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Calixarene-Based Oxovanadium Complexes as Molecular Models for Catalytically Active Surface Species and Homogeneous Catalysts

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There are several reasons that make the combination of calixarenes with oxovanadium moieties attractive. Calixarenes are capable of simulating the surfaces of oxide bulk materials and supports, and on the other hand, supported vanadium oxides are an important class of heterogeneous catalysts, whose reactivity is still discussed controversially with respect to the effective mechanisms. Oxovanadium calixarene complexes can thus represent molecular models whose investigation in the homogeneous phase can shed some light into surface processes. This review describes the recent achievements in the synthesis of oxovanadium calixarene, thiacalixarene, and oxacalixarene complexes and the investigation of their reactivity. It has been shown that they represent active catalysts for the oxidation of alcohols and the polymerization/copolymerization of olefins.

1. Introduction

Heterogeneous catalysts play an important role in the chemical and pharmaceutical industry where 90% of all compounds produced require at least one *catalytic* step during their synthesis.[1] While in comparison to homogeneous catalysts the employment of heterogeneous catalysts has certain advantages with respect to product separation, stability (for instance at higher temperatures), and technical issues,[1] the unequivocal identification of their surface constitution and active sites poses problems. These properties are best studied by a combination of physical and chemical methods such as IR, Raman, Mössbauer, and solid-state NMR spectroscopy as well as EXAFS, XANES, and XPS.[2] However, these techniques involve bulk measurements, and their sensitivity is often inadequate for obtaining accurate data from the various sites that are present on the surface in low concentration.[3] Furthermore, even if the active sites are known, the clarification of mechanistic questions is far more difficult for heterogeneous catalysts than for homogeneous catalysts, as in situ studies on surfaces under catalytic conditions require methods far from routine. Naturally, the results of such investigations as well as hypotheses derived from kinetic investigations and isotopic enrichment studies provide a stimulus for the synthesis of molecular models: these can be investigated in the homogeneous phase and may serve to support or defeat mechanistic proposals, thus offering hope that heterogeneous catalysts can be designed rationally. In addition, such models can in turn prove themselves as novel homogeneous catalysts, independently of the heterogeneous process that led to their synthesis.

One important class of heterogeneous catalysts consists of metal oxides on inert supports which are employed, for instance, to mediate oxidations with O_2 as well as other processes like polymerizations.[4] The construction of molecular models for oxometal (the terms “oxo” and “chloro” are used as ligand names throughout this Microreview as in the original articles) surface sites requires ligands that are capable of mimicking the oxide environments surrounding oxometal moieties on oxide supports or in bulk materials,

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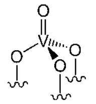
Christian Limberg was born in 1965 in Essen and studied chemistry from 1985 to 1990 in Bochum. He earned his doctorate with Professor A. Haas in 1992 and concluded his postdoctoral work together with Professor A. J. Downs at Oxford University with a further Ph. D. thesis and Inauguration (D. Phil.). In 1995 he then joined the research group of Professor G. Huttner in Heidelberg to start his Habilitation work, which was finished in 1999. Having received a Heisenberg scholarship, he stayed in Heidelberg until 2001, when he moved to the TU Munich to lead the Inorganic Chemistry chair on behalf of Professor Herrmann. In 2002 he accepted an offer to become full professor at the Humboldt-University of Berlin, where he is currently Dean of the Faculty I for Mathematics and Natural Sciences. The author of this contribution is mainly concerned with oxometal complexes and their reactivity under synthetic and mechanistic viewpoints. He received the ADUC prize for Habilitanden and was further awarded a Karl-Winnacker-Stipendium, the academy prize of the Academy of Science in Göttingen, as well as the Carl-Duisberg-Gedächtnispreis of the GDCh.

and in this context in particular, two ligand systems have established themselves: silsesquioxanes[3,5a–5d] and calixarenes.[5e,5f] This review focuses on the most recent research concerning oxovanadium calixarene complexes that were synthesized in order to model supported vanadium catalysts, finding applications for instance in the oxidative dehydrogenation (ODH)[6] of light alkanes and methanol. Various surface species have been found to be active during the heterogeneous processes in one way or the other, and hence these structural motifs represent an inspiration for attempts to mimic them in molecular compounds.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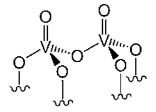
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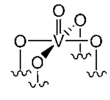
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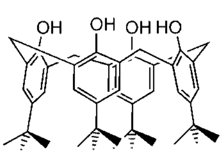
On the other hand, silica-supported vanadium materials have proved to be efficient as heterogeneous catalysts for olefin polymerization,[7a–7d] and oxovanadium complexes with multipodal ligands were shown to catalyze such polymerizations homogeneously.[7e] It follows that oxovanadium calixarene complexes were also investigated in this respect.

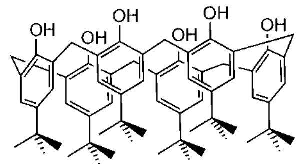
The results of studies on both aspects are discussed below.

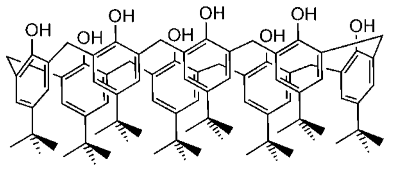
2. Synthesis of Oxovanadium Calixarene Complexes and Their Properties

2.1. Complexes with “Classical” Calixarene Ligands

In addition to silsesquioxane ligands, calixarene ligands such as H_4**C**, H_6**C**′, and H_8**C**′′ have recommended themselves for the simulation of oxide surfaces in recent years.[5e,5f] While H_4**C** yields a tetrapodal ligand after deprotonation, H_3**C**$^{\mathbf{R}}$ (a derivative of H_4**C** where one of the phenolic protons is replaced by an alkyl group R) leads to a tripodal ligand. Employing H_4**C** and H_3**C**$^{\mathbf{R}}$ thus enables modelling the embedding of a transition metal ion in the midst of three and four oxygen atoms of an oxide surface (for instance a support), respectively. On the other hand, ligands like [**C**′]$^{6-}$ or a calix[8]arene with eight phenolate units ([**C**′′]$^{8-}$) provide more extended platforms of oxygen atoms, where polynuclear moieties can arrange themselves, too.

