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Communication

Dinitrogen Partial Reduction by Formally Zero- and Divalent Vanadium Complexes Supported by the Bis-iminopyridine System

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Reduction of the two trivalent 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N═C(CH$_3$)}$_2$-(C$_5$H$_3$N)VCl$_3$ and {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N—C═(CH$_2$)}$_2$(C$_5$H$_3$N)]-VCl(THF) complexes with excess NaH afforded two corresponding end-on dinitrogen-bridged complexes [2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N═C-(CH$_3$)}$_2$(C$_5$H$_3$N)V]$_2$(*m*-N$_2$)·(hexane) (**1**) and [{[2,6-{[2,6-(i-Pr)$_2$C$_6$-H$_3$]N—C═(CH$_2$)}$_2$(C$_5$H$_3$N)]V]$_2$(*m*-N$_2$)·(hexane) (**3**). Despite their very close structural similarity, the two species have completely different natures. The first is paramagnetic and may be regarded as generated by the two-electron attack of two formally zerovalent vanadium moieties on the same N$_2$ unit. In the nearly diamagnetic **3** instead, the N$_2$ unit has been reduced by two vanadium atoms, formally divalent. Structural analysis and DFT calculations have indicated that partial reduction of the bridging nitrogen occurred for both complexes while, in the case of **1**, substantial metal-to-ligand electron transfer also occurs.

The ability of conjugated bis-imines to sustain high catalytic activity in olefin polymerization with a large variety of metals[1] has renewed the interest for this family of ligands which traditionally were confined to the domain of classical coordination chemistry.[2] Their remarkable versatility in terms of stabilization of highly reactive species[3] may be ascribed to the capacity of these molecules to engage in redox processes with the metal center and to efficiently delocalize negative charge.[4] The bis-iminopyridine ligand 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N═C(CH$_3$)}$_2$(C$_5$H$_3$N),[5] in particular, can accept up to three electrons into the delocalized π-system to form a paramagnetic radical anion.[6] This indicates that the occasional appearance of these complexes as low-valent species may be deceiving since in reality the metal might be in a higher oxidation state, one or more electrons being efficiently stored into the extended iminopyridine π-system.[4] Nonetheless, depending on the extent of charge-transfer, the reducing power of the metal is not necessarily quenched. For example, highly reactive zerovalent Fe[3] and monovalent Co[7] complexes of this ligand system are sufficiently reactive to coordinate dinitrogen.

There are limitations though. It is now well-established that the bis-iminopyridine ligand may engage, particularly during alkylation processes, in a variety of transformations which span from alkylation at virtually any position of the pyridine ring,[8] including the N atom,[9] and of the imine functions,[10] to deprotonation of one[9] or both methyl imine

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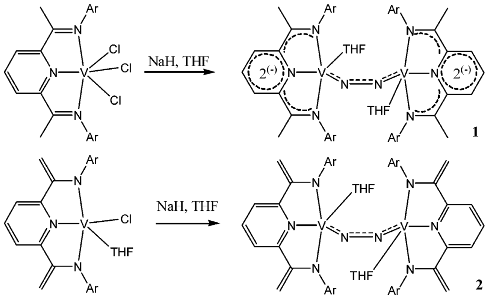
Scheme 1



substituents.[11] In both ligand-alkylation and ligand-deprotonation processes, the primary transformation undergone by the ligand system is to become either mono- or dianionic, thus providing accessibility to a new family of anionic ligands. Besides supporting new catalysts for olefin and diolefin polymerization,[11] these ligands may also store additional electron density in C−C bonds via dimerization reactions.[4,8b] This redox dimerization may occur not only with the intervention of external reducing agents but also spontaneously and at the expense of the metal center. This was the case of a Co(II) species which was reduced by the anionic ligand to the monovalent state and became the precursor to dinitrogen fixation.[12]

These considerations prompted us to revisit the reactivity of the bis-iminopyridine complexes of vanadium which have already provided a potent ethylene polymerization catalyst but which also gave the first indication about how ligand alkylation may provide reduction pathways for the metal center.[8a] A recurrent feature of di- and trivalent vanadium supported by N-donor based ligand systems (amides and amidinates) is the ability to form dinitrogen complexes[13] which in two instances have provided the basis for further dinitrogen cleavage.[14] We have therefore attempted the hydride-reduction of the vanadium center supported by both the neutral and dianionic forms of the bis-imine pyridine ligand system to probe the possibility to stabilize formal low oxidation states without quenching the reactivity of the metal center.

The reaction of the 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$-(C$_5$H$_3$N)VCl$_3$ adduct[8a] with an excess of NaH proceeded slowly at room temperature affording a dark-colored suspension from which dark crystals of the paramagnetic dinitrogen complex [2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N=C(CH$_3$)}$_2$(C$_5$H$_3$N)V]$_2$(μ-N$_2$)·(hexane) (**1**) were isolated in 35% yield (Scheme 1).

