1 Introduction

Since its discovery in 1772 by Joseph Priestley, nitrous oxide has had a remarkable career.\(^1\) First, it became a popular recreational drug among the British upper class. In the second part of the 19th century, \(\text{N}_2\text{O}\) was employed as an anesthetic by dentists. This application is less common today, but in some countries, \(\text{N}_2\text{O}\) is given as a pain relief during childbirth.\(^2\) Very preliminary results indicate that \(\text{N}_2\text{O}\) could be used as a drug for patients with treatment-resistant depression.\(^3\) More technical applications include its utilization as a whipping agent for cream or as a fuel additive for rockets and motors.\(^4\) But there is also a ‘dark side’ of \(\text{N}_2\text{O}\), and that is its environmental impact. In fact, \(\text{N}_2\text{O}\) has been identified as the most potent ozone-depleting substance emitted in the 21st century.\(^5\) In addition, \(\text{N}_2\text{O}\) is a very effective greenhouse gas.\(^5\) The concentration of \(\text{N}_2\text{O}\) in the atmosphere is increasing, and human activities contribute significantly to \(\text{N}_2\text{O}\) emissions.\(^5\) The extensive use of fertilizers fosters the formation of \(\text{N}_2\text{O}\) during enzymatic nitrification and denitrification.\(^5\) Furthermore, there are industrial processes in which \(\text{N}_2\text{O}\) is produced as side product, and part of this \(\text{N}_2\text{O}\) is released in the atmosphere.\(^7\)

For a synthetic chemist, \(\text{N}_2\text{O}\) is of interest because it is a very strong oxidant from a thermodynamic point of view.\(^8\) Oxidation reactions typically result in the release of dinitrogen, which is an environmentally benign side product. However, reactions with \(\text{N}_2\text{O}\) are hampered by the highly inert character of \(\text{N}_2\text{O}\). These kinds of reactions have been summarized before,\(^9\) and they are not discussed in this overview. Instead, the focus will be on reactions which are carried out in homogeneous solution under (relatively) mild conditions. As described in Section 2, \(\text{N}_2\text{O}\) can be used as a very selective oxidant for highly reactive compounds such as disilenes or low-valent metallocenes. Transition metal-catalyzed oxidation reactions are also possible (Section 3), and recent results have shown that high turnover numbers can be achieved.

Another interesting avenue is the utilization of \(\text{N}_2\text{O}\) as a nitrogen atom donor for the synthesis of more complex organic molecules. Since many years, it is known that reactions of \(\text{N}_2\text{O}\) with organometallic reagents can give nitrogen-containing products. However, efficient synthetic procedures which employ \(\text{N}_2\text{O}\) as N-atom donor have only been discovered recently. Section 4 provides an overview of these transformations.

To better define the scope of this review article, it should be noted that the extensive bioinorganic chemistry of \(\text{N}_2\text{O}\) will not be discussed. For a description of the ligand properties of \(\text{N}_2\text{O}\), the reader is referred to an excellent review article by Tolman.\(^10\)

2 \(\text{N}_2\text{O}\) as O-atom donor

Chemical reactions with \(\text{N}_2\text{O}\) typically proceed via oxygen atom transfer and release of \(\text{N}_2\). Due to the very inert character of \(\text{N}_2\text{O}\), only highly reactive compounds are able to react with \(\text{N}_2\text{O}\) under mild conditions. For plain organic compounds such as olefins, on the other hand, rather harsh conditions are required. For example, it is possible to perform a solution-based oxidation of cyclohexene and cyclopentene to the corresponding cyclic ketones, but temperatures above 200 °C and elevated pressures (>25 bar) are needed to achieve good conversions.\(^11,12\)

