Theoretical investigation of the pathway for reductive cleavage of dinitrogen by a vanadium diamidoamine complex

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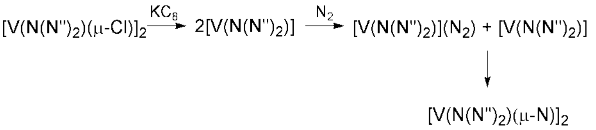
Received (in Cambridge, UK) 30th March 2000, Accepted 19th April 2000

Density functional calculations show that $[HN(CH_2CH_2NH)_2V]$ will bind N_2 in a sideways fashion; further reaction with another molecule of $[HN(CH_2CH_2NH)_2V]$ leads to reductive cleavage of the N_2 moiety to form a bridged nitrido dimer, $[HN(CH_2CH_2NH)_2V(\mu\text{-}N)]_2$; this study provides a model for the formation of $[RN(CH_2CH_2NR)_2V(\mu\text{-}N)]_2$ (R = $SiMe_3$) by reduction of $[RN(CH_2CH_2NR)_2V(\mu\text{-}Cl)]_2$ under an N_2 atmosphere.

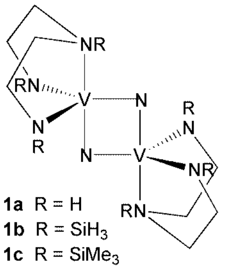
Examples of well-defined molecular systems which completely reductively cleave the dinitrogen molecule are extremely rare. The original case is the neutral Mo(III)–tris(anilide) complex of Laplaza and Cummins which yields a Mo(VI) terminal nitride upon reaction with N_2;[1] a comprehensive study has demonstrated that the mechanism of formation of the latter involves formation of a binuclear complex containing a linear μ-dinitrogen ligand which subsequently cleaves symmetrically *via* a transition state in which the μ-dinitrogen ligand is bound in a zigzag fashion.[2] Subsequently Floriani and coworkers reported an anionic Nb(III)–calixarene dinitrogen complex which affords an anionic nitrido-bridged dimer on further reduction.[3] The very recent report that reduction of the V(III) complex $[V(N\{N''\}_2)Cl]_2$, where $N\{N''\}_2 = (Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2$, under a dinitrogen atmosphere completely cleaves the N≡N bond to afford the doubly nitrido-bridged V(V)–V(V) dimer $[V(N\{N''\}_2)(\mu\text{-}N)]_2$,[4] has prompted us to investigate a possible pathway for this unusual reaction using density functional methods.[5]

Use of a mixture of $^{14}N_2$ and $^{15}N_2$ shows that both nitrido bridging atoms in the dimer molecule originate from the same dinitrogen molecule. If the reduction is carried out under argon and N_2 is subsequently introduced the nitrido-bridged dimer is not isolated. On the assumption that reaction of $[V(N\{N''\}_2)Cl]_2$ with potassium graphite in toluene results in the V(II) species $[V(N\{N''\}_2)]$, a possible route is given by eqn. (1). The V(II) species first binds dinitrogen and then reacts with a further V(II) species to give the product.

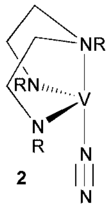


$$[V(N(N'')_2)(\mu\text{-}Cl)]_2 \xrightarrow{KC_8} 2[V(N(N'')_2)] \xrightarrow{N_2} [V(N(N'')_2)](N_2) + [V(N(N'')_2)] \longrightarrow [V(N(N'')_2)(\mu\text{-}N)]_2 \quad (1)$$

We first tested whether theoretical calculations produced a good model of $[V(N\{N''\}_2)(\mu\text{-}N)]_2$, and whether the structural features could be reproduced with the $SiMe_3$ groups being replaced by SiH_3 and by H. Geometry optimization of these three dimers, **1a**, **1b** and **1c** reproduced the trigonal bipyramidal coordination found for $[V(N\{N''\}_2)(\mu\text{-}N)]_2$, and gave the V–N distances listed in Table 1. Frequency calculations showed **1a** to be a local minimum. Good agreement with the experimental distances (Table 1) was found for **1c**, and the only significant change on substitution was the magnitude of the long V–N (amino) distance which was calculated to be reduced by 0.3 Å on replacing $SiMe_3$ by the smaller H atom. We thus felt justified in modeling possible intermediates with the simpler $[HN(CH_2CH_2NH)_2]$ ligand (denoted L).



