Synthesis, Molecular Structure and Reactivity of a Calix[4]arene Monomethyl Ether Supported Nitridomolybdenum Complex

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The calix[4]arene monomethyl ether supported nitridomolybdenum complex [MoN(MeCalix)] (**1**) was obtained in high yield from the reaction of [MoN(O*t*Bu)$_3$] and calix[4]arene methyl ether (H_3MeCalix). Contrary to the calix[4]arene dimethyl ether supported dioxomolybdenum complex [MoO_2(*paco*-Me_2Calix)] published earlier, the calix[4]arene ligand in **1** adopts a cone conformation. Complex **1** reacts smoothly with $GaCl_3$ and $GaEt_3$ to yield the compounds [Mo($NGaCl_3$)(MeCalix)] (**2**) and [Mo($NGaEt_3$)(MeCalix)] (**3**), respectively. Complex **2** is the first structurally characterized example of a nitrido-bridged dinuclear compound of a group 6 metal and a group 13 halide (EX_3). The [Mo≡N–$GaCl_3$] unit, in which both metal atoms are unsymmetrically bridged with a short Mo≡N and a long Ga–N contact, shows significant bending at the nitrido bridge. This deviation from a linear alignment is attributed to packing forces.

Introduction

Calix[*n*]arenes are macrocyclic molecules made of *n* phenol units connected by *ortho* methylene groups.[1–3] Calix[4]arenes (*p*-*tert*-butylcalix[4]arene = H_4Calix) are the simplest and most common compounds of this family, with four phenolic residues in the macrocyclic ring. Because of these four phenoxy groups in the calix[4]arenes, reactions with transition metal complexes can produce metal phenolate complexes with substitution of one to four hydrogen atoms.[4] The fully deprotonated form of the parent calix[4]arene acts as a tetraanionic ligand and almost exclusively assumes the cone conformation in metallacalix[4]arenes, which keeps the set of oxygen donor atoms quasi planar. The charge of the O_4 set can be tuned by etherification or esterification of the lower rim of the calix[4]arene. The Me_2-Calix homologues, in particular, have received much attention in organotransition metal chemistry over the last 10 years, and a rich chemistry has emerged comprising mainly mononuclear group 4 and 5 metals. In these complexes, the $[R_2Calix]^{2-}$ ligands usually provide two negatively charged phenolate oxygen donor atoms and two neutral anisole oxygen donors to a transition metal. If the calix[4]arene ethers coordinate in their elliptically distorted cone conformations, these ligands provide a robust and well-defined O_4 coordination environment, similar to other widely used supporting dianionic ligands such as the O_2,N_2-donor ligands of salen-type Schiff bases or N_4-donor ligands such as porphyrins and dibenzotetraaza[14]annulenes.[5–7] In contrast to these nitrogen-containing ligand systems, the calix[4]arene dialkyl ethers are conformationally flexible.

The coordination form of calix[4]arene alkyl ethers is largely determined by the nature of the ether group, the coordination number of the metal, and the nature of the co-ligands. We have shown that the calix[4]arene ligand in the d^0 transition metal complex [$TiCl_2$(Me_2Calix)] (**A**) adopts an elliptically distorted cone conformation, whereas in the related d^0-transition metal complex [MoO_2(*paco*-Me_2-Calix)] (**B**) the metalated calix[4]arene ligand is coordinated in a partially flattened cone conformation, a form reminiscent of the partial cone (*paco*) conformation of calix[4]arene, in the solid state as well as in solution (see Scheme 1).[8] In compound **B**, the [Mo(Me_2Calix)] complex fragment is further stabilized by two additional oxo ligands, which exhibit a strong *trans* influence, and DFT calculations on models of different isomers of **A** and **B** indicate that this phenomenon is mainly driven by the co-ligands employed in these complexes.

Furthermore, in compounds of the type [Ti(O-4-C_6H_4R)$_2$-(Me_2Calix)] (R = Me or *t*Bu; **C**), both types of coordination behavior have been observed.[9] Bis(phenolate) compounds with *para*-substituted phenolate ligands have been isolated in good to excellent yields from reaction of the imidotitanium complex [Ti(N*t*Bu)(Me_2Calix)] and two equivalents of the corresponding phenol to afford complexes in which the calix[4]arene is coordinated in an elliptically distorted cone conformation. These complexes undergo elimination and/or rearrangement reactions in non-

