



# Models of Vanadate-dependent Peroxidases and Their Properties in Catalytic Sulfoxidation

Thesis

for the Ph.D. (Dr. rer. nat.) degree

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Hamburg 2008

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Disputationstermin: 12. Oct. 2008

## Aknowledgement

This reserach project has been carried out from Feb. 2005 to Jul. 2008 under the supervision of Professor Dieter Rehder in the Chemistry Department of the Hamburg University.

I would like to give my deepest gratitude to my supervisor, Prof. Dr. D. Rehder. I am deeply indebted for Prof. Rehder's abundant help and support, as well as his invaluable guidance. Not only his profound knowledge, but also his charm of personality has impressed me deeply, and will inspire me in my future life.

I would like to express my great gratitude to Dr. E. Haupt and Prof. Dr. U. Behrens for the generous help and the time spent for me; their precise attitude towards science has also made me benefit.

Thanks to Dr. F. Olbrich, Prof. Dr. J. A. C. Broekaert, and Dr. K. Hofmann (inorganic and physical department of the Eduard-Zintl Institute, Darmstadt) for the crystal structure and elemental analyses;

To Ms. C. Wikete, Ms. C. Wontorra, Ms. J. Gätjens, Ms. V. Kraehmer, Mr. A. Behrens, Mr. H. Esbak, and Mr. M. Ebel, I give my thanks for their help. I treasure the nice time we spent together. Also, to all my other colleagues, professors, and friends, who have helped me, I would give my deep thanks.

I further acknowledge support by the Deutsche Forschungsgemeinschaft in the frame of the Graduate School 611 ("Design and Characterisation of Functional Materials") at the University of Hamburg.

At last, I would thank my dear mother and father, as well as all my other family members, for their understanding and endless love.

感谢我亲爱的父母和其他所有家人给予我的理解和无尽的爱。

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Ligands used:

$$H_{HO}$$
  $H_{OH}$   $H_{OH}$  Lig. 1

$$\begin{array}{c} Ph \\ HO \\ HO \\ HO \end{array}$$

$$\begin{array}{c} Ph & \begin{array}{c} & & \\ &$$

## **General Overview**

Vanadium locates in the 23rd position in the Periodic Table. The free element is a soft and ductile metal which is very stable at normal conditions, with good resistance towards corrosion by alkalis, acids, and towards oxidation. Only at high temperature above 933 K can it be oxidized.

The abundance of vanadium is 0.015% in the Earth's crust; it is widely distributed in many minerals, such as vanadinite  $[3Pb_3(VO_4)_2 \cdot PbCl_2]$ , carnotite  $[K(UO_2)(VO_4) \cdot 1.5H_2O]$ , and roscoelite  $[2K_2O \cdot 2Al_2O_3 - (Mg,Fe)O \cdot 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O]$ .

Vanadium also exists in various organisms and plays a vital role in metabolism. It is one of the 16 essential trace elements in the human body. The amount of vanadium people need is estimated to range from 10 to 30  $\mu$ g daily, which is about one millionth of the amount of calcium people need. Though human deficiencies have not been reported, goats fed a low-vanadium diet have developed birth defects <sup>[1]</sup>.

People take in vanadium from a wide variety of foods, including cereals, canned fruit juices, wine, beer, buckwheat, parsley, soy, oats, olive oil, sunflower seeds, corn, green beans, peanut oil, carrots, cabbage, and garlic. The average daily American diet provides between 10 and 60  $\mu$ g of vanadium<sup>[1]</sup>. Certain plants and sea creatures accumulate vanadium from their environment. Sea squirts (ascidians), e.g., can accumulate vanadium (in the form of V<sup>III</sup>) in specialized blood cells, the so-called vanadocytes, up to a concentration of 0.3 M, which is higher by 7 orders of magnitude than the concentration of vanadium in seawater (about 30 nM).<sup>[8c]</sup>

Vanadium is a fascinating element which can exist in eight oxidation states ranging from –III to +V. With different oxidation states, vanadium presents different characteristic beautiful colors. Due to this character, it was named by its discoverer, the Swedish chemist Nils Gabriel Sefström, after Vanadis, the Norse Goddess of beauty, youth, and luster.

In biological systems, the most common oxidation states of vanadium are +III, +IV and  $+V^{[2]}$ , and under ordinary conditions, the +IV and +V oxidation states are the most stable ones<sup>[3]</sup>.

Most vanadium(IV) compounds contain the VO<sup>2+</sup> unit (vanadyl or oxidovanadium(IV) ion). These complexes usually have square pyramidal or bipyramidal geometries with an axial oxido group. Vanadium(IV) complexes lacking the oxido group are scarce. An example is amavadin, a naturally occurring (in *Amanita* mushrooms) vanadium compound containing hydroxamate and carboxylate functions. Vanadium(V) compounds contain the VO<sup>3+</sup> or the VO<sub>2</sub><sup>+</sup> moiety. The V<sup>4+</sup> and V<sup>5+</sup> ions have very small radii of 0.61 Å and 0.59 Å, respectively, even smaller than lithium (the radius of a Li<sup>+</sup> ion is 0.78 Å).

Vanadium(IV) compounds are paramagnetic due to the  $d^1$  configuration of the V<sup>IV</sup> ion, and therefore can be easily identified by EPR spectroscopy with typical eight-line patterns because of hyperfine interaction of the electron with the <sup>51</sup>V nucleus (I = 7/2). V<sup>V</sup> is diamagnetic due to its  $d^0$  electron configuration, and therefore EPR silent. For V<sup>V</sup> compounds, NMR is a very useful method of characterization, since the chemical shifts of  $\delta(^{51}V)$  are very sensitive to the nature of the coordination environment<sup>[4]</sup>.

So far there are two kinds of vanadium-containing enzymes that have been discovered. One is vanadium-dependent nitrogenase, the other one encompasses vanadium-dependent haloperoxidases.

Vanadium-dependent nitrogenases (see Fig. 1 for the coordination environment of vanadium), which reduce dinitrogen to ammonia<sup>[5]</sup>, exist in certain nitrogen-fixing bacteria, such as *Azotobacter chroococcum*<sup>[6]</sup> and *A. vinelandii*<sup>[7]</sup>. These enzymes are multicomponent metalloenzyme complexes, containing Fe-S clusters in their active centers<sup>[8a]</sup>.



Figure 1 Proposed V-environment in vanadium nitrogenase<sup>[8]</sup>

Vanadium-dependent haloperoxidases, which catalyze the oxidation of halides (X<sup>-</sup>) to the corresponding hypohalous acids (or to a related two-electron oxidized halogenating intermediate, such as OX<sup>-</sup>, X<sub>3</sub><sup>-</sup> or X<sup>+</sup>) by hydrogen peroxide as the oxidant, exist in algae, lichens and fungi. <sup>[8b]</sup> These enzymes have been drawing more and more attentions in recent years, and our work – including the present thesis – also focuses onto this field.

## 1. Introduction

## 1.1 Vanadium-dependent Haloperoxidases

### 1.1.1 Haloperoxidases

Haloperoxidases (HPOs) are a group of enzymes, which take part in the halogenation of organic substrates with hydrogen peroxide as oxidant.

The whole process consists of two steps. First, with the catalysis of HPOs, hydrogen peroxide oxidizes the halide to a halogen species with the +I oxidation state, e.g., hypohalous acid (equation [1]); second, this intermediate species non-enzymatically halogenate the organic substrates to organic halides (equation [2])<sup>[9]</sup>.

$$X^{-} + H_2O_2 + H^{+} \xrightarrow{enzyme} HOX + H_2O \qquad [1]$$
$$HOX + R - H \xrightarrow{} R - X + H_2O \qquad [2]$$
$$X = CI, Br, I, SCN$$

The first HPO was found in 1961, when Hager and coworkers separated a chlorinating enzyme from *Caldariomyces fumago*<sup>[10]</sup>. Since then, a large number of HPOs have been found in a broad range of organisms, including algae, bacteria, ferns, molds, higher plants, and mammals<sup>[11]</sup>.

On the basis of their different cofactors, HPOs are classified into three groups: metal-free HPOs, heme-depending HPOs, and vanadium-depending HPOs<sup>[12]</sup>. Among them, vanadium-dependent haloperoxidases (VHPOs) are the most prevalent ones<sup>[13-14]</sup>.

#### 1.1.2 Vanadium-dependent Haloperoxidases

VHPOs exist in certain brown and red marine algae, lichen, and fungi<sup>[15]</sup>. In 1983, Vilter discovered the first VHPO in *Ascophyllum nodosum*<sup>[16]</sup>; in 1996, Messerschmidt and Wever resolved the crystal structure of an azide inhibited vanadium chloroperoxidase (V-CPO), which was isolated from the fungus *Curvularia inaequalis*<sup>[17]</sup>; and in 1999, Schomburg's group published the crystal structure of vanadium bromoperoxidase (V-BPO) from the marine brown alga *Ascophyllum nodosum*<sup>[18]</sup>.



inaequalis

The crystal structure of

V-CPO from Curvularia

Figure 1.1

The structure analysis revealed that in these native enzymes, vanadium(V) resides in the center of a trigonal-bipyramid<sup>[15]</sup>; Fig. 1.2. The V-BPO from the brown marine alga Ascophyllum nodosum (AnPO) and the V-CPO from the fungus *Curvularia inaequalis* (CiPO) both contain vanadate(V), with vanadium covalently bonded in one of the axial

positions to NE of a proximal histidine (His 486 in

AnPO), and further hydrogen-bonded, via its oxido- and hydroxido ligands, to several active site amino acid residues, including serine and one (CiPO) or two (AnPO) additional histidines. The active sites of AnPO and CiPO are very similar, the main difference being the exchange of Phe397 in CiPO by His411 in AnPO<sup>[9]</sup>. The electron density in the second axial position of vanadium has been interpreted, depending on the V–O distances (2.2 to 1.8 Å), as a water ligand, or as an OH group, hydrogen-bonded to a distal histidine (His404 in CiPO, His418 in AnPO), providing more information for the elucidation of the working mechanism of haloperoxidases<sup>[9]</sup>.





Ascophyllum nodosum (AnPO)<sup>[9]</sup>;
(b) the active center in the VCPO from the fungus Curvularia inaequalis (CiPO)<sup>[20]</sup>

In order to arrive at a better understanding of the working mechanism of these active sites of V-HPOs, many investigations have been carried out on these native enzymes as well as their model complexes to reveal the nature of these enzymes. The proposed common mechanism for the halide oxidation by V-HPOs is as follows (Figure 1.3):

At the attack of hydrogen peroxide, the catalytic reaction is initiated by the substitution of the axial hydroxido group by the peroxido group, which is protonated; then the halide ion attacks the hydroperoxido group nucleophilicly and causes the oxido group to transfer from the catalyst to halide. As an evidence, the peroxido form of the CiPO<sup>[19]</sup>, as well as of several derivatives and mutants of CiPO, has been characterized<sup>[21-22]</sup>. In this structure, a rearrangement occurred by transforming the original trigonal bipyramid to a distorted tetragonal pyramid (Figure 1.4).



Figure 1.3 Proposal for a common reaction mechanism for the halide oxidation by VHPOs



Figure 1.4 Comparison of the geometric structures of the native and peroxido sites of CiPO

These enzymes cannot only catalyze the oxidation of halides, but also catalyze the oxidation of sulfides.

### 1.2 Chiral Sulfoxidation

#### 1.2.1 The Importance of Chiral Sulfides

Chiral sulfoxides have been widely used in pharmaceutical and organic asymmetric synthesis as chiral auxiliaries and also as ligands<sup>[23]</sup>. The successful application of chiral sulfoxides is due to their high optical stability as well as high asymmetry.

Enantiomers may undergo a process known as racemization by transforming into their mirror images to a certain degree. In the case of sp<sup>3</sup> central chirality, when the stereocenter has a lone electron pair, such as in amines and sulfoxides, both enantiomers can interconvert through a process called pyramidal inversion (Fig. 1.5), in which the mirror image of the pyramid is formed through a trigonal planar transition state<sup>[24]</sup>. When the transition is hampered by a high inversion barrier, or is at a considerably slow rate, then an enantiomer is said to be optically stable.



Figure 1.5 Pyramidal inversion of sulfoxides

Fortunately, the racemization of enantiopure sulfoxides occurs only at high temperature above 200°C; sulfoxides therefore are optically stable. Furthermore, enantiopure sulfoxides are highly asymmetric, because they contain three types of very different substituents, i.e. oxygen, a lone electron pair, and two organic groups, and as a result they may induce a strongly asymmetric environment both electronically and sterically.

Based on these advantages, optically active sulfoxides have played an important role as valuable asymmetric starting materials and chiral auxiliaries in asymmetric synthesis of biologically active compounds.

#### 1.2.2 Methods in Synthesizing Chiral Sulfides

Several synthetic methods have been developed in order to obtain chiral sulfoxides. Their preparation has been well documented by either chemical<sup>[25-28]</sup>, microbiological<sup>[29-31]</sup> or enzymatic methods<sup>[32-37]</sup>.

In terms of chemical methods, two general techniques are used:

- Nucleophilic substitution in optically active sulfur derivatives. In this method, enatiopure sulfoxides are obtained by action of a nucleophilic reagent onto an optically active sulfur compound<sup>[25, 38]</sup>.
- Asymmetric oxidation of prochiral sulfides, i.e. chiral sulfoxidation. In most cases, chiral sulfoxidations are activated by metal-complexes as catalysts. Titanium complexes were introduced first into this reaction system.

In 1984, the research groups of Kagan and Modena applied Ti-alcoholates, which have very good catalytic performance in Sharpless epoxidation of allylic alcohols<sup>[39]</sup>, in the asymmetric oxidation of sulfides<sup>[40]</sup>. They found that, at -20 °C in CH<sub>2</sub>Cl<sub>2</sub> and with *tert*-butyl hydroperoxide (TBHP) as oxidant, the system Ti(*i*-PrO)<sub>4</sub>/(*R*,*R*)-det/H<sub>2</sub>O in a ratio of 1:2:1 (det = diethyltartrate) catalyzed the oxidation of some prochiral sulfides with surprisingly high stereoselectivity.

Inspired by this achievement, other metal complexes, with a diversity of metal centers like vanadium, manganese, or iron, as well as a variety of ligands such as  $C_2$ -symmetric diols,  $C_3$ -symmetric triols, Schiff bases and double Schiff bases (e.g. salen, the Schiff base derived from ethylenediamine and salicylaldehyde), amino acids, and amino alcohols were introduced. Among them, vanadium-Schiff base, vanadium-amino acid, and vanadium-amino alcohol systems have been developed as models for VHPO.

Biologically, chiral sulfoxidations are done by enzymes in plants or microorganisms, particularly by peroxidases. Among them, vanadium-dependent haloperoxidases are an important class of enzymes which possess this function.

## 1.3 VHPOs in chiral sulfoxidation

Recently it was demonstrated that VHPOs are also capable of mediating selective sulfoxidation reactions in the presence of hydroperoxides<sup>[41]</sup>. VHPOs of different origin have different selectivity on different sulfide substrates. As an example, the VBPO from the brown seaweed *Asophyllum nodosum* promotes formation of the *R*-enantiomer of methylphenylsulfoxide with 91% enantiomeric excess (ee) and 52% in yield under optimal reaction conditions, whereas another VBPO from the red seaweed *Corallina pilulifera* mediates the formation of the *S*-enantiomer with 55% ee and 45% in yield. Recombinant VCPO produces a racemic mixture of the sulfoxides. This selectivity pattern appears to be an intrinsic characteristic of the enzyme.

#### 1.4 Models of Vanadium-dependent Haloperoxidases

#### 1.4.1 Models of VHPOs

In 1986, Fujita et al. reported on the first VHPO models, based on the vanadium-salen system, in enantioselective sulfoxidation <sup>[42]</sup>. With 10 mol% of the tetradentate ONNO-type salicylidene Schiff base-oxidovanadium(IV) complexes as catalysts (Fig. 1.6) in  $CH_2Cl_2$ , cumyl-hydroperoxide (CHP) as oxidant, and methylphenylsulfide as the substrate, 40% optimal enantioselectivity was achieved with 96% yield at 0°C. But the reaction rate was fairly slow; the overall reaction took 120 hours.





VO(sal-(RR)-chxn): X=H VO(3-MeOsal-(RR)-chxn): X=OCH<sub>3</sub> VO(3-EtOsal-(RR)-chxn): X=OC<sub>2</sub>H<sub>5</sub> VO(3-Bu<sup>t</sup>sal-(RR)-chxn): X=C(CH<sub>3</sub>)<sub>3</sub>

VO(sal-(R)-pn): Y=H VO(7-Mesal-(R)-pn): Y=CH<sub>3</sub>

Figure 1.6 The first VHPO models

Later, Fujita and coworkers reported on another chiral sulfoxidation, catalyzed by structurally well characterized V<sup>V</sup> complexes with aminoacid-derived tridentate ONO-type Schiff bases as ligands, viz.  $[V^{V}O(sal-L-aa)(OCH_3)(CH_3OH)]$  (sal-L-aa = N-salicylidene-L-alaninate, N-salicylidene-L-phenylalaninate, N-salicylidene-L-valinate, and N-salicylidene-L-leucinate)<sup>[43]</sup>. With the same molar amount of catalysts and TBHP as oxidant, at 4°C in dichloromethane, the reaction rate was improved, i.e. the oxidation was completed after 5.5 to 8 hours. The ee values for the methylphenylsulfoxide were, however, only 14% at the best.

In their further studies with tetradentate salen type VHPO models, the best result was no better than 40% in enantioselectivity with yields ranging from 56-96% and reaction times between 15 and 120 hours at 0  $^{\circ}C^{[44]}$ .

In 1996 and 1997, Bolm et al. studied the catalytic asymmetric sulfoxidation with vanadium(IV) complexes of  $C_2$ -symmetric *bis*(sulfoximines)<sup>[45]</sup> (Fig. 1.7a) and oxazolinylphenols<sup>[46]</sup> as ligands. Both catalyst systems showed high activity, but unfortunately, the products were racemic.



**Figure 1.7a** The VO<sup>2+</sup>*bis*(sulfoximine) VHPO model by Bolm

Among the earlier VHPO models, an *in situ* catalytic system of vanadyl acetylacetonate and Schiff bases (Fig.1.7b) was introduced by Bolm and Bienewald in 1995, which can be considered a milestone in the investigation of VHPO models. This catalytic system provided remarkable results with respect to the chiral oxidation of certain aryl-alkylsulfides<sup>[47]</sup>.

The exceptional feature of this catalytic system lies in the following aspects:

- 1. Excellent enantioselectivity of the oxidation products (53-85 %) accompanied by good yields (54-94 %).
- 2. The use of non-toxic and inexpensive aqueous  $H_2O_2$  (30%) as the oxidant. In this catalytic system, aqueous  $H_2O_2$  proved to be the most efficient oxidant, while in some other VHPO model systems, in which TBHP was used as the oxygen source, the oxidations were often inhibited by the presence of water.

- 3. The reaction conditions are unusually simple: The oxidation may be conducted in open air at room temperature. The atmospheric oxygen and water have no affect on the reaction, which fact makes this catalysis particularly attractive for large scale applications.
- 4. Only very small amounts of the catalyst are needed. The catalytic system is extremely efficient; only 0.01 mol-% of the catalyst suffices to ensure an efficient reaction and optimal turnout.
- 5. The four Schiff base ligands can readily be prepared from salicylaldehyde and amino alcohols.

This study showed the importance of electronic and steric factors, as indicated by the influence of the substituents R and X at the phenyl ring on the enantioselectivity of the sulfoxidation products. For different substrates, the substituents on the phenyl ring had to be different for achieving the optimal enantioselectivity.

If, e.g., both R positions were occupied by a *tert*-butyl group, catalyst **a** with a nitro group in the X position gave the best enantioselectivity for simple substrates like methylphenylsulfide (ee = 70%), while catalyst **b** with a *tert*-butyl group in the X position gave the best enantioselectivity for the oxygenation of the dithioacetal of benzaldehyde (ee = 85%).

HC (S)a: R=tBu, X=NO2 c: R=SiPh2tBu, X=tBu

Figure 1.7b Schiff base ligands

developed by Bolm et al<sup>[47]</sup>

d: R=H, X=NO;

b' R=X=tBu

Inspired by these results, other research groups hav engaged in the extensive investigation of vanadiun base system as VHPO models by variation of the a aldehyde and the amino alcohol<sup>[48-52]</sup>.

Among these investigations, a result of Ellman and coworkers is of particular interest. They successfully oxidized *tert*-butyl disulfide to give mono-oxidized optically active thiosulfinate (Fig. 1.8) with 91% ee and 98% yield.

This chiral sulfoxide has been the starting material for several synthetically interesting

<sup>12</sup> 

products including amines and  $\beta$ -amino acids<sup>[53-54]</sup>.



Figure 1.8 Chiral oxidation of *tert*-butyl disulfide by the catalytic system developed by Ellman et at.<sup>[53, 55]</sup>

In stead of the *in situ* catalytic systems with which excellent ee values were obtained, Gau and coworkers used a series vanadium(V)-Schiff base complexes as catalysts in the chiral oxidation of methyl phenyl sulfide<sup>[56]</sup>. With hydrogen peroxide as oxidant at -20 °C in CH<sub>2</sub>Cl<sub>2</sub>, the best results (98% ee, 61% yield) were obtained when the substituents on the complex are R1 = R2 = H, R3 = *t*Bu, and R4 = I (Figure 1.9).



Figure 1.9 Catalytic system developed by Gau et al.<sup>[56]</sup>

So far, the tridentate ONO salicylidene type vanadium-Schiff base complexes mentioned above are the most widely studied VHPO model systems.

For the tetradentate ONNO type vanadium-salen complexes or analogoues thereof, used in Fujita's initial work, Hu and co-workers made further investigation and reported satisfying results in  $2004^{[57]}$ . They used salan or salen ligands and vanadyl acetylacetonate *in situ* (Figure 1.10) to catalyze the oxidation of methyl-phenylsulfide at 0 °C with H<sub>2</sub>O<sub>2</sub> as oxidant in CH<sub>2</sub>Cl<sub>2</sub>, and acquired chiral products with 95% ee in 81% yield at an optimum.



Figure 1.10 Salan or salen ligands developed by Hu et al<sup>[57]</sup>.

There have also been some investigations on the catalytic properties of vanadium-amino acid and vanadium-amino alcohol type VHPO models in chiral catalysis. The catalytic data on these two model systems are so far scarce.

In 2007, Rehder and coworkers reported on the catalytic property of  $[VO(HOMe)(OMe)L^{D}]$  (HL<sup>D</sup> = N(1-phenyl-2-hydroxyethyl)glycine) (Figure 1.11) in the oxidation of methyl-*p*-tolylsulfide (MeS*p*Tol) and benzyl phenylsulfide (BnSPh) by CHP at -20 °C in CH<sub>2</sub>Cl<sub>2</sub>. Although the products were almost racemic, the catalytic reaction systems showed excellent reactivity and selectivity: The reaction was finished after 2.5 hours (for MeS*p*Tol) and 5 hours (or BnSPh) with 98% and 100% in yield, respectively <sup>[58]</sup>.

Rehder's group was also engaged in the study of VHPO models based on vanadiumamino alcoholates. In 2003, they reported on reactions with the amino alcohol ligands **1**, **2**, **3** and **4** in Fig. 1.12, and also synthesized their vanadium(V) complexes (**5**, **6**, **7** and **8** 



in Fig. 1.12), among which the complexes of ligands **1** and **2** were crystallographically characterized<sup>[59]</sup>.

Figure 1.11 Amino acid-vanadium complex modeling VHPO developed by Rehder et al.<sup>[58]</sup>.

The catalytic systems based on these vanadium complexes showed excellent reactivity and selectivity in the oxidation of methyl-*p*tolylsulfide by cumylhydroperoxide (CHP) in



Figure 1.12 Scheme for the synthesis of amino alcohol vanadium complexes that model VHPO<sup>[59]</sup>

 $CH_2Cl_2$  at 0 °C. The reactions were terminated after 120 to 720 minutes, with selectivity from 72-95%. The enantioselectivity ranged from 11% to 31%.

Comparing the catalytic properties of the *in situ* system ligand  $4/VO(OiPr)_3$  and its related complex **8** revealed that the *in situ* system provided better reactivity: the reaction was terminated within 30 minutes, as compared to 120 minutes with the complex as catalyst. The yield of the sulfoxide in the *in situ* system was 95%, a little bit higher than for the complex (88%). The enantioselectivities of these two systems were similar, viz. 25% (*in situ*) and 26% (complex **8**), respectively.

## 1.4.2 Catalytic Mechanism of VHPOs, and Models of Intermediate Active Species

So far, the exact mechanism, by which the oxidation of sulfides catalyzed by VHPOs is accomplished, still remains a subject of study. Usually it is believed that the possible catalytic process is similar to that in the oxidation of halides catalyzed by VHPOs, and also that the peroxidovanadium complex generated as an intermediate facilitates nucleophilic attack by the substrate and thus is employed in the process of transfer of an oxido group from the oxidant to the substrate<sup>[15]</sup>. Accordingly, the mechanism could be described as follows (Fig. 1.13): The vanadium complex is first associated with a peroxide to form an active peroxido species which is further activated by protonation. Then the sulfide attacks the hydroperoxide nucleophilically, and finally enables transfer of the oxido group from the hydroperoxide intermediate to the sulfide<sup>[60]</sup>.



Figure 1.13 The possible mechanism of sulfoxidations catalyzed by VHPOs

The active intermediate of the VHPOs contains a histidine covalently attached to peroxidovanadate  $[H_xVO_3(O_2)]^{(3-x)-}$ , where *x* possibly equals 1 under the slightly acidic conditions for the optimal action of the enzyme. Several groups hydrogen-bonded to the active center may be considered to shuttle protons to the peroxido intermediate, such as interstitial water, and the protein side chain groups of serine, protonated lysine and distal histidine.<sup>[15]</sup>

In order to elucidate the mechanism, many oxido-peroxidovanadium complexes, particularly those with amino acid type of ligands, have been synthesized and crystallographically characterized to model the structural features of the intermediate state of the VHPO active centers.

In 1996, Pecoraro and coworkers published crystal structures of oxido-peroxidovanadium complexes with amino acid ligands as VHPO models:  $K[VO(O_2)Hheida]$ ,  $K[VO(O_2)ada]$ ,  $[VO(O_2)bpg]$ , and  $H[VO(O_2)bpg]_2(ClO_4)$  [H<sub>3</sub>heida = *N*-(2-hydroxyethyl)iminodiacetic acid; H<sub>2</sub>ada = N-(2-amidomethyl)iminodiacetic acid, Hbpg = N,N-*bis*(2-pyridylmethyl)-glycine]<sup>[61]</sup>.

In 2001, the crystal structure of the oxido-peroxidovanadium amino acid complex  $[VO(O_2)(bpaH)](CIO_4)\cdot 2H_2O$  [bpaH = *N*,*N*-*bis*(2-pyridylmethyl)- $\beta$ -alanine] (Fig. 1.14) reported by Rehder and coworkers revealed tight binding of the carboxylic acid function to the vanadium center through its doubly bonded oxygen. The H-bond interaction between the carboxylic acid proton and the vanadium(V) bounded peroxido moiety is mediated by two waters of crystallization. This special arrangement of carboxylic acid, water and peroxide provides a basis for a mechanism for rapid – and reversible – transfer of a proton to the activated (by coordination to vanadium) peroxido function, and hence a mechanism by which the electrophilicity of this site can be adapted to an appropriate substrate to be oxidized, such as sulfide or halide<sup>[62]</sup>.



In 2002, Butler and coworkers reported on the complexes K[VO(O<sub>2</sub>)(NH<sub>2</sub>pyg<sub>2</sub>)] and K[VO(O<sub>2</sub>)-(BrNH<sub>2</sub>pyg<sub>2</sub>)] [NH<sub>2</sub>pyg<sub>2</sub> = N-(2pyridylmethyl-6-amino)-iminodiacetic acid] (Fig. 1.15) which demonstrated direct intramolecular H-bonding between an amine functionality and V<sup>V</sup>-bonded peroxide<sup>[63]</sup>. The intramolecular H-bond strength in [VO(O<sub>2</sub>)(BrNH<sub>2</sub>pyg<sub>2</sub>)] is estimated to 25 kJ/mol by <sup>1</sup>H NMR studies, and thus is significant. As

such, these complexes mimic the direct H-bond

Figure 1.14 Structure of an oxidoperoxidovanadium amino acid complex, including the H-bonds (dashed lines)<sup>[62]</sup>.

between Lys353 and the peroxido moiety in VCIPO of *C. inaequalis*, and further support the notion that similar H-bonding occurs in VBrPOs.

In 2004, Rehder et al. reported on molecular and supramolecular features of some oxido-

peroxidovanadium complexes containing O<sub>3</sub>N, O<sub>2</sub>N<sub>2</sub> and ON<sub>3</sub> donor sets<sup>[15]</sup>. The supramolecular pattern of these complexed featured by intermolecular hydrogen bonds between lattice water molecules (as donors) and vanadium-bonded oxido and peroidxo groups, as well as the doubly bonded oxygen from carboxylic groups (as acceptors).



Figure 1.15 ORTEP views of [VO(O<sub>2</sub>)(NH<sub>2</sub>pyg<sub>2</sub>)]<sup>-</sup> (i) and [VO(O<sub>2</sub>)(BrNH<sub>2</sub>pyg<sub>2</sub>)]<sup>-</sup> (ii)<sup>[63]</sup>.

All these oxido-peroxidovandadium models with inter- or intra-molecular H-bonds have manifested the possible proton transfer pathways which are involved in the sulfoxidation process at VHPO active sites.

#### 1.5 Generation of Chirality

The generation of chirality is considered as the result of the 'conspiracy' of spatial effects and electronic effects in the reaction system. Spatial and electronic effects work together and determine the difference in energy barriers as well as in free energy changes in the reaction process; and these differences in energy finally result in the discrimination of different possible stereo-structures of the product by favoring the formation of specific sterical arrangements with fixed spatial configuration.

In order to create a substantial difference in energy in asymmetric synthesis, a chiral moiety with a well defined and stable structure is usually introduced into the reaction





 $\label{eq:second} \mbox{Figure 1.16} \quad \mbox{Enantiomeric (above) and diastereomeric (below) energy profiles in the $S_N$1 reaction$^{[64]}$}$ 

The two graphs in Fig. 1.16 stand for the simple  $S_N1$  reaction. The nucleophilic attack on the carbon cation may happen from either side of the trigonal plane in which the carbon cation resides. When the chemical environments on both sides of this trigonal plane are exactly the same, the probability for nucleophilic attack from either side is alike, i.e. the energy barrier which has to be overcome is the same, and *R* and *S* enantiomers form in equal amounts. Because enantiomers have exactly the same energy (potential energy, internal energy, enthalpic and free energy), the Gibbs free energy changes for the formation of both enantiomers are the same, resulting in a racemic mixture with a 1:1 ratio of *R* an *S* enantiomers; Fig. 1.16, top. Unlike enantiomers, diastereomers have clearly different energies. That reaction is thus favored, which is characterized by a lower energy barrier and greater Gibbs free energy change. As a result, one of the diastereomers is formed as the main product (Fig. 1.16, bottom).

One way of introducing chirality into the reaction system to form diastereomers is by catalysis with a chiral catalyst, which is the most convenient and promising asymmetric synthetic route.

During the chiral catalytic process, the enantioselectivity is also, like in all the other cases, controlled by spatial and electronic properties of the reaction system. Ellman and coworkers have demonstrated this in their work by having further studied Bolm's vanadium-salicylidene catalytic system<sup>[47]</sup>, introducing a wide variety of substituents into the Schiff base ligand <sup>[53]</sup>.

First, they tested Bolm's catalytic system with a different substrate, i.e. with *t*-butyl disulfide instead of methyl-phenylsulfide. The optimal catalytic results in the two systems are displayed in Fig. 1.17, clearly demonstrating that yield and ee are better in Bolm's system.



**Figure 1.17** V-salicylidene Schiff base catalytic systems and catalytic results of Bolm (up)<sup>[47]</sup> and Ellman (down)<sup>[53]</sup>

To test the salicylidene Schiff base ligands, different substituents were used in the position R1, R2, R3, R4, and R5 (Fig. 1.18).



Figure 1.18 Ellman's V-salicylidene Schiff base catalytic systems with ligands having different substituents<sup>[53]</sup>

The same reaction condition provided, the enantioselectivity is 82% for  $R^1 = R^2 = R^3 = t$ butyl and  $R^4 = R^5 =$  hydrogen. Replacing the *t*-butyl group in position  $R^3$  for *i*-propyl diminishes the ee value to 60%; replacing *t*Bu at  $R^3$  for Ph, reduces the ee to 25%.

The significant influence of the substituents in  $\mathbb{R}^3$  position on the enantioselectivity is due to the vicinity of  $\mathbb{R}^3$  to the nitrogen atom directly coordinated to the vanadium atom, around which the formation of the active intermediate state of the catalyst and the nucleophilic attack of the substrate would take place. When the most bulky *t*-butyl group was used, the hindrance in space near the metal center increases the asymmetry around the metal center, which is in favor of high enantioselectivity (82%); for the same reason, when the least bulky phenyl group was used, the ee value was the lowest among these three cases (25%). Along with the steric effect, these different substituents also influence the electron density around the vanadium.

The substituents in position  $R^1$ ,  $R^4$  and  $R^5$  also play an important role in the enantioselectivity due to the same reason as the substituent in in position  $R^3$ . As to position  $R^2$ , the bulk of the substituents has almost no influence on the enantioselectivity: No matter if  $R^2$  is *t*-butyl, the methoxido group, or a hydrogen atom (A, C and D in Table 1.1), the ee values remain almost the same, viz. 82%, 79% and 83%, because  $R^2$  is too far away from the metal center. But it still exerts influence through electronic effects: when the electron-donating groups are substituted by the strong electron-withdrawing substituent NO<sub>2</sub> (B in Table 1.1), the ee value decreased to 45%.

F. Maseras, et al., have computationally studied Ellman's catalytic system and calculated the energy changes<sup>[65]</sup>. They illustrated the origin of enantioselectivity with the energy profile shown in Fig.1.19.

<b>Table 1.1</b> Comparison of catalytic results of V- salicylidene Schiff base catalytic system
--

	$\mathbb{R}^1$	$\mathbf{R}^2$	conv. %	ee %		R3	R4	R5	conv. %	ee %
Α	t-Bu	t-Bu	94	82	Α	t-Bu (S)	Н	Н	94	82 (R)
В	t-Bu	NO <sub>2</sub>	18	45	К	<i>i</i> -Pr (S)	Н	Н	65	60 (R)
С	t-Bu	OMe	85	79	L	Ph ( <i>R</i> )	Н	Н	47	25 (R)
D	t-Bu	Н	88	83	Μ	Bn (S)	Н	Н	69	53 (R)
Е	Н	Н	50	46	Ν	Ph (S)	Ph ( <i>R</i> )	Н	60	44 (S)
F	OMe	Н	17	<10	0	Н	Me (S)	Н	40	19 (R)
G	$NO_2$	Br	15	<10	Р	Me ( <i>R</i> )	Ph (S)	Н	85	41 (R)
Н	Br	Br	10	25	Q	<i>i</i> -Pr (S)	Н	Me	16	53 (R)
Ι	Cl	Cl	12	<10	R	t-Bu (S)	Н	Me	10	19 (R)
J	Br	Me	23	50	S	Me (S)	Н	Me	16	41 (R)

When the salicylidene Schiff base reacts with VO(acac)<sub>2</sub> to form the vanadium complex, and further with peroxide, the V=O bond may be oriented in two alternative directions along the axis which is perpendicular to the ONOO plane spanned by the ONO ligand and one of the peroxido-oxygens, giving rise to two configurations, denoted **a** and **b** in Fig. 1.19, which possibly are in equilibrium in solution. Since the vanadium atom is now constituent of an asymmetric chelate ring, it is also a chiral center, along with the chiral ligand center (the carbon carrying R<sup>3</sup>). Configurations **a** and **b** are diastereomers of different energy. Both catalyze the enantioselective oxidation of *t*-butyl disulfide with hydrogen peroxide. If the energy difference  $\Delta E_{AB} < \Delta E_A$  (cf. Fig. 1.19), the enantioselectivity induced by **a** and **b** is determined by the energy difference  $\Delta E_{AB}$ between the most stable pro-*R* and pro-*S* transition states associated with each diastereomer; if  $\Delta E_{AB} \approx \Delta E_A$ , the enantioselectivity induced is determined by both  $\Delta E_{AB}$ and  $\Delta E_A$ ; when  $\Delta E_{AB} > \Delta E_A$ , the extent of enantioselectivity will be determined by  $\Delta E_A$ . All the differences in energy in these transition states come about by the cooperativity of spatial and electronic effect in the reaction system.



Figure 1.19 Origin of enantioselectivity<sup>[65]</sup>



2. Aim of the Project

## 2. Aim of the Project

## 2.1 Synthesis of New Vanadium-Aminoalcohol Complexes as VHPO Models

The development of asymmetric catalysts generally requires time-consuming screening of a large number of chiral ligands, metal centers, and reaction condition<sup>[66]</sup>.

To the present time, different kinds of vanadium complexes have been synthesized and tested as models for VHPOs (see ch. 1). Among these, salicylidene type Schiff base ligands have been widely studied, and some of the corresponding complexes have shown promising catalytic properties with good selectivity (with respect to the ratio sulfide:sulfone), and/or enantioselectivity.

In contrast, work on aminoalcohols as ligands in model complexes of VHPOs is so far less developed; and most of the respective work has been carried out by former members in our group<sup>[59]</sup>. The present work aims towards new synthetic approaches and a more profound understanding of the mechanisms of the catalytically conducted sulfoxidation, leading to high yields, high selectivities and a reasonable enantiomeric excess.

## 2.2 Immobilization of Vanadium-Aminoalcohol Complexes

#### 2.2.1 Immobilization of Catalysts

Immobilization of the catalytically active complex provides rigidity otherwise not necessarily encountered in solution. Further, recycling of the catalysts is always in the spotlight of the investigation, and immobilization of a catalysts onto a solid supporter is an important approach to address this issue.

For metal-complex catalysts, immobilization is in most cases based on the tethering of corresponding ligands, with which the metal precursor forms an immobilized complex in a second reaction step<sup>[67-68]</sup>. There are two commonly used strategies to immobilize ligands:

- 1. Anchoring ('Tail-tie') the ligand directly onto the backbone of a solid support<sup>[69-71]</sup>;
- applying a combinatorial method to develop the catalysts, i. e. firstly tethering the initial building block containing the anchoring group(s) to the solid support; secondly a step-by-step solid state synthesis of the ligand, based on the anchored building block<sup>[66, 72-73]</sup>.

