

# Preparation, Characterization, and Reactivity of a Diamagnetic Vanadium Nitride

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**Abstract:** The reactions of  $(\text{Ph}_2\text{N})_3\text{V}(\text{THF})$  (**1**) with  $[(\text{CH}_3)_3\text{Si}]_3\text{N}_3$  and  $[(\text{CH}_3)_3\text{Si}]\text{CHN}_2$  proceed at room temperature to afford the corresponding derivatives  $(\text{Ph}_2\text{N})_3\text{V}[\text{N}-\text{Si}(\text{CH}_3)_3]$  (**2a**) and  $(\text{Ph}_2\text{N})_3\text{V}[\text{N}_2\text{CHSi}(\text{CH}_3)_3]$  (**3**). Reactions of both **2a** and **3** with lithium isopropylamide provide the unprecedented

anionic vanadium nitride species  $[(\text{Ph}_2\text{N})_3\text{V}(\mu\text{-N})\text{Li}(\text{THF})_3] \cdot (\text{THF})_{0.5}$  (**4**), which displays moderate nucleophilicity.

## Keywords

dinitrogen activation · nitrides · structure elucidation · vanadium complexes

It reacts with  $(\text{CH}_3)_3\text{SiCl}$  and  $\text{MeI}$  to form the complex  $(\text{Ph}_2\text{N})_3\text{V}(\text{N-R})$  [ $\text{R} = \text{Si}(\text{CH}_3)_3$  (**2a**),  $\text{Me}$  (**2b**)]. Reactions with  $\text{Cp}^*_2\text{ZrCl}_2$  and  $\text{CpTiCl}_3$  lead to the formation of the heterodinuclear bridged nitride complexes  $[(\text{Ph}_2\text{N})_3\text{V}(\mu\text{-N})\text{ZrClCp}^*_2]$  [ $\text{Cp}^* = \text{Cp}^* = \text{Cp}$  (**6a**),  $\text{CH}_3\text{C}_5\text{H}_4$  (**6b**)] and  $\{[(\text{Ph}_2\text{N})_3\text{V}(\mu\text{-N})]_2\text{TiClCp}\}$  (**8**).

## Introduction

In the past few years, the current literature has experienced a spectacular revival of interest in the preparation and characterization of transition metal nitrides.<sup>[1]</sup> This was mainly motivated by the tendency of the nitride atom to bridge two or more metal centers, thus making these species particularly versatile building blocks for cluster chemistry,<sup>[2]</sup> material science,<sup>[3,4]</sup> and precursors to inorganic polymers.<sup>[5]</sup> In addition, transition and non-transition metal nitrides display interesting and useful physical properties.<sup>[6]</sup>

Our interest in this field focuses on the transition metal nitride's role as a plausible reactive intermediate in the metal promoted activation of dinitrogen<sup>[7]</sup> and subsequent incorporation of nitrogen into organic substrates.<sup>[8]</sup> Although formation of the nitride species was long regarded as a pivotal step in the activation of dinitrogen, its generation by dinitrogen cleavage has only recently been unequivocally demonstrated.<sup>[9]</sup> Di- and trivalent vanadium species are particularly promising substrates for studying this chemistry owing to their ability to interact with dinitrogen,<sup>[10]</sup> promote catalytic formation of ammonia and hydrazine,<sup>[11]</sup> and generate stable nitride and imido functionalities.<sup>[5d-e, 7a, 12]</sup> A recent study reported the preparation of the mixed-valence anion  $\{[(\text{CH}_3)_3\text{Si}]_2\text{N}\}_2\text{V}(\mu\text{-N})_2\text{V}^-$  obtained during hydrogenolysis experiments carried out in the presence of nitrogen gas.<sup>[13]</sup> A protonated form of vanadium nitride has also been prepared by the reaction of a  $\text{V}^{\text{III}}$  amide with aziridine.<sup>[14]</sup> Vanadium nitrides prepared by synthetic routes other than dinitrogen cleavage are well established.<sup>[15]</sup> These species, which are significant as possible intermediates for the dinitrogen reduction process, display puzzling structures and

interesting magnetic behavior.<sup>[16]</sup> However, they are characterized by pronounced chemical inertness. In order to understand the activation of dinitrogen, it is important to prepare reactive vanadium nitride species which are able to readily interact with both organic and inorganic substrates.

In this paper we describe the preparation and characterization of an anionic vanadium nitride species and a preliminary study of its chemical reactivity.

## Experimental Section

**General:** All operations were performed under the inert atmosphere of a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques.  $\text{Ph}_2\text{NH}$  and  $i\text{PrNH}_2$  were sublimed or distilled prior to use.  $\text{NaH}$ ,  $n\text{BuLi}$ ,  $(\text{TMS})\text{N}_3$ ,  $(\text{TMS})\text{CHN}_2$ , and  $\text{CH}_3\text{I}$  were used as received (Aldrich).  $(\text{Ph}_2\text{N})_3\text{V}(\text{THF})$  (**1**) [17],  $\text{Cp}^*_2\text{ZrCl}_2$  [18],  $\text{Cp}^*\text{ZrCl}_2$  [18],  $\text{Cp}^*\text{ZrCl}_3$  [19], and  $\text{CpTiCl}_3$  [20] were prepared according to published procedures. Lithium isopropylamide (LIA) was prepared by treating a solution of  $i\text{PrNH}_2$  in hexane with a stoichiometric amount of  $\text{BuLi}$ . Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a dry-box. Elemental analyses were carried out with a Perkin Elmer PE 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence with a Philips XRF 2400 instrument. NMR spectra were obtained with a Varian 500 MHz instrument. Data for X-ray crystal structures were obtained with a Rigaku AFC 6S diffractometer. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and were sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods [21] and corrections for underlying diamagnetism were applied to the data [22].

