Catalysis of Oxo Transfer to Prochiral Sulfides by Oxovanadium(V) Compounds That Model the Active Center of Haloperoxidases

Gabriella Santoni,[a] Giulia Licini,[b] and Dieter Rehder*[a]

Abstract: The catalytic properties of a new class of chiral vanadium compounds—[(*S*,*S*,*S*)-VO(OMe)L1] (**5**), [(*S*,*S*)-VO(OMe)L2] (**6**), [(*S*,*S*)-VO(OMe)L3] (**7**), and [(*R*,*R*,*R*)-VO(OMe)L4] (**8**), as well as the system $VO(OiPr)_3$/(*R*,*R*,*R*)-H_2L4 [H_2L1 = (*S*,*S*)-bis(2-hydroxypropyl)-(*S*)-1-phenylethylamine, **1**; H_2L2 = (*S*,*S*)-bis(2-hydroxypropyl)-benzylamine, **2**; H_2L3 = (*S*,*S*)-bis(2-hydroxypropyl)isopropylamine), **3**; (H_2L4) = (*R*,*R*)-bis(2-phenylethanol)-(*R*)-1-phenylethylamine, **4**]—in the asymmetric oxidation of prochiral sulfides by organic hydroperoxides have been investigated. Particular attention has been paid to the factors that guide the discrimination between the two prochiral faces of the sulfides (methyl *p*-tolyl sulfide and benzyl phenyl sulfide), to steric implications stemming from the oxidant (cumyl hydroperoxide and *tert*-butyl hydroperoxide), and to the specific complex used. As an example, (*S*)-methyl *p*-tolyl sulfoxide was obtained in a 31% enantiomeric excess by use of cumyl hydroperoxide as oxidant and complex **5** as the catalyst, after 150 min at 0 °C and with 100% conversion of the sulfide. The crystal and molecular structures of **5** and **6** reveal the close relationship between these complexes and the active center of vanadate-dependent haloperoxidases: the vanadium is in a slightly distorted trigonal-bipyramidal environment with the nitrogen and the methoxy group in the axial positions, and the oxo and alkoxide functions of L2 and L3 are the plane. The presence and equilibrium situation of isomers of the catalysts in solution has been investigated by ^{51}V EXSY and variable-temperature multinuclear NMR spectroscopy. An intermediately formed peroxo (ROO^-) vanadium complex was detected by ^{51}V NMR spectroscopy.

Keywords: amino alcohols · oxo-transfer catalysis · sulfides · sulfoxides · vanadium

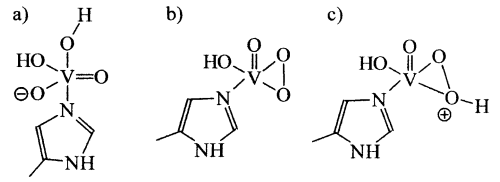
Introduction

Vanadate-dependent haloperoxidases are enzymes responsible for the production of a variety of halogenated compounds through the initial formation of hypohalous acids as the halogenating agents.[1–3] The enzymes are capable of withstanding temperatures of up to 70 °C, they remain functional in the presence of several organic solvents, and—in contrast to heme peroxidases—they are not inactivated by H_2O_2 during catalysis.[4] Like other natural receptors, vanadate-dependent haloperoxidases are also capable of recognizing substrates with a specific chirality: it has recently been demonstrated that these enzymes mediate enantioselective sulfoxidation by hydrogen peroxide.[5–8] Thus, the asymmetric oxidation of bicyclic aromatic sulfides with hydrogen peroxide as oxidant and the bromoperoxidase from the seaweed *Corallina officinalis* as catalyst yields the corresponding (*S*)-sulfoxides with high enantiomeric excesses (*ee*s), while this enzyme is not able to oxidize methyl phenyl sulfide at all.[7, 8] If, however, this reaction is mediated by the bromoperoxidase from the brown seaweed *Ascophyllum nodosum,* the *R* enantiomer of the sulfoxide is obtained in 91% *ee*, with a yield of 55%, after 20 h at room temperature under slightly acidic conditions.[4] The sulfoxide with the opposite configuration was obtained (30% *ee*, 45% yield) in the oxidation mediated by the bromoperoxidase from the red seaweed *Corallina pilulifera*.[5] In contrast, use of the chloroperoxidase from the mold *Curvularia inaequalis* or of recombinant chloroperoxidases led to racemic mixtures.[5] This difference in reactivity suggests a specific orientation of the substrate in the vicinity of the active sites,[9] even though the molecular structures of the chloroperoxidase from *C. inaequalis*[10] and the bromoperoxidase from *A. nodosum*[11] revealed a high degree of amino acid homology in the active sites, with the only difference being the replacement of His411 by Phe397. The vanadate core in these enzymes is covalently bound to the Nε of a proximal histidine; vanadium is in a trigonal-bipyramidal array (Scheme 1a), with the apical OH group hydrogen-

[a] Prof. Dr. D. Rehder, Dott.ssa G. Santoni
Institut für Anorganische und Angewandte Chemie der Universität Hamburg
20146 Hamburg (Germany)
Fax: (+49) 40-42838-2893
E-mail: dieter.rehder@chemie.uni-hamburg.de

[b] Prof. Dr. G. Licini
Universitá degli Studi di Padova
Dipartimento di Chimica Organica, 35131 Padova (Italy)
Fax: (+39) 049-8275289
E-mail: giulia.licini@unipd.it

DOI: 10.1002/chem.200304595



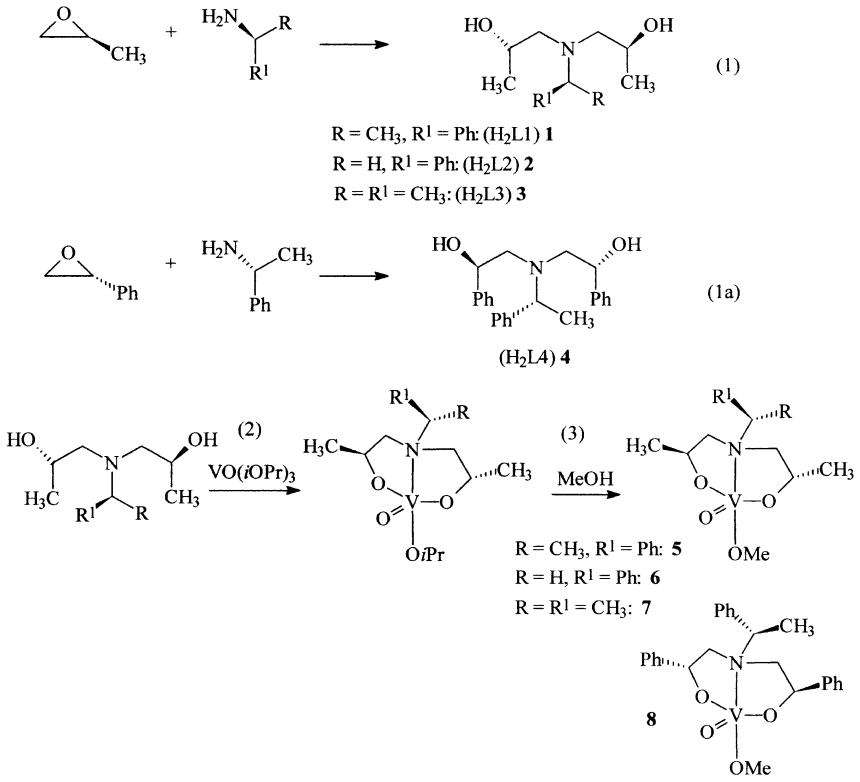
Scheme 1. The active centers of vanadate-dependent haloperoxidases from: (a) native *A. nodosum* bromoperoxidase, (b) the peroxo from of *C. inaequalis* chloroperoxidase, and (c) the hydroperoxo intermediate proposed for the *A. nodosum* peroxidase.

bonded to a distal His residue. When a molecule of oxidant (H_2O_2) coordinates to the metal center, a structural rearrangement from a trigonal-bipyramidal geometry to square-pyramidal occurs. In the peroxo form, vanadium carries an axial oxo group, while the plane is occupied by a side-on coordinated peroxide, histidine, and an oxo/hydroxo ligand (Scheme 1b).[12] For the turnover, a hydroperoxo intermediate has been proposed; the resulting asymmetric side-on coordination of hydroperoxide has been suggested on the basis of ^{17}O NMR studies of solutions of the *A. nodosum* peroxidase after treatment with ^{17}O-enriched H_2O_2 (Scheme 1c).[13] The formation of a mono-hydroperoxo species plays a fundamental role for the enzymatic reactivity[14] in the sense that a positive charge on the peroxo-O provided by protonation[15–17] furnishes a favorable site for the nucleophilic attack of the substrate to be oxidized.[18] The oxidation of prochiral sulfides to the corresponding optically active sulfoxides is believed to work according to this mechanism (see also below).

