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Vanadium(V) Complexes of a Chelating Dianionic [ONNO]-Type Amine Bis(Phenolate) Ligand: Synthesis and Solid State and Solution Structures

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The reaction between $VO(OR)_3$ (R = ^{i}Pr, ^{t}Bu, CH_2CF_3) and the chelating dianionic bis(phenoxy)amine ligand [ONNO]-H_2 affords a mixture of two isomers (**A** and **B** in a ratio **A**:**B** ∼ 3:1) formulated as VO(OR)[ONNO] (**1a**–**c**) (R = ^{i}Pr (**1a**), ^{t}Bu (**1b**), CH_2CF_3 (**1c**)). Multinuclear and NOESY NMR spectroscopy experiments were able to determine the structure in solution of the complexes. Both isomers have the symmetry-related phenolate groups in a trans configuration, the difference arising from the different configuration of the oxo and alkoxo ligands being located either cis (in isomer **A**) or trans (in isomer **B**) to the tripodal amino nitrogen donor atom and the (dimethylamino)-ethyl sidearm respectively for the oxo and the alkoxo ligands. Crystals of isomer **A** (*cis*-**1a**) were obtained, and the structure determination confirms the arrangement of the ligands around the vanadium center. Analogue complexes VO(X)[ONNO] (X = Cl (**2**); X = N_3 (**3**)) were prepared by reacting equimolar amount of [ONNO]H_2 and $VO(X)_n(OR)_{3-n}$ (X = Cl, R = Et, n = 1; X = N_3, R = ^{i}Pr, n = 2) at ambient temperature. Compounds **2** and **3** were further characterized by NMR spectroscopy experiments and X-ray structure determination. For both **2** and **3**, a single isomer is obtained, having a *trans*-(O,O) configuration for the phenolate groups and a trans configuration of the oxo ligand in respect to the tripodal amino nitrogen donor atom. Finally, complex **2** could also be obtained by chlorination of **1a** or **3** using a large excess of $ClSiMe_3$ in refluxing toluene.

Introduction

The increased interest in the development of new ancillary ligand systems for early transition metals is driven by the quest for new α-olefin polymerization catalysts.[1] Particularly, group IV nonmetallocene complexes based on chelating diamido[1a,2−4] or dialkoxo[1a,5−6] ligands have attracted considerable attention, with report of the first living polymerization of 1-hexene at ambient temperature[2a,3a] or the highly isospecific living polymerization of 1-hexene.[5a] Furthermore, vanadium-based catalysts in homogeneous Ziegler−Natta polymerization have been known for about half a century.[7]

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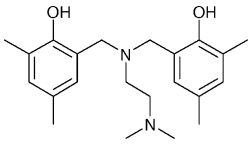

[ONNO]H$_2$

Figure 1. Structure of [ONNO]-type bis(phenoxy)amine ligand.

Although generally less active, their use presents a number of interesting advantages:[8] (1) the synthesis of high molecular weight polymers with narrow polydispersity; (2) the preparation of ethylene/α-olefin copolymers with high α-olefin incorporation; (3) the preparation of syndiotactic polypropylene. The major reason for the low activity of these systems is their deactivation during the polymerization process, probably due to reduction of catalytically active vanadium species to low-valent, less active or inactive species. As part of an ongoing study of vanadium chemistry with various supporting ligands,[9] in particular directed toward vanadium complexes for olefin polymerization, we have recently used ancillary diamido with sterically demanding protecting groups[10] or imido ligands[11] on vanadium(IV) complexes as a way to overcome the problem of deactivation by stabilization of the formal oxidation state of the vanadium center. In this study, we describe the synthesis and structure of oxo−vanadium(V) complexes of a chelating dianionic [ONNO]-type bis(phenoxy)amine ligand (Figure 1), a ligand family that was successfully introduced by Kol et al. for group IV metals.[5a]

Experimental Section

General Remarks. Starting materials for ligand precursor synthesis were purchased from Aldrich Inc. or Fluka Inc. and used as received. All experiments requiring a dry atmosphere were performed using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon, collected by distillation, and stored in the drybox over 4 Å molecular sieves. The ligand [ONNO]H$_2$ was prepared according to a known synthesis.[5e] All vanadium precursors $VO(NEt_2)_3$, $VO(O^tBu)_3$, $VO(OCH_2CF_3)_3$, and $VO(O^iPr)(N_3)_2$ were prepared as published previously.[12−15] $VO(O^iPr)_3$, $VOCl_3$, and $VO(OEt)_3$ were purchased from Aldrich Inc. NMR solvents were sparged with argon and stored over 4 Å molecular sieves in a drybox. NMR data were recorded using AMX-400, DPX-300, or AC-200 MHz Bruker spectrometers and referenced internally to residual protonated-solvent (^{1}H) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F NMR (188.298 MHz) spectra were recorded on a Bruker AC-200 spectrometer (reference CF_3CO_2H). ^{51}V NMR (105.17 MHz) spectra were recorded on a Bruker AMX-400 spectrometer (reference $VOCl_3$ in C_6D_6: 9:1). NOESY experiments were performed on a 400 MHz spectrometer at room temperature. Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France).

VO(OR)[ONNO] (1a−c) (R = ^{i}Pr, ^{t}Bu, CH_2CF_3). General Procedure. A solution of ligand precursor [ONNO]H$_2$ (0.56 mmol) in toluene (2 mL) was added dropwise to a solution of $VO(OR)_3$ (R = ^{i}Pr, ^{t}Bu, CH_2CF_3) (0.56 mmol) in toluene (2 mL) at room temperature. The reaction mixture was stirred during 2 h, and the volatiles were removed under vacuum.

