

**Reductive Cleavage of Dinitrogen by a Vanadium Diamidoamine Complex: the Molecular Structures of  $[V(\text{Me}_3\text{SiN}\{\text{CH}_2\text{CH}_2\text{NSiMe}_3\}_2)(\mu\text{-N})_2]$  and  $\text{K}[V(\text{Me}_3\text{SiN}\{\text{CH}_2\text{CH}_2\text{NSiMe}_3\}_2)(\mu\text{-N})_2]$**

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There has been a considerable resurgence of interest in the coordination chemistry of the dinitrogen ligand in recent years,<sup>1</sup> and much attention has focused on reducing, electron-deficient early transition and f-element systems to activate<sup>2</sup> and indeed ultimately completely cleave the N≡N triple bond. However, there are only two unequivocal examples of the latter: the neutral Mo(III)–tris(anilide) complex of Cummins which yields a Mo(VI) terminal nitride upon reaction with N<sub>2</sub>,<sup>3</sup> and the anionic Nb(III)–calixarene dinitrogen complex of Floriani which affords an anionic nitrido-bridged dimer on further reduction.<sup>4</sup> Gambarotta has also reported an anionic nitrido-bridged vanadium dimer; however, the origin of the (μ-N)<sub>2</sub> unit in the latter was not established.<sup>5</sup>

The bulky, chelating silylamino(disilylamido) ligand [(Me<sub>3</sub>Si)N{CH<sub>2</sub>CH<sub>2</sub>N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub><sup>2-</sup> ([N{N''}]<sub>2</sub><sup>2-</sup>) has been employed by us and others to prepare a series of group IV complexes,<sup>6,7,8</sup> which are moderate olefin polymerization catalysts and which also includes the novel titanium(III) hydride [Ti(N{N''})<sub>2</sub>(μ-H)]<sub>2</sub>.<sup>9</sup> We were interested in extending this chemistry to vanadium, especially in the context of activation of dinitrogen, given the established role of vanadium in biological nitrogen-fixing enzymes.<sup>10</sup> In this paper we report that reduction of the V(III) complex [V(N{N''})<sub>2</sub>(Cl)]<sub>2</sub> under a dinitrogen atmosphere completely cleaves the N≡N bond to afford the doubly nitrido-bridged V(V)–V(V) dimer [V(N{N''})<sub>2</sub>(μ-N)]<sub>2</sub>, which may be further reduced to the anionic V(V)–V(IV) dimer [V(N{N''})<sub>2</sub>(μ-N)]<sub>2</sub><sup>-</sup>.

Treatment of [V(N{N''})<sub>2</sub>Cl]<sub>2</sub><sup>11</sup> in toluene with one equivalent of KC<sub>8</sub> under N<sub>2</sub> yields deep red [V(N{N''})<sub>2</sub>(μ-N)]<sub>2</sub> **1** (see Scheme 1) after work-up, together with some pentane-insoluble green material (vide infra).<sup>12</sup>

(1) (a) Leigh, G. J. *Science* **1998**, 279, 506. (b) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, 1995, 1115. (c) Gambarotta, S. *J. Organomet. Chem.* **1995**, 500, 117.

(2) For most recent references, see: (a) Basch, H.; Musaev, D. G.; Morokuma, K.; Fryzuk, M. D.; Love, J. B.; Seidel, W. W.; Albinati, A.; Koetzle, T. F.; Klooster, W. T.; Mason, S. A.; Eckert, J. *J. Am. Chem. Soc.* **1999**, 121, 523. (b) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. *Inorg. Chem.* **1999**, 38, 243. (c) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, 120, 11024. (d) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, 120, 5836. (e) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, 120, 1070. (f) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, 275, 1445. (g) O'Donoghue, M. B.; Zanetti, N. C.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, 119, 2753. (h) Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *J. Chem. Soc., Chem. Commun.* **1997**, 2603.

(3) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, 268, 861.

(4) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, 120, 437.

(5) Berno, P.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 822.

(6) Horton, A. D.; De With, J.; Van de Linden, A. J.; Van de Weg, H. *Organometallics* **1996**, 15, 2672.

