Vanadium-Catalysed Aerobic Cleavage of C−C Bonds in Substituted Cyclohexanones To Afford Carboxylic Acids: Two Model Complexes with Tetrahedral Geometry around Vanadium(V)

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Two monosilanol/disilanol derivatives were synthesised by treatment of Ph_3SiOH or $Ph_2Si(OH)_2$ with $[nBu_4N]VO_3$ (**3**) in ethanol solution. The mononuclear anionic dioxo vanadium(V) species $[\{Ph_3SiO\}_2VO_2]^-$ (**4**) and the dinuclear complex anion $[\{Ph_2SiO_2VO_2\}_2]^{2-}$ (**5**) thus obtained are unusual and novel model compounds with ≡Si–O–V(O)$_2$O linkages characterised by single-crystal X-ray diffraction. The catalytic activities of these *tert*-butylammonium complexes, together with those of the simple vanadium derivatives **3** and **5**, of the vanadyl precursors $VOSO_4{\cdot}5H_2O$ (**1**) and $[VO(acac)_2]$ (**2**), and also of "$H_6[PMo_9V_3O_{40}]{\cdot}aq$", were tested for aerobic C–C bond cleavage in 2-hydroxycyclohexanone and 2-methylcyclohexanone. Monomeric vanadium species show the same chemistry as the polyoxometalate but with lower yields of acids or keto acids, and so the redox and acid properties of HPA-*n* (*n* = 3, 4) are better tuned. Mechanisms for these oxidation reaction, including electron transfer from a substrate coordinated to vanadium, are proposed.

Introduction

Vanadium(V) oxoalkoxides such as $[VO(OEt)_3]$ or heteropolyacids containing vanadium(V) ions with common formula $H_{3+n}[PMo_{12-n}V_nO_{40}]{\cdot}xH_2O$ (denoted HPA-*n*, where *n* = 1, 2, 3 etc.) have been proposed as precursors for the catalytic oxidation of α-ketols and ketones by dioxygen.[1−4] It has also been demonstrated that aqueous solutions of HPA-*n* are multicomponent systems: the higher the value of *n*, the more complex the system. These solutions contain a great number of polyanions, positional isomers of these, as well as monomeric metallo species such as *cis*-dioxo $[VO_2]^+$ (pervanadyl moieties) in equilibrium with lacunary heteropolyanion.[5] The ^{31}P NMR spectrum of "aqueous $H_6[PMo_9V_3O_{40}]$", for example, attests to the existence of several species containing P, Mo and V (Figure 1).

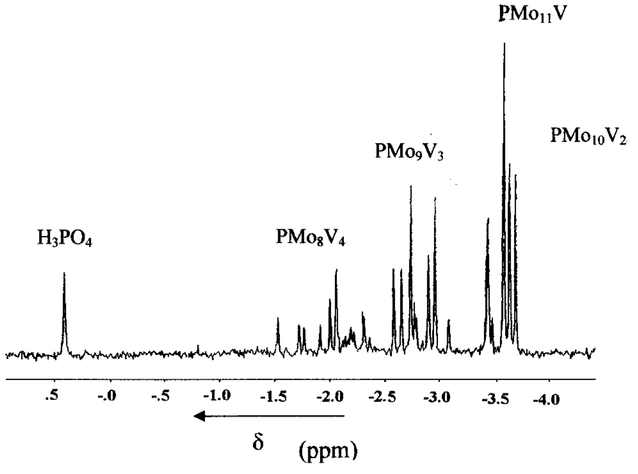

Figure 1. ^{31}P NMR spectrum of "$H_6[PMo_9V_3O_{40}]$" (1 mol·dm^{-3}; pH 0.8) prepared by treatment of $MoO_3.xH_2O$, V_2O_5 and H_3PO_4 with H_2O_2 at room temperature (the identification is supported by solutions and solids prepared with $2 \leqslant n \leqslant 10$ − see ref.[5,7,47]

Preparations of HPA-*n* obtained by diethyl ether extraction[6] or by an oxo-peroxo route[7] give EPR signals attributable to $[VO]^{2+}$ species, as do catalytic systems with vanadium(V) oxoalkoxides. At low pH (<2), heteropolyanion solutions contain a solvated *cis*-dioxo cation $[VO_2(H_2O)_4]^+$, usually written as $[VO_2]^+$.[8,9] This is considered to be one of the catalytically active species.[5] Such complexity makes mechanistic studies very difficult. Moreover, in aerobic ketone oxidations, HPA-*n* species are active not only as redox systems but also play a very important role as Brønsted acids for the enolisation process.[3,10] To the best of our

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knowledge there is no iono-covalent crystal structure containing the pervanadyl cation $[VO_2(H_2O)_4]^+$.

In this work we have prepared and characterised two novel dioxovanadium(V) complexes with two organosilanolato ligands. As other catalyst precursors we have also used simple vanadium(V) and vanadium(IV) derivatives, mainly mononuclear compounds, which − unlike HPA-*n* − are not strong acids. Naturally, it was very interesting to study the influence of acids on the oxidation reactions. We hoped that combinations of simple vanadium complexes with added acids would provide models of catalytically active systems based on various V-containing HPA-*n* species. Work on the use of these complexes in homogeneous catalytic systems (oxidation of 2-hydroxycyclohexanone and 2-methylcyclohexanone) with other precursors and comparison of conversions and selectivities with those obtained with HPA-*n* has made us refine our previous mechanism.[3] The novel four-coordinate complexes should open perspectives for incorporation of oxovanadium catalysts into polymeric materials.[11] Organosilanols model the hydroxy groups that lie on silica surfaces,[12] and the complexes synthesised can be regarded as models for metal oxides supported on silica surfaces.[13]

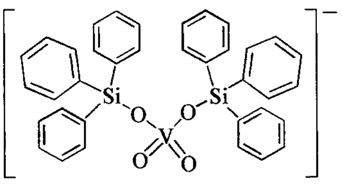
Results and Discussion

As catalyst precursors we used simple derivatives of vanadium(IV), such as $VOSO_4{\cdot}5H_2O$ (**1**) and $[VO(acac)_2]$ (**2**), as well as vanadium(V) derivatives in the form of tetrabutylammonium salts: $[nBu_4N]VO_3$ (**3**) and two pervanadyl complexes, $[nBu_4N][\{Ph_3SiO\}_2VO_2]$ (**4a**) and $[nBu_4N]_2[\{Ph_2SiO_2VO_2\}_2]$ (**5a**).