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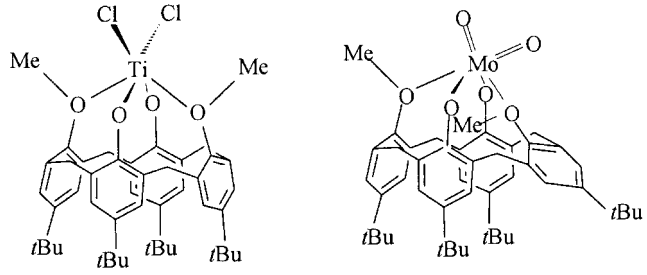


Scheme 1. Coordination of the calix[4]arene ligands in $[TiCl_2(Me_2$-Calix)] (**A**) and $[MoO_2$(*paco*-Me_2Calix)] (**B**).

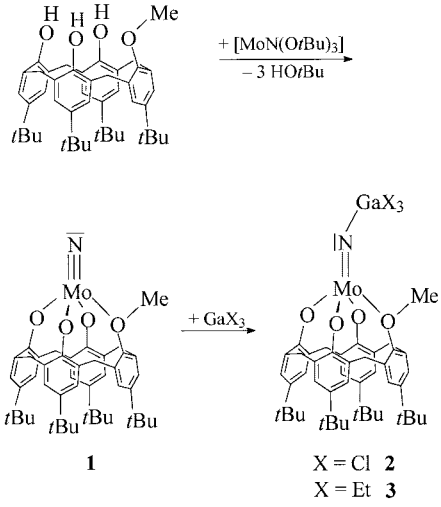
polar solvents such as pentane or hexane. The metal-containing products of the elimination reactions are dinuclear complexes $[\{Ti(O\text{-}4\text{-}C_6H_4R)(MeCalix)\}_2]$ and the products of the rearrangement reactions are $[Ti(O\text{-}4\text{-}C_6H_4R)_2$(*paco*-$Me_2$Calix)]. In these compounds, one of the methoxy groups is located inside the cavity of the calix[4]arene ligand. DFT calculations on model compounds $[Ti(OC_6H_5)_2$(*cone*-Me_2Calix)] and $[Ti(OC_6H_5)_2$(*paco*-Me_2Calix)] reveal a slight thermodynamic preference for the *paco* isomer. Furthermore, *paco* coordination has only been observed in complexes of the calix[4]arene dimethyl ether in distorted octahedrally coordinated compounds of the type $[MX_2(Me_2$-Calix)].

In titanium complexes of the type [TiX(MeCalix)] (X = Cl, OR, SR, NR_2)[10] the calix[4]arene ligand adopts an elliptically distorted cone conformation in which the Ti–O distances to the anisole oxygen atoms vary in the solid-state structures in a range between 234.2 and 243.8 pm.[11] MP2 calculations on model complexes have revealed that this titanium–anisole oxygen bond is relatively weak, and, particularly in the region between 230 and 280 pm, the potential energy surface is very shallow. Thus, the MeCalix ligand acts in these complexes as a tris(phenolate) ligand with a hemilabile anisole group. Despite the labile anisole ether–titanium bond, isomerization reactions of the calix[4]arene ligand leading to a *paco* coordination have never been observed in these complexes and MP2 calculations have revealed a considerable thermodynamic preference for the cone isomers.

At this point we were interested in extending our studies to calix[4]arene monomethyl ether stabilized complexes of the type [MoX(MeCalix)] (X = ligand with *trans* directing properties), and we wish to report here our first results on the synthesis and molecular structure of the nitridomolybdenum complex [MoN(MeCalix)] and its reaction with Lewis acids of the type GaX_3 (X = Cl, Et).

Results and Discussion

Most of the calix[4]arene-stabilized molybdenum complexes known so far are compounds of the parent *p-tert*-butylcalix[4]arene.[11,12] For calix[4]arene ethers there are, to the best of our knowledge, three complexes available in the literature, $[MoOCl_2(R_2Calix)]$ (R = Me, Et) synthesized by Young et al. starting from $[MoOCl_4]$ and calix[4]arene dialkyl ether,[12j] and a dinuclear complex $[Mo_2(MeCalix)_2]$, prepared in Chisholm's group, in which the metal–metal triple bond is supported by calix[4]arene methyl ethers.[12g] This complex was synthesized by amine or butanol elimination starting from $[Mo_2(NMe_2)_6]$ or $[Mo_2(OtBu)_6]$, respectively, and the calix[4]arene ether. For the preparation of [MoN(MeCalix)] (**1**) we decided to follow a similar strategy and treated $[MoN(OtBu)_3]$[13] with H_3MeCalix in toluene (Scheme 2).



