Forschungsbericht – Research Report

Calix[4]arene stabilized Transition Metal Imido Complexes

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Abstract. The usage of calix[n]arenes as ancillary poly(phenolate) ligands is a rapidly developing area in coordination chemistry. This article focuses on the synthesis, structure and reactivity of calix[4]-arene- and calix[4]arene ether-stabilized imido complexes of group 4 - 6 transition metals as well as on the comparison of calix[4]arene dialkyl ethers in particular with other widely employed related ligand systems such as salenes, porphyrins and tetraazaannulenes. Contrary to these nitrogen containing systems, it is much easier to control the charge of the ligand system through the degree of alkylation of the calixarene's lower rim without a major change in the

geometry of the resulting metal complex. This could lead to isoelectronic and structurally closely related transition metal complex fragments for metals in neighboring groups of the periodic table or for metals in different oxidation states. The "intrinsic" reactivity of metal imido linkages might therefore be explored using calix[4]arenes and calix[4]arene ethers and first results are summarized in this research report.

Keywords: Transition metal complexes; Group 4 – 6 metals; Calix[4]arene complexes; Imido complexes

Calix[4]aren-stabilisierte Übergangsmetall-Imido-Komplexe

Inhaltsübersicht. Der Einsatz von Calix[n]arenen als Poly(phenolat)liganden hat in den letzten Jahren zunehmendes Interesse in der Koordinationschemie gefunden. Dieser Forschungsbericht beschreibt Synthesewege, Strukturen und Reaktivität von Übergangsmetall-Imidokomplexen der Elemente der vierten bis sechsten Gruppe, die durch Calix[4]arene bzw. Calix[4]aren-Ether stabilisiert sind. Ferner werden die Komplexe der Calix[4]aren-Di(alkyl)ether mit anderen verwandten, vielfach eingesetzten Ligandensystemen wie den Salenen, Porphyrinen und Tetraazaannulenen verglichen. Im Gegensatz zu den Stickstoff-haltigen Ligandensystemen ist es in der Chemie von Calix[4]arenkomplexen durch Variation des Alkylierungsgrades am sog. "unteren Kegelrand" einfach, die Ladung des Liganden zu kontrollieren, ohne die Koordinationssphäre am Metallatom des resultierenden Komplexes tiefgreifend zu verändern. Der Einsatz von Calix[4]arenen und Calix[4]aren-Ethern sollte so zu isoelektronischen und strukturell ähnlichen Übergangsmetall-Komplexen von benachbarten Metallen im Periodensystem oder von identischen Metallen in unterschiedlichen Oxidationsstufen führen. Auf diese Weise können "intrinsische" Reaktivitäten von Calix[4]aren-stabilisierten Metall-Imidoverbindungen in Abhängigkeit vom Metall bzw. dessen Oxidationsstufe untersucht werden. Erste Ergebnisse sind in diesem Forschungsbericht zusammengefasst.

1 Introduction

Calix[n]arenes are macrocyclic molecules made of *n* phenol units connected by *ortho* methylene groups [1, 2]. Calix[4]arenes are the simplest and most common members of this family with four phenolic residues in the macrocyclic ring. These molecules and their derivatives have been extensively studied for their interesting properties, e.g. as hosts to cations, anions and neutral molecules, and for the formation of supramolecular assemblies [3]. Because of the four phenoxyl groups in the calix[4]arenes (*p-tert*-butyl-calix[4]arene = H₄calix, see Scheme 1) [4], reactions with transition

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metal complexes can produce metal phenolate complexes with substitution of one to four hydrogen atoms [5]. The fully deprotonated form of the parent calix[4]arenes act as tetraanionic ligands and usually assume the *cone* conformation in metalla-calix[4]arenes, which keeps the set of the 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, as pointed out in Scheme 1 for methylation products of H₄calix.



Scheme 1 Calix[4]arenes and calix[4]arene ethers as ancillary poly(phenolate)ligands.

Curriculum vitae of the author

Udo Radius was born in Nuremberg, Germany in 1965 and studied chemistry from 1986 to 1991 at the University of Würzburg. He received his doctoral degree in the group of Prof. Helmut Werner under the guidance of Prof. Jörg Sundermeyer in 1994. He continued his scientific education as a postdoctoral fellow with Prof. Roald Hoffmann (1995 – 1996) at the Cornell University, Ithaca, NY, where he was introduced into theoretical chemistry. Funded by a Liebig-Stipendium of the Fonds



der Chemischen Industrie, he returned to Germany for his habilitation, which was completed at the Universität Karlsruhe (TH) in 2001. His general research interests are in the fields of coordination chemistry and organometallic chemistry of the d-block elements including catalysis, material science, and bioinorganic chemistry. His group focuses currently on the usage of macrocyclic ligands in these areas, especially on calixarenes and thiacalixarenes as poly(phenolate) ligands.

The degree of functionalization of the metal atom can be controlled by alkylation or silvlation of the oxygen atoms, which also offers steric protection. The Me₂calix 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 [5]. In these complexes, the $[R_2 calix]^{2-}$ ligands usually provide two negatively charged phenolate oxygen donor atoms and two neutral anisole oxygen donors to a transition metal atom - a robust and welldefined O₄-coordination environment, similar to other widely used supporting dianionic ligands such as the O2,N2donor ligands of salene type Schiff bases or N4-donor ligands such as porphyrins and dibenzotetraaza[14]annulenes [6-8]. In contrast to these nitrogen containing ligand systems, the calix[4]arene dialkyl ethers are conformationally much more flexible (as shown below). Moreover, it is much easier to change the charge of the ligand system through the degree of alkylation without a major change in the structure of the resulting metal complex. Modifying the above mentioned nitrogen containing ligands in the same way would require significant synthetic effort, if at all possible. Therefore, calix[4]arenes seem to be ideal ancillary ligands for systematic investigations. Isoelectronic and structurally closely related transition metal complexes fragments, for example, are available for metals in neighboring groups of the periodic table. Similar compounds of the complex fragments [M(R₂calix)], [M'(Rcalix)], and [M"(calix)], can be synthesized, if the degree of alkylation of the calix[4]arene ligand is decreased and the central atom of the complex is substituted with a metal atom of the next group of the periodic table (M < M' < M'') or the same metal atom in its next higher oxidation state (M < M' < M''). This is exemplified in Scheme 2 for multiply bonded dianionic ligands E such as oxo, sulfido, imido, phosphinidene or carbene. In the case that (i) the metal atoms M, M', and M" are of group 4, 5, or 6 and of the same d electron configuration and (ii) that the metal atoms M, M', and M" are of the same group and differ in their formal oxidation states by one unit, these complexes are isoelectronic and structurally closely related. With these complexes in hand, it should

be possible to isolate and stabilize [M=E] functionalities and to study their "intrinsic" reactivity depending on the metal atom and its oxidation state, provided that the calix-[4]arene ligand binds in a *cone* or *elliptically distorted cone* conformation and the resulting complexes are monomeric as illustrated in Scheme 2.



