Nitrogen Oxides

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# Covalent Capture of Nitrous Oxide by N-Heterocyclic Carbenes**

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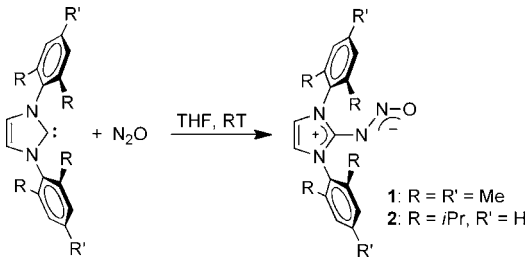
In a recent publication, Ravishankara and et al. conclude that nitrous oxide will be "the dominant ozone-depleting substance emitted in the 21st century".[1,2] $N_2O$ is also a greenhouse gas which is around 300 times more potent than $CO_2$.[3] The environmental impact of $N_2O$ should be regarded as a strong incentive to study the basic chemistry of this gas in more detail. In principle, $N_2O$ is a very interesting oxidizing agent.[3,4] It has a high oxidation potential and it is environmentally benign (side product: $N_2$). However, $N_2O$ is kinetically very inert and this has hampered its utilization as an oxidant or as a building block for more complex molecules. It is thus not surprising that considerable efforts have been made to activate $N_2O$ chemically.[3,4] Transition-metal complexes have emerged as promising activation agents.[5] Notwithstanding, $N_2O$ is a very poor ligand and structurally characterized $N_2O$ complexes have only been reported recently.[6] The reaction of $N_2O$ with organic compounds typically requires elevated temperatures or pressures.[3,4] Olefins, for example, are converted into carbonyl compounds in the presence of $N_2O$ at 150–250 °C and pressures of more than 10 bar.[4c] The oxidation of $PPh_3$ was found to occur at temperatures below 100 °C but supercritical $N_2O$ was employed ($p > 100$ bar).[7] Only highly reactive molecules such as triethylborane[8] and certain silicon-containing compounds (e.g., silaethenes or disilenes)[9] are oxidized by $N_2O$ under ambient conditions. An exciting recent finding was the fact that frustrated Lewis pairs (FLPs) are able to bind $N_2O$.[10] In contrast to the oxygen-transfer reactions mentioned above, $N_2O$ is bound intact between the Lewis acid (fluoroarylboranes) and the Lewis base (trialkylphosphines) as evidenced by crystallographic analyses. Herein we report that N-heterocyclic carbenes (NHCs) are also able to capture $N_2O$ to give stable adducts. The adducts display unique reactivity as evidenced by an alkylation reaction which results in rupture of the N–N bond.

N-heterocyclic carbenes such as the commercially available 1,3-dimesitylimidazol-2-ylidene (IMes) are highly Lewis-basic compounds,[11] which are able to form adducts with the inert gas $CO_2$.[12] These findings prompted us to explore the reactivity of NHCs towards $N_2O$. When a solution of IMes in THF (33 mM) was subjected to an atmosphere of $N_2O$, the solution slowly became yellow along with the formation of a yellow precipitate (**1**). Isolation (yield: 90 %) and analysis of **1** by NMR spectroscopy, mass spectrometry, and elemental analysis suggested the formation of an $N_2O$ adduct (Scheme 1). This structure was confirmed by a crystallographic analysis (see below). In a related fashion, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) reacted with $N_2O$ to give the adduct **2**. Purification of **2** required column chromatography on silica gel which reduced the yield of the isolated adduct to 41 %.[13] The fact that **2** could be purified by chromatography was a first indication of its high stability.




***Scheme 1.*** Synthesis of the $N_2O$ adducts **1** and **2**.

The adducts **1** and **2** are very soluble in polar organic solvents (e.g., $CHCl_3$, $CH_2Cl_2$, or THF). Crystallization was achieved by slow evaporation of $CH_2Cl_2$/*n*-hexane (for **1**) or $Et_2O$/*n*-hexane (for **2**) solutions. Single-crystal X-ray diffraction analyses were performed for both complexes[14] and graphical representations of the molecular structures are depicted in Figure 1.

