Vanadium calixarene complexes as molecular models for supported vanadia

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Abstract

Reaction of dimethylated *tert*-butyl calix[4]arene, H_2A^{Me2}, with O=VCl$_2$(thf)$_2$ unexpectedly led to the isolation of Cl−V^{IV}A^{Me}, **2**, whose crystal structure was determined. Hence, one of the MeO–C bonds present in H_2A^{Me2} has been cleaved and one equivalent of HCl eliminated leaving three phenolate and one phenolether function to coordinate at the V centre. **2** smoothly reacts with O$_2$ to give O=V^{V}A^{Me}, **B**, i.e. the chloride ligand has been replaced by a terminal oxo ligand with concomitant oxidation of the vanadium atom to the oxidation state +5. **B** crystallises isostructurally with **2**; crystallisation of a mixture of **2** and **B** even leads to crystals that contain both compounds beside each other. However, when **B** was co-crystallised together with H_2A^{Me2}, from acetonitrile a different structure with a partial cone conformation was obtained. The mechanism by which **B** is formed from **2** is discussed. To obtain information concerning the fate of the chloride ligand in **2**, a derivative, Ph$_3$SiO–V^{IV}A^{Me}, **3**, has been synthesised and investigated with respect to its behaviour in the presence of O$_2$: it reacts the same way as **2**.
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1. Introduction

Despite significant research efforts directed toward understanding the general features and reaction steps of oxidation catalysis mechanisms *on surfaces*, many systems can still be regarded as poorly defined [1], which may in part be due to the fact that a lot of difficulties are encountered during characterisation of reaction intermediates on surfaces [2]. For several years, we have been dealing with the modelling of surface intermediates occurring during heterogeneous processes with *molecular compounds* as well as with the possibilities and limits of such an approach [3].

This contribution deals with reactive moieties and intermediates playing relevant roles on the surfaces of vanadiumoxide-based catalysts during the oxygenation/dehydrogenation of organic substrates. A portfolio of different surface species has been considered to be involved in one way or the other [4]. A representative example is the oxidative dehydrogenation (ODH) of alkanes for which heterogeneous vanadiumoxide catalysts containing SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$, MgO as well as zeolite supports proved to represent efficient catalysts [5]. One of the

various working hypotheses assumes that the active and selective sites contain mononuclear tetrahedrally coordinated V^{5+} centres [4] (Chart 1).

Calix[4]aren ligands, **A**, have established themselves in the past for the modelling of oxidic surfaces characteristic for transition metal catalysts or the support belonging to a certain catalyst [6], and their valency can be adjusted by successive methylation of the phenolate units. Here, we report the employment of such ligands for the mimicking of V=O sites.

2. Experimental

2.1. General procedures

All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^{1}H, ^{13}C and ^{51}V NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (^{1}H 400.13 MHz, ^{13}C 100.63 MHz, ^{51}V 105.25 MHz) with toluene-d_8 or C$_6$D$_6$ as solvent at 20 °C. The ^{1}H NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent (toluene-d_8 δ_H 2.10 ppm and C$_6$D$_6$ δ_H 7.15 ppm), the ^{51}V NMR spectra against VOCl$_3$ as a standard. The ESR spectra were recorded on a ERS 300

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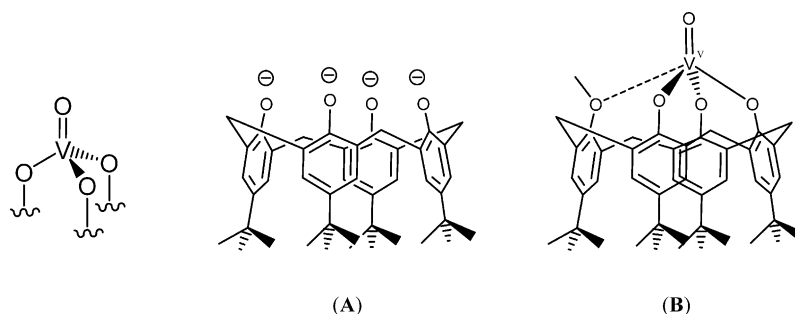
Chart 1.

spectrometer (X-Band (9 GHz) ZWG) on solid and liquid assays with CH_2Cl_2 as solvent at 20 °C. Microanalyses were performed on a Leco CHNS-932 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Digilab Excalibur FTS 4000 FTIR-spectrometer.

