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Surface-Inspired Molecular Vanadium Oxide Catalysts for the Oxidative Dehydrogenation of Alcohols: Evidence for Metal Cooperation and Peroxide Intermediates

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Abstract: On the basis that thiacalix[4]arene (H₄T4A) complex (PPh₄)₂- $[H_2T4A(VO_2)]_2$ (Ia) was found to be an adequate functional model for surface species occurring on vanadium oxide based catalysts and itself catalyses the oxidative dehydrogenation (ODH) of alcohols, an analogue containing 2,2'-thiobis(2,4-di-tert-butylphenolate), ^sL²⁻, as ligand, namely, $(PPh_4)_2[^{S}LVO_2]_2$ (II) was investigated in the same context. Despite the apparent similarity of Ia and II, studies on II revealed several novel insights, which are also valuable in connection with surfaces of vanadia catalysts: 1) For Ia and **II** similar turnover numbers (TONs) were found for the ODH of activated alcohols, which indicates that the addi-

Introduction

Supported vanadium oxide catalysts are among the most efficient catalysts for the oxidative dehydrogenation (ODH) of alcohols and alkanes,^[1] and for a couple of years we have been interested in their active sites on the molecular level. Hence, we have pursued the synthesis of molecular compounds which can simulate the structure, reactivity and/or the spectroscopic properties of corresponding sites postulated to occur on the surfaces of such catalysts.^[2-8] For simulation of the oxidic environments that oxidovanadium moieties experience on the surfaces of oxidic support materials we have successfully employed two different types of ligands: The deprotonated forms of calixarenes^[2-5] and the deprotonated forms of incompletely condensed silsesquioxanes.^[6-8] Recently we reported the results of structure–function analyses of calixarene-based oxidovanadium model

tional OH units inherent to **Ia** do not contribute particularly to the activity of this complex, for instance, through prebinding of the alcohol. 2) On dissolution **II** enters into an equilibrium with a monomeric form, which is the predominant species in solution; nevertheless, ODH proceeds exclusively at the dimeric form, and this stresses the need for cooperation of two vanadium centres. 3) By omitting O_2 from the system during the oxidation of 9-fluorenol, the reduced form of the catalyst

Keywords: dehydrogenation • homogeneous catalysis • peroxo ligands • reaction mechanisms • vanadium could be isolated and fully characterised (including single-crystal X-ray analysis). The corresponding intermediate had been elusive in case of thiacalixarene system Ia. 4) Reoxidation was found to proceed via a peroxide intermediate that also oxidises one alcohol equivalent. As the peroxide can also perform mono- and dioxygenation of the thioether group in II, after a number of turnovers the active catalyst contains a sulfone group. The reduced form of this ultimate catalyst was also isolated and structurally characterised. Possible implications of 1)-4) for the function of heterogeneous vanadia catalysts are discussed.

compounds with respect to the ODH of alcohols.^[2,4] It turned out that dinuclear compounds are more active than mononuclear ones, and that thiacalixarene complexes are more efficient than complexes containing the classical calixarene ligands.

Oxidovanadium(V) complex Ia (see Scheme 1) reached the highest turnover numbers (TONs), and the results of more detailed mechanistic investigations, inter alia isolation of intermediate Ic, led to the proposal of a catalytic cycle as exemplified in Scheme 1 for the substrate 9-fluorenol. While it was not clear whether pre-binding of the alcohol is necessary prior to the oxidation step, in any case starting from Ia the next step was proposed to be a dehydrogenation (presumably in form of two consecutive H-atom abstractions) leading to 9-fluorenone and an oxidovanadium(IV) complex with two hydroxide bridges (Ib). To transform Ib into intermediate Ic, which could be isolated, an excess of alcohol has to replace one of the two hydroxide bridges by an alcoholate ligand under elimination of water, and it is reasonable to assume that this step proceeds sufficiently fast at 80 °C, especially in the presence of molecular sieves, which were added to constantly remove the water formed in this process. Starting from Ic, O_2 is then capable of regenerating the starting situation, as shown independently, and for this it has to use all of its four oxidation equivalents.^[4]



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Scheme 1. Proposed catalytic cycle for the oxidation of alcohols (exemplified for 9-fluorenol) catalysed by thiacalix[4]arene-based compound Ia.