Scheme 2 Similar isoelectronic and structurally closely related complexes of the type $[M(=E)(R_2calix)]$ D, [M'(=E)(Rcalix)] E, and [M''(=E)(calix)] F.

The chemistry of organoimido complexes has experienced a considerable development during the last two decades [9]. The imido ligand $[NR]^{2-}$ (R = alkyl, aryl) usually coordinates to a transition metal atom through one σ and up to two π orbital interactions, similar to the ubiquitous cyclopentadienyl ligand [10] or to phosphorane iminato ligands [11]. With respect to the fundamental importance of group 4 metallocenes as catalysts in olefin polymerizations and other catalytic transformations, this similarity has become a strategic tool for the development of new classes of catalytically active imido complexes [12, 13]. Furthermore, organoimido complexes of the transition metals have been implicated in catalytic processes such as propylene ammoxidation [14] and nitrile reduction [15] and have been shown to function as imido transfer intermediates in aziridination [16] and amination reactions [17, 18]. The importance of these fields led to a growing number of imido complexes of both later [18, 19] and earlier [17, 20] transition metals. The reactivity of group IV and group V organoimido complexes include C-H activation, cycloaddition of unsaturated C-C and C-X bonds, as well as addition of H₂ and alkylsilanes to the metal imido group. Moreover, group IV imido complexes participate in imine metathesis and catalyze the hydroamination of alkynes to enamines. By contrast, the metal nitrogen multiple bonds in imido complexes of group VI and group VII metals rarely display reactivity at the [M=NR] bond. Imido groups of diimido molybdenum, tungsten and rhenium compounds, for example, can act as spectator ligands in numerous reaction processes including metathesis reactions [20], whereas mononuclear imido compounds of more electron rich metals such as $[(\eta^5 C_5Me_5$ [Ir(NR)] [19b - h] and [(η^6 -arene)Os(NR)] [19a] show extensive cycloaddition chemistry. Following a conceptual model by Nugent et al. [9, 22], this reactivity follows largely the relative energy and the composition of the π or π^* orbital of the [M=NR] linkage, which is mainly influenced by the following factors: (i) the nature of the transition metal, (ii) the oxidation state of the transition metal, (iii) the ancillary ligands and (iv) the ligand R of the NR moiety [9, 22, 23]. However, to date there is no study on organoimido complexes available, which describes comprehensively the reactivity over several groups of transition metals or the dependence of the particular oxidation state of the metal atom in complexes, in which the metal atoms experience a similar ligand environment. Such a comparable surrounding might be provided by calix[4]arene ligands. One prerequisite is that the calix[4]arene bind to these complexes while maintaining the cone-like appearance of the macrocyclic ligand.

2 Coordination of calix[4]arene dimethyl ethers in metallacalix[4]arenes: *cone* vs. *paco* coordination mode

As mentioned above, like the successfully applied nitrogen containing ligand systems such as salenes, porphyrins and tetraazaannulenes the R2calix ligands provide a robust and well-defined O₄-coordination environment, which should be less rigid compared to TPP and TAA ligands. This raises the question of what the possible coordination modes of calix[4]arene ethers in metal complexes are. The calix[4]arene system [calix]⁴⁻ usually binds in a tetradentate fashion and retains its cone-like appearance in square pyramidal complexes of the type [ML(calix)] or in octahedral complexes [ML₂(calix)], if both ligands L are oriented *trans* to each other. In the latter case, one of the ligands coordinates endohedrally to the metal atom and is located in the cage of the calix[4]arene ligand. For group 6 chemistry, imido compounds [M(NR)L(calix)] (R = tBu, Mes; L' = NCMe, CNtBu, see below) are good examples of this type of coordination. Furthermore, it has been found in mononuclear complexes, that the calix[4]arene is capable of adopting alternative conformations when binding to metal centers, usually in an elliptical cone conformation, in which the calix[4]arene oxygen atoms adopt cis and trans sites in octahedral [ML₂(calix)] complexes. In these compounds, the ligands L are mutually *cis* oriented, as has been found in the structurally characterized calixarene molybdenum dichloride [MoCl₂(calix)] [24]. According to DFT calculations, the cis isomer of [MoCl₂(calix)] is approximately 18.1 kJ/mol higher in energy compared to the *trans* isomer, and a detailed analysis has shown that this difference in energy is almost exclusively due to the deformation energy needed to distort the calix[4]arene ligand. *Floriani* and coworkers have demonstrated that the conversion of *cis*-[WCl₂(calix)] to the thermodynamically more favorable *trans* isomer is facilitated by reactions with Lewis acids such as AlCl₃ [25].

For the Me₂calix ligand system, DFT analyses as well as experimental results have shown, that the macrocyclic ligand can bind in an elliptically distorted cone conformation to a metal atom, as adopted in [TiCl₂(Me₂calix)] (1), but also in a way which is reminiscent of the *partial* cone (paco) conformation of calixarenes. In this coordination mode, the ligand coordinates under loss of its regular cone-like appearance and its hydrophobic cavity with one of the anisole methoxy groups located *inside* the cavity. This was exemplified by the synthesis of [Mo(O)2-(paco-Me₂calix)] (2) and has been proven spectroscopically as well as crystallographically [26]. The formal change of a d^{0} -[TiCl₂] with a d^{0} -[MoO₂] complex fragment completely changes the coordination form of the calixarene dimethyl ether dianion. The results of the crystal structure determinations of 1 and 2 are shown in Figure 1.



Figure 1 Schakal plots of the molecular structures of [TiCl₂-(Me₂calix)] (1, left) and [Mo(O)₂(*paco*-Me₂calix)] (2, right) [26].

In complex 1 the calix[4]arene ether ligand binds with two anisole ether and two phenolate groups to the titanium atom and adopts an elliptically distorted *cone* conformation. This coordination mode leads to a pseudo C_{2v} symmetric structure with two different sets of Ti-O distances, 178.3(2) pm and 180.6(2) pm to the phenolate oxygen atoms and 210.1(2) pm and 213.3(2) pm to the ether oxygen atoms, as well as two sets of different Ti-O-C angles 116.6(1)° and 115.6(1)° (ether moiety) and 153.5(2)° and 163.8(2)° (phenolate moiety). The chlorine ligands *trans* to the phenolate units complete the distorted octahedron around the titanium atom.