Immobilization of the catalysts has solved the problem of product isolation and recovery, as well as the potential re-use of the catalyst in many cases. However, with heterogeneous catalysts, it is usually found that the catalytic activity and enantioselectivity are decreased with respect to structurally related, homogeneous catalytic systems<sup>[74-75]</sup>.

The decrease in catalytic activity may be due to the insufficient contact of the catalyst with the reactants. Pu and coworkers attributed the drawback in the decrease of enantioselectivity to the microenvironment of the catalytic centers, which are not systematically modified to achieve the desired stereoselectivity<sup>[76]</sup>.

This drawback might be overcome by immobilizing the structurally defined metal complex directly onto the support without disturbing its original structure. When the complex is formed by reacting the metal source with the immobilized ligand, the metal cations may form extra active centers with certain functional groups of the support, consequently decreasing the loading of the ligand-attached metal ion. Thus the catalytic activity will be reduced. Furthermore, the existence of the extra active centers with less asymmetric environment may reduce the enantioselectivity of the catalytic system. If the metal cations are fixed to the ligand in a rigid configuration prior to the attachment to the supporter, their contact with the solid supporter will not occur. This may prevent the formation of extra active centers if the metal complex is stable enough not to be decomposed by reaction with the support.

There are few reports so far about anchoring the metal complex as an entire moiety onto a solid support. This is probably due to the lability of metal complexes under the reaction

condition in the process of immobilization. The few reports about direct immobilization of metal complexes are limited to those with metal cations the complexes of which are very stable at ambient conditions, like Pd(II), Cr(III) and Co(II).

1n 1998, Clark and coworkers reported on a silica gel supported Schiff base-chromium complex as catalyst in the oxidation of alkyl-substitutet aromatic compounds (Fig. 2.1)<sup>[77]</sup>.



Figure 2.1 Anchoring of a Schiff base-chromium complex onto silica gel

A palladium complex supported by silica gel as a heterogeneous catalyst for the Suzuki reaction was reported by García in 2003 (Fig. 2.2)<sup>[78]</sup>.



Figure 2.2 Immobilization of an oxime-carbapallada cyclic complex onto silica gel

In 2004, Styring and coworkers described the immobilization of another palladium complex, a salen-type palladium(II) complex, onto Merrifield resin as an effective recyclable heterogeneous catalyst for the Suzuki cross-coupling reaction (Fig. 2.3)<sup>[79]</sup>.


Figure 2.3 The immobilization of the salen-type palladium(II) complex onto Merrifield resin

With a similar approach to Clark's work shown in Fig. 2.1, Macquarrie and coworkers immobilized Schiff base-cobalt complexes onto silica gel (Fig. 2.4) in 2005<sup>[80]</sup>.



Figure 2.4 Anchoring of a Schiff base-cobalt complex onto silica gel

# 2.2.2 Immobilization of VHPO Models

There hasn't been any (published) immobilized model for VHPOs reported so far. Our former group member Gabriella Santoni has endeavored to study the immobilization of model complexes onto mesoporous silica gel MCM-41 by the following strategy (Figure 2.5):



Figure 2.5 Immobilization of a VHPO model onto MCM-41

The catalytic results for the free vanadium complex and the corresponding immobilized complex are listed in Table 2.1.

Catalyst	Conver. %	SO : SO2	ee %	Time
Free catalyst (in situ)	100	89:11	25	3 h
Catalyst on MCM-41	100	83 :17	13	24 h

Table 2.1 Catalytic results of sulfoxidation

(0.1 M reactants, in 1,2-dichloroethane,

[benzyl phenylsulfide] : [CHP] : [catalyst] = 1:1: 0.1; -20 °C)

As shown in Table 2.1, the catalytic activity and enantioselectivity decreased obviously, while the selectivity decreased slightly. This may be explained by comparing the solid state <sup>51</sup>V NMR spectra of the catalyst in the homo- and heterogeneous systems: The solid state <sup>51</sup>V NMR spectrum of the free complex is represented by a signal at -470 ppm, while that of the immobilized complex resonates at -600 ppm (Fig. 2.6), corresponding to VO(-OSi-)<sub>3</sub>, and indicating that the complex has (partly) decomposed.



Figure 2.6 Solid state MAS <sup>51</sup>V NMR of an immobilized V-complex on MCM-41

On the basis of former work, new strategies in immobilizing V-aminoalcohol models of VHPOs are explored in the present work to obtain heterogeneous catalysts with well defined and stable structures.

Vanadium complexes with amino alcohol ligands were synthesized and studied as part of our systematic investigation into the amino alcohol type models of VHPOs. The investigation focused on three aspects: syntheses and structural characterization of model VHPOs, immobilization of these model compounds, and catalytic properties in selective sulfoxidations.

# 3.1 Synthesis and Characterization of Aminoalcohol Type Model VHPOs

In continuation of exploring the new aminoalcohol type models of VHPOs, R-styrene oxide and amines with different functional groups were used to synthesize aminoalcohol ligands, and oxido-*tris*(*iso*propoxido)vanadium VO(O*i*Pr)<sub>3</sub> was employed as vanadium source in the syntheses of the complexes. The overall reaction scheme is as follows:

$$+ H^{N} + H^{R} \longrightarrow Ligand \xrightarrow{VO(O_iP_{r})_3} V-Complex$$

Scheme 3.1 Synthesis of aminoalcohol type models of VHPOs

In most cases of the syntheses of the ligands, two isomers were obtained as the main products by nucleophilic attack of the amines on one of the two carbon atoms of the epoxyethyl moiety. Under basic reaction conditions, the ratio of the two isomeric products depends on the spatial hindrance of the amines. Reasonably, when the ratio of styreneoxide:amine is 2:1, the yield of the ligand obtained by 1,3/1,3 cleavage of the epoxyethyl group is larger than for the ligand obtained by 1,2/1,3 cleavage.

# 3.1.1 Model VHPOs with ligands from R-styreneoxide and allylamine

3.1.1.1 Syntheses and Characterization of the Ligands N,N-*bis*(hydroxy-phenylehtyl)-propene(1)-amine [**Lig. 1**] and N-2-hydroxyphenylehtyl-N-1-phenyl-2-hydroxy-ethyl-propene(1)-amine [**Lig. 2**]

By refluxing R-styreneoxide and allylamine (2:1 molar ratio) in *iso*propanol (scheme 3.1.1), colorless block-shaped crystals of ligand **1** (Lig.1) and a light-yellow sticky liquid of ligand **2** (Lig.2) were obtained in yields of 56% and 23%, respectively.



Scheme 3.1.1 Synthesis of Lig.1 and Lig.2

The two ligands were characterized by their 1-D and 2-D  $^{1}$ H and  $^{13}$ C NMR spectra. The spectra and the assignment of the protons in the molecules are shown in Fig. 3.1.



Figure 3.1 <sup>1</sup>H NMR of Lig.1 and Lig.2 in CDCl<sub>3</sub> at room temperature

The X-ray crystallographic analysis of Lig.**1** indicates that it crystallizes in the orthorhombic  $P2_12_12_1$  space group with a = 7.3912(6) Å, b = 13.0062(11) Å, c = 17.3285(15) Å, V = 1665.8(2) Å<sup>3</sup>, Z = 4 and R ( $wR_2$ ) = 0.0439 (0.0642); Figure 3.2. All bond lengths and bond angles are within normal ranges. The three N-C bond lengths are almost the same within experimental error, with an average value of 1.474(3)Å; d(O1-C7) and d(O2-C17) are 1.438(2) Å and 1.427(3) Å, respectively. The bond angles C8-N-C31, C8-N-C18 and C18-N-C31 are 111.70(18)°, 109.26(19)° and 110.41(18)°. N is 0.4669 Å above the plane defined by C8, C18, and C31. The two stereo centers at C7 and C17 remain in the R configuration.

There are intermolecular bonds between O1-H1O…N [ x-1/2, -y+3/2, -z ] and O2-H2O…O1 [ x+1, y, z ].



Figure 3.2 Crystal structure of Lig.1

Table 3.1	Selected bond	lengths and bo	ond angles of	Lig.1
		0	0	~

Bond lengths (Å)		Bond angles (°)		
N - C31	1.473(3)	C31- N - C8	111.70(18)	
N - C8	1.473(3)	C31 - N - C18	110.41(18)	
N - C18	1.477(3)	C8 – N - C18	109.26(19)	
O1 - C7	1.438(2)	C7 - O1 - H1O	110.0(15)	
O2 - C17	1.427(3)	С17 - О2 - Н2О	112(2)	
01-H10N*	1.933	01-H10N	168.16	
O2-H2OO1**	1.932	O2-H2OO1	174.87	

\* N is from a symmetry-related molecule [x-1/2, -y+3/2, -z]; \*\*O is from a symmetry-related molecule [ x+1, y, z ]

3.1.1.2 Synthesis and Characterization of Model VHPOs: (R,R)-Methoxido-[N,N-bis(2hydroxyphenylethyl)-propene(1)amine]-oxidovanadium(V) (Complex 1) and Methoxido[(R)-N-2-hydroxy-2-phenylethyl-(S)-N-1-phenyl-2-hydroxyethylpropenenamine]-oxidovanadium(V) (Complex 2)

3.1.1.2.1 Synthesis and Crystal Structure of the Vanadium Complexes

The reaction between Lig.1 and VO(OiPr)<sub>3</sub> (molar ratio 1:1) in anhydrous THF under N<sub>2</sub> yielded a green solution, from which a green sticky residue was obtained after removal of the solvent in vacuo. The residue was redissolved in dry methanol, and kept at -20 °C to yield yellow needle-shaped crystals of R,R-[VO(OMe)L<sup>1</sup>] (Complex 1). The complex

R,S-[VO(OMe)L<sup>2</sup>] (Complex **2**) has been prepared accordingly from Lig.2 and  $VO(OiPr)_3$ . Both complexes exhibit strong characteristic (V=O) stretching vibrations at 978 cm<sup>-1</sup> (KBr pellets) in their IR spectra.



Figure 3.3 Molecular Structure of Complex 1 (left) and Complex 2 (right)

Compl.1 crystallizes in the orthorhombic space group  $P2_12_12_1$  with a = 6.4827(4) Å, b = 7.7631(5) Å, c = 38.15(2) Å, V = 1921.2(2) Å<sup>3</sup>, Z = 4 and R ( $wR_2$ ) = 0.0328 (0.0799); Compl.2 crystallizes in the monoclinic  $P2_1$  space group with a = 11.1327(13) Å, b = 5.9643(7) Å, c = 14.6191(18) Å,  $\beta = 93.347(2)^\circ$ , V = 969.0(2) Å<sup>3</sup>, Z = 4 and R ( $wR_2$ ) = 0.0467 (0.0906); Figure 3.3.

The vanadium center in both structures is five-coordinated. Selected bond lengths and angles are listed in Table **2**. In complex **1**, the two largest angles at vanadium are 164.75(7)° (O4-V-N) and 125.15(7)° (O3-V-O2); in complex **2**, the two largest angles at vanadium are 163.88(14)° (O4-V-N) and 132.19(14)° (O3-V-O2). The angular parameters  $\tau$  (the  $\tau$  parameter is 0 for an ideal square pyramid, and 1 for an ideal trigonal bipyramid) amounts to 0.66 for complex **1** and 0.53 for complex **2**. Since the  $\tau$  values are close to 0.5, the coordination geometry for these two complexes is in-between trigonal-bipyramidal and square-pyramidal.

As in the other five-coordinated aminoalkoxido-vanadium complexes that have been reported<sup>[59]</sup>, the methoxy group in **1** and **2** is in the *trans* position of the N donor of the ligand – as expected, considering that this structural arrangement minimizes the strain in the molecules.

The V-N bond lengths in complex **1** is 2.2251(16) Å, which is rather long as a consequence of the *trans* influence exerted by the OMe group, but in the normal range of V-N(amine) bond lengths (around 2.1-2.3 Å) observed in other vanadium(V) complexes<sup>[81]</sup>, and also in other five coordinated vanadium complexes containing the NO<sub>4</sub> donor set including an amino alcohol <sup>[59]</sup>. The V-N bond length in complex **2** is 2.413(3) Å. This particularly prolonged *d*(V-N) may reflect steric crowding due to the fact that one of the phenyl groups is adjacent to the coordinating ligand function.

The V=O bond lengths are 1.5914(14) Å in **1**, and 1.600(3)Å in **2**, which is in the normal range <sup>[81-85]</sup>. The V-O distances for V-O2 and V-O3 in the two complexes are similar, varying between 1.8127(14) Å and 1.8303(3) Å, nearly in the normal range when compared to d(V-O<sub>alkoxido</sub>) observed for a variety of *mono*oxidovanadium complexes, viz. 1.719-1.819Å <sup>[85-86]</sup>. The d(V-O<sub>methoxido</sub>) for of V-O4 is 1.7930(14) Å in **1** and 1.759(3)Å in **2**, comparing well with corresponding bond lengths found in other vanadium complexes with the methoxido ligand <sup>[59]</sup>.

In complex **1**, the distances of O2 and O3 to their bonding carbon atoms are indistinguishable within experimental error, 1.415(2) Å and 1.417(2) Å, i. e. slightly shorter than in the free ligand 1 (1.438(2) Å and 1.427(3) Å). In complex **2**, the corresponding O-C distances are 1.414(5) and 1.425(5) Å.

Due to the multidentate coordination to V, the distance from N to the plane of C8, C18, and C31 in complex **1**, 0.4262 Å, is shorter than that in Lig.1, 0.4669 Å, and consequently, the angle C8-N-C18 becomes larger by more than  $4^{\circ}$ , opening from 109.26(19)° in Lig.1 to 113.32(15)° in complex **1**.

Complex 1		Complex 2			
	Bond lengths (Å)				
V-O(1)	1.5914(14)	V-O(1)	1.600(3)		
V-O(4)	1.7930(14)	V-O(4)	1.759(3)		
V-O(3)	1.8127(14)	V-O(3)	1.820(3)		
V-O(2)	1.8251(13)	V-O(2)	1.830(3)		
V-N	2.2251(16)	V-N	2.413(3)		
O(2)-C(7)	1.415(2)	O(2)-C(7)	1.414(5)		
	2				

 Table 3.2
 Selected bond lengths and bond angles of complex 1 and complex 2

O(3)-C(17)	1.417(2)	O(3)-C(19)	1.425(5)
O(4)-C(20)	1.407(3)	O(4)-C(20)	1.414(5)
	Bond an	gles (°)	
O(1)-V-O(4)	103.96(7)	O(1)-V-O(4)	105.40(17)
O(1)-V-O(3)	115.89(8)	O(1)-V-O(3)	107.06(14)
O(4)-V-O(3)	93.57(6)	O(4)-V-O(3)	98.20(13)
O(1)-V-O(2)	113.33(7)	O(1)-V-O(2)	110.92(15)
O(4)-V-O(2)	96.83(6)	O(4)-V-O(2)	98.61(14)
O(3)-V-O(2)	125.15(7)	O(3)-V-O(2)	132.19(14)
O(1)-V-N	91.23(7)	O(1)-V-N	90.71(13)
O(4)-V-N	164.75(7)	O(4)-V-N	163.88(14)
O(3)-V-N	78.33(6)	O(3)-V-N	76.11(11)
O(2)-V-N	77.94(6)	O(2)-V-N	75.48(12)
C(8)-N-C(18)	113.32(15)	C(8)-N-C(12)	114.1(3)

# 3.1.1.2.2 Structures of the Vanadium Complexes in Solution

The <sup>51</sup>V NMR spectra of complex **1** and complex **2** in CDCl<sub>3</sub> are shown in Figure 3.7. More than one resonance signal were observed in the range typical of five-coordinated vanadium complexes with an O<sub>4</sub>N donor set <sup>[86]</sup>, indicating that more than one vanadium species is present in chloroform solution. The resonance peaks of **1** are at  $\delta$  = -418, -446 and -455 ppm; those of **2** at  $\delta$  = -443, -449, and -457 ppm (Fig. 3.4).



**Figure 3.4** <sup>51</sup>V NMR spectra of complexes **1** (a) and **2** (b) in CDCl<sub>3</sub> at room temperature

Rehder et al. have carried out a detailed elucidation on the creation of these multiresonance peaks of aminoalcoholatovanadium complexes <sup>[59]</sup>. Alkoxidovanadium compounds tend to associate to dimers and/or oligomers (Fig. 3.5) in certain solvents through alkoxido bridges, and provide resonance in higher field regions. In Figure 3.7, the broad peaks at  $\delta = -$ 455 ppm (complex **1**) and  $\delta = -477$  ppm (complex **2**) are assigned to these dimers.

The intensity of these signals increases with an increase of the concentration of these complexes.



Figure 3.5 Equilibrium between monomer and dimers and/or oligomers [59]

The high-field resonances disappear when methanol is used as solvent (Fig. 3.6). This is due to an additional (weak) coordination of methanol to these five-coordinated complexes leading to six-coordinated vanadium species, and thus preventing the formation of dimers and/or oligomers.





For entropic reasons, the equilibrium should be directed towards the monomers. Therefore, the predominant resonance signals at -418 for **1** and -443 ppm for **2** are assigned to the monomers, whose solution structures supposedly are the same as in the crystallographically characterized solid state, i.e. with the methoxido group in the *trans* position of the N-V bond. The smaller signals at -446 ppm for **1** and -449 ppm for **2** are provisionally assigned to the isomers of these two complexes with the *oxido* group in the *trans* position with respect to the N-V bond (Fig. 3.7).

$$\begin{array}{c} \stackrel{0}{\overset{}_{\scriptstyle \downarrow}} \\ \stackrel{0}{\overset{0}{\overset{}}} \\ \stackrel{0}{\overset{}_{\scriptstyle \downarrow}} \\ \stackrel{0}{\overset{}_{\scriptstyle \scriptstyle}} \\ \stackrel{0}{\overset{}_{\scriptstyle \scriptstyle}} \\ \stackrel{0}{\overset{}_{\scriptstyle \scriptstyle}} \\ \stackrel{0}{\overset{}} \stackrel{0}{\overset{}} \\ \stackrel{0}{\overset{}} \\ \stackrel{0}{\overset{}} \stackrel{}} \stackrel{} \\ } \stackrel{0}{\overset{}} \stackrel{} \overset{}} \stackrel{}$$

Figure 3.7 The two isomers with different trans groups with respect to the N-V bond

Unlike the aminoalcohol-vanadium complexes reported in our former work<sup>[59]</sup>, which exhibited obvious exchange correlation in the <sup>51</sup>V EXSY spectra in CDCl<sub>3</sub> at a mixing time of 2 ms at room temperature, neither complex **1** nor complex **2** showed any exchange correlation in CDCl<sub>3</sub> or THF at a mixing time of 1 ms, even not at a higher temperature of 330 K.

# 3.1.2 Model VHPOs with ligands derived from R-styreneoxide and 3amino-1,2-propanediol

3.1.2.1 Synthesis and Characterization of the Ligands 3-[N,N-*bis*(2-hydroxyphenylethyl)]amino-1,2-propanediol [**Lig. 3**] and N-2-hydroxyphenylehtyl-N-1-phenyl-2hydroxy-ethyl-amino-1,2-propanediol [**Lig. 4**]

By refluxing R-styreneoxide and racemic 3-amino-1,2-propandiol (2:1 molar ratio) in *iso*propanol (Scheme 3.2), colorless block-shaped crystals of Lig.3 and a colorless sticky, gel-like substance of Lig.4 were synthesized in yields of 58.6% and 31.8%, respectively.



Scheme 3.2 Synthesis of Lig.3 and Lig.4

Lig.3 is obtained in the R,R,S and Lig.4 in R,R configuration with an unknown configuration at the carbon-2 of the propanediol side-chain. Their <sup>1</sup>H NMR spectra are shown in Fig. 3.8.



**Figure 3.8** <sup>1</sup>H NMR of Lig.**3** (left) and Lig.**4** (right) in CDCl<sub>3</sub> at RT

According to the X-ray crystallographic analysis, of Lig.3 crystallizes in the orthorhombic space group  $P2_12_12_1$  with a = 9.3360(8) Å, b = 10.7743(10) Å, c = 17.3992(15) Å, V = 1750.2(3) Å<sup>3</sup>, Z = 4 and R ( $wR_2$ ) = 0.0398 (0.0923); Fig. 3.9. In this structure, the three R stereo centers are at C7, C27 and C32. All bond lengths and bond angles are in the normal range. The bond lengths d(N-C) are between 1.420(3) and 1.427(3) Å, i.e. almost the same within experimental error; the bond



Figure 3.9 Crystal structure of Lig.3

lengths of d(C-O) are around 142.6 Å. The bond angles of C8-N-C31, C8-N-C28 and C28-N-C31 are 113.11(17)°, 114.96(17)° and 113.02(18)°, respectively. The distance from N to the plane spanned by C8, C28 and C31 is 0.3738 Å.

Because of the multihydroxy characteristic of Lig.3, the structure is rich of intra- and intermolecular H-bonds (Table 3.3).

 Table 3.3
 Selected bond lengths and angles of Lig.3

Bond lengths (Å)						
C(8)-N(1)	146.9(3)					
C(31)-N(1)	146.7(3)	C(7)-O(1)	142.6(3)			
C(27)-O(2)	143.1(3)	C(32)-O(3)	142.0(3)			
C(33)-O(4)	142.6(3)	O3-H30…N1	2.106			
O1-H10…O2	2.090	O4-H40…O1**	2.094			
O2-H20…O4*	2.022	N1-HN1O3	2.226			
Bond angles (°)						
O1-H10O2	117.85					
O2-H20O4*	158.14	O4-H40O1**	163.54			
N1-HN103	119.27					

\*O4 is from the related molecule [ x+1/2, -y+1/2, -z ]; \*\*O1 is from the related molecule [ x-1, y, z ]

3.1.2.2 Synthesis and Characterization of Model VHPOs: (R,R)-[N,N-*bis*(2-oxo-2-phenylethyl)-N-2-oxo-3-hydroxopropylamine]oxidovanadium(V) (Complexe **3**) and

(R,R)-[N,N-bis(2-oxo-2-phenylethyl)-N-2-oxo-3-hydroxypropylamine]oxidovanadium(V) (Complexe ${\bf 3'}$ )

## 3.1.2.2.1 Synthesis and Crystal Structure of the Vanadium Complexes

The reaction of Lig.3 and VO(O*i*Pr)<sub>3</sub> (molar ratio 1:1) in anhydrous ethanol under N<sub>2</sub> results in a red-brown solution and a light yellow amorphous precipitate. After having kept the red-brown solution at -20 °C for several days, yellow-green cubic crystals of complex **3** had formed. The complex dissolves well in DMSO and methanol, slightly in THF. The IR spectrum of **3** exhibits a characteristic V=O stretching vibration at 967 cm<sup>-1</sup> (KBr pellet).

The amorphous precipitate dissolves well in DMSO. Put in the open air, fine, needle-like light-yellow crystals formed two weeks later (complex **3'**). The IR spectrum of **3'** exhibits a characteristic V=O stretching vibration at 965 cm<sup>-1</sup>. The ratio of the yields of complexes **3** and **3'** is about 1 : 1.5.

Complex **3** crystallizes in the tetragonal space group *P*4(1) with a = 11.5705(5) Å, b = 11.5705(5) Å, c = 31.755(2) Å, V = 4251.3(4) Å<sup>3</sup>, Z = 8 and R (*wR*2) = 0.0404 (0.0486); Fig. **3.10**.

Vanadium is six-coordinated, forming an almost perfect octahedron. The four oxygen atoms O11, O12, O13, and O14 from the ligand are positioned on the four corners of the square plane which is vertical to the N-V-O1 axis. The deviations of the four O atoms from this plane are 0.0378 Å (O11), -0.0383 Å (O12), -0.0436 Å (O13), and 0.0441 Å (O14), respectively, and the V atom resides 0.3631 Å above this plane; the distances of the axial N and the oxido functions to this plane are -1.9326 Å and 1.9671 Å, respectively. The angle of N-V-O1 is 178.15(9)°, almost a completely straight line, and d(V-N) is 2.297(2) Å, d(V=O) is 1.6065(17) Å. The N-V distance is a little bit longer than usual (see the discussion in the previous section) due to the *trans* effect by the oxido ligand and the crowded environment around the vanadium atom.



Figure 3.10 Crystal structure of complex 3 (left) and complex 3' (right)

The four angles O1-V-O11, O1-V-O12, O1-V-O13 and O1-V-O14 are 100.08(9)°, 99.58(9)°, 105.31(9)° and 99.56(9)°, respectively; the distances of V to the four O atoms are d(V-O11) = 1.8236(17) Å, d(V-O12) = 1.8423(18) Å, d(V-O13) = 1.9324(18) Å, and d(V-O14) = 2.0753(19) Å.

The long bond length V-O14 indicates weak coordination of O14. In fact, O14 still carries its hydrogen atom as in the free ligand. And in Complex **3**', this hydroxy group is completely free, not coordinating to V at all (Fig. **3.10**).

Complex 3						
Bond lengths (Å)						
V-O(1)	V-O(1) 1.6065(17) V-O(13)					
V-O(11)	1.8236(17)	V-O(14)	2.0753(19)			
V-O(12)	1.8423(18)	V-N(1)	2.297(2)			
	Bonc	l angles (°)				
O(1)-V-N	178.15(9)	O(1)-V-O(12)	99.58(9)			
O(12)-V-O(13)	149.77(8)	O(1)-V-O(13)	105.31(9)			
O(11)-V-O(14)	158.38(9)	O(1)-V-O(14)	99.56(9)			
O(1)-V-O(11)	100.08(9)					
	Co	mplex 3'				
	Bond	lengths (Å)				
V-O(1)	1.6074(15)	V-O(4)	1.8097(16)			
V-O(2)	1.8183(16)	V-N(1)	2.2987(17)			
V-O(3)	1.8024(15)	O(5)H(5)O(2')	2.015			
Bond angles (°)						
O(1)-V-N	179.74(10)	O(2)-V-O(4)	117.73(8)			
O(2)-V-O(3)	115.38(8)	O(5) - (5)O(2')	178.24			
O(3)-V-O(4)	116.33(8)					

 Table 3.3
 Selected Bond Lengths and Bond Angles of Complex 3 and 3'

Complex **3'** crystallizes in the orthorhombic space group  $P2_12_12_1$  with a = 7.7973(8) Å, b = 11.9461(12) Å, c = 18.8807(19) Å, V = 1758.7(3) Å<sup>3</sup>, Z = 4 and R (wR2) = 0.0368 (0.0628). It represents a five coordinated V-complex, with a primary hydroxyl group on the ligand completely free. The vanadium resides in an ideal trigonal bipyramidal geometry with the V-N and V=O bonds oriented along the axis: The bond angle N-V-O is 179.74(10)°, and the angular parameters  $\tau$  is 1.03. The distance of V to the plane defined by O2, O3, and O4 is 0.3439 Å, and the distances of V and N to this plane are 1.9512 Å and -1.9545 Å, respectively. All the bond length are comparable with those in Complex **3** (Table **3.3**): the d(V-O) lengths are distributed over the range 1.8024(15) Å to 1.8183(16) Å; d(V=O) is 1.6074(15) Å and d(V-N) is 2.2987(17) Å. The free hydroxyl group forms a hydrogen bond with O2' from another molecule.

## 3.1.2.2.2 Structures of the Vanadium Complexes 3 and 3' in Solution

Unlike the complexes **1** and **2**, complexes **3** and **3'** exhibit only one <sup>51</sup>V NMR signal in solution. In methanol-d<sub>4</sub> at room temperature, the <sup>51</sup>V NMR of complex **3** is at  $\delta$  = -411.4 ppm (Fig. **3.12**). The peak at -553 ppm is VO(OMe)<sub>3</sub>, formed by partial decomposition of the complex in methanol. When DMSO-d<sub>6</sub> is used as a solvent, the peak at -553 ppm is absent, and the chemical shift for **3** is at  $\delta$  = -396 ppm. The <sup>51</sup>V NMR of complex **3'** in DMSO-d<sub>6</sub> at room temperature is at  $\delta$  = -381 ppm.



This difference in the number of <sup>51</sup>V NMR signals between **1** and **2** on the one hand, and **3** on the other hand, arises from the different denticities of the ligands: The six-coordinated complex **3** is in a rigid



octahedral geometry at the structural request of the ligand, with the axial orientation of the oxido group opposite to the N-V bond as the preferential orientation. Although complex **3'** is also in a five- coordinated trigonal coordinated trigonal bipyramidal geometry as complex **1** and **2**, its coordinating atoms are all from the same single ligand, and the fixed structure of the

ligand allows no exchange of the positions of the coordinating atoms.



# 3.1.3 Model VHPOs with ligands derived from R-styreneoxide and *tris*(hydroxymethyl)-methylamine

3.1.3.1 Synthesis and Characterization N,N-*bis*(hydroxyphenylehtyl)-*tris*(hydroxymethyl)methylamine [**Lig. 5**] and N-2-hydroxyphenyl-ehtyl-N-1-phenyl-2-hydroxy*tris*(hydroxy-methyl)methylamine [**Lig. 6**]

In order to immobilize model VHPOs on resins, vanadium complexes with free hydroxy groups in the coordination periphery were envisaged. For this purpose, a multi-hydroxy grouped precursor was chosen to synthesize an appropriate ligand (Scheme 3.3).



Scheme 3.3 Synthesis of Lig.5 and Lig.6

Lig.**5** and Lig.**6** were synthesized by refluxing R-styreneoxide and *tris*(hydroxymethyl)methylamine in *iso*propanol. The products were purified by column chromatography with hexane/ethylacetate and ethylacetate/ethanol as eluants with gradually increased polarity. Both ligands are colorless sticky gel-like substances, and were obtained in yields of 52.4% (Lig.**5**) and 21.9% (Lig.**6**), respectively.

The two ligands were characterized by IR, elemental analysis as well as 1D <sup>1</sup>H NMR and 2D <sup>1</sup>H-<sup>1</sup>H COSY NMR, HMBC and HSQC techniques. The <sup>1</sup>H NMR spectra of Lig.5 and Lig.6 are shown in Figure 3.14.



Figure 3.14 <sup>1</sup>H NMR of Lig.5 (up) and Lig.6 (down) in acetone-d<sub>6</sub> at RT

## 3.1.3.2 Synthesis of the Vanadium Complex 5, and Characterization in Solution

Complex **5** was synthesized by the reaction of Lig.5 and VO(OiPr)<sub>3</sub> (molar ratio 1:1) in anhydrous THF under N<sub>2</sub>. On slow addition of a THF solution of VO(OiPr)<sub>3</sub> to a THF solution of Lig.5, an initially red-brown solution formed, which turned yellow on further addition of VO(OiPr)<sub>3</sub>, accompanied by the formation of a yellow amorphous precipitate. Any attempts to get crystals from the original red brown mother liquor, or from different solvents, failed. The yellow precipitate (complex **5**) was slightly soluble in CHCl<sub>3</sub> and THF, and easily dissolved in DMSO.

NMR, IR and elemental analyses indicated that the yellow precipitate is the vanadium(V) complex of Lig.5. The vanadium in complex **5** easily got reduced to the +IV oxidation state. This could be observed from the back-ground noise of its <sup>51</sup>V NMR spectra. Figure **3.15** shows the <sup>51</sup>V



**Figure 3.15** <sup>51</sup>V NMR of complex **5** in CDCl<sub>3</sub> at RT

NMR spectrum of a freshly prepared solution of **5** in CDCl<sub>3</sub> at room temperature with the chemical shift  $\delta = -402$  ppm.

Two to three weeks later, yellow **5** had turned green, and a <sup>51</sup>V NMR signal could no longer be observed.

Instead, EPR spectra of its reduced form, complex **5'**, were obtained at 115 K (Fig. **3.16**). The  $A_{\perp}$  value obtained from the EPR spectrum is  $68.0 \times 10^{-4}$  cm<sup>-1</sup>, and  $A_{\parallel}$  172.0 × 10<sup>-4</sup> cm<sup>-1</sup>; the  $g_{\perp}$  is 1.988 and  $g_{\parallel}$  1.950.



Figure 3.16 EPR of complex 5' in acetone at 115K (left) & its simulation (right)

Considering that Lig.5 has structural characteristics similar to Lig.3, the oxido group in complex 5 should reasonably have the same position as in complexes 3 or 3', i. e. along the axis vertical to the plane defined by the alkoxido donors from the ligand, and opposite the V-N vector. The question that still remains is: how many O atoms from the ligand are coordinated to the vanadium atom?

EPR and the additivity relationship have been used to reveal the structures of many vanadyl complexes <sup>[99]</sup>, because different coordinating moieties in the equatorial plane have different contributions to the parallel component of the hyperfine coupling constant,  $A_{\#}$ . Partial  $A_{\#}$  are  $35.3 \cdot 10^{-4}$  cm<sup>-1</sup> for alkoxido (RO),  $43 \sim 45 \cdot 10^{-4}$  cm<sup>-1</sup> for an alcohol (ROH), and  $40 \cdot 10^{-4}$  cm<sup>-1</sup> for acetone (C=O). The overall number of O atoms coordinating in the equatorial plane to vanadium should be 4, with two of which deprotonated to provide the overall neutral charge, providing the structure shown in Fig. **3.17**. In this case, the calculated value of  $A_{\#}$  is  $2 \times 35.3 \cdot 10^{-4} + 2 \times 43 \cdot 10^{-4} = 156.6 \cdot 10^{-4}$  cm<sup>-1</sup>. The considerably larger experimental value of  $172 \cdot 10^{-4}$  cm<sup>-1</sup> suggests, however, that alkoxido functions are replaced by the polar solvent acetone, or that there are strong rhombic distortions.



**Figure 3.17** The putative structure of complex 5 ( $V^{4+}$ )

# 3.1.4 Model VHPOs with ligands derived from R-styreneoxide and 3trimethoxy-silylpropylamine

3.1.4.1 Syntheses and Characterization of Methoxy  $\{N,N',N''-2,2',3-[bis(R-1-phenylethanolato)(propyl)]$ amino $\}$  silane **[Lig. 7]** and methoxy- $\{N,N',N''-2,2',3-[(R-1-phenylethanolato)(S-2-phenylethanolato)(propyl)]$ amino $\}$  silane **[Lig. 8]** 

In this part of the work, carbasilatrane ligands were developed with the intention to produce heterogeneous model VHPO catalyst systems.

Silatranes have a cage structure in which N-(CH<sub>2</sub>)<sub>3</sub> and X-Si(Y)<sub>3</sub> (Y = O, C, N) fragments face each other (Fig. 3.18). Si is five coordinated, residing in a trigonal bipyramid with the Y atoms nearly in equatorial positions. When Y is O plus C, or exclusively C, the silatranes are called carbasilatranes; when Y is O plus N, or exclusively N, they are called azasilatranes. The axial N is pyramidalized with its lone electron pair pointing towards Si, forming an intramolecular N $\rightarrow$ Si donor – acceptor bond <sup>[87]</sup>.

Carbasilatranes containing amino-alcoholate groups covalently attached to Si might be very useful in the stereoselective and enantioselective





catalysis of the synthesis of oxygen transfer based on immobilized vanadium(V) compounds <sup>[88]</sup>. The design of these carbasilatranes was accomplished by using amines with methoxysilyl groups, allowing for an introduction of the corresponding functional group into the ligands for subsequent immobilization.





Scheme 3.4 Syntheses of Lig.7 and Lig.8

As shown in Scheme 3.4, Lig.7 and Lig.8 were synthesized from the reaction of Rstyreneoxide and 3-trimethoxysilylpropylamine by refluxing in *iso*propanol under the protection of N<sub>2</sub>. The product was purified by column chromatography with eluants (hexane/ethylacetate followed by ethylacetate/ethanol) of gradually increased polarity. After evaporation of the solvent, colorless, big block-shaped crystals of Lig.7 and Lig.8 were obtained in yields of 54.2% and 25.2%, respectively.

The chemical shift  $\delta$ (<sup>29</sup>Si) of Lig.7 is  $\delta$  = -66.1 ppm, and that of Lig.8  $\delta$  = -60.3 ppm. The <sup>1</sup>H and <sup>1</sup>H-<sup>29</sup>Si HMBC NMR spectra of the two ligands (Fig. 3.19 and 3.20) show a long distance coupling between Si and the protons at positions 3, 3', 4, 5, 6, and 7 in Lig.7, and with the protons at positions 2, 3, 5, 6, 7, 8, and 9 in Lig. 8, reflecting the cyclic structures in the carbasilatranes.



Figure 3.19 <sup>1</sup>H NMR of Lig.7 (left) and Lig.8 (right) in CDCl<sub>3</sub> at RT



Figure 3.20 <sup>1</sup>H-<sup>29</sup>Si HMBC NMR of Lig.7 (left) and Lig.8 (right) in THF at RT

According to the X-ray crystallographic analysis, Lig.7 crystallizes in the hexagonal space group  $P6_1$  with a = 10.8032(5) Å, b = 10.8032(5) Å, c = 27.4597(17) Å,  $\gamma = 120^\circ$ , V = 2775.4(3) Å<sup>3</sup>, Z = 6, and R(wR2) = 0.0354 (0.0409) (Fig. 3.24). Lig.8 crystallizes in the monoclinic space group P2(1) with a = 7.7061(9) Å, b = 9.2717(11) Å, c = 12.4967(15) Å,  $\beta = 99.633(2)^\circ$ , V = 880.28(18) Å<sup>3</sup>, Z = 2, and R(wR2) = 0.0378 (0.0650) (Fig. **3.21**).



Figure 3.21 Crystal structures of Lig.7 (left) and Lig.8 (right)
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The N-Si bond lengths in Lig.7 and Lig.8 are 2.2031(19) Å and 2.2284(16) Å, respectively. The N-Si-O3 bond in Lig.7 is almost linear (bond angle 178.99(9)°) while, in Lig.8, this angle is 175.40(7)°. In most silanes which have been characterized crystallographically, the N-Si bond lengths vary between 1.97 and 2.24 Å, which exceeds the usual N-Si bonds (1.7 - 1.8 Å), but is distinctly shorter than the sum of the van der Waals radii (~ 3.5Å) <sup>[89]</sup>. The length of the transannular N-Si bond depends in part on the nature of the substituent X on Si. Generally, a more electronegative substituent X shortens the N-Si bond, because an increase in the electron-withdrawing power of X increases the positive charge on Si, resulting in stronger attraction between N and Si <sup>[90]</sup>. Additionally, carbasilatranes have longer N-Si bonds than other kinds of silatranes (azasilatranes have the shortest N-Si bonds). <sup>[87, 91]</sup>

While the key role of the N-2p lone pair is indisputable, the nature of the N $\rightarrow$ Si bond is far from being well understood. Controversies mainly arise on the question of whether the N-2p lone pair is attracted only by the positive charge of Si, or whether there is also a charge transfer to the unoccupied Si 3d, 4s, or 4p atomic orbitals <sup>[89]</sup>. Further, there is still no agreement about the nature of the covalent component of the N $\rightarrow$ Si bond, which has been predicted to be a three center (X-Si-N) four-electron (3c4e) interaction mode <sup>[92]</sup>. The recent calculations of Ortiz et al. indicate, however, that the N $\rightarrow$ Si bond is chiefly electrostatic in nature, with no appreciable covalent N-Si bonding being found. <sup>[89]</sup> It is known that the N $\rightarrow$ Si interaction is weak and the potential energy surface is very flat. Thus it is expected that there may be no actual N $\rightarrow$ Si bond in the gas phase, in which the bond length is typically increased by 0.28 Å as compared to that in the crystalline solid state.