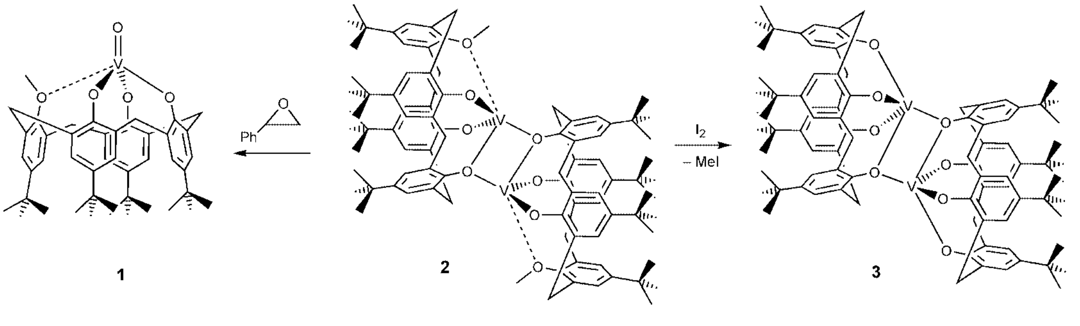

H_4**C**


H_6**C**'

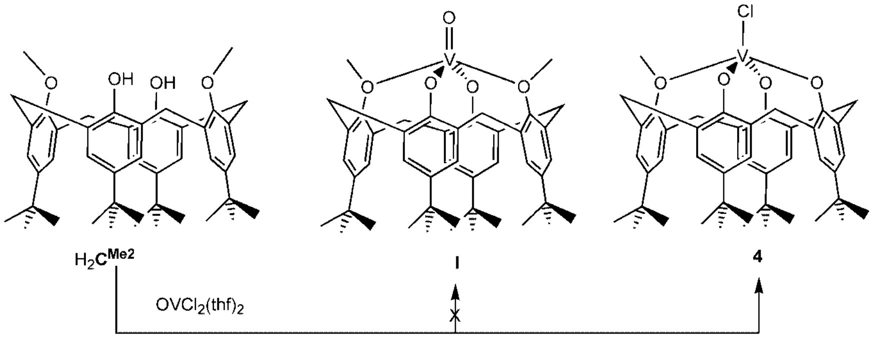

H_8**C**''

Until recently, oxovanadium complexes of calix[4]arenes (**C**$^{4-}$) were not known, and the literature on the coordination of oxovanadium units by other calixarene-based ligands was scarce, too: one complex with a ligand derived from H_4**C** by monomethylation of a phenolic function, **C**$^{\mathbf{Me}}$$V^V$=O (**1**), (see Scheme 1) had been reported[8] as well as a few others containing calix[3]-, calix[6]-, and calix[8]arene ligands, which, however, were either not characterized structurally or contained vanadium centers that were not exclusively ligated by O donor atoms.[9,8]

Whereas these examples all involve V^V, naturally, there is also interest in reduced complexes that could model reduced species formed after oxidation reactions on surfaces, and in this context V^{IV} and V^{III} are important. The chemistry of a vanadium(III) center complexed by calix[4]arene has been investigated by C. Floriani et al.[8] Metalation of H_3**C**$^{\mathbf{Me}}$ with [$VMes_3$·thf] led to the collapse of the coordinatively unsaturated V^{III}-d^2 fragment **C**$^{\mathbf{Me}}$$V^{III}$ to the dimer [{μ-**C**$^{\mathbf{Me}}$}V]$_2$ (**2**). In addition to reactions with *t*BuNC, PhCN, pyridine, and 4,4′-bipyridine, the one-electron oxidation with I_2, which led to the V^{IV} complex [{μ-**C**}V]$_2$ (**3**), was investigated. A two-electron oxidation of the V^{III}-d^2 system to the oxovanadium(V) derivative **C**$^{\mathbf{Me}}$$V^V$=O (**1**), has been achieved by using styrene oxide. Very recently, Redshaw et al.[10] published synthetic methods that lead to a complex **3**$^{\mathbf{AN}}$, which is closely related to **3**: **3**$^{\mathbf{AN}}$ differs from **3** (Scheme 1) in that it additionally contains two metal-bound acetonitrile molecules within the two calyx cavities, which results in pseudo-octahedral coordination spheres for the vanadium atoms, and it can be obtained by starting from H_4**C** upon treatment with [V(N*p*-tolyl)-



Scheme 1.



Scheme 2.

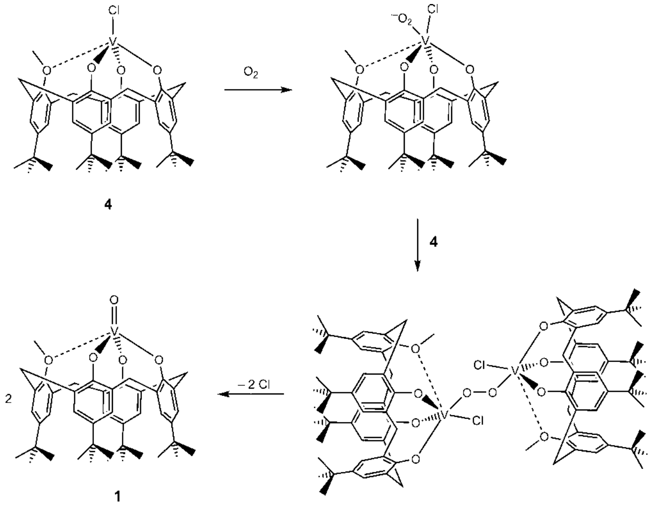
$(OnPr)_3]$ or $[VCl_3(thf)_3]$ followed by recrystallization from acetonitrile. Moreover, it was found that **1** is also accessible by the use of $H_3\mathbf{C}^{Me}$ and $[VO(OnPr)_3]$.[10]

We set out to investigate the chemistry of V^{IV} on an oxo surface modeled by calixarene ligands in order to study possible reoxidation reactions. Accordingly, we treated $[VOCl_2(thf)_2]$ with dimethylated $H_4\mathbf{C}$ and $H_2\mathbf{C}^{Me2}$, in order to synthesize a complex **I** as depicted in Scheme 2. A pure product was obtained in good yield, whose characterization, however, showed that the expected complex **I** had not been formed, but a compound that had been previously suggested by Floriani et al.[11] as the product of the reaction between the complex $\mathbf{C}^{Me2}V^{III}$-Cl and iodine on the basis of an elemental analysis and decomposition studies: $\mathbf{C}^{Me}V^{IV}$-Cl (**4**).[12] The preparation of **4** by the route shown in Scheme 2 allowed its full characterization, and its crystal structure could be determined, too (very recently it has also been identified as the product of the reaction between $H_3\mathbf{C}^{Me}$ and $[RN{=}VCl_3]$).[13] Compound **4** was found to be sensitive to both water and O_2.

Hydrolysis leads to $H_3\mathbf{C}^{Me}$ as well as unidentified oxovanadium halides. The reaction with oxygen astonishingly leads to **1**, which crystallizes isotypically with **4**, so that both compounds can be present side by side (cocrystallized) within the same crystal. Naturally, the question arose as to how **1** is formed from **4** and dioxygen. Most likely, the initiating step consists of an end-on addition of O_2 to the Lewis acidic V^{IV} center to form a $V^{IV}Cl(\eta^1\text{-O=O})$ unit. Subsequently, an electron can be expected to flow from the vanadium center to the oxygen ligand so that a vanadium(V)superoxide moiety is produced (Scheme 3).