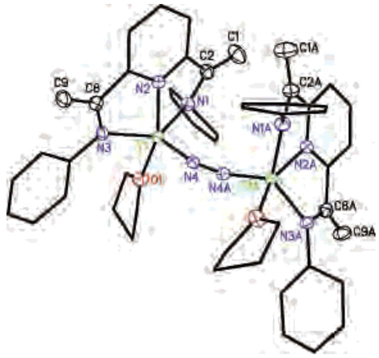


Figure 1. Partial thermal ellipsoid plot with ellipsoids drawn at the 30% probability level. i-Pr groups have been removed for clarity. Bond distances (Å) and angles (deg): **1**, N(4)−N(4a) = 1.259(6), V(1)−N(4) = 1.777(3), V(1)−N(1) = 2.141(3), V(1)−N(2) = 1.931(3), V(1)−N(3) = 2.084(3), C(1)−C(2) = 1.500(6), C(8)−C(9) = 1.497(6), C(2)−N(1) = 1.341(5), C(8)−N(3) = 1.370(5), O(1)−V(1)−N(1) = 92.44(12), O(1)−V(1)−N(2) = 151.68(12), O(1)−V(1)−N(3) = 97.97(12), O(1)−V(1)−N(4) = 103.81(12), N(1)−V(1)−N(2)= 75.24(13), N(1)−V(1)−N(3) = 138.05(13), N(1)−V(1)−N(4) = 109.87(13), N(2)−V(1)−N(3) = 76.62(13), N(2)−V(1)−N(4) = 104.36(14), N(3)−V(1)−N(4) = 106.82(13), V(1)−N(4)−N(4a) = 162.42(17); **3**, N(4)−N(4a) = 1.242(5), V(1)−N(4) = 1.777(2), V(1)−N(1) = 2.024(3), V(1)−N(2) = 2.029(3), V(1)−N(3) = 2.049(2), C(1)−C(2) = 1.317(5), C(8)−C(9) = 1.350(4), C(2)−N(1) = 1.401(4), C(8)−N(3) = 1.387(4), O(1)−V(1)−N(1) = 97.18(10), O(1)−V(1)−N(2) = 157.55(10), O(1)−V(1)−N(3) = 94.45(10), O(1)−V(1)−N(4) = 103.38(10), N(1)−V(1)−N(2)= 76.97(10), N(1)−V(1)−N(3) = 135.83(11), N(1)−V(1)−N(4) = 107.39(11), N(2)−V(1)−N(3) = 76.25(10), N(2)−V(1)−N(4) = 99.04(10), N(3)−V(1)−N(4) = 111.01(10), V(1)−N(4)−N(4a) = 167.18(8).

Attempts to use other reductants, such as potassium, afforded intractable materials. The formation of **1** was accompanied by H$_2$ gas evolution which was recovered in significant yield (79% of the expected amount based on a presumed 100% conversion) by carrying the reaction in a sealed vessel connected to a Toepler pump.

The connectivity of **1** was yielded by an X-ray crystal structure (Figure 1) showing a dinuclear complex with the two vanadium atoms bridged by one end-on bonded dinitrogen unit and each surrounded by one ligand and one molecule of coordinated THF. The ligand system appears to have undergone no significant modification with respect to the starting trivalent complex.[8a] The $C_{imine}-C_{Me}$ bonds are rather long and clearly are C−C single bonds. This rules out the possibility that the ligand might have been deprotonated by the strongly basic NaH. The V−N and N−N distances compare rather well with those of the other existing V(II) and V(III) dinitrogen complexes.[15] The N−N bond is elongated relative to that of free N$_2$, indicating reduction to $[N_2]^{2-}$. This alone would make each V atom monovalent. However, the $C_{imine}{=}N_{imine}$ bonds are much longer than those in the free ligand or in its "innocent" complexes, while the $C_{py}-C_{imine}$ bonds are shortened. The bond length changes indicate a transfer of more than 1.5 electron from the metal to the ligand.[16] Thus, the structure is best regarded as

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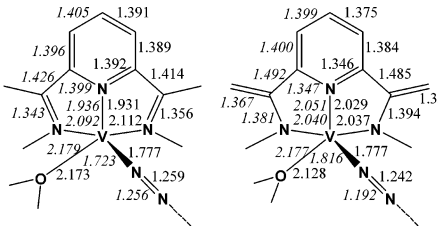
containing two V(III) atoms, bridged by an N_2^{2-} unit and each bearing a ligand dianion.

The structure does not show any distortion which may possibly be indicative of the presence of one or more hydrides. In addition, chemical degradation experiments carried out with the Toepler pump did not yield any significant amount of H_2. The IR spectrum ruled out the possibility that the N atoms may have been protonated.