The low intrinsic reactivity of \(\text{N}_2\text{O}\) can be advantageous because it allows performing very selective oxidation reactions,
which would be difficult to achieve with other oxidants such as O$_2$. Selective O-atom transfer reactions with N$_2$O have been used in particular in the context of synthetic inorganic chemistry. Low valent silicon compounds are suited substrates. For example, N$_2$O has been used to oxidize disilenes (Scheme 1a), silanamines, silaethenes, silylenes (Scheme 1b), and carbene-stabilized Si(0) compounds. It is worth noting that a metallosilylene and an osmium silylene complex were also found to react with N$_2$O. Recently, it was shown that low-valent germanium compounds can be oxidized with N$_2$O as well. A β-diketiminato germanium(II) hydride, for example, was converted into a hydroxide compound and donor-stabilized germylenes were oxidized to give germanones. Other main group compounds which react with N$_2$O under mild conditions are basic phosphines, methylenetriphenylphosphorane (PPh$_3$QCH$_2$), sodium sulphite, and boranes. However, these reactions are less interesting from a synthetic point of view.

Reaction of transition metal complexes with N$_2$O are hampered by the fact that N$_2$O is a very poor ligand. Accordingly, there are very few well-characterized L$_n$M(N$_2$O) complexes described in the literature. A first example was reported by Armor and Taube in 1969. They showed that N$_2$O can displace the water ligand in [Ru(NH$_3$)$_5$(OH$_2$)]$^{2+}$ to give the adduct [Ru(NH$_3$)$_5$(N$_2$O)]$^{2+}$ in a reversible fashion. Despite this early success, it was not until recently that a high-resolution crystallographic analysis of an N$_2$O vanadium complex was reported (Scheme 2). As in the case of [Ru(NH$_3$)$_5$(N$_2$O)]$^{2+}$, the coordination of N$_2$O is weak and ligand release is triggered by applying a vacuum. The intermediate formation of an osmium–N$_2$O complex was proposed for the reaction of (PNP)OsH$_3$ (PNP = N(SiMe$_2$CH$_2$P$_t$Bu$_2$)) with N$_2$O, which ultimately leads to the formation of a dinitrogen complex and water (hydrogenation of N$_2$O).

Even though the coordination of intact N$_2$O to a metal complex is a rarely observed phenomenon, there are numerous reports about transition metal complexes which react with N$_2$O in a stoichiometric fashion. In the majority of these cases, N$_2$O acts as oxygen atom donor. Selected examples are summarized below.

Early studies by Bottomley et al. focused on cyclopentadienyl titanium complexes. The reaction of the Ti(III) complex (Cp$_2$TiCl)$_2$ (Cp = η$^5$-C$_5$H$_5$) with N$_2$O was shown to give (Cp$_2$TiCl)$_2$O, whereas the Ti(II) complex Cp$_2$Ti gave the dinuclear complex (Cp$_2$Ti)$_2$O (Scheme 3a). Subsequently, other cyclopentadienyl complexes of the early transition metals were oxidized with N$_2$O. The reaction of Cp$_2$Cr gave the tetramer (CpCrO)$_4$, which features...
a heterocubane structure (Scheme 3b). A similar reaction was observed for the pentamethycyclopentadienyl complex Cp*₂Cr. Oxygen atom transfer was also demonstrated for cyclopentadienyl complexes of vanadium, tantalum, zirconium, and hafnium.

Oxygen atom transfer reactions are not restricted to complexes with cyclopentadienyl co-ligands. The Mindiola group has shown that vanadium and titanium alkyl complexes can be oxidized with N₂O to give complexes with terminal oxo ligands. A representative example is depicted in Scheme 3c. L₃M(O) complexes were also obtained by reaction of N₂O with a titanium tellurido complex, with a niobium hydride complex, or with the V(m) complex V[[Me₃SiCH₂CH₂]₂]₃. A detailed kinetic study of the O-atom transfer reaction from N₂O to the V(m) complex V[N(tBu)[3,5-C₆H₃Me₂)]₃ revealed that the reaction at room temperature is second order in concentration of the vanadium complex and first order in concentration of N₂O. At low temperature, however, an overall second order was observed. These data suggest that the oxygen atom transfer proceeds via a bimetallic L₃V(N₂O)VL₃ complex with a bridging N₂O ligand.

