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Sequential N−O and N−N Bond Cleavage of N-Heterocyclic Carbene-Activated Nitrous Oxide with a Vanadium Complex

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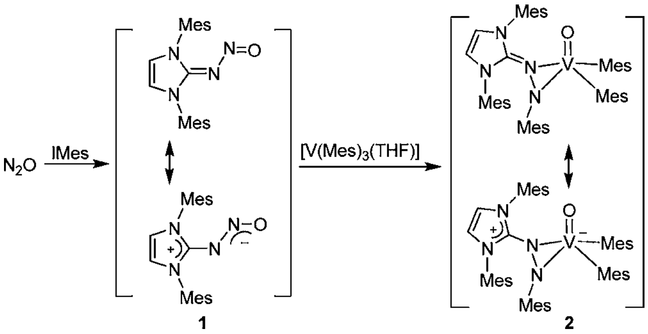
Supporting Information

ABSTRACT: Chemically induced bond cleavage of nitrous oxide typically proceeds by rupture of the N−O bond with concomitant O-atom transfer and liberation of dinitrogen. On a few occasions, N−N bond scission has been observed instead. We report a reaction sequence involving an N-heterocyclic carbene and a vanadium complex that results in cleavage of both the N−O bond *and* the N−N bond.

Nitrous oxide is a problematic compound from an environmental point of view because it is an ozone-depleting substance[1] and a very efficient greenhouse gas.[2] From a synthetic point of view, on the other hand, N_2O is interesting because of its high oxidation potential.[3] A severe hurdle for developing the chemistry of N_2O is its inert character. Over the last years, considerable efforts have been made to activate N_2O chemically.[2,4] Most investigations in this direction have focused on transition-metal complexes. Today, there are abundant reports about transition-metal complexes that react with N_2O under mild conditions.[4,5] In most cases, the reactions proceed by rupture of the N−O bond with concomitant O-atom transfer and liberation of dinitrogen. Chemical transformations that preserve the N_2O unit[6] or lead to cleavage of the N−N bond[7] are very rare. Here we describe a reaction sequence involving an N-heterocyclic carbene and a vanadium complex that results in cleavage of both the N−O bond *and* the N−N bond.

We recently reported that the N-heterocyclic carbene 1,3-dimesitylimidazol-2-ylidene (IMes) is able to form a stable covalent adduct (**1**) with N_2O at ambient pressure and temperature (Scheme 1).[8] The adduct can be described as a nitrosyl imine[9] or an imidazolium diazotate. The importance of the zwitterionic form is supported by a computational analysis of the Hirschfeld-I charges and by the results of a crystallographic analysis, which showed that the plane defined by the bent N_2O group is markedly inclined with respect to the plane defined by the heterocycle.[8] A noteworthy feature of **1** is the long N−N bond [1.333(2) Å], which is in contrast to what has been observed for N_2O adducts of frustrated Lewis pairs (N−N ≈ 1.25 Å).[10] This structural characteristic suggests that the activation of N_2O by IMes might facilitate N−N bond rupture, and preliminary results obtained for an alkylation reaction have shown that this is indeed the case.[8]

Scheme 1. Synthesis of Complex 2



Intrigued by the results of these initial investigations, we examined the reaction of **1** with $V(Mes)_3(THF)$.[11] The complex $V(Mes)_3(THF)$ is highly oxophilic, as evidenced by the fact that it can abstract oxygen atoms from epoxides[12] and nitrosyl complexes.[13] Furthermore, it is known that low-valent vanadium complexes are able to react with N_2O.[14] Exploring the combined effect of an N-heterocyclic carbene (which weakens the N−N bond) and $V(Mes)_3(THF)$ (which "pulls" on the O atom) on N_2O appeared to be a worthwhile endeavor.

When equimolar amounts of **1** and $V(Mes)_3(THF)$ were mixed in THF, the color of the solution quickly changed from blue to purple-red. Precipitation with *n*-hexane allowed complex **2** to be isolated in 53% yield (Scheme 1) Complex **2** is sensitive to oxygen and moisture both in solution and in the solid state. It is very soluble in common organic solvents such as dichloromethane, THF, and toluene. Single crystals of **2** were analyzed by X-ray diffraction, and the solid-state structure of **2** is depicted in Figure 1.