2.2. Materials

Solvents were purified, dried and degassed prior to use. Pure $VOCl_2(thf)_2$ [7] and dimethyl-*p-tert*-butyl-calix[4]arene [8] were prepared according to the literature procedure. $NaOSiPh_3$ was prepared using NaH and $HOSiPh_3$ in THF.

2.3. (O-methyl-p-tert-butyl-calix[4]arene)-chloro-vanadium(IV) (2)

2.3.1. Method A

A solution of $VOCl_2(thf)_2$ (0.52 g, 1.85 mmol) in toluene (15 ml) was added to a solution of dimethyl-*p-tert*-butyl-calix[4]arene (1.25 g, 1.85 mmol) in toluene (15 ml) and this mixture was refluxed for 24 h. From the resulting red-brown solution all volatiles were removed and the residue was extracted with hexane (2 × 10 ml). Cooling a hexane solution to −30 °C yields 1.28 g (92.7%) of 2.

2.3.2. Method B

A solution of $VCl_4(thf)_2$ (0.25 g, 0.68 mmol) in toluene (5 ml) was added to a solution of dimethyl-*p-tert*-butyl-calix[4]arene (0.46 g, 0.68 mmol) in toluene (5 ml) and this mixture was refluxed for 16 h. From the resulting red-brown solution all volatiles were removed. The residue was extracted with CH_2Cl_2 (10 ml) and after evaporation to dryness again with hexane (10 ml). Removal of the solvent yields complex 2 (0.37 g, 72.6%).

ESR: $g = 1.88328$, $a = 0.203$ GHz (solution in CH_2Cl_2) and $g = 1.86430$, $a = 0.401$ GHz (solid), mp 119 °C, anal. found: C 73.14, H 7.92, Cl 5.25. Calc. for $C_{45}H_{55}O_4VCl$: C 72.42, H 7.43, Cl 4.75%.

2.4. (O-methyl-p-tert-butyl-calix[4]arene)-oxo-vanadium(V) (B)

To a stirred black brown solution of 2 (0.15 g, 0.20 mmol) in acetonitrile (5 ml) a 1000-fold excess of dry oxygen was added via a syringe. While stirring at r.t. over night the colour of the solution turned red-brown and small amounts of a brown solid precipitated. Subsequently, all volatiles were removed, and the residue was extracted with hexane (5 ml). Evaporation of the solvent yields B as a brown powder (0.13 g, 89.0%).

The analytical as well as the IR and ^1H NMR spectroscopic data were in agreement with those described in the literature [9b] before. ^{51}V NMR (toluene-d_8, δ [ppm]): −352 (br).

2.5. (O-methyl-p-tert-butyl-calix[4]arene)-triphenylsilyloxy-vanadium(IV) (3)

To a stirred red-brown solution of 2 (0.25 g, 0.335 mmol) in THF (5 ml) a solution of $NaOSiPh_3$ (0.10 g, 0.335 mmol) in THF (5 ml) was added. The colour changed rapidly to yellow brown. After stirring for 1 h at r.t. the solvent was evaporated in vacuum. Extracting with hexane and cooling of the saturated solution to 4 °C yields fine black needles of 3 (0.24 g, 74.1%).

ESR of the solid: $g = 1.88328$, $a = 0.405$ GHz, mp 213–215 °C. IR (KBr): $\tilde{v}$ [cm^{-1}] 3047 w, 2958 s, 2823 m, 2871 m, 1428 s, 1304 w, 1262 w, 1203 w, 1187 w, 1117 s, 1005 m, 905 vs b, 740 w, 712 s, 697 s, 622 w, 602 w, 510 s, 458 w. Anal. found: C 76.20, H 7.93, calc. for $C_{63}H_{70}O_5SiV$: C 76.72, H 7.15%.

2.6. Crystal structure determinations

Single crystals of 2 were obtained by cooling a saturated pentane solution to −30 °C or else by slow evaporation of the solvent from a saturated solution of 2 in toluene in a glovebox. Single crystals of 3 were obtained by slowly cooling a saturated hexane solution to 4 °C. Suitable crystals of B in the paco conformation were obtained by evaporation of the solvent from a saturated acetonitrile solution. The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer (Stoe IPDS for 2 and 3, Stoe IPDS2T for B) using Mo Kα radiation, λ = 0.71073 Å, and the structures were solved by direct methods (SHELXS-97) [10], refined versus F^2 (SHELXL-97) [11] with anisotropic temperature factors for all non-hydrogen atoms (Table 1). All hydrogen atoms were added geometrically and refined by using a riding model.

