

V₂O₅/SiO₂ surface inspired, silsesquioxane-derived oxovanadium complexes and their properties†‡

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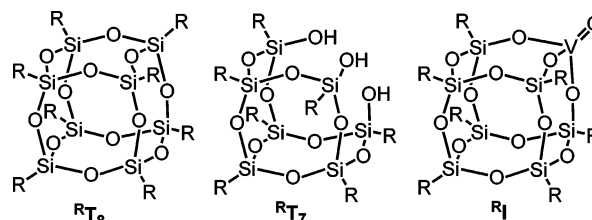
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Inspired by surface species proposed to occur on heterogeneous catalysts novel oxovanadium(v) silsesquioxanes were synthesised. Reaction of a T₈-silsesquioxane containing two geminal OH groups with O=V(OⁱPr)₃ led to a dinuclear compound where the geminal disiloxide functions of two silsesquioxanes are bridging two O=V(OⁱPr) moieties (**2**). Formation of **2** shows that—in contrast to proposals made for silica surfaces—in molecular chemistry a bidentate coordination of geminal siloxides to one vanadium centre is not favourable. With the background that species being doubly anchored to a support have been suggested to play active roles on V₂O₅/SiO₂ catalysts an anionic complex has been prepared where a divalent dioxovanadium unit replaces one Si corner of a (RSiO_{1.5})₈ cube (a Si–OH function remains pending) (**3**). **3** has been intensely investigated by vibrational spectroscopy, and to support assignments not only of the ν(V=O) bands but also of the ν(V–O–Si) bands, whose positions are of interest in the area of heterogeneous catalysis, isotopic enrichment studies and DFT calculations have been performed. The corresponding investigations were aided by the synthesis and analysis of a silylated derivative of **3**, **4**. Moreover, with regard to their potential as structural and spectroscopic models all complexes were characterised by single crystal X-ray diffraction. Finally, **2** and **3** were tested as potential catalysts for the photooxidation of cyclohexane and benzene with O₂. While **2** shows a slightly higher activity than vanadylacetylacetonate, **3** leads to significantly increased turnover numbers for the conversion of benzene to phenol.

Introduction

Vanadia dispersed on oxidic supports has been shown to be a versatile catalyst for the oxidation of hydrocarbons. Depending on the individual process under consideration numerous different species are discussed as active/selective sites: they range from mononuclear tetrahedrally coordinated O=V³⁺, via dinuclear assemblies and polynuclear moieties to “monolayers”,¹ and one of the various working hypotheses suggests, that oxygenations occur mainly at di- or polynuclear sites. We are interested in using some of these structural motifs as an inspiration for the preparation of molecular model compounds.² One ligand system that has established itself in the past for the modelling of oxidic surfaces characteristic for transition metal catalysts or the support belonging to a certain catalyst is based on silsesquioxanes ((RSiO_{1.5})_n), which thus play an important role in the development of heterogeneous catalysts.³

Octameric silsesquioxanes, T₈, resemble skeletal frameworks found in crystalline forms of silica, and silsesquioxanes in general are therefore suitable models for silica surfaces.³ Of particular interest are the incompletely condensed silsesquioxanes which have



one silicon atom removed from a corner of the T₈ cube. This “T₇” structure possesses both structural and electronic similarities to hydroxylated silica surface sites. F. J. Feher and co-workers have investigated the coordination chemistry of deprotonated ^RT₇,— also with respect to vanadium(v) centres.⁴ They were able to synthesise a mononuclear complex ^RI (with R = cyclohexyl) and found that in solution it forms an equilibrium with a dimeric version, **II**, in which each V atom is bonded to O atoms of two different T₇ cages. Attempts to crystallise a compound from this system always led to the crystal structure of **II**. Investigations concerning the reactivity in solution showed that **I/II** represent active catalysts for olefin polymerisations (in combination with MAO)⁴ and for the photooxidation of certain hydrocarbons (R = cyclopentyl).⁵ Despite the importance of supported V₂O₅-based catalysts ^RI (with R = cyclohexyl,⁴ cyclopentyl,⁵ *iso*-butyl⁶) and its dimer (both originally synthesised in 1991!) are still the only known vanadium-silsesquioxane complexes up to now; the crystal data for **II** so far provide the only structural information for O=V³⁺ units in a silica-like environment.

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‡ Electronic supplementary information (ESI) available: Oxidation results, further IR and Raman spectra for NBu₄V(¹⁸O)₃, **3**^{NBu₄} and **4**^{NBu₄}. See DOI: 10.1039/b714933f

Results and discussion

Complex formation

On silica surfaces isolated Si–OH groups, vicinal Si–OH groups and also geminal Si(OH)₂ moieties can be found. Studies concerning the surface reactivity in contact with (iPrO)₃V=O have shown that at room temperature only one alcohol equivalent is liberated during the grafting process, independent of the pretreatment temperature of the support.⁷ At higher temperatures two alcohol equivalents are generated indicating a bidentate nature of the alkoxide surface complex.^{8,9} Trying to rationalise this finding molecular modelling studies were performed for β-cristobalite surfaces which suggested that the vicinity of the geminal OH groups on the (100) face allows the bidentate binding of the precursor.⁹