The next step should represent a reaction with a second molecule of **4** to give a peroxide unit. To generate **1**, the O–O bond then has to be cleaved homolytically, but since the V centers are already in their highest oxidation states, a V=O bond can only form if an additional electron is provided, and at the same time the chloride ligands have to leave the molecule. How these subsequent steps proceed remains unclear; they result in chloride and organic decomposition products. This type of reactivity is not restricted to **4**: replacement of chloride by triphenylsiloxide followed by exposure to O_2 leads to the same results.[12]

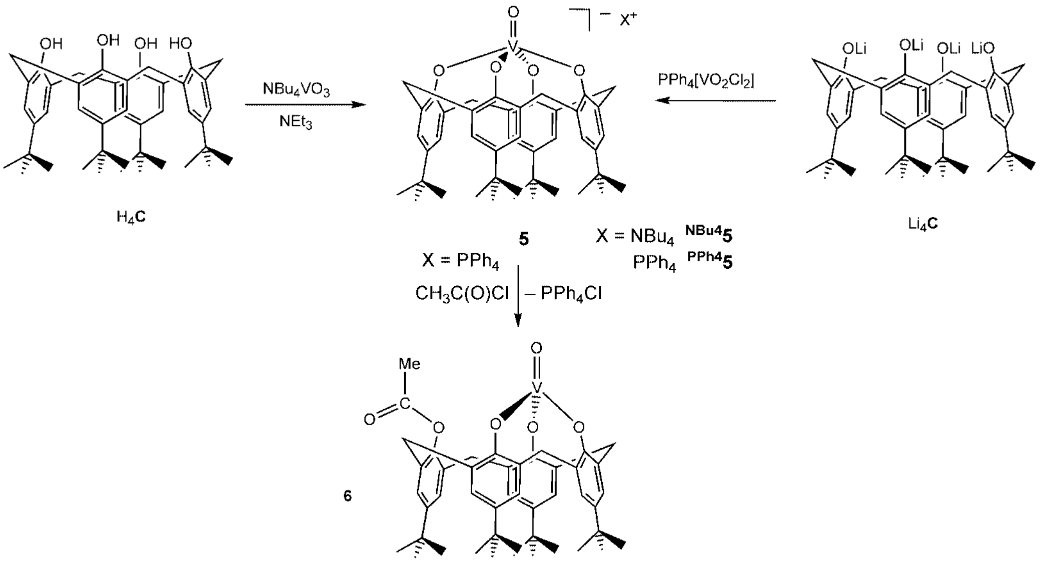
We next turned our attention to the synthesis and reactivity of oxovanadium(V) complexes. Would a complex like **1** behave as a functional model for oxovanadium sites on surfaces, that is, would it show any oxidation chemistry? How would an additional charge alter the situation, and would polynuclear species behave differently? In order to address these questions, systematic studies on the preparation of calixarene oxovanadium complexes with varying nuclearity and charge were performed. This was followed by an investigation of their reactivity and potential as structural or functional models for active sites on surfaces.[14,15]



Scheme 3.

In order to obtain a complex containing an $O{=}V^{3+}$ unit embedded in a tetragonal oxo coordination environment, tetrabutylammonium metavanadate was treated with $H_4\mathbf{C}$ in the presence of NEt_3, and indeed the envisioned complex, $NBu_4[\mathbf{C}V{=}O]$ ($^{\mathbf{NBu4}}\mathbf{5}$) (Scheme 4) formed in good yields.[14] Alternatively, the complex anion **5** can be synthesized starting from the lithium salt $Li_4\mathbf{C}$ that can be obtained by treatment of $H_4\mathbf{C}$ with lithium naphthalenide: The corresponding reaction with tetraphenylphosphonium dichlorodioxovanadate $PPh_4[VO_2Cl_2]$ leads to the elimination of LiCl (and apparently also Li_2O), yielding $PPh_4[\mathbf{C}V{=}O]$ ($^{\mathbf{PPh4}}\mathbf{5}$) (Scheme 4).[14]

According to a crystal structure analysis, the V=O group in **5** is surrounded symmetrically by an O_4 donor set as expected, and **5** therefore represents the first model for such a situation on an oxide support.



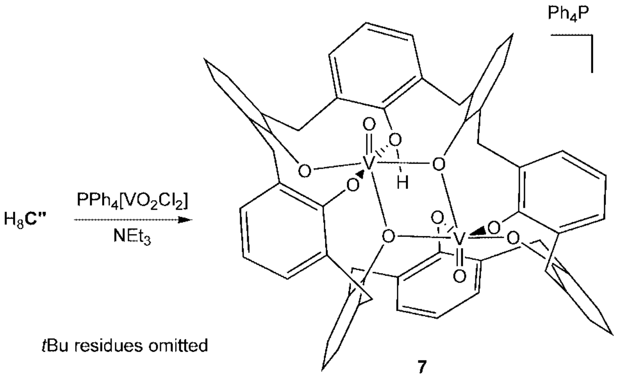
Scheme 4.

For comparative reactivity studies it seemed desirable to also investigate a neutral calixarene oxovanadium(V) complex. As mentioned, there is one complex known, **1**, which, however, is difficult to isolate in larger quantities and in a pure state free from V^{IV} impurities by the reactions shown in Scheme 1 and Scheme 3. Hence, we contemplated the synthesis of a more easily accessible derivative. Indeed, starting from $^{\mathbf{PPh4}}$**5** such a neutral complex can be obtained in a clean and facile synthesis: addition of $CH_3C(O)Cl$ leads to the precipitation of PPh_4Cl and formation of $\mathbf{C}^{\mathbf{OAc}}V^V{=}O$ (**6**) (see Scheme 4).[14]

Whereas the coordination geometry around V in **1** – due to the fact that the methoxy group binds at a longer distance to V, too (compare Scheme 1) – has to be described most appropriately as distorted trigonal bipyramidal, the vanadium center in **6** is coordinated tetrahedrally; there is no interaction with the O atom of the acetyl unit, and **6** can thus be regarded as a model for a species **a**.

We next turned our attention to the synthesis of compounds containing two oxovanadium units to also allow a comparison of the reactivities of dinuclear and mononuclear complexes. Accordingly, higher calixarenes were employed as starting materials, as these offer room for more than one vanadium center. First of all, $H_8\mathbf{C}''$ was chosen to be treated with $PPh_4[VO_2Cl_2]$ in the presence of Et_3N as a base. The resulting product was fully characterized, and a single-crystal X-ray analysis revealed the structure (Scheme 5) and constitution of $PPh_4[H\mathbf{C}''V_2O_2]$ (**7**).[14]

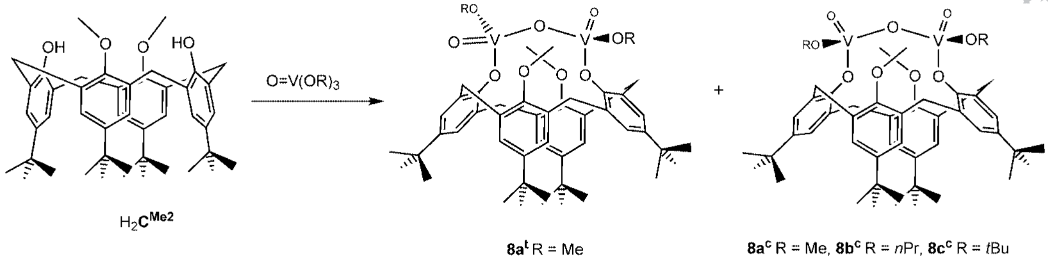
It turned out that a salt containing the anion of **7** in combination with a different cation had been reported before by Pedersen and co-workers[16] as the product of the conversion of $VO(O\mathit{i}Pr)_3$ with $H_8\mathbf{C}''$ in the presence of (*R*)-(+)-1-(1-naphthyl)ethylamine. A single-crystal X-ray diffraction study had not been performed, but the constitution was suggested correctly on the basis of a structure determination for a similar titanium complex. The formation of **7** must have proceeded by reaction of OH functions with V–Cl and V=O groups under elimination of HCl and water, so that two – at first independent – $O{=}V^{3+}$ units are initially coordinated by four aryloxo ligands each, as in **5**. However, two facts prohibit a description of **7** as a dinuclear version of **5**: First of all, one of the phenol functions in $H_8\mathbf{C}''$ is *not* deprotonated (i.e. a coordinated alcohol function results), so that **7** contains only a monoanion, and secondly, the arene band folds in a way that allows two of the phenoxy functions to adopt a bridging binding mode, such that the two vanadium atoms are located in pseudo-octahedral environments.