In contrast, the Me₂calix ligand in **2** coordinates in a form which is reminiscent of the *paco* conformation of the calix[4]arene. In this complex, the ether groups of the calix-[4]arene ligand are in *trans* positions relative to the oxo $[O]^{2-}$ ligands. As a consequence, one of the methoxy groups is located *inside* the cavity of the calix[4]arene ligand leading to an 'up, up, up, down' arrangement of the aryloxy units of the macrocycle. The molybdenum phenolate oxygen bond lengths (191.6(3) pm and 192.0(3) pm) and molybdenum oxide ligand distances (169.4(3) pm and 169.0(3) pm) are

unexceptional. The molybdenum anisole oxygen distances (Mo-O(1) 239.4(3) pm and Mo-O(3) 255.9(3) pm), are considerably longer. The Mo-O(3) distance is very large, probably due to structural constraints imposed by the calix[4]arene ligand, and suggests only weak interaction of O(3) with the metal atom. The strong *trans* effect of the multiply bonded oxo ligand [27] explains the alignment of the ligands. The oxo ligands are coordinated *cis* to each other with an O(5)-Mo-O(6) angle of 101.5(2)°, increased from an idealized value of 90° so as to maximize π overlap to the high valent molybdenum atom.

A powerful tool to investigate this behavior in solution is ¹H NMR spectroscopy, where different signal patterns depending on the coordination mode of the calix[4]arene ligand are found, i.e. for the *paco* form signals which are typical for the macrocyclic ligand in a local pseudo C_s symmetry are detected. More significantly, two signals for the methyl groups of the calix[4]arene ether of **2** are observed: one for the *exohedrally* coordinated anisole unit at 4.18 ppm, which is similar to the chemical shift of 4.19 ppm found in **1**, and the other resonance for the *endohedrally* coordinated anisole ether unit at 0.79 ppm, which is shifted due to ring current effects of the calix[4]arene phenyl rings within the calix[4]arene cavity.

In compounds of the type $[Ti(O-4-C_6H_4R)_2(Me_2calix)]$ (R = Me 3, *t*Bu 4), both kinds of coordination mode have been observed [28b]. These calixarene-stabilized titanium bis(phenolate) compounds with *para*-substituted phenolate ligands have been isolated in good to excellent yields from the reaction of the titanium imido complex $[Ti(NtBu)(Me_2$ calix)] and two equivalents of the corresponding phenol (see below) 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 polar solvents such as pentane and hexane (see equation (1)).



The dinuclear compounds [{Ti(O-4-C₆H₄R)(Mecalix)}₂] (5, R = Me; 6, R = *t*Bu) are the result of the elimination of one equivalent of aryl methyl ether. The products of the rearrangement reaction are [Ti(O-4-C₆H₄Me)₂(*paco*-Me₂calix)] (7) and [Ti(O-4-C₆H₄*t*Bu)₂(*paco*-Me₂calix)] (8), in which the calix[4]arene ligand is coordinated in the *paco* conformation. This was established by NMR spectroscopy and X-ray crystallography. The proton NMR spectra of both isomers of [Ti(O-4-C₆H₄*t*Bu)₂(Me₂calix)] are shown in Figure 2.



Figure 2 Proton NMR spectra of $[Ti(O-4-C_6H_4tBu)_2(Me_2calix)]$ (4; upper part) and $[Ti(O-4-C_6H_4tBu)_2(paco-Me_2calix)]$ (8; lower part) in CDCl₃ [28b].

For the pseudo C_{2v} symmetric *cone* isomer **4**, three signals arise for the *tert*.-butyl groups of the calix[4]arene and the *tert*.-butyl-phenolate ligand, two doublets for the methylene protons of the calix[4]arene ligand and a singlet for the methyl groups of the anisole moiety. In the aryl region there are, in addition to the resonances of the protons of the calix[4]arene ligand, the signals of toluene, originally located in the cavity of the calix[4]arene ligand in the isolated compound **4**. In the proton NMR spectrum of C_s

symmetric **8**, the *tert*-butyl groups of the calix[4]arene and the phenolate ligands appear as signals at 1.33, 1.24, 1.23, 1.14, and 1.07 ppm in an integration ratio of 1:1:2:1:1 and four doublets can be found for the diastereotopic protons of the methylene bridges. Most relevant here are two signals for the methoxide groups of the anisole units, one at 4.30 ppm, while the other resonance is significantly shifted upfield to 0.82 ppm, as observed for the molybdenum complex **2**.

DFT calculations on model compounds [Ti(O-C₆H₅)₂-(cone-Me₂calix^H)] and [Ti(O-C₆H₅)₂(paco-Me₂calix^H)] reveal a slight thermodynamic preference for the paco-isomer, but the pathway of this isomerization process remains unclear. The rearrangment reaction is sensitive to changes in the sterics of the $M(OAr)_2$ fragment. Complexes $[Ti(O-2,6-C_6H_3R_2)_2(Me_2calix)]$ (9) and $[Zr(O-4-C_6H_4Me)_2-$ (Me₂calix)] (10) do not rearrange. The rearrangement reaction described here therefore implies a delicate steric balance. Whereas the complexes with para substituted phenoxide ligands 4 and 5 rearrange in apolar solvents, the complexes with the sterically more demanding phenoxides such as 9 and the zirconium compound 10 do not undergo analogous rearrangements in benzene, pentane or hexane, which might be due to a kinetic stabilization of the cone isomer or different ionic radii of the metal ions. We have not yet found similar rearrangements in complexes of calix[4]arene mono(methyl) ether Mecalix, as for example in compounds of the type [TiX(Mecalix)] [29] and [Mo(N)-(Mecalix)] [30].

These investigations show two major features of the R₂calix ligand compared to similar nitrogen based ligands: (i) a more flexible calix[4]arene backbone and (ii) the ease of dealkylation of the calixarene ether, especially in early transition metal complexes. Dealkylation reactions have already been observed in the synthesis of [TiCl₂(Me₂calix)] starting from H₂Me₂calix and [TiCl₄(thf)₂]. The outcome of this reaction critically depends upon the reaction conditions. Whereas the reaction of H2Me2calix and [TiCl₄(thf)₂] in toluene for one day at 60 °C affords the dimethyl ether titanacalix[4]arene [TiCl₂(Me₂calix)], a longer reaction time in refluxing toluene leads to elimination of MeCl to give [TiCl(Mecalix)]. The thermal stability of the calixarene ether dichloride complexes [TiCl₂(R₂calix)] with respect to RCl elimination to form the [TiCl(Rcalix)] compounds is $SiMe_3 < Bz << Me$, which reflects the stability of possible radical species R, probable intermediates during the cleavage reaction, as well as the steric demand of the R group [29].

3 Calix[4]arene-supported Group 4 – 6 Imido Complexes

3.1 Calix[4]arene-supported group 4 imido complexes

Synthesis and Characterization

Feasible routes to complexes of the type $[Ti(NtBu)(R_2calix)]$ and $[Ti(NAr)(R_2calix)]$ are depicted in Scheme 3 [28]. The reactions of the dichloro compound [TiCl₂(Me₂calix)] with two equivalents of alkali metal amides MNH*t*Bu or MNHAr (Ar = 2,6-C₆H₃Me₂, 2,4,6-C₆H₂Me₃, or 2,6-C₆H₃*i*Pr₂), proceed cleanly and usually in high yield. On NMR tube scale, reactions of [TiCl₂(Me₂calix)] and two equivalents of LiNHR' form in >95 % the imido complexes, and one equivalent of the corresponding R'NH₂ is eliminated during the reaction. There is no evidence for interaction between the ArNH₂ and the imido complexes which, in principle, could form either an adduct with the free amines or significant equilibrium concentrations of bis(amido) species [Ti(NHR')₂(Me₂calix)]. Alternative pathways are the reaction of the imido complexes [Ti(NR')Cl₂(py)₃] or [Ti(NR')Cl₂(NHMe₂)₂] (R' = *t*Bu or aryl) with metallated calix[4]arenes such as [{Na₂(Me₂calix)}₂] [30].