Scheme 2. Synthesis of [MoN(MeCalix)] (**1**) and reaction of **1** with $GaCl_3$ and $GaEt_3$.

This reaction proceeds cleanly with elimination of *tert*-butyl alcohol to afford the calix[4]arene ether-stabilized, neutral nitridomolybdenum(VI) complex **1** in excellent yield. Contrary to the calix[4]arene oxomolybdenum(VI) compound $[MoO(Calix)(H_2O)(PhNO_2)(H_4Calix)]$ reported by Floriani et al.,[12a] the nitrido compound is readily soluble in most organic solvents such as benzene or toluene. Compound **1** is stable with respect to either isomerization of the calix[4]arene ligand or rearrangement to a calix[4]arene-stabilized imidomolybdenum complex [Mo(NMe)(Calix)]. Analytical and spectroscopic data are in accordance with monomeric molecular units in solution as well as in the solid state, in which the calix[4]arene binds in a distorted cone conformation to the molybdenum atom. The ^1H NMR spectrum of **1** reveals a signal pattern typically found for those ligand systems in C_s symmetrical complexes, with three resonances for the *tert*-butyl protons at δ = 0.71, 0.79, and 1.37 ppm in the ratio 1:1:2 and four doublets between δ = 3.10 and 4.71 ppm with coupling constants of 12.4 Hz and 12.7 Hz. Most significantly, the methoxide resonance is detected as a sharp singlet at δ = 4.25 ppm and is not shifted to lower field as usually observed for endohedrally located anisole methyl groups, which are typically found at approximately δ = 0.8 ppm. In the IR spectrum of the complex, an intense absorption is detected in the region of the [Mo≡N] stretch at 1045 cm^{-1}.

Crystals of **1** suitable for X-ray diffraction were obtained by cooling saturated diethyl ether solutions to –40 °C. The molecular structure of **1** is shown in Figure 1; selected bond lengths and bond angles are given in the figure caption. The structural analysis confirms the proposed mononuclear nature of **1** in the solid state and the cone conformation of the calix[4]arene ligand. In contrast to many solid-state structures of nitrido complexes, in which molecules aggregate through Mo–N···Mo contacts, we observe no intermolecular molybdenum–nitrogen interactions here. The coordination polyhedron at the molybdenum atom is best described as a square pyramid with the calixarene oxygen atoms O(1) to O(4) in the basal plane and the nitrogen atom occupying the apex. The molybdenum atom is displaced out of the calixarene O_4 plane towards the nitrogen atom of the complex, which is indicated by the N–Mo–O angles in a range between 92.4(2)° and 102.7(2)°. The Mo–O distances to the phenoxide entities [191.4(4) pm to 192.5(4) pm] and to the anisole unit [226.3(4) pm] of the calix[4]arene ligand are unexceptional. The Mo–N distance of 163.9(5) pm in **1** is significantly (approximately 8 pm) shorter than Mo–N bonds observed in calix[4]arene imidomolybdenum(VI) complexes[12b,12d] but similar to those found in other mononuclear nitridomolybdenum(VI) complexes such as $[MoN(NtBuPh)_3]$ [165.8(5) pm],[14a] $[MoN(NPh_2)_3]$ [163.4(3) pm],[14b] $[MoN(OtBu)_3]$ [166.1(4) and 167.3(5) pm],[13] $[MoN(Mes)_3]$ [164.9(4) pm],[14c] and $(Ph_4P)[MoNX_4]$ (X = Cl, Br) [163.7(4) and 162.8(15) pm].[14e,f]

