Oxovanadium(IV) complexes as molecular catalysts in epoxidation: Simple access to pyridylalkoxide derivatives

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Abstract

Reaction of bis(aryl)-2-pyridylmethanol ligands (**1a–7a**) with $VO(SO_4) \cdot 5H_2O$ results in the formation of metal-oxo complexes $[VO(N-O)_2]$ (**1–7**), with N-O = bis(aryl)-2-pyridylmethanol. A molecular structure of (**4**) has been determined by single crystals X-ray diffraction study, which showed the expected square planar pyramidal geometry with the pyridine ring nitrogens in *trans*-position to each other. The metal-oxo complexes (**1–4,6,7**) demonstrated the ability to catalyse epoxidation reactions of alkenes with molecular oxygen.
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1. Introduction

An application of oxovanadium(IV) compounds as oxidation catalysts was first discovered by Sharpless in the case of the regioselective epoxidation of allylic alcohols [1]. Although these oxovanadium(IV) complexes were studied intensively with *tert*-butylhydrogenperoxide as oxidant [2–4], these complexes have – with one exception: VO-(acac)$_2$ (**8**) – never been employed in oxidation catalysis with molecular oxygen [5]. To investigate the potential of these oxovanadium(IV) compounds in epoxidation catalysis with molecular oxygen, the class of vanadium complexes with bidentate N,O-ligands was synthesized [6]. Pyridyl alcohols, which consist of an aliphatic alkoxy function and an aromatic nitrogen donor atom, were used as N,O-ligands for the syntheses, because it has been shown,
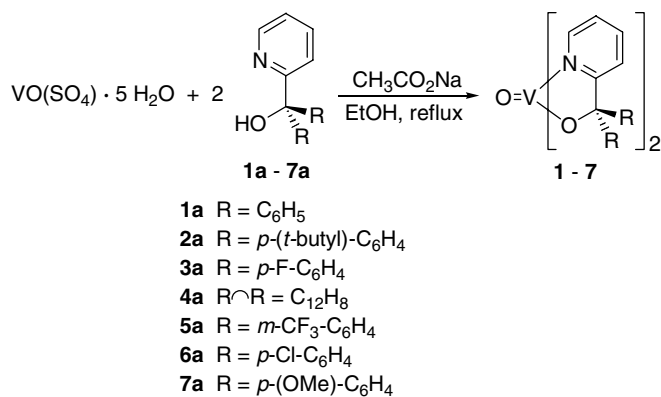
that these ligands are perfectly stable in oxidation catalysis with dioxomolybdenum(VI) complexes [7,8].

2. Results and Discussion

The new oxovanadium(IV)-complexes build up a big variety of vanadium(IV)-complexes with a bidentate N,O-ligand, which consist of an aliphatic hydroxy function combined with a nitrogen-donor of a pyridine ring and two phenyl groups at the backbone, bound to a $(VO)^{2+}$-unit. The used ligands were made by nucleophilic attack of 2-lithiumpyridine on various aromatic ketones [9,10]. After hydrolisation the prepared ligands were received pure and in high yields.

The new oxovanadium(IV) catalysts **1–7** were synthesized by a simple ligand exchange reaction of the sulphate counter ion of the starting reagent $VO(SO_4) \cdot 5H_2O$ with two equivalents of various pyridyl alcohols **1a–7a** (Scheme 1). To deprotonate each equivalent of the chelating alcohol sodium acetate was used. The driving force of this reaction

Scheme 1. Synthesis of the complexes 1–7.

1a R = C_6H_5
2a R = p-(t-butyl)-C_6H_4
3a R = p-F-C_6H_4
4a R⌒R = $C_{12}H_8$
5a R = m-CF_3-C_6H_4
6a R = p-Cl-C_6H_4
7a R = p-(OMe)-C_6H_4
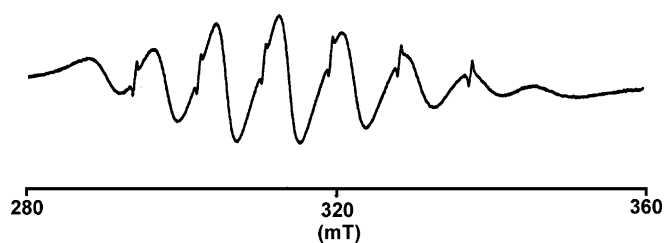

Fig. 2. ESR spectra of complex 2 at 133 K.

