Dinitrogen Fixation versus Metal-Metal Bond Formation in the Chemistry of Vanadium(II) Amidinates

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The considerable growth of interest in the chemistry of noncyclopentadienyl derivatives of divalent vanadium[1] is mainly stimulated by two remarkable reactions discovered for this oxidation state: dinitrogen fixation/activation[2] and formation of V–V triple bonds of unusual shortness.[3] This study, which describes the preliminary preparation and the stability of a series of vanadium(II) amidinates, was conceived with the aim of studying the effect of the ligand steric bulk on both the stability and the nuclearity of d^3 V(II) complexes. The choice of amidinate anions was prompted by the well-known ability of these chelating ligands to stabilize the low oxidation states of early transition metals[4] and lanthanides[5] and the possibility to adjust the ligand's bite by modifying the steric interaction between the amidinate organic substituents. In addition, the three-atom bite and the electronic structure of these ligands assign them to the family of the three-center chelating ligands which have yielded an impressive number of dimers with both transition[6] and nontransition metals.[7]

The predominance of the ligand steric hindrance in determining the result of the reaction of $VCl_2(TMEDA)_2$ with 2 equiv of amidinate lithium salt is clearly shown by the data summarized in Scheme 1. In all cases, monomeric and paramagnetic complexes were initially formed in THF solutions. The reaction yielded air-sensitive crystals of $[CyNC(H)NCy]_2V(TMEDA)$ (**1**) in the case of the formamidinate derivative,[8] while employment of the more sterically demanding amidinates $[RNC(R')NR]^-$ gave *trans*-$[RNC(R')NR]_2V(THF)_2$ [R = Cy, R′ = Me (**2a**); R = $SiMe_3$, R′ = Ph (**2b**)],[8] where the chelating TMEDA was eliminated and replaced by two molecules of THF in order to relieve the very high steric congestion.

The residual molecule of TMEDA present in complex **1** could be removed upon reflux in toluene with consequent formation of green air-sensitive crystals of the dinuclear and diamagnetic $\{[CyNC(H)NCy]_2V\}_2$ (**3**).[9] While the formula of this new complex was revealed by combustion analysis results, the chemical connectivity was elucidated by an X-ray crystal structure.

The structure of **3** shows the typical dimeric arrangement (lantern-type) invariably observed in formamidinate complexes (Scheme 1).[4b] The molecule consists of a V_2 unit bridged by four formamidinate groups placed *trans* with respect to each other, with each pair of *trans*-positioned ligands defining two perpendicular planes.

The V–V distance in the diamagnetic **3** [V1–V2 = 1.968(2) Å] is even shorter than that in the less bulky $\{[(tolyl)NC(H)N(tolyl)]_2V\}_2$,[3e] which has the shortest reported V–V distance. The fact that the increased steric hindrance of **3** gives a shorter intermetallic distance is in line with the recent finding in the chemistry of lantern-type Cr(II) complexes,[10] showing that nonbonding contacts between the amidinate organic substituents determine both the nuclearity and the M–M distances via deformation of the ligand's bite. However, in spite of the exceedingly short V–V distance, the dinuclear frame of **3** is rather labile and could be easily cleaved. Treatment with excess pyridine formed large blue crystals of the monomeric and paramagnetic $[CyNC(H)NCy]_2V(Py)_2$ (**4**) which, similar to the case of the quadruply bonded dichromium complexes,[11] reformed the starting dimeric **3** upon dissociation of pyridine in toluene at 100 °C for 1 h. This result indicates that, in spite of the remarkable shortness, the strength of the V–V multiple bond of **3** must be comparable to only twice the strength of the vanadium–pyridine bond. Conversely, we found no evidence that similar cleavage could be achieved with TMEDA, which indicates that the dimeric **3** is probably thermodynamically more stable with respect to the very crowded **1**. The fact that rather harsh reaction conditions are required for the transformation **1** → **3** may be explained by assuming that the dissociation of the TMEDA ligand requires a rather high activation barrier. The dimeric **3** could also be prepared via reduction of the nearly diamagnetic and dinuclear $[(CyNC(H)NCy)_2VCl]_2$ (**8**)[8] carried out with potassium in either THF or toluene at room temperature.

In the cases of the more bulkyl acetamidinate and silylbenzamidinate, attempts to obtain lantern-type dinuclear structures via thermal elimination of THF from **2a** and **2b** were unsuccessful. While in the case of **2b** the reaction gave only intractable solutions, thermolysis of **2a** in toluene afforded the monomeric and paramagnetic V(III) complex $[CyNC(Me)NCy]_3V$ (**5**), which

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(1) See, for example: (a) Luneva, N.; Mironova, S. A.; Shilov, A. E.; Antipin, M. Y.; Struchkov, Y. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *23*, 1178 and references cited therein. (b) Money, J. K.; Huffmann, J. C.; Christou, G. *Inorg. Chem.* **1988**, *27*, 507 and references cited therein. (c) Money, J. K.; Huffmann, J. C.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 2210. (d) Minhas, R. K.; Edema, J. J. H.; Gambarotta, S.; Meetsma, A. *J. Am. Chem. Soc.* **1993**, *115*, 6710 and references cited therein. (e) Edema, J. J. H.; Meetsma, A.; Van Bolhuis, F.; Gambarotta, S. *Inorg. Chem.* **1991**, *30*, 2056. (f) Scott, M. J.; Wilish, W. C. A.; Armstrong, W. H. *J. Am. Chem. Soc.* **1990**, *112*, 2429.