During the last few years, the synthesis of enantiopure sulfoxides has received much attention[19] because of the use of these compounds as chiral auxiliaries,[20–22] synthetic intermediates, and bioactive compounds.[23] Several inorganic chiral vanadium compounds have been employed in the catalytically conducted oxidation of prochiral sulfides to chiral sulfoxides (and further to sulfones), usually based on vanadium systems containing Schiff base ligands.[24–26] These reactions have further been extended to thioacetals and thioketals,[27] and to disulfides.[28] Here, as a contribution to the elucidation of the chiral recognition mechanism of the haloperoxidases, we report on a study of the catalytic properties of new oxovanadium(v) complexes, containing bi- and trichiral amino-bis(alcoholates) as ligands, in the asymmetric oxidation of prochiral thioethers.

Results and Discussion

Syntheses: A new class of chiral vanadium complexes mimicking the active site of the vanadate-dependent haloperoxidases was synthesized through the use of enantiopure amino alcohols (H_2L1, H_2L2, and H_2L3, **1**–**3**), obtained by treatment of (*S*)-propene oxide with three different amines (Scheme 2, (1)), and with H_2L4 (**4**), obtained by treatment of (*R*)-(+)-styrene oxide with (*R*)-(+)-phenylethylamine



Scheme 2. Syntheses of the new class of chiral vanadium complexes.

(Scheme 2). Treatment of the amino alcohols with $VO(OiPr)_3$ in dichloromethane resulted in the formation of the complexes [VO(O*i*Pr)L] (Scheme 2, (2)) with an asymmetric environment around the metal center. Transesterification with methanol (Scheme 2, (3)) yielded [VO(OMe)L] (**5**–**8**). Compounds **5** and **6** were obtained in crystalline form suitable for X-ray diffraction analysis.

Structure description: ORTEP plots of **5** and **6** are shown in Figure 1; Table 1 contains selected bonding parameters. In both molecules, vanadium is in a somewhat distorted trigonal-bipyramidal environment ($\tau = 0.75$ for **5** and $\tau = 0.66$ for **6**; the angular parameter τ is 1 for an ideal trigonal-bipyramid and 0 for an ideal square pyramid), with the doubly bonded oxo group in the plane. The vanadium center is displaced by 0.2321 Å (**5**) and by 0.2618 Å (**6**) from the basal plane towards the nitrogen atom. The angle between the two apical ligands and the vanadium center, O2-V1-N1, is 167°. The deviations of the basal angles from the idealized value of 120° is more

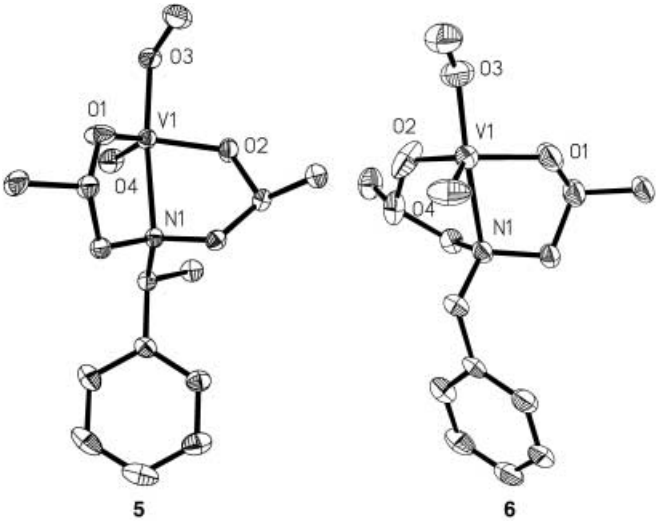


Figure 1. Structures of **5** and **6** (ORTEP plots (50% probability level).

Table 1. Selected bond lengths [Å] and bond angles [°] for **5** and **6**.

[VO(OMe)L1] (**5**)		[VO(OMe)L2] (**6**)	
V1−O4	1.6043(11)	V1−O4	1.591(2)
V1−O1	1.7947(11)	V1−O1	1.792(2)
V1−O3	1.7991(10)	V1−O3	1.787(3)
V1−O2	1.8119(10)	V1−O2	1.787(2)
V1−N1	2.2615(11)	V1−N1	2.338(3)
N1−C16	1.4813(16)	N1−C11	1.480(3)
N1−C3	1.4886(15)	N1−C8	1.484(3)
N1−C15	1.5216(16)	N1−C1	1.493(3)
O4-V1-O1	114.72(6)	O4-V1-O1	111.10(16)
O4-V1-O3	102.26(6)	O4-V1-O3	101.91(13)
O1-V1-O3	95.63(5)	O3-V1-O1	98.05(12)
O4-V1-O2	117.72(6)	O4-V1-O2	114.29(15)
O1-V1-O2	122.26(6)	O2-V1-O1	127.71(15)
O3-V1-O2	95.44(5)	O3-V1-O2	96.74(13)
O4-V1-N1	90.25(5)	O4-V1-N1	91.01(11)
O1-V1-N1	78.98(4)	O1-V1-N1	77.58(10)
O3-V1-N1	167.49(5)	O3-V1-N1	167.06(11)
O2-V1-N1	78.35(4)	O2-V1-N1	77.06(11)

pronounced in **6**, in which the ligand **2** bears a sterically less demanding benzyl residue instead of a phenylethyl moiety. This steric influence is also reflected in the two different *d*(V−N1) values, of 2.2615(11) Å in **5** and 2.338(3) Å in **6**. Both are surprisingly elongated and reminiscent of V−N(amine) bonds in V^{IV} and V^{V} complexes with the nitrogen atom *trans* to a doubly bonded oxo group.[29–31] For complexes with the amine function *cis* to an oxo group, bond lengths in the range of 2.13–2.21 Å have been reported.[32–34] The upper limit for *d*[V−N(amine)] is about 2.52 Å, as observed in [VO(acac)L′], in which H_2L' is bis-(2-hydroxyethyl)-(*S*/*R*)-1-phenylethylamine.[35] The *d*(V−OMe) distances of 1.799 and 1.787 Å are within the expected range,[36] as are the bonds to the remaining functions.

Solution studies: In the ^{51}V NMR spectra, the observation of more than one signal in the range typical of five-coordinate vanadium complexes with an O_4N donor set,[37] with the main components for compound **6** at $\delta = -420$, -447, and -457 ppm (Figure 2), suggests the presence of isomers in solution. Variations in the solvent (CH_2Cl_2, toluene, THF, 2-Me-THF) did not cause variation in the signal pattern or in

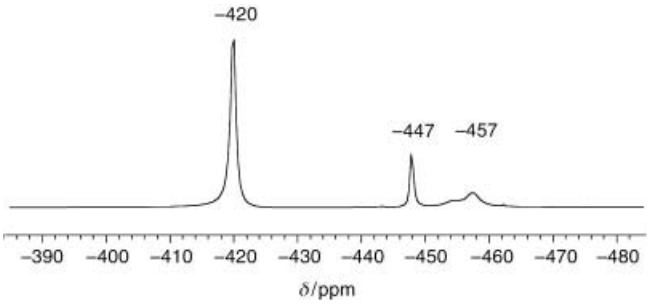
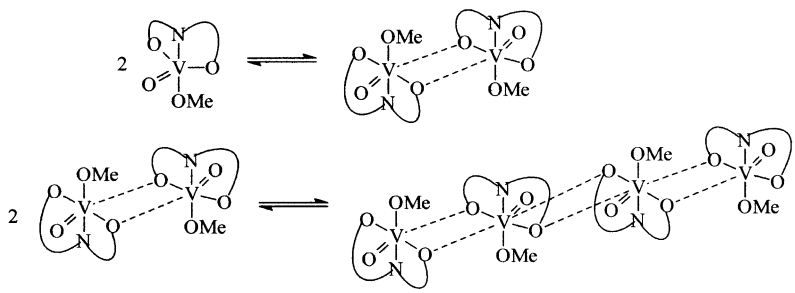