Scheme 5.

Having accessed a dinuclear, singly charged oxovanadium complex, we also pursued the synthesis of a corresponding neutral complex, ideally containing V–O–V units. Heating a mixture of $H_2\mathbf{C}^{\mathbf{Me2}}$ with $[VO(OCH_3)_3]$ in acetonitrile solution at reflux led to such a compound, $[\mathbf{C}^{\mathbf{Me2}}\text{-}[O{=}V(OMe)]_2\mu\text{-}O]$ (**8a**), which also represents the first dinuclear calix[4]arene complex in general (see Scheme 6).[14]

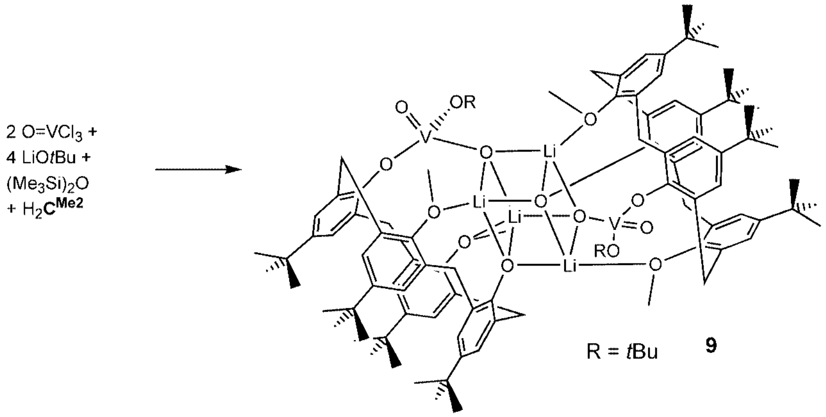
The two phenoxy functions in $\mathbf{C}^{\mathbf{Me2}}$ bind two V=O units that are connected by a bridging oxo ligand. The residual coordination sphere is completed for each V center by



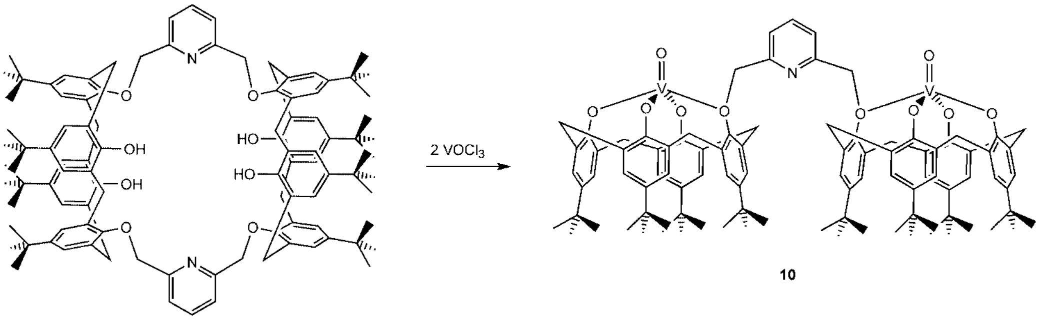
Scheme 6.

methoxy ligands, which can either be located *cis* or *trans* to each other (a mixture of isomers is obtained), i.e. the geometries around the V atoms can be assigned as tetrahedral. At the same time and independently, Redshaw and coworkers reported the analogous syntheses of the corresponding *n*-propyl and *tert*-butyl derivatives **8b**^{c} and **8c**^{c}.[10] The origin of the µ-O bridge is still unclear. Whereas in alkoxide chemistry there is sufficient precedence for the formation of oxo ligands by ether elimination, Redshaw and co-workers contemplated a fortuitous hydrolysis reaction of the vanadyl esters prior to the reaction with $H_2\mathbf{C}^{\mathbf{Me2}}$. Envisioning that a more rational route might involve the initial formation of a chloro alkoxide complex of the form [VOCl(O*t*Bu)$_2$] to which an oxo bridge could be introduced by reaction with $(Me_3Si)_2O$ before the addition to $H_2\mathbf{C}^{\mathbf{Me2}}$, a corresponding investigation was carried out: After reaction of [$VOCl_3$] with a twofold excess of LiO*t*Bu, first $(Me_3Si)_2O$ and then $H_2\mathbf{C}^{\mathbf{Me2}}$ were added to the resulting mixture in order to obtain **8c**^{c}. However, [{$\mathbf{C}^{\mathbf{Me2}}$V-(O*t*Bu)(O)}$_2Li_4O_4$] (**9**) was isolated instead, where a Li_4O_4 cubane-type core is trapped between two oxovanadium calix[4]arene units (Scheme 7).[10]

With the aim of preparing a different type of dinuclear oxovanadium calix[4]arene complex, a special type of ligand was employed where two calix[4]arene units are linked by two lutidene moieties. Reaction with [$VOCl_3$] in refluxing toluene led to the loss of one of these linkers and to the formation of the bimetallic complex **10** (Scheme 8). As in the mononuclear "version" **1**, each vanadium atom here adopts a trigonal bipyramidal geometry, for which both vanadyl groups are oriented in the same direction with respect to the lutidene bridge.[10]



Scheme 7.



Scheme 8.

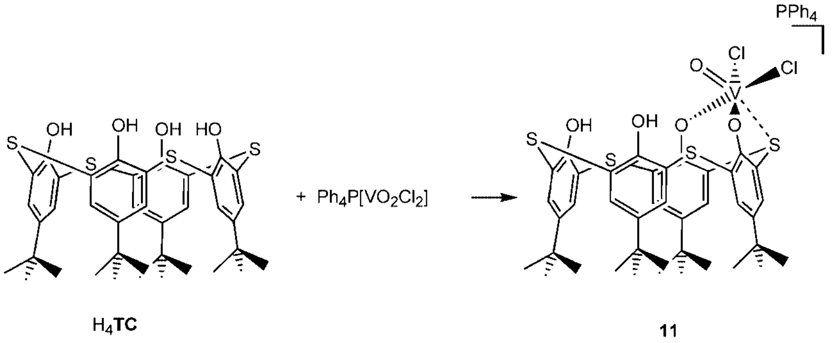
2.2. Complexes with Thiacalixarene Ligands

Compared with that of the related *p-tert*-butylcalix[4]-arene, the chemistry of thiacalixarenes is still in its infancy, as the synthesis of thiacalixarenes and their sulfinyl and sulfonyl derivatives has been known only since the late 1990's.[17] Recent publications provide evidence that the thioether units can take part in metal ion coordination, which leads to a stronger interaction with transition metals relative to calixarenes.[18] As such interactions can be anticipated to lead to significant chemical differences, it seemed interesting to also prepare oxovanadium thiacalix[4]arene complexes in order to compare their reactivities with those of the corresponding complexes based on the "classical" calixarenes. First, a reaction of *p-tert*-butyltetrathiacalix[4]-arene (H_4**TC**) with $Ph_4P[VO_2Cl_2]$ was carried out in the absence of an external base; this led to $PPh_4[(H_2$**TC**$)VOCl_2]$ (**11**), as demonstrated by single-crystal X-ray crystallography, elemental analysis, and IR and NMR spectroscopy (Scheme 9).[15]