We were thus interested in the behaviour of *molecules* containing geminal Si(OH)₂ moieties in contact with (iPrO)₃V=O, and the question of whether a vanadium centre could possibly coordinate both geminal O atoms at the same time, as proposed for the surface chemistry. Therefore the silsesquioxane **1** (Scheme 1) containing the required Si(OH)₂ unit¹⁰ was reacted with one equivalent of (iPrO)₃V=O at r.t. Recrystallisation of the raw material thus obtained from hexane led to colourless crystals of a product **2** which was investigated by NMR and IR spectroscopy as well as by single crystal X-ray analysis. The molecular structure of **2** is shown in Fig. 1. Obviously, one vanadium centre *cannot* efficiently bind to both geminal siloxide functions: Subsequent to the reaction of the first Si–OH group with (iPrO)₃V=O the resulting (HO)Si–O–V(O)(OⁱPr)₂ moiety prefers the reaction with a second molecule **1** over an intramolecular alcohol elimination. This leaves one SiOH group at each silsesquioxane unit unreacted, allowing for an analogous reaction of a second (iPrO)₃V=O molecule. Hence, a structure results where two V=O units bridge two silsesquioxane moieties, and the coordination sphere at each V centre is completed by a conserved iso-propoxide ligand. The bond lengths and angles of the ([Si]O)₂(iPrO)V=O entities lie in the usual ranges expected for vanadium oxo-alkoxides¹¹ so that the structure can be regarded as undistorted.

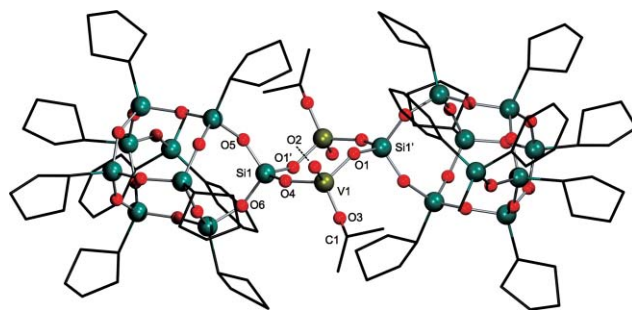
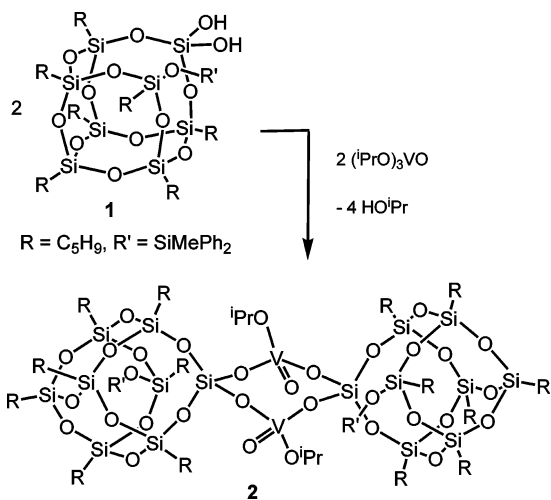


Fig. 1 Molecular structure of **2**. Selected bond lengths (atom distances) [Å] and angles [°]: V1–O1 1.736(6), V1–O2 1.663(12), V1–O3 1.561(13), V1–O4 1.734(6), O3–C1 1.49(2), Si1–O4 1.609(7), Si1–O1' 1.618(7), Si1–O5 1.565(8), Si1–O6 1.602(6), O2–V1–O3 98.4(10), O4–V1–O1 111.5(3), Si1–O4–V1 148.0(5), O4–Si1–O1' 109.7(3), V1–O3–C1 136.9(18), V1–O1–Si1' 144.8(5), O5–Si1–O6 110.9(3).

From the experimental observation that during the grafting process at silica surfaces one equivalent of alcohol is eliminated at r.t. while two are liberated at elevated temperatures it has been inferred that higher temperatures are needed to activate the precursor after the first alcohol elimination.⁹ Facile formation of **2** shows that this cannot be the role of the temperature for the generation of two-coordinate species on surfaces: both the silanol and the vanadium oxo alkoxide are sufficiently reactive to eliminate two alcohol equivalents.

This discussion indicates that species being doubly anchored to a support do play relevant roles during the grafting process,^{8,9,12} and it has been suggested that the possibility of only one or two V–O–M_{support} bonds instead of three should be considered also for the final catalysts.¹³

In order to obtain a new type of silsesquioxane-based complex that is *mononuclear* and contains *two V–O–Si units* we reacted *c*-C₅H₉¹⁹ **T₇** with PPh₄[VO₂Cl₂]. Workup led to the isolation of colourless crystals in good yields that were characterised and investigated, also by means of XRD (Fig. 2). It turned out that a dioxovanadate unit had replaced two of the protons in **T₇** to yield the complex **3**^{PH4}. This leaves one Si–OH group untouched that principally could undergo H bonding to one of the two terminal oxo ligands (O2) at the tetrahedrally coordinated vanadium atom.