Figure 2. ^{51}V NMR spectrum of **6** in $CDCl_3$ at room temperature. See text for discussion.

their ratio; coordination of solvent molecules to the complex in a sixth position can therefore be excluded. Note that even the polar alcohols employed in the preparation did not lead to the formation of a six-coordinate complex. An equilibrium between structural isomers is possibly responsible for the signals at $\delta = -420$ and -447 (see the discussion for complex **5** below). In addition, dimers and/or oligomers in equilibrium with the monomer (Scheme 3; dashed lines represent weak bonds[39]) may provide additional signals in the higher field region. Alkoxovanadium compounds tend to associate into dimers/oligomers through alkoxo bridges.[38–41] This notion is corroborated here by the ^{51}V NMR analyses of solutions of **6** at different concentrations: an increase in concentration increases the integral intensity of the signal at $\delta = -457$ at the expense of the other signals. For entropic reasons these equilibria should be directed towards the monomer; we therefore assign the predominant resonance signal at $\delta = -420$ to the monomer. The ^{1}H NMR spectrum (Figure 3) seems to validate this thesis; the signals corresponding to complex **6** have been marked with an asterisk, while those marked with an arrow should be attributed to the dimeric (or oligomeric) species. The ratio between monomer and dimer is the same as found in the ^{51}V NMR spectra.

Further insight into the equilibrium situation was obtained by a variable-temperature NMR analysis of complex **5**, the



Scheme 3. Equilibrium between the monomer and dimers and/or oligomers.

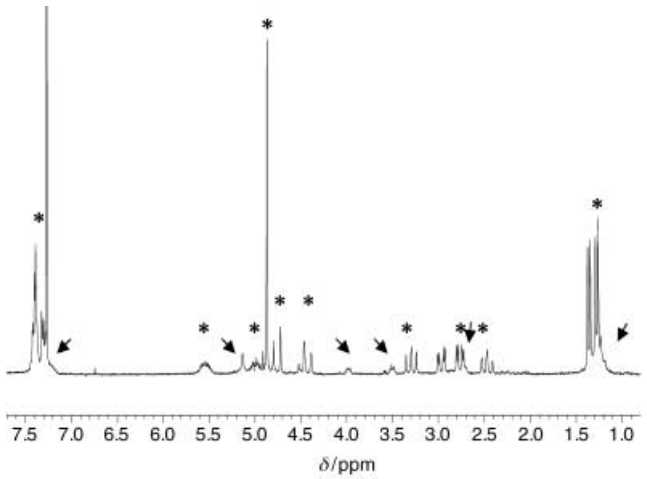


Figure 3. ^{1}H NMR spectrum of **6** in $CDCl_3$ at room temperature. The resonances indicated by asterisks and arrows are assigned to monomers and dimers (or oligomers) of **6**, respectively (cf. Scheme 3).

^{51}V and ^{1}H NMR spectra of which in chloroform and THF show broad signals at ambient temperature. Figure 4 shows the ^{51}V NMR spectra in THF in the 193 to 323 K range, affirming an exchange process involving the species characterized by the two main signals at $\delta = -411$ and -453.

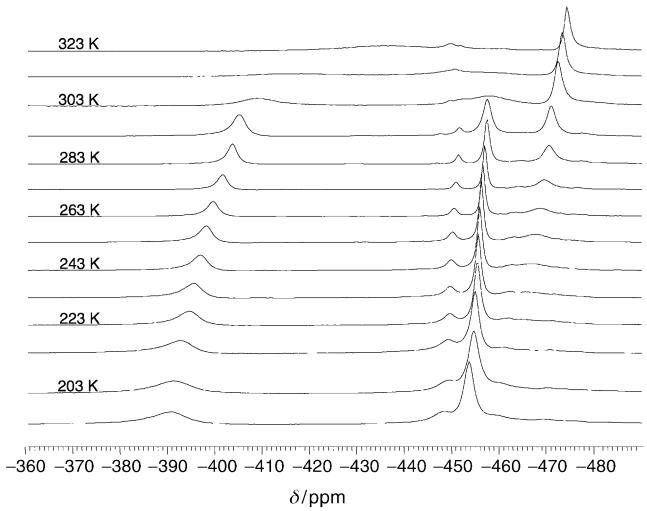
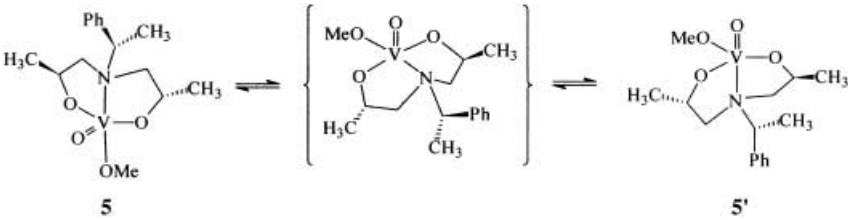


Figure 4. Variable-temperature ^{51}V NMR spectra of **5** in [D_8]THF. The signals at $\delta = -391$ and -451 (193 K) [$\delta = -411$ and -453 at 292 K] are taking part in an exchange equilibrium (Scheme 4). The signal at $\delta \approx -470$, which is particularly broad at low temperatures, presumably corresponds to a larger (i.e., oligomeric) species of **5** (Scheme 3). The sharpening of the signals with rising temperature is a consequence of decreasing quadrupolar relaxation (decreasing molecular correlation time) with increasing temperature.

Beyond 303 K, coalescence is reached. We suggest an equilibrium between the two isomers **5** and **5′** as shown in Scheme 4, coming about through a rearrangement in the coordination sphere through a tetragonal-pyramidal transient. Compounds **5**/**5′** and **6** differ in as far as in **5**/**5′** there is an additional methyl group on the carbon atom adjacent to the nitrogen atom, which apparently slows down the geometrical rearrangement to the extent to which the two species in equilibrium can be detected in the NMR spectra. The signal at lower field should be attributable to the species **5′**, with reference to data reported in the literature for trigonal-bipyramidal vanadium complexes with N(amine) *trans* to the oxo group.[29] The presence of two isomers is confirmed by the ^{1}H NMR spectra (Figure 5): the signals at $\delta = 5.05$ and 4.52 assigned to V-OCH_3, in an approximate ratio of 1:1, coalesce at about 280 K (not shown). Partial ligand dissociation can be excluded on the basis of the ^{1}H NMR pattern. Chemical exchange is further confirmed by the ^{51}V NMR EXSY spectrum of **5** in $CDCl_3$ solution, taken at room temperature (Figure 6).



5 5′

Scheme 4. Equilibrium between the two isomers **5** and **5′**.

Catalytic oxidation of sulfides: Vanadium complexes bearing amino alcohol ligands have not so far been employed as catalysts in the enantioselective oxidation of organic sulfides. There are a few reported examples of vanadium catalysts with chiral Schiff base ligands, in which the asymmetric component is supplied by the amine component.[24–26] These catalysts have usually been employed in situ (i.e., as mixtures of a vanadium precursor and the ligand), with hydrogen peroxide or alkyl hydroperoxides as oxidant. In the oxidation reactions reported here, alkyl hydroperoxides (cumyl hydroperoxide (CHP), and *tert*-butyl hydroperoxide (TBHP)) have been used, because the reactions had to be carried out in organic solvents, due to the water sensitivity of the catalysts. The reactions have been conducted with the sulfides and oxidants at 0.1M, and the catalyst at 0.01M concentrations in 1,2-dichloroethane. The results are summarized in Table 2 for methyl *p*-tolyl sulfide and CHP and varying catalysts, and in Table 3 for complex **5** as the catalyst with varying sulfide and oxidant. For the overall reaction, see Scheme 5.