The crystallographic data (apart from structure factors) of 2, 3 and B were deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 282429, 282427

Table 1
Crystal data and experimental parameters for the crystal structure analyses of **2**, **3** and **B**

	2	3	B
Formula	$C_{45}H_{55}ClO_4V \cdot 1.5C_7H_8$	$C_{63}H_{70}O_5SiV$	$C_{45}H_{55}O_5V \cdot C_{46}H_{60}O_4 \cdot 3C_2H_3N$
Weight (g·mol^{-1})	884.48	986.254	1526.93
Temperature (K)	180(2)	180(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorombic	Triclinic
Space group	$I2/a$	$Pn2_1a$	$P\bar{1}$
a (Å)	24.976(3)	21.556(4)	11.9765(13)
b (Å)	13.2350(10)	23.200(3)	18.105(2)
c (Å)	29.927(3)	25.196(3)	20.653(3)
α (°)	90	90	94.147(9)
β (°)	94.91(2)	90	91.838(9)
γ (°)	90	90	100.667(9)
V (Å^3)	9856.3(17)	12600(3)	4384.7(8)
Z	8	8	2
Density (g cm^{-3})	1.192	1.04	1.157
μ(Mo Kα) (mm^{-1})	0.299	0.216	0.171
$F(000)$	3776	4136	1644
GoF	0.787	1.026	1.075
R_{ind} [$I > 2\sigma(I)$]	$R_1 = 0.0492$	$R_1 = 0.0634$	$R_1 = 0.1244$
	$wR_2 = 0.0868$	$wR_2 = 0.1723$	$wR_2 = 0.1856$
R_{ind} (all data)	$R_1 = 0.1196$	$R_1 = 0.0828$	$R_1 = 0.2432$
	$wR_2 = 0.1029$	$wR_2 = 0.1789$	$wR_2 = 0.2272$
$\Delta\rho_{min}/\Delta\rho_{max}$ (eÅ^{-3})	−0.341/0.273	−0.449/1.094	−0.486/0.570

and 282428. Copies of the data can be ordered free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

With regard to calixarene based vanadium oxo complexes, only one precedent complex has been reported containing a ligand derived from **A** by monomethylation of one phenolic function, **A^{Me}**, and an [O=V]$^{3+}$ unit [9b] (see **B** in Chart). Naturally, there is also interest in reduced complexes that could model reduced species formed after oxidation reactions, and in this context V^{IV} and V^{III} are important. We therefore decided to investigate the chemistry of V^{IV} on an oxo surface modelled by calixarene ligands in order to study possible reoxidation reactions. Accordingly, we reacted O=VCl$_2$(thf)$_2$ with dimethylated