Complexes *cis*-1a and *trans*-1a. A mixture of *cis*-**1a** and *trans*-**1a** was obtained as a blue solid (73% yield, ratio 75:25). IR: 946 and 953 ($\nu_{V=O}$). Anal. Calcd for $C_{25}H_{37}N_2O_4V$: C, 62.49; H, 7.76; N, 5.83. Found: C, 62. 42; H, 7.99; N, 5.80.

***cis*-1a.** ^{1}H NMR (C_6D_6): δ 7.14 (s, 2H, Ar), 6.82 (s, 2H, Ar), 6.23 (sept, $J = 5.2$ Hz, 1H, C*H*$(CH_3)_2$), 3.92 (d, $J = 13.6$ Hz, 1H, CH_2), 3.55 (d, $J = 13.6$ Hz, 1H, CH_2), 2.61 (s, 6H, ArCH_3), 2.47 (s, 6H, N(CH_3)$_2$), 2.42 (s, 6H, ArCH_3), 2.12 (m, 2H, CH_2), 2.07 (m, 2H, CH_2), 1.65 (d, $J = 6.0$ Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 164.6, 131.1, 127.0 (Ar), 86.2 (*C*H$(CH_3)_2$), 62.2 (Ar*C*H$_2$), 56.4 (*C*H$_2$), 54.2 (*C*H$_2$), 48.7 (N(*C*H$_3$)$_2$), 25.7 (CH(*C*H$_3$)$_2$), 21.1 (*C*H$_3$), 17.2 (*C*H$_3$). ^{51}V NMR (C_6D_6): δ −471.

***trans*-1a.** ^{1}H NMR (C_6D_6): δ 7.05 (s, 2H, Ar), 6.76 (s, 2H, Ar), 5.81 (sept, $J = 6.0$ Hz, 1H, C*H*$(CH_3)_2$), 4.19 (d, $J = 13.2$ Hz, 2H, CH_2), 3.12 (d, $J = 13.2$ Hz, 2H, CH_2), 2.63 (s, 6H, ArCH_3), 2.54 (s, 6H, N(CH_3)$_2$), 2.38 (s, 6H, ArCH_3), 2.06 (m, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.32 (d, $J = 6.0$ Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 163.8, 131.2, 127.5 (Ar), 85.0 (*C*H$(CH_3)_2$), 62.5 (Ar*C*H$_2$), 58.2 (*C*H$_2$), 50.8 (N(*C*H$_3$)$_2$), 50.7 (*C*H$_2$), 25.2 (CH(*C*H$_3$)$_2$), 21.0 (*C*H$_3$), 17.5 (*C*H$_3$). ^{51}V NMR (C_6D_6): δ −440.

Complexes *cis*-1b and *trans*-1b. A mixture of *cis*-**1b** and *trans*-**1b** was obtained as blue solid (76% yield, ratio 73:27). Anal. Calcd for $C_{26}H_{39}N_2O_4V$: C, 63.15; H, 7.95; N, 5.66. Found: C, 63.41; H, 8.07; N, 6.01.

***cis*-1b.** ^{1}H NMR (C_6D_6): δ 7.09 (s, 2H, Ar), 6.81 (s, 2H, Ar), 3.98 (d, $J = 14.0$ Hz, 2H, CH_2), 3.54 (d, $J = 14.0$ Hz, 2H, CH_2), 2.55 (s, 6H, ArCH_3), 2.42 (s, 6H, N(C*H3*)$_2$), 2.41 (s, 6H, ArCH_3), 2.19 (m, 2H, CH_2), 2.07 (m, 2H, *CH*$_2$), 1.80 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 164.4, 131.0, 127.0 (Ar), 86.0 (*C*$(CH_3)_3$), 62.6 (Ar*C*H$_2$), 56.2, 54.2 (*C*H$_2$), 48.7 (N(*C*H$_3$)$_2$), 31.7 (C(*C*H$_3$)$_3$), 21.1, 17.4 (*C*H$_3$). ^{51}V NMR (C_6D_6): δ −523.

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Table 1. Crystal Data and Structure Refinement Parameters for **1a**, **2,** and **3**

	1a	**2**	**3**
chem formula	$C_{25}H_{37}N_2O_4V$	$C_{44}H_{60}Cl_2N_4O_6V_2$	$C_{22}H_{30}N_5O_3V$
fw	480.51	913.74	463.45
cryst system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	Ia	$Pna2_1$
a, Å	14.008(5)	15.035(2)	15.370(2)
b, Å	13.075(5)	11.1489(6)	7.968(7)
c, Å	13.863(5)	27.935(2)	18.324(2)
α, deg	90.0	90.0	90.0
β, deg	103.462(5)	105.296(8)	90.0
γ, deg	90.0	90.0	90.0
V, Å^3	2469.3(16)	4516.6(7)	2244.1(6)
Z	4	4	4
D_{calc}, g cm^{-3}	1.293	1.344	1.372
μ(Mo Kα), mm^{-1}	0.434	0.582	0.475
F(000)	1024	1920	976
2*θ* range, deg	3.3−52.1	3.3−52.1	2.9−48.4
measd reflcns	18 908	17 555	12 304
unique reflcns/R_{int}	4820/0.0303	8710/0.0624	3205/0.0890
params/restraints	297/0	535/2	287/1
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0344$, $wR_2 = 0.0876$	$R_1 = 0.0485$, $wR_2 = 0.1043$	$R_1 = 0.0430$, $wR_2 = 0.0972$
Final R indices all data	$R_1 = 0.0468$, $wR_2 = 0.0927$	$R_1 = 0.0775$, $wR_2 = 0.1186$	$R_1 = 0.0578$, $wR_2 = 0.1044$
Flack param		0.51(3)	−0.03(2)
goodness of fit	1.021	0.994	0.976
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^3	0.353, −0.319	0.422, −0.323	0.317, −0.304

trans-1b. ^{1}H NMR (C_6D_6): *δ* 7.03 (s, 2H, Ar), 6.78 (s, 2H, Ar), 4.05 (d, J = 13.6 Hz, 2H, CH_2), 3.20 (d, J = 13.6 Hz, 2H, CH_2), 2.63 (s, 6H, N(C*H*3)$_2$), 2.60 (s, 6H, ArCH_3), 2.38 (s, 6H, ArCH_3), 2.07 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 1.42 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (C_6D_6): *δ* 164.5, 130.9, 127.3 (Ar), 86.3 (C(CH$_3$)$_3$), 62.2 (ArCH$_2$), 58.0 (CH$_2$), 51.0 (CH$_2$), 48.7 (N(CH$_3$)$_2$), 31.1 (C(CH$_3$)$_3$), 21.1, 17.5 (CH$_3$). ^{51}V NMR (C_6D_6): *δ* −477.

