Syntheses and Molecular Structures of New Calix[4]arene Molybdenum and Tungsten Complexes

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Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Abstract: An unusual disproportionation reaction of the molybdenum(IV) and tungsten(IV) chlorides $[MCl_4L_2]$ (M = Mo, L = Et_2S, Et_2O; M = W; L = Et_2S) in the presence of *p*-*t*Bu-calix[4]-arene (Cax(OH)$_4$) and triethylamine leads to d^0 complexes $[(CaxO_4)\{CaxO_2(OH)_2\}M]$ (**1**) and d^3 compounds $(HNEt_3)_2[(CaxO_4)_2M_2]$ (**2**). Complexes **1a** (M = Mo), **1b** (M = W), and the HCl adduct of **2a** (M = Mo) have been structurally characterized. Compound **1a** represents one of the few examples of a well-characterized molybdenum(VI) hexa-alkoxide complex of the type $[Mo(OR)_6]$. Isolation and structural characterization of the side product $[(CaxO_4W)\{\kappa^2(O)\text{-}\kappa^1(O)\text{-}CaxO_3(OH)\}(CaxO_4WCl)]$ (**3**) suggests the intermediacy of chloro-containing calix[4]arene complexes in these reaction mixtures. The reaction of **1a** with HCl provides $[CaxO_4MoCl_2]$ (**4a**), the first well-defined example of a mixed molybdenum(VI) alkoxide halide compound of the general formula $[MoCl_x(OR)_{6-x}]$.

Keywords: calixarenes · coordination chemistry · molybdenum · tungsten

Introduction

Transition metal calix[4]arene complexes, in which metal atoms are coordinated to the phenolic oxygen atoms of the macrocycle, have been known for almost 15 years. In 1985, Power and co-workers reported the syntheses and structures of dinuclear and trinuclear calix[4]arene complexes of titanium, iron, and cobalt.[1] These compounds were obtained from the reaction of *p*-*t*Bu-calix[4]arene (Cax(OH)$_4$; Cax = carbonhydride backbone of the *p*-*t*Bu-calix[4]arene, $C_{44}H_{52}$) with homoleptic amides $[Ti(NMe_2)_4]$, $[Fe\{N(SiMe_3)_2\}_3]$ and $[\{Co\{N(SiMe_3)_2\}_2\}_2]$. The first mononuclear calix[4]arene complex, a calix[4]arene molybdenum oxide, was reported five years later by Floriani and co-workers.[2] This compound was structurally characterized as the calix[4]arene complex $[CaxO_4Mo(=O)(OH_2)\{Cax(OH)_4\}(PhNO_2)]$, which is almost insoluble in common organic solvents. In the last few years, the potential of calix[4]arene complexes in organometallic and coordination chemistry has been demonstrated in several contributions, particularly from Floriani's group.[3–7] For mononuclear calix[4]arene tungsten complexes, it has been shown that they are useful precursors for the reductive generation of dinuclear compounds with metal–metal multiple bonds,[6d, 6f] and that they are of interest in materials science[6k, 6l] and organic synthesis.[6j] The interconversion of carbenes, carbynes, and alkenes[6g] as well as olefin rearrangements[6h] in calix[4]arene tungsten complexes by simple protonation and deprotonation steps are facilitated by the basic environment of the phenoxide oxygen atoms of the macrocylic ligand. The isolation and characterization of these different compounds was of particular interest, as it was demonstrated that calix[4]arene complexes might serve as a molecular model for oxo surfaces that bind a metal in an appropriate way to drive catalytic or stoichiometric reactions. The overall processes described in these studies mimic reactions supposed to proceed on metal–oxo surfaces.

Studies on molybdenum complex fragments coordinated through this unique set of oxygen donor atoms provided by the calix[4]arene ligand might be also of some significance, since molybdenum oxides are important materials in heterogenous catalysis, for example, in the allylic oxygenation over bismuth molybdate oxides in the so called SOHIO process[8a] or in the hydrodesulfurization process (HDS).[8b] However, the chemistry of calix[4]arene molybdenum complexes is almost unexplored in contrast to compounds of the heavier congener tungsten or the Group 5 metals, niobium and tantalum. A mononuclear calix[4]arene molybdenum oxide reported by Floriani and co-workers,[2] which is sparingly soluble in common organic solvents, and some calix[4]arene molybdenum imido complexes reported from Gibson's group[7h] and ourselves,[4b] are the few mononuclear calix[4]arene molybdenum compounds known so far. Dinuclear anionic molybdenum calix[4]arene complexes $[(CaxO_4)_2Mo_2]^{2-}$ reported by us[4a] and Chisholm et al.[7f, 7g]

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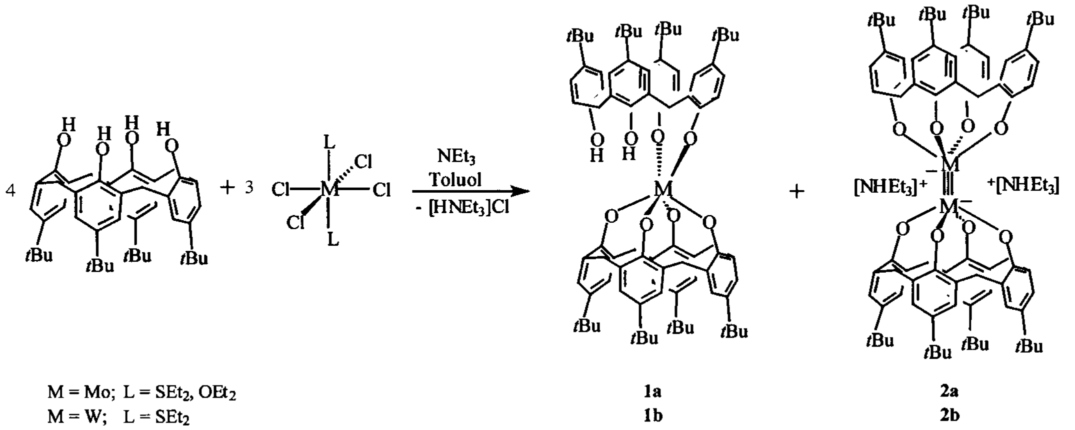

(1)

are rather unreactive with respect to cleavage of the metal–metal multiple bond. None of these complexes seems to be a desirable starting material for calix[4]arene molybdenum chemistry. This led us to investigate reactions of calix[4]arene Cax(OH)$_4$ with higher valent molybdenum chloride compounds.

Results and Discussion

Whereas the tungsten(VI)chloride [(CaxO$_4$)WCl$_2$] is easily synthesized in high yields from the reaction of calix[4]arene CaxOH$_4$ with [WCl$_6$],[6f] we were unable to isolate any mononuclear molybdenum species, for example, [CaxO$_4$MoCl$_2$] or [CaxO$_4$MoCl], from reactions of CaxOH$_4$ with [MoCl$_5$] under several different sets of reaction conditions. These reactions lead in most cases to decomposition of the calix[4]arene ligand, for example, in scission of *t*Bu groups from the ligand system. The cleavage of *t*Bu groups from p-*t*Bu-calix[4]arenes in the presence of HCl and strong Lewis-acids, like AlCl$_3$, in a retro-Friedel-Crafts type alkylation reaction is well known in calixarene chemistry.[9] On the other hand, there are presumably more complicated decomposition pathways working in these mixtures, because the reaction of the parent *p*-H-calix[4]arene with [MoCl$_5$] does also not lead to isolable, mononuclear calix[4]arene molybdenum chlorides. The reactivity of [MoCl$_5$] with alcohols was reinvestigated only recently, and it was shown that these reactions proceed under partial cleavage of the alcohol yielding alkyl halides, mononuclear molybdenum(oxo)chlorides and multinuclear molybdenum(oxy)(alkoxy)halides.[10]