L	ig.7	L	ig.8				
	Bond lengths (Å)						
Si-O(1)	1.6562(17)	Si-O(1)	1.6757(13)				
Si-O(2)	1.6637(16)	Si-O(2)	1.6597(13)				
Si-O(3)	1.6713(15)	Si-O(3)	1.6810(14)				
Si-C(19)	1.873(2)	Si-C(19)	1.885(2)				
Si-N	2.2031(19)	Si-N	2.2284(16)				
O(1)-C(2)	1.421(2)	O(1)-C(2)	1.415(2)				
		10					

**Table 3.4**Selected bond lengths and bond angles of Lig.7 and Lig.8

O(2)-C(10) 1.423(2)		O(2)-C(9)	1.425(2)					
O(3)-C(20)	1.418(3)	O(3)-C(20)	1.417(2)					
	Bond angles (°)							
O(1)-Si-O(2)	117.96(9)	O(1)-Si-O(2)	116.85(7)					
O(1)-Si-C(19)	120.66(10)	O(1)-Si-C(19)	118.82(8)					
O(2)-Si-C(19)	116.52(10)	O(2)-Si-C(19)	119.47(8)					
O(1)-Si-N	82.32(8)	O(1)-Si-N	81.36(6)					
O(2)-Si-N	82.85(8)	O(2)-Si-N	83.40(6)					
O(3)-Si-N	178.99(9)	O(3)-Si-N	175.40(7)					
C(19)-Si-N	82.76(10)	C(19)-Si-N	83.12(8)					
C(1)-N-C(17)	112.33(19)	C(1)-N-C(17)	112.70(15)					
C(1)-N-C(9)	114.51(18)	C(1)-N-C(10)	114.72(15)					
C(17)-N-C(9)	112.66(19)	C(17)-N-C(10)	113.86(15)					

In Lig.7, the chiral centers at C2 and C10 are both in R-configuration, while in Lig.8 the chiral centers at C2 and C9 are in the R and S configuration, respectively. In both ligands, the Si-O bond lengths are in the range of 1.6562 - 1.68(10) Å, and the C-O bond lengths in the range 1.415(2) - 1.425(2) Å. All these bond lengths are in the normal range.

3.1.4.2 Syntheses and Characterization of the Vanadium Complexes 7 and 8

The aqueous carbasilatrane-NaVO<sub>3</sub> system has been studied by Keramidas et al. <sup>[93]</sup>, in which vanadosilicates and vanadium chelate complexes were generated. Different from this system, the vanadium complexes of the carbasilatrane ligands Lig.7 and Lig.8 were studied in the system carbasilatrane-VO(O*i*Pr)<sub>3</sub> (L:V=1:1) in DMSO solution.



Figure 3.22 <sup>1</sup>H NMR of complex 7 (left) and 8 (right) in DMSO-d<sub>6</sub> at RT

During the first several hours after the reaction between the ligands and  $VO(OiPr)_3$  had started, the systems were studied by <sup>1</sup>H and <sup>51</sup>V, as well as by <sup>1</sup>H-<sup>29</sup>Si HMBC NMR.



Figure 3.23 <sup>51</sup>V NMR of complex 7 (left) and 8 (right) in DMSO-d<sub>6</sub> at RT

In the Lig.**7**-VO(O*i*Pr)<sub>3</sub> system (Fig. **3.23** left), <sup>51</sup>V NMR was measured 10 minutes after the reaction had begun. The spectrum shows several resonances due to vanadium species present in the solution. The resonance at the lowest field,  $\delta = -469.0$  ppm, indicates that the aminoalcoholato-vanadium complex already had formed, while the resonance for VO(O*i*Pr)<sub>3</sub> in the high-field region ( $\delta = -621.7$  ppm) is still dominant. The signals inbetween are assigned to a series of intermediate products; the small peaks of very weak intensity (-648, -652, -655 ppm) found at higher field are assigned to vanadosilicates.<sup>[93]</sup> In the Lig.8-VO(O*i*Pr)<sub>3</sub> system (Fig. **3.23** right), the <sup>51</sup>V NMR was measured six hours after the reaction had been started. Resonances are observed between -472 ppm and -616 ppm. 48 hours later, the originally red-brown solutions of the Lig-V systems had turned completely to green, indicating the reduction of V(V) to V(IV). The <sup>1</sup>H-<sup>29</sup>Si HMBC NMR spectra of these solutions are shown in Fig. **3.24**.



Fig. 3.24 <sup>1</sup>H-<sup>29</sup>Si HMBC NMR of complexes 7 (left) & 8 (right) in DMSO-d<sub>6</sub> at RT

There is only one silicon species which shows <sup>1</sup>H-<sup>29</sup>Si correlations in each Lig-V system. In the Lig.**7**-V system, the resonance of <sup>29</sup>Si is at -66.0 ppm, and in the Lig.8-V system, this resonance is at -62.2 ppm. If there were any silicon species which involves vanadosilicate, its <sup>29</sup>Si signals could possibly not be observed because the <sup>51</sup>V-<sup>29</sup>Si coupling would broaden the <sup>29</sup>Si signals. Therefore the silicon species for which <sup>1</sup>H-<sup>29</sup>Si correlations were detected are most probably those which either contain no vanadium (the pure ligand), or contain vanadium coordinating only to the amino alcoholic group.

## 3.1.5 Aminoalcohol Ligands Containing the Chlorosilyl Group: Synthesis and Characterization of the Ligand Chloro-[(R,R)-N,N-bis(2-hydroxyphenylethyl)-propylamine]silicate [Lig. 9]

Although carbasilatrane ligands based on amino-alcohols have a promising potential in the synthesis of immobilized model VHPOs, a disadvantage might arise from the competition between silicon and vanadium in the ligation of the chelate moiety as a result of the affinity of amino alcohols to silicium. This affinity could also be seen in the syntheses of Lig.9: although the hydroxy groups of the amino alcohol ligand had been protected by methylation, the oxygen atoms also became attached, together with the nitrogen, to silicium during hydrosilylation (Schema. 3.5 ). The synthesis of Lig.9 proceeds in two steps as shown in Scheme 3.5.



Scheme 3.5 Synthesis of Lig. 9

In the first step, the hydroxyl groups of Lig.1 were methylated with methyl iodide by refluxing overnight after having been reacted with NaH (in paraffin, 60%) in anhydrous THF. The methylated product, a light-yellow liquid, was obtained in yields of 92.1% after purification by column chromatography with the eluants hexane-ethylacetate (4:1 v/v).

The methylated ligand 1 was characterized by <sup>1</sup>H and <sup>13</sup>C NMR. Its <sup>1</sup>H NMR is shown in Fig. **3.25**. The <sup>1</sup>H NMR signal of the -OCH<sub>3</sub> groups appears at  $\delta$  = 3.2 ppm.



In a second step, methylated Lig.1 was then, with the catalysis by H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, hydrosilylated at the vinyl moiety by refluxing with HSiCl<sub>3</sub> for 4 days in anhydrous *iso*propanol under the protection of nitrogen. The final reaction mixture is a red-brown solution.



Figure 3.26 <sup>1</sup>H NMR (left) and <sup>29</sup>Si NMR (right) of Lig.9 in CDCl<sub>3</sub> at RT

After having been concentrated, the red-brown product was roughly purified by quick passage through a short column of silica gel with the eluants hexane/ethylacetate (4:1), ethylacetate/ethanol (4:1), and finally ethanol. A red-brown substance got stuck onto the silica gel (for further processing see ch. 3.1.6.1), while the eluate coming out was colorless. Several days later, Lig.9 crystallized in colorless, big block-shaped crystals from the collected colorless eluates.



Figure 3.27 Crystal Structure of Lig.9

Lig.9 crystallizes in the orthorhombic space group P2(1)2(1)2(1) with a = 8.6210(7) Å, b = 11.4337(9) Å, c = 18.4090(14) Å, V = 1814.6(2) Å3, Z = 4, and R(wR2) = 0.0373 (0.0819). Compared with Lig.7, the only difference between the two ligands in structure lies in the groups attached to the silicium in the axial position: in Lig.9, this is a chlorine atom, while in Lig.7 it is the methoxy group. The distance from N to the plane of C8, C9, and C28 is 0.4004 Å, a little bit longer than in Lig.7.

Table 3.4	Selected bond	lengths and	angles of	Lig.9
				0

Bond lengths (Å)						
Cl(1)-Si(1) 2.1699(7) Si(1)-O(2) 1.6637(14)						
Si(1)-O(1)	1.6546(13)	Si(1)-C(11)	1.869(2)			
Si(1)-N(1)	2.0661(17)	O(1)-C(27)	1.439(2)			
O(2)-C(7)	1.418(2)					
	Bond	angles (°)				
O(1)-Si(1)-O(2)	105.63(11)					
O(1)-Si(1)-C(11)	O(1)-Si(1)-C(11) 119.11(9)		104.12(12)			
O(2)-Si(1)-C(11)	120.59(9)	C(9)-N(1)-Si(1)	107.34(12)			
O(1)-Si(1)-N(1)	86.33(7)	N(1)-Si(1)-Cl(1)	175.98(5)			
O(2)-Si(1)-N(1)	85.78(7)	C(11)-Si(1)-N(1)	86.80(8)			

In Lig.9, the N-Si bond length is 2.0661(17) Å, much shorter than that in Lig.7, due to the greater effective electronegativity of Cl than of the methoxy group, as discussed in ch. 3.1.4.1. The Si-Cl bond length is 2.1699(7) Å, the N-Si-Cl bond angle is 175.98(5)°. The two Si-O bonds are 1.6546(13) and 1.6637(14) Å, almost the same as those in Lig.7, where they are 1.6562(17) and 1.6637(16) Å.

The two chiral centers in Lig.9, C2 and C10, are both in the R configuration.

# 3.1.6. Synthesis and Characterization of N,N-*bis*(2-methoxy-2phenylethyl)-ammonium hydrochloride [Lig.10]

The red-brown silica gel obtained during preparation of Lig.9 (see previous chapter) was treated with a mixture of methanol and concentrated hydrochloric acid (37%, CH<sub>3</sub>OH:HCl  $\approx 6:1 \text{ v/v}$ ) with stirring overnight. During slow evaporation of the wash solvents, colorless plate-shaped crystals of Lig.10 were obtained.



Lig.10 crystallizes in orthorhombic space group *P*2(1)2(1)2(1) with *a* = 11.9238(10) Å, *b* = 21.1466(17) Å, *c* = 21.6386(17) Å, *V* = 5456.1(8) Å3, *Z* = 12, and *R*(*wR*2) = 0.0468 (0.0590).

Lig.10 is the chloride of a secondary amine which can be regarded as being obtained from

methylated ligand 1 with the allyl group missing. In the unit cell, the ligands are stacked one by one. The molecules are connected via a hydrogen bond line H-N-H…Cl…H-N-H…Cl (Fig. **3.29**). All bond length and angles are in the normal range. The H bond lengths and bond angle are collated in Table 3.5. This formation of Lig.10 was unexpected, because the strong C-N bond in tertiary amines is not easily broken. The mechanism is so far unknown.



Figure 3.29 Crystal structure of Lig.10

Table 3.5	Selected	bond	lengths	and a	ngles	for	Lig.	10
							4.2.	

Bond lengths (Å)					
Cl(1)-H(101)	2.2624	Cl(1)-H(202)	2.2074		
Cl(2)-H(201)	2.2919	Cl(2)-H(301)	2.2522		
Cl(3)-H(102)	2.2110	Cl(3)-H(302)	2.2491		
N(1)-H(101)	0.9200	N(1)-H(102)	0.9200		
Bond angles (°)					
H(101)-Cl(1)-H(202)	83.815	H(201)- Cl(2)-H(301)	92.257		
H(102)- Cl(3)-H(302)	104.638	H(101)-N(1)-H(102)	107.901		
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## 3.2 Immobilization of Aminoalcohol Type Model VHPOs

With the aim to exploit the advantages of heterogeneous catalysis, model VHPOs synthesized in Part 3.1. have been immobilized. Four different methods were studied: (i) self aggregation, (ii) immobilization on silica gel, (iii) immobilization on Merrifield resin, and (iv) immobilization on Barlos resin. The strategy is to choose ligands or V-complexes with functional groups which are suitable for being anchored to the support without disturbing the catalytic active center.

# 3.2.1 Synthesis and Characterization of Immobilized Carbasilatrane Derived Model VHPOs

Carbasilatranes of the type discussed in ch. 3.1.4.1 have the potential to be starting products to synthesize, stereo- and enantioselectively, immobilized oxygen transfer catalysts as model VHPOs. A disadvantage of these compounds might be the high affinity of the amino-alcoholates to silicium, which competes with V for the ligation of the chelate moiety. Further, vanadium may also coordinate to the alkoxysilyl group to form a V-O-Si moiety. Due to the complexity caused by complex structures, carbasilatrane ligands as such are less suitable to be used directly in synthesizing V-complexes with certain unique structural features. More appropriate is the cleavage of the amino-alkoxo-silicon fragment first, and then to stabilize the silicon part before vanadium is introduced.

Silatranes are relatively stable to moisture compared with the triethoxysilanes. They hydrolyze, however, at significantly faster rates in the presence of acid. The first and slowest step of the acid hydrolysis is protonation at the oxygen with simultaneous nucleophilic attack of the hydration shell of the acid anion at the silicon.<sup>[87]</sup> The subsequent steps, cleavage of the endo-cyclic Si-O bonds and protonation to form silanol groups, proceed very fast.<sup>[95]</sup> The mechanism of the acid hydrolysis is depicted in Figure **3.35**; see ch. 3.2.1.1.

Based on this behavior of carbasilatranes, immobilized model VHPOs derived from carbasilatranes were synthesized following two strategies: (i) self aggregation, and (ii) immobilization on silica gel.

# 3.2.1.1 Synthesis and characterization of immobilized complex 11 by self-aggregation

The carbasilatranes Lig.7 was dissolved in the minimum amount of methanol, followed by drop-wise addition of hydrochloric acid (pH  $\approx$  1) under vigorous stirring. After the carbasilatrane had undergone acidic hydrolysis, the product of hydrolysis, the silane, like other silanes, began to aggregate by dehydration,<sup>[94, 95, 98]</sup> as show in Fig. **3.30**. 12 Hours later, the precipitate was collected by centrifugation and washed with deionized water, NaHCO<sub>3</sub> (0.5 M), and again with deionized water (each 5 times) in an ultrasonic bath. The powder was finally dried at 70°. Comparing the IR spectra of Lig.7 and its aggregate, the two IR spectra are almost congruent (Fig. **3.31**).



Figure 3.30 Mechanism of the synthesis of complex 11









Figure 3.32 SEM image of aggregated Lig.7

Figure 3.31 IR of Lig.7 (magenta) and aggregated Lig.7 (green) The scanning electron microscope (SEM) image of the aggregate of Lig.7 shows a homogeneous system with the particle size around a few hundred nanometers (Fig. 3.32).

> The vanadium complex of this aggregated product, complex 11, was obtained by reaction of VO(OiPr)3 in anhydrous THF under N2 with stirring overnight. An ultrasonic bath was used at the beginning to

finely disperse the powdery ligand.

After the reaction, the green powdery product was washed several times with anhydrous THF in an ultrasonic bath, and then dried in vacuo. The characteristic V=O stretching vibration of the complex was found at 987 cm<sup>-1</sup> (Fig.3.33).



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For the SEM image (Fig. **3.34**) of complex **11**, a backscattered electron beam was used. From the brightness pattern it could be concluded that the distribution of V in this sample is very uniform.

Complex **11** was also analyzed semi-quantitatively by EDX [Energy Dispersive X-ray Analysis] (Fig. **3.35**). The peak of N is overlapped



Figure 3.34 SEM image of complex 11

with that of C. The average weight percentages of carbon by EDX is C 69.9%. Vanadium was quantitatively determined by ICP-OES, providing 24.46% V in the aggregate. The expected ratio V:C is 1:19; the ratio V:C obtained from the analyses is 1:12, corresponding to a ratio V:ligand = 1.6:1. This indicates that part of the ligand was lost and thus some VO is directly coordinated to the silica matrix.



Figure 3.35 EDX of complex 11

3.2.1.2 Synthesis and Characterization of immobilized complex **12** on silica gel

The carbasilatrane Lig.7 was immobilized on silica gel (Scheme 3.6) employing the method for immobilizing compounds containing trialkoxidosilyl groups, i.e. by refluxing in xylene in the presence of triethylamine.<sup>[96]</sup>



Scheme 3.6 Synthesis of the V-complex 12

Infrared spectroscopy confirmed that the ligand actually had been immobilized. An attenuated total reflectance (ATR)-IR spectrum of the product showed characteristic bands of Lig.7: the CH out-of-plane vibration of the phenyl ring is observed at 700 cm<sup>-1</sup>; the C-C vibration of the phenyl ring at 1500 cm<sup>-1</sup>; and the alkyl C-H stretching vibrations at 1455 cm<sup>-1</sup>. A broad band between 730-760 cm<sup>-1</sup> is due to overlapping vibrations of the propyl group (Fig. **3.36**). The CHN elemental analysis provided a loading of 0.24 mmol of ligand per gram of silica gel, and a N:C ratio of 1:19, consistent with the ratio in the original ligand.



Figure 3.36 ATR-IR spectra of silica gel (b) and Lig. 7 immobilized on silica gel (c), compared with the IR spectrum of Lig. 7 (a)

In order to deactivate the remaining -Si-OH groups on the surface of the support, these were capped with trimethylsilyl (TMS) by refluxing with hexamethyldisiloxane (HMDS) prior to the synthesis of the immobilized vanadium complex of Lig.7.



Figure 3.37 ATR-IR spectra of Lig.7 immobilized on silica gel (a), after additional capping with TMS (b), and of the V-complex 12 (c)

The V-complex of the immobilized ligand was synthesized by reaction with excess  $VO(OiPr)_3$  (molar ratio 1:1.2) in anhydrous THF under the protection of N<sub>2</sub> at RT. The green powder thus obtained was washed with anhydrous THF 5 times, and then with methanol until the solution became colorless. The powder was then dried in vacuo.



The immobilized V-complex (complex 12) was light pale-green in color. The characteristic v(V=O) was covered by the broad and strong Si-O band in the range of 900-1400 cm<sup>-1</sup>, while other characteristic bands of the ligand at 700, 730-760, 1455, and 1500 cm<sup>-1</sup> were still observable. The presence of vanadium was established qualitatively by EDX, as shown in Fig. **3.38**.

The elemental analysis provided contents of C and N of 4.69% and 0.2%, respectively. The ratio N:C is about 1:27, higher than that in the original ligand (1:19), due to the TMS on the surface of the silica gel. The concentration of V, measured by ICP-OES, is 0.377 %. Based on the nitrogen contents, the molar ratio V:ligand is 1:1.9, i.e. only about half of the immobilized ligands have taken up vanadium.

The surface area, pore volume, and the mean pore dimensions were determined by  $N_2$  absorption employing the BET method (Fig. 3.39). The results are listed in Table **3.6**.

	Surface area,	Pore volume,	Pore diameter,
	m²/g	cm³/g	mm
Activated silica gel	430.986	0.717	7.411
Lig.7-silica gel	462.729	0.628	7.396
Lig.7-silica gel-TMS	383.099	0.599	7.384
Lig.7-silica gel-TMS-V*	361.030	0.568	3.701

 Table 3. Characterization of the products in the process of the synthesis of complex 12 by comparison of the average pore diameters and the specific surface areas (calculated according to the BET method)

\*Complex 12

The surface area the of silica gel functionalized by Lig.7 is larger than that of the original activated silica gel, which might be explained by the newly introduced Si-O groups from the ligand.



Figure 3.39 Nitrogen physisorption isotherms and BJH pore diameter distribution of a) activated silica gel; b) Lig.7-silica gel; c) Lig.7-silica gel-TMS; and d) Lig.7-silica gel-TMS-V (complex 12)

This appears to be the first report on the immobilization of carbasilatranes or their complexes. A disadvantage in the use of these immobilized catalysts as models of VHPO lies, as shown in the section dealing with the catalytic activity, in a rapid loss of the

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activity after three catalytic cycles. This is most probably due to the decomposition of the complex, forming V-O-Si moieties on the silica gel surface. This drawback might be avoided by using organic polymers as support instead of silica gel. In the following chapter, this will be exemplified with resins.

# 3.2.2 Synthesis and Characterization of Immobilized Complex 13 on Merrifield Resin

The widely used Merrifield resin was chosen for anchoring Lig.3, since the hydroxy groups contained in this ligand provide a convenient means by which to tether the ligand to the solid support (Scheme 3.7). Moreover, Merrifield resin swells well and becomes highly solvated in organic solvents of intermediate polarity, such as dichloromethane, toluene, or dimethylformamide, and the first one is a suitable solvent for testing the catalytic properties of model VHPOs.

In Lig.3, there are one primary and three secondary hydroxy groups. When reacted with a base, the primary OH group reacts faster than secondary ones. Therefore, this unique OH group makes possible stoichiometric reaction with NaH in a molar ratio of 1:1. The main reaction of Lig.3 and NaH will thus take place at this primary -OH, forming -O<sup>\*</sup>Na<sup>+</sup>, which further reacts with Merrifield resin to get anchored.



Scheme 3.7 Synthesis of the V-complex 13

The IR spectrum confirmed the immobilization of Lig.3. The strong characteristic band of Lig.3 at 1065 cm<sup>-1</sup>, which is assigned to the C-O stretching vibration, was also observed in the spectrum of the immobilized Lig.3 on Merrifield resin (Fig. 3.40).
The loading of the ligand could be calculated by the content of N, because only the ligand contains N. Elemental analysis indicates that the content of N in the functionalized resin is 0.37%, giving a loading of the ligand of 0.27 mmol/g.



Figure 3.40 ATR-IR spectra of (a) Lig.3; (b) Merrifield resin; (c) Lig.3 immobilized on Merrifield resin

The V-complex of this functionalized resin (complex **13**) was synthesized by reacting immobilized Lig.3 with excess  $VO(OiPr)_3$  (molar ratio 1:1.2) in anhydrous THF under the protection of N<sub>2</sub> at RT. The brown-colored resin was washed with anhydrous THF several times and then dried in vacuum.

Because the primary hydroxyl group on Lig.3 has been anchored to the Merrifield resin, vanadium in complex **13** is supposed to have the same coordination environment as in



Figure 3.41 ATR-IR spectra of (a) complex 3'; (b) Lig.3 immobilized on Merrifield resin; (c) complex 13

The IR spectrum shows that the characteristic band for v(V=O) in complex 3' at 965 cm<sup>-1</sup> could be observed as a broad band around 970 - 1000 cm<sup>-1</sup> (Fig. 3.41). The concentration

of V, measured by ICP-OES, is 0.219 mmol per gram functionalized Merrifield resin. The molar ratio of V:ligand amounts to about 1:1.

### 3.2.3 Synthesis and Characterization of Immobilized Complexes on Barlos Resin

Barlos resin is increasingly considered as a convenient support in solid-phase syntheses.<sup>[97]</sup> It possesses essentially the same backbone as the Merrifield resin (a co-polymer from styrene and 1% of vinylbenzene), except for a 2-chlorotrityl chloride anchor instead of a chloromethyl one.

Compared with Merrifield resin, Barlos resin has undoubtedly advantages in immobilizing aminoalcohols through binding to the alcoholato function(s) because of the mild reaction conditions. There have been reports in which the use of NaH resulted in partial decomposition of the ligands, and the secondary hydroxy groups may also become deprotonated to some degree. In the case of Barlos resin, these drawbacks could be circumvented with the use of Hünig's base (di*iso*propylethylamine) instead of the reactive NaH to capture the HCl released in the course of the reaction.

Because of the bulky 2-chlorotrityl chloride present in Barlos resin, a nucleophilic reaction at the (tertiary) N atom of the amino alcohol could be avoided even when the tertiary N atom is not coordinated to any metal cation (see ch. 3.2.3.1). And the immobilization reaction conditions are mild enough to ensure the structures of the model V-complexes to remain intact. The stability and integrity of the complex was tested by <sup>51</sup>V NMR of mixtures of complex **3** plus Hünig's base, and of complex **3** plus the tritylhydrochloride of Hünig's base in the same molar ratio as in the immobilization reaction. The chemical shifts of these mixtures were identical within the limits of medium effects to that observed in <sup>51</sup>V NMR of the original pure complex **3** (Fig. 3.42). (Complex **3** was chosen, because it has no free -OH group to react with tritylchloride; thus the electron density around V would not be changed by any factors beyond the change in the coordination environment of the V center.) An additional advantage of using Barlos resin



arises from the fact that the bulkiness of this resin may fulfill the structural requirement for enantioselectivity in the catalytic reaction.

Figure 3.42 Comparison of the <sup>51</sup>V NMR spectra of a): complex 3; b): complex 3 - Hünig's base; and c): complex 3 - Hünig's base - tritylchloride

Based on these virtues of Barlos resin, the vanadium complexes **3'** and **5** (see ch. **3.1**) were successfully anchored directly onto the solid support (Scheme **3.8** and **3.9**).

To our knowledge, this is the first attempt that a vanadium complex was directly immobilized, while in other procedures reported so far in synthesizing immobilized V-complexes (see also the discussion in ch. 2), it is always the ligand which is anchored first to the solid support, followed by the synthesis of the vanadium complex in the heterogeneous reaction system.

#### 3.2.3.1 Syntheses and Characterization of Immobilized Complex 14 on Barlos Resin

Complex **3'** was anchored to the 2-chlorotrityl group on Barlos resin by stirring with a mixture of the resin and Hünig's base in  $CH_2Cl_2$  under  $N_2$  at room temperature for 24 hours, yielding complex **14** (Scheme 3.8). Complex **3'** is only sparingly soluble in  $CH_2Cl_2$ ; it dissolves completely, however, when Hünig's base is added.



The ATR-IR spectrum of complex **14** shows the characteristic resonances of complex **3'**, e.g. the V=O stretching vibration peak at 963 cm<sup>-1</sup>, and the V-O vibrations around 905 cm<sup>-1</sup>. Several of the characteristic resonances from the ligand could be observed between 1400 and 1200 cm<sup>-1</sup> (Fig. 3.43).



Figure 3.43 ATR-IR spectra of (a): Barlos resin; (b): complex 14; (c) complex 3'

The loading of the functionalized resin, determined by ICP-OES analysis of vanadium, is 0.342 mmol per gram of functionalized Barlos resin.

The structural unit representing the interaction of Lig.3 with Barlos resin was imitated by reacting the Lig.3 with Hünig's base and trityl chloride in CH<sub>2</sub>Cl<sub>2</sub>. X-ray crystallographic analysis of the reaction product (ligand 3') thus obtained indicates that it crystallizes in the orthorhombic space group  $P2_12_12_1$  with a = 7.2471(8) Å, b = 17.8576(19) Å, c = 23.712(3) Å, V = 3068.7(6) Å<sup>3</sup>, Z = 4 and R ( $wR_2$ ) = 0.0457 (0.0668). The crystal structure (Fig. 3.44) shows that incorporation of the trityl group has taken place on the primary hydroxy group as expected. This indicates that the trityl group is bulky enough for the amino alcohol ligand to avoid substitution at the secondary OH or anchoring to the amine-N.



#### 3. Results and Discussion



Figure 3.44 Molecular structure of Lig.3'

Lig.3' was obtained in the R,R,R-configuration. All bond lengths and angles are in the normal range. The d(N-C) are around 1.474 Å; the d(O-C) around 1.43 Å. There are intraand intermolecular hydrogen bonds: Intramolecular H-bond: O1-H1…O3, O2-H2…N1, and O2-H2…O3. The hydroxy group O3-H3 forms an H-bond with O2 from another molecule [x-1/2, -y+3/2, -z+2]. Selected bond lengths and angles are listed in Table 3.7.

 Table 3.7
 Selected bond lengths and angles of Lig.3'

	Bond le	ngths (Å)	
N1 - C28	1.469(4)	N1 - C31	1.474(4)
N1 - C18	1.481(3)	O1 - C17	1.441(3)
O1 - H1	0.8400	O2 - C27	1.429(4)
O3 - C32	1.423(3)	O4 - C33	1.425(3)
O4 - C34	1.448(3)	O1-H1…O3	1.943
O2-H2…N1	2.217	O2-H2···O3	2.293
O3-H3····O2*	1.875		
	Bond a	ngles (°)	
C33 - O4 - C34	119.0(2)	O1-H1…O3	172.37
O2-H2…N1	118.61	O2-H2···O3	165.82
O3-H3····O2*	170.47		

\* O2 is from a related molecule [ x-1/2, -y+3/2, -z+2 ]

3.2.3.2 Syntheses and Characterization of Immobilized Complex 15 on Barlos Resin

Complex **5** was anchored to the 2-chlorotrityl group on Barlos resin by stirring a mixture of the resin and Hünig's base in saturated  $CH_2Cl_2$  solution of complex **5** or DMSO/CH<sub>2</sub>Cl<sub>2</sub> (1:2.5) under N<sub>2</sub> at room temperature for 24 hours to yield complex **15**.

Like complex 3', complex 5 easily dissolves the mixture of  $CH_2Cl_2$  and Hünig's base, therefore the method for preparing complex 14 is also suitable for preparing complex 15. But unlike preparing complex 14, in which Barlos resin was first added to a mixture of complex 3' in  $CH_2Cl_2$ , the preparation of complex 15 was carried out by adding Barlos resin to a clear solution containing complex 5 and Hünig's base in  $CH_2Cl_2$  plus a small amount of DMSO (to ascertain complete dissolution).



Scheme 3.9 Synthesis of complex 15 (a: Hünig's base in CH<sub>2</sub>Cl<sub>2</sub> solution at RT)

In the IR spectrum of complex **15**, the characteristic v(V=O) band of complex **5** at 965 cm<sup>-1</sup> is observed at 978 cm<sup>-1</sup> (Fig. 3.45).

In order to test the stability of complex **5** in  $CH_2Cl_2$  solution in the presence of Hünig's base and Barlos resin, <sup>51</sup>V NMR spectra were measured of mixtures of complex **5**, Hünig's base and trityl-chloride. The spectra showed the same chemical shift as that of complex **5** alone.



Figure 3.45 ATR-IR of (a): complex 5; (b): Barlos resin; and (c) complex 15 69



A semi-quantitative elemental analysis of complex 15 was carried out by EDX, as shown in Fig. 3.46. The loading of the functionalized resin, determined by analysis of the vanadium contents via ICP-OES, amounted to 0.279 mmol per gram of functionalized Barlos resin.

3.3 Catalytic Properties of Model VHPOs

The catalytic properties of complexes 1, 2, 3, 5 and 7 were studied in homogeneous reaction systems, while those of complexes 11, 12, 13 and 14 were studied in heterogeneous systems.

In the homogeneous systems, cumyl hydroperoxide (CHP) or  $H_2O_2$  were used as oxidant, methyl phenylsulfide (MPS) as substrate, chloroform, dichloromethane, or dichloroethane as solvent. The concentration of the sulfide and the oxidant were 0.1, and that of the catalyst 0.01 or 0.02 M. In the heterogeneous systems, CHP was used as oxidant, MPS as substrate, chloroform or dichloromethane as solvent. The concentration of the sulfide and the oxidant was 0.1 M, and that of the catalyst was variable. The reaction is shown as in Scheme 3.10.



Scheme 3.10 Oxidation of methylphenylsulfide with CHP

During the process of generation of the sulfoxide, usually the undesired by-product, sulfone, is also formed. For each V-complex studied as model VHPO in homogeneous reaction systems, the changes of the <sup>51</sup>V NMR pattern during the reaction were detected

(Fig. 3.48 - 3.50), and all of these reactions were supposed to follow the same mechanism as depicted in Fig. 3.47.

Spectrum I in Fig. 3.48 corresponds to complex 2 in CDCl<sub>3</sub>. After CHP is added, a peroxidovanadium complex forms, as spectrum II indicates, which is supposed to be the active catalytic species in the oxidation reaction. After the substrate is added, one oxo of the peroxo group in



Figure 3.47 Supposed oxo transfer process in the oxidation of sulfides

the active species is transferred to the substrate. After the reaction, as shown in spectrum III, the peroxide is consumed, and the catalyst is recovered. The extra peaks are from the isomers of the V-complex.

Usually, when CHP is used as oxidant, cumyl alcohol forms as the reduction product of CHP. The cumyl alcohol can react with the catalyst, forming V species containing cumyloxido ligands. Thus, the <sup>51</sup>V NMR signal of *tris*(cumyloxido)oxidovanadium has been detected at -685 ppm when complex 1 is used as catalyst both in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> solutions. For complex 2, this peak is observed only several days after the end of the reaction, but another peak, at -392 ppm, could often be observed after the reaction was finished. Fig. 3.49 shows the <sup>51</sup>V NMR spectra of the V species in the oxidation of sulfide with CHP in CD<sub>3</sub>OD, with complex **3** as the catalyst.



8 V species in the oxidation of sulfide with CHP with complex 2 as  $\frac{1}{1} - \frac{-492}{-532}$ 1  $\frac{1}{-350} - 400 - 450 - 500 \text{ ppm}$ 

Figure 3.48 V species in the oxidation of sulfide with CHP with complex 2 as catalyst in CDCl<sub>3</sub>

Figure 3.49 V species in the oxidation of sulfide with CHP with complex 3 as catalyst in CD<sub>3</sub>OD

When  $H_2O_2$  is used as the oxidant, partial decomposition of the complex is observed during the catalytic process. For example, in case of complex **2** used as catalyst in CDCl<sub>3</sub> solution, a main peak at -773 ppm appeared, which represents diperoxidovanadate formed by decomposition of complex **2**. After the oxidation of MPS is finished, only the main signal at -443 ppm, attributed to the main species of complex **2** in the CDCl<sub>3</sub> solution, was detected.



Figure 3.50 V species in the oxidation of sulfide with  $H_2O_2$  with complex 2 as catalyst in CDCl<sub>3</sub>

When  $H_2O_2$  was added to the CDCl<sub>3</sub> solution of complex **1**, a strong peak appeared at -727 ppm, accompanied by a very weak signal at -663 ppm, comparable to the situation found for complex **2**. Different from CHP as oxidant, where the oxidizing species is a monoperoxido complex, the peroxido species of complex 1 and 2 in the presence of  $H_2O_2$  as oxidant are diperoxido complexes.

#### 3.3.1 Oxidation of Sulfide Catalyzed with model VHPOs in Homogeneous Systems

### Catalytic reaction systems with CHP at 0 $^\circ C$ (I)

In this catalytic reaction system, the concentration of the reactants are 0.1 M, and the catalyst makes up 10%, i.e. the ratio of sulfide:oxidant:catalyst is 1:1:0.1. Chloroform was used as the solvent, and the reaction temperature was set to 0°C. The results are listed in Table 3.8 for the complexes and the *in situ* systems, i.e. mixtures of the ligand and the precursor  $VO(OiPr)_3$ . Figs. 3.51 and 3.52 are graphical representations of the reaction course for the *in situ* systems with ligand 1 and ligand 2, respectively.

Cat.	$SO:SO_2$	Conver. (%)	ee ( % )	Time
Lig.1 + V O(O <sub>i</sub> Pr) <sub>3</sub>	84.5 : 15.5	100	6.2 R	20 min
Complex 1	92.3 : 7.7	100	5.5 R	3h
$Lig.2 + V O(O_i Pr)_3$	98.6 : 1.4	100	11.1 R	5h
Complex 2	94.4 : 5.6	93.8	4.6 R	3h
$Lig.3 + V O(O_i Pr)_3$	98.0 : 2.0	100	6.0 S	3h
Complex 3	97.3 : 2.7	100	4.6 S	3h
$Lig.5 + V O(O_i Pr)_3$	94.7 : 5.3	60.3	37.0 R	5h
Complex 5	97.1 : 2.9	88.58	2.0 S	3h
$Lig.6 + V O(O_i Pr)_3$	94.5 : 5.5	88.6	7.4 S	3h
Lig.7 + V O(O <sub>i</sub> Pr) <sub>3</sub>	84.5 : 15.5	100	7.4 S	10 min

Table 3.8 Catalytic results  $(V = VO(O_iPr)_3)$ 

T: 0°C ; Solvent: CHCl3; Sulfide: MPS; Oxidant: CHP

In these homogeneous catalytic reaction systems at 0°C, all model VHPOs exhibited good selectivity and turn-overs. The conversion rate of complex 5 in the *in situ* system was relatively low, possibly because the system became slightly gel-like after addition of VO(O*i*Pr)<sub>3</sub>; the enantio-selectivity in this system was, however, clearly more favorable than in the other ones.



Figure 3.51 Complex 1 in situ catalytic system in the oxidation of methylphenylsulfide at 0°C in CHCl<sub>3</sub>



Figure 3.52 Complex 2 in situ catalytic system in the oxidation of methylphenylsulfide at 0°C in CHCl<sub>3</sub>

#### Catalytic reaction systems with CHP at -20 °C (II)

In the second catalytic reaction system, the catalytic properties of complexes **1** and **2** were studied at -20 °C in dichloromethane or dichloroethane, instead of chloroform as in system I. Concentrations were the same as in system I, but in the *in situ* systems, the molar ratio ligand:VO( $O_i$ Pr)<sub>3</sub> was varied between 1:1 and 2:1 (i.e. the concentration of the ligand was 0.01 or 0.02 M, the concentration of VO( $O_i$ Pr)<sub>3</sub> 0.01 M). The results were evaluated by <sup>1</sup>H NMR 72 hours after the reactions were started; Table 3.9; in all cases, the conversion was 100 %.

Compared with system I, the enantio-selectivity for complexes **1** and **2** in system II were improved both in the *in situ* system and when employing the pre-synthesized complexes.

