Multinuclear NMR study of the reactive intermediates in enantioselective epoxidations of allylic alcohols catalyzed by a vanadium complex derived from a planar-chiral hydroxamic acid

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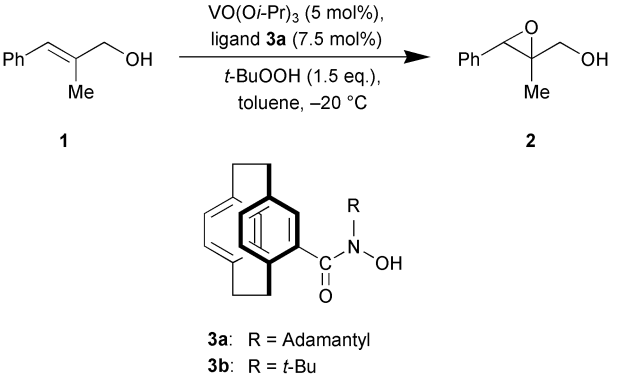
Structure and reactivity of vanadium(v) complexes formed *in situ* in the catalytic system $VO(Oalkyl)_3$/hydroxamic acid/*tert*-butylhydroperoxide (TBHP) have been examined by means of ^{51}V, ^{13}C and ^{17}O NMR spectroscopy. For the first time, reactive vanadium(v) alkylperoxo intermediates in vanadium/hydroxamic acid epoxidations were observed and spectroscopically characterized. With a planar-chiral [2.2]paracyclophane-derived hydroxamate as ligand two diastereomeric alkylperoxo vanadium(v) complexes were formed in a 3:1 ratio. They differ in the relative positioning of the V=O group and the planar-chiral aromatic part. Upon addition of geraniol as substrate, these complexes disappear in a parallel manner, and geraniol epoxide is formed. Probably, the existence of these two diastereomeric complexes and their comparable reactivity account for the observed enantioselectivity level (≤71% ee) and hence sets a fundamental limitation for the use of such ligands in this asymmetric catalysis.

Introduction

In epoxidations of allylic alcohols synthetically useful levels of enantioselectivity were first achieved in 1980 by Katsuki and Sharpless, who introduced a titanium tartrate-based catalytic system with TBHP as oxidant.[1,2] Since then, several other catalysts for stereoselective epoxidations have been developed.[3] Unfortunately, however, most of them have severe limitations in turnover numbers and frequencies, and thus the finding of new catalysts for epoxidation reactions is most desirable.

Vanadium-catalyzed epoxidations of allylic alcohols with TBHP as oxidant are well known,[4–9] and a number of asymmetric versions with chiral vanadium complexes have been developed.[7–9] In 1977 Sharpless and co-workers introduced a protocol which utilized hydroxamates as ligands.[7] As possible reactive intermediates alkylperoxo vanadium(v) complexes were proposed. Since then, several modifications of this process have been described and good enantioselectivities could be reached.[8,9] For example, by using [2.2]paracyclophane-based hydroxamic acid **3a** as ligand in the vanadium-catalyzed epoxidation of allylic alcohol **1**, epoxide **2** was obtained with 71% ee in 85% yield (Scheme 1).[9]

Vanadium(v) alkylperoxo complexes are widely accepted as intermediates in catalytic systems derived from combinations of $[VO(acac)_2]$ and TBHP in the absence[4a–c] or the presence of a ligand.[5a,b,7b,8b] For the corresponding vanadium(v) complex derived from dipicolinic acid, [VO(OO*t*-Bu)(dipic)-(H_2O)], Mimoun and co-workers established the molecular structure by X-ray crystallography.[5] In vanadium/hydroxamic acids/ROOH systems,[7–9] however, the presence of alkylperoxo complexes has been neither observed nor confirmed by any physical methods. Here, we report on a detailed multinuclear NMR spectroscopic study of the vanadium(v) complexes formed in a catalytic system obtained from $VO(Oalkyl)_3$, hydroxamic acid **3b**, and TBHP. The reactive intermediates were identified, and their structure, stability and reactivity were characterized by means of ^{51}V, ^{13}C, ^{17}O NMR spectroscopy.