(7) Cloke, F. G. N.; Love, J. B.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

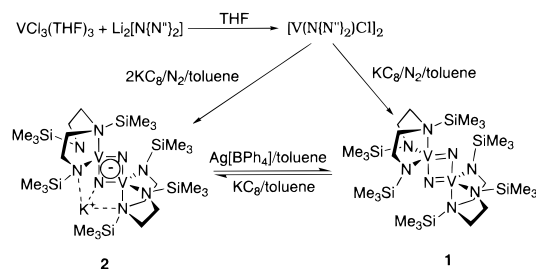
(8) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, 503, 333.

(9) Love, J. B.; Clark, H. C. S.; Cloke, F. G. N.; Green, J. C.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1999**, 121, 6843.

(10) Rehder, D. *Coord. Chem. Rev.* **1999**, 182, 297 and references therein.

(11) Clancy, G. P.; Clentsmith, G. K. B.; Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.*, **1999**, 3345.

**Scheme 1**



**1** is diamagnetic and displays a parent ion in the mass spectrum with the appropriate isotopic intensity ratios.<sup>12</sup> Repeating the experiment under an atmosphere of <sup>15</sup>N<sub>2</sub> affords the labeled nitride [V(N{N''})<sub>2</sub>(μ-<sup>15</sup>N)]<sub>2</sub> **1-<sup>15</sup>N**, identified by mass spectrometry,<sup>12</sup> thus unambiguously confirming the origin of the doubly bridging nitrido unit in **1** to be external N<sub>2</sub>. The <sup>15</sup>N NMR spectrum<sup>12</sup> of **1-<sup>15</sup>N** shows a single peak at δ 561.6 ppm which compares to the value of 460 ppm (corrected to the same reference) found for the terminal nitride in [Mo(NAr)<sub>3</sub>N].<sup>3,13</sup> The <sup>51</sup>V NMR spectrum displays a broad singlet at δ 265.7,<sup>12</sup> somewhat downfield of that in [V(Cp\*)<sub>2</sub>(μ-N)Cl]<sub>2</sub> (δ -144 ppm).<sup>14,15</sup>

The nature of the double nitrido bridge in **1** was confirmed by X-ray crystallography,<sup>16</sup> and the molecular structure, together with selected bond distances and angles, is shown in Figure 1.

The molecule lies on a crystallographic inversion center. The geometry about vanadium is best described as distorted trigonal bipyramidal with N(2), N(3), and N(4') equatorial and N(4) and N(1) axial. The amino nitrogen (N(1))–V bond is long at

