Paramagnetic Chloro-, Alkoxo-, or Azidovanadium(IV) Complexes Supported by an [ONNO]-Type Amine Bis(phenolate) Ligand

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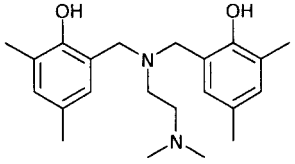
The reactions between $V(N_3)_2(NMe_2)_2$ or $V(OiPr)_4$ and the chelating dianionic bis(phenoxy)amine ligand $[ONNO]H_2$ afford complexes formulated as $[V(N_3)_2\{ONNO\}]$ (**1**) and $[V(OiPr)_2\{ONNO\}]$ (**2**). When refluxed in toluene with an excess of Me_3SiCl, compound **2** leads to mono- or dichloro derivatives $[V(Cl)(OiPr)\{ONNO\}]$ (**3**) and $[VCl_2\{ONNO\}]$ (**4**) depending on the experimental conditions. The crystal structures of complexes **1**–**4** were solved and show in all cases an [ONNO] ligand that has phenolate groups in a *trans* configuration, with both amino-nitrogen donor atoms of the ligand coordinated to the octahedral vanadium center. Complexes **1**–**4** were further characterized by EPR spectroscopy and susceptibility measurement studies typical of d^1-paramagnetic V^{IV} species.

Introduction

In the past decade, ''non-metallocene'' complexes have attracted considerable attention due to their activity as α-olefin polymerization catalysts.[1] Chelating diamide,[1a,2–4] dialkoxide,[1a,5–6] or phenoxyimine[7,8] ligands in particular have been extensively studied as rigid supporting environments for group 4 transition metals. As a result a great deal of novel and useful chemistry has emerged, including the discovery of highly active olefin polymerization precatalysts. Among these new ligands, chelating dianionic [ONNO]-type amine bis(phenolate) ligands, recently introduced by Kol et al.[5] and associated to group 4 metal complexes, have proved to give highly active 1-hexene polymerization catalysts, and in some cases even isospecific living polymerization was possible.[5a] As our interest lies strongly in vanadium chemistry with various supporting ligand environments,[9] in particular those that could help stabilize the formal oxidation state (+III or +IV) of the vanadium center (and thus avoid the reduction to inactive V^{II} species by the alkylaluminum cocatalyst) during the vanadium-catalyzed polymerization of olefins,[10,11] we have recently described the synthesis of a series of oxovanadium(V) complexes with the ancillary amine bis(phenolate) [ONNO]-type ligand (Figure 1),[12] and demonstrated interesting features in the solution and the solid-state structure of these complexes. In the present article, we wish to report on the synthesis, structure, EPR spectroscopy, and magnetism of new d^1-paramagnetic vanadium(IV) complexes supported by the same [ONNO]-type bis(phenoxy)amine ligand.



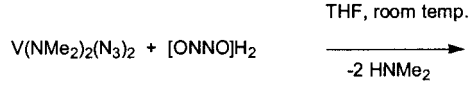
[ONNO]H$_2$

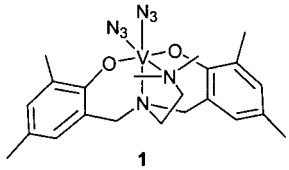
Figure 1. Structure of [ONNO]-type bis(phenoxy)amine ligand

Results and Discussion

1. Syntheses

In the past few years we have successfully used tetrakis(dialkylamido)vanadium(IV) $V(NR_2)_4$ as a precursor to various families of vanadium complexes.[9b,19,20] Logically, therefore, we first attempted the reaction between $V(NR_2)_4$





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Scheme 1. Synthesis of azido-[ONNO] vanadium(IV) complex