Scheme 1 Vanadium-catalyzed enantioselective epoxidation with hydroxamic acids **3** as ligands.

Results and discussion

Interaction of hydroxamic acid 3b with the vanadium catalyst precursor [VO(O*n*-Bu)$_3$]

Upon addition of 1 equiv. of hydroxamic acid **3b** to a solution of $VO(On\text{-}Bu)_3$ in CH_2Cl_2, the ^{51}V NMR signal for $VO(On\text{-}Bu)_3$ at $\delta = -594$ ppm disappeared, and the narrow line (width at half-hight $= \Delta\upsilon_{1/2} = 93$ Hz) at −508 ppm indicated the formation of a new vanadium(v) species **4** (Figs. 1a,b). At higher ligand-to-vanadium ratios, the concentration of **4** decreased to form four vanadium(v) complexes further denoted as complexes of type **5** (Figs. 1c,d).

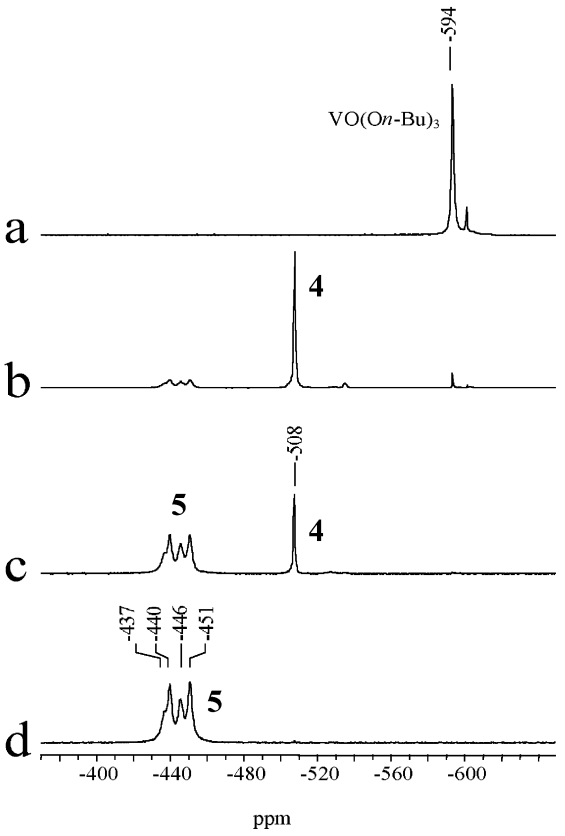


Fig. 1 ^{51}V NMR spectra of the vanadium(v) complexes formed in the system VO(O*n*-Bu)$_3$/**3b** studied in CH_2Cl_2 at 20 °C {[VO(O*n*-Bu)$_3$] = 0.05 M}: (a) VO(O*n*-Bu)$_3$; (b) VO(O*n*-Bu)$_3$:**3b** = 1:1; (c) VO(O*n*-Bu)$_3$:**3b** = 1:1.5; (d) VO(O*n*-Bu)$_3$:**3b** = 1:1.73.

The detailed composition and the structure of complexes **4** and **5** were studied by ^{13}C NMR spectroscopy. In Table 1, ^{13}C NMR chemical shifts of those carbons that could be affected by coordination to vanadium as well as characteristic ^{51}V and ^{17}O NMR shift data are summarized.

Complex **4** contains one molecule of the chiral ligand and two *n*-butoxides (*n*-BuO$^-$) per vanadium atom. Thus, **4** is likely to be a VO(O*n*-Bu)$_2$(**3b**′) species, where **3b**′ stands for the anionic form of **3b** (Scheme 2). Complexes of type **5** are formed at higher ligand-to-vanadium ratios, giving a side product with ^{13}C NMR signals at 163.7 (*C*=O) and 65.6 (N–*C*(CH$_3$)$_3$) ppm, which were attributed to the anionic form of the ligand, **3b**′. Since **3b**′ prepared independently by reacting **3b** with NaOH has the respective ^{13}C NMR signals at 165.6 and 62.4 ppm (Table 1), we propose that in the reaction solution the anionic form, **3b**′, exists as a counter-anion of the ionic pair **5**·**3b**′ shown in Scheme 2.