While this mechanism is plausible and was supported by several observations, it still posed some questions, for instance, concerning the role of the remaining OH groups in the ligand system. Are they beneficial in terms of precoordination of alcohols via H-bonds? We addressed this and other questions by preparing a derivative without these groups: by employing the 2,2'-thiobis(2,4-di-*tert*-butylphenolate) ligand ^sL²⁻ (Scheme 2a), which can be regarded as the relevant section of the thiacalixarene framework needed for construction of **Ia**, we managed to prepare analogous complex **II** (Scheme 2b),^[9] which, however, was found to be mainly monomeric in solution.

Results and Discussion

Influence of dangling OH groups in Ia: To determine the contribution of the dangling OH groups in **Ia** to its high activity, for instance, through pre-binding of alcohol substrates, it was of interest to test **II**, which lacks such OH groups, as a catalyst for the ODH of alcohols under the same conditions as **Ia** (Table 1).

While the trend is somewhat non-uniform, it is clear that reduction of the thiacalixarene ligand system to ${}^{s}L^{2-}$ does not lead to a loss in activity that would point to the OH groups being responsible for the superiority of **Ia** over other



calixarene-based catalysts. This holds all the more given that only a fraction of **II** employed, namely, the equilibrium concentration of $\mathbf{II}^{\mathbf{D}}$, can be effective during the catalytic procedure (see below), so that it has to be concluded, that $\mathbf{II}^{\mathbf{D}}$ is even superior to **Ia**. Hence, we can now be sure that the free OH groups of the thiacalix[4]arene ligand in **Ia** do not serve any particular purpose during catalysis.

Recently, we reported on bioinspired investigations concerning haloperoxidase-like behaviour of **II** and its catalytic activity in sulfoxidation with *t*BuOOH.^[9] We now report its properties as an ODH catalyst and detailed insight into its function, which at the same time improve and extend the mechanistic view on systems such as **Ia**.

Table 1. TONs for the ODH of selected alcohols to the respective aldehydes/ketones with O_2 , catalysed by 1 mol% of **Ia** or **II**, after 60 min.

Catalyst	Benzyl alcohol	9-Fluorenol	Cinnamic alcohol
Ia	34	83	45
II	50	83	25

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Dinuclearity as a prerequisite: Since **II** crystallises as a dimer ($\mathbf{II}^{\mathbf{D}}$) but after dissolution mainly exists in form of a monomeric species ($\mathbf{II}^{\mathbf{M}}$, $K_{eq} = 20 \text{ mol } \mathbf{L}^{-1}$ for the equilibrium shown in Scheme 2 b), the question arose whether the mechanism shown in Scheme 1 even holds for **II**. However, all subsequent investigations as outlined below confirmed that the ODH reactivity is exhibited exclusively by the dimer $\mathbf{II}^{\mathbf{D}}$, which is a further important finding, also with regard to the model character of these compounds and inferences for surface chemistry.

Provided that a rate law for a pseudo-first-order reaction applies, a linear dependence between the concentration of the catalytically active species and the reaction rate should be observed. Figure 1 shows corresponding plots for various



Figure 1. Observed reaction rate in dependence on the amount of used catalyst for ODH of 9-fluorenol to 9-fluorenone with O_2 catalysed by various amounts of **II**.

