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# The (Calix[4]arene)chloromolybdate(IV) Anion [MoCl(Calix)]$^-$: A Convenient Entry into Molybdenum Calix[4]arene Chemistry

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The complex (HNEt$_3$)[MoCl(NCMe)(Calix)] (**1**), prepared from the reaction of [MoCl$_4$(NCMe)$_2$] with *p-tert*-butylcalix[4]arene, H$_4$Calix, in the presence of triethylamine, has been used as a source of the d$^2$-[Mo(NCMe)(Calix)] fragment. Complex **1** is readily oxidized with PhICl$_2$ to afford the molybdenum(VI) dichloro complex [MoCl$_2$(Calix)] (**2**). Both complexes are a convenient entry point into molybdenum(VI) and molybdenum(IV) calixarene chemistry. The reaction of **1** with trimethylphosphine and pyridine in the presence of catalytic amounts [Ag(OTf)] led to the formation of neutral d$^2$ complexes [Mo(PMe$_3$)(NCMe)(Calix)] (**3**) and [Mo(NC$_5$H$_5$)(NCMe)(Calix)] (**4**). The role of the silver salt in the reaction mixture is presumably the oxidation of the chloromolybdate anion of **1** to give a reactive molybdenum(V) species. The same reactions can also be initiated with ferrocenium cations such as [Cp$_2$Fe](BF$_4$). Without the presence of coordinating ligands, the dimeric complex [{Mo(NCMe)(Calix)}$_2$] (**5**) was isolated. The reaction of **1** with Ph$_2$CN$_2$ led to the formation of a metallahydrazone complex [Mo(N$_2$CPh$_2$)(NCMe)(Calix)] (**6**), in which the diphenyldiazomethane has been formally reduced by two electrons. Molybdenum(VI) complexes were also obtained from reaction of **1** with azobenzene and sodium azide in the presence of catalytic amounts of silver salt. The reaction with azobenzene led under cleavage of the nitrogen nitrogen bond to an imido complex [Mo(NPh)(NCMe)(Calix)] (**7**), whereas the reaction with sodium azide afforded the mononuclear molybdenum(VI) nitrido complex (HNEt$_3$)[MoN(Calix)] (**8**).

## Introduction

In recent years there has been considerable and growing interest in the metal coordination chemistry of calixarenes and calixarene ethers as poly(phenolate) ligands, partly due to the ability to generate reactive metal−ligand fragments in an unusual coordination environment made up of four oxygen donor atoms.[1] This has been the case in organometallic functionalization or in the synthesis and reactivity of reduced, low-valent early transition metals. The d$^2$-[Nb$^{III}$(Calix)] (H$_4$Calix = *p-tert*-butylcalix[4]arene) moiety assists, by way of example, the reduction of dinitrogen and carbon monoxide to nitride and carbide,[2] respectively, and also for the d$^2$-[W$^{IV}$(Calix)] fragment[3] a high reactivity was observed. These d$^2$-[W$^{IV}$(Calix)] and d$^2$-[Nb$^{III}$(Calix)] derivatives do not have a counterpart in molybdenum−calix[4]arene chemistry. Contrary to calix[4]arene tungsten complexes, the chemistry of calix[4]arene-supported complexes of its congener molybdenum is hampered by the unavailability of suitable starting material.[4,5] Calix[4]arene complexes of molybdenum are mainly restricted to nonreactive dimeric compounds such as [Mo$_2$(Calix)$_2$] and [Mo$_2$(Calix)$_2$]$^{2-}$ or oxo, imido, and hydrazido complexes [Mo(E)(Calix)] (E = O, NR, NNR). None of these complexes can serve as

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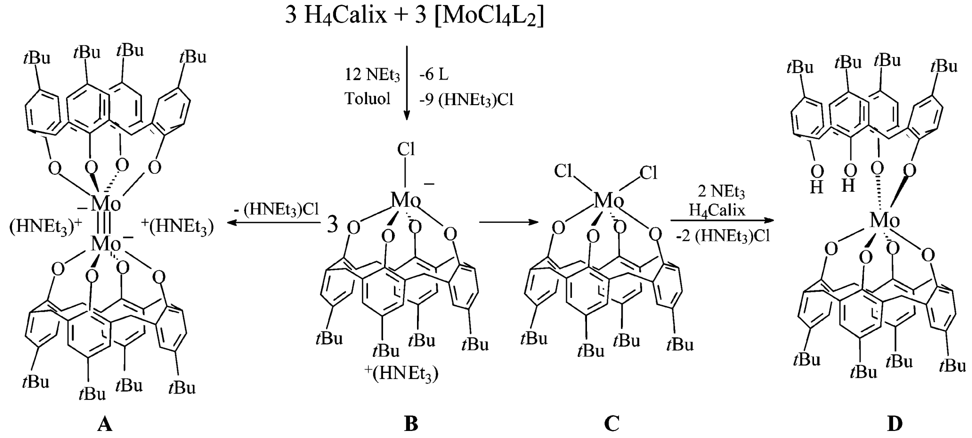
**Scheme 1.** Proposed Mechanism for the Reaction of $[MoCl_4L_2]$ (L = $Et_2S$, $Et_2O$) with *p-tert*-Butylcalix[4]arene in the Presence of Triethylamine

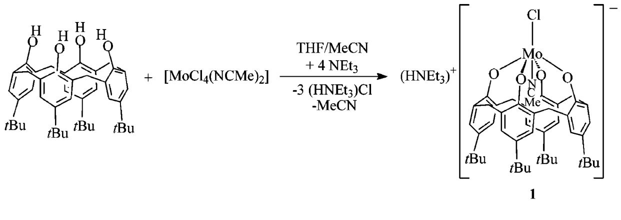


a convenient and general starting material in molybdenum chemistry. Recently, Floriani and co-workers reported the in situ generation of a reactive molybdenum calix[4]arene complex fragment, which presumably contains a $d^2$-[$Mo^{IV}$-(Calix)] moiety, starting from the sodium or lithium salt of calixarene and $[MoCl_4(THF)_2]$, consistent with its reactivity toward alkynes and azobenzene.[5j] In previous contributions we reported the stabilization and isolation of this fragment, which dimerizes without an additional ligands in the coordination sphere.[4] The complex $[Mo(NHMe_2)(NCMe)(Calix)]$ was synthesized starting from $[Mo(NMe_2)_4]$ and *p-tert*-butylcalix[4]arene and isolated in good to moderate yield.[4e] Furthermore, we reported the isolation of a molybdenum(VI) dichloro complex $[MoCl_2(Calix)]$ via disproportionation of molybdenum(IV) chlorides $[MoCl_4L_2]$ (L = $Et_2S$, $Et_2O$) in the presence of calix[4]arene and triethylamine (see Scheme 1) and a subsequent reaction of product **D** with HCl.[4c] This disproportionation reaction afforded the $d^3$ compound $[(HNEt_3)_2[M_2(Calix)_2]$ (**A**) and the $d^0$ complex $[Mo(H_2Calix)(Calix)]$ (**D**). Complex **D** and the HCl adduct of **A** have been structurally characterized. The reaction of **D** with HCl provides $[MoCl_2(Calix)]$, albeit in moderate yield and under an immense loss of calixarene and metal as well. Therefore, we were interested to improve the synthesis of complex **C** and to establish further useful synthetic approaches into (calix[4]arene)molybdenum chemistry.

## Results

For the mechanism of the disproportionation reaction shown in Scheme 1, we proposed a pathway via a key (calix[4]arene)chloromolybdate intermediate $(HNEt_3)[MoCl(Calix)]$ (**B**). Experimental hints have been the only outcome of the reaction, i.e., the isolation of **A** and **D** and analogous tungsten compounds for the reaction using base-stabilized W(IV) chlorides. Additionally, the side product [{(Calix)W}{$\kappa^2$(*O*)-$\kappa^1$(*O*)-HCalix)}{WCl(Calix)}] was isolated and structurally characterized,[4c] a compound which seemed to be formed from a reaction of $[WCl_2(Calix)]$ and *p-tert*-butylcalix[4]arene. The dichlorides $[MCl_2(Calix)]$ themselves react cleanly with calix[4]arene under the reaction conditions employed in the disproportionation reaction, which supports the idea of the intermediacy of chloro-containing species. To stabilize and isolate the chloromolybdate intermediate of type **B**, we used a procedure that was already successfully applied in the stabilization of the $[Mo(NHMe_2)(Calix)]$ complex fragment.[4e] Whereas the reaction of $Mo(NMe_2)_4]$ with calix[4]arene in equimolar amounts at 80 °C in toluene affords a mixture of $[Mo(NHMe_2)(Calix)]$ and $[Mo_2(Calix)_2]$, the same reaction carried out in acetonitrile or in mixtures of toluene and acetonitrile leads to stabilization of the amine complex to yield $[Mo(NHMe_2)(NCMe)(Calix)]$ and therefore to a suppression of the formation of the dinuclear compound.

Following this strategy, the acetonitrile adduct of molybdenum tetrachloride, $[MoCl_4(NCMe)_2]$ reacts with equimolar amounts of calixarene in the presence of triethylamine in a THF/acetonitrile solvent mixture without the formation of any product emerging from a disproportionation reaction. From the resulting red brownish reaction mixture the (calix[4]arene)chloromolybdate $(HNEt_3)[MoCl(NCMe)(Calix)]$ (**1**) was isolated in good yields.



(1)

First evidence for a complete deprotonation of the calix[4]arene was revealed by IR spectroscopy. A band at 2498 $cm^{-1}$ is in a typical region for N−H− absorption of ammonia salts,[6] and two bands at 2311 and 2282 $cm^{-1}$ were assigned to a C≡N stretching frequency and a combination band,

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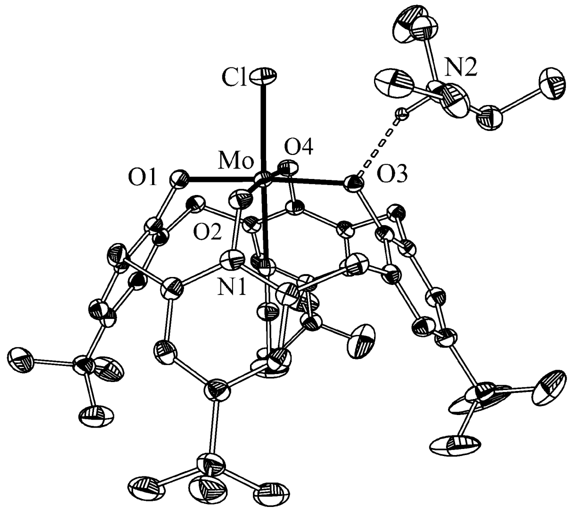