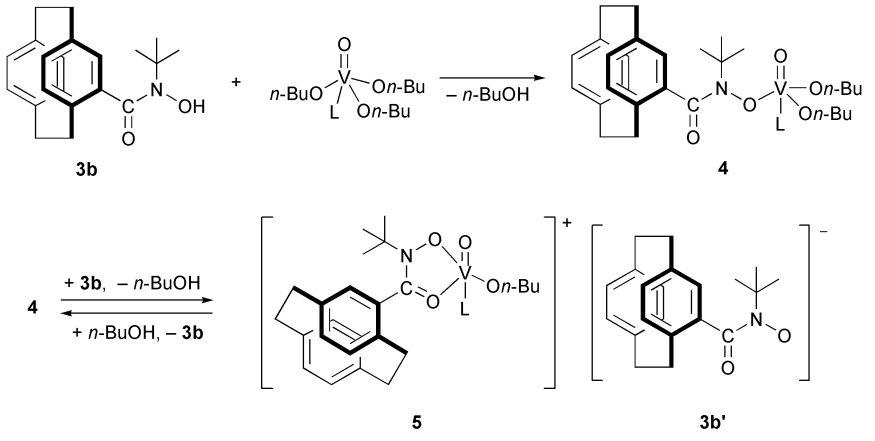
Cationic complexes **5** contain one *n*-BuO$^-$ and one [2.2]paracyclophane ligand per vanadium. The higher ^{51}V NMR shift values are typical for vanadium complexes containing bi- or multidentate O-coordinating ligands and V=O moieties,[11] and the existence of four distinct ^{51}V NMR signals indicates the presence of at least four complexes. If these complexes **5** differed by the axial ligand, one could change their relative concentrations by adding coordinating molecules. However, the relative concentrations of complexes **5** were found to be insensitive to the addition of H_2O and *n*-BuOH, suggesting that the various complexes **5** have a diastereomeric relationship to each other (Schemes 2, 3). Furthermore, there are two groups of V–O*C*H$_2$ resonances in **5**: first, a single line at 86.8 ppm with $\Delta\upsilon_{1/2} = 44$ Hz and a relative intensity of 1.0, and second, two lines at 83.5 and 83.8 ppm with $\Delta\upsilon_{1/2} = 18$ and 12 Hz, respectively, and a summed relative intensity of 1.8. We suggest that the line at 86.8 ppm is a super-position of the peaks of the minor two complexes of **5** having the ^{51}V NMR signals at −446 and −437 ppm, and that the signals at 83.5 and 83.8 ppm relate to the major complexes of **5** having ^{51}V NMR signals at −451 and −440 ppm. The structures proposed for the diastereomeric complexes of type **5** are presented in Scheme 3. They can be easily deduced by varying the relative positions of the arene parts, the V=O moieties, and the *N*–*t*-Bu groups with respect to the horizontal plane (Scheme 3). Since racemic hydroxamic acid **3b** was employed, there also exist the enantiomeric counterparts to the shown structures.

Another result of the NMR studies directly relates to the optimized protocol of the asymmetric catalysis (ligand-to-vanadium ratio of 1.5).[9] In order to form **5** quantitatively, the ratio of **3b**-to-vanadium has to be close to 1.5–1.7. This phenomenon is due to the thermodynamic parameters of the equilibrium in Scheme 2 (which in fact could be a product of several equilibria), and it explains the fact that the highest enantioselectivities were obtained in catalysis with a ligand-to-vanadium ratio of 1.5:1. Under these conditions most of complex **4** is transformed into **5**, and furthermore, a possible inhibition of the catalysis due to a too high ligand-to-metal ratio[9] is no point of concern.