The transfer of multiple oxygen atoms was observed for the reaction of Ar'CrCrAr' (Ar' = C₆H₄₂,6-2,6-C₆H₃Ph₂) with an excess of N₂O (Scheme 3d). This reaction is good evidence for the utility of N₂O as a mild and selective oxidant because the product, Ar'Cr[O]₂CrAr', is extremely air and moisture sensitive. Accordingly, no defined product could be isolated when O₂ was used instead of N₂O.

Reactions of N₂O with complexes of the late transition metal nickel were examined by the group of Hillhouse. They observed that complexes of the general formula L₃NiR₂ (L = neutral P- or N-donor; R = alkyl, aryl) give alkoxide or aryloxide complexes of the formula L₃Ni(OR). For example, the metallacyclopentane (bipy)Ni(C₄H₈O) upon reaction with N₂O (Scheme 3e). Chemically induced demetallation of the latter results in the formation of 1-butanol, tetrahydrofuran or δ-valerolactone, respectively. It should be noted that the oxametallocycle cannot be prepared with O₂, because cyclobutane is formed instead. More recently, it was shown that a Ni-carbene complex is able to react with N₂O to give an oxametallocyclopropane. The oxidation of a Ni(0) carbonyl complex with N₂O was reported to give a complex with a chelating alkoxy ligand (Scheme 3f).

As mentioned above, some ruthenium complexes are able to bind intact N₂O in a reversible fashion. However, oxygen atom transfer has also been observed. Cauthon et al. have shown that the Ru(IV) nitride complex [PNP]RuN is converted into the corresponding nitrosyl complex [PNP]RuNO upon exposure to N₂O. Insertion of oxygen into a Ru-hydride bond was observed by Kaplan and Bergman. They found that Ru₂H₂(DMPE) (DMPE = Me₂PCH₂CH₂PMe₂) reacts with N₂O in a step-wise fashion to give first the hydroxo complex RuH(OH)(DMPE) and then the dihydroxo complex Ru(OH)₂(DMPE). We have examined the reaction of dinuclear organometallic Ru complexes with N₂O. When a solution of (p-cymene)Ru(m-Cl)₂Ru(IMes)₂(C₄H₄)Cl (IMes = 1,3-dimesitylimidazol-2-ylidene) was subjected to an atmosphere of N₂O, we observed the formation of a mixed-valence Ru(n)–Ru(m) complex with a chelating alkoxy ligand (Scheme 3f).

### 3 Metal-catalyzed reactions with N₂O

The fact that transition metal complexes are able to activate N₂O suggests that metal-catalyzed oxidation reactions with N₂O can be performed. A generic catalytic cycle is shown in Scheme 4. Reactions of this kind have been realized with heterogeneous catalysts or in the gas phase, but these systems are not discussed here. This section summarizes catalytic oxidation reactions with N₂O which are performed in homogeneous solution.

Initial attempts to use N₂O as an oxidant in metal-catalyzed reactions have focused on a rather ‘easy’ reaction: the oxidation of phosphines to phosphine oxides. It was shown that the hydride complex CoH(N₃)(PPh₃)₂ is able to catalyze the oxidation of PPh₃ to give OPPH₃ (Scheme 5a). The reaction was performed under ambient conditions and at least six turnovers were achieved. These findings are in line with observations by Pratt et al., who showed that Co(II) complexes are able to reduce N₂O to N₂. The cobalt-catalyzed oxidation of PPh₃ was recently re-investigated by Beloglazkina et al. using different Co complexes and higher turnover numbers were obtained (≤ 73).

![Scheme 4](image_url)
Another competent catalyst system for the conversion of phosphines to phosphine oxides by N$_2$O is a mixture of NiCl$_2$(DPPP) (DPPP = 1,3-bis(diphenylphosphino)propane) and n-BuLi (Scheme 5b). The active catalyst is assumed to be a low-valent Ni complex which is formed upon reduction of NiCl$_2$(DPPP) with n-BuLi.