Complexes *cis*-1c and *trans*-1c. A mixture of *cis*-**1c** and *trans*-**1c** is obtained as a dark blue solid (80% yield, ratio 72:28). IR: 951 and 959 ($\nu_{V=O}$). Anal. Calcd for $C_{24}H_{32}F_3N_2O4V$: C, 55.39; H, 6.20; N, 5.38. Found: C, 55.10; H, 6.28; N, 5.21.

cis-1c. ^{1}H NMR (C_6D_6): *δ* 6.98 (s, 2H, Ar), 6.68 (s, 2H, Ar), 5.47 (q, $^3J_{H-F}$ = 8.4 Hz, CH_2CF$_3$), 4.42 (d, J = 13.5 Hz, 2H, CH_2), 2.87 (d, J = 13.5 Hz, 2H, CH_2), 2.55 (s, 6H, Ar−CH_3), 2.33 (s, 6H, Ar−CH_3), 2.27 (s, 6H, N(CH_3)$_2$), 1.96 (m, 2H, CH_2), 1.47 (m, 2H, CH_2). ^{13}C NMR (C_6D_6): *δ* 162.7, 131.5, 128.5 (Ar), 125.9 (q, $^1J_{C-F}$ = 275.1 Hz, CH$_2$$CF_3$), 76.0 (q, $^2J_{C-F}$ = 33.1 Hz, CH$_2$CF$_3$), 63.3 (ArCH$_2$), 58.9 (CH$_2$), 50.7 (N(CH$_3$)$_2$), 49.6 (CH$_2$), 21.0, 17.2 (CH$_3$). ^{51}V NMR (C_6D_6): *δ* −445. ^{19}F NMR (C_6D_6): *δ* 0.55 (t; $^3J_{H-F}$ = 9.6 Hz).

***trans*-1c.** ^{1}H NMR (C_6D_6): *δ* 7.08 (s, 2H, Ar), 6.77 (s, 2H, Ar), 5.70 (q, $^3J_{H-F}$ = 8.4 Hz, CH_2CF$_3$), 3.85 (d, J = 13.6 Hz, 2H, CH_2), 3.45 (d, J = 13.6 Hz, 2H, CH_2), 2.53 (s, 6H, ArCH_3), 2.41 (s, 6H, N(CH_3)$_2$), 2.39 (s, 6H, ArCH_3), 2.01 (m, 2H, CH_2), 1.95 (m, 2H, CH_2). ^{13}C NMR (C_6D_6): *δ* 164.7, 131.2, 126.8 (Ar), 125.3 (q, $^1J_{C-F}$ = 271.2 Hz, CH$_2$$CF_3$), 78.1 (q, $^2J_{C-F}$ = 33.1 Hz, CH$_2$CF$_3$), 62.4 (ArCH$_2$), 56.3 (CH$_2$), 54.6 (CH$_2$), 48.4 (N(CH$_3$)$_2$), 21.0 (CH$_3$), 16.8 (CH$_3$). ^{51}V NMR (C_6D_6): *δ* −477. ^{19}F NMR (C_6D_6): *δ* 0.19 (t; $^3J_{H-F}$ = 9.0 Hz).

VO(Cl)[ONNO] (2). Method 1. A solution of ligand precursor [ONNO]H$_2$ (200 mg, 0.56 mmol) in toluene (2 mL) was added dropwise to a solution of VO(OEt)$_2$Cl (108 mg, 0.56 mmol) in toluene (2 mL) at room temperature. The color changed immediately from pale yellow to dark blue. The reaction mixture was stirred for 1 h, and the volatiles were removed under reduced pressure to give a dark oil. This oil was washed with pentane and dried to give a dark blue solid. Anal. Calcd for $C_{22}H_{30}ClN_2O_3V$: C, 57.83; H, 6.62; N, 6.13. Found: C, 57.08; H, 6.34; N, 5.89. IR: 947 ($\nu_{V=O}$). ^{1}H NMR ($CDCl_3$): *δ* 7.07 (s, 2H), 6.89 (s, 2H), 4.44 (d, J = 13.8 Hz, 2H, ArCH_2), 3.31 (d, J = 13.8 Hz, 2H, ArCH_2), 2.63 (s, 6H, ArCH_3), 2.51 (s, 6H, N(CH_3)$_2$), 2.49 (m, 2H, CH_2), 2.37 (s, 6H, ArCH_3), 2.07 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): *δ* 165.5, 133.7, 132.1, 129.8, 127.5, 124.3 (Ar), 63.5 (ArCH$_2$), 59.6 (CH$_2$), 51.2 (N(CH$_3$)$_2$), 50.8 (CH$_2$), 21.02, 16.92 (CH$_3$). ^{51}V NMR (C_6D_6): *δ* −355.