weigh-ins of catalyst II. Interestingly, doubling the amount of added catalyst from 0.125 to 0.25 mol% or from 0.25 to 0.5 mol% leads to an approximately fourfold (4.1 and 3.6, respectively) increase in reaction rate, which can only be explained if the ODH proceeds not through the monomeric but through the dimeric form: On the basis of the equilibrium equation $K_{eq} = [\mathbf{II}^{\mathbf{M}}]^2 / [\mathbf{II}^{\mathbf{D}}]$ for the equilibrium shown in Scheme 2b, at these low concentrations a doubling of the overall amount of catalyst added leads to a fourfold increase of $[\mathbf{H}^{\mathbf{D}}]$, while $[\mathbf{H}^{\mathbf{M}}]$ is only doubled. When the weigh-in is doubled at higher catalyst concentrations, the multiplying factor for $\mathbf{II}^{\mathbf{D}}$ should be somewhat lower than four, as the equilibrium gradually shifts more to the side of the dimer, and this is observed here, too. However, the decrease of the observed factor is more pronounced than should be theoretically (2.45 from 1 to 2 mol%), which we cannot rationalise at present.

Nevertheless, the behaviour of the reaction rates with variation of the overall concentration at low catalyst weigh-ins clearly indicates that $\mathbf{II}^{\mathbf{D}}$ mediates alcohol oxidation, while $\mathbf{II}^{\mathbf{M}}$ itself is inactive, which nicely illustrates the advantage of the cooperation of two vanadium ions: Referring to

Scheme 1, the V centres in Π^{D} must switch their oxidation states only between +V and +IV, while function of Π^{M} would require a change between +V and +III.

The rate-determining step: To obtain information on the rate-determining step of the catalytic oxidation, 9-deutero-9-fluorenol was employed to compare its reaction rate with that of undeuterated 9-fluorenol (Figure 2). This gave a ki-



Figure 2. Reaction rates for the oxidation of 9-fluorenol and 9-deutero-9-fluorenol with O_2 catalysed by 1 mol % **II**.

netic isotope effect (KIE) of 2.8. Considering, that the maximum KIE reachable at 80 °C is about 5, a value of 2.8 is certainly indicative of a rate-determining step with significant involvement of the C–H bond and a quite symmetric transition state along the H-atom transfer coordinate O···H···C. This finding is consistent with recent investigations concerning the H-atom abstraction reactivity of ligated $[VO_2]^+$ units.^[8,10]

Isolation of the reduced catalyst: As in the case of **Ia**, we also tried to identify reaction intermediates of the catalytic system involving **II**. Interestingly, omitting O₂ during conversion of 9-fluorenol led to isolation of $(PPh_4)_2[^{S}LVO(\mu OH)_2VO^{S}L]$ (1), which is an analogue of **Ib**. Compound **Ib** itself had been elusive, supposedly as it quickly reacts with excess alcohol to give **1c**. Its existence was only inferred,^[4] but isolation of **1** now confirms that its proposed intermediacy was reasonable. Furthermore, it provides additional support that the ODH indeed proceeds via dimer **II**^D.

The structure of the dianion of **1** (Figure 3) is nearly identical with that of $\mathbf{II}^{\mathbf{D}}$, from which it can be derived formally by replacing the μ -O bridges by μ -OH groups. The protons could be located in the X-ray analysis, and the appearance of a corresponding OH stretching band at $\tilde{\nu} = 3678 \text{ cm}^{-1}$ in the IR spectrum of **1** further proved their existence. The replacement of the bridging divalent oxido ligands by monovalent OH ligands leads to lengthening of corresponding V– O distances from approximately 1.84 Å in $\mathbf{II}^{\mathbf{D}}$ to 1.9870(11) Å (O1–V1) and 2.0103(11) Å (O1'–V1) in **1**. Fur-

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Figure 3. Structure of 1-2 MeCN in the crystal. All hydrogen atoms except H1 and H1', the Ph_4P^+ cations and co-crystallised acetonitrile solvent molecules are omitted. Selected bond lengths [Å] and angles [°]: O1-H1 0.8489, O1-V1 1.9870(11), O1'-V1 2.0103(11), O2-V1 1.6050(12), O3-V1 1.9669(11), O4-V1 1.9842(11), S1-V1 2.8229(5), V1-V1' 3.1705(4), V1-(O1, O1', O3, O4) 0.3991(3), O1-V1-O1' 75.04(5), O1-V1-O2 104.22(6), O1'-V1-O2 102.96(5), O2-V1-O3 100.56(6), O2-V1-O4 99.19(6), O2-V1-S 170.01(5), V1-O1-V1' 104.96(5).