The oxidation of different organic substrates in the presence of Ru–porphyrin complexes was investigated by Yamada et al. First, they were able to show that the Ru(II) complex Ru(TMP)(O)$_2$ (TMP = tetramesitylporphyrinato) is a catalyst for the epoxidation of olefins, including structurally complex substrates such a steroids (Scheme 6a). The reactions were performed under rather forcing conditions (140 °C, 10 bar) and aromatic solvents, in particular fluoro- and chlorobenzene, gave the best results. Soon after, the same group reported that Ru(TMP)(O)$_2$ can be used as a catalyst for the oxidation of secondary and primary benzylic alcohols (Scheme 6b), as well as for the oxidation of 9,10-dihydroanthracene derivatives (Scheme 6c). Again, rather harsh reactions conditions were applied. In this context, a study by Groves and Roman is worth mentioning. They have shown that the Ru(II) complex Ru(TMP)(THF)$_2$ can be oxidized with N$_2$O to give Ru(TMP)(O)(THF) or Ru(TMP)(O)$_2$, depending on the reaction conditions.

The utilization of polyoxometalates as catalysts for N$_2$O-based oxidation reactions was investigated by the group of Neumann. The vanadium-containing polyoxometalate [PV$_2$Mo$_{10}$O$_{40}$]$_5^-$ was shown to catalyze the oxidation of alcohols (Scheme 7a) and alkylarenes (Scheme 7b). The reactions were performed at ambient pressure and a temperature of 150 °C. The combination of H$_5$PV$_2$Mo$_{10}$O$_{40}$ with a Pd complex featuring a phenanthroline ligand decorated with a crown ether allowed to perform Wacker-type oxidation reactions of olefins with N$_2$O (Scheme 7c).

The Sita group has investigated oxygen atom transfer reactions mediated by organometallic Mo complexes. They were able to demonstrate the catalytic oxidation of an isocyanide to an isocyanate (Scheme 8). During the reaction, the catalysts cycles between Mo(II) and Mo(IV). At present, the reaction is less interesting from a synthetic point of view because low turnover numbers and frequencies (1 per week) were achieved. Still, the reaction is quite remarkable because catalysis occurs under ambient conditions (1 bar N$_2$O, 25 °C).

We have recently reported that N$_2$O can be used as an oxidant for the metal-catalyzed homo-coupling of Grignard...
reagents (Scheme 9). Simple metal salts such as Fe(acac)₃, CoCl₂, or Li₂CuCl₄ were employed as catalyst precursors. For most reactions, catalyst concentrations of 0.1–1.0 mol% were sufficient to obtain good yields. Coupling reactions of some arylmagnesium compounds could be performed with less than 0.01 mol% under very mild conditions. The corresponding turnover numbers of up to 9400 are unprecedented for solution-based oxidation reactions with N₂O. Compared to alternative procedures which utilize O₂ as oxidant, our method offers some important advantages. First, it is possible to use lower amounts of catalyst since N₂O is less prone to undergo metal-independent side reactions. Second, sterically demanding aryl Grignard reagents as well as highly reactive alkyl Grignard reagents can be used as substrates. Another noteworthy feature is the fact that aryl-alkyl and alkyl-alkyl cross-coupling reactions can be achieved with good selectivity. All these characteristics should make the method attractive for applications in organic synthesis.

Interestingly, it is also possible to perform metal-catalyzed reductions in the presence of N₂O. A system of this kind was recently described in a communication by Higuchi. They were able to show that alkenes can be reductively dimerized in the presence of N₂O. A system of this kind was reported in 1892 by Wislicenus. He showed that sodium azide is obtained upon exposure of NaNH₂ to N₂O at elevated temperatures (Scheme 11a). KNH₂ and Zn(NH₂)₂ were found to react in a similar fashion. The ‘Wislicenus reaction’ is nowadays used by industry to produce sodium azide on a larger scale. The mechanism of the reaction has been investigated by Clusius et al. Using ¹⁵N-labelled nitrous oxide (N¹⁵NO and ¹⁵NNO) can be prepared by decomposition of either NH₄¹⁵NO₃ or ¹⁵NH₄NO₃, they were able to show that two reaction pathways are operational. An attack of the amide at the terminal and the central nitrogen atom were proposed.

