Monomeric and dimeric V(III) complexes supported by organic amides

Pietro Berno, Mark Moore, Ravinder Minhas, and Sandro Gambarotta

Abstract: Reaction of $VCl_3(THF)_3$ with two equivalents of R_2NLi (R = Cy, Me_3Si) yielded the two corresponding complexes $(Cy_2N)_2V(\mu\text{-}Cl)_2Li(THF)_2$ (**1**) and $[(Me_3Si)_2N]_2VCl(THF)$ (**2**). Both complexes decomposed in hot toluene. In the case of complex **1** the reaction led to dimerization and formation of the dimeric $[(Cy_2N)_2V(\mu\text{-}Cl)]_2$ (**3**). Reaction of **2** with $NaBH_4$ yielded the unprecedented borohydride derivative $[(Me_3Si)_2N]_2V(BH_4)(THF)$ (**4**). The structures of all the complexes were elucidated by X-ray analysis.

Key words: vanadium, trivalent, amide, borohydride, dinuclear.

Résumé : La réaction du $VCl_3(THF)_3$ avec deux équivalents de R_2NLi (R = Cy, Me_3Si) conduit aux deux complexes correspondants $(Cy_2N)_2V(\mu\text{-}Cl)_2Li(THF)_2$ (**1**) et $[(Me_3Si)_2N]_2VCl(THF)$ (**2**). Les deux complexes se décomposent dans le toluène bouillant. Dans le cas du complexe **1**, la réaction conduit à une dimérisation et à la formation du dimère $[(Cy_2N)_2V(\mu\text{-}Cl)]_2$, **3**. La réaction du composé **2** avec le $NaBH_4$ conduit au dérivé borohydrure inconnu $[(Me_3Si)_2N]_2V(BH_4)(THF)$, **4**. Les structures de tous les complexes ont été élucidées par diffraction des rayons X.

Mots clés : vanadium, trivalent, amide, borohydrure, dinucléaire.

[Traduit par la rédaction]

Introduction

There has been a steady growth of interest in the recent literature (1) in the chemistry of medium-valent vanadium complexes and, in particular, those containing the metal in the oxidation state +3. This is probably due to the rich and diversified chemical reactivity displayed by these derivatives which includes dinitrogen fixation (2), possible relevance for desulfurization processes (3), and formation of precursors for hydrogenation (4) and of reactive moieties such as nitrides (5), carbenes (6), alkyls (7), and hydrides (5*c*, 8). In fact, this particular oxidation state of vanadium combines a medium Lewis acidity with the presence of available *d* electrons, which together contribute to its fairly high reactivity. Last but not least, trivalent vanadium seems to play an important role in some naturally occurring systems such as vanadium nitrogenase (9) and others (see for example ref. 10), where remarkable transformations are carried out in a catalytic manner and under mild reaction conditions.

Anionic organic amides seem to be particularly versatile supporting ligands with which to study the chemistry of trivalent vanadium. There are several characteristics that make them unique. First of all, there is a virtually unlimited possibility of fine tuning the steric hindrance via the appropriate selection of the substituents attached to the nitrogen atom. Their rather strong reducing power (11) and electronic flexibility allow the stabilization of a rather wide range of oxidation states and, in particular, of the lower states. Finally, these ligands are readily available via simple deprotonation of commercially available primary or secondary amines.

We recently reported the preparation of several V(III) complexes supported by nitrogen-donor-based ligands and described their involvement in dinitrogen activation (2, 12) and hydrogen transfer processes (4, 5*c*). These findings encouraged us to extend further the chemistry of these derivatives toward further functionalization and in particular to attempt the preparation of hydrides and alkyls. In this perspective, complexes such as $(R_2N)_2VCl$, containing a chlorine atom that should be easy to replace, will be the most promising starting materials.

In this paper we describe the convenient and straightforward preparation of monomeric and dimeric V(III) halide complexes supported by organic amides and the transformation of one of them into an unusual borohydride derivative.

Experimental

All operations were performed under the inert atmosphere of a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. Cy_2NLi (13) and $VCl_3(THF)_3$ (14) were prepared according to published procedures. $NaBH_4$ (Aldrich) was used as received. $(Me_3Si)_2NLi$ (Aldrich) was recrystallized from hexane. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in the dry-box. Samples for magnetic susceptibility measurements were weighed inside the dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson

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Matthey) at room temperature. The magnetic moment was calculated following standard methods (15), and corrections for underlying diamagnetism were applied to the data (16). Elemental analyses were carried out with a Perkin Elmer PE 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence by using a Philips XRF 2400 instrument.