H$_4$A, **H$_2$A^{Me2}**, in toluene at 111 °C for 24 h in order to synthesise a complex **1** as depicted in Scheme 1. A pure product was obtained in good yield, whose spectroscopic characterisation, however, showed that the expected product **1** had not been formed. Finally, an X-ray crystal structure analysis revealed the constitution **2** for the product, a compound that had been previously suggested by Floriani and co-workers for the product of the a reaction between the complex Cl–V^{III}**A^{Me2}** and iodine on the basis of an elemental analysis and decomposition studies [9a]. The crystal structure of complex **2** is depicted in Fig. 1. Each molecule hosts a toluene molecule in the cavity and additional 0.5 equivalents of co-crystallised toluene are present within the unit cell. The coordination polyhedron around the vanadium centre resembles a distorted trigonal bipyramid ($\tau = 0.6$) [12], with O2, O4 and Cl atoms defining the equatorial plane and the O1 and O3 atoms in the axial positions. The distortions from a
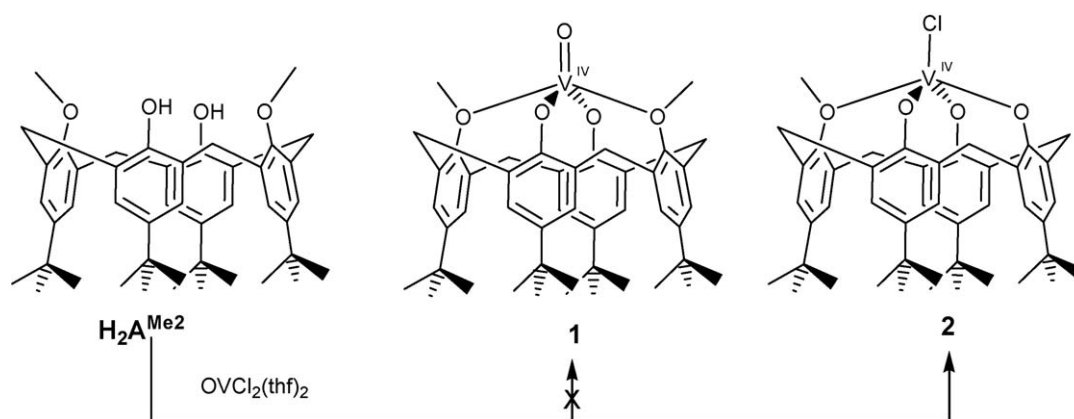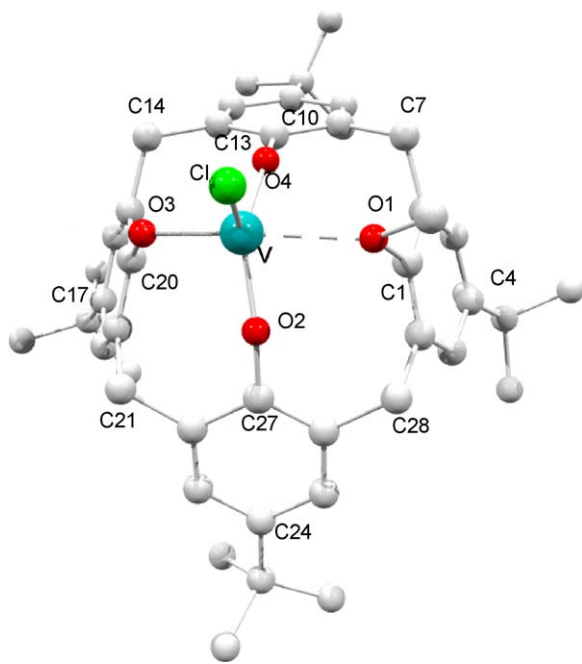

Scheme 1.

Fig. 1. Molecular structure of complex **2**. Solvent molecules and all hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): V–Cl 2.2327(11), V–O1 2.324(2), V–O2 1.759(3), V–O3 1.825(2), V–O4 1.767(3), Cl–V–O1 91.44(6), Cl–V–O2 109.74(8), Cl–V–O3 96.24(7), Cl–V–O4 109.67(8), O1–V–O3 172.32(9), O2–V–O4 136.11(13), V–O1–C1 117.5(2), V–O2–C13 156.1(2), V–O3–C20 115.6(2), V–O4–C27 152.8(2).

Table 2
Dihedral angles (°) between planar moieties (E (reference plane) refers to the least-squares mean plane defined by the C7, C14, C21 and C28 bridging methylenic carbons)

	2	**3**	**B**
E A	113.18(6)	111.1(3)	114.5(2)
E B	135.99(8)	132.62(12)	123.7(2)
E C	93.90(2)	119.74(11)	115.0(1)
E D	133.50(7)	146.38(11)	170.2(2)
A C	130.94(5)	132.24(13)	130.2(2)
B D	91.27(6)	99.03(14)	114.0(2)
Contact distances (Å) between *para*-carbon atoms of opposite aromatic rings			
C4–C17	7.650(1)	8.192(9)	7.602(10)
C10–C24	9.039(6)	9.427(9)	9.609(9)
Displacement of vanadium to the O3-atom in a trigonale bipyramide			
Δ	0.2256(7)	0.2384(9)	0.2211(13)

regular trigonal bipyramid are indicated by the O1–V–O3 angle (172.32(1)°) and by the displacement of the metal atom from the equatorial plane toward the O3 atom (0.2256(7) Å). The V–O2, V–O3 and V–O4 bond distances (1.758(3), 1.824(2), 1.767(2) Å) as well as the wide angles V–O2–C13 (156.1(2)°) and V–O4–C27 (152.8(2)°) are in agreement with the existence of V–O π bonding. However, the V–O3–C20 angle (115.6(2)°) is particularly acute [13], and this value is close to the V–O1–C1 angle (117.5(2)°) defined by the coordinated methoxy group. As a consequence of the presence of the methoxy group (V–O1: 2.324(2) Å) the macrocycle adopts an elliptical cross section conformation with the opposite A and C aryl rings (C contains the methoxy group) pushed outward and the opposite B and D rings inward to the cavity, as indicated by the dihedral angles they form with the "reference" plane and by the distances between opposite *para*-carbon atoms (Table 2). Within the cavity the methyl group of guest molecule toluene points towards the vanadium centre.