**Figure 1.** Molecular structure of (HNEt$_3$)[MoCl(NCMe)(Calix)] (**1**) in **1**·C$_7$H$_8$ in the solid state (ellipsoids at 40% probability level). Non-hydrogen-bonding H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo−N(1) 2.156(3), Mo−Cl 2.388(1), Mo−O(1) 1.950(2), Mo−O(2) 1.982(2), Mo−O(3) 2.032(2), Mo−O(4) 1.961(2), N(1)−C(5) 1.121(4), Cl−Mo−N(1) 178.1(1); Cl−Mo−O(1) 93.0(1), Cl−Mo−O(2) 92.4(1), Cl−Mo−O(3) 90.1(1), Cl−Mo−O(4) 92.1(1), O(1)−Mo−N(1) 88.9(1), O(1)−Mo−O(2) 91.2(1), O(1)−Mo−O(4) 92.5(1), O(1)−Mo−O(3) 176.9(1), O(2)−Mo−N(1) 87.6(1), O(2)−Mo−O(3) 88.1(1), O(2)−Mo−O(4) 174.1(1), O(3)−Mo−N(1) 88.1(1), O(3)−Mo−O(4) 88.0(1), O(4)−Mo−N(1) 87.8(1), Mo−N(1)−C(5) 179.3(3), Mo−O(1)−C(10) 122.1(2), Mo−O(2)−C(20) 122.2(2), Mo−O(3)−C(30) 121.5(2), Mo−O(4)−C(40) 122.9(2).

which results from coupling of a symmetric CH$_3$ deformation mode and a C−C stretching frequency. The proton resonance spectrum of **1** is not suitable for a complete elucidation of the structure of the compound showing signals at 0.89, 2.45, 4.85, and 11.06 ppm with uncharacteristic intensities. The position as well as the form of the signals is temperature dependent. At −60 °C four broad signals were observed in the region between 0 and 15.0 ppm at 0.44, 3.10, 3.48, and 14.71 ppm. In accordance with the elemental analysis, all data indicated a compound of the composition (HNEt$_3$)[MoCl(NCMe)(Calix)] (**1**). Cyclovoltammetry of methylene chloride solutions of **1** against the ferrocene/ferrocenium couple revealed three redox waves of one electron transitions at +727, +75, and −524 mV. Both oxidation waves are quasi reversible processes, whereas the redoxwave at negative potential is not reversible, presumably a one electron transition under subsequent formation of a dinuclear (calix[4]arene)molybdenum compound.

Crystals of **1** suitable for X-ray diffraction were grown from saturated toluene solutions (see Figure 1). The distorted octahedrally coordinated molybdenum atom of monomeric **1** is almost ideally located within the calixarene O$_4$ plane (0.066(1) Å distorted toward Cl). The chlorine atom and the nitrogen atom of the acetonitrile ligand are with respect to the O$_4$ plane in axial positions (angle Cl−Mo−N(1): 178.1(1)°). All distances to the oxygen atoms O(1), O(2), and O(4) (1.950(2)−1.982(2) Å) are longer compared to (calix[4]arene)molybdenum(VI) complexes[4,5] but in a range typically observed for mononuclear (calixarene)molybdenum(IV) compounds (see below). The Mo−O(3) bond of 2.032(2) Å is elongated due to the interaction of O(3) with the hydrogen atom of the ammonium cation. The distance O(3)−N(2) to the ammonium nitrogen atom is 2.747 Å. The Mo−Cl bond length of 2.388(1) Å and the Mo−N distance of 2.156(3) Å are with the expected range;[7] the Mo−N bond length is especially similar to those found in other acetontrile-stabilized calix[4]arene complexes such as [{Mo(NCMe)(Calix)}$_2$] (2.158 Å) and [Mo(NHMe$_2$)(NCMe)(Calix)].[4e]

The reactivity of **1** toward selected substrates is summarized in Scheme 2. Generally, we were interested in ligand addition and substitution reactions of **1** under maintenance or an increase of the formal oxidation state of the metal atom, in particular in oxidization reactions to improve the synthesis of the molybdenum(VI) dichloro complex [MoCl$_2$(Calix)] (**2**). For a controlled chlorination of **1**, PhICl$_2$ has proven to be an ideal chlorine transfer reagent. This reaction led to [MoCl$_2$(Calix)] (**2**) in 64% yield, which is a significant improvement compared with the protocol of the synthesis for **2** given earlier. Details of the characterization including an X-ray crystal structure determination have been given previously.[4c]

All attempts to directly substitute the chloro ligand with neutral 2 electron donor ligands L such as PMe$_3$ and pyridine under elimination of ammonium chloride and formation of a neutral complex [MoL(NCMe)(Calix)] failed even after prolonged reaction times in toluene at 100−110 °C. The nucleophilicity of these ligands is presumably insufficient to attack at the metal atom to initiate the substitution. If catalytic amounts (approximately 10%) of silver triflate are added to the reaction mixture, this behavior changes drastically and the neutral calix[4]arene complexes [Mo(PMe$_3$)(NCMe)(Calix)] (**3**) and [Mo(NC$_5$H$_5$)(NCMe)(Calix)] (**4**) are formed in good to excellent yields. Similarly to **1**, the proton NMR spectra of these compounds are not very informative showing broad resonances at 0.91, 1.10, 7.70, and 13.77 ppm in an intensity ratio of approximately 18:3:4:2 for **3** and three broad signals at 0.98, 6.21, and 11.43 ppm in the ratio 9:2:1. The mass spectra of these complexes reveal peaks for the molecular ion at $m/z = 818$ (**3**) and at $m/z = 862$ (**4**). Reaction of **1** under similar conditions without any ligand L in the reaction mixture afforded the dimeric d$^2$ complex [{Mo(NCMe)(Calix)}$_2$] (**5**) published earlier.[4e]

Crystals of **3** and **4** suitable for X-ray diffraction were grown from saturated benzene (**3**) or acetonitrile (**4**) solutions of the compounds. The molecular structures of these complexes as well as important structural data are given in Figures 2 and 3.

In both cases the molybdenum atoms are located in a slightly distorted octahedral coordination sphere spanned by the calixarene oxygen atoms, the acetonitrile nitrogen atom, and the donor atom of the phosphine or pyridine ligand, respectively. The Mo−O distances and the M−O−C angles are within a narrow range (1.957(4)−1.976(3) Å; 121.0(3)−124.2(3)°). The metal atom is almost ideally located within

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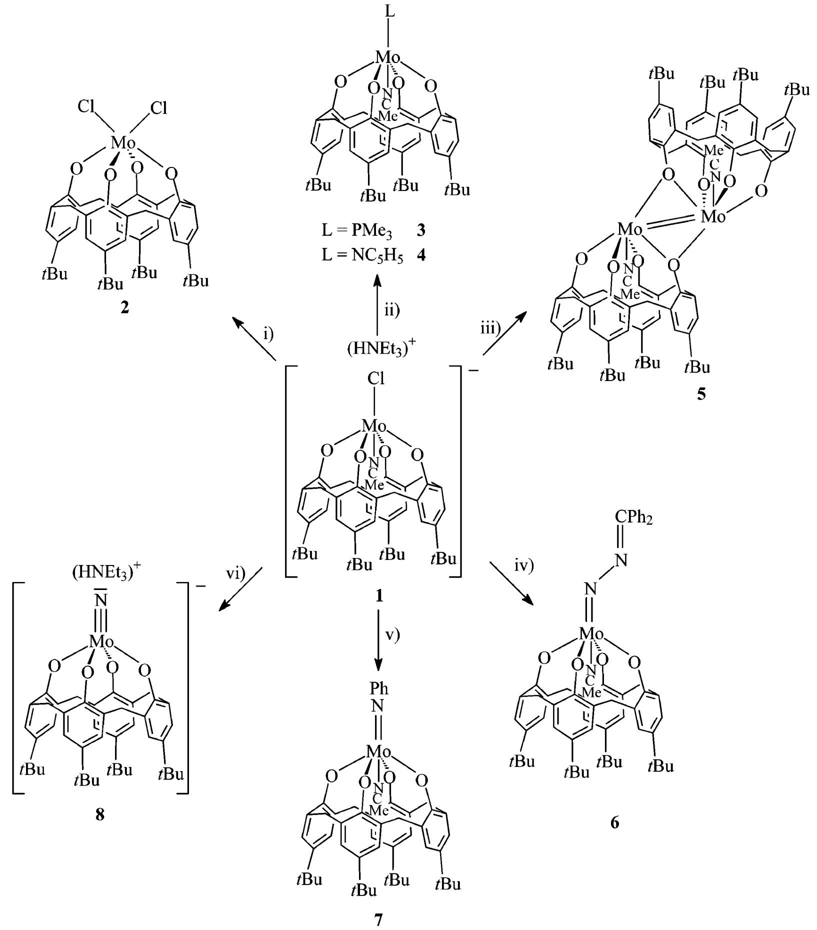
**Scheme 2.** Reactivity of $(HNEt_3)[MoCl(NCMe)(Calix)]$ (**1**)[a]



[a] Reagents and conditions (i) $PhICl_2$, 8 h, 60 °C, toluene, 64%; (ii) L, 10% [Ag(OTf)], 4 h, 80 °C, toluene, >84%; (iii) 10% [Ag(OTf)], 12 h, 110 °C, toluene, 84%; (iv) $Ph_2CN_2$, 10% [Ag(OTf)], 8 h, 80 °C, toluene, 86%; (v) $Ph_2N_2$, 10% [Ag(OTf)], 8 h, 80 °C, toluene, 72%; (vi) $NaN_3$, 10% [Ag(OTf)], 8 h, 80 °C, toluene, 70%.

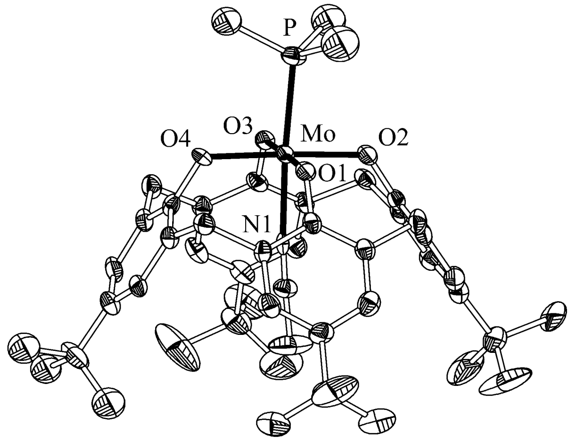


**Figure 2.** Molecular structure of $[Mo(PMe_3)(NCMe)(Calix)]$ (**3**) in **3**·$1.5C_6H_6$ in the solid state (ellipsoids at 40% probability level). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo−P 2.454(2), Mo−O(1) 1.968(3), Mo−O(2) 1.961(4), Mo−O(3) 1.959(3), Mo−O(4) 1.976(3), Mo−N 2.238(5), N−C(50) 111.7(7); O(1)−Mo−O(3) 177.5(1), O(2)−Mo−O(4) 177.3(1), P−Mo−N(1) 176.8(1), Mo−O(1)−C(10) 121.4(3), Mo−O(2)−C(20) 124.2(3), Mo−O(3)−C(30) 121.0(3), Mo−O(4)−C(40) 121.4(3), N−C(50)−C(51) 178.0(8).

the $O_4$ donor set of the calix[4]arene ligand, pointing 0.044(1) Å (**3**) and 0.045(1) Å (**4**) away from the acetonitrile ligand toward the better donor ligand $PMe_3$ and pyridine, respectively. The Mo−N and Mo−P distances in **3** and **4** are unexceptional.[7]

