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Adducts of Nitrous Oxide and N-Heterocyclic Carbenes: Syntheses, Structures, and Reactivity

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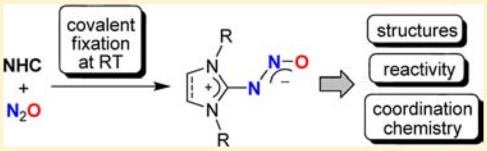
Supporting Information



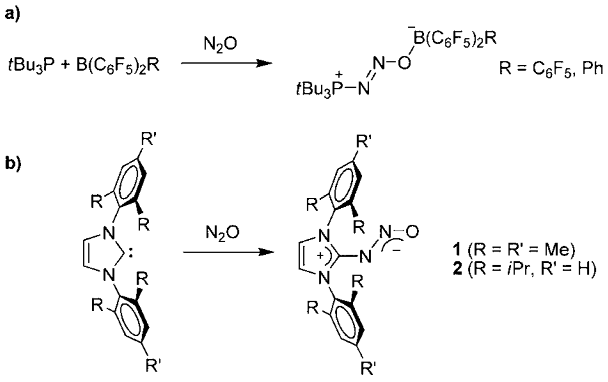
ABSTRACT: N-Heterocyclic carbenes (NHCs) react at ambient conditions with nitrous oxide to give covalent adducts. In the crystal, all compounds show a bent N_2O group connected via the N-atom to the former carbene carbon atom. Most adducts are stable at room temperature, but heating induces decomposition into the corresponding ureas. Kinetic experiments show that the thermal stability of the NHC–N_2O adducts depends on steric as well as electronic effects. The coordination of N_2O to NHCs weakens the N–N bond substantially, and facile N–N bond rupture was observed in reactions with acid or acetyl chloride. On the other hand, reaction with tritylium tetrafluoroborate resulted in a covalent modification of the terminal O-atom, and cleavage of the C–N_2O bond was observed in a reaction with thionyl chloride. The coordination chemistry of IMes–N_2O (IMes = 1,3-dimesitylimidazol-2-ylidene) was explored in reactions with the complexes CuOTf, $Fe(OTf)_2$, $PhSnCl_3$, $CuCl_2$, and $Zn(C_6F_5)_2$. Structural analyses show that IMes–N_2O is able to act as a N-donor, as an O-donor, or as a chelating N,O-donor. The different coordination modes go along with pronounced electronic changes as evidenced by a bond length analysis.

■ INTRODUCTION

Nitrous oxide is a very inert gas, and its chemical activation under ambient conditions is a challenging task.[1] Transition-metal complexes have been used with good success for this purpose.[2] With few exceptions,[3−5] these reactions proceed via oxygen atom transfer to the metal complex and release of dinitrogen. In principle, the oxygen atom can be further transferred to organic substrates, resulting in a metal-catalyzed oxidation process. However, turnover is difficult to achieve, and only a few catalytic processes have been reported so far.[6] Highly oxophilic compounds such as low-valent silicon compounds,[7] BEt_3,[8] and PCy_3[9] are also known to react with N_2O under mild conditions, with oxygen atom transfer being the exclusive reaction mode. The utilization of N_2O as a nitrogen atom transfer agent has been realized in a few cases. Reactions of lithium–organic[10] and calcium–organic[11] compounds with N_2O can give azines, hydrazones, or diazo compounds, but the yields of these transformations are typically poor. Of industrial importance is the reaction of sodium amide with N_2O, which gives NaN_3.[12] Deprotonated amines and hydrazines can also react with N_2O in nitrogen atom transfer reactions.[13] The incorporation of all three atoms of N_2O was achieved in reactions with strained alkynes.[14]

In 2009, the group of Stephan reported the fixation of N_2O by frustrated Lewis pairs (FLPs) (Scheme 1a).[15,16] This type of reaction is remarkable as it leaves the N–N–O unit intact.[4] We have recently reported another example of covalent fixation of intact N_2O.[17] The N-heterocyclic carbenes 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IDipp) were shown to react with N_2O to give the stable adducts **1** and **2** (Scheme 1b). Preliminary studies indicate that the carbene-based adducts are quite distinct from N_2O adducts of FLPs, in terms of both structure and reactivity.[17,18] Detailed investigations about the chemistry of N-heterocyclic carbene (NHC)–N_2O adducts are reported below.

