

## Fixation of nitrous oxide by mesoionic and carbanionic N-heterocyclic carbenes

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A ditopic carbanionic N-heterocyclic carbene was found to react with the inert gas nitrous oxide, resulting in a stable covalent adduct with two intact N<sub>2</sub>O groups attached to the heterocycle. Mesoionic N-heterocyclic carbenes derived from C2-arylated 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene are also able to form adducts with one or two N<sub>2</sub>O groups. Crystallographic analyses of all adducts reveal bent N<sub>2</sub>O groups, which can adopt a *cis* or *trans* configuration.

N-Heterocyclic carbenes (NHCs, Fig. 1) are able to react with nitrous oxide under ambient conditions.<sup>1</sup> The products are covalent adducts, in which the N<sub>2</sub>O group is bound via the terminal nitrogen atom to the C2 atom of the carbene. The formation of stable N<sub>2</sub>O adducts is unusual, because most chemical reactions with N<sub>2</sub>O result in oxygen atom transfer and liberation of N<sub>2</sub>.<sup>2</sup> The connection of N<sub>2</sub>O to the carbene weakens the nitrogen-nitrogen bond, and N-N cleavage reactions can be induced by electrophiles (e.g. MeI or acetyl chloride)<sup>1b,d</sup> or by a low valent Ni(0) complex.<sup>3</sup> The addition of AlCl<sub>3</sub>, on the other hand, results in N-O bond cleavage.<sup>4,5</sup> We have exploited this reactivity to convert NHC-N<sub>2</sub>O adducts into azoimidazolium dyes.<sup>4</sup> These kind of dyes are of industrial importance, and they are used for numerous applications such as the dyeing of hair and synthetic fibers.<sup>6</sup> Another noteworthy feature of azoimidazolium dyes is the fact that they can be converted into stable neutral aminyl radicals.<sup>7</sup>

In continuation of our studies about the chemical activation of N<sub>2</sub>O, we have examined the reaction of nitrous oxide with mesoionic and ditopic carbanionic N-heterocyclic carbenes (m-NHCs and dc-NHCs, Fig. 1). The results of these investigation are described below.

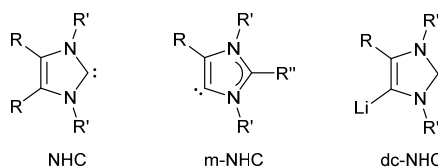


Fig. 1 General structure of N-heterocyclic carbenes (NHCs), mesoionic N-heterocyclic carbenes (m-NHCs), and ditopic carbanionic N-heterocyclic carbenes (dc-NHCs)

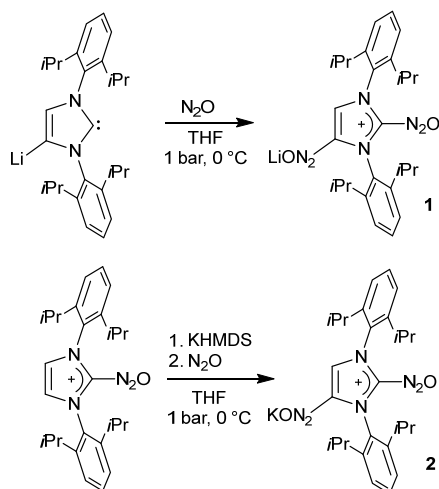
The chemistry of anionic NHCs has flourished over the last years, and numerous applications in transition metal catalysis and main group chemistry have been reported.<sup>8</sup> The C4 deprotonation of NHCs with *n*BuLi gives dc-NHCs,<sup>9</sup> which represent an interesting subclass of anionic NHCs.<sup>10</sup> An example of small molecule activation by dc-NHCs was reported by Ashfeld et al.<sup>11</sup> Reaction with CO<sub>2</sub> was shown to result in carboxylation at C4 position, but not at the C2 position. This behavior was unexpected, because normal NHCs rapidly react with CO<sub>2</sub> at the C2 position.<sup>12</sup> Apparently, the carboxylate group in 4 position reduces the reactivity of the C2 carbene atom substantially.