**$(\text{Ph}_2\text{N})_3\text{V}(\text{N-TMS})$  (**2a**):** A deep green solution of **1** (3.5 g, 5.6 mmol) in THF was treated at  $-20^\circ\text{C}$  with neat azidotrimethylsilane (0.65 g, 5.6 mmol). The color of the solution turned intense blood red and vigorous gas evolution was observed. The solution was evaporated to dryness and the residue redissolved in hexane (70 mL). Deep red, moderately air-stable crystals of **2a** separated upon standing at  $-30^\circ\text{C}$  (3.1 g, 4.8 mmol, 86%). Anal. calcd. (found) for  $\text{C}_{39}\text{H}_{39}\text{N}_4\text{SiV}$ : C 72.87 (72.65), H 6.12 (6.01), N 8.72 (8.63). IR (KBr, Nujol,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 1583$  (s), 1497 (s), 1377 (m), 1267 (m), 1243 (m), 1210 (w), 1186 (s), 1168 (s), 1074 (m), 1052 (w), 1026 (s), 926 (s), 877 (s), 860 (m), 800 (m), 753 (s), 694 (s).  $^1\text{H}$  NMR (500 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.11$ , 6.82 (m, 30H, Ph),  $-0.23$  (s, 9H, TMS).  $^{13}\text{C}$  NMR (125.7 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ):  $\delta = 155.8$  (quat C, Ph), 129.5, 124.6, 124.1 (Ph), 0.7 (TMS).  $^{51}\text{V}$  NMR (131.4 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ):  $\delta = -156.2$ .

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**(Ph<sub>2</sub>N)<sub>3</sub>V(N-CH<sub>3</sub>) (2b):** A solution of **4** (2.0 g, 2.4 mmol) in THF (70 mL) was treated at room temperature with neat MeI (0.35 g, 2.4 mmol). The resulting deep red solution was evaporated to dryness and the residual mixture redissolved in hexane (30 mL). After filtration, dark red crystals of **2b** separated from the solution upon standing for 4 d at 4 °C (1.1 g, 1.9 mmol, 79%). Anal. calcd. (found) for C<sub>7</sub>H<sub>13</sub>N<sub>4</sub>V: C 76.01 (75.54), H 5.69 (5.57), N 9.58 (9.73). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1583 (m), 1479 (sh), 1465 (s), 1376 (m), 1261 (s), 1184 (w), 1176 (w), 1164 (w), 1081 (w), 1070 (w), 1041 (w), 1027 (m), 937 (m), 883 (m), 865 (w), 800 (m), 752 (s), 694 (s). <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 6.97, 6.81 (m, 30H, Ph), 3.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 154.2, (quat C, Ph), 129.1, 123.8, 123.3 (Ph), 68.1 (CH<sub>3</sub>). <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -250.5.

**(Ph<sub>2</sub>N)<sub>3</sub>V[N<sub>2</sub>CH(TMS)] (3):** A solution of **1** (3.2 g, 5.0 mmol) in THF (100 mL) at -20 °C was treated with neat trimethylsilyldiazomethane (0.6 g, 5.2 mmol). The resulting deep orange solution was warmed up to room temperature and evaporated to dryness. The residual solid was resuspended in hexane (40 mL), the resulting slurry boiled, and the mixture filtered while hot. The filtrate was allowed to cool and stand at room temperature overnight during which dark orange crystals of **3** separated (2.8 g, 4.2 mmol, 84%). Anal. calcd. (found) for C<sub>40</sub>H<sub>60</sub>N<sub>6</sub>VSi: C 71.73 (71.66), H 6.02 (5.97), N 10.46 (10.35). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1581 (s), 1469 (s), 1376 (m), 1261 (s), 1183 (s), 1172 (s), 1161 (s), 1085 (m), 1027 (m), 937 (s), 883 (s), 862 (s), 842 (s), 752 (s), 692 (s), 662 (w), 527 (m), 507 (s). <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.2, 6.8 (m, 31H, Ph and CH<sub>diaz</sub>), -0.08 (s, 9H, TMS). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 154.0, (quat C, Ph), 129.2, 124.0, 123.5 (Ph), 118.1 (CH<sub>diaz</sub>), -2.8 (TMS). <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -12.8.

**[(Ph<sub>2</sub>N)<sub>3</sub>V(μ-N)Li(THF)<sub>3</sub>](THF)<sub>0.5</sub> (4):**

**Method A:** A solution of **2a** (2.5 g, 3.9 mmol) in THF (70 mL) was treated at -40 °C with LIA (0.27 g, 4.1 mmol). A sudden color change from dark red to bright orange was observed. The resulting solution was filtered and evaporated to dryness. The residual gummy material was redissolved in a mixture of toluene/hexane 20:80 (100 mL) and allowed to stand at 4 °C. After 2 d, large, bright orange, cubic, extremely air-sensitive crystals of **4** separated (2.25 g, 2.7 mmol, 69%). Anal. calcd. (found) for C<sub>50</sub>H<sub>58</sub>N<sub>6</sub>LiVO<sub>3</sub>: C 72.45 (72.13), H 7.05 (7.09), N 6.76 (7.03). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1586 (s), 1481 (sh), 1333 (w), 1304 (m), 1263 (s), 1192 (s), 1173 (s), 1073 (w), 1035 (s), 990 (w), 926 (s), 875 (s), 865 (s), 836 (w), 811 (w), 750 (s), 698 (s), 695 (sh), 670 (w), 615 (w), 580 (w), 509 (s). <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.20, 6.97, 6.78, 6.70 (m, 30H, Ph), 3.11 (m, 14H, THF), 1.07 (m, 14H, THF). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 156.9, 155.0, (quat C, Ph), 129.5, 128.8, 128.0, 123.1, 122.3, 118.2, 116.1 (Ph), 67.9 (THF), 24.8 (THF). <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -159.4. <sup>7</sup>Li NMR (194.3 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -1.38.

