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Vanadium(III) and Vanadium(V) Amine Tris(Phenolate) Complexes

Stanislav Groysman,† Israel Goldberg,† Zeev Goldschmidt,*,‡ and Moshe Kol*,†

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel, and Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel

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The coordination chemistry of amine tris(phenolate) ligands around V(III) and V(V) is described for the first time. Three amine tris(phenolate) ligands were employed featuring different steric and electronic influence exerted by the phenolate substituents in the *ortho* and *para* positions being either t-Bu, Me, or Cl. V(III) complexes of all ligands (**1**–**3**) were readily obtained by reaction between the ligand precursors and $VCl_3(THF)_3$ in the presence of triethylamine. The complexes obtained were pentacoordinate, a THF ligand completing the coordination sphere of the metal, which was found to be of almost perfect TBP geometry, as revealed by crystallography. V(V) oxo complexes of all the ligands (**4**–**6**) were readily obtained by a reaction between the ligand precursors and $VO(OPr)_3$. The oxo complexes of the alkyl-bearing ligands (**4** and **5**) could also be synthesized by the air oxidation of the corresponding V(III) complexes (**1** and **2**); however, the attempted air oxidation of the V(III) complex bound to the electron-poor ligand (**3**) did not yield the corresponding oxo complex **6**. ^1H NMR and crystallographic analysis of complexes **4** and **5** supported their TBP structures. Complex **6**, on the other hand, was found to be composed of a TBP complex (**6a**) and an octahedral complex (**6b**) in equilibrium, the octahedral complex being more stable at lower temperatures. An X-ray structure of **6b** revealed a mononuclear oxo complex, the sixth coordination site being occupied by an aqua ligand to which two THF molecules are H-bonded. Complexes **4**–**6** catalyze the epoxidation of olefins by t-BuOOH, albeit slowly. These complexes may thus be considered as structural and functional models of vanadium-dependent haloperoxidase enzymes.

Introduction

The growing interest in vanadium chemistry has been inspired by the discovery of its bioinorganic functions.[1,2] For example, the vanadium-dependent nitrogenase enzyme features vanadium in medium oxidation states of V(II)−V(IV), postulated to bind and reduce dinitrogen.[1,2] Vanadium-dependent haloperoxidases feature vanadium in its highest oxidation state of V(V) in the active center, where it possesses a trigonal bipyramidal geometry in the resting state, being surrounded by three (equatorial) oxygen donors and axial oxygen and nitrogen (hystidine residue) donors.[3] Relying on these structural motifs, model compounds are being designed that mimic the metal coordination sphere in the active sites of vanadium-dependent enzymes, especially haloperoxidases.[1, 4−6]

We, and others, have been exploring the chemistry of the tetradentate dianionic amine bis(phenolate) ligands and tetradentate trianionic amine tris(phenolate) ligands with early transition metals.[7−10] In the course of our studies of the amine tris(phenolate) ligands chemistry, we have shown that these

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* Authors to whom correspondence should be addressed. E-mail: moshekol@post.tau.ac.il (M.K.); goldz@mail.biu.ac.il (Z.G.).

† Tel Aviv University.

‡ Bar-Ilan University.

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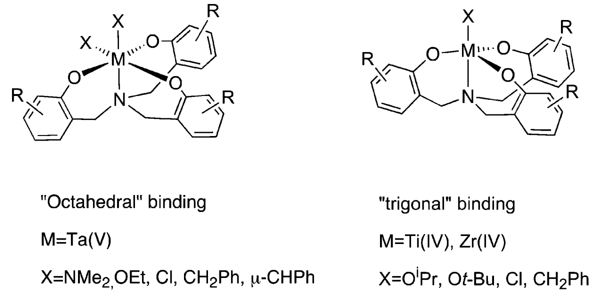

Figure 1. Two possible binding modes of the amine tris(phenolate) ligands.

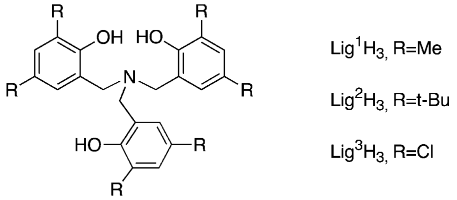

Figure 2. Amine tris(phenolate) ligands chosen for the current investigation.

ligands may coordinate to the metal in two modes. For Ti(IV), these ligands bind in a "trigonal" fashion, leading to a TBP geometry at the metal center, in which the three indistinguishable phenolate oxygens occupy equatorial positions.[7] In contrast, the "heavy" group V member (Ta) forms octahedral complexes, featuring two different types of phenolates on the NMR time scale (Figure 1).[11] The chemistry of V (IV) and (V) complexes with amine bis(phenolate) ligands was recently investigated.[12] In addition, V(V) complexes of the structurally related tris(ethanol) amine ligand were studied as a V(V) protein model.[13] However, no study concerning V chemistry with the amine tris(phenolate) ligands, which seem to provide a "natural environment" for vanadium, was reported. In addition to the expected strong binding to the metal, this ligand family may enable "fine tuning" of the complex structure and reactivity by the choice of substituents on the phenolate rings. To this end, we decided to explore the chemistry of V in different oxidation states in the amine tris(phenolate) ligand environment. Three amine tris(phenolate) ligand precursors featuring different steric and electronic effects were employed in this study and are presented in Figure 2.

Results and Discussion

$VCl_3(THF)_3$ provides a useful starting material for the entry into V(III) chemistry. The reaction of Lig^1H_3 with $VCl_3(THF)_3$ in the presence of 3 equiv of Et_3N produced a heterogeneous yellow-brown solution. Filtering off of the $Et_3N{\cdot}HCl$ and removing the solvent in vacuo gave a yellow solid. Bright-yellow crystals of **1** were obtained upon recrystallization from ether at −30 °C in 53% yield. The magnetic moment of this compound, measured by Evans' method,[14] was 2.8 μ_B, being consistent with a V(III) d^2 metal center. The ^{1}H NMR spectrum of this paramagnetic complex featured two broad absorptions of equal intensity at ca. −1 and −4 ppm that may probably be attributed to the *ortho* and *para* Me groups.