Method 2 (Starting from 1a−c or 3). A solution of **1a**−**c** or **3** (0.80 mmol) in toluene (4 mL) was treated with 5 equiv of Me$_3$SiCl (4 mmol) and heated at 110 °C in a screw cap vial during 14 h (*caution*: *closed flask heating*). The dark solution was filtered off, washed with pentane, and dried to give quantitatively VO(Cl)(ONNO) as a dark blue solid.

VO(N$_3$)[ONNO] (3). A solution of ligand precursor [ONNO]H$_2$ (200 mg, 0.56 mmol) in THF (2 mL) was added dropwise to a solution of VO(O^{i}Pr)(N$_3$)$_2$ (118 mg, 0.56 mmol) in THF (2 mL) at room temperature (*caution*: *azido compounds are potent explosives*). The color changed immediately from yellow to dark blue. After 15 min, orange crystals were filtered off and dried (78% yield). Anal. Calcd for $C_{22}H_{30}N_5O_3V$: C, 57.02; H, 6.52; N, 15.11. Found: C, 56.91; H, 6.65; N, 14.83. IR: 954 ($\nu_{V=O}$). ^{1}H NMR (CD_2Cl_2): *δ* 7.05 (s, 2H), 6.86 (s, 2H), 4.18 (d, J = 13.7 Hz, 2H, ArCH_2), 3.33 (d, J = 13.7 Hz, 2H, ArCH_2), 2.55 (s, 6H, ArCH_3), 2.47 (s, 6H, N(CH_3)$_2$), 2.44 (m, 2H, CH_2), 2.33 (s, 6H, ArCH_3), 2.00 (m, 2H, CH_2). ^{13}C NMR (CD_2Cl_2): *δ* 164.0, 133.6, 131.6, 129.0, 126.9, 124.9 (Ar), 63.6 (ArCH$_2$), 60.0, 52.0 (CH$_2$), 50.8 (N(CH$_3$)$_2$), 21.3, 17.2 (CH$_3$). ^{51}V NMR (C_6D_6) *δ* −356.

Crystal Structure Determination of 1a, 2, and 3. For the three compounds data collection were collected at low temperature (T = 180 K) on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using a graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) (see Table 1). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and the crystal decay was monitored during data collection by measuring 200 reflections by image; no significant fluctuation of intensities has been observed. Structures have been solved by means of direct methods with the program SIR92;[16] subsequent difference Fourier maps and models were

(16) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

refined by least-squares procedures on F^2 by using SHELXL-97[17] integrated in the package WINGX version 1.64,[18] and empirical absorption corrections were applied to the data.[19] All hydrogen atoms have been located on difference Fourier maps and introduced in the refinement as fixed contributors using a riding model with an isotropic thermal parameter fixed at 20% higher than those of the C sp^2 atoms and 50% for the C sp^3 atoms to which they were connected; concerning the methyls groups, they were refined with the torsion angle as free variable. For the three compounds all non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement weighting schemes have been used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. For the compounds **2** and **3** the absolute configuration was assigned on the basis of the refinement of Flack's enantiopole parameter x,[20] which is the fractional contribution of $F(-h)$ to the observed structure amplitude as depicted in the formula $F_o^2 = (1 - x)F(h)^2 + xF(-h)^2$; this parameter is sensitive to the polarity of the structure. This parameter was found close to 0 for **3** which clearly indicated the good choice of the enantiomer refined but was found near to 0.5 for **2** which indicates the possibility of the presence of racemic twin. All attempts to solve compound **2** in the corresponding centrosymmetric space group failed; this seems to prove the presence of twin problem. Consequently **2** was refined using the following twin law: $\bar{1}00$, $0\bar{1}0$, $00\bar{1}$. For all compounds the criteria for a satisfactory complete analysis were the ratios of root-mean-square shift standard deviation being less than 0.1 and no significant features in final difference Fourier maps.

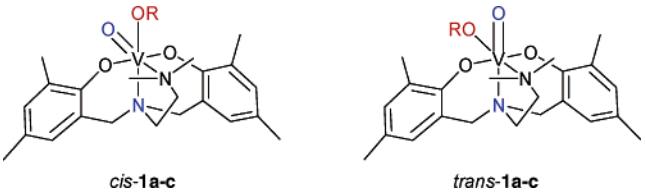
Results and Discussion

An entry to the desired vanadium(V) amine bis(phenolate) complexes was first sought via the metathesis reaction between $VOCl_3$ and the dipotassium salt of the ligand precursor K_2[ONNO] (obtained by the reaction of [ONNO]-H_2 over excess K in THF). Attempting this reaction at low (−78 °C) or ambient temperature did not lead to the desired product, and only unidentified, possibly reduced vanadium, species were obtained. Another approach was the reaction between $VO(NEt_2)_3$ and [ONNO]H_2. However, even under forcing conditions (toluene, reflux), we did not observe the metathesis reaction. We therefore reacted alkoxide starting complexes $VO(OR)_3$ (R = ^{i}Pr, ^{t}Bu, CH_2CF_3) directly with the bisphenol ligand [ONNO]H_2 in toluene at room temperature. Under these conditions, the reactions proceeded rapidly, the colorless solution turning dark blue, yielding the corresponding oxo−alkoxo complexes VO(OR)[ONNO] (**1a**−**c**) (R = ^{i}Pr (**1a**), ^{t}Bu (**1b**), CH_2CF_3 (**1c**)) as dark blue solids (Scheme 1).

Scheme 1. Synthesis of Alkoxo−[ONNO] Vanadium(V) Complexes

$$VO(OR)_3 + [ONNO]H_2 \xrightarrow{\text{toluene, RT}} VO(OR)[ONNO]$$

R = ^{i}Pr (**1a**), ^{t}Bu (**1b**), CH_2CF_3 (**1c**)



cis-**1a-c** *trans*-**1a-c**

Figure 2. Cis and trans oxo configurations with a *trans*-phenoxy configuration.