Table 3.9	Catalytic	results
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Catalyst	Lig. : V	Solvent	SO:SO <sub>2</sub>	Conver. (%)	ee (%)	Time <sup>a</sup>
Lig.1+VO(O <sub>i</sub> Pr) <sub>3</sub>	1:1	$CH_2Cl_2$	100: 0	100	18 R	72 h
Lig.1+VO(O <sub>i</sub> Pr) <sub>3</sub>	1:1	CH <sub>2</sub> ClCH <sub>2</sub> Cl	93.3 : 6.7	100	22 R	72 h
Lig.1+VO(O <sub>i</sub> Pr) <sub>3</sub>	2:1	$CH_2Cl_2$	97.4 : 2.6	100	24 R	72 h
Lig.1+VO(O <sub>i</sub> Pr) <sub>3</sub>	2:1	CH <sub>2</sub> ClCH <sub>2</sub> Cl	65.4 : 34.6	100	15 R	72 h
Lig.2+VO(O <sub>i</sub> Pr) <sub>3</sub>	1:1	$CH_2Cl_2$	72.8 : 27.2	100	17 R	72 h
Lig.2+VO(O <sub>i</sub> Pr) <sub>3</sub>	1:1	CH <sub>2</sub> ClCH <sub>2</sub> Cl	63.6 : 36.4	100	11 R	72 h
Lig.2+VO(O <sub>i</sub> Pr) <sub>3</sub>	2:1	$CH_2Cl_2$	63.4 : 36.6	100	11 R	72 h
Lig.2+VO(O <sub>i</sub> Pr) <sub>3</sub>	2:1	CH <sub>2</sub> ClCH <sub>2</sub> Cl	89.9 : 10.1	100	6 R	72 h
Complex 1		$CH_2Cl_2$	64.8 : 35.2	100	16 R	72 h
Complex 1		CH <sub>2</sub> ClCH <sub>2</sub> Cl	87.7 : 22.3	100	18 R	72 h
Complex 2		$CH_2Cl_2$	97.6 : 2.4	100	5 S	72 h
Complex 2		CH <sub>2</sub> ClCH <sub>2</sub> Cl	97.1 : 2.9	100	11 S	72 h

T: -20°C ; Sulfide: MPS; Oxidant: CHP

a: The time when the ee value was determined, not the time when the reaction was finished

For complex **1**, the best results with respect to selectivity and chiral induction were obtained in  $CH_2Cl_2$  *in situ* with a Lig:V ratio of 2:1; for complex **2**, the best selectivity was obtained with the pre-formed complex in  $CH_2Cl_2$  or  $CH_2ClCH_2Cl$  solution, while the best result in *ee* were obtained *in situ* in  $CH_2Cl_2$  with the ratio Lig:V = 1:1.

### Catalytic reaction systems with H<sub>2</sub>O<sub>2</sub> (III)

When  $H_2O_2$  is used as the oxidant instead of CHP in the temperature range 8-12 or 8-17 °C, complexes 1 and 2 also exhibit good selectivity both *in situ* and with the pre-formed complexes. Enantio-selectivity was similar to system I and II. But the rate of conversion is slow. For the pre-synthesized complexes the reaction is somewhat faster, possibly due to the higher reaction temperature.

Table 3.10Catalytic results	Fable	le 3.10.	Catalytic	results
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Cat.	Lig. : V	<b>T</b> (°C)	SO: SO <sub>2</sub>	Conver. (%)	ee (%)	Time
Lig.1+VO(O <sub>i</sub> Pr) <sub>3</sub>	2:1	8-12	94.6 : 5.4	49.6	10.0 S	24h
Lig.2+VO(O <sub>i</sub> Pr) <sub>3</sub>	2:1	8-12	92.5 : 7.5	48.2	23.4 S	24h
Complex 1		8-17	92.8 : 7.2	89.37	8.6 S	24h
Complex 2		8-17	95.4 : 4.6	85.1	15.6 S	24h

Solvent: CH2Cl2; Sulfide: MPS; Oxidant: H2O2

<sup>75</sup> 

#### 3.3.2 Oxidation of Sulfide Catalyzed with model VHPOs in Heterogeneous Systems

In heterogeneous catalytic reaction systems, CHP was used as the oxidant and MPS as the substrate. The concentration of the reactants were 0.1M. The molar ratios reactant:catalyst were around 1:0.1 (except for complex **12**). The results are listed in Tables 3.12-3.14.

Among these heterogeneous catalytic reactions, complex **11**, which was synthesized by self-aggregation of the carbasilatrane (Lig.7), and complexes **13**, **14**, and **15**, which represent vanadium complexes anchored to resins, exhibit relatively high structural stability and good catalytic activities. After several catalytic cycles, the selectivities and the reaction rates remain almost unchanged, except for complex **12** (the complex system prepared by immobilization of carbasilatrane on silicagel followed by complexation with the vanadium precursor). As an example, after complex **11** (Table 3.12) had been used four times, the oxidation still finished within 60 minutes with the same enantioselectivity and high selectivity.

For complex **12** (Table 3.13) however, though the selectivity is also excellent, the conversion is rather low: The conversion of the substrate is 54.4% within 90 min. in the first run, while, in the third run, the conversion is only 8.5% within 120 minutes, indicating the decomposition of the catalyst.

Table 3.12....Catalytic results

Cat.	Experiment No.	$SO:SO_2$	Conver. (%)	ee (%)	Time <sup>a</sup> ( min )
Complex 11	1	91:9	100		180
	2	98:2	100	16 S	120
	3	98:2	100	25 S	60
	4	91:9	100	20 S	180

T: 0-8°C; Solvent: CH<sub>3</sub>; Sulfide: MPS; Oxidant: CHP; Cat.: CHP : MPS= 0.12 : 1 : 1

a: The time where the ee value was measured, not the time when the reaction is finished

Cat.	Experiment No.	$SO:SO_2$	Conver. (%)	ee (%)	Time <sup>a</sup> ( min )
	1	99:1	54.4		90
Complex 12	1	98:2	100	14 S	180
	2	100:0	21.5		30
		100:0	68	10 S	90
	3	100:0	5		60
		100:0	8.5	19 S	120

T: 0-8°C; Solvent: CH<sub>3</sub>; Sulfide: MPS; Oxidant: CHP; Cat.: CHP : MPS= 0.03 : 1 : 1

a: The time where the ee value was measured, not the time when the reaction is finished.

#### Table 3.14....Catalytic results

Catalyst	Cat.:CHP:MPS	Solvent	<b>Т</b> (°С)	SO : SO2	Conver. (%)	ee <sup>a</sup> (%)	Time <sup>b</sup>
Complex 11	0.12:1:1	CHCl <sub>3</sub>	0-8	98 : 2	100	25 S	50 min
Complex 12	0.03 : 1 : 1	CHCl <sub>3</sub>	0-8	98:2	100	19 S	180 min
Complex 13	0.09:1:1	CHCl <sub>3</sub>	0-8	97 : 4	100	16 S	40 min
Complex 14	0.11:1:1	$CH_2Cl_2$	8-15	98:2	100	19 S	24 h
Complex 15	0.09 : 1 : 1	$CH_2Cl_2$	8 - 17	86.5 : 13.5	100	14.4 S	24 h

Sulfide: MPS; Oxidant: CHP;

a: The best *ee* value of all cycles of reaction;

b: The time where the *ee* value was measured, not the time when the reaction was finished

### 4. Summary

Vanadate-dependent haloperoxidases (VHPOs) isolated from marine algae and terrestrial fungi and lichen contain dihydrogenvanadate(V) in their active centre, covalently linked to a histidine of the protein matrix. Vanadium is in a trigonal-bipyramidal environment, with the imidazole-N and an OH group in the axial positions. The genuine reaction catalyzed by these enzymes is the two-electron oxidation, by  $H_2O_2$ , of halide to hypohalous acid, with concomitant (non-enzymatic) halogenation of organic molecules. Organic (prochiral) sulfides can also be substrates for these peroxidases, resulting in the formation of (chiral) sulfoxides along with some sulfone. The present work addresses the synthesis and characterization of oxidovanadium(V) complexes which are structural and functional models, for the sulfoxigenation reaction, of the active centers of the VHPOs. Suitable model complexes have been obtained with ligands derived from chiral aminodiethanols. The ligands, prepared by reaction of *R*-styreneoxide with various amines, are collated in Figure S1.

Reaction of the ligands with VO(O*i*Pr)<sub>3</sub> yields complexes, structures of which are shown in Figure S2. The coordination geometries attained by the complexes are distorted trigonal-bipyramidal (Compl.**1** and Compl.**2**; the  $\tau$  parameters are 0.66 and 0.53, respectively), ideally trigonal-bipyramidal (Compl.**3**') or octahedral (Compl.**3**). Characterization in solution has been achieved by <sup>51</sup>V NMR spectroscopy. An illustrative example is displayed in Figure S3.



Figure S1. Ligands synthesized in the present work. Except of Lig.5 and Lig.6, all of the ligands have been structurally characterized.



igure S2. Structurally characterized vanadium complexes. The numbering of the complexes readopts to the numbering of ligands (Fig. S1).



Figure S3: <sup>51</sup>V NMR spectrum of a solution of

of three isomers.

Compl.1 in CDCl<sub>3</sub>, showing the presence

Additional complex systems have been prepared by aggregation of the carbasilatrane Lig.**7**, followed by reaction with the vanadium precursor (Compl.**11**; Fig. S4), and by immobilization on silica gel (Compl.**12**), Merrifield and Barlos resins (Compl.**13-15**; for Compl.**14** see Fig. S5).



Figure S4. Preparation of the polymeric aggregate Compl.**11** from Lig.**7** and VO(O<sub>i</sub>Pr)<sub>3</sub>. The SEM picture shows a sponge-like structure with a regular size distribution of the granular components.



Figure S5. Synthesis of Compl.**14** by reacting Compl.**3'** with Barlos resin in the presence of Hünig's base NEt(*i*Pr)<sub>2</sub>.

Catalytically conducted reactions have been carried out in homogenous systems, using the complexes or mixtures of the ligand and VO(OiPr)<sub>3</sub> ("*in situ*"), or – with the aggregated and immobilized complexes – under heterogeneous conditions. All of the systems investigated are catalytically active in the sulfoxigenation of methylphenylsulfide by cumylhydroperoxide in chlorinated hydrocarbons. As evidenced by <sup>51</sup>V NMR, the active catalyst is a peroxido intermediate; see eqn. (1). The turn-over rate, selectivity and enantiomeric excess vary with the systems under investigation and the reaction conditions such as temperature. Selected results are collated in Table S1. Figure S6 represents the reaction course for the *in situ* Compl.1. While the chirality (*R*) of the catalyst system is commonly induced upon the product under homogeneous reaction conditions ( $\rightarrow R$ -sulfoxide), chiral conversion occurs in the heterogeneous systems ( $\rightarrow S$ -sulfoxide).



Figure S6. Time course of the oxygenation of methylphenylsulfide by cumylhydroperoxide, catalyzed by Compl.1 formed *in situ* from Lig.1 and VO(OiPr)3.

Entry #	System	°C	SO:SO2 <sup>a</sup>	Conver. %	ее %,	Time h
1	Compl.1	0	92:8	100	6 R	3
2	Compl.1	-20	65:35	100	16 R	72
3	$Lig.1 + VO(OiPr)_3$	-20	97:3	100	24 R	72
4	$Lig.5 + VO(OiPr)_3$	0	95:5	60	37 R	5
$5^b$	$Compl.1 / H_2O_2$	8-17	93:7	89	7 S	24
6	Compl.11	0	98:2	100	25 S	0.8
7	Compl.12	0	98:2	100	19 S	0.8
8	Compl.13	0	97:3	100	16 S	0.6
9	Compl.14	8-15	98:2	100	19 S	24

 Table S1.
 Results from selected catalytic reactions (in CHCl3 or CH2Cl2; oxidant: cumylhydroperoxide, except for entry #5). Entries #6-9 are heterogeneous systems.

<sup>a</sup>Ratio sulfoxide:sulfone. <sup>b</sup>Oxidant is H<sub>2</sub>O<sub>2</sub>.

#### Zusammenfassung

Vanadat-abhängige Haloperoxidasen (VHPOs) aus Meeresalgen sowie terrestrischen primitiven Pilzen und Flechten enthalten Dihydrogenvanadat(V) im aktiven Zentrum, kovalent gebunden an ein Histidin der Proteinmatrix. Das Vanadium befindet sich in trigonal-bipyramidaler Umgebung, mit dem Imidazol-N und einer OH-Gruppe in den axialen Positionen. Die von diesem Enzym katalysierte Reaktion ist die Zwei-Elektronen-Oxidation, mittels H<sub>2</sub>O<sub>2</sub>, von Halogenid zu Unterhalogeniger Säure, gefolgt von der (nicht-enzymatischen) Halogenierung organischer Moleküle. Organische (prochirale) Sulfide können gleichfalls Substrate dieser Peroxidasen sein, wobei (chirale) Sulfide neben etwas Sulfon gebildet werden. In der vorliegenden Arbeit wird die Synthese und Charakterisierung solcher Komplexe behandelt, die strukturelle und (für die Sulfoxigenierung) funktionelle Modelle der aktiven Zentren der VHPOs sind. Geeignete Modellkomplexe wurden mit Liganden erhalten, die sich von chiralen Aminodialkoholen herleiten. Die Liganden, die durch Umsetzung von *R*-Styrenoxid mit primären Aminen erhalten werden, sind in Abbildung Z1 zusammengestellt.

Die Reaktion der Liganden mit VO(OiPr)<sub>3</sub> führt zu Komplexen, deren Strukturen in Abbildung Z2 gezeigt sind. Die Koordinationsgeometrie dieser Komplexe variiert zwischen verzerrt trigonal-bipyramidal (Compl.**1** und Compl.**2**; die  $\tau$ -Parameter betragen 0.66 bzw. 0.53), ideal trigonal-bipyramidal (Compl.**3**') oder oktaedrisch (Compl.**3**). Die Charakterisierung in Lösung erfolgte durch <sup>51</sup>V NMR-Spektroskopie. Ein illustratives Beispiel zeigt Abbildung Z3.



<u>Abbildung Z1</u>. In der vorliegenden Arbeit synthetisierte Liganden. Außer Lig.**5** and Lig.**6** wurden allen Liganden strukturell charakterisiert.



Abbildung Z S2. Strukturell charakterisierte Vanadiumkomplexe. Die Nummerierung der Komplexe nimmt die der Liganden (Abb. Z1) wieder auf.



<u>Abbildung Z3</u>: Das <sup>51</sup>V NMR-Spektrum einer Lösung von Compl.**1** 

in CDCl3 zeigt drei Isomere

Weitere komplexe Systeme wurden durch Aggregation des Carbasilatrens Lig.7 und anschließende Reaktion mit dem Vanadium-Precursor synthetisiert (Compl.11; Abb. Z4), sowie durch Immobilisierung auf Kieselgel (Compl.12), Merrifield- und Barlos-Harzen (Compl.13-15; für Compl.14, s. Abbildung Z5).



<u>Abbildung Z4</u>. Darstellung des polymeren Aggregats Compl.**11** ausLig.**7** und VO(OiPr)<sub>3</sub>. Die SEM-Aufnahme zeigt eine schwammartige Struktur mit regulärer Größenverteilung der granulären Komponenten.



<u>Abbildung Z5</u>. Synthese von Compl.**14** durch Umsetzung von Compl.**3'** mit Barlos-Harz in Gegenwart von Hünigs Base NEt(*i*Pr)<sub>2</sub>.

Katalytisch geführte Reaktionen wurden in homogenen Systemen einerseits mit den Komplexen, andererseits mit Mischungen aus Ligand und VO(OiPr)<sub>3</sub> ("*in situ*") durchgeführt, oder – mit dem aggregierten und den immobilisierten Komplexen – unter heterogenen Bedingungen. Alle untersuchten Systeme sind katalytisch aktiv in der Sulfoxigenierung von Methylphenylsulfid durch Cumylhydroperoxid in Chlorkohlenwasserstoffen. Wie <sup>51</sup>V NMR-spektroskopische Untersuchungen zeigen, ist der eigentliche aktive Katalysator ein intermediär gebildeter Peroxidokomplex; s. Gl. (1). Turn-over Raten, Selektivität und Enantiomeren-Überschüsse variieren mit dem katalytische System und den Reaktionsbedingungen, etwa der Temperatur. Ausgewählte Ergebnisse sind in Tabelle Z1 zusammengestellt. Abbildung Z6 zeigt beispielhaft für den *in situ* Compl.**1** den zeitlichen Ablauf der Reaktion. Während die Chiralität (*R*) des Katalysatorsystems unter homogenen Reaktionsbedingungen für gewöhnlich im Produkt wieder auftaucht ( $\rightarrow R$ -Sulfoxid), kommt es in heterogenen Systemen zu einer Chiralitätsumkehr ( $\rightarrow S$ -sulfoxide).



<u>Abbildung Z6</u>. Zeitlicher Verlauf der Oxigenierung von Methylphenylsulfid durch Cumylhydroperoxid, katalysiert durch den *in situ* aus Lig.**1** and VO(OiPr)<sub>3</sub> gebildeten Compl.**1**.

Eintrag #	System	T °C	SO:SO2 <sup>a</sup>	Umsatz %	ee %,	Zeit h
1	Compl.1	0	92:8	100	6 R	3
2	Compl.1	-20	65:35	100	16 R	72
3	$Lig.1 + VO(OiPr)_3$	-20	97:3	100	24 R	72
4	$Lig.5 + VO(OiPr)_3$	0	95:5	60	37 R	5
$5^b$	Compl.1 / H <sub>2</sub> O <sub>2</sub>	8-17	93:7	89	7 S	24
6	Compl.11	0	98:2	100	25 S	0.8
7	Compl.12	0	98:2	100	19 S	0.8
8	Compl.13	0	97:3	100	16 S	0.6
9	Compl.14	8-15	98:2	100	19 <i>S</i>	24

 

 Tabelle Z1.
 Ergebnisse ausgewählter katalytischer Reaktionen (in CHCl3 oder CH2Cl2; Oxidans: Cumylhydroperoxid, außer für den Eintrag #5). Die Einträge #6-9 entsprechen den heterogenen Systemen.

<sup>a</sup>Verhältnis Sulfoxid:Sulfon. <sup>b</sup>Oxidans ist H<sub>2</sub>O<sub>2</sub>.

# 5 Experimental Part

### 5.1 Materials and Methods

All chemicals used were of analytical-reagent grade. The solvents were purified and deoxygenated by standard methods. Water was deionized.

Elemental analyses for C, H and N were measured on a Heraeus CHN-O-Rapid analyzer; V in the immobilized complexes was determined by ICP-OES on a SPECTRO CIROS CCD spectrometer.

EDX semi-quantitative analyses were carried out with a transmission electron microscope (Philips CM12, LaB<sub>6</sub>-cathode, 120 kV) equipped with an EDX spectrometer (EDAX, Fa. Ametek, SUTW window).

Normal IR spectra were recorded on a Perkin-Elmer 1720 spectrometer, using KBr pellets for solid samples and films between NaCl crystal plates for liquid samples; ATR-IR spectra were recorded on Bruker VERTEX 70 FT-IR spectrometer.

<sup>1</sup>H NMR spectra were measured on a Varian Gemini (200 MHz) or a Bruker AM 360 spectrometer; all <sup>51</sup>V NMR chemical shifts were referenced against VOCl<sub>3</sub> as external standard.

EPR spectra were obtained with a Bruker ESP 300E spectrometer.

BET N2 absorption experiments were carried out on Quantachrome Autosorb 6.

Crystal structures were measured on a Hilger & Watts Y 290 diffractometer in the  $\theta/2\theta$  scan mode with monochromated Mo-K<sub>a</sub> irradiation ( $\lambda = 0.71073$  Å). Calculations were carried out with SHELXL-97.

Silica gel 60, 230 - 400 mesh ASTM (0.040-0.063 mm) was purchased Merck; Merrifield resin with 0.7 mmol Cl/g resin from Fluka, and Barlos resin 200-400 mesh, 1% DVB (divinylbenzene), 1.0-1.6 mmol/g, from Merck.

## 5.2 Syntheses of Ligands and Complexes

The preparation of all of the vanadium complexes was conducted under inert gas atmosphere.

# 5.2.1 Synthesis of N,N-*bis*(hydroxyphenylehtyl)- propene(1)amine [Lig.1] and N-2-hydroxyphenylehtyl-N-1-phenyl-2hydroxyethyl-propene(1)amine [Lig.2]

1.43 mL of R-styrene oxide and 0.46 mL of allylamine were dissolved in 10 mL of *iso*propanol in a small flask and refluxed for four days. The products were purified by chromatography on silica gel, using hexane and ethyl acetate with gradually increasing polarity as elutant. Lig.1 was recrystallized from ethylacetate in hexane atmosphere. Yield: Lig.1, 55.69%; Lig.2, 22.50%.

### Lig.1

Chemical formula:  $C_{19}H_{23}NO_2$ ; molar mass: 297.38 g/mol. Elemental analysis % (cal.): C, 76.18 (76.67); H, 7.82 (7.73); N, 4.48 (4.7) <sup>1</sup>H NMR (acetone-d<sub>6</sub>)  $\delta$  (ppm) 7.24-7.42 (m, 10H, aromatic); 5.88 (m, 1H, NCH<sub>2</sub>CHCH<sub>2</sub>); 5.17 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>); 4.72 (H<sub>x</sub> of an ABX system, 2H, PhCHOHCH<sub>2</sub>); 3.38, 3.19 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>); 2.66 (H<sub>A</sub> and H<sub>B</sub> of an ABX system, 4H, PhCHOHCH<sub>2</sub>);

<sup>13</sup>C NMR (acetone-d<sub>6</sub>) δ (ppm) 146.6, 128.8, 128.2 (phenyl ring); 134.6 (NCH<sub>2</sub>CHCH<sub>2</sub>);
 117.3 (NCH<sub>2</sub>CHCH<sub>2</sub>); 70.0 (PhCHOHCH<sub>2</sub>N); 62.0 (PhCHOHCH<sub>2</sub>N)

# Lig.2

Chemical formula: C19H23NO2; molar mass: 297.38 g/mol

Elemental analysis % (cal.): C, 75.33 (76.67); H, 7.61 (7.73); N, 4.49 (4.7) <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ(ppm) 7.24-7.42 (m, 10H, aromatic); 5.79 (m, 1H, NCH<sub>2</sub>CHCH<sub>2</sub>); 5.12 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>);4.67 (H<sub>X</sub> of ABX system, 1H, PhCHOHCH<sub>2</sub>N); 3.90 (H<sub>X</sub> of ABX system, 1H, NCHPhCH<sub>2</sub>OH); 3.86, 3.67 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, NCHPhCH<sub>2</sub>OH); 3.29, 3.02 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>); 2.86, 2.58 (m, 2H, PhCHOHCH<sub>2</sub>N)

<sup>13</sup>C NMR (Aceton-d<sub>6</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 137.5 (NCH<sub>2</sub>CHCH<sub>2</sub>);
117.0 (NCH<sub>2</sub>CHCH<sub>2</sub>); 71.7 (PhCHOHCH<sub>2</sub>N); 66.3 (NCHPhCH<sub>2</sub>OH); 61.3 (NCHPhCH<sub>2</sub>OH) 59.4 (PhCHOHCH<sub>2</sub>N); 54.4 (NCH<sub>2</sub>CHCH<sub>2</sub>)

# 5.2.2 Synthesis of R,R-methoxido-[N,N-*bis*(2-hydroxidophenyl-ethyl)-N-propene(1)amine]-oxidovanadium [Complex 1]

0.18 g of Lig.1 were dissolved in 3 mL of dry THF, forming a colorless solution To this solution was added drop wise 0.21 mL of  $VO(iOPr)_3$  dissolved in 4 mL of dry THF. The reaction mixture was stirred at room temp. for 10 hours and then dried by removing the solvent in vacuo to yield a green sticky residue, which was filtered off. The yellow filtrate was kept at -20°C. Several days later, needle-shaped colorless crystals of complex 1 were obtained.

Chemical formula:  $C_{20}H_{24}NO_4V$ ; molar mass: 393.34 g/mol <sup>51</sup>V NMR (CDCl<sub>3</sub>)  $\delta$  (ppm) -418, -446, -455 IR (KBr, cm<sup>-1</sup>) 978 (V=O)

# 5.2.3 Synthesis of methoxido[(R)-N-2-hydroxido-2-phenylethyl-(S)-N-1-phenyl-2-hydroxidoethyl-N-propenen(1)amine]oxidovanadium [Complex 2]

0.18 g of Lig.2 were dissolved in 3 mL of dry THF, forming a colorless solution To this solution was added drop wise 0.21 mL of  $VO(iOPr)_3$  dissolved in 4 mL of dry THF. The reaction mixture was stirred at room temperature for 10 hours, and the solvent removed in vacuo, getting a green sticky residue. The solid materials were filtered off, and the yellow

filtrate kept at -20°C. After two days, bar shaped colorless crystals [Compl.2] were obtained.

Chemical formula:  $C_{20}H_{24}NO_4V$ ; molar mass: 393.34 g/mol <sup>51</sup>V NMR (CDCl<sub>3</sub>)  $\delta$ (ppm) -443, -449, -457 IR (KBr, cm<sup>-1</sup>) 978 (V=O)

# 5.2.4 Syntheses of 3-[N,N-bis(2-hydroxyphenyl-ethyl)]amino-1,2propanediol [Lig. 3] and (N-2-hydroxyphenylehtyl-N-1-phenyl-2hydroxyethyl) amino-1,2-propanediol [Lig. 4]

1.43 mL of R-styrene oxide (0.01252mol) and 0.4865 mL of 3-amino-1,2-propanediol (0.00626mol) were dissolved in 10 mL of *iso*propanol in a small flask and refluxed for four days. The products were then purified by chromatography on silica gel, using hexane/ethyl acetate as elutant, followed by ethyl acetate/ethanol with gradually increasing polarity. Lig.3 was isolated as a colorless solid, Lig.4 as a colorless liquid. Yields: Lig.3, 58.6 %; Lig.4, 31.8%.

#### Lig.3

Chemical formula: C<sub>19</sub> H<sub>25</sub> N O<sub>4</sub>; molar mass: 331.40 g/mol Elemental analysis % (cal.): C, 68.24 (68.80); H, 7.58 (7.54); N, 4.10 (4.22) <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ(ppm) 7.24-7.42 (m, 10H, aromatic); 4.82 (Hx of ABX system, 2H, PhC**H**OHCH<sub>2</sub>); 3.78 (m, 1H, CH<sub>2</sub>C**H**OHCH<sub>2</sub>); 3.5 (m, 2H, CHOHC**H**<sub>2</sub>OH); 2.90, 2.73 (m, 2H, NC**H**<sub>2</sub>CHOH); 2.80, 2.72 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHC**H**<sub>2</sub>N);

<sup>13</sup>C NMR (CD<sub>3</sub>OD) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 70.8 (PhCHOHCH<sub>2</sub>N);
68.1 (NCH<sub>2</sub>CHOHCH<sub>2</sub>OH); 63.9 (NCH<sub>2</sub>CHOHCH<sub>2</sub>OH); 58.7 (NCH<sub>2</sub>COHCH<sub>2</sub>OH)

# Lig.4

Chemical formula: C<sub>19</sub> H<sub>25</sub> N O<sub>4</sub>; molar mass: 331.40 g/mol Elemental analysis % (cal.): C, 66.07 (68.80); H, 7.65 (7.54); N, 3.88 (4.22) <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ(ppm) 7.24-7.42 (m, 10H, aromatic); 4.82 (Hx of ABX system, 1H, PhC**H**OHCH<sub>2</sub>N); 3.98 (Hx of ABX system, 1H, NC**H**PhCH<sub>2</sub>OH); 4.0, 3.8 (H<sub>A</sub> and H<sub>B</sub>

of ABX system, 2H, PhCHOHC**H**<sub>2</sub>OH); 3.7 (m, 1H, CH<sub>2</sub>CHOHCH<sub>2</sub>); 3.39, 3.47 (m, 2H, CHOHC**H**<sub>2</sub>OH); 2.80, 2.53 (m, 2H, NCH<sub>2</sub>CHOH); 2.80, 2.63 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHCH<sub>2</sub>N)

<sup>13</sup>C NMR (CD<sub>3</sub>OD) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 69.1 (PhCHOHCH<sub>2</sub>); 68 (CHOHCH<sub>2</sub>OH); 66.2 (NCHPhCH<sub>2</sub>); 62.1 (CHOHCH<sub>2</sub>OH); 60 (PhCHOHCH<sub>2</sub>OH); 52.5 (NCH<sub>2</sub>COH)

# 5.2.5 Syntheses of (R,R)-[N,N-bis(2-oxido-2 phenyl- ethyl)-N-2oxido-3 hydroxopropylamine]- oxidovanadium(V) (Complex 3) and (R,R)-[N,N-bis(2-oxido-2-phenylethyl)-N-2-oxido-3 hydroxy- propylamine]oxido- vanadium(V) (Complex 3')

To the solution of 0.3502 g (1.058mmol) Lig.3 in 2mL of anhydrous THF (or ethanol) was added drop wise and with stirring 0.25 mL VO(OiPr)<sub>3</sub> in 10.0 mL of anhydrous THF (or ethanol). The solution became red brown, and a light yellow precipitate formed. After the precipitate was filtered off, the transparent solution was kept at -20°C. Several days later, yellow-green cubic (in ethanol) or fine needle-like (in THF) crystals formed (Complex **3**).

The light yellow precipitate was washed with THF or ethanol and then dissolved in DMSO and put aside at RT in the open air. Several days later, bar-shaped colorless crystals appeared (Complex  $3^{\circ}$ ).

Complex **3** Chemical formula:  $C_{19}H_{22}NO_4V$ ; molar mass: 379 g/mol <sup>51</sup>V NMR (DMSO-d<sub>6</sub>)  $\delta$  (ppm) -411 IR (KBr, cm<sup>-1</sup>) 967 (V=O) Complex **3**' Chemical formula:  $C_{19}H_{22}NO_4V$ ; molar mass: 379 g/mol <sup>51</sup>V NMR (DMSO-d<sub>6</sub>)  $\delta$ (ppm) -381 IR (KBr, cm<sup>-1</sup>) 965 (V=O)

# 5.2.6 Syntheses of (R,R)-[N,N-*bis*(hydroxyphenylehtyl)-N*tris*(hydroxymethyl)methylamine [Lig. 5] and N-2hydroxyphenylehtyl-N-1-phenyl-2-hydroxy-*tris*(hydroxymethyl)methylamine [Lig. 6]

### 1.43 mL of R-styrene oxide (0.01252 mol) and 0.7583 g of

*tris*(hydroxymethyl)methylamine (0.00626 mol) were refluxed in 15mL of anhydrous *iso*propanol with stirring for four days (the amine does not dissolve in *iso*propanol at room temp.; as the temperature goes up, the amine gradually becomes dissolved). The product was purified by column chromatography on silica gel, using the elutants ① hexane/ethyl acetate and then ② ethyl acetate/ethanol with gradually increased polarity. Both Lig.5 and Lig.6 are colorless sticky gel-like substances. Yields: Lig.5, 52.35%; Lig.6, 21.88%.

### Lig.5

Chemical formula: C<sub>20</sub>H<sub>27</sub>O<sub>5</sub>N; molar mass: 361.44 g/mol Elemental analysis % (cal.): C, 65.82 (66.46); H, 8.49 (7.53); N, 3.41 (3.88) <sup>1</sup>H NMR (aceton-d<sub>6</sub>) δ(ppm) 7.24-7.42 (m, 10H, aromatic); 4.944 (Hx of ABX system, 2H, PhC**H**OHCH<sub>2</sub>N); 3.75 (s, 6H, C(C**H**<sub>2</sub>OH)<sub>3</sub>); 3.27 (H<sub>A</sub> of ABX system, 2H, CH<sub>2</sub>); 2.88 (H<sub>B</sub> of ABX system, 2H, PhCHOHC**H**<sub>2</sub>N)

<sup>13</sup>C NMR (aceton-d<sub>6</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 72.4 (PhCHOHCH<sub>2</sub>N);
64.4 (NC(CH<sub>2</sub>OH)<sub>3</sub>); 63.9 (NC(CH<sub>2</sub>OH)<sub>3</sub>); 58.5 (PhCHOHCH<sub>2</sub>N)

IR (KBr) cm<sup>-1</sup> 3399.8 (-OH) 2923.5 (CH) 1635.5 (phenyl) 1494.2 1453.8 1245.6 1230.7 1120.1 1060.6 1028.5 915.7 861.0 761.4 701.1 Lig.6 Chemical formula:  $C_{20}H_{27}O_5N$ ; molar mass: 361.44 g/mol <sup>1</sup>H NMR (aceton-d<sub>6</sub>)  $\delta$ (ppm) 7.24-7.42 (m, 10H, aromatic); 4.80 (Hx of ABX system, 1H, PhCHOHCH<sub>2</sub>N); 4.15 (Hx of ABX system, 1H, NCHPhCH<sub>2</sub>OH); 3.58, 3.44 (H<sub>A</sub> and H<sub>B</sub>

of ABX system, 2H, NCHPhC $\mathbf{H}_2$ OH); 3.55 (s, 6H, C(C $\mathbf{H}_2$ OH)<sub>3</sub>); 2.91 and 2.78 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHC $\mathbf{H}_2$ N)

<sup>13</sup>C NMR (aceton-d<sub>6</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 73.5 (PhCHOHCH<sub>2</sub>N);
64.4 (NC(CH<sub>2</sub>OH)<sub>3</sub>); 62.6 (NCHPhCH<sub>2</sub>OH); 62.0 (NC(CH<sub>2</sub>OH)<sub>3</sub>); 67.1 (NCHPhCH<sub>2</sub>OH); 52.4 (PhCHOHCH<sub>2</sub>N)

# 5.2.7 Synthesis of (R,R)-[N,N-*bis*(2-hydroxidophenyl- ehtyl)-N *tris*(hydroxymethyl)methylamine]-oxidovanadium(V) (Complex 5)

To a solution of 0.1513 g Lig.5 (0.419 mmol) in 2 mL of anhydrous THF was added drop wise and with stirring 0.1000mL of  $VO(OiPr)_3$  (0.423mmol) in 4.5 mL of anhydrous THF. The solution became orange, and later deep in color, and a yellow amorphous precipitate formed. 10 hours later, the precipitate was filtered off and washed with anhydrous THF.

Chemical formula:  $C_{20}H_{25}NO_6V$ ; molar mass: 426 g/mol <sup>51</sup>V NMR (CDCl<sub>3</sub>)  $\delta$  (ppm) -411 EPR (DMSO, 115K):  $A_{\perp} = 68.0 \times 10^{-4} \text{ cm}^{-1}$ ;  $A_{\#} = 172.0 \times 10^{-4} \text{ cm}^{-1}$ ;  $g_{\perp} = 1.988$ ;  $g_{\#} = 1.950$ .

# 5.2.8 Syntheses of methoxido{N,N',N''-2,2',3-[*bis*(R-1phenylethanolato)- (propyl)]amino}silane [Lig.7] and {N,N',N''-2,2',3-[(R-1-phenyl- ethanolato)- (S-2phenylethanolato)(propyl)]amino}silane [Lig.8]

To 1.43 mL of R-styreneoxide in 10 mL of dry *iso* propanol was added 1.127mL of 97% trioxomethylsilyl-propylamine. The mixture was refluxed for 4 days. The products were purified by chromatography on silica gel, using the elutant hexane/ethyl acetate and then ethyl acetate/ethanol with gradually increased polarity. The two products were recrystallized from acetone. Yield: Lig.7, 54.15%; Lig.8, 25.22%

### Lig.7

Chemical formula:  $C_{20}H_{25}NO_3Si$ ; molar mass: 355.50 g/mol <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm) 7.24-7.42 (m, 10H, aromatic); 4.934 (Hx of ABX system, 1H, PhCHOHCH<sub>2</sub>N); 4.878 (Hx of ABX system, 1H, PhCHOHCH<sub>2</sub>N); 3.57 (s, 3H, SiOCH<sub>3</sub>); 2.92 and 2.46 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHCH<sub>2</sub>N); 3.09 and 2.57 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHCH<sub>2</sub>N); 2.86 and 2.52 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.77, 1.64 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 0.99, 0.67 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si)

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 70.8 (PhCHOHCH<sub>2</sub>N); 70.3 (PhCHOHCH<sub>2</sub>N); 60.6 (PhCHOHCH<sub>2</sub>N); 60.5 (PhCHOHCH<sub>2</sub>N) 50.6 (SiOCH<sub>3</sub>); 53.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 20.9 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 8.6 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si)

# Lig.8

Chemical formula:  $C_{20}H_{25}NO_3Si$ ; molar mass: 355.50 g/mol <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm) 7.24-7.42 (m, 10H, aromatic); 5.07 (Hx of AB-x system, 1H, phCH(OSi)CH<sub>2</sub>N); 4.03 (Hx of AB-x system, 1H, NCHphCH<sub>2</sub>OSi); 4.11 and 4.39 (H<sub>A</sub> and H<sub>B</sub> of AB-x system, 2H, NCHphCH<sub>2</sub>OSi); 3.29 and 2.30 (H<sub>A</sub> and H<sub>B</sub> of AB-x system, 2H, phCH(OSi)CH<sub>2</sub>N); 2.79 and 2.26 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>Si); 1.6 and 1.8 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 0.85 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>Si); 3.59 (s, 3H, SiOCH<sub>3</sub>)

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 72.1 (PhCH(OSi)CH<sub>2</sub>N); 64 (NCHPhCH<sub>2</sub>OSi); 62.6 (NCHPhCH<sub>2</sub>OSi); 54.2 (PhCH(OSi)CH<sub>2</sub>N); 50.1 (SiOCH<sub>3</sub>); 53.9 (NCH<sub>2</sub>CHCH<sub>2</sub>Si); 21.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 8.65 (NCH<sub>2</sub>CHCH<sub>2</sub>Si)

### 5.2.9 Syntheses of the vanadium complex of ligand 7 [Complex 7]

To a solution of 0.0326 g Lig.7 (0.1mmol) in 1 mL of anhydrous DMSO was added 0.022 mL of  $VO(iOPr)_3$  (0.1mmol). The mixture was stirred overnight at RT.

<sup>51</sup>V NMR (CDCl<sub>3</sub>) δ (ppm) -469.0, -621.7;
 <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ (ppm) -66.0

#### 5.2.10 Syntheses of the vanadium complex of ligand 8 [Complex 8]

To the solution of 0.0326 g Lig.8 (0.1mmol) in 1 mL of anhydrous DMSO was added 0.0216 mL of VO(*i*OPr)<sub>3</sub> (0.1mmol). The mixture was stirred overnight at RT.