**Method B:** A solution of **3** (2.7 g, 4.0 mmol) in THF (70 mL) at -40 °C was treated with LIA (0.30 g, 4.6 mmol). The color of the solution changed instantaneously to bright orange. After warming up to room temperature, the solution was filtered and evaporated to dryness. The residual solid was redissolved in a mixture of toluene/hexane 20:80 (70 mL) and allowed to stand overnight at 4 °C during which large crystals of **4** separated (1.85 g, 2.2 mmol, 55%).

**[(Ph<sub>2</sub>N)<sub>3</sub>V]Li(THF)<sub>4</sub> (5):** A solution of **4** (1.8 g, 2.2 mmol) in THF (70 mL) at -40 °C was treated with LIA (0.15 g, 2.3 mmol). The color of the solution changed from bright orange to deep green. The solution was allowed to warm up to room temperature and the solvent was removed in vacuo. The residual solid was redissolved in a 30:70 mixture of THF/toluene (50 mL), filtered, and allowed to stand at 4 °C overnight during which deep green, moderately air-sensitive crystals of **5** separated (0.9 g, 0.9 mmol, 4%). Anal. calcd. (found) for C<sub>64</sub>H<sub>72</sub>N<sub>6</sub>O<sub>4</sub>VLi: C 75.42 (75.38), H 7.12 (7.03), N 5.50 (5.43). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1585 (s), 1479 (s), 1463 (s), 1376 (m), 1253 (s), 1176 (s), 1152 (m), 1140 (w), 1078 (m), 1016 (m), 991 (s), 935 (s), 877 (m), 862 (w), 800 (s), 752 (s), 700 (s), 671 (w).  $\mu_{\text{eff}}$  = 2.97 μ<sub>B</sub>.

**[(Ph<sub>2</sub>N)<sub>3</sub>V(μ-N)ZrClCp\*] [Cp\* = C<sub>5</sub>H<sub>5</sub> (6a), CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub> (6b)]:** A solution of **4** (2.3 g, 2.8 mmol) in THF (70 mL) was treated with Cp\*<sub>2</sub>ZrCl<sub>2</sub> (2.8 mmol) at room temperature. The resulting deep red solution was filtered and evaporated to dryness. The residual solid was redissolved in hexane, filtered while hot, and allowed to stand overnight at room temperature during which dark crystals of **6** separated [**6a**: 1.7 g, 2.1 mmol, 75%; **6b**: 1.5 g, 1.7 mmol, 63%].

**6a:** Anal. calcd. (found) for C<sub>66</sub>H<sub>40</sub>N<sub>4</sub>VZrCl: C 66.85 (66.79), H 4.88 (4.72), N 6.78 (6.73). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1590 (s), 1482 (s), 1475 (s), 1375 (m), 1251 (s), 1178 (m), 1140 (m), 1078 (w), 1059 (w), 1030 (m), 990 (s), 935 (s), 890 (m), 750 (s), 700 (s), 660 (w). <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.12 (dd, 12H, Ph), 7.08 (dt, 12H, Ph), 6.83 (tt, 6H, Ph), 5.73 (s, 10H, Cp). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 155.9 (quat C, Ph), 129.1, 124.0, 123.7 (Ph), 115.4 (Cp). <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -31.2.

**6b:** Anal. calcd. (found) for C<sub>68</sub>H<sub>44</sub>N<sub>4</sub>VZrCl: C 67.47 (67.40), H 5.19 (5.11), N 6.56 (6.49). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1587 (m), 1479 (s), 1253 (s), 1186 (m), 1176 (m), 1078 (w), 1052 (w), 1029 (m), 985 (s), 933 (m), 881 (m), 800 (s), 754 (m), 700 (s), 669 (w). <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.08 (dt, 20H, Ph), 6.84 (dt, 10H, Ph), 6.30 (quartet, 2H, Cp), 5.62 (quartet, 2H, Cp), 5.38 (quartet, 2H, Cp), 5.20

(quartet, 2H, Cp), 1.85 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 156.0 (quat C, Ph), 129.1, 124.0, 123.6 (Ph), 121.5, 118.7, 110.5, 109.2 (Cp), 15.6 (Me). <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -30.5.

**[(Ph<sub>2</sub>N)<sub>3</sub>V(μ-N)ZrCp\*Cl<sub>2</sub>] (7):** A solution of **4** (2.5 g, 3.0 mmol) in THF (70 mL) was treated with Cp\*<sub>2</sub>ZrCl<sub>2</sub> (1.0 g, 3.0 mmol) at room temperature. The resulting deep red solution was evaporated to dryness and the residual solid redissolved in hexane (70 mL). The resulting solution was filtered and allowed to stand at 4 °C overnight during which dark red crystals of **7** separated (1.72 g, 2.0 mmol, 67%). Anal. calcd. (found) for C<sub>66</sub>H<sub>43</sub>N<sub>4</sub>VZrCl<sub>2</sub>: C 63.73 (63.66), H 5.23 (5.19), N 6.46 (6.41). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1592 (s), 1476 (s), 1454 (s), 1372 (m), 1200 (s), 1154 (m), 1119 (m), 1078 (w), 1055 (w), 1029 (m), 985 (s), 930 (s), 881 (m), 754 (s), 700 (s), 685 (w), 1253 (s), 1186 (m), 1176 (m), 1078 (w), 1052 (w), 1029 (m), 985 (s), 933 (m), 881 (m), 800 (s), 754 (m), 700 (s), 669 (w). <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.2, 6.4 (m, 30H, Ph), 1.92 (s, 15H, CH<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 158.0 (quat C, Ph), 128.9, 125.2, 121.9, 119.2, 116.2, 108.4 (Ph), 12.8 (Me). No resonance could conclusively be attributed to the quaternary Cp\* carbon atoms. <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -35.5.