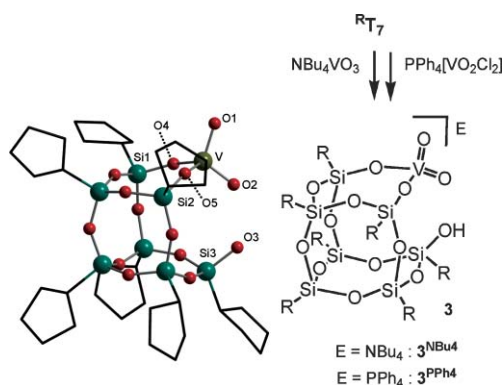


Fig. 2 Synthesis of **3^E** (R = cyclopentyl) and the molecular structure of the anion **3**. Selected bond lengths (atom distances) [Å] and angles [°]: V–O1 1.621(5), V–O2 1.596(5), V–O4 1.797(5), V–O5 1.791(6), Si1–O4 1.615(5), Si2–O5 1.609(6), Si3–O3 1.620(5), O2, O3 2.65(2), O1–V–O2 110.0(3), O1–V–O4 107.5(3), O2–V–O5 106.2(3), O4–V–O5 108.8(3).

However, both V=O bond distances are basically identical which argues against a strong H bridge. A vibrational analysis points into the same direction (*vide infra*). A derivative of 3^{PPH_4} containing a NBu_4^+ instead of a PPh_4^+ cation in combination with the anion 3 , 3^{NBu_4} , can be obtained if NBu_4VO_3 is reacted with $c\text{-}C_5H_9T_7$.

Properties as photooxidation catalysts

Heterogeneous vanadium containing catalysts usually act at temperatures above 300 °C where molecular models are not stable; it is therefore difficult to test, whether they could also represent functional models. Supplying the required energy in the form of light rather than heat might be an approach to circumvent this problem (compare with ref. 5), and we thus decided to investigate the potential of 2 and 3^{PPH_4} to act as catalysts for the oxidation of benzene with O_2 under photolytic conditions. A mixture of 10 ml acetonitrile and 10 ml benzene was filled into a PyrexTM tube equipped with a TeflonTM tap, the gas phase above the solution was replaced by O_2 , complex added (25 μmol) and after closing of the tap the tube was exposed to the light of a 200 W Hg-medium-pressure arc lamp for 6 h. After workup the mixtures were investigated by means of GC-MS. It turned out that 2 exhibits a catalytic activity for the oxidation of benzene to phenol (TON = 2.0/6 h^{-1}) that is higher than the one observed for $OV(acac)_2$ (1.6/6 h^{-1}) but lower than that determined for $c\text{-}C_5H_9I/II$ (2.6/6 h^{-1}), possibly due to a higher steric constraint around the metal centres of 2 . However, 3^{PPH_4} proved even more efficient than $c\text{-}C_5H_9I/II$ leading to a TON of 3.4/6 h^{-1} , and it therefore seems to indeed possess superior properties for the benzene oxidation/reactivation by dioxygen. All compounds were also employed as catalysts for the oxidation of cyclohexane which had to be employed in neat form as it forms two phases with polar solvents such as acetonitrile. $c\text{-}C_5H_9I/II$ proved far more active than 2 (TON = 27.1/6 h^{-1} vs. 5.0/6 h^{-1}). However, 2 is more selective producing cyclohexanol and cyclohexanone in a ratio of 5.6 : 1 while the product ratio equals 1 in the case of I/II . Based on the results for the benzene oxidation the highest TON would be expected for 3^{PPH_4} . However, due to its ionic character 3^{PPH_4} is only sparingly soluble in cyclohexane so that not even 25 μmol can be completely dissolved. Performing the catalysis with a suspension led to a TON twice as high as the one observed for 2 which already supports the expected trend even though it only represents a lower limit.

Vibrational analysis

Furthermore we were interested in the vibrational analysis of the IR and Raman spectra belonging to 3 : it is well known that the choice of the support material influences the activity of vanadia catalysts (compare literature cited in 14, 15), and this in turn has led to the hypotheses that V–O–support bonds might be the true active sites in supported vanadia catalysts. Investigations based on vibrational spectroscopy seemed to support this suggestion, even though the corresponding bands could not be observed directly in the Raman studies. Only recently this problem has led to a systematic investigation combining experimental studies on solid state model catalysts and on powder catalysts with cluster calculations.¹⁴ It turned out that it is possible to find a unique interpretation of the spectra, and it would certainly also be instructive to fit molecular model compounds into the pattern. However, there is a

pronounced lack of molecular compounds that on the one hand can adequately mimic the surface species and for which at the same time the V–O–Si absorptions have been unequivocally identified. While, for instance, II certainly would have been a suitable object for such a study, the IR spectrum reported has not been interpreted in detail. Recently, it was claimed⁶ that the reaction of $i\text{-}BuT_7$ with $(iPrO)_3VO$ leads to $i\text{-}BuI$, that—unlike $c\text{-}C_6H_{11}I^4$ —is resistant towards dimerisation to II and can thus be isolated in monomeric form. The product obtained has been subjected to a vibrational spectroscopic analysis. In comparison to the ligand spectrum the strongest new band appeared at 910 cm^{-1} and this was assigned to $\nu_{as}(Si-O-V)$; all other new bands in the region between 1400 and 800 cm^{-1} have less than half of its intensity. In the Raman spectrum only one new band of reasonable intensity could be made out at 1020 cm^{-1} which was assigned to the O=V stretching vibration. Previous calculations concerning HI ,¹⁴ with scaling of force constants applying recently derived factors of 0.985 for V=O stretch and 1.036 for all other constants¹⁶ predict $\nu(V=O)$ to cause the strongest absorption in the IR at 1033 cm^{-1} and $\nu_{as}(Si-O-V)$ to give rise to a band at 908 cm^{-1} ; hence, they would support the assignment.