1a R = H
1b R = SiH_3
1c R = $SiMe_3$



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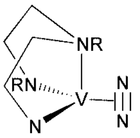

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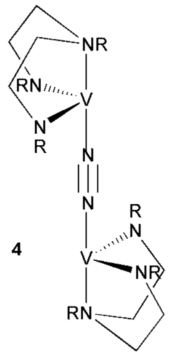

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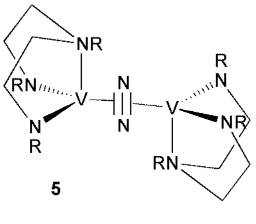

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A search for stable $[LV(N_2)]$ intermediates yielded two promising candidates, **2** and **3**. Structure **2** had the N_2 moiety bound in an end on fashion in the axial site of a trigonal bipyramid and the quartet spin state was found to be lower in energy than a doublet for this intermediate. In **3** the N_2 was bound sideways in an equatorial site and in this case a doublet spin state was lower in energy. V–N and N–N distances for **2** and **3** are listed in Table 2 together with the energy of the various spin states relative to [LV] and N_2. Frequency calculations showed both **2** and **3** to be local minima. It should be noted that both $[LVN_2]$ intermediates show substantial binding energies for the N_2 molecule and also that **3** is predicted to be marginally more stable than **2** and to have a longer N–N

Table 1 Calculated and experimental V–N distances (Å) for $[V\{RN(CH_2CH_2NR)\}N]_2$ (R = H, SiH_3 or $SiMe_3$)

	H (calc.)	SiH_3 (calc.)	$SiMe_3$ (calc.)	$SiMe_3$ (exptl.)
V1–N1	1.88	1.86	1.86	1.862, 1.912
V1–N2	1.68	1.67	1.67	1.713, 1.769
V1–N3	2.34	2.48	2.64	2.539
V1–N4	1.87	1.87	1.87	1.877
V1–N5	1.87	1.87	1.87	1.897

DOI: 10.1039/b002534h

Table 2 Calculated V–N and N–N distances (Å) and energies (eV) relative to LV and N2 for **1a**, **2**, **3**, **4** and **5**

	1a (S = 0)	**2** (S = 3/2)	**2** (S = 1/2)	**3** (S = 3/2)	**3** (S = 1/2)	**4** (S = 1)	**5** (S = 1)
V–N	1.88, 1.68	1.92	1.85	2.10, 2.12	1.95, 1.90	1.72	1.93, 1.81
N–N	2.49	1.13	1.15	1.16	1.20	1.23	1.41
Energy	−7.09	−2.94	−2.47	−2.49	−2.99	−4.75	−5.04

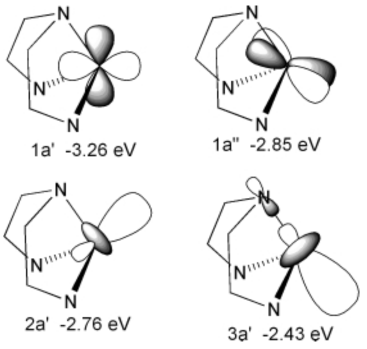

Fig. 1 Frontier orbitalS of the [HN(CH$_2$CH$_2$NH)$_2$V] (LV) fragment.

distance. As the N$_2$ unit in **3** lies close to the substituent on the amino N we were concerned that this binding mode might be sterically hindered. However, geometry optimization of the fully trimethylsilylated analogue resulted in a similar structure with the N$_2$ only slightly displaced away from the amino substituent. The V–N (amino) distance was also lengthened by 0.061 Å.

Attachment of a second [LV] unit to **2** yielded the minimum energy structure **4** which had a triplet as the lowest spin state. The N–N bond was lengthened further (Table 2).

