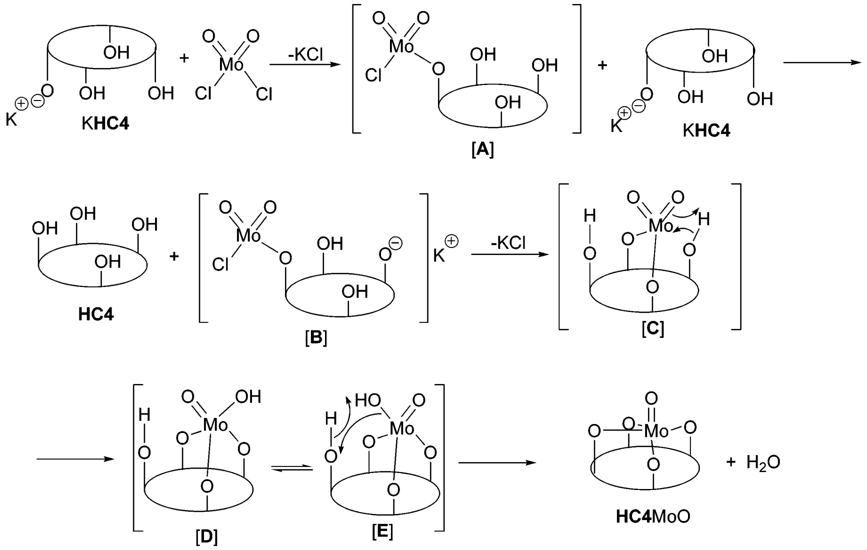
Scheme 1



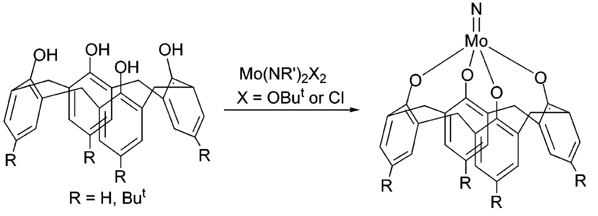
is the first reported structure to include all three types of bridging interaction in a single molecule.

Discussion

The formation of the dioxomolybdenum calixarene dianions from the corresponding calixarene tetranions is very similar to reactions observed by previous workers, such as Petrella et al.'s synthesis of dianionic Ti/calixarene complexes[8] and several examples by Floriani and co-workers.[1,38] The mechanism is likely a simple substitution of the Mo−Cl group with the anionic phenolic groups of the calixarene precursor. Although this is formally a transmetalation, i.e., replacement of the alkali metal cation with the molybdenum moiety, we do not see significant differences in the reaction based on the identity of the alkali metal. The structural characteristics of the products, in contrast, do differ substantially (vide infra). Floriani et al. reported the crystal structures of the tetraanions for the Li^+, Na^+, and K^+ salts,[4] which are dominated by exo coordination to form alkali metal/oxygen cores bridging two calixarene units. The dissociation of these units to allow substitution reactions is apparently facile in solution.

The formation of the monooxo molybdenum calixarene complex was not expected, but its general mechanism may be deduced on the basis of literature precedent. Scheme 1 shows the proposed mechanism, ignoring the conformation of the calixarene rings and nature of the alkali metal. Calix[4]arene monoanion K**HC4** first reacts with MoO_2Cl_2 to form intermediate [**A**]. Introduction of the MoO_2Cl- moiety makes the remaining calix-OH groups more acidic, so [**A**] can further react with K**HC4** to give intermediate [**B**] and **HC4**. (We suggest a deprotonation in the 3 position for [**B**] and a 1,3-substitution pattern for [**C**] based on the structure of dioxomolybdenum calixarene dianions K_2**HC4**MoO_2. The structure of [**B**] as depicted also allows for maximum H-bonding stabilization of the anionic oxygen). Intramolecular elimination of KCl forms intermediate [**C**]. Proton transfer with concurrent Mo−O bond formation leads to the hydroxy complex [**D**]. The second proton transfer may either form an oxo/aquo or a dihydroxomolybdenum moiety which eliminates H_2O to form **HC4**MoO**.** The oxo/aquo intermediate is shown, as this intermediate would be stabilized by the "spectator oxo effect",[39] and is thus more likely. Finally, the released H_2O molecule coordinates to Mo inside the cavity of the calix[4]arene.