Preparation of $(Cy_2N)_2V(\mu\text{-}Cl)_2Li(THF)_2$ (1)

Freshly prepared Cy_2NLi (6.96 g, 37.1 mmol) was added to a red suspension of $VCl_3(THF)_3$ (6.94 g, 18.6 mmol) in THF (100 mL) at −30°C. The color immediately turned green and the resulting suspension was stirred overnight at room temperature. After evaporation to dryness, toluene (120 mL) was added to the solid residue. The resulting suspension was filtered and the solution was concentrated to small volume. The addition of diethyl ether (150 mL) caused the precipitation of a dark microcrystalline solid (3.7 g, 5.8 mmol, 31%). Crystals suitable for X-ray analysis were obtained upon addition of hexane to a concentrated THF solution of **1** and storage at −25°C. IR (Nujol mull, cm^{-1}): 2671(br), 1449(vs), 1365(sh), 1343(m), 1248(br), 1162(s), 1145(s), 1121(br), 1034(vs), 980(w), 955(vs), 890(vs), 842(s), 804(m), 779(m), 728(w), 698(vs), 587(s), 513(s), 451(w). Anal. calcd. (found) for $C_{32}H_{60}O_2N_2Cl_2LiV$: C 60.66(60.11), H 9.54(8.99), N 4.41(4.21). $\mu_{eff} = 2.68\mu_B$.

Preparation of $\{[(CH_3)_3Si]_2N\}_2VCl(THF)$ (2)

A suspension of $VCl_3(THF)_3$ (7.06 g, 18.9 mmol) in THF (80 mL) was treated at room temperature with $(Me_3Si)_2NLi$ (6.3 g, 38 mmol). The color rapidly turned deep blue-green. After stirring for 3 h at room temperature, the solvent was evaporated in vacuo. The residual solid was redissolved in hexane (70 mL) and the resulting solution was filtered and allowed to stand overnight at −30°C. Dark blue-green crystals of **2** separated (7.9 g, 16.4 mmol, 87%). IR (Nujol mull, cm^{-1}): 1462(vs), 1376(m), 1249(s), 1001(w), 906(s), 890(s), 846(s), 784(m), 759(w), 690(m), 665(s). Anal. calcd. (found) for $C_{16}H_{44}N_2ClSi_4OV$: C 40.10(39.91), H 9.25(9.17), N 5.85(5.72). $\mu_{eff} = 2.79\mu_B$.

Preparation of $[(Cy_2N)_2V(\mu\text{-}Cl)]_2$ (3)

Solid Cy_2NLi (24.98 g, 133.4 mmol) was added to a red suspension of $VCl_3(THF)_3$ (24.92 g, 66.7 mmol) in THF (200 mL) at −30°C. The resulting dark green suspension was stirred overnight at room temperature. After evaporation of the solvent in vacuo, the dark brown solid residue was suspended in toluene (250 mL) and the resulting solution was boiled and filtered while hot. Dark brown crystals of **3** (14.98 g, 17 mmol, 51%) separated after allowing the resulting brown solution to stand at −25°C for 2 days. IR (Nujol mull, cm^{-1}): 2667(br), 1449(vs), 1364(sp), 1343(m), 1296(w), 1285(w), 1250(s), 1160(s), 1146(s), 1119(vs), 1067(w), 1037(vs), 980(w), 956(vs), 890(s), 841(s), 803(w), 778(m), 697(s), 612(w), 585(m), 514(s), 495(w), 484(w), 449(w), 424(w). Anal. calcd. (found) for $C_{24}H_{44}N_2ClV$: C 64.48(64.31), H 9.92(9.77), N 6.27(6.22). $\mu_{eff} = 1.79\mu_B$.