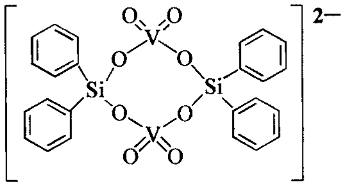
Synthesis of New Vanadium Pre-Catalysts

Only a few examples of mono- and dioxovanadium(V) complexes derived from silanols or disilanols have been described in the literature.[13,14] Compounds $(Ph_3SiO)_3VO$[15−19] and $[(tBu)_2Si(O)_2VOCl]_3$ [20] have been structurally characterised. The latter contains a twelve-membered ring, $\{VOSiO\}_3$, in which the vanadium and silicon atoms exist in distorted tetrahedral coordinations. Trisilanols such as $R_7Si_7O_9(OH)_3$ [R = cyclopentyl, cyclohexyl (cy), phenyl, etc.] are known to react with $VOCl_3$, $VO(O\text{-}nPr)_3$ or $VO(CH_2SiMe_3)_3$ to afford mixtures of the monomeric and dimeric vanadium(V) silsesquioxanes $[(cy)_7Si_7O_{12}VO]$ and $[(cy)_7Si_7O_{12}VO]_2$.[13,18,21] An anionic dioxo complex $(H_2NEt_2)_2[\{Ph_2SiO_2VO_2\}_2]$ was prepared in low yield (29%)[22] from diphenylsilanediol and vanadium(V) dialkylamides, $VO(NEt_2)_3$.

We focused our initial efforts on synthesising oxo-peroxo species and in this paper *cis*-dioxoanionic complexes by undemanding reactions, with the goal of using them to generate catalytic intermediates with the $[VO_2]^+$ group for carbon−carbon bond cleavage in α-hydroxy ketones, cycloalkanones, etc. with dioxygen. Treatment of Ph_3SiOH or $Ph_2Si(OH)_2$ with compound **3**, dissolved in ROH (R = Me, Et), resulted in the formation of a mononuclear anionic dioxo species $[nBu_4N][\{Ph_3SiO\}_2VO_2]$ (**4a**) or a dinuclear complex $[nBu_4N]_2[\{Ph_2SiO_2VO_2\}_2]$ (**5a**), respectively, in fair to nearly quantitative yields. Formulae of the anions of both complexes are presented in Scheme 1.



Anion of compounds **4a** and **4b**



Anion of compound **5a**

Scheme 1

The new vanadium-siloxane complexes were fully characterised by elemental analysis, vibrational spectroscopy and room-temperature single-crystal X-ray diffraction studies. Crystals of $[PPh_4][\{Ph_3SiO\}_2VO_2]$ (**4b**; the nBu_4N cation was replaced by PPh_4 to prepare crystals for X-ray analysis) and of **5a** present novel anionic structures, shown in Figures 2 and 3. Selected bond lengths and angles are listed in Table 1 and 2.

Solid-State Structure of the Mononuclear Complex $[PPh_4][\{Ph_3SiO\}_2VO_2]$ (4b)

Compound **4b** consists of tetraphenylphosphonium cations and monomeric vanadosiloxane anions. There is one independent anionic species in the asymmetric unit, loosely connected through a series of phenyl ring interactions. The crystal packing is determined by van der Waals forces, the closest C···C approach being 3.6 Å, greater than the sum of the van der Waals radii. The geometry at vanadium(V) is a tetrahedral coordination unusual for mononuclear complexes (Figure 2), with the oxygen atoms of the Ph_3SiO ligands occupying two sites and two terminal oxygen atoms occupying the remaining sites. The VO_2 arrangement is no doubt favoured (as in some other d^0 systems) because this allows better $O_{p\pi} \rightarrow M_{d\pi}$ bonding than a linear arrangement would. The characteristic lengths in **4b** are similar to those observed in **5a** (vide infra); the VO bond lengths to the terminal oxygens are 1.621(3) and 1.607(3) Å to O(1) and O(2), respectively; this suggests a bond order approaching two for the V=O linkages in the VO_2 group. The average V−O(Si) bond length is 1.8145 Å. The Si−O bond lengths are similar to those found in the parent siloxane rings.[23−26]

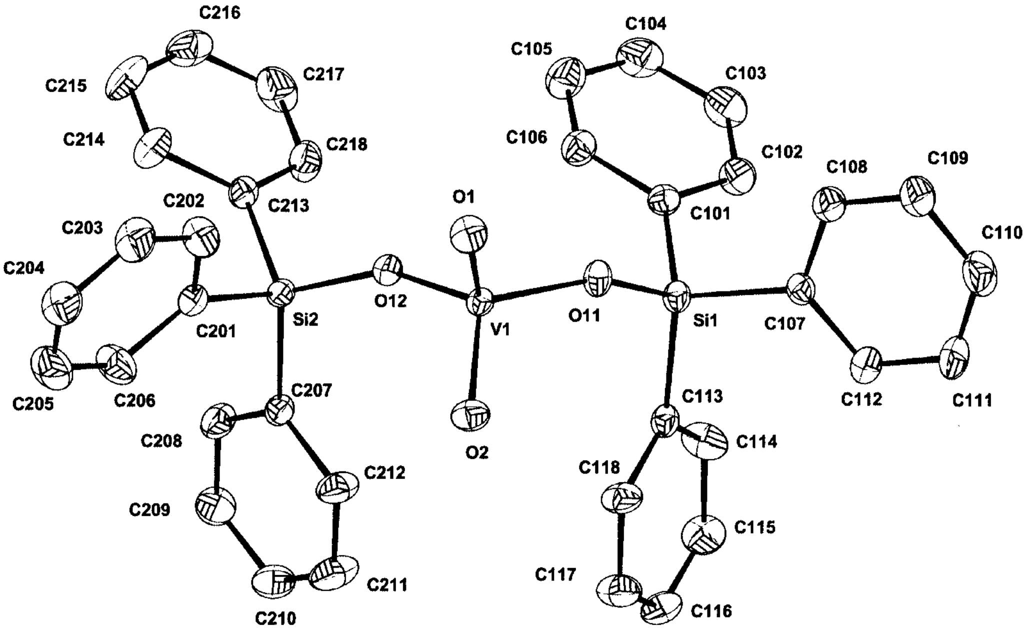


Figure 2. CAMERON representation[61] (ellipsoids at 30% probability level) of $[\{Ph_3SiO\}_2VO_2]^-$, showing the atom-labelling scheme (H atoms omitted for clarity)