The X-ray structure of **1** revealed a mononuclear pentacoordinate complex of V(III), the fifth coordination site being occupied by a THF ligand (Figure 3). The amine tris(phenolate) ligand binds to the metal in a trigonal fashion and approximate C_3 symmetry, with the phenolate oxygens lying in equatorial positions and the amine functionality and THF ligand occupying the axial positions. The geometry around the metal center is almost perfectly trigonal bipyramidal, with the vanadium lying in the plane defined by the three phenolate oxygens (O−V−O angles sum of 359.95°). Thus, the O(THF)−V−N (179.48(7)°), O(THF)−V−O(Ph) (89.0−89.7°), and N−V−O(Ph) (90.6−90.7°) angles are very close to the expected values of 180, 90, and 90°, respectively. All V−O(Ph) bonds and V−O(Ph)−C angles lie in narrow ranges of 1.86−1.88 Å and 118.7−120.7°, respectively. The V−O(THF) and V−N dative bonds are both short, and similar, being 2.107(2) and 2.121(2) Å, respectively.

For the V(III) triamidoamine complexes, it has been shown that the occupancy (lability) of the remaining axial position in the TBP geometry may be affected by the steric bulk of the amido substituents.[15] In contrast, the relatively distant ortho Me groups on Lig^1 do not induce any steric influence on the binding of the THF ligand in the axial position. To estimate the influence of bulkier (t-Bu) groups in the *ortho* position of the phenolate rings on the structure of the resulting V(III) complex, we reacted the ligand precursor Lig^2H_3 with $VCl_3(THF)_3$. Under similar reaction conditions, and following the same workup procedure, we obtained a yellow solid (**2**). Recrystallization of **2** from saturated ether or pentane solutions upon cooling yielded only noncrystalline material, whose EA, however, was consistent with Lig^{2}V(THF) molecular formula. On the other hand, a slow evaporation of a pentane solution of **2** led to bright yellow crystals. The X-ray structure of **2** is analogous to **1**, presenting a TBP complex bearing THF ligand in the remaining axial position (Figure 4).[16] The similarity in coordination behavior of Lig^1 and Lig^2 that feature different bulk of the phenolate substituents may be correlated to their coordination tendency around Ti(IV).[7] On the other hand,

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(11) For the hexacoordinate dibenzyl complexes, a fluxional C_{3v} structure was observed in solution.[10b]

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(16) The overall structure of **2** was of low quality, being complicated by twinning, as evidenced by the disorder in the ligand's conformation, i.e., the existence of two enantiomers at the same positions. In addition, the t-Bu groups exhibit a substantial conformational disorder.

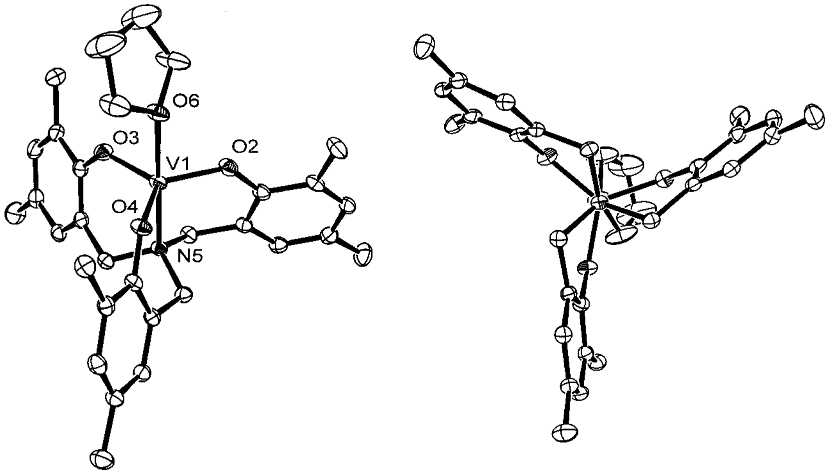


Figure 3. Crystal structure of **1**: side view and bottom view (along the N−V−O axis). This ORTEP representation shows 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): V1−O4 1.864(2), V1−O2 1.872(2), V1−O3 1.880(2), V1−O6 2.107(2), V1−N5 2.121(2); O4−V1−O2 120.51(7), O4−V1−O3 118.72(7), O2−V1−O3 120.72(7), O4−V1−O6 89.69(7), O2−V1−O6 88.94(7), O3−V1−O6 89.19(7), O4−V1−N5 90.69(7), O2−V1−N5 90.56(7), O3−V1−N5 90.93(7), O6−V1−N5 179.48(7).

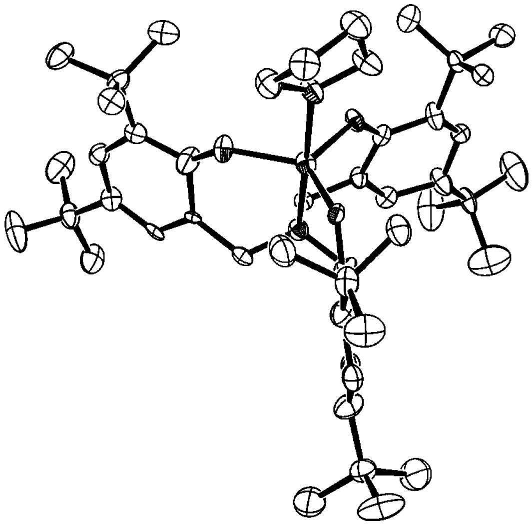
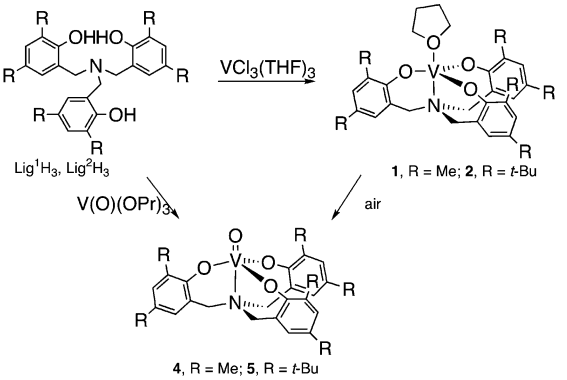


Figure 4. Crystal structure of **2**. This ORTEP representation shows 30% probability ellipsoids.[16]

the coordination of these ligands around an octahedral Ta(V) center was different: the bulky t-Bu groups precluded the straightforward reaction of the corresponding ligand precursor with $Ta(CH_2Ph)_5$ and slowed its reaction with $Ta(OEt)_5$ and $Ta(NMe_2)_5$.[10c] It may be concluded that steric effects via the phenolate ortho substituents play a less significant role when these amine tris(phenolate) ligands bind around a pentacoordinate metal center. The reaction of the electron-deficient ligand precusor, Lig^3H_3, resulted in the formation of a yellow-brown solid (**3**). ^{1}H NMR of the products indicated that no free ligand is present. **3** may be recrystallized from ether in good yield, as yellow crystals. However, the diffraction of these crystals was poor, and no structural data was obtained for this complex. Nevertheless, EA data for the recrystallized **3** supported a similar LigV(THF) structure.