Scheme 1. Fixation of N_2O by FLPs (a) or NHCs (b)



■ RESULTS AND DISCUSSION

Having established that NHCs with bulky aromatic mesityl (Mes) or 2,6-diisopropylphenyl (Dipp) groups are able to fix N_2O,[17] we were interested in whether other N-substituents would be tolerated as well. To facilitate the synthetic access, we decided to generate the carbenes in situ by reaction of the corresponding imidazolium salts with potassium bis(trimethylsilyl)amide (KHMDS) in THF. After filtration of the resulting potassium salt, the solution of the carbenes was

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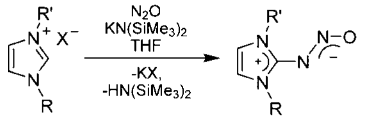
stirred at room temperature under an atmosphere of N_2O. After 24 h, the volume of the solution was reduced, which resulted in precipitation of the N_2O adducts **1**−**7** (isolated yields 40−56%). This simple in situ methodology worked not only for the known compounds **1** and **2**, but also for adducts with aliphatic substituents at the N-atoms, including small methyl and large isopropyl groups (Scheme 2).

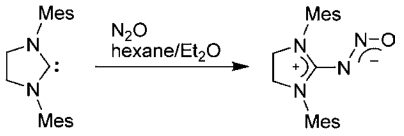
Scheme 2. Synthesis of NHC−N_2O Adducts from Imidazolium Salts



	R	R'
1	Mes	Mes
2	Dipp	Dipp
3	Cy	Cy
4	Xyl	Xyl
5	Me	Me
6	*i*Pr	*i*Pr
7	Me	Et

The synthesis of a N_2O adduct of a saturated carbene proved to be more challenging. Reaction of 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene (SIMes) with N_2O in THF resulted in adduct formation, but the product decomposed into the corresponding urea (see below), making isolation of a pure compound difficult. Key to success was the utilization of a hexane/Et_2O mixture (1:2) instead of THF as the solvent. Under these conditions, the N_2O adduct **8** precipitated directly from the reaction mixture, which allowed its isolation in 62% yield (Scheme 3).

Scheme 3. Synthesis of the N_2O Adduct 8



8

The new compounds **3**−**8** were comprehensively characterized by elemental analysis (C, H, N), high-resolution ESI$^+$ mass spectrometry, UV/vis and NMR spectroscopy, and single-crystal X-ray diffraction. All compounds are soluble in dichloromethane and chloroform. Interestingly, the alkyl-substituted adducts **5**−**7** are also soluble in water. A noteworthy feature of the NHC−N_2O adducts is their color. Solutions appear yellow, and the UV/vis spectra show absorption bands at ~300 and 450 nm. NMR spectroscopic analyses (CD_2Cl_2 or $CDCl_3$) of the adducts **3**−**6** and **8** revealed an apparent C_{2v} symmetry. Attempts to "freeze out" rotational isomers were not successful. The low-temperature NMR spectrum of **1** in CD_2Cl_2 at −80 °C was very similar to that recorded at room temperature. Similar results were observed for the asymmetrically substituted (Me/Et) adduct **7**. It should be noted that rotational isomers have been detected by NMR spectroscopy for thiazole- and 1,3,4-thiadiazole-2-nitrosamines.[19] These compounds also feature a terminal N_2O group. In addition to the standard ^1H and ^{13}C NMR measurements, we have recorded ^{15}N NMR spectra of the adducts **1** and **6** in $CDCl_3$. The signals of the N_2O group appear at 336.9 and 617.6 ppm for **1** and at 341.8 and 604.6 ppm for **6**. These values are shifted to lower field compared to what is observed for free N_2O (135 and 218 ppm),[20] but they are close to those reported for FLP−N_2O adducts (~380 and 575 ppm).[16c]

The solid-state structures of **3**−**8** were determined by X-ray diffraction. In addition, we have analyzed a new structure of **1** containing a cocrystallized water molecule. Graphic representations of the structures are depicted in Figure 1, and selected bond lengths and angles are given in Table 1. For comparison, we have also listed the values for the structures of **1** and **2**, which we had reported earlier.[17] All adducts show a bent N−N−O group (α = 110.19(17)−118.7(4)°) which is connected via the terminal N-atom to the carbon atom of the heterocycle. The C−N−N−O unit is in all cases nearly flat, with dihedral angles between 172.65(7)° and 180.0(3)°. While the lengths observed for the N−O and C−N(N) bonds are very similar for the eight compounds, the N−N bond lengths vary between 1.270(5) and 1.33(2) Å. Despite these variations, the N−O bonds are always shorter than the N−N bonds. This trend is in contrast to what has been reported for N_2O adducts of FLPs, which feature shorter N−N bonds than N−O bonds.[15,16]