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(8) Full experimental part and cell parameters of complexes **1**, **2a**, **2b**, **5**, **6a**, **6b**, and **8** are available as Supplementary Material.

(9) Complex 3. A suspension of $VCl_2(TMEDA)_2$ (2.23 g, 6.3 mmol) in toluene (100 mL) was refluxed and stirred overnight in the presence of [CyNC(H)NCy]Li (2.86 g, 13.4 mmol). The resulting deep-yellow suspension was filtered at 80 °C to eliminate gray solid (0.2 g). The resulting dark yellow solution was concentrated to small volume until crystallization of emerald-green solid started. The suspension was boiled to redissolve the solid and slowly cooled to room temperature. Emerald-green air-sensitive crystals of **3** were obtained upon standing 2 days at room temperature. (0.4 g, 0.43 mmol, 13%). ^{1}H NMR [C_6D_6, 200 MHz, 25 °C]: δ 9.85 (s, 4H, formamidine), 2.75 (pseudoquintet, 8H, cyclohexyl), 1.90 (pseudodoublet, 16H, cyclohexyl), 17.5 (pseudodoublet, 16H, cyclohexyl), 1.63 (pseudodoublet, 8H, cyclohexyl), 1.20 (m, 40H, cyclohexyl). Satisfactory combustion analysis data were obtained.

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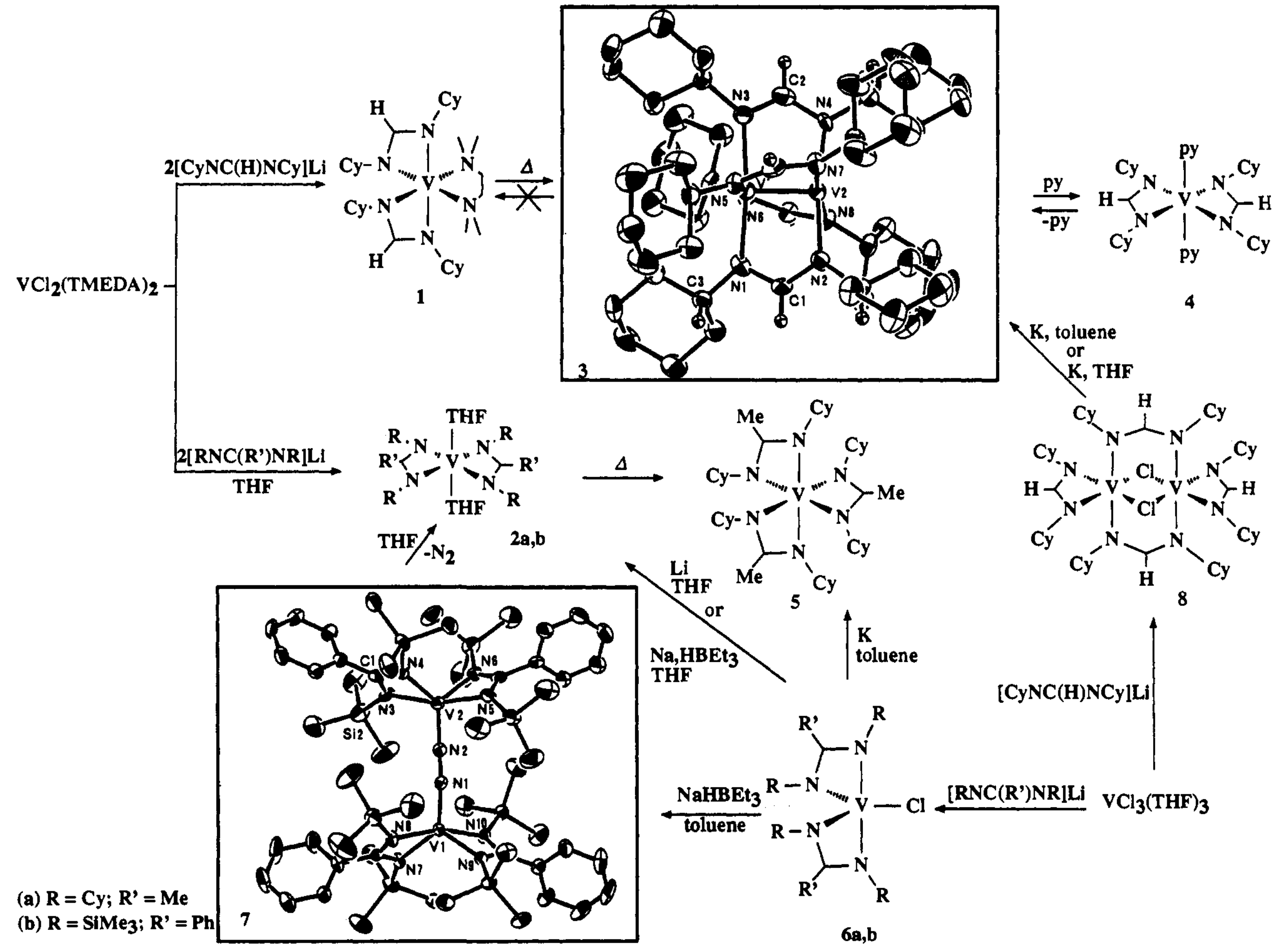
Scheme 1[a]