The most interesting step of this mechanism is the attack of the calixarene phenolic group on a Mo═O group, implying nucleophilicity of the terminal oxo group. Although this reactivity has rarely been reported in MoO_2^{2+} complexes, attack of protons and other cationic groups on metal oxo groups is well-precedented for several metals,[40] as well as for other molybdenum-containing moieties.[41−46] Indeed, Kühn and co-workers recently proposed a similar precoordination then protonation of a MoO_2^{2+} group by *tert*-butylhydroperoxide.[47] This reaction may also be compared with the formation of molybdenum monoimido calixarenes from diimido precursors with elimination of amine (eq 6) via what is presumably a parallel mechanism of nucleophilic attack of a phenol hydrogen on a terminal molybdenum imido group.[22,32]



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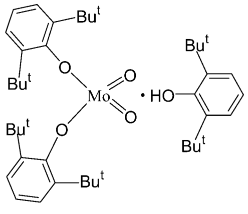
The attack of phenol on the oxo group in this calixarene-ligated molybdenum complex may be contrasted with our previously reported molybdenum dioxo diaryloxide (**1**),



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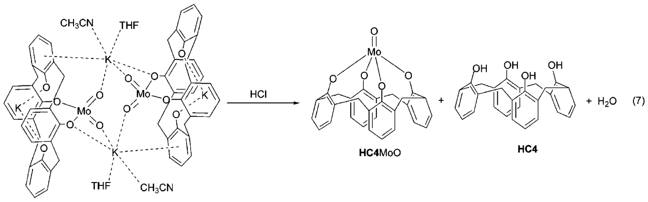
which co-crystallizes with 1 equiv of phenol. No evidence of proton transfer is found in that system.[28] Presumably, the difference is due to the favorable configuration of the calixarene phenol with respect to the metal center, allowing pre-coordination to the molybdenum and therefore increased acidity of the hydrogen.[47] In complex **1**, the steric bulk inhibits phenol coordination, and the free phenol is not sufficiently acidic to protonate the terminal oxo group. The less sterically crowded molybdenum dioxo diaryloxides do undergo an equivalent reaction to form the monooxo tetraaryloxides, as described in our recent communication.[17]

Unfortunately, this reaction occurs too quickly to be amenable to kinetic studies. The following observations, however, are consistent with our proposed mechanism.

The calix[4]arene tetraanions react with MoO_2Cl_2 to give compound K_2**HC4**MoO_2 by elimination of 2 MCl molecules, as described above. Compound K_2**HC4**MoO_2, in the absence of −OH groups, cannot undergo proton transfer. When compound K_2**HC4**MoO_2 was treated with ca. 2 equiv of HCl in THF, however, compounds **HC4**MoO and **HC4** (3:4 molar ratio) were immediately formed (eq 7) and the eliminated H_2O molecule entered into the cavity (identified by ^{1}H NMR, one broad peak at −0.35 ppm). Compound K_2**HC4**MoO_2 presumably reacts with HCl to form intermediate [**C**] (or else an oxo group, then a hydroxo group, is directly protonated by the HCl).



In a separate experiment, parent calix[4]arene was treated with $MoO_2(OBu^t)_2$ in ether (analogous to Gibson's synthesis of Mo imido calix[4]arene complexes[22]), and compounds **HC4**MoO and **HC4** were obtained. Here the first step is to substitute the calixarene OH groups in the 1,3 positions to again give [**C**], which follows the pathway above to form compound **HC4**MoO (Scheme 1). These experiments indicate that it is possible to form compound **HC4**MoO from intermediate [**C**] by proton transfer and water elimination.

This discussion has again ignored the nature of the alkali metal and calixarene conformation, but in this case, their role bears examination. It has been established that both the calixanion conformations[5] and the Mo dioxo dianion conformations (vide supra) do change according to the nature of the alkali metal. We have also found that for monooxo formation the nature of the alkali metal affects the progress of the reaction. The calixarene monoanions for $M^+ = Li^+$, Na^+, and K^+ have been shown to have exo coordination of the cations; for all of these precursors, we obtain similar reactivity in the formation of **HC4**MoO. In contrast, the calix[4]arene monoanions with Cs and Rb cations have polymeric endo/exo coordination geometries in the solid state. These two precursors lead to slow reactions and very low yields of molybdenum complex. The inaccessibility of the cation apparently inhibits the transmetalation of calixarene anion from alkali metal to molybdenum.