thermore, the distance between the two vanadium atoms, which are now in the oxidation state +IV, is lengthened from 2.7782(7) Å in $\mathbf{H}^{\mathbf{p}}$ to 3.1705(4) Å. The widening of the V_2O_2 core is in agreement with the observations made for intermediate Ic containing thiacalixarene ligands. In solution 1 exhibits a magnetic moment of 2.27 μ_B at room temperature, which is indicative of weak antiferromagnetic coupling of the two V^{IV} ions. EPR studies on 1 (in frozen THF, MeCN or CH₂Cl₂ solution) at 77 or 293 K (THF or CH₂Cl₂ solutions) revealed, if at all, only a very weak and broad signal (see Supporting Information for selected EPR spectra of 1), which excludes the presence of a monomeric form of 1 and again suggests a magnetic communication between the two V^{IV} ions. We were not able to isolate a derivative of 1 containing an alkoxide bridge as in Ic even when using a fivefold excess of the substrate.

The reoxidation step: We also investigated the reoxidation step starting from 1. Treatment of 1 with O_2 at room temperature led to an immediate colour change from green to violet. Monitoring this reaction by ⁵¹V NMR spectroscopy revealed, in addition to a signal at $\delta = -502$ ppm, which corresponds to the starting compound \mathbf{II}^{M} , a further signal at $\delta = -448$ ppm. The latter belonged to peroxide III (Scheme 3b), which was identified previously as a product of the reaction between II and H_2O_2 .^[9] On storing of the sample at room temperature the peroxide signal decreased in intensity in favour of a new one at $\delta = -512$ ppm, characteristic of the monomer of singly S-oxidised compound IV^M (Scheme 3a), generated from III in the course of an intramolecular transfer of a peroxidic oxygen atom to the thioether linker. Like \mathbf{II}^{M} , also \mathbf{IV}^{M} enters into an equilibrium with a dimeric form, $IV^{D,[9]}$ and it is reasonable to assume that **IV^D** will oxidise a further alcohol equivalent; reoxidation can then be anticipated to lead to IV^M and V. Finally, the peroxide group of V will transfer another oxygen atom



Scheme 3. Products resulting from the oxygenation of **II**. Compounds **IV** and **VI** are involved in monomer/dimer equilibrium (a), whereas peroxides **III**, **V** and **VII** exist only in monomeric form (b).^[9]

to the sulfoxide group to yield VI^{M} , which was identified previously as the final product of H_2O_2 oxidation of $II^{[9]}$ and here represents the monomer of the ultimate catalyst.

Consistently, the reaction of **VI** with 9-fluorenol led to isolation of V^{IV} intermediate $(PPh_4)_2[^{SO2}LVO(\mu-OH)_2VO^{SO2}L]$ (2). The structure of the dianion of 2 (Figure 4) can be derived from that of 1 by replacement of the thioether groups by sulfone units, which interact with the vanadium centres through one of their oxygen atoms. The protons of the bridging OH unit could be located in the



Figure 4. Structure of $2\cdot 8 CH_2CI_2$ in the crystal. All hydrogen atoms except H2 and H2', the Ph₄P⁺ cations and co-crystallised CH₂Cl₂ solvent molecules are omitted. Selected bond lengths [Å] and angles [°]: O2–H2 0.74(6), O1–V1 1.596(2), O2–V1 2.004(2), O2'–V1 2.000(2), O3–V1 1.957(2), O4–V1 1.980(2), O5–V1 2.410(2), V1–V1' 3.1378(7), V–(O2, O2', O3, O4) 0.3798(6), O1-V1-O2 102.65(11), O1-V1-O2' 103.78(11), O1-V1-O3 100.43(11), O1-V1-O4 97.76(11), O1-V1-O5 176.65(10), V1-O2-V2 103.20(11).