With methyl *p*-tolyl sulfide and CHP, the reactions proceeded with a turnover of 100% (related to the oxidant). Along with the sulfoxide as the main product, obtained with the same absolute configuration as the catalyst, some sulfone is also formed. Figure 7 represents the reaction path as a function of time for complex **5** as the catalyst. The *ee* (about 31% (*S*)) remains constant during the complete oxidation process. The reaction is thus kinetically controlled (i.e., there is no chiral distinction for the oxidation of the sulfoxide to the sulfone), contrasting with other catalytic sulfoxidation systems such as those using amino alcoholates of Ti^{IV} and Zr^{IV}.[42]

Compounds **5** and **8**—as compared to **6** and **7**—contain an additional chiral center, and this is possibly responsible for the better chiral discrimination (Table 2). Of the reactions catalyzed by **6** and **7** (i.e., the complexes with only two chiral

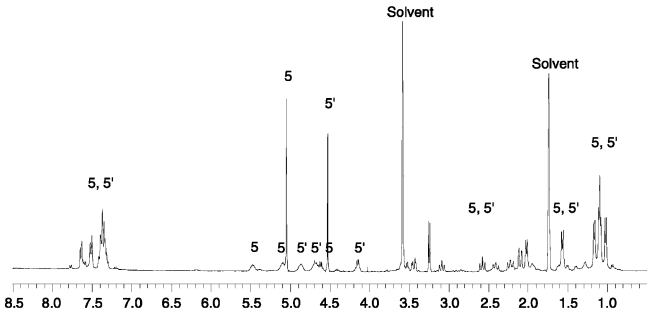


Figure 5. ^{1}H NMR spectrum of **5** in [D$_8$]THF. For assignments cf. Scheme 4. The signals at $\delta = 5.05$ and 4.52 correspond to V-OCH_3.

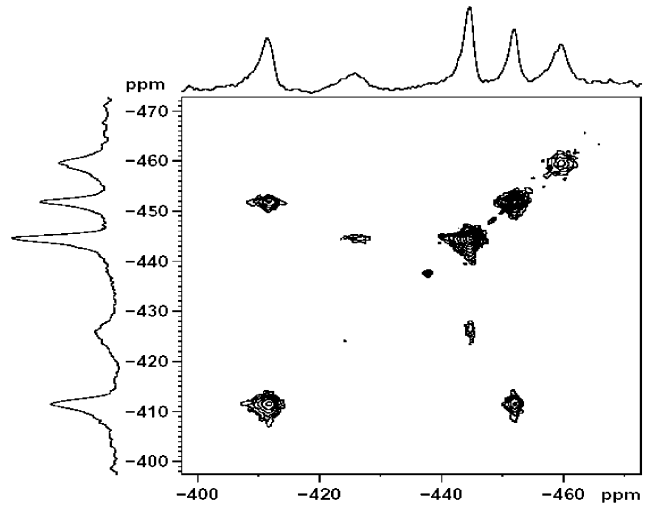


Figure 6. Room temperature ^{51}V EXSY spectrum of complex **5** in $CDCl_3$, at a mixing time of 2 ms, showing the exchange correlation between the signals at $\delta = -411$ and -453 and (less pronounced) the two inner signals at $\delta = -426$ and -444.

Table 2. Oxidation of methyl *p*-tolyl sulfide with CHP in the presence of varying catalysts.

Entry	SO:SO$_2$[a]	*ee* [%][b]	Turnover [%][c]	Time [min]	Catalyst
1	85:15	31.2 (*S*)	100	150	**5**
2	72:28	23.0 (*S*)	100	720	**6**
3	94:6	11.0 (*S*)	100	540	**7**
4	88:12	26.0 (*R*)	100	120	**8**
5	94:6	25.0 (*R*)	100	30	VOL4(O*i*Pr)[d]

[a] determined by GC analysis. [b] Determined by HPLC analysis. [c] Related to the oxidant. [d] Complex prepared in situ by treatment of VO(O*i*Pr)$_3$ with H$_2$L4.

Table 3. Oxidation of alkyl aryl sulfides by organic peroxides in the presence of catalyst **5**.[a]

Entry	Sulfide	Oxidant	SO:SO$_2$	*ee* [%] (*S*)	Turnover [%]	Time [min]
1	MeS*p*Tol	CHP	85:15	31.2	100	150
2	BzSPh	CHP	79:21	23.6	100	270
3	MeS*p*Tol	TBHP	100:0	24.8	58	120
4	BzSPh	TBHP	87:13	4.7	72	120

[a] Compare legend to Table 2. CHP = cumyl hydroperoxide; TBHP = *tert*-butyl hydroperoxide.

centers), the oxidation proceeds with a better *ee* in the case of **6**, which is the compound with less steric hindrance.

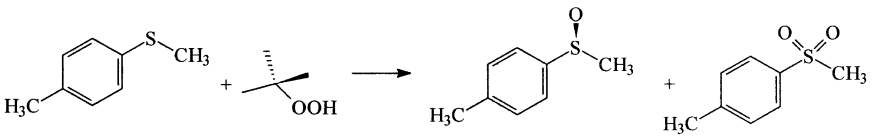
In an attempt to elucidate the mechanism operative in chiral recognition, we studied the asymmetric oxidation of two different sulfides—methyl *p*-tolyl and benzylphenyl sulfide—with two peroxides (CHP and TBHP) exhibiting different steric conditions, in the presence of **5** as the catalyst (Table 3), in more detail. In the case of the MeS*p*Tol (Table 3, entries 1 and 3), better results both in terms of turnover and in *ee* were obtained with CPH. The bulky *tert*-butyl group in TBHP probably creates an intermediate peroxo species that does not allow the substrate to approach with the appropriate orientation. If we consider the same oxidant, CHP, but two different substrates (Table 3, entries 1 and 2), better discrimination between the two prochiral faces of the sulfide is observed as the two residues on the sulfur are unbalanced, (i.e., in the case of MeS*p*Tol). This observation is markedly accentuated with THBP as oxidant (Table 3, entries 3 and 4); here, the *ee* drops from 24.8 to 4.7%. The selectivity with respect to a high percentage of sulfoxide in the sulfoxide/sulfone mixture is particularly pronounced for catalyst **7** (with methyl groups on the ethanol arms) and the in situ system VO(O*i*Pr)$_3$/H$_2$L4 (with phenyl groups on the ethanol arms) (Table 2, entries 3 and 5). The very short reaction time (30 min for 100% consumption of the oxidant) in the case of the in situ system may be accounted for by the better accessibility for the ligand, the oxidant and/or the substrate in four-coordinate VO(O*i*Pr)$_3$, although this unprecedented observation, which may be related to the "ligand accelerating effect in catalysis",[43] still needs to be explored.

A possible mechanism for the catalysis, depicted in Scheme 6, is based on the proposal that a peroxo intermediate with the peroxide coordinating to vanadium in the η^2 mode is formed, consistent with what is known of peroxovanadium complexes.[12, 44–47]

The formation of a peroxo intermediate is corroborated by ^{51}V NMR spectra (Figure 8). This intermediate has been detected in methanolic solutions of [VO(O*i*Pr)L4], containing [VO(OMe)L4] (**8**) treated with CHP, as well as in solutions containing the precursor components [VO(O*i*Pr)$_3$ + H$_2$L4] and CHP. Along with the two main signals for **8** and [VO(O*i*Pr)L4], respectively, the spectra each show a new signal at -510, which is only present if the peroxide is added and is thus assigned to [VO(O$_2$R)L4], formed by exchange of the isopropoxo or methoxo ligand by RO$_2^-$. In agreement with what one would expect,[37] the shielding in six-coordinate [VO(O$_2$R)L4] is lower than in seven-coordinate monoperoxovanadium complexes by about 100 ppm.[37, 44, 48]

Conclusion

Three five-coordinate oxovanadium(v) complexes, each containing an O_4N donor set consisting of a chiral tridentate amino-bis(alcoholate), a methoxy group, and a basal oxo group, have been characterized. The complexes are essentially trigonal-bipyramidal ($\tau = 0.66 - 0.75$) and so are rare examples of oxovanadium complexes exhibiting this geometry (for a Schiff base complex with a comparable $\tau = 0.70$ see[49]). The



Scheme 5. Catalytic oxidation of sulfides.