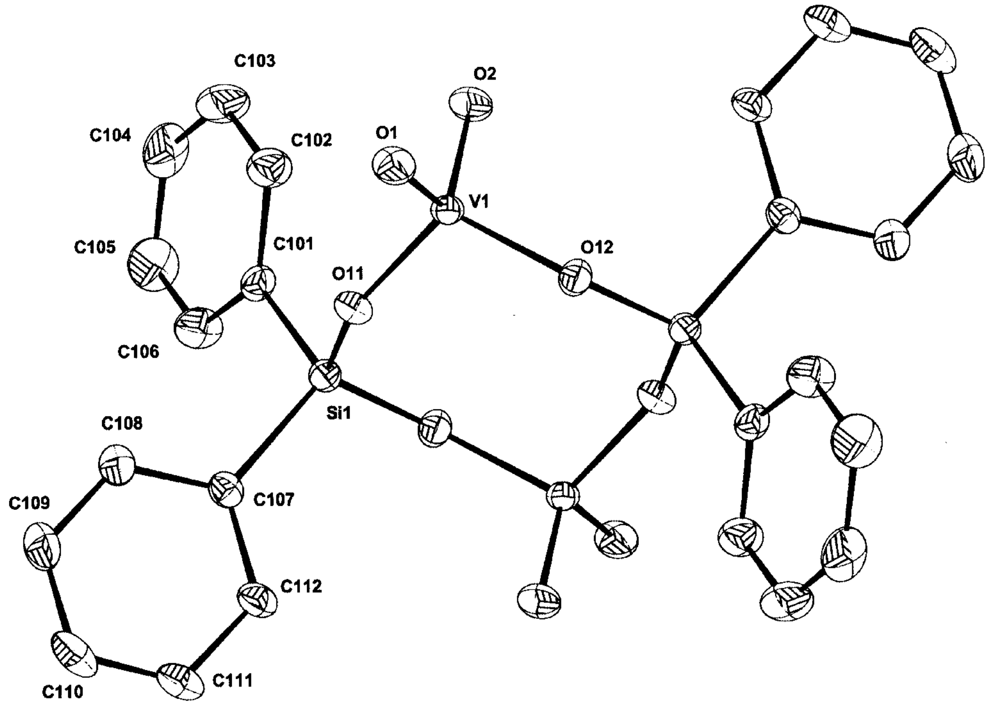


Figure 3. CAMERON representation[61] (ellipsoids at 30% probability level) of $[\{Ph_2SiO_2VO_2\}_2]^{2-}$, showing the atom-labelling scheme (H atoms omitted for clarity)

Table 1. Selected bond lengths [Å] and angles [°] for **4b**

Bond length		Bond angle	
V(1)−O(1)	1.621(3)	O(1)−V(1)−O(2)	108.4(2)
V(1)−O(2)	1.607(3)	O(1)−V(1)−O(11)	109.5(2)
V(1)−O(11)	1.815(3)	O(2)−V(1)−O(11)	110.8(2)
V(1)−O(12)	1.814(3)	O(1)−V(1)−O(12)	109.7(2)
Si(1)−O(11)	1.612(3)	O(2)−V(1)−O(12)	110.6(2)
Si(1)−C(101)	1.853(5)	O(11)−V(1)−O(12)	107.8(2)
Si(1)−C(107)	1.869(5)		
Si(1)−C(113)	1.865(5)		
Si(2)−O(12)	1.601(3)		
Si(2)−C(201)	1.864(5)		
Si(2)−C(207)	1.865(5)		
Si(2)−C(213)	1.862(5)		

Table 2. Selected bond lengths [Å] and angles [°] for **5a**

Bond length		Bond angle	
V(1)−O(1)	1.613(3)	O(1)−V(1)−O(2)	109.0(2)
V(1)−O(2)	1.619(3)	O(1)−V(1)−O(11)	108.9(2)
V(1)−O(11)	1.817(3)	O(2)−V(1)−O(11)	111.5(2)
V(1)−O(12)	1.807(3)	O(1)−V(1)−O(12)	108.2(2)
Si(1)−O(11)	1.613(4)	O(2)−V(1)−O(12)	109.3(2)
Si(1)−O(12′)	1.618(3)	O(11)−V(1)−O(12)	109.9(2)
Si(1)−C(101)	1.872(5)		
Si(1)−C(107)	1.872(5)		

The Si(1)O(11)V(1)O(12)Si(2) moiety in **4b** is almost planar, the largest deviation from the least-squares plane being 0.17 Å for V(1). The angle between the O(1)V(1)O(2) and Si(1)V(1)Si(2) planes is 88.7°. In the siloxane $(Ph_2SiO)_4$ the $\{Si-O\}_4$ ring is somewhat closer to planarity, the maximum deviation from the root-mean square plane being 0.1 Å.[24]

In **4b**, the V−O−Si bond angles are 151.4(2)° and 146.7(2)°. The formation of the tetrahedral VO_2 species was recently evaluated by a theoretical study of the extended Hückel (EH) type, this species being excluded in the cases of SiO_2, TiO_2 and γ-Al_2O_3.[27] To the best of our knowledge, no monomeric tetrahedral vanadium(v) species containing oxo organic ligands has yet been observed in aqueous solution, and such tetrahedral units are also not common for dioxovanadium(v) moieties in the solid state: only distorted square-pyramidal,[28] trigonal-bipyramidal[29] and octahedral[30] geometries have recently been characterised with *cis*-dioxo groups,[28−30] but tetrahedral species exist in some chains of inorganic vanadates. With large metal cations such as Ba^{2+}, the structures adopted by dinegative metavanadates, MV_2O_6, contains chains of vertex-shared VO_4 tetrahedra.[31,32] This structural motif is typically found in orthovanadates such as $LiMnVO_4$[33] and $LnVO_4$.[34] The $[V_4O_{12}]^{4-}$ ion has a cyclic tetrametaphosphate-like structure with an O*t*-V-O*t* angle of only 102.3(1)°,[35] the three others being 111°, while $[V_5O_{14}]^{3-}$ is pentanuclear with O−V−O angles ranging from 107.6(4) to 112.7(3)°.[36] In **4b**, the tetraphenyl phosphonium cations are well behaved and have the expected dimensions.

Solid-State Structure of the Dinuclear Complex $[nBu_4N]_2[\{Ph_2SiO_2VO_2\}_2]$ (5a)

Compound **5a** consists of discrete dimeric anions and tetrabutylammonium cations. The complex possesses crystallographic site symmetry $\bar{1}$, and there is one half of the complex anion per crystallographically independent unit. The anionic moiety has two vanadium(v) atoms bridged by two diphenylsiloxy ligands to form an eight-membered ring, "$\{VOSiO\}_2$", in an extended chair conformation. In addition, each vanadium is bonded to two terminal oxygen atoms. For a side view of the anion showing the conformation of the ring, see Figure 3. The O(1) and O(2) bond lengths to V(1) are 1.613(3) and 1.619(3) Å, respectively; these correspond to V=O linkages in compound **4b**. Similar V=O bond lengths are found for the trigonal-bipyramidal environment of $[VO_2(pic)(HMPA)]$, with 1.600(5) and 1.606(5) Å,[37] and for $[nBu_4][VO_2(pca)_2]$ (pcaH = pyrazine-2-carboxylic acid), for which the vanadium is found to have an octahedral coordination geometry with two terminal oxo ligands in the *cis* positions [d(V=O) ≈ 1.620(1) and 1.634(1) Å].[38]

The V−O(Si) bond lengths of 1.817(3) and of 1.807(3) Å are short in comparison with the chelate ligand V−O(C) bond lengths of 1.990(1) and 1.996(1) Å found in the pyrazine-2-carboxylato complex.[38] We consider that the V−O(Si) distances in **4b** and in **5a** indicate very strong bonds. The Si−O and Si−C bond lengths are in good agreement with values found in other cyclotetrasiloxanes[23−26] and in **4b** (vide supra).