Preparation of $\{[(CH_3)_3Si]_2N\}_2V(BH_4)(THF)$ (4)

A solution of **2** (3.0 g, 6.3 mmol) in THF (100 mL) was stirred with $NaBH_4$ (1.9 g, 50.2 mmol) for 24 h at room temperature. The resulting deep blue mixture was filtered and the solvent evaporated in vacuo. The oily residue was dried overnight in vacuo at room temperature and the resulting solid was redissolved in hexane. The mixture was filtered to remove the small amount of insoluble material, concentrated, and allowed to stand at −30°C. Dark blue crystals of **4** (0.160 g, 0.3 mmol, 6%) were obtained. IR (Nujol mull, cm^{-1}): 2434(s), 2396(s), 2240(m), 2134(s), 1463(s), 1373(s), 1351(w), 1243(vs), 1167(w), 1129(m), 1020(w), 999(s), 881(v br), 663(s), 441(s). The extreme air sensitivity prevented elemental analysis determination. $\mu_{eff} = 2.91\mu_B$.

X-ray crystallography

Data were collected in the temperature range −144 to −161°C. The ω–2θ scan technique was used for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 centered reflections. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects, but no absorption corrections were applied to the data except for complex **4**. In this case, absorption corrections (DIFABS) significantly improved the agreement factors. The structures of **1**, **2**, and **3** were solved by direct methods by locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were introduced at their calculated positions except for complex **4** where the positions of the hydrogens connected to the boron atom were located from difference Fourier maps. The data were processed using the TEXSAN software package on a Digital VAX workstation. Refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o2/\sigma2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources (Cromer and Waber) (17). Details on the data collections and structure refinements are listed in Table 1. The final atomic coordinates are given as supplementary material.[2] Selected bond distances and angles are given in Table 2.

Results

According to Scheme 1, the reaction of $VCl_3(THF)_3$ with two equivalents of R_2NLi (R = Cy, $(CH_3)_3Si$) led to the formation of the corresponding derivatives $(Cy_2N)_2V(\mu\text{-}Cl)_2Li(THF)_2$ (**1**) and $\{[(CH_3)_3Si]_2N\}_2VCl(THF)$ (**2**). In both cases, the reactions were instantaneous and were accompanied by a rapid color change to dark green or blue-green. The two complexes were isolated in crystalline form. The formulation of the two species was indicated by the values of the combustion analy-

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[2] Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Tables of atomic coordinates and bond lengths and angles have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Table 1. Crystal data and structure analysis results.

	1	2	3	4
Formula	$C_{32}H_{60}O_2N_2VCl_2Li$	$C_{16}H_{44}N_2OVSi_4Cl$	$C_{24}H_{44}N_2VCl$	$C_{16}H_{48}OBN_2VSi_4$
Formula weight	633.63	479.27	447.02	458.66
Space group	P2₁/n (No. 14)	*P*-1 (No. 2)	*P*2₁/*n* (No. 14)	*P*2₁/*n* (No. 14)
a (Å)	14.188(1)	11.636(3)	9.310(1)	11.732(1)
b (Å)	17.113(1)	15.767(4)	21.5129(9)	19.199(1)
c (Å)	14.499(2)	8.561(2)	12.680(2)	12.086(1)
α (deg)		94.08(2)		
β (deg)	97.332(9)	108.98(2)	99.10(1)	97.77(1)
γ (deg)		105.55(2)		
V ($Å^3$)	3492(1)	1409.2(6)	2507.6(8)	2697.3(8)
Z	4	2	4	4
Radiation (Mo Kα, Å)	0.71069	0.71069	0.71069	1.54178
T (°C)	-161	-150	-144	-162
D_{calcd} (g cm^{-3})	1.205	1.129	1.184	1.129
μ_{calcd} (cm^{-1})	4.56	6.11	5.01	49.02
R, R_w	0.034, 0.047	0.045, 0.045	0.054, 0.068	0.068, 0.078

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (deg).