Amides of aromatic amines can also be converted into azides. Meier showed that lithium anilide reacts with N₂O to give azobenzene, biphenyl, and a small amount of a yellow oil, which he assumed to be phenyl azide. The reaction was later reinvestigated by Koga and Anselme. By optimizing the reaction conditions, they were able to increase the amount of phenyl azide to 35% (Scheme 11b). Amides derived from p-toluidine, p-anisidine, and cyclohexylamine were found to react in a similar fashion, but the yields were likewise low. Apart from simple amides, hydrazine anions are also able to react with N₂O, giving rise to a mixture of products.

Organometallic compounds of the alkali and the alkaline-earth metals often react with N₂O under mild conditions. Already in 1928, it was shown that the sodium salt of triphenylmethane adds N₂O to give a diazotate. The latter is converted into triphenylcarbinol upon reaction with ethanol (Scheme 12a). A first comprehensive study about the reaction of organolithium compounds with N₂O was published by Beringer et al. They showed that primary, secondary, and tertiary alkyl lithium compounds and most aryllithium compounds are able to react with N₂O. For example, the reaction of nBuLi with N₂O gave a hydrzone, which could be isolated with a yield of 24% (Scheme 12b).
For phenyl lithium, they observed a complex mixture of products including biphenyl, azobenzene, triphenylhydrazine and phenol. The mechanism this reaction was investigated by Meier.\textsuperscript{77,83} He proposed that the initially formed phenyldiazotate reacts with a second equivalent of PhLi to give azobenzene and Li\textsubscript{2}O. Side products arise from decomposition of the diazotate and from the fact that azobenzene can react further with PhLi.

The reaction of N\textsubscript{2}O with the simplest organolithium compound, CH\textsubscript{3}Li, was investigated by the group of Müller.\textsuperscript{84} They were able to show that diazomethane is formed after basic workup (Scheme 12c). Under optimized conditions, a yield of 70\% can be obtained.

The reaction of lithiated ferrocene with N\textsubscript{2}O allows the preparation of azoferrocene in 25\% yield (Scheme 12d). A similar reaction was used to synthesize azo-bridged ferrocene oligomers, albeit in very low yield.\textsuperscript{85} For the preparation of simple aromatic azo compounds, aryl calcium reagents appear to be best suited. This was first shown by Meier and Rappold, who isolated azobenzene along with larger amounts of biphenyl from the reaction of PhCaI with N\textsubscript{2}O in diethyl ether.\textsuperscript{87} More recently, the reaction was reinvestigated by Hays and Hanusa.\textsuperscript{88} Under optimized reaction conditions, they were able to increase the yield of azobenzene to 61\% (Scheme 12e), but they mentioned problems with reproducibility and the substrate scope was very narrow.

In contrast to organocalcium reagents, Grignard reagents were believed to be inert towards N\textsubscript{2}O. An early attempt to combine an organomagnesium compound with N\textsubscript{2}O was reported by Zerner in 1913.\textsuperscript{89} He observed that solutions of MeMgI in Et\textsubscript{2}O did not react with N\textsubscript{2}O even upon heating. Since then, statements about the unreactivity of Grignard reagents towards N\textsubscript{2}O have appeared in several articles.\textsuperscript{8,87,88} We have recently demonstrated that this generalization is not correct. Some primary and secondary aliphatic Grignard reagents such as EtMgCl, BnMgCl or iPrMgCl (Scheme 12f) are converted to hydrazones when THF solutions are subjected to an atmosphere of N\textsubscript{2}O. When the reactions are combined with an acidic work-up, it is possible to obtain alkylhydrazinium salts on a preparative scale.