Scheme 3 Feasible routes to calix[4]arene stabilized titanium imido complexes.

For the synthesis of analogous titanium imido complexes of other 1,3-disubstituted ether *p-tert*.-butyl-calix[4]arene ligands, i.e. Bz_2calix ($Bz = CH_2Ph$) and (Me_3Si)₂calix, the synthesis via the dichloro compound [TiCl₂(R₂calix)] $(R = Bz, SiMe_3)$ is not a practicable way since the dichlorides themselves are not stable and rapidly eliminate RCl. For the Bz₂calix systems, reaction of one equivalent of Li₂(Bz₂calix) with [Ti(NR)Cl₂(py)₃] gave complexes $[Ti(NR)(Bz_2calix)]$ (R = tBu, 2,6-C₆H₃Me₂, C₆H₃iPr₂) in good yield, whereas the reaction of the disodium salt of $(Me_3Si)_2$ calix with $[Ti(NR)Cl_2(py)_3]$ gave only a mixture of products and neither the target complexes nor any other imido containing compound. All NMR spectra of the complexes 11 - 17 are consistent with molecular $C_{2\nu}$ symmetry with the molecular C_2 axis passing through the R'-N=Ti bond vector. The result of the X-ray crystal structure determination of [Ti(NtBu)(Me₂calix)] (11) as determined in $[Ti(NtBu)(Me_2calix)] \cdot 2(C_7H_8)$ 1 · 2(C₇H₈) is shown in Figure 3. One of the toluene solvent molecules is included in the cavity of the calix[4]arene ligand (not shown in Figure 3), the other solvent molecule occupies a general position in the lattice and gives rise to no significant contacts with the molecules of **11**.

The five-coordinate metal center in **11** possesses a trigonal bipyramidal arrangement with the imido and aryloxide donors lying in the equatorial plane as is typically the case for Group 4 imido complexes of the type



Figure 3 Schakal plot of the molecular structure of $[Ti(NtBu)-(Me_2calix)]$ (11) [28b].

 $[M(NR)X_2L_2]$ (X = amide or alkoxide/aryloxide; L = Lewis base donor) [31]. The Ti=NtBu, Ti-Oaryloxide and Ti-O_{ether} distances are within the usual range for complexes with fivefold coordinated metal atoms [31, 32]. The Ti-N bond distance of 170.9(2) pm as well as the Ti=N-tBu bond angle of $175.7(2)^{\circ}$ is consistent with the imido ligand acting as a 6-electron donor to the titanium atom (heterolytic cleavage of the Ti-N-bond), while the Ti-Oarvloxide-C angles of 149.8(2)° and 177.6(2)° suggest that the aryloxide O-donors can act as at least 4-electron donors potentially giving the titanium atom an 18 valence electron count. The structure of 1 is similar to that of the mesityl homologue 4 [28a], but the Ti=NR distance (171.8(3) pm in 14) is slightly shorter and the Ti-OR slightly longer for the tert.-butyl species. This is consistent with the general observation that Ti=NR bonds for arylimido complexes are typically longer than those in their tert.-butyl homologues, and that tert.butylimido ligands are generally more labilising towards other ligands present than arylimido ligands in homologous complexes.

Ab initio and DFT calculations [33-36] were performed on model compounds to gain a better understanding of the main electronic and structural properties of the titanium imido complexes supported by the calix[4]arene methyl ether ligand. Two models have been considered in the calculations: a detailed model [Ti(NR)(Me₂calix^H)], in which the ligand has been slightly modified through a replacement of the tert.-butyl groups with hydrogen atoms, and a second, more simplified model [Ti(NR)(OMe)₂(OMe₂)₂], in which the coordination environment at the titanium atom has been maintained to resemble the main features of the ligand, but the aryl groups have been replaced by methyl. Calculations on different detailed model complexes have shown that DFT methods (BP86/SV(P)) describe the geometry very well compared to the structurally obtained data. The structure of [Ti(NtBu)(Me₂calix^H)] optimizes in a C_s symmetric structure with a Ti-N distance of 171.10 pm and an Ti-N-C- angle of 176.05°. Replacement of the imido tert.-butyl group with methyl or hydrogen leads to a small decrease of the Ti-N bond length to 170.34 pm (R = Me)and 169.52 pm (R = H).



[Ti(Me₂calix)]²⁺ [Ti(NR)(Me₂calix)] [NR]²⁻

Figure 4 Orbital plots of relevant metal fragment orbitals of the simplified model $[Ti(OMe)_2(OMe_2)_2]^{2+}$ of the calixarene complexes (left side) and a schematic FMO diagram of the interaction of an imido ligand $[NR]^{2-}$ with the metallacalixarene fragment $[Ti(Me_2calix)]^{2+}$ (right side).

A schematic FMO diagram of the interactions of an imido ligand [NR]²⁻ with the metallacalixarene fragment $[Ti(Me_2calix)]^{2+}$ is depicted on the right side of Figure 4. The lowest unoccupied, metal-centered orbitals of the $[Ti(Me_2calix)]^{2+}$ fragment are depicted on the left side of the FMO scheme in Figure 4, whereas orbital plots of these relevant orbitals drawn for the simplified model are given on the left side of Figure 4. For this Ti^{IV} complex fragment with a d⁰ electron count the highest occupied orbitals are ligand centered, Ti-O non bonding orbitals. There are four low-lying unoccupied metal-centered orbitals which are higher in energy. The orbital $2a_1$, $d_{x^2-v^2}$ in character, points closely towards the oxygen atoms of the ligand and is pushed up higher in energy while the remaining four d orbitals are found within 1.5 eV. Because of a relatively strong π -overlap of the phenolate oxygen atoms of the ligands with the titanium atom, the Ti-O π -antibondung orbitals $1a_2(d_{xy})$ and $1b_1(d_{yz})$ lie higher in energy than the LUMO $1b_2$ (mainly titanium d_{z^2} in character). Due to the lower interaction with the anisole oxygen donor atoms in the xz plane, the orbital 1b₂ is approximately 1.00 eV lower in energy than $1b_1$. The $[Ti(Me_2calix)]^{2+}$ fragment is therefore ideally suited to stabilize good σ , 2π donor ligands. In complexes [Ti(NR)(Me₂calix)] with fivefold coordinated titanium atoms, in which the imido ligand lies along the z axis, there exists a strong bonding interaction between the $la_1(d_{z^2})$ and the σ -orbital of the imido ligand as shown schematically in the FMO diagram in Figure 4. For π donating ligands the remaining low-lying metal centered orbitals can interact with the high lying π -donor orbitals, which leads to a stabilization of 1b₂ and 1b₁ to form two titanium imido π bonds, which are slightly different in energy. For the model [Ti(NtBu)(Me₂calix^H)] these π bonding orbitals are