Conclusion

We have reported a series of calix[4]arene Mo(VI) dioxo complexes that were fully characterized by NMR, X-ray, IR, UV/vis, and elemental analysis. Molybdocalix[4]arene structures can be controlled via lower rim deprotonation, groups at para positions of calix[4]arene, and alkali metal counterions. Mono deprotonation at the lower rim leads to calix[4]arene Mo(VI) monooxo complexes, and full deprotonation gives rise to calix[4]arene Mo(VI) dioxo complexes. Structural studies indicate that **HC4** Mo(VI) dioxo complexes easily form polymeric structures via cation−π interaction and coordination between different calixarene units. However, **Bu^{t}C**4 Mo(VI) dioxo complexes tend to form dimers or tetramers due to steric hindrance of the *tert*-butyl groups at para positions in calixarene. The structures of the reduced side products **A** and **C** were determined by X-ray diffraction studies. These early results promise an interesting redox chemistry of our new compounds, which we are investigating. The mechanism of **RC4**MoO formation from the reaction of calixarene monoanions with MoO_2Cl_2 appears to include the addition of a calixarene −OH group across a Mo═O bond, similar to the chemistry we recently reported for Mo(VI) oxo aryloxides.[17]

Experimental Section

1. General Information. Unless otherwise noted, all manipulations were carried out in a nitrogen-filled glovebox and starting materials were obtained from commercial suppliers and used without further purification. Calix[4]arene,[48] *p-tert*-butylcalix-

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[4]arene,[49] *p*-allylcalix[4]arene (**AC4**),[50] calix[4]arene monoanions,[5] and $MoO_2(OBu^t)_2$[51] were prepared by literature procedures. Calixarenes were *not* vacuum oven-dried to remove encapsulated water molecules before use. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone; other anhydrous solvents were purchased from Aldrich and stored over molecular sieves under nitrogen before using. Deuterated THF was dried over CaH_2 and Na/benzophenone, and DMSO-d_6, C_6D_6, and CD_3CN were dried over CaH_2. The melting points of all compounds were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 400 °C thermometer calibrated against a thermocouple. The melting points are uncorrected. A melting temperature preceded by a “>” sign indicates that the compound starts to decompose at that temperature but appears to actually melt at some higher temperature. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer at 300 and 75 MHz, respectively. Analytical samples were dried in a drying pistol under vacuum for at least 24 h. Microanalyses were performed by Microanalysis Laboratory, University of Illinois, Urbana−Champaign, Urbana, IL. 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.

2. RC4MoO [R = H, Bu^t, and A (allyl)]. 2.1. Method A. To a stirred suspension of potassium salt of monoanionic calix[4]arene (**HC4**) (0.140 g, 0.325 mmol) in THF (10 mL) was added a solution of MoO_2Cl_2 (0.060 g, 0.31 mmol) in THF (5 mL) causing immediate formation of a dark red suspension. The reaction mixture was stirred for 4 h, the solvent was removed under vacuum to give a dark red solid, which was brought up with benzene, and the beige insoluble material was removed by filtration. The filtrate was dried under vacuum to give a dark red solid (this is a mixture of **HC4**MoO and **HC4**). The mixture was recrystallized by hexane diffusion into the benzene solution of **HC4**MoO and **HC4** to produce two kinds of crystals. Compound **HC4**MoO formed small dark needle crystals and **HC4** formed large colorless ones. The two kinds of crystals were manually separated, and compound **HC4**MoO (0.067 g, 38% yield) was obtained.

The same procedure was used for other monoanion salts **HC4**M (M = Li, Na, Rb, Cs). The yield was similar when Li or Na was used (40% yield for Li, 35% yield for Na). The yield was much smaller when Rb or Cs was used (11% yield for Rb, 10% yield for Cs).