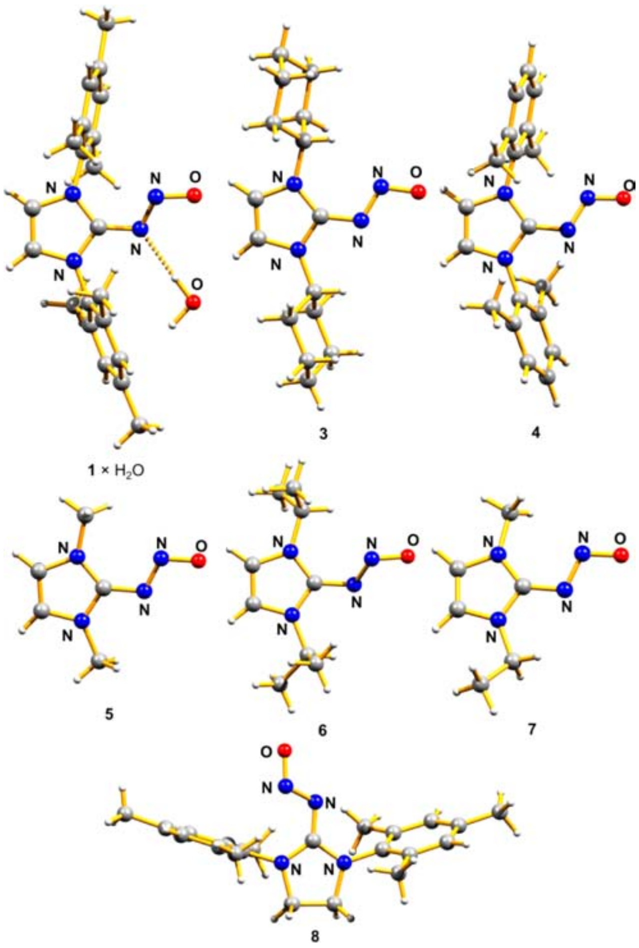


Figure 1. Ball-and-stick representations of the molecular structures of the NHC−N_2O adducts **1**·H_2O and **3**−**8** in the crystal.

Large structural differences are found for the dihedral N−C−N−N angles, which correspond to the angle between the planes defined by the bent N_2O group and the heterocycle. At first glance, there seems to be a correlation between the size of the *N*-R groups and the bending of the N_2O group, with smaller groups resulting in reduced bending. For the *N*,*N*′-dimethyl-substituted adduct **5**, for example, the two planes are nearly coplanar (N−C−N−N = 8.06°), whereas a large inclination of 46.56° is found for adduct **6** with isopropyl groups attached to

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1·H_2O and 3−8

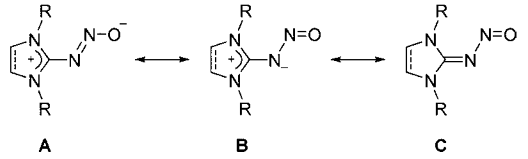
	N−N	N−O	C−N(N)	C−N−N−O	N−C−N−N[b]
1[a]	1.333(2)	1.250(2)	1.360(2)	175.36(13)	25.4(2)
1·H_2O	1.328(3)	1.245(3)	1.362(4)	176.0(2)	31.9(4)
2[a]	1.352(4)	1.250(4)	1.358(4)	178.4(3)	39.5(5)
3[c]	1.293(3)	1.273(3)	1.376(4)	178.8(2)	10.2(5)
	1.312(4)	1.265(3)	1.375(4)	180.0(3)	29.8(5)
4	1.270(5)	1.240(5)	1.355(6)	178.0(4)	16.4(8)
5	1.3039(15)	1.2609(14)	1.3743(16)	179.86(9)	8.07(18)
6	1.3223(11)	1.2644(11)	1.3783(12)	172.65(7)	46.52(13)
7	1.3124(17)	1.2693(15)	1.3771(18)	179.72(11)	14.3(2)
8	1.343(2)	1.247(2)	1.354(2)	174.78(16)	22.0(3)

[a] Data taken from ref 17. [b] The two terminal N-atoms of the N−C−N−N unit are *cis* to each other. [c] Two independent molecules are found in the crystal.