**[(Ph<sub>2</sub>N)<sub>3</sub>V(μ-N)<sub>2</sub>TiCpCl] (8):** A solution of **4** (2.2 g, 2.6 mmol) in THF (70 mL) was treated with CpTiCl<sub>3</sub> (0.30 g, 1.4 mmol) at room temperature whereby the color of the solution changed from bright orange to deep red. The resulting solution was evaporated to dryness and the residual solid redissolved in hexane (70 mL). After filtration and 1 d at room temperature moderately air stable, deep red needles of **8** separated (2.4 g, 1.8 mmol, 69%). Anal. calcd. (found) for C<sub>79</sub>H<sub>65</sub>N<sub>6</sub>V<sub>2</sub>TiCl: C 72.34 (72.28), H 5.00 (4.95), N 8.54 (8.48). IR (KBr, Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1589 (s), 1474 (s), 1460 (s), 1375 (m), 1251 (s), 1178 (m), 1148 (s), 1080 (m), 1047 (s), 991 (s), 931 (s), 891 (m), 751 (s), 704 (m), 640 (w). <sup>1</sup>H NMR (500 MHz, 25 °C, [D<sub>6</sub>]THF):  $\delta$  = 7.05 (quartet, 24H, Ph), 6.99 (d, 12H, Ph), 6.83 (d, 24H, Ph), 5.62 (s, 5H, Cp). <sup>13</sup>C NMR (125.7 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 155.9 (quat C, Ph), 129.9, 125.3, 124.2 (Ph), 121.6 (Cp). <sup>51</sup>V NMR (131.4 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 32.3.

**X-Ray Crystallography:** Data were collected at temperatures in the range of -142 to -160 °C by using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of 50.0° for suitable air-sensitive crystals mounted on glass fibres. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were averaged. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct as well as Fourier methods. The positions of the non-hydrogen atoms were anisotropically refined. Hydrogen atom positions were located in the difference Fourier maps but not refined. In the case of complex **3**, the TMS carbon atoms display rather large thermal parameters, possibly indicative of disorder. The disorder was modeled by splitting the occupancy of the three carbon atoms over the two positions, and arbitrarily attributing a 50:50 occupancy, as shown by the difference Fourier maps. Successful refinement confirmed the goodness of the model. Similarly, the structure of complex **4** showed that the carbon atoms of one of the three THF molecules attached to lithium were disordered over two positions. The disorder was successfully modeled by attributing a relative occupancy of 80:20. In addition, half a THF molecule, disordered over two positions, was found in the lattice. In this case the refinement succeeded by attributing a 50:50 occupancy to the two positions. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with  $I > 2.5\sigma(I)$ . Neutral atomic scattering factors were taken from Cromer and Waber [23]. Anomalous dispersion effects were included in  $F_{\text{calc}}$ . All calculations were performed using the TEXSAN package on a Digital VAX station. Details on crystal data and structure solution are given in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-24. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code + (1223)336-033; e-mail: teched@chemcryst.cam.ac.uk).

## Results and Discussion

Vigorous evolution of dinitrogen and a color change were observed upon treatment of a toluene solution of (Ph<sub>2</sub>N)<sub>3</sub>V(THF) (1) with trimethylsilylazide (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub>. A crystalline, diamagnetic compound, formulated as (Ph<sub>2</sub>N)<sub>3</sub>V[N-Si(CH<sub>3</sub>)<sub>3</sub>] (2a), was isolated in 57% yield upon crystallization from ether (Scheme 1). This complex was characterized by elemental analysis and NMR spectroscopy. Combustion analysis data are consistent with the proposed formulation and both the <sup>1</sup>H and <sup>13</sup>C NMR spectra show the aromatic and (CH<sub>3</sub>)<sub>3</sub>Si group resonances in the expected regions. This compound belongs to the

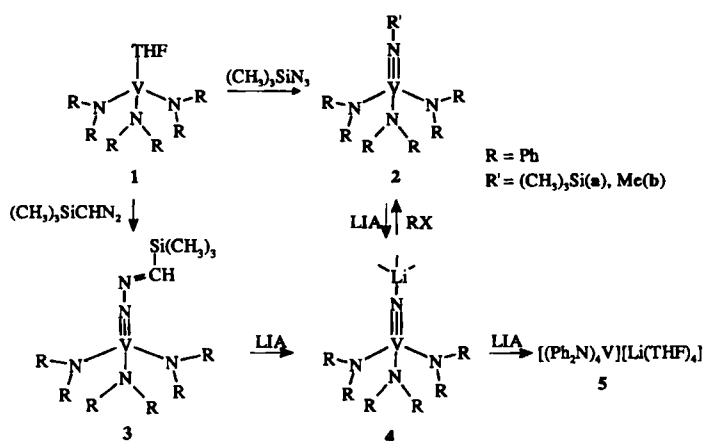
Table 1. Crystal data and results of structure analysis.