Table 1 The ^{13}C, ^{51}V and ^{17}O NMR chemical shifts in ppm for hydroxamic acid **3b** and vanadium(v) complexes **4**–**6** in CH_2Cl_2 at 20 °C

Species	*C*=O	N–*C*(CH$_3$)$_3$	O*C*H$_2$	OO*C*(CH$_3$)$_3$	^{51}V	V=^{17}O
VO(O*n*-Bu)$_3$	—	—	84.3[a]	—	−594	1162[a]
3b	170.1	62.5	—	—	—	—
4	165.2	66.5	82.2[b]	—	−508	n. o.[c]
5 + **3b**′[d]	165.4	65.3	86.8, 83.5, 83.8[e]	—	−451, −440 (major)	1244
	(163.7)[d]	(65.6)[d]			−446, −437 (minor)	n. o.[c]
6 + **3b**′[d]	165.6	66.0, 66.2	—	84.9, 85.0[f]	−355 (major)	1265
	(163.7)[d]	(65.6)[d]			−361 (minor)	
3b′[g]	165.6	62.4	—	—	—	—
n-BuOH	—	—	63.7	—	—	—
t-BuOOH	—	—	—	81.6	—	—[h]

[a] Adopted from ref. 10. [b] The ^{13}C NMR shifts of *n*-BuOH are: 14.8, 20.0, 36.2, 63.7 ppm. [c] n. o. = not observed. [d] Species **5** and **3b**′ appear in solution in a parallel manner. Thus, the ^{13}C NMR signals of **5** and **3b**′ can only be distinguished by comparison of ^{13}C NMR spectra of **5** + **3b**′ and **6** + **3b**′. The chemical shifts of **3b**′ (given in parentheses) are regarded as independent of *t*-BuOOH addition. [e] The ^{13}C NMR shifts of the *n*-BuOV groups are: 15.1, 20.8, 37.0, 83.5, 83.8 (narrow lines) and 86.8 (wider line) ppm. [f] The ^{13}C NMR shift of V-OOC(*C*H$_3$)$_3$ is 27.8 ppm. [g] Obtained in the course of the following experiment: A CH_2Cl_2 solution of hydroxamic acid **3b** was shaken with solid NaOH at −20 °C until the ^{13}C NMR shifts remained constant. [h] The ^{17}O NMR chemical shifts of *t*-BuOOH oxygens were 210 and 264 ppm.



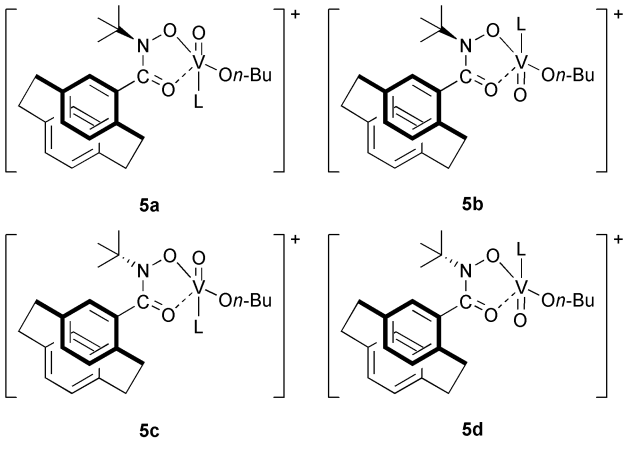
Scheme 2 Vanadium species formed from **3b** and VO(O*n*-Bu)$_3$.

Detection of the vanadium(v) reactive intermediates

When a high excess of TBHP was added to the solution containing the four complexes of type **5**, the formation of new species (further denoted as complexes of type **6**) was revealed by ^{51}V NMR spectroscopy (Scheme 4, Fig. 2). Two complexes in a ratio of *ca.* 3:1 (probably diastereomers such as **6a** and **6b**) with ^{51}V NMR resonances at −355 and −361 ppm dominated besides some residual **5** (giving multiple signals in the range of −420 to −450 ppm). The relative concentrations of the complexes adopted constant values within 10–12 h, suggesting the species to be in equilibrium.