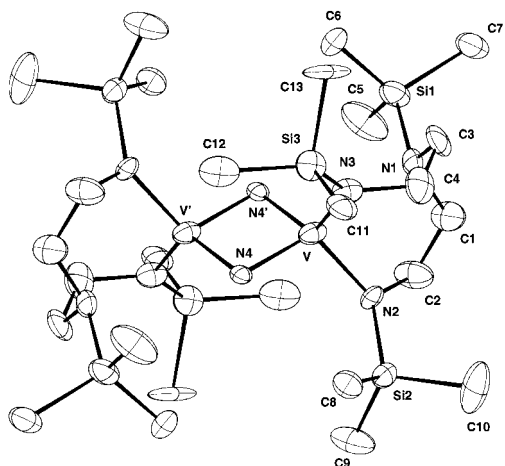
(12) **K**[{V(N{N''})<sub>2</sub>(μ-N)}<sub>2</sub>] **2** (i) To a mixture of [V(N{N''})<sub>2</sub>Cl]<sub>2</sub> (0.520 g, 1.28 × 10<sup>-3</sup> mol) and KC<sub>8</sub> (0.174 g, 1.28 × 10<sup>-3</sup> mol) in an ampule was added toluene (15 mL) chilled to -78 °C. The ampule was cooled to -196 °C, evacuated, and then charged with dinitrogen gas (~20 equiv) and warmed slowly to room temperature. As the solvent melted, a green color was observed in solution, which intensified to give a deep green-brown solution and a black deposit of carbon. The mixture was stirred for a further 48 h. The mixture was then filtered via cannula, and the solvent was removed from the resultant solution to yield a green-brown powder. This residue was washed with pentane (2 × 5 mL volumes), and the red pentane washings were collected. The deep green pentane-insoluble powder remaining was dissolved in toluene (2 mL) to give a deep green solution, which was filtered via cannula and cooled to -20 °C to yield large green crystals of **2** (0.095 g, 19%). μ<sub>eff</sub> (d<sub>8</sub>-toluene) = 1.77 μ<sub>B</sub>. ESR (293 K, toluene): 15 lines, g<sub>iso</sub> = 1.998, A<sub>iso</sub> = 45.7 G. Anal. Calcd for C<sub>26</sub>H<sub>70</sub>KN<sub>8</sub>Si<sub>6</sub>V<sub>2</sub>: C, 38.82; H, 8.77; N, 13.93. Found: C, 38.70; H, 8.75; N, 14.20. (ii) As before with [V(N{N''})<sub>2</sub>Cl] (0.366 g, 9.06 × 10<sup>-4</sup> mol) and KC<sub>8</sub> (0.245 g, 1.81 × 10<sup>-3</sup> mol). Recrystallization from toluene (4 mL) gave green crystals of **2** (0.220 g, 60%). [V(N{N''})<sub>2</sub>(μ-N)<sub>2</sub>] **1** (i) The pentane washings from the initial synthesis of **2** were pumped to dryness to yield a red-purple powder. This was recrystallized from pentane (3 mL) to give deep red crystals which were a mixture of **1** and [V(N{N''})<sub>2</sub>Cl]<sub>2</sub> starting material (0.060 g). MS (70 eV) (%): m/z 764 (20, M<sup>+</sup>). (ii) To **2** (0.100 g, 1.24 × 10<sup>-4</sup> mol) and AgBPh<sub>4</sub> (0.053 g, 1.24 × 10<sup>-4</sup> mol) was added toluene (5 mL) at -78 °C. Upon dissolution the initial green color discharged to give a deep red-purple color, and a black precipitate deposited. The mixture was warmed to room temperature and filtered via cannula, and the solvent was removed from the filtrate to give a red oil. The oil was taken up in pentane (2 mL) and cooled to -50 °C to give red crystals of pure **1** (0.040 g, 42%). <sup>1</sup>H NMR (293K, d<sub>6</sub>-benzene): δ 3.57, 3.47, 2.70, 2.19 (all m, 2H, N(CHH'CHH')<sub>2</sub>), 0.54 (s, 18H, SiMe<sub>3</sub>), 0.21 (s, 9H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (293 K, d<sub>6</sub>-benzene): δ 55.71, 50.63 (both CH<sub>2</sub>), 1.36, -1.07 (both SiMe<sub>3</sub>). Anal. Calcd for C<sub>26</sub>H<sub>70</sub>N<sub>8</sub>Si<sub>6</sub>V<sub>2</sub>: C, 40.81; H, 9.22; N, 14, 64. Found: C, 41.08; H, 9.05; N, 14.40. [V(N{N''})<sub>2</sub>(μ-<sup>15</sup>N)]<sub>2</sub> **1-<sup>15</sup>N** was prepared similarly to **1** (using method (i)), but using <sup>15</sup>N<sub>2</sub> (99.5%, ~15 equiv) which was transferred by Toepler pump. MS (70 eV) (%): m/z 766 (15, M<sup>+</sup>). <sup>15</sup>N{<sup>1</sup>H} NMR (d<sub>8</sub>-toluene, 298 K): δ 561.6 (s, Δν<sub>1/2</sub> = 200 Hz). <sup>51</sup>V NMR (d<sub>8</sub>-toluene, 298 K): δ 265.7 (s, Δν<sub>1/2</sub> = 400 Hz).

(13) von Philipsborn, W.; Muller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 383.

(14) Haddad, T. S.; Aistars, A.; Ziller, J. W.; Doherty, N. M. *Organometallics* **1993**, 12, 2420.

(15) Rehder, D. *Coord. Chem. Rev.* **1991**, 110, 161.

(16) Crystal data for **1**: Triclinic, FW 765.3, deep red, space group P $\bar{1}$  (No. 2); a = 10.668(12) Å, b = 11.227(19) Å, c = 19.29(3) Å, α = 93.88(14)°, β = 91.02(12)°, γ = 113.47(12)°, Z = 2. Final residual wR2(all data) = 0.349 (R = 0.109, with goodness of fit 0.954 on F<sup>2</sup>).

