Chlorination of a Pyrazole Ligand in Vanadium(V)alkoxo Complexes[1]

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Received December 5, 1997

Introduction

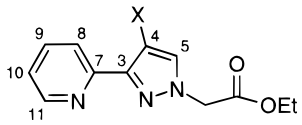
Vanadium(V) plays an important role as catalyst in a variety of oxidation reactions, in nature (vanadium bromo peroxidases[2]) as well as in technical processes (sulfuric acid production,[3] synthesis of phthalic acid[4]). Additionally, vanadium species were among the first transition metal compounds to be applied for catalytic olefin epoxidations.[5] As a consequence of the low radius/charge ratio, vanadium(V) centers are usually strong Lewis acidic, which makes them perfect candidates for the activation of peroxidic reagents. However, one-electron oxidation processes ($V^V + e^- \rightarrow V^{IV}$) may lead to radical side reactions in V(V)-catalyzed reactions. Owing to ligand exchange reactions, there is only little information on the actual structures of V(V) catalysts.[6] We are interested in structurally defined catalysts for mechanistic studies of oxidation reactions by means of spectroscopic and kinetic methods. For that reason, we developed new bidentate pyrazolylpyridine ligands equipped with long side chains to increase the solubility of the derived high-valent transition metal complexes in nonpolar organic solvents.[7−10] In the present paper, we describe the synthesis and reactivity of new vanadium oxoalkoxo complexes bearing those pyrazolylpyridine ligands.

Experimental Section

All syntheses were performed under a nitrogen atmosphere; solvents were dried and distilled before use. The NMR spectra are assigned according to Chart 1.[11]

Synthesis of (pypzCH$_2$COOEt)VO(Cl)$_2$(O-^{t}Bu) (1). PypzCH$_2$-COOEt[7] (463 mg, 2.00 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and treated with $VOCl_3$ (346 mg, 2.00 mmol) dissolved in CH_2Cl_2 (20 cm^3). After 15 min of stirring at room temperature, ^{t}BuOH (178 mg, 2.40 mmol) dissolved in CH_2Cl_2 (20 cm^3) was added dropwise to the deep red solution, which was stirred for an additional 3 h. The solution was filtered over a Whatman filter, the solvent was stripped off, the residue was washed with diethyl ether (3 × 30 cm^3), and the resulting microcrystalline, orange-colored product was dried in vacuo (486 mg, 55%). Mp: 130 °C. Anal. Calcd for $C_{16}H_{22}Cl_2N_3O_4V$ (442.22 g/mol): C, 43.46; H, 5.01; N, 9.50. Found: C, 43.07; H, 4.79; N, 9.77. IR (KBr, cm^{-1}): ν 1749 vs $\nu_{C=O}$, 983 vs $\nu_{V=O}$. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): isomer **A** δ 9.39 (d, $^3J_{10,11}$ = 5.0 Hz, 11-H), 8.38 (d, 8-H), 7.94 (dt, $^3J_{8,9}$ = 7.5 Hz, $^3J_{9,10}$ = 7.0 Hz, 9-H), 7.77 (d, $^3J_{4,5}$ = 2.0 Hz, 5-H), 7.48 (t, 10-H), 6.85 (d, 4-H), 5.44 (s, NCH$_2$), 4.20 (q, OCH$_2$), 1.90 (s, ^{t}Bu), 1.24 (t, CH$_3$); isomer **B** δ 8.94 (d, $^3J_{10,11}$ = 5.0 Hz, 11-H), 8.38 (d, 8-H), 7.89 (dt, $^3J_{8,9}$ = 7.5 Hz, $^3J_{9,10}$ = 7.0 Hz, 9-H), 7.66 (d, $^3J_{4,5}$ = 2.0 Hz, 5-H), 7.42 (t, $^3J_{9,10}$ = 7.0 Hz, 10-H), 6.89 (d, 4-H), 5.58 (s, NCH$_2$), 4.27 (q, OCH$_2$), 1.90 (s, ^{t}Bu), 1.25 (t, CH$_3$); isomer ratio **A**:**B** 1.6:1. ^{51}V NMR (105.2 MHz, 25 °C, $CDCl_3$): isomer **A** δ −464.8; isomer **B** δ − 488.4.