Abstract in German: *Eine ungewöhnliche Disproportionierungs-Reaktion der vierwertigen Molybdän- und Wolframchloride [MCl$_4$L$_2$] (M = Mo, L = Et$_2$S, Et$_2$O; M = W; L = Et$_2$S) in Gegenwart von p-tBu-Calix[4]aren und Triethylamin führt zu den d^0-Komplexen [(CaxO$_4$){CaxO$_2$(OH)$_2$}M] (**1**) und den d^3-Verbindungen (HNEt$_3$)$_2$[(CaxO$_4$)$_2$M$_2$] (**2**). Sowohl **1a** (M = Mo) und **1b** (M = W) als auch das HCl Addukt der Verbindung **2a** (M = Mo) konnten strukturell charakterisiert werden. Verbindung **1a** ist eine der wenigen bislang charakterisierten Verbindungen vom Typ [Mo(OR)$_6$] des sechswertigen Molybdäns. Die Isolierung und strukturelle Charakterisierung des Nebenproduktes [(CaxO$_4$W){κ^2(O)-κ^1(O)-CaxO$_3$-(OH)}(CaxO$_4$WCl)] (**3**) lässt vermuten, daß Calix[4]aren-Molybdän- und Wolframchloride am Reaktionsgeschehen beteiligt sind. Die Reaktion von **1a** mit HCl führt zu [CaxO$_4$MoCl$_2$] (**4a**), dem ersten bekannten Beispiel für ein heteroleptisches Molybdän(VI)chloroalkoxid der allgemeinen Formel [MoCl$_x$(OR)$_{6-x}$].*

Molybdenum(IV)chlorides are far less Lewis acidic than molybdenum pentachloride, and this might be the reason why calix[4]arene does not react with compounds of the type [MoCl$_4$L$_2$] (L = Et$_2$S, Et$_2$O)[11] at elevated temperatures. If a base like triethylamine is added to the reaction mixture, typically solutions of the calix[4]arene and the molybdenum chloride at 100 °C in toluene, the color of these solutions turns from red to purple. The proton NMR spectrum of the crude product shows a variety of signals for diamagnetic reaction products, but there were no indications that molybdenum(IV) species—presumably paramagnetic—are formed. According to Equation (1), two calix[4]arene molybdenum complexes were isolated from these reaction mixtures, the molybdenum(VI) complex [(CaxO$_4$){CaxO$_2$(OH)$_2$}Mo] (**1a**) and a dinuclear molybdenum(III) compound (HNEt$_3$)$_2$-[(CaxO$_4$)$_2$Mo$_2$] (**2a**).

In contrast to the yellow compound **2a**, the dark purple complex **1a** is very soluble in pentane or hexane, therefore **1a** can be easily separated from **2a** by extraction in the organic solvent. The ^{1}H NMR spectrum of **2a** shows one resonance for the *t*Bu protons, two doublets for the methylene protons, and one resonance due to the protons of the aromatic ring; this reveals the high local C_{4v} symmetry for the calix[4]arene complex. In the electron impact mass spectrum of **2a**, a signal at m/z 1484 is detectable for the [(CaxO$_4$)$_2$Mo$_2$]$^{2-}$ entity.

The ^{1}H NMR spectrum of the molybdenum(VI) complex [(CaxO$_4$){CaxO$_2$(OH)$_2$}Mo] (**1a**) reveals low local symmetry at the metal atom. Five signals can be observed in the intensity ratio 1:1:2:2:2 for the resonances of the *t*Bu protons, furthermore ten doublets for the methylene protons and six signals for the aromatic ring protons are observed. A resonance at $\delta = 8.33$ indicated O–H groups in the molecule, which was confirmed in the infrared spectrum by a resonance at $\tilde{\nu} = 3442\,cm^{-1}$. According to the spectroscopic data, one calix[4]arene ligand in **1a** coordinates to the central metal atom in a tetradentate fashion, the other in a bidentate fashion.

We were interested to know about the reactivity of tungsten(IV)halides with calix[4]arene CaxOH$_4$ under similar conditions. The thioether adduct $[WCl_4(SEt_2)_2]$,[12a] for example, reacts cleanly with Cax(OH)$_4$ in the presence of NEt$_3$ in toluene at 100 °C to give, after work up, the brick red hexane soluble compound $[(CaxO_4)\{CaxO_2(OH)_2\}W]$ (**1b**) and the green dinuclear compound **2b** in good yields. Compound **1b** can also be obtained in somewhat lower yield from $[WCl_4]$, prepared by the reduction of $[WCl_6]$ with red phosphorous.[12b] ^1H and ^{13}C NMR spectroscopic data of **1b** are almost identical with those of **1a**. From the fraction of the crude product that was insoluble in hexane a green powder can be obtained in small yields; this was identified as $(HNEt_3)_2[(CaxO_4)_2W_2]$ (**2b**) by NMR spectroscopy.

As one moves across the transition series of the periodic table, the effect of the oxidation state of the metal on the stability of complexes becomes more notable in a group. For Group 6 transition elements, the relative oxidation power of the M^{6+} oxidation state is quite pronounced (Cr > Mo > W) and reaches its minimum at the heaviest element tungsten. The formation of $[CrF_6]$ requires a fluorine pressure of 200–300 atm, and reduction of this pressure causes the dissociation of the compound to $[CrF_5]$ and F_2, even at temperatures as low as −100 °C. The complex $[MoCl_6]$ is similarily unstable with respect to the formation of $[MoCl_5]$ and Cl_2.[13] For tungsten, $[WX_6]$ complexes are stable with respect to decomposition of the metal halide for X = F, Cl, and Br. Compounds of the type $[MX_6]$ of hexavalent tungsten with monoanionic carbon, nitrogen, or oxygen ligands are also well known, such as the homoleptic compounds $[WMe_6]$,[14] $[W(NMe_2)_6]$,[15] $[W(OMe)_6]$,[16] and $[W(OPh)_6]$.[17]

For the lighter congener molybdenum, hexavalent complexes $[MX_6]$ with monoanionic carbon, nitrogen, oxygen, or halide ligands seem only to be sufficiently stable for the element with the highest electronegativity, that is, fluoride, and for good σ or σ/π donor ligands, as in $[Mo(NMe_2)_6]$[18] or $[MoMe_6]$.[19] These ligands reduce the electron deficiency of the metal in its highest formal oxidation state. Electrochemical studies on octahedral molybdenum and tungsten chlorides, chloride oxides, and chloride nitrides have shown that there are systematic differences in the electrode potentials of molybdenum and tungsten redox couples and that the relative stability of the higher oxidation states is directly linked to the donor properties of the ligands.[20] For the hexachlorometalate system, the electrochemically reversible reduction step for $[MCl_6]^{0/1-}$ (d^0/d^1) has been observed at 1.59 V for M = W and at 2.20 V for M = Mo.[20, 21] The high reducing power of $[MoCl_6]$—the d^0/d^1 redox step for the fluoride system $[MoF_6]^{0/1-}$ has been observed at 2.08 V—might be the reason for the experimental inaccessibility of molybdenum hexachloride $[MoCl_6]$.[21–23]

In contrast to the lack of molybdenum(VI) hexachlorides, a few molybdenum(VI) hexaalkoxides have been found so far. One of them, $[Mo(OMe)_6]$, has been prepared as a thermally unstable and moisture-sensitive compound from the co-condensation of $[MoF_6]$ and $[Si(OMe)_4]$.[24] For the synthesis of monomeric molybdenum hexaalkoxides, there is, in addition to the instability of the +6 oxidation state, another problem to overcome, that is, the inherent instability of an $[Mo(OR)_2]$ unit with respect to ether elimination or hydrolysis to give the very stable $[Mo({=}O)]$ functionality.[24a] The majority of molybdenum(VI) complexes are stabilized by multiple bonded ligands, and $[Mo({=}E)]$ or $[Mo({=}E)_2]$ (E = O, S, NR) entities are very common in molybdenum(VI) chemistry. Complexes of the general formula $[Mo({=}O)X_4]$ or $[Mo({=}O)_2X_2]$, in which X is an alkoxide or halide ligand, are usually very stable compounds.[25] One way to stabilize alkoxides with respect to decomposition of $[M(OR)_6]$ is the use of multidendate ligands. Following this strategy, tris(glycolato) and tris(pinakolato) molybdenum(VI) complexes $[Mo(OCR_2CR_2O)_3]$ (R = H, Me) have been synthesized by Dehnicke and co-workers.[26] In this sense, the synthesis of $[(CaxO_4)\{CaxO_2(OH)_2\}Mo]$ (**1a**) is a continuation of this synthetic strategy and compound **1a** is one of the few molybdenum(VI) hexaalkoxides reported so far. Thus, we were very interested to confirm our analytical data by a structural investigation of this compound. Crystals of **1a** in the form of thin plates were obtained from layering saturated solutions of **1a** in hexane with acetonitrile. The molecular structure of **1a**, though not crystallographically satisfactory, is depicted in Figure 1 because of the above-mentioned significance of this complex and as a confirmation of our structural proposal given in Equation (1). However, to clarify the composition of the complexes **1** beyond any doubt, we