The tetrahedral geometry around vanadium is evidenced by an average O−V−O bond angle of 109.5°. Again, four-coordination is not very common for inorganic anionic dinuclear V^V complexes; another typical dioxovanadium(v) salt that has been found to have a tetrahedral structure with chains is KVO_3.[39] The average V−O−Si bond angle in **5a** − of 144.1(2)° − is smaller than those found in **4b** and similar to the values of 145° found for the Si−O−Si angle in $[(Me_2SiO)_4]$,[40] but significantly smaller than those found for the previously reported tetrasiloxane compounds (ca. 159.5°),[23−26] also with a puckered eight-membered ring, and for V−O−V in $[V_4O_{12}]^{4-}$ [158.2(2)°].[35] The O−Si−O angle of 111.5(2)°, the C−Si−C of 108.1(2)° and the O−Si−C angles (mean ca. 109.3°) are close to the expected values commonly found for tetrahedral geometry in cyclic siloxanes;[23−26] this may indicate that no strain is involved in bridging the nearly 4.4 Å V···V distance. The closest C···C approach being 3.7 Å, the crystal packing must be determined by van der Waals forces .

Main Features of Vibrational Studies of Synthesised Complexes

The infrared spectra of the complexes are consistent with the deprotonation of the silanol functionalities in the complexes. They show features similar to those observed for other mono- or dinuclear pervanadyl species;[41] in addition a band at 1588 cm^{-1} may be assigned as ν(C−C) of the phenyl ring,[42,43] and a very sharp band at 1113 for **4a** and 1117 cm^{-1} for **5a** is due to an in-plane deformation of the phenyl ring δ(C−H), with some ν(Si−C) character. Consistently with the structural data (vide supra) and the existence of short V=O bonds, there are strong ν(V=O) bands at ca. 939 and 927 cm^{-1} (sh.) for **4a**, and at 941 and 925 cm^{-1} for **5a**; peaks observed in the two above regions for previous $[VO_2]^+$ complexes are assigned to ν_{as} and ν_s modes of the VO_2 group, respectively.[44] A maximum at 925 cm^{-1} for **5a** and a shoulder (**4a**) are tentatively attributed to Si−O(V) stretching. Si−C stretches appear at ca. 743 cm^{-1} for both compounds. In the Raman spectra, comparison of the ν(V=O) at 943 cm^{-1} for solid **4a** with the maximum at 935 cm^{-1} (**4a** in methanol), together with other unattributed maxima, suggests that the overall structure of the pervanadyl complex **4a** is conserved in methanol at room temperature, as would be expected for a compound originally prepared in methanol or ethanol.

Catalytic Oxidative Cleavage of α-Ketols (α-Hydroxy Ketones)

For the oxidation of 2-hydroxycyclohexanone (**6**) we used simple vanadium derivatives **1**, **2** and **3**, the synthesised compounds **4a** and **5a**, and also "$H_6[PMo_9V_3O_{40}]\cdot 11H_2O$" (HPA-3). Methanol was employed as solvent and the reactions were carried out at two temperatures, 20 and 60 °C (Table 3). The main product was adipic acid (Scheme 2), and the concentration of this compound was measured after esterification by addition of ethereal diazomethane. The course of the reaction was followed by dioxygen consumption, monitored by a gas burette system, and by GC analysis. Dioxygen uptake was observed in the reactions catalysed by mononuclear complexes, with moderate conversion even at room temperature (Table 3, entries 1, 3, 5). An induction period was only found in the case of $[VO(acac)_2]$. During this period the active catalyst precursor probably changes; this transformation may be de-coordination of one of the acac ligands strongly bound to vanadium.

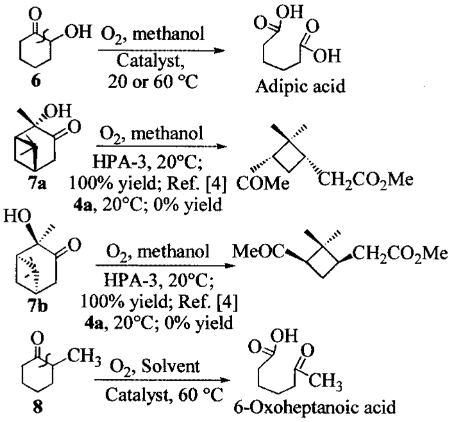
Higher degrees of conversion were obtained at 60 °C (entries 2, 4, 6). It can be seen that mono-oxovanadium(IV) complexes and polyoxovanadium(V) species are moderately active but the selectivity is rather low. Thus, oxidation catalysed by VO_3^- results in the formation of undesired products (cyclohexanedione in a yield ≤ 20%, dimethyl pentanedioate, butanedioate etc.). Catalysis by **4a** or **5a**, and especially by HPA-3, favours the formation of dimethyl adipate. It should be noted that the oxidative cleavage of 2-hydroxycyclohexanone[45] to produce adipic acid, as well as of various substituted α-hydroxy ketones,[4] does not require the presence of a strong Brønsted acid and occurs with both mononuclear vanadium(IV) and (V) species; $[VOCl_3]/MeCN/O_2$ systems give only α-diketones.[46]

Recently the "HPA-3/O_2/MeOH" system has been successfully used in the oxidative cleavage at room temperature of (1*S*,2*S*,5*S*)-2-hydroxypinan-3-one (**7a**) and its (1*R*,2*R*,5*R*) enantiomer **7b** (see Scheme 2). The diastereoselective formation of the esters of 3-acetyl-2,2-dimethylcyclobutaneacetic acid (methyl esters of the *cis*-pinonic acids) was observed, with 100% conversion and high diastereoselectivity (99:1 for 1*S*,3*S*:1*S*,3*R* and 1*R*,3*R*:1*R*,3*S*, respectively).[4] As found in this work, compound **4a** does not catalyse the oxidative transformations of **7** at all at room temperature. We assume that steric hindrance is a crucial factor governing the activity of complex **4a**; the bulkiness of the three C_6H_5 groups on Si(1) and Si(2) (Figure 2) and the methyl group of the 2-hydroxypinan-3-one may prevent the interaction of the VO_2 group with the α-hydroxy group of **7**. The inactivity of **4a** in reaction with **7** is in agreement with the assumption that only relatively small mononuclear *cis*-dioxo species are responsible for the catalytic activity. It seems that the HPA-3 anion is also too bulky and that direct coordination of this anion with **7** is sterically restricted. However, the dissociation of HPA-3 to produce, inter alia, a small reactive species such as $[VO_2]^+$ would explain the high efficiency of HPA-3 in the oxidative transformation of sterically hindered **7**.