	2b	3	4	5	6b
formula	C <sub>37</sub> H <sub>33</sub> VN <sub>4</sub>	C <sub>40</sub> H <sub>40</sub> N <sub>5</sub> SiV	C <sub>50</sub> H <sub>58</sub> N <sub>4</sub> O <sub>3.5</sub> VLi	C <sub>64</sub> H <sub>72</sub> VN <sub>4</sub> O <sub>4</sub> Li	C <sub>48</sub> H <sub>44</sub> N <sub>4</sub> VZrCl
M <sub>r</sub>	584.64	669.82	828.92	1019.18	854.52
space group	P2 <sub>1</sub> /n (No. 14)	P2 <sub>1</sub> /c (No. 14)	P1 (No. 2)	P2 <sub>1</sub> (No. 4)	P2 <sub>1</sub> /n (No. 14)
a (Å)	13.847 (9)	9.177 (3)	13.590 (1)	10.872 (2)	13.677 (1)
b (Å)	12.134 (6)	14.678 (2)	13.813 (1)	13.830 (1)	14.2892 (9)
c (Å)	18.57 (1)	26.877 (3)	13.265 (2)	18.948 (2)	20.425 (1)
α (deg)			104.55 (1)		
β (deg)	101.77 (4)	96.59 (2)	107.30 (2)	98.07 (1)	93.659 (9)
γ (deg)			73.00 (2)		
V (Å <sup>3</sup> )	3055 (3)	3596 (2)	2237 (1)	2821 (1)	3983.5 (8)
Z	4	4	2	4	4
radiation (MoKα, Å)	0.71069	0.71069	0.71069	0.71069	0.71069
T (°C)	-155	-150	-160	-148	-142
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.271	1.237	1.231	1.200	1.425
μ <sub>calcd</sub> (cm <sup>-1</sup> )	3.44	3.32	2.58	2.17	5.90
R, R <sub>w</sub> [a]	0.047, 0.058	0.070, 0.084	0.053, 0.070	0.067, 0.083	0.048, 0.063

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

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

Compound 2b		Compound 3		Compound 4		Compound 5		Compound 6b	
V1-N1	1.918(3)	V1-N1	1.901(4)	V1-N2	1.954(2)	V1-N1	2.004(7)	V1-N1	1.920(4)
V1-N2	1.925(3)	V1-N2	1.905(4)	V1-N3	1.958(2)	V1-N2	1.995(7)	V1-N2	1.909(4)
V1-N3	1.894(3)	V1-N3	1.909(3)	V1-N4	1.942(2)	V1-N3	1.988(7)	V1-N3	1.918(4)
V1-N4	1.637(3)	V1-N4	1.665(4)	V1-N5	1.582(3)	V1-N4	1.988(7)	V1-N4	1.638(4)
N4-C37	1.427(5)	N4-N5	1.333(5)	N5-Li1	2.017(6)	O1-Li1	1.82(3)	N4-Zr1	2.128(4)
N1-C1	1.411(5)	N5-C37	1.192(7)	Li1-O1	1.985(6)	O2-Li1	1.86(3)	Zr1-Cl1	2.428(1)
N1-C7	1.447(5)	Si1-C37	1.858(6)	N2-C1	1.401(4)	O3-Li1	1.99(2)	N1-V1-N2	114.2(2)
N1-V1-N2	116.0(1)	N1-C1	1.415(5)	N2-C6	1.442(4)	O4-Li1	1.96(3)	N1-V1-N3	112.8(1)
N1-V1-N3	109.8(1)	N1-C7	1.448(5)	N2-V1-N3	114.4(1)	N1-V1-N2	108.3(3)	N1-V1-N4	106.3(2)
N1-V1-N4	105.3(2)	N1-V1-N2	114.8(2)	N2-V1-N4	116.1(1)	N1-V1-N3	113.2(3)	N2-V1-N3	107.4(2)
N2-V1-N3	115.5(1)	N1-V1-N3	112.3(2)	N2-V1-N5	104.3(1)	N1-V1-N4	107.8(3)	N2-V1-N4	106.1(2)
N2-V1-N4	104.1(2)	N1-V1-N4	104.9(2)	N3-V1-N4	112.80(9)	N2-V1-N3	107.0(3)	N3-V1-N4	109.8(2)
N3-V1-N4	104.8(2)	N2-V1-N3	110.8(2)	N3-V1-N5	103.3(1)	N2-V1-N4	109.4(3)	V1-N4-Zr1	174.6(2)
V1-N4-C37	177.9(3)	N2-V1-N4	104.2(2)	N4-V1-N5	104.0(1)	N3-V1-N4	111.1(3)	Cl1-Zr1-N4	96.7(1)
V1-N1-C1	126.7(2)	N3-V1-N4	109.3(2)	V1-N5-Li1	171.0(2)	O1-Li1-O2	116(2)		
V1-N1-C7	116.8(2)	V1-N4-N5	172.5(3)	V1-N2-C1	124.2(2)	O1-Li1-O3	113(1)		
		N4-N5-C37	123.7(5)	V1-N2-C6	119.5(2)	O1-Li1-O4	108(1)		
		N5-C37-Si1	126.6(5)	O1-Li1-N5	115.0(3)	O2-Li1-O3	103(1)		
		V1-N1-C1	131.1(3)	O2-Li1-N5	115.4(3)				
		V1-N1-C7	112.2(3)	O3-Li1-N5	118.1(3)				