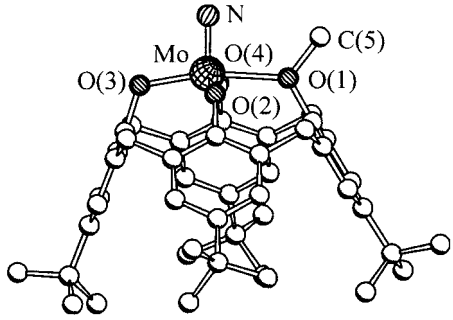


Figure 1. Schakal plot of the molecular structure of the [MoN(MeCalix)] (**1**) unit in **1**·1.5 Et_2O. H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Mo–N 163.9(5), Mo–O(1) 226.3(4), Mo–O(2) 191.4(4), Mo–O(3) 192.5(4), Mo–O(4) 192.0(4); N–Mo–O(1) 92.4(2), N–Mo–O(2) 102.8(2), N–Mo–O(3) 100.7(2), N–Mo–O(4) 102.7(2), O(1)–Mo–O(2) 81.29(16), O(1)–Mo–O(3) 166.92(14), O(1)–Mo–O(4) 81.41(15), O(2)–Mo–O(3) 96.21(18), O(2)–Mo–O(4) 149.62(16), O(3)–Mo–O(4) 95.03(17), Mo–O(1)–C(10) 121.7(3), Mo–O(1)–C(5) 124.5(3), Mo–O(2)–C(20) 137.4(4), Mo–O(3)–C(30) 117.6(3), Mo–O(4)–C(40) 138.1(3).

Transition metal nitrido complexes with a terminal nitrido ligand usually show Lewis basic behavior and can thus form nitrido bridges to Lewis acidic species. Compounds that contain a transition metal–nitrogen–main group element linkage have been proven to be a versatile class of compounds that exhibit vastly different chemical behavior depending on the nature of the transition metal and the main group element.[15] The structure of the compounds can range from species that have a linear transition metal–nitrogen–main group element moiety up to molecules where the nitrido linkage is strongly bent. Some compounds are monomeric while others are oligomeric or polymeric. Because of their rich chemistry, nitrido complexes have been the subject of experimental as well as theoretical studies. Whereas the formation and the chemistry of complexes with an $[Re{\equiv}N–EX_3]$ (E = group 13 element) linkage has been rather thoroughly investigated, mainly by the groups of Strähle and Abram,[16] there are few known examples of similar complexes of group 6 metals. With the exception of the complex [*trans*-$Mo(N–BPh_3)(OTf)$(*anti*-Me_8[16]aneS_4)] (Me_8[16]aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane, OTf = SO_3CF_3) published by Yoshida et al.,[17] this type of compound is, to the best of our knowledge, unknown in group 6 chemistry. Therefore we were interested in the adduct formation of complex **1** with group 13 tris(halide) and tris(alkyl) compounds. Calculations published by Frenking and coworkers[18] on model complexes of the type $[Re({\equiv}N–EX_3)(PH_3)_3Cl_2]$ have shown that in the series EH_3 (E = B, Al, Ga) the $[Re{\equiv}N–GaH_3]$ linkage is particularly weakly bonded. The zero-point-corrected dissociation energies at the MP2 level given in this paper are, for the trihydrides, 29.3 kcal mol^{-1} for E = B, 25.3 kcal mol^{-1} for E = Al, and 17.0 kcal mol^{-1} for E = Ga, and in the case of the trichlorides 31.2 kcal mol^{-1} for E = B, 42.6 kcal mol^{-1} for E = Al, and 33.5 kcal mol^{-1} for E = Ga. Because of the lack of known ER_3 and EX_3 adducts of nitridomolybdenum compounds, and the presumably weak interaction with gallium Lewis acids, we decided

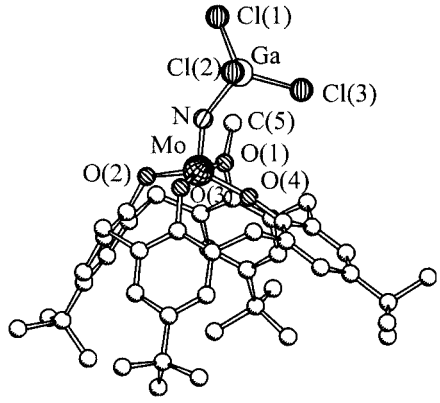


Figure 2. Schakal plot of the molecular structure of the [Mo(N-$GaCl_3$)(MeCalix)] (**2**) unit in **2**·3 C_7H_8. H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Mo–N 168.0(5), Mo–O(1) 223.5(4), Mo–O(2) 187.9(4), Mo–O(3) 191.6(3), Mo–O(4) 182.9(4), Ga–N 196.0(5), Ga–Cl(1) 214.1(2), Ga–Cl(2) 213.2(2), Ga–Cl(3) 218.3(3), C(5)–O(1) 146.0(7); Mo–N–Ga 147.2(3), N–Ga–Cl(1) 107.60(14), N–Ga–Cl(2) 104.27(16), N–Ga–Cl(3) 104.11(19), N–Mo–O(1) 91.3(2), N–Mo–O(2) 104.9(2), N–Mo–O(4) 111.2(3), N–Mo–O(3) 98.4(2), O(1)–Mo–O(2) 84.98(15), O(1)–Mo–O(3) 168.97(14), O(1)–Mo–O(4) 79.77(16), O(2)–Mo–O(3) 97.55(16), O(2)–Mo–O(4) 140.9(2), O(3)–Mo–O(4) 91.72(16), Cl(1)–Ga–Cl(2) 113.50(10), Cl(2)–Ga–Cl(3) 115.44(13), Cl(1)–Ga–Cl(3) 110.93(10), Mo–O(1)–C(10) 118.9(3), Mo–O(1)–C(5) 127.5(4), Mo–O(2)–C(20) 130.2(3), Mo–O(3)–C(30) 117.2(3), Mo–O(4)–C(40) 170.7(4).