For many transition metal complexes, it is known that they catalytically decompose diorganyl diazomethanes to form carbene complexes.[8,9] In the case of $(HNEt_3)[MoCl(NCMe)(Calix)]$ (**1**), the reaction with 1 equiv of diphenyldiazomethane in the presence of catalytic amounts of silver triflate afforded the violet molybdenum(VI) diazoalkane complex $[Mo(N_2CPh_2)(NCMe)(Calix)]$ (**6**). In contrast to the $d^2$-molybdenum complexes **1**, **3**, and **4** a proton and carbon NMR spectrum typically found for pseudo $C_{4v}$ symmetrically coordinated calix[4]arene $d^0$ metal complexes were recorded for **6**. The proton NMR revealed one singlet for the protons of the *tert*-butyl group at 1.15 ppm, two doublets at 3.15 and 4.30 ppm with coupling constants of 12.2 Hz for the protons of the methylene bridges, and a resonance at 7.04 ppm for the phenolate protons. The protons of the diazoalkane ligand were detected as multiplets at 7.45, 7.90, and

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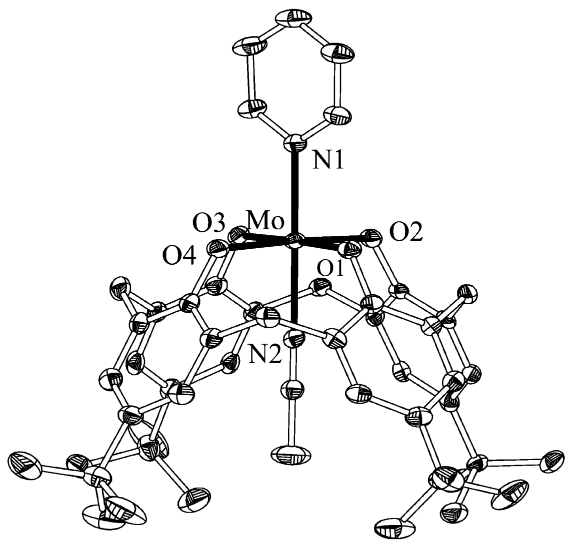

**Figure 3.** Molecular structure of [Mo($NC_5H_5$)(NCMe)(Calix)] (**4**) in the solid state (ellipsoids at 40% probability level). H atoms molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo−N(1) 2.155(5), Mo−O(1) 1.976(4), Mo−O(2) 1.957(4), Mo−O(3) 1.975(4), Mo−O(4) 1.974(4), Mo−N(2) 2.157(5), N(2)−C(55) 1.335(7); O(1)−Mo−O(3) 177.8(2), O(2)−Mo−O(4) 176.6(2), Mo−O(1)−C(10) 123.1(4), Mo−O(2)−C(20) 121.1(3), Mo−O(3)−C(30) 122.3(4), Mo−O(4)−C(40) 123.0(3), N(1)−Mo−N(2) 179.3(2), N(2)−C(55)−C(56) 179.3(9).

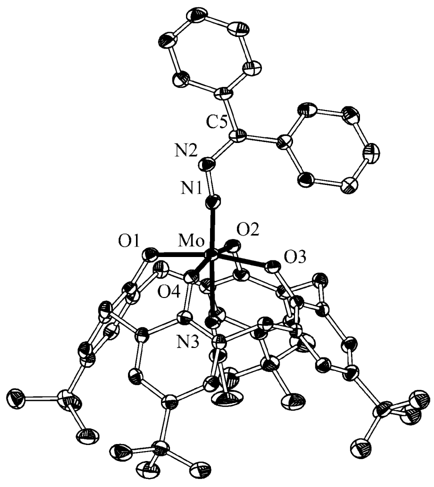

**Figure 4.** Molecular structure of [Mo($N_2CPh_2$)(NCMe)(Calix)] (**6**) in **6**·2MeCN in the solid state (ellipsoids at 40% probability level). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo−N(1) 1.762(4), Mo−O(1) 1.969(3), Mo−O(2) 1.949(3), Mo−O(3) 1.952(3), Mo−O(4) 1.949(3), Mo−N(3) 2.284(3), N(1)−N(2) 1.291(5), N(3)−C(6) 1.124(5), N(2)−C(5) 1.315(5); O(1)−Mo−O(3) 167.3(1), O(2)−Mo−O(4) 165.9(1), N(1)−Mo−N(3) 178.2(1), Mo−O(1)−C(10) 124.6(2), Mo−O(2)−C(20) 129.7(3), Mo−O(3)−C(30) 130.8(2), Mo−O(4)−C(40) 127.0(2), Mo−N(1)−N(2) 170.2(3), Mo−N(3)−C(6) 172.0(3), N(1)−N(2)−C(5) 123.4(3), C(50)−C(5)−C(56) 119.1(4), N(3)−C(6)−C(7) 177.7(5).

8.16 ppm and the protons of the acetonitrile ligand as a significantly shifted resonance at −0.11 ppm. Most relevant, in the $^{13}C$ NMR spectrum a resonance at 175.6 ppm for a quarternary carbon atom accounting for the [NN*C*$Ph_2$] fragment coordinated to the [Mo(NCMe)(Calix)] fragment was detected. Carbene ligands [*C*$Ph_2$] usually show resonances above 200 ppm. Both carbon and proton NMR spectra are in accordance with a pseudo-$C_{4v}$ symmetric structure of **6**, in which a diphenyldiazo ligand can easily rotate around the Mo−N and/or N−C bond axis. The composition of **6** was also verified by elemental analysis as well as mass spectroscopy. Complex **6** is very stable under an inert atmosphere and does not undergo nitrogen loss under thermal or photochemical conditions.

The molecular structure of **4** (Figure 4) confirms the spectroscopic data. The diphenyldiazoalkane ligand is terminally bound to the molybdenum atom of the [Mo(NCMe)(Calix)] complex fragment. In the [Mo(Calix)] fragment, the Mo−O distances are in a range between 1.949(3) and 1.969(3) Å, which is significantly shorter compared to **1**, **3**, and **4** but similar to distances found in other molybdenum(VI) calix[4]arene complexes.[4] The Mo−N(1) distance of 1.762(4) Å is very close to Mo−N bond lengths found in molybdacalixarene imido complexes (for example: 1.718(10) Å in [Mo(N*t*Bu)(NCMe)(Calix)] and 1.724(3) Å in [Mo(NMes)(NCMe)(Calix)]),[4b] which indicates multiple bond character in the Mo−N bond. The bond angles Mo−N(1)−N(2) of 170.2(3)° and N(1)−N(2)−C(5) of 123.5(3)° are almost ideal for sp- and $sp^2$-hybridized nitrogen atoms. The bond lengths N(1)−N(2) (1.291(5) Å) and N(2)−C(5) (1.315(5) Å) are between the values typically found for a single and a double bond.[10]

Whereas **6** is unreactive with respect to N−N cleavage, the reaction of **1** with azobenzene led after activation with silver triflate to scission of the N═N double bond of the substrate under subsequent formation of the mononuclear imido complex [Mo(NPh)(NCMe)(Calix)] (**7**) (see Scheme 2). The analytic and spectroscopic data for **7** are similar to those obtained earlier for other imido complexes such as [Mo(N*t*Bu)(NCMe)(Calix)] and [Mo(NMes)(NCMe)(Calix)][4b] and indicate the presence of a mononuclear complex in solution. Contrary to a dinuclear calix[4]arene-bridged complex [{Mo(NPh)(Calix)}$_2$] reported by Floriani and coworkers,[5j] the acetonitrile-stabilized compound [Mo(NPh)(NCMe)(Calix)] (**7**) is also monomer in the solid state (see Figure 5).

The molecular structure of **7** fits well in the series of structures obtained for other *p*-*tert*-butylcalix[4]arene-stabilized molybdenum imido complexes.[4b] The Mo−N(1) distance (1.716(3) Å) as well as the angle Mo−N(1)−C(50) (176.1(4)°) indicate a significant triple bond character of the molybdenum imido linkage.[11] The bond length Mo−N(2) (2.322(3) Å) to the nitrogen atom of the acetonitrile ligand is significantly elongated compared to the Mo−N(acetonitrile) distances in the molybdenum(IV) complexes described above but comparable to those of other (calixarene)-

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(10) (a) The N−N distance of hydrazine amounts to 1.459 Å, and that of diazine to 1.21 Å; see: Holleman, A. F.; Wiberg, E. *Handbook of Inorganic Chemistry*; deGruyter: Berlin, 1985; Vol. 100, pp 553−568. (b) The calculated N−N distance for *trans*-diazine is 1.266 Å: Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 4385. (c) In a dinuclear iron complex a distance of 1.288(15) Å was found: Sellmann, D.; Hennige, A. *Angew. Chem.* **1997**, *109*, 270; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 276. (d) In *trans*-azobenzene the N−N distance is 1.243(3) Å: Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146. (e) Traetteberg, M.; Hilmo, I.; Hagen, K. *J. Mol. Struct.* **1977**, *39*, 231. (f) Typical values for $sp^2$ C−N bonds are 1.36 Å, and those for $sp^2$ C═N, 1.28 Å: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985.

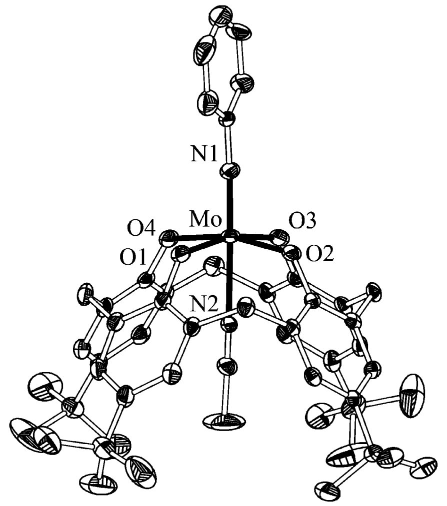

**Figure 5.** Molecular structure of [Mo(NPh)(NCMe)(Calix)] (**7**) in the solid state (ellipsoids at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo−N(1) 1.716(3), Mo−N(2) 2.322(3), Mo−O(1) 1.944(3), Mo−O(2) 1.936(3), Mo−O(3) 1.944(3), Mo−O(4) 1.940(3), N(2)−C(5) 1.107(5); Mo−N(1)−C(50) 176.1(4), Mo−N(2)−C(5) 178.4(4), N(1)−Mo−N(2) 178.6(2), N(1)−Mo−O(1) 96.7(2), N(1)−Mo−O(2) 97.9(1), N(1)−Mo−O(3) 98.7(2), N(1)−Mo−O(4) 97.3(1), O(1)−Mo−O(2) 89.4(1), O(1)−Mo−O(3) 164.6(1), O(1)−Mo−O(4) 88.5(1), O(2)−Mo−O(3) 89.2(1), O(2)−Mo−O(4) 164.8(1), O(3)−Mo−O(4) 88.9(1), Mo−O(1)−C(10) 129.9(3), Mo−O(2)−C(20) 128.1(2), Mo−O(3)−C(30) 129.5(2), Mo−O(4)−C(40) 129.5(2).

molybdenum and -tungsten imido complexes such as [Mo(N*t*Bu)(NCMe)(Calix)] (2.344(9) Å), [Mo(NMes)(NCMe)(Calix)] (2.303(3) Å), and [W(N*t*Bu)(NCMe)(Calix)] (2.314(3) Å). The molybdenum atom is only 0.258(1) Å displaced out of the calix[4]arene O$_4$ plane toward N(1), which seems to provide enough steric protection to keep the compound mononuclear.