1	2	3	4
V1—Cl1 = 2.375(1)	V1—Cl1 = 2.276(2)	V1—Cl1 = 2.391(2)	V1—O1 = 2.057(7)
V1—Cl2 = 2.355(1)	V1—O1 = 2.034(3)	V1—Cl1a = 2.347(2)	V1—B1 = 2.38(2)
V1—N1 = 1.902(3)	V1—N1 = 1.918(4)	V1—N1 = 1.856(4)	V1—N1 = 1.876(8)
V1—N2 = 1.864(3)	V1—N3 = 1.953(3)	V1—N2 = 1.875(4)	V1—N2 = 1.940(8)
N1—C9 = 1.459(5)	N1—Si1 = 1.741(4)	Cl1-V1-N1 =105.7(1)	N2—Si1 = 1.737(9)
N1—C15 = 1.474(4)	N1—Si2 = 1.745(4)	Cl1-V1-N2 = 113.3(1)	N1—Si2 = 1.755(8)
Li1—O1 = 1.920(7)	Cl1-V1-O1 = 95.2(1)	Cl1-V1-Cl1a = 92.85(5)	V1—H48 = 1.711(7)
Li1—O2 =1.916(6)	Cl1-V1-N1 = 106.9(1)	V1-Cl1-V1a = 87.15(5)	V1—H47 =1.916(6)
Li1—Cl1 = 2.344(6)	Cl1-V1-N3 = 114.8(1)	C1-N1-C7 =116.0(4)	B1—H47 = 0.943
Li1—Cl2 = 2.400(7)	O1-V1-N1 = 113.2(1)	V1-N1-C1 = 107.0(3)	B1—H48 = 1.43(7)
N1-V1-Cl1 = 106.0(1)	O1-V1-N3 = 100.5(1)	V1-N1-C7 = 137.0(3)	N1-V1-O1 = 119.0(4)
N1-V1-Cl2 = 113.25(9)	N1-V1-N3 = 122.7(1)	V1-N2-C13 = 111.7(3)	N1-V1-N2 = 113.9(4)
N1-V1-N2 = 120.9(1)	Si1-N1-Si2 = 120.5(2)	V1-N2-C18 = 131.2(3)	N2-V1-O1 = 99.3(3)
N2-V1-Cl1 = 105.55(9)	V1-N1-Si1 = 122.2(2)	C13-N2-C18 = 117.0(4)	Si2-N1-Si4 = 117.7(5)
N2-V1-Cl2 = 112.30(9)	V1-N1-Si2 = 114.9(2)	N1-V1-N2 = 120.8(2)	V1-N1-Si4 = 123.4(4)
Cl1-V1-Cl2 = 94.89(4)		V1..V1a = 3.266(2)	V1-N1-Si2 = 117.5(5)
V1-Cl1-Li1 = 85.6(2)			
V1-Cl2-Li1 = 84.8(1)			
Cl1-Li1-Cl2 = 94.5(2)			
V1-N1-C9 = 131.1(2)			

ses. The X-ray fluorescence spectrum confirmed the presence of chlorine in the expected ratio with the metal centers. Both complexes are paramagnetic at room temperature with magnetic moments as expected for the d^2 electronic formulation of V(III) metal centers.

The chemical connectivity of both complexes was elucidated by X-ray analysis. Complex **1** features a vanadium atom residing in the center of a distorted tetrahedron (N1-V1-N2 = 120.9(1)°, N1-V1-Cl1 = 106.0(1)°, Cl1-V1-Cl2 = 94.89(4)°) defined by the two nitrogen atoms of the two amide groups (V1—N1 = 1.902(3) Å, V1—N2 = 1.864(3) Å) and two chlorides (V1—Cl1 = 2.375(1) Å, V1—Cl2 = 2.355(1) Å). Similar to the case of the closely related titanium derivative $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2(Li(TMEDA)]$ (18), the distortion of the coordination geometry is probably due to the large steric bulk of the amide groups since the angle subtended at vanadium by the two amide groups is significantly wider than expected for a normal tetrahedral angle. The two chloride atoms bridge to one lithium cation (Cl1—Li1 = 2.344(6) Å, Cl2—Li1 = 2.400(7) Å) forming an almost planar VCl_2Li core (torsion angle V1-Cl1-Li1-Cl2 = 3.7(2)°). Two molecules of THF complete the tetrahedral coordination geometry of the alkali

Scheme 1.