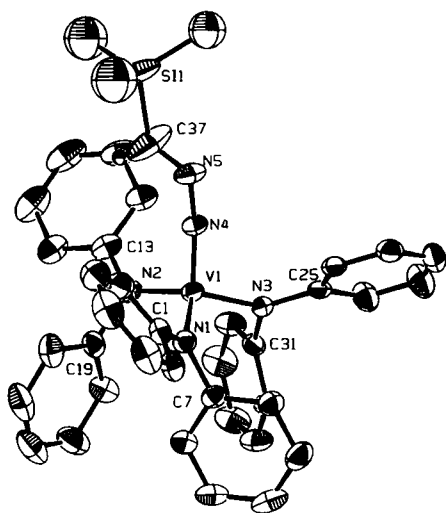
Scheme 1.

large family of vanadium imido complexes for which synthetic procedures and chemical reactivity have largely been established.<sup>[24]</sup>

Complex 1 also reacted with trimethylsilyl diazomethane. The reaction afforded the corresponding adduct (Ph<sub>2</sub>N)<sub>3</sub>V-

[N<sub>2</sub>CHSi(CH<sub>3</sub>)<sub>3</sub>] (3) which was isolated as a dark orange, crystalline material after recrystallization from hexane. The formulation of 3 was indicated by combustion analysis data. The IR spectrum shows an intense absorption at 1582 cm<sup>-1</sup>, characteristic for a C=N double bond stretch. This suggests a considerable extent of reduction of the coordinated diazo group. Accordingly, the diamagnetic complex 3 shows resonances for the Si(CH<sub>3</sub>)<sub>3</sub> and phenyl groups in the expected regions. The diazo C-H resonance could not be properly identified in the <sup>1</sup>H NMR spectrum since it overlapped with multiplets associated with the phenyl groups. Nevertheless, the corresponding carbon atom was clearly identified in the <sup>13</sup>C NMR spectrum at δ = 118.1.

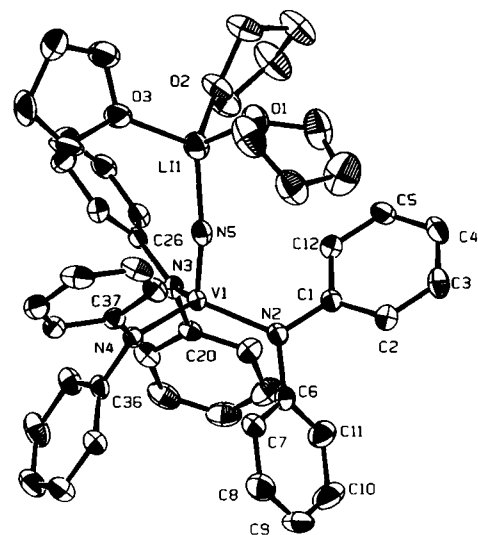
The connectivity of 3 was confirmed by an X-ray crystal structure analysis. The complex is monomeric with the vanadium atom at the center of a distorted tetrahedron [N1-V1-N2 = 114.8(2)°, N1-V1-N3 = 112.3(2)°, N1-V1-N4 = 104.9(2)°, N2-V1-N4 = 104.2(2)°] defined by three amide nitrogen atoms [V1-N1 = 1.901(4) Å, V1-N2 = 1.905(4) Å, V1-N3 = 1.909(3) Å] and the terminal nitrogen of one diazo group (Fig. 1). The V-N bond formed with the diazo nitrogen [V1-N4 = 1.665(4) Å] is remarkably short, possibly indicating some V≡N triple bond character. Accordingly, the V-N-N vec-

Fig. 1 ORTEP plot of **3** (thermal ellipsoids at the 50% probability level).

tor is almost linear [ $V1-N4-N5 = 172.5(2)^\circ$ ], while the coordinated diazo moiety is bent at the central nitrogen atom forming an angle [ $N4-N5-C37 = 123.7(5)^\circ$ ] which is typical for  $sp^2$  hybridization of the nitrogen atom. The C–N bond length is in the expected range for a double bond [ $N5-C37 = 1.192(7) \text{ \AA}$ ]. The N–N bond is somewhat elongated [ $N4-N5 = 1.333(5) \text{ \AA}$ ] with respect to a N=N double bond, but still shorter than expected for a N–N single bond.

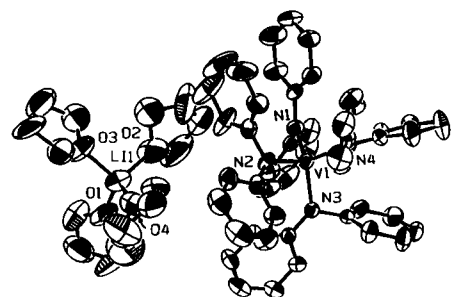
The  $(CH_3)_3Si$  group of **2a** was readily displaced by strong nucleophiles such as MeLi or  $(iPr)NHLi$  (LIA) to form the corresponding anionic nitrido derivative  $[(Ph_2N)_3V \equiv N-Li(THF)_3](THF)_{0.5}$  (**4**). This new diamagnetic species was isolated as beige-yellow, extremely air-sensitive, well-formed crystals by crystallization from hexane at  $4^\circ C$ . Combustion analysis data obtained are in agreement with the suggested formulation. Both IR and NMR data display the resonances for the aromatic rings and the coordinated THF in the expected regions. The  $^{13}C$  NMR spectrum shows two different types of phenyl rings.