to investigate adduct formation of **1** with alkylgallium compounds and gallium halides.

Surprisingly, complex **1** reacts swiftly with $GaCl_3$ and $GaEt_3$ (see Scheme 2). According to NMR investigations, these compounds form the adducts [Mo(N$GaCl_3$)(MeCalix)] (**2**) and [Mo(N$GaEt_3$)(MeCalix)] (**3**) quantitatively without decomposition of the starting material. In the reaction products, the [Mo≡N] stretch does not change very much after coordination of the GaX_3 moieties: we observe these stretching frequencies in the IR spectra at 1046 cm^{-1} (**2**) and 1055 cm^{-1} (**3**). In the NMR spectra of these complexes, the resonances of the calix[4]arene ligands are slightly shifted compared to the resonances found for **1**. In the case of complex **3** the proton and carbon resonances of the $GaEt_3$ group are significantly shifted with respect to the noncoordinated molecule. By way of an example, in the ^1H NMR spectrum they are shifted from δ = 0.56 and 1.28 ppm to δ = 1.02 and 1.74 ppm. To confirm the adduct formation beyond doubt single crystals of the chloride complex **2** were grown from saturated toluene solutions at –40 °C and an X-ray diffraction study was undertaken. The molecular structure of **2** is shown in Figure selected bond lengths and bond angles are given in the figure caption.

Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with three additional toluene molecules in the asymmetric unit. One of these solvent molecules is located inside the calix[4]arene cavity, whereas the others occupy general positions in the lattice. The endohedrally bound toluene molecule does not interact with the metal atom. The molecular structure confirms the composition of **2** as the $GaCl_3$ adduct of [MoN(MeCalix)] (**1**), in which the gallium atom is mounted on the nitrido nitrogen atom of **1**. Although various complexes of group 6 metal nitrido complexes with homoatomic and heteroatomic nitrido bridges [M≡N–M′] to other transition metal complex fragments are known,[19,20] complex **2** is the first structurally characterized example of a dinuclear compound of a group 6 metal complex and a group 13 halide EX_3 (E = B, Al, Ga, In; X = F, Cl, Br) with a central [M≡N–EX_3] nitrido bridge. This nitrido bridge is asymmetric; the molecular structure reveals a short Mo–N bond and a long Ga–N contact. The Mo–N distance of 168.0(5) pm in **2** is approximately 4 pm longer than the Mo–N bond observed in **1**. The Ga–N distance of 196.0(5) pm is similar to other Ga–N distances found in adducts of $GaCl_3$ with nitridorhenium complexes such as [Re(N$GaCl_3$)Cl_2(PMe_2Ph)$_3$] [197(1) pm], [Re(N$GaCl_3$)-Cl(PMe_2Ph)$_3$(NCMe)]$^+$[$GaCl_4$]$^-$ [195.9(4) pm], [Re(N$GaCl_3$)(PMe_2Ph)(Et_2dtc)] [191.6(6) pm; Et_2dtc = diethyldithiocarbamato], or [Re(N$GaCl_3$)Cl(PMe_2Ph)(H_2Et_2tcb)]$^+$-[$GaCl_4$]$^-$ [194.5(3) pm; Et_2tcb = *N*,*N*-diethylcarbamoylbenzamidate].[16b,21] The [Mo–N–Ga] linkage is significantly bent towards O(4) with an angle of 147.2(3)° at the nitrogen atom. The best planes defined by Mo, N, Ga and N, Mo, O(4) intersect each other with an angle of 5.8(6)°. This deviation from linearity is presumably due to packing forces in the lattice, since the distance of one of the chlorine atoms [Cl(1)] to the *tert*-butyl and ring *meta* carbon atoms of the phenolate entities at O(3) and O(4) of the next molecule in the lattice is slightly below 400 pm and would get even closer for an almost linear coordination. Furthermore, the coordination of $GaCl_3$ to [MoN(MeCalix)] (**1**) is accompanied by a distortion of the first coordination sphere at the molybdenum atom. The electron density at the molybdenum atom in **2** is lower than that in complex **1** due to the electron-withdrawing properties of the $GaCl_3$ moiety in the molecule. This is reflected by the shorter Mo–O contacts observed for complex **2** in general. Most significantly, the Mo–O(4) bond length is reduced from 192.0(4) pm in **1** to 182.9(4) pm in **2**, and this phenolate unit of the calixarene ligand coordinates almost linearly to the molybdenum atom [Mo–O(4)–C(40): 170.7(4)°].