N−N cleavage was also achieved in the reaction of **1** with sodium azide in the presence of silver triflate, which afforded the nitrido complex (HNEt$_3$)[MoN(Calix)] (**8**) (see Scheme 2). We used this reaction as a first test for the reactivity of **1** toward anionic nucleophiles. The reaction proceeds presumably via a molybdenum(VI) azide intermediate (HNEt$_3$)[Mo(N$_3$)(NCMe)(Calix)] under N$_2$ elimination and formal oxidation of the metal atom. Due to the excellent trans influence of the nitrido ligand N$^{3-}$,[11c,12,13] the endohedrally coordinated acetonitrile ligand is lost during formation of the nitrido complex.

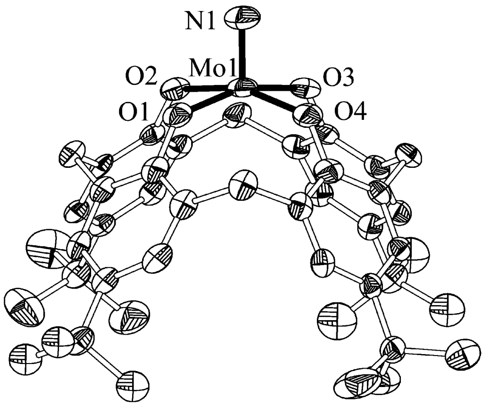

**Figure 6.** Molecular structure of the complex anion of (HNEt$_3$)[MoN(Calix)] (**8**) in the solid state (ellipsoids at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) in the molecule of Mo(1): Mo(1)−N(1) 1.641(6), Mo(1)−O(1) 2.001(5), Mo(1)−O(2) 2.000(5), Mo(1)−O(3) 1.987(5), Mo(1)−O(4) 1.988(5); N(1)−Mo(1)−O(1) 99.5(3), N(1)−Mo(1)−O(2) 99.3(3), N(1)−Mo(1)−O(3) 100.1(3), N(1)−Mo(1)−O(4) 100.5(3), O(1)−Mo(1)−O(2) 85.6(2), O(1)−Mo(1)−O(3) 160.4(2), O(2)−Mo(1)−O(3) 89.9(2), O(2)−Mo(1)−O(4) 160.1(2), O(1)−Mo(1)−O(4) 90.0(2), O(3)−Mo(1)−O(4) 87.8(2), Mo(1)−O(1)−C(10) 130.0(4), Mo(1)−O(2)−C(20) 130.3(4), Mo(1)−O(3)−C(30) 128.9(4), Mo(1)−O(4)−C(40) 127.7(4). Selected bond lengths (Å) and angles (deg) in the molecule of Mo(2): Mo(2)−N(2) 1.667(7), Mo(2)−O(5) 1.964(6), Mo(2)−O(6) 2.016(4), Mo(2)−O(7) 1.939(5), Mo(2)−O(6′) 2.017(4); N(2)−Mo(2)−O(5) 102.8(3), N(2)−Mo(2)−O(6) 99.0(1), N(2)−Mo(2)−O(7) 99.1(3), N(2)−Mo(2)−O(6′) 99.0(1), O(5)−Mo(2)−O(6) 87.1(1), O(5)−Mo(2)−O(7) 158.1(2), O(5)−Mo(2)−O(6′) 87.1(1), O(6)−Mo(2)−O(7) 89.5(1), O(6)−Mo(2)−O(6′) 161.9(2), O(7)−Mo(2)−O(6′) 89.5(1), Mo(2)−O(5)−C(50) 136.4(4), Mo(2)−O(6)−C(60) 124.3(3), Mo(2)−O(7)−C(70) 126.8(5).

Contrary to a neutral (calix[4]arene)molybdenum oxo compound reported by Floriani et al.,[5a] the ionic nitrido complex is soluble in organic solvents such as benzene and toluene. Analytic and spectroscopic data indicate monomeric units in solution as well as in the solid state. Proton as well as carbon NMR spectra of **8** are those typical found for a pseudo-$C_{4v}$ symmetric calix[4]arene complex in solution, and the presence of a transition metal nitrido group was confirmed in the infrared spectrum by a very intense absorption in the region of the [M≡N] stretch at 1047 cm$^{-1}$. In the mass spectrum of **8**, the peak of the molecular ion at $m/z = 769$ was detected.

Complex **8** crystallizes from saturated acetonitrile solutions in the orthorhombic space group *Pnma* with 1.5 independent molecules and 2.5 additional solvent molecules in the asymmetric unit. The complex molecules differ in the location of the [HNEt$_3$]$^+$ counterion: for the anion of Mo(1), it is located near N(1), and for the anion around Mo(2), near O(6). Since there are no significant differences between the two sets of bond distances and angles in the complex anion [MoN(Calix)]$^-$ shown in Figure 6, we will refer specifically only to those from one of the molecules (at Mo(1)); the parameters of the other molecules are given in the caption of Figure 6. The molecular structure confirms the mononuclear nature of this compound in the solid state, in which the molybdenum atom has square pyramidally coordination. The oxygen atoms of the calixarene ligand occupy the basal positions whereas the nitrido ligand is located in the apex of the coordination polyhedron.

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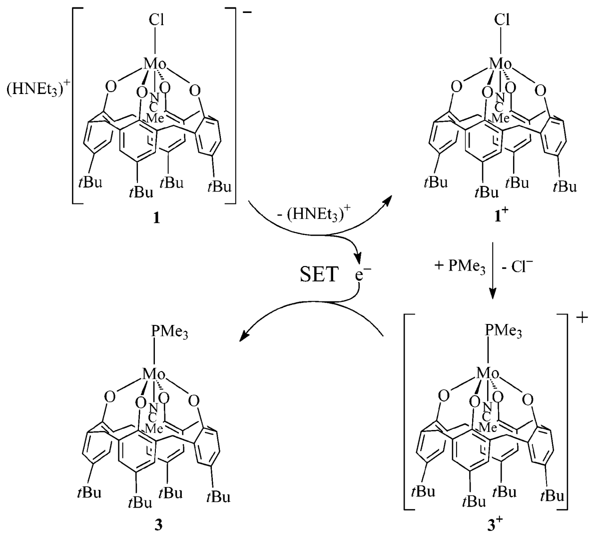
The molybdenum nitrido distances of 1.641(6) Å (Mo(1)−N(1)) and 1.667(7) Å (Mo(2)−N(2)) in **8** are approximately 0.008 Å shorter compared to Mo−N distances observed in imido complexes but in the usual range for molybdenum(VI) nitrido complexes,[11c,t,13] such as [($t$BuPhN)$_3$MoN] (1.658(5) Å),[14a] [(Ph$_2$N)$_3$MoN] (1.634(3) Å),[14b] [($t$BuO)$_3$MoN] (1.661(4) and 1.673(5) Å),[14c] [Mes$_3$MoN] (1.649(4) Å),[14d] and (Ph$_4$P)[X$_4$MoN] (X = Cl, Br).[14e,f] (1.637(4) and 1.628(15) Å). Whereas many nitrido complexes are aggregated via Mo−N···Mo contacts in the solid state, both independent molecules located in the structure of **8** are not stacked this way.

## Discussion

The reaction of [MoCl$_4$(NCMe)$_2$] with calixarene H$_4$Calix in the presence of triethylamine is a feasible entry into (calix[4]arene)molybdenum chemistry. This reaction affords the (calix[4]arene)chloromolybdate (HNEt$_3$)[MoCl(NCMe)(Calix)] (**1**) in good yield, which can easily be chlorinated with PhICl$_2$ to give [MoCl$_2$(Calix)] (**2**). Complexes **1** and **2** can serve as key entry points into Mo(IV) and Mo(VI) calix[4]arene chemistry, and some representative examples for the use of **1** to generate Mo(IV) and Mo(VI) calix[4]arene complexes via ligand substitution and oxidation reactions are given in this contribution. The reaction of **1** with neutral Lewis bases such as PMe$_3$ or pyridine in the presence of catalytic amounts of [Ag(OTf)] affords the neutral complexes **3** and **4** in good to excellent yield. The mechanism of this reaction, however, is not clear yet. The nucleophilicity of these bases is not good enough to attack the metal center directly under formation of an associate that initiates the substitution reaction. Addition of the silver salt was initially planned to push the reaction toward a dissociative reaction mechanism under chloride abstraction and formation of a reactive neutral intermediate [Mo(Calix)] which finally reacts with the nucleophile to give complexes **3** and **4**. In continuing experiments we recognized that substoichiometric amounts of silver salt are sufficient for reaction completion. Therefore, another reaction mechanism is likely in which redox reactions play an important part as outlined in Scheme 3. The decisive step in this reaction seems to be a single electron transfer (SET), in which the complex anion [Mo$^{IV}$Cl(NCMe)(Calix)]$^-$ in **1** is oxidized with the silver salt to form a neutral molybdenum d$^1$ intermediate [Mo$^V$Cl(NCMe)(Calix)] (**1**$^+$), which is more reactive compared to **1** with respect to an initial attack for substitution.

Whereas for a dissociative mechanism the substitution of the chloro ligand of **1** should be favored compared to **1**$^+$ due to electrostatic interactions between the leaving group and the complex fragment, we expect for an associative mechanism a preferred substitution of the chloro ligand of **1**$^+$ compared to **1**. A neutral ligand such as PMe$_3$ should attack the neutral molybdenum d$^1$ complex more easily to substitute a chloro ligand to yield the cationic complex **3**$^+$ (see Scheme 3), which in turn is reduced with complex **1** to give **1**$^+$ and **3**. The rate-limiting step of this procedure should be the ligand exchange. The overall reaction is the substitution of the chlorine ligand in **1** under formation of a neutral compound **3** and 1 equiv of ammonium chloride, and the main task of the silver salt in this process is the oxidation of **1**. We are currently exploring this reaction in more detail, but the presumably active molybdenum d$^1$ species has defied isolation so far. Cyclovoltammetric measurements in methylene chloride, however, revealed quasireversible one electron redox waves at a very low potential of $E_{1/2} = 0.075$ V (with respect of ferrocene at $E_{1/2} = 0.460$ V). To substantiate the hypothesis of electron transfer we investigated substitution reactions initiated with ferrocenium cations. Usually these reactions proceed without any loss of yield using catalytic amounts of complexes such as [Cp$_2$Fe](BF$_4$).