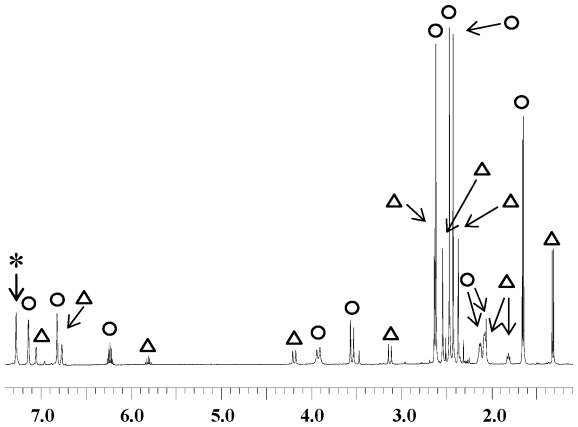


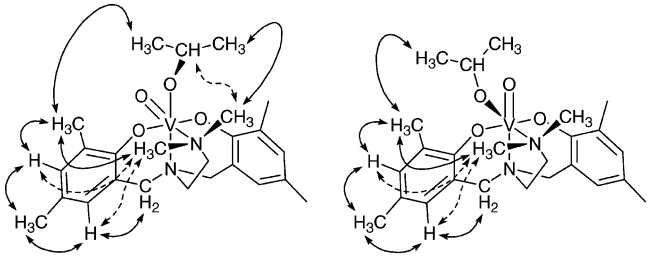
Figure 3. 400-MHz ^{1}H NMR spectrum of a mixture of isomers **A** (○) and **B** (△) of complex **1a** in benzene-d_6. (The asterisk denotes protio impurities in benzene-d_6.)

For such VO(OR)[ONNO] octachedral complexes we could expect four different isomers. First, two possible geometries of the phenolate rings in an octahedral complex are cis and trans configurations, leading to C_1 and C_s symmetry, respectively. The second possibility would be isomers of position of the oxo and alkoxo group in regard to the [ONNO] fragment, i.e., the oxo ligand in cis or trans configuration from the tripodal nitrogen atom (see Figure 2 for the isomers having a trans configuration of the phenoxy groups).

The ^{1}H NMR spectra of all complexes **1a**−**c** (see Experimental Section) are similar and reveal the presence of only two isomers (**A** and **B**) in a ratio major:minor **A**:**B** ∼ 3:1 (see Figure 3 for **1a**),[21] both of them featuring symmetry-related phenolate rings that exclude a cis geometry for those groups. Two signals are also observed in the ^{51}V NMR spectra of **1a**−**c** compounds for the two isomers (i.e. −440 and −471 ppm for **1a**). In addition to the two symmetry-related phenolate rings, the ^{1}H NMR spectrum of both isomers consists of an AB system for the Ar−CH_2−N methylene units and a single signal for the OR group (i.e. for complex **1a**, one septuplet at 6.10 ppm and one doublet at 1.56 ppm for the O^{i}Pr ligand of isomer **A**).

Addition of pyridine to complex **1a** did not affect the ^{1}H NMR spectrum, suggesting that the sidearm NMe_2 group is sufficiently tightly bound to the metal not to be displaced by strong donors. Moreover, variable-temperature NMR studies on these systems did not show any significant differences (in toluene-d_8, from −90 to +90 °C), suggesting

(17) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis (Release 97-2)*; Institüt für Anorganische Chemie: Tammanstrasse 4, D-3400 Göttingen, Germany, 1998 (includes SHELXS97, SHELXL97, CIFTAB).
(18) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(19) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1983**, *39*, 158−166.
(20) Flack, H. D *Acta Crystallogr. A* **1983**, *39*, 876−881.
(21) Conducting the reaction between $VO(OR)_3$ and [ONNO]H_2 in various solvents (toluene, pentane, or THF) and at low or high temperature did not affect the final ratio (∼3:1) of the two isomers of complexes **1**. At this point, it is also unclear why this ratio does not depend on the steric or electronic properties of the alkoxide precursors $VO(OR)_3$.



***cis*-1a** ***trans*-1a**

Figure 4. Main observed ^{1}H NMR NOESY correlations on a mixture of **1a** isomers (weak correlations in dashed curves).

that the interconversion between the two isomers is not possible within the temperature range studied. Altogether, this indicates the formation of rigid, mononuclear C_s-symmetrical isomer complexes in which the phenoxy groups are in a trans configuration, with oxo and alkoxo ligands being either in cis or in trans configuration to the tripodal N donor atom.

Other NMR studies were necessary to determine the nature of each isomer, and in particular, with the help of NOESY experiments, we were able to determine spatial relations between different groups in the molecules. On Figure 4 are shown the most significant correlations observed for the mixture of two isomers in complex **1a**.

The assignment of the two Me groups on the phenolate rings were verified by their correlations with the aromatic protons of the phenolate rings (see Figure 4). In both isomers, the *ortho*-Me group was found to correlate with the Me groups on the sidearm N atom (proving that this nitrogen atom is bound to the metal in solution). Most importantly, *only* in one isomer (isomer **A**) did we find a correlation between the Me groups on the sidearm N donor and *both* the *ortho*-Me group of the phenolate fragment and of the Me group of the isopropoxide ligand (and to a less extent to the $CH_{^iPr}$). The close spatial proximity of these groups is only possible in the isomer in which the O^{i}Pr ligand is located cis to the NMe_2 group (i.e. *cis*-**1a**); thus, the NOESY experiments clearly indicates that the major isomer **A** is the *cis*-**1a** complex, whereas the minor isomer **B** is the *trans*-**1a** complex (in which a spatial correlation between the Me groups of the sidearm NMe_2 donor and the alkoxide is not possible).

Similar NOESY experiments were performed on the other alkoxides complexes **1b**−**c**, in which similar features were observed, allowing discrimination between the two isomers.