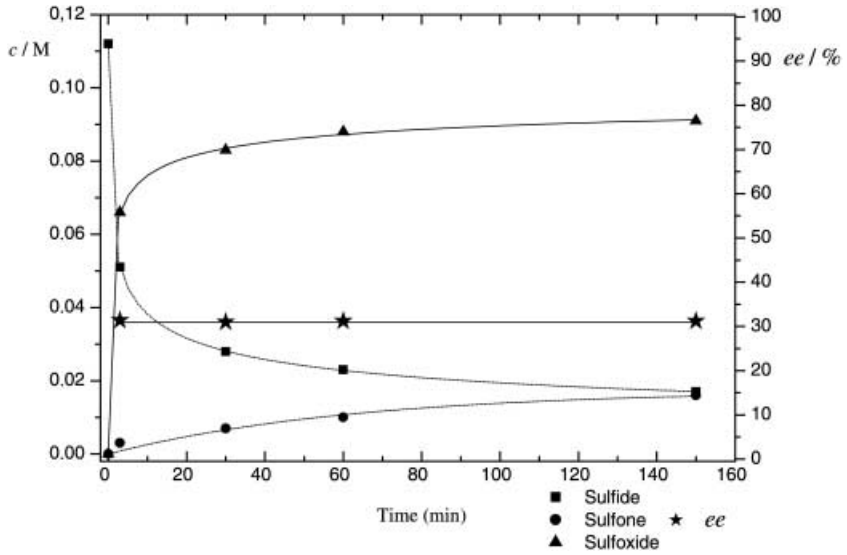
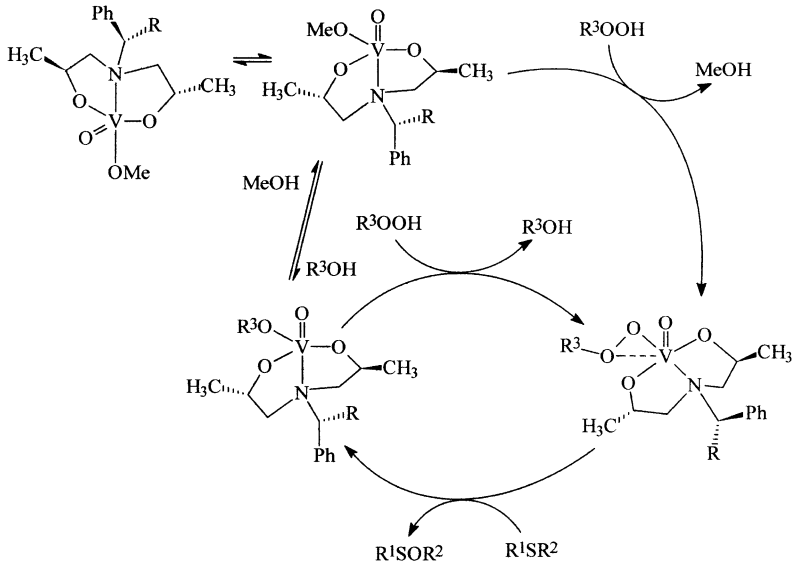


Figure 7. Time dependence of the oxidation of methyl *p*-tolyl sulfide with CHP in the presence of catalyst **5**.



Scheme 6. Possible mechanism for the catalysis.

complexes model specific features of vanadate-dependent haloperoxidases, such as the trigonal-bipyramidal O_4N coordination of V^V and the chiral environment at the active center. Like most of the native enzymes, the model compounds enantioselectively catalyze the peroxide oxidation of prochiral sulfides to chiral sulfoxides. In the optimal system in our series, (*S*)-methyl *p*-tolyl sulfoxide has been obtained with an *ee* of 31% in the presence of catalyst **5** and CHP as the oxidant. The reaction times are in general faster (about 2 h), and the turnover and selectivities (with respect to the formation of sulfoxide) better than those seen in other systems containing vanadium-based catalysts.[24–26] The dynamic behavior of our complexes (i.e., equilibria between stereoisomers and possibly also monomers/oligomers) is

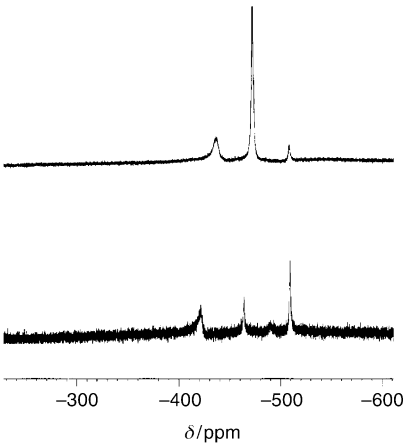


Figure 8. ^{51}V NMR spectra of **8** dissolved in $CDCl_3$ at 273 K, treated with CHP (bottom), and of $VO(OiPr)_3$ + H_2L4 + CHP (top). The signal indicated at −510 belongs to the peroxo complex $[VO(O_2R)L4]$, and the two low-field signals to [VO(OMe)L4] (**8**) and [VO(O*i*Pr)L4], respectively.

likely to be responsible for the relatively inefficient (with respect to the *ee)* asymmetric induction. The degree of enantioselectivity is also influenced by the substrate and the oxidant in that the less "symmetrical" sulfides (methyl *p*-tolyl versus phenyl benzyl sulfide) and the less bulky peroxide (cumyl versus *tert*-butyl hydroperoxide) gave the better *ee* values. The latter factor suggests the formation of an intermediate with the hydroperoxide coordinated to the catalyst center, an intermediate detectable by ^{51}V NMR in the systems **8** + CHP and $VO(OiPr)_3$ + H_2L4 (**4**) + CHP.

Experimental Section

Materials and instrumentation: All solvents and liquid reagents used in this work were stored under nitrogen over molecular sieves (4 Å). Dichloromethane was distilled over CaH_2. 1,2-Dichloroethane was treated with concentrated sulfuric acid (four times with 100 mL of H_2SO_4 per 1 L of dichloroethane), washed with water, dried overnight with $CaCl_2$, and distilled over P_2O_5. Methanol was distilled over sodium. Cumyl hydroperoxide (Fluka, 80% in cumene) was stored at 0 °C. *tert*-Butyl hydroperoxide (Fluka) was purified by distillation at reduced pressure (b.p. = 33 °C/16 mm Hg) and stored at 0 °C. Benzyl phenyl sulfide was prepared according to reference [43] by alkylation of the corresponding thiol, and its identity was established by ^1H NMR spectroscopy and elemental analysis. Silica gel 60 (Mecherey–Nagel, 230–400 mesh ASTM), $[VO(OiPr)_3]$ (Aldrich), (*S*)-(−)propene oxide (Fluka), (*S*)-(−)1-phenylethylamine, isopropylamine, 4-methyl-benzophenone (Acros Organics), benzylamine (Merck), benzophenone (Carlo Erba), methyl *p*-tolyl sulfide, and bis(*n*-butyl) sulfide (Aldrich) were used as obtained. The ligand H_2L4 (**4**) and the complex (*R*,*R*,*R*)-[VO(OMe)L4] · ½CH_3OH (**8** · ½CH_3OH) were prepared as described previously.[50]

The quantitative product analyses for the catalytically conducted sulfide oxidations were carried out with a Hewlett–Packard 5890 series II chromatograph, equipped with a capillary column with a FFAP EC-1000 stationary phase (30 m × 0.25 mm, film thickness 0.25 μm). The instrument conditions for the analysis were as follows: initial temperature 55 °C for 1 min, rate = 15 °C min^{-1}, final temperature 200 °C for 30 min. The enantiomeric excesses of the sulfoxides were determined by HPLC analysis, with a Shimadzu LC-10AT chromatograph, UV Shimadzu SPD-10A (λ = 241 nm) detector, and a C-R5A Shimadzu chromatopac integrator. The chromatograph was fitted with a chiral column packed with Lichrosorb S 100, (*R,R*)-diaminocyclohexane DNB spherical 250 × 4.0 mm. The eluent employed was a mixture of *n*-hexane/2-propanol 9:1, flow = 0.6 mL min^{-1}, pressure = 17 kg cm^{-2}. The retention times of the methyl *p*-tolyl sulfoxide were 16.2 min (*R* enantiomer) and 18.7 min (*S* enantiomer). The retention times of the benzyl phenyl sulfoxide were 23.9 min (*R* enantiomer) and 30.2 min (*S* enantiomer).

IR spectra were obtained on a Perkin–Elmer FT 1720 spectrometer. NMR spectra were measured on a Bruker AM 360 (at 94.726 MHz for ^{51}V, and 360.134 MHz for ^1H) or on a Varian Gemini 200 instrument (at 52.577 MHz for ^{51}V, 50.285 MHz for ^{13}C, and 199.962 MHz for ^1H) with the usual spectrometer settings. 2D EXSY spectroscopy: the ^{51}V homonuclear exchange (EXSY) experiments were conducted on a Bruker Avance 400 instrument (at 105.198 MHz) by use of the standard NOESYPH pulse sequence ($90° - \tau_1 - 90° - T_m - 90°$), 2 ms mixing time. All ^{51}V NMR chemical shifts are referenced against external $VOCl_3$.