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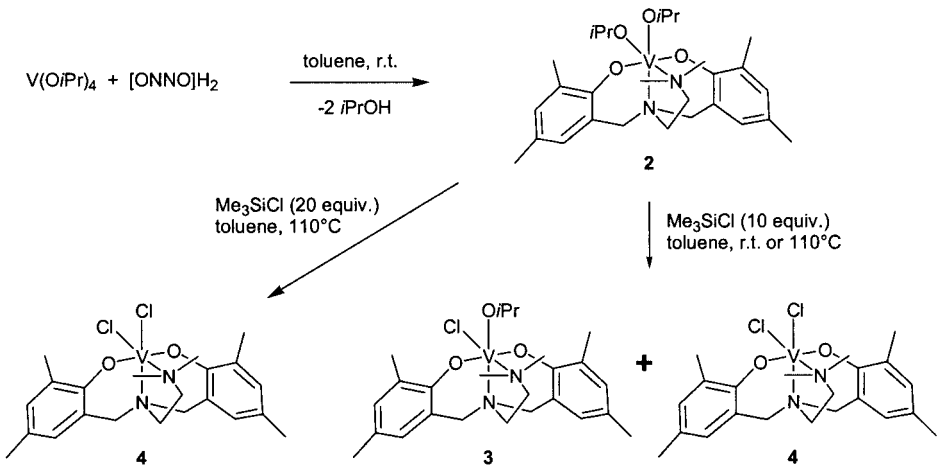

Scheme 2. Synthesis of alkoxo- and chloro- [ONNO] vanadium(IV) complexes

(R = Me; Et)[21] and an equimolar amount of the bisphenol ligand [ONNO]H_2, but although a reaction occurred we failed to isolate the pure [V(NMe_2)$_2${ONNO}] derivatives resulting from the amine elimination reaction. We then conducted the room temperature reaction of the new [V(N_3)$_2$(NMe_2)$_2$] complex (see Exp. Sect.) with [ONNO]H_2 in THF, which yielded the brown microcrystalline vanadium(IV) complex [V(N_3)$_2${ONNO}] (**1**) (yield: 40%) (Scheme 1). Brown crystals were further obtained by slow diffusion of pentane into a THF solution of **1**.

Reacting [ONNO]H_2 with an equimolar amount of V(O*i*Pr)$_4$ in toluene at room temperature for two hours afforded a dark red solution from which the complex [V(O*i*Pr)$_2${ONNO}] (**2**) was isolated with good yield (86%) as a dark red microcrystalline solid (Scheme 2). Compound **2** was recrystallized from a concentrated cold (−40 °C) pentane solution as dark red crystals.

Trimethylchlorosilane is known for its ability to substitute −NMe_2, −OR, or oxo groups by chlorine atoms in lanthanides [22] and in group 4−6 transition metal complexes;[3,4,9b,23] for vanadium complexes forcing conditions are generally required.[9b,20] We showed previously that Me_3SiCl could replace an azido group by a chlorine atom in oxo-vanadium(V) complexes,[12] and thus it was interesting to react the bis-azido complex **1** with Me_3SiCl. Unfortunately, the reaction did not proceed to completion even under forcing conditions in refluxing toluene.[24] However, when 10 equiv. of Me_3SiCl were used to chlorinate complex **2** in toluene at room temp. or 110 °C, a reaction occurred giving a mixture of the monochloro [V(Cl)(O*i*Pr){ONNO}] (**3**) and the dichloro [VCl_2{ONNO}] (**4**) derivatives. From that mixture of complexes, compound **3** was accidentally isolated as purple crystals (Scheme 2). In order to achieve a complete chlorination of **2**, a larger excess of Me_3SiCl (20 equiv.) was necessary, in dilute refluxing toluene solution, followed by slow cooling of the solution to room temperature, to afford dark blue crystals of the dichloro complex [VCl_2{ONNO}] (**4**) (yield: 96%) (Scheme 2).