<sup>51</sup>V NMR (CDCl<sub>3</sub>) δ (ppm) -472, -616; <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ (ppm) -62.2

# 5.2.11 Syntheses of chloro-[(R,R)-N,N-*bis*(2-hydroxy-nylethyl)propylamine]-silicate [Lig. 9] and N,N-*bis*(2-methoxy-2-phenyl ethyl)ammonium hydrochloride [Lig.10]

1. Methylation of ligand 1: Synthesis of Lig.1'

0.32 g NaH (in paraffin, 60%) contained in a flask was washed with anhydrous hexane 5 times. Then 0.8950 g Lig.1 dissolved in 6 mL of anhydrous THF were added. When no more bubbles were produced, 0.466 mL of CH<sub>3</sub>I was added, and the reaction system refluxed overnight.

The reaction mixture was washed with saturated NaCl aqueous solution, and the organic phase was transferred to a second flask. The aqueous phase was extracted three times with ethylacetate, and the organic phases were combined.

The combined organic phase were washed with saturated NaCl aqueous solution and dried with sodium sulfate, and then purified by column chromatography on silica gel with the elutant hexane/ethylacetate (4:1). The methylated product, Lig.1', a yellow liquid substance, was obtained in a yield of 92.1%.

Lig.1'

Chemical formula: C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>; molar mass: 325 g/mol.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ(ppm) 7.24-7.42 (m, 10H, aromatic); 5.78 (m, 1H, NCH<sub>2</sub>CHCH<sub>2</sub>); 5.07 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>); 4.28 (Hx of ABX system, 2H, PhCHOHCH<sub>2</sub>N); 3.27 (m, 2H, NCH<sub>2</sub>CHCH<sub>2</sub>); 3.22 (s, 3H, CHOCH<sub>3</sub>); 2.92, 2.76 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 4H, PhCHOHCH<sub>2</sub>N);

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 136.2 (NCH<sub>2</sub>CHCH<sub>2</sub>); 116.6 (NCH<sub>2</sub>CHCH<sub>2</sub>); 83.26 (PhCHOHCH<sub>2</sub>N); 62.1 (PhCHOHCH<sub>2</sub>N); 59.2 (NCH<sub>2</sub>CHCH<sub>2</sub>); 56.9 (COCH<sub>3</sub>)

2. Hydrosilylation of Lig.1': Preparation of Lig.9 and Lig.10

The whole process was conducted under N<sub>2</sub>. 1.3624 g of Lig.1' (4.192mmol) was added to 0.434 mL of a solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in dry 2-propanol (containing 21.706 mg of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O). A light yellow precipitates formed immediately. Then 0.928 mL of HSiCl<sub>3</sub> was introduced and the temperature of the reaction system increased. After cooling back to room temperature with a water bath, the reaction system was heated on an oil bath. At 80 °C, 15 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added, resulting in the immediate dissolution of the precipitates. At 110 °C, the solution began to reflux; refluxing was continued for 5 days.

The product dissolved in  $CH_2Cl_2$  was passed quickly through a short column of silica gel with hexane/ethylacetate, ethylacetate/ethanol (4:1 in volume ratio), and ethanol as elutant. The colorless crystalline Lig.9 was isolated from the collected eluates and recrystallized from ethylacetate. The yield of Lig.9 was about 21.6%.

The remaining silica gel was washed with a mixture of methanol and concentrated hydrochloric acid (36%) in a ratio about 5:1 in volume, and stirring overnight. Lig.**10** crystallized from this solution.

#### Lig.9

Chemical formula:  $C_{19}H_{22}CINO_2Si$ ; molar mass: 359.92 g/mol. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm) 7.24-7.42 (m, 10H, aromatic); 5.05 (Hx of ABX system, 1H, PhCHOHCH<sub>2</sub>N); 5.01 (H<sub>X</sub> of ABX system, 1H, PhCHOHCH<sub>2</sub>N); 3.26 and 2.82 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHCH<sub>2</sub>N); 3.08 and 2.69 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 2H, PhCHOHCH<sub>2</sub>N); 3.00 and 2.73 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.90, 1.2 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 1.76, 1.32 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si)

<sup>97</sup> 

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 70.7 (PhCHOHCH<sub>2</sub>N); 70.7 (PhCHOHCH<sub>2</sub>N); 60.2 (PhCHOHCH<sub>2</sub>N); 59.4 (PhCHOHCH<sub>2</sub>N); 52.9 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>);
20.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 19.8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)

# Lig.10

Chemical formula:  $C_{18}H_{24}NO_2Cl$ ; molar mass: 321.8 g/mol. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ (ppm) 7.24-7.42 (m, 10H, aromatic); 9.69 (s, 2H, H<sub>2</sub>N<sup>+</sup>); 4.87 (H<sub>X</sub> of ABX system, 2H, PhCHOHCH<sub>2</sub>N); 3.49, 3.25 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 4H, phCHOHCH<sub>2</sub>N); 3.31 (s, 6H, COCH<sub>3</sub>)

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm) 146.6, 128.8, 128.2 (phenyl ring); 72.3 (PhCHOHCH<sub>2</sub>N); 63.6 (PhCHOHCH<sub>2</sub>N); 53.9 (COCH<sub>3</sub>)

#### 5.2.12 Synthesis of Complex 11

### 1. Synthesis of aggregated Lig.7

0.0523g Lig.7 was dissolved in the least amount of MeOH. 1.5 mL of concentrated HCl (12M) was diluted with 30 mL H<sub>2</sub>O ( [HCl]~0.4M). This aqueous HCl was added slowly and drop wise to the MeOH solution of Lig.7 with vigorous stirring, until a precipitate formed. Then the acid solution left was added with a syringe, and the mixture stirred overnight.

The white precipitate which had formed was separated by centrifugation and washed first with deionized water for several times, then with aqueous saturated NaHCO<sub>3</sub>. At last, the product was washed again with deionized water for several times; separation was always carried out by centrifugation. All of the washing procedures were carried out in an ultrasonic bath. The final product was dried in a drying oven at 75°C overnight. Yield: about 45%.

2. Synthesis of Complex **11** 

0.010 g of aggregated Lig.7 was well dispersed ultrasonically in 5 mL of anhydrous THF, followed by addition of an excess  $VO(OiPr)_3$  under the protection of N<sub>2</sub>. The reaction was assisted with ultrasonic for 30-40 minutes, and then allowed to stay overnight. The product was separated by centrifugation, washed with dry THF several times, and dried in vacuo.

Elemental analysis (%): C, 69.9; V, 24.46.

# 5.2.13 Synthesis of Complex 12

#### 1. Preparation of activated silica gel

5.00 g silica gel 60 (0.040-0.063 mm) was refluxed in 6 M HCl solution for 24 hours. After cooling back to room temp., the silica gel was thoroughly washed with deionized water and then dried at 100 °C overnight.

#### 2. Immobilization of Lig.7 on activated silica gel

Under the protection of  $N_2$ , 2.00 g activated silica gel and the solution of 0.10 g (0.14 mmol) of Lig.7 in 10 mL of toluene were mixed and refluxed for 48 hours with stirring. The functionalized silica gel thus obtained was washed with toluene, THF, ethanol, deionized water, and finally with THF again, each for 3 times, and then dried at 80 °C in a drying oven for 24 hours.

Elemental analysis (%): C, 4.73; H, 0.95; N, 0.33; loading of Lig.7 per gram of functionalized silica gel: 0.24 mmol/g.

3. Protection of the unreacted (free) OH-groups with trimethylsilyl

Under the protection of  $N_2$ , the mixture of 0.056 g functionalized silica gel in 9 mL of THF was treated with 0.03 mL (0.2 mmol) of hexamethyldisiloxane, and the mixture refluxed for 36 hours. Then the silica gel was washed three times with THF and dried at 75°C for two hours.

Elemental analysis (%): C, 4.69; H, 0.95; N, 0.2

<sup>99</sup>
#### 4. Synthesis of Complex 12

To the mixture of 1 g of functionalized silica gel in 10 mL of THF was added 0.075 mL of  $VO(OiPr)_3$  (0.32 mmol, excess to the ligand). The reaction mixture was stirred overnight at room temp.

The silica gel grafted with the vanadium compound was washed with THF, ethanol and methanol several times, and then dried in vacuo.

Elemental analysis (%): N, 0.2; V, 0.377. Loading of Complex **12** per gram of functionalized silica gel: 0.074 mmol/g

#### 5.2.14 Synthesis of Complex 13

The whole process was performed under the protection of N2

1. Synthesis of immobilized Lig.3 on Merrifield resin

0.0650 g (1.625 mmol) NaH (60% in paraffin) was washed with anhydrous hexane 5 times and dried in vacuo. To this NaH was introduced 0.5300 g (1.60 mmol) Lig.3 dissolved in 6 mL of anhydrous THF. The slurry was stirred for 4 hours at room temperature, and then 0.3600 g Merrifield resin (0.7mmol Cl/g), previously swelled in 6 ml of anhydrous THF for 6 hours, was added to the slurry and stirred overnight. The slurry was washed with deionized water, ethanol, and dry THF, each for 3 times, and pumped to dryness.

Elemental analysis (%): N, 0.37; C, 88.51; H, 7.65; loading of Lig.3 per gram of functionalized Merrifield resin: 0.27mmol/g (calculated by N).

#### 2. Synthesis of Complex 13

To the mixture of 0.2526 g of functionalized Merrifield resin in 4 mL anhydrous THF was added 0.075 mL of  $VO(OiPr)_3$  (0.32 mmol, excess with respect to the ligand). The mixture was stirred overnight at room temperature. The resin was then filtered off and

washed with anhydrous THF, ethanol, and acetone, each for 5 times, and vacuumed to dryness.

Elemental analysis (%): V, 1.12; loading of complex **13** per gram of functionalized Merrifield resin: 0.219 mmol/g

#### 5.2.15 Synthesis of Complex 14

0.1005 g Barlos resin (0.1005 mmol, calculated as 1.0 mmol/g) was added to 1.0 mL of an anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.0796 g (0.2013 mmol) complex 3' (complex3' dissolves only slightly in CH<sub>2</sub>Cl<sub>2</sub>). Then 0.1403 mL (0.8054 mmol) of Hünig's base was added with stirring, resulting in complete dissolution of complex 3'. The resin was filtered off after 24 hours, washed thoroughly (6×) with anhydrous CH<sub>2</sub>Cl<sub>2</sub>, and pumped to dryness.

Elemental analysis (%): V, 1.74; loading of complex **14** per gram of functionalized Barlos resin: 0.342 mmol/g.

#### 5.2.16 Synthesis of Complex 15

To a mixture of 0.0966 g (0.2278 mmol) of complex **5** in 1.0 mL of a  $CH_2Cl_2$  solution (complex **5** dissolves only slightly in  $CH_2Cl_2$ ) was added, with stirring, 0.4 mL of dry DMSO. A clear solution formed. Then 0.1018 g Barlos resin and 0.1600 mL (0.9185mmol) of Hünig's base was added. 24 hours later, the resin was filtered off and washed with anhydrous  $CH_2Cl_2$  thoroughly (6 ×) and pumped dry. Elemental analysis (%): V, 1.40; loading of complex **14** per gram of functionalized Barlos resin: 0.279 mmol/g.

#### 5.2.17 Synthesis of 1-[*bis*(2-hydroxyphenylethyl)]amino-3-(trityloxy)propan-2-ol [Lig.3']

0.1009 g (0.3058 mmol) of Lig.3 was dissolved in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> solution. To this solution 0.0853 g (0.3058 mmol) of trityl chloride (triphenylchloromethane) and 0.1010 mL (0.5783mmol) of Hünig's base were added. After stirring the reaction mixture for 24

hours, the solvent was evaporated off in the open air, and the residue redissolved in anhydrous acetone. The acetone was then evaporated slowly. Several days later, needle-shaped colorless crystals had formed. Yield: 100%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.46-7.20 (m, 25H, phenyl ring); 4.70 (H<sub>X</sub> of ABX system, 2H, PhC**H**OHCH<sub>2</sub>); 3.92 (m, 1H, NCH<sub>2</sub>CHOHCH<sub>2</sub>); 3.2 (m, 2H, CH<sub>2</sub>CHOHC**H**<sub>2</sub>OC); 2.80, 2.76 (H<sub>A</sub> and H<sub>B</sub> of ABX system, 4H, PhCHOHC**H**<sub>2</sub>N); 2.60, 2.49 (m, 2H, NC**H**<sub>2</sub>CHOH)

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm): 148-126 (phenyl ring); 87 (Ph<sub>3</sub>COCH<sub>2</sub>); 71 (PhCHOHCH<sub>2</sub>);
 70 (Ph<sub>3</sub>COCH<sub>2</sub>); 68 (NCH<sub>2</sub>CHOH); 63 (PhCHOHCH<sub>2</sub>N); 58 (NCH<sub>2</sub>CHOH)

#### 5.3 Catalytic Oxidations of Methylphenylsulfide (MPS)

The reactions and/or results of the reactions were monitored by NMR. The NMR solvent  $CDCl_3$  was dried with 4 Å molecular sieve and neutralized with  $K_2CO_3$  before use. All catalytic processes were conducted under the protection of  $N_2$ .

# 5.3.1 Catalytic oxidation of MPS with cumyl hydroperoxide (CHP) at $0^{\circ}C$

5.3.1.1 Catalysis with complex 1 formed in situ

0.0026 g (0.008 mmol) of Lig.1 was dissolved in 0.8 mL of CDCl<sub>3</sub>. To this solution, 1.9  $\mu$ L of VO(O*i*Pr)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 14.90  $\mu$ L of CHP (0.08 mmol) was introduced to this solution with stirring. The solution was transferred to an NMR tube, and cooled down to 0°C in an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

5.3.1.2 Catalysis with complex 2 formed in situ

0.0026 g (0.008 mmol) of Lig.2 was dissolved in 0.8 mL of CDCl<sub>3</sub>. To this solution, 1.9  $\mu$ L of VO(O*i*Pr)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 14.90  $\mu$ L of CHP (0.08 mmol) was introduced to the solution with stirring. The solution was transferred to an NMR tube, and cooled down to 0°C with an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

#### 5.3.1.3 Catalysis with complex 3 formed in situ

0.0027 g (0.008 mmol) of Lig.3 was dissolved in 0.8 mL of CDCl<sub>3</sub>. To this solution 1.9  $\mu$ L of VO(*OiPr*)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 14.90  $\mu$ L of CHP (0.08 mmol) was introduced to the solution with stirring. The solution was transferred to an NMR tube, and cooled down to 0°C with an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

#### 5.3.1.4 Catalysis with complex 5 formed in situ

0.0029 g (0.008 mmol) of Lig.5 was dissolved in 0.8 mL of CDCl<sub>3</sub>. To this solution 1.9  $\mu$ L of VO(*OiPr*)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 14.90  $\mu$ L of CHP (0.08 mmol) was introduced with stirring. The solution was transferred to an NMR tube, and cooled down to 0°C with an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

#### 5.3.1.5 Catalysis with complex 7 formed in situ

0.0028 g (0.008 mmol) of Lig.7 was dissolved in 0.8 mL of CDCl<sub>3</sub>. To this solution 1.9  $\mu$ L of VO(*Oi*Pr)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 14.90  $\mu$ L of CHP (0.08 mmol) was introduced with stirring. The solution was transferred to an NMR tube, and cooled down to 0°C with an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

5.3.1.6 Catalysis with complex 1

0.0033 g (0.008 mmol) of complex **1** was dissolved in 0.8 mL CDCl<sub>3</sub>, followed by the addition of 14.90  $\mu$ L of CHP (0.08 mmol). The solution was transferred to an NMR tube and cooled down to 0°C with an ice bath. Then, 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

#### 5.3.1.7 Catalysis with complex 2

0.0033 g (0.008 mmol) of complex **2** was dissolved in 0.8 mL of CDCl<sub>3</sub>, followed by 14.90 µL of CHP (0.08 mmol). The solution was transfer to an NMR tube and cooled down to 0°C with an ice bath. Then 9.46 µL of MPS (0.08 mmol, 0°C) was added.

#### 5.3.1.8 Catalysis with complex 3

0.0032 g (0.008 mmol) of complex **3** was dissolved in 0.8 mL CDCl<sub>3</sub>, followed by 14.90  $\mu$ L of CHP (0.08 mmol). The solution was transfer to an NMR tube and cooled down to 0°C with an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

5.3.1.9 Catalysis with complex 5

0.0034 g (0.008 mmol) of complex **5** was dissolved in 0.8mL CDCl<sub>3</sub>, followed by 14.90  $\mu$ L of CHP (0.08 mmol). The solution was transfer to an NMR tube and cooled down to 0°C with an ice bath. Then 9.46  $\mu$ L of MPS (0.08 mmol, 0°C) was added.

# 5.3.2 Catalytic oxidation of MPS with cumyl hydroperoxide (CHP) at - $20^{\circ}C$

5.3.2.1 Catalyses with complex 1

#### Lig:V = 1:1 in *situ* in $CH_2Cl_2$ solution:

0.0026 g (0.008 mmol) of Lig.1 was dissolved in 0.8 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub>. To this solution 1.9  $\mu$ L of VO(O*i*Pr)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 14.90  $\mu$ L of CHP (0.08 mmol) was introduced to the solution with stirring. The solution was cooled down to -20°C in a low-temperature refrigerator. Then to this solution 9.46  $\mu$ L

of MPS (0.08 mmol, -20°C) was added. The reaction system was kept at -20°C in a low-temperature refrigerator still. 3 days later the reaction system was dried in vacuo and redissolved in CDCl<sub>3</sub>. The catalytic results were detected by NMR.

#### Lig:V = 2:1 in *situ* in $CH_2Cl_2$ solution

The reaction was carried out accordingly with 0.0052 g (0.016 mmol) of Lig.1 in 0.8 mL of anhydrous  $CH_2Cl_2$  plus 1.9  $\mu$ L of VO(O*i*Pr)<sub>3</sub> (0.008 mmol).

#### Lig: V = 1:1 in *situ* in CH<sub>2</sub>ClCH<sub>2</sub>Cl solution

The experiment process was the same; just CH<sub>2</sub>Cl<sub>2</sub> was substituted with CH<sub>2</sub>ClCH<sub>2</sub>Cl.

#### Lig: V = 2:1 in *situ* in CH<sub>2</sub>ClCH<sub>2</sub>Cl solution

The experiment process was the same, just CH2Cl2 was substituted with CH2ClCH2Cl.

#### Pre-formed complex 1 in CH2Cl2 solution

0.0033 g (0.008 mmol) of complex **1** was dissolved in 0.8 mL of anhydrous  $CH_2Cl_2$ , followed by the addition of 14.90 µL of CHP (0.08 mmol). The solution was cooled down to -20°C in a low-temperature refrigerator. Then to this solution 9.46 µL of MPS (0.08 mmol, -20°C) was added with stirring. The reaction system was kept at -20°C in a low-temperature refrigerator still. 3 days later the reaction system was dried in vacuo and redissolved in CDCl<sub>3</sub>. The catalytic results were detected by NMR.

#### Pre-formed complex 1 in CH<sub>2</sub>ClCH<sub>2</sub>Cl solution

0.0033 g (0.008 mmol) of complex **1** was dissolved in 0.8 mL of anhydrous  $CH_2ClCH_2Cl$ . The remaining procedure follows the one described for Pre-formed complex **1** in  $CH_2Cl_2$  solution.

5.3.2.2 Catalyses with complex 2

#### Lig:V = 1:1 in *situ* in $CH_2Cl_2$ solution

0.0026 g (0.008 mmol) of Lig.2 was dissolved in 0.8 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub>. To this solution 1.9  $\mu$ L of VO(O*i*Pr)<sub>3</sub> (0.008 mmol) was added with stirring. After half an hour,

14.90  $\mu$ L of CHP (0.08 mmol) was introduced. The solution was cooled down to -20 °C. Then 9.46  $\mu$ L of MPS (0.08 mmol, -20°C) was added. The reaction system was kept at -20°C for 3 days. The reaction system was then dried in vacuo, and redissolved in CDCl<sub>3</sub>.

#### Lig:V = 2:1 in *situ* in $CH_2Cl_2$ solution

The procedure follows the one described above, using the following amounts of reactants: 0.0052 g (0.016 mmol) of Lig.2 in 0.8 mL CH<sub>2</sub>Cl<sub>2</sub>; 1.9  $\mu$ L of VO(O*i*Pr)<sub>3</sub> (0.008 mmol); 14.90  $\mu$ L (0.08 mmol) of CHP; 9.46  $\mu$ L (0.08 mmol) of MPS.

#### Lig: V = 1:1 in *situ* in CH<sub>2</sub>ClCH<sub>2</sub>Cl solution

The experiment process was the same, just CH<sub>2</sub>Cl<sub>2</sub> was substituted with CH<sub>2</sub>ClCH<sub>2</sub>Cl.

Lig:V = 2:1 in *situ* in  $CH_2ClCH_2Cl$  solution

The experiment process was the same, just CH2Cl2 was substituted with CH2ClCH2Cl.

#### Pre-formed complex 2 in CH<sub>2</sub>Cl<sub>2</sub> solution

0.0033 g (0.008 mmol) of complex **2** was dissolved in 0.8 mL of anhydrous  $CH_2Cl_2$ , followed by the addition of 14.90 µL of CHP (0.08 mmol). The solution was cooled down to -20°C in a low-temperature refrigerator. Then to this solution 9.46 µL of MPS (0.08 mmol, -20°C) was added with stirring. The reaction system was kept at -20°C in a low-temperature refrigerator still. 3 days later the reaction system was dried in vacuo and redissolved in CDCl<sub>3</sub>. The catalytic results were detected by NMR.

Pre-formed complex 2 in CH<sub>2</sub>ClCH<sub>2</sub>Cl solution

0.0033 g (0.008 mmol) of complex **2** was dissolved in 0.8 mL of anhydrous  $CH_2ClCH_2Cl$ . The remaining procedure follows the one described for Pre-formed complex **2** in  $CH_2Cl_2$  solution.

#### 5.3.3 Catalytic oxidation of MPS with hydrogen peroxide

5.3.3.1 Catalysis with complex 1 in situ

0.0026 g (0.008 mmol) of Lig.1 was dissolved in 0.8 mL of anhydrous  $CH_2Cl_2$ . To this solution 1.9 µL of VO(OiPr)<sub>3</sub> (0.008 mmol) was added with stirring. Half an hour later, 9.46 µL of MPS (0.08 mmol) was added. The solution was cooled in an ice water bath to 4 °C. To this solution, 8.17 µL of  $H_2O_2$  (0.08 mmol, 4°C) was added. The reaction mixture was stirred with the temperature controlled between 8-12°C. 24 hours later, the reaction system was dried in vacuo and redissolved in CDCl<sub>3</sub>.

#### Catalysis with complex 2 in situ

The same procedure as described for complex 1 was applied.

5.3.3.3 Catalyses with the pre-formed complexes 1 and 2 0.0033 g (0.008 mmol) of complex 1 or 2, respectively, was dissolved in 0.8 mL of anhydrous  $CH_2Cl_2$  and processed as described for the *in situ* systems.

# 5.3.4 Oxidation of MPS with CHP catalyzed by immobilized model complexes

5.3.4.1 Catalysis with complex 11

0.0082 g of complex **11** (V: 0.0384 mmol) was dispersed in 3.2 mL of CDCl<sub>3</sub>. Then 37.84  $\mu$ L of MPS (0.32 mmol) was added with stirring. The solution was cooled down in an ice/water bath to 0 °C. To this solution was added 59.6  $\mu$ L of CHP (0.08 mmol, 4°C). The reaction mixture was stirred, with the temperature controlled at 0°C. The solution was taken out in fractions at different reaction times and centrifuged. Then the clear fraction was measured by NMR.

After the catalytic reaction was finished, the catalyst was washed with CHCl<sub>3</sub> for 3 times by centrifugation, and then used in the next run of experiment.

5.3.4.2 Catalysis with complex 12

0.1335 g of complex **12** (V: 0.0099 mmol) was dispersed in 3.2 mL of CDCl<sub>3</sub>. The further procedure follows that described for complex **11**.

#### 5.3.4.3 Catalysis with complex 13

0.1651 g of complex **13** (V: 0.036 mmol) was dispersed in 4.0 mL of CDCl<sub>3</sub> solution. For further processing, see 5.3.4.1.

#### 5.3.4.4 Catalysis with complex **14**

0.0271 g of complex **14** (V: 0.0092 mmol) was dispersed in 0.8 mL of  $CH_2Cl_2$  solution. Then 9.46 µL of MPS (0.08 mmol) was added with stirring. The solution was cooled down in an ice/water bath to 4°C and treated with 14.9 µL of CHP (0.40 mmol, 4°C). The reaction mixture was stirred with the temperature controlled between 8-17°C. After 24 hours, the reaction system was vacuumed to dryness, and redissolved in CDCl<sub>3</sub>. After the catalytic reaction was finished, the catalyst was washed with anhydrous THF for 3 times, and then used in the next run of experiment.

#### 5.3.4.5 Catalysis with complex 15

0.0269g of complex **15** (V: 0.0075mmol) was dispersed in 0.8mL of  $CH_2Cl_2$  solution. For the following reaction steps, cf. 5.3.4.4.

#### 5.4 Crystallgraphic Data

#### 5.4.1 Crystal data and structure refinement for Lig.1

Empirical formula	C <sub>19</sub> H <sub>23</sub> N O <sub>2</sub>	
Formula weight	297.38	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.3912(6)	Å
	b = 13.0062(11)	Å
	$\alpha = 90$	0
	$\beta = 90^{\circ}$ .	
	c = 17.3285(15)	Å
	$\gamma = 90^{\circ}$ .	
Volume	1665.8(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.186 Mg/m <sup>3</sup>	
Absorption coefficient	0.076 mm <sup>-1</sup>	
F(000)	640	
Crystal size	0.38 x 0.22 x 0.12 mm	3
Theta range for data collection	1.96 to 27.50°	
-	108	

Index ranges	-9<=h<=9, -16<=k<=16, -22<=l<=22
Reflections collected	19986
Independent reflections	2194 [R(int) = 0.0859]
Completeness to theta = 27.50°	99.6 %
Max. and min. transmission	0.9909 and 0.9716
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2194 / 0 / 207
Goodness-of-fit on F <sup>2</sup>	0.904
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.0642
R indices (all data)	R1 = 0.0682, wR2 = 0.0697
Absolute structure parameter	0(10)
Largest diff. peak and hole	$0.143 and -0.136 e.Å^{-3}$

Bond lengths [Å] and angles [°] for Lig. 1

Bond lengths [Å]					
N-C(31)	1.473(3)	C(5)-C(6)	1.382(3)	C(14)-H(14)	0.9500
N-C(8)	1.473(3)	C(5)-H(5)	0.9500	C(15)-C(16)	1.380(3)
N-C(18)	1.477(3)	C(6)-H(6)	0.9500	C(15)-H(15)	0.9500
O(1)-C(7)	1.438(2)	C(7)-C(8)	1.516(3)	C(16)-H(16)	0.9500
O(1)-H(1)	0.96(2)	C(7)-H(7)	1.0000	C(17)-C(18)	1.517(3)
O(2)-C(17)	1.427(3)	C(8)-H(8A)	0.9900	C(17)-H(17)	1.0000
O(2)-H(2)	0.89(3)	C(8)-H(8B)	0.9900	C(18)-H(18A)	0.9900
C(1)-C(6)	1.377(3)	C(11)-C(16)	1.376(3)	C(18)-H(18B)	0.9900
C(1) - C(2)	1.377(3)	C(11)-C(12)	1.387(3)	C(31)-C(32)	1.486(3)
C(1)-C(7)	1.505(3)	C(11)-C(17)	1.503(3)	C(31)-H(31A)	0.9900
C(2)-C(3)	1.380(3)	C(12)-C(13)	1.379(3)	C(31)-H(31B)	0.9900
C(2)-H(2)	0.9500	C(12)-H(12)	0.9500	C(32)-C(33)	1.301(3)
C(3)-C(4)	1.376(3)	C(13)-C(14)	1.376(3)	C(32)-H(32)	0.9500
C(3)-H(3)	0.9500	C(13)-H(13)	0.9500	C(33)-H(33A)	0.9500
C(4)-C(5)	1.376(3)	C(14)-C(15)	1.374(4)	C(33)-H(33B)	0.9500
C(4)-H(4)	0.9500				
		ang	les [°]		
C(31)-N-C(8)	111 70(18)	C(13)-C(12)-C(1	1) 121 2(3)	C(15)-C(16)-H(1)	6) 119.7
C(31)-N- $C(18)$	110 41(18)	O(1)-C(7)-H(7)	108 5	O(2)-C(17)-C(11)	112.87(18)
C(8)-N-C(18)	109 26(19)	C(1)-C(7)-H(7)	108.5	O(2)-C(17)-C(18)	107.31(19)
C(7)-O(1)-H(1)	110.0(15)	C(8)-C(7)-H(7)	108.5	C(11)-C(17)-C(18	8) 111 50
C(17)-O(2)-H(1)	(12) $(12)$	N-C(8)-C(7)	114 84(19)	O(2)-C(17)-H(17)	108.3
C(6)-C(1)-C(2)	118.3(2)	N-C(8)-H(8A)	108.6	C(11)-C(17)-H(1)	7) 108.3
C(6)-C(1)-C(7)	120.7(2)	C(7)-C(8)-H(8A)	108.6	C(18)-C(17)-H(1)	7) 108.3
C(2)-C(1)-C(7)	120 9(2)	N-C(8)-H(8B)	108.6	N-C(18)-C(17)	112 03(17)
C(1)-C(2)-C(3)	121.0(3)	C(7)-C(8)-H(8B)	108.6	N-C(18)-H(18A)	109.2
C(1)-C(2)-H(2)	119.5	H(8A)-C(8)-H(8H	3) 107.5	C(17)-C(18)-H(1	8A) 109.2
C(3)-C(2)-H(2)	119.5	C(16)-C(11)-C(12	2) 118.4(2)	N-C(18)-H(18B)	109.2
C(4)-C(3)-C(2)	120.2(3)	C(16)-C(11)-C(1	7) 123.0(2)	C(17)-C(18)-H(1	8B) 109.2
C(4)-C(3)-H(3)	119.9	C(12)-C(11)-C(1	7) 118.6(2)	H(18A)-C(18)-H	(18B) 107.9
C(2)-C(3)-H(3)	) 119.9	C(13)-C(12)-H(12	2) 119.4	N-C(31)-C(32)	112.7(2)
C(3)-C(4)-C(5)	119.4(3)	C(11)-C(12)-H(12	2) 119.4	N-C(31)-H(31A)	109.1
C(3)-C(4)-H(4)	120.3	C(14)-C(13)-C(12	2) 119.6(3)	C(32)-C(31)-H(3	1A) 109.1
C(5)-C(4)-H(4)	) 120.3	C(14)-C(13)-H(1	3) 120.2	N-C(31)-H(31B)	109.1
C(4)-C(5)-C(6)	119.9(3)	C(12)-C(13)-H(1	3) 120.2	C(32)-C(31)-H(3	1B) 109.1
C(4)-C(5)-H(5)	) 120.0	C(15)-C(14)-C(12	3) 119.7(3)	H(31A)-C(31)-H	(31B) 107.8
C(6)-C(5)-H(5)	) 120.0	C(15)-C(14)-H(14	4) 120.1	C(33)-C(32)-C(3	1) 124.5(3)
C(1)-C(6)-C(5)	121.2(3)	C(13)-C(14)-H(14	4) 120.1	C(33)-C(32)-H(3	2) 117.7
C(1)-C(6)-H(6)	) 119.4	C(14)-C(15)-C(10	6) 120.5(3)	C(31)-C(32)-H(32	2) 117.7
C(5)-C(6)-H(6)	) 119.4	C(14)-C(15)-H(1	5) 119.8	C(32)-C(33)-H(3	3A) 120.0
O(1)-C(7)-C(1)	) 110.48(18)	C(16)-C(15)-H(1	5) 119.8	C(32)-C(33)-H(3	3B) 120.0
O(1)-C(7)-C(8)	) 109.62(18)	C(11)-C(16)-C(15	5) 120.6(2)	H(33A)-C(33)-H	(33B) 120.0
C(1)-C(7)-C(8)	111.28(19)	C(11)-C(16)-H(1	6) 119.7		

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions	$C_{20} H_{24} N O_4 V$ 393.34 153(2) K 0.71073 Å ORTHORHOMBIC P2(1)2(1)2(1) a = 6.4827(4) Å. b = 7.7631(5) Å c = 38.175(2) Å $\alpha = 90^{\circ}$ $\beta = 90^{\circ}$ . $\gamma = 90^{\circ}$
Volume	1921.2(2) Å <sup>3</sup>
Z	4
Density (calculated)	1.360 Mg/m <sup>3</sup>
Absorption coefficient	0.540 mm <sup>-1</sup>
F(000)	824
Crystal size	0.91 x 0.22 x 0.20 mm <sup>3</sup>
Theta range for data collection	2.13 to 27.00°.
Index ranges	-8<=h<=8, -9<=k<=9, -48<=l<=48
Reflections collected	22650
Independent reflections	4191 [R(int) = 0.0752]
Completeness to theta = 27.00°	100.0 %
Max. and min. Transmission	0.8996 and 0.6392
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4191 / 0 / 236
Goodness-of-fit on F <sup>2</sup>	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0799
R indices (all data)	R1 = 0.0352, wR2 = 0.0810
Absolute structure parameter	0.010(17)
Largest diff, peak and hole	0.419 and -0.168 e.Å <sup>-3</sup>

## 5.4.2 Crystal data and structure refinement for Complex 1

Bond lengths [Å] and angles [°] for Complex 1

	Bond lengths [Å]				
V(1)-O(1)	1.5914(14)	O(3)-C(17)	1.417(2)	C(17)-C(11)	1.511(3)
V(1)-O(4)	1.7930(14)	C(8)-C(7)	1.519(2)	C(3)-C(4)	1.381(3)
V(1)-O(3)	1.8127(14)	C(7)-C(1)	1.513(3)	C(3)-C(2)	1.387(3)
V(1)-O(2)	1.8251(13)	C(1)-C(2)	1.387(3)	C(11)-C(16)	1.386(3)
V(1)-N	2.2251(16)	C(1)-C(6)	1.389(3)	C(11)-C(12)	1.388(3)
O(2)-C(7)	1.415(2)	C(18)-C(17)	1.516(3)	C(16)-C(15)	1.387(3)
N-C(8)	1.485(2)	C(32)-C(33)	1.311(3)	C(12)-C(13)	1.393(3)
N-C(18)	1.485(2)	C(32)-C(31)	1.505(3)	C(13)-C(14)	1.366(4)
N-C(31)	1.486(3)	C(5)-C(6)	1.378(3)	C(15)-C(14)	1.383(4)
O(4)-C(20)	1.407(3)	C(5)-C(4)	1.390(3)		
angles [°]					
O(1)-V(1)-O(	4) 103.96(7)	C(18)-N-V(1)	105.73(11)	O(3)-C(17)-C(18)	106.40(15)
O(1)-V(1)-O(	3) 115.89(8)	C(31)-N-V(1)	111.45(12)	C(11)-C(17)-C(18)	111.69(16)
O(4)-V(1)-O(	3) 93.57(6)	C(20)-O(4)-V(1)	119.13(13)	C(5)-C(6)-C(1)	120.80(18)
O(1)-V(1)-O(	2) 113.33(7)	C(17)-O(3)-V(1)	125.89(12)	N-C(31)-C(32)	115.06(17)

O(4)-V(1)-O(2)	96.83(6)	N-C(8)-C(7)	107.09(14)	C(4)-C(3)-C(2)	120.0(2)
O(3)-V(1)-O(2)	125.15(7)	O(2)-C(7)-C(1)	109.87(15)	C(16)-C(11)-C(12)	119.51(19)
O(1)-V(1)-N	91.23(7)	O(2)-C(7)-C(8)	106.83(14)	C(16)-C(11)-C(17)	119.64(19)
O(4)-V(1)-N	164.75(7)	C(1)-C(7)-C(8)	113.01(16)	C(12)-C(11)-C(17)	120.83(19)
O(3)-V(1)-N	78.33(6)	C(2)-C(1)-C(6)	118.53(18)	C(3)-C(4)-C(5)	119.42(19)
O(2)-V(1)-N	77.94(6)	C(2)-C(1)-C(7)	120.72(18)	C(11)-C(16)-C(15)	120.0(2)
C(7)-O(2)-V(1)	125.28(11)	C(6)-C(1)-C(7)	120.74(16)	C(11)-C(12)-C(13)	119.8(2)
C(8)-N-C(18)	113.32(15)	N-C(18)-C(17)	107.98(15)	C(14)-C(13)-C(12)	120.5(2)
C(8)-N-C(31)	111.66(14)	C(33)-C(32)-C(31)	122.0(2)	C(14)-C(15)-C(16)	120.2(2)
C(18)-N-C(31)	111.37(15)	C(6)-C(5)-C(4)	120.30(19)	C(1)-C(2)-C(3)	121.0(2)
C(8)-N-V(1)	102.85(11)	O(3)-C(17)-C(11)	112.21(16)	C(13)-C(14)-C(15)	120.0(2)

## 5.4.3 Crystal data and structure refinement for Complex 2

Empirical formula	C <sub>20</sub> H <sub>24</sub> N O <sub>4</sub> V
Formula weight	393.34
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2(1)
Unit cell dimensions	a = 11.1327(13) A
	b = 5.9643(7) A
	c = 14.6191(18)A
	$\alpha = 90^{\circ}$ .
	$\beta = 93.347(2)^{\circ}$
	$\gamma = 90^{\circ}$ .
Volume	969.0(2) Å <sup>3</sup>
Z	2
Density (calculated)	1.242 Mg/m <sup>3</sup>
Absorption coefficient	0.526 mm <sup>-1</sup>
F(000)	378
Crystal size	$0.67 \times 0.10 \times 0.07 \text{ mm}^3$
Theta range for data collection	1 40 to 27 00°
Index ranges	-14<=h<=14 -7<=k<=7 -18<=l<=18
Reflections collected	11188
Independent reflections	4204 [R(int) = 0.0734]
Completeness to theta = $27.00^{\circ}$	99.7 %
Max. and min. Transmission	0.9641 and 0.7195
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / narameters	4204 / 1 / 237
$C = 1 + C C + E^2$	0.015
Goodness-of-fit on F <sup>-</sup>	0.915
Final R indices [1>2sigma(1)]	R1 = 0.046/, WR2 = 0.0906
A hashita atmatuma manamatan	R1 = 0.0/41, WR2 = 0.1293
Austration apofficient	0.07(5)
Extinction coefficient	0.014(2)
Largest diff. peak and hole	0.327 and -0.416 e.Å <sup>-3</sup>

Bond lengths [Å] and angles [°] for Complex 2

Bond lengths [Å]					
V(1)-O(1)	1.600(3)	N-C(12)	1.505(5)	C(10)-C(11)	1.320(6)
V(1)-O(4)	1.759(3)	C(1)-C(2)	1.391(6)	C(12)-C(13)	1.519(6)