If a substrate was added, the concentrations of complexes **6** decreased whereas those of **5** increased. Figs. 2b–c show the difference within 24 h after the addition of geraniol. ^{13}C NMR spectra of the sample depicted in Fig. 2c indicated a complete transformation of geraniol into the respective 2,3-epoxide. The ratio of the concentration of residual TBHP to that of *t*-BuOH was *ca.* 1:3. If geraniol and TBHP were combined in CH_2Cl_2, no epoxide was formed after several days. These facts clearly demonstrate that complexes of type **6** were responsible for the epoxidation of the allylic alcohol. When geraniol (180 μL) was added to a mixture of TBHP (200 μL) and complexes **6** prepared from a ligand-to-vanadium ratio of 3, the geraniol to epoxide conversion estimated by ^{13}C NMR within 48 h after the addition was lower than 15% (at TBHP conversion *ca.* 25%). This is in agreement with the described inhibition of the catalytic system at ligand-to-vanadium ratios of ≥3.[9] According to ^{51}V and ^{13}C NMR spectra, no complexes other than **5** and **6** were observed in the reaction mixture at ratios of ligand-to-vanadium in a range of 1.7 up to 3.0. The possible explanation of this phenomenon is discussed below.

Interestingly, both processes (the formation of complexes **6** and their reaction with the allylic alcohol) appear to be rather slow. This observation parallels the experimental data for vanadium catalysis with other hydroxamates as ligands and TBHP as oxidant which often require reaction times of up to 7 d.[7–9]



Scheme 3 Diastereomeric vanadium complexes **5** (with L = *n*-BuOH).

The nature of the vanadium(v) reactive intermediates

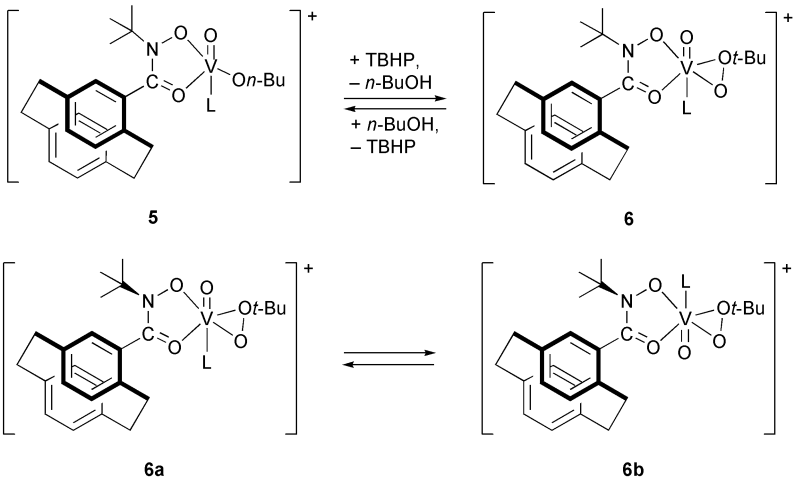
For the oxygen-transfer step of the catalysis the question about the nature of the key intermediates is of particular importance. Most commonly, pathways involving peroxometal and oxometal species are being discussed for metal-catalyzed oxidations with alkyl hydroperoxides.[12] Vanadium-catalyzed epoxidations with such oxidants are proposed to proceed *via* alkylperoxometal complexes as the active oxidants.[4*a*–*c*,5,7] The ^{51}V, ^{13}C and ^{17}O NMR spectra of the intermediates **6** are combined in Fig. 3.