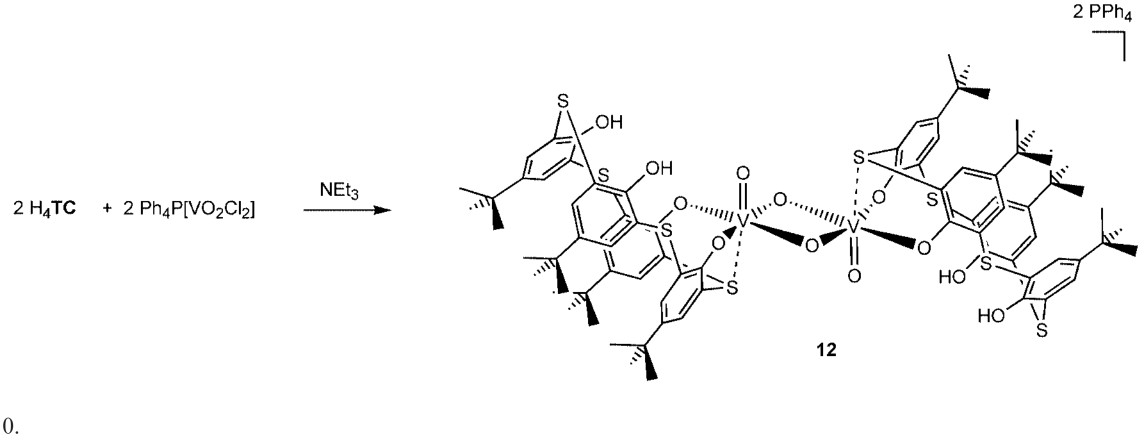
In **11** a vanadyl unit is positioned somewhat above the plane defined by the O atoms belonging to the two calixarene phenolate functions and the two terminal chloride ligands. The coordination sphere of V is completed by one of the thioether functions belonging to the ligand: The distance to the closest S atom is significantly shorter than the sum of the van der Waals radii of vanadium and sulfur, indicating a coordinative interaction.

The formation of **11** must have proceeded by addition of two OH functions to one of the V=O groups belonging to the starting material with elimination of water. Accordingly, in the absence of an external base, the protons of H_4**TC** are acidic enough to attack one of the nucleophilic oxygen atoms of $[VO_2Cl_2]^-$, as in the case of the "normal" calixarenes. However, they are not acidic enough to further induce intramolecular HCl elimination: the anion of **11** formally still contains two equivalents of HCl, whose elimination would lead to the thia analog of **5**. The fact that such a complex is not formed spontaneously may to some extent be a result of the coordinative support of the sulfur atom at the vanadium center. On the other hand, the formation of **5** – as mentioned before – required the addition of a base at least as strong as NEt_3. Therefore, the reaction in Scheme 9 was repeated in the presence of NEt_3, which led to the precipitation of a red solid. After purification and crystallization, this solid was identified as $(PPh_4)_2$-$[H_2$**TC**$V(O)(\mu\text{-}O)]_2$ (**12**) with the aid of X-ray crystal structure determination, elemental analysis, and IR and NMR spectroscopy (Scheme 10).[15]

In the molecular structure of the anion of **12**, two O=V groups are linked by two bridging oxo ligands in a way that positions the terminal O ligands in an *anti* fashion, and a noncrystallographic mirror plane runs through them. Furthermore, each vanadium center coordinates a calixarene ligand in a cone conformation through two phenolate



Scheme 9.



Scheme 10.

functions and again also through interaction with a thioether function.

2.3. Complexes with Oxacalixarene Ligands

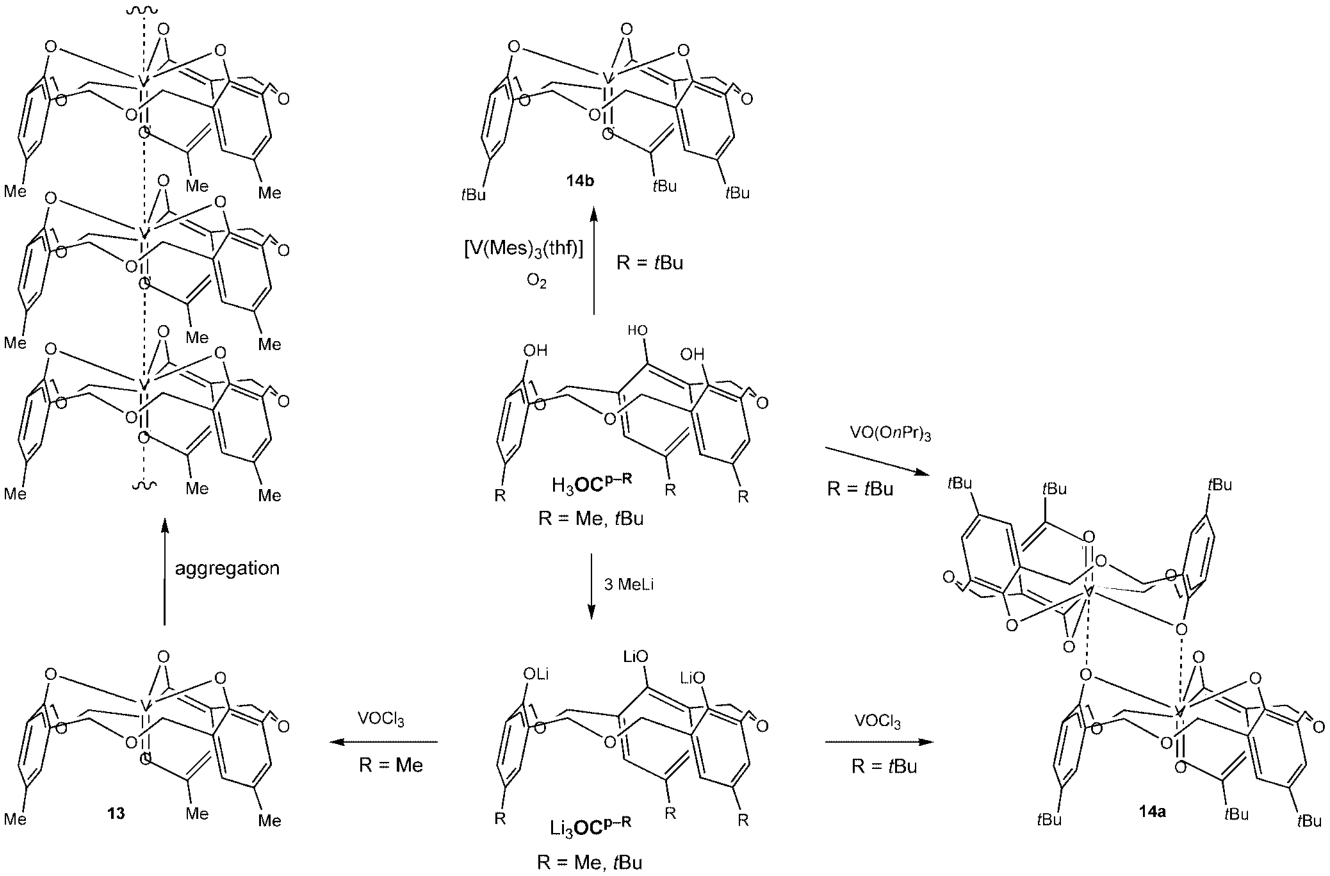
In 1997, Hampton et al. treated lithiated *p*-methylhexahomotrioxacalix[3]arene, H_3**OC**$^{\mathbf{p-Me}}$, with [$VOCl_3$], in order to prepare linear chain polymers, and obtained a compound of the expected stoichiometry, [**OC**$^{\mathbf{p-Me}}$V=O] (**13**).[9b] On the basis of spectroscopic data obtained for solutions of **13**, a structure in which the vanadyl group is positioned within the calyx (Scheme 11) was proposed, even though the corresponding "oxo-out" structure could not be ruled out. A fibrous solid precipitated from such solutions after several days, and the spectroscopic data obtained for this solid indicated that an asymmetric μ-oxo-bridged linear chain polymer had formed. Unfortunately, single crystals suitable for an X-ray diffraction study could not be grown for any of the forms of **13**.