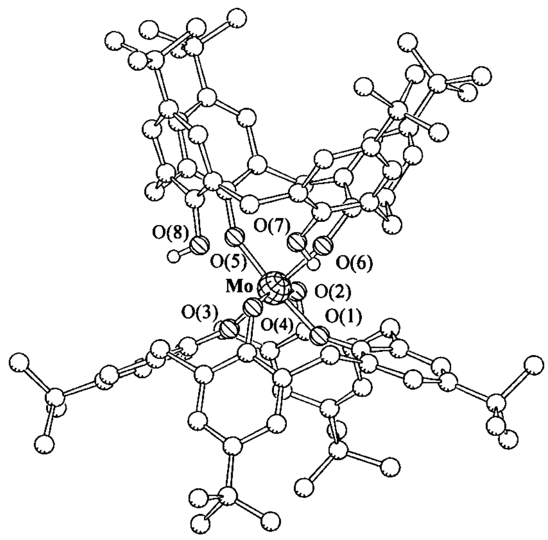

Figure 1. Schakal plot of the molecular structure of $[(CaxO_4)\{CaxO_2(OH)_2\}Mo]$ (**1a**) in **1a** · 4.5 MeCN. The disorder of the *t*Bu groups is not resolved in the drawing, and the hydrogen atoms are omitted for clarity. The hydrogen atoms at O(7) and O(8) were calculated in idealized positions. Selected bond lengths [pm] and angles [°]: Mo–O(1): 190.3(9), Mo–O(2): 193.2(9), Mo–O(3): 185.8(9), Mo–O(4): 190.9(9), Mo–O(5): 187.7(8), Mo–O(6): 194.7(9), O(1)-Mo-O(2): 82.4(3), O(1)-Mo-O(3): 93.4(4), O(1)-Mo-O(4): 83.5(3), O(1)-Mo-O(5): 173.9(4), O(1)-Mo-O(6): 85.9(4), O(2)-Mo-O(3): 82.0(4), O(2)-Mo-O(4): 160.1(3), O(2)-Mo-O(5): 98.9(4), O(2)-Mo-O(6): 95.8(4), O(3)-Mo-O(4): 84.9(4), O(3)-Mo-O(5): 92.7(4), O(3)-Mo-O(6): 177.8(4), O(4)-Mo-O(5): 96.6(4), O(4)-Mo-O(6): 97.1(4), O(5)-Mo-O(6): 88.0(4), C(10)-O(1)-Mo: 150.6(8), C(20)-O(2)-Mo: 125.2(9), C(30)-O(3)-Mo: 162.5(8), C(40)-O(4)-Mo: 124.4(7), C(50)-O(5)-Mo: 152.8(7), C(60)-O(6)-Mo: 151.2(8).

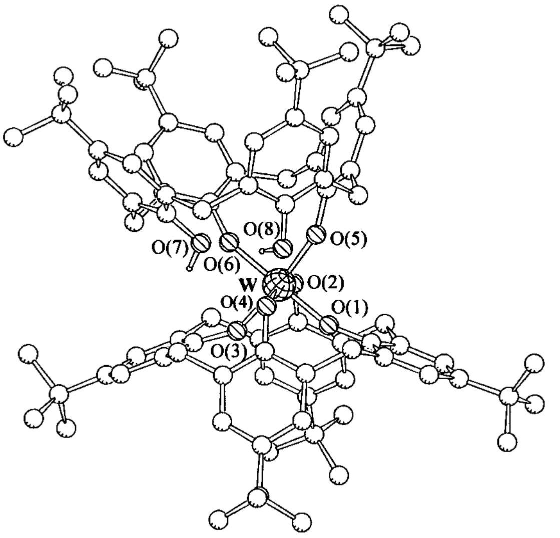

Figure 2. Schakal plot of the molecular structure of $[(CaxO_4)\{CaxO_2(OH)_2\}W]$ (**1b**) in **1b**$\cdot$3MeCN. The disorder of the *t*Bu groups are not resolved in the drawing, and the hydrogen atoms are omitted for clarity. The hydrogen atoms at O(7) and O(8) were calculated in idealized positions. Selected bond lengths [pm] and angles [°]: W–O(1): 186.3(3), W–O(2): 193.7(3), W–O(3): 188.5(3), W–O(4): 191.8(3), W–O(5): 188.7(3), W–O(6): 191.6(3), O(1)-W-O(2): 83.45(13), O(1)-W-O(3): 92.97(13), O(1)-W-O(4): 84.24(13), O(1)-W-O(5): 92.85(13), O(1)-W-O(6):177.68(14), O(2)-W-O(4): 161.79(12), O(3)-W-O(4): 83.60(12), O(3)-W-O(6): 87.18(13), C(10)-O(1)-W: 162.6(3), C(20)-O(2)-W: 124.6(3), C(30)-O(3)-W: 148.7(3), C(40)-O(4)-W: 124.1(3), C(50)-O(5)-W: 152.2(3), C(60)-O(6)-W: 151.6(3).

decided to resolve the structure of tungsten analogue as well. The X-ray crystal structure of the isostructural complex **1b** is given in Figure 2.

Both complexes **1a** and **1b** crystallize with acetonitrile in the unit cell. The metal atoms in these compounds are surrounded by six phenoxide oxygen atoms of two calix[4]arene ligands. In each case, one of the macrocyclic ligands is fourfold coordinated to the metal atom through the oxygen atoms O(1) to O(4), the second calix[4]arene ligand is twofold coordinated, with O(5) and O(6) attached to the metal center. The metal oxygen bond lengths of 186.3(3) – 193.7(3) pm in the case of the tungsten compound and 185.8(9) – 194.7(9) pm for the molybdenum complex are in a range that is observed for comparable compounds like $[CaxO_4WCl_2]$[6a], $[CaxO_4W(OPh)_2]$,[6b] or $[Mo(OCR_2CR_2O)_3]$ (R = H, Me).[26] The basis of the resulting distorted octahedron is best described by the oxygen atoms O(1), O(3), O(5), and O(6). The sum of the O-M-O angles to neighboring oxygen atoms in the basal plane of **1b** is 360.06°; in the case of the molybdenum compound **1a** this sum is exactly 360°. In **1b**, the O-W-O angles to neighboring oxygen atoms are enlarged to some degree at O(1), 92.97(13)° for O(1)-W-O(3) and 92.85(13)° for O(1)-W-O(5), as compared with 87.18(13)° for O(3)-W-O(6) and 87.06° for O(5)-W-O(6). The same effect can be observed for the angles at O(3) in **1a**. This distortion might be due to steric interactions or to favorable π-bonding effects in the molecule, because the W–O(1) and Mo–O(3) bond lengths of 186.3(3) and 185.8(9) pm, respectively, are the shortest metal – oxygen interactions in the molecules, and the bond angles at the coordinated oxygen atoms W-O(1)-C and Mo-O(3)-C of 162.6(3)° and 162.5(8)°, respectively, are the largest M–O–C angles observed. The M–O(2) and M–O(4) vectors form the heavily distorted axis of the octahedron, as demonstrated with an angle O(2)-W-O(4) of 161.79(12)° and O(2)-Mo-O(4) of 160.1(3)°. The metal oxygen bond lengths of 193.7(3) and 191.8(3) pm for W–O(2) and W–O(3), respectively, as well as the bond lengths of 193.2(9) and 194.7(9) pm for Mo–O(2) and Mo–O(6), respectively, are the largest observed in **1a** and **1b**, whereas the angles W-O(2)-C(20) 124.6(3)°, W-O(4)-C(40) 124.1(3)°, Mo-O(2)-C(20) 125.2(9)°, and Mo-O(4)-C(40) 124.4(7)° are the smallest in these molecules. Thus, the calixarene rings of O(1) to O(4) define an *elliptical cone* section for the κ^4 calix[4]arene ligand.