In solution, [ONNO]-vanadium(IV) compounds **1**−**4** are all d^1-paramagnetic species presenting well-resolved electron paramagnetic resonance (EPR) spectra with the characteristic octet pattern at about g = 1.97 [A_{iso}(^{51}V) = 94.0 G (**1**), 70.9 G (**2**), 77.3 G (**3**), 82.7 G (**4**)] expected for the interaction of an unpaired electron of V^{IV} with the ^{51}V nucleus (I = 7/2). Accordingly, susceptibility measurements show magnetic moments consistent with a d^1 electronic configuration [μ_{eff} = 1.80 μ_B (**1**), 1.79 μ_B (**2**), 1.77 μ_B (**3**), 1.82 μ_B (**4**)].

Addition of pyridine or PMe_3 to complex **2** did not affect its EPR spectrum (in particular, no coupling with the ^{31}P phosphorus nucleus of PMe_3 was observed) or the color of the solution, suggesting that the sidearm NMe_2 group is sufficiently tightly bound to the metal not to be displaced by strong donors (as in our vanadium(V)[ONNO] complexes[12]).

2. Solid State Structures

In contrast to diamagnetic [ONNO]-vanadium(V) complexes for which ^{1}H NMR spectroscopy and NOESY experiments are very helpful tools in determining the structure in solution and in particular the conformation of the [ONNO] fragment, for paramagnetic d^1-vanadium(IV) species it is of tremendous importance to have a crystal structure in order to assess their formulation without ambiguity, as we have already stated in other articles dealing with vanadium(IV) complexes.[9a,9b]

Crystals suitable for X-ray structure determination were obtained for all complexes described in this article, either by diffusion of pentane into a THF solution of the complex (for **1** and **3**), cold pentane solution (for **2**), or slow cooling of a toluene solution from 110 °C to ambient temperature (for **4**). ORTEP drawings are given in Figure 2−5, with selected bond lengths and angles in Table 1 (complex **2** presents two independent molecules in the cell with very similar structural parameters, therefore only one of these molecules will be described here).

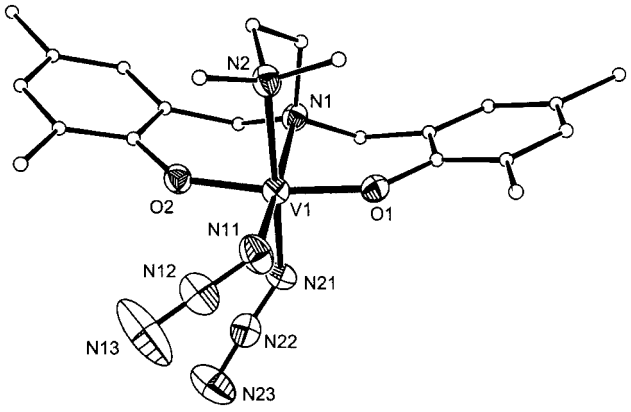

Figure 2. ORTEP drawing of the molecular structure of **1** showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity

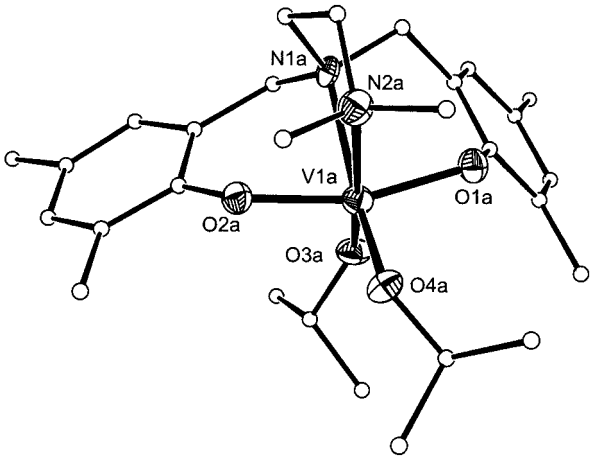

Figure 3. ORTEP drawing of the molecular structure of **2** (independent molecule A) showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity

The solid-state structures confirm our first formulation for complexes **1**−**4** as mononuclear vanadium complexes with one [ONNO] ligand in association with either two N_3 groups (**1**), two O*iPr* groups (**2**), two Cl groups (**4**), or one chlorine atom and one O*iPr* group (**3**). Furthermore, all complexes have a slightly distorted octahedral geometry with a *trans* configuration for the two phenolate rings of the [ONNO] ligand, as well as coordination of both amino-nitrogen donor atoms to the metal center, features that they share with their group 4 and oxo-[ONNO] vanadium(V) analogs.[5b,5d,5e,5f,12]

In contrast to the latter oxo complexes in which a *trans* effect due to the oxo ligand was observed, resulting in an elongated V−N bond of the amino-nitrogen atom of the [ONNO] ligand *trans* to the oxo group compared to the one in *cis*, here in the vanadium(IV) systems the two V−N bonds (formed between the metal center and the tripodal

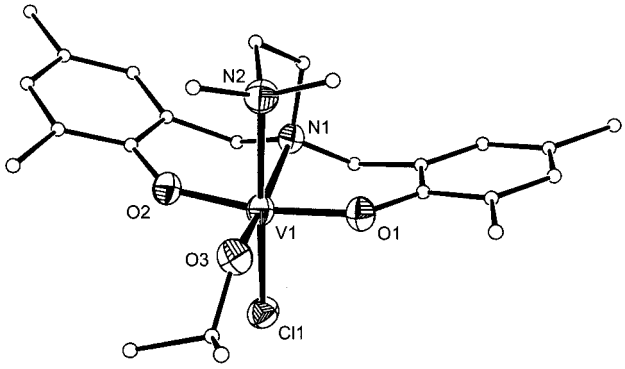

Figure 4. ORTEP drawing of the molecular structure of **3** showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity

Table 1. Selected structural parameters for complexes [V(X)(Y){ONNO}], X = Y = N_3 (**1**), O*i*Pr (**2**), or Cl (**4**), or X = O*i*Pr and Y = Cl (**3**) (distances are given in Å and angles in deg, X is the group *cis* to the NMe_2 sidearm whereas Y is the group *trans*)

	[V(N_3)$_2${ONNO}] (**1**)	[V(O*iPr*)$_2${ONNO}] (**2**)[a]	[V(Cl)(O*iPr*){ONNO}] (**3**)	[VCl_2{ONNO}] (**4**)
V−O1	1.780(2)	1.919(4)	1.801(1)	1.794(2)
V−O2	1.816(2)	1.882(4)	1.794(1)	
V−N1	2.193(3)	2.273(4)	2.226(1)	2.209(4)
V−N2	2.224(3)	2.313(5)	2.227(2)	2.209(4)
V−X	1.981(3) (*N11*)	1.793(4) (*O4*)	1.782(1) (*O3*)	2.308(2) (*Cl2*)
V−Y	2.029(3) (*N21*)	1.787(4) (*O3*)	2.3468(9) (*Cl1*)	2.354(2) (*Cl1*)
O1−V−O2	170.7(1)	162.6(2)	167.32(5)	168.9(2) [b]
N1−V−N2	82.0(1)	76.8(2)	80.11(5)	82.1(2)
X−V−Y	96.0(1)	104.1(2)	98.38(4)	95.51(6)
V−O1−C7	143.2(2)	116.6(3)	142.7(1)	143.2(2)
V−O2−C8	141.4(2)	129.8(4)	142.0(1)	
V−O3−C23		133.9(4)	131.7(1)	
V−O4−C26		131.0(3)		
α, β[c]	+6.5, −3.1	+2.6, +3.6	−4.0, +9.4	+4.1, −4.1
δ [d]	−148	+106	−149	−140

[a] For independent molecule A. [b] For **4**, angle O1−V−O1′. [c] Dihedral angle: α = C1−C2−C7−O1, β = C14−C13−C8−O2. [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 towards the NMe_2 sidearm.