Table 3. Oxidation of 2-hydroxycyclohexanone (**6**) to adipic acid (Scheme 2)

Entry[a]	Catalyst precursor	*T* (°C)	Conversion (%)[b]	Yield (%)[c]
1	$VOSO_4\cdot 5H_2O$ (**1**)	20	46	26
2		60	95	56
3	$[VO(acac)_2]$ (**2**)	20	42	43
4		60	96	51
5	$[nBu_4N]VO_3$ (**3**)	20	40	39
6		60	77	30
7	**4a**	20	77	61
8		60	100	60
9	**5a**	20	72	66
10		60	100	71
11	HPA-3	60	100	90

[a] Conditions: vanadium complex, 0.076 mmol; 2-hydroxycyclohexanone, 7.6 mmol; methanol, 5 mL; dioxygen, 0.1 MPa; reaction time 24 h. [b] Conversion is percentage of the substrate consumed. [c] Yield (%) is (mmol of dimethyl adipate per mmol of the substrate)×100 (determined after addition of ethereal diazomethane).



Scheme 2

Catalytic Oxidative Cleavage of 2-Methylcyclohexanone (8)

Unlike 2-hydroxycyclohexanone, 2-methylcyclohexanone is not oxidised in methanol by the V^V-based catalytic systems without an induction period if there is no Brønsted acid present in the reaction solution (Table 4, entries 6 and 8). None of the quaternary ammonium salts of HPA-*n* was active in these oxidations (not shown here) and only the heteropolyacids HPA-*n*, which are known to be strong acids, catalyse C−C bond cleavage (entries 10 and 11). However, these results with alkylammonium may be ambiguous, because these salts are not only less acidic but also less efficient oxidants (change of redox potentials and stabilisation of the $[VO_2]^+$ moieties in the Keggin unit). Addition of only 2−10 equivalents (relative to one vanadium) of *para*-toluenesulfonic acid (PTSA) to the reaction solutions containing catalyst precursors **3** or **4a** results in the formation of 6-oxoheptanoic acid in the form of its methyl ester (see Scheme 2; Table 4, entries 7 and 9). However, it should be noted that the yields for all mononuclear dioxo catalysts are lower than those of HPA-*n* (*n* = 4 or 3; see entries 10 and 11, respectively). Hence, the redox and acid properties of HPA-3 and mixed valence HPA-4 $[[V^{IV}/V^V]$ are better tuned than those of the mononuclear species. In the case of the "**4a**/O_2/MeOH" system at 60 °C in the absence of added acid, Ph_3SiOMe was formed and characterised by GC-MS (see Exp. Sect.). We conclude that even without addition of strong acid the Ph_3SiO ligands in **4a** are partly replaced to generate oxohydroxo- and/or alkoxo-anionic or neutral vanadium(v) species. As 2-hydroxypinan-3-one is not oxidised by this system at 20 °C, probably due to the bulkiness of this molecule and of **4a** (see above), it is certain that this catalyst precursor does not decompose with formation of small mononuclear species at room temperature (vide supra: vibrational studies).

It is noteworthy that vanadyl precursors (entries 1 and 3) exhibit some activity even in the absence of an acid. Dioxygen consumption has an induction period during which the acac ligand is replaced by other ligands. Addition of 10 equivalents of PTSA increases the yield only in the case of **2** (entry 4). Replacement of PTSA by trifluoromethanesulfonic acid gives the highest yield (entry 5). The addition of either PTSA or CF_3SO_3H (entries 4 and 5) results in O_2 uptake without an induction period. The "$VOSO_4{\cdot}5H_2O$/MeOH/O_2" system gives a blue solution, which turns green immediately after the addition of 2-methylcyclohexanone (**8**). This change in colour is apparently due to the formation of a complex between vanadium-containing species and **8**.

Table 4. Oxidation of 2-methylcyclohexanone (**8**) to 6-oxoheptanoic acid (Scheme 2)

Entry[a]	Catalyst	[PTSA]/[V]	Conversion (%)[b]	Yield (%)[c]
1	$VOSO_4{\cdot}5H_2O$ (**1**)	0	34	26
2		10	41	21
3	$[VO(acac)_2]$ (**2**)	0	20	18
4		10	66	34
5		10[d]	100	50
6	$[nBu_4N]VO_3$ (**3**)	0	0	0
7		10	48	25
8	**4a**	0	0	0
9		2	50	40
10	HPA-4 ($V^{IV}V^V$)	0	100	90
11	HPA-3[e]	0	99	97

[a] Conditions: vanadium complex, 0.076 mmol; 2-methylcyclohexanone, 7.6 mmol; methanol, 5 mL; dioxygen, 0.1 Mpa; reaction temperature 60 °C; reaction time 24 h. [b] See corresponding footnotes to Table 3. [c] See corresponding footnotes to Table 3. [d] The catalytic species was prepared by the reaction between CF_3SO_3H and $[VO(acac)_2]$ (ratio 1.1) in methanol at 60 °C during 8 h. [e] Reaction in water; reaction time 8 h.

We also investigated the oxidation of **8** in acetonitrile, which is aprotic, although residual water cannot be excluded. It turned out that, in the absence of any other additives, catalyst precursor **3** induces slow consumption of molecular oxygen (Figure 4, curve 1). The oxidation occurs with auto-acceleration after an induction period (ca. 4 hours) during which the colour of the reaction solution changes from very pale yellow to intense orange-yellow. Addition of acetic acid (≈ 4 equivalents relative to **3**) accelerates the reaction insignificantly, the induction period remaining the same (curve 3, see Figure 4). The reaction also proceeds very similarly (curve 4, see Figure 4) in the presence of a chelating amino acid (pyrazine-2-carboxylic acid, PCA) that has been shown to accelerate V-catalysed oxygenations with hydrogen peroxide or air dramatically.[38] Addition of PTSA (only 2 equivalents) considerably increases the rate, and the induction period is eliminated (curve 2; see Figure 4). If 4 equivalents of PCA are added

