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# Dinitrogen Fixation, Ligand Dehydrogenation, and Cyclometalation in the Chemistry of Vanadium(III) Amides

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Divalent vanadium complexes with oxygen-containing ligands (catecholate, hydroxide) are known to catalytically convert dinitrogen into ammonia and hydrazine.[1] In the long-term perspective of understanding the factors which affect this remarkable transformation, we recently prepared and characterized a class of vanadium(II) and -(III) aryl oxides,[2] finding no indication that these systems might be capable of interacting with dinitrogen[2,3] or that they may work as models for dinitrogen activation processes.[4] On the other hand, the environment of vanadium in nitrogenase[5] and related systems[6] indicates that the employment of other donor atoms, such as sulfur or phosphorus,[7] might be a valid alternative. The three cases of dinitrogen fixation determined for V(II)[8,9] and V(III)[10] have been obtained using carbon-based ligands. Unfortunately, low-valent vanadium alkyls and aryls are still rare, and therefore the chemistry of vanadium–dinitrogen complexes remains somewhat haphazard.

We became interested in exploring the ability of vanadium complexes of nitrogen donor ligands to coordinate $N_2$. The choice of organic anionic amides as supporting ligands was stimulated by recent results showing that vanadium amide complexes are very reactive, sufficiently so to give fragmentation of THF[11] or to support highly reactive functions including vanadacyclobutane rings.[12] For this preliminary study, we have used organic amides which are sterically less demanding and more inert than the bulky silazane $(Me_3Si)_2N$, for which a unique case of V(III) homoleptic complex $V(NR_2)_3$ has been reported.[13] Herein we describe our findings.

The reaction of $VCl_3(THF)_3$ with 3 equiv of $R_2NLi$ [R = *i*-Pr, Cy, Ph] proceeded at low temperature (–40 °C) to produce green solutions. Although the high solubility of the cyclohexyl and isopropyl derivatives prevented the isolation of any characterizable products, in the case of the $Ph_2N$ derivative, large deep-green crystals of the monomeric, paramagnetic $(Ph_2N)_3V(THF)$ (**1**) were isolated in 78% yield from toluene.[14] The monomeric nature of **1** and its tetrahedral geometry were elucidated by an X-ray crystal structure analysis (Scheme 1).

In contrast to the cyclohexyl and isopropyl derivatives, complex **1** is thermally stable and does not show any appreciable decomposition when THF is replaced by toluene or hexane. Conversely, in the case of the two green cyclohexyl and isopropyl complexes, the color turned brown-red during the solvent replacement. Diamagnetic brown crystals of $[(R_2N)_3V]_2(\mu\text{-}N_2)$ [R = *i*-Pr (**2a**), Cy (**2b**)] were isolated in 57 and 32% yields, respectively, upon cooling.[15] The presence of dinitrogen in complex **2** has been unambiguously demonstrated by elemental analysis, degradation experiments with MeI (8 equiv) or HCl (12 equiv) carried out with a Toepler pump [dinitrogen recovered, respectively 84% (**2a**)(MeI), 40% (**2a**)(HCl), and 69% (**2b**)(HCl)], and X-ray analysis. The most distinctive feature of the crystal structure of **2a** is the presence of a molecule of dinitrogen, bridging the two vanadium atoms in an end-on fashion. The $V–N_2–V$ frame of **2a** is surprisingly robust and unreactive toward several reagents (azide, diazo), and even attempts to replace dinitrogen with other ligands ($PR_3$, CO, RNC) were unsuccessful. Nevertheless, dinitrogen was released by MeI and HCl without forming detectable amounts of the corresponding hydrazines.

The cyclic voltammogram of **2a** showed a reversible one-electron reduction at –0.6 V in THF–$TBABF_4$ solution ($TBABF_4$ = *n*-tetrabutylammonium tetrafluoroborate, $E_{pa} - E_{pc}$ = 72 mV vs $Fc/Fc^+$, room temperature, scan rate 200 mV $s^{-1}$). The fact that no oxidation wave could be detected up to +1.2 V suggests, together with the diamagnetism, that vanadium might be in the oxidation state 5+. On the other hand, the bond distances and angles, as determined by the X-ray crystal structure, although certainly indicative of some extent of dinitrogen reduction, show that the N–N multiple bond reduction is not very extensive. Therefore, the attribution of the formal oxidation state of vanadium in complex **2** remains puzzling since the formal oxidation state 3+ for vanadium would be expected to yield a paramagnetic complex, given the $C_{3v}$ symmetry of each vanadium atom with consequent degeneracy of the low-lying $d_{xz}$ and $d_{yz}$ orbitals.

The reaction of $VCl_3(THF)_3$ with LDA gave a surprisingly different result when carried out with a 1:6 stoichiometric ratio.