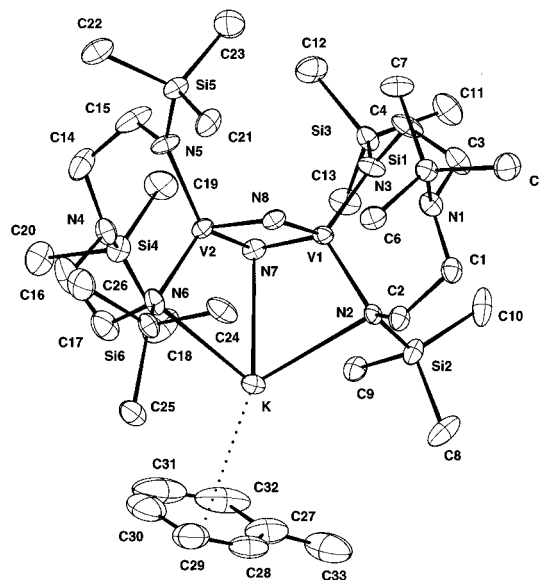


**Figure 1.** ORTEP<sup>20</sup> of **1** (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (deg): V–N1, 2.539(10); V–N2, 1.877(9); V–N3, 1.897(10); V···V', 2.632(6); N4···N4', 2.50(2); V–N4, 1.769(10); V–N4', 1.862(10); N4–V–N2, 107.7(4); N4–V–N3, 104.4(5); N2–V–N3, 110.1(4); N1–V–N4', 89.6(4); N1–V–N3, 79.3(4); N1–V–N2, 78.4(4); N1–V–N4, 175.2(4); N4–V–N4', 87.1(5); V–N4–V', 92.9(5).

2.539(10) Å, but the observation of four distinct multiplets, assigned to two pairs of diastereotopic hydrogens, for the backbone protons in the room temperature <sup>1</sup>H NMR spectrum of **1** confirms that the amino nitrogen is at least partially coordinated.<sup>12</sup> Only at 373 K does the backbone region of the spectrum simplify to two triplets due to rapid dissociation of the amino nitrogen. This contrasts with the situation in [Ti(N{N''})<sub>2</sub>Me<sub>2</sub>], in which the ligand binding is fluxional at room temperature on the NMR time scale and the amino N–Ti bond length is somewhat longer at 2.732(2) Å.<sup>8</sup> The other structural parameters of the V(N{N''})<sub>2</sub> fragment are unexceptional, so that the discussion will now focus on the V<sub>2</sub>N<sub>2</sub> core. The latter is planar and virtually square, with a N(4)···N(4') separation of 2.50(2) Å, thus confirming complete cleavage of the N<sub>2</sub> triple bond to form two bridging nitrido ligands with concomitant oxidation of vanadium to V(V). The V···V' separation is 2.632(6) Å, a distance presumably imposed by the nitride bridges and not indicative of any metal–metal interaction since both metal centers in **1** are formally d<sup>0</sup>. The bond lengths and angles (Figure 1) within the V<sub>2</sub>N<sub>2</sub> unit are very similar to those in [V(N{SiMe<sub>3</sub>})<sub>2</sub>(μ-N)]<sub>2</sub><sup>-</sup> and [V(Cp\*)(μ-N)Cl]<sub>2</sub>.<sup>5,14</sup>

Reduction of [V(N{N''})<sub>2</sub>Cl]<sub>2</sub> in toluene with two equivalents of KC<sub>8</sub> under N<sub>2</sub> affords deep green K[V(N{N''})<sub>2</sub>(μ-N)]<sub>2</sub> **2** (see Scheme 1).<sup>12</sup> **2** is also obtained during the synthesis of **1** (vide supra), presumably due to the fact that **1** reacts faster with KC<sub>8</sub> than does [V(N{N''})<sub>2</sub>Cl]<sub>2</sub>; hence, some of the latter is also recovered during the synthesis of **1**. The reduction of **1** to **2** is readily reversible, and **1** may be quantitatively regenerated by treatment of **2** with one equivalent of Ag[BPh<sub>4</sub>] in toluene; the latter provides a convenient alternative route to analytically pure **1** (see Scheme).<sup>12</sup> **2** is paramagnetic, with μ<sub>eff</sub> = 1.77 μ<sub>B</sub> at 293 K in solution (Evans' method,<sup>17</sup> d<sub>8</sub>-toluene) and displays a 15-line EPR spectrum (<sup>51</sup>V, 99.75%, I = 7/2) at 293 K in toluene with g<sub>iso</sub> = 1.998 and A<sub>iso</sub> = 45.7 G;<sup>12</sup> these features are entirely consistent with a d<sup>1</sup> V(V)–V(IV) dimer in which the single electron is delocalized in solution.<sup>18</sup> **2** has also been structurally characterized, and the molecular structure, together with selected bond distances and angles, is shown in Figure 2.<sup>19</sup>