As mentioned above, the diminopyridine molecule 2,6-{[2,6-(i-Pr)$_2$C$_6$H$_5$]N═C(CH$_3$)}$_2$(C$_5$H$_3$N) can be transformed into the corresponding dianion {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N─C═(CH$_2$)}$_2$(C$_5$H$_3$N)]$^{2-}$ via simple treatment with 2 equiv of LiCH$_2$SiMe$_3$.[4] In turn, the reaction of this dianion with VCl$_3$(THF)$_3$ afforded the corresponding vanadium complex {[2,6-{[2,6-(i-Pr)$_2$C$_6$H$_3$]N─C═(CH$_2$)}$_2$(C$_5$H$_3$N)]VCl(THF) (**2**) which also is a versatile catalyst for ethylene homo- and copolymerization.[17] Its treatment with K in THF resulted in a slow color change and yielded dark-colored crystals (60%) of the nearly diamagnetic dinitrogen complex [{[2,6-{[2,6-(i-Pr)$_2$-C$_6$H$_3$]N─C═(CH$_2$)}$_2$(C$_5$H$_3$N)]V]$_2$(μ-N$_2$)·(hexane) (**3**).

The crystal structure of **3** is very similar to that of **1**, and not surprisingly, the two species display almost identical crystallographic cell parameters (Figure 1). However, the former $C_{imine}-C_{Me}$ bonds are much shorter than those in **1** and are evidently double bonds. Thus, while in **1** a ligand dianion is formed through metal-to-ligand electron transfer, in **3** it has been formed by deprotonation. The V─N distances seem to be unaffected by this change.

The geometries of simplified models of complexes **1** and **3** (Me groups at N) were optimized using unrestricted DFT calculations. For both complexes, spin "states" from $S = 0$ to $S = 4$ were considered. All $S = 2$ or higher states were found to be too high in energy to be relevant. The $S = 0$ state was calculated to be somewhat lower in energy than $S = 1$; the difference depends on the functional but is smaller for **1** (RI-bp86, 1.2 kcal/mol; b3-lyp, 7.4 kcal/mol) than for **3** (4.5 and 7.8 kcal/mol). The $S = 0$ "state" is heavily spin-contaminated. Therefore, although the absolute energies are probably not very meaningful, the general picture (singlet and triplet close, triplet relatively more stable for **1**) should be reliable. The experimental results suggest that we overestimate the stability of the singlet, possibly because of the use of a model ligand, and that for the real systems **1** has a triplet ground state, while **3** is actually a singlet.



1 **3**

Figure 2. Observed and *calculated* bond lengths (Å) for complexes **1** ($S = 1$) and **3** ($S = 0$).

The calculated geometries for $S = 0$ and $S = 1$ are very similar. Figure 2 compares the observed and calculated ($S = 1$ for **1**, $S = 0$ for **3**) geometries. The agreement is sufficient to give credibility to the computational results. The bonding picture that emerges for **1** is perhaps clearer if we start with two V^0 centers, each with the occupation $d_{xz}^2 d_{yz}^2 d_{xy}$ where each V center has its own local axis system, with the z axis parallel to the V─N$_2$ bond and the x axis along V─N$_{py}$. The d_{yz} electrons (both α and β) back-donate into the N$_2$ π^*-orbitals, whereas the d_{xz} electrons are mostly transferred into ligand π^* orbitals (only one π^*-orbital of each ligand participates). The d_{xy} orbitals on the two V centers interact only weakly, and the coupling between these two gives rise to the singlet and triplet states. For **3**, the ligand, N$_2$ π^* and metal d orbitals are strongly mixed and the analysis is not as clear. The highest occupied orbitals show back-donation from d_{xz} and d_{yz} to the N$_2$ π^* orbitals just like in **1**. The activation of N$_2$ is therefore not much different in the two complexes. However, there is now only one metal electron left to interact with the bis-iminopyridine π^* orbitals, and these π^* orbitals are higher in energy for the dianionic ligand in **3** than for the originally neutral ligand in **1**. Thus, the metal─ligand bonding in **3** is more concentrated in the iminate─V σ-bonds, as is evident from the longer V─N$_{py}$ and shorter V─N$_{imine}$ bonds and the smaller C─C/C─N distances of the pyridine ring in **3** as compared to **1**. The strong mixing in the orbitals just below the frontier orbitals may explain why the coupling between the remaining electrons on the two V centers is stronger than in **1** and results in a diamagnetic ground state. Partial thermal depopulation of the HOMO provides a reasonable explanation for the little residual paramagnetism observed at room temperature.

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Supporting Information Available: Complete crystallographic data (CIF) for complex **1** and **3**; calculated energies, S^2 values, and geometrical parameters for model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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