**Scheme 3.** Proposed Reaction Mechanism of the Silver Triflate Catalyzed Substitution of the Chloro Ligand in (HNEt$_3$)[MoCl(NCMe)(Calix)] (**1**) with Neutral Ligands Such as PMe$_3$



DFT calculations[15−20] were performed on model compounds [MoXY(Calix$^H$)] (H$_4$Calix$^H$ = $p$-H-calix[4]arene), to

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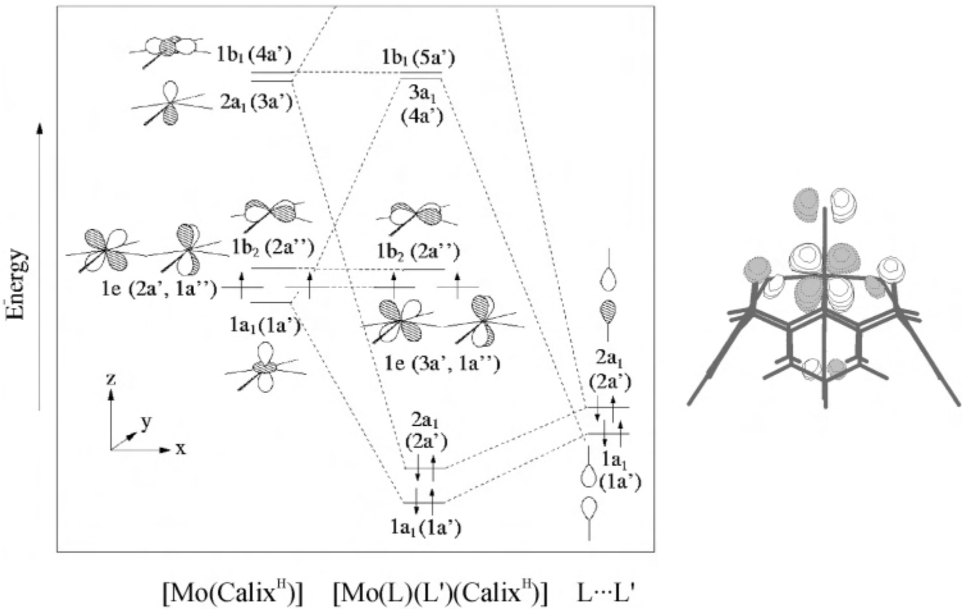

**Figure 7.** Schematic FMO diagram (left) of the orbital interactions of a metal complex fragment [Mo(Calix$^{H}$)] with two mutually trans oriented neutral ligands under formation of [Mo(L)(L′)(Calix$^{H}$)] (L′ = endohedrally coordinated ligand). The occupation drawn for the [Mo$^{IV}$(Calix)] fragment is not the ground state of this fragment (see text). The right side shows a MO plot of the HOMO 1e of [MoCl(NCH)(Calix$^{H}$)]$^{-}$.

gain a better understanding of the main electronic and structural properties of the molybdenum complexes supported by the calix[4]arene ligand. In this model the ligand has been slightly modified through replacement of the *t*Bu groups with hydrogen atoms to reduce computation time. The aim of these calculations was to study the main features of the molybdenum complexes described above as well as the frontier orbitals of the (calix[4]arene)molybdenum complex fragment and their structural consequences.

The orbital interactions of a metal center with the $O_4$ donor set under the geometrical restriction imposed by the calix[4]arene ligand are given elsewhere.[4b] The complex fragment [Mo$^{VI}$(Calix$^{H}$)]$^{2+}$ converges without symmetry restrictions at the RIDFT/SVP level in an ideal $C_{4v}$-symmetrical geometry. The bond lengths calculated are 1.9016 Å for Mo−O, the angles Mo−O−C are 135.84°, and the angles O−Mo−O are 160.81°. The HOMO of the complex fragment is a ligand-centered orbital of $b_1$ symmetry at −12.19 eV. The metal-centered orbitals, energetically above the HOMO, are depicted schematically on the left side of the FMO diagram given in Figure 7. The LUMO of [Mo$^{VI}$(Calix)]$^{2+}$ is a molecular orbital of $a_1$ symmetry at −11.95 eV, predominantly molybdenum $d_{z^2}$ in character. Energetically slightly above this orbital is a degenerate set of orbitals of e symmetry at −10.78 eV, predominantly molybdenum $d_{xz}$ and $d_{yz}$, and an orbital $b_2$ at −10.27 eV, which has significant contributions of molybdenum $d_{xy}$. Both e and $b_2$ orbitals are significantly shifted to higher energies due to Mo−O $\pi$ antibonding interactions.

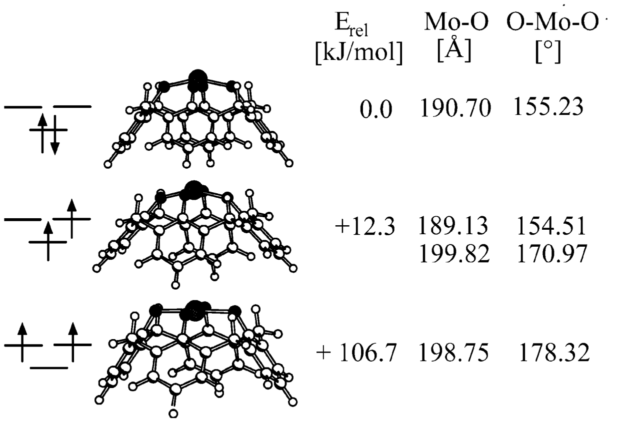

**Figure 8.** Comparison of singlet and triplet metal complex fragment [Mo(Calix$^{H}$)].

The ground state of a neutral molybdenum $d^2$ complex fragment [Mo$^{IV}$(Calix$^{H}$)] is a singlet state, in which the orbital $1a_1$ is occupied with two electrons. A comparison of the relative energies of this singlet state with two low-lying triplet states of the [Mo$^{IV}$(Calix$^{H}$)] fragment as well as a comparison of Mo−O distances and O−Mo−O-angles is given in Figure 8. A $C_{2v}$-symmetric triplet state, in which the molecular orbital $1a_1$ and one of the 1e orbitals are singly occupied, is 12.3 kJ/mol higher in energy. The occupation of one of the Mo−O antibonding e typ orbital ($b_1$ in $C_{2v}$ symmetry) leads to a significant increase of one of the Mo−O distances (1.9982 Å vs 1.8913 Å) and of one O−Mo−O angle (170.97° vs 154.51°). The $C_{4v}$-symmetric triplet state that is schematically shown on the left side of the FMO diagram of Figure 7 and at the bottom of Figure 8, in which the degenerate e orbitals are doubly occupied, is 106.7 kJ/mol higher in energy relative to the ground state. The population of these Mo−O antibonding e orbitals leads to an increase of the Mo−O distances to 1.9875 Å and to a decrease of the angle Mo−O−C to 121.85°. Moreover, the molybdenum

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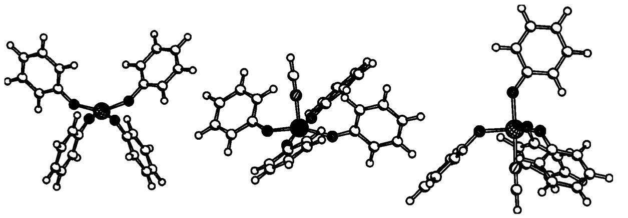

**Figure 9.** Calculated geometries of complexes [Mo(OPh)$_4$] and [Mo(NCH)(OPh)$_4$].

atom in [Mo$^{IV}$(Calix$^H$)] is almost ideally located within the calixarene O$_4$ plane. The angles O−Mo−O of oxide donor atoms mutually in trans positions converge at 178.32°.

Due to the geometrical constraints imposed by the calixarene ligand the metal atom supported by this macrocyclic ligand has anomalous coordination and reactivity compared to metals supported by four monomeric phenolate moieties. These geometrical constraints influence the electronic structure and the reactivity of the molybdenum complexes, as might be demonstrated by a comparison with the calculated geometric and electronic structures of mononuclear molybdenum tetraphenolate complexes. The d$^0$ complex [Mo(OPh)$_4$]$^{2+}$ optimizes in an essentially tetrahedral geometry. The structurally characterized d$^2$ complexes of the type [M(SR)$_4$] (M = Mo, W) and [W(OAr)$_4$][21] show a flattened tetrahedral geometry. For the calculated d$^2$ complex [Mo(OPh)$_4$] we found a singlet ground state of $C_2$ symmetry. The optimized geometry of the complex is shown on the left side of Figure 9 and can be described as a “gull’s wing” structure with two orthogonally intersecting “W” moieties $C_{ipso}$−O−Mo−O−$C_{ipso}$. The calculated Mo−O distances are 1.901 Å, and the O−Mo−O angles of trans phenolate ligands are 148.95°.

The coordination of an endohedrally coordinated nitrile ligand completely changes the electronic situation of the calix[4]arene complexes. For the molecule [Mo(NCH)(Calix$^H$)] we calculate a triplet ground state of $C_{4v}$ symmetry 27.5 kJ/mol lower in energy compared to the lowest singlet state. The geometrical parameters are similar as those found for triplet $C_{4v}$ [Mo(Calix$^H$)], Mo−O distances of 1.978 Å and O−Mo−O angles of 176.73° for trans phenolate entities of the calixarene ligand. This is in sharp contrast to complexes of the type [Mo(NCH)(OPh)$_4$]. We calculate for quadratic pyramidal [Mo(NCH)(OPh)$_4$] as shown in the middle of Figure 9 for $^3$[Mo(NCH)(OPh)$_4$] a singlet and a triplet state which are very close in energy, 2.8 kJ/mol in favor of the triplet state. At 39.4 kJ/mol below this triplet state we find another triplet state of this complex in which the molybdenum atom is trigonal bipyramidally coordinated as depicted at the right side of Figure 9. Three of the phenolate ligands occupy equatorial sites, wheras the remaining phenolate and the nitrile ligand are in the axis of the coordination polyhedron. For both square pyramidal and trigonal bipyramidal complexes of the type [M(L)(ER)$_4$][22] (M = Mo, W; E = O, S) are examples in the literature; the molybdenum complexes [Mo(NHMe$_2$)(OAdamantyl)$_4$] and Mo(NCMe)(S-2,4,6-$i$Pr$_3$C$_6$H$_2$)$_4$], however, closely resemble the global minimum structure calculated for [Mo(NCH)(OPh)$_4$]. The structural maintenance of the [Mo(NCMe)(Calix)] unit imposed by the calixarene ligand during the reactions reported here is the key to a chemistry which is different compared to non-calix species.

The coordination of two mutually trans ligands to this triplet [Mo$^{IV}$(Calix$^H$)] complex fragment leads to an interaction of the occupied ligand donor orbitals with the metal-centered orbitals 1a$_1$ and 2a$_1$ as schematically depicted in Figure 7. For the resulting molecule [Mo(L)(L′)(Calix$^H$)], we generally calculate triplet ground states, in which both of the 1e orbitals are singly occupied. For the model compound [MoCl(NCH)(Calix$^H$)]$^-$, an orbital plot of one of these degenerate orbitals is provided at the right side of Figure 7. In addition to metal $d_{xz}$ and $d_{yz}$ contributions significant Mo−Cl antibonding and Mo−O antibonding contributions of the ligands mix into this molecular orbital.

