H-9b), 2.51 (dd, $J=4.8$, 13.8 Hz, 1H; H-3eq), 1.90, 1.88, 1.80, 1.77 (each s, 3H; Me); HR-FAB-MS: calcd for $C_{29}H_{38}N_2O_{13}SNa$ $[M+Na^+]$: 677.1993; found: 677.1997.

[9] A. Marra, P. Sinaÿ, *Carbohydr. Res.* **1989**, *187*, 35–42.

[10] The CPG was used for the solid-phase synthesis of glycopeptide: M. Schuster, P. Wang, J. C. Paulson, C. H. Wong, *J. Am. Chem. Soc.* **1994**, *116*, 1135–1136.

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[12] Immobilized CMP-NeuAc **7** was suspended in 0.5 mL of $D_2O$, and the $^{31}P$ NMR spectrum was measured in a conventional manner: W. L. Fitch, G. Detre, C. P. Holmes, *J. Org. Chem.* **1994**, *59*, 7955–7956.

[13] Prior to the assays, **7** was washed with BSA (2 mg of BSA in 1 mL of HEPES buffer) in a 1.5-mL eppendorf tube in order to prevent nonspecific absorption of STase or glycoprotein acceptor to the CPG. After centrifugation, the supernatant was removed. This treatment was repeated three times, and then **7** was washed with water. After lyophylization, CMP-Neu5Ac **7** was used for assays.

[14] S. Sabesan, S. Neira, F. Davidson, J. Ø. Duus, K. Bock, *J. Am. Chem. Soc.* **1994**, *116*, 1616–1634.

[15] After incubation (panels A–H) the mixture was filtered, and the CPG remaining on the filter paper was washed with water twice (3 mL). The filter paper and CPG were inserted into a scintillation vial for counting. The radioactivity on the CPG was measured by a liquid scintillation counter, and the amount of [$^{14}$C]-LacNAc incorporated on the CPG was estimated. The transfer rates after subtraction of control values are summarized in Figure 3 (panels A–F). The data given (panels A–H) are averages values.

[16] The transfer assays were performed by one of the following two methods. The assays of CMP-NeuAc were carried out at 37 °C with a solution of HEPES buffer (total 35 µL) containing CMP-[U-$^{14}$C]-NeuAc (12.1 KBq nmol$^{-1}$, 20 µM), LacNAc (1 µM), BSA, and 3STase (0.8 µU). The amounts that were transferred were estimated by the conventional method.[17] For immobilized CMP-NeuAc, a solution of HEPES buffer (total 35 µL) containing **7** (1 mg: the concentration of CMP-NeuAc corresponds to 20 µM based on 721 pmol of CMP-NeuAc on 1 mg of CPG), [$^{14}$C]-LacNAc (1 µM), BSA, and 3STase (0.8 µU) was incubated at 37 °C, and the transferred amount was estimated with the above method.[15]

[17] Y. Kajihara, H. Kodama, T. Wakabayashi, K.-I. Sato, H. Hashimoto, *Carbohydr. Res.* **1993**, *247*, 179–193.

[18] $\alpha_1$-Acidic asialoglycoprotein with [U-$^{14}$C]-galactoside was prepared from $\alpha_1$-acidic asialo-agalacto-glycoprotein by the action of UDP-[U-$^{14}$C]-galactose and $\beta$-(1→4)-galactosyltransferase: Y. Kajihara, T. Endo, H. Ogasawara, H. Kodama, H. Hashimoto, *Carbohydr. Res.* **1995**, *269*, 273–294.

[19] Immobilization of the STase as a side reaction of this method could not be detected in several self-immobilization assays of STase.

[20] Immobilization yields are estimated to be about 4.5% and 5.8% in the case of LacNAc and asialoglycoprotein, respectively, based on the sialylacceptors added.