The model complex [Mo(N$GaCl_3$)(MeCalix^H)] $\mathbf{2^H}$, in which the *tert*-butyl groups of the calix[4]arene have been replaced by hydrogen atoms to reduce computational effort, optimizes in DFT calculations[22] with a structure with slightly longer Mo–N and Ga–N distances of 169.74 pm (Mo–N) and Ga–N 202.12 pm (Ga–N) compared to the molecular structure of **2**. The calculated Mo–N–Ga angle of 169.74°, however, is closer to linearity than the angle observed in the molecular structure. The distortion of the calix[4]arene ligand in the coordination sphere of the molybdenum atom is also well reproduced in the computations. The zero-point-corrected dissociation energies calculated at the level employed here for the gallium–nitrogen bond in $\mathbf{2^H}$ is 25.8 kcal mol^{-1} and therefore slightly smaller than the dissociation energies computed by Frenking and coworkers for the nitridorhenium system mentioned above (33.5 kcal mol^{-1}) and similar to the dissociation energy calculated for [Cl_3W≡N–$AlCl_3$] (22.06 kcal mol^{-1}) by the same group.[23]

Conclusions

We have shown that [MoN(MeCalix)] (**1**) can be synthesized in high yield in an alcohol elimination reaction starting from [MoN(O*t*Bu)$_3$] and the calix[4]arene H_3MeCalix. Contrary to the dioxomolybdenum complex [MoO_2(*paco*-Me_2Calix)] (**B**) the calixarene ligand in **1** is coordinated in the cone conformation. Complex **1** is stable with respect to either isomerization of the calix[4]arene ligand or rearrangement to a calix[4]arene-stabilized imidomolybdenum complex. The calix[4]arene ether ligand provides enough electron density to the [Mo≡N] moiety in **1** that reactions with $GaCl_3$ and $GaEt_3$ proceed smoothly and afford the complexes [Mo(N$GaCl_3$)(MeCalix)] (**2**) and [Mo(N$GaEt_3$)(MeCalix)] (**3**). Complex **2** is the first structurally characterized nitrido-bridged compound of a group 6 metal complex and a group 13 metal halide [EX_3]. The [M≡N–EX_3] linkage is significantly bent at the nitrido nitrogen atom, which is attributed to packing forces.

Experimental Section

General Remarks: All air/moisture-sensitive manipulations were performed using standard Schlenk-line (N_2) and dry-box (Ar) tech-

niques. Solvents were pre-dried and refluxed over sodium, potassium, or sodium-potassium alloy (1:3 w/w; benzene, toluene, pentane, hexane, diethyl ether, THF), or P_2O_5 (acetonitrile, dichloromethane) under N_2. Solvents were distilled at atmospheric pressure prior to use. Deuterated solvents were dried with sodium. $GaEt_3$ was obtained from commercial sources and distilled prior to use.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer at 298 K. Spectra are referenced internally to residual protonated solvent resonances (^1H; C_6D_6: δ = 7.15 ppm) or solvent (^{13}C; C_6D_6: δ = 128.0 ppm) and are reported relative to tetramethylsilane (δ = 0.00 ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. 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. IR spectra were recorded on a Bruker IFS28 spectrometer as KBr pellets. All data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded on a Finnigan MAT 900 XLT. All data are quoted as their mass/charge (*m*/*z*) ratios. Elemental analyses were carried out by the analytical laboratory of the Institute of Inorganic Chemistry of the University Karlsruhe (TH). [Mo(N)(O*t*Bu)$_3$][13] and H_3MeCalix[24] were synthesized according to literature procedures.