the N-atoms. However, a more detailed inspection shows that there are also large differences of the dihedral angle for compounds with sterically very similar *N*-R groups (**1** and **3**, or **4** and **6**). We therefore conclude that the energy potential for a rotation around the C−N(N) bond is rather flat and packing effects are likely to contribute to the observed differences in dihedral angles. The suggestion that rotation around the C−N(N) bond is facile is in line with the NMR spectra, which show one set of signals for the two *N*-R groups. For compound **1**·H_2O with a cocrystallized water molecule, one can observe a hydrogen bond between the water and the N_2O group. Interestingly, the bond is formed between the OH group and the N(C)-atom (N···H = 1.940(19) Å) and not between the OH group and the terminal O-atom. This observation is evidence for the basicity of the N(C)-atom. The presence of the hydrogen bond has only a minor influence on the bond lengths of the N_2O group.

In principle, the structures of NHC−N_2O adducts can be described by three mesomeric forms: the diazotate **A**, the nitrosamide **B**, and the nitrosoimine **C** (Scheme 4). Structurally characterized diazotates are scarce, but data for the thallium salt *trans*-Tl(ONNMe) have been reported.[21] In the crystal, the salt shows a long N−O bond (1.35(4) Å) and a short N−N bond (1.24(5) Å), similar to what has been reported for N_2O adducts of FLPs.[15,16] The opposite trend is observed for the NHC−N_2O adducts. This comparison indicates a smaller contribution of the mesomeric form **A**. The relevance of form **B**, with a negatively charged N(C)-atom, is underlined by the presence of a N···HO hydrogen bond in **1**·H_2O, by the facile rotation around the N−C bond, and by a computational study that we had performed earlier on compound **1**.[17]

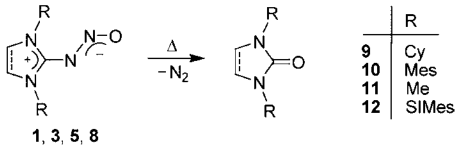
Scheme 4. Mesomeric Structures of NHC−N_2O Adducts



The mesomeric forms **A** and **B** are both zwitterions, reminiscent of what is found for NHC adducts of heteroallenes such as CO_2 and CS_2.[22] Mesomeric form **C** represents an *N*-nitrosoimine. *N*-Nitrosoimines have been known for more than 100 years.[23] They can be obtained by nitrosation of imines.[24] Generally, *N*-nitrosoimines decompose rapidly to give dinitrogen and the corresponding carbonyl compound.[25] The *N*-nitrosoimine derived from benzophenone, for example, has a half-life of around 3 min at room temperature in methanol.[24] More stable *N*-nitrosoimines can be obtained by nitrosation of heterocyclic imines, but liberation of dinitrogen is still observed.[22−24] Upon irradiation, however, some *N*-nitrosoimines were found to release NO.[26] As potential NO donors, *N*-nitrosoimines have been examined for their antithrombotic, antiplatelet, and vasodilating activities.[23,27] To the best of our knowledge, crystallographic analyses of *N*-nitrosoimines have not been reported so far.

To determine the thermal stability of the NHC−N_2O adducts, we have monitored the decomposition in THF-d_8 at 60 °C by ^1H NMR spectroscopy. For this study, adducts with an aromatic mesityl substituent (**1**), as well as with a large (**3**) and small alkyl substituent (**5**), were chosen. Furthermore, we have examined adduct **8** with a saturated backbone. In all cases the solution became colorless, and we observed the clean decomposition into the corresponding ureas (Scheme 5).

Scheme 5. Thermolysis of NHC−N_2O Adducts

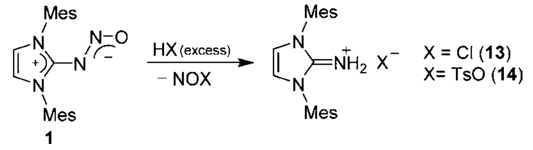


The decomposition reactions followed first-order kinetics (see the Supporting Information, Figures S1−S4) and did not depend on the concentration. These observations are in line with what has been observed for other *N*-nitrosoimines,[25] and they suggest that the reactions proceed in an intramolecular fashion. The highest stability was observed for adduct **5** with $t_{1/2}$ = 15.1 h, whereas **8** was the least stable one ($t_{1/2}$ = 0.4 h). Compounds **1** and **3** decomposed with $t_{1/2}$ of 2.3 and 5.6 h, respectively. The enhanced stability of **1**, **3**, and **5** over that of **8** can be explained by the presence of the C=C bond in the heterocyclic ring, leading to additional resonance stabilization and a decreased electrophilicity of the C(NNO)-atom. The higher stability of the adducts **3** and **5** with aliphatic *N*-Cy and *N*-Me groups over that of adduct **1** with aromatic *N*-Mes groups is likely due to electronic effects as well.