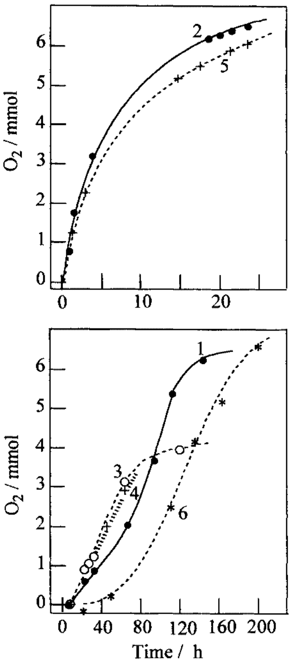


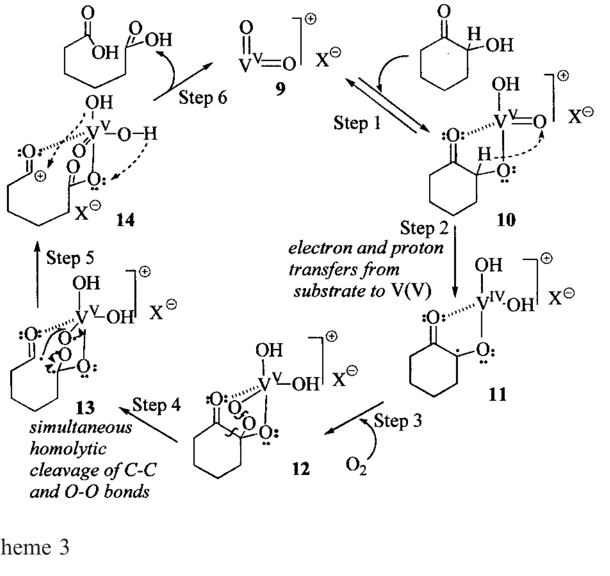
Figure 4. Consumption of O_2 in reaction of 2-methylcyclohexanone (7.6 mmol) in MeCN (total volume of reaction solution 6 mL), catalysed by $[nBu_4N]VO_3$ (0.076 mmol) at 63 °C without additives (curve 1) and with PTSA (0.155 mmol) (2), CH_3COOH (0.32 mmol) (3), PCA (0.306 mmol) (4), PTSA (0.155 mmol) + PCA (0.306 mmol) (5), and pyridine (0.755 mmol) (6)

to the same mixture the oxidation proceeds at practically the same rate (curve 5). It may thus be concluded that acids accelerate the oxidation of **8**, the rate of this reaction rising significantly on going from weak acids to strong ones. When pyridine is added, there is a long induction period (curve 6; see Figure 4), a reduced initial rate and a reduction in the yield of keto acid ($\leq$ 15%).

A study of immobilised $[VO_2]^+/[VO]^{2+}$ on several perfluorinated supports with highly acidic and noncoordinating groups such as $-SO_3^-H^+$ has been presented.[11] This system produces highly selective C−C bond cleavage and low-leaching catalysts; mononuclear vanadium(V/IV) moieties are the most likely active species interacting with SO_3^- groups.[11,47]

On the Mechanism of the Oxidative Cleavage of C−C Bonds

On the basis of our results and others in the literature we propose a mechanism as depicted in Scheme 3 for C−C bond cleavage of 2-hydroxycyclohexanone. This scheme represents a formally closed catalytic cycle, although it is likely that other steps occur and that the equilibria are more complex. The reaction begins with the formation of a catalytically active oxovanadium(V) species **9**, depicted as $[VO_2]^+X^-$, this species containing additional ligands such as coordinated water or organic solvent. Species **9** coordinates to the α-ketol monoanion through its hydroxy oxygen to produce complex **10**. One-electron and proton transfers from the carbon atom to the vanadium moieties give rise to the formation of complex **11**. Naturally, the proton transfer occurs not intramolecularly as schematically depicted as step 2, but through deprotonation and protonation with participation of the solvent, substrate or water (the latter is present at relatively low concentrations in all reaction solutions). The one-electron transfer from the electron-rich organic moiety to the V^V-oxo part of the complex produces species **11**, which contains the organic part of the complex σ, *n*-coordinated to V^{IV}. There is an unpaired electron on the organic ligand, and one of the mesomeric forms of **11** would be a carbon-centred radical. In the presence of molecular oxygen species, **11** would react rapidly with O_2. Indeed, it is well known[48] that carbon-centred radicals add to oxygen molecules in a very fast reaction (Scheme 3).



Scheme 3

$$R\cdot + O_2 \rightarrow ROO\cdot$$

It is reasonable to assume that the peroxyl radical formed after addition of O_2 to the carbon atom in **11** would add to the V^{IV} ion of the same complex to form V^V peroxo derivative **12**. In this step, radical ROO· oxidises V^{IV} to V^V. An example of the direct formation of a vanadium(V) peroxo complex in the reaction between a vanadyl(IV) complex and molecular oxygen was recently described.[49]

$$2\,[V^{IV}(=O)(OH)]^+ + O_2 \rightleftarrows [V^V(=O)_2]^+ + [V^V(=O)(O_2)]^+ + H_2O$$

Vanadium(IV) oxo complexes can also be reoxidised by the usual four-electron overall oxidation process shown below.

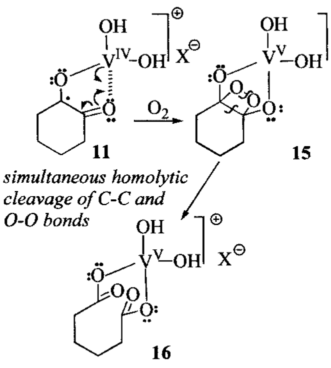
$$4\,[V^{IV}(=O)]^{2+} + 2\,H_2O + O_2 \rightleftarrows 4\,[V^V(=O)_2]^+ + 4\,H^+$$

Vanadium(V) oxo and peroxo complexes have been reported to hydroxylate aromatic compounds in the presence of acids or/and under light irradiation.[50,51] The mechanism of this oxidation appears to include an electron-transfer step.

Vanadium(V) peroxo complexes are unstable and can decompose by homolytic fission of O−O bonds.[52,53] In our case, we propose that homolytic C−C bond cleavage in **12** occurs simultaneously, possibly through a six-membered transition state. Structure **13** represents one of the species on the reaction coordinate for this electron redistribution. As a result we obtain structure **14** with an acylium cation, which could explain the formation of adipaldehyde and lactones.[45] Addition of hydroxy anion (or methoxy anion when methanol is used as a solvent) gives rise to the formation of adipic acid (or its methyl ester) in Step 6. The hydroxy anion from the V^V species in Scheme 3 is used only conventionally to close the catalytic cycle.