In both adducts, a bent $N_2O$ group is connected through the N atom (N3) to the carbon atom (C1) of the heterocycle. Overall, the bond lengths and angles are similar for the two adducts (Table 1). The bonds of the C1 atom to the three adjacent nitrogen atoms (N1–N3) all have lengths of approximately 1.36 Å. With 1.25 Å, the N4-O1 bond is significantly shorter than the N3-N4 bond (1.333(2) and 1.352(4) Å for **1** and **2** respectively). This difference is in contrast to what has been observed for $N_2O$ adducts of FLPs, for which the N–N bond [(1.25 ± 0.01) Å)] is shorter than the N–O bond [(1.33 ± 0.01) Å].[10] The degree of bending, in contrast, is similar for FLP/$N_2O$ adducts and for **1** and **2** (ca. 110°). The rather long bond between the two adjacent nitrogen atoms is reminiscent of what has been observed for imidazolylidene triazines, the coupling products of NHCs and azides. In these compounds, the length of the central N–N bond is typically on the order of 1.33–1.37 Å.[15] The plane defined by the bent $N_2O$ group is

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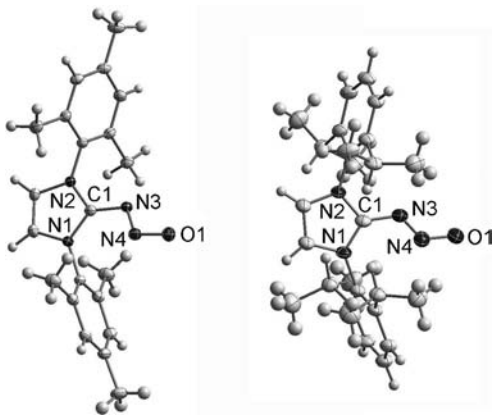


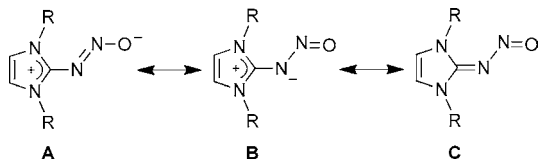

***Figure 1.*** Molecular structures of **1** (left) and **2** (right) in the crystal. Thermal ellipsoids shown at the 50% probability level.

***Table 1:*** Selected bond lengths and angles for **1** and **2**.

| | **1** (exptl.) | **2** (exptl.) | **1** (theor.) | **2** (theor.) |
|---|---|---|---|---|
| C1-N1 [Å] | 1.366(2) | 1.354(4) | 1.365 | 1.361 |
| C1-N2 [Å] | 1.360(2) | 1.368(4) | 1.361 | 1.357 |
| C1-N3 [Å] | 1.360(2) | 1.358(4) | 1.323 | 1.327 |
| N3-N4 [Å] | 1.333(2) | 1.352(4) | 1.352 | 1.346 |
| N4-O1 [Å] | 1.250(2) | 1.250(4) | 1.202 | 1.205 |
| C1-N3-N4 [°] | 109.6(1) | 110.7(3) | 110.9 | 110.5 |
| N3-N4-O1 [°] | 113.1(1) | 112.9(3) | 113.9 | 114.1 |
| N4-N3-C1-N1 [°] | 25.4(2) | 39.5(5) | 24.07 | 26.25 |

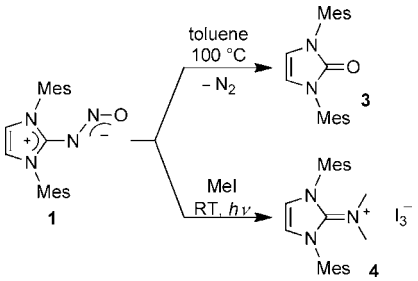
markedly inclined with respect to the plane defined by the heterocycle: the dihedral angle N1-C1-N3-N4 found for **1** is 25.4(2)° and that found for **2** is 39.5(5)°.