As mentioned above, compound **5** is soluble in water. Surprisingly, heating a solution of **5** in D_2O at 100 °C for 60 h did not lead to a detectable decomposition. Similarly, a solution of compound **5** in CD_3OD could be tempered at 60 °C for 60 h without significant degradation. A plausible explanation for the remarkable stability in water and methanol is a selective stabilization of the ground state by hydrogen bonds. This hypothesis is supported by the fact that compound **5** displays solvatochromism (Figure S23, Supporting Information). Interestingly, a completely different behavior was observed for the *N*-nitrosoimine derived from benzophenone, with decomposition being faster in methanol than in THF.[24]

The good stability of the NHC−N_2O adducts at ambient temperature provided the opportunity to study the chemical reactivity of this class of compounds in more detail. Compound **1** was used as a representative example for these investigations. First, we examined the reactivity of **1** toward acids. Addition of an excess of aqueous HCl or HOTs to a solution of **1** in dichloromethane or THF led to the immediate formation of a colorless solution, from which the guanidinium salt **13** or **14** could be isolated in 45% and 47% yield, respectively (Scheme 6). 2-Fold deprotonation of the guanidinium salt **13** or **14** would give imidazolin-2-iminato ligands. The latter have emerged as versatile 2σ,4π-electron donors for early transition metals.[28] The reaction of NHC−N_2O adducts with acids could therefore be used as a new pathway for the synthesis of these important ligands.

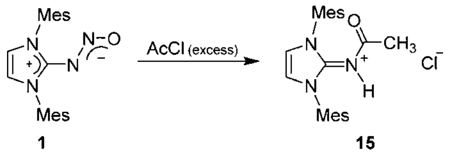
Scheme 6. Reactions of 1 with Acids



A plausible mechanism for the reaction of **1** with acids is a protonation of the N(C)-atom, followed by heterolytic cleavage of the N−N bond to give NO^+ and a 2-iminoimidazoline. The latter is immediately protonated to give **13** and **14**. The released NO^+ can undergo subsequent reactions with the solvent THF.[29] The formation of NO^+ is supported by the following experiment: addition of aqueous HCl to a solution of **1** in MeOH in the presence of a mixture of sulfanilic acid and 1-naphthylamine[30] gave a red-pink color due to the formation of an azo dye.

Reaction of a solution of **1** in THF with an excess of acetyl chloride (3 equiv) also resulted in N−N bond rupture to give the acetylguanidinium salt **15** in 84% isolated yield (Scheme 7).

Scheme 7. Reaction of 1 with Acetyl Chloride



The source of the NH proton in **15** is presently not clear. It could be derived from the solvent or from impurities in the reagent (AcOH, H_2O). NO^+ is again a likely side product in this reaction.

Single-crystal X-ray analyses confirmed the proposed structures of **14** and **15** (Figure 2). The C−N bond, which connects the N_2O group to the heterocycle, is longer in **15** (1.369(5) Å) than in **14** (1.344(4) Å). This difference can be attributed to conjugation to the C═O bond of the acetyl group. The C−N bond in **14** is slightly longer compared to what has been observed for neutral 2-iminoimidazolines (1.294(3)−1.298(1) Å).[31]

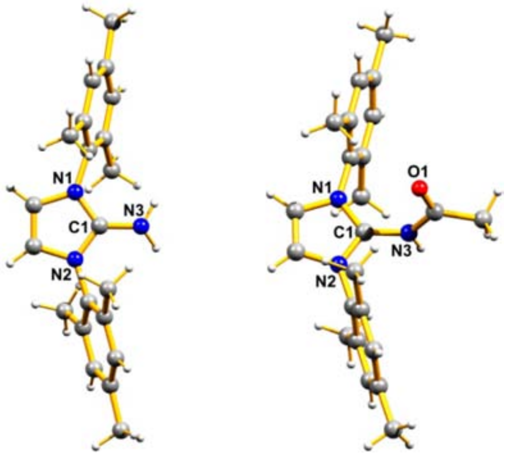
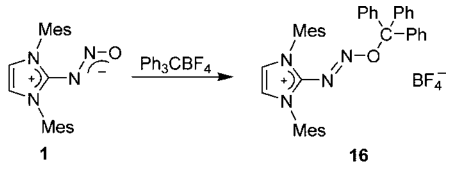


Figure 2. Ball-and-stick representations of the molecular structures of **14** (left) and **15** (right) in the crystal. Anions are omitted.