As mentioned in Section 2, olefins are able to react with N\textsubscript{2}O under forcing conditions to give ketones.\textsuperscript{11,12} Calculations suggest that these reactions proceed via 1,3-dipolar cycloadditions of N\textsubscript{2}O to the double bond of the olefins.\textsuperscript{90} The latter decomposes to give the ketone and dinitrogen. Banert and Plefka have shown that cyclic alkynes are much more reactive towards N\textsubscript{2}O than simple olefins.\textsuperscript{91} Reactions were found to proceed at temperatures between -25 °C and RT using pressures between 15 and 50 bar. Interestingly, they were able to obtain products which contain all three atoms of nitrous oxide (Scheme 13).

The incorporation of all three atoms of N\textsubscript{2}O into the final product was also observed for reactions with some transition metal complexes. The diphenylacetylene complexes of permethyltitanocene and zirconocene react with N\textsubscript{2}O to give azoxymetallacyclopentene complexes (Scheme 14a).\textsuperscript{92} The Zr complex is thermally labile and undergoes extrusion of dinitrogen to give an oxametallacyclobutane complex. The carbon–metal bond of the latter can be cleaved with a variety of substrates processing acidic protons. It is noteworthy that the oxametallacyclobutane complex can be obtained in quantitative yield by exposure of the solid Zr diphenylacetylene complex to N\textsubscript{2}O. Recently, it was shown that the labile azoxymetallacyclopentene complex can be trapped by reactions with MeO\textsubscript{3}SCF\textsubscript{3} (alkylation of the β-N-atom).\textsuperscript{93} The reaction product can be isolated and is stable as a solid if stored at -35 °C. In case of Ti, the initial N\textsubscript{2}O adduct is more stable and can be used for further reactions. Apart from an alkylation reaction with MeO\textsubscript{3}SCF\textsubscript{3} (O- and β-N-alkylation), it was shown that the complex can be reduced to give a stable radical anion.\textsuperscript{93}

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Some organometallic samarium complexes are also able to insert \( \text{N}_2\text{O} \) into metal–carbon bonds. When a solution of \( \text{Cp}^*\text{Zn}(\text{THF}) \) was subjected to an atmosphere of \( \text{N}_2\text{O} \), a dinuclear complex was formed (Scheme 14b).\(^{94}\) A related reaction was observed for allyl complexes of the formula \( \text{Cp}^*\text{M}(\eta^3\text{-C}_3\text{H}_5) \) (\( \text{M} = \text{Y}, \text{Sm}, \text{La} \)).\(^{95}\)

A rarely observed phenomenon is the addition of \( \text{N}_2\text{O} \) to transition metal complexes with concomitant cleavage of the N–N bond.\(^{96–100}\) Cummins has shown that three-coordinate Mo(III) complexes are able to react with \( \text{N}_2\text{O} \) in this fashion to give a nitrosyl complex along with a nitride complex (Scheme 15a).\(^{96,97}\) It is interesting to note that the reverse reaction, the formation of \( \text{N}_2\text{O} \) from a metal nitride complex and nitric oxide, has been observed for an osmium\(^{101}\) and a ruthenium\(^{49}\) nitride complex. More recently, the Sita group has shown that a Mo carbonyl complex (generated in situ by photolysis of a dicarbonyl complex) can add \( \text{N}_2\text{O} \) to give a nitrosyl, isocyanate complex (Scheme 15b).\(^{98,99}\)