Fig. 1. ESR spectra of complex 2 at 293 K.

is the chelating effect of the two bidentate N,O-ligands. The same reactions were carried out with vanadium acetylacetonate as starting material, but in this case the yields were lower in comparison to the method described above.

The characterization of 1–7 is based on infrared spectroscopy. The characteristic oxovanadium stretching frequency was detected in the range between 958 and 982 cm^{-1}, which is 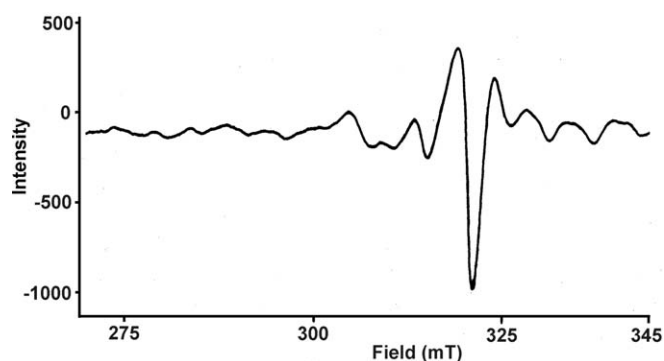in accordance to the literature (970–985 cm^{-1}) [6,11]. Additionally the aromatic stretching frequencies of the pyridine ring indicate the complexation of the oxovanadium-fragment by the ligands. The elemental analyses clearly prove the existence of the resulting complexes. Since vanadium(IV) complexes are known to be paramagnetic systems, ESR methods are applied to prove this. At room temperature, the ESR spectrum of 2 clearly shows 8 lines, as expected for an $I = 7/2$ nucleus (Fig. 1). The low temperature (133 K) ESR spectrum of 2 depicts the anisotropic behaviour, as published by Attanasio et al. for oxovanadium(IV) salen complexes (Fig. 2) [12]. In the case of 1–5 a magnetic moment of about 1.8 Bohr magnetons was detected in accordance to published data [13].

Suitable single crystals of the fluorenyl-derivative 4 for X-ray diffraction study were grown from a dichloromethane/n-hexane mixture (Fig. 3).

The structure of complex 4 can be described as a square planar pyramid. The nitrogen atoms in the pyridine rings of the ligands are positioned trans to each other. This is
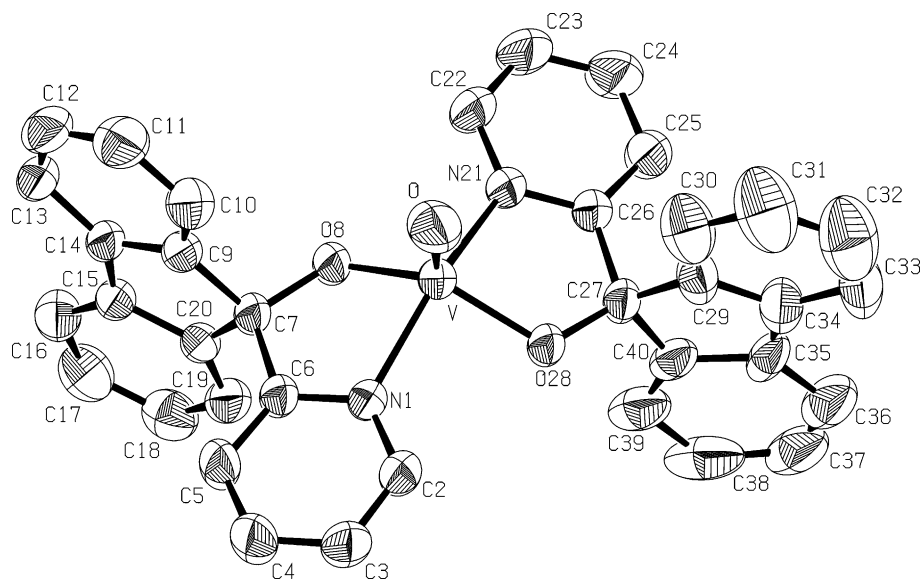