[a] Selected values of bond distances (Å) and angles (deg). Complex **3**: V1–V2 = 1.968(2), V1–N1 = 2.075(7), V1–N3 = 2.142(7), V1–N5 = 2.080(6), N1–V1–N3 = 173.0(3), N5–V1–N6 = 171.7(2), N1–V1–V2 = 93.5(2), N1–C1–N2 = 102.6(8), C1–N1–C3 = 112.6(7), N1–V1–V2–N2 = 18.1(3). Complex **7**: V1–N1 = 1.756(5), N1–N2 = 1.235(6), V2–N2 = 1.757(5), V1–N7 = 2.074(5), V1–N8 = 2.137(5), N7–Si6 = 1.741(5), V1–N1–N2 = 173.7(4), N1–N2–V2 = 179.3(4), N1–V1–N7 = 129.2(2), N1–V1–N8 = 97.4(2), N7–V1–N8 = 64.9(2), N7–C27–N8 = 116.5(5), Si6–N7–C27 = 130.5(4).

could be isolated in good yield as orange crystalline solid from hexane solutions.[8] The fact that the trivalent **5** was also obtained in significant yield (41%) as the only identifiable product of the reaction of the monomeric $[CyNC(Me)NCy]_2VCl$ (**6a**)[8] with potassium in toluene substantiates the hypothesis that complex **5** might likely be originated by disproportionation of a metastable and coordinatively unsaturated V(II) "$[CyNC(Me)NCy]_2V$" intermediate. Conversely, the V(II) compounds **2a** and **2b** were formed in good yield when the reductions of **6a** and **6b** were carried out in THF with either Li or $NaHBEt_3$ reducing agents.

When carried out in toluene, the reduction of **6b** with $NaHBEt_3$ gave the new dinuclear paramagnetic dinitrogen complex $\{[(Me_3Si)NC(Ph)N(SiMe_3)]_2V\}_2(\mu\text{-}N_2)$ (**7**) [$\mu_{eff} = 0.91\ \mu_B$ per dimer].[12] The presence in **7** of weakly bonded dinitrogen has been unambiguously demonstrated by analytical results, chemical degradation experiments carried out with THF in a closed vessel connected with a Toepler pump (87% of N_2 recovered during the formation of **2b**), and an X-ray crystal structure (Scheme 1). The rather short N–N distance [N1–N2 = 1.235(6) Å] and the lability of the coordination suggest minimal extent of dinitrogen reduction.

In summary, the results described in this work clearly show that each of the amidinate ligands employed for this work behaves in a very distinctive manner with respect to the nuclearity and the stabilization of the oxidation state of the metal. The fact that the formamidinate ligand gives a dinuclear and diamagnetic species regardless of both the metal oxidation state [II or III] and the synthetic procedure employed for the preparation of the complex indicates an intrinsic ability of the formamidinate ligand to form dimers and to enforce very short intermetallic contacts. However, the contribution of the V–V multiple bond to the stabilization energy of the dimer is probably minimal. The situation is reversed in the case of the extremely bulky silyl-amidinate, where the systematic failure to form dimers is complemented by the ability to stabilize divalent vanadium and to perform reversible dinitrogen fixation.

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Supplementary Material Available: Full details on preparation of all complexes including ORTEP drawing showing the full labeling scheme and tables listing atomic positional and anisotropic thermal parameters and complete bond distances and angles (87 pages); listing of observed and calculated structure factors for **3** and **7** (75 pages). 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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[12] A solution of **6b** (6.35 g, 10.4 mmol) in toluene (60 mL) was treated with $NaHBEt_3$ (10.5 mL, 1 M in toluene). The color rapidly turned brown during a vigorous gas evolution. The suspension was stirred overnight at room temperature, during which time a slow gas uptake occurred. The mixture was filtered and evaporated to dryness, and the residual solid was redissolved in hexane. Dark-green crystals of **7** separated almost immediately (2.69 g, 43%). Satisfactory combustion analysis data were obtained. $\mu_{eff} = 0.91\ \mu_B$ per dimer. ^1H NMR [200 MHz, C_6D_6, 25 °C]: δ 7.69 (5H, $\Delta\nu_{1/2}$ = 66 Hz, phenyl), 0.36 (18H, $\Delta\nu_{1/2}$ = 87 Hz, Me_3Si).