The reactions with acids (Scheme 6) and with acetyl chloride (Scheme 7) both result in cleavage of the N−N bond. These results corroborate our previous findings[17,18] that coordination to NHCs alters the chemical reactivity of the N_2O group substantially: instead of the commonly observed oxygen atom transfer, rupture of the N−N bond is now a viable alternative. It should be noted that N−N bond cleavage of N_2O has also been observed in reactions with metal complexes, but only a very few examples have been described so far.[3]

In contrast to small electrophiles, reaction of **1** with tritylium tetrafluoroborate in CH_2Cl_2 did not lead to N−N bond rupture. Instead, the immediate formation of adduct **16** was observed (Scheme 8).

Scheme 8. Reaction of 1 with Ph_3CBF_4



In the product, the Ph_3C group is bound to the oxygen atom of the N_2O group as evidenced by a crystallographic analysis (Figure 3). The C(1)−N(3) (1.392(2) Å) and N(4)−O(1) (1.3651(17) Å) bonds in **16** are longer than in **1**, while the N(3)−N(4) bond is shorter (1.2572(19) Å). The differences indicate a larger contribution of the resonance form **A** in **16** when compared to **1**. The dihedral angle N(4)−N(3)−C(1)−N(2) (24.9(3)°) in **16** is almost the same as in **1** (25.4(2)°). The angle N(3)−N(4)−O(1) (107.32(13)°), on the other hand, is slightly smaller than in **1** (113.1(1)°). The close relation of **16** to N_2O adducts of FLPs described by Stephan et al.[15,16] is noteworthy. In **16**, the N_2O group is sandwiched between a Lewis-basic NHC and a Lewis-acidic tritylium group, whereas phosphines and boranes have been used by Stephan. Not surprisingly, the bond lengths and angles observed for **16** are comparable to what has been reported for FLP−N_2O adducts.[15,16]

Furthermore, we examined the reactivity of **1** toward the chlorinating agent thionyl chloride. Treatment of a THF

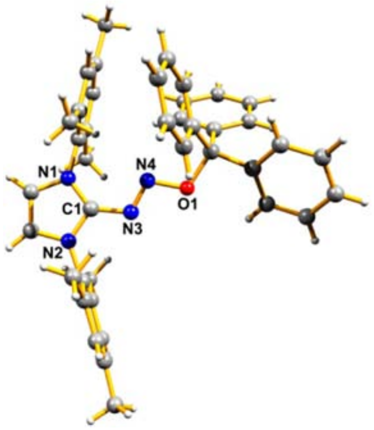
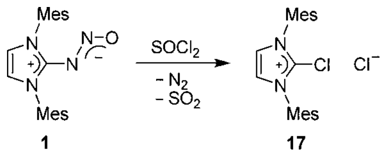


Figure 3. Ball-and-stick representations of the molecular structure of **16** in the crystal. The BF_4^- anion is omitted.

solution of **1** with an excess of $SOCl_2$ at ambient temperature resulted in intensive bubbling and formation of a yellow solution, from which **17** was isolated in 76% yield (Scheme 9).