Fig. 3. ORTEP style plot [14f] of the solid state structure of complex 4. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: V–O 1.609(3), V–O8 1.885(2), V–O28 1.893(2), V–N1 2.090(3), V–N21 2.097(4), O8–C7 1.411(4), O28–C27 1.397(4); O–V–O8 114.7(1), O–V–O28 114.3(1), O–V–N1 101.9(1), O–V–N21 104.3(1), O8–V–O28 131.0(1), O8–V–N1 79.22(9), O8–V–N21 88.9(1), O28–V–N1 90.61(9), O28–V–N21 79.63(9), N1–V–N21 153.8(1), V–O8–C7 119.1(2), V–O28–C27 119.8(2).

in contrast to the structures of oxovanadium(IV) salen complexes, in which the nitrogen atoms are forced to coordinate *cis* to the vanadium center. Especially the geometry of the (*trans-O*)$_2$(*trans-N*)$_2$-V=O core is in accordance to those found in C$_{18}$H$_{20}$N$_2$O$_5$V [15] and C$_{18}$H$_{16}$N$_2$O$_3$V [16]. The V=O bond distance of 1.609(3) Å is typical for a five coordinated vanadyl species [6,17].

For a catalytic application of these complexes it is important that no possibility is given for a solvent molecule to coordinate to the vanadium center. In this case a solvent molecule could block the sixth co-ordination position and disfavour the interaction with an oxidizing agent.

If complexes **1–4**, **6** and **7** are used to change the product distribution of the autoxidation reaction with 1-octene and molecular oxygen, we found a selectivity of ~30% based on the epoxide (**1**, 33; **2**, 29; **3**, 27; **4**, 30; **6**, 27; **7**, 26% product selectivity). This is a slight improvement in selectivity compared to the autoxidation data without any catalyst (23%). The corresponding conversion curves are depicted in (Fig. 4).
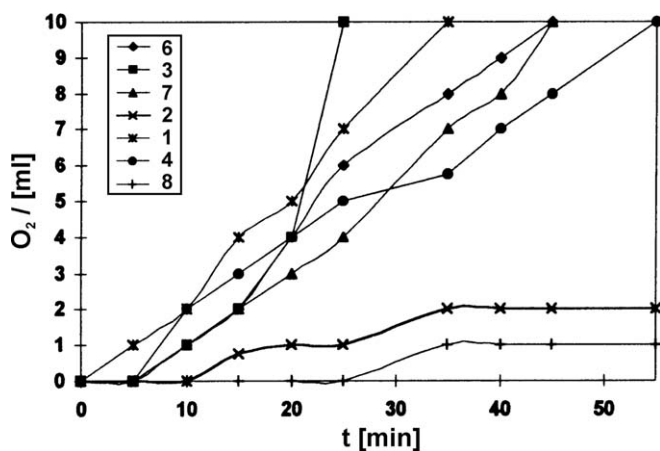
The catalytical conversion of geraniole to the corresponding epoxide was also possible (see Fig. 5). A regioselectivity of >99% corresponding to allylic double bonds was detected for the complexes **1–4**, **6** and **7** with turnover numbers (TON's) of 100–400 and turnover frequencies (TOF) of about 100 [h^{-1} (average over the first 2 h)].

3. Conclusion

The class of oxo-vandium(IV) compounds with aliphatic pyridyl alcohols can be synthesized easily via the vanadium sulphate route. A single crystal X-ray structure determination shows a square-planar pyramidal co-ordination sphere of the central vanadium atom. Contrary to the effects known for dioxomolybdenum(VI) complexes with the described pyridyl alcohols, the oxovanadium(IV) complexes feature only slight improvement in catalytic selectivity when terminal alkenes are oxidized with molecular oxygen. Further investigations are in progress to learn more about the catalytic potential of these complexes on various substrates.