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# Cationic Homoleptic Vanadium(II), (IV), and (V) Complexes Arising from Protonolysis of $[V(NEt_2)_4]$

Robert Choukroun,* Pierre Moumboko, Sandrine Chevalier, Michel Etienne, and Bruno Donnadieu

Although the chemistry of cations containing Group 4 metals is very well documented[1] and a subject of ongoing investigations, with regard to the modeling of the Ziegler–Natta polymerization, the chemistry of cationic vanadium complexes has not been as thoroughly studied as that of their neutral complexes.[2–4] The recent interest in complexes in which amido and imido groups are directly bound to a Group 4 or 5 metal atom has led to new catalysts in alkene polymerization.[5] Hydridotris(pyrazolyl)borate imidovanadium(V) in the presence of a methylaluminoxane (MAO) activator shows modest ethylene polymerization activity.[6] We reported that the protonolysis of $[Cp_2VMe_2]$ or $[Cp_2Zr(BH_4)_2]$ can lead to a disproportionation redox reaction resulting in cationic vanadium(III) or zirconium(III) complexes.[7,8] In this context we report here the formation of new cationic vanadium(II), (IV), and (V) species when $[V(NEt_2)_4]$ (**1**) is treated with the ammonium salt $[NHMe_2Ph][BR_4]$ (R = Ph, $C_6F_5$).

Treatment of **1** with one equivalent of $[NHMe_2Ph][BPh_4]$ in thf at room or low temperature (−78 °C) causes precipitation of the unexpected air-sensitive, dicationic, heteroleptic dialkylamidovanadium(IV) complex **2** with one thf molecule of crystallization (yield: 26%). This crystalline red product was characterized by X-ray structure analysis (Figure 1).[9] The environment around the metal is octahedral and the V–N and V–O distances (2.054 and 2.11 Å (average), respectively) are comparable to those in other vanadium compounds containing the bis(trimethylsilyl)amide ligand and a coordinated thf molecule.[10] The sum of the angles about each N center is close to 360°, indicating that the amide ligands are probably acting as three-electron donors. We also observe that a small, nonquantifiable amount of an uncharacterized green precipitate is present among the crystals of **2**, providing evidence that the reaction is not simple.

$[V(NEt_2)_4]$ **1**

$[V(NEt_2)_2(thf)_4][BPh_4]_2 \cdot thf$ **2**

Reconsidering the formation of **2**, we repeated our experiment with **1** and two equivalents of $[NHMe_2Ph][BR_4]$ (R = Ph or $C_6F_5$) in thf at room temperature. Compound **1** was treated with two equivalents of $[NHMe_2Ph][B(C_6F_5)_4]$ in thf, and pentane was allowed to diffuse slowly into the solution to give a mixture of crystalline, highly air-sensitive, red products.

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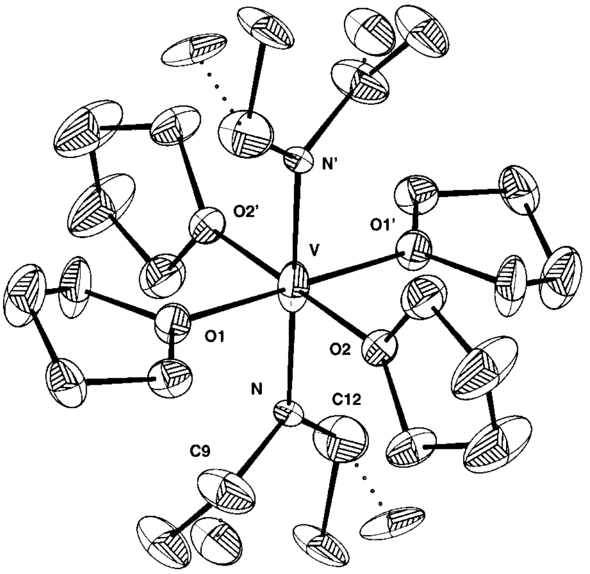


Figure 1. Molecular structure of the cation in **2** showing the labeling scheme; hydrogen atoms are omitted for clarity. The structure of the $[BPh_4]^-$ ion is normal. Selected bond lengths [Å] and angles [°]: V–O1 2.108(3), V–O2 2.121(3), V–N 2.050(3); O1-V-O2 89.4(1), O1-V-N 89.2(1), O2-V-N 89.8(1), V-N-C9 125.6(3), V-N-C11 126.6(3), C9-N-C11 107.7(4).