Reaction of **1** with $V(Mes)_3(THF)$ resulted in O-atom transfer from **1** to vanadium and insertion of the $IMesN_2$ fragment into the V−Mes bond, providing a $VO(Mes)_2$ complex with a side-on bound $IMesN_2Mes$ ligand. The bonding situation of the latter is of special interest. The V−N bond lengths of 1.981(3) and 1.948(3) Å are shorter than what has been observed for side-on coordinated hydrazine complexes of V(V) (V−N ≈ 2.1 Å).[15,16] On the other hand, the N1−N2 bond [1.474(5) Å] is long, exceeding the N−N bond lengths observed for hydrazines (N−N ≈ 1.45 Å).[17] Formally, $IMesN_2Mes$ can be regarded as a deprotonated mesitylhydrazone ligand. However, the geometry around the N1 atom is not planar: the C1−N1−N2−V1 dihedral angle is 116° instead of 180°. These data suggest a strong contribution from a mesomeric form with an imidazolium group connected to a hydrazido(2−) ligand. The computed Hirschfeld-I charges for

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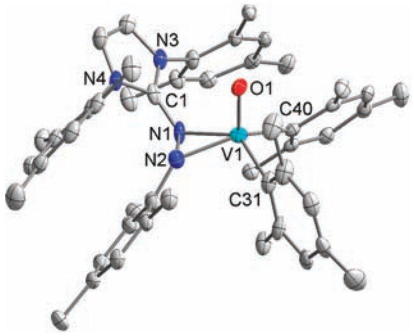


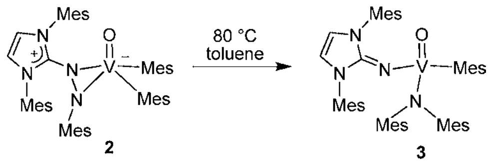
Figure 1. Molecular structure of complex **2** in the crystal. Thermal ellipsoids are at 50% probability.

complex **2** are in line with this description [see the Supporting Information (SI)].

The ^{1}H NMR spectrum of **2** in THF-d_8 was found to be strongly temperature-dependent. At room temperature, broad peaks were observed. At −80 °C, a well-resolved spectrum indicated the presence of five chemically distinct mesityl groups devoid of local C_2 symmetry. The peak broadening at ambient temperature was not unexpected in view of the fact that complex **2** is a sterically highly congested molecule with close contacts between the different mesityl groups. Hindered rotation around the N−C_{Mes} and V−C_{Mes} bonds would thus be expected.

When a toluene-d_8 solution of complex **2** was heated to 80 °C (Scheme 2), a clean transformation into a new complex (**3**) was observed by ^{1}H NMR spectroscopy (see the SI). The reaction, which was accompanied by color change from purple-red to orange-red, was complete after 70 min. Complex **3** (75% isolated yield) was crystallized from *n*-hexane/THF, and its solid-state structure is depicted in Figure 2.

Scheme 2. Thermally Induced Rearrangement of Complex 2 into 3



The crystallographic analysis revealed that the elevated temperature had induced the migration of a vanadium-bound mesityl group to the N2 atom and cleavage of the N1−N2 bond. As a result, we observed a vanadium oxo complex bound to a mesityl ligand, a dimesitylamide ligand, and an imidazolin-2-iminato ligand.[18] The bond lengths found for V1−O1 [1.598(3) Å], V1−N2 [1.919(3) Å], and V1−C22 [2.109(4) Å] are unremarkable. The guanidinate ligand is coordinated in a bent fashion [C1−N1−V1 = 144.7(3)°] with an N1−V1 bond distance of only 1.779(3) Å. This value points to a partial double-bond character of the V1−N1 bond.[18,19] The apparent symmetry of complex **3** as revealed by ^{1}H NMR spectroscopy is higher than that of **2**, indicating increased rotational freedom of the mesityl groups in solution. The release of steric congestion upon rearrangement of **2** into **3** likely contributes to the energy required for N−N bond splitting.

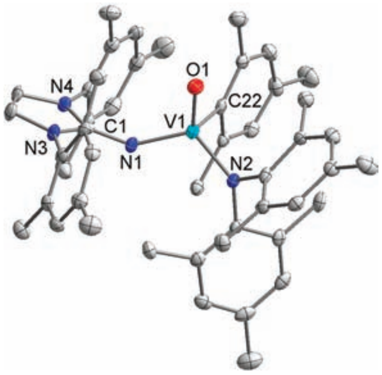


Figure 2. Molecular structure of complex **3** in the crystal. Thermal ellipsoids are at 50% probability.

In summary, we have shown that the reaction of a vanadium complex with IMes-activated N_2O results in consecutive cleavage of first the N−O bond and then the N−N bond. Such behavior is unusual because metal-induced N−O bond rupture of N_2O typically results in release of N_2, whereas N−N bond cleavage gives NO. We were able to overcome the bias to form N_2 or NO by using two reagents with complementary reactivity profiles: a highly oxophilic vanadium complex that acts as deoxygenation agent and a highly Lewis basic N-heterocyclic carbene that weakens the N−N bond of N_2O.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and crystallographic data for complexes **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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