4. Experimental

4.1. General comments

The ligands **1a**, **4a**, **6a** and **7a** [9], **2a** [10,20], and ligand **5a** [18] were prepared according to the literature. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried over activated molecular sieves and refluxed over appropriate drying agents under argon. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents. NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 (EI) or a Varian MAT 311a (CI) instrument. IR spectra were recorded on a Perkin–Elmer 1650 FT-IR spectrophotometer using KBr discs. GC–MS spectra were measured on a Hewlett–Packard gas chromatograph HP 5890A equipped with a mass selective detector HP 5970 B. To measure the magnetic moments via paramagnetic proton NMR, a method described by Evans was used [19].

4.2. Preparation of bis(4-fluorophenyl)-2-pyridylmethanol (3a)

Bis(4-fluorophenyl)-2-pyridylmethanol was synthesized by the published procedure [20]. To a −78 °C kept diethyl ether solution (200 ml) 80.0 ml BuLi (1.6 M in *n*-hexane) was added over 10 min. 11.5 ml (0.123 mol) of 2-bromopyridine dissolved in 25 ml diethyl ether was added over

Fig. 4. Diagram of the conversion of oxygen [in ml] vs. reaction time (*t*) of the epoxidation reaction of 1-octene at 100 °C. Complex **8** [bis(acetylacetonato)oxovanadium(IV)] was used for comparison.
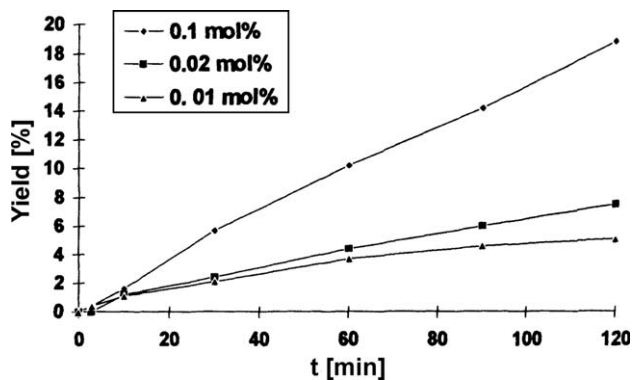
Fig. 5. Diagram of the conversion of geraniole [in %] vs. reaction time (*t*) with different concentration of catalyst **6** at 50 °C. 50 mmol geraniole, 50 mmol of a *tert*-butylhydrogenperoxide/*n*-decane solution, *x* mol% catalyst, *T* = 50 °C.

10 min. The reaction was left stirring below −40 °C for 2 h after which 0.123 mol of 4,4′-di-fluorobenzophenone dissolved in 30 ml diethyl ether was added slowly. The resulting solution was stirred for 1 h at −40 °C and overnight at room temperature. Hydrolysis was achieved using 50 ml of a saturated NH_4Cl solution. After evaporation of the ether phase, the resulting white solid was washed with methanol and recrystallized from hot methanol, giving 27.3 g (75%) of the product.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.57 (1H ($H^{6'}$), d, $^3J_{H6',H5'}$ = 4 Hz), 7.63 (1H ($H^{4'}$), dd, $^3J_{H4',H3'}$ = 8 Hz, $^3J_{H4',H5'}$ = 8 Hz), 7.33 (1H ($H^{3'}$), d, $^3J_{H3',H4'}$ = 8 Hz), 7.25 (1H ($H^{5'}$), dd, $^3J_{H5',H6'}$ = 4 Hz, $^3J_{H5',H4'}$ = 8 Hz), 7.24 (4H($H^{2'',6'',2''',6'''}$), dd, $^3J_{HH}$ = 8 Hz, $^3J_{FH}$ = 5 Hz), 7.02 (4H($H^{3'',5'',3''',5'''}$), dd, $^3J_{HH}$ = 8 Hz, $^3J_{FH}$ = 8 Hz), 6.22 (1H, s, OH). ^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): δ = 162.8 ($C^{2'}$), 161.9 ($C^{4'',4'''}$, d, $^1J_{FC}$ = 246 Hz), 147.9 ($C^{6'}$), 141.8 ($C^{1'',1'''}$, d, $^1J_{FC}$ = 21 Hz), 136.6 ($C^{4'}$), 129.5 ($C^{2',6',2'',6''}$, d, $^1J_{FC}$ = 8 Hz), 114.8 ($C^{3'',5'',3''',5'''}$, d, $^1J_{FC}$ = 21 Hz), 122.6 ($C^{3'}$), 122.5 ($C^{5'}$), 80.0 (COH). ^{19}F NMR (282 MHz, CDCl$_3$): δ = 115.8. IR (KBr, cm^{-1}): v = 3396 (s), 1590 (s), 1504 (s), 1435 (m), 1225 (s), 1156 (m), 1039 (m), 831 (s).