V(1)-O(3)	1.820(3)	C(1)-C(6)	1.394(5)	C(12)-C(19)	1.524(5)
V(1)-O(2)	1.830(3)	C(2)-C(3)	1.379(7)	C(13)-C(18)	1.395(6)
V(1)-N	2.413(3)	C(3)-C(4)	1.385(6)	C(13)-C(14)	1.399(6)
O(2)-C(7)	1.414(5)	C(4)-C(5)	1.386(6)	C(14)-C(15)	1.390(6)
O(3)-C(19)	1.425(5)	C(5)-C(6)	1.379(6)	C(15)-C(16)	1.386(7)
O(4)-C(20)	1.414(5)	C(6)-C(7)	1.516(5)	C(16)-C(17)	1.366(6)
N-C(8)	1.470(5)	C(7)-C(8)	1.530(5)	C(17)-C(18)	1.398(6)
N-C(9)	1.494(5)	C(9)-C(10)	1.514(5)		
		angle	es [°]		
O(1)-V(1)-O(4)	105.40(17)	C(9)-N-C(12)	114.6(3)	N-C(8)-C(7)	107.2(3)
O(1)-V(1)-O(3)	107.06(14)	C(8)-N-V(1)	102.5(2)	N-C(9)-C(10)	116.5(4)
O(4)-V(1)-O(3)	98.20(13)	C(9)-N-V(1)	107.6(2)	C(11)-C(10)-C(9)	121.4(4)
O(1)-V(1)-O(2)	110.92(15)	C(12)-N-V(1)	104.4(2)	N-C(12)-C(13)	116.8(3)
O(4)-V(1)-O(2)	98.61(14)	C(2)-C(1)-C(6)	120.2(4)	N-C(12)-C(19)	105.1(3)
O(3)-V(1)-O(2)	132.19(14)	C(3)-C(2)-C(1)	120.2(4)	C(13)-C(12)-C(19)	115.2(3)
O(1)-V(1)-N	90.71(13)	C(2)-C(3)-C(4)	119.6(4)	C(18)-C(13)-C(14)	118.1(4)
O(4)-V(1)-N	163.88(14)	C(3)-C(4)-C(5)	120.4(4)	C(18)-C(13)-C(12)	122.6(4)
O(3)-V(1)-N	76.11(11)	C(6)-C(5)-C(4)	120.5(4)	C(14)-C(13)-C(12)	119.3(4)
O(2)-V(1)-N	75.48(12)	C(5)-C(6)-C(1)	119.2(4)	C(15)-C(14)-C(13)	121.5(4)
C(7)-O(2)-V(1)	125.9(3)	C(5)-C(6)-C(7)	122.2(4)	C(16)-C(15)-C(14)	119.2(5)
C(19)-O(3)-V(1)	121.1(2)	C(1)-C(6)-C(7)	118.4(4)	C(17)-C(16)-C(15)	120.3(4)
C(20)-O(4)-V(1)	130.8(3)	O(2)-C(7)-C(6)	112.5(3)	C(16)-C(17)-C(18)	120.9(5)
C(8)-N-C(9)	112.4(3)	O(2)-C(7)-C(8)	105.3(3)	C(13)-C(18)-C(17)	120.1(4)
C(8)-N-C(12)	114.1(3)	C(6)-C(7)-C(8)	110.6(3)	O(3)-C(19)-C(12)	107.3(3)

## 5.4.4 Crystal data and structure refinement for Lig. 3

Empirical formula	C <sub>19</sub> H <sub>25</sub> N O <sub>4</sub>
Formula weight	331.40
Temperature	153(2) K
Wavelength	71.073 pm
Crystal system	orthorhombic
Space group	P 2(1) 2(1) 2(1)
Unit cell dimensions	a = 933.60(8)  pm
	b = 1077.43(10)  pm
	c = 1739.92(15)  pm
	α= 90°
	$\beta = 90^{\circ}$ .
	$\gamma = 90^{\circ}$
Volume	1.7502(3) nm <sup>3</sup>
Ζ	4
Density (calculated)	1.258 Mg/m <sup>3</sup>
Absorption coefficient	0.088 mm <sup>-1</sup>
F(000)	712
Crystal size	0.38 x 0.29 x 0.12 mm <sup>3</sup>
Theta range for data collection	2.22 to 27.50°.
Index ranges	-12<=h<=11, -13<=k<=13, -22<=l<=22
Reflections collected	20789
Independent reflections	2284 [R(int) = 0.0454]
Completeness to theta = $27.50^{\circ}$	99.6 %
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2284 / 14 / 237
Dual, restante, parameters	22017 117 257

Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Absolute structure parameter Largest diff. peak and hole

 $\begin{array}{c} 0.997 \\ R1 = 0.0398, wR2 = 0.0923 \\ R1 = 0.0504, wR2 = 0.0963 \\ 0(10) \\ 0.328 \mbox{ and } -0.166 \mbox{ e.Å}^{-3} \end{array}$ 

Bond lengths [Å] and angles [°] for Lig. 3

Bond lengths [pm]					
C(1)-C(2)	138.8(3)	C(8)-H(8B)	99.00	C(28)-H(28A)	99.00
C(1)-C(6)	139.4(3)	C(21)-C(26)	139.0(3)	C(28)-H(28B)	99.00
C(1)-C(7)	151.4(3)	C(21)-C(22)	139.4(3)	C(31)-N(1)	146.7(3)
C(2)-C(3)	139.5(3)	C(21)-C(27)	152.1(3)	C(31)-C(32)	152.2(3)
C(2)-H(2)	95.00	C(22)-C(23)	138.5(3)	C(31)-H(31A)	99.00
C(3)-C(4)	138.5(3)	C(22)-H(22)	95.00	C(31)-H(31B)	99.00
C(3)-H(3)	95.00	C(23)-C(24)	138.9(4)	C(32)-O(3)	142.0(3)
C(4)-C(5)	137.3(3)	C(23)-H(23)	95.00	C(32)-C(33)	151.4(3)
C(4)-H(4)	95.00	C(24)-C(25)	137.2(4)	C(32)-H(32)	100.00
C(5)-C(6)	139.2(3)	C(24)-H(24)	95.00	C(33)-O(4)	142.6(3)
C(5)-H(5)	95.00	C(25)-C(26)	139.2(3)	C(33)-H(33A)	99.00
C(6)-H(6)	95.00	C(25)-H(25)	95.00	C(33)-H(33B)	99.00
C(7)-O(1)	142.6(3)	C(26)-H(26)	95.00	O(1)-HO1	84.00(11)
C(7)-C(8)	153.4(3)	C(27)-O(2)	143.1(3)	O(2)-HO2	84.00(11)
C(7)-H(7)	100.00	C(27)-C(28)	152.4(3)	O(3)-HO3	84.02(11)
C(8)-N(1)	145.6(3)	C(27)-H(27)	100.00	O(4)-HO4	83.99(11)
C(8)-H(8A)	99.00	C(28)-N(1)	146.9(3)	N(1)-HN1	88.00(11)
		angles	[°]		
C(2)-C(1)-C(6)	118.8(2)	C(26)-C(21)-C(27)	121.6(2)	N(1)-C(31)-C(32)	111.32(18)
C(2)-C(1)-C(7)	120.6(2)	C(22)-C(21)-C(27)	120.0(2)	N(1)-C(31)-H(31/	A) 109.4
C(6)-C(1)-C(7)	120.4(2)	C(23)-C(22)-C(21)	120.8(2)	C(32)-C(31)-H(31	Á) 109.4
C(1)-C(2)-C(3)	120.7(2)	C(23)-C(22)-H(22)	119.6	N(1)-C(31)-H(31I	3) 109.4
C(1)-C(2)-H(2)	119.7	C(21) C(22) H(22)	110.6	C(32)-C(31)-H(31	B) 109.4
C(3)-C(2)-H(2)	119.7	$C(21)$ - $C(22)$ - $\Pi(22)$	117.0	H(31A)-C(31)-H(	31B) 108.0
C(4)-C(3)-C(2)	119.9(2)	C(22)- $C(23)$ - $C(24)$	120.2(2)	O(3)-C(32)-C(33)	109.6(2)
C(4)-C(3)-H(3)	120.0	C(22)-C(23)-H(23)	119.9	O(3)-C(32)-C(31)	108,99(19)
C(2)-C(3)-H(3)	120.0	C(24)-C(23)-H(23)	119.9	C(33)-C(32)-C(31	) 111.73(19)
C(5)-C(4)-C(3)	119.8(2)	C(25)-C(24)-C(23)	119.4(2)	O(3)-C(32)-H(32)	108.8
C(5)-C(4)-H(4)	120.1	C(25)- $C(24)$ - $H(24)$	120.3	C(33)-C(32)-H(32	2) 108.8
C(3)-C(4)-H(4)	120.1	C(23) - C(24) - H(24)	120.5	C(31)-C(32)-H(32	2) 108.8
C(4)-C(5)-C(6)	120.7(2)	C(23)-C(24)-H(24)	120.3	O(4)-C(33)-C(32)	110.43(18)
C(4)-C(5)-H(5)	119.6	C(24)-C(25)-C(26)	120.6(2)	O(4)-C(33)-H(33/	A) 109.6
C(6)-C(5)-H(5)	119.6	C(24)-C(25)-H(25)	119.7	C(32)-C(33)-H(33	A) 109.6
C(5)-C(6)-C(1)	120.1(2)	C(26)-C(25)-H(25)	119.7	O(4)-C(33)-H(33H	3) 109.6
C(5)-C(6)-H(6)	119.9	C(21)-C(26)-C(25)	120.5(2)	C(32)-C(33)-H(33	B) 109.6
C(1)-C(6)-H(6)	119.9	C(21)-C(26)-H(26)	119.7	H(33A)-C(33)-H(	33B) 108.1
O(1)-C(7)-C(1)	109.59(18)	C(25)-C(26)-H(26)	119.7	C(7)-O(1)-HO1	108.7(11)
O(1)-C(7)-C(8)	111.26(18)	O(2)-C(27)-C(21)	111.7(2)	C(27)-O(2)-HO2	108.2(11)
C(1)-C(7)-C(8)	108.95(17)	O(2)-C(27)-C(28)	106.10(18)	C(22) O(2) HO2	100.2(11)
O(1)-C(7)-H(7)	109.0	C(21)-C(27)-C(28)	110.78(18)	C(32)-O(3)-1103	109.2(11)
C(1)-C(7)-H(7)	109.0	O(2)-C(27)-H(27)	109.4	C(33)-O(4)-HO4	108.7(11)
C(8)-C(7)-H(7)	109.0	C(21)-C(27)-H(27)	109.4	C(8)-N(1)-C(31)	113.11(17)
N(1)-C(8)-C(7)	113.68(18)	C(28)-C(27)-H(27)	109.4	C(8)-N(1)-C(28)	114.96(17)
N(1)-C(8)-H(8A)	108.8	N(1)-C(28)-C(27)	111.03(18)	C(31)-N(1)-C(28)	113 02(18)
C(7)-C(8)-H(8A)	108.8	N(1)-C(28)-H(28A)	109.4	C(0) N(1) ID(1)	105 4(2)
N(1)-C(8)-H(8B)	108.8	C(27)-C(28)-H(28A	) 109.4	C(8)-N(1)-HNI	105.4(2)
C(7)-C(8)-H(8B)	108.8	N(1)-C(28)-H(28B)	109.4	C(31)-N(1)-HN1	104.6(2)
H(8A)-C(8)-H(8B)	107.7	C(27)-C(28)-H(28B	) 109.4	C(28)-N(1)-HN1	104.4(2)
C(26)-C(21)-C(22)	118.4(2)	H(28A)-C(28)-H(28	B) 108.0		

Empirical formula	C <sub>38</sub> H <sub>39</sub> N O <sub>4</sub>
Formula weight	573.70
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.2471(8) Å
	b = 17.8576(19) Å
	$\beta = 90^{\circ}$ .
	c = 23.712(3) Å
	$\gamma = 90^{\circ}.$
Volume	3068.7(6) Å <sup>3</sup>
Z	4
Density (calculated)	1.242 Mg/m <sup>3</sup>
Absorption coefficient	0.080 mm <sup>-1</sup>
F(000)	1224
Crystal size	$0.50 \ge 0.10 \ge 0.07 \text{ mm}^3$
Theta range for data collection	2.82 to 27.50°.
Index ranges	-9<=h<=9, -23<=k<=23, -30<=l<=30
Reflections collected	36989
Independent reflections	3985 [R(int) = 0.1362]
Completeness to theta = $27.50^{\circ}$	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9944 and 0.9613
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3985 / 0 / 391
Goodness-of-fit on F <sup>2</sup>	0.803
Final R indices [I>2sigma(I)]	R1 = 0.0457, $wR2 = 0.0668$
R indices (all data)	R1 = 0.1084, WR2 = 0.0782
Absolute structure parameter	0(10)
Largest diff. peak and hole	0.210 and -0.222 e.Å <sup>-3</sup>

## 5.4.5 Crystal data and structure refinement for Lig. 3'

Bond lengths [Å] and angles [°] for Lig. 3'

Bond lengths [Å]					
N(1)-C(28)	1.469(4)	C(21)-C(27)	1.530(4)	C(43)-H(43)	0.9500
N(1)-C(31)	1.474(4)	C(22)-C(23)	1.388(4)	C(44)-C(45)	1.375(5)
N(1)-C(18)	1.481(3)	C(22)-H(22)	0.9500	C(44)-H(44)	0.9500
O(1)-C(17)	1.441(3)	C(23)-C(24)	1.374(5)	C(45)-C(46)	1.392(4)
O(1)-H(1)	0.8400	C(23)-H(23)	0.9500	C(45)-H(45)	0.9500
O(2)-C(27)	1.429(4)	C(24)-C(25)	1.371(4)	C(46)-H(46)	0.9500
O(2)-H(2)	0.8400	C(24)-H(24)	0.9500	C(51)-C(56)	1.393(4)
O(3)-C(32)	1.423(3)	C(25)-C(26)	1.392(4)	C(51)-C(52)	1.394(4)
O(3)-H(3)	0.8400	C(25)-H(25)	0.9500	C(52)-C(53)	1.390(4)
O(4)-C(33)	1.425(3)	C(26)-H(26)	0.9500	C(52)-H(52)	0.9500
O(4)-C(34)	1.448(3)	C(27)-C(28)	1.526(4)	C(53)-C(54)	1.383(4)
C(11)-C(12)	1.380(4)	C(27)-H(27)	1.0000	C(53)-H(53)	0.9500
C(11)-C(16)	1.383(4)	C(28)-H(28A)	0.9900	C(54)-C(55)	1.377(4)

C(11)-C(17) 1.511(4)	C(28)-H(28B) 0.9900	C(54)-H(54) 0.9500
C(12)-C(13) 1.380(4)	C(31)-C(32) 1.527(4)	C(55)-C(56) 1.394(4)
C(12)-H(12) 0.9500	C(31)-H(31A) 0.9900	C(55)-H(55) 0.9500
C(13)-C(14) 1.375(4)	C(31)-H(31B) 0.9900	C(56)-H(56) 0.9500
C(13)-H(13) = 0.9500	C(32)-C(33) = 1.527(4)	C(61)-C(62) 1 389(4)
C(14) C(15) = 1.382(4)	C(32) H(32) = 1.027(1)	C(61) C(62) = 1.305(4)
C(14) + C(15) = 1.582(4)	C(32) + H(32) 1.0000 C(32) + H(32) 0.0000	C(61)- $C(60)$ 1.555(4) C(62) $C(62)$ 1.401(4)
C(14)-H(14) 0.9500	C(33)-H(33A) 0.9900	C(02)-C(03) 1.401(4)
C(15)-C(16) 1.380(4)	C(33)-H(33B) 0.9900	C(62)-H(62) 0.9500
C(15)-H(15) 0.9500	C(34)-C(51) 1.536(4)	C(63)-C(64) 1.381(4)
C(16)-H(16) 0.9500	C(34)-C(41) 1.540(4)	C(63)-H(63) 0.9500
C(17)-C(18) 1.517(4)	C(34)-C(61) 1.541(4)	C(64)-C(65) 1.381(4)
C(17)-H(17) 1.0000	C(41)-C(42) 1.383(4)	C(64)-H(64) 0.9500
C(18)-H(18A) 0.9900	C(41)-C(46) 1.391(4)	C(65)-C(66) 1.375(4)
C(18)-H(18B) 0.9900	C(42)-C(43) 1.386(4)	C(65)-H(65) 0.9500
C(21)-C(22) 1.381(4)	C(42)-H(42) 0.9500	C(66)-H(66) 0.9500
C(21)-C(26) 1.385(4)	C(43)-C(44) 1.378(5)	
	angles [°]	
C(28)-N(1)-C(31) 115.4(3)	C(24)-C(25)-C(26) 120.7(3)	C(44)-C(43)-H(43) 120.2
C(28)-N(1)-C(18) 115.4(3)	C(24)-C(25)-H(25) 119.6	C(42)-C(43)-H(43) 120.3
C(31)-N(1)-C(18) 113.9(2)	C(26)-C(25)-H(25) 119.6	C(45)-C(44)-C(43) 119.5(4)
C(17)-O(1)-H(1) 109.5 C(27)-O(2)-H(2) 109.5	C(21)- $C(26)$ - $C(25)$ 120.3(3) C(21)- $C(26)$ - $H(26)$ -110.0	C(45)-C(44)-H(44) 120.2 C(42)-C(44)-H(44) 120.2
C(27)-O(2)-H(2) 109.5 C(32)-O(3)-H(3) 109.5	C(21)-C(20)-H(20) 119.9 C(25)-C(26)-H(26) 119.9	C(43)-C(44)-H(44) 120.2 C(44)-C(45)-C(46) 120.8(4)
C(32)-O(4)-C(34) 119 $O(2)$	O(2)-C(27)-C(28) 108 1(3)	C(44)-C(45)-H(45) 119 6
C(12)-C(11)-C(16) 118.9(3)	O(2)-C(27)-C(21) 111.6(3)	C(46)-C(45)-H(45) 119.6
C(12)-C(11)-C(17) 120.8(3)	C(28)-C(27)-C(21) 114.5(3)	C(41)-C(46)-C(45) 120.3(4)
C(16)-C(11)-C(17) 120.3(3)	O(2)-C(27)-H(27) 107.4	C(41)-C(46)-H(46) 119.9
C(11)-C(12)-C(13) 120.6(3)	C(28)-C(27)-H(27) 107.4	C(45)-C(46)-H(46) 119.9
C(11)-C(12)-H(12) 119.7	C(21)-C(27)-H(27) 107.4	C(56)-C(51)-C(52) 117.6(3)
C(13)- $C(12)$ - $H(12)$ 119.7	N(1)-C(28)-C(27) = 110.0(3) N(1)-C(28) = 1/(28A) = 100.7	C(56)-C(51)-C(34) 121.0(3) C(52) $C(51)$ $C(24)$ 121.2(3)
C(14)-C(13)-C(12) 120.5(3) C(14)-C(13)-H(13) 119.9	C(27)-C(28)-H(28A) 109.7	C(52)- $C(51)$ - $C(54)$ 121.3(3) C(53)- $C(52)$ - $C(51)$ 121.2(3)
C(12)-C(13)-H(13) 119.9	N(1)-C(28)-H(28B) 109.7	C(53)-C(52)-H(52) 119.4
C(13)-C(14)-C(15) 119.6(3)	C(27)-C(28)-H(28B) 109.7	C(51)-C(52)-H(52) 119.4
С(13)-С(14)-Н(14) 120.2	H(28A)-C(28)-H(28B) 108.2	C(54)-C(53)-C(52) 120.3(3)
C(15)-C(14)-H(14) 120.2	N(1)-C(31)-C(32) 112.6(2)	C(54)-C(53)-H(53) 119.8
C(16)-C(15)-C(14) 120.0(3)	N(1)-C(31)-H(31A) 109.1	C(52)-C(53)-H(53) 119.8
C(16)-C(15)-H(15) 120.0	C(32)-C(31)-H(31A) 109.1	C(55)-C(54)-C(53) 119.4(3)
C(14)-C(15)-H(15) 120.0	N(1)-C(31)-H(31B) 109.1	C(55)-C(54)-H(54) 120.3
C(15)- $C(16)$ - $C(11)$ 120.6(3)	U(32)-U(31)-H(31B) = 109.1	C(53)- $C(54)$ - $H(54)$ 120.3
C(13)- $C(16)$ - $H(16)$ 119.7	$\Pi(31A)$ - $C(31)$ - $\Pi(31B)$ 107.8 $\Omega(3)$ $C(32)$ $C(31)$ 108 5(2)	C(54) - C(55) - C(50) - 120.3(5) C(54) - C(55) - H(55) - 110.8
O(1)-C(17)-C(11) 107 2(3)	O(3)-C(32)-C(33) 113 5(3)	C(54)-C(55)-H(55) 119.8
O(1)-C(17)-C(18) 110 2(3)	C(31)-C(32)-C(33) 110 4(3)	C(51)-C(56)-C(55) = 121.2(3)
C(11)-C(17)-C(18) 111 3(3)	O(3)-C(32)-H(32) 108 1	C(51)- $C(56)$ - $H(56)$ 1194
O(1)-C(17)-H(17) 109.4	C(31)-C(32)-H(32) 108.1	C(55)-C(56)-H(56) 119.4
C(11)-C(17)-H(17) 109.4	C(33)-C(32)-H(32) 108.1	C(62)-C(61)-C(66) 118.1(3)
С(18)-С(17)-Н(17) 109.4	O(4)-C(33)-C(32) 107.1(2)	C(62)-C(61)-C(34) 120.9(3)
N(1)-C(18)-C(17) 110.9(3)	O(4)-C(33)-H(33A) 110.3	C(66)-C(61)-C(34) 120.9(3)
N(1)-C(18)-H(18A) 109.5	C(32)-C(33)-H(33A) 110.3	C(61)-C(62)-C(63) 120.4(3)
C(17)-C(18)-H(18A) 109.5	O(4)-C(33)-H(33B) 110.3	C(61)-C(62)-H(62) 119.8
N(1)-C(18)-H(18B) 109.5	C(32)-C(33)-H(33B) 110.3	C(63)- $C(62)$ - $H(62)$ 119.8
U(17)-U(18)-H(18B) 109.5 H(18A) C(18) H(19B) 109.5	$\Pi(33A)-U(33)-\Pi(33B)$ 108.6 $\Omega(4) C(34) C(51) 100 G(2)$	C(04)- $C(03)$ - $C(02)$ 120.2(3) C(64) $C(63)$ $H(63)$ 110.0
C(22)-C(21)-C(26) = 118.7(2)	O(4)-C(34)-C(31) 109.0(2) O(4)-C(34)-C(41) 110.9(3)	C(0+)-C(03)-H(03) 119.9 C(62)-C(63)-H(63) 119.9
C(22) = C(21) = C(20) = 110.7(3) C(22) = C(21) = C(27) = 120.1(3)	C(51) = C(34) = C(41) = 113.7(3)	C(65)-C(64)-C(63) 119.9
C(26)-C(21)-C(27) 120.1(3) C(26)-C(21)-C(27) 121.2(3)	O(4)-C(34)-C(61) 103 4(2)	C(65)-C(64)-H(64) 120 2
C(21)-C(22)-C(23) 120.6(3)	C(51)-C(34)-C(61) 110.9(3)	C(63)-C(64)-H(64) 120.2
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$\begin{array}{llllllllllllllllllllllllllllllllllll$			
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(21)-C(22)-H(22) 119.7	C(41)-C(34)-C(61) 108.0(2)	C(66)-C(65)-C(64) 120.3(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(23)-C(22)-H(22) 119.7	C(42)-C(41)-C(46) 117.8(3)	C(66)-C(65)-H(65) 119.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(24)-C(23)-C(22) 120.6(3)	C(42)-C(41)-C(34) 123.1(3)	C(64)-C(65)-H(65) 119.9
C(22)-C(23)-H(23)         119.7         C(41)-C(42)-C(43)         122.0(4)         C(65)-C(66)-H(66)         119.3           C(25)-C(24)-C(23)         119.1(3)         C(41)-C(42)-H(42)         119.0         C(61)-C(66)-H(66)         119.3           C(25)-C(24)-H(24)         120.4         C(43)-C(42)-H(42)         119.0         C(61)-C(66)-H(66)         119.3           C(25)-C(24)-H(24)         120.4         C(43)-C(42)-H(42)         119.0         C(43)-C(42)-H(42)         119.0           C(23)-C(24)-H(24)         120.4         C(44)-C(43)-C(42)         119.5(4)         C(43)-C(42)         C(43)-C(42)	C(24)-C(23)-H(23) 119.7	C(46)-C(41)-C(34) 118.9(3)	C(65)-C(66)-C(61) 121.4(3)
C(25)-C(24)-C(23) 119.1(3) C(25)-C(24)-H(24) 120.4 C(25)-C(24)-H(24) 120.4 C(23)-C(24)-H(24) 120.4 C(24)-C(43)-C(42) 119.0 C(24)-H(24) 120.4 C(44)-C(43)-C(42) 119.5(4)	C(22)-C(23)-H(23) 119.7	C(41)-C(42)-C(43) 122.0(4)	C(65)-C(66)-H(66) 119.3
C(25)-C(24)-H(24) 120.4 C(43)-C(42)-H(42) 119.0 C(23)-C(24)-H(24) 120.4 C(44)-C(43)-C(42) 119.5(4)	C(25)-C(24)-C(23) 119.1(3)	C(41)-C(42)-H(42) 119.0	C(61)-C(66)-H(66) 119.3
C(23)-C(24)-H(24) 120.4 C(44)-C(43)-C(42) 119.5(4)	C(25)-C(24)-H(24) 120.4	C(43)-C(42)-H(42) 119.0	
	C(23)-C(24)-H(24) 120.4	C(44)-C(43)-C(42) 119.5(4)	

## 5.4.6 Crystal data and structure refinement for Complex 3

C <sub>19</sub> H <sub>22</sub> N O <sub>5</sub> V, C <sub>2</sub> H <sub>6</sub> O 441.38 153(2) K 0.71073 Å tetragonal P4 (1) a = 11.5705(5) Å b = 11.5705(5) Å $\beta = 90^{\circ}$ . c = 31.755(2) Å $\gamma = 90^{\circ}$ .
4251.3(4) Å <sup>3</sup> 8
1.379 Mg/m <sup>3</sup>
0.503 mm <sup>-1</sup> 1856
$\begin{array}{c} 0.43 \ x \ 0.29 \ x \ 0.14 \ mm^3 \\ 1.87 \ to \ 27.50^\circ. \\ -14 <=h <=15, \ -15 <=k <=15, \ -41 <=l <=41 \\ 51404 \\ 9699 \ [R(int) = 0.0783] \\ 99.9 \ \% \\ 0.9329 \ and \ 0.8127 \end{array}$
Full-matrix least-squares on F <sup>2</sup> 9699 / 3 / 533
$\begin{array}{c} 0.754 \\ \text{R1} = 0.0404, \ \text{wR2} = 0.0486 \\ \text{R1} = 0.0695, \ \text{wR2} = 0.0526 \\ -0.005(12) \\ 0.603 \ \text{and} \ -0.343 \ \text{e.}\text{\AA}^{-3} \end{array}$

Bond lengths  $[\text{\AA}]$  and angles  $[^\circ]$  for Complex 3

		Bond 1	engths [Å]		
V(1)-O(1)	1.6065(17)	C(17)-H(17)	1.0000	C(48)-H(48A)	0.9900
V(1)-(11)	1.8236(17)	C(18)-H(18A)	0.9900	C(48)-H(48B)	0.9900
V(1)-O(12)	1.8423(18)	C(18)-H(18B)	0.9900	C(51)-C(52)	1.380(3)
V(1)-(13)	1.9324(18)	C(21)-C(22)	1.373(4)	C(51)-C(56)	1.392(4)
V(1)-(14)	2.0753(19)	C(21)-C(26)	1.380(4)	C(51)-C(57)	1.516(3)
V(1)-N(1)	2.297(2)	C(21)-C(27)	1.534(3)	C(52)-C(53)	1.393(4)
V(2)-O(2)	1.5989(17)	C(22)-C(23)	1.391(4)	C(52)-H(52)	0.9500
V(2)-O(2)	1.5969(17)	C(22)-C(25)	1.391(4)	C(32)-H(32)	0.9300

V(2)-(21)	1.8255(19)	C(22)-H(22)	0.9500	C(53)-C(54) 1.384(4)
V(2)-O(22)	1.8313(17)	C(23)-C(24)	1.364(4)	C(53)-H(53) 0.9500
V(2)-O(23)	1.9358(18)	C(23)-H(23)	0.9500	C(54)-C(55) 1.382(4)
V(2)-O(24)	2 097(2)	C(24)-C(25)	1.391(4)	C(54)-H(54) 0 9500
V(2)-N(2)	2 291(2)	C(24)-H(24)	0.9500	C(55)- $C(56)$ 1 394(4)
O(11)- $C(17)$	1419(3)	C(25)- $C(26)$	1 387(3)	C(55)-H(55) 0.9500
O(12)-C(27)	1 430(3)	C(25) = H(25)	0.9500	C(56)-H(56) 0.9500
O(12) - C(27)	1.430(3)	C(25)- $H(25)$	0.9500	C(57) C(58) = 1.524(3)
O(13) - C(32)	1.419(3)	$C(20)=\Pi(20)$	1.540(4)	C(57) + C(58) = 1.52 + (5)
O(14) - C(33)	(3) $(3)$ $(3)$ $(3)$	C(27) - C(28)	1.0000	C(57)- $H(57)$ 1.0000 C(58) $H(58A)$ 0.0000
O(14)-H(14	0) 0.8401(11)	C(27)-H(27)	1.0000	C(58)-H(58A) 0.9900
0(21)-C(47	) 1.422(3)	C(28)-H(28A)	0.9900	С(58)-Н(58В) 0.9900
O(22)-C(57	) 1.421(3)	C(28)-H(28B)	0.9900	C(61)-C(62) 1.525(4)
O(23)-C(62	) 1.428(3)	C(31)-C(32)	1.528(4)	C(61)-H(61A) 0.9900
O(24)-C(63	) 1.439(3)	C(31)-H(31A)	0.9900	C(61)-H(61B) 0.9900
O(24)-H(24	O) 0.8403(11)	C(31)-H(31B)	0.9900	C(62)-C(63) 1.520(3)
N(1)-C(28)	1.470(3)	C(32)-C(33)	1.511(3)	C(62)-H(62) 1.0000
N(1)-C(18)	1.481(3)	C(32)-H(32)	1.0000	C(63)-H(63A) 0.9900
N(1)-C(31)	1.494(3)	C(33)-H(33A)	0.9900	C(63)-H(63B) 0.9900
N(2)-C(48)	1.462(3)	C(33)-H(33B)	0.9900	O(7)-C(71) 1.405(4)
N(2)-C(61)	1.482(3)	C(41)-C(42)	1.369(4)	O(7)-H(7) 0.8400
N(2)-C(58)	1.483(3)	C(41)-C(46)	1.384(4)	C(71)-C(72) 1.477(4)
C(11)-C(16)	1.379(3)	C(41)-C(47)	1.535(4)	C(71)-H(71A) 0.9900
C(11)-C(12)	1401(3)	C(42)-C(43)	1.385(4)	C(71)-H(71B) 0 9900
C(11)-C(17)	) 1512(3)	C(42)-H(42)	0.9500	C(72)-H(72A) = 0.9800
C(12)- $C(13)$	1390(4)	C(43)- $C(44)$	1 361(4)	C(72)-H(72B) 0.9800
C(12) = H(12)	) 0.9500	C(43)-H(43)	0.9500	C(72)-H(72C) 0.9800
$C(12)$ - $\Pi(12)$	1 384(4)	C(44)- $C(45)$	1 366(4)	O(8) C(81) = 1.405(4)
C(13) - C(14)	) 0.0500	C(44)-H(44)	0.9500	O(8) + O(81) = 0.8400
$C(13)-\Pi(13)$	1.276(4)	C(45) C(46)	1 277(2)	O(8)-H(8) = 0.8400 O(81) O(82) = 1.551(5)
C(14)-C(15)	) 1.376(4)	C(45) = C(40)	0.0500	C(81) - C(82) = 1.551(5)
C(14)-H(14)	) 0.9300	C(43)- $H(43)$	0.9500	C(81)-H(81A) 0.9900
C(15)-C(16)	) 1.395(4)	C(40)- $H(40)$	0.9500	C(81)-H(81B) 0.9900
С(15)-Н(15	) 0.9500	C(47) - C(48)	1.551(4)	C(82)-H(82A) 0.9800
C(17)-C(18)	) 1.539(3)	C(4/)-H(4/)	1.0000	C(82)-H(82B) 0.9800
				C(82)-H(82C) 0.9800
		an	gles [°]	
O(1)-V(1)-O	D(11) 100.08(9)	N(1)-C(18)-H(1	8A) 110.4	C(47)-C(48)-H(48A) 109.9
O(1)-V(1)-C	O(12) 99.58(9)	C(17)-C(18)-H(	18A) 1104	N(2)-C(48)-H(48B) 109 9
O(11)-V(1)-	-O(12) 102 39(8)	N(1)-C(18)-H(1)	8B) 110.4	C(47)-C(48)-H(48B) = 109.9
O(1) - V(1) - C	D(13) = 105 31(9)	C(17)-C(18)-H(1	18B) 110.4	H(48A) - C(48) - H(48B) - 108 - 3
O(11) - V(1)	-O(13) 89.97(8)	H(18A)-C(18)-F	I(18B) 108.6	C(52)- $C(51)$ - $C(56)$ 119 $O(3)$
O(12)-V(1)	-O(13) 149 77(8)	C(22)-C(21)-C(2)	(10D) 100.0 (1) 118 7(3)	C(52)- $C(51)$ - $C(57)$ 121 7(3)
O(12) = V(1) = O(1) = O(1) = O(1) = V(1) = O(1) =	P(14) = 99.56(9)	C(22)-C(21)-C(2)	(20) 110.7(3) (27) 120.5(3)	C(52)- $C(51)$ - $C(57)$ 119 3(3)
O(1) = V(1) = O(1)	O(14) 158 28(0)	C(22) - C(21) - C(21)	(7) 120.0(3)	C(51) C(52) C(52) 120 8(3)
O(11) - V(1) - O(12) V(1)	O(14) 138.38(9) O(14) 82.00(8)	C(20)- $C(21)$ - $C(2)$	(27) 120.9(3)	C(51) - C(52) - C(53) - 120.8(5)
O(12) - V(1)	O(14) = 7(-18(8))	C(21)- $C(22)$ - $C(2)$	(25) $(121.2(5))$	C(51)- $C(52)$ - $H(52)$ 119.0
O(13)-V(1)-O(1)	-0(14) /6.18(8)	C(21)-C(22)-H(2	22) 119.4	C(53)- $C(52)$ - $H(52)$ 119.6
O(1)-V(1)-P	N(1) 1/8.15(9)	C(23)-C(22)-H(2	22) 119.4	C(54)- $C(53)$ - $C(52)$ 119.6(3)
O(11)-V(1)-	-N(1) 80.79(8)	C(24)-C(23)-C(2	22) 119.5(3)	C(54)-C(53)-H(53) 120.2
O(12)-V(1)-	-N(1) 78.62(8)	C(24)-C(23)-H(2	23) 120.3	C(52)-C(53)-H(53) 120.2
O(13)-V(1)-	-N(1) 76.28(8)	C(22)-C(23)-H(2	23) 120.3	C(55)-C(54)-C(53) 120.3(3)
O(14)-V(1)-	-N(1) 79.85(8)	C(23)-C(24)-C(2	25) 120.5(3)	C(55)-C(54)-H(54) 119.9
O(2)-V(2)-O	D(21) 100.47(9)	C(23)-C(24)-H(2	24) 119.7	C(53)-C(54)-H(54) 119.9
O(2)-V(2)-O	0(22) 99.38(9)	C(25)-C(24)-H(2	24) 119.7	C(54)-C(55)-C(56) 119.6(3)
O(21)-V(2)-	-O(22) 103.25(8)	C(26)-C(25)-C(2	24) 119.0(3)	C(54)-C(55)-H(55) 120.2
O(2)-V(2)-O	D(23) 104.54(9)	C(26)-C(25)-H(2	25) 120.5	C(56)-C(55)-H(55) 120.2
O(21)-V(2)-	-O(23) 149.07(8)	C(24)-C(25)-H(2	25) 120.5	C(51)-C(56)-C(55) 120.6(3)
O(22)-V(2)-	-O(23) 90.41(8)	C(21)-C(26)-C(2	25) 121.1(3)	C(51)-C(56)-H(56) 119.7
O(2)-V(2)-O	D(24) 99.78(8)	C(21)-C(26)-H(2	26) 119.5	C(55)-C(56)-H(56) 119.7
O(21)-V(2)-	-O(24) 82.07(8)	C(25)-C(26)-H(2	26) 119.5	O(22)-C(57)-C(51) 111.8(2)
O(22)-V(2)-	-O(24) 158.79(8)	O(12)-C(27)-C(2	21) 110.3(2)	O(22)-C(57)-C(58) 108.4(2)
			,	· · · · · · · · · · · · · · · · · · ·