Complexes **1**−**3** are extremely air-sensitive materials. Even in the crystalline state in the glovebox freezer, these yellow compounds slowly change color to violet-blue.[17] When exposed to air, C_6D_6 solutions of **1** and **2** readily change color to dark-red, forming diamagnetic complexes **4** and **5** in seconds. The IR spectra of these compounds contained signals at 956 cm^{-1} (**4**) and 962 cm^{-1} (**5**), indicative of V═O stretching.

Scheme 1. Routes to V(III) and V(V) Complexes of the Amine Tris(phenolate) Ligands Lig^1 and Lig^2



The same dark red products could be synthesized directly from the ligand precursors and the V(V) precursor $V(O)(OPr)_3$ (Scheme 1). The ^{51}V NMR spectrum for both complexes exhibited a single peak at −366 ppm (**4**) and −365 ppm (**5**) (relative to $VOCl_3$), signifying a single species in solution. These values are close to those previously reported for the vanadium oxo triethanolamine species (−387 to −380 ppm).[13] ^{1}H NMR spectra of these complexes feature 2 aromatic signals and 2 signals for the alkyl substituents, indicating a C_3 symmetry.

According to the flat broad resonance of the ligand methylene protons in **4**, both enantiomers of C_3 symmetry readily interconvert at RT (room temperature). In contrast, the ^{1}H NMR spectrum of the sterically congested **5** displays a well-defined AB system for the methylene protons at RT, indicating a higher barrier for interconversion. To quantify the inversion barrier, both complexes were subjected to

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[17] These partially oxidized species are presumed to be V(IV) hydroxo or μ-oxo. For example, see the following: Rosenberger, C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1997**, *36*, 123.

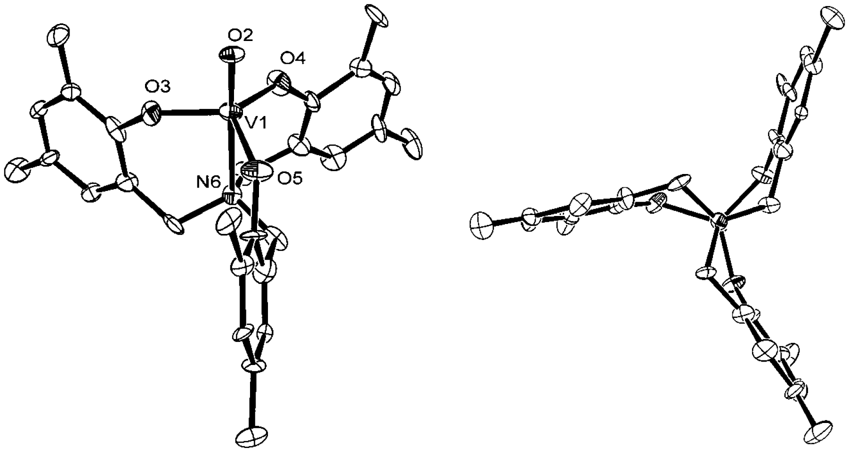

Figure 5. ORTEP representation of **4** (side view and bottom view, along the N−V−O axis), with 50% probability ellipsoids. Only 1 of 4 molecules, occupying the asymmetric unit, is shown. Selected bond distances (Å) and angles (deg): V1−O2 1.6031(3), V1−O5 1.7984(4), V1−O4 1.8018(4), V1−O3 1.8159(4), V1−N6 2.4697(4); O2−V1−O5 97.52(2), O2−V1−O4 99.14(2), O5−V1−O4 120.85(2), O2−V1−O3 99.32(2), O5−V1−O3 114.47(2), O4−V1−O3 117.99(2), O2−V1−N6 178.35(2), O5−V1−N6 81.51(1), O4−V1−N6 80.28(1), O3−V1−N6 82.30(1).

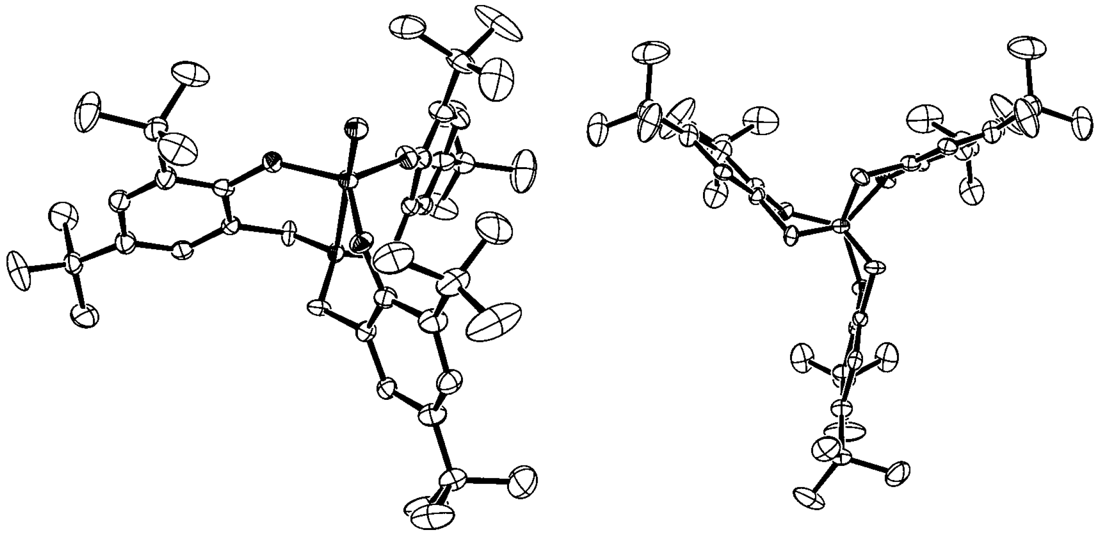

Figure 6. ORTEP representation of **5** (side view and bottom view), with 50% probability ellipsoids. Similar to the structure of **2**, both ligand conformations (both enantiomers of **5**) exist at the same positions, indicating a twinned structure. These enantiomeric conformations are well resolved and occur with equal occupancy in **5**. The second conformation and the toluene solvent were omitted for clarity.