Chart 1



X = H: pypzCH$_2$COOEt

X = Cl: py(4-Cl-pz)CH$_2$COOEt

Synthesis of [py(4-Cl-pz)CH$_2$COOEt]VO(Cl)$_2$(O-^{t}Bu) (2). The synthesis was carried out analogous to **1**, but ^{t}BuOOH (0.34 cm^3 of a 6.5 M solution in $CHCl_3$) was used instead of ^{t}BuOH, yielding an orange-colored, microcrystalline solid (562 mg, 59%). Mp: 148 °C. Anal. Calcd for $C_{16}H_{21}Cl_3N_3O_4V$ (476.66 g/mol): C, 40.31; H, 4.44; N 8.81 Found: C, 39.74; H, 4.41; N, 8.65. IR (KBr, cm^{-1}): ν 1738 vs $\nu_{C=O}$, 981 s $\nu_{V=O}$. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): isomer **A** δ 9.46 (d, $^3J_{10,11}$ = 5.0 Hz, 11-H), 8.47 (d, $^3J_{8,9}$ = 8.0 Hz, 8-H), 8.00 (dt, $^3J_{9,10}$ = 6.5 Hz, 9-H), 7.73 (s, 5-H), 7.52 (t, $^3J_{9,10}$ = 6.5 Hz, 10-H), 5.45 (s, NCH$_2$), 4.23 (q, $^3J_{HH}$ = 7.0 Hz, OCH$_2$), 1.87 (s, ^{t}Bu), 1.25 (t, $^3J_{HH}$ = 7.0 Hz, CH$_3$); isomer **B** δ 9.35 (d, $^3J_{10,11}$ = 5.0 Hz, 11-H), 8.39 (d, $^3J_{8,9}$ = 8.0 Hz, 8-H), 8.03 (dt, $^3J_{9,10}$ = 6.5 Hz, 9-H), 7.84 (s, 5-H), 7.47 (t, $^3J_{9,10}$ = 6.5 Hz, 10-H), 5.58 (s, NCH$_2$), 4.28 (q, $^3J_{HH}$ = 7.0 Hz, OC*H*$_2$), 1.90 (s, ^{t}Bu), 1.27 (t, $^3J_{HH}$ = 7.0 Hz, CH$_3$); isomer ratio **A**:**B** 2.0:1. ^{51}V NMR (105.2 MHz, 25 °C, $CDCl_3$): isomer **A** δ −465.4; isomer **B** δ − 487.5.

Single-Crystal Structure Determination of 1 and 2. **1** and **2** were crystallized by slow diffusion of hexane into a solution of the complexes in dichloromethane. The intensity data were obtained at 223 K (**1**) and 293 K (**2**) with graphite-monochromated Mo Kα radiation on a STOE IPDS (**1**) and a CAD4 diffractometer (**2**). Preliminary positions of heavy atoms were found by direct methods (SIR92[12]), while the positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with an initially isotropic least-squares refinement (SHELXL93[13]). Hydrogen atoms were placed in calculated positions and included in the structure factor calculations but were not refined. Additional crystal data, data collection, and refinement parameters are presented in Table 1.[14]

Results and Discussion

Treatment of pypzCH$_2$COOEt with $VOCl_3$ in dichloromethane solution does not give the desired chelate complex

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(14) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101339. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, +44 1223 336 033; e-mail, teched@chemcrys.cam.ac.uk).

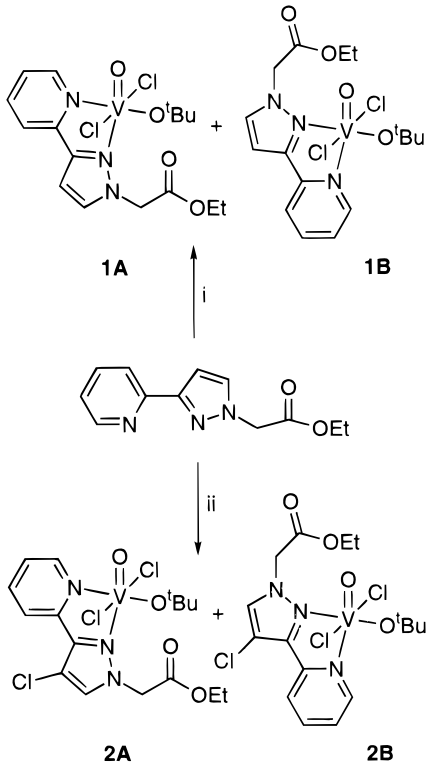
S0020-1669(97)01535-8 CCC: $15.00
Published on Web 06/25/1998