LUMO-2 and LUMO-3 and separate fairly well from other ligand type orbitals, as shown in Figure 5. The importance of π -contributions to Ti-N-bonding can be substantiated by population analyses. In a Roby-Davidson analysis [37] of C_{2v} -[Ti(NH)(Me₂calix^H)] a total of 1.20 electrons for the Ti-N-bond is divided into 0.41 electrons emerging from interactions of b₂ symmetry, 0.40 electrons from interactions of b₂ symmetry, and only 0.39 electrons due to G interaction of a₁ type orbitals. A similar picture arises from an analysis of C_s-[Ti(N*t*Bu)(Me₂calix^H)], where out of a total of 1.12 electrons for the Ti-N-bond, 0.74 electrons emerge from interactions of a' symmetry (i. e. $\sigma + \pi$, the π bonding orbital LUMO-2 itself contributes 0.33 electrons !) and 0.38 electrons from π interactions of a" symmetry.



Figure 5 Orbital plots of the titanium nitrogen π type orbitals LUMO-2 (left) and LUMO-3 (right) calculated for [Ti(N*t*Bu)-(Me₂calix^H)].

¹³C-NMR spectroscopy has a prominent role in the characterization of tert.-butylimido complexes. Nugent and Haymore [9, 22] proposed the difference in ¹³C-NMR shifts $\Delta\delta$ of α -(= NC(CH₃)₃) and β -(= NC(CH₃)₃) carbon atoms of the tert.-butyl group as an approximation of electron density at the imido nitrogen atom and an experimental hint on the donor strength of the imido ligand to the metal center. A decrease of the electron density at the metal atom leads to an increase of the metal nitrogen bond and therefore to a decrease of the electron density at the nitrogen atom of the imido ligand, which can be observed experimentally by an increase of $\Delta\delta$. On the other hand, the donor capabilities of ancillary ligands in complexes of similar coordination environment as found in complexes of the type $[L_n Ti(NtBu)]$ can be compared. ¹³C-NMR-resonances of the α - and β - carbon atoms as well as the $\Delta\delta$ values of some selected examples of titanium(IV) imido complexes are given in Table 1 [28].

The $\Delta\delta$ value of 36.5 ppm (11) and 36.7 ppm (15) found for the calix[4]arene complexes are similar to those observed for other titanium imido phenolate complexes. They correspond to values found for salene compounds, but are larger than those of the TAA system. According to these $\Delta\delta$ values the calixarene dialkyl ether ligands are similar in

Table 1 $\Delta\delta$ values of titanium(IV) imido complexes.

Complex	$\delta(NC(CH_3)_3)$	$\delta(NC(CH_3)_3)$	Δδ	Lit.
[Ti(NtBu)Cl ₂ (py) ₃]	73.6	30.6	43.0	[20r, t]
$[Ti(NtBu)(ODIP)_2(py)_2]$	68.8	31.7	37.1	[31a]
[Ti(NtBu)(Et ₂ salene)]	68.3	31.4	36.9	[32f]
$[Ti(NtBu)(tBu_4salene)]$	69.1	32.3	36.8	[32f]
[Ti(NtBu)(Me ₂ calix)] 11	69.9	33.4	36.5	[28]
$[Ti(NtBu)(Bz_2calix)]$ 15	70.7	34.0	36.7	[28]
[Ti(NtBu)(Me ₈ TAA)]	67.0	31.8	35.2	[32b]

their donor capabilities to salene type ligands but worse than tetraazaannulene systems.

Floriani et al. have reported the synthesis of a structurally characterized, binuclear zirconium phenylimido complex $[{Zr(\mu_2-NPh)(Me_2calix)}_2]$ from PhN₃ and $[Zr(\eta^4-C_4H_6)-$ (Me₂calix)] [38]. Non-azide routes to zirconium imido complexes based on those discussed for the titanium systems above are not straight forward. Unlike the titanium set of synthons $[Ti(NR)Cl_2(L)_n]$, no such convenient set of entry points to zirconium imido chemistry have yet been established, although Wigley and co-worker have reported $[Zr(N-2,6-C_6H_3iPr_2)Cl_2(L)_n]$ $[(L)_n = (THF)_2 \text{ or } (py)_3]$ [39]. While the reaction of [Na2(Me2calix)]2 with [Zr(N-2,6- $C_6H_3iPr_2)Cl_2(THF)_2$ appeared to form the desired product $[Zr(N-2,6-C_6H_3iPr_2)(Me_2calix)]$ (18), the reaction does not proceed cleanly. The salt elimination starting from [ZrCl₂(Me₂calix)] and two equivalents of LiNH-2,6- $C_6H_3iPr_2$ is the superior route that gave the imido complex in the case of the sterically demanding aryl substituent. Like its titanium congeners [Ti(NR)(Me2calix)], the compound **18** affords ¹H and ¹³C $\{^{1}H\}$ NMR spectra consistent with molecular $C_{2\nu}$ symmetry. The usage of other amides LiNHR (R = tBu, Ph, 2,6-C₆H₃Me₂ or 2-C₆H₄tBu) leads to no isolable zirconium imido products. When these reactions were followed by ¹H NMR spectroscopy the data suggested that in all cases (except where R = Ph) mixtures of imido and bis(amido) complexes, namely [Zr(NR)(Me₂calix)] and [Zr(NHR)₂(Me₂calix)], were formed in apparent equilibrium with each other, the relative amounts depending on the steric demands of the N-substituent. In the case of R = Ph, the only identifiable carbon-containing product of the NMR tube scale reaction between [ZrCl₂(Me₂calix)] and two equivalents of LiNHPh appeared to be [Zr(NHPh)₂(Me₂calix)] (19) with no evidence for Floriani's binuclear phenylimido complex [{Zr(µ2-NPh)- (Me_2calix) ₂]. In these calix[4]arene zirconium complexes, the Me₂calix ligand provides a satisfactory match with the zirconium atomic radius, but the imido N-substituent still needs to provide adequate steric bulk to avoid reaction of [Zr(NR)(Me₂calix)] complexes with amines that may be present in the reaction mixture.

Reactivity of 11

Our investigations on the reactivity of complex 11 are summarized in Schemes 4 and 5. Compound 11 reacts swiftly



Scheme 4 Reactions of [Ti(NtBu)(Me₂calix)] (11) with heterocumulenes.

and quantitatively with CO_2 in benzene at room temperature. The spectroscopic data are consistent with the formation of a *N*,*O*-bound organocarbamate complex [Ti{N(*t*Bu)C(O)O}(Me₂calix)] (**20**) as illustrated in Scheme 4.