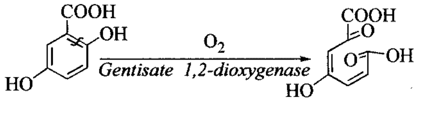
An alternative is that in the interaction between **11** and O_2 the latter adds to the two carbon atoms to produce an endoperoxide species **15** (Scheme 4). It can be seen that this process is also accompanied by the oxidation of V^{IV} to V^V. The simultaneous fission of C−C and O−O bonds in **15** gives adipic acid directly coordinated to vanadium(V) (**16**).

A similar mechanism has previously been proposed for oxidative C−C bond cleavage in acetylacetonate ligand coordinated to palladium(II) to afford acetate.[48,54] In this case the reaction proceeds smoothly at room temperature under irradiation by visible light. Another ligand, *ortho*-metallated azobenzene, coordinated to Pd^{II} plays the role of an "antenna", absorbing light energy necessary for electron transfer from the acac ligand to the palladium centre. It



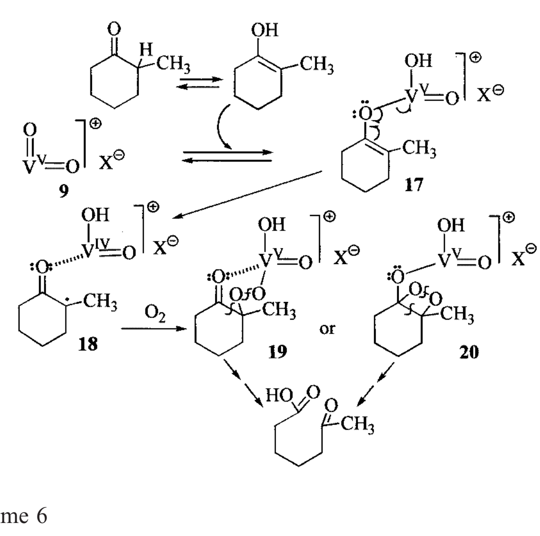
Scheme 4

should be noted that such a mechanism is related to that of C−C bond cleavage in substituted phenols and catechols under the action of O_2 and catalysed by non-heme iron dioxygenase enzymes.[48,55] For example, gentisate 1,2-dioxygenase induces the ring cleavage shown in Scheme 5, and so the oxidative systems described in this paper can be regarded as models of dioxygenases.



Scheme 5

For the oxidation of 2-methylcyclohexanone, direct σ-coordination of the substrate with vanadium-containing catalytically active species is unlikely. However (see above), this compound could react in the enol form, since addition of weak or, especially, strong acids (see Figure 4) dramatically accelerates the oxidation. The reaction starts with the coordination of the enol species to produce species **17** (Scheme 6). Subsequent electron transfer and dioxygen addition give rise to species **19** or/and **20**. After the cleavage of the C−C and O−O bonds, 6-oxoheptanoic acid is formed.



Scheme 6

Conclusion

Despite the advantage of the use of air or dioxygen as the oxidant, there are relatively few known methods that use homogeneous catalysts under very mild conditions. It has been demonstrated here that C−C bond cleavage can be performed efficiently in the presence of dioxygen with simple vanadium-containing precursors or catalysts. Novel anionic vanadium(V) complexes $[nBu_4N][\{Ph_3SiO\}_2VO_2]$ (**4a**) and $[nBu_4N]_2[\{Ph_2SiO_2VO_2\}_2]$ (**5a**) have been synthesised and used as models of catalytic homogeneous systems in order to generate $[VO_2]^+$ moieties.

Comparison of the activities of substituted heteropolyacids $H_{3+n}[PMo_{12-n}V_nO_{40}]\cdot aq.$, HPA-*n*, with these pervanadyl precursors and other vanadyl complexes with different substrates has caused us to refine our previous mechanism involving mononuclear vanadium(IV) and (V) oxo species and substrate coordination to these $[VO_2]^+$ species.[3] HPA-*n* species are practical and highly efficient reagents for vanadium-based catalysts because their counterions are H_3O^+; they are reversible oxidants, capable of undergoing repeated cycles of reduction and of re-oxidation with dioxygen. Moreover, they can readily be formed from inexpensive reagents: V_2O_5, MoO_3, H_3PO_4 and H_2O_2.[7] We believe that these results can help understanding of systems based on the $[VO_2]^+/[VO]^{2+}$ couple or on modified HPA-*n* species for *linear alkane and cyclohexane oxidation under study in our group.* These systems also give oxygenated intermediates (keto acids, α,ω-diacids, alcohols, ketones, *etc.*) and will be further developed.

Experimental Section

Synthesis

$[nBu_4N][\{Ph_3SiO\}_2VO_2]$ (4a): $[nBu_4N]VO_3$ [56] (0.68 g; 2 mmol) in ethanol (5 mL) was added to a solution of Ph_3SiOH (1.1 g; 4 mmol) in the same solvent (10 mL). After addition of aqueous ammonia (1.25 M; 3.2 mL), the solution was slowly stirred for 45 min. The white precipitate was isolated by filtration, and then washed with diethyl ether and dried over P_4O_{10} (yield 50−70%). $C_{52}H_{66}NO_4Si_2V$ (876.22): calcd. C 71.28, H 7.59, N 1.60, Si 6.41, V 5.81; found C 71.47, H 7.55, N 1.63, Si 5.58, V 5.40. The structure shows disorder of the tetrabutylammonium cations, but the tetraphenylphosphonium salt gave crystals suitable for an X-ray diffraction study.

$[Ph_4P][\{Ph_3SiO\}_2VO_2]$ (4b): This salt was prepared by dissolving **4a** (0.90 g; 1 mmol) in methanol (10 mL). The complex anion was then precipitated by slow addition of an aqueous solution (10 mL) of PPh_4Cl (0.42 g; 1 mmol). The white solid was isolated by filtration, washed with diethyl ether and then dried in air (yield 95%). $C_{60}H_{50}O_4PSi_2V$ (973.15): calcd. C 74.05, H 5.18, P 3.18, Si 5.77, V 5.23; found C 73.52, H 5.07, P 2.35, Si 5.40, V 5.09.

$[nBu_4N]_2[\{Ph_2SiO_2VO_2\}_2]$ (5a): $[nBu_4N]VO_3$ [56] (1.36 g; 4 mmol) in ethanol (10 mL) was added to a solution of $Ph_2Si(OH)_2$ (0.86 g; 4 mmol) in the same solvent (10 mL). After 45 min the white precipitate was filtered off, washed with diethyl ether and then dried over P_4O_{10} (yield 50−75%). $C_{56}H_{92}N_2O_8Si_2V_2$ (1079.42): calcd. C 62.31, H 8.59, N 2.59, Si 5.20, V 9.44; found C 62.29, H 8.76, N 2.61, Si 5.30, V 9.38.