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of 1 and 2

	1	**2**
empirical formula	$C_{16}H_{22}Cl_2N_3O_4V$	$C_{16}H_{21}Cl_3N_3O_4V$
fw	442.22	476.66
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	8.406(1)	9.119(1)
b/Å	9.695(1)	12.095(1)
c/Å	13.756(2)	19.438(2)
α/deg	107.23(1)	90
β/deg	99.70(1)	102.43(1)
γ/deg	103.57(1)	90
V/Å^3	1006.1(2)	2093.6(4)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.460	1.512
μ/cm^{-1}	7.8	8.8
diffractometer	STOE-IPDS	CAD4
scan type	oscillation	ω scan
λ/Å	0.710 73	0.710 73
T/K	223	293
R^a (all data)	0.0433	0.0375
$\omega R_2{}^b$ (all data)	0.1241	0.1096

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^4]^{1/2}$. ^{c} GOF $= [\Sigma\omega(F_o^2 - F_c^2)^2/(N_O - N_V)]^{1/2}$.

Scheme 1 I. $VOCl_3$, CH_2Cl_2, ^{t}BuOH, rt, 3 h; $VOCl_3$, CH_2Cl_2, ^{t}BuOOH, rt, 3 h.



i. $VOCl_3$, CH_2Cl_2, ^{t}BuOH, room. temp., 3 h
ii. $VOCl_3$, CH_2Cl_2, ^{t}BuOOH, room. temp., 3 h.

(PypzCH$_2$COOEt)VOCl$_3$, but decomposition is observed. However, if the reaction is carried out in the presence of 1.2 equiv of ^{t}BuOH, the new six-coordinate vanadium oxoalkoxo complex **1** is obtained in good yield (Scheme 1). Owing to the asymmetric nature of the ligand, featuring two different coordinating nitrogen donor centers, complex **1** exists in two isomeric forms **A** and **B**, differing in the orientation of the aromatic rings relative to the oxo ligand. They can easily be identified by means of NMR spectroscopy, especially by ^{51}V

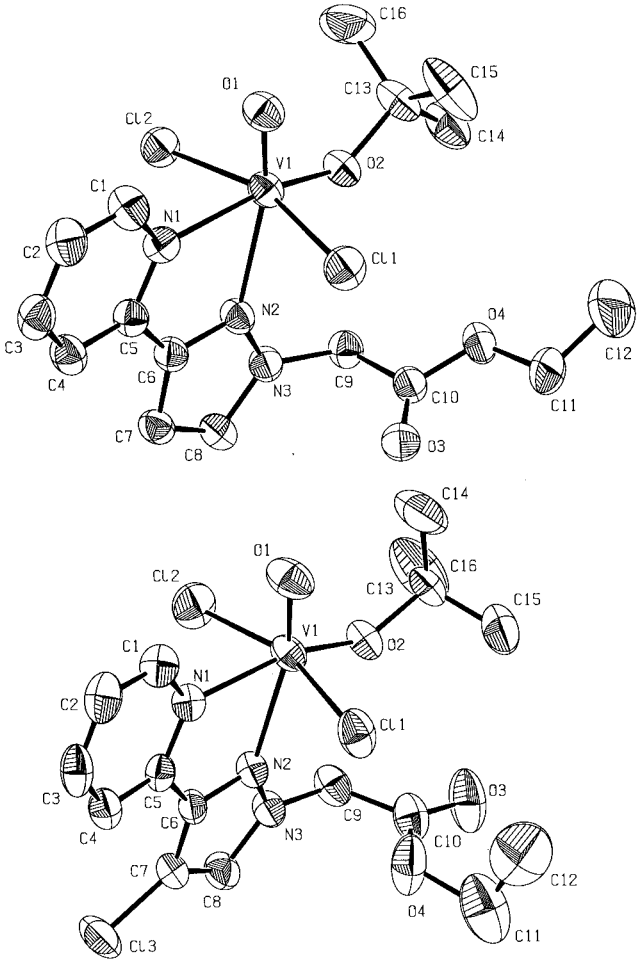


Figure 1. PLATON[26] plots of the solid-state structures of **1** (top) and **2** (bottom).