After careful and lengthy separation, we were able to elucidate their composition by X-ray crystal structure analysis.[9] Dark red crystals were identified as the unanticipated cationic homoleptic vanadium(v) complex **3** and bright red crystals as the dicationic vanadium(II) species **4**, which crystallizes with two molecules of thf.

$[V(NEt_2)_4][B(C_6F_5)_4]$ **3**

$[V(thf)_6][B(C_6F_5)_4]_2 \cdot 2\,thf$ **4**

The crystal structure of **3** (Figure 2) shows that the complex has a tetrahedral core; the vanadium center is bound to four dialkylamido ligands. The sum of the angles around each nitrogen atom is nearly 360° and the V–N distances are in the expected range of 1.817 – 1.847 Å. These distances are shorter than those in **2** but consistent with the electronic contribution of the oxygen atom from the thf ligand in **3**. The angles of the four $VNC_2$ moieties in **3** are slightly different owing to the steric bulk of the ligand and the coordination number of the metal.

The X-ray structure of **4** (Figure 3) reveals an octahedral geometry in which the metal center is surrounded by six thf ligands, two $[B(C_6F_5)_4]$ counteranions, and two thf molecules. Similar $[VL_6]^{2+}$ compounds ($L = CH_3OH$, $H_2O$, $CH_3CN$)[11–14] have been characterized, but the thf analogue was described as $[V(thf)_4]^{2+}$.[12] The V–O distances are in the range of 2.13 – 2.15 Å, slightly longer than in **2**. In the compounds characterized by three X-ray crystallography the counteranions display the expected geometry.

The $^1H$ NMR spectrum of complex **3** exhibits the set of $CH_2CH_3$ resonances. The solution of **2** in $CH_3CN$ gives a clearly resolved EPR spectrum ($g = 1.988$; $a(^{51}V) = 79.1$ G), indicating that the impurities observed with **2** are EPR-silent vanadium species. The $^1H$ NMR spectrum of **2** in $CD_3CN$ shows free thf, which indicates that ligand exchange occurs between thf and $CD_3CN$ to give presumably $[V(NEt_2)_2(CD_3CN)_4][BPh_4]_2$. Complex **4** was also characterized by EPR spectroscopy ($g = 1.979$; $a(^{51}V) = 91.0$ G).