With this background we made an effort to achieve vibrational assignments for 3 . As this had to include the selective isotopic labelling of the terminal oxo ligands, which can be achieved starting from $NBu_4V(^{18}O)_3$, the discussion focuses here on 3^{NBu_4} and not on 3^{PPH_4} (it is far more difficult to label the starting material $PPh_4[VO_2Cl_2]$).

The vibrations for the VO_2 and $V(O[Si])_2$ units are expected to appear in the region between 1050 and 900 cm^{-1} of the IR spectrum. Both units should give rise to a symmetric and an anti-symmetric mode so that altogether four bands should be visible—provided that no overlaps occur. Five bands are observed in this region for 3^{NBu_4} at 1048, 1013, 945, 936 and 913 (shoulder) cm^{-1} (Fig. 3) and by comparison with the spectrum belonging to the ligand $c\text{-}C_5H_9T_7$, the bands at 1048 and 913 could be identified as ligand absorptions (see ESI[†]). In the case of $PPh_4[VO_2Cl_2]$ the $\nu_s(VO_2)$ and $\nu_{as}(VO_2)$ vibrations correspond to bands at 968 and 957 cm^{-1} . This suggests an assignment of the bands at 945 and 936 cm^{-1} (which can also be observed in the Raman spectrum; see ESI[†]) to the VO_2 unit of 3 . In order to further support this and to also

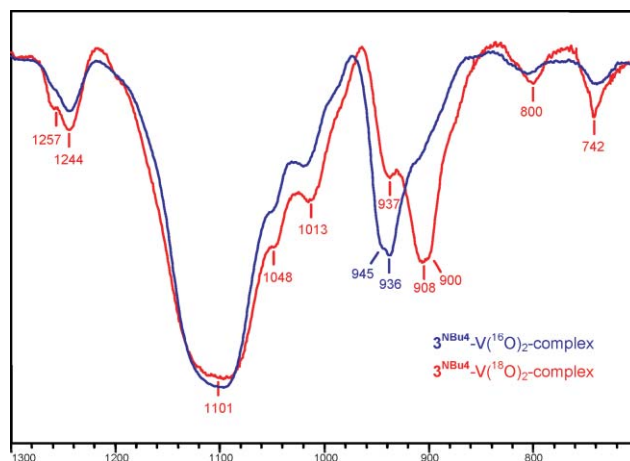


Fig. 3 Infrared spectrum of 3^{NBu_4} (blue) and the product obtained after the reaction of $c\text{-}C_5H_9T_7$ with $NBu_4V(^{18}O)_3$ (red).

identify the $V(O[Si])_2$ bands, DFT calculations were carried out. The result of the X-ray crystal structure analysis served as an input for a geometry optimisation which, however, always established a strong hydrogen bond between the Si–OH function and a V=O group. This not only leads to two quite different V=O bond lengths (V–O1 = 1.625 Å, V–O2 = 1.656 Å) but also significantly affects the vibrations of the VO_2 unit: the two VO_2 motions are decoupled into isolated V=O modes. One mode with high intensity is found at higher wavenumber (V=O1 bond) and one red-shifted with lower intensity (V=O2...H). As the strong hydrogen bond contrasts the experimental observations, a derivative of 3^{NBu4} was synthesised, where the proton of the Si–OH group is replaced by a Me_3Si group, so that definitely no interaction occurs. The corresponding complexes 4^{PPh4} and 4^{NBu4} could be obtained in analogy to the route leading to 3^{PPh4} and 3^{NBu4} but employing the monosilylated ligand $c\text{-}C_5H_9T_7$. Fig. 4 shows the molecular structure of **4** as revealed by a single crystal X-ray analysis of 4^{PPh4} . The two V=O bond lengths are almost identical to those observed for **3**, and furthermore in the region around 950 cm^{-1} the IR and Raman spectra are very similar to the ones of **3**, too. All that shows that the SiOH function—if at all—interacts only weakly with the VO_2 moiety. This discrepancy with the theoretical results, which suggest a very strong interaction, might be attributed to the fact that naturally the calculations are performed for gas phase molecules, whereas in the solid salt the ion is subjected to the electrostatic field of other ions. Hence, the results of a theoretical analysis of **4** are better suited for a comparison with the experimental data of **3** because the artificial strong hydrogen bond cannot occur there (at the same time the *experimental* data of **4** are *less* informative than those of **3** since the area around 1010 cm^{-1} gets masked in **4** by a $\nu(\text{Si–O–SiMe}_3)$ mode). After scaling of the force constants, calculations for **4** predict the V=O vibrations at 950 cm^{-1} and 917 cm^{-1} . Their splitting is larger than in the experiment, which might be caused by strong mixing with bending motions of the cyclopentyl ligands in the calculation. Still, this result in combination with the calculated isotopic shifts (*vide infra*) supports the assignment of the experimental $945/936\text{ cm}^{-1}$ doublet band in the IR spectrum of 3^{NBu4} to the V=O vibrations. The symmetric V–O–Si vibration