Metal $d_{xz}$ and $d_{yz}$ are the orbitals which are ideally suited for nucleophilic attack, because they are not involved in the construction of the $\sigma$ framework and spatially accessible for an incoming nucleophile, whereas all other metal-centered d orbitals lie within the plane of the relatively rigid ligand regime. Assuming an associative mechanism, the nucleophilic attack should take place at one of these orbitals, which are singly occupied in the case of **1**. Substitution is therefore hampered by a repulsive interaction with the incoming nucleophile. Oxidation of **1** and depopulation of 1e as a consequence thereof facilitates an associative substitution of the chlorine ligand.

Further experiments mainly concern the use of the molybdenum calixarene complex **1** as a source of a d$^2$-Mo$^{IV}$−calix[4]arene fragment in the reaction with diazoalkanes and azides. Such reactions led either to two-electron reduction of the substrate or to the cleavage of nitrogen nitrogen multiple bonds with the formation of a metal imido species. The reductions of diazoalkane and organic azides have been chosen for their relationship with the N$_2$ reduction and N−N bond cleavage reactions, in general.

The coordination of diphenyldiazoalkane to the [Mo(NCMe)(Calix)] complex fragment led to an intramolecular electron transfer from the metal atom to the organic substrate, formally a two-electron reduction to afford a metallahydrazone. Due to the formal oxidation state +VI of the metal atom, meaningful NMR spectra of **6** were recorded for this diamagnetic compound. The Mo−N distance of 1.762(4) Å is an indication for the existence of a stable Mo═N multiple bond in **6**, which is is comparable with the imido complex **7** or other calix[4]arene-stabilized molybdenum imido complexes synthesized earlier.[4b] The deformation of the diazoalkane ligand is a clear indication for the population of the

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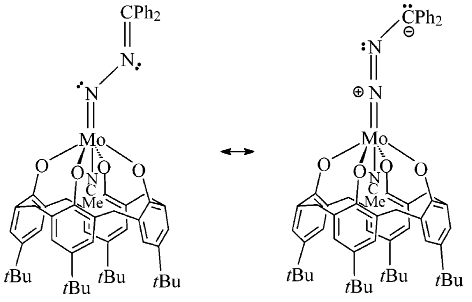
[21] (a) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207−7208. (b) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264−271. (c) Roland, E.; Walborsky, E. C.; Schrock, R. *J. Am. Chem. Soc.* **1985**, *107*, 5795−5797.

[22] See for example: (a) Bickelhaupt, F. M.; Neumüller, B. Plate, M.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1455. (b) Bishop, P. T.; Dilworth, J. R.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2535. (c) Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 901.

former LUMO of the diazoalkane. The N(1)−N(2) (1.291(5) Å) and N(2)−C(5) (1.315(5) Å) bond lengths are between the values typically found for a single and a double bond,[10] and the following two resonance structures seem therefore to be important in the description of the molybdenum−diazoalkane moiety:



The bond angles Mo−N(1)−N(2) of 170.2(3)° and N(1)−N(2)−C(5) of 123.5(3)° observed in the solid state are an indication for the significant contribution of the resonance structure given on the right side with sp- and $sp^2$-hybridized nitrogen atom. The formation of a stable metal nitrogen multiple bond is one point that prevents decomposition of **6** to a possible carbene complex [$Mo(CPh_2)(NCMe)(Calix)$] under thermal or photolytical conditions. Similar behavior was observed in Chisholm's group for [$Mo(OtBu)_4(N_2CPh_2)$].[23] In addition, the calix[4]arene ligand presumably prevents a possible reaction pathway via a 1,3 addition product of the diazoalkane, which is one of the postulated decomposition pathways for diazoalkane complexes.[8,9]

The formation of the imido complex **7** involves the utilization of the [Mo(NCMe)(Calix)] complex fragment for N═N cleavage of diazobenzene. In general, the mechanism of the metal-catalyzed diazene cleavage is discussed frequently currently. Initial reasoning for a $\eta^2$-diazene complex as the key intermediate[24] was rebutted by the observation of Schrock and co-workers[24g] that the decomposition of [$Cp^*WMe_3(\eta^2\text{-}MeNNMe)$] to afford an imido complex [$Cp^*WMe_3(NMe)$] does not follow a first-order rate law. Bergman et al. nicely demonstrated the importance of $\eta^1$-coordinated diazene ligands exemplified by [$Cp_2TaMe(\eta^1\text{-}PhNNPh)$] as a key intermediate in the decomposition of tantalum diazene complexes to give an imido compound [$Cp_2Ta(NPh)Me$]. If one starts from [$Cp_2TaMe(\eta^2\text{-}PhNNPh)$], no imido complex was observed and the formation of the $\eta^2$-diazene complex therefore seems to be the mechanistic dead end for this type of conversion. However, possible intermediates of the reaction of **1** with $Ph_2N_2$ such as a dinuclear complex [{(Calix)Mo(NCMe)}N(Ph)−(Ph)N{Mo(NCMe)(Calix)}] or a mononuclear complexes [$Mo(\eta^1\text{-}N_2Ph_2)(NCMe)(Calix)$] or [$Mo(\eta^2\text{-}N_2Ph_2)(NCMe)(Calix)$] have not been observed so far in the reaction mixture.

A dinuclear molybdenum phenylimido complex was synthesized in Floriani's group in a one-pot reaction starting from [$MoCl_4(thf)_2$], the perlithiated calix[4]arene, and diazobenzene.[5j] The spectroscopic data for this complex are typical for a pseudo-$C_s$ symmetrical molecule in solution, and the molecular structure of this complex revealed a dinuclear compound with exohedrally bonded imido ligands. The dimeric form derives from the sharing of one of the calix[4]arene oxygen atoms, whereas the imido nitrogen atoms are terminally bound to the metal atoms. In the case of compound **7**, spectroscopic as well as analytical data confirm a mononuclear structure of the imido complex in solution and in the solid state. This difference might be explained by the lack of an efficient donor ligand trans to the imido group in the case of Floriani's compound, which makes the metal atom available for dimerization. In square pyramidal complexes of the type [M(L)(calix)] the metal atom is displaced significantly out of the calix[4]arene $O_4$ plane toward the ligand whereas in octahedral complexes [M(L)(L′)(Calix)] the metal atom is more or less located within the $O_4$ plane. Similar monomeric/dimeric pairs of complexes [$\{M(L)(calix)\}_2$]/[M(L)(calix)(L′)] are available in the literature, noteworthy examples being the hydrazido complexes [$W(NNR_2)(calix^H)(NCMe)$] (monomer) and [$\{W(NNR_2)(calix^H)\}_2$] (dimer) published by Redshaw et al.[25]

## Conclusions

Contrary to the poly(phenolate) metallacalix[4]arene chemistry of group 4 and 5 metals as well as tungsten, the chemistry of *p-tert*-butylcalix[4]arene-supported complexes of molybdenum was hampered by the unavailability of suitable starting material. The reaction of [$MoCl_4(NCMe)_2$] with calixarene $H_4Calix$ in the presence of triethylamine is a feasible entry point into calix[4]arene molybdenum chemistry and results in the formation of the (calix[4]arene)chloromolybdate ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in good yield, which is a useful starting material for the preparation of Mo(IV) and Mo(VI) calix[4]arene complexes. It can easily be chlorinated with $PhICl_2$ to afford the molybdenum(VI) dichloro complex [$MoCl_2(Calix)$] (**2**). ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) is also an appropriate source for the $d^2$-[Mo(NCMe)(Calix)] fragment, if the reaction is catalyzed with small amounts of an oxidizing reagent such as [Ag(OTf)] or $[Cp_2Fe]^+$. Neutral $d^2$ complexes [$Mo(PMe_3)(NCMe)(Calix)$] (**3**) and [$Mo(NC_5H_5)(NCMe)(Calix)$] (**4**) were obtained from reaction of **1** with trimethylphosphine and pyridine, respectively, in the presence of [Ag(OTf)]. Without coordinating ligands, this reaction accomplished the dimerization of the molybdenum calixarene complex fragment to

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(23) Chisholm, M. H.; Folting, K.; Huffmann, J. C.; Ratermann, A. L. *Inorg. Chem.* **1984**, *23*, 2303.

(24) See for example: (a) Barry, J.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Streib, W. E. *Polyhedron* **1997**, *16*, 2113. (b) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem.* **1990**, *102*, 7213; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (c) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143. (d) Hansert, B.; Vahrenkamp, H. *J. Organomet. Chem.* **1993**, *459*, 265. (e) Gray, S. D.; Thorman, J. L.; Adamian, V. A.; Kasdish, K. M.; Woo, L. K. *Inorg. Chem.* **1998**, *37*, 1. (f) Lockwood, M. A.; Fanwick, P. E.; Eisenstein, O.; Rothwell, I. P. *J. Am. Chem. Soc.* **1996**, *118*, 2762. (g) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760. (h) Zambrano, C. H.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1994**, *13*, 1174. (i) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem.* **1998**, *110*, 1005; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 959. (j) Aubart, M. A.; Bergman, R. G. *Organometallics* **1999**, *18*, 811.

(25) Redshaw, C.; Elsegood, M. R. J. *Inorg. Chem.* **2000**, *39*, 5164.

give the dinuclear compound [{Mo(NCMe)(Calix)}$_2$] (**5**). The reaction of **1** with $Ph_2CN_2$ afforded the formation of a metallahydrazone [Mo($N_2CPh_2$)(NCMe)(Calix)] (**6**), in which the diphenyldiazomethane ligand has been formally reduced with two electrons. A formal oxidation of the metal atom has also been achieved in the reaction of **1** with azobenzene and sodium azide. The reaction with azobenzene led under cleavage of the nitrogen nitrogen double bond to an imido complex [Mo(NPh)(NCMe)(Calix)] (**7**), whereas the reaction with sodium azide afforded the mononuclear molybdenum(VI) nitrido complex ($HNEt_3$)[MoN(Calix)] (**8**).

## Experimental Section

**General Methods.** All reactions and subsequent manipulations involving organometallic reagents were performed under nitrogen or argon atmosphere using standard Schlenk techniques as reported previously.[4b] Elemental analyses were performed in the microanalytical laboratory of the author's department. EI and FD mass spectra were recorded on a Varian MAT 3830 (70 eV), and the field desorption spectra were recorded from toluene solutions. NMR spectra were recorded on a Bruker AC 250 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 carbon atoms from $-C$ or $-CH_2$ type carbon atoms 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: $CDCl_3$, 7.24 ppm ($^1$H), $C_6D_6$, 7.15 ppm ($^1$H), or natural-abundance carbon signal at 77.0 ppm for $CDCl_3$ and 128.0 ppm for $C_6D_6$. Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 and are reported in cm$^{-1}$. *p-tert*-Butylcalix[4]arene[26] and [$MoCl_4L(MeCN)_2$][27] were prepared as described in the literature; all other reagents were purchased from commercial sources and purified by standard techniques.