NMR.[15] Since **1** catalyzes the epoxidation of both unfunctionalized olefins and allylic alcohols in the presence of ^{t}BuOOH, we investigated the reaction of $VOCl_3$ with pypzCH$_2$COOEt and ^{t}BuOOH with the intention to isolate a ^{t}BuOO$^-$ derivative, which may be considered as the active intermediate of the epoxidation.[16,17] However, the desired complex is not obtained, but quantitative chlorination at the 4-position of the pyrazole ring does occur. The active chlorine species, which may either be Cl_2 or ^{t}BuOCl, is generated from Cl$^-$ and ^{t}BuOOH in a vanadium haloperoxidase-like reaction.[18−20] Both elemental chlorine[10] and ^{t}BuOCl are capable to chlorinate pyrazolylpyridines in the 4-position of pyrazole. The resulting *tert*-butyl alcoholato complex **2** is obtained in good yield (Scheme 1). The isomer ratio A:B, which gives an idea about the individual donor capacities of the heteroaromatic rings, is shifted slightly toward isomer **A** for **2** (2.0:1) with respect to **1** (1.6:1), in the same manner as previously reported for a series of molybdenum peroxo complexes.[1,10]

(15) The NMR spectra of **1** and **2** were assigned according to the data of the complex (L)VOCl$_2$ with L = [3-(2-pyridyl)-1-pyrazolyl]cyclohexanolate ($C_5H_4N-C_3H_2N_2-C_6H_{10}-O^-$), where the oxo ligand selectively occupies, owing to the meridionally coordinating, tridentate ligand, the trans position to the pyrazolyl moiety (isomer **A**).
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The rate of chlorination is efficiently decreased when the protons liberated during the reaction (V−Cl + HOOR → VOOR + HCl) are eliminated by the addition of amines or K_2CO_3. However, even under these milder conditions, no *tert*-butylperoxovanadium(V) complex could be isolated, but mixtures of **1** and **2** are obtained. Further treatment of **2** with excess ^{t}BuOOH does not give a *tert*-butylperoxovanadium(V) complex but leads to decomposition of the oxidizing agent.

Since only a few solid-state structures of neutral alkoxochlorooxovanadium(V) complexes have been described,[21−25] we carried out X-ray structure analyses of **1** and **2** (both isomer **A**), which finally proved the coordination geometry at the vanadium(V) centers. **1** and **2** crystallize from dichloromethane/diethyl ether as orange-red plates and needles, respectively. Figure 1 shows the molecular structures of both compounds, and a selection of characteristic bond lengths and angles is given in Table 2.

Both complexes differ only marginally in their geometries. The central vanadium atoms are coordinated in a distorted octahedrally mode, wherein the *axial* positions are occupied by the oxo ligand and the pyrazole ring of the chelate ligand and the two chloro ligands are found in trans orientation. Owing to the different trans influences of O(1) and O(2), the distance V−N(2) is about 11 pm longer than V−N(1). The larger V−O(2)−C(13) angle of **2** (about 7° with respect to **1**) indicates an increased Lewis acidity due to the chlorinated chelate ligand, which is compensated by a stronger π-back-bonding from O(2) to vanadium.

Table 2. Bond Lengths (Å) and Angles (deg) for **1** and **2**

1		**2**	
	Bond Lengths		
V−O(1)	1.575(3)	V−O(1)	1.579(2)
V−O(2)	1.740(2)	V−O(2)	1.735(2)
V−N(1)	2.216(3)	V−N(1)	2.219(2)
V−N(2)	2.310(3)	V−N(2)	2.338(2)
V−Cl(1)	2.296(1)	V−Cl(1)	2.320(1)
V−Cl(2)	2.359(1)	V−Cl(2)	2.324(1)
	Bond Angles		
O(1)−V−N(1)	91.3(1)	O(1)−V−N(1)	92.1(1)
N(1)−V−N(2)	71.0(1)	N(1)−V−N(2)	70.5(1)
O(1)−V−O(2)	104.2(1)	O(1)−V−O(2)	104.9(1)
O(1)−V−Cl(1)	96.5(1)	O(1)−V−Cl(1)	96.(1)
O(1)−V−Cl(2)	95.5(1)	O(1)−V−Cl(2)	95.1(1)
N(1)−V−Cl(1)	84.8(1)	N(1)−V−Cl(1)	81.9(1)
N(1)−V−Cl(2)	81.6(1)	N(1)−V−Cl(2)	83.5(1)
V−O(2)−C(13)	136.1(2)	V−O(2)−C(13)	142.8(2)

The vanadium complexes **1** and **2** are high active catalysts for the epoxidation of allylic alcohols in the presence of ^{t}BuOOH. Unfunctionalized olefins such as cycloalkenes are converted into the corresponding epoxides with moderate activity. Further work to investigate the catalytic potential of the complexes **1** and **2** in oxidation reactions is underway.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of complexes **1A** and **2A** is available on the Internet (as well as with the CCDC[14]). Access information is given on any current masthead page.

IC9715355

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