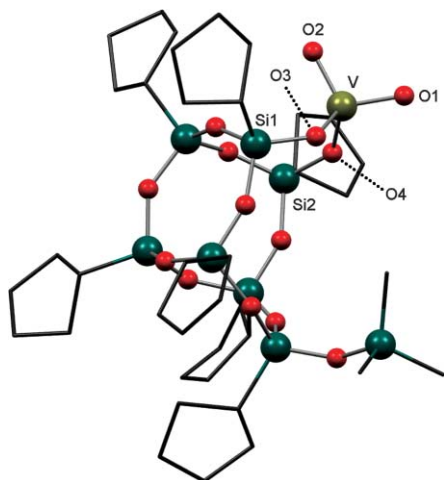


Fig. 4 The molecular structure of the anion **4**. Selected bond lengths [Å] and angles [°]: V–O1 1.617(2), V–O2 1.616(3), V–O3 1.842(2), V–O4 1.832(2), Si1–O3 1.609(2), Si2–O4 1.605(2), O1–V–O2 109.0(1), O1–V–O4 109.0(1), O2–V–O3 111.5(1), O3–V–O4 107.3(1).

is predicted at 1013 cm^{-1} , which suggests an assignment of the remaining new band at 1013 cm^{-1} (which is not Raman active) to $\nu_s(\text{V–O–Si})$. The calculations further suggest $\nu_{as}(\text{V–O–Si})$ absorbs at 935 cm^{-1} , in which case it would get covered by the VO_2 bands.

It is well known that terminal oxo ligands undergo isotopic substitution on addition of $^{18}OH_2$, and hence such studies were performed for 3^{NBu4} in order to further support the $\nu(VO_2)$ assignments as well as to uncover the $\nu_{as}(\text{V–O–Si})$ band. To this end, 3^{NBu4} , which is—at least for short periods—stable in the presence of water, was dissolved in THF and stirred for 10 min in the presence of $^{18}OH_2$. Subsequent workup gave back 3^{NBu4} . The IR spectrum, however, now revealed that the $945/936\text{ cm}^{-1}$ bands had lost a lot of their intensities in favour of new bands at $908/900\text{ cm}^{-1}$. The 1013 cm^{-1} band is not shifted, confirming that it does not belong to a V=O bond (*vide supra*). To reassure that in fact the V=O bands were shifted and not, for instance, V–O–Si bands the VO_2 unit in **3** was labelled selectively with ^{18}O *via* employment of $NBu_4V^{18}O_3$ in the reaction shown in Fig. 2 (in the presence of molecular sieves to immediately remove the $^{18}OH_2$ generated in addition). The same shift was observed, and the labelling achieved this way could be expected to be almost complete (see ESI†). Nevertheless, a—now less intense—band at 937 cm^{-1} remained. When this selectively labelled complex was stirred for 10 min. in the presence of $^{18}OH_2$ no changes could be observed subsequently in the IR spectrum, which confirms that the residual 937 cm^{-1} band cannot belong exclusively to residual V = ^{16}O units. It is thus reasonable to assign this band to $\nu_{as}(\text{V–O–Si})$. In the calculation of **4** we find a red shift of 38 cm^{-1} for the V=O modes, while the influence on V–O–Si modes is small (asym: no shift, sym: 3 cm^{-1} red shift). The magnitude of the isotope shift of the V=O frequencies is in excellent agreement with the experiment.

Hence, we can now safely conclude that the assignments made above for the $\nu(\text{V–O–Si})$ vibrations are correct.

The lack of any changes occurring in the IR spectrum of **3** selectively labelled at the terminal positions after stirring in THF solution in the presence of $^{18}OH_2$ shows in addition that the V–O–Si moieties are reluctant to isotopic exchange reactions with water. The ease with which the *terminal* positions are exchanged is nicely demonstrated in Fig. 5.

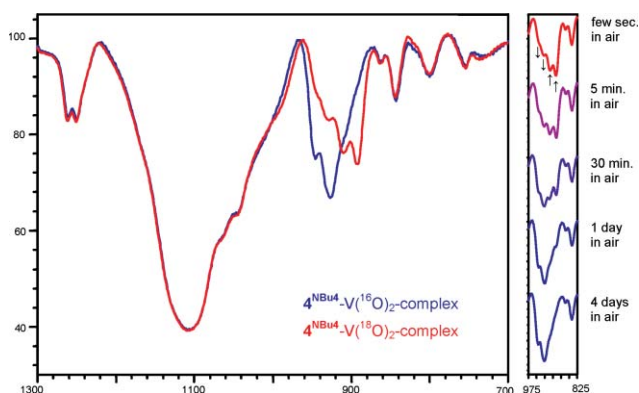


Fig. 5 Left hand side shows a section of the IR spectrum recorded for a KBr disc of ^{18}O enriched (*ca.* 90%) 4^{NBu4} . Residual bands for $\nu_s(V(^{16}O)_2)$ and $\nu_{as}(V(^{16}O)_2)$ can be observed, but the spectrum is dominated by $\nu_s(V(^{18}O)_2)$ and $\nu_{as}(V(^{18}O)_2)$ ($\nu(V^{16}O^{18}O)$ are hidden). If this KBr disc is exposed to air, immediately a $^{18}O/^{16}O$ exchange occurs, initiated by the moisture entering the disc. Exchange reaches a level of *ca.* 50% after only 0.5 h.