First, both complexes **6** exhibit ^{17}O NMR peaks in the same region, giving a superposition at 1265 ppm ($\Delta\upsilon_{1/2}$ = 600 Hz, Fig. 3b). This is characteristic of an O^{2-} moiety in a six-coordinated vanadium(v) complex.[10,13] The ^{51}V NMR shifts of **6** (−355, −361 ppm, Fig. 3a) are very close to those detected for the alkyl peroxovanadium(v) complex [VO(acac)$_2$OO*t*-Bu] (δ = −350 ppm).[14]

Based on the ^{13}C NMR spectra, complexes **6** contain one molecule of **3b** and one *t*-BuOO$^-$ group per vanadium atom. The *t*-BuOO$^-$ groups were identified by means of a J-modulated ^{13}C NMR pulse program optimized for quaternary carbons (Fig. 3d). There are two ^{13}C NMR signals for coordinated *t*-BuOO$^-$ groups (84.9, 85.0 ppm) as well as two signals for the N–*C*(CH$_3$)$_3$ carbons of **6** (66.0, 66.2 ppm). The evident reason for this doubling is the existence of two vanadium(v) complexes of type **6**, which is consistent with the two peaks in the ^{51}V NMR spectrum at −355 and −361 ppm. Presumably, those two complexes are diastereomers **6a** and **6b** as indicated in Scheme 4. Two more stereoisomers with different positions of the *N*–*t*-Bu groups are revealed as minor species displaying ^{51}V NMR signals at −349 and −373 ppm. Based on earlier work,[5,10,14] we also suppose the side-on coordination of TBHP to vanadium.

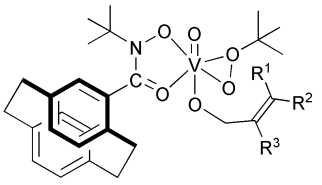
As shown in Scheme 4, complexes **6** also bear a labile axial ligand L which could be *n*-BuOH or an allylic alcohol as substrate. Note that the addition of an allylic alcohol results in a slight downfield shift of the ^{51}V NMR peaks of complexes **6** (*cf.* Figs. 2a,b), indicating a replacement of *n*-BuOH by the substrate as axial ligand.

Summarizing all structural information on the intermediates, we conclude that a reactive complex **7** could be



Scheme 4 Formation of diastereomeric vanadium complexes **6** (with L = *n*-BuOH).

responsible for the oxygen transfer in the catalyzed epoxidation. This arrangement is in excellent agreement with those suggested for other vanadium catalysts bearing hydroxamates as ligands.[7,8]



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Unfortunately, the question of which particular diastereoisomer (**6a** or **6b**) is more reactive towards the substrate cannot be answered by the NMR spectroscopy data, since the concentrations of both complexes decrease in a parallel manner. It could well be that the comparable reactivities of these two diastereomers are the decisive factor for the upper limit of the observed enantioselectivity in the asymmetric catalysis (71% ee for 2-methyl-3-phenylpropen-1-ol and 42% ee for geraniol as substrates with **3a** and **3b** as ligands, respectively).[9]

The observed inhibition of the catalyst at ligand-to-vanadium ratios > 3.0 can be accounted for by an additional ligand ligation to complex **6**, which blocks the approach of the substrate to the axial position of the catalyst. Evidence for such coordination stems from ^{51}V NMR data which demonstrate a small (*ca.* 1 ppm) shift of the signals of complexes **5** in the system with ligand-to-vanadium ratio ≥ 3 with respect to those in the system with ligand-to-vanadium ratio 1.7. Furthermore, the ^{13}C NMR shift data of the excess ligand present in solution [170.1 ppm for (*C*=O) and 62.5 ppm for (N–*C*(CH$_3$)$_3$) ppm] are close to those of free hydroxamic acid **3b**, which indicates a rapid exchange between axially coordinated and non-coordinated **3b**.