Scheme 9. Reaction of 1 with $SOCl_2$

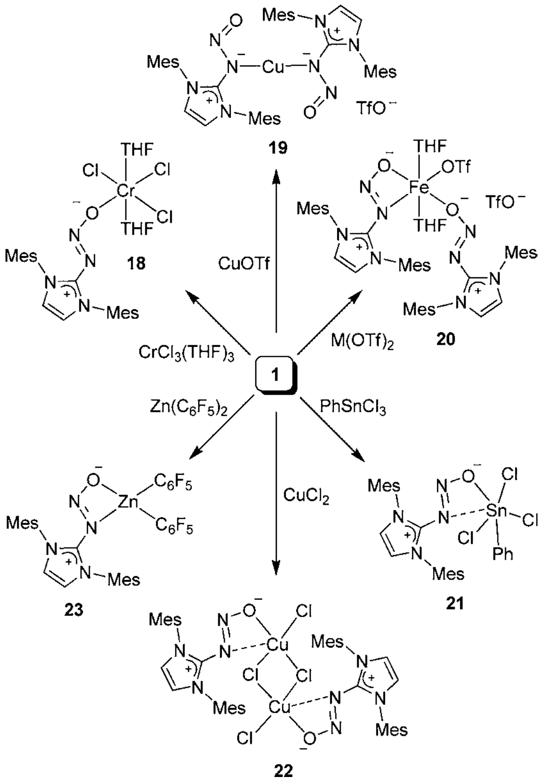


The reaction likely proceeds via liberation of N_2 and SO_2; the latter was detected experimentally by a qualitative test with $Na_2Cr_2O_7$. Chloroimidazolium chlorides such as **17** are known.[32] They are generally prepared by reaction of mild chlorinating agents such as CCl_4 and C_2Cl_6 with NHCs.

The formation of **17** by chlorination with $SOCl_2$ is remarkable because it requires the cleavage of a strong C–N bond. As a potential mechanism for this reaction, one can propose the coordination of $SOCl^+$ to the terminal oxygen atom of the N_2O group, followed by an intramolecular rearrangement to give **17** along with N_2 and SO_2.

Finally, we were interested to explore the reactivity of **1** toward Lewis-acidic transition-metal complexes. For reactions with the complexes CuOTf, $Fe(OTf)_2$, $PhSnCl_3$, $CuCl_2$, and $Zn(C_6F_5)_2$ we were able to isolate defined adducts (**18**–**23**, Scheme 10). The complexes were isolated in good yields (46–94%), with the exception of the Fe(II) complex **20**, for which only a few crystals were obtained. The structures of all adducts were determined by single-crystal X-ray analysis (Figure 4). The structural analyses revealed that **1** displays remarkably versatile coordination chemistry. In the solid state, one can observe η^1-coordination via the N(C)-atom (**19**) or via the terminal O-atom (**18**, **20**). Furthermore, ligand **1** is able to act as a chelating ligand with η^2-coordination via the N(C)-atom and the O-atom (**20**–**23**). For the Sn(IV) complex **21** and the Cu(II) complex **22**, the N,O-chelate features a short M–O bond and a long N–M bond, whereas a more equilibrated situation is found for the chelate in the Fe(II) complex **20** and the Zn(II) complex **23** (Table 2). The different coordination modes have a strong influence on the bond lengths in the N_2O group of ligand **1**. The nearly planar *trans* configuration of the C–N–N–O unit, on the other hand, is conserved for all complexes. For the O-bound IMes–N_2O ligands in **18** and **20**, the C–N and N–O bonds are significantly longer than in free **1**, while the N–N bonds are shorter (Table 2). These data indicate an increased electron density on the O-atom and a significant contribution of the resonance form **A**. The bond lengths in **18** and **20** are close to those found for FLP–N_2O adducts which contain PNNO–M linkages.[16] The bond lengths in the N_2O group of chelates **20**–**23** are close to each other. The C–N and N–O bonds in the chelates are shorter than those found for monodentately coordinated **1**, but longer than in free **1**. The N–N bonds are shorter than in free **1**, but longer compared to those in η^1-coordinated **1**, indicating that the contribution of the resonance form **A** is more pronounced for η^1-coordination than for η^2-coordination. A unique coordination mode of the IMes–N_2O ligand is observed for complex **19**. Here, we observe exclusive coordination via the N(C)-atom. As expected, the bond lengths in the N_2O unit of **19** indicate a large contribution of the resonance form **B** (Table 2).

Scheme 10. Reaction of 1 with Different Transition-Metal Complexes



CONCLUSIONS

Covalent capture of the inert gas N_2O can be achieved at ambient conditions using NHCs. The latter can conveniently be prepared in situ by deprotonation of imidazolium salts. The adducts contain intact N_2O groups, which are bound via the terminal N-atom to the heterocycle. They can thus be described as imidazolium diazoates or as *N*-nitrosoimines. Compared to other *N*-nitrosoimines reported previously, the NHC–N_2O adducts are remarkably stable. When dissolved in THF, only slow thermal decomposition into ureas was observed at elevated temperatures. Further stabilization was achieved by using protic solvents. The good thermal stability of these *N*-nitrosoimines allowed for the first time a detailed structural characterization of this class of compounds. A distinctive