"$H_6[PMo_9V_3O_{40}]\cdot 11H_2O$": The heteropolyacids "HPA-3" were prepared by described procedures.[7] $PMo_9V_3O_{51}H_{28}$ (1891.45): calcd. P 1.64, Mo 45.65; V 8.08; found P 1.70, Mo 45.50, V 7.75. Solid HPA-*n* species and their aqueous solutions are multicomponent systems: they contain several polyanions, positional isomers of these, $[VO_2]^+$ and often traces of V^{IV}. The identification is supported by solutions prepared with $2 \leq n \leq 10$ (see refs.[5,7,47]). Incomplete Keggin species or lacunary HPA-*n* are also formed and only equilibrium exchange-average resonances are observed.

Structure Determinations

Single crystals of **4b** and **5a** were grown from solutions in methanol at room temperature.

$[Ph_4P][\{Ph_3SiO\}_2VO_2]$ (4b): $C_{60}H_{50}O_4PSi_2V$, M_r = 973.14, monoclinic, space group $P2_1/n$ (no. 14); a = 2233.7(4), b = 1118.5(3), c = 2268.2(7) pm, β = 118.59(2)°, V = 4.976 (2) nm^3, Z = 4, $\rho_{calcd.}$ = 1.30 $Mg\cdot m^{-3}$, $F(000)$ = 2034, λ = 71.069 pm, T = 293 K, μ (Mo-K_α) = 0.317 mm^{-1}, crystal dimensions 0.2 × 0.3 × 0.5 mm^3, $2 \leq 2\theta \leq 50°$, 9487 measured reflections, 8729 were unique; 614 parameters refined in full-matrix, R_1 = 0.046 with 3730 reflections [$I > 3\sigma$ (I)], wR_2 = 0.054, $w \neq 1$ [weighting scheme of the form $w = w'[1-(||F_o| - |F_c||) / 6\sigma\ (Fo))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 3.55, −0.579 and 2.62 for a Chebyshev series for which X = Fc/Fc(max)].[57] Min./max. residual electron density − 250/320 e nm^{-3}.

$[nBu_4N]_2[\{Ph_2SiO_2VO_2\}_2]$ (5a): $C_{56}H_{92}N_2O_8Si_2V_2$, M_r = 1079.42, monoclinic, space group $P2_1/n$ (no.14); a = 1207.2(2), b = 1567.8(2), c = 1778.6(2) pm, β = 114.28(1)°, V = 3.068 (2) nm^3, Z = 2, $\rho_{calcd.}$ = 1.17 $Mg\cdot m^{-3}$, $F(000)$ = 1167, λ = 71.069 pm, T = 293 K, μ (Mo-K_α) = 0.379 mm^{-1}, crystal dimensions 0.1 × 0.3 × 0.4 mm^3, $2 \leq 2\theta \leq 50°$, 5896 measured reflections, 5388 were unique; 317 parameters refined in full-matrix, R_1 = 0.047 with 2386 reflections [$I > 3\sigma$ (I)], wR_2 = 0.056, $w \neq 1$ (weighting scheme of the form $w = w'\{1-[(||F_o| - |F_c||)/6\sigma\ (Fo)]^2\}^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 3.16, 0.109 and 2.29 for a Chebyshev series for which X = Fc/Fc(max)).[57] Min./max. residual electron density −290/300 e nm^{-3}. The data were collected on a Enraf−Nonius CAD4 four-circle diffractometer (ω-2θ scans). All measurements were made at room temperature; two standard reflections showed no significant variation in intensity. Corrections were made for Lorentzian and polarisation effects; an extinction correction was also applied;[58] an empirical absorption correction on the basis of Ψ scan data was introduced. The structures were solved by direct methods (SHELX-86 program)[59] and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found on difference Fourier maps; their positions were not refined and they were given one overall isotropic thermal parameter. Refinements were carried out by minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors (program CRYSTALS).[60]

CCDC-167421 (**4b**) and CCDC-167420 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

General

The solvents were purified by standard procedures and distilled under nitrogen.[62] Triphenyl silanol, Ph_3SiOH and diphenylsilanediol $Ph_2Si(OH)_2$ are commercial products; they were purified by fractional crystallisation. 2-Hydroxycyclohexanone (**6**), (1*S*, 2*S*, 5*S*)-2-hydroxypinane-3-one (**7a**), its (1*R*,2*R*,5*R*) enantiomer **7b**, and 2-methylcyclohexanone (**8**), were better than 99% pure by GC and NMR analysis; they were used without further purification. ^1H and ^{13}C NMR spectra were recorded at ambient temperature, on a Fourier transform apparatus (Bruker WP200), using $CDCl_3$ as solvent.

The ^{31}P NMR spectra were recorded with 10 mm o.d. tubes on a Bruker WM 250 apparatus operating at 101.2 MHz. From these NMR measurements it was found that the HPA-*n* precursors ($n \geq 2$) are not pure heteropolyacids: they contains a certain fraction of HPA-1, HPA-2, −3 and −4 with several isomers and excess H_3PO_4. We were unable to prepare a 99% pure isomer.

Raman spectra were recorded at room temperature with a Jobin−Yvon U1000 spectrometer with a resolution of 4 cm^{-1}. Solid samples of the complexes were mounted on a disk rotating at about 1000 rpm in order to avoid decomposition and/or photoreduction by the laser beam (excitation line, 514.5 nm of an Ar^+ laser; source power 30−50 mW; scanning time ca. 2 h). Solutions (0.1 M) of the mononuclear complex **4a** were studied. IR spectra (resolution: 2 cm^{-1}) were measured in a Fourier transform apparatus (Bruker Vector 22) in Nujol suspension either between two caesium bromide plates or in KBr pellets. Elemental analyses (C, H, N, Si, V) were carried out at the Service Central d'Analyses CNRS, Lyon.

Oxidation of 6, 7a or b, or 8 by Dioxygen in the Presence of a Vanadium Precursor

Typical experiments were performed in an all-glass reactor vessel (40 mL) attached to a vacuum line, with a manometer and a gas inlet. This was charged with the vanadium precursor (0.076 mmol V), the solvent (5 mL) and the substrate (ca. 7.6 mmol), and the mixture was stirred magnetically under O_2 for 24 h at 60 °C. Dioxygen uptake was determined by use of a gas burette system. The mixture was cooled and analysed by GC (OV 1701). An aliquot portion (usually 1 mL) including a standard (methyl heptanoate or naphthalene) was esterified by addition of ethereal diazomethane to the crude mixture or after removal of the vanadium on active charcoal (GC-MS experiments). Products were identified by GC-MS.

The GC-MS analyses were performed on a TRACE GC 2000 gas chromatograph (50 m capillary column) interfaced with a mass selective detector (RTX5-MS). ^1H and ^{13}C NMR spectra and MS (70 eV or CI, NH_3) data correspond to our previous findings[45] or to literature references.

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