VT NMR experiments in the temperature range of 213−353 K. For **4**, coalescence takes place at 296 K and for **5** at 346 K, corresponding to $\Delta G^{\ddagger}$ values of 58.5 and 66.7 kJ mol^{-1}, respectively.[18] In comparison, the Ti complexes of this ligand family exhibited similar, albeit slightly higher, interconversion barriers, probably due to the bulkier ligand in the axial position (O−i-Pr or 2,6-di-i-Pr−Ph).[7,8a] Notably, the differences in $\Delta G^{\ddagger}$ values between Lig^1 and Lig^2 in the Ti and V series are similar, being ca. 9 kJ mol^{-1}. It should be also noted that, due to poor solubility of **4** at low temperatures, an additional species of low symmetry could be observed below ca. 273 K.

4 is poorly soluble in most organic solvents, including THF, so its controlled crystallization was unsuccessful. Therefore, we attempted to take advantage of the higher solubility of **1** vs **4**. A saturated homogeneous yellow THF solution of **1** in a capped vial (to slow the oxidation rate) was taken out the glovebox and stored at RT for several days. The color of the solution slowly turned red, and big red prismatic crystals formed. The more soluble **5** was recrystallized from toluene. The solid-state structures of **4** and **5** (Figures 5 and 6, respectively) reveal monomeric pentacoordinate complexes of nearly TBP geometry, with the oxo function occupying the axial position, trans to the central nitrogen. These structures represent the first amine tris(phenolate) complexes featuring a doubly bonded ligand in the axial position. In the crystal structure of **4**, the symmetry was lower than expected, leading to four independent molecules in the asymmetric unit, presenting slightly different structural data. In all molecules, the V center is positioned slightly above the phenolate oxygens plane, pointing toward the oxo function. The structure of **5** is complicated by overlapping enantiomers of C_3 symmetry; however, they are well resolved in this crystal structure. The V−N bonds in both crystal structures are weak, being affected by the trans effect of a strong π-donor (oxo). The V(V) complex (**4**) exhibits shorter V−OPh bonds (1.79−1.81 Å) than the

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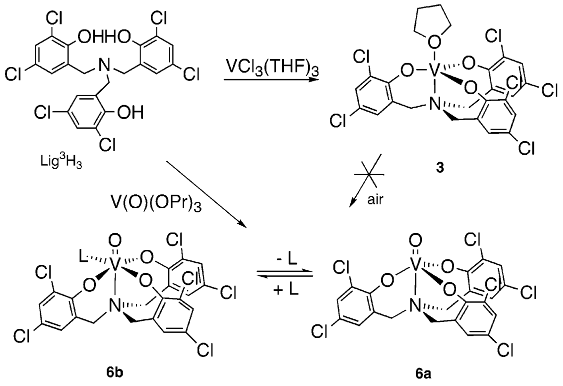
[18] The calculations were performed using the equation $\Delta G^{\ddagger} = 19.14 T_c[9.97 + \log(T_c/\delta\nu)]$: Günther, H. *NMR Spectroscopy-an Introduction*; Wiley: New York, 1980.

Scheme 2. Routes to V(III) and V(V) Complexes of the Amine Tris(phenolate) Ligand Lig^3



corresponding V(III) complex (1.87−1.88 Å). The coordination environment of V in both structures mimicks, to a large extent, the coordination environment of the metal center in vanadate-dependent HPO: both structures are TBP, in both cases the ligand set around the metal is [O$_4$N], with the amine (imine in the enzyme) ligand occupying an axial position. In the amine tris(phenolate) complexes the oxo function occupies the second axial position, whereas in the active site of the enzyme this position is occupied by a hydroxo or an aqua ligand.[3]

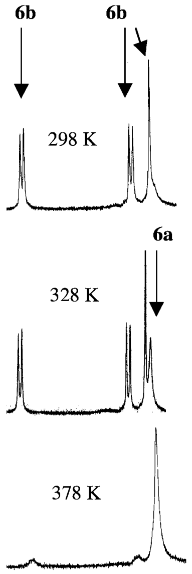


Figure 7. Benzyl (methylene) region (2.5−6 ppm) of the **6a**,**b** mixture at various temperatures.