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(14) Complex **1**: A solution of $Ph_2NH$ (3.5 g, 20.7 mmol) in THF (75 mL) was treated with NaH (0.50 g, 20.8 mmol) at –70 °C. The resulting suspension was allowed to warm up to room temperature, upon which a vigorous reaction took place. The addition of $VCl_3(THF)_3$ (2.6 g, 6.9 mmol) to the resulting solution turned the color green. The resulting mixture was evaporated to dryness and the residual solid redissolved in toluene. Moderately air-sensitive green crystals of **1** (3.3 g, 5.3 mmol, 78% yield) separated after standing for 3 days at 4 °C. [$\mu_{eff} = 2.99\ \mu_B$]

(15) Complex **2a**: A suspension of $VCl_3(THF)_3$ (1.0 g, 2.7 mmol) in THF was treated with lithium diisopropylamide (0.9 g, 8.1 mmol) at –40 °C under $N_2$. The resulting deep-green solution was allowed to warm up to room temperature and evaporated to dryness. The residual solid was redissolved in hexane. Deep-orange, moderately air-stable crystals of **2a** (1.5 g, 1.1 mmol, 57% yield after double recrystallization) separated after standing for 5 days at 4 °C. $^1$H-NMR ($C_6D_6$, 200 MHz, $\delta_{ppm}$) 1.42 (d, 6H, $-CH_3$), 4.19 (septet, 1H, -CH-); $^{13}$C-NMR ($C_6D_6$, 75 MHz, $\delta_{ppm}$) 27.2 ($-CH_3$), 55.4 (-CH-); $^{51}$V-NMR ($C_6D_6$, $\delta_{ppm}$, referenced to $VOCl_3$) 137.4 (s). Complex **2b**: A solution of $VCl_3(THF)_3$ (2.03, 5.44 mmol) in THF (50 mL) was treated with $Cy_2NLi$(TMEDA) at room temperature. A blood-red color immediately developed, and stirring was continued overnight. After evaporation to dryness, the dark-red residue was redissolved in toluene (50 mL). The suspension was filtered to eliminate LiCl and concentrated to small volume. Dark-red microcrystalline **2b** (1.0 g, 32%) separated upon addition of $Et_2O$ (50 mL). $^1$H-NMR ($C_6D_6$, 200 MHz, $\delta_{ppm}$) 3.97 (m, 1H, Cy), 1.0–2.3 (m, 10H, Cy); $^{13}$C-NMR ($C_6D_6$, 75 MHz, $\delta_{ppm}$) 66.81, 37.23, 27.49, 26.15.

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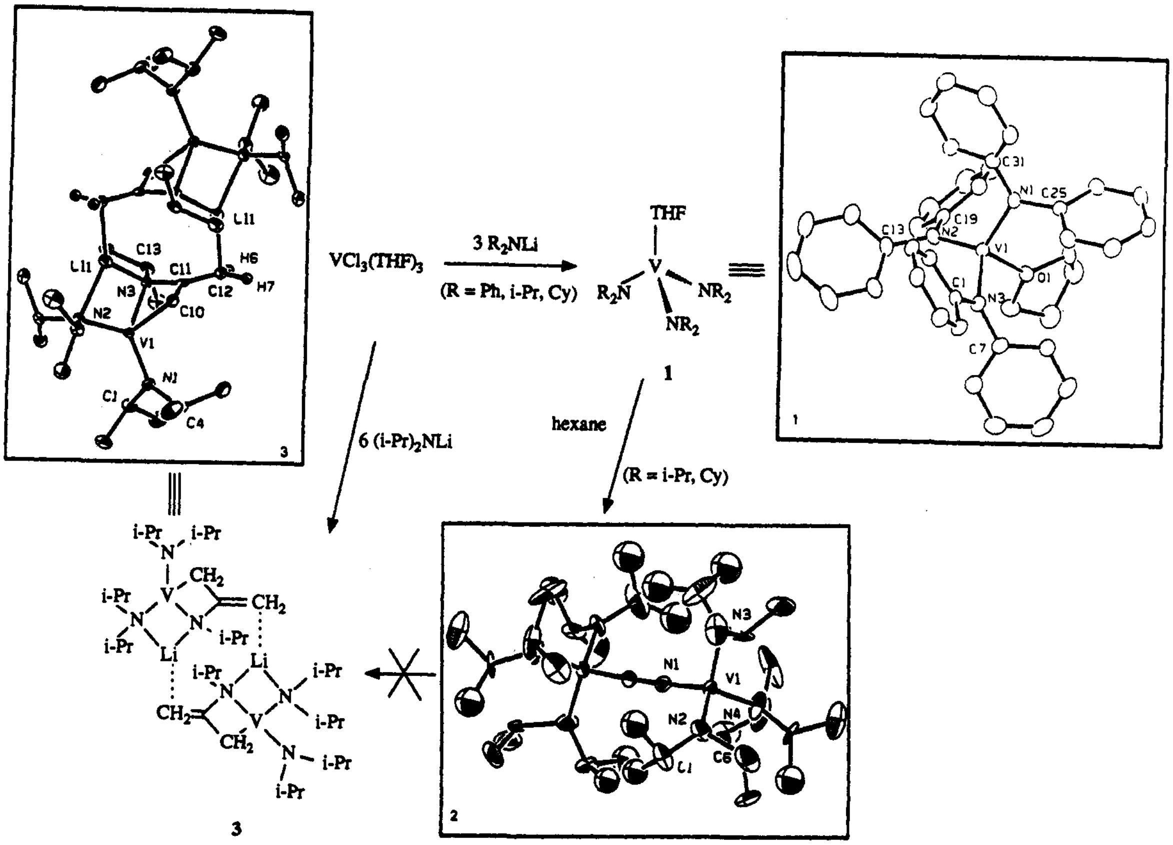
**Scheme 1**[a]