O(23)-V(2)-O(24) 76.05(8)	O(12)-C(27)-C(28) 110.7(2)	C(51)-C(57)-C(58) 111.7(2)
O(2)-V(2)-N(2) 178.96(9)	C(21)-C(27)-C(28) 112.0(2)	O(22)-C(57)-H(57) 108.3
O(21)-V(2)-N(2) 78.65(8)	O(12)-C(27)-H(27) 107.9	C(51)-C(57)-H(57) 108.3
O(22)-V(2)-N(2) 81.38(8)	C(21)-C(27)-H(27) 107.9	C(58)-C(57)-H(57) 108.3
O(23)-V(2)-N(2) 76.13(8)	C(28)-C(27)-H(27) 107.9	N(2)-C(58)-C(57) 108.1(2)
O(24)-V(2)-N(2) 79.58(8)	N(1)-C(28)-C(27) 109.9(2)	N(2)-C(58)-H(58A) 110.1
C(17)-O(11)-V(1) 117.44(16)	N(1)-C(28)-H(28A) 109.7	C(57)-C(58)-H(58A) 110.1
C(27)-O(12)-V(1) 124.65(16)	C(27)-C(28)-H(28A) 109.7	N(2)-C(58)-H(58B) 110.1
C(32)-O(13)-V(1) 110.52(15)	N(1)-C(28)-H(28B) 109.7	C(57)-C(58)-H(58B) 110.1
C(33)-O(14)-V(1) 115 38(16)	C(27)-C(28)-H(28B) = 109.7	H(58A)-C(58)-H(58B) 108 4
C(33)-O(14)-H(14O) 111(2)	H(28A)-C(28)-H(28B) 108.2	N(2)-C(61)-C(62) = 108.2(2)
V(1)-O(14)-H(14O) = 108(2)	N(1)-C(31)-C(32) = 107.8(2)	N(2)-C(61)-H(61A) = 110.1
$C(47) = O(21) = V(2) = 124 \ 70(17)$	N(1)-C(31)-H(31A) = 110.1	C(62)- $C(61)$ - $H(61A)$ 110.1
C(57)-O(22)-V(2) 117 71(16)	C(32)-C(31)-H(31A) = 110.1	N(2)-C(61)-H(61B) = 110.1
C(57) - O(22) - V(2) - 117.71(10) C(52) - O(22) - V(2) - 110.68(16)	N(1)-C(31)-H(31B) = 110.1	C(62) C(61) H(61B) = 110.1
C(62) - O(24) V(2) 115.17(16)	C(22) C(21) H(21B) 110.1	U(61A) C(61) U(61B) 1084
C(63)-O(24)-V(2) 115.17(16)	H(31A) C(31) H(31B) 1085	H(01A)-C(01)-H(01B) 108.4
C(63)-O(24)-H(24O) = 110(2)	O(12) C(22) C(22) 105 2(2)	O(23)- $C(62)$ - $C(63)$ 105.2(2)
V(2)-O(24)-H(24O) = 105(2)	O(13)-O(32)-O(33) = 105.3(2) O(12)-O(32)-O(21) = 107.4(2)	O(23)- $C(62)$ - $C(61)$ 106.9(2)
C(28)-N(1)-C(18) 113.8(2)	O(13)-C(32)-C(31) = 107.4(2)	C(63)-C(62)-C(61) 114./(2)
C(28)-N(1)-C(31) 114.3(2)	C(33)-C(32)-C(31) 114.6(2)	O(23)-C(62)-H(62) 109.9
C(18)-N(1)-C(31) 112.4(2)	O(13)-C(32)-H(32) = 109.8	C(63)-C(62)-H(62) 109.9
C(28)-N(1)-V(1) 105.00(16)	C(33)-C(32)-H(32) 109.8	C(61)-C(62)-H(62) 109.9
C(18)-N(1)-V(1) 102.77(16)	C(31)-C(32)-H(32) 109.8	O(24)-C(63)-C(62) 104.8(2)
C(31)-N(1)-V(1) 107.43(16)	O(14)-C(33)-C(32) 104.7(2)	O(24)-C(63)-H(63A) 110.8
C(48)-N(2)-C(61) 114.6(2)	O(14)-C(33)-H(33A) 110.8	C(62)-C(63)-H(63A) 110.8
C(48)-N(2)-C(58) 113.1(2)	C(32)-C(33)-H(33A) 110.8	O(24)-C(63)-H(63B) 110.8
C(61)-N(2)-C(58) 112.7(2)	O(14)-C(33)-H(33B) 110.8	C(62)-C(63)-H(63B) 110.8
C(48)-N(2)-V(2) 104.69(16)	C(32)-C(33)-H(33B) 110.8	H(63A)-C(63)-H(63B) 108.9
C(61)-N(2)-V(2) 107.88(16)	H(33A)-C(33)-H(33B) 108.9	C(71)-O(7)-H(7) 109.5
C(58)-N(2)-V(2) 102.69(15)	C(42)-C(41)-C(46) 118.5(3)	O(7)-C(71)-C(72) 112.0(3)
C(16)-C(11)-C(12) = 119.4(3)	C(42)-C(41)-C(47) 120.1(3)	O(7)-C(71)-H(71A) 109.2
C(16)-C(11)-C(17) 122.0(3)	C(46)-C(41)-C(47) 121.4(3)	C(72)- $C(71)$ - $H(71A)$ 109.2
C(12)-C(11)-C(17) = 118.5(3)	C(41)-C(42)-C(43) 120.4(3)	O(7)-C(71)-H(71B) 109.2
C(13)-C(12)-C(11) 119 8(3)	C(41)-C(42)-H(42) 119.8	C(72)-C(71)-H(71B) = 109.2
C(13)-C(12)-H(12) 120.1	C(43)-C(42)-H(42) 119.8	H(71A)-C(71)-H(71B) 107.9
C(11)-C(12)-H(12) 120.1	C(44)-C(43)-C(42) 120.7(4)	C(71)-C(72)-H(72A) 109 5
C(14)-C(13)-C(12) = 120.1(3)	C(44)-C(43)-H(43) 119.7	C(71)- $C(72)$ - $H(72B)$ 109.5
C(14)-C(13)-H(13) 120.1(5)	C(42)-C(43)-H(43) 1197	C(71)-C(72)-H(72C) = 109.5
C(12)-C(13)-H(13) 120.0	C(43)-C(44)-C(45) 119 3(3)	H(72A)-C(72)-H(72C) 109.5
$C(12) - C(13) - \Pi(13) = 120.0$ C(15) - C(14) - C(13) = 120.3(2)	C(43)- $C(44)$ - $H(44)$ 120.3	H(72R) C(72) H(72C) 109.5
C(15) - C(14) - C(15) - 120.5(5)	C(45)-C(44)-H(44) = 120.3	C(81) O(8) H(8) = 100.5
C(13)-C(14)-H(14) 119.8	C(44)-C(45)-C(46) 120.5	C(81)-O(8)-H(8) 109.5 C(81)-C(82) = 107.0(2)
C(13)-C(14)-H(14) 119.8 C(14)-C(15)-C(14)-110-0(2)	C(44) C(45) H(45) = 110.7	O(8) - C(81) - C(82) - 107.9(3)
C(14) - C(15) - C(16) - 119.9(3)	C(44) - C(45) - H(45) = 119.7	O(8)- $C(81)$ - $H(81A)$ 110.1
C(14)-C(15)-H(15) 120.0	C(46)- $C(45)$ - $H(45)$ 119.7	C(82)-C(81)-H(81A) 110.1
С(16)-С(15)-Н(15) 120.0	C(45)- $C(46)$ - $C(41)$ 120.5(3)	O(8)-C(81)-H(81B) 110.1
C(11)-C(16)-C(15) = 120.5(3)	C(45)-C(46)-H(46) 119.8	C(82)-C(81)-H(81B) 110.1
C(11)-C(16)-H(16) 119.8	C(41)-C(46)-H(46) 119.8	H(81A)-C(81)-H(81B) 108.4
С(15)-С(16)-Н(16) 119.8	O(21)- $C(47)$ - $C(48)$ 110.1(2)	C(81)-C(82)-H(82A) 109.5
O(11)-C(17)-C(11) 112.5(2)	O(21)- $C(47)$ - $C(41)$ 111.4(2)	C(81)-C(82)-H(82B) 109.5
O(11)-C(17)-C(18) 106.9(2)	C(48)-C(47)-C(41) 111.0(2)	H(82A)-C(82)-H(82B) 109.5
C(11)-C(17)-C(18) 113.5(2)	O(21)-C(47)-H(47) 108.1	C(81)-C(82)-H(82C) 109.5
O(11)-C(17)-H(17) 107.9	C(48)-C(47)-H(47) 108.1	H(82A)-C(82)-H(82C) 109.5
С(11)-С(17)-Н(17) 107.9	C(41)-C(47)-H(47) 108.1	H(82B)-C(82)-H(82C) 109.5
C(18)-C(17)-H(17) 107.9	N(2)-C(48)-C(47) 109.1(2)	
N(1)-C(18)-C(17) 106.7(2)	N(2)-C(48)-H(48A) 109.9	

5.4.7 Crystal data and structure refinement for Complex 3'

C<sub>19</sub> H<sub>22</sub> N O<sub>5</sub> V 395.32 Empirical formula Formula weight Temperature 103(2) K Wavelength 0.71073 Å Crystal system orthorhombic Space group P2(1)2(1)2(1) Unit cell dimensions a = 7.7973(8) Å  $\alpha = 90^{\circ}$ . b = 11.9461(12) Å  $\beta = 90^{\circ}$ . c = 18.8807(19) Å $\gamma = 90^{\circ}$ . 1758.7(3) Å<sup>3</sup> Volume Ζ 4 1.493 Mg/m<sup>3</sup> Density (calculated) 0.595 mm<sup>-1</sup> Absorption coefficient F(000) 824  $0.50 \ge 0.07 \ge 0.05 \text{ mm}^3$ Crystal size Theta range for data collection 2.02 to 27.49°. Index ranges Reflections collected -10<=h<=10, -15<=k<=15, -24<=l<=24 21132 Independent reflections Completeness to theta = 27.49° 4018 [R(int) = 0.0742] 99.9 % 0.9709 and 0.7553 Max. and min. transmission Full-matrix least-squares on F<sup>2</sup> Refinement method 4018 / 1 / 239 Data / restraints / parameters  ${\small Goodness-of-fit} \text{ on } \mathbb{F}^2$ 0.876 Final R indices [I>2sigma(I)] R1 = 0.0368, wR2 = 0.0628 R indices (all data) R1 = 0.0526, wR2 = 0.06630.01(2) Absolute structure parameter 0.584 and -0.323 e.Å<sup>-3</sup> Largest diff. peak and hole

Bond lengths [Å] and angles [°] for Complex 3'

		Bond le	ngths [Å]		
V(1)-O(1)	1.6074(15)	C(13)-C(14)	1.385(4)	C(24)-C(25) 1.3	99(4)
V(1)-O(3)	1.8024(15)	C(13)-H(13)	0.9500	C(24)-H(24) 0.	9500
V(1)-O(4)	1.8097(16)	C(14)-C(15)	1.381(4)	C(25)-C(26) 1.3	382(3)
V(1)-O(2)	1.8183(16)	C(14)-H(14)	0.9500	C(25)-H(25) 0.	9500
V(1)-N(1)	2.2987(17)	C(15)-C(16)	1.399(3)	C(26)-H(26) 0.	.9500
O(2)-C(17)	1.436(3)	C(15)-H(15)	0.9500	C(27)-C(28) 1.5	530(3)
O(3)-C(27)	1.447(3)	C(16)-H(16)	0.9500	C(27)-H(27) 1.	0000
O(4)-C(32)	1.434(3)	C(17)-C(18)	1.537(3)	C(28)-H(28A) 0	.9900
O(5)-C(33)	1.422(3)	C(17)-H(17)	1.0000	C(28)-H(28B) 0	.9900
O(5)-H(5)	0.846(10)	C(18)-H(18A)	0.9900	C(31)-C(32) 1.5	25(3)
N(1)-C(18)	1.480(3)	C(18)-H(18B)	0.9900	C(31)-H(31A) 0	.9900
N(1)-C(28)	1.482(3)	C(21)-C(26)	1.387(3)	C(31)-H(31B) 0	.9900
N(1)-C(31)	1.485(3)	C(21)-C(22)	1.400(3)	C(32)-C(33) 1.5	20(3)
C(11)-C(16)	1.388(3)	C(21)-C(27)	1.514(3)	C(32)-H(32) 1.	.0000
C(11)-C(12)	1.392(3)	C(22)-C(23)	1.392(3)	C(33)-H(33A) 0	.9900
C(11)-C(17)	1.523(3)	C(22)-H(22)	0.9500	C(33)-H(33B) 0	.9900
C(12)-C(13)	1.387(3)	C(23)-C(24)	1.392(3)	H(5)O(2')	2.015

C(12)-H(12) 0.9500	C(23)-H(23) 0.9500	
	angles [°]	
O(1)-V(1)-O(3)100.51(9)	C(14)-C(15)-C(16) 120.3(3)	C(25)-C(26)-C(21) 120.8(3)
O(1)-V(1)-O(4)101.37(8)	C(14)-C(15)-H(15) 119.9	C(25)-C(26)-H(26) 119.6
O(3)-V(1)-O(4)116.33(8)	C(16)-C(15)-H(15) 119.9	C(21)-C(26)-H(26) 119.6
O(1)-V(1)-O(2)100.97(8)	C(11)-C(16)-C(15) 120.2(2)	O(3)-C(27)-C(21) 110.92(19)
O(3)-V(1)-O(2)115.38(8)	C(11)-C(16)-H(16) 119.9	O(3)-C(27)-C(28) 107.54(18)
O(4)-V(1)-O(2)117.73(8)	C(15)-C(16)-H(16) 119.9	C(21)-C(27)-C(28) 113.2(2)
O(1)-V(1)-N(1)179.74(9)	O(2)-C(17)-C(11) 110.21(19)	O(3)-C(27)-H(27) 108.4
O(3)-V(1)-N(1) 79.75(8)	O(2)-C(17)-C(18) 109.58(19)	C(21)-C(27)-H(27) 108.4
O(4)-V(1)-N(1) 78.47(7)	C(11)-C(17)-C(18) 109.1(2)	C(28)-C(27)-H(27) 108.4
O(2)-V(1)-N(1) 78.93(7)	O(2)-C(17)-H(17) 109.3	N(1)-C(28)-C(27) 107.4(2)
C(17)-O(2)-V(1) 125.40	C(11)-C(17)-H(17) 109.3	N(1)-C(28)-H(28A) 110.2
C(27)-O(3)-V(1)122.29(14)	C(18)-C(17)-H(17) 109.3	C(27)-C(28)-H(28A) 110.2
C(32)-O(4)-V(1) 124.52(14)	N(1)-C(18)-C(17) 109.30(19)	N(1)-C(28)-H(28B) 110.2
C(33)-O(5)-H(5) 108(2)	N(1)-C(18)-H(18A) 109.8	C(27)-C(28)-H(28B) 110.2
C(18)-N(1)-C(28) 115.45(17)	C(17)-C(18)-H(18A) 109.8	H(28A)-C(28)-H(28B) 108.5
C(18)-N(1)-C(31) 112.04(19)	N(1)-C(18)-H(18B) 109.8	N(1)-C(31)-C(32) 107.44(18)
C(28)-N(1)-C(31) 113.1(2)	C(17)-C(18)-H(18B) 109.8	N(1)-C(31)-H(31A) 110.2
C(18)-N(1)-V(1) 105.50(15)	H(18A)-C(18)-H(18B) 108.3	C(32)-C(31)-H(31A) 10.2
C(28)-N(1)-V(1) 104.04(13)	C(26)-C(21)-C(22) 119.1(2)	N(1)-C(31)-H(31B) 10.2
C(31)-N(1)-V(1) 105.57(12)	C(26)-C(21)-C(27) 120.6(2)	C(32)-C(31)-H(31B) 110.2
C(16)-C(11)-C(12) 119.0(2)	C(22)-C(21)-C(27) 120.3(2)	H(31A)-C(31)-H(31B) 108.5
C(16)-C(11)-C(17) 120.3(2)	C(23)-C(22)-C(21) 120.2(2)	O(4)-C(32)-C(33) 111.1(2)
C(12)-C(11)-C(17) 120.4(2)	C(23)-C(22)-H(22) 119.9	O(4)-C(32)-C(31) 108.55(19)
C(13)-C(12)-C(11) 120.5(2)	C(21)-C(22)-H(22) 119.9	C(33)-C(32)-C(31) 113.0(2)
C(13)-C(12)-H(12) 119.8	C(24)-C(23)-C(22) 120.4(2)	O(4)-C(32)-H(32) 108.0
C(11)-C(12)-H(12) 119.8	C(24)-C(23)-H(23) 119.8	C(33)-C(32)-H(32) 108.0
C(14)-C(13)-C(12) 120.3(2)	C(22)-C(23)-H(23) 119.8	C(31)-C(32)-H(32) 108.0
C(14)-C(13)-H(13) 119.8	C(23)-C(24)-C(25) 119.1(2)	O(5)-C(33)-C(32) 113.97(19)
C(12)-C(13)-H(13) 119.8	C(23)-C(24)-H(24) 120.4	O(5)-C(33)-H(33A) 108.8
C(15)-C(14)-C(13) 119.6(2)	C(25)-C(24)-H(24) 120.4	C(32)-C(33)-H(33A) 108.8
C(15)-C(14)-H(14) 120.2	C(26)-C(25)-C(24) 120.3(2)	O(5)-C(33)-H(33B) 108.8
C(13)-C(14)-H(14) 120.2	C(26)-C(25)-H(25) 119.8	C(32)-C(33)-H(33B) 108.8
	C(24)-C(25)-H(25) 119.8	H(33A)-C(33)-H(33B) 107.7
		O(5) - (5)O(2') 178.24

## 5.4.8 Crystal data and structure refinement for Lig. 7

Empirical formula Formula weight	C <sub>20</sub> H <sub>25</sub> N O <sub>3</sub> Si 355.50
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	P6(1)
Unit cell dimensions	a = 10.8032(5) Å
	$\alpha = 90^{\circ}$ .
	b = 10.8032(5)  Å
	$\beta = 90^{\circ}$ .
	c = 27.4597(17)  Å
	$\gamma = 120^{\circ}$ .
Volume	2775.4(3) Å <sup>3</sup>
Z	6
Density (calculated)	1.276 Mg/m <sup>3</sup>
Absorption coefficient	0.145 mm <sup>-1</sup>
F(000)	1140

Crystal size	0.48 x 0.43 x 0.19 mm <sup>3</sup>
Theta range for data collection	2.18 to 24.98°.
Index ranges	-12<=h<=12, -12<=k<=12, -32<=l<=32
Reflections collected	28314
Independent reflections	3250 [R(int) = 0.0944]
Completeness to theta = 24.98°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max and min transmission	0.9729 and 0.9335
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3250 / 1 / 231
Goodness-of-fit on F <sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Absolute structure parameter Extinction coefficient	$\begin{array}{c} 0.896\\ R1 = 0.0354, \ wR2 = 0.0409\\ R1 = 0.0547, \ wR2 = 0.0429\\ -0.17(10)\\ 0\end{array}$
Largest diff. peak and hole	0.189 and -0.172 e.Å <sup>-3</sup>

Bond lengths [Å] and angles [°] for Lig. 7  $\,$ 

		Bond ler	gths [Å]	
Si-O(1)	1.6562(17)	C(4)-C(5)	1.381(3)	C(13)-C(14) 1.370(3)
Si-O(2)	1.6637(16)	C(4)-H(4)	0.9500	C(13)-H(13) 0.9500
Si-O(3)	1.6713(15)	C(5)-C(6)	1.374(4)	C(14)-C(15) 1.354(4)
Si-C(19)	1.873(2)	C(5)-H(5)	0.9500	C(14)-H(14) 0.9500
Si-N	2.2031(19)	C(6)-C(7)	1.377(3)	C(15)-C(16) 1.399(3)
O(1)-C(2)	1.421(2)	C(6)-H(6)	0.9500	C(15)-H(15) 0.9500
O(2)-C(10)	1.423(2)	C(7)-C(8)	1.378(3)	C(16)-H(16) 0.9500
O(3)-C(20)	1.418(3)	C(7)-H(7)	0.9500	C(17)-C(18) 1.516(3)
N-C(1)	1.469(3)	C(8)-H(8)	0.9500	C(17)-H(17A) 0.9900
N-C(17)	1.477(3)	C(9)-C(10)	1.530(3)	C(17)-H(17B) 0.9900
N-C(9)	1.478(3)	C(9)-H(9A)	0.9900	C(18)-C(19) 1.524(3)
C(1)-C(2)	1.531(3)	C(9)-H(9B)	0.9900	C(18)-H(18A) 0.9900
C(1)-H(1A)	0.9900	C(10)-C(11)	1.509(3)	C(18)-H(18B) 0.9900
C(1)-H(1B)	0.9900	C(10)-H(10)	1.0000	C(19)-H(19A) 0.9900
C(2)-C(3)	1.518(3)	C(11)-C(12)	1.373(3)	C(19)-H(19B) 0.9900
C(2)-H(2)	1.0000	C(11)-C(16)	1.376(3)	C(20)-H(20A) 0.9800
C(3)-C(8)	1.380(3)	C(12)-C(13)	1.389(3)	C(20)-H(20B) 0.9800
C(3)-C(4)	1.391(3)	C(12)-H(12)	0.9500	C(20)-H(20C) 0.9800
		angle	es [°]	
O(1)-Si-O(2)	117.96(9)	C(5)-C(4)-H(4)	119.9	С(12)-С(13)-Н(13) 120.1
O(1)-Si-O(3)	96.68(8)	C(3)-C(4)-H(4)	119.9	C(15)-C(14)-C(13) 120.4(3)
O(2)-Si-O(3)	97.50(9)	C(6)-C(5)-C(4)	120.7(3)	C(15)-C(14)-H(14) 119.8
O(1)-Si-C(19)	120.66(10)	C(6)-C(5)-H(5)	119.7	C(13)-C(14)-H(14) 119.8
O(2)-Si-C(19)	116.52(10)	C(4)-C(5)-H(5)	119.7	C(14)-C(15)-C(16) 120.2(3)
O(3)-Si-C(19)	97.91(10)	C(5)-C(6)-C(7)	119.2(3)	C(14)-C(15)-H(15) 119.9
O(1)-Si-N	82.32(8)	C(5)-C(6)-H(6)	120.4	C(16)-C(15)-H(15) 119.9
O(2)-Si-N	82.85(8)	C(7)-C(6)-H(6)	120.4	C(11)-C(16)-C(15) 119.8(3)
O(3)-Si-N	178.99(9)	C(6)-C(7)-C(8)	120.6(2)	C(11)-C(16)-H(16) 120.1
C(19)-Si-N	82.76(10)	C(6)-C(7)-H(7)	119.7	C(15)-C(16)-H(16) 120.1
C(2)-O(1)-Si	124.84(15)	C(8)-C(7)-H(7)	119.7	N-C(17)-C(18) 107.17(19)
C(10)-O(2)-Si	121.47(14)	C(7)-C(8)-C(3)	120.6(2)	N-C(17)-H(17A) 110.3
C(20)-O(3)-Si	122.65(15)	C(7)-C(8)-H(8)	119.7	C(18)-C(17)-H(1A) 110.3
C(1)-N-C(17)	112.33(19)	C(3)-C(8)-H(8)	119.7	N-C(17)-H(17B) 110.3
C(1)-N-C(9)	114.51(18)	N-C(9)-C(10)	105.72(18)	C(18)-C(17)-H(17B) 110.3
C(17)-N-C(9)	112.66(19)	N-C(9)-H(9A)	110.6	H(17A)-C(17)-H(17B) 108.5
C(1)-N-Si	105.02(14)	C(10)-C(9)-H(9A)	110.6	C(17)-C(18)-C(19) 108.7(2)
C(17)-N-Si	107.65(14)	N-C(9)-H(9B)	110.6	C(17)-C(18)-H(18A) 109.9
C(9)-N-Si	103.74(14)	C(10)-C(9)-H(9B)	110.6	C(19)-C(18)-H(18A) 109.9
N-C(1)-C(2)	107.5(2)	H(9A)-C(9)-H(9B)	108.7	C(17)-C(18)-H(18B) 109.9

N-C(1)-H(1A)	110.2	O(2)-C(10)-C(11)	111.9(2)	C(19)-C(18)-H(18B) 109.9
C(2)-C(1)-H(1A)	110.2	O(2)-C(10)-C(9)	107.00(19)	H(18A)-C(18)-H(18B) 108.3
N-C(1)-H(1B)	110.2	C(11)-C(10)-C(9)	112.7(2)	C(18)-C(19)-Si 113.76(17)
C(2)-C(1)-H(1B)	110.2	O(2)-C(10)-H(10)	108.4	C(18)-C(19)-H(19A) 108.8
H(1A)-C(1)-H(1B)	108.5	C(11)-C(10)-H(10)	108.4	Si-C(19)-H(19A) 108.8
O(1)-C(2)-C(3)	110.2(2)	C(9)-C(10)-H(10)	108.4	C(18)-C(19)-H(19B) 108.8
O(1)-C(2)-C(1)	108.29(19)	C(12)-C(11)-C(16)	119.5(3)	Si-C(19)-H(19B) 108.8
C(3)-C(2)-C(1)	110.1(2)	C(12)-C(11)-C(10)	120.3(2)	H(19A)-C(19)-H(19B) 107.7
O(1)-C(2)-H(2)	109.4	C(16)-C(11)-C(10)	120.1(2)	O(3)-C(20)-H(20A) 109.5
C(3)-C(2)-H(2)	109.4	C(11)-C(12)-C(13)	120.2(3)	O(3)-C(20)-H(20B) 109.5
C(1)-C(2)-H(2)	109.4	C(11)-C(12)-H(12)	119.9	H(20A)-C(20)-H(20B) 109.5
C(8)-C(3)-C(4)	118.8(2)	C(13)-C(12)-H(12)	119.9	O(3)-C(20)-H(20C) 109.5
C(8)-C(3)-C(2)	121.3(2)	C(14)-C(13)-C(12)	119.9(3)	H(20A)-C(20)-H(20C) 109.5
C(4)-C(3)-C(2)	119.8(2)	C(14)-C(13)-H(13)	120.1	H(20B)-C(20)-H(20C) 109.5
C(5)-C(4)-C(3)	120.2(3)			

5.4.9 Crystal data and structure refinement for Lig. 8

Empirical formula	C <sub>20</sub> H <sub>25</sub> NO <sub>3</sub> Si
Formula weight	355.50
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 7.7061(9)  Å
	$\alpha = 90^{\circ}$ .
	b = 9.2717(11)  Å
	$\beta = 99.633(2)^{\circ}.$
	c = 12.4967(15)  Å
	$\gamma = 90^{\circ}$ .
Volume	880.28(18) Å <sup>3</sup>
Z	2
Density (calculated)	1.341 Mg/m <sup>3</sup>
Absorption coefficient	0.153 mm <sup>-1</sup>
F(000)	380
Crystal size	0.36 x 0.29 x 0.07 mm <sup>3</sup>
Theta range for data collection	2.68 to 27.50°.
Index ranges	-9<=h<=9, -11<=k<=12, -16<=l<=16
Reflections collected	10584
Independent reflections	3972 [R(int) = 0.0504]
Completeness to theta = $27.50^{\circ}$	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9894 and 0.9470
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3972 / 1 / 231
Coodness of fit on $F^2$	1.001
Final P indices [1>2sigma(1)]	$P_1 = 0.0278 \text{ wP}_2 = 0.0650$
P indices (all data)	R1 = 0.0378, $WR2 = 0.0030P1 = 0.0454$ $WP2 = 0.0665$
Absolute structure parameter	$R_1 = 0.0454, WR_2 = 0.0005$ 0.15(10)
Extinction coefficient	0.15(10)
	0.050 1.0.001 3-3
Largest diff. peak and hole	$0.370 \text{ and } -0.301 \text{ e.A}^{-5}$

Bond lengths [Å] and angles [°] for Lig. 8

		Bond lengt	hs [Å]		
Si-O(2)	1.6597(13)	C(4)-C(5)	1.389(2)	C(13)-C(14)	1.388(3)
Si-O(1)	1.6757(13)	C(4)-H(4)	0.9500	C(13)-H(13)	0.9500
Si-O(3)	1.6810(14)	C(5)-C(6)	1.396(3)	C(14)-C(15)	1.388(3)
Si-C(19)	1.885(2)	C(5)-H(5)	0.9500	C(14)-H(14)	0.9500
Si-N	2.2284(16)	C(6)-C(7)	1.377(3)	C(15)-C(16)	1.390(3)
O(1)-C(2)	1.415(2)	C(6)-H(6)	0.9500	C(15)-H(15)	0.9500
O(2)-C(9)	1.425(2)	C(7)-C(8)	1.391(3)	C(16)-H(16)	0.9500
O(3)-C(20)	1.417(2)	C(7)-H(7)	0.9500	C(17)-C(18)	1.526(3)
N-C(1)	1 467(2)	C(8)-H(8)	0.9500	C(17)-H(17A)	0 9900
N-C(17)	1.484(2)	C(9)-C(10)	1.519(3)	C(17)-H(17B)	0.9900
N-C(10)	1.500(2)	C(9)-H(9A)	0.9900	C(18)-C(19)	1.536(3)
C(1)-C(2)	1.540(3)	C(9)-H(9B)	0 9900	C(18)-H(18A)	0 9900
C(1)-H(1A)	0 9900	C(10)- $C(11)$	1 530(3)	C(18)-H(18B)	0 9900
C(1)-H(1B)	0.9900	C(10)-H(10)	1.0000	C(19)-H(19A)	0.9900
C(2)- $C(3)$	1 530(3)	C(11)- $C(12)$	1 387(3)	C(19)-H(19B)	0.9900
C(2) = H(2)	1.0000	C(11) = C(16)	1 401(3)	C(20)-H(20A)	0.9800
C(3)- $C(8)$	1 392(3)	C(12)- $C(13)$	1 385(3)	C(20) - H(20R)	0.9800
C(3)-C(4)	1.392(3)	C(12)-H(12)	0.9500	C(20)-H(20D)	0.9800
0(5) 0(1)	1.595(5)	angles	[°]	0(20) 11(200)	0.9000
O(2)-Si- $O(1)$	116 85(7)	C(5)-C(4)-H(4)	119.5	C(14)-C(13)-H(13)	120.3
O(2)-Si- $O(3)$	94 30(7)	C(3)- $C(4)$ - $H(4)$	119.5	C(15)-C(14)-C(13)	120 3(2)
O(1)-Si- $O(3)$	96 21(6)	C(4)- $C(5)$ - $C(6)$	119.96(19)	C(15) = C(14) = H(14)	119.9
O(2)-Si- $C(19)$	119 47(8)	C(4)- $C(5)$ - $H(5)$	120.0	C(13) - C(14) - H(14)	119.9
O(2)-Si- $C(19)$	118.82(8)	C(4)-C(5)-H(5)	120.0	C(14)-C(15)-C(16)	119.86(19)
O(3)-Si-C(19)	101 49(9)	C(7)- $C(6)$ - $C(5)$	119 49(19)	C(14) - C(15) - H(15)	120.1
O(2)-Si-N	83 40(6)	C(7)-C(6)-H(6)	120.3	C(16)-C(15)-H(15)	120.1
O(1) Si N	81.36(6)	C(5) C(6) H(6)	120.3	C(15) C(16) C(11)	120.1
O(3) Si N	175 40(7)	$C(5)-C(0)-\Pi(0)$ C(6) C(7) C(8)	120.3	C(15) - C(16) - U(16)	110.4(2)
C(10) S: N	175.40(7) 93.12(9)	C(6) - C(7) - C(8)	110.8	C(13)- $C(16)$ - $H(16)$	119.8
C(1) = 0(1) Si	126 11(11)	C(0)-C(7)-H(7)	119.8	C(11)-C(10)-H(10)	108 49(16)
C(2) - O(1) - Si	120.11(11)	$C(3)-C(7)-\Pi(7)$	119.0	N-C(17)-C(18)	110.49(10)
C(9) - O(2) - SI	121.26(11)	C(7) - C(8) - C(3)	121.1(2)	$\Gamma(17) - \Gamma(17A)$	110.0
C(20) - O(3) - 31	121.37(12)	C(7)-C(8)-H(8)	119.5	C(16)-C(17)-H(17A)	110.0
C(1)-N- $C(17)$	112.70(15)	C(3)-C(8)-H(8)	100 50(16)	$N-C(17)-\Pi(1/B)$	110.0
C(1)-N- $C(10)$	114.72(15)	O(2)-C(9)-C(10)	109.30(16)	U(18) - U(17) - H(1/B)	110.0
C(1) N S	115.80(15)	O(2)-C(9)-H(9A)	109.8	H(1/A)-C(1/)-H(1/B)	108.4
C(1)-IN-SI	105.59(11)	C(10)-C(9)-H(9A)	109.8	C(17) - C(18) - C(19)	108.10(10)
C(17)-N-SI	106.09(12)	O(2)-C(9)-H(9B)	109.8	C(17)-C(18)-H(18A)	110.1
C(10)-N-SI	102.75(11)	C(10)-C(9)-H(9B)	109.8	C(19)-C(18)-H(18A)	110.1
N-C(1)-C(2)	108.17(15)	H(9A)-C(9)-H(9B)	108.2	C(17)-C(18)-H(18B)	110.1
N-C(1)-H(1A)	110.1	N-C(10)-C(9)	105.00(15)	C(19)-C(18)-H(18B)	110.1
C(2)-C(1)-H(1A)	110.1	N-C(10)-C(11)	115.06(16)	H(18A)-C(18)-H(18B)	108.4
N-C(1)-H(1B)	110.1	C(9)- $C(10)$ - $C(11)$	115.68(17)	C(18)-C(19)-Si	114./6(14)
C(2)-C(1)-H(1B)	110.1	N-C(10)-H(10)	106.8	C(18)-C(19)-H(19A)	108.6
H(1A)-C(1)-H(1B)	108.4	C(9)-C(10)-H(10)	106.8	S1-C(19)-H(19A)	108.6
O(1)-C(2)-C(3)	111.86(16)	C(11)-C(10)-H(10)	106.8	C(18)-C(19)-H(19B)	108.6
O(1)-C(2)-C(1)	108.44(15)	C(12)-C(11)-C(16)	118.55(19)	Si-C(19)-H(19B)	108.6
C(3)-C(2)-C(1)	116.67(16)	C(12)-C(11)-C(10)	119.43(18)	H(19A)-C(19)-H(19B)	107.6
O(1)-C(2)-H(2)	106.4	C(16)-C(11)-C(10)	122.01(18)	O(3)-C(20)-H(20A)	109.5
C(3)-C(2)-H(2)	106.4	C(13)-C(12)-C(11)	121.4(2)	O(3)-C(20)-H(20B)	109.5
C(1)-C(2)-H(2)	106.4	C(13)-C(12)-H(12)	119.3	H(20A)-C(20)-H(20B)	109.5

C(8)-C(3)-C(4)	118.13(18)	C(11)-C(12)-H(12)	119.3	O(3)-C(20)-H(20C)	109.5
C(8)-C(3)-C(2)	120.30(18)	C(12)-C(13)-C(14)	119.5(2)	H(20A)-C(20)-H(20C)	109.5
C(4)-C(3)-C(2)	121.23(17)	C(12)-C(13)-H(13)	120.3	H(20B)-C(20)-H(20C)	109.5
C(5)-C(4)-C(3)	121.01(18)				

## 5.4.10 Crystal data and structure refinement for Lig. 9

Empirical formula Formula weight Temperature	C <sub>19</sub> H <sub>22</sub> Cl N O <sub>2</sub> Si 359.92 153(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 8.6210(7)Å
	b = 11.4337(9) Å
	c = 18.4090(14)  Å
	$\alpha = 90^{\circ}$
	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$ .
Volume	1814.6(2) Å <sup>3</sup>
Z	4
Density (calculated)	1.317 Mg/m <sup>3</sup>
Absorption coefficient	0.288 mm <sup>-1</sup>
F(000)	760
Crystal size	$1.10 \ge 0.46 \ge 0.24 \text{ mm}^3$
Theta range for data collection	2.10 to 27.50°.
Index ranges	-10<=h<=11, -14<=k<=14, -23<=l<=23
Reflections collected	21385
Independent reflections	4114 [R(int) = 0.0659]
Completeness to theta = $27.50^{\circ}$	99.7 %
Max. and min. Transmission	0.9342 and 0.7426
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4114 / 0 / 217
Goodness-of-fit on $F^2$	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0373, $wR2 = 0.0819$
R indices (all data)	R1 = 0.0424, $wR2 = 0.0838$
Absolute structure parameter	-0.01(6)
Largest diff. peak and hole	0.435 and -0.178 e.Å <sup>-3</sup>

Bond lengths [Å] and angles [°] for Lig. 9

		Bond le	engths [Å]		
Cl(1)-Si(1)	2.1699(7)	C(4)-C(5)	1.381(3)	C(21)-C(22)	1.377(3)
Si(1)-O(1)	1.6546(13)	C(4)-H(4)	0.9500	C(21)-C(26)	1.383(3)
Si(1)-O(2)	1.6637(14)	C(5)-C(6)	1.384(3)	C(21)-C(27)	1.503(3)
Si(1)-C(11)	1.869(2)	C(5)-H(5)	0.9500	C(22)-C(23)	1.389(3)
Si(1)-N(1)	2.0661(17)	C(6)-H(6)	0.9500	C(22)-H(22)	0.9500
O(1)-C(27)	1.439(2)	C(7)-C(8)	1.536(3)	C(23)-C(24)	1.368(4)
O(2)-C(7)	1.418(2)	C(7)-H(7)	1.0000	C(23)-H(23)	0.9500