**Synthesis of ($HNEt_3$)[MoCl(NCMe)(Calix)] (1).** $NEt_3$ (11.1 mL, 81.5 mmol) and 10.6 mL (202 mmol) of acetonitrile were added at room temperature to a suspension of 6.47 g (20.2 mmol) of [$MoCl_4(NCMe)_2$] and 15.0 g (20.2 mmol) of $H_4Calix\cdot C_7H_8$ in 250 mL of THF. The resulting mixture was stirred for 8 h at reflux, and unsolved components were filtered off. The filtrate was stored at −40 °C overnight. During this time the product precipitates in form of fine yellow needles. The precipitate was filtered off, washed with three 10 mL portions of diethyl ether, and dried in vacuo. Remaining traces of triethylammonium chloride were removed by sublimation in vacuo. Yield: 12.6 g (68%), yellow powder. Bright orange crystals suitable for X-ray diffraction were obtained from saturated benzene or toluene solutions of **1**. Anal. Calcd (found) for $C_{52}H_{70}ClN_2O_4Mo$ ($M_r$ = 918.5): C, 68.00 (67.84); H, 7.68 (7.58); N, 3.05 (3.03). IR (KBr, cm$^{-1}$): 2498 br, m $\nu(N^{+}-H)$. $^1$H NMR ($CDCl_3$): $\delta = 0.89$ (s, br, 36 H), 2.45 (s, sbr, 15 H), 4.85 (s, br, 8 H), 11.06 (s, br, 4 H).

**Synthesis of [$MoCl_2$(Calix)] (2).** $PhICl_2$ (1.49 g, 5.45 mmol) was added to a solution of 5.00 g (5.45 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in toluene. The color of the reaction mixture changed immediately after addition to deep violet. After 8 h of stirring at 60 °C all volatiles were removed in vacuo and the remaining residue was extracted into 150 mL of THF and filtered over a pad of Celite. The filtrate was evaporated to dryness, and resulting [$MoCl_2$(Calix)] (**2**) was dried in vacuo. Yield: 2.83 g (64%), violet powder. Anal. Calcd (found) for $C_{44}H_{52}Cl_2O_4Mo$ ($M_r$ = 811.7): C, 65.11 (64.80); H, 6.46 (6.61). EI/MS [*m/z* (%)]: 812 (50), [M]$^+$; 797 (7), [M − $CH_3$]$^+$; 777 (46), [M − Cl]$^+$. $^1$H NMR ($CDCl_3$): $\delta = 1.19$ (s, 18 H, C($CH_3$)$_3$), 1.38 (s, 18 H, C($CH_3$)$_3$), 3.42 (d, 2 H, $^2J_{HH} = 13.9$ Hz, $CH_2$), 4.71 (d, 2 H, $^2J_{HH} = 13.9$ Hz, $CH_2$), 7.07 (s, 4 H, aryl-$H_m$), 7.29 (s, 4 H, aryl-$H_m$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.76$, 31.89 (C($CH_3$)$_3$), 34.10, 34.30 ($C$($CH_3$)$_3$), 35.46 ($CH_2$), 124.66, 127.33 (aryl-$C_m$), 132.94, 143.87, 149.97, 152.20, 164.06, 172.17 (aryl-$C$).

**Synthesis of [Mo($PMe_3$)(NCMe)(Calix)] (3). (a) Activation with [Ag(OTf)].** $PMe_3$ (0.28 mL, 2.62 mmol) was added to a solution of 2.00 g (2.18 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 80 mL of toluene. After addition of 56.0 mg (0.22 mmol) of [Ag(OTf)], the initially bright orange solution changed its color to red. After 4 h of stirring at 80 °C the solution was filtered, concentrated to approximately 40 mL, and stored at −30 °C overnight. During this time, a red crystal powder was formed, which was filtered off, washed with two 5 mL portions of hexane, and dried in vacuo. Yield: 1.97 g (95%), red crystal powder. Red crystals suitable for X-ray diffraction were obtained from repeated crystallization from toluene.

**(b) Activation with [$Cp_2Fe$]($BF_4$).** $PMe_3$ (0.14 mL, 1.31 mmol) and 28.0 mg (0.11 mmol) of [$Cp_2Fe$]($BF_4$) were added to a solution of 1.00 g (1.09 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 40 mL of toluene. After 8 h of stirring at 60 °C the reaction mixture was filtered through a pad of Celite; all volatiles were removed from the resulting red solution. The red residue was washed with 5 mL of hexane and recrystallized from hot toluene solutions. Yield: 819 mg (92%), red crystals. Anal. Calcd (found) for $C_{49}H_{64}NO_4PMo$ ($M_r$ = 858.0): C, 68.60 (68.55); H, 7.52 (7.87); N, 1.63 (1.61). EI/MS [*m/z* (%)]: 817 (31), [M − NCMe]$^+$; 803 (1), [M − NCMe − $CH_3$]$^+$; 742 (40), [M − NCMe − $PMe_3$]$^+$. IR (KBr, cm$^{-1}$): 2318 m, 2290 m $\nu(-C{\equiv}N)$. $^1$H NMR ($CDCl_3$): $\delta = 0.91$ (s, br, 36 H, C($CH_3$)$_3$), 1.10 (s, 6 H), 7.70 (s, br, 8 H), 13.77 (s, br, 4 H).

**Synthesis of [Mo($NC_5H_5$)(NCMe)(Calix)] (4).** Pyridine (0.21 mL, 2.62 mmol) was added to a solution of 2.00 g (2.18 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 80 mL of toluene. After addition of 56.0 mg (0.22 mmol) of [Ag(OTf)], the reaction mixture was stirred for 4 h at 80 °C and filtered while hot over a pad of Celite. The filtrate was reduced to dryness to afford [Mo($NC_5H_5$)(NCMe)(Calix)] (**4**) as a reddish brown solid. Yield: 1.57 g (84%), red brown solid. Crystals suitable for X-ray diffraction were obtained from saturated acetonitrile solutions. Anal. Calcd (found) for $C_{51}H_{60}N_2O_4Mo$ ($M_r$ = 861.0): C, 71.15 (70.55); H, 7.02 (7.35); N, 3.25 (3.33). FD/MS (10 kV) [*m/z* (%)]: 863 (100), [M + 2H]$^+$. IR (KBr, cm$^{-1}$): 2320 w, 2292 w $\nu(-C{\equiv}N)$. $^1$H NMR ($CDCl_3$): $\delta = 1.03$ (s, br, 36 H, C($CH_3$)$_3$), 6.18 (s, br, 8 H), 11.37 (s, br, 4 H).

**Synthesis of [{Mo(NCMe)(Calix)}$_2$]** (**5**)**.** Silver triflate (0.013 g, 0.05 mmol) was added to a solution of 480 mg (0.52 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 30 mL of toluene. After 12 h of stirring at 110 °C, the reaction mixture was evaporated to dryness and extracted with 30 mL of THF. After filtration over a pad of Celite, the solvent was removed and the resulting solid was dried in vacuo to afford [{Mo(NCMe)(Calix)}$_2$] (**5**) as a green powder. Yield: 287 mg (70%), green powder. Anal. Calcd (found) for $C_{92}H_{110}N_2O_8Mo_2$ ($M_r$ = 1563,8]: C, 70.66 (72.07); H, 7.09 (8.19); N, 1.79 (1.74). EI/MS (70 eV): *m/z* = 1482 ([M − 2MeCN]$^+$, 5%), 741 ([M − 2MeCN]$^{2+}$/2, 41%). IR (KBr, cm$^{-1}$):

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(26) (a) Gutsche, C. D.; Iqbal, M.; Watson, A. T.; Heathcock, C. H. *Org. Synth.* **1989**, *68*, 234. (b) Arduini, A.; Casnati, A. *Macrocycle Synthesis, A Practical Approach*; Oxford University Press: New York, 1996.

(27) Dilworth, J. R.; Richards, R. L.; Chen, G. J.-J.; McDonald, J. W. *Inorg. Synth.* **1980**, *20*, 119.

2326 m, 2298 w $\nu(-C{\equiv}N)$. $^1H$ NMR ($CDCl_3$): $\delta = 0.23$ (s, 3 H, C$H_3$CN), 1.13 (s, 9 H, C(C$H_3$)$_3$), 1.20 (s, 18 H, C(C$H_3$)$_3$), 1.22 (s, 9 H, C(C$H_3$)$_3$), 3.17 (d, 2 H, $^2J_{HH} = 12.4$ Hz, C$H_2$), 3.33 (d, 2 H, $^2J_{HH} = 12.3$ Hz, C$H_2$), 4.39 (d, 2 H, $^2J_{HH} = 12.3$ Hz, C$H_2$), 5.26 (d, 2 H, $^2J_{HH} = 12.4$ Hz, C$H_2$), 7.01 (s, 2 H, aryl-$H_m$), 7.09 (d, 2 H, $^4J_{HH} = 2.4$ Hz, aryl-$H_m$), 7.14 (d, 2 H, $^4J_{HH} = 2.4$ Hz, aryl-$H_m$), 7.20 (s, 2 H, aryl-$H_m$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 0.85$ ($C$H$_3$CN), 31.74, 31.79, 31.90 (C($C$H$_3$)$_3$), 32.34, 33.09 ($C$H$_2$), 34.07, 34.20, 34.47 ($C$(CH$_3$)$_3$), 116.96 (CH$_3$$C$N), 123.94, 124.11, 124.20, 124.48 (aryl-$C_m$), 127.47, 129.45, 129.74, 135.81 (aryl-$C_o$), 143.29, 143.48, 147.34 (aryl-$C_p$), 159.89, 161.88, 167.62 (aryl-$C_i$).

**Synthesis of [Mo($N_2CPh_2$)(NCMe)(Calix)] (6).** A solution of 0.196 g (1.09 mmol) of diphenyldiazomethane in 10 mL of toluene was added at room temperature to a solution of 1.00 g (1.09 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 60 mL of toluene. After addition of 28.0 mg (0.11 mmol) of [Ag(OTf)], the reaction mixture was stirred for 8 h at 80 °C and was filtered over a pad of Celite. The filtrate was evaporated to dryness. The remaining powder was washed with 5 mL of pentane and dried in vacuo to afford [Mo($N_2CPh_2$)(NCMe)(Calix)] (**6**) as a red violet powder. Yield: 915 mg (86%), red violet powder. Dark red crystals of **6** suitable for X-ray diffraction were obtained from recrystallization in acetonitrile. Anal. Calcd (found) for $C_{59}H_{65}N_3O_4Mo$ ($M_r = 976.1$): C, 72.60 (72.21); H, 6.71 (6.40); N, 4.30 (4.12). EI/MS [$m/z$ (%)]: 936 (2), $[M - MeCN]^+$; 921 (11), $[M - MeCN - CH_3]^+$. IR (KBr, $cm^{-1}$): 2324 w, 2294 w $\nu(-C{\equiv}N)$. $^1H$ NMR ($CDCl_3$): $\delta = -0.11$ (s, 3 H, C$H_3$CN) 1.15 (s, 36 H, C(C$H_3$)$_3$), 3.15 (d, 4 H, $^2J_{HH} = 12.2$ Hz, C$H_2$), 4.30 (d, 4 H, $^2J_{HH} = 12.2$ Hz, C$H_2$), 7.04 (s, 8 H, aryl-$H_m$), 7.45 (m, 6 H, Ph$H$), 7.90 (d, 2 H, $^3J_{HH} = 7.7$ Hz, Ph$H$), 8.16 (m, 2 H, Ph$H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -2.04$ ($C$H$_3$CN), 31.47 (C($C$H$_3$)$_3$), 32.51 ($C$H$_2$), 33.77 ($C$(CH$_3$)$_3$), 116.94 (CH$_3$$C$N), 123.45 (aryl-$C_m$), 128.02 (Ph-$C$), 128.30, 128.83 (Ph-$C$H), 129.10 (aryl-$C_o$), 130.46 (Ph-$C$H), 143.44 (aryl-$C_p$), 161.73 (aryl-$C_i$), 175.63 (NN$C$Ph$_2$).