For the second product of the reaction shown in Equation (1), we were able to isolate crystals which at least clarify the connectivity of the reaction product in the case of the molybdenum compound **2a**. Yellow needles of the composition $(HNEt_3)_2[(CaxO_4)_2Mo_2H]\cdot Cl\cdot 4C_7H_8\cdot MeCN$ can be obtained from concentrated solutions of the crude reaction product in toluene/acetonitrile (10:1). The structure of the central $(HNEt_3)_2[(CaxO_4)_2Mo_2H]^-Cl^-$ unit is shown in Figure 3. This compound may be regarded as the HCl adduct of **2a** and can be nicely compared with $(H_2NMe_2)_2[(CaxO_4)_2Mo_2]\cdot 4py$ or $[(CaxO_4)_2Mo_2H_2]\cdot xC_6H_6$ reported by Chisholm and co-workers recently.[7g] However, in contrast to their work we were not able to spectroscopically locate OH protons in any of our several isolated dinuclear species. Therefore, we propose compounds of the formula $(HNEt_3)_2[(CaxO_4)_2M_2]$

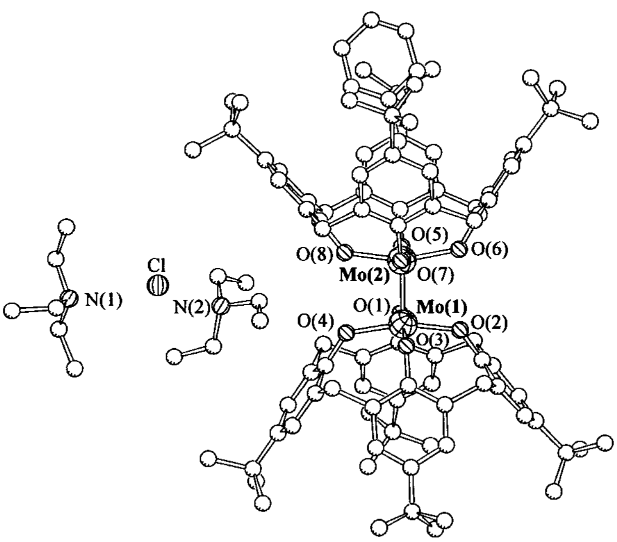

Figure 3. Schakal plot of the molecular structure of $(HNEt_3)_2[(CaxO_4)_2Mo_2H]\cdot Cl$ (**2a·HCl**) in **2a**$\cdot$HCl$\cdot 4C_7H_8\cdot$MeCN. The disorder of the *t*Bu groups is not resolved in the drawing, and the hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Mo(1)–Mo(2): 224.1(1), Mo(1)–O(1): 209.4(8), Mo(1)–O(2): 196.0(7), Mo(1)–O(3): 195.5(8), Mo(1)–O(4): 195.7(7), Mo(2)–O(5): 211.4(8), Mo(2)–O(6): 196.5(7), Mo(2)–O(7): 195.6(7), Mo(2)–O(8): 196.2(7), O(1)-Mo(1)-O(2): 85.3(3), O(2)-Mo(1)-O(3): 92.4(3), O(3)-Mo(1)-O(4): 93.0(3), O(1)-Mo(1)-O(4): 85.2(3), O(5)-Mo(2)-O(6): 85.8(3), O(6)-Mo(2)-O(7): 93.3(3), O(7)-Mo(2)-O(8): 93.7(3), O(5)-Mo(2)-O(8): 83.3(3), O(1)-Mo(1)-Mo(2): 91.3(2), O(2)-Mo(1)-Mo(2): 98.9(2), O(3)-Mo(1)-Mo(2): 101.6(2), O(4)-Mo(1)-Mo(2): 98.4(2), O(5)-Mo(2)-Mo(1): 91.8(2), O(6)-Mo(2)-Mo(1): 99.1(2), O(7)-Mo(2)-Mo(1): 100.5(2), O(8)-Mo(2)-Mo(1): 97.8(2).

(**2**)—in accordance with spectroscopical and analytical data—as the product of the reaction in Equation (1). The result of the X-ray crystal structure analysis confirms the dumbbell-like structure of **2a**. The molybdenum–molybdenum bond length of 224.1(1) pm is in accordance with a triple bond and compares well with the bond lengths of 222.6(1), 222.6(6), and 221.4(7) pm in Chisholm's compounds. Both calix[4]arene ligands are terminally coordinated to the central $[Mo{\equiv}Mo]^{6+}$ core. The molybdenum–oxygen bond lengths to O(1) of 209.4(8) pm and O(5) of 211.4(8) pm (positioned *cis* to each other) are exceptionally long relative to other molybdenum–oxygen bond lengths in the compound, which are in the range 195.5(8)–196.5(7) pm. This elongation suggests some bridging hydrogen interaction O(1)-H-O(5), but we were unable to locate a hydrogen atom between these oxygen atoms required for charge balance. The distances between the nitrogen and chlorine atoms are 3.02 and 3.03 pm for N(1)–Cl and N(2)–Cl, respectively.

Currently, we have no detailed knowledge for the mechanism of reaction in Equation (1). Independent of the relative amount of calix[4]arene and metal chloride used in the reaction, we observe both reaction products. Currently, we propose a reaction intermediate of the type d^2-$(HNEt_3)[CaxO_4MCl]$, which disproportionates to $(HNEt_3)_2[(CaxO_4)_2M_2]$ and $[CaxO_4MCl_2]$. We were unable to isolate any compound of the composition d^2-$(HNEt_3)[CaxO_4MCl]$[33] or $[CaxO_4MCl_2]$ so far from these reactions, but compounds of the type $[CaxO_4MCl_2]$ (**4**) (see below) react cleanly with calix[4]arene to yield **1** under the reaction conditions given.

We favor this mechanistic pathway with the inclusion of intermediates of the type d^2-$(HNEt_3)[CaxO_4MCl]$ and $[(CaxO_4)_2MCl_2]$, because in one case we could isolate red crystals of a dinuclear chloride containing side product $[(CaxO_4W)\{\kappa^2(O)\text{-}\kappa^1(O)\text{-}CaxO_3(OH)\}(CaxO_4WCl)]$ (**3**), besides the compounds **1b** and **2b**, from the reaction of the tungsten complex $[WCl_4(SEt_2)_2]$. The result of the X-ray structure analysis of this compound is shown in Figure 4.

The dinuclear compound **3** is formally the condensation product of the bis(calixarene)compound **1b** and the calixarene tungsten dichloride $[CaxO_4WCl_2]$ (**4b**). The bonding parameters at W(1) in compound **3** are almost identical to those found in $[(CaxO_4)\{CaxO_2(OH)_2\}W]$ (**1b**), and the geometrical data at W(2) compare well with those found for **4b**.[6a] The W(2)–O and W(2)–Cl bond lengths are on average slightly longer than the corresponding bond lengths found for **4b**. Both complex fragments at W(1) and W(2) are connected through a bridging calix[4]arene ligand, which forms two bonds to W(1) through O(6) and O(5) and one bond to W(2) through O(7). The W(2)–O(7) bond length of 188.9(9) pm is unexceptional. Further HCl cleavage to give a symmetrically calix[4]arene-bridged molecule of the type $[(CaxO_4W)_2\{\kappa^2(O)\text{-}\kappa^2(O)\text{-}Cax\}]$ seems to be unfavorable for sterical reasons.