[MoN(MeCalix)] (1): Toluene (50 mL) was added to a mixture of H_3MeCalix (15.00 g, 22.6 mmol) and [MoN(O*t*Bu)$_3$] (7.44 g, 22.6 mmol). The initially orange-colored solution turned red after a short time and the resulting reaction mixture was stirred for three hours and then filtered through a pad of Celite. The filtrate was evaporated to dryness to afford [MoN(MeCalix)] (**1**) as an orange-red powder. Yield: 16.50 g (21.5 mmol, 95%). Crystals suitable for X-ray diffraction were obtained either from hot saturated toluene solutions or from saturated diethyl ether solutions at –40 °C. $C_{45}H_{55}MoNO_4$ (769.9): calcd. C 70.21, H 7.20, N 1.82; found C 70.48, H 7.30, N 1.84. EI/MS: *m*/*z* (%) = 769 (27) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 1045 cm^{-1} (vs) ν(Mo≡N). ^1H NMR (C_6D_6): δ = 0.71 [s, 9 H, C(CH_3)$_3$], 0.79 [s, 9 H, C(CH_3)$_3$], 1.37 [s, 18 H, C(CH_3)$_3$], 3.10 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH_2), 3.16 (d, $^2J_{H,H}$ = 12.4 Hz, 2 H, CH_2), 4.25 (s, 3 H, OCH_3), 4.35 (d, $^2J_{H,H}$ = 12.4 Hz, 2 H, CH_2), 4.70 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH_2), 6.81 (s, 2 H, Aryl-H_m), 6.88 (s, 2 H, Aryl-H_m), 7.19 (s, 4 H, Aryl-H_m) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 30.5, 30.9, 31.9 [C(*C*H$_3$)$_3$], 32.8, 33.4 (*C*H$_2$), 33.7, 33.9, 34.3 [*C*(CH$_3$)$_3$], 76.2 (O*C*H$_3$), 124.4, 125.9, 126.0, 127.0 (Aryl-C_m), 129.5, 129.6, 131.1, 134.7 (Aryl-C_o), 144.7, 146.2, 150.8 (Aryl-C_p), 149.4, 151.6, 156.1 (Aryl-C_i) ppm.

[Mo(NGaCl$_3$)(MeCalix)] (2): [MoN(MeCalix)] (**1**; 0.77 g, 0.99 mmol) was dissolved in toluene (20 mL) and a solution of $GaCl_3$ (0.18 g, 1.01 mmol) in toluene (10 mL) was slowly added at room temperature. The resulting reaction mixture was stirred overnight at room temperature, filtered through a pad of Celite, and the volatile components of the filtrate were removed in vacuo. The resulting solid was suspended in hexane and filtered off to afford **2** as a brown powder Yield: 0.72 mg (0.76 mmol, 77%). Crystals suitable for X-ray diffraction were obtained from saturated toluene solutions at –40 °C. $C_{45}H_{55}Cl_3GaMoNO_4$ (946.0): calcd. C 57.74, H 5.86, N 1.48; found C 58.19, H 5.60, N 1.42. IR (KBr): $\tilde{\nu}$ = 1046 cm^{-1} (vs) ν(Mo≡N). ^1H NMR (C_6D_6): δ = 0.63 [s, 9 H, C(CH_3)$_3$], 0.72 [s, 9 H, C(CH_3)$_3$], 1.33 [s, 18 H, C(CH_3)$_3$], 2.97 (d, $^2J_{H,H}$ = 13.3 Hz, 2 H, CH_2), 3.08 (d, $^2J_{H,H}$ = 12.9 Hz, 2 H, CH_2), 4.07 (d, $^2J_{H,H}$ = 12.9 Hz, 2 H, CH_2), 4.26 (s, 3 H, OCH_3), 4.29 (d, $^2J_{H,H}$ = 13.3 Hz, 2 H, CH_2), 6.72 (s, 2 H, Aryl-H_m), 6.75 (s, 2 H, Aryl-H_m), 7.13 (s, 2 H, Aryl-H_m), 7.14 (s, 2 H, Aryl-H_m) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 30.4, 30.7, 31.9 [C(*C*H$_3$)$_3$], 32.6, 33.1 (*C*H$_2$), 33.8, 33.9, 34.6 [*C*(CH$_3$)$_3$], 76.1 (O*C*H$_3$), 125.7, 125.0, 126.0, 126.6 (Aryl-C_m), 129.7, 129.9, 131.9, 133.0 (Aryl-C_o), 149.3, 149.0, 151.0 (Aryl-C_p), 149.1, 151.6, 155.9 (Aryl-C_i) ppm.