Single crystals of one isomer of **1a**, suitable for an X-ray structure determination, were obtained from cold pentane solutions, and an ORTEP drawing is shown in Figure 5, with selected bond distances and angles in Table 2. The solid-state structure confirms our solution-structure NMR investigations (i.e. a mononuclear complex with a trans configuration for the phenolate rings and a coordination of the sidearm NMe_2 to the vanadium) and reveals that we crystallized the isomer *cis*-**1a** with the oxo ligand in cis configuration to the tripodal N atom.[22] The complex has a slightly distorted octahedral geometry with a sidearm nitrogen V−N2 distance of 2.3773(16) Å, significantly longer

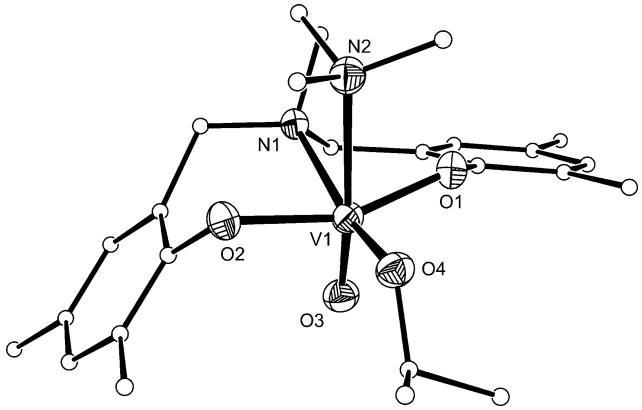


Figure 5. ORTEP drawing of the molecular structure of *cis*-**1a** showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Table 2. Selected Structural Parameters for Complexes VO(X)[ONNO] (X = O^{i}Pr (**1a**), Cl (**2**), and N_3 (**3**)) (Distances in Å and Angles in deg)

	VO(O^{i}Pr)[ONNO] (**1a**)	VO(Cl)[ONNO] (**2**)[a]	VO(N_3)[ONNO] (**3**)
V−O1	1.8651(13)	1.854(3)	1.848(3)
V−O2	1.9078(13)	1.841(3)	1.833(3)
V−O3	1.5969(13)	1.600(3)	1.591(3)
V−N1	2.2959(15)	2.354(4)	2.360(3)
V−N2	2.3773(16)	2.213(4)	2.228(3)
V−X	1.7782(13)	2.3361(14)	2.021(4)
O1−V−O2	157.62(6)	165.91(14)	165.99(15)
N1−V−N2	77.68(6)	78.29(13)	78.54(12)
O3−V−X	104.20(6)	101.85(13)	102.76(15)
α, β[c]	−5.2, −8.4	−8.0, +4.1	−6.3, +7.5
δ[d]	+121	−149	−158

[a] For independent molecule **A**. [b] X = O^{i}Pr (**1a**), Cl (**2**), or N_3 (**3**). [c] Dihedral angle: α = C1C2C7O1; β = C14C13C8O2. [d] Angle defined by the two planes containing the two phenolate aromatic rings; the + sign refers to a folding away from the NMe_2 sidearm whereas the − sign refers to a folding in toward the NMe_2 sidearm.

than the tripodal N1−V bond of 2.2959(15) Å, suggesting a weaker binding of the sidearm NMe_2 group to the vanadium that might well result from a trans effect of the oxo group reflecting its trans-labilizing ability. The vanadium−oxo distance is in the normal range for such a bond (V−O3 = 1.5669(13) Å),[9f,23] whereas the vanadium−isopropoxide V−O distance is rather short (V−O4 = 1.7782(13) Å) with a wider V−O−$C_{^iPr}$ angle (V−O4−C23 = 127.06(11)°) in agreement with some character of π-donation to the metal.

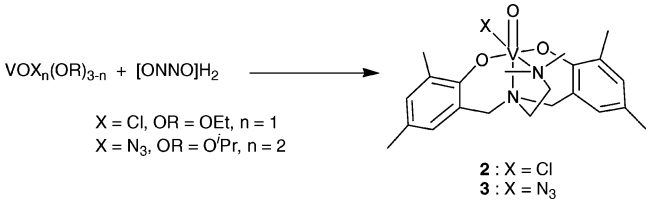
The phenolate groups of the tetradentate ligand fold back away from the pendant (dimethylamino)ethyl sidearm; the angle δ between the two planes of the aromatic rings is ca. +121°.

At this point, it clearly appears from the crystal structure that the two phenolate rings in complex *cis*-**1a** are nonsymmetry-related (due to the helicoidal distortion of the tripodal amino nitrogen donor that induce a dissymmetry in the ligand framework; vide infra), whereas the solution structure determined by NMR spectroscopy revealed two symmetry-

(22) ^{1}H NMR studies of a few crystals of **1a** still present features of both cis and trans isomers. As we have shown that the interconversion between the isomers is not possible, it suggests that we may have obtained mixture of crystals of the two isomers.

(23) Nugent, W. A.; Mayer, J. M. In *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

Scheme 2. Synthesis of Chloro− and Azido−[ONNO] Vanadium(V) Complexes



related phenolate groups, thus proving some degree of flexibility of the ligand.[24]

Reacting $[ONNO]H_2$ with an equimolar amount of $VO(X)_n(OR)_{3-n}$ ($X = Cl$, $R = Et$, $n = 1$; $X = N_3$, $R = {}^i Pr$, $n = 2$) in toluene (for **2**) or THF (for **3**) at room temperature afforded a blue solution from which dark crystals of VO(X)[ONNO] ($X = Cl$ (**2**), $X = N_3$ (**3**)) were obtained upon crystallization (Scheme 2).