During our investigations we became interested in the synthesis and characterization of calix[4]arene molybdenum dichloride **4a** for several reasons. First of all, it was of interest to us to know whether this complex reacts with calix[4]arene in the presence of triethylamine to give **1a** or not. Beyond that, this compound seems to be a useful starting material to enter calix[4]arene molybdenum chemistry. Finally, there might be some more general interest in this compound, because it would be the first fully characterized compound of the type $[MoCl_x(OR)_{6-x}]$ in the long history of molybdenum alkoxide chemistry (vide supra).[27] For the heavier congener tungsten, for example, each member of the family of compounds of the type $[WCl_x(OR)_{6-x}]$ is known.[28]

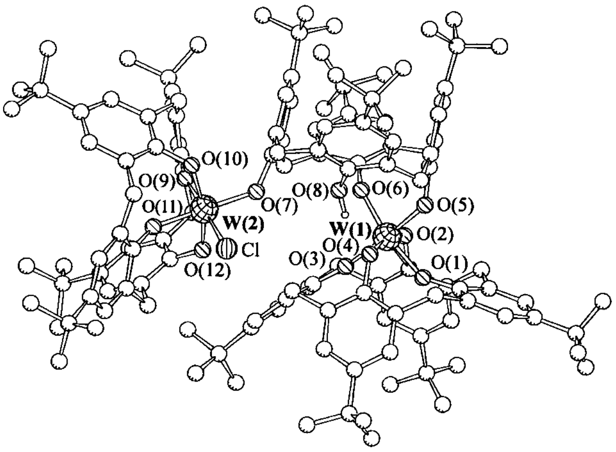

Figure 4. Schakal plot of the molecular structure of $[CaxO_4W\{\kappa^2(O)\text{-}\kappa^1(O)\text{-}CaxO_3(OH)\}(CaxO_4WCl)]$ (**3**) in **3** · 3 MeCN. The disorder of the *t*Bu groups is not resolved in the drawing, and the hydrogen atoms are omitted for clarity. The hydrogen atom at O(8) was calculated in an idealized position. Selected bond lengths [pm] and angles [°]: W(1)–O(1): 187.3(9), W(1)–O(2): 193.6(9), W(1)–O(3): 185.3(10), W(1)–O(4): 194.1(9), W(1)–O(5): 189.6(10), W(1)–O(6): 187.7(10), W(2)–O(7): 188.9(9), W(2)–O(9): 187.1(9), W(2)–O(10): 191.8(9), W(2)–O(11): 189.0(9), W(2)–O(12): 190.9(9), W(2)–Cl: 233.8(3), O(1)-W(1)-O(2): 83.5(4), O(1)-W(1)-O(3): 96.4(4), O(1)-W(1)-O(4): 84.1(4), O(1)-W(1)-O(5): 87.4(4), O(1)-W(1)-O(6): 166.4(4), O(2)-W(1)-O(3): 85.5(4), O(2)-W(1)-O(4): 162.7(4), O(2)-W(1)-O(5): 102.6(4), O(2)-W(1)-O(6): 87.2(4), O(3)-W(1)-O(4): 84.1(4), O(3)-W(1)-O(5): 171.5(4), O(3)-W(1)-O(6): 92.7(4), O(4)-W(1)-O(5): 88.8(4), O(4)-W(1)-O(6): 107.0(4), O(5)-W(1)-O(6): 85.0(4), O(7)-W(2)-O(9): 93.7(4), O(7)-W(2)-O(10): 91.2(4), O(7)-W(2)-O(11): 171.5(4), O(7)-W(2)-O(12): 100.7(4), O(9)-W(2)-O(10): 83.6(4), O(9)-W(2)-O(11): 93.3(4), O(9)-W(2)-O(12): 84.8(4), O(10)-W(2)-O(11): 84.6(4), O(10)-W(2)-O(12): 163.9(4), O(11)-W(2)-O(12): 84.9(4), O(7)-W(2)-Cl: 87.1(3), O(9)-W(2)-Cl: 179.1(3), O(10)-W(2)-Cl: 96.8(3), O(11)-W(2)-Cl: 86.0(3), O(12)-W(2)-Cl: 94.6(3), C(10)-O(1)-W(1): 147.8(10), C(20)-O(2)-W(1): 123.4(8), C(30)-O(3)-W(1): 173.6(9), C(40)-O(4)-W(1): 123.5(7), C(50)-O(5)-W(1): 136.8(9), C(60)-O(6)-W(1): 139.5(9), C(70)-O(7)-W(2): 132.0(8), C(90)-O(9)-W(2): 166.7(9), C(100)-O(10)-W(2): 125.6(8), C(110)-O(11)-W(2): 144.5(9), C(120)-O(12)-W(2): 123.9(8).

Compound **1a** reacts with two equivalents HCl to give the first isolated and fully characterized molybdenum(VI) chloro phenoxide $[CaxO_4MoCl_2]$ (**4a**). The molecular structure of **4a** in the solid state has been determined by X-ray diffraction, see Figure 5.

The central atom in $[CaxO_4MoCl_2]$ **4a** is sixfold coordinated by four oxygen atoms of the calix[4]arene ligand and two chlorine atoms, which are in mutual *cis* positions. As a result of this, two phenoxide rings, those at O(1) and O(3), are pushed away from the macrocycle to define an *elliptical cone* section for the calix[4]arene ligand. Similar distortions were found in comparable compounds like $[CaxO_4WCl_2]$[6a] or $[CaxO_4W(OPh)_2]$.[6b] The molybdenum atom lies exactly in the best plane defined by the atoms Cl(1), Cl(2), O(2), and O(4), which describe the basis of an distorted octahedron around the central atom. The angles between the vectors

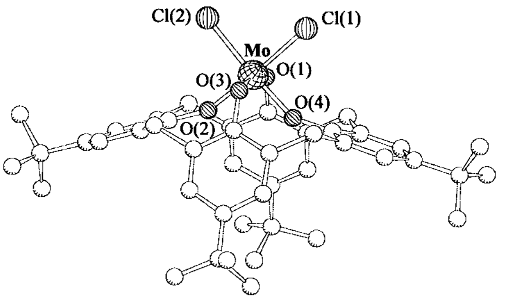

Figure 5. Schakal plot of the molecular structure of $[CaxO_4MoCl_2]$ (**4a**) in **4a**·4MeCN. The disorder of the *t*Bu groups is not resolved in the drawing, and the hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Mo−Cl(1): 233.6(1), Mo−Cl(2): 235.6(1), Mo−O(1): 189.6(2), Mo−O(2): 187.2(2), Mo−O(3): 190.9(2), Mo−O(4): 187.3(2), Cl(1)-Mo-Cl(2): 87.63(4), O(1)-Mo-Cl(1): 98.11(7), O(2)-Mo-Cl(1): 175.94(6), O(3)-Mo-Cl(1): 94.23(7), O(4)-Mo-Cl(1): 88.76(8), O(1)-Mo-Cl(2): 93.88(7), O(2)-Mo-Cl(2): 89.16(8), O(3)-Mo-Cl(2): 98.46(7), O(4)-Mo-Cl(2): 175.45(8), O(1)-Mo-O(2): 84.59(9), O(1)-Mo-O(3): 162.88(9), O(1)-Mo-O(4): 83.88(9), O(2)-Mo-O(3): 83.78(9), O(2)-Mo-O(4): 94.56(10), O(3)-Mo-O(4): 84.56(9), C(10)-O(1)-Mo: 125.71(19), C(20)-O(2)-Mo: 156.9(2), C(30)-O(3)-Mo: 124.79(15), C(40)-O(4)-Mo: 151.6(2).