How was **2** formed? Obviously, instead of the expected two equivalents of HCl only one equivalent was eliminated. Furthermore, the oxo ligand and also a methyl group of the original ligand A^{Me2} is missing. Thus, formally MeOH has been eliminated (probably as a result of Lewis acid catalysed ether cleavage) in addition to HCl; MeOH can of course react with HCl under elimination of water to give MeCl. In order to clarify the fate of the methyl group GC/MS measurements were performed both with the gas phase and the liquid phase after a corresponding reaction in toluene. However, no additional organic product could be detected this way. Correspondingly, a reaction was carried out

in a flame-sealed NMR tube. After the reaction no resonance could be detected for MeOH or MeCl. There was only one new signal with the expected integral: a singlet at 2.2 ppm, which we assign to heptadeuterated *o*-xylene that could have formed via Lewis acid catalysed methylation of d_8-toluene solvent with MeCl.

During the characterisation of **2** we noticed, that it is sensitive to both water and O_2. Hydrolysis leads to H_3A^{Me} as well as unidentified vanadium oxo halides. The reaction with oxygen astonishingly leads to **B**, which crystallises isotypically with **2** [9b]. Hence, if oxygen is not rigorously excluded during the synthesis of **2** and the product finally purified by crystallisation, the crystals contain cocrystallised **2** and **B**. This leads to peculiar effects: subsequent to an experiment during which some O_2 had been present, the crystals obtained were selected and their cell determined, in order to make sure that it is identical with the cell found for **2**. Having confirmed that, the crystals were dissolved in d_8-toluene. A ^{1}H NMR spectrum then showed a sharp set of signals belonging to **B**, and a ^{51}V NMR spectrum displayed a resonance at −352 ppm. However, at the same time the solution can be investigated by ESR revealing a signal at $g = 1.88328$ characteristic for an uncoupled d^1-system (**2**). Accordingly, the crystals contain mainly **2** but also some **B** and the only evidence for that in the crystal structure would be an apparent shortening of the V–Cl bond with rising concentration of **B**.

As shown by Radius [14] by X-ray crystallography and NMR investigation d^0 calix[4]arene complexes (e.g. those of Mo and Ti) can undergo isomerisation reactions: the cone conformation can change into the partial cone conformation ("paco"). DF calculations gave evidence that this phenomenon is mainly driven by the co-ligands at the metal centers (strongly directing co-ligands favour the "paco" conformation). We found evidence for this kind of isomerism also in the case of **B**: when **2** was synthesised the way depicted in Scheme 1 (that left some H_2A^{Me2} unreacted) and treated straight away with O_2 without further purification, the crystals obtained from such a reaction mixture in acetonitrile contained **B** in a paco-conformation (Fig. 2) together with co-crystallised H_2A^{Me2} and three acetonitrile molecules, two of which are hosted in the calixarene
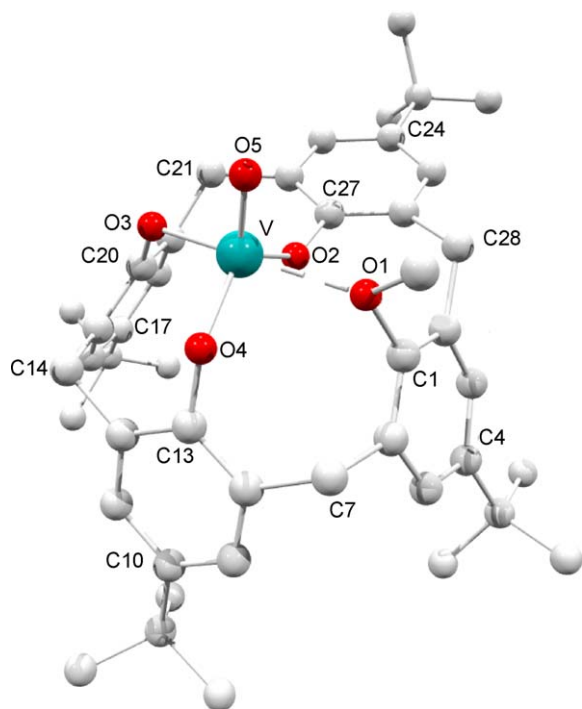
Fig. 2. Molecular structure of complex **B**. Uncoordinated ligand, solvent molecules and all hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): V–O1 2.244(6), V–O2 1.793(5), V–O3 1.811(6), V–O4 1.825(5), V–O5 1.598(5), O5–V–O1 86.3(2), O5–V–O2 121.3(2), O5–V–O3 99.5(2), O5–V–O4 109.2(2), O1–V–O3 171.6(2), O2–V–O4 124.6(2), V–O1–C1 143.6(5), V–O2–C13 119.1(4), V–O3–C20 117.9(4), V–O4–C27 130.2(4).