Recently, the *p-tert*-butyl derivative of **13** was prepared by treating the corresponding calix[3]arene H_3**OC**$^{\mathbf{p-Bu}}$ with [VO(O*n*Pr)$_3$] or by treating Li_3**OC**$^{\mathbf{p-Bu}}$ with [$VOCl_3$].[10] A single-crystal X-ray analysis showed that the resulting complex **14a** (Scheme 11) is monomeric with a trigonal pyramidal coordination of the vanadium atom. In the solid state, there are only very weak intermolecular interactions between the vanadium center of one molecule and a phenoxy function of another molecule. This gives rise to a pair of molecules that lie face to face over an inversion center, which contrasts the identification of a polymeric structure for **13**. Interestingly, the reaction of [$VMes_3$·thf] with H_3**OC**$^{\mathbf{p-Bu}}$ followed by treatment with O_2 provided a complex that could be identified as a discretely monomeric molecule **14b** by means of X-ray diffraction after crystallization of the compound.[10]

3. Catalytic Activity

3.1. Evaluation of the Potential of the Compounds as Functional Models for ODH

As outlined in the introduction, the most prominent conversions that can be carried out by using vanadia on oxide supports as heterogeneous catalysts are the ODH of methanol and alkanes. Naturally, molecular models such as those described here will prove to be unreactive in contact with alkanes, as the rate-determining step of ODH is the first C–H bond cleavage, which has a large activation barrier (which means that heterogeneous catalysis at elevated temperatures is required for the reaction to take place). However, methanol and higher alcohols are less inert as substrates, so that their reactions can also be investigated with molecular compounds in the liquid phase. Any information derived from such studies might contribute to a



Scheme 11.

more comprehensive understanding of methanol oxidation at vanadia catalysts, and they might as well provide ideas for the (probably) more complex ODH of alkanes.

In order to test the compounds described above for reactivity in relation to ODH and to establish their suitability as models, we therefore decided to investigate the oxidation of a palette of various alcohols to the corresponding carbonyl compounds with O_2 as the reagent.[14,15] Of course there are numerous methods to oxidize alcohols with organic or inorganic reagents,[19] which, however, are often stoichiometric and/or lead to toxic waste products. Hence, at present, the performance of catalytic oxidations with O_2 is still an attractive topic, and a lot of research has been devoted to it in the past.[19] Certainly, the background of the study presented here – as mentioned – was an inquiry as to whether oxovanadium calixarene and thiacalixarene complexes could represent not only structural but also functional models for the heterogeneously catalyzed ODH, and we did not have the aim of finding an improved catalyst for the aerobic oxidation of alcohols. Nevertheless, the latter aspect was borne in mind as a potential, beneficial part of the investigation.

As we consider the V^V compounds **5**–**8**, **11**, and **12** as functional models, they are expected to contain functional moieties already, i.e. the first step of a possible catalytic cycle should consist of a reaction with the chosen alcohol (vide infra). After a potential oxidation reaction, O_2 could serve to regenerate the active species. As a reference, a system was chosen that has been recently shown to efficiently catalyze the aerobic oxidation of 1-phenyl-1-propargyl alcohol,[20] $OV(acac)_2$. This system probably belongs to the category of complexes that activate O_2 first. Figure 1 combines the list of alcohols chosen and the complexes tested with the turnover frequencies (TOFs) measured at 80 °C in the presence of molecular sieves to remove the water generated during the ODH.

For none of the nonactivated aliphatic alcohols was any activity observed by employing the catalysts depicted. When focusing on the complexes with the classical calixarene ligands first, the following picture emerged on employment of 1-phenyl-1-propargylic alcohol and fluorenol: the mononuclear complexes **5** and **6** only led to low conversions. However, the dinuclear complexes and the reference system led to much higher TOFs between 7.7 and 43 h^{-1}. With a TOF of 43 h^{-1}, the activity of **7** for the oxidation of fluorenol was even almost twice as high as that of $OV(acac)_2$.[14]

Subsequent studies even showed that the singly charged mononuclear complex **5** is completely inert under various conditions also towards other substrates, whereas the two dinuclear complexes were also capable of oxidizing a nonfunctionalized hydrocarbon such as 9,10-dihydroanthracene, although the TOFs are much lower in than those for the alcohol oxidations. The oxidation products were identified as 10.0% (1.0%) anthracene, 13.0% (1.5%) 10*H*-anthracene-9-one, and 7% (1.5%) 9,10-dihydroanthracene-

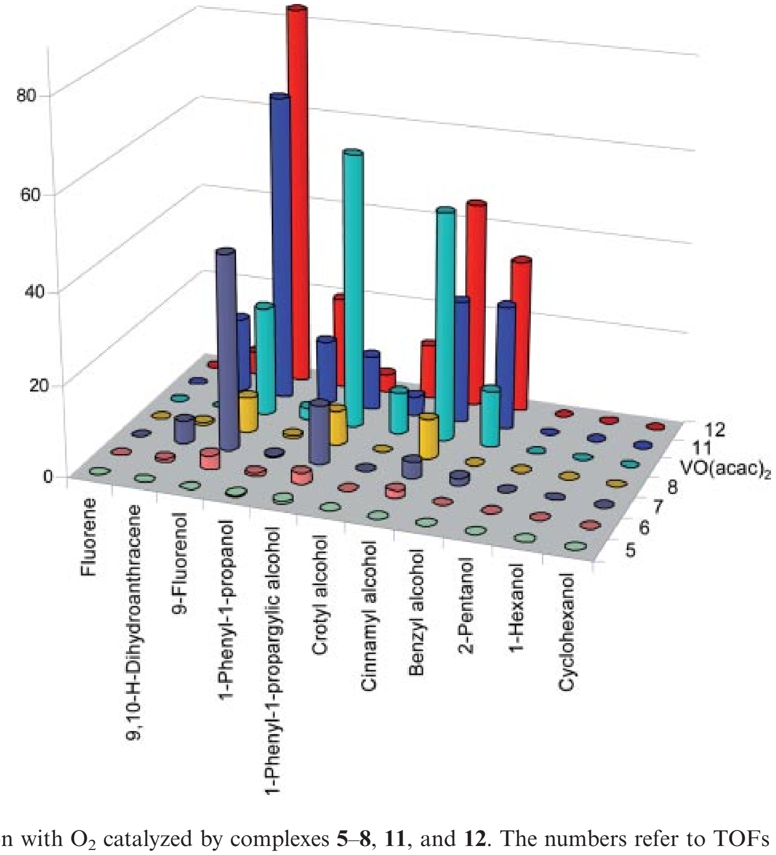


Figure 1. Substrate oxidation with O_2 catalyzed by complexes **5**–**8**, **11**, and **12**. The numbers refer to TOFs (h^{-1}), calculated per V center present.[15]

9,10-diol (the percentage values specify the yield of oxidation product obtained by employing **7** (**8**) [1 mol-%] within 3 h with respect to the alcohol employed).