4.3. General method for the preparation of the complexes 1–7

A solution of 10 mmol of ligand **1a**–**7a** dissolved in 10 ml ethanol was added to a refluxing aqueous solution of VO(SO$_4$) · 5H$_2$O (5 mmol) in 5 ml water. After refluxing for 1 h, sodium acetate (15 mmol) dissolved in 10 ml water was added to the mixture and refluxed for another 2 h. The brown precipitate was collected, washed three times with 10 ml water, 10 ml ethanol, 10 ml diethyl ether, 10 ml n-pentane and dried in vacuo for 8 h. (Scheme 1). The compounds were purified by crystallization from CH$_2$Cl$_2$/n-hexane.

4.3.1. Bis{N,O-[1,1-diphenyl-1-(2′-pyridyl)methanolato]}-oxovanadium(IV) (1)

Yield: 2.13 g (73%). Anal. Calc. for C$_{36}$H$_{28}$N$_2$O$_3$V (587.56): C, 73.59; H, 4.80; N, 4.77; O, 8.17. Found: C, 73.6; H, 4.9; N, 4.8; O, 7.7%. CI-MS: m/z (%) = 587 (21, [M$^+$]), 510 (13, [M$^+$−C$_6$H$_5$]), 326 (100). IR (KBr, cm^{-1}): v = 3054 (C–H, m), 1603 (C=N, s), 1490 (C–C, s), 1470 (C–C, s), 1445 (C–C, s), 981.5 (V=O, s). μ_{eff} (293 K) = 1.81 B.M.

4.3.2. Bis{N,O-[1,1-di(4-tert-butylphenyl)-1-(2′-pyridyl)-methanolato]}oxovanadium(IV) (2)

Yield: 3.19 g (77%). Anal. Calc. for C$_{52}$H$_{60}$N$_2$O$_3$·V · H$_2$O (830.00): C, 75.25; H, 7.53; N, 3.38; O, 7.71. Found: C, 75.0; H, 7.3; N, 3.3; O, 8.2%. FAB-MS: m/z (%) = 811 (16, [M$^+$]), 678 (12, [M$^+$−(C$_6$H$_4$+ C(CH$_3$)$_3$)]), 440 (100). IR (KBr, cm^{-1}): v = 3033 (C–H, arom, m), 2962 (C–H, aliph, s), 2903 (C–H, aliph, s), 1602 (C=N, s), 1506 (C–C, arom, s), 1471 (C–C, arom, s), 1435 (C–C, arom, s), 1362 (C(CH$_3$)$_3$, m), 958 (V=O, s). μ_{eff} (293 K) = 1.85 B.M.

4.3.3. Bis{N,O-[1,1-di(4-fluorophenyl)-1-(2′-pyridyl)-methanolato]}oxovanadium(IV) (3)

Yield: 2.33 g (71%). Anal. Calc. for C$_{36}$H$_{24}$F$_4$N$_2$O$_3$V (659.52): C, 65.56; H, 3.67; F, 11.52; N, 4.25; O, 7.28; V, 7.72. Found: C, 65.7; H, 3.9; F, 11.2; N, 4.2; O, 7.3; V, 7.2%. CI-MS: m/z (%) = 659 (22, [M$^+$]), 563 (18, [M$^+$−(C$_6$H$_4$+F)]), 362 (100). IR (KBr, cm^{-1}): v = 3025 (C–H, m), 1603 (C=N, s), 1504 (C–C, s), 1472 (C–C, m), 968 (V=O, s). μ_{eff} (293 K) = 1.81 B.M.