2.2. Method B. To a stirred suspension of **HC4** (0.168 g, 0.398 mmol) in Et_2O (15 mL) was added a solution of $MoO_2(OBu^t)_2$ (0.110 g, 0.401 mmol) in DME (3 mL) to give a dark red suspension. The reaction mixture was stirred for 12 h at room temperature. The suspension was filtered to give a dark red solid. The dark red solid was suspended in THF (10 mL) to give a dark red suspension. The THF-insoluble green material was removed by filtration. The filtrate was dried under vacuum to give a dark red solid. The solid was recrystallized by hexane diffusion into its benzene solution to obtain compound **HC4**MoO (0.11 g, 44% yield). ^1H NMR (C_6D_6): δ 6.80 (d, $^3J_{H,H} = 7.5$ Hz, *m-H*-Ar), 6.62 (t, $^3J_{H,H} = 7.5$ Hz, *p-H*-Ar), 4.46 (d, $^2J_{H,H} = 12.6$ Hz, $ArCH_2Ar$), 2.94 (d, $^2J_{H,H} = 12.7$ Hz, $ArCH_2Ar$). ^{13}C NMR (C_6D_6): δ 161.8, 133.2, 131.6, 127.2 (aromatic carbons), 35.7 (methylene carbons). IR (KBr, cm^{-1}): 1573m, 1446vs, 1430 vs, 1265s, 1248vs, 1198vs, 1076s, 956vs (Mo═O), 920s, 897s, 863s, 758s. UV/vis (C_6H_6) λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 273 (1797), 342 (1749). MS (HRFAB): found, 541.0524; calcd for $C_{28}H_{20}O_5LiMo$, 541.0524 (MS was operated on the Li target platform). Due to the difficulty in separation of **HC4**MoO and **HC4**, a satisfactory result of elemental analysis is unavailable.

Complex **AC4**MoO was prepared by the same procedure as that of **HC4**MoO. The product **AC4**MoO could not be separated from the reaction mixture. However, it was characterized by NMR and FTIR spectroscopies. ^1H NMR (C_6D_6): δ 6.76 (s, *m-H*-Ar, 8H), 5.75 (m, $CH_2{=}C\mathit{H}{-}CH_2$, 4H), 4.96 (m, $C\mathit{H}_2{=}CH{-}CH_2$, 8H), 4.52 (d, $^2J_{H,H} = 12.3$ Hz, $ArC\mathit{H}_2Ar$, 4H), 3.07 (d, $^2J_{H,H} = 6.2$ Hz, $CH_2{=}CH{-}C\mathit{H}_2$, 8H), 2.99 (d, $^2J_{H,H} = 12.8$ Hz, $ArC\mathit{H}_2Ar$, 4H). ^{13}C NMR (C_6D_6): δ 153.1, 138.0, 133.4, 129.2 (aromatic carbons), 128.4 ($CH_2 = \mathit{C}H{-}CH_2$), 115.6 ($\mathit{C}H_2{=}CH{-}CH_2$), 39.7 ($CH_2{=}CH\text{-}\mathit{C}H_2$), 33.0 (methylene carbons). IR (KBr, cm^{-1}): 3430vs, 3077vs, 2976s, 2926s, 1638s, 1576m, 1540w, 1505w, 1478w, 1458vs, 1431s, 1411m, 1333w, 1277m, 1244m, 1216s, 1162m, 1149m, 1127m, 1102w, 992m, 965s (Mo═O), 913s, 828s, 787m, 753w. UV/vis (C_6H_6) λ_{max}/nm: 281, 328.

For **Bu^{t}C4**, the same procedure was used to synthesize **Bu^{t}C4**MoO. No NMR data are available due to its poor solubility in organic solvents. Compound **Bu^{t}C4**MoO was identified with IR and MS spectra. IR (KBr, cm^{-1}): 3440m, 3189m, 2960s, 2688m, 2836m, 1605w, 1480s, 1462s, 1414m, 1394w, 1362m, 1305m, 1268m, 1241m, 1195s, 1106m, 968 (vs, Mo═O), 917m, 872m, 837s, 797m, 762w. MS (EI): [M] (*m/z*) = 756.90, calcd for $C_{44}H_{52}O_5Mo$, 756.83.