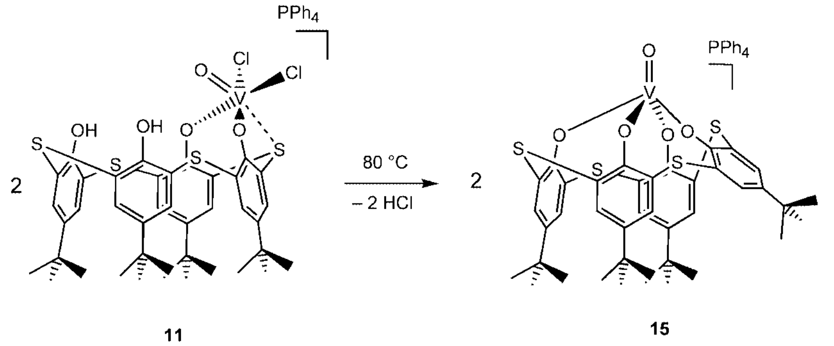
Turning our attention now to the thiacalixarene complexes, it can be noted that **11** and **12** are significantly more active than **5**–**8**,[15] and **12** catalyzes the oxidation of benzyl alcohol (33.6 h^{-1}) and crotyl alcohol (12.0 h^{-1}) even more efficiently than the reference system. The outstanding behavior of **12** fits the observation that dinuclear complexes are more active than the corresponding mononuclear ones, as was already evident during the investigation of the classical calixarenes.[14] In fact, **12** is more active than **11** for all alcohols except for one: 1-phenyl-1-propargyl alcohol. At the same time, this is the only case where **11** and **12** are less active than **7** and **8**, so that something seems to be special about the reactivity of this alcohol in combination with the thiacalixarene complexes. In contrast, the TOF observed for the oxidation of fluorenol catalyzed by **12** (83.4 h^{-1}) is twice as high as that observed for **7** (43.0 h^{-1}), and **11** is also very active (67.0 h^{-1}), whereas the two mononuclear calixarene complexes **5** and **6** – as mentioned previously – show hardly any activity. With reference to 9,10-dihydroanthracene, it becomes evident that, of all complexes investigated, **11** performs best (13.0 h^{-1}), whereas **12** is three times more active than **8** but only half as active as **7**. With fluorene, whose C–H bonds are somewhat (ca. 23 kJ/mol) stronger, as the substrate, none of the compounds employed showed any activity.

Having identified **11** and **12** as the most active catalysts, we subjected them to studies concerning mechanistic questions. Hence, the effects of the individual reagents and reaction conditions were analyzed, and it was found that heating dissolved **11** to 80 °C in the absence of alcohol and O_2 leads to the thia analog of **5**, $PPh_4[(\mathbf{TC})V{=}O]$ (**15**) (Scheme 12).

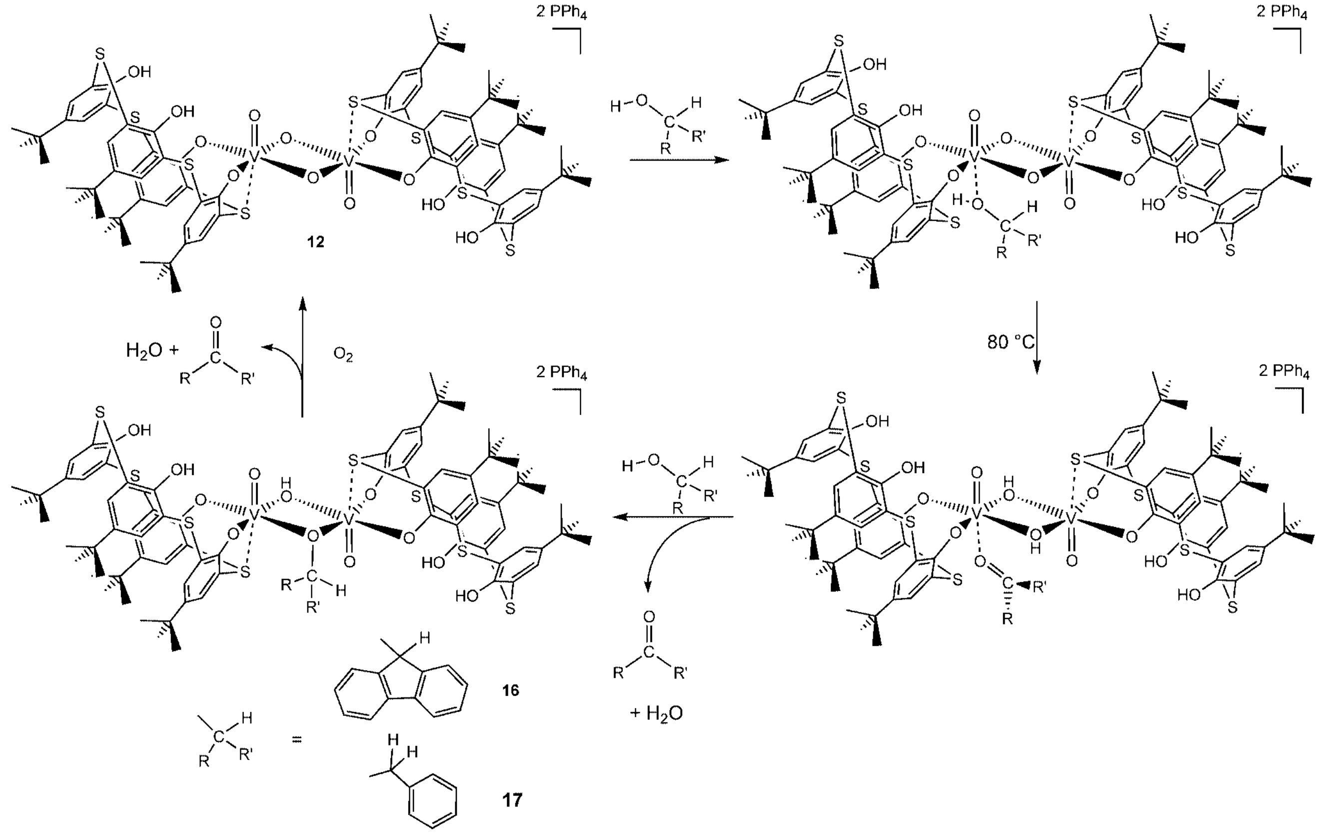
This indicates that, whenever **11** is employed as a catalyst for conversions at 80 °C, **15** will be the active species being generated from **11** in situ by a double intramolecular HCl elimination. Compound **15** then reacts with convertible alcohols, as indicated by a further color change, and most likely this leads to the carbonyl compounds. O_2 is then needed to reoxidize the V center, which apparently yields **15** again. So far we were not able to identify any of the intermediates occurring in the catalytic cycle involving **15** in contact with alcohols. However, we were more successful in the case of **12**: Treating **12** with two equivalents of fluorenol at 80 °C in the absence of O_2 led to a light green solution from which $(PPh_4)_2[\{H_2\mathbf{TC}V(O)\}_2(\mu\text{-}OH)(\mu\text{-}OC_{13}H_9)]$ (**16**) could be isolated in good yields.[15] Compound **16** can be derived from **12** by formally replacing one of the two divalent μ-O ligands in **12** by one μ-OH and one μ-fluorenolate ligand, and in consequence both vanadium atoms are then in the oxidation state +IV. How is **16** formed? Scheme 13 shows a possible catalytic cycle involving **16**.