4.3.4. Bis{N,O-[9-(2′-pyridyl)fluoren-9-olato]}-oxovanadium(IV) (4)

Yield: 2.21 g (76%). Anal. Calc. for C$_{36}$H$_{24}$N$_2$O$_3$V · H$_2$O (601.54): C, 71.88; H, 4.36; N, 4.66; O, 10.64; V, 8.47. Found: C, 71.2; H, 4.9; N, 4.9; O, 11.7; V, 8.4%. CI-MS: m/z (%) = 583 (45, [M$^+$]), 324 (100). IR (KBr, cm^{-1}): v = 3034 (C–H, m), 1602 (C–N, m), 1473 (C–C, s), 1437 (C–C, s), 969 (V=O, s). μ_{eff} (293 K) = 1.84 B.M.

4.3.5. Bis{N,O-[1,1-di(3-trifluoromethylphenyl)-1-(2′-pyridyl)methanolato]}oxovanadium(IV) (5)

Yield: 1.50 g (35%). Anal. Calc. for C$_{40}$H$_{24}$F$_{12}$N$_2$O$_3$V (859.55): C, 55.89; H, 2.81; F, 26.52; N, 3.26. Found: C, 55.5; H, 3.1; F, 26.0; N, 3.1%. CI-MS: m/z (%) = 857 (32, [M$^+$]), 713 (25, [M$^+$−C$_6$H$_4$CF$_3$]), 396 (100). IR (KBr, cm^{-1}): v = 3031 (C–H, m), 1603 (C–N, m), 1474 (m), 1441 (m), 1329 (s), 1162 (s), 1070 (m), 1050 (m), 964 (V=O, s), 819 (m), 763(s), 698 (m). μ_{eff} (293 K) = 1.83 B.M.

4.3.6. Bis{N,O-[1,1-di(4-chlorophenyl)-1-(2′-pyridyl)-methanolato]}oxovanadium(IV) (6)

Yield: 2.83 g (78%). Anal. Calc. for C$_{36}$H$_{24}$Cl$_4$N$_2$O$_3$V (725.34): C, 59.61; H, 3.34; Cl, 19.55; N, 3.86; O, 6.62; V, 7.02. Found: C, 60.2; H, 3.5; Cl, 20.0; N, 3.8; O, 6.3; V, 7.0%. CI-MS: m/z (%) = 725 (27, [M$^+$]), 614 (18, [M$^+$−(C$_6$H$_4$+Cl)]), 394 (100). IR (KBr, cm^{-1}): v = 3020 (m), 1603 (m), 1486 (s), 1471 (s), 1436 (m), 1396 (m), 1091 (s), 1040 (s), 1013 (s), 981 (V=O, s), 833 (s), 773 (m), 674 (m), 555 (w).

4.3.7. Bis{N,O-[1,1-di(4-anisyl)-1-(2′-pyridyl)-methanolato]}oxovanadium(IV) (7)

Yield: 2.40 g (68%). Anal. Calc. for C$_{40}$H$_{36}$N$_2$O$_7$V (707.66): C, 67.89; H, 5.13; N, 3.96; O, 15.83. Found: C, 67.8; H, 5.1; N, 4.0; O, 15.4%. CI-MS: m/z (%) = 707 (23, [M$^+$]). IR (KBr, cm^{-1}): v = 977 (V=O, s). μ_{eff} (293 K) = 1.71 B.M.

4.4. Procedure for the epoxidation of 1-octene with oxygen

In a Schlenk tube equipped with a stirring bar 2 ml 1-octene, 50 µml n-heptane as internal standard and 1 mol% catalyst were added. The flask was filled with 1 bar of oxygen. After thermostating at 100 °C continuously the oxygen conversion was monitored by a gasvolume-apparatus. After 10 ml of oxygen was converted the

reaction mixture was quenched to room temperature. The solution was analyzed on a gas chromatograph.