Mo−O(1) and Mo−O(3) and this plane are 81.15(7)° and 81.45(7)°, respectively. The Mo−Cl bond lengths of 233.6(1) and 235.6(1) pm are in accordance with other molybdenum chlorides.[29] The molybdenum–oxygen bond lengths in **4a** are shorter that those found for the d^0 molybdenum calix[4]arene imido complexes (approximately 194.0 pm),[4b] in which instead of two chlorine atoms the imido ligand, an excellent σ,π-donor ligand, is mounted on the $[CaxO_4Mo]$ moiety. In **4a**, the Mo−O bond lengths of 189.6(2) pm to O(1) and 190.9(2) pm to O(3) are significantly longer than those to the oxygen atoms O(2) and O(4), *trans* to the chlorine atoms, of 187.2(2) pm and 187.3(2) pm, respectively. This might be attributed to the worse donor properties of the chlorine ligand relative to a phenoxide ligand. According to NMR spectroscopy, a similar structure with a pseudo-C_{2v} arrangement of **4a** as observed in the solid state can also be found in solution.

In summary, the unusual reaction of the molybdenum(IV) and tungsten(IV) chlorides $[MCl_4L_2]$ with *p*-*t*Bu-calix[4]arene $Cax(OH)_4$ in the presence of triethylamine leads to mononuclear molybdenum(VI) and tungsten(VI) calix[4]arene complexes $[(CaxO_4)\{CaxO_2(OH)_2\}M]$ (**1**) and binuclear molybdenum(III) and tungsten(III) calix[4]arene complexes $(HNEt_3)_2[(CaxO_4)_2M_2]$ (**2**). Compound **1a** represents one of the few examples of a molybdenum(VI) hexaalkoxide complex of the type $[Mo(OR)_6]$. We propose for the mechanism of this unusual reaction a pathway via calix[4]arene molybdenum and tungsten chlorine intermediates, that is, $(HNEt_3)[CaxO_4MCl]$ and $[CaxO_4MCl_2]$. The isolation and characterization of the side product $[(CaxO_4W)\{\kappa^2(O)\text{-}\kappa^1(O)\text{-}CaxO_3(OH)\}(CaxO_4WCl)]$ (**3**), as well as the observation that the dichlorides $[CaxO_4MoCl_2]$ react cleanly with calix[4]arene under the reaction conditions reported, support the idea of the intermediacy of these chloro-containing species. The reaction of **1a** with HCl provides the novel compound $[CaxO_4MoCl_2]$ (**4a**), the first well-defined examples of a mixed molybdenum(VI) alkoxide halide compound of the general formula $[MoCl_x(OR)_{6-x}]$ in good yield. Our further interest in this chemistry is to isolate d^2-calix[4]arene compounds, to improve the synthesis of **4a** and to explore the reactivity of these compounds.

Experimental Section

General: All reactions and subsequent manipulations involving organometallic reagents were performed under argon atmosphere by using standard Schlenk techniques as reported previously.[4b] Elemental analyses were performed in the microanalytical laboratory of the author's department. NMR spectra were recorded on a Bruker AC250 at 298 K. ^{13}C NMR spectra are broad-band proton decoupled ($^{13}C\{^1H\}$). Standard DEPT-135 experiments were recorded to distinguish $-CH_3$ and $-CH$ type carbons from $-C$ or $-CH_2$ type carbons in the ^{13}C NMR spectrum; NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane. Coupling constants are quoted in Hertz. Residual solvent peaks used as internal standards were as follows: $CDCl_3$ $\delta = 7.24$ (^1H), C_6D_6 $\delta = 7.15$ (^1H) or natural-abundance carbon signal at $\delta = 77.0$ for $CDCl_3$ and $\delta = 128.0$ for C_6D_6. Infrared spectra were recorded as KBr pellets on a Bruker IFS28 and are reported in cm^{-1}. P-*t*Bu-calix[4]arene[30] and $[MCl_4L_2]$ (M = Mo, $L = Et_2S$, Et_2O; W, $L = Et_2S$)[11, 12] were prepared as described in the literature, all other reagents were purchased from commercial sources and purified by standard techniques.

$[(CaxO_4)\{CaxO_2(OH)_2\}Mo]$ (1a) and $(HNEt_3)_2[(CaxO_4)_2Mo_2]$ (2a): NEt_3 (1.12 mL, 8.10 mmol) was added to a reaction mixture of $[MoCl_4L_2]$ (0.722 g, $L = SEt_2$; 0.670 g, $L = OEt_2$, 1.74 mmol) and $Cax(OH)_4$ (1.5 g, 2.31 mmol) in toluene (60 mL). The solution was stirred for 8 h at 100 °C, all volatiles were removed in vacuo, and the residue was suspended in hexane (60 mL) to give a pale brown precipitate in a purple solution. After filtration, the mother liquor was evaporated in vacuo to give compound **1a** as a purple powder (0.352 g, 44%, $L = SEt_2$; 0.385 g, 48%, $L = OEt_2$). Crystals of **1a** were obtained as thin plates from layering concentrated hexane solutions of **1a** with acetonitrile. The hexane insoluble residue was extracted in hot toluene (60 mL) and filtered through a pad of Celite. Cooling the toluene solution gave yellow brown needles of **2a.** Traces of ammonium chloride were removed by sublimation in vacuo. Yield: 0.117 g (12%); $L = SEt_2$; 0.176 g (18%; $L = OEt_2$).

$[(CaxO_4)\{CaxO_2(OH)_2\}Mo]$ (1a): ^1H NMR (C_6D_6): $\delta = 0.78$ (s, 9H; $C(CH_3)_3$), 0.83 (s, 9H; $C(CH_3)_3$), 1.07 (s, 18H; $C(CH_3)_3$), 1.12 (s, 18H; $C(CH_3)_3$), 1.30 (s, 18H; $C(CH_3)_3$), 3.16 (d, $^2J(H,H) = 13.7$ Hz, 2H; CH_2), 3.36 (d, $^2J(H,H) = 13.7$ Hz, 2H; CH_2), 3.41–3.46 (2d, 2H; CH_2), 3.65 (d, $^2J(H,H) = 14.0$ Hz, 2H; CH_2), 4.43 (d, $^2J(H,H) = 13.8$ Hz, 1H; CH_2), 4.76 (d, $^2J(H,H) = 13.5$ Hz, 2H; CH_2), 4.94 (d, $^2J(H,H) = 13.5$ Hz, 2H; CH_2), 5.83 (d, $^2J(H,H) = 13.7$ Hz, 2H; CH_2), 6.92 (s, 2H; aromatic H), 6.97 (d, $^4J(H,H) = 2.3$ Hz, 2H; aromatic H), 7.05 (d, $^4J(H,H) = 2.5$ Hz, 2H; aromatic H), 7.08 (d, $^4J(H,H) = 2.4$ Hz, 4H; aromatic H), 7.13 (s, 4H; aromatic H), 7.37 (d, $^4J(H,H) = 2.0$ Hz, 2H; aromatic H), 7.55 (d, $^2J(H,H) = 13.9$ Hz, 1H; CH_2), 8.32 (s, 2H; OH); ^1H NMR ($CDCl_3$): $\delta = 1.12$ (s, 18H; $C(CH_3)_3$), 1.17 (s, 18H; $C(CH_3)_3$), 1.18 (s, 9H; $C(CH_3)_3$), 1.21 (s, 9H; $C(CH_3)_3$), 1.38 (s, 18H; $C(CH_3)_3$), 3.10–3.27 (3d, 5H; CH_2), 3.42 (d, $^2J(H,H) = 13.9$ Hz, 1H; CH_2), 3.44 (d, $^2J(H,H) = 14.0$ Hz, 2H; CH_2), 4.02 (d, $^2J(H,H) = 13.8$ Hz, 1H; CH_2), 4.26 (d, $^2J(H,H) = 13.9$ Hz, 2H; CH_2), 4.34 (d, $^2J(H,H) = 13.7$ Hz, 2H; CH_2), 5.11 (d, $^2J(H,H) = 14.0$ Hz, 2H; CH_2), 6.59 (d, $^2J(H,H) = 14.1$ Hz, 1H; CH_2), 6.85 (d, $^4J(H,H) = 2.3$ Hz, 2H; aromatic H), 6.91 (d, $^4J(H,H) = 2.4$ Hz, 4H; aromatic H), 6.97 (d, $^4J(H,H) = 2.4$ Hz, 2H; aromatic H), 7.06 (s, 2H; aromatic H), 7.12 (s, 2H; aromatic H), 7.15 (d, $^4J(H,H) = 1.9$ Hz, 2H; aromatic H), 7.25 (d, $^4J(H,H) = 1.9$ Hz, 2H; aromatic H), 7.56 (s, 2H; OH); ^{13}C NMR ($CDCl_3$): $\delta = 31.45$, 31.56, 31.64, 31.81, 31.95 (s, $C(CH_3)_3$)), 32.79 (s, $C(CH_3)_3$)), 33.41 (s, CH_2), 34.01, 34.24, 34.31, 34.90 (s, $C(CH_3)_3$)), 35.58, 35.87, 36.34 (s, CH_2), 124.02, 124.28, 125.07, 125.16, 125.84, 126.09, 126.73, 127.04 (s, aromatic CH), 128.05, 128.21, 130.64, 131.04, 131.81, 136.81, 137.11, 137.48, 142.79, 146.51, 147.04, 147.27, 147.57, 148.98, 159.96, 163.06, 167.43, 168.22 (s, aromatic C); MS (70 eV, EI): m/z (%): 1388 (5) $[M]^+$, 1375 (1) $[M - CH_3]^+$; IR: $\tilde{\nu} = 3442$ cm^{-1} (O−H); elemental analysis calcd (%) for $C_{88}H_{106}O_8Mo$ (1388): C 76.16, H 7.70; found C 76.46, H 7.99.