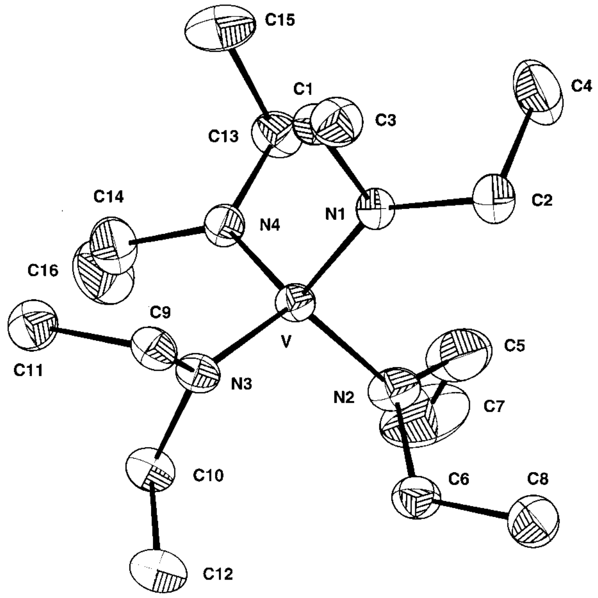


Figure 2. Molecular structure of the cation in **3** showing the labeling scheme; hydrogen atoms are omitted for clarity. The structure of the $[B(C_6F_5)_4]^-$ ion is normal. Selected bond lengths [Å] and angles [°]: V–N1 1.817(3), V–N2 1.826(3), V–N3 1.826(3), V–N4 1.847(3); N1-V-N2 104.1(1), N1-V-N3 111.8(1), N2-V-N3 114.5(1), N1-V-N4 107.6(1), N2-V-N4 109.0(1), N3-V-N4 109.5(1), V-N1-C1 115.7(2), V1-N1-C2 130.1(2), V1-N2-C5 122.9(3),V-N2-C6 122.0(3), V-N3-C9 131.4(2), V-N3-C10 114.1(2), V-N4-C13 120.6(2), V-N4-C14 125.0(2).

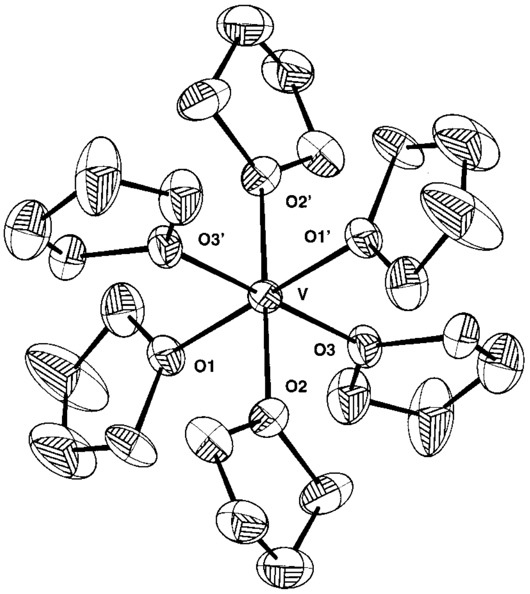
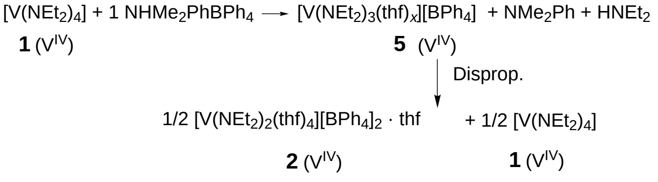


Figure 3. Molecular structure of the cation in **4** showing the labeling scheme; hydrogen atoms are omitted for clarity. The structure of the $[B(C_6F_5)_4]^-$ ion is normal. Selected bond lengths [Å] and angles [°]: V–O1 2.149(4), V–O2 2.146(4), V–O3 2.131(4); O1-V-O2 91.5(2), O1-V-O3 89.5(2), O2-V-O3 89.9(2), *trans* O-V-O 180.0 (av).

When **1** was treated with two equivalents of $[NHMe_2Ph][BPh_4]$ in thf, a red powder precipitated immediately, which we identified as **2** by its EPR spectrum; however, complete conversion into **2** was not possible (30–40% yield, in different experiments). The $^{11}B$ NMR spectrum of the filtrate shows a signal for $[BPh_4]^-$ at $\delta = -6.3$ and a broad resonance at $\delta = 2$, which we assign to a $BPh_3 \cdot NR_3$ adduct ($NR_3 = HNEt_2$) (an authentic sample of $BPh_3$ and $HNR_2$ was prepared). This indicates that a redox reaction probably occurs in the reaction with $[BPh_4]^-$, like that which we have already observed in the redox reaction of $[Cp_2V(CH_3)(thf)][BPh_4]$.[7] Addition of pentane to the green filtrate gave an oily product, which was then triturated with pentane to give a mixture of **3** and **4** (characterized by $^1H$ NMR and by EPR spectroscopy, respectively, but the yield was not quantified).