Mass analysis measurements were conducted on a Mariner instrument (Perspective Biosystem), in the electron spray ionization mode and with a time-of-flight analyzer (ESI/TOF). The sample concentration was 2×10^{-5} M in methanol. Mobile phase: methanol; rate 5 μL min^{-1}.

X-ray structure analyses were carried out at 153(2) K with $Mo_{K\alpha}$ irradiation (λ = 0.71073 Å, graphite monochromator) on a Smart Apex CCD diffractometer. Hydrogen atoms were calculated in idealized positions and included in the last cycles of refinement. Absorption corrections were not performed. For crystal data and structure refinement see Table 4

CCDC-176660 (**5**) and CCDC-187671 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Table 4. Crystal data and structure refinement for **5** and **6**.

	VO(OMe)L1 (**5**)	VO(OMe)L2 (**6**)
empirical formula	$C_{15}H_{24}NO_4V$	$C_{14}H_{22}NO_4V$
formula weight [g mol^{-1}]	333.29	319.27
crystal system	monoclinic	orthorhombic
space group	*P*2(1)	*P*2(1)2(1)2(1)
unit cell dimensions		
a [Å]	8.2684(3)	10.1615(10)
b [Å]	10.9118(4)	13.4671(13)
c [Å]	8.9816(3)	33.682(3)
β [°]	95.0470(10)	
volume [Å^3]	807.21(5)	4609.3(8)
Z	2	12
ρ_{calcd} [g^{-1} cm^{-3}]	1.371	1.380
μ [mm^{-1}]	0.629	0.657
F(000)	352	2016
crystal size [mm^3]	0.30 × 0.10 × 0.10	0.60 × 0.57 × 0.41
θ range for data collection [°]	2.28 to 32.53	2.36 to 27.50
index ranges	$-12 < h < 12$	$-13 < h < 11$,
	$-16 < k < 16$	$-17 < k < 17$
	$-13 < l < 13$	$-43 < l < 33$
reflections collected	22075	56674
independent reflections, (R_{int})	5677 (0.0293)	10570 (0.2201)
completeness to θ [%]	98.9	99.9
data/restraints/parameters	5677/1/190	10570/0/541
goodness of fit	1.024	1.061
final *R* ind. [$I > 2\sigma(I)$]		
*R*1	0.0311	0.0515
*wR*2	0.0724	0.1146
R indices (all data)		
*R*1	0.0337	0.0576
*wR*2	0.0731	0.1191
absolute structure param.	−0.002(12)	0.048(17)
largest diff. peak and hole [eÅ^{-3}]	0.479 and −0.279	0.773 and −0.512

General procedure for the catalytically conducted sulfide oxidations

Oxidation of methyl *p*-tolyl sulfide (cf. Table 2, and entries 1 and 3 in Table 3 in the Results and Discussion section): Methyl *p*-tolyl sulfide

(15.48 mg, 0.11 mmol), complex **5** (3.66 mg, 0.01mmol), and benzophenone (12.75 mg, 0.07mmol) as internal standard were dissolved in anhydrous 1,2-dichloromethane in a 1 mL flask. The solution was then cooled to 0 °C. With stirring and under a nitrogen atmosphere, cumyl hydroperoxide (20 μL, 0.11 mmol) (Table 2, entry 1) or *tert*-butyl hydroperoxide (5 ML, 0.11 mmol) was added (Table 3, entry 3). For entries 2 and 3 in Table 2, the same procedure as for entry 1 was employed, with complex **6** (3.19 mg, 0.01 mmol, entry 2), complex **7** (2.71 mg, 0.01 mmol, entry 3), or complex **8** (5.12 mg, 0.01 mmol, entry 4).

Oxidation of benzyl phenyl sulfide (Table 3, entries 2 and 4): Benzyl phenyl sulfide (20.03 mg, 0.11 mmol), complex **5** (3.66 mg, 0.01 mmol), and 4-methyl-benzophenone (20.68 mg, 0.10 mmol) as internal standard were dissolved in anhydrous 1,2-dichloromethane in a 1 mL flask. After the mixture had been cooled to 0 °C, cumyl hydroperoxide (20 μL, 0.11 mmol, Table 3, entry 2) or *tert*-butyl hydroperoxide (5 μL, 0.11 mmol, Table 3, entry 4) was added with stirring, under a nitrogen atmosphere.

After defined intervals of time, 50 μL portions were removed from the reaction mixtures and immediately quenched by addition to an excess of bis(*n*-butyl) sulfide, and the product spectrum was analyzed by GC and HPLC (determination of the enantiomeric excess; see above).

Preparation of compounds

(*S*,*S*)-Bis(2-hydroxy-propyl)-(*S*)-1-phenyl-ethylamine, (PhMeCH)N(CH$_2$CHMeOH)$_2$ (H$_2$L1), 1: (*S*)-(−)-Propene oxide (1.00 g, 17.2 mmol) and (*S*)-(−)phenyl-ethylamine (1.04 g, 8.6 mmol) were placed in a 5 mL round-bottomed flask. The reaction mixture was stirred at 40 °C for four days. The crude product obtained was purified by flash chromatography on silica gel, with hexane/ethyl acetate 1:1 as eluent. The product was obtained as a pale yellow oil. Yield 1.47 g (72 %). ^{1}H NMR (CDCl$_3$): δ = 7.42 – 7.28 (m, 5H; aromatic), 4.06 – 3.98 (q, J = 6.8 Hz, 1H; N−C*H*Ph−CH$_3$), 3.90 – 3.74 (m, 2H; CH$_2$−C*H*CH$_3$−OH), 2.61 – 2.19 (dd, J = 13.4 and 2.4 Hz, 2H; N−C*H*$_2$−CHPhOH), 2.58 (b, 2H; CHCH$_3$−O*H*), 1.38 (d, J = 6.8 Hz, 3H; NCHPh−C*H*$_3$), 1.08 (d, J = 6.3 Hz, 6H; CHC*H*$_3$–OH) ppm; ^{13}C NMR (CDCl$_3$): δ = 128.50, 127.78, and 127.27 (aromatic carbons), 64.45 (CH$_2$−*C*HMe−OH), 58.10 (N−*C*HPhCH$_3$), 57.95 (N−*C*H$_2$−CHPhOH), 20.05 (CH*C*H$_3$OH), 10.99 (NCHPh−*C*H$_3$) ppm; IR (NaCl): $\tilde{\nu}$ = 3400 (ν(OH)), 3086, 3062, and 3029 (ν(CH)), 2855 (ν(R$_2$N−CH)), 1602, 1495, and 1451 (CC ring stretch), 1071 (ν(CO)), 738 and 701 (δ(CH) and δ(CC)) cm^{-1}; elemental analysis calcd (%) for C$_{14}$H$_{27}$NO$_2$ (237.33): C 73.80, H 9.56, N 7.81; found: C 73.33, H 9.56, N 7.83.

(*S*,*S*)-Bis(2-hydroxypropyl)benzylamine, (PhCH$_2$)N(CH$_2$CHMeOH)$_2$ (H$_2$L2), 2: (*S*)-(−)-Propene oxide (1.66 g, 28.5 mmol) and benzylamine (1.51 g, 14.3 mmol) dissolved in dichloromethane (5 mL) were placed in a 10 mL round-bottomed flask. The reaction mixture was stirred at 40 °C for seven days. The crude product obtained was purified by flash chromatography on silica gel, with hexane/ethyl acetate 7:3 as eluent. The product was obtained as a pale yellow oil. Yield 2.51 g (78.6 %). ^{1}H NMR (CDCl$_3$): δ = 7.35 – 7.28 (m, 5H; aromatic), 3.94 – 3.78 (m, 2H; CH$_2$−C*H*CH$_3$−OH), 3.89 (d, J = 13.6 Hz, 1H; N−C*H*$_2$Ph), 3.51 (d, J = 13.6 Hz, 1H; N−C*H*$_2$Ph), 2.65 (br, 2H; CHCH$_3$−O*H*), 2.45 (d, J = 6.1 Hz, 4H; N−C*H*$_2$−CHMeOH), 1.10 (d, J = 6.1 Hz, 6H; CHC*H*$_3$−OH) ppm; ^{13}C NMR (CDCl$_3$): δ = 138.38, 128.94, 128.50, and 127.36 (aromatic carbons), 63.97 (CH$_2$−*C*HMe−OH), 62.07 (N−*C*H$_2$−CHMeOH), 59.76 (N−*C*H$_2$Ph), 20.26 (CH*C*H$_3$OH); IR (NaCl): $\tilde{\nu}$ = 3399 (ν(OH)), 3085, 3062, and 3027 (ν(CH)), 2822 (ν(R$_2$N−CH)). 1602, 1495, and 1453 (CC ring stretch), 1055 (ν(CO)), 742 and 699 (δ(CH) and δ(CC)) cm^{-1}; elemental analysis calcd (%) for C$_{13}$H$_{21}$NO$_2$ (223.32): C 69.92, H 9.48, N 6.27; found: C 69.63, H 9.43, N 6.52.