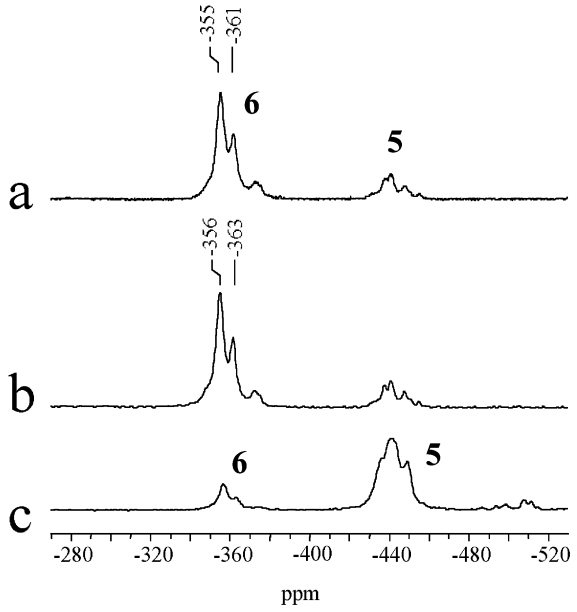

Fig. 2 ^{51}V NMR spectra of the vanadium(v) complexes formed in the system VO(O*n*-Bu)$_3$/**3b**/TBHP studied in CH_2Cl_2 at 20 °C: (a) [VO(O*n*-Bu)$_3$] = 0.05 M, **3b**-to-vanadium ratio = 1.73:1, and [TBHP] = 0.67 M, 12 h after the addition of TBHP; (b) after the addition of geraniol, [geraniol] = 0.35 M; (c) 24 h after the addition of geraniol.

Summary and conclusions

^{51}V, ^{13}C and ^{17}O NMR spectroscopy were used to determine the structures and reactivities of vanadium(v) complexes obtained from VO(O*n*-Bu)$_3$ and hydroxamic acid **3b** in the presence and absence of TBHP (as oxidant) and geraniol (as substrate). As reactive intermediates two diastereomeric vanadium(v) alkylperoxo complexes were identified. They were formed in a ratio of *ca.* 3:1, and possible structural arrangements differing in the relative positioning of the V=O group and the planar-chiral arene part were proposed. When geraniol was added as a substrate, these complexes disappeared in a parallel manner, and 2,3-geraniol epoxide formed. It is very possible that the current level of enantioselectivity in the asymmetric epoxidation with chiral vanadium complexes stemming from mixtures of VO(OR)$_3$ and hydroxamic acids **3** (ee_{max} = 71%) is a result of the presence of the identified diastereomeric complexes and their comparable reactivity. Further studies are therefore directed towards the goal of overcoming this limitation by optimizing the ligand structure. Those investigations are currently being pursued in our laboratories.

Experimental

Materials

Geraniol [3,7-dimethyl-2,6-octadien-1-ol], methylene chloride, *tert*-butyl alcohol, were purchased from Aldrich and used as received. *N*-Butyl *ortho*-vanadate [VO(O*n*-Bu)$_3$],[15] *tert*-butyl