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X-ray analysis, and the appearance of a corresponding OH stretching band at 3664 cm⁻¹ in the IR spectrum of 2 further proved their existence. As in the case of 1, treatment of 2 with O_2 leads to a colour change from green to violet, and a ⁵¹V NMR spectrum recorded directly afterwards indicated the presence of equimolar amounts of starting compound VI^M and known peroxide VII^{M.[9]} Independent reactivity studies with peroxide VII^M itself showed that it does not oxidise intermediate 2, but it is capable of oxidising the alcohol, although this reaction proceeds more slowly than oxidation of the alcohol by VI. Hence, this is the route through which the peroxide, formed in the course of reoxidation of the reduced catalyst, re-enters the catalytic cycle after the thioether group has been fully oxidised: it oxidises a further alcohol equivalent. In the course of catalytic alcohol oxidations setting out with VI no new signals belonging to any other V species could be observed, which supports that VI (and VII) are the sole species responsible for substrate oxidation in the later stage of the catalytic process.

Catalytic cycle: Based on all these results, it is reasonable to propose the mechanism exemplified for the substrate 9-fluorenol in Scheme 4: Starting from $\mathbf{II}^{\mathbf{D}}$ ODH of one alcohol equivalent occurs in the form of two H-atom abstractions, whereas the rate-determining step consists of an H-atom transfer from the ^{HO}CH unit to the oxidovanadium core. This produces 1 and one equivalent of the carbonyl compound. Reoxidation of 1 with O₂ leads to one equivalent of the monomer of the starting material, $\mathbf{II}^{\mathbf{M}}$, and one equivalent of peroxide **III**. The peroxide then oxidises a further alcohol equivalent to close the cycle, as shown in Scheme 4. This cycle, however, is somewhat simplified: As the peroxide **III** can also oxidise the thioether group of the thiobisphenolate ligand, after approximately 6–7 turnovers the catalytic system works exactly as shown in Scheme 4 but



Scheme 4. Catalytic cycle for the oxidation of alcohols (exemplified for 9-fluorenol) with II as catalyst.

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with all of the S atoms being doubly oxidised. This leads to **VI** as the actual catalytically active species, as proved by NMR spectroscopy.

Considering these findings the question arises how they relate to the thiacalixarene system and the proposed catalytic cycle shown in Scheme 1? First, they indicate, that catalysis with **Ia** need not necessarily proceed via an alcoholate intermediate **Ic**. In the case of **II**, the reduced bis(μ -hydroxido) intermediate is readily reoxidized by O₂, and now the same seems possible also for **I**, although there was no evidence for a peroxide intermediate in this system. Perhaps catalysis with **Ia** proceeds by two simultaneous cycles, one as shown in Scheme 1 and one according to Scheme 4. A further possibility is that **I** exclusively utilises the Scheme 4 cycle, too, and that **1c** was only isolated under non-turnover conditions as it is thermodynamically more stable than **Ib**.

Implications for surface chemistry: By investigating system II as an ODH catalyst two important findings could be made: 1) catalysis proceeds (in the temperature regime that applies here) exclusively via dinuclear species, and 2) re-oxidation proceeds via the participation of peroxides. One hypothesis which 1) thus poses for heterogeneous catalysts is that, also on their surfaces, dinuclear species are more reactive than mononuclear ones, and this nicely complements from the molecular side corresponding proposals based on experimental and theoretical results concerning heterogeneous catalysts.^[11] Considering 2), it is noteworthy that only recently after detailed spectroscopic investigations and comparison with peroxido model compounds was it concluded that "an umbrella-type vanadium oxido peroxido structure does not exist for hydrated or dehydrated V2O5/SiO2 catalysts",^[12] although DFT results suggested that reoxidation takes place via peroxide species.^[13] In this context it is important to note that the failure to detect peroxides does not

> mean that they are not formed intermediately; they may just not be stable under the conditions of analysis or do not accumulate due to their high reactivity. Dissolved in MeCN, peroxide **VII**, for instance, only has a half-life of 12 h at room temperature and merely 5 min at 80 °C.^[9] With this background our results support the peroxide route for reoxidation.