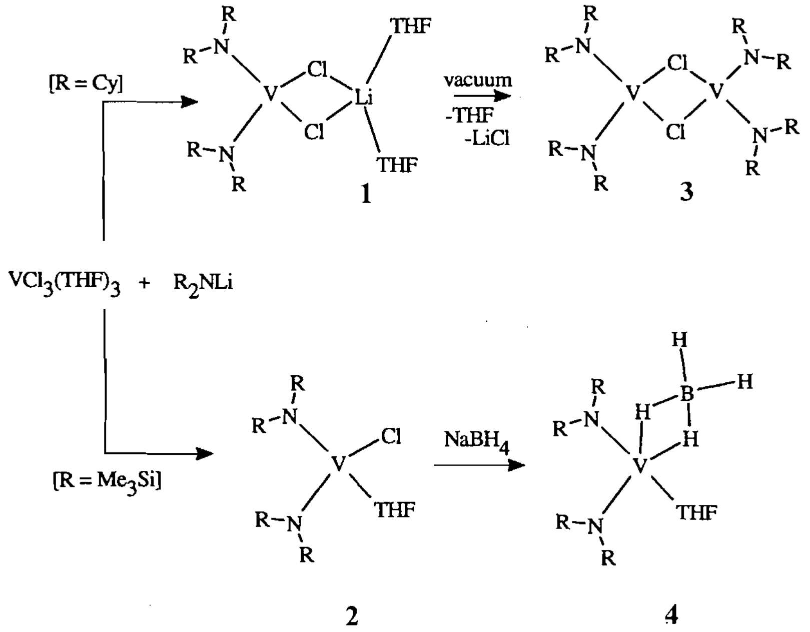


Fig. 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

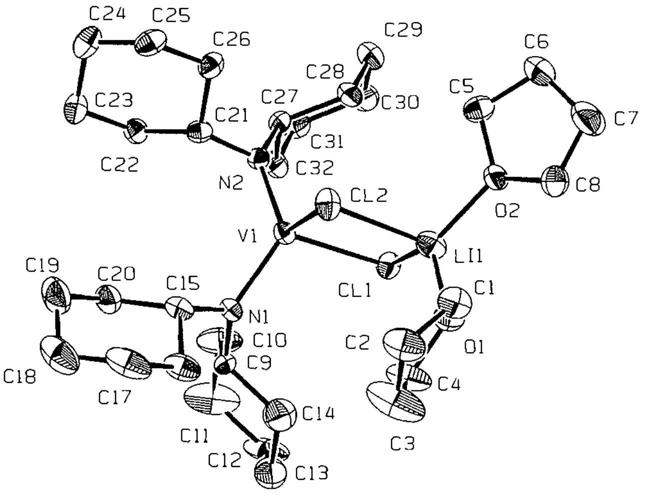
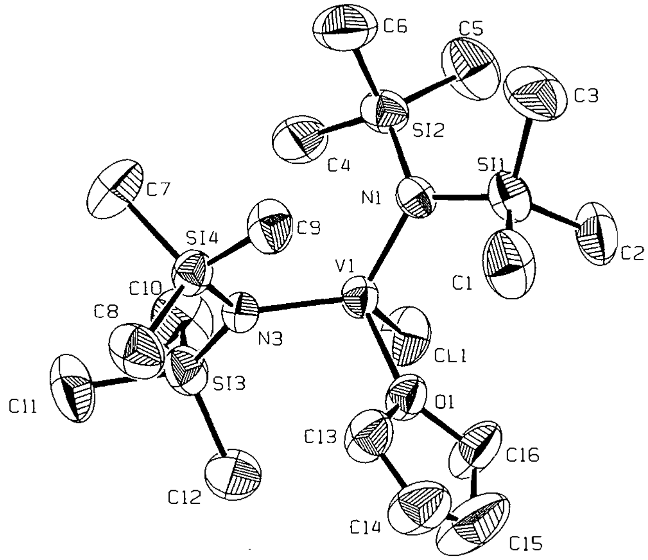


Fig. 2. ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level.



cation (Li1—O1 = 1.920(7) Å, Li1—O2 = 1.916(6) Å). The coordination geometry around each amide nitrogen atom is trigonal planar (C9-N1-C15 = 114.2(3)°, C9-N1-V1 = 131.1(2)°, C15-N1-V1 = 113.6(2)°), possibly suggesting some extent of π-interaction of the amide groups with the metal center.