The ^{51}V NMR spectra of both complexes **2** and **3** consist of a unique signal at −355 ppm (**2**) and −356 ppm (**3**). Moreover, the ^1H NMR spectra of **2** and **3** are very similar, confirming the presence of a single isomer in which the phenolate rings are again symmetry related and consist of an AB system for the Ar−CH_2−N methylene units. As for compounds **1a**−**c**, we conclude that complexes **2** and **3** possess a rigid C_s-symmetrical framework in which the phenoxy groups are in a trans configuration. The solution structure, in particular the determination of the configuration of the oxo and X ligands in respect to the [ONNO] ligand, was determined with the help of NOESY experiments and by comparison with the ^1H NMR pattern of both isomers of complexes **1a**−**c**. According to all these ^1H NMR studies, in solution, complexes **2** and **3** present the same features as those of *trans*-**1a**−**c** (isomer **B**) and then would have the same structural configuration (i.e. the oxo group located in trans to the tripodal N donor atom).[25]

Crystals of **2** (dark blue) and **3** (dark with hints of copper) were obtained at room temperature from toluene−pentane or THF solutions of **2** and **3**, respectively, and their solid-state structure was determined. Thermal ellipsoid plots are shown in Figures 6 and 7, and Table 2 shows a comparison of their structural parameters. (Complex **2** presents two independent molecules in the cell with very similar structural parameters; therefore, only one of these molecules will be described here.) The X-ray structures confirm the solution-structures established by the way of the NMR studies: (1) Both complexes have a trans configuration for the phenolate rings and (2) coordination of the sidearm NMe_2 to the vanadium, and (3) the oxo ligand is located in trans configuration to the tripodal N atom (the Cl or N_3 ligand being trans to the NMe_2 sidearm donor atom). Overall, the geometry of **2** and **3** is distorted octahedral, with a sidearm nitrogen V−N distance of 2.213(4) Å (**2**) and 2.228(3) Å (**3**), shorter than the tripodal N−V bond of 2.354(4) Å (**2**) and 2.360(3) Å (**3**) by ca. 0.14 Å. This stronger binding of the sidearm NMe_2 group to the metal (as compared with *cis*-**1a**) results, again, from a trans effect of the oxo group now labilizing the tripodal N amino group. The vanadium−oxo and vanadium−X ($X = Cl$, N_3) distances are in the expected range for such bonds (V−O3 = 1.600(3) Å in **2**, V−O3 = 1.591(3) Å in **3**, V−Cl1 = 2.3361(14) Å, V−N11 = 2.021(4) Å).[9b,f,10,12,26]

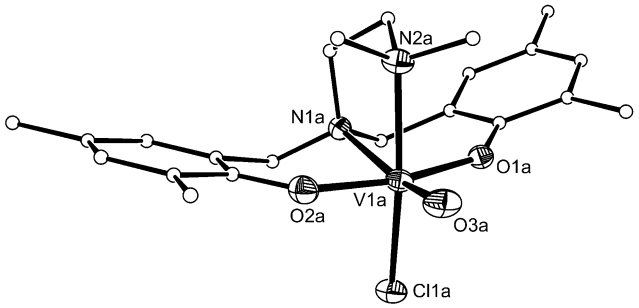


Figure 6. ORTEP drawing of the molecular structure of **2** showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

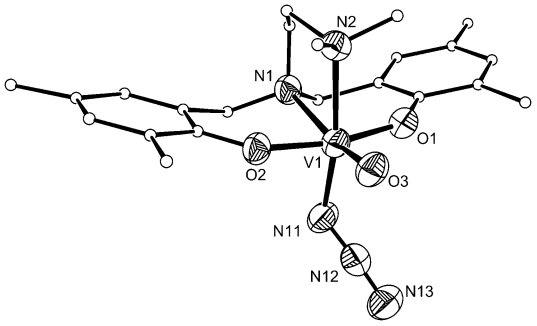


Figure 7. ORTEP drawing of the molecular structure of **3** showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Thus, interestingly, only one isomer of complexes **2** and **3** is formed (the trans) although we could expect (as in **1a**−**c**) the formation of two isomers (cis and trans) when the [ONNO] ligand approaches the $V(X)_n(OR)_{3-n}$ starting complexes. If we exclude steric reasons (because for **1a**−**c** the ratio between the isomers does not seem to be dependent on the OR group), it is conceivable that because oxo and alkoxo

(24) In addition, the intensities of NOESY correlations between the proton at the *ortho* benzylic position and the two diastereotopic Ar−CH_2−N methylenic protons are found to be very different in the minor isomer **B** *trans*-**1a**−**c** (that means that the distance between this aryl proton and the two diastereotopic Ar−CH_2−N methylenic protons is different), whereas they are almost identical in the major **A** *cis*-**1a**−**c**, suggesting that in solution the [ONNO] framework adopts a different geometry in the two isomers. By comparison with a molecular model, this suggests that isomer **B** has a solution structure very similar to that of **2** and **3** (determined by X-ray, with the phenolate groups of the [ONNO] framework that fold in toward the pendant (dimethylamino)ethyl sidearm; vide infra). By contrast, the solution structure of isomer **A** would be slightly different, still with the phenolate groups of the [ONNO] framework that fold in toward the pendant NMe_2 sidearm but now with a smaller angle between the planes formed by the two phenolate rings. This hypothesis is further corroborated by the intensities of the correlations found between the methyl group at the *ortho* position to the phenoxy oxygen atom and the methyl group of the NMe_2 sidearm that are less intense in isomer **A** than in isomer **B**.

(25) As previously discussed in ref 24, there is strong evidence that the structures of compounds **2** and **3** in solution are very close to those determined in the solid state (vide infra), as revealed by the very different intensities of NOESY correlations observed between the proton at the *ortho* benzylic position and the two diastereotopic Ar−CH_2−N methylenic protons.