The formation of stable covalent adducts of \( \text{N}_2\text{O} \) can be achieved without transition metals. In 2009, the group of Stephan has shown that the frustrated Lewis pair (FLP) \( \text{tBu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3 \) reacts with \( \text{N}_2\text{O} \) at ambient conditions to give the adduct \( \text{tBu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3 \) (Scheme 16a).\(^{102,103}\) A crystallographic analysis of the product revealed that the \( \text{tBu}_3\text{P} \) and the \( \text{OB}(\text{C}_6\text{F}_5)_3 \) group are oriented \textit{trans} with respect the N–N double bond. Upon thermal or photochemical activation, the adduct liberates dinitrogen to give \( (\text{tBu}_3\text{PO})\text{B}(\text{C}_6\text{F}_5)_3 \). The \( \text{B}(\text{C}_6\text{F}_5)_3 \) group in the adduct \( \text{tBu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3 \) is labile and can be replaced by the Lewis acid \( \text{Zn}(\text{C}_6\text{F}_5)_2 \).\(^{104}\) Subsequent studies showed that the adduct \( \text{tBu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{H}_4\text{F})_3 \) is particularly well suited for exchange reactions, since it features the relatively weak Lewis acid \( \text{B}(\text{C}_6\text{H}_4\text{F})_3 \). Clean exchange reactions were observed for boron-based Lewis acids such as \( \text{PhB}(\text{C}_6\text{F}_5)_2 \) and \( \text{MesB}(\text{C}_6\text{F}_5)_3 \), as well as for cationic metallocene complexes and the tritylium cation (Scheme 16b).\(^{22}\) The Al analogue \( \text{tBu}_3\text{P}(\text{N}_2\text{O})\text{Al}(\text{C}_6\text{F}_5)_3 \) can be prepared by slow addition of \( \text{N}_2\text{O} \) to a cooled (\(-78 \degree \text{C}\)) solution containing \( \text{tBu}_3\text{P} \) (2 eq.) and \( \text{Al}(\text{C}_6\text{F}_5)_3 \text{tol.} \) Subsequent reaction with additional \( \text{Al}(\text{C}_6\text{F}_5)_3 \text{tol.} \) results in cleavage of the N–O bond to generate the highly reactive radical ion pair \( (\text{tBu}_3\text{PO})\text{Al}(\text{C}_6\text{F}_5)_3\text{Al}^\text{+}(\text{C}_6\text{F}_5)_3\text{thf}^- \) that can activate C–H bonds. First steps towards the preparation of \( \text{N}_2\text{O} \) sensors based on FLPS were recently reported by the groups of Aldridge and Tamm.\(^{106}\) They showed that FLPS containing organometallic sandwich complexes (e.g. ferrocene, Scheme 16c) change their color upon binding to \( \text{N}_2\text{O} \).

Covalent capture of intact \( \text{N}_2\text{O} \) can also be achieved by N-heterocyclic carbenes (NHCs).\(^{107–110}\) This was first demonstrated by our group in 2012.\(^{107}\) The reactions occur at room temperature and ambient pressure to give the adducts \( \text{NCH–N}_2\text{O} \) in (mostly) good yields (Scheme 17). Conveniently, the carbenes can be prepared \textit{in situ} by deprotonation of the corresponding imidazolium salts.\(^{108}\) Owing to the strong C–N bond, most adducts show a good stability at room temperature. On heating, however, they decompose to give dinitrogen and the corresponding urea. The decomposition reaction was found to depend strongly on the nature of the carbene and the solvent. Aqueous solutions of the adduct derived from 1,2-dimethylimidazol-2-ylidine (\( R = R' = \text{Me} \)), for example, could be heated to 100 \degree \text{C} for a prolonged period of time without significant decomposition.\(^{108}\) A noteworthy characteristic of NHC–\( \text{N}_2\text{O} \) adducts is the long N–N bond (1.27–1.33 \AA), which is in contrast to what has been observed for \( \text{N}_2\text{O} \) adducts.
of frustrated Lewis pairs (N–N ~ 1.25 Å). This structural feature suggests that the activation of N₂O by carbenes might facilitate N–N bond rupture. In fact, when NHC–N₂O adducts were allowed to react with MeI, HCl (Scheme 18a), or acetyl chloride, rupture of the N–N bond was observed.107,108 Reaction with the tritylium tetrafluoroborate, on the other hand, led to the formation of the adduct (IMes–N₂O–CPh₃)(BF₄) (Scheme 18b).