The structure of complex **2** was more straightforward and predictable, consisting of a tetrahedral vanadium atom also placed in the center of a distorted tetrahedron (N1-V1-N3 = 122.7(1)°, N1-V1-Cl1 = 106.9(1)°, N1-V1-O1 = 113.2(1)°, Cl1-V1-O1 = 95.2(1)°) defined by two nitrogen atoms of two amide ligands (V1—N1 = 1.918(4) Å, V1—N3 = 1.953(3) Å), one chlorine (V1—Cl1 = 2.276(2) Å), and one oxygen atom of one molecule of THF (V1—O1 = 2.034(3) Å). Even in this case the distortion of the coordination geometry around vanadium is probably due to the large steric bulk of the two amide groups. The V—Cl and V—O distances are in the expected range for such bonds. The coordination geometry around each nitrogen atom is trigonal planar, again suggesting the possibility of some extent of π-interaction with the metal center (Si1-N1-V1 = 122.2(2)°, Si2-N1-V1 = 114.9(2)°, Si1-N1-Si2 = 102.5(2)°).

Both complexes were extremely air sensitive but stable at room temperature in both the solid state and solution under inert atmosphere. Nevertheless, a rather rapid color change to

Fig. 3. ORTEP plot of **3**. Thermal ellipsoids are drawn at the 50% probability level.

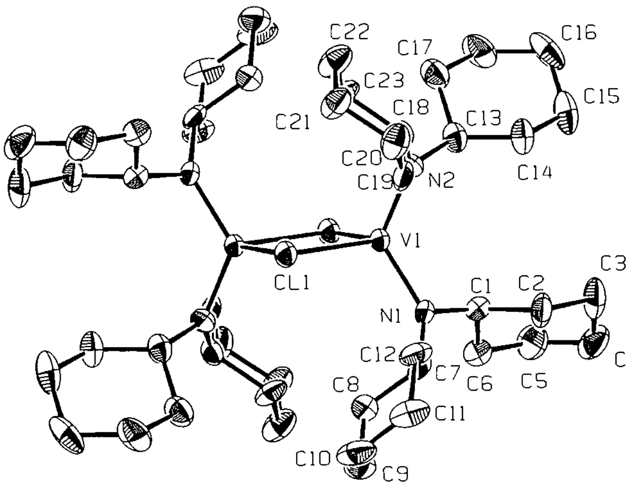
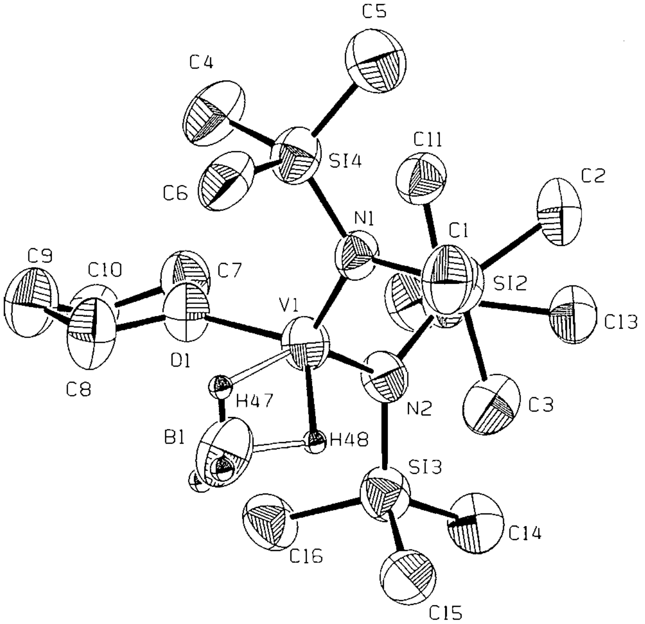


Fig. 4. ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.



brown was observed upon heating toluene solutions of both complexes. While in the case of complex **2** this behavior may be attributed to the dissociation of THF from the coordination sphere of the metal center, in the case of complex **1** the thermal instability was unexpected since the heating should lead only to desolvation of the lithium cation. Nevertheless, the color change indicated that a reaction involving the vanadium center probably occurred. After suitable work-up, a new brown crystalline material **3** was isolated. Conversely, in the case of complex **2** the thermolysis led only to intractable solutions. The combustion analysis and X-ray fluorescence of **3** clearly indicated the loss of one chlorine atom per vanadium atom with respect to **1**. These data were in agreement with the formulation $[(Cy_2N)_2VCl]_2$. Further, the magnetic moment calculated on the basis of the proposed formula was found to be considerably reduced with respect to the value expected for a d^2 electronic configuration of the V(III) metal center, possibly indicating the presence of a magnetic coupling between the metal centers. To unambiguously characterize the complex, the molecular structure was elucidated by an X-ray analysis.