Compound **20** is unstable at room temperature with respect to extrusion of *tert*.-butylisocyanate and formation of the dimeric oxo complex [$\{Ti(\mu-O)(Me_2calix)\}_2$] (**21**). This elimination reaction goes quite slowly in the dark, but under ambient lighting is complete within one hour. The reaction of **11** with CO₂ under ambient light is the most efficient and clean method for synthesizing the oxo compound **21**. The corresponding reaction of **11** with CS₂ proceeds much more slowly. This is attributed to the lower electrophilicity of the carbon atom in CS₂ and the softer nature of the sulfur atom which would disfavour coordination to the hard titanium center as compared to CO₂. The only observed products of this reaction are the bridging sulfido complex [$\{Ti(\mu-S)(Me_2calix)\}_2$] (**22**) and *tert*.-butyl isothiocyanate, *t*BuNCS. The reaction is presumed to

proceed via an intermediate thiocarbamate complex $[Ti{N(tBu)C(S)S}(Me_2calix)]$ analogous to **20**, but this intermediate was not observed. In contrast to **21** and **22**, the porphyrin complexes [Ti(O)(OEP)] and tetraaza[14]annulene analogues $[Ti(O)(Me_ntaa)]$ and $[Ti(S)(Me_ntaa)]$ are monomeric, as are certain heavier chalcogen derivatives [40-42], suggesting that the Me₂calix ligand provides a less sterically protecting environment for stabilising sterically unprotected metal-ligand multiple bonds.

The reaction of $[Ti(NtBu)(Me_2calix)]$ **11** with *p*-tolyl isocyanate gave clean conversion to the *N*,*N'*-bound ureate complex $[Ti\{N(tBu)C(O)N(-4-C_6H_4Me)\}(Me_2calix)]$ **(23)**, which is stable with respect to cycloreversion or extrusion of *t*BuNCO to afford a tolylimido complex. The molecular structure of **23** is shown in Figure 6.

The solid state structure of **23** shows the *p*-tolylisocyanate moiety coupled across the former Ti-N(2) imide bond. The titanium atom has an approximately octahedral coordination arrangement with the etheral O-donors of Me₂calix occupying mutually *trans* coordination sites, and with the

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Figure 6 Schakal plot of the molecular structure of $[Ti{N(tBu)C(O)N(-4-C_6H_4Me)}(Me_2calix)]$ (23) [28b].

four anionic donors [N(1), N(2), O(2) and O(4)] forming the equatorial plane of the octahedron. The distances and angles within the structure are as expected [28b].

In recent years the reaction chemistry of Group 4 imido complexes with CO_2 and isocyanates has become better established and a diversity of behaviour is starting to emerge, which depends on the ancilliary ligand(s) and the imide and isocyanate N-substituents. Reactions of [Ti(N*t*Bu)(Me₄taa)] with aryl isocyanates failed to give any tractable products. However, reaction of [Ti(N*t*Bu)(Me₄taa)] with *t*BuNCO gives an N,O-bound ureate product as do a number of other *tert.*-butylimido titanium complexes. In some cases the *N*,*O*- bound ureate intermediates are unstable with respect to cycloreversion to form cyclopentadienyl-amidinate titanium oxo complexes and the corresponding carbodiimides *t*BuNCNR. The reaction of $[Ti(NtBu)(Me_2calix)]$ (11) with *p*-tolyl isocycanate to form the stable, N,N'-bound ureate 23 is therefore unusual in the still emerging field of Group 4 imide/heterocumulene reaction chemistry.

Protonolysis reactions of $[Ti(NtBu)(Me_2calix)]$ (11) with N-H, O-H, S-H and Cl-H bond substrates are summarized in Scheme 5. Complex 11 easily loses $tBuNH_2$ and new N-and O- or Cl-donor functional groups are introduced.

The *tert.*-butyl imide/arylamine exchange reactions are rather slow requiring prolonged heating to ensure complete reaction. The reactions to form **12** and **13** proceed quantitatively on an NMR tube scale, but require about three days at 65 °C to go to completion. The analogous reaction with $H_2N-4-C_6H_4Me$ to form [Ti(N-4-C₆H₄Me)(Me₂calix)] (**24**) is slightly faster, presumably due to formation of a less sterically crowded 6-coordinate titanium atom of the bis(amide) intermediate. However, this intermediate has not been detected spectroscopically.

The reactions of **11** with H₂O, H₂S and HCl afforded the expected products $[{Ti(\mu-O)(Me_2calix)}_2]$ (**21**), $[{Ti(\mu-S)(Me_2calix)}_2]$ (**22**), and $[TiCl_2(Me_2calix)]$ (**1**) in greater than 90 % yield. The reaction of **11** with H₂S to form **12** proceeds cleanly and completely within 30 minutes and is therefore a more convenient synthesis of this compound than that from **1** and CS₂. Phenols react similarly in



Scheme 5 Protonolysis reactions of [Ti(NtBu)(Me₂calix)] (11) with N-H, O-H, S-H and Cl-H bond substrates.

a smooth reaction to afford the bis(phenolate) complexes, as exemplified here by the formation of the *cone* isomers $[Ti(O-4-C_6H_4Me)_2(Me_2calix)]$ (3) and $[Ti(O-4-C_6H_4tBu)_2-(Me_2calix)]$ (5) mentioned above.

3.2 Calix [4] arene-supported group 5 imido complexes

Calix[4]arene stabilized imido complexes of group 5 metals are rare and have not been systematically explored. Calix[4]arene complexes with M-N multiple bonds (M = V, Nb, Ta) have been synthesized from the reaction of V_2 (Mecalix)₂] with diphenyldiazomethane to afford the diazoalkane complex [V(=N-N=CPh₂)(Mecalix)] [43] or prepared in the stepwise process of N₂ activation using $[Nb_2(calix)_2]^{2-}$ [44]. During the latter investigations, the synthesis of the phenyl imido complex $[{Nb(NPh)(calix)}_2]^-$ was achieved, which is – in contrast to the isoelectronic molybdenum complex – a dinuclear, calixarene-bridged compound. This complex and $[{Ta(NPh)(Mecalix)}_2]$, synthesized from the reaction of $[Ta(\eta^4-C_4H_6)(Mecalix)]$ and phenyl azide [45], are the only examples of calix[4]arene stabilized imido complexes known in the literature so far. In our group, mononuclear calix[4]arene vanadium imido complexes, prepared from the reaction of $[\{V(NR)Cl_3\}]$ (R = tBu, Ph, 4-C₆H₄Me) and dinuclear [{Li₃Mecalix}₂], as well as imido complexes of its higher congener are currently under investigation [46]. The result of the structural analysis of [V(NtBu)(Mecalix)] (25) is shown in Figure 7. This complex is less reactive with respect to cycloaddition reactions and protonolysis reactions compared to the titanium complex [Ti(NtBu)(Me₂calix)] (11).