amino-N atom and the dimethylamino sidearm N atom) have almost identical distances ranging from 2.19 to 2.31 Å. Short phenoxide V−O bond lengths of 1.78 to 1.82 Å are found in **1**, **3** and **4** (which correspond to the complexes that adopt a similar "symmetric" configuration, vide infra),[25] whereas they are about 0.1 Å longer in complex **2**. All other bonds are in the normal range; alkoxide V−O bond lengths are about 1.79 Å, V−Cl bond lengths are about 2.35 Å, and V−N_{azido} bond lengths are about 2.00 Å. V−O−$C_{phenolate}$ angles are around 141−143° in **1**, **3** and **4**, whereas for **2** they are 117−130° (vide infra). In **2**−**3**, V−O−C_{iPr} angles are between 132−134° which reflect only weak π interactions in the V−alkoxide bonds.

More importantly, if we have a closer look at the four crystal structures of **1**−**4** [see also Figure 6 that represents a view along the tripodal nitrogen atom N1−V−X axis for **1**−**4**, X being N11 (**1**), O4 (**2**), O3 (**3**), Cl2 (**4**)], in complexes **1**, **3** and **4** the [ONNO] fragment adopts the same, almost superimposable, configuration which is probably due to the very similar electronegativity of the chloride and azide ligands. 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 **2**. As a result, the phenolate groups of the [ONNO] framework in **1**, **3** and **4** fold in towards the pendant (dimethylamino)ethyl sidearm, the angle between the two planes of the aromatic rings is about −148° (**1**), −149° (**3**) and −140° (**4**) (the minus sign refers to a folding towards the NMe_2 sidearm, in contrast to the folding away from the NMe_2 sidearm that has a positive sign), whereas in complex **2** 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 about +106°. As a consequence, the V−$O_{phenolate}$ and V−N_{amino} bond lengths are longer by about 0.05−0.10 Å in **2** (compared to **1**, **3** or **4**), and the O1−V−O2 angle are smaller in **2** by about 5−10° as well as the V−O−$C_{phenolate}$ by 13° (V−O2−C8) to 26° (V−O1−C7).

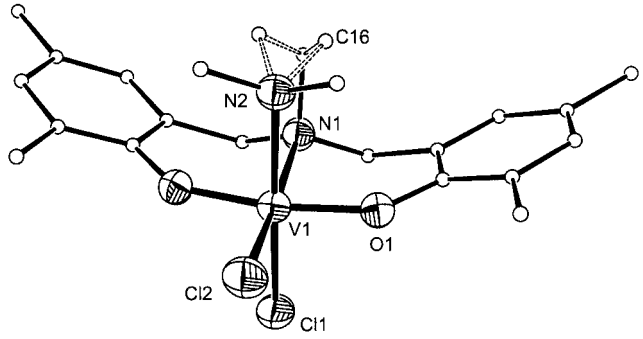

Figure 5. ORTEP drawing of the molecular structure of **4** showing 50% probability ellipsoids (except on C atoms for clarity) and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity

A similar observation was already mentioned in our oxo-[ONNO]-vanadium(v) series of complexes in which, in the solid state and in solution, the amine(bisphenolate) ligand accommodates different arrangements that allows the aromatic rings to flip above and under the plane defined by the vanadium center, the tripodal N atom and the two phenolate O atoms. Now, on the basis of all the crystal structures collected on our [ONNO]-vanadium systems,[26] it ap-