Complex **3** is dimeric and consists of two distorted tetrahedral vanadium centers linked together by two bridging chlorides, forming a planar V_2Cl_2 core (torsion angle V1-Cl1-V1a-Cl1a = 0.0°). The coordination geometry around each vanadium center is distorted tetrahedral (N1-V1-N2 = 120.8(2)°, N1-V1-Cl1 = 105.7(1)°, Cl1-V1-Cl1a = 92.85(5)°, N2-V1-Cl1 = 113.3(1)°) and is defined by two nitrogens of two amide groups (V1—N1 = 1.856(4) Å, V1—N2 = 1.875(4) Å) and two bridging chlorides. The V—Cl distances (V1—Cl1 = 2.391(2) Å, V1—Cl1a = 2.347(2) Å) are normal although slightly longer than in complexes **1** and **2**. As in the cases of complexes **1** and **2**, the distortion of the tetrahedral geometry around the metal centers can be ascribed to the large steric bulk of the amides. The coordination geometry around each nitrogen atom is also trigonal planar (V1-N1-C1 = 107.0(3)°, V1-N1-C7 = 137.0(3)°, C1-N1-C7 = 116.0(4)°), again suggesting some extent of π-interaction between the nitrogen atoms and the metal center. The intermetallic distance (V1—V1a = 3.266(2) Å) is rather long and excludes the presence of a direct bonding interaction.

Chlorine replacement reactions were attempted with $NaBH_4$. While in the case of **1** and **3** the work-up afforded only intractable materials, a clean reaction was observed with **2**. The reaction proceeded smoothly, resulting in the formation of a deep blue solution from which a new complex $\{[(CH_3)_3Si]_2N\}_2V(BH_4)(THF)$ (**4**) was isolated in low yield as a homogeneous crystalline mass. Unfortunately, the extreme air sensitivity prevented the obtaining of reproducible and meaningful values of the combustion analysis data. The magnetic moment, calculated on the basis of the formula where the chlorine atom of **2** has been replaced by a BH_4^- group, was as expected for the d^2 electronic configuration of a V(III) metal center. The IR spectrum of these species shows a rather unusual pattern with three intense absorptions at 2434, 2396, and 2134 cm^{-1} and a medium-intensity band at 2240 cm^{-1}. This spectrum is not in agreement with any of those commonly observed for the η^1-, η^2-, and η^3-bonded BH_4 groups (19). Since we were unable to understand the spectroscopic data and to obtain meaningful analytical data we have undertaken a crystallographic analysis.

The molecular structure of **4** was elucidated by X-ray analysis. The complex is virtually isostructural with complex **2**, with comparable bond distances (V1—N1 = 1.876(8) Å, V1—N2 = 1.940(8) Å, V1—O1 = 2.057(7) Å) and angles (N1-V1-N2 = 113.9(4)°, N1-V1-O1 = 119.0(4)°, N2-V1-O1 = 99.3(3)°). Even in this case the tetrahedral coordination geometry around the vanadium center is distorted. The V—B distance is rather long (V1—B1 = 2.38(2) Å) and falls in the expected range for a η^2-bonded BH_4 group. The hydrogen atom positions for the BH_4 group were obtained from difference Fourier maps. Although the crystal structure was not of sufficient accuracy to permit drawing definite conclusions about the positions of the hydrogen atoms, it indicates, as an interesting possibility, that the bonding mode of the BH_4^-

group may be regarded as somewhat intermediate between η^2-BH_4 and the limiting case of an aggregation of a V—H complex with BH_3. In fact, the two bridging hydrogens were found to possess significantly different bond distances with the vanadium and boron centers. In particular, one of the two bridging hydrogens was found in the normal bonding range with the boron atom (B1—H47 = 0.943 Å) while the second was significantly closer to the vanadium center (V1—H48 = 1.711(7) Å) and significantly further from the boron atom (B1—H48 = 1.43(7) Å).

Complex **4** represents one of the rare examples of a vanadium borohydride derivative (20) and we are actively investigating its chemical reactivity.

Supplementary information available

A full list of atomic coordinates, anisotropic thermal parameters, bond distances and angles for **1**, **2**, **3**, and **4** has been deposited.[2]

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