Figure 7 Schakal plot of the molecular structure of [V(NtBu)-(Mecalix)] (25).

3.3 Calix[4]arene-supported group 6 imido complexes

Synthesis and Characterization

Despite the fact that calix[4]arene complexes of molybdenum (VI) and tungsten (VI) have been investigated by a number of groups there is no unified picture regarding the structure of these complexes. Studies by ourselves [47] and by *Redshaw* et al. [48] revealed that mononuclear imido complexes [M(NR)(calix)] and [M(NR)(calix^H)] (M = Mo, W) are affordable in good to excellent yields from H₄calix with compounds of the type [M(NR)₂(NHR)₂], [M(NR)₂Cl₂L₂] or [M(NR)₂(OSiMe₃)₂], as shown in Scheme 6.



Scheme 6 Calix[4]arene-stabilized imido complexes from H₄calix.

These compounds [M(NR)(calix)] can be synthesized in the fivefold coordinated form as presented in Scheme 6, but as soon as a sterically non demanding coordinating solvent is present, adducts of the type [M(NR)(calix)(L)] are obtained. In these compounds an additional donor ligand L coordinates *endohedrally* (i.e. within the calix[4]arene cavity) to form octahedrally coordinated metal atoms, which are located almost ideally within the O₄ plane of the calixarene ligand. Spectroscopic and analytical data suggest monomeric units with local pseudo C4v symmetry in solution as well as in the solid state. Similar chromium complexes [Cr(NR)(calix)] are unknown so far. $[Cr(NtBu)_2(OtBu)_2]$ eliminates from the reaction with calix[4]arene two equivalents tert.-butanol and both imido ligands to yield a mononuclear complex with two calix[4]arene ligands coordinated at the metal atom [49].

Whereas the reaction of calix[4]arene and $[WOCl_4]$ affords cleanly the oxo complexes [WO(calix)] [25a], the corresponding reaction of different imidoyl chlorides [W(NAr)Cl₄] seems to be more sluggish. Jablonski and coworker isolated from these reactions the known dichloro compound [WCl₂(calix)] as well as the HCl adducts $[W(NAr)(Hcalix)]^+Cl^-$ [50] instead of the desired complex [W(NAr)(calix)]. Elimination of both the imido and the chloro ligands from the starting material seems to be important in this case. The complexes [W(NAr)(Hcalix)]⁺Cl⁻ are also available via reaction of aniline derivatives with [WCl₂(calix)] in refluxing toluene. A possible diamido complex, a likely intermediate in the course of this reaction, has not been reported. The usage of metallated calix[4]arenes leads here to isolated imido complexes, as exemplifies the reaction of $[\{Na_4calix\}_2(thf)_4]$ with $[W(N-4-C_6H_4Me)Cl_4]$ to yield $[W(N-4-C_6H_4Me)(calix)]$ (30). This complex is in equilibrium with its dimeric form $[{W(N-4-C_6H_4Me)-(calix)}_2]$ in solution [51a].

Another important route to calixarene stabilized imido complexes is the reduction of azides. Floriani et. al. used $[W(\eta^2-C_6H_{10})(calix)]$ as a source of calix[4]arene stabilized $W^{IV} - W^{VI}$ complexes [51], since the olefin is easily displaced by other ligands. The outcome of the reaction with organic azides RN₃ (R = SiMe₃, CPh₃, Ph, H) strongly depends on the nature of the R substituent, because the calix[4]arene cavity is able to discriminate between two possible reaction pathways (see Scheme 7). In the case of R =SiMe₃ or CPh₃ the reaction occurs *exohedrally* at the metal atom under loss of dinitrogen to yield monomeric alkylimido derivatives [W(NR)(calix)] (R = SiMe₃, 31; R = CPh₃, 32). The reaction with PhN₃, however, occurs inside the calixarene cavity, leading under two electron reduction of the phenyl azide to a diazenylimido derivative [{W(calix)-(=N-N=NPh)₂ (33). These results were interpreted with two different reaction pathways that are followed at the metal atom in exo and endo positions. In the case of the sterically demanding azides ($R = SiMe_3$, CPh₃) the 1,3 dipolar addition of the azide to the carbenoid metal atom proceeds for steric reasons with an initial attack from the exohedral side. In the exo-conformation, the complex provides two cis-coordination sides which enables a 1.3 addition of the azide to the metal atom, which according to Bergman et al. [52] is a prerequisite for dinitrogen loss. The net result of this sequence is the formation of an alkylimido complex under loss of N₂.



Scheme 7 Reactivity of $[W(\eta^2-C_6H_{10})(calix)]$ toward organic azides RN₃ [52].

In the case of PhN₃, the azide adds *endohedrally* to $[W(\eta^2-C_6H_{10})(calix)]$ and the size of the calixarene cavity prevents 1,3 addition. [51a] The resulting diazenylimido complex **33** is stable even at elevated temperatures. In the case of HN₃ the dinuclear imido complex

 $[{W(calix)(NH)}_2]$ (34) has been isolated and structurally characterized. This reaction is supposed to proceed via *en-dohedral* HN₃ binding to the Lewis-acidic metal atom with the protonated nitrogen atom inside the cavity and decomposition under dinitrogen cleavage to give the imido functionality.

A dinuclear molybdenum phenyl imido complex was synthesized in Floriani's group in a one pot reaction starting from [MoCl₄(thf)₂], the perlithiated calix[4]arene and phenyl azide [51b]. The spectroscopic data of this complex are typical for a pseudo C_s symmetrical molecule in solution and the molecular structure of this complex reveals 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. This geometry can be explained with the reduced steric hindrance at the aryl group (no ortho alkyl groups), but also with the lack of a donor ligand trans to the imido group, which makes the metal atom readily available for dimerization. In our group, four electron reduction of azobenzene was performed starting with two equivalents of the d² complex ion [MoCl(calix)(NCMe)]⁻ and azobenzene to afford the mononuclear complex [Mo(NPh)(calix)(NCMe)] (35) [53]. The molecular structure of this compound is shown as an example for several X-ray analyses performed on calix[4]arene imido complexes of molybdenum (VI) and tungsten (VI) [47] in Figure 8.



Figure 8 Schakal plot of the molecular structure of [Mo(NPh)-(calix)(NCMe)] (35).

In square pyramidal complexes of the type [M(L)(calix)]the metal atom is displaced significantly out of the calix[4]arene O₄ plane towards the ligand in contrast to octahedral complexes [M(L)(calix)(L')], in which the metal atom lies more or less exactly within the O₄ plane. Thus, similar monomeric/dimeric complexes $[\{M(L)(calix)\}_2]/[M(L)-(calix)(L')]$ are described 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. [54].