To gain further information about the electronic situation in NHC/$N_2O$ adducts, we performed density functional computations at the M06-2X/cc-pVTZ level of theory.[16–18] Computational geometric data generally agrees well with the experimental data, although shorter N4-O1 (by ca. 0.05 Å) and C1-N3 (by ca. 0.03 Å) bond lengths are predicted. Additionally, the differences in dihedral angles (N4-N3-C1-N1) between **1** and **2**, which measure the planarity of the $N_2O$ relative to the plane of the heterocycle, are not observed: both structures are predicted to be 24–27° out of plane. To assess the resonance picture depicted in Scheme 2, we computed Hirshfeld-I charges[19] at the M06-2X/6-31G(d) level of theory as implemented in an in-house version of QChem.[20,21] Both structures **1** and **2** reveal the N3 atom (−0.57, −0.55) to be more negative than the O1 atom (−0.32), which is indicative of a significant contribution from the resonance structure **B**.




***Scheme 2.*** Resonance structures of NHC/$N_2O$ adducts.

The reactivity of adduct **1** was examined in a series of experiments. Solutions of **1** are stable towards water and air. This was evidenced by dissolving **1** in a mixture of [$D_8$]THF and $H_2O$ (10:1) under air. No significant decomposition was observed by $^1$H NMR spectroscopy after three days. Crossover experiments were performed with THF solutions containing equal amounts of **1** and free carbene IPr, or **2** and free carbene IMes. After three days at room temperature, transfer of $N_2O$ was not observed by $^1$H NMR spectroscopy. These results imply a high stability of the adducts **1** and **2**. At elevated temperatures, **1** was found to decompose into the urea **3**: heating a toluene solution of **1** for 3 hours at 100 °C gave **3** in 60% yield (Scheme 3). In situ NMR experiments in $C_2D_2Cl_4$ at 130 °C revealed a clean and quantitative **1**→**3** transformation within 30 minutes. This type of reactivity is in line with what has been found for FLP/$N_2O$ adducts[10] and for nitrosylimines,[22] both of which decompose thermally with liberation of dinitrogen.




***Scheme 3.*** Reactivity of the $N_2O$ adduct **1**.

The reactivity of **1** towards electrophiles was examined using methyliodide. When **1** was added to a mixture of toluene and MeI (1:1) a solution formed which slowly turned red. The speed of the transformation could be accelerated by placing the reaction flask next to a mercury lamp.[23] After 5 hours, we were able to isolate the alkylation product **4** in 60% yield (Scheme 3). Compound **4** was examined spectroscopically as well as by single-crystal X-ray analysis (Figure 2).[14] The data reveal the formation of a salt composed of a guanidinium-type cation and a triiodide anion. The formation of this salt might proceed through an alkylation of the central N3 atom with subsequent liberation of nitrosyl iodine, which decomposes to give $I_2$.[24] A second

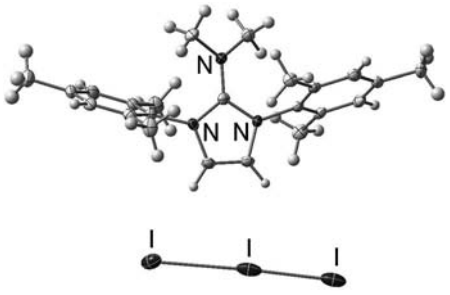



***Figure 2.*** Molecular structure of **4** in the crystal. Thermal ellipsoids shown at the 50% probability level.

methylation would give the cation along with the triiodide anion. However, a more detailed study is needed to corroborate this mechanistic hypothesis. The formation of **4** is significant because it demonstrates that NHC-activated $N_2O$ can undergo reactions which lead to a rupture of the N–N bond. One should note that this type of reactivity if very rare for $N_2O$.[25] The fact that we observe alkylation at N3 also confirms the importance of the resonance structure **B** in agreement with the results of the computational study.

In summary, we have demonstrated that N-heterocyclic carbenes are able to form stable adducts with $N_2O$ under ambient conditions. The adducts display a bent $N_2O$ group, which is bound to the heterocycle through the N atom. Alkylation of the $N_2O$ adduct **1** by MeI was shown to induce a rupture of the N–N bond, a rarely observed reactivity pattern in $N_2O$ chemistry. Current efforts in our laboratory aim to provide a more detailed understanding of the chemistry of imidazolium-2-diazotates. Additional results will be reported in due course.

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