The electron-deficient Lig^{3}H$_3$, bearing the chloro groups in *ortho* and *para* positions presented a completely different mode of reactivity (Scheme 2). When a C_6D_6 solution of the presumed **3** was exposed to air, a rapid color change (from bright yellow to blue) took place; however, no diamagnetic V species was observed by proton NMR. The reaction of V(O)(OPr)$_3$ with the electron-deficient Lig^{3}H$_3$ led to a blue diamagnetic product **6**. Unexpectedly, the ^{1}H NMR spectrum of **6** revealed two compounds, **6a**,**b**, possessing different ligand coordination environments. The minor compound, **6a**, features two aromatic signals and a broad signal in the benzyl region. Therefore, its structure is consistent with the structures of **4** and **5**, being a TBP vanadium oxo complex. The major product, **6b** (ca. 80% in C_6D_6 at RT), presents two sets of aromatic protons (2:1), an AB system for four methylene (benzyl) groups, and a sharp singlet for the remaining methylene group. This spectrum is reminiscent of the spectra of Ta(V) complexes with the amine tris(phenolate) ligands, being characteristic of the "octahedral" type of ligand binding, with a hexacoordinate metal center. An additional support for the hexacoordinate metal center comes from the ^{51}V NMR spectrum, containing a broad resonance at −226 ppm, ca. 140 ppm downfield relative to the resonance for ^{51}V nucleus in **4** and **5**. For similar ligand systems, a downfield shift is expected upon the increase in coordination number at the metal center.[19] Since the amine tris(phenolate) ligand provides only four donors, two general structural possibilities for the hexacoordinate complex may be considered. The first possibility encounters the (μ-O)$_2$ dimeric structure for the [Lig^{3}VO] (**6**) complex. Several considerations seem to support a dimeric structure. First, a similar dimeric structure (μ-X)$_2$ (X = benzylidene) was observed for the Ta complex with the amine tris(phenolate) ligands, thus showing a preference for octahedral geometry in these complexes.[10d] Second, the vanadyl tris(alkoxides) are well-known to form dimers (and higher nuclear species), making the dimeric structure of **6b** possible, if favorable thermodynamically.[19b] The second possibility is a hexacoordinate complex, containing propanol, or some other donor ligand molecules that complete the octahedral geometry. This possibility looked feasible as well, as the spectrum of **6b** contained broad signals that may be attributed to a coordinated propanol molecule (ca. 3.3, 1.3, and 0.8 ppm), even after prolonged evaporation. However, the assumed propanol could be removed in large by further evaporating a benzene solution of this material. The monomeric structure, containing a V═O function, was supported by the presence of the corresponding signal in the IR spectrum.

VT NMR experiments of **6** were performed in chlorobenzene-*d*$_5$. During the heating to ca. 378 K, two dynamic processes were observed for this mixture. First, the spectrum of **6a** is temperature-dependent (as those of **4** and **5**), exhibiting a broad signal for the ligand methylenes at RT that sharpens at elevated temperatures. More significantly, the relative ratio of **6a**/**6b** is also affected by temperature. At RT, **6a** constitutes less than 20%, while heating to 358 K leads to ca. 55% of **6a** in the products mixture. At the highest temperature employed, only traces of **6b** could be observed (Figure 7). Cooling to RT results again in a substantially higher fraction of the hexacoordinate species **6b** in the products mixture. It might be concluded that **6** is a dynamic mixture of the penta- and the hexacoordinate species and that the hexacoordinate species are more stable at lower temperature.

X-ray-quality crystals of **6b** were obtained from a saturated pentane solution at −30 °C. Two crystallographically non-

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[19] (a) Rehder, D.; Weidemann, C.; Duch, A.; Priebsch, W. *Inorg Chem.* **1988**, *27*, 584. (b) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013.

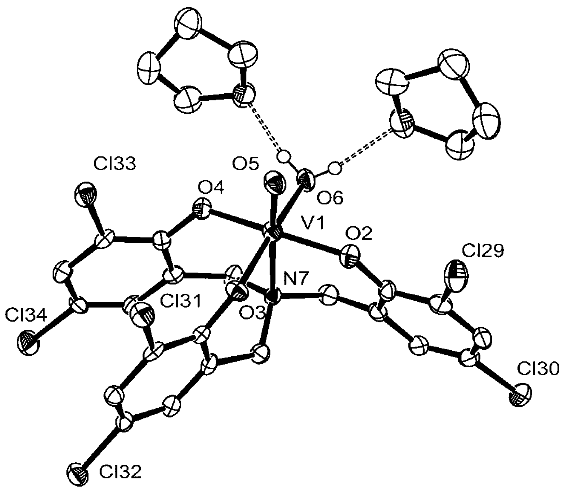
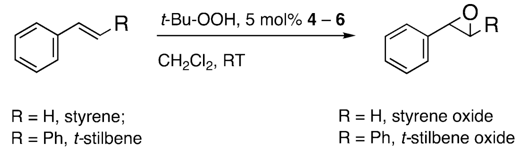


Figure 8. ORTEP representation of **6b** (50% probability ellipsoids), showing the hydrogen bonds between coordinated water molecule and two THF molecules. Selected bond distances (Å) and angles (deg): V1−O2 1.855(3), V1−O3 1.844(3), V1−O4 1.899(3), V1−O5 1.596(3), V1−O6 2.083(4), V1−N7 2.444(4); H6A−O6−H6B 111(6), O5−V1−O3 100.0 (2), O5−V1−O2 96.9(2), O3−V1−O2 97.1(2), O5−V1−O4 97.2(2), O3−V1−O4 93.4(2), O2−V1−O4 160.6(1), O5−V1−O6 94.0(2), O3−V1−O6 165.6(2), O2−V1−O6 84.2(2), O4−V1−O6 81.6 (2), O5−V1−N7 175.5(2), O3−V1−N7 84.6(1), O4−V1−N7 82.5(1), O6−V1−N7 81.4-(1).

equivalent molecules of **6b**, along with four THF molecules, comprise the asymmetric unit in this crystal structure (Figure 8). As expected, the coordination mode of the amine tris(phenolate) ligand in this complex is analogous to that of the Ta(V) amine tris(phenolate) complexes, presenting an octahedral *mer* geometry for the phenolate donors. According to its solid-state structure, **6b** is a mononuclear hexacoordinate complex, bearing an oxo function (V−O 1.596(3) Å) and an aqua ligand (V−O 2.083(4) Å), hydrogen-bonded to two THF molecules. The overall geometry of this complex is of a distorted octahedron. The V−OPh bond distances are longer in this complex than in the corresponding pentacoordinate complexes, ranging from 1.84 to 1.90 Å. In contrast, the V−N bond length in this species is substantially shorter, ranging between 2.40 and 2.44 Å.

The coordination of a water molecule to the metal center in vanadate-dependent haloperoxidases was proposed.[20] Rehder and co-workers prepared several model compounds, demonstrating water molecule(s) bound directly to vanadium, thus making the presence of water in the active center of the enzyme feasible. The structure of **6b** clearly indicates that water ligation to the V(V) metal center could switch between TBP and octahedral geometries, as a function of phenolate substituents. For the first time, the amine tris(phenolate) ligand presents a different binding mode for the same metal having the same oxidation state.[21] Assuming that Lig^3 binds in a TBP geometry in **3**, it is also noteworthy that the same ligand stabilizes different geometries around the same metal as a function of oxidation state. The different coordination geometry of the V(V) oxo center bound to Lig^3 may stem from its overall electron deficiency caused by the electron-withdrawing chloro groups. Moreover, this finding may probably point to the ability of this ligand type to undergo a reversible change of the coordination mode during the chemical reaction. Not less importantly, the structure presents a rare example of hydrogen bonding between a coordinated water molecule and H-bond acceptors (2.8−3.0 Å in the solid state).