We have investigated the reaction of a dc-NHC derived from 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with N<sub>2</sub>O. The ditopic carbene was obtained by reaction with *n*BuLi in hexane as described by Robinson et al.<sup>9</sup> The lithium salt was isolated and dissolved in THF. Addition of nitrous oxide (1 bar) resulted in the formation of the bis-N<sub>2</sub>O adduct **1** (Scheme 1). Even though it was possible to crystallize compound **1** (see below), its isolation was challenging because **1** has a tendency to form a sticky oil. In order to prepare the bis-N<sub>2</sub>O adduct on a preparative scale, it is advantageous to start with the known N<sub>2</sub>O adduct of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. Deprotonation with potassium hexamethyldisilazide (KHMDs) followed by addition of N<sub>2</sub>O gave the potassium salt **2**, which could be isolated in the form of a yellow powder in 71% yield (Scheme 1).

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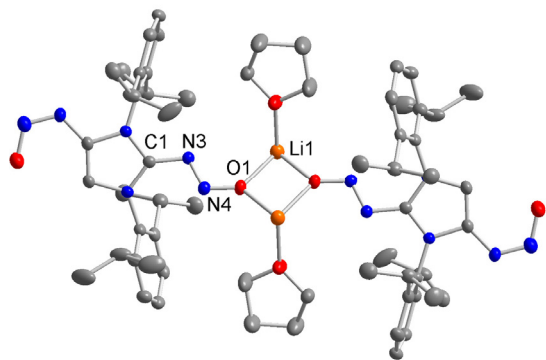
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**Scheme 1** Syntheses of the bis- $\text{N}_2\text{O}$  adducts **1** and **2**.

The molecular structure of **1** in the crystal was analyzed by X-ray crystallography. Compound **1** features two  $\text{N}_2\text{O}$  groups, which are connected to the C2 and the C4 atoms of the heterocycle (Fig. 2). The  $\text{N}_2\text{O}$  group at C2 adopt a *trans* configuration, whereas the  $\text{N}_2\text{O}$  group at C4 position adopts a *cis* configuration. For the latter, we observe some disorder, with 17% of  $\text{N}_2\text{O}$  being bound to C5 instead of C4 (likewise in *cis* configuration). Due to this disorder, we do not discuss the bond lengths found for this subunit. The *trans*  $\text{N}_2\text{O}$  group shows an N-N bond length of 1.3041(17) Å, and an N-O bond length of 1.2701(16) Å. These values are comparable to what was observed for neutral mono  $\text{N}_2\text{O}$  adducts of NHCs.<sup>1</sup> The oxygen atoms of both  $\text{N}_2\text{O}$  group are coordinated to lithium ions, resulting in the formation of a 2-dimensional coordination polymer. The lithium ions are tetra-coordinated, with the fourth coordination site being occupied by a THF molecule.



**Fig. 2** Part of the polymeric structure of the bis- $\text{N}_2\text{O}$  adduct **1** in the crystal. Hydrogen atoms are not shown for clarity. The thermal ellipsoids are at 50% probability level. Selected bond lengths (Å): O1-N4 = 1.2701(16), N3-N4 = 1.3041(17), N3-C1 = 1.3717(19), O1-Li1 = 1.966(3).

The NMR spectra of solutions of **1** or **2** in  $\text{CD}_3\text{CN}$  shows two sets of signals, suggesting the presence of isomers. Most likely, the

$\text{N}_2\text{O}$  group attached to C4 can adopt a *cis* and a *trans* configuration. For the  $\text{N}_2\text{O}$  group attached to C2, the formation of a *cis* form seems also possible,<sup>1c</sup> but overall, the published structural data indicate a strong preference for a *trans* configuration when the  $\text{N}_2\text{O}$  group is bound to C2.<sup>1</sup>

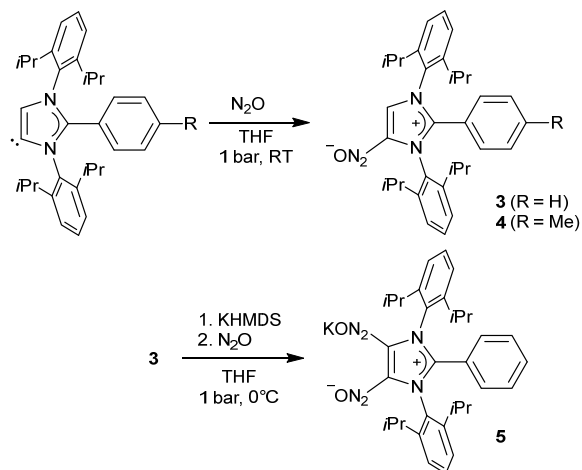
The thermal stability of **1** was investigated by heating a solution of **1** in  $\text{CD}_3\text{CN}$  to 70 °C. Time dependent NMR spectra showed no detectable decomposition over a period of 70 h. It is worth noting that two sets of NMR signals are still detected at 70 °C, indication that *cis-trans* isomerization of the diazotate group is slow on the NMR time scale.