(*S*,*S*)-Bis(2-hydroxypropyl)isopropylamine, {(CH$_3$)$_2$CH}N(CH$_2$CHMeOH)$_2$ (H$_2$L3), 3: (*S*)-(−)-Propene oxide (1.660 g, 28.05 mmol) and isopropylamine (0.845 g, 14.3 mmol) were dissolved in 1,2-dichloromethane (5 mL). The reaction mixture was stirred at 40 °C for four days. The crude product was purified as described for **2**. Compound **3** was obtained as a pale yellow oil. Yield 1.47 g (71.4 %). ^{1}H NMR (CDCl$_3$): δ = 3.79 (br, 2H; CHCH$_3$−O*H*), 3.72 – 3.56 (m, 2H; CH$_2$−C*H*CH$_3$−OH), 2.95 – 2.75 (heptet, J = 6.6 Hz, 1H; N−C*H*(CH$_3$)$_2$), 2.34 – 2.06 (m, 4H; N−C*H*$_2$−CHMeOH), 1.01 – 0.98 (d, J = 5.86 Hz, 6H; CHC*H*$_3$−OH), 0.96 – 0.93 (d, J = 6.6 Hz, 3H; N−CH(C*H*$_3$)$_2$), 0.84 – 0.81 (d, J = 6.6 Hz, 3H; N−CH(C*H*$_3$)$_2$) ppm; ^{13}C NMR (CDCl$_3$): δ = 63.90 (CH$_2$−*C*HMe−OH), 57.69 (N−*C*H$_2$−CHMeOH), 50.65 (N−*C*H(CH$_3$)$_2$), 20.42 (N−CH(*C*H$_3$)$_2$), 20.07 (CH*C*H$_3$OH), 15.17 (N−CH(*C*H$_3$)$_2$) ppm; elemental analysis calcd (%) for C$_9$H$_{21}$NO$_2$ (117.19): C 61.68, H 7.99, N 7.99; found: C 60.98, H 12.03, N 7.51.

(*S*,*S*,*S*)-[VO(OMe)L1], 5: Ligand **1** (0.5055 g, 2.13 mmol) was dissolved in 1,1-dichloromethane (15 mL) in a double-necked 50 mL round-bottomed flask. Oxo-tris(isopropoxo)vanadium(v) (0.4954 g, 2.03 mmol) dissolved in dichloromethane (10 mL) was added dropwise to this solution. During the addition, the color changed to yellow. After 30 min stirring under nitrogen, the solvent was removed under vacuum. The product ([VO(O*i*Pr)L1]) was obtained quantitatively as a yellow-green solid, which was recrystallized from methanol to yield **5** quantitatively. Crystals were grown by keeping a concentrated methanolic solution at −20 °C for about two weeks. ^{51}V NMR ([D$_8$]toluene): δ = −421.0, −455.4, −463.1, −473.7 ppm; ([D$_8$]THF): δ = −404.5, −450.9, −456.7, −470.2 ppm; (CDCl$_3$): δ = −412.7, −445.4, −452.3, −460.7 ppm; IR (KBr,): $\tilde{\nu}$ = 2969 and 2929 (ν(CH)), 2789 (ν(R$_2$N−CH)), 1636 and 1451 (CC ring stretch), 1090 (ν(CO)), 968 (ν(VO)), 746 and 706 (δ(CH) and δ(CC)) cm^{-1}; MS: *m*/*z* (%): 333.9 (42) [**5**+H]$^+$, 355.9 (100) [**5**+Na]$^+$; elemental analysis calcd (%) for C$_{15}$H$_{24}$NO$_4$V (333.11): C 54.05, H 7.26, N 4.20; found: C 53.31, H 7.12, N 4.06.

(*S*,*S*)-[VO(OMe)L2], 6: Complex **6** was prepared according to the procedure described for **5** by treatment of ligand **2** (0.790 g, 3.53 mmol) with VO(O*i*Pr)$_3$ (0.8227 g, 3.30 mmol). The product, [VO(*i*PrO)L2], was obtained as a yellow-green solid, and was recrystallized from methanol to yield **6** quantitatively. Crystals were grown by keeping a concentrated methanolic solution at −20 °C for about two weeks. ^{1}H NMR (CDCl$_3$): δ = 7.40 – 7.28 (m, 5H; aromatic), 5.55 (m, 1H; CH$_2$C*H*CH$_3$−OV), 4.99 (m, 1H; CH$_2$C*H*MeO−V), 4.87 (s, 3H; C*H*$_3$O−V), 4.75 (d, J = 15.0 Hz, 1H; NC*H*$_2$Ph), 4.42 (d, J = 15.0 Hz, 1H; NC*H*$_2$Ph), 2.88 (m, 4H; NC*H*$_2$CHMeO), 1.36 (d, J = 6.1 Hz, 3H; CHC*H*$_3$OV), 1.27 (d, J = 5.9 Hz, 3H; CHC*H*$_3$O−V) ppm; ^{13}C NMR (CDCl$_3$): δ = 133.07, 131.05, and 128.70 (aromatic carbons), 81.10 (CH$_2$*C*HMeO−V), 80.60 (CH$_2$*C*HMeO−V), 70.76 (*C*H$_3$O−V), 66.83 (N*C*H$_2$Ph), 62.00 (N*C*H$_2$CHMeO−V), 59.12 (N*C*H$_2$CHMeO−V), 21.42 (CH*C*H$_3$O−V), 21.24 (CH*C*H$_3$O−V) ppm; ^{51}V NMR (CDCl$_3$): δ (relative integral intensity) = −419.8 (1.0), −447.5 (0.2), −457.5 (0.2) ppm; IR (KBr): $\tilde{\nu}$ = 3028, 2969, and 2926 (ν(CH)), 2867, (ν(R$_2$N−CH)), 1630, 1494, and 1454 (CC ring stretch), 1067 (ν(CO)); 9.58 and 974 (ν(VO)), 755 and 707 (δ(CH) and δ(CC)) cm^{-1}; elemental analysis calcd (%) for C$_{14}$H$_{22}$NO$_4$V (319.27): C 52.67, H 6.95, N 4.39; found: C 50.95, H 6.74, N 4.14.

(*S*,*S*)-[VO(OMe)L3], 7: Complex **7** was prepared by the procedure described for **5**, by treatment of ligand **3** (0.790 g, 3.53 mmol) with oxo-tris(isopropoxo)vanadium(v) (0.8227 g, 3.30 mmol). The primary product, [VO(*i*PrO)$_3$L3], was quantitatively transesterificated with methanol to yield **7** as a yellow oil. Yield = 0.6149g (68.7 %). ^{1}H NMR (CDCl$_3$): δ = 5.26 (br, 1H; CH$_2$CHCH$_3$−OV), 5.03 (br, 1H; CH$_2$CHMeO−V), 4.81 (br, 3H; CH$_3$O−V), 3.67 – 2.18 (m, 5H; NCH$_2$CH and NCH(CH$_3$)$_2$), 1.36 – 1.33 (d, J = 5.8 Hz, 6H; CH$_2$CHCH$_3$O−V), 1.29 – 1.24 (d, J = 5.8 Hz, 6H; NCH(CH$_3$)$_2$) ppm; ^{51}V NMR (CDCl$_3$): δ (relative integral intensity) = −418.7 (1), −444.3 (0.1), −454.5 (0.3) ppm; elemental analysis calcd (%) for C$_{10}$H$_{22}$NO$_4$V (271.23 g mol^{-1}): C 44.28, H 8.18, N 5.16; found: C 43.71, H 7.74, N 5.07.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (grant RE 431/13 – 4), the European Union (COST D12 – 0027/99), the Ufficio Formazione *post lauream*, University of Padova, the Deutsche Akademische Austauschdienst (grant to G.S.), and the Fonds der Chemischen Industrie.