Scheme 3. Epoxidation Reactions Catalyzed by V(V) Complexes **4**−**6**



As aforementioned, the V(V) complexes, especially those bearing oxygen-donor ligands, may be viewed as structural models for the active sites of the vanadium-dependent haloperoxidases. Overall, the V center in HPO catalyzes the oxidation (halogenation) of organic substrates. At the first step of this process, the V(V) metal center activates a peroxide molecule, whose oxygen atom will further oxidize the halide ion (X^-) to the halonium intermediate (X^+) at the subsequent steps.[1] Preliminary results suggest that the amine tris(phenolate) complexes **4**−**6** are indeed able to promote a peroxide-driven oxidation of an organic substrate (olefin). In the absence of a vanadium complex, t-BuOOH has shown no reactivity toward styrene. Adding ca. 5 mol % of **4** to a C_6D_6 solution of styrene/t-BuOOH led to the formation of styrene oxide, which was identified by ^{1}H NMR, along with some additional products. Larger-scale oxidation experiments, employing ca. 5 mol % of **4**−**6**, were carried out in dichloromethane at RT. For all vanadium complexes under investigation (**4**−**6**), epoxidation of styrene was observed (Scheme 3). The rate of the oxidation reaction was slow (4−5 turnovers/day for **4** and **5**; 2−3/day for **6**), and additional products formed, which might be attributed to the instability of the olefin employed (styrene) in the reaction medium. For the more stable albeit bulky olefin, *trans*-stilbene, epoxidation reaction involving **4** led cleanly to *trans*-stilbene oxide. The rate of stilbene oxidation using **4** was similar to the rate of styrene oxidation, i.e., ca. 2−3 turnovers/day, while both **5** and **6** led to a single turnover in 2 days. These preliminary findings indicate that V(V) complexes may be regarded as models of vanadium-dependent HPO.

In conclusion, this work demonstrates that amine tris(phenolate) ligands are suitable for stabilizing vanadium complexes in oxidation states of III and V. The preferred coordination number for V(III) complexes is 5, wherein the fifth coordination site is occupied by an additional neutral ligand (THF), even for a bulky amine tris(phenolate) ligand. Ligand electronic parameters were found to play a significant role on the oxidation chemistry of these complexes. Thus, the V(III) complexes of the amine tris(phenolate) ligands bearing electron-donating groups underwent ready oxidation to V(V) oxo complexes upon exposure to air, whereas the V(III) complex of the electron-deficient ligand did not lead

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(20) Rehder, D.; Schulzke, C.; Dau, H.; Meinke, C.; Hanss, J.; Epple, M. *J. Inorg. Biochem.* **2000**, *80*, 115 and references therein.

(21) After the submission of this manuscript, a paper describing hexacoordinate Ti(IV) complexes of an amine tris(phenolate) ligand was published. See: Fortner, K. C.; Bigi, J. P.; Brown, S. N. *Inorg. Chem.* **2005**, *44*, 2803.

Table 1. Crystallographic Experimental Details

	1	**2**	**4**	**5**	**6b**
formula	$C_{31}H_{38}NO_4V$	$C_{49}H_{66}NO_4V$	$C_{27}H_{30}NO_4V$	$C_{73}H_{98}NO_4V$	$C_{58}H_{60}Cl_{12}N_2O_{14}V_2$
fw	539.56	783.9	483.46	1104.46	1536.42
a (Å)	9.4930(2)	10.379(2)	18.4310(8)	15.5830(2)	18.5420(4)
b (Å)	17.4150(3)	11.033(2)	16.3800(3)	18.4250(3)	14.6950(4)
c (Å)	16.5300(4)	20.604(3)	31.9740(13)	22.8020(5)	23.9320(5)
α (deg)	90.00	91.93(1)	90.00	90.00	90.00
β (deg)	98.3660(7)	100.20(1)	91.853(1)	90.00	101.223(2)
γ (deg)	90.00	96.43(1)	90.00	90.00	90.00
cryst syst	monoclinic	triclinic	monoclinic	orthorombic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	Pnma	$P2_1/c$
V (Å^3)	2703.67(10)	2304.1(6)	9647.9(6)	6546.8(2)	6396.2(3)
D_c (g cm^{-1})	1.326	1.130	1.331	1.121	1.595
μ (cm^{-1})	0.404	0.256	0.444	0.199	0.859
Z	4	2	16	4	4
no. of measd reflcns	6313	7733	16 181	5956	11 759
no. of reflcns [$I > 2\sigma(I)$]	4834	3973	5535	4554	6825
R_1 [$I > 2\sigma(I)$]	0.0516	0.1327	0.0596	0.0811	0.0628
wR_2 [$I > 2\sigma(I)$]	0.1098	0.3073	0.1285	0.2266	0.1151
GOF	1.022	1.130	0.947	1.039	0.968

to V(V) species. In addition, the electronic parameters were found to affect the coordination mode of the V(V) oxo complexes. The coordination modes and the oxidation catalytic activity of these complexes make them relevant models for the active site of vanadium-containing haloperoxidase enzymes. Further studies in our laboratory are currently under way.