4.5. Procedure for the epoxidation of geraniole with tert-butylhydrogenperoxide

In a Schlenk tube equipped with a stirring bar 6.8 ml (50 mmol) geraniole, 50 μml diethyl ether as internal standard and catalyst **6** were added. After thermostating at 50 °C a *tert*-butylhydrogenperoxide/*n*-decane solution (50 mmol) was added. Every 30 min a probe was analyzed on a gas chromatograph.

4.6. Single crystal X-ray structure determination of complex $4 \cdot 1/2CH_2Cl_2$

X-ray-quality crystals of $4 \cdot 1/2CH_2Cl_2$ were obtained directly from the preparation as described above. Preliminary examination and data collection was carried out on a four-circle diffractometer (NONIUS CAD4) with graphite monochromated Mo Kα radiation (0.71073 Å). A dark red single crystal of $4 \cdot 1/2CH_2Cl_2$ with dimensions $0.51 \times 0.51 \times 0.46$ mm was sealed in a capillary. Cell constants were obtained from least-squares refinements using a setting angles of 25 carefully centered reflections in the range $20.2° < \theta < 24.3°$. The intensities of three representative reflections monitored every 200 reflections showed no sign of significant decay [14a]. The data were corrected for Lorentz and Polarisation effects. No absorption correction was applied. A total number of 6393 reflections were collected. Seven hundred and forty two negative intensities together with 186 systematically absent reflections were rejected from the original data set. After merging ($R_{int} = 0.0190$), a sum of 5284 independent reflections remained and were used for all calculations [14b]. The structure was solved by a combination of direct methods [14c] and difference Fourier syntheses [14d]. All "heavy atoms" of the asymmetric unit were refined anisotropically. All hydrogen atoms were calculated in ideal positions. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)_2$ with SHELXL-93 weighting scheme. Maximum shift/esd < 0.001 and maximum and minimum peaks in the final difference Fourier Synthesis were 0.84 and -0.53 e Å^{-3}, respectively. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for X-Ray Crystallography* [14e]. Crystallographic data for $4 \cdot 1/2CH_2Cl_2$ are summarized in Table 1.

Appendix A. Supplementary data

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-289230 ($4 \cdot 1/2CH_2Cl_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.11.034.

Table 1
Crystallographic data for $\{[(C_{12}H_8)(NC_5H_4)CO]_2V{=}O\} \cdot 1/2CH_2Cl_2$ ($4 \cdot 1/2CH_2Cl_2$)

	$4 \cdot 1/2CH_2Cl_2$
Formula	$C_{73}H_{50}Cl_2N_4O_6V_2$
F_w	1251.95
Color/habit	Dark red/octahedron
Crystal dimensions (mm^3)	$0.51 \times 0.51 \times 0.46$
Crystal system	Monoclinic
Space group	$I2/a$ (No. 15)
a (Å)	18.728(5)
b (Å)	19.507(2)
c (Å)	17.144(4)
β (°)	102.79(1)
V (Å^3)	6108(2)
Z	4
T (K)	293
D_{calc} (g cm^{-3})	1.361
μ (mm^{-1})	0.452
$F(000)$	2576
θ Range (°)	1.53–26.02
Index ranges (h,k,l)	h: -23 to $22/k$: 0–24/l: 0–21
No. of reflections collected	6393
No. of independent reflections/R_{int}	5284/0.0190
No. of observed reflections ($I > 2\sigma(I)$)	4691
No. of data/restraints/parameters	5284/0/393
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0557/0.1520
R_1/wR_2 (all data)[a]	0.0628/0.1563
GOF (on F^2)[a]	1.038
Largest differential peak and hole (e Å^{-3})	$+0.84/-0.53$

[a] $R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\Sigma[w(F_o^2 F_c^2)^2]/(n - p)\}^{1/2}$.

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