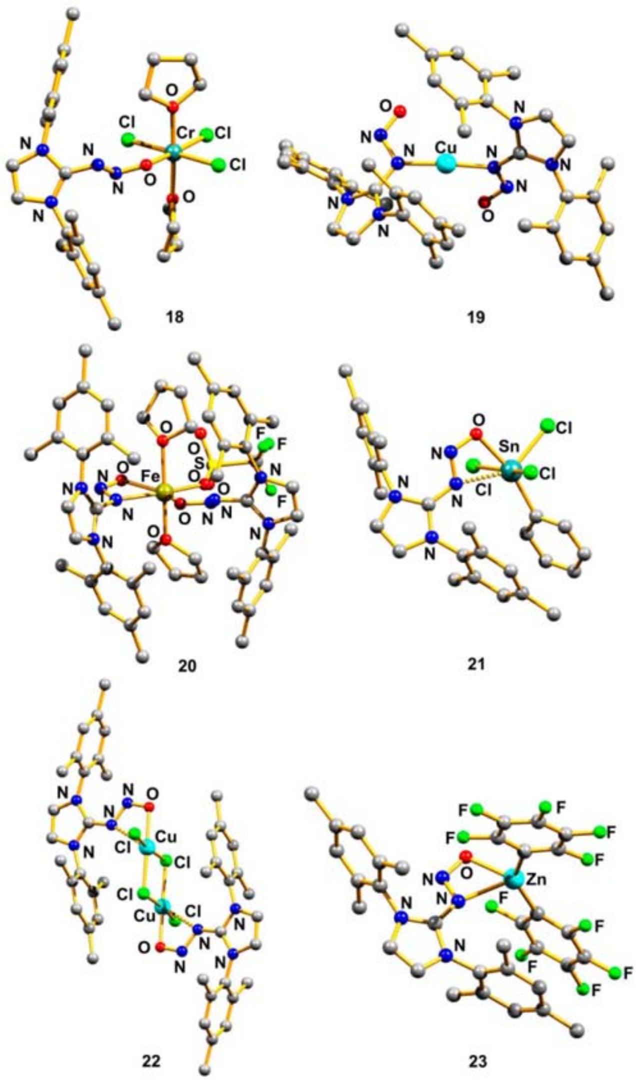


Figure 4. Ball-and-stick representations of the molecular structures of **18**−**23** in the crystal. Anions and H-atoms are omitted.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 18−23

	N−N	N−O	C−N(N)	C−N−N−O	N−C−N−N[b]
18	1.261(5)	1.318(4)	1.395(5)	178.2(3)	71.9(5)
19[a]	1.358(8)	1.225(8)	1.369(8)	173.6(6)	37.2(1)
	1.355(8)	1.231(8)	1.379(8)	174.6(6)	27.9(1)
20 η^1	1.268(3)	1.294(3)	1.374(3)	177.6(2)	63.7(4)
20 η^2	1.300(3)	1.279(3)	1.384(3)	179.9(2)	88.0(3)
21	1.294(3)	1.290(2)	1.384(3)	173.75(18)	30.0(3)
22	1.296(4)	1.274(4)	1.371(5)	176.4(3)	14.4(6)
23	1.301(2)	1.265(2)	1.362(3)	175.24(16)	26.6(3)

[a] The complex contains two ligands with different metrical parameters.

structural feature of the NHC−N_2O adducts is the presence of long N−N and short N−O bonds. The opposite trend has been observed for diazotates and N_2O adducts of FLPs. The structural data suggest that the N−N bond of NHC−N_2O adducts is rather weak. This was confirmed in reactions with acids or with acetyl chloride, which resulted in rupture of the N−N bond. In contrast, reaction with the bulky Lewis acid Ph_3C^+ led to the formation of a stable adduct with coordination via the O-atom. The coordination chemistry of NHC−N_2O adducts was explored using the IMes-derived **1** as a representative example. Structural analyses of six different transition-metal complexes revealed a remarkably versatile coordination behavior: **1** is able to act as a N-donor, as an O-donor, or as a chelating N,O-donor. The different coordination modes go along with pronounced electronic changes as evidenced by a bond length analysis.

Overall, the results presented in this work contribute to the understanding of the basic chemistry of N_2O, an inert gas with a highly negative environmental impact.[33] Furthermore, our work demonstrates that *N*-nitrosoimines display a rich chemistry, which goes far beyond the simple decomposition into ureas.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and analytical data as well as crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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