Experimental Section

General Methods. All syntheses of metal complexes were performed under an atmosphere of dry nitrogen in a nitrogen-filled glovebox. Ether and tetrahydrofuran were purified by reflux and distillation under dry argon atmosphere from Na/benzophenone. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. Dichloromethane was distilled over CaH_2. $VCl_3(THF)_3$, $VO(OPr)_3$, styrene, and *trans*-stilbene were purchased from Aldrich Inc and used without purification. The ligand precursors Lig^1H_3 ({2,2′,2″-[nitrilotris(methylene)]tris(4,6-dimethylphenol)}),[7] Lig^2H_3 ({2,2′,2″-[nitrilotris(methylene)]tris(4,6-di-*tert*-Bu-phenol)}),[7] and Lig^3H_3 ({2,2′,2″-[nitrilotris(methylene)]tris(4,6-dichlorophenol)})[10d] were synthesized according to previously published procedures. NMR data were recorded on a Bruker AC-200 and a Bruker Avance AC-400 spectrometers and referenced to protio impurities in benzene-d_6 (δ 7.15) and to ^{13}C chemical shift of benzene (δ 128.70). ^{51}V NMR spectra were collected on a Bruker Avance AC-400 spectrometer and referenced to $VOCl_3$ (δ 0) as an external standard. Magnetic moment determinations (according to the Evans' method)[14] were performed by measuring the chemical shift difference between a solvent peak of the dissolved paramagnetic compound (in an insert tube) and the neat solvent peak on an AC-200 spectrometer. IR measurements were done on Nicolet FT-IR 205 spectrometer using KBr disks. The ratio of olefin/epoxide was determined by ^{1}H NMR. Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem. The metal complexes were analyzed within a few hours of being taken out of the freezer of the glovebox. The X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using Mo Kα (λ = 0.7107 Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using the SIR-92 software[22] and were refined by full-matrix least squares with SHELXL-97.[23] X-ray details are provided in Table 1.

Synthesis of Complex 1. A 30 mg (0.072 mmol) amount of Lig^1H_3 and 21 mg (0.21 mmol) of Et_3N were dissolved in tetrahydrofuran (2 mL) at RT. $VCl_3(THF)_3$ (28 mg, 0.075 mmol) was dissolved in tetrahydrofuran (2 mL), forming a pink-violet solution, and cooled to −35 °C. The ligand/base solution was added dropwise to a stirred solution of $VCl_3(THF)_3$. Upon addition, the reaction color changed to yellow-brown and an off-white solid had formed. The reaction mixture was stirred at RT for 2 h, after which it was filtered and concentrated in vacuo. The resulting yellow solid was extracted with ether and left at −35 °C for 3 days, leading to formation of bright-yellow crystals. The crystals were separated from the solution, washed with ca. 2 mL of ether, and dried in vacuo for 3 h. The final yield was 52% (20 mg, 0.037 mmol). Anal. Calcd for $C_{31}H_{38}NO_4V$ ($M_r = 539.22$): C, 69.00; H, 7.10; N, 2.60. Found: C, 68.64; H, 7.29; N, 2.63.

Synthesis of Complex 2. A 111 mg (0.165 mmol) amount of Lig^1H_3 and 50 mg (0.50 mmol) of Et_3N were dissolved in tetrahydrofuran (2 mL) at RT. $VCl_3(THF)_3$ (60 mg, 0.16 mmol) was dissolved in tetrahydrofuran (2 mL), forming a pink-violet solution, and cooled to −35 °C. The ligand/base solution was added dropwise to the stirred solution of $VCl_3(THF)_3$. Upon addition, the reaction color changed to yellow-brown and an off-white solid had formed. The reaction mixture was stirred at RT for 2 h, after which it was filtered and concentrated in vacuo. The resulting yellow-brown solid was extracted with pentane and ether and left at −35 °C. After several weeks, a bright-yellow solid had formed. The solution was decanted, and the solid was washed with a small volume of a cold solvent and dried in vacuo for 3 h. The final yield was 41% (52 mg, 0.065 mmol). Anal. Calcd for $C_{49}H_{74}NO_4V$ ($M_r = 792.06$): C, 74.30; H, 9.42; N, 1.77. Found: C, 74.23; H, 9.57; N, 1.98.

Synthesis of Complex 3. A 45 mg (0.083 mmol) amount of Lig^3H_3 and 25 mg (0.16 mmol) of Et_3N in THF (2 mL) were added dropwise to a stirred solution of $VCl_3(THF)_3$ (31 mg, 0.083 mmol) in THF. The resulting heterogeneous yellow-brown mixture was stirred for 2 h at RT, after which it was filtered and concentrated in vacuo. The resulting yellow solid was extracted twice (2 mL) with ether and kept in the freezer (−33 °C) for 3 days to give bright-yellow crystals (38 mg, 0.057 mmol) in 70% yield. The crystals were dried in vacuo and subjected to elemental analysis. Anal. Calcd

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[22] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camali, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[23] Sheldrick, G. M. *SHELXL-97 Program*; University of Göttingen: Göttingen, Germany, 1996.

for $C_{25}H_{20}NO_4V$ (M_r = 539.22): C, 45.35; H, 3.04; N, 2.12. Found: C, 44.79; H, 3.52; N, 2.08.

Synthesis of Complex 4 (5) via the Oxidation of 1 (2). A yellow C_6D_6 solution of **1** (**2**) in an NMR tube was taken out the glovebox and exposed to air. The color of the solution turned dark-red immediately. According to ^{1}H NMR spectroscopy (for the spectrum of **4** (**5**), see below), no other metal species besides **4** (**5**) had formed. According to the internal standard used (hexamethylbenzene), the formation of the diamagnetic V(V) complexes was nearly quantitative.

Synthesis of 4 via V(O)(OPr)$_3$. A 38 mg (0.091 mmol) amount of Lig^{1}H$_3$ was dissolved in CH_2Cl_2 (ca. 2 mL, colorless solution), and the solution was added dropwise to a stirred pale-yellow solution of V(O)(OPr)$_3$ (22 mg, 0.090 mmol) in 1 mL of ether. The solution color changed to dark-red immediately upon mixing of the reagents. The reaction was stirred at RT for 2 h, after which the solvent was removed. The resulting red solid was washed with 2 mL of pentane and dried in vacuo for several hours, affording pure **4** in 70% yield. Anal. Calcd for $C_{27}H_{30}NO_4V$ (M_r = 483.47): C, 67.07; H, 6.25; N, 2.90. Found: C, 66.89; H, 6.28; N, 2.93. ^{1}H NMR (200 MHz, C_6D_6): δ 6.68 (br s, 3H), 6.47 (d, J = 2.1 Hz, 3H), ca. 3 (very br s), 2.41 (s, 12 H), 2.11 (s, 12H). ^{13}C NMR (100.61 MHz, C_6D_6): δ 132.89 (C), 130.75 (*C*H), 128.72 (*C*H), 128.59 (*C*), 126.45 (*C*), 125.27 (*C*), 32.75, 23.34 (*C*H$_3$), 17.29 (*C*H$_3$). ^{51}V NMR (105.26 MHz, C_6D_6): δ −366. IR (KBr): 426 (m), 573 (m), 610 (m), 690 (w), 750 (m), 862 (s), 955 (m), 1038 (w), 1094 (w), 1159 (m), 1215 (m), 1239 (s), 1377 (w), 1392 (w), 1472 (s), 2917 (m) cm^{-1}.