cavity of **B**; the residual one is found in the cavity of H_2A^{Me2}. Apparently, in case of this d^0–V=O complex both conformations are very close in energy and the environment from which the compound is crystallised (solvent, co-crystallised molecules) determine which conformation is adopted in the crystal. It was not possible to freeze this process out on the NMR time scale. While the cone structure of **B** [9b] is – as mentioned – very similar to the structure discussed above for **2** displaying quite different V–O bonds, in the paco structure all aryloxidic V–O bonds are comparable (O2–V 1.793(5), O3–V 1.811(6), O4–V 1.825(5) Å), and in this conformation the methoxy group can approach the V centre more closely (O1–V 2.244(6) Å). The coordination sphere can still be described as trigonal bipyramidal ($\tau = 0.78$) [12], and the V=O bond length (1.598(5) Å) is similar to the one reported for the cone conformation (1.585(8) Å) [9b].

As we were interested in the conversion of **2** to **B** via molecular oxygen, the reaction was investigated in another NMR tube experiment. A solution of **2** in d_8-toluene was treated with a 50-fold excess of dry oxygen, and the reaction was followed with the aid of ^{1}H NMR spectroscopy. Directly after the addition of dioxygen the characteristic signal set for **B** could be observed, and its intensity continuously rose at the expense of the rather broad signals belonging to paramagnetic **2**. The reaction took 2 days to reach completion (it is of course much faster in a flask that can be stirred), and during this time a diamagnetic reaction intermediate containing ligand A^{Me} became apparent that could not be detected anymore at the end of the reaction. How is **B** formed
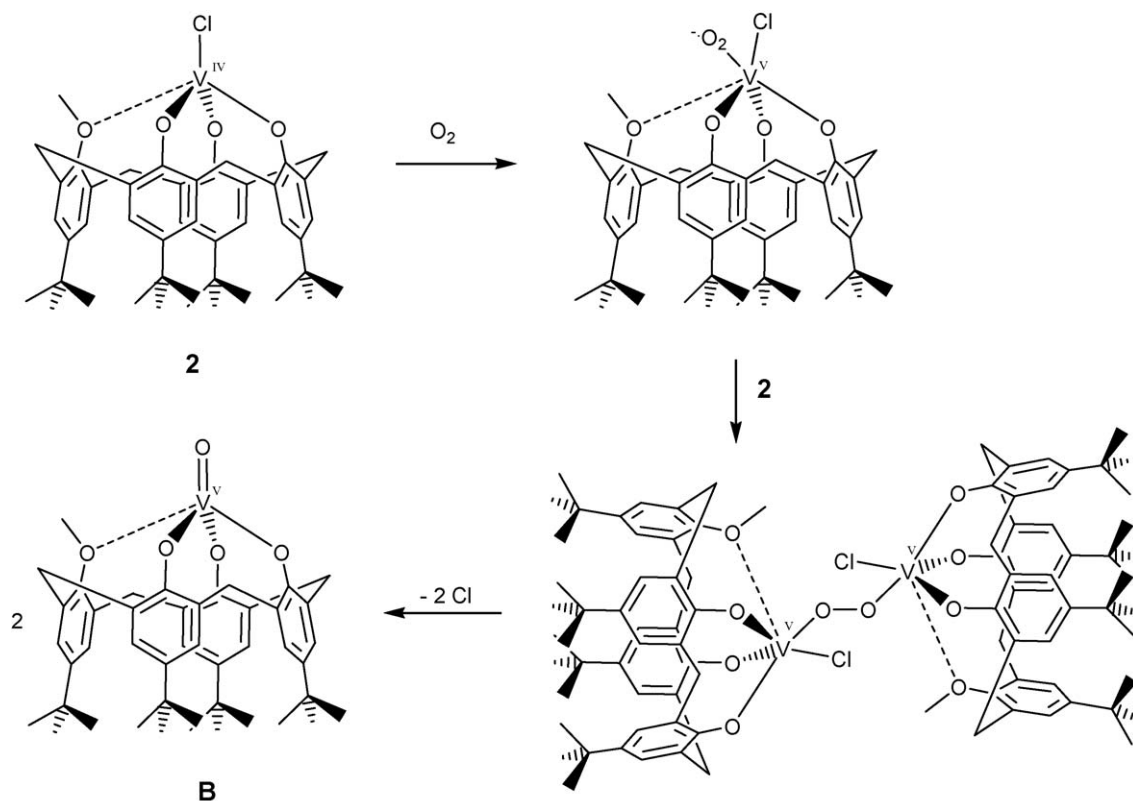
Scheme 2.