[Mo(NGaEt$_3$)(MeCalix)] (3): [MoN(MeCalix)] (**1**; 0.40 g, 0.52 mmol) was dissolved in toluene (20 mL) and a solution of $GaEt_3$ (0.08 g, 0.52 mmol) in toluene (10 mL) was slowly added at room temperature and stirred for an hour. The volatile components of the reaction mixture were removed in vacuo to afford **3** as an orange-brown powder. Yield: 0.48 g (0.51 mmol, 98%). $C_{51}H_{70}GaMoNO_4$ (926.8): calcd. C 66.10, H 7.61, N 1.51; found C 65.98, H 7.39, N 1.41. IR (KBr): $\tilde{\nu}$ = 1055 cm^{-1} (vs) ν(Mo≡N). ^1H NMR (C_6D_6): δ = 0.67 [s, 9 H, C(CH$_3$)$_3$], 0.75 [s, 9 H, C(CH$_3$)$_3$], 1.08 (q, $^3J_{HH}$ = 8.0 Hz, 6 H, GaCH_2R), 1.36 [s, 18 H, C(CH$_3$)$_3$], 1.74 (t, $^3J_{HH}$ = 8.0 Hz, 9 H, GaCH$_2$CH_3), 3.05 (d, $^2J_{H,H}$ = 12.9 Hz, 2 H, CH$_2$), 3.11 (d, $^2J_{H,H}$ = 12.7 Hz, 2 H, CH$_2$), 4.24 (d, $^2J_{H,H}$ = 12.5 Hz, 2 H, CH$_2$), 4.32 (s, 3 H, OCH$_3$), 4.59 (d, $^2J_{H,H}$ = 12.8 Hz, 2 H, CH$_2$), 6.77 (s, 2 H, Aryl-H_m), 6.82 (s, 2 H, Aryl-H_m), 7.15 (s, 4 H, Aryl-H_m) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 7.2 (Ga*C*H$_2$CH$_3$), 11.7 (GaCH$_2$*C*H$_3$), 30.5, 30.8, 31.9 [C(*C*H$_3$)$_3$], 32.7, 33.4 (*C*H$_2$), 33.7, 33.9, 34.3 [*C*(CH$_3$)$_3$], 76.0 (O*C*H$_3$), 124.5, 125.9, 126.1, 127.2 (Aryl-C_m), 129.4, 129.5, 130.9, 134.4 (Aryl-C_o), 145.3, 146.8, 149.1 (Aryl-C_p), 150.9, 151.0., 155.8 (Aryl-C_i) ppm.

X-ray Crystallographic Study of [MoN(MeCalix)]·1.5 Et$_2$O and [Mo(NGaCl$_3$)(MeCalix)]·3 C$_7$H$_8$: Crystal data collection and processing parameters are given in Table 1. The crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-STADI 4 (**1**·1.5 Et_2O, Mo-K_α radiation) or Stoe IPDS I diffractometer (**2**·3 C_7H_8, Ag-K_α radiation) equipped with an FTS AirJet low-temperature device. Data were collected at 203 K. The IPDS images were processed with the Stoe IPDS software package and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms; hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed with SHELXS-97 and SHELXL-97.[25] For compound **2**·3 C_7H_8 the methyl carbon atoms of two *tert*-butyl groups of the calixarene ligand [C(27) to C(29)] and [C(47) to C(49)] were disordered over two sites and were isotropically refined with occupancy factors of 70 and 30%. The visualization of the molecular structures was performed with the program Schakal 99.[26]

CCDC-256140 (for **1**·1.5 Et_2O) and CCDC-256141 (for **2**·3 C_7H_8) contain the supplementary crystallographic data for this paper.

Table 1. X-ray data collection and processing parameters.

	1·1.5 Et_2O	**2**·3 C_7H_8
Formula	$C_{51}H_{70}MoNO_{5.50}$	$C_{66}H_{79}Cl_3GaMoNO_4$
Formula mass	881.02	1222.31
Crystal system	monoclinic	monoclinic
Space group	*I*2/*a*	$P2_1/c$
a [Å]	24.716(3)	11.3554(6)
b [Å]	13.033(3)	23.4224(12)
c [Å]	30.483(3)	23.7856(14)
β [°]	96.040(3)	94.514(7)
V [Å^3]	9765(3)	6306.6(6)
Z	8	4
μ [mm^{-1}]	0.314	1.053
Total/indep. reflns.	6784/5954	25466/10079
Observed reflns.[a]	4446	7065
Parameters	531	616
Final *R*,[b] wR_2[c][d]	0.0575/0.1260	0.0676/0.1686

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

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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