[a] Selected values of bond distances (Å) and angles (deg). Complex **1**: V1–O1 = 2.059(2), V1–N1 = 1.944(2), V1–N2 = 1.961(2), V1–N3 = 1.937(2); N1–V1–N2 = 118.31(9), O1–V1–N3 = 97.98(8), V1–N3–C1 = 114.5(1), V1–N3–C7 = 126.6(1), C1–N3–C7 = 118.3(2), C1–N3–C7–C12 = 67.6(3). Complex **2a**: V1–N1 = 1.744(6), V1–N2 = 1.891(7), V1–N3 = 1.886(8), V1–N4 = 1.888(6), N1–N1 = 1.27(1), N1–V1–N3 = 107.7(3), N1–V1–N4 = 109.7(3), V1–N1–N1 = 177.4(3), V1–N1–N1–V1 = 29(28). Complex **3**: V1–N1 = 1.894(3), V1–N2 = 1.963(3), V1–N3 = 2.029(3), V1–C10 = 2.150(3), C12–Li1 = 2.223(7), N2–Li1 = 2.191(6), N3–Li1 = 2.135(6), N3–C11 = 1.390(4), N1–V1–N2 = 127.9(1), N1–V1–N3 = 126.5(1), N3–V1–C10 = 66.3(1), N2–V1–N3 = 104.5(1), N1–V1–C10 = 109.1(1), C11–C12–Li1 = 91.9(3).

In order to obtain a complete reaction and to avoid the formation of the dinitrogen complex **2a**, the reaction mixture must be heated at about 60 °C after removal of THF and prior to the addition of hexane. The reaction produced blue-violet crystals of a new paramagnetic complex (**3**) which could be isolated from hexane solution upon slow cooling.[16] Much lower yields were obtained when a 1:4 stoichiometric ratio was employed. Complex **3** did not release gas during decomposition experiments carried out with HCl, while the IR spectrum showed a narrow resonance at 1536 cm$^{-1}$, which might suggest the presence of a C=C double bond. The crystal structure of this new species revealed the formula and the surprising chemical connectivity. The dimeric complex is formed by two identical vanadaaminocyclobutane $[(i\text{-}Pr_2)N]_2V[\mu\text{-}CH_2C(=CH_2)N(i\text{-}Pr)]$ units. The metallacycle is formed by one amido group which chelates the vanadium atom by using both the nitrogen [V1–N3 = 2.029(3) Å, V1–C10 = 2.150(3) Å] and one deprotonated methyl group, thus forming a four-membered vanadacyclobutane ring. The second carbon atom and the methylene carbon of the same isopropyl group engaged in the formation of the metallacycle have also been dehydrogenated to form an exocyclic $C=CH_2$ double bond [C11–C12 = 1.367(5) Å] (Scheme 1). The bridging between the two monomeric moieties is realized through two tricoordinated lithium cations which bond two nitrogens from two amido groups and the $C=CH_2$ moiety of the other unit.

By analogy with recent findings,[12] the origin of the metallacycle may be explained through a C–H σ-bond metathesis mediated by a fourth amido group of a hypothetical homoleptic $[(i\text{-}Pr)_2N]_4VLi$ intermediate. However, the formation of the C=C double bond of complex **3**, which implies ligand oxidation and which seems to require an extra 3 equiv of LDA reagent, is somewhat reminiscent of that obtained during attempts to reduce $[(i\text{-}Pr)_2PhO]_3NbCl_2$.[17] However, the process leading to the dehydrogenation has to be of a different nature in the present case, since the oxidation state of vanadium remained unchanged during the formation of **3** ($\mu_{eff}$ = 2.89 $\mu_B$ per vanadium).

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**Supplementary Material Available:** Details of the structure determination; ORTEP drawings showing the full labeling schemes; tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles (94 pages); listing of observed and calculated structure factors (65 pages) for **1**, **2**, and **3**. This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(16) Complex 3: A suspension of $VCl_3(THF)_3$ (2.8 g, 7.5 mmol) in THF was mixed with lithium diisopropylamide (4.9 g, 49.8 mmol) at −40 °C. The resulting solution was allowed to warm to room temperature and evaporated to dryness. The residual oily material was heated at about 100 °C in vacuo for about 30 min and redissolved in hexane, and the resulting solution was filtered to eliminate the insoluble residue. Blue-violet air-sensitive crystals of 3 (1.8 g, 2.5 mmol, 34%) separated from the resulting brown solution after standing for 5 days at 4 °C. [$\mu_{eff}$ = 2.89 $\mu_B$ per vanadium.]

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