Fig. 5 shows on the left hand side a section of the IR spectrum recorded for a KBr disc of ^{18}O enriched (*ca.* 90%) 4^{NBu_4} . Residual bands for $\nu_s(\text{V}^{16}\text{O}_2)$ and $\nu_{\text{as}}(\text{V}^{16}\text{O}_2)$ can be observed, but the spectrum is dominated by $\nu_s(\text{V}^{18}\text{O}_2)$ and $\nu_{\text{as}}(\text{V}^{18}\text{O}_2)$ ($\nu(\text{V}^{16}\text{O}^{18}\text{O})$ are hidden). If this KBr disc is exposed to air, immediately a $^{18}\text{O}/^{16}\text{O}$ exchange occurs, initiated by the moisture entering the disc. Exchange reaches already a level of *ca.* 50% after 0.5 h.

Conclusions

Despite the need for well-defined oxovanada silsequioxanes only one representative was hitherto known (**I/II**). **2** and **3** constitute two novel silsequioxane-based oxovanadium complexes which represent effective catalysts for photooxidations of cyclohexene and benzene, and whose formation processes, structures and spectroscopic properties provide helpful information concerning the formation and analysis of surface species. For instance, formation of **2** shows that geminal $\text{Si}(\text{OH})_2$ units will not bind vanadium-oxo units *via* both siloxide functions if vicinal OH groups are available, and the analysis of the vibrational spectra displayed by **3** allows for an assignment of $\nu(\text{V}=\text{O})$ and $\nu(\text{V}-\text{O}-\text{Si})$.

Experimental

General remarks

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 ^1H , ^{13}C , ^{29}Si and ^{51}V NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (^1H 400.13 MHz; ^{13}C 100.63 MHz, ^{29}Si 79.49 MHz, ^{51}V 105.25 MHz) with CDCl_3 as solvent at 20 °C. The ^1H NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent the ^{29}Si NMR spectra against TMS and the ^{51}V NMR spectra against VOCl_3 as standards. Coupling constants are given in Hz. Microanalyses were performed on a Leco CHNS-932 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR 8400S FTIR-spectrometer. Raman spectra were recorded using a solid sample in a sintered glass tube with a Bruker VERTEX 70/RAM II spectrometer.

Synthesis of **2**

0.08 ml (0.34 mmol) of $\text{OV}(\text{O}^i\text{Pr})_3$ were added drop wise to a solution of 0.71 g (0.63 mmol) of **1**, and the solution was stirred for 65 h. After removing all the volatiles, recrystallisation of the residual white powder from hexane yielded 0.21 g (84 μmol) of **2** (50%). ^1H NMR (CDCl_3 , 400 MHz): 0.78 (s, 6 H, SiCH_3), 0.82–1.16 (m(br), 14 H, c-pent. CH), 1.26 (d, $^3J_{\text{HH}} = 6.11$ Hz, 12 H, $^i\text{PrCH}_3$), 1.30–1.88 (m(br), 112 H, c-pent. CH_2), 5.14 (sept, $^3J_{\text{CH}} = 6.16$ Hz, 2 H, $^i\text{PrCH}$), 7.28–7.44 (m, 6 H, CAr H), 7.55–7.71 (m, 4 H, CArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz): –0.86 (s, SiCH_3), 23.01 (s, $^i\text{PrCH}_3$), 23.98, 24.35, 24.52, 24.71, 24.89 (s, c-pent. CH), 27.06, 27.35, 27.56, 27.92 (m(br), c-pent. CH_2), 87.74 (s, VOCH), 127.53, 129.20, 134.14, 137.93 (s, CAr). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.5 MHz): –67.9, –66.1, –65.8, –65.6, –65.1 (s, O_3SiC), –21.9 (s, $\text{O}_3\text{Si}(\text{OV})_2$), –10.5 (s, OSiPh_2Me). $^{51}\text{V}\{^1\text{H}\}$ NMR (CDCl_3 , 105.2 MHz): –682. IR (KBr, cm^{-1}): 2950 m, 2866 m, 1451 vw, 1428 vw, 1260 vw, 1248 sh, 1117 vs, 1098 sh,

1058 sh, 1041 sh, 914 vw, 879 vw, 797 m, 760 vw, 730 m, 697 m, 490 s, 453 sh, 431 sh, 383 vw. Raman (solid, cm^{-1}): 3048 m, 2957 vs, 2907 sh, 2866 vs, 1590 w, 1568 w, 1474 vw, 1448 m, 1324 vw, 1295 vw, 1255 vw, 1192 vw, 1157 vw, 1113 vw, 1027 m, 999 s, 961 vw, 892 m, 854 w, 801 vw, 750 vw, 709 vw, 673 vw, 637 vw, 619 w, 490 w, 427 vw, 400 vw, 324 vw, 243 vw, 219 vw. mp 192 °C. Anal. calcd. for $\text{C}_{102}\text{H}_{166}\text{O}_{32}\text{Si}_{18}\text{V}_2$ (2511.84): C 48.77, H 6.66. Found: C 47.25, H 6.62%.