The binding of one of the N{N''})<sub>2</sub> ligands in **2** shows some



**Figure 2.** ORTEP<sup>20</sup> of **2** (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (deg): V1···N1, 3.062(8); V1–N2, 1.992(8); V1–N3, 1.900(8); V2–N4, 2.603(10); V2–N5, 1.931(8); V2–N6, 1.977(9); V1···V2, 2.575(3); N7···N8, 2.44(1); V1–N7, 1.758(8); V1–N8, 1.754(8); V2–N7, 1.807(8); V2–N8, 1.781(8); K–N2, 2.918(8); K–N7, 3.027(9); K–N8, 3.712(9); K–N6, 2.882(10); K···toluene ring centroid, 3.17(2); N3–V1–N2, 113.9(4); N3–V1–N7, 111.2(4); N3–V1–N8, 118.6(4); N2–V1–N7, 112.0(3); N2–V1–N8, 110.4(3); N7–V1–N8, 88.1(4); V1–N7–V2, 92.5(4); V1–N8–V2, 93.5(4); N7–V2–N8, 85.7(4); N7–V2–N6, 112.0(4); N7–V2–N5, 121.2(4); N8–V2–N6, 109.0(4); N8–V2–N5, 102.6(4); N6–V2–N5, 119.1(4); N4–V2–N8, 172.6(4).

distortion compared with those in **1**. The V2–N4 distance of 2.603(10) Å is consistent with weak coordination of the amino nitrogen and adoption of a distorted trigonal bipyramidal geometry about V2 with N4 and N8 axial and N5, N6, and N7 equatorial (cf. **1**). However, the analogous distance (V1–N1) for the ligand bound to V1 is considerably longer at 3.062(8) Å, indicating noncoordination of the amino nitrogen N1 and adoption of a distorted tetrahedral geometry about V1. This distortion may be reasonably associated with a localized V(IV)–V(V) mixed valence structure for **2** in the solid state; in the planar V<sub>2</sub>N<sub>2</sub> core the bond distances for N7 and N8 to V2 are also slightly shorter than those to V1 (see Figure 2). The potassium counterion in **2** is coordinated virtually symmetrically to one of the amide groups of each N{N''})<sub>2</sub> ligand, and also to one of the bridging nitrides (N7); ligation of the potassium ion is completed by a weak π interaction with a toluene solvent molecule.

The formation of **1** presumably proceeds via the intermediacy of a V(II) complex of the type [V(N{N''})<sub>2</sub>]<sub>n</sub> which subsequently binds, reduces, and cleaves N<sub>2</sub>, and work is in progress to isolate such a species.

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**Supporting Information Available:** Experimental details for the preparation of **1** and **2**; X-ray data and figures for **1** and **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Crystal data for **2**: Monoclinic, FW 896.5, deep green, space group Cc (No. 9); a = 11.203(3) Å, b = 24.256(12) Å, c = 18.889(19) Å, α = 90°, β = 105.21(6)°, γ = 90°, Z = 4. Final residual wR2(all data) = 0.189 (R = 0.068, with goodness of fit 1.049 on F<sup>2</sup>).

(20) Johnson, C. K. ORTEP II, Report ORNL-5738; Oak Ridge National Laboratory: Oakridge, TN, 1976.

(17) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(18) Dutta, S. K.; Samanta, S.; Kumar, S. B.; Han, O. H.; Burckel, P.; Pinkerton, A. A.; Chaudhury, M. *Inorg. Chem.* **1999**, *38*, 1982.