from **2** and dioxygen? Most likely the initiating step consists of an end-on addition of O_2 to the Lewis acidic V^{IV} centre to form a $V^{IV}Cl(\eta^1–O=O)$ unit. Subsequently, an electron can be expected to flow from the vanadium centre to the oxygen ligand so that a vanadium(V)superoxide moiety is produced (Scheme 2). The next step should represent a reaction with a second molecule of **1** so that a peroxide unit is formed. In order to give **2** the O—O bond then has to cleave homolytically, but since the V-centres are already in their highest oxidation states, a V=O bond can only form if an additional electron is provided. As, moreover, at some stage the chloro atom has to leave the molecule, one possibility that would solve both of these issues is the elimination of Cl radicals that subsequently abstract H atoms from the solvent. In order to test for this, we first of all repeated the reaction in the presence of PMe_3 (a chloro radical would abstract an H atom anywhere to yield HCl which could be trapped by PMe_3, and the resulting phosphonium cation could easily be identified via ^{31}P NMR). However, the whole system behaved differently in the presence of PMe_3 and we were not able to draw any conclusions from that approach (O=PMe$_3$ formed but the active species might not have been **B**).

Of course, there is the possibility that not Cl atoms but chloride anions are eliminated in the last step of Scheme 2, but then electrons would have to be provided externally. Assumed, one calixarene molecule decomposes, this could bare reducing equivalents for many V centres at the same time, so that the partial decomposition of calixarene molecules could account for all electrons the reaction in Scheme 2 needs. After the reaction of **2** with O_2 in acetonitrile and extraction of **B** with hexane, the residue contains a white solid. This solid tested positively for chloride and it also contained organic compounds that derive from the calixarene moiety as evidenced by ^1H NMR spectroscopy. However, we were not able to identify its detailed constitution.

A further option has to be mentioned: if the dinuclear species shown in Scheme 2 were capable of transferring chloro atoms to unreacted molecules of **2**, the mechanism shown in Scheme 2 could apply without the generation of free Cl radicals: instead, $Cl_2V^V\mathbf{A^{Me}}$ molecules would result, whose hydrolysis would yield further equivalents of **B** and HCl. As stated above all reactions were performed under rigorously dry conditions so that there should not have been any scope for hydrolysis, but as it is difficult to be absolutely sure, we decided to test this hypothesis. We synthesised complex **3** via reaction of **2** with $NaOSiPh_3$ in thf, and crystals were grown from hexane. The crystal structure is shown in Fig. 3. The arrangement of the ligand donor atoms around the V centre is very similar to the one of **2**.