Synthesis of **3**^{PPH₄}

A solution of 0.85 g (1.72 mmol) $[\text{PPh}_4][\text{VO}_2\text{Cl}_2]$ in 30 ml CH_2Cl_2 was added to a solution of 1.53 g (1.75 mmol) $^{\text{c-CSH}^9}\text{T}_7$ in 50 ml THF. After addition of 1.1 ml (7.61 mmol) Et_3N the mixture was stirred for 22 h at room temperature. All volatiles were removed and the resulting grey solid was extracted with 30 ml THF. The suspension was filtered. Removal of all the volatiles from the filtrate afforded a grey powder. Recrystallisation from a CH_2Cl_2 /*n*-hexane mixture yielded 1.52 g (1.17 mmol; 67%) **3** in the form of colourless crystals. ^1H NMR (CDCl_3 , 400 MHz): δ 0.80–1.00 (m, 7 H, c-pent. CH), 1.24–1.78 (m, 56 H, c-pent. CH_2), 6.28 (s, 1 H, SiOH), 7.62–7.69 (m, 8 H, CArH), 7.76–7.83 (m, 8 H, CArH), 7.86–7.92 (m, 4 H, CArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.4 MHz): δ 22.50, 22.69, 23.23, 23.58 (s, c-pent. CH), 27.00, 27.05, 27.09, 27.31, 27.48, 27.56, 27.62, 27.88 (s, c-pent. CH_2), 117.46 (d, $^1J_{\text{CP}} = 89.6$ Hz, CAr), 130.78 (d, $^2J_{\text{CP}} = 12.9$ Hz, CAr), 134.41 (d, $^3J_{\text{CP}} = 10.3$ Hz, CAr), 135.72 (d, $^4J_{\text{CP}} = 2.7$ Hz, CAr). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.5 MHz): δ –59.9 (s), –62.8 (s (br)), –66.0 (s), –67.1 (s), –68.9 (s). $^{51}\text{V}\{^1\text{H}\}$ NMR (CDCl_3 , 105.2 MHz): δ –587. IR (KBr, cm^{-1}): 3060 vw, 2948 s, 2863 m, 1482 vw, 1439 m, 1319 vw, 1243 w, 1107 vs, 1088 sh, 1047 vw, 1021 w, 998 sh, 945 s, 923 sh, 910 sh, 853 vw, 810 vw, 753 vw, 724 m, 690 w, 527 m, 494 m. Raman (solid, cm^{-1}): 3061 s, 2952 s, 2866 s, 2588 vw(br), 2223 vw, 1586 s, 1575 m, 1476 w, 1447 m, 1321 vw, 1296 w, 1241 w, 1188 w, 1169 w, 1107 w, 1098 m, 1028 s, 1000 vs, 951 s, 892 s, 726 w, 678 m, 644 w, 617 m, 439 w, 365 w, 285w, 256 s, 245 m, 200 m. Anal. calcd. for $\text{C}_{59}\text{H}_{84}\text{O}_{14}\text{PSi}_7\text{V}$ (1295.8): C 54.69, H 6.53. Found: C 54.46, H 6.47%.

Synthesis of **3**^{NBu₄}

A solution of 0.08 g (0.23 mmol) $[\text{NBu}_4][\text{VO}_3]$ in 10 ml CH_2Cl_2 was added to a solution of 0.20 g (0.23 mmol) $^{\text{c-CSH}^9}\text{T}_7$ in 10 ml THF. The mixture was stirred for 20 h at room temperature. All volatiles were removed in vacuum. The resulting grey powder of **3**^{NBu₄} was used for IR and Raman studies.

The formed complex can be easily transformed into **3**^{PPH₄} by dissolution in MeCN and addition of an equimolar amount of PPh_4Cl . Within two days colourless crystals are formed. The spectroscopic data of these crystals are identical to those listed above.

Synthesis of **4**^{PPH₄}

40 ml THF were added to a mixture of 400 mg (0.42 mmol) $(\text{C}_5\text{H}_9)_3\text{Si}_7\text{O}_9(\text{OTMS})(\text{OH})_2^{17}$ and 210 mg (0.43 mmol) $[\text{PPh}_4][\text{VO}_2\text{Cl}_2]$. The resulting solution was treated drop wise with 1.2 ml (8.7 mmol) NEt_3 , leading to a suspension that was stirred for 15 h at room temperature. After removing half of the solvent under reduced pressure, the precipitate was filtered off. Removing of all volatiles from the filtrate afforded a grey powder. Recrystallisation