Reactions of IMes–N₂O with different transition metal complexes have been investigated. When combined with simple 3d transition metal salts, IMes–N₂O can act as an N-donor, as an O-donor, or as a chelating N,O-donor.108 More interesting results were obtained with the low-valent vanadium complex V(Mes)₃(THF) and the Ni(0) complex Ni(COD)₂. In case of the highly oxophilic V(Mes)₃(THF), the addition of IMes–N₂O resulted in N–O bond cleavage with oxygen atom transfer to the metal center and formation of a deprotonated hydrazone ligand (Scheme 18c).111 With Ni(COD)₂, on the other hand, insertion of the metal in the N–N bond was observed.112 The product of the reaction is an unusual three-coordinate Ni nitrosyl complex with bridging imidazolin-2-iminato ligands (Scheme 18d).

Recently, we found that AlCl₃ is able to induce cleavage of the N–O bond of NHC–N₂O adducts. When the reactions are performed in the presence of an aromatic compound, azoimidazolium salts are formed in good yields (Scheme 19).113 These kinds of salts are of interest because they are strongly colored dyes. They are produced industrially (e.g. Basic Red 51) and used for a variety of applications such as dying of synthetic and natural fibers. An advantage of the N₂O-based procedure is its flexibility. The heterocyclic coupling partner can have aliphatic as well as aromatic substituents on the nitrogen atoms. Furthermore, it is possible to use a wide range of aromatic coupling partners including deactivated arenes such as C₆H₅F, heterocycles, and polycyclic arenes such as pyrene and azulene (Scheme 19). As such, the method complements existing procedures for the synthesis of these dyes, each of which has its own limitations.

Triazenes are compounds of the general formula R–N═N–NR′R″. They have been used extensively in synthetic organic chemistry.114 Furthermore, triazenes have been examined as potential anti-tumor drugs, and the triazenes dacarbazine and temozolomide are currently used in the clinic for the treatment of cancer.115 We have recently shown that triazenes can be prepared by coupling of lithium amides and organomagnesium compounds with N₂O.116 The reaction is best performed in a sequential fashion, with initial addition of N₂O to a solution of the amide, followed by reaction with the Grignard reagent (Scheme 20). A key advantage of the new procedure is the ability to access triazenes with alkenyl and alkynyl substituents (some selected examples are show in Scheme 20). These compounds are difficult to synthesize by conventional methods.
because the required starting materials are unstable. Interestingly, some of the new alkylnitriazines were found to display high cytotoxicity in in vitro tests on ovarian and breast cancer cell lines. Recent results from our laboratory show that alkylnitriazines are versatile starting materials for subsequent reactions, and details about these reactions will be reported in due course.

5 Conclusions
The examples discussed above show that nitrous oxide is an interesting reagent for synthetic organic and inorganic chemistry. The inert character of N₂O allows selective oxygen atom transfer reactions to highly reactive species, while minimizing the risk of over-oxidation. Stoichiometric reactions of this kind have been used in particular for the oxidation of low-valent silicon compounds and for transition metal complexes.

Catalytic reactions with N₂O have been examined extensively because N₂O is a cheap and environmentally benign oxidant. Initially, solution-based reactions with transition metal catalysts have shown only very limited success. High temperatures and/or pressures were needed, and low turnover numbers were achieved. However, recent results demonstrate that efficient catalytic processes at ambient conditions are possible. Based on these initial results, it appears that catalytic reactions which involve low-valent transition metal complexes are particularly well suited.

For reactions with N₂O, the transfer of oxygen is the most commonly observed mode of reactivity. Nevertheless, it is possible to use N₂O as a donor of nitrogen atoms. Reactions of this kind are known for many decades, but applications in organic synthesis were sparse. The formation of side products, low yields, and the existence of more attractive alternative procedures have hampered the utilization of N₂O in N-atom transfer reactions. But this might change in the future. As demonstrated by synthesis of triazines and azoimidazolium dyes, it is possible to perform high yield N-atom transfer reactions with N₂O. Notably, the N₂O-based methods can offer distinct advantages over more established synthetic procedures.

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