The formation of the moisture-sensitive compounds **2**–**4** is not a straightforward process, and different pathways seem to occur. First, the oxidation state of the vanadium center is preserved on going from **1** to **2**, whereas it loses two dialkylamido ligands. This reaction was monitored by EPR spectroscopy, and the characteristic signal of $[V(NEt_2)_4]$ ($g = 1.980$; $a(^{51}V) = 65.0$ G)[15] was continually observed together with that of a transient species **5** ($g = 1.977$; $a(^{51}V) = 72.0$ G). The red insoluble precipitate **2** was filtered off, and the EPR spectrum of the filtrate shows the sole presence of **1**, which is at roughly half of the concentration before its reaction with the ammonium salt. A disproportionation reaction is mainly responsible for the pathway (Scheme 1), and we tentatively suggest formula **5** ($x = 1$) for the intermediate species.

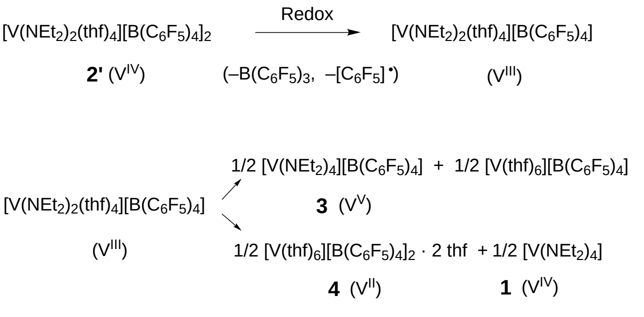


Scheme 1. Reaction of **1** with one equivalent of $[NHMe_2Ph][BPh_4]$ to give **2** by means of a disproportionation mechanism.

The reaction of **1** with two equivalents of the ammonium salt is more complicated, and we tentatively propose an idealized pathway involving redox and disproportionation reactions (Scheme 2). After monitoring the reaction with the tetraperfluoroborate ammonium salt by EPR spectroscopy for two days, we observed overlapping eight-line signals of different species. Compounds **1** and **4** were easily identified at the beginning and at the end of the reaction, respectively. Two other species were also identified, **2′** and the presumed cation **5′** associated with the $[B(C_6F_5)_4]$ counteranion, based on the

$[V(NEt_2)_3(thf)]^+$ **5′**

similarity with the EPR spectra of the analogues **2** and **5**. Both appear as transient species (the EPR signal of **2′** was observed only during the first 30 min of the reaction until it overlapped with the signal of **4**; **5′** was seen for roughly 15 h). Peak positions and relative intensities of different spectra monitored during the course of the reaction validate these assumptions. After one week the diamagnetic species **3** had entirely precipitated and only **4** was observed by EPR spectroscopy (25–30% yield based on **1** (100%) in several experiments, with a small amount of an uncharacterized vanadium species).



Scheme 2. Postulated mechanism deduced from the isolation of **3** and **4** from the reaction of **1** with two equivalents of $[NHMe_2Ph][B(C_6F_5)_4]$.

The presence of **5′** can be explained on the basis of Scheme 1. We presume that the excess of the perfluoroborate ammonium salt serves either to trap **1**, which is formed in the disproportionation of **5′**,[16] or to convert **5′** directly into **2′**. Moreover, there is no evidence that the putative **5** (or **5′**) intermediate does not undergo a redox reaction with the neutral $[V(NEt_2)_3]$ being formed.[17] The vanadium atom in product **3** has increased its oxidation state from the starting state $V^{IV}$ to $V^{V}$, whereas in **4** it has lowered its oxidation state to $V^{II}$. A competitive disproportionation reaction from $2\,V^{III}$ to $V^{V}/V^{I}$ and $V^{IV}/V^{II}$ is suggested. The mechanism involves the formation of the $V^{III}$ species $[V(NEt_2)_2(thf)_4]^+$ from **2′** by means of a redox reaction with the $[B(C_6F_5)_4]^-$ ion[7,8] (the transfer of a $C_6F_5$ group from a $[B(C_6F_5)_4]^-$ ion to a metal is a recognized mechanism[18]). The reaction was analyzed by $^{11}B$ NMR spectroscopy. The spectrum shows the expected peak of the $[B(C_6F_5)_4]^-$ ion ($\delta = -16$) and a broad peak at $\delta = -2.5$ which may be due to the adduct $B(C_6F_5)_x(NEt_2)_{3-x} \cdot HNEt_2$ (by comparison with a sample prepared from $B(C_6F_5)_3$ and $HNEt_2$). However, the protonolysis of **1** was not further studied in detail due to its complexity.[19]