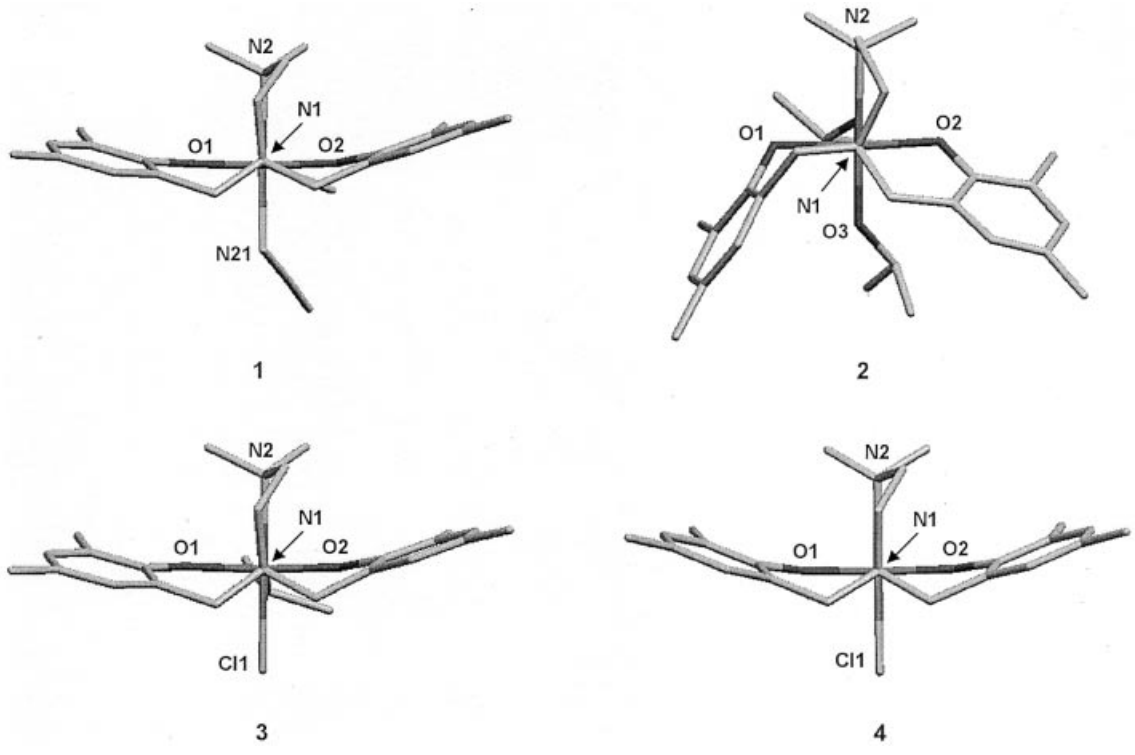

Figure 6. View along the tripodal N1−V−X axis of complexes **1**−**4** [X = N11 (**1**), O4 (**2**), O3 (**3**), Cl2 (**4**)]

pears that the "dissymmetric" configuration (never observed for group 4 metal complexes) in which the phenolate ligand folds back away from the pendant (dimethylamino)-ethyl sidearm (as in complex **2** and *cis*-[$V^{V}O(OiPr)\{ONNO\}$][12]) is due to the presence of an *O*-ligated anionic ligand (alkoxo, oxo, ···) *trans* to the (dimethylamino)ethyl sidearm nitrogen donor atom in these complexes.

Interestingly, we crystallized only one isomer for [V(Cl)(O*i*Pr){ONNO}] (**3**) although we could expect the formation of two isomers during the chlorination process with Me_3SiCl. Nevertheless, as the two groups (Cl and O*i*Pr) are *trans* to amino nitrogen donor atoms of similar electronic properties, there is probably no reason why in solution the two isomers would not coexist (and have not been distinguished by EPR spectroscopy).

Conclusion

New vanadium(IV) complexes **1**−**4** containing the amine bis(phenolate) [ONNO] ligand and additional azido, isopropoxo or chloro groups are reported. All complexes are d^1-paramagnetic species, whose crystal structures show an [ONNO] moiety that can adopt two different geometries depending on the nature of the ligand located *trans* to the NMe_2 sidearm nitrogen donor atom. Next, we will present the reactivity of these [ONNO]-vanadium complexes towards olefin polymerization.