The chemical connectivity of **4** was elucidated by an X-ray crystal structure analysis. The vanadium atom lies in the center of a slightly distorted tetrahedron [ $N2-V1-N3 = 114.4(1)^\circ$ ,  $N2-V1-N4 = 116.1(1)^\circ$ ,  $N3-V1-N4 = 112.80(9)^\circ$ ,  $N2-V1-N5 = 104.3(1)^\circ$ ,  $N3-V1-N5 = 103.3(1)^\circ$ ] defined by the three amide nitrogen atoms [ $V1-N2 = 1.954(2) \text{ \AA}$ ,  $V1-N3 = 1.958(2) \text{ \AA}$ ,  $V1-N4 = 1.942(2) \text{ \AA}$ ] and the nitrido nitrogen (Fig. 2). The V–N bond formed by the vanadium atom with the nitrido group is remarkably short [ $V1-N5 = 1.582(3) \text{ \AA}$ ]; those formed by the imido and diazo groups of complex **2b** (vide infra) and **3** are significantly longer. Nevertheless, it compares well with that of other vanadium nitrides.<sup>15d–6, 7a, 12</sup> The nitride functionality is bonded to a lithium cation [ $N5-Li1 = 2.017(6) \text{ \AA}$ ], which lies along a slightly bent V–N–Li vector [ $V1-N5-Li1 = 171.0(2)^\circ$ ]. Three molecule of THF complete the coordination sphere of the alkali cation [ $Li1-O1 = 1.985(6) \text{ \AA}$ ]. One disordered THF molecule per two molecules of complex was found in the unit cell. Of the two phenyl groups for each amide ligand, one is pointing towards the nitride group, while the other is pointing in the opposite direction. Given the considerable steric bulk around the vanadium center it is conceivable that the inequivalency of the phenyl rings observed in the solid state is also preserved in solution. This explains the  $^{13}C$  NMR spectrum.

Fig. 2 ORTEP plot of **4** (thermal ellipsoids at the 50% probability level).

The formation of **4** was probably achieved through nucleophilic attack by LIA at the silicon atom of the  $Si(CH_3)_3$  group with formation of the corresponding  $(CH_3)_3SiN(iPr)H$ . Consistent with this hypothesis, a GC-MS of the mother liquor showed significant amounts of a material with the appropriate parent peak at 119.3 and the fragmentation pattern expected for  $(CH_3)_3SiN(iPr)H$ .

Complex **4** was also obtained by treatment of the diazo complex **3** with LIA. In this case the hydrazone  $iPr(H)NN=CHSi(CH_3)_3$  is the likely co-product. Unfortunately, attempts to isolate and identify this species failed. Complex **4** also reacted with one equivalent of LIA to give a mixture from which the new complex  $[(Ph_2N)_4V][Li(THF)_4]$  (**5**) was isolated in significant yields as the only characterizable species. Interestingly, the same result was obtained upon reaction of both **2** and **3** with an excess of LIA. Attempts to isolate other species from the mother liquor yielded only intractable materials. This new paramagnetic product was characterized on the basis of its analytical and spectroscopic data as well as X-ray diffraction analysis (Fig. 3). Its formation is a reproducible process, which to us

Fig. 3 ORTEP plot of **5** (thermal ellipsoids at the 50% probability level).

does not have a straightforward explanation. In fact, we do not yet understand which series of steps actually lead to reduction of the vanadium metal center and scrambling of the  $Ph_2N$  ligands.

Complex **4** displays moderate nucleophilicity. It reacts readily at room temperature with a number of alkyl halides, including  $(CH_3)_3SiCl$  and MeI, to eliminate LiCl and form the corresponding crystalline imido derivatives **2** [ $(CH_3)_3Si$  (**a**); Me (**b**)].

In the case of **2b**, the imide methyl group resonances are unusually broad in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Remarkably, the resonances became narrower upon lowering the temperature. This behavior, which cannot be ascribed to fluxionality, is due to the rapid relaxation of spin states of the  $^{14}\text{N}$  quadrupolar nucleus.<sup>[25]</sup> In other words, as the temperature decreases the rate of relaxation between the  $^{14}\text{N}$  spin states increases. This results in self-decoupling since both the  $^{13}\text{C}$  and  $^1\text{H}$  nuclei "see" an average of all three  $^{14}\text{N}$  spin states. The 1:1:1 triplets due to spin-spin coupling with  $^{14}\text{N}$ ,<sup>[24]</sup> expected for both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra at higher temperature, were not observed in the present case since the boiling point of the solvent was well below this temperature limit.

Crystals of **2b** suitable for X-ray analysis were grown from ether/hexane mixtures. The structure shows a tetrahedrally coordinated vanadium atom [N1-V1-N2 = 116.0(1)°, N1-V1-N3 = 109.8(1)°, N1-V1-N4 = 105.3(2)°, N2-V1-N4 = 104.1(2)°, N3-V1-N4 = 104.8(2)°] with the coordination geometry defined by the three amide groups [V1-N1 = 1.918(3) Å, V1-N2 = 1.925(3) Å, V1-N3 = 1.894(3) Å] and the imido function (Fig. 4). The V-N bond formed by vanadium with the imido nitrogen [V1-N4 = 1.637(3) Å] is very short and falls in the expected range. The V-N-C array [V1-N4-C37 = 177.9(3)°] is almost linear.