$(HNEt_3)_2[(CaxO_4)_2Mo_2]$ (2a): ^1H NMR ($CDCl_3$): $\delta = 1.17$ (s, 36H; $C(CH_3)_3$), 1.35 (t, $^3J(H,H) = 7.2$ Hz, 9H; NCH_2CH_3), 2.96 (q, $^3J(H,H) = 7.3$ Hz, 6H; NCH_2CH_3), 3.26 (d, $^2J(H,H) = 11.9$ Hz, 4H; CH_2), 4.94 (d,

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^2J(H,H) = 11.8 Hz, 4H; CH_2), 7.00 (s, 8H; aromatic H); ^{13}C NMR ($CDCl_3$): δ = 9.26 (s, NCH_2CH_3), 31.66 (s, C(CH_3)$_3$), 34.03 (s, CH_2), 34.12 (s, C(CH_3)$_3$), 46.22 (s, N$CH_2$$CH_3$), 124.71 (s, aromatic CH), 131.74, 143.61, 154.05 (s, aromatic C); MS (70 eV, EI): m/z (%): 1484 (0.2) [M]$^+$; elemental analysis calcd (%) for $C_{100}H_{136}O_8Mo_2N_2$ (1686): C 71.26, H 8.08, N 1.66; found C 71.05, H 7.98, N 1.62.

[(CaxO$_4$){CaxO$_2$(OH)$_2$}W] (1b) and (HNEt$_3$)$_2$[(CaxO$_4$)$_2$W$_2$] (2b). Excess NEt_3 (1.12 mL, 8.10 mmol) was added to a reaction mixture of $WCl_4(SEt_2)_2$ (0.879 g, 1.74 mmol) and Cax(OH)$_4$ (1.5 g, 2.31 mmol) in toluene (60 mL). The solution was stirred for 8 h at 100 °C, all volatiles were removed in vacuo, and the residue was suspended in hexane (60 mL) to give a pale green precipitate in a red solution. After filtration, the mother liquor was evaporated in vacuo to give compound **1b** as a red powder (0.810 g, 95%). Crystals of **1b** were obtained as thin plates from layering concentrated hexane solutions of **1b** with acetonitrile. The hexane insoluble residue was extracted in hot THF (60 mL) and filtered through a pad of celite. Traces of ammonium chloride were removed by sublimation in vacuo. Yield: 0.571 g 53%.

[(CaxO$_4$){CaxO$_2$(OH)$_2$}W] (1b): ^{1}H NMR (C_6D_6): δ = 0.80 (s, 9H; C(CH_3)$_3$), 0.84 (s, 9H; C(CH_3)$_3$), 1.08 (s, 18H; C(CH_3)$_3$), 1.12 (s, 18H; C(CH_3)$_3$), 1.31 (s, 18H; C(CH_3)$_3$), 3.23 (d, ^2J(H,H) = 13.7 Hz, 2H; CH_2), 3.38 (d, ^2J(H,H) = 14.0 Hz, 2H; CH_2), 3.49 (d, ^2J(H,H) = 14.0 Hz, 1H; CH_2), 3.52 (d, ^2J(H,H) = 14.1 Hz, 1H; CH_2), 3.71 (d, ^2J(H,H) = 13.8 Hz, 2H; CH_2), 4.32 (d, ^2J(H,H) = 13.9 Hz, 1H; CH_2), 4.83 (d, ^2J(H,H) = 13.4 Hz, 2H; CH_2), 4.91 (d, ^2J(H,H) = 13.8 Hz, 2H; CH_2), 5.78 (d, ^2J(H,H) = 13.5 Hz, 2H; CH_2), 6.95 (s, 2H; aromatic H), 6.96 (d, ^4J(H,H) = 2.4 Hz, 2H; aromatic H), 7.06 (d, ^4J(H,H) = 2.1 Hz, 4H; aromatic H), 7.10 (s, 4H; aromatic H), 7.12 (s, 4 H aromatic H), 7.28 (d, ^2J(H,H) = 14.0 Hz, 1H; CH_2), 7.41 (d, ^4J(H,H) = 2.1 Hz, 2H; aromatic H), 8.06 (s, 2H; OH); ^{1}H NMR ($CDCl_3$): δ = 1.12 (s, 18H; C(CH_3)$_3$), 1.19 (s, 18H; C(CH_3)$_3$), 1.20 (s, 9H; C(CH_3)$_3$), 1.22 (s, 9H; C(CH_3)$_3$), 1.39 (s, 18H; C(CH_3)$_3$), 3.25–3.36 (3d, 5H; CH_2), 3.44 (d, ^2J(H,H) = 14.0 Hz, 2H; CH_2), 3.53 (d, ^2J(H,H) = 14.0 Hz, 1H; CH_2), 3.95 (d, ^2J(H,H) = 14.1 Hz, 1H; CH_2), 4.21 (d, ^2J(H,H) = 14.4 Hz, 2H; CH_2), 4.44 (d, ^2J(H,H) = 13.7 Hz, 2H; CH_2), 5.03 (d, ^2J(H,H) = 13.9 Hz, 2H; CH_2), 6.49 (d, ^2J(H,H) = 14.0 Hz, 1H; CH_2), 6.87 (d, ^4J(H,H) = 2.3 Hz, 2H; aromatic H), 6.91 (d, ^4J(H,H) = 2.3 Hz, 2H; aromatic H), 7.00 (d, ^4J(H,H) = 2.5 Hz, 2H; aromatic H), 7.06 (d, ^4J(H,H) = 2.5 Hz, 2H; aromatic H), 7.09 (s, 2H; aromatic H), 7.12 (s, 2H; aromatic H), 7.16 (s, 2H; aromatic H), 7.29 (s, 2H; aromatic H), 10.43 (s, 2H; OH); ^{13}C NMR ($CDCl_3$): δ = 31.62, 31.65, 31.78, 31.98, 32.13 (s, C(CH_3)$_3$), 33.41 (s, CH_2), 34.05, 34.23, 34.74 (s, C(CH_3)$_3$), 35.11, 35.36, 36.12 (s, CH_2), 123.82, 124.02, 125.13, 125.29, 126.01, 126.51, 126.83 (s, aromatic CH), 127.37, 128.22, 128.40, 129.22, 130.68, 131.21, 134.84, 135.16, 135.69, 142.81, 146.30, 146.78, 147.12, 149.09, 156.41, 158.43, 161.82, 162.38 (s, aromatic C); IR: (KBr [cm^{-1}]): $\tilde{\nu}$ = 3454 cm^{-1} (O–H); MS (70 eV, EI): m/z (%): 1475 (100) [M]$^+$, 1460 (3) [M – CH_3]$^+$; elemental analysis calcd (%) for $C_{88}H_{106}O_8W$ (1475.65): C 71.63, H 7.24, found C 71.41, H 7.52.