Experimental Section

General Remarks: All manipulations were carried out using standard Schlenk line or drybox techniques under argon. Starting materials were purchased from Aldrich Inc. or Fluka Inc. and used without further purification. Solvents were refluxed and dried with appropriate drying agents under argon, collected by distillation and stored in a drybox over activated 4-Å molecular sieves. Trimethylchlorosilane and azidotrimethylsilane were distilled and stored over 4-Å molecular sieves under argon. $[ONNO]H_2$ and $V(OiPr)_4$ were prepared according to known procedures.[5e,13] EPR spectra were recorded on a Bruker ESP300E spectrometer. Infrared spectra were prepared as KBr pellets under argon in a glove box and were recorded on a Perkin−Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumber (cm^{-1}). Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). Magnetic susceptibility data were collected on powdered samples of the different compounds using a homemade Faraday-type automatic magnetometer with mercury tetra(thiocyanato)cobaltate susceptibility (at 20 °C, 16.44×10^{-6} $cm^3 \cdot mol^{-1}$). Diamagnetic corrections were applied using Pascal's constants as described previously.[9b]

CAUTION: Organic and inorganic azides are potentially explosive compounds and should be handled with great care.[14]

$[V(N_3)_2(NMe_2)_2]$: A large excess of azidotrimethylsilane (2.5 g, 22.0 mmol) was added to a pentane solution (15 mL) of $V(NMe_2)_4$ (1.1 g, 5.0 mmol). The solution was kept at room temperature overnight without stirring. A brown-red microcrystalline solid was filtered off, washed with pentane and dried (yield 96%). IR: $\tilde{\nu}$ = 2050 (s, ν_{N3}) cm^{-1}. $C_4H_{12}N_8V$ (223.1): calcd. C 21.53, H 5.42; found C 21.51, H 5.25 (Caution: we encountered an explosion during the combustion analysis).

$[V(N_3)_2\{ONNO\}]$ (1): Solid $[ONNO]H_2$ ligand (195 mg, 0.45 mmol) was added at room temperature to a THF suspension (2 mL) of $[V(N_3)_2(NMe_2)_2]$ (100 mg, 0.45 mmol). The brown solution was stirred at room temperature for 2 h and a brown solid was filtered off (yield 40%). EPR (THF, 20 °C): g = 1.968, $A(^{51}V)$ = 94.0 G. IR: $\tilde{\nu}$ = 2057 (s, ν_{N3}) cm^{-1}. μ_{eff} (20 °C) = 1.80 μ_B. $C_{22}H_{30}N_8O_2V$ (489.5): calcd. C 53.98, H 6.18, N 22.89; found C 53.81, H 6.31, N 23.11.

$[V(OiPr)_2\{ONNO\}]$ (2): Solid $[ONNO]H_2$ ligand (125 mg, 0.35 mmol) was added at room temperature to a toluene solution (2 mL) of $V(OiPr)_4$ (100 mg, 0.35 mmol). The blue-green solution immediately turned dark red and was stirred at room temperature for 2 h. Removal of the volatiles under vacuum and washing with pentane afforded a dark red solid (yield 86%). EPR (pentane, 20 °C): g = 1.967, $A(^{51}V)$ = 70.9 G. μ_{eff} (20 °C) = 1.79 μ_B. $C_{28}H_{44}N_2O_2V$ (491.6): calcd. C 64.23, H 8.47, N 5.35; found C 63.97, H 8.40, N 5.49.

[V(O*i*Pr)(Cl){ONNO}] (3): An excess of Me_3SiCl (1.90 mmol) was slowly added at room temperature to a toluene solution (2 mL) of **2** (100 mg, 0.19 mmol). The reaction mixture was placed in a 25 mL screw-cap vial and heated at 110 °C for 14 h. Removal of the volatiles afforded a dark solid containing a mixture of **3** and **4** from which **3** could be recrystallized from a pentane/THF solution at room temperature giving 11 mg of **3** (yield 11%). EPR (CH_2Cl_2, 20 °C): g = 1.973, $A(^{51}V)$ = 77.3 G. μ_{eff} (20 °C) = 1.77 μ_B. $C_{25}H_{37}ClN_2O_3V$ (500.0): calcd. C 60.06, H 7.46, N 5.60; found C 59.72, H 7.51, N 5.44.