It is not clear whether a prebinding of the alcohol is necessary for the oxidation step, but if this were the case, it most likely occurs at one of the V centers through a replacement of the weakly bound, "soft" thioether donor belonging to the calixarene ligand as shown in Scheme 13. The next steps might consist of a dehydrogenation (possibly in the form of two consecutive H atom abstractions) leading to fluorenone and a complex with two hydroxo bridges. To get from there to **16** a replacement of one of the two hydroxo bridges by an alcoholate ligand with elimination of water has to occur, a step that should be sufficiently fast at 80 °C, especially in the presence of molecular sieves that constantly remove the water out of the equilibrium. By the mechanism in Scheme 13, one equivalent of fluorenone should be formed simultaneously with **16**, and indeed this could be detected. O_2 can then oxidize **16** to give a second equivalent of fluorenone and the starting material **12**, and this was independently shown to proceed already at room temp.; the process involves four electrons and two protons, which, in combination with O_2, lead to one equivalent of water and the O^{2-} ligand necessary to regenerate **12**.

Hence, this catalytic cycle for the oxidation of fluorenol with O_2 mediated by **12** is plausible, and it additionally even seems to be conferrable to the oxidations of other alcohols: After analogous treatment of **12** with benzyl alcohol, **17**, the derivative corresponding to **16**, (Scheme 13) was isolated. It is interesting to note that oxidation chemistry preferably takes place at the bridging oxo functions and not at the terminal oxo ligands present. This in turn means that the conclusion drawn for the functioning of **12** can not be valid as such for the other calixarene-based catalysts (**5**–**8** and **11**/**15**), since each of those has its individual features



Scheme 12.



Scheme 13.

and none of them contains a bis(μ-oxo) unit. However, the mechanism in Scheme 13 exemplifies why it might be advantageous for a catalyst to contain two V centers, putting across the observation that dinuclear catalysts are more effective: all oxidation equivalents of O_2 are consumed within one cycle, and the vanadium centers only have to switch oxidation states between +V and +IV, whereas the functioning of mononuclear catalysts requires a change between +V and +III. This finding could, in principle, apply to the ODH of alcohols by surface sites, too, i.e. dinuclear sites containing bridging oxo functions should be more active than mononuclear ones. It will be interesting to follow up this working hypothesis in the future.

3.2. Olefin Polymerization

With the background described above in the Introduction, a number of the above-mentioned compounds were screened as potential catalysts for the polymerization of ethylene and for ethylene/propylene copolymerization in the presence of a number of organoaluminum cocatalysts as for instance MAO, and dimethylaluminum chloride (DMAC); the effect of the presence of the reactivating substance ethyl trichloroacetate (ETA) was tested, too.[10]

Among the oxovanadium calixarene compounds tested as catalysts, **1**, **3^{AN}**, **8b^{c}**, **9**, **10**, and **14**, **14** in combination with DMAC/ETA displayed the highest activity for ethylene polymerization [up to 130,000 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ at 80 °C, yielding ultra-high-molecular-weight (>5,500,000) linear polyethylene], and ethylene/propylene copolymerization (up to 10,000 $g\,mmol^{-1}\,h^{-1}\,bar^{-1}$ at 25 °C) with about 14.5 mol-% propylene incorporation. These activities are amongst the highest reported to date for nonmetallocene systems.[21] An additional advantageous property of **14** is its stability to prolonged exposure to air. If other organoaluminum cocatalysts are employed such as MAO, much poorer catalytic activities are observed. In comparison to the oxacalix[3]arene complex **14** calix[4]arene-based procatalysts are at best an order of magnitude less active. Hence, the variation from oxa(-CH_2OCH_2-)- to methylene (-CH_2-)-bridged calixarenes as ancillary ligands leads to clear differences in catalytic performance for α-olefin polymerization systems. Although the nature of the active species formed upon addition of excess DMAC remains uncertain, the reasons are thought to be both steric and electronic in nature and relate to the ease with which the macrocycle can be disconnected from the vanadium center.[10] The shape and size of the oxacalix[3]arene ligand (and associated cavity) is very different from that of the calix[4]arene ligand, and this clearly leads, for instance, to different binding modes (exo vs. endo) for the V=O group: in oxacalixarene complexes this unit is located in the cavity, and this renders the vanadium somewhat exposed, whereas in vanadyl calix[4]arene complexes an exo orientation is observed. The depths of each type of cavity are also very different.[10]

Among the vanadyl calix[4]arene complexes investigated, those containing two vanadium centers (**8b**^{c} and **10**) exhibit the highest activities, which may be the result of cooperative effects between the vanadium centers upon formation of the active species.

4. Conclusions and Outlook

Taken together, all the findings described in 3.1. may have implications on the discussion of which kind of species are active in oxidative dehydrogenation with vanadia catalysts, as they suggest an increase of activity through the cooperative behavior of two metal centers. However, a larger number of complexes has to be synthesized, and more detailed mechanistic investigations have to be performed to support this hypothesis.

With regard to the mechanism suggested for catalyst **12**, it seems interesting to investigate the kind of reactivity that forms the basis for the activity of mononuclear complexes: the identity of the products generated after addition of the alcohols to **15** at 80 °C or the other mononuclear complexes remains unclear, as we were so far not able to identify any of these potential intermediates. A further question concerns the reasons for the better performance of the thiacalixarene complexes relative to **5**–**8**. A striking result is the high activity observed for **15** (which is identical with the one ascribed to **11**), whereas the calixarene analog **5** is absolutely inert. The rate-determining step (probably the alcohol conversion) seems to be accelerated by the interaction of the thioether functions with the vanadium centers. More detailed and extensive studies might provide some insight in the future.

Interestingly, the results of the investigations concerning the catalytic activity for olefin polymerization (section 3.2) seem to suggest the same general trends as in the alcohol oxidation: the heterocalixarenes (here oxacalixarenes) are more active, and dinuclear complexes display higher activities than mononuclear compounds. It will be interesting to examine the reasons in the future and to investigate other open questions concerning the exact role played by DMAC, which is still far from clear. Success in the identification of the active species in these vanadium-based systems would be a major step forward in the current understanding and provide information vital to the future design of new vanadium-based catalytic systems.

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