Conclusion

Investigation of the thiobisphenolato oxidovanadium complex $(PPh_4)_2[(^{S}LVO_2)_2]$ (II) as a catalyst for the ODH of alcohols revealed valuable insights into oxidation catalysis at vanadium

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centres. First, it was shown that dangling OH groups present in a related thiacalix[4]arene-based catalyst do not contribute particularly to its activity, and the proposal of an "OVIV- $(\mu$ -OH)₂V^{IV}O" intermediate, which was elusive in the case of that system, was supported: An analogue (1) has now successfully been isolated by employing the simplified thiobisphenolate ligand ^SL²⁻. Reoxidation of 1 was found to proceed through a peroxide intermediate and, importantly, it was shown that ODH proceeds via a dinuclear species, while the corresponding monomer is inactive. The rate-determining step is an H-atom abstraction from the CH unit connected to the OH group. Altogether these results allowed a plausible reaction mechanism to be proposed. They suggest that also on surfaces dinuclear species are more reactive than mononuclear ones and that the reoxidation proceeds via a peroxide route.

Experimental Section

General remarks: All manipulations were carried out in a glove box or by Schlenk-type techniques under a dry argon atmosphere. The ¹H and ⁵¹V NMR spectra were recorded on a Bruker AV-400 NMR or DPX-300 spectrometer. The ¹H NMR spectra were calibrated against the residual protons of the deuterated solvent, and the ⁵¹V NMR spectra against VOCl₃ as external standard. Microanalyses were performed on a Leco CHNS-932 or HEKAtech Euro EA 3000 elemental analyser. Infrared spectra were recorded on samples prepared as KBr pellets with a Shimadzu FTIR 8400S spectrometer. The high-resolution mass spectra were recorded with an Agilent Technologies 1200 Series mass spectrometer with a time-of-flight analyser. EPR spectra were measured on an ERS 300 (ZWG/Magnettech GmbH, Berlin Adlershof, Germany). Solution magnetic susceptibilities were determined by the Evans method^[14] with a Bruker AV-400 NMR spectrometer. Compounds **II**, **VI** and **VII** were obtained by literature procedure.^[9]

Synthesis of 1: Compound **II-**2MeCN (90 mg, 50 µmol, 1 equiv), 9-fluorenol (9.1 mg, 50 µmol, 1 equiv) and 3 Å molecular sieves (500 mg) were suspended in 10 mL of acetonitrile and stirred at 80 °C. After 1.5 h the solvent was removed thoroughly, the residue was extracted with 5 mL of CH₂Cl₂ and layered with 10 mL of hexane. Removal of the solvent by filtration after 3 d and drying of the remaining crystalline solid afforded 40 mg of **1-**2CH₂Cl₂ (21 µmol, 42 %). IR (KBr): $\tilde{\nu} = 3678$ (w), 3062 (w), 2948 (s), 2900 (m), 2865 (m), 1586 (w), 1467 (s), 1436 (vs), 1381 (m), 1357 (w), 1312 (s), 1299 (w), 1256 (m), 1200 (w), 1108 (vs), 995 (w), 959 (s), 838 (m), 758 (m), 723 (s), 688 (s), 527 cm⁻¹ (vs); elemental analysis calcd (%) for C₁₀₄H₁₂₂O₁₂P₂S₂V₂·1CH₂Cl₂ (1897.9): C 67.08, H 6.69, S 3.37; found: C 67.54, H 7.05, S 2.99. Crystals that were suitable for X-ray diffraction analysis were obtained by slowly evaporating a saturated solution of **1** in acetonitrile.