Attachment of a further [LV] fragment to **3** and geometry optimization of a triplet state led to **5**. This was more stable than **4** and had a considerably stretched N–N distance of 1.41 Å (Table 2) indicative of a bond order of 2 between the N atoms. The two half filled orbitals of **5** lay very close in energy and were of a$_u$ and b$_u$ symmetry. This closeness in energy led to problems with SCF convergence for geometry optimization of the singlet state. However, when the configuration was fixed with both electrons occupying the b$_u$ orbital, the molecule optimized to a structure in which the N–N bond was broken and which was indistinguishable from **1a**.

Inspection of the frontier orbitals (Fig. 1) of the [LV] fragment neatly explains the two different coordination modes and sites for the N$_2$ molecule in **2** and **3**. The 2a′ and 3a′ orbitals are those that form σ bonds in a trigonal bipyramidal geometry, 2a′ providing equatorial coordination and the higher lying 3a′ axial coordination. In **2**, with the quartet ground state, the end on axially coordinated [LV(N$_2$)] intermediate, 3a′ is the acceptor orbital and 1a′ and 1a″ back donate in a π fashion to the antibonding π$_g$ orbitals of the nitrogen molecule. Both of the back-donation MOs are singly occupied. The third unpaired electron occupies the 2a′ orbital. In **3**, the doublet ground state, the side-on bound [LV(N$_2$)] intermediate, the 2a′ orbital accepts electron density from the bonding π$_u$ orbital and back donates in a π fashion from the 1a′ orbital (doubly occupied) and in δ fashion from the 1a″ orbital (singly occupied). The 3a′ orbital is unoccupied. Thus in **3,** more electrons are involved in back-donation to the N$_2$ unit. This results in a longer N–N distance.

In **4** additional back donation ensues from the π type orbitals, which are doubly occupied, and further lengthening of the N–N bond results. However, two unpaired electrons still occupy non-bonding orbitals of 2a′ origin.

The a$_u$ and b$_u$ half-occupied orbitals of **5** are shown in Fig. 2. The b$_u$ orbital has N–N σ$_u$ character and its partial occupancy results in further lengthening of the N–N bond. When it is doubly occupied, in the singlet state, all three N–N antibonding orbitals are receiving maximum input from the electron-rich vanadium centres and rupture of the N–N bond is achieved.

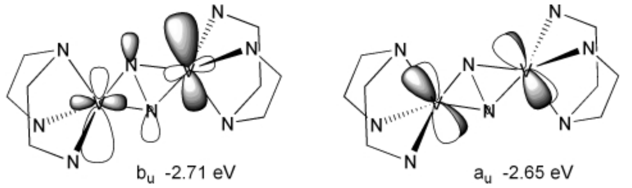

Fig. 2 RepresentationS of the b$_u$ and a$_u$ half-occupied orbitalS of **5**.

In essence, cleavage of the N$_2$ unit requires not only donation into its π$_g$ orbitals but also into the antibonding σ$_u$ orbital. This can only be sensibly achieved by sideways bonding of the N$_2$ unit where the acceptor function of the metal fragment is spatially separated from the interaction with the σ$_u$ N$_2$ orbital. There are parallels between the N$_2$ cleavage discussed here and the relative stabilities of (μ-η^2:η^2-peroxo)dicopper(II) and bis(μ-oxo)dicopper(III) complexes, where donation into the σ$_u$* orbitals of O$_2$ is a key step in breaking the O–O bond.[11,12]

In conclusion a promising pathway for N$_2$ cleavage by [V(N{N″}$_2$)] to give [V(N{N″}$_2$)(μ-N)]$_2$, is side-on binding of N$_2$ by [V(N{N″}$_2$)] followed by association of a further molecule of [V(N{N″}$_2$)]. In a singlet state the N–N bond in the resultant sideways dinitrogen-bridged dimer will break and the nitrido bridged dimer is formed.

We thank EPSRC (ROPA) for support. Results were obtained using the resources of the Oxford Supercomputing Centre.

Notes and references

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