(26) Hanich, J.; Krestel, M.; Muller, U.; Denicke, K.; Rehder, D. *Z. Naturforsch. B* **1984**, *39*, 1686−1690.

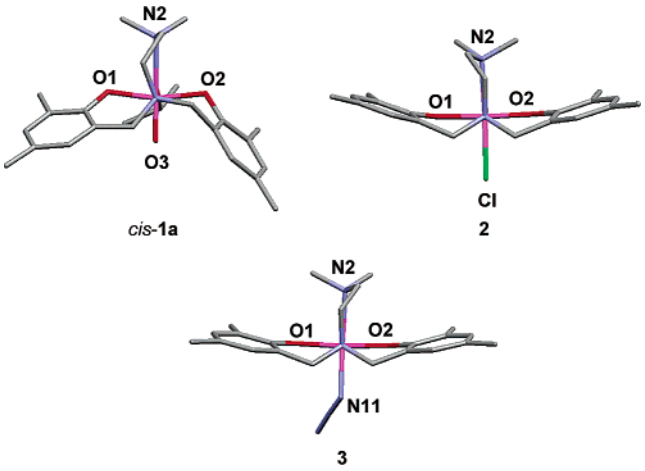


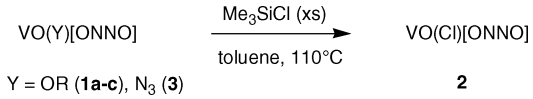
Figure 8. View along the tripodal nitrogen atom N1−V axis of complexes **1a**, **2**, and **3**.

ligands have similar properties (σ- and π-donors), the discrimination between both groups is rather difficult, therefore leading to the formation of two isomers. By contrast, the electronic properties of an oxo ligand and a Cl or a N_3 groups are not comparable, resulting in a strong discrimination favoring the formation of only one type of isomer.

It is noteworthy that if we have a closer look at all the crystal structures of **1a**, **2,** and **3** (see also Figure 8 that represents a view along the tripodal nitrogen atom N1−V axis), in complexes **2** and **3** the [ONNO] fragment is almost superimposable, which is probably due to the very similar electronegativity of the chloride and azide ligand. Interestingly, the arrangement of the three groups attached to the tripodal N donor atom (the two benzylic groups and the ethylenic arm) is not helicoidal as observed in the crystal structure of *cis*-**1a**. As a result, the phenolate groups of the [ONNO] framework now fold in toward the pendant (dimethylamino)ethyl sidearm; the angle between the two planes of the aromatic rings is ca. −149° (**2**) and −158° (**3**) (the minus sign refers to a folding toward the NMe_2 sidearm, by contrast to the folding away from the NMe_2 sidearm that has a positive sign). In contrast to *cis*-**1a**, the two aromatic rings of the bis(phenolate) framework (without the sidearm) are symmetry-related in the solid-state structure of **2** and **3**, in agreement with the structure in solution as determined by NMR spectroscopy studies, and the [ONNO] ligand adopts a geometry similar to that observed in titanium(IV) and zirconium(IV) analogue complexes.[5e−f]

Therefore, although the [ONNO] framework was previously qualified as rigid in the sense that it does not decoordinate (in particular through the NMe_2 donor atom as previously discussed), it has enough flexibility (as observed in solution and in the different X-ray structures of *cis*-**1a** vs **2**−**3**) around the tripodal amino N donor atom to accommodate various arrangements that allows the aromatic rings

Scheme 3. Synthesis of Chloro−[ONNO] Vanadium(V) Complex **2** by Chlorination of **1a**−**c** and **3** with Me_3SiCl



to flip above and under the plane defined by the vanadium center, the tripodal N atom, and the two phenolate O atoms.

Alternatively, the chlorine derivative **2**, VO(Cl)[ONNO], could be prepared by reacting excess of chlorotrimethylsilane (5 equiv) over the alkoxo- or azido- complexes **1a**−**c** and **3**, in toluene at 110 °C for 14 h in a screw cap vial (Scheme 3).[27]

All these oxo−vanadium(V) V(O)(X)[ONNO] complexes exhibit in thf a first chemically quasi-reversible redox step at −0.635, −0.748, −0.355, −0.110, and −0.154 V vs SCE respectively for **1a**−**c**, **2**, and **3**, following the electronic property of the ligand X, that most certainly correspond to the reduction of the metal center. Full details of the electrochemistry studies of these compounds and others will be given elsewhere.

Conclusion

In summary, new oxo−vanadium(V) complexes containing the chelating dianionic bis(phenoxy)amine [ONNO] ligand have been prepared in good yields. Information on their structural conformation and configuration was available both in solution (by NMR spectroscopy) and in the solid state (by X-ray determination), allowing the identification of two isomers for the alkoxo complexes VO(OR)[ONNO] in contrast to the single isomer obtained for complexes VO(X)[ONNO] (X = Cl, N_3).

In future articles, we will report on the synthesis of vanadium complexes with various valencies (from vanadium(II) to vanadium(IV)) stabilized by the same [ONNO] ligand, together with their olefin homo- and copolymerization activity.

Acknowledgment. This research was supported by the Centre National de la Recherche Scientifique (CNRS). The authors thank Prof. M. Kol for helpful discussions. We thank F. Lacassin, Dr. Y. Coppel, and S. Parrès for the ^{1}H NMR NOESY and ^{51}V NMR experiments and Dr. A. Sournia-Saquet for the electrochemical measurements.

Supporting Information Available: Tables of atomic coordinates and bond distances and angles for complexes **1a**, **2,** and **3**, results of ^{1}H NMR NOESY experiments with the main correlations observed for *cis*- and *trans*-**1a** complexes, and results of electrochemical studies of complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) It is unclear why starting from a mixture of two isomers of **1a**−**c** we end up with a single isomer of **2**; one possible reason would be the intrinsic instability of the unobserved isomer.