N(1)-C(8)	1.469(3)	C(8)-H(8A)	0.9900	C(24)-C(25)	1.366(3)
N(1)-C(28)	1.482(2)	C(8)-H(8B)	0.9900	C(24)-H(24)	0.9500
N(1)-C(9)	1.491(2)	C(9)-C(10)	1.522(3)	C(25)-C(26)	1.385(3)
C(1)-C(6)	1.381(3)	C(9)-H(9A)	0.9900	C(25)-H(25)	0.9500
C(1)-C(2)	1.387(3)	C(9)-H(9B)	0.9900	C(26)-H(26)	0.9500
C(1)-C(7)	1.507(3)	C(10)-C(11)	1.539(3)	C(27)-C(28)	1.514(3)
C(2)-C(3)	1.383(3)	C(10)-H(10A)	0.9900	C(27)-H(27)	1.0000
C(2)-H(2)	0.9500	C(10)-H(10B)	0.9900	C(28)-H(28A)	0.9900
C(3)-C(4)	1.384(3)	C(11)-H(11A)	0.9900	C(28)-H(28B)	0.9900
C(3)-H(3)	0.9500	C(11)-H(11B)	0.9900		
		angles [°	]		
O(1)-Si(1)-O(2)	119.06(8)	C(7)-C(8)-H(8B)	110.1	C(27)-C(28)-H(28A)	110.6
O(1)-Si(1)-C(11)	119.11(9)	H(8A)-C(8)-H(8B)	108.5	N(1)-C(28)-H(28B)	110.6
O(2)-Si(1)-C(11)	120.59(9)	N(1)-C(9)-C(10)	108.15(16)	C(27)-C(28)-H(28B)	110.6
O(1)-Si(1)-N(1)	86.33(7)	N(1)-C(9)-H(9A)	110.1	H(28A)-C(28)-H(28B)	108.7
O(2)-Si(1)-N(1)	85.78(7)	C(10)-C(9)-H(9A)	110.1	H(9A)-C(9)-H(9B)	108.4
C(11)-Si(1)-N(1)	86.80(8)	N(1)-C(9)-H(9B)	110.1	C(9)-C(10)-C(11)	108.18(16)
O(1)-Si(1)-Cl(1)	92.49(5)	C(10)-C(9)-H(9B)	110.1	C(9)-C(10)-H(10A)	110.1
O(2)-Si(1)-Cl(1)	91.45(5)	H(9A)-C(9)-H(9B)	108.4	C(11)-C(10)-H(10A)	110.1
C(11)-Si(1)-Cl(1)	97.13(7)	C(9)-C(10)-C(11)	108.18(16)	C(9)-C(10)-H(10B)	110.1
N(1)-Si(1)-Cl(1)	175.98(5)	C(9)-C(10)-H(10A)	110.1	C(11)-C(10)-H(10B)	110.1
C(27)-O(1)-Si(1)	119.08(12)	C(11)-C(10)-H(10A)	110.1	H(10A)-C(10)-H(10B)	108.4
C(7)-O(2)-Si(1)	122.16(12)	C(9)-C(10)-H(10B)	110.1	C(10)-C(11)-Si(1)	112.04(15)
C(8)-N(1)-C(28)	113 92(16)	C(11)-C(10)-H(10B)	110.1	C(10)- $C(11)$ - $H(11A)$	109.2
C(8)-N(1)-C(9)	112.06(15)	H(10A)-C(10)-H(10B)	108.4	Si(1)-C(11)-H(11A)	109.2
C(28)-N(1)-(9)	112.00(12)	C(10)-C(11)-Si(1)	112 04(15)	C(10)- $C(11)$ -H(11B)	109.2
C(20)-N(1)-Si(1)	112.94(17) 105.63(11)	C(10)-C(11)-H(11A)	109.2	$S_{i}(1)-C(11)-H(11B)$	109.2
C(28) N(1) S(1)	105.05(11) 104.12(12)	$S_{i}(1) C(11) H(11A)$	109.2	H(11A) C(11) H(11B)	107.2
C(20) = N(1) = Si(1)	104.12(12) 107.24(12)	C(10) C(11) H(11R)	109.2	$\Gamma(11X) = C(11) = \Pi(11B)$	118 0(2)
C(9) - N(1) - SI(1)	118 60(10)	C(10)-C(11)-H(11B) S(1) C(11) H(11B)	109.2	C(22)- $C(21)$ - $C(20)$	120.2(2)
C(0)-C(1)-C(2)	121.42(19)	$SI(1) - C(11) - \Pi(11D)$	109.2	C(22)- $C(21)$ - $C(27)$	120.5(2)
C(0)-C(1)-C(7)	121.42(18)	H(11A)-C(11)-H(11B)	107.9	C(20)-C(21)-C(27)	121.08(18)
C(2)-C(1)-C(7)	119.76(18)	C(22)- $C(21)$ - $C(26)$	118.0(2)	C(21)-C(22)-C(23)	120.9(2)
C(3)-C(2)-C(1)	121.1(2)	C(22)-C(21)-C(27)	120.3(2)	C(21)-C(22)-H(22)	119.6
C(3)- $C(2)$ - $H(2)$	119.5	C(26)-C(21)-C(27)	121.68(18)	C(23)-C(22)-H(22)	119.6
C(1)- $C(2)$ -H(2)	119.5	C(21)-C(22)-C(23)	120.9(2)	C(24)-C(23)-C(22)	120.2(2)
C(2)-C(3)-C(4)	119.8(2)	C(21)-C(22)-H(22)	119.6	C(24)-C(23)-H(23)	119.9
C(2)-C(3)-H(3)	120.1	C(23)-C(22)-H(22)	119.6	C(22)-C(23)-H(23)	119.9
C(4)-C(3)-H(3)	120.1	C(24)-C(23)-C(22)	120.2(2)	C(25)-C(24)-C(23)	119.9(2)
C(5)-C(4)-C(3)	119.5(2)	C(24)-C(23)-H(23)	119.9	C(25)-C(24)-H(24)	120.1
C(5)-C(4)-H(4)	120.3	C(22)-C(23)-H(23)	119.9	C(23)-C(24)-H(24)	120.1
C(3)-C(4)-H(4)	120.3	C(25)-C(24)-C(23)	119.9(2)	C(24)-C(25)-C(26)	119.9(2)
C(4)-C(5)-C(6)	120.5(2)	C(25)-C(24)-H(24)	120.1	C(24)-C(25)-H(25)	120.0
C(4)-C(5)-H(5)	119.8	C(23)-C(24)-H(24)	120.1	C(26)-C(25)-H(25)	120.0
C(6)-C(5)-H(5)	119.8	C(24)-C(25)-C(26)	119.9(2)	C(21)-C(26)-C(25)	121.2(2)
C(1)-C(6)-C(5)	120.5(2)	C(24)-C(25)-H(25)	120.0	C(21)-C(26)-H(26)	119.4
C(1)-C(6)-H(6)	119.7	C(26)-C(25)-H(25)	120.0	C(25)-C(26)-H(26)	119.4
C(5)-C(6)-H(6)	119.7	C(21)-C(26)-C(25)	121.2(2)	O(1)-C(27)-C(21)	110.71(15)
O(2)-C(7)-C(1)	111.14(16)	C(21)-C(26)-H(26)	119.4	O(1)-C(27)-C(28)	106.35(15)
O(2)-C(7)-C(8)	107.84(15)	C(25)-C(26)-H(26)	119.4	C(21)-C(27)-C(28)	113.93(17)
C(1)-C(7)-C(8)	110.17(16)	O(1)-C(27)-C(21)	110.71(15)	O(1)-C(27)-H(27)	108.6
O(2)-C(7)-H(7)	109.2	O(1)-C(27)-C(28)	106.35(15)	C(21)-C(27)-H(27)	108.6

C(1)-C(7)-H(7)	109.2	C(21)-C(27)-C(28)	113.93(17)	C(28)-C(27)-H(27)	108.6
C(8)-C(7)-H(7)	109.2	O(1)-C(27)-H(27)	108.6	N(1)-C(28)-C(27)	105.78(16)
N(1)-C(8)-C(7)	107.83(15)	C(21)-C(27)-H(27)	108.6	N(1)-C(28)-H(28A)	110.6
N(1)-C(8)-H(8A)	110.1	C(28)-C(27)-H(27)	108.6	C(27)-C(28)-H(28A)	110.6
C(7)-C(8)-H(8A)	110.1	N(1)-C(28)-C(27)	105.78(16)	N(1)-C(28)-H(28B)	110.6
N(1)-C(8)-H(8B)	110.1	N(1)-C(28)-H(28A)	110.6	C(27)-C(28)-H(28B)	110.6
				H(28A)-C(28)-H(28B)	108 7

## 5.4.11 Crystal data and structure refinement for Lig. 10

Empirical formula Formula weight	C <sub>18</sub> H <sub>24</sub> ClNO <sub>2</sub> 321 83
Temperature	153 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Snace group	$P2_{1}2_{1}2_{1}$
Unit cell dimensions	a = 11.9238(10)  Å
	b = 21.1466(17)  Å
	c = 21.6386(17) Å
Volume	5456.1(8) Å <sup>3</sup>
Ζ	12
Density (calculated)	1.175 Mg/m <sup>3</sup>
Absorption coefficient	0.217 mm <sup>-1</sup>
F(000)	2064
Crystal size	0.41 x 0.22 x 0.05 mm <sup>3</sup>
Theta range for data collection	1.88 to 25.00°.
Index range	-14<=h<=14, -25<=k<=24, -25<=l<=25
Reflections collected	55769
Independent reflections	9599 [R(int) = 0.1602]
Completeness to theta = $25.00^{\circ}$	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.9893 and 0.9165
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	959̂9 / 0 / 605
Goodness-of-fit on F <sup>2</sup>	0.782
Final R indices [I>2sigma(I)]	R1 = 0.0468, WR2 = 0.0590
R indices (all data)	R1 = 0.1164, WR2 = 0.0681
Absolute structure parameter	-0.01(5)
Extinction coefficient	0
Largest diff. peak and hole	0.220 and -0.224 e.Å <sup>-3</sup>

Bond lengths  $[\text{\AA}]$  and angles  $[^\circ]$  for Lig. 10

		Bond le	engths [Å]			
N(1)-C(1)	1.487(4)	C(11)-C(13)	1.512(5)	C(34)-H(34)	0.9500	
N(1)-C(10)	1.488(4)	C(11)-H(11)	1.0000	C(35)-C(36)	1.393(5)	
N(1)-H(101)	0.9200	C(12)-H(12A)	0.9800	C(35)-H(35)	0.9500	
N(1)-H(102)	0.9200	C(12)-H(12B)	0.9800	C(36)-C(37)	1.394(5)	
N(2)-C(30)	1.487(4)	C(12)-H(12C)	0.9800	C(36)-H(36)	0.9500	
N(2)-C(21)	1.502(4)	C(13)-C(14)	1.386(5)	C(37)-C(38)	1.374(5)	

N(2)-H(201)	0.920	00	C(13)-C(18)	1.390(	5)	C(37)-H(37)	0.950	00
N(2)-H(202)	0.9200		C(14)-C(15)	1.3950	5)	C(38)-H(38)	0.950	00
N(3)-C(50)	1 494(4	4)	C(14)-H(14)	0.950	0	C(41)-C(42)	1 508	3(5)
N(3)-C(41)	1 502(4	4)	C(15)-C(16)	1 391(	6	C(41)-H(41A)	0.9	9900
N(3)-H(301)	0.920	0	C(15)-H(15)	0.9500	)	C(41)-H(41B)	0.9	9900
N(3) - H(302)	0.920	ů 0	C(16)- $C(17)$	1 383	(5)	C(42)- $C(44)$	1 506	5(5)
O(1)-C(2)	1 4120	4)	C(16)-H(16)	0.950	0	C(42) = H(42)	1.000	0
O(1) - C(2)	1 424(4		C(17) C(18)	1 277	(5)	$C(42) - \Pi(42)$ $C(42) - \Pi(42A)$	1.000	200
O(2) C(12)	1 / 180	4)	C(17) = C(18)	0.04	500	C(43) = H(43R)	0.0	800
O(2) - C(12)	1 4280	+) 4)	$C(17) = \Pi(17)$ $C(18) = \Pi(18)$	0.9.	0	$C(43) = \Pi(43D)$	0.9	800
O(2)- $C(11)$	1.420(4	+) 4)	$C(18) - \Pi(18)$	1 400	(4)	$C(43) - \Pi(43C)$	1 2 7 1	800
O(3)-C(23)	1.424(4	+) 4)	C(21)-C(22)	1.499	(4)	C(44)- $C(45)$	1.3/1	I(5)
O(3)-O(22)	1.430(4	+) 4)	C(21)- $H(21A)$	0.95	200	C(44)- $C(49)$	1.383	D(5)
O(4) - C(31)	1.427(4	4)	C(21)-H(21B)	0.99	00	C(45)-C(46)	1.383	5(5)
O(4)-C(32)	1.432(4	4)	C(22)-C(24)	1.501	(5)	C(45)-H(45)	0.950	00
O(5)-C(42)	1.415(4	4)	C(22)-H(22)	1.000	00	C(46)-C(47)	1.368	3(5)
O(5)-C(43)	1.433(4	4)	C(23)-H(23A)	0.9	9800	C(46)-H(46)	0.95	00
O(6)-C(51)	1.441(4	4)	C(23)-H(23B)	0.9	800	C(47)-C(48)	1.38	4(6)
O(6)-C(52)	1.443(	(4)	C(23)-H(23C)	0.9	800	C(47)-H(47)	0.95	00
C(1)-C(2)	1.509(5)	)	C(24)-C(29)	1.357	(6)	C(48)-C(49)	1.407	7(6)
C(1)-H(1A)	0.990	0	C(24)-C(25)	1.358	8(6)	C(48)-H(48)	0.950	00
C(1)-H(1B)	0.990	0	C(25)-C(26)	1.383	(7)	C(49)-H(49)	0.95	00
C(2)-C(4)	1.500(5)	)	C(25)-H(25)	0.950	0	C(50)-C(51)	1.510	)(5)
C(2)-H(2)	1.0000		C(26)-C(27)	1.343	(8)	C(50)-H(50A)	0.9	900
C(3)-H(3A)	0.980	0	C(26)-H(26)	0.950	00	C(50)-H(50B)	0.9	900
C(3)-H(3B)	0.9800	)	C(27)-C(28)	1.344	(7)	C(51)-C(53)	1.494	4(5)
C(3)-H(3C)	0.9800	)	C(27)-H(27)	0.950	0	C(51)-H(51)	1.000	ò
C(4)-C(9)	1.380(5)	)	C(28)-C(29)	1 404	(6)	C(52)-H(52A)	0.9	800
C(4)- $C(5)$	1 383(5)		C(28)-H(28)	0.950	0	C(52)-H(52B)	0.9	0800
C(5)- $C(6)$	1 393(5)	, ,	C(29)-H(29)	0.950	ñ	C(52)-H(52C)	0.9	800
C(5)-H(5)	0.9500	,	C(20)-C(21)	1 / 100	(5)	$C(52)$ - $\Pi(52C)$	1 363	8(5)
$C(5) - \Pi(3)$	1 281(5)		C(30) + C(31)	1.400	000	C(53) - C(54)	1 202	D(5)
C(0) - C(7)	0.0500	,	$C(30) - \Pi(30A)$	0.95	000	C(53)- $C(58)$	1.392	2(5)
C(0)-H(0)	1.200(6)		$C(30)$ - $\Pi(30B)$	1 5 1 1	(5)	C(54)- $C(55)$	1.362	2(0)
C(7) - C(8)	1.309(0)	)	C(31)-C(33)	1.000	(5)	C(54) - H(54)	1.266	JU 5(7)
C(7)-H(7)	0.9500		C(31)-H(31)	1.000	0	C(55) - C(56)	1.300	D(7)
C(8) - C(9)	1.3/0(0)	)	C(32)- $H(32A)$	0.98	800	C(55)-H(55)	0.95	00
C(8) - H(8)	0.9500		C(32)-H(32B)	0.98	800	C(50)-C(57)	1.35	0(7)
$C(9) - \Pi(9)$	0.9500	5(4)	C(32) - H(32C)	1 205	000 (5)	C(50)-H(50)	0.95	00
C(10) - C(11)	1.480	0(4)	C(33)-C(34)	1.385	(5)	C(57) - C(58)	1.397	(0)
C(10)-H(10A)	0.9	900	C(33)-C(38)	1.410	J(S)	C(5/)-H(5/)	0.95	00
C(10)-H(10B)	0.99	00	C(34)-C(35)	1.376	(5)	C(58)-H(58)	0.95	00
			ang	gles [°]				
C(1)-N(1)-C(10	)	112.3(3)	C(18)-C(13)-C(	(11)	120.2(4)	C(33)-C(38)-H	(38)	120.2
C(1)-N(1)-H(10	1)	109.1	C(17)-C(18)-C(	(13)	121.9(5)	N(3)-C(41)-C(4	12)	111.0(3)
C(10)-N(1)-H(1	01)	109.1	C(17)-C(18)-H	(18)	119.1	N(3)-C(41)-H(4	41A)	109.4
C(1)-N(1)-H(10	2)	109.1	C(13)-C(18)-H	(18)	119.1	C(42)-C(41)-H	(41Å)	109.4
C(10)-N(1)-H(1	02)	109.1	C(22)-C(21)-N	(2)	112.9(3)	N(3)-C(41)-H(4	41B)	109.4
H(101)-N(1)-H	102)	107.9	C(22)-C(21)-H	(21A)	109.0	C(42)-C(41)-H	(41É)	109.4
C(30)-N(2)-C(2	n í	114.3(3)	N(2)-C(21)-H(2	21A)	109.0	H(41A)-C(41)-	H(41B)	108.0
C(30)-N(2)-H(2)	01)	108.7	C(22)-C(21)-H	(21B)	109.0	O(5)-C(42)-C(4	44)	113 2(4)
C(21)-N(2)-H(2)	01)	108.7	N(2)-C(21)-H(2	21B)	109.0	O(5)-C(42)-C(4	ŧń –	103.8(3)
C(30)-N(2)-H(2	02)	108 7	H(21A)-C(21)-I	H(21B)	107.8	C(44)-C(42)-C(	(41)	113 4(3)
C(21)-N(2)-H(2	02)	108 7	0(3)-C(22)-C(2	21)	106 7(3)	O(5)-C(42)-H(4	42)	108.8
H(201)-N(2) H	202)	107.6	0(3) - C(22) - C(2)	24)	111 2(4)	$C(44) = C(42) = \Pi(42)$	(42)	108.8
C(50) - N(2) - C(4)	1)	115 2(2)	C(21) C(22) C(22)	) (24)	100 0(4)	C(41) C(42)-H	(42)	108.8
C(50) = IN(3) = C(4)	01)	108.5	O(2) C(22) U(2)	( <u>≁</u> +)	109.9(4)	O(5) C(42) II(42)	(74) 13 A)	100.0
C(30)-IN(3)-H(3) C(41) N(2) H(2)	01)	100.5	C(3) - C(22) - H(2)	(22)	109.0	O(5) - C(45) - H(4)	12D)	109.5
C(41)-N(3)-H(3) C(50) N(2) H(2)	01)	108.5	C(21)- $C(22)$ -H(	(22)	109.0	C(4) C(43)-H(4	(19)	120.2
C(50)-N(3)-H(3)	02)	108.5	C(24)-C(22)-H(	(22)	109.6	C(49)-C(48)-H	(48)	120.2
C(41)-N(3)-H(3	02)	108.5	O(3)-C(23)-H(2	(3A)	109.5	C(44)-C(49)-C(	(48)	118.9(5)
H(301)-N(3)-H(	302)	107.5	O(3)-C(23)-H(2	23B)	109.5	C(44)-C(49)-H	(49)	120.5
C(2)-O(1)-C(3)		111.8(3)	H(23A)-C(23)-	H(23B)	109.5	C(48)-C(49)-H	(49)	120.5
C(12)-O(2)-C(1	1)	111.8(3)	O(3)-C(23)-H(2	23C)	109.5	N(3)-C(50)-C(5	,1)	113.4(3)
C(23)-O(3)-C(2	2)	110.3(3)	H(23A)-C(23)-	H(23C)	109.5	N(3)-C(50)-H(5	50A)	108.9
C(31)-O(4)-C(3	2)	12.6(3)	H(23B)-C(23)-I	H(23C)	109.5	C(51)-C(50)-H	(50A)	108.9

C(42)-O(5)-C(43)	112.0(3)	C(29)-C(24)-C(25)	116.0(5)	N(3)-C(50)-H(50B)	108.9
C(51)-O(6)-C(52)	111.5(3)	C(29)-C(24)-C(22)	121.4(5)	C(51)- $C(50)$ - $H(50B)$	108.9
N(1)-C(1)-C(2)	113 7(3)	C(25) - C(24) - C(22)	121.9(5)	H(50A)-C(50)-H(50B)	107.7
N(1)-C(1)-H(1A)	108.8	C(24)-C(25)-C(26)	123.2(6)	$\Omega(6) - C(51) - C(53)$	111 8(3)
C(2)-C(1)-H(1A)	108.8	C(24)-C(25)-U(25)	118.4	O(6)-C(51)-C(50)	106.0(3)
N(1) C(1) H(1R)	108.8	C(24) - C(25) - H(25)	118.4	C(53) C(51) C(50)	112 2(3)
R(1)-C(1)-R(1B)	100.0	C(20)-C(23)-H(23)	110.4	C(53)-C(51)-C(50)	102.2(5)
U(2)-U(1)-H(1B)	108.8	C(27) - C(26) - C(25)	118.7(7)	O(6)-C(51)-H(51)	108.9
H(IA)-C(I)-H(IB)	10/./	C(27)-C(26)-H(26)	120.6	C(53)-C(51)-H(51)	108.9
O(1)-C(2)-C(4)	114.0(3)	C(25)-C(26)-H(26)	120.6	C(35)-C(36)-H(36)	120.4
O(1)-C(2)-C(1)	106.1(3)	C(13)-C(14)-C(15)	120.1(5)	C(37)-C(36)-H(36)	120.4
C(4)-C(2)-C(1)	108.1(3)	C(13)-C(14)-H(14)	120.0	C(38)-C(37)-C(36)	121.0(4)
O(1)-C(2)-H(2)	109.5	C(15)-C(14)-H(14)	120.0	C(38)-C(37)-H(37)	119.5
C(4)-C(2)-H(2)	109.5	C(16)-C(15)-C(14)	120.0(5)	C(36)-C(37)-H(37)	119.5
C(1)-C(2)-H(2)	109.5	C(16)-C(15)-H(15)	120.0	C(37)-C(38)-C(33)	119.6(4)
O(1)-C(3)-H(3A)	109.5	C(14)-C(15)-H(15)	120.0	C(37)-C(38)-H(38)	109.5
O(1)-C(3)-H(3B)	109.5	C(17)-C(16)-C(15)	120.1(5)	H(43A)-C(43)-H(43B)	109.5
H(3A)-C(3)-H(3B)	109.5	C(17)-C(16)-H(16)	120.0	O(5)-C(43)-H(43C)	109.5
O(1)-C(3)-H(3C)	109.5	C(15)-C(16)-H(16)	120.0	H(43A)-C(43)-H(43C)	109.5
H(3A)-C(3)-H(3C)	109.5	C(18)-C(17)-C(16)	119.3(5)	H(43B)-C(43)-H(43C)	109.5
H(3B)-C(3)-H(3C)	109.5	C(18)-C(17)-H(17)	120.4	C(45)-C(44)-C(49)	120.2(4)
C(9)-C(4)-C(5)	118.1(4)	C(16)-C(17)-H(17)	120.4	C(45)-C(44)-C(42)	120.8(4)
C(9)- $C(4)$ - $C(2)$	120.3(4)	C(26)-C(27)-C(28)	120.9(7)	C(49)- $C(44)$ - $C(42)$	119.0(4)
C(5)-C(4)-C(2)	121 3(4)	C(26)-C(27)-H(27)	119.5	C(44)- $C(45)$ - $C(46)$	121.0(5)
C(4)-C(5)-C(6)	121.9(4)	C(28)-C(27)-H(27)	119.5	C(44)- $C(45)$ - $H(45)$	119.5
C(4)-C(5)-H(5)	110.1	C(27)-C(28)-C(29)	118.9(7)	C(46)-C(45)-H(45)	119.5
C(6) C(5) H(5)	110.1	C(27) - C(28) - U(29)	120.6	C(47) C(46) C(45)	110.4(5)
$C(0)$ - $C(5)$ - $\Pi(5)$	119.1	C(27) - C(28) - H(28)	120.0	C(47) - C(40) - C(45)	120.2
C(7) - C(0) - C(3)	110.5(5)	C(29)-C(20)-H(20)	120.0	C(47)- $C(40)$ - $H(40)$	120.5
C(7)- $C(0)$ - $H(0)$	120.9	C(24) - C(29) - C(28)	122.0(6)	C(45)- $C(46)$ - $H(46)$	120.5
C(5)-C(6)-H(6)	120.9	C(24)-C(29)-H(29)	119.0	C(46)-C(47)-C(48)	120.8(5)
C(8)-C(7)-C(6)	120.3(5)	C(28)-C(29)-H(29)	119.0	C(46)-C(47)-H(47)	119.6
C(8)-C(7)-H(7)	119.8	N(2)-C(30)-C(31)	111.6(3)	C(48)-C(47)-H(47)	119.6
C(6)-C(7)-H(7)	119.8	N(2)-C(30)-H(30A)	109.3	C(47)-C(48)-C(49)	119.6(5)
C(7)-C(8)-C(9)	120.7(5)	C(31)-C(30)-H(30A)	109.3	C(47)-C(48)-H(48)	120.2
C(7)-C(8)-H(8)	119.6	N(2)-C(30)-H(30B)	109.3	C(50)-C(51)-H(51)	108.9
C(9)-C(8)-H(8)	119.6	C(31)-C(30)-H(30B)	109.3	O(6)-C(52)-H(52A)	109.5
C(8)-C(9)-C(4)	120.6(5)	H(30A)-C(30)-H(30B)	108.0	O(6)-C(52)-H(52B)	109.5
C(8)-C(9)-H(9)	119.7	O(4)-C(31)-C(30)	105.4(3)	H(52A)-C(52)-H(52B)	109.5
C(4)-C(9)-H(9)	119.7	O(4)-C(31)-C(33)	113.5(3)	O(6)-C(52)-H(52C)	109.5
C(11)-C(10)-N(1)	114.0(3)	C(30)-C(31)-C(33)	109.2(4)	H(52A)-C(52)-H(52C)	109.5
C(11)-C(10)-H(10A)	108.8	O(4)-C(31)-H(31)	109.5	H(52B)-C(52)-H(52C)	109.5
N(1)-C(10)-H(10A)	108.8	C(30)-C(31)-H(31)	109.5	C(54)-C(53)-C(58)	117.7(5)
C(11)-C(10)-H(10B)	108.8	C(33)-C(31)-H(31)	109.5	C(54)-C(53)-C(51)	121.0(4)
N(1)-C(10)-H(10B)	108.8	O(4)-C(32)-H(32A)	109.5	C(58)-C(53)-C(51)	121.3(4)
H(10A)-C(10)-H(10B)	107.7	O(4)-C(32)-H(32B)	109.5	C(53)-C(54)-C(55)	120.7(5)
O(2)-C(11)-C(10)	106.8(3)	H(32A)-C(32)-H(32B)	109.5	C(53)-C(54)-H(54)	119.7
O(2)-C(11)-C(13)	111.6(4)	O(4)-C(32)-H(32C)	109.5	C(55)-C(54)-H(54)	119.7
C(10)- $C(11)$ - $C(13)$	110 4(3)	H(32A)-C(32)-H(32C)	109.5	C(56)-C(55)-C(54)	121 4(6)
O(2)-C(11)-H(11)	109.4	H(32B)-C(32)-H(32C)	109.5	C(56)- $C(55)$ - $H(55)$	119.3
C(10)-C(11)-H(11)	109.4	C(34)-C(33)-C(38)	119.0(4)	C(54)- $C(55)$ -H(55)	119.3
C(13)-C(11)-H(11)	109.4	C(34)-C(33)-C(31)	122.0(4)	C(57)-C(56)-C(55)	119.4(6)
O(2) C(12) U(12A)	109.4	C(38) C(22) C(21)	1122.0(4)	C(57) = C(50) = C(55) C(57) = C(56) = H(56)	120.2
O(2) - O(12) - H(12A)	109.5	C(35) - C(33) - C(31)	118.9(4)	C(57) - C(50) - H(50)	120.5
U(2)-U(12)-H(12B)	109.5	C(35)-C(34)-C(33)	121.2(4)	C(55)-C(56)-H(56)	120.5
H(12A)-C(12)-H(12B)	109.5	C(35)-C(34)-H(34)	119.4	C(56)-C(57)-C(58)	119.6(6)
U(2)-U(12)-H(12U)	109.5	C(33)-C(34)-H(34)	119.4	C(56)-C(57)-H(57)	120.2
H(12A)-C(12)-H(12C)	109.5	C(34)-C(35)-C(36)	120.0(5)	C(58)-C(57)-H(57)	120.2
H(12B)-C(12)-H(12C)	109.5	C(34)-C(35)-H(35)	120.0	C(53)-C(58)-C(57)	121.3(5)
C(14)-C(13)-C(18)	118.7(4)	C(36)-C(35)-H(35)	120.0	C(53)-C(58)-H(58)	119.4
C(14) $C(12)$ $C(11)$	1211(4)	C(35)-C(36)-C(37)	119 2(5)	C(57)-C(58)-H(58)	119.4

#### 6. Toxicity of Vanadium Compounds

#### 6.1 General

Basically, vanadium compounds are toxic. The toxicity increases with their oxidation states and solubility in fluids and air. Vanadium compounds with vanadium in the +V oxidation state are more toxic than those with lower oxidation states; the compounds, which show higher solubility in air, water and biological media, exhibit a higher toxicity due to better absorption. For example, tetravalent VOSO<sub>4</sub> has been reported to be more than 5 times as toxic as trivalent  $V_2O_3$ ;<sup>[99]</sup>  $V_2O_5$  is highly toxic also because it forms aerosols in the air and can be easily inhaled and then be absorbed by the respiratory system.

In humans, exposure by inhalation causes diverse toxic effects on the respiratory, digestive, and central nervous systems, the kidney and the skin. So far there are very few reported cases of vanadium toxicity in humans for vanadium compounds getting into and being absorbed by the gastrointestinal system. Experiments have shown that human volunteers subjected to oral doses of vanadyl compounds of 50-125 mg/day suffered from cramps, loosened stool, and 'green tongue' in all patients, and fatigue and lethargy in a minority. The 'green tongue' phenomenon has also been observed with laborers subjected to the inhalation of  $V_2O_5$  in mines and industrial processing of vanadium.

Absorbed vanadium is widely distributed in the body, but short-term localization occurs primarily in bone, kidneys, and liver. In the body, vanadium can undergo changes in oxidation state (interconversion of vanadyl (+IV) and vanadate (+V)), and it can also bind in both oxidation states to blood protein (transferrin).

Vanadium is excreted primarily in the feces following oral exposures, and primarily in the urine following inhalation exposures.<sup>[100]</sup>

# 6.2 Laboratory and Environmental Protection – Labor und Umweltschutz

#### 6.2.1 Rechtliches Umfeld und Reglementierung des Chemikers

In seinem weiten Tätigkeitsfeld wird der Chemiker mit einer Fülle von Gesetzen und Verordnungen konfrontiert, die alle dem Schutz von Mensch und Umwelt dienen. Die Verordnungen des Chemikalienrechts, vor allem über Gefahrstoffe, stellen einen Teil der Rechtsordnung dar. Diese regeln einerseits die Tätigkeit des Chemikers, andererseits werden sie selbst von seinen Erkenntnissen und Erfahrungen beeinflusst. Im Chemikaliegesetz werden Gefahrstoffe folgendermaßen definiert:

- gefährliche Stoffe, Zubereitungen oder Erzeugnisse nach §3a sowie Stoffe und Zubereitungen, die sonstige chronisch schädigende Eigenschaften besitzen;
- 2. exploisionsgefährliche Stoffe, Zubereitungen und Erzeugnisse;
- Stoffe, Zubereitungen und Erzeugnisse, die explosionsgefährliche Stoffe freisetzen können;
- Stoffe, Zubereitungen und Erzeugnisse, die erfahrungsgemäß krankheitserreger übertragen können

Wenn sehr giftige oder giftige Stoffe in den Verkehr gebracht oder abgegeben werden, ist dies nur dann rechtlich zulässig, wenn die verantwortliche Person volljährig ist, die erforderliche Zuverlässigkeit besitzt und die Sachkenntnis nach der Chemikalienverbotsverordnung (ChemverbotsV) nachweisen kann. Für einen verantwortungsvollen Umgang mit Chemikalien müssen dem Chemiker die wesentlichen Eigenschaften der Gefahrstoffe, die mit ihrer Verwendung verbundenen Gefahren und die einschlägigen Vorschriften bekannt sein, so wie dies nach §5 des ChemverbotsV bestimmt wird.

Die Kenntnis der dazugehörigen Vorschriften setzt die rechtlichen Definitionen der Gefährlichkeitsmerkmale, die Kennzeichnung und Einstufung gefährlicher Stoffe und Zubereitungen anhand der Gefahreigenschaften voraus. Die letztgenannten erfolgen gemäß dem Listenprinzip, wenn die Stoffe in der maßgeblichen Liste erfasst sind, und gemäß dem Definitionsprinzip, wenn die Stoffe nach der Operationalisierung der Gefährlichkeitsmerkmale dies nicht sind.

Außerdem sind für den Chemiker auch das Wissen über die Tatbestände der fahrlässigen Tötung und Körperverletzung, der Vergiftung (§§220, 230, 229 StGB), sowie des strafbaren Inverkehrbringens von Giften und über die Ordnungswidrigkeiten beim Inverkehrbringen von und beim Umgang mit Giften von Bedeutung. Er sollt sich im weiteren über das Gefahrguttransportrecht, das Abfallrecht, das Lebensmittelgesetz, das Bundsimmisionsschutzgesetz, das Wasserhaushaltsgesetz sowie über die Technischen Regeln für Gefahrstoffe (TRGS) unterrichten, die teilweise die geltenden Regeln und Erkenntnisse inhaltlich näher bestimmen.

Durch die TRGS 451 wird z. B. der Umgang mit Gefahrstoffen im Hochschulbereich definiert. Die TRGS 555 das Aussehen und den Inhalt von Betriebsanweisungen, die in chemischen Labors, in denen mit Gefahrstoffen gearbeitet wird, vorhanden sind und die auf sämtliche Gefahren der betreffenden Stoffe hinweisen müssen, eingehender fest als es die Gefahrstoffverordnung (GefStofV) tut. Die TRGS hast als Ziel, ein Maximum an Sicherheit zu gewähren und dient folglich dazu, Gefahrstoffe unter sicherheitstechnischen, arbeitsmedizinschen, hygienischen und arbeiswissenschaftlichen Aspekten eindeutig einzuordnen.

All chemists have the responsibility and obligation to follow the laws and regulations related to human and environment protection.

How to deal with hazardous chemicals is a very important part among the rules about chemical regulation. Hazardous chemicals are defined as follows:

1. toxic materials, preparation and manufacture (according to § 3a), as well as materials and preparations that can cause chronic hazard;

- 2. explosive materials, preparation and manufacture;
- 3. materials, preparation and manufacture that may release explosive materials;
- 4. materials, preparation and manufacture that may cause illness.

When hazardous chemicals are transported or delivered, there must be legal permission, and the responsible persons must be adults who possess and are able to prove the required knowledge and experience according to the Chemilalienverordung (ChemverbotsV).

The chemist has to possess knowledge about the properties of the toxic chemicals, their hazards when in application, as well as the related regulations (according to §5).

In addition, chemists should also have available knowledge about death, injury, and intoxication caused by careless handling (§§220, 230, and 229 StGB).

Further, the chemist also has to be informed on the facts of negligent homicide and bodily harm, poisoning, and the criminal bringing into circulation of toxic materials, and on the marketing of regulatory offense and in dealing with toxins of significance.

For a responsible handling of chemicals, the chemist has to be aware of the essential characteristics of dangerous substances associated with their use, and of the relevant regulations.

#### 6.2.2 Examples of toxic chemicals used in this work

1. Tris(isopropoxido)oxidovanadium VO(OiPr)3

① Workplace: Room 517, Institute of Inorganic and Applied Chemistry

<sup>(2)</sup> Hazards to humans and the environment: R10 inflammable; R36/37/38 eyes, respiratory organs, and skin irritant.

③ Protective methods: keep away from ignition sources; work with uniform, protecting glasses and gloves;

④ First aid: once the skin or eyes get contaminated, wash with water immediately and go to the doctor when necessary.

2. Dichloromethane CH<sub>2</sub>Cl<sub>2</sub>

① Workplace: Room 517, Institute of Inorganic and Applied Chemistry

Hazards to humans and the environment: R40 may cause irreversible injury; possibly carcinogenic in humans. Possibly mutagenic.

2 MWC value: 360 mg/m<sup>3</sup>

③ Protective methods: keep away from ignition sources; work with uniform, protecting glasses and gloves; operate in fume cupboard with good ventilation;

④ First aid:

#### Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention immediately. *Skin Contact*:

immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Get medical attention

Inhalation:

move to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention if symptoms appear.

Ingestion:

Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

#### 6.2.3 Entsorgung

Zu einem verantwortungsvollen Arbeiten mit Chemikalien aller Art gehört auch die sachgerechte Entsorgung, die in der BRD durch das 1986 erneuerte Gesetz über die Vermeidung und Entsorgung von Abfällen (AbfG) reglementiert ist. Demgemäß soll die Entsorgung nicht nur auf die Sammlung und die regelgerechte Umwandlung gefährlicher Stoffe in weniger gefährliche Substanzen begrenzt sein, sonder soll, soweit möglich, durch die Wahl geeigneter Verfahren die bereits im Labor entstehenden Abfallmengen auf ein Minimum reduzieren. Dabei sind verschiedene Maßnahmen möglich, wie z. B. entsprechend kleinen dimensionierte Forschungsansätze, die Wiedergewinnung bestimmter Lösungsmittel wie Aceton und Ethanol, die in erster Linie zu Reinigungswecken verwendet werden, oder aber die Wiedergewinnung sehr teurer Lösungsmittel wie deuteriertes THF. Auch ist der Ersatz sehr gefährlicher Stoffe durch weniger gefährliche Stoffe zu testen und wenn möglich auch vorzunehmen. So ist bei

vielen Synthesen der Ersatz von Benzol und Methanol durch die weniger gefährlichen Lösungsmittel Toluol und Ethanol durchaus möglich.

Im Folgenden werden die wichtigsten Entsorgungsarten der in der Arbeit verwendeten Stoffe aufgezählt:

- Die getrennte Sammlung von halogenierten und nicht -halogenierten Lösungsmitteln erfolgte in lösungsmittelbeständigen und bruchsicheren PE-Kanistern (rot für halogenhaltige und blau für halogenfreie Lösungsmittel) mit einem maximalen Fassungsvermögen von 5 Litern. Dabei wurden die Lösungsmittel vor der Entsorgung durch Destillation von etwaigen Metallverbindungen getrennt.
- Mit Chemikalien kontaminierte Papierfilter, Butylschläuche, DC-Folien etc. wurden dem Sammelbehälter f
  ür kontaminierte Betriebsmittel zugef
  ührt.
- 3. Glasgefäße wurden nach entsprechender Reinigung und Entfernung aller Etiketten dem normalen Glasmüll zugeführt.
- 4. Verunreinigte Heizbäder und Öl aus Vakuumpumpen gelten als stark kontaminiertes Altöl und wurden als Sondermull der Entsorgung zugeführt.
- 5. Alle metallhaltigen Rückstände wurden mit einem Gemisch aus konzentrierter Schwefelsäure und 30%igem Wasserstoffperoxid oxidativ aufgeschlossen und nach Verkochen des überschüssigen Peroxids und Abstumpfung mit Soda oder Natriumhydroxid dem Abfallbehälter für metallhaltige anorganische Säuren zugeführt.

#### 6.2.4 Balance of chemical materials

The consumptions of the main chemicals used in this research are listed below:

- R-Styrene oxide, 20 g; *tris(iso*propoxido)oxidovanadium, 5 g; allylamine, 5 mL; 3amino-1,2-propanediol, 2 g; *tris*(hydroxymethyl)methylamine, 3.5 g; trioxomethylsilyl-propylamine, 6 mL;
- 2. Ethanol, 5 L; ethylacetate, 5 L; hexane, 3 L; acetone, 5 L.

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Hiermit versichere ich, alle dieser Arbeit zugrundeliegenden Experimente selbständig durchgeführt und keine anderen als die angegebenen Hilfsmittel verwendet zu haben.

Ferner versichere ich, mit der vorliegenden Arbeit noch keine weiteren Promotionsversuche unternommen zu haben.

Hamburg, August 2008

(Wu Pingsong)