from a THF/n-hexane mixture yielded 0.28 g (0.20 mmol; 48%) **4^{PPH4}** in the form of colourless crystals. ¹H NMR (CDCl₃, 400 MHz): δ 0.11 (s, 9 H, SiCH₃), 0.78–0.98 (m, 7 H, c-pent. CH), 1.21–1.80 (m, 56 H, c-pent. CH₂), 7.64–7.72 (m, 8 H, CArH), 7.79–7.85 (m, 8 H, CArH), 7.84–7.93 (m, 4 H, CArH). ¹³C{¹H} NMR (CDCl₃, 100.4 MHz): δ 1.90 (s, SiCH₃), 22.62, 22.68, 23.63, 23.82, 24.59 (s, c-pent. CH), 27.00, 27.07, 27.12, 27.15, 27.41, 27.46, 27.64, 27.68, 27.73, 27.84 (s, c-pent. CH₂), 117.56 (d, ¹J_{CP} = 89.23 Hz, CAr), 130.84 (d, ²J_{CP} = 12.49 Hz, CAr), 134.51 (d, ³J_{CP} = 10.71 Hz, CAr), 135.70 (d, ⁴J_{CP} = 3.57 Hz, CAr). ²⁹Si{¹H} NMR: δ 9.4 (s, SiMe₃), –62.9 (s (br)), –65.9 (s), –66.8 (s), –67.4 (s), –69.3 (s). ⁵¹V{¹H} NMR: δ –573 (s). IR (KBr, cm^{–1}): 3060 vw, 2947 s, 2864 m, 1482 vw, 1437 m, 1319 vw, 1248 w, 1105 vs, 1040 vw, 1021 w, 995 sh, 945 s, 935 s, 860 vw, 841 vw, 810 vw, 754 vw, 723 m, 698 w, 527 m, 496 m. Anal. calcd. for C₆₂H₉₂O₁₄PSi₈V (1368.0): C 54.44 H 6.78. Found: C 54.25, H 6.72%.

Synthesis of **4^{NBu4}**

A solution of 0.07 g (0.21 mmol) [NBu₄][VO₃] in 10 ml CH₂Cl₂ was added to a solution of 0.20 g (0.21 mmol) (C₅H₉)₇Si₇O₆(OTMS)(OH)₂ in 10 ml THF. The mixture was stirred for 20 h at room temperature. All volatiles were removed in vacuum. The resulting grey powder of **4^{NBu4}** was used for IR and Raman studies.

X-Ray diffraction studies

Crystal data for **2**: C₅₁H₈₃O₁₆Si₉V, *M_r* = 2511.84, *T* = 180(2) K, λ = 0.71073 Å, triclinic, space group *P*-1, *a* = 13.076(4) Å, *b* = 14.748(3) Å, *c* = 18.540(5) Å, *a* = 77.43(3)°, *β* = 77.90(3)°, *γ* = 67.34(3)°, *U* = 3188.7(5) Å³, *Z* = 2, *D_c* = 1.308 Mg m^{–3}, *μ* = 0.386 mm^{–1}; 20 620 reflections measured, 8447 unique (*R_{int}* = 0.1061); Final *R* indices [*I* > 2σ(*I*)] *R* = 0.0948, *wR* = 0.2591. Crystal data for **3^{PPH4}** · 2 CH₂Cl₂: C₆₁H₈₈C₁₄O₁₄PSi₇V, *M_r* = 1464.65, *T* = 180(2) K, λ = 0.71073 Å, triclinic, space group *P*-1, *a* = 10.292(3) Å, *b* = 14.543(3) Å, *c* = 24.244(6) Å, *a* = 87.33(3)°, *β* = 88.66(3)°, *γ* = 85.85(3)°, *U* = 3614.6(17) Å³, *Z* = 2, *D_c* = 1.347 Mg m^{–3}, *μ* = 0.482 mm^{–1}; 20 103 reflections measured, 10 157 unique (*R_{int}* = 0.0921); Final *R* indices [*I* > 2σ(*I*)] *R* = 0.0987, *wR* = 0.2416. Crystal data for **4^{PPH4}**: C₆₂H₉₂O₁₄PSi₈V, *M_r* = 1367.99, *T* = 100(2) K, λ = 0.71073 Å, triclinic, space group *P*-1, *a* = 12.2305(8) Å, *b* = 13.1509(9) Å, *c* = 22.780(2) Å, *a* = 91.236(6)°, *β* = 96.081(6)°, *γ* = 110.382(5)°, *U* = 3408.5(4) Å³, *Z* = 2, *D_c* = 1.333 Mg m^{–3}, *μ* = 0.371 mm^{–1}; 47 577 reflections measured, 16 343 unique (*R_{int}* = 0.0925); Final *R* indices [*I* > 2σ(*I*)] *R* = 0.0566, *wR* = 0.1183. The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer Stoe IPDS using Mo-Kα radiation. The structure was solved by direct methods (SHELXS-97), refined versus *F*² (SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms.^{18,19} All hydrogen atoms were added geometrically and refined by using a riding model.

Computations

All calculations were performed with TURBOMOLE 5.9²⁰ and employed the BP86 DFT functional²¹ and the TZVP basis set²² as well as the resolution of identity method.²³ Vibrational frequencies were calculated from analytical second derivatives of the energy

in the harmonic approximation. To correct for systematic errors in the calculated force constants, the V=O stretch contribution is separated from the hessian and is scaled by a factor of 0.985. The remaining hessian is scaled by 1.036 and added to the V=O stretch part and the resulting hessian is diagonalised in the usual way to obtain harmonic frequencies and normal modes.

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Notes and references

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