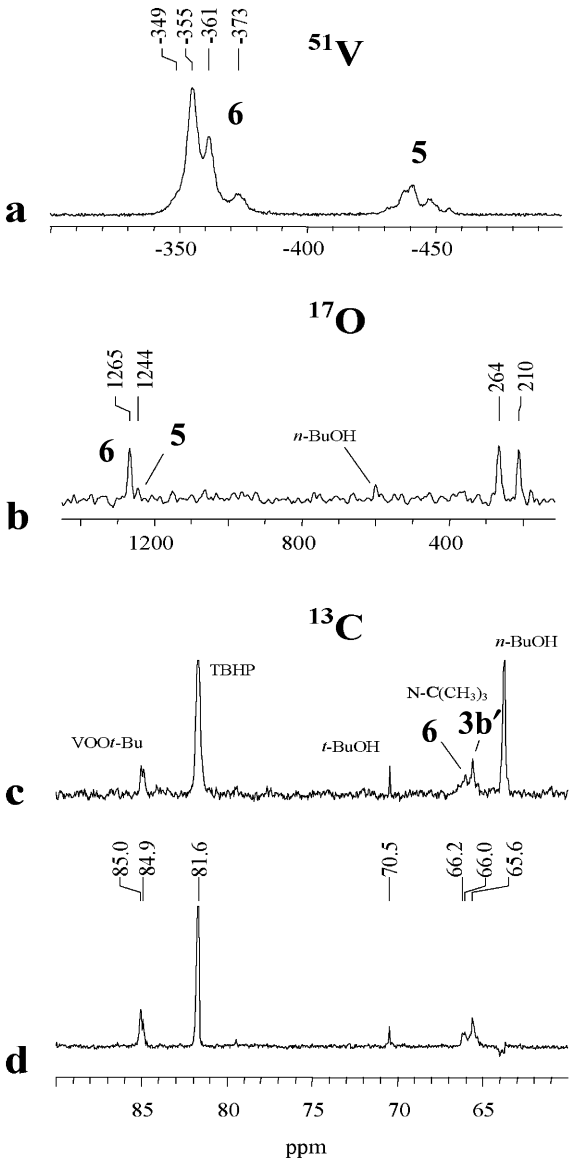

Fig. 3 NMR spectra of the vanadium(v) complexes formed in the system VO(O*n*-Bu)$_3$/**3b**/TBHP studied in CH_2Cl_2 at 20 °C {[VO(O*n*-Bu)$_3$] = 0.05 M, **3b**-to-vanadium ratio = 1.73:1, and [TBHP] = 0.67 M}: (a) ^{51}V NMR spectrum; (b) ^{17}O NMR spectrum; (c) ^{1}H-decoupled ^{13}C NMR spectrum; (d) ^{1}H-decoupled ^{13}C NMR sub-spectrum (quaternary carbons only).

hydroperoxide (100%),[10,16] and racemic *N*-hydroxy-[2.2]paracyclophane-4-carboxylic amide **3b**[9] were prepared as previously described.

NMR measurements

^{13}C, ^{51}V and ^{17}O NMR spectra were recorded on a Bruker MSL-400 spectrometer at 100.614, 105.191 and 54.245 MHz, respectively, using 5 mm or 10 mm cylindrical tubes. For ^{17}O NMR spectra, high-power probehead was used to increase the sensitivity. Chemical shifts were measured with respect to residual CH_2Cl_2 carbons (δ 55.0 ppm) for ^{13}C, external reference $VOCl_3$ for ^{51}V spectra, and internal reference H_2O for ^{17}O NMR spectra, with positive values in the low-field direction. Typical operation conditions for ^{51}V measurements were as follows: sweep widths 125 000 Hz, spectrum accumulation frequency 20 Hz, number of scans 4096, 10 μs radio-frequency pulse, 2 K data points. Typical operation conditions for ^{17}O measurements were the following: sweep widths 125 000 Hz, spectrum accumulation frequency 50 Hz, number of scans 4096, 45° pulse at 10 μs, 2 K data points. ^{1}H-decoupled ^{13}C NMR measurements: sweep widths 30 000 Hz, spectrum accumulation frequency 0.2 Hz, number of scans 1000, 10 μs radio-frequency pulse. ^{13}C NMR data were collected with 32 K points and zero filled to 64 K. ^{13}C measurements for the quantitative determination of relative intensities of the resonances in the same spectrum were made using an inverse gated decoupling procedure.

Samples for NMR measurements were prepared as follows: an appropriate amount (60–150 μmol) of VO(O*n*-Bu)$_3$ was dissolved in 3 mL of CH_2Cl_2 in a 10 mm glass NMR tube. Then, hydroxamic acid **3b** was added as a solid to obtain the desired **3b**/V ratio (1:1 to 3:1). If necessary, *t*-BuOOH, geraniol, *etc.* were added. Samples were kept at an appropriate temperature in the probe-head, and ^{51}V and ^{13}C spectra were collected with the parameters stated above. To record ^{17}O NMR, 0.010 mL of $H_2{}^{17}O$ (4.6% in ^{17}O) was added to the sample containing the solution of VO(O*n*-Bu)$_3$ and **3b** (**3b**/V = 1.7) in 3 mL of CH_2Cl_2.

Acknowledgements

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