[1] R. Wever, *Nature* **1988**, *335*, 501; R. Wever, W. Hemrika, *Vanadium in the Environment* (Ed.: J. O. Nriagu), Wiley, New York, **1998**, *30*, 285 – 305.
[2] A. Butler, J. V. Walker, *Chem. Rev.* **1993**, *93*, 1937 – 1944.
[3] A. Butler, A. H. Baldwin, *Structure & Bonding: Metal Sites in Proteins & Models* (Eds.: P. Sadler, H. A. O. Hill, A. Thompson), Springer, **1997**, 109 – 131.

[4] H. B. ten Brink, H. E. Schoemaker, R. Wever, *Eur. J. Biochem.* **2001**, *268*, 132 – 138, and references therein.
[5] H. B. ten Brink, A. Tuynman, H. L. Dekker, W. Hemrika, Y. Izumi, T. Oshiro, H. E. Schoemaker, R. Wever, *Inorg. Chem.* **1998**, *37*, 6780 – 6784.
[6] H. B. ten Brink, H. L. Holland, H. E. Schoemaker, H. von Lingen, R. Wever, *Tetrahedron Asymmetry* **1999**, *10*, 4563 – 4572.
[7] M. A. Andersson, A. Willets, S. G. Allenmark, *J. Org. Chem.* **1997**, *62*, 8455 – 8458.
[8] M. A. Andersson, S. G. Allenmark, *Tetrahedron* **1998**, *54*, 15293 – 15304.
[9] J. S. Martinez, G. L. Carroll, R. A. Tschirret-Guth, G. Altenhoff, R. D. Little, A. Butler, *J. Am. Chem. Soc.* **2001**, *123*, 3289 – 3294.
[10] A. Messerschmidt, R. Wever, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 392 – 396.
[11] M. Weyand, H.-J. Hecht, M. Kieß, M.-F. Liaud, H. Vilter, D. Schomburg, *J. Mol. Biol.* **1999**, *293*, 595 – 611.
[12] A. Messerschmidt, R. Prade, R. Wever, *Biol. Chem.* **1997**, *378*, 309 – 315.
[13] M. Časný, D. Rehder, H. Schmidt, H. Vilter, V. Conte, *J. Inorg. Biochem.* **2000**, *80*, 157 – 169
[14] T. L. Poulus, J. Kraut, *J. Biol. Chem.* **1980**, *255*, 8199 – 8205.
[15] C. Kimblin, X. Bu, A. Butler, *Inorg. Chem.* **2002**, *41*, 161 – 163.
[16] M. Časný, D. Rehder, *Chem. Commun.* **2001**, *10*, 921 – 922.
[17] G. Colpas, B. J. Hamstra, J. W. Kampf, V. L. Pecoraro, *J. Am. Chem. Soc.* **1996**, *118*, 3469 – 3478.
[18] A. Butler, *Coord. Chem. Rev.* **1999**, *187*, 17 – 35.
[19] H. B. Kagan, *Asymmetric Oxidation of Sulfides* 2nd ed. (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, ch. 6c.
[20] M. C. Carreño, *Chem. Rev.* **1995**, *95*, 1717.
[21] G. Solladié, *Synthesis* **1981**, 185.
[22] M. C. Andersen, *The Chemistry of Sulfones and Sulfoxides* (Eds.: S. Patai, Z. Rappoport, C. J. M. Stirling), Wiley, Chichester, England, **1988**, ch. 3 and ch. 16.
[23] a) H. L. Holland, F. M. Brown, *Tetrahedron Asymmetry* **1998**, *9*, 535; b) V. Conte, F. Di Furia, G. Licini, *Appl. Catal. A: General* **1997**, *157*, 335 – 361, and references therein.
[24] K. Nakajima, M. Kojima, K. Toriumi, K. Saito, J. Fujita, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 760 – 767.
[25] K. Nakajima, M. Kojima, K. Kojima, J. Fujita, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2620 – 2630.
[26] C. Bolm, F. Bienewald, *Angew. Chem.* **1996**, *108*, 1767 – 1769; *Angew. Chem. Int. Engl.* **1996**, *34*, 1657 – 1659; .
[27] C. Bolm, F. Bienewald, *Synlett.* **1998**, 1327 – 1328.
[28] G. Liu, D. A. Cogan, J. A. Ellman, *J. Am. Chem. Soc.* **1997**, *119*, 9913 – 9914.
[29] D. C. Crans, C. Haojiang, O. P. Anderson, M. M. Miller, *J. Am. Chem. Soc.* **1993**, *115*, 6769 – 6776.
[30] S. Ooi, M. Nishizawa, K. Matzsumoto, K. Saito, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 452 – 457.
[31] M. Mahroof-Tahir, A. D. Keramidas, R. B. Goldfarb, O. P. Anderson, M. M. Miller, D. C. Crans, *Inorg. Chem.* **1997**, *36*, 1657 – 1668.
[32] A. D. Keramidas, M. M. Miller, O. P. Anderson, D. C. Crans, *J. Am. Chem. Soc.* **1997**, *119*, 8901 – 8915.
[33] K. Kawabe, M. Tadokoro, A. Ichimura, Y. Kojima, T. Takino, H. Sakurai, *J. Am. Chem. Soc.* **1999**, *121*, 7937 – 7938.
[34] Y. Chen, Q. Liu, Y. Deng, H. Zhu, H. F. Chen, D. Liao, E. Gao, *Inorg. Chem.* **2001**, *40*, 3725 – 3733.
[35] M. Bashirpoor, H. Schmidt, C. Schulzke, D. Rehder, *Chem. Ber./ Recueil* **1997**, *130*, 651 – 657.
[36] I. D. Brown, D. Altermatt, *Acta Crystallogr. B* **1985**, *41*, 244 – 247.
[37] D. Rehder, C. Weidemann, A. Duch, W. Priebsch, *Inorg. Chem.* **1988**, *27*, 584 – 587.
[38] W. Priebsch, D. Rehder, *Inorg. Chem.* **1990**, *29*, 3013 – 3019.
[39] F. Hillerns, F. Olbrich, U. Behrens, D. Rehder, *Angew. Chem.* **1992**, *104*, 479 – 480; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 447 – 448.
[40] O. W. Howarth, J. R. Trainor, *Inorg. Chim. Acta* **1987**, *127*, L27.
[41] D. C. Crans, F. Jiang, J. Chen, O. P. Anderson, M. M. Miller, *Inorg. Chem.* **1997**, *36*, 1038 – 1047.
[42] a) F. di Furia, G. M. Licini, G. Modena, R. Motterle *J. Org. Chem.* **1996**, *61*, 5175—5177; b) M. Bonchio, G. M. Licini, F. di Furia, S. Mantovani, G. Modena, W. A. Nugent, *J. Org. Chem.* **1999**, *64*, 1326 – 1330.
[43] a) D. J. Berrisford, C. Bolm, K. B. Sharpless, *Angew. Chem.* **1995**, *107*, 1159 – 1171; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1059 – 1070; b) C. Bolm, *Coord. Chem. Rev.* **2003**, *237*, 245 – 256.
[44] H. Mimoun, P. Chaumette, M. Mignard, L. Saussine, J. Fischer, R. Weiss, *Nouv. J. Chim.* **1983**, *7*, 467 – 475.
[45] M. Sivák, M. Madarová, J. Marek, J. Benko, *Chem. Listy* **2000**, *94*, 906 – 907.
[46] V. Conte, F. di Furia, G. M. Licini, *Appl. Catal.* **1997**, *157*, 335 – 361.
[47] L. Kuchta, M. Sivák, J. Marek, F. Pavelčik, M. Časný, *New. J. Chem.* **1998**, *17*, 43 – 46.
[48] H. Schmidt, I. Andersson, D. Rehder, L. Pettersson, *Chem. Eur. J.* **2001**, *7*, 251 – 257.
[49] C. R. Cornman, K. M. Geiser-Bush, S. P. Rowley, P. D. Boyle, *Inorg. Chem.* **1997**, *36*, 6401.
[50] D. Rehder, G. Santoni, G. M. Licini, C. Schulzke, B. Meier, *Coord. Chem. Rev.* **2003**, *237*, 53 – 63.

Received: November 21, 2002
Revised: May 27, 2003 [F4595]