The mechanism for the formation of **2** is fully rationalized, but the pathways leading to **3** and **4** are not obvious and the mechanisms remain unknown. We do not yet have mechanistic details concerning these transformations owing to the propensity of the $[VNR_2]$ moiety to undergo amine elimination and redistribution/redox reaction in the presence of the ammonium salt. The different reactivity observed when the protonolysis of **1** is performed with the ammonium salt $[NHMe_2Ph]^+$ associated with the $[BPh_4]^-$ or the $[B(C_6F_5)_4]^-$ counterion is mainly due to the insolubility of **2**, which precipitates from the reaction mixture before it can react further, whereas the presence of the tetraperfluoroborate ion, leading to a more soluble complex **2′**, permits further degradation. Due to the tendency for the vanadium to assume different oxidation states, octahedral $V^{II}$ and $V^{IV}$ and tetrahedral $V^{V}$ cationic complexes were obtained. The ability of the amido ligand to act as a three-electron ligand is worth underlining. The presence of different oxidation states in the cationic vanadium chemistry observed in this work further supports the recognized complexity of vanadium chemistry in Ziegler–Natta catalysis.[20] Procedures to convert species **2**–**4** into active cationic species for olefin polymerization[3b,5e] are in progress and will be reported elsewhere.

## *Experimental Section*

**2**: Solid $[NHMe_2Ph][BPh_4]$ (344 mg, 0.78 mmol) was added to $[V(NEt_2)_4]$ (266 mg, 0.78 mmol) in thf (15 mL) at −78 °C. The resulting solution was stirred for 1 h and allowed to warm to room temperature. After 12 h red crystals of **2** were obtained and filtered, washed with thf, and dried in vacuo. Yield: 244 mg (26%). Elemental analysis calcd for $C_{76}H_{100}B_2O_5N_2V$: C 76.45, H 8.38, V 4.27; found: C 75.82, H 7.92, V 4.40.

**3**, **4**: Solid $[NHMe_2Ph][B(C_6F_5)_4]$ (727 mg, 0.90 mmol) was added to $[V(NEt_2)_4]$ (154 mg, 0.45 mmol) in thf (15 mL) at room temperature. The resulting solution was stirred for 1 h, and pentane (20 mL) was slowly added to the solution. After slow diffusion of the pentane into the solution in thf, red-black **3** and bright red **4** crystals were obtained overnight, filtered, washed rapidly with thf (2 × 5 mL), and dried in vacuo (total mass: 304 mg). After careful and lengthy separation in the glove box, analytical analysis of **3** and **4** was attempted for characterization**,** but only **3** gave reproducible results. Elemental analysis calcd for $C_{40}H_{40}BF_{20}N_4V$: C 47.16, H 3.93, N 5.50; found: C 46.60, H 3.26, N 5.00; $^1H$ NMR (200 MHz, $[D_8]$thf): $\delta = 1.40$ (t, $CH_3$), 4.32 (q, $CH_2$); $^{11}B$ NMR (25.7 MHz, $[D_8]$thf): $\delta = -16.2$.

EPR experiments: In a typical experiment a solution of **1** in thf was prepared, and an aliquot of the solution was introduced into a standardized capillary tube for EPR measurements. This EPR spectrum served as a standard for the reaction. The solid ammonium salt was then added to the solution, and aliquots were removed by syringe periodically, introduced into the capillary tubes, and analyzed by EPR over one week. The acquisition parameters were kept constant for both the unknown and the standard sample measurements.