The unit cell contains two independent molecules of **3** (neither of which hosts a solvent molecule) with similar bond distances and angles. For the discussion, the data of one molecule were selected. The V–O5–Si angle ($146.6(2)°$) is in a normal range for a V–O–SiPh$_3$ group [15]. The coordination sphere around the silicon atom is almost perfectly tetrahedral with bond angles O5–Si–C1$'$ ($109.8(2)°$), O5–Si–C2$'$ ($110.0(2)°$) and O5–Si–C3$'$ ($107.3(2)°$) as well as C1$'$–Si–C2$'$ ($106.8(2)°$), C1$'$–Si–C3$'$ ($112.3(2)°$) and C2$'$–Si–C3$'$ ($110.6(2)°$).
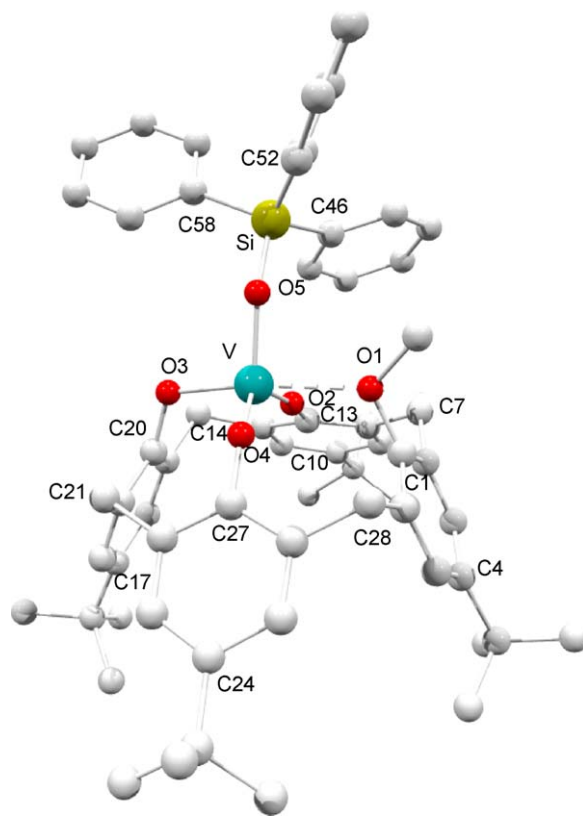

Fig. 3. Molecular structure of complex **3**. The second independent molecule and all hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (°): V–O1 2.325(4), V–O2 1.756(4), V–O3 1.844(4), V–O4 1.790(4), V–O5 1.807(3), Si–O5 1.639(4), Si–C46 1.897(5), Si–C52 1.875(5), Si–C58 1.873(5), O5–V–O1 86.9(1), O5–V–O2 111.2(2), O5–V–O3 100.5(2), O5–V–O4 111.2(2), O1–V–O3 172.3(2), O2–V–O4 132.1(2), V–O1–C1 114.5(3), V–O2–C13 145.8(3), V–O3–C20 115.9(3), V–O4–C27 168.8(4), V–O5–Si 146.6(2), C46–Si–C52 106.8(2), C52–Si–C58 110.6(2), C46–Si–C58 112.3(2), O5–Si–C46 109.8(2), O5–Si–C52 110.0(2), O5–Si–C58 107.3(2).

The reaction of **3** with O_2 was investigated again in an NMR tube experiment. As in the case of **2**, the characteristic signals for **B** appeared, whose integral rose until the reaction had reached completion. As in contrast to two Cl ligands two Ph_3SiO ligands would hardly find sufficient space at a VA^{Me} complex metal fragment, the last mechanistic suggestion mentioned above (requiring the presence of water) can be excluded. Moreover, – considering that the formation of $Ph_3SiO^\bullet$ radicals is even more unlikely than the formation of $Cl^\bullet$ (for comparison, the bond dissociation energy of $H_3SiO–H$ is significantly higher than the one of HCl [16]) – the mechanism involving the elimination of radicals does not seem feasible. We thus prefer the suggestion that Cl as well as Ph_3SiO leave the corresponding peroxo complexes as *anionic* species supported by an external electron source.

4. Conclusions

In conclusion, we have synthesised the calixarene vanadium(IV) chloro complex, **2**, in a reaction that was meant to produce a vanadium(IV)oxo complex. Apparently, the starting

material O=VCl$_2$(thf)$_2$ prefers to react with the potential ligand **H$_2$A^{Me2}** via cleavage of a aryl–O–Me unit and retains a chloro rather than an oxo ligand. The chloro complex reacts with dioxygen to give the vanadium(V)oxo complex **B**, which is conformationally flexible and crystallises in the cone or partial cone conformation. The first step leading to the formation of **B** certainly represents the binding of O$_2$ to the V^{IV} centre. The O–O bond cleavage probably involves a second molecule of **2**. The subsequent steps remain unclear; they result in chloride and organic decomposition products. This type of reactivity is not restricted to **2**: replacement of chloride by triphenylsiloxide (**3**) leads to the same results.

Acknowledgements

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