The successful  $\text{N}_2\text{O}$  addition to the C4 position of the ditopic carbene prompted us to investigate the reaction of  $\text{N}_2\text{O}$  with mesoionic carbenes ('abnormal carbenes').<sup>13</sup> It should be noted that attempts to bind  $\text{N}_2\text{O}$  to m-NHCs have been reported before. Thakur et al. have studied the reaction of  $\text{N}_2\text{O}$  with a mesoionic carbene having phenyl groups in position C2 and C4, but they failed to isolate an m-NHC- $\text{N}_2\text{O}$  adduct. Successful  $\text{N}_2\text{O}$  fixation was only possible upon addition of  $\text{B}(\text{C}_6\text{F}_5)_3$ , resulting in the formation of the ternary adduct m-NHC- $\text{N}_2\text{O}$ - $\text{B}(\text{C}_6\text{F}_5)_3$  with a bridging  $\text{N}_2\text{O}$  group.<sup>14</sup>

We have examined the reaction of  $\text{N}_2\text{O}$  with mesoionic N-heterocyclic carbenes derived from C2-arylated 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.<sup>15</sup> In contrast to what was reported by Thakur et al., we were able to isolate the  $\text{N}_2\text{O}$  adducts **2** and **3** without difficulty in high yield (Scheme 2).

As it was observed for **1** and **2**, two sets of NMR signals were observed for solutions of **3** or **4** in  $\text{CD}_3\text{CN}$ , suggesting that the  $\text{N}_2\text{O}$  group can adopt a *cis* and a *trans* configuration. The thermal stability of **3** and **4** in  $\text{CD}_3\text{CN}$  was again very good, with no detectable decomposition upon heating for 75 h at 70 °C.

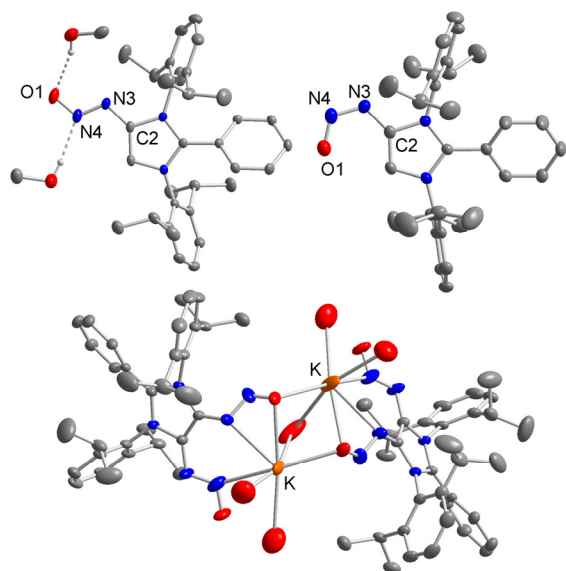
Starting with zwitterionic **3**, we were able to install a second  $\text{N}_2\text{O}$  group by reaction with KHMDS, followed by addition of  $\text{N}_2\text{O}$  (Scheme 2). The potassium salt **5** was isolated in the form of an orange powder in 84% yield. The higher polarity of **5** allows dissolving the compound not only in organic solvents such as acetonitrile, but also in water. Despite the presence of two  $\text{N}_2\text{O}$  groups, the thermal stability of **5** ( $\text{CD}_3\text{OD}$  at 50 °C) was again good.



Scheme 2 Syntheses of the N<sub>2</sub>O adducts 3–5.

The N<sub>2</sub>O adducts **3**–**5** were all analyzed by single crystal X-ray diffraction. For compound **3**, we were able to crystallize two distinct forms. Compound **3a** was obtained from methanol and features a *trans* N<sub>2</sub>O group which is bound via hydrogen bonds to two co-crystallized methanol molecules (Fig. 3, top left). Compound **3b** was obtained from dichloromethane and shows a *cis* N<sub>2</sub>O group (Fig. 3, top right). For compound **4**, we observed a disordered N<sub>2</sub>O group (for graphic see ESI). The disorder can be resolved by assuming the presence of *cis-trans* isomers within the same crystal.