Synthesis of 2: Compound **VI** (90 mg, 50 µmol, 1 equiv), 9-fluorenol (9.1 mg, 50 µmol, 1 equiv) and 3 Å molecular sieves (500 mg) were suspended in 5 mL of CH₂Cl₂. After 1 h of stirring the solution was filtered and layered with 5 mL of hexane. Removal of the solvent by filtration after 3 d and drying of the remaining crystalline solid afforded 58 mg of **2**·CH₂Cl₂ (31 µmol, 62 %). IR (KBr): $\tilde{\nu}$ =3681 (w), 3061 (w), 2950 (s), 2902 (m), 2864 (m), 1598 (w), 1530 (w), 1480 (vs), 1441 (s), 1436 (s), 1381 (w), 1358 (m), 1336 (s), 1273 (s), 1256 (m), 1193 (w), 1139 (w), 1122(m), 1108 (vs), 1085 (m), 995 (w), 972 (s), 868 (w), 841 (w), 786 (m), 777(m), 750 (w), 723 (s), 689 (s), 619 (vs), 526 (vs), 486 cm⁻¹ (w); elemental analysis calcd (%) for C₁₀₄H₁₂₂O₈P₂S₂V₂·CH₂Cl₂ (1877.0): C 67.18, H 6.66, S 3.41, Cl 3.77; found: C 66.91, H 6.71, S 3.25, Cl 3.24.

General procedure for oxidation studies: Alcohol, catalyst (mol% with respect to V centres) and 1.5 g of 3 Å molecular sieves were suspended in 6 mL of acetonitrile under an argon atmosphere. Then the vessel was

partially degassed, flushed with 1.2 bar of O₂ and heated to 80 °C. Conversions were determined by ¹H NMR spectroscopic analysis of samples taken at the depicted times under a dioxygen stream. Blind studies in the absence of the catalyst showed no alcohol conversion.

Crystal structure determinations: Data for **1**·2 MeCN and **2**·8 CH₂Cl₂ were collected at 100 K on a Stoe IPDS 2T diffractometer with Mo_{Ka} radiation ($\lambda = 0.71073$ Å) from a sealed-tube generator with graphite monochromator. Numerical absorption correction^[15] were applied for **1**·2 MeCN and **2**·8 CH₂Cl₂. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 with all measured reflections.^[16] All non-hydrogen atoms were refined anisotropic cally. H atoms were introduced in their idealised positions and refined by using a riding model. CCDC-817517 (**1**·2 MeCN) and CCDC-817518 (**2**·8 CH₂Cl₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **1**·2 MeCN: $C_{108}H_{128}N_2O_8P_2S_2V_2$, M_r =1810.06, T= 100(2) K, λ =0.71073 Å, monoclinic, space group $P2_1/n$, a=12.5041(4), b=31.2121(6), c=13.9180(4) Å, β =114.478(2)°, V=4943.7(2) Å³, Z=2, ρ_{calcd} =1.216 mg m⁻³, μ =0.320 mm⁻¹; 42882 reflections measured, 9715 unique (R_{int} =0.0380); final R indices [$I > 2\sigma(I)$]: R=0.0379, wR=0.0924. Crystal data for **2**·8 CH₂Cl₂: $C_{112}H_{138}Cl_{12}O_{12}P_2S_2V_2$. M_r =2471.49, T= 100(2) K, λ =0.71073 Å, triclinic, space group $P\overline{1}$, a=13.1043(4), b= 14.8568(5), c=17.0432(6) Å, a=75.750(3)°, β =83.516(3)°, γ =70.633(3)°, V=3032.25(19) Å³, Z=1, ρ_{calcd} =1.352 mg m⁻³, μ =0.623 mm⁻¹; 31167 reflections measured, 11841 unique (R_{int} =0.0423); final R indices [$I > 2\sigma(I)$]: R=0.0544, wR=0.1390.

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