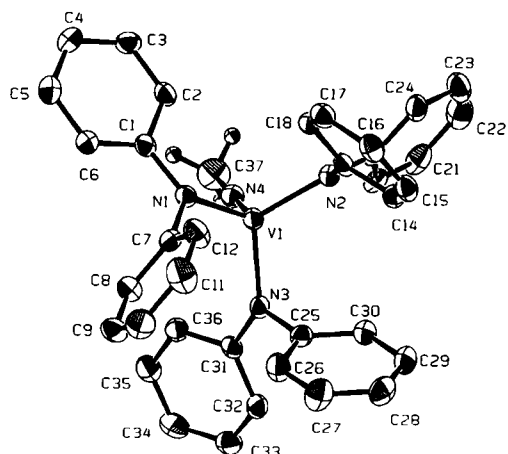
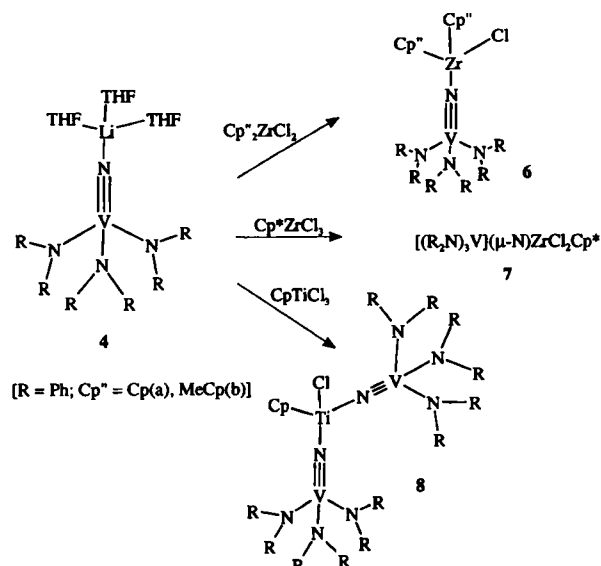


Fig. 4 ORTEP plot of **2b** (thermal ellipsoids at the 50% probability level).



Scheme 2.

Complex **4** reacts readily with organometallic complexes to yield heterodimetallic bridged nitride species (Scheme 2). In the case of  $\text{Cp}^*_2\text{ZrCl}_2$  [ $\text{Cp}^* = \text{C}_5\text{H}_5$ ,  $\text{CH}_3\text{C}_5\text{H}_4$ ] the reaction led to the formation of the corresponding diamagnetic [ $\text{Cp}^*_2\text{ZrCl}-\text{N}=\text{V}(\text{Ph}_2\text{N})_3$ ] [ $\text{Cp}^* = \text{C}_5\text{H}_5$  (**6a**),  $\text{CH}_3\text{C}_5\text{H}_4$  (**6b**)]. Spectroscopic and analytical data consistent with the proposed formulation were obtained in both cases.

In the case of **6b** the chemical connectivity was elucidated by an X-ray crystal structure analysis. The structure shows the zirconium and vanadium metal centers linked together by a bridging nitride atom forming an almost linear V-N-Zr vector [V1-N4-Zr1 = 174.6(2)°] (Fig. 5). The nitrogen atom forms a

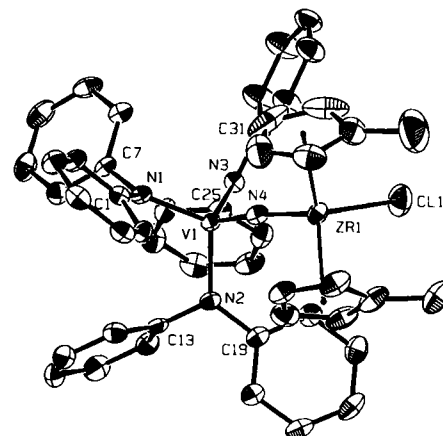


Fig. 5 ORTEP plot of **6b** (thermal ellipsoids at the 50% probability level).

very short bond with vanadium [V1-N4 = 1.638(4) Å], but a remarkably long one with zirconium [Zr1-N4 = 2.128(4) Å]. This suggests the presence of a V-N multiple bond and a Zr-N single bond. The coordination geometry around vanadium is tetrahedral [N1-V1-N2 = 114.2(2)°, N1-V1-N3 = 112.8(1)°, N1-V1-N4 = 106.3(2)°, N2-V1-N4 = 106.1(2)°] and is made up of three amide nitrogen atoms [V1-N1 = 1.920(4) Å, V1-N2 = 1.909(4) Å, V1-N3 = 1.918(4) Å] and the bridging nitride. The geometry around zirconium is also pseudotetrahedral and is defined by the two Cp rings centroids, one chlorine atom [Zr1-C11 = 2.428(1) Å], and the bridging nitride. Curiously, the two cyclopentadienyl rings are in an eclipsed conformation with both the cyclopentadienyl ring methyl substituents pointing away from the nitride atom.

Attempts to replace the second chlorine atom at zirconium by reaction with a second equivalent of **4** were unsuccessful. A similar result was obtained in the case of the reaction of **4** with  $\text{Cp}^*\text{ZrCl}_3$  where only formation of the corresponding 1:1 adduct [( $\text{Ph}_2\text{N}$ )<sub>3</sub>V( $\mu$ -N)ZrCp\*Cl<sub>2</sub>] (**7**) was observed.

Conversely, reaction of **3** with the less bulky  $\text{CpTiCl}_3$  in either a 1:1 or 1:2 ratio led to the formation of the corresponding bisnitride derivative [( $\text{Ph}_2\text{N}$ )<sub>3</sub>V( $\mu$ -N)<sub>2</sub>TiCpCl] (**8**). Although unfavorable crystal shape prevented structural determination by X-ray diffraction methods, the structure of **8** is confidently proposed on the basis of analytical and spectroscopic data.

Further exploration into the reactivity of complex **4** with main group compounds and a variety of organic substrates is in progress and will be published elsewhere.

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