(HNEt$_3$)$_2$[(CaxO$_4$)$_2$W$_2$] (2a): ^{1}H NMR (CD_2Cl_2): δ = 1.13 (s, 36H; C(CH_3)$_3$), 1.22 (t, ^3J(H,H) = 7.3 Hz, 9H; NCH_2CH_3), 2.43 (q, ^3J(H,H) = 7.3 Hz, 12H; N$CH_2$$CH_3$), 3.22 (d, ^2J(H,H) = 11.8 Hz, 4H; CH_2), 4.86 (d, ^2J(H,H) = 11.8 Hz, 4H; CH_2), 6.99 (s, 8H; aromatic H); ^{13}C NMR (CD_2Cl_2): δ = 9.31 (s, CH_3), 31.53 (s, C(CH_3)$_3$), 33.64 (s, C(CH_3)$_3$), 34.01 (s, CH_2), 46.37 (s, CH_2), 124.42 (s, aromatic CH), 132.41, 144.06, 153.34 (s, aromatic C); elemental analysis calcd (%) for $C_{100}H_{136}O_8W_2N_2$ (1860): C 64.52, H 7.31, N 1.51; found C 64.54, H 7.51, N 1.56.

[CaxO$_4$MoCl$_2$] (4a): Two HCl equivalents of a saturated solution of gaseous HCl in diethyl ether was added dropwise to a solution of **1a** (1.39 g, 1.00 mmol) in $CHCl_3$ (60 mL). The mixture was stirred for 8 h, then filtered through a pad of Celite and evaporated to dryness. The dark violet residue was washed with hexane (5 mL), collected, and dried in vacuo (0.472 g, 58%). Crystals of **4a** were obtained by recrystallization from acetonitrile. ^{1}H NMR ($CDCl_3$): δ = 1.19 (s, 18H; C(CH_3)$_3$), 1.38 (s, 18H; C(CH_3)$_3$), 3.42 (d, ^2J(H,H) = 13.9 Hz, 2H; CH_2), 4.71 (d, ^2J(H,H) = 13.8 Hz, 2H; CH_2), 7.07 (s, 4H; aromatic H), 7.29 (s, 4H; aromatic H); ^{13}C NMR ($CDCl_3$): δ = 31.76, 31.89 (s, C(CH_3)$_3$), 34.30 (s, C(CH_3)$_3$), 35.46 (s, CH_2), 124.66, 127.33 (s, aromatic CH), 132.94, 143.87, 149.97, 152.20, 164.06, 172.17 (s, aromatic C); MS (70 eV, EI): m/z (%): 812 (50) [M]$^+$, 797 (7) [M – CH_3]$^+$, 777 (46) [M – Cl]$^+$; elemental analysis calcd (%) for $C_{44}H_{52}O_4MoCl_2$ (812): C 65.11, H 6.46; found C 64.80, H 6.61.

Crystal structure analysis of 1a · 4.5 MeCN: Stoe-IPDS diffractometer (Mo$_{K\alpha}$ radiation), T = 190(2) K; data collection and refinement: SHELXS-97[31] and SHELXL-97[32]; monoclinic, space group $C2$; lattice constants a = 23.557(5), b = 12.381(3), c = 32.851(7) Å, β = 110.90(3)°, V = 8951(3) Å^3, Z = 4, μ(Mo$_{K\alpha}$) = 0.203 mm^{-1}, $2\Theta_{max}$ = 49.8°; 15042 independent reflections measured, of which 10212 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 1.740 and –0.940 e Å^{-3}. 941 parameters (Mo, O, N, C anisotropic except solvent molecules, the positions of the H atoms were calculated for idealized positions); R_1 = 0.1131; wR_2 = 0.2986.

Crystal structure analysis of 1b · 3 MeCN: Stoe-IPDS diffractometer (Mo$_{K\alpha}$ radiation), T = 203(2) K; data collection and refinement: SHELXS-97[32] and SHELXL-97[33]; monoclinic, space group $C2$; lattice constants a = 23.459(5), b = 12.393(3), c = 32.773(7) Å, β = 110.88(3)°, V = 8903(3) Å^3, Z = 4, μ(Mo$_{K\alpha}$) = 1.351 mm^{-1}, $2\Theta_{max}$ = 52.0°; 16270 independent reflections measured, of which 15676 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 2.168 and –0.665 e Å^{-3}. 905 parameters (W, O, N, C anisotropic except solvent molecules, the positions of the H atoms were calculated for idealized positions); R_1 = 0.0335; wR_2 = 0.0984.

Crystal structure analysis of 2a · HCl · 4 C$_7$H$_8$ · MeCN: Stoe-IPDS diffractometer (Mo$_{K\alpha}$ radiation), T = 183(2) K; data collection and refinement: SHELXS-97[31] and SHELXL-97[32]; triclinic, space group $P\bar{1}$; lattice constants a = 17.693(4), b = 19.718(4), c = 22.731(5) Å, α = 79.85(3)°, β = 75.62(3)°, γ = 65.31(3)°, V = 6956(2) Å^3, Z = 2, μ(Mo$_{K\alpha}$) = 0.247 mm^{-1}, $2\Theta_{max}$ = 44.0°; 13521 independent reflections measured, of which 8860 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 1.139 and –0.490 e Å^{-3}. 1162 parameters (Mo, O, N, C anisotropic except solvent molecules, the positions of the H atoms were calculated for idealized positions); R_1 = 0.0985; wR_2 = 0.2868.

Crystal structure analysis of 3 · 3 MeCN: Stoe-STADI IV diffractometer (Mo$_{K\alpha}$ radiation), T = 200(2) K; data collection and refinement: SHELXS-97[31] and SHELXL-97[32]; triclinic, space group $P\bar{1}$; lattice constants a = 17.630(4), b = 17.905(4), c = 24.405(5) Å, α = 73.07(3)°, β = 76.47(3)°, γ = 86.75(3)°, V = 7165(2) Å^3, Z = 2, μ(Mo$_{K\alpha}$) = 1.675 mm^{-1}, $2\Theta_{max}$ = 50.0°; 25223 independent reflections measured, of which 15145 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 1.738 and –1.033 e Å^{-3}. 1372 parameters (W, O, N, C anisotropic except solvent molecules, the positions of the H atoms were calculated for idealized positions); R_1 = 0.0930; wR_2 = 0.2021.

Crystal structure analysis of 4a · 4 MeCN: Stoe-IPDS diffractometer (Mo$_{K\alpha}$ radiation), T = 203(2) K; data collection and refinement: SHELXS-97[31] and SHELXL-97[32]; triclinic, space group $P\bar{1}$; lattice constants a = 12.990(3), b = 13.651(4), c = 15.864(4) Å, α = 81.20(3), β = 78.38(3)°, γ = 66.42(3) , V = 2517.2(9) Å^3, Z = 2, μ(Mo$_{K\alpha}$) = 0.413 mm^{-1}, $2\Theta_{max}$ = 52.0°; 7669 independent reflections measured, of which 6816 were considered observed with $I > 2\sigma(I)$; max./min. residual electronic density 0.720 and –0.665 e Å^{-3}. 524 parameters (Mo, O, N, C anisotropic except solvent molecules, the positions of the H atoms were calculated for idealized positions); R_1 = 0.0442; wR_2 = 0.1168.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144193 to CCDC-144197. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We wish to thank Professor D. Fenske for his continuing support and interest in our work. A donation of metal chlorides of Fa. H. C. Starck GmbH, Goslar, is gratefully acknowledged.

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Received: May 16, 2000 [F2492]