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[9] Crystal structure data of **2** [the data for **3**, **4** are given in square brackets]**:** Chemical formula $[V\{N(C_2H_5)_2\}_2(C_4H_8O)_4][B(C_6H_5)_4]\cdot C_4H_8O$ $[[\{V[N(C_2H_5)_2]_2\}_4][B(C_6F_5)_4]$, $[V(C_4H_8O)_6][B(C_6H_5)_4]_2\cdot 2\,C_4H_8O]$, $M_r = 1174.04$ [1018.4; 1981.84], monoclinic [triclinic, monoclinic], space group $P21/n$ [$P1$, $P21/n$], $a = 11.9261(8)$ [11.095(2), 12.557(1)], $b = 13.2215(8)$ [11.181(2), 22.158(2)], $c = 21.126(2)$ [18.095(2), 15.648(2)] Å, $\alpha = 90$ [77.663(1), 90], $\beta = 92.527(7)$ [84.22(2), 106.368(8)], $\gamma = 90$ [89.13(1), 90], $V = 3327.8$ [2171, 4177] Å$^3$, $Z = 2$ [4,2], $\rho =$ 1.17 [1.56, 1.58] g cm$^{-1}$, $\mu = 1.92$ [3.38, 2.50] cm$^{-1}$, $F(000) = 1033$ [1033, 1996], crystal size 0.32 × 0.25 × 0.05 [0.32 × 0.25 × 0.07, 0.4 × 0.2 × 0.05] mm$^3$, crystal form: platelet [plate, thin plate], crystal color: red [dark red, bright red], $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 170$ [180, 180] K, number of measured reflections: 20817 [17214, 25545], number of independent reflections: 4508 [6422, 5741], $R_{av} = 0.09$ [0.05, 0.04], $R_a = 0.059$ [0.059, 0.056], $R_{wb} = 0.064$ [0.067; 0.063], weighting scheme Chebyshev, Ar coefficients: 3.67/−1.72/2.79/−0.081 [2.22/0.39/1.71, 2.75/−1.13/2.04/−0.336], GOF = 1.1 [1.1, 1.05], number of reflections used: 2174 [3033; 4870], observation criterion $I > \sigma(I)$ [$I > 1.5\sigma(I)$, $I > 3\sigma(I)$], number of parameters 402 [472, 596]. The selected crystal, sensitive to air and moisture, was protected in vaseline oil and placed in a capillary. The data were collected with a STOE IPDS diffractometer. Whole structures were solved by direct methods and refined by least-squares procedures on $F_o$. In **2** disorder was observed on one ethyl ligand; the electron density of $CH_3$ groups is statistically distributed over two sites with a 1:1 ratio. A similar situation has been observed for one molecule of the thf solvent molecule of **4** for which one C atom is also distributed over two positions. All non-hydrogen atoms were refined anisotropically except for the C atom of free thf molecule of **4**, which was only isotropically refined. 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-101352. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] The following reactions were investigated as an alternative approach to provide assignable compounds. When **1** was treated with one equivalent of the perfluoborate ammonium salt, the same EPR spectra were observed (but we were unabled to isolate a vanadium complex). After complex **1** was treated with one or two equivalents of $B(C_6F_5)_3$ in thf at room temperature, the EPR spectrum of **5** was observed**;** the signals disappear after three days to again give the EPR signal of **1**. This is probably due to a disproportionation reaction, but we were unable, in both cases, to isolate any vanadium complex.

[17] This neutral $V^{III}$ complex could react further with the ammonium salt to give the cationic $V^{III}$ species leading to **3** and **4**. This possibility is under investigation.

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[19] We did not observe the formation of the perfluorinated biphenyl $(C_6F_5)_2$, whereas $C_6F_5H$ was identified in the reaction mixture (by comparison with the $^{19}F$ NMR spectrum of an authentic sample and by a characteristic peak in its mass spectrum (*m*/*z* 168)). Nevertheless, the formation of $C_6F_5H$ was also observed by $^{19}F$ NMR spectroscopy when $B(C_6F_5)_3$ and $HNEt_2$ were allowed to react. Therefore, a redox reaction could be inferred from the existence of $C_6F_5H$.

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