For the three mono-N<sub>2</sub>O adducts **3a**, **3b** and **4**, the N<sub>2</sub>O groups are nearly co-planar with the imidazolium heterocycle. The bond lengths observed for the N<sub>2</sub>O groups are very similar for the *trans* form **3a** and the *cis* form **3b**. As it was observed for **1** and for N<sub>2</sub>O adducts normal NHCs, the N–N bond is longer than the N–O bond.

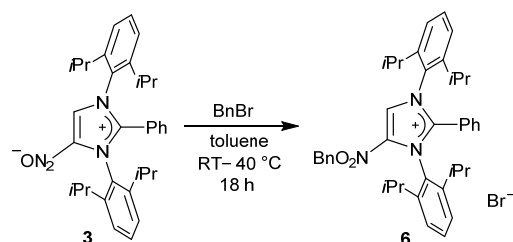


**Fig. 3** Molecular structures of the N<sub>2</sub>O adducts **3a** (top left), **3b** (top right) and **5** (bottom) in the crystal. Most hydrogen atoms and the carbon atoms of the THF ligands of **5** are not shown for clarity. The thermal ellipsoids are at 50% probability level. Selected bond lengths (Å): **3a**: O1–N4 = 1.2580(19), N3–N4 = 1.300(2), N3–C2 = 1.3797(17); **3b**: O1–N4 = 1.252(3), N3–N4 = 1.303(3), N3–C2 = 1.384(3).

The bis-N<sub>2</sub>O adduct **5** forms a solvated dimer in the solid state. The central part, which consists of N<sub>2</sub>O groups bound to two potassium ions, is highly disordered. Therefore, we refrain from a discussion of bond lengths and angles. The disorder can be resolved by assuming two conformations, and the dominant form in the crystal (occupancy: 74%) is shown in Figure 3. The anionic bis-N<sub>2</sub>O adduct is bound via two nitrogen atoms and one oxygen atom to the potassium ion. One N<sub>2</sub>O group thus acts as a chelate, and the other N<sub>2</sub>O group is bound in a monodentate fashion via the central nitrogen atom. The oxygen atom of the chelating N<sub>2</sub>O group also coordinates to the second K<sup>+</sup> ion, resulting in the formation of a central K(μ-O)<sub>2</sub>K unit. Each K<sup>+</sup> ion is further coordinated to one water molecule and two THF

molecules (carbon atoms not shown), one of which is bound to both potassium ions.

As outlined above, N<sub>2</sub>O adducts of ‘normal’ NHCs show a diverse and interesting chemistry in reactions with organic and inorganic reagents.<sup>3–5</sup> At present, we have just started to investigate the reactivity of the new N<sub>2</sub>O adducts **1**–**5**. However, we have already made an interesting observation: alkylation of **3** with benzyl bromide resulted in the formation of the O-alkylation product **6** (Scheme 3; for a detailed characterization including a crystallographic analysis see ESI). In contrast, attempts to alkylate N<sub>2</sub>O adducts of ‘normal’ NHCs had resulted in cleavage of the N–N bond.<sup>1d</sup> This first result indicates that we can expect a different reactivity for these new N<sub>2</sub>O adducts.



**Scheme 3** Alkylation of the N<sub>2</sub>O adduct **3**.

To conclude: we have shown that a carbanionic NHC is able to form a stable covalent adduct with two equivalents of N<sub>2</sub>O. This behavior is in contrast to what has been observed for CO<sub>2</sub>, where the reaction stops at the mono adduct stage.<sup>11</sup> Starting from mesoionic carbenes, we have been able to attach one or two intact N<sub>2</sub>O groups. All adducts show a good thermal stability in solution. Therefore, we are optimistic that we can use these compounds as starting materials for subsequent chemical transformation. The successful isolation of the alkylation product **6** is evidence that the reactivity of these new imidazolium diazotates may differ from the previously described N<sub>2</sub>O adducts of ‘normal’ NHCs.

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**Graphic for the TOC:**

Double fixation of laughing gas ( $\text{N}_2\text{O}$ ) can be achieved under mild conditions using mesoionic or ditopic carbanionic carbenes.