$[VCl_2\{ONNO\}]$ (4) (*CAUTION*: *closed flask heating*): A large excess of Me_3SiCl (3.80 mmol) was slowly added at room temperature to a toluene solution (4 mL) of $[V(OiPr)_2\{ONNO\}]$ (100 mg, 0.19 mmol). The reaction mixture was placed in a 25 mL screw-cap vial and heated at 110 °C for 14 h and then cooled to room temperature. Dark blue needles were filtered off, washed with pentane and dried under vacuum (yield 96%). EPR (CH_2Cl_2, 20 °C): g = 1.975, $A(^{51}V)$ = 82.7 G. μ_{eff} (20 °C) = 1.82 μ_B. $C_{22}H_{30}Cl_2N_2O_2V$ (476.3): calcd. C 55.47, H 6.35, N 5.88; found C 55.60, H 6.33, N 5.96.

Crystal Structure Determination of 1−4: For the four compounds, data 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 graphite-monochromated Mo-K_α radiation (λ = 0.71073Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections. The crystal decay was monitored during data collection by measuring 200 reflections by image; no significant fluctuation of intensities was observed. Structures were solved by means of Direct Methods with the program SIR92.[15] Subsequent difference Fourier maps and models were refined by least-squares procedures on F^2 by using SHELXL-97[16] integrated in the package WINGX version 1.64,[17] and empirical absorption corrections were applied to the data.[18] All hydrogen atoms were 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. The methyl groups were refined with the torsion angle as free variable. For the four compounds all non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement weighting schemes were used, where weights were calculated from

Table 2. Crystal data and structure refinement parameters for **1**−**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{22}H_{30}N_8O_2V$	$C_{56}H_{88}N_4O_8V_2$	$C_{50}H_{74}Cl_2N_4O_6V_2$	$C_{22}H_{26}Cl_2N_2O_2V$
Molecular mass	489.48	1047.18	999.91	476.32
Crystal system	monoclinic	triclinic	tetragonal	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$I4_1/a$	$Pnma$
a (Å)	19.703(5)	9.411(5)	28.174(5)	16.455(2)
b (Å)	14.479(5)	12.537(5)	28.174(5)	16.2959(15)
c (Å)	8.321(5)	24.800(5)	12.630(5)	8.1845(7)
α (deg)	90.0	80.763(5)	90.0	90.0
β (deg)	92.875(5)	83.429(5)	90.0	90.0
γ (deg)	90.0	77.161(5)	90.0	90.0
V (Å)^3	2370.8(17)	2806.4(19)	10025(5)	2275.2(4)
Z	4	2	8	8
$D_{calcd.}$ (g·cm^{-3})	1.371	1.239	1.325	1.379
μ (Mo-K_α) (mm^{-1})	0.454	0.387	0.531	0.691
F(000)	1028	1124	4240	980
θ Range (deg)	2.07 to 23.26	2.82 to 22.46	1.65 to 26.05	2.48 to 25.97
Measured reflections	13661	15083	40093	16946
Unique reflections/R_{int}	3398/0.0672	7296/0.0951	5097/0.0352	2237/0.1104
Parameters/restraints	304/0	651/0	297/0	158/0
Final R indices [$I > \sigma 2(I)$]	$R_1 = 0.0392$ $wR_2 = 0.0791$	$R_1 = 0.0712$ $wR_2 = 0.1081$	$R_1 = 0.0353$ $wR_2 = 0.0928$	$R_1 = 0.0546$ $wR_2 = 0.1409$
Final R indices all data	$R_1 = 0.0753$ $wR_2 = 0.0909$	$R_1 = 0.1396$ $wR_2 = 0.1277$	$R_1 = 0.0425$ $wR_2 = 0.0980$	$R_1 = 0.0808$ $wR_2 = 0.1556$
Goodness of fit	0.925	0.962	1.018	1.051
$\Delta\rho_{max.} - \Delta\rho_{min.}$, e·Å^3	0.222 and −0.233	0.340 and −0.296	0.507 and −0.363	0.478 and −0.416

the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

CCDC-226148, -226149, -226150 and -226151 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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