3. Typical Procedure for Making Calix[4]arene Mo(VI) Dioxo Complexes. To a solution of **HC4** (0.220 g, 0.518 mmol) in THF (8 mL) was added a solution of $LiOBu^t$ (0.167 g, 2.09 mmol) in THF (5 mL). The reaction mixture was stirred for 2 h at room temperature. A solution of MoO_2Cl_2 (0.103 g, 0.518 mmol) in THF (3 mL) was then added to the stirring light blue solution, and immediately a dark red suspension was obtained. The resulting mixture was stirred for 12 h at room temperature, and an orange yellow suspension was obtained. The side product LiCl was removed by centrifugation, and the solution was pumped dry in vacuo to give an orange-yellow solid. The product was purified by recrystallization with THF−hexane, and Li$_2$**HC4**MoO$_2$ yellow crystals (0.205 g, 58% yield) were obtained. Single crystals were obtained by diffusion of pentane into a concentrated THF solution.

All spectroscopic data and analytical data are given in the Supporting Information.

4. General X-ray Crystal Structure Information. All data were collected on a Bruker SMART APEX CCD diffractometer at low temperature using Mo Kα radiation. The crystallographic data and some details of the data collections and refinements of the structures are given in Table 6. Absorption corrections in all cases were applied by SADABS. Structures were solved using direct methods or the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. Some solvent THF and CH_3CN molecules and *t*-Bu groups as well (in Li$_2$**HC4**MoO$_2$, K$_2$**Bu^{t}C4**MoO$_2$, side product **A**) are disordered over two positions. Some of these molecules were refined with restrictions on the bond distances; in the refinement, typical average values were used as targets for corresponding bond distances. Two highly disordered CH_3CN solvent molecules in

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Table 6. Crystallographic Data and Summary of the Data Collection and Structure Refinement

	HC4 MoO·C_6H_6	Li_2**Bu^{t}C4**MoO_2· THF·3.5CH_3CN	Li_2**Br$_2$C4**MoO_2· 6THF·3CH_3CN	K_2**Bu^{t}C4**MoO_2· 6THF	Cs_2**Bu^{t}C4**MoO_2· 3.5THF
formula	$C_{34}H_{28}MoO_6$	$C_{55}H_{70.5}Li_2MoN_{3.5}O_7$	$C_{94}H_{109}Br_4Li_4Mo_2N_3O_{20}$	$C_{68}H_{90}K_2MoO_{12}$	$C_{58}H_{80}Cs_2MoO_{9.5}$
fw	628.50	1002.47	2140.12	1273.54	1290.98
cryst syst	monoclinic	triclinic	monoclinic	triclinic	tetragonal
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P4_2/n$
T, K	213(2)	150(2)	100(2)	150(2)	100(2)
a, Å	9.9482(7)	12.3203(15)	18.0459(11)	12.1548(7)	24.3614(6)
b, Å	17.0987(11)	13.7772(17)	15.3228(9)	14.1043(8)	24.3614(6)
c, Å	15.8339(10)	17.857(2)	19.2400(12)	22.5902(13)	19.2140(9)
α, deg	90	89.568(2)	90	95.1550(10)	90
β, deg	97.7040(10)	71.825(2)	115.5800(10)	105.5130(10)	90
γ, deg	90	67.398(2)	90	112.4380(10)	90
V, Å^3	2669.1(3)	2636.8(6)	4798.7(5)	3368.1(3)	11403.1(7)
Z, Z'	4, 1	2, 1	2, 0.5	2, 1	8, 1
cryst dimens mm^3	0.30 × 0.20 × 0.10	0.05 × 0.15 × 0.25	0.20 × 0.15 × 0.12	0.35 × 0.25 × 0.20	0.26 × 0.22 × 0.18
d_{calcd}, g·cm^{-3}	1.564	1.263	1.481	1.256	1.504
μ, mm^{-1}	0.540	0.302	1.995	0.376	1.542
$2\theta_{max}$, deg	56.44	56.72	55.04	56.52	55.06
T_{min}/T_{max}	0.805	0.846	0.847	0.931	0.857
N measd [R_{int}]	19 115 [0.0302]	16 555 [0.0201]	29 665 [0.0272]	20 640 [0.0151]	70 264 [0.0260]
N ind	6261	11 566	10 946	14 479	12 939
N obs ($I \geq 2(I)$)	5481	9849	8954	13 217	11 692
no. of params	482	669	532	693	631
R ($I \geq 2\sigma(I)$)	0.0393	0.0508	0.0418	0.0663	0.0471
R_w ($I \geq 2\sigma(I)$)	0.0970	0.1527	0.1180	0.1809	0.1002
GOF	1.082	1.067	1.045	1.096	1.172