The calix[4]arene metal fragments of mononuclear imido compounds [M(NR)(calix)(donor)] investigated by X-ray crystallography retain pseudo C_{4v} symmetry in the solid state and produce circular calix[4]arene cavities, similar to the uncoordinated ligand. The molybdenum oxygen and tungsten oxygen bond distances are in a very narrow range between 192 pm and 196 pm, the angles N1-M-O are between 97° and 99°, and the angles M-O-C are approximately 130°. The short Mo-N1 and W-N1 bonds of 171.6(5) - 174.3(4) pm and the almost linear M-N1-C entities with angles larger than 170° suggest sp hybridized imido nitrogen atoms with triple bond character of the metal-imido linkage, which was confirmed by theoretical calculations.

Reactivity

Currently there is not very much known about the reactivity of the calix[4]arene stabilized group 6 imido complexes. Investigations in our group have shown that the molybdenum and tungsten complexes are far less reactive compared to the titanium imido compounds. The metal imido linkage in these complexes is usually not reactive with respect to cycloaddition reactions and protonations and therefore not sensitive against hydrolysis. Imido exchange reactions as observed for the titanium and vanadium compounds are not viable reactions for the molybdenum and tungsten tert.butyl imido complexes. Electron rich, sterically nondemanding substrates usually do not react with the imido nitrogen atom but rather add to the acidic metal atom inside the calix[4]arene cavity to afford complexes with octahedrally coordinated metal atom (endo coordination), as observed for example in the structurally characterized complexes [Mo(NtBu)(calix)(CNtBu)](26)(CNtBu), [Mo(NtBu)(calix)(NCMe)] (26)(NCMe), [Mo(NMes)(calix)(NCMe)] (27)(NCMe), [W(NtBu)(calix)(CNtBu)] (28)(CNtBu), $[W(NtBu)(calix)(OH_2)]$ (28)(OH₂) and [W(NMes)(calix)(NCMe)] (29)(NCMe) [47a].

Whereas the imido ligand of [W(NtBu)(calix)] (28) can be replaced selectively with two chloride ligands via reaction of the imido complex with HCl, the reactivity of the analogous molybdenum compound 26 with respect to hydrochlorination is totally different [47b]. The reaction of 28 with one equivalent of HCl affords a dark violet solution which contains, according to NMR spectroscopy, a compound with local C_s symmetry, presumably [Mo(NtBu)Cl(Hcalix)] (36). A larger amount of HCl during the reaction does not lead to the scission of the imido group, but results in decomposition of 36. Until now, complex 36 could not be isolated since it decomposes to the starting material 26, when solutions of this compound are concentrated in vacuo. The addition of HCl to 26 is totally reversible for some cycles. All attempts to remove 35 from equilibrium or to crystallize this complex have failed so far.

Similarly unreactive is the molybdenum imido function of **26** with respect to chlorine transfer reagents. The addition of an equimolar amount of PhICl₂ to a toluene solution of yellow **26** causes a spontaneous color change of the reaction mixture to dark violet and the addition product [Mo(N*t*Bu)Cl(calix^{*t*Bu₄Cl)}] (**37**) was isolated in good yield. Spectroscopic data of the reaction product were in good agreement with addition of Cl_2 to **26**, which was confirmed by an X-ray analysis (Figure 9).



Figure 9 Schakal plot of the molecular structure of $[Mo(NtBu)-Cl(calix^{Bu_4Cl})]$ (37).

The molybdenum atom in 37 is sixfold coordinated with four oxygen atoms of the calix[4]arene ligand, the imido nitrogen atom and the chlorine atom Cl(1). The distances Mo-O(2), Mo-O(3), and Mo-O(4) as well as Mo-Cl(1) are unexceptional, but the molybdenum nitrogen distance of 170.3(4) pm is approximately 1.5 pm shorter than the Mo-N distance observed in the starting compound. The N-Mo-O(1) arrangement is almost linear with an angle of $176.2(2)^{\circ}$. Significantly elongated with respect to the other molybdenum oxygen bond lengths is the distance Mo-O(1) of 216.0(3) pm, which correlates with a short O(1)-C(10)contact of 122.1(5) pm (C=O double bond). The carbon atoms C(10) to C(15) of the carbon ring system connected to O(1) show alternating C-C bond lengths of 145.2(5) pm on average for C_{ipso}-C_{ortho}, 132.8(6) pm and for C_{ortho}-C_{meta} and 150.4(6) pm for C_{meta}-C_{para}, which is in accordance with a description of the previously aromatic unit of the calix[4] arene as an α , β -unsaturated ring system. The distance C(15)-Cl(2) of 183.3(5) pm corresponds to a chlorine bound to a sp^3 -hybridized carbon atom. As a net result, the structure of complex 37 in solution and in the solid state is best described as the 1,6-addition product of chlorine to 26. To our knowledge, a selective 1,6-addition of chlorine to an organic or inorganic substrate has never been observed before. Furthermore, the cyclohexadienone part of the macrocyclic ligand in 36 is the first example of a structurally characterized 4-halo-4-alkyl-2,5-cyclohexadienone in the coordination sphere of a transition metal complex. This moiety is stabilized with the highly Lewis acidic molybdenum(VI) complex fragment. After initial chlorine attack at the negatively charged and therefore activated ring system of the calix[4]arene ligand, the molecule does not recover its aromatic system but remains with an intact cyclohexadienone system and stabilizes itself with attack of chlorine at the (positively charged) metal atom.

Perspectives

Macrocyclic complexes are usually associated with high thermodynamic and kinetic stability and are therefore used as templates in supramolecular chemistry, in multi component assembly processes, as molecular receptors for guest molecules or as spectator ligands for organometallic transformations at the metal atom. Calix[4]arenes and calix[4]arene ethers used as poly(phenolate) ligands in transition metal chemistry provide the metal atom with a robust and well-defined O₄-coordination environment, similar to other widely and successfully used supporting dianionic ligands such as the O₂,N₂-donor ligands of salene type Schiff bases or N₄-donor ligands such as porphyrins and dibenzotetraaza[14]annulene systems. Results in titanium imido chemistry led to the suggestion, that calixarene bis(alkyl)ethers are in their donor capabilities similar to salene type ligands but worse compared to the tetraazaannulene system. Furthermore, the Me₂calix ligand seems to provide a less sterically protecting environment for stabilizing sterically unprotected metal-ligand multiple bonds. Calix[4]arene dialkyl ethers are conformationally much more flexible compared to the nitrogen containing ligand systems, which culminates in a change of the coordination mode for complexes of the type [ML₂(Me₂calix)], in which L is a ligand which exhibits a fairly good *trans* influence. However, it is much easier to change the charge of the ligand system, in this case through the degree of alkylation of the calixarene lower rim, without a major change of the structure of the resulting metal complex. This concept might be exploited for systematic investigations across oxidation states and rows of transition metals of different groups ("intrinsic reactivity of M=E bonds"), and we started such a model investigation for metal imido linkages. The first results of this project are given in this research report. Moreover, transition metal imido precursors have been proven to be convenient entry points into metallacalixarene chemistry, i. e. to introduce metal complexes into the lower rim of the macrocyclic ligand. This quite general protocol for group 4 - 6 metals is currently being expanded to transition metals beyond group 6.

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