**Synthesis of [Mo(NPh)(NCMe)(Calix)] (7).** Azobenzene (119 mg, 1.09 mmol) was added to a solution of 1.00 g (1.09 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 30 mL of toluene. After addition of 28.0 mg (0.11 mmol) of [Ag(OTf)], the reaction mixture was stirred for 8 h at 80 °C and was filtered over a pad of Celite. The filtrate was evaporated to dryness, and the remaining powder was suspended in 15 mL of hexane, filtered off, and dried in vacuo to afford [Mo(NPh)(NCMe)(Calix)] (**7**) as an orange brown solid. Yield: 654 mg (72%), orange brown solid. Crystals suitable for X-ray diffraction were obtained from recrystallization of **7** in acetonitrile. Anal. Calcd (found) for $C_{52}H_{60}N_2O_4Mo$ ($M_r = 873.0$]: C, 71.54 (70.92); H, 6.93 (6.70); N, 3.21 (2.94). EI/MS [$m/z$ (%)]: 833 (4), $[M - MeCN]^+$. IR (KBr, $cm^{-1}$): 2322 m, 2291 m $\nu(-C{\equiv}N)$. $^1H$ NMR ($CDCl_3$): $\delta = -0.09$ (s, 3 H, C$H_3$CN), 1.17 (s, 36 H, C(C$H_3$)$_3$), 3.21 (d, 4 H, $^2J_{HH} = 12.4$ Hz, C$H_2$), 4.42 (d, 4 H, $^2J_{HH} = 12.4$ Hz, C$H_2$), 7.08 (s, 8 H, aryl-$H_m$), 7.12 (d, 1 H, $^3J_{HH} = 7.2$ Hz, Ph$H$), 7.48−7.54 (dd, 2 H, Ph$H$), 7.89 (d, 2 H, $^3J_{HH} = 7.2$ Hz, Ph$H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -2.02$ ($C$H$_3$CN), 31.79 (C($C$H$_3$)$_3$), 32.93 ($C$H$_2$), 34.16 ($C$(CH$_3$)$_3$), 116.27 (CH$_3$$C$N), 123.88 (aryl-$C_m$), 125.24 (Ph-$C_m$), 127.62 (Ph-$C_o$), 130.50 (aryl-$C_o$, Ph-$C_p$), 144.31 (aryl-$C_p$), 155.21 (Ph-$C_i$), 161.21 (aryl-$C_i$).

**Synthesis of ($HNEt_3$)[MoN(Calix)] (8).** Sodium azide (71.0 mg, 1.09 mmol) and 28.0 mg (0.11 mmol) of [Ag(OTf)] were added to a solution of 1.00 g (1.09 mmol) of ($HNEt_3$)[MoCl(NCMe)(Calix)] (**1**) in 30 mL of toluene. The reaction mixture was stirred for 8 h at 80 °C and filtered afterward over a pad of Celite. The filtrate was evaporated to dryness, and the remaining solid was suspended in 30 mL of hexane and filtered. The filtrate was evaporated to dryness to afford ($HNEt_3$)[MoN(Calix)] (**8**) as an orange solid, which was dried in vacuo. Yield: 608 mg (70%), orange powder. Crystals suitable for X-ray diffraction were obtained from recrystallization of **8** in acetonitrile. Anal. Calcd (found) for $C_{50}H_{68}N_2O_4$-Mo ($M_r = 857.0$): C, 70.07 (69.21); H, 8.00 (8.40); N, 3.27 (2.98). FD/MS (10 kV) [$m/z$ (%)]: 757 (100), $[M - NEt_3 + H]^+$. IR (KBr, $cm^{-1}$): 2677 m, br $\nu(N^{+}{-}H)$, 1047 s $\nu(Mo{\equiv}N)$. $^1H$ NMR ($CDCl_3$): $\delta = 1.18$ (s, 36 H, C(C$H_3$)$_3$), 1.52 (t, 9 H, $^3J_{HH} = 7.2$ Hz, NCH$_2$C$H_3$), 3.11 (d, 4 H, $^2J_{HH} = 12.0$ Hz, C$H_2$), 3.34 (m, 6 H. NC$H_2$CH$_3$), 3.39 (d, 4 H, $^2J_{HH} = 12.0$ Hz, C$H_2$), 6.98 (s, 8 H, aryl-$H_m$), 9.53 (s, br, 1 H, N$H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 9.08$ (NCH$_2$$C$H$_3$), 31.53 (C($C$H$_3$)$_3$), 33.59 ($C$H$_2$), 33.87 ($C$(CH$_3$)$_3$), 47.69 (N$C$H$_2$CH$_3$), 124.37 (aryl-$C_m$), 130.50 (aryl-$C_o$), 143.33 (aryl-$C_p$), 154.60 (aryl-$C_i$).

**Computational Details.** All density functional calculations were carried out by using the TURBOMOLE set of programs, developed by Ahlrichs and co-workers, within the RI-J approximation.[15,16] Standard SV(P) basis sets and auxiliary basis sets as implemented in the TURBOMOLE package were used for all atoms.[16,17] The acronym SV(P) (split valence plus polarization) refers to TURBOMOLE split valence basis sets, augmented by a shell of polarization functions. Quasi-relativistic pseudo potentials were used for Mo.[18] All calculations were performed including gradient corrections, Becke's nonlocal correction for exchange, and Perdew's nonlocal correction for correlation to the local density approximation part of the density functional.[19]

**Crystal Structure Determinations of ($HNEt_3$)[MoCl(NCMe)(Calix)]·$C_7H_8$ (1·$C_7H_8$), [Mo($PMe_3$)(NCMe)(Calix)]·1.5$C_6H_6$ (3·1.5$C_6H_6$), [Mo($NC_5H_5$)(NCMe)(Calix)] (4), [Mo($N_2CPh_2$)(NCMe)(Calix)]·2$CH_3CN$ (6·2$CH_3CN$), [Mo(NPh)(NCMe)(Calix)] (7), and 1.5($HNEt_3$)[MoN(Calix)]·2.5$CH_3CN$ [1.5(8)·2.5$CH_3CN$].** CCDC-243079 to CCDC-243084 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.; fax (+44) 1223-336-033 or deposit@ccdc.cam.uk).

Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS (Ag Kα radiation, **1**·$C_7H_8$, **7**, 1.5(**8**)·2.5$CH_3CN$; Mo Kα radiation, **6**·2$CH_3CN$) or a Stoe STADI 4 diffractometer (Mo Kα radiation, **4**) equipped with a FTS AirJet low-temperature device or a Stoe-CCD (Mo Kα radiation, **3**·1.5$C_6H_6$) equipped with an Oxford Cryosystems low-temperature device. Data were collected 203 K; equivalent reflections were merged, and the images were processed with the appropriate STOE software package. Corrections for Lorentz−polarization effects and absorption were performed, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.[28]

For compound **3**·1.5$C_6H_6$ the methyl carbons of the phosphine ligand C(5)−C(7) were disordered over two sites and isotropically refined with occupancy factors of 70% and 30%. Furthermore, one of the calix[4]arene *tert*-butyl groups, C(47)−C(49), as well as one of the additional solvent molecules C(70)−C(75) was disordered over two sites and isotropically refined with 50% occupancy each. The calix[4]arene *tert*-butyl groups containing C(37)−C(39) and

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(28) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Universität Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.

**Table 1.** X-ray Data Collection and Processing Parameters

| | **1**·$C_7H_8$ | **3**·1.5$C_6H_6$ | **4** | **6**·2$CH_3CN$ | **7** | 1.5(**8**)·2.5$CH_3CN$ |
|---|---|---|---|---|---|---|
| formula | $C_{59}H_{79}ClMoN_2O_4$ | $C_{58}H_{73}MoNO_4P$ | $C_{51}H_{60}MoN_2O_4$ | $C_{63}H_{71}MoN_5O_4$ | $C_{52}H_{60}MoN_2O_4$ | $C_{80}H_{109.5}Mo_{1.5}N_{5.5}O_6$ |
| fw | 1011.7 | 975.1 | 861.0 | 1058.2 | 873.0 | 1388.1 |
| cryst system | monoclinic | orthorhombic | monoclinic | triclinic | monoclinic | orthorhombic |
| space group | $P2_1/c$ | $P2_12_12_1$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | *Pnma* |
| $a$/Å | 16.205(1) | 12.777(3) | 19.024(4) | 12.732(3) | 18.450(4) | 13.499(3) |
| $b$/Å | 13.250(1) | 18.352(4) | 12.263(3) | 14.487(3) | 12.621(3) | 24.289(5) |
| $c$/Å | 25.903(1) | 24.604(5) | 20.140(4) | 16.634(3) | 20.521(4) | 46.879(9) |
| $\alpha$/deg | | | | 77.47(3) | | |
| $\beta$/deg | 102.761(6) | | 109.84(3) | 67.54(3) | 108.46(3) | |
| $\gamma$/deg | | | | 84.50(3) | | |
| $V$/Å$^3$ | 5424.4(6) | 5769(2) | 4419.7(15) | 2767(10) | 4532.4(16) | 15 371(5) |
| $Z$ | 4 | 4 | 4 | 2 | 4 | 8 |
| $\mu$/mm$^{-1}$ | 0.916 | 0.296 | 0.343 | 0.289 | 1.061 | 0.941 |
| tot./indpdt reflcns | 38 899/9483 | 64 707/9123 | 8245/7822 | 16 004/8208 | 31 747/9182 | 49 028/9509 |
| obsd reflcns [$I > 2\sigma(I)$] | 7483 | 6911 | 5240 | 10866 | 5907 | 6379 |
| params | 586 | 683 | 536 | 655 | 545 | 814 |
| final R,[a] wR2[b] | 0.0441, 0.1101 | 0.0593, 0.1544 | 0.0684, 0.1296 | 0.0657, 0.1731 | 0.0544, 0.1201 | 0.0647, 0.1609 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, for data with $I > 2\sigma(I)$.

an additional acetonitrile molecule [N(5), C(64), C(65)] were positionally disordered for compound **6**·2$CH_3CN$. These carbon atoms were refined in an isotropic approximation with occupancy factors of 60% and 40% or 50% each, respectively. For compound 1.5(**8**)·2.5$CH_3CN$, the positionally disordered calixarene *tert*-butyl group containing C(17)−C(19) and C(37)−C(39) was refined in an isotropic approximation with occupancy factors of 70% and 30%, and those containing C(67)−C(69) were refined with occupancy factors of 60% and 70%. The disordered nitrogen atom of one of the solvent molecules, N(6), was isotropically refined with occupancy factors of 60% and 40%.

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**Supporting Information Available:** X-ray crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC numbers for these CIFs are 243079−243084.

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