	Li_2HC4MoO_2· 6THF·3LiCl	K_2HC4MoO_2· 3THF·2CH_3CN	Rb_2HC4MoO_2· 6THF	**A**	**C**
formula	$C_{80}H_{88}Cl_2Li_6Mo_2O_{18}$	$C_{36}H_{34}K_2MoN_2O_7$	$C_{30}H_{26}MoO_7Rb_2S$	$C_{124}H_{131}K_8N_{15}O_{25}$	$C_{113}H_{138}K_3Mo_1O_{15}$
fw	1641.92	780.79	797.45	3142.51	1949.48
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$Pbca$	$P2_1/c$	$C2/c$	$P\bar{1}$
T, K	150(2)	147(2)	213(2)	150(2)	100(2)
a, Å	11.6946(7)	12.5343(8)	10.0905(8)	32.783(3)	15.8192(8)
b, Å	26.3105(15)	20.9472(14)	21.1785(17)	32.918(3)	18.9347(9)
c, Å	26.4358(15)	25.0840(17)	14.1137(11)	29.183(2)	19.2990(10)
α, deg	94.6690(10)	90	90	90	85.2640(10)
β, deg	91.9040(10)	90	109.035(10)	101.314(2)	73.1320(10)
γ, deg	92.9690(10)	90	90	90	74.0610(10)
V, Å^3	8090.4(8)	6586.0(8)	2851.2(4)	30880(4)	5319.3(5)
Z, Z'	4, 2	8, 1	4, 1	8, 1	2, 1
cryst dimens mm^3	0.30 × 0.25 × 0.15	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.30	0.35 × 0.25 × 0.20	0.35 × 0.30 × 0.25
d_{calcd}, g·cm^{-3}	1.348	1.575	1.858	1.353	1.217
μ, mm^{-1}	0.441	0.705	3.973	0.602	0.302
$2\theta_{max}$, deg	56.46	56.54	56.40	48.00	54.92
T_{min}/T_{max}	0.938	0.936	1.00	0.731	0.859
N measd [R_{int}]	51 598 [0.0387]	39 317 [0.0495]	21 744 [0.0272]	72 734 [0.0970]	33 621 [0.0193]
N ind	36 017	7832	6734	24 269	23 378
N obs ($I \geq 2\sigma(I)$)	24 587	5984	5509	13 017	19 376
no. of params	1935	433	370	1580	1117
R ($I \geq 2\sigma(I)$)	0.0753	0.0520	0.0328	0.0727	0.0784
R_w ($I \geq 2\sigma(I)$)	0.1906	0.1532	0.0822	0.1991	0.2259
GOF	1.056	1.138	1.020	1.065	1.038

Li_2**Br$_2$C4**MoO_2 (one in a general and one in a special position) were treated by SQUEEZE; the correction of the data by SQUEEZE, 131 e/cell, is close to the required value, 132 e/cell. All non-hydrogen atoms were refined with anisotropic displacement coefficients, except atoms of disordered fragments which were refined with isotropic thermal parameters. The H atoms in **HC4**MoO and Rb_2**HC4**MoO_2 were found on the F-map and refined with isotropic thermal parameters. The H atoms in other structures were taken in calculated positions, except the H atoms in disordered THF molecules in Li_2**HC4**MoO_2·6THF·3LiCl and solvent water molecules in side product **A**, which were not taken into consideration. The values of peaks corresponding to the O atoms of solvent water and the structure refinement show that positions of these solvent water molecules in **A** could be not fully occupied.

Acknowledgment. We are grateful to the Welch Foundation (Grant No. P-1459) and the National Science Foundation (Grant No. CHE -133866) for research funding.

Supporting Information Available: Detailed Experimental Section; NMR data, IR data, UV/vis data, elemental analysis, and melting points of calix[4]arene Mo(VI) dioxo complexes; X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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