Synthesis of Complex 5 via V(O)(OPr)$_3$. Bright-yellow V(O)(OPr)$_3$ (40 mg, 0.16 mmol) was dissolved in CH_2Cl_2 (2 mL), and the solution was slowly added to the colorless solution of Lig^{2}H$_3$ (111 mg, 0.17 mg) in CH_2Cl_2 (3 mL). The reaction color immediately changed to dark-red. After the solution was stirred for 1 h at RT, the solvent was evaporated, leading to a dark-red solid (138 mg). According to ^{1}H NMR spectrum, the crude product consisted mostly of **5**, along with minor impurities. A 62 mg amount of the crude product was employed for recrystallization from toluene (2 mL), giving red needles (43 mg) in two crops at −35 °C (ca. 70% yield). Anal. Calcd for $C_{45}H_{66}NO_4V$ (M_r = 735.44): C, 73.44; H, 9.04; N, 1.90. Found: C, 73.19; H, 8.93; N, 2.00. ^{1}H NMR (200 MHz, C_6D_6): δ 7.43 (d, J = 2.4 Hz, 3H), 6.80 (d, J = 2.4 Hz, 3H), 3.75 (d, J = 13.1 Hz, 3H), 2.45 (d, J = 13.3 Hz, 3H), 1.75 (s, 27H), 1.31 (s, 27H). ^{13}C NMR (200 MHz, C_6D_6): δ 146.28 (*C*), 129.00 (*C*), 127.41 (*C*), 125.45 (*C*H), 123.03 (*C*H), 58.87 (*C*H$_2$), 36.27 (*C*), 35.39 (*C*), 32.46 (*C*H$_3$), 30.76 (*C*H$_3$). ^{51}V NMR (105.26 MHz, C_6D_6): δ −365. IR (KBr): 491 (m), 571 (m), 588 (m), 602 (m), 763 (m), 862 (s), 876 (m), 917 (m), 962 (m), 1127 (w), 1171 (m), 1203 (m), 1238 (s), 1362 (m), 1392 (w), 1410 (w), 1466 (s), 2960 (s) cm^{-1}.

Synthesis of Complex 6. A 133 mg (0.245 mmol) amount of Lig^{3}H$_3$ was dissolved in 2 mL of CH_2Cl_2, and the solution was added dropwise to a stirred yellow solution of V(O)(OPr)$_3$ (60 mg, 0.246 mmol) in CH_2Cl_2 (1 mL). The color of the reaction changed upon addition to dark blue. The solution was stirred for 2 h at RT, after which the solvent was evaporated, leading to a blue crude product (165 mg). The ^{1}H NMR spectrum of the crude product revealed **6**, along with some impurities. A 90 mg amount of the crude product was dissolved in ether and stored at −30 °C overnight. After removal of the solvent, **6** was obtained in 49% yield (44 mg), as dark blue needles. Anal. Calcd for $C_{25}H_{24}Cl_6NO_6V$ (**6**·$C_4H_{10}O$; M_r = 694.92): C, 43.01; H, 3.47; N, 2.01. Found: C, 42.87; H, 3.59; N, 1.84. ^{1}H NMR (200 MHz, C_6D_6): δ 7.08 (br s, Ar-H, **6a**), 7.03 (m, 3H, **6b**), 6.77 (d, J = 2.5 Hz, 2H, **6b**), 6.42 (br s, Ar-H, **6a**), 6.07 (d, J = 2.5 Hz, 1H, **6b**), 5.18 (d, J = 14.1 Hz, 2H, **6b**), ca. 2.8 (br flat s, Ar-C*H*$_2$N, **6a**), 2.78 (d, J = 13.9 Hz, 2H, **6b**), 2.40 (s, 2H, **6b**). For the spectra of **6** in chlorobenzene-d_5 at VT, see the Supporting Information. ^{13}C NMR (200 MHz, C_6D_6): δ 162.93 (*C*), 161.88 (*C*), 130.36 (*C*), 130.10 (*C*), 129.78 (*C*H), 129.60 (*C*H), 128.99 (*C*), 128.64 (*C*H), 128.49 (*C*H), 126.77 (*C*), 122.17 (*C*), 120.97 (*C*), 64.18 (*C*H$_2$), 58.31 (*C*H$_2$). ^{51}V NMR (105.26 MHz, C_6D_6): δ −226, broad. IR (KBr): 476 (w), 520 (w), 573 (m), 781 (s), 868 (s), 968 (m), 1100 (w), 1178 (s), 1219 (m), 1295 (m), 1382 (w), 1451 (s), 1558 (w), 1579 (w) cm^{-1}.

General Procedure for the Epoxidation Reaction. The appropriate metal complex was weighed in a glovebox and dissolved in dichloromethane (ca. 10 mL), and the solution was transferred to a Schlenk flask. A suitable amount (generally 20 equiv) of olefin was measured and added to the metal complex. The flask was purged with Ar for 1 min, sealed with a septum, and left under Ar atmosphere henceforth. TBHP (t-Bu hydroperoxide, 5.5 M in decane) was then added to the stirring mixture via syringe, resulting in homogeneous dark-red (blue for the solution of **6**) solution. A slow change of color (to bright-yellow) was observed during several hours. In the end of the reaction, 10 mL of water was added, and the biphasic mixture was stirred for ca. 10 min. The organic phase was separated, dried with sodium sulfate, filtered, and removed in vacuo. The final product was subjected to ^{1}H NMR.

Acknowledgment. We thank Elisheva Genizi and Sima Alfi (BIU) for technical assistance.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of complexes **1**, **2**, **4**, **5**, and **6b** and scanned VT-NMR spectra of complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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