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Activation of Ammonia by a Si═O Double Bond and Formation of a Unique Pair of Sila-Hemiaminal and Silanoic Amide Tautomers

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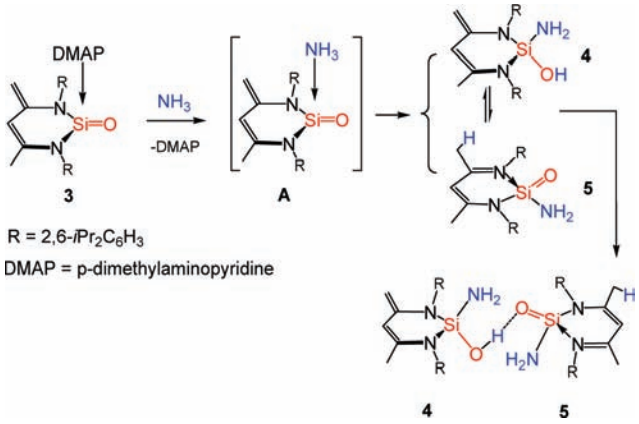
Currently, the activation of ammonia is attracting considerable interest because of its promising role for the development of facile transformations into value-added products. Striking examples comprise N−H bond splitting by a transition metal,[1] N-heterocyclic carbenes (NHCs)[2] and even by heavier group 14 element carbene analogues,[3,4] including ylide-like silylene **1**, LSi: (L = N(R)C(═CH_2)CH═C(Me)N(R), R = 2,6-$i$$Pr_2C_6H_3$)[5] and its $Ni(CO)_3$ complex.[6] In spite of recent progress, the activation of N−H bonds of ammonia by coordinatively unsaturated sites (nonmetals or metals) is still surprisingly rare. Perhaps the earliest precedent reported for N−H activation of ammonia and primary organoamines by Lewis acidic substrates is their nucleophilic addition to C═O double bonds in aldehydes and ketones (R_2C═O) to give hemiaminals followed by an elimination step to form imines and water.[7] Since hemiaminals are generally unstable and imines with a N−H moiety spontaneously polymerize, they need special environments to be detectable.[8] These classical features inspired us to investigate whether ammonia reacts with a Si═O double bond to give isolable sila-hemiaminals ($R_2Si(OH)NH_2$) and/or iminosilanes (R_2Si═NH). To the best of our knowledge, the chemistry of silanones toward ammonia is currently unknown. Since silicon analogues of ketones are elusive species, it seems appealing to explore the chemistry of Si═O double bonds by using donor-stabilized silanone precursors. Recently, we reported the synthesis and isolation of the first *N*-donor supported silanoic ester (L′Si(═O)OR; L′ = LH)[9a] and remarkably stable NHC−silanone complexes (NHC→Si(L)═O),[9b,c,10] starting from silylene **1**.[5b] We now learned that the NHC donor in the latter system can be replaced by the weaker coordinated *p*-dimethylaminopyridine (DMAP) ligand, leading to the corresponding silanone precursor **3** (Scheme 1) via oxidation of the silylene−DMAP adduct **2** (see Supporting Information). Strikingly and in contrast to related NHC-stabilized Si═O complexes, **3** reacts readily with ammonia under mild conditions. Herein we report for the first time the addition of ammonia to the Si═O double bond of **3**, affording a unique pair of tautomer products.

Similar to procedures previously reported,[9,10] **3** is simply accessible in 83% yield by oxygenation of **2** with N_2O in toluene. It has been fully characterized, including by X-ray diffraction analysis. The spectroscopic and structural features of **3** are similar to those of related NHC−silanone adducts (see Supporting Information).

Crystals of **3** are even stable in dry air, marginally soluble in hydrocarbons and ethereal solvents, but very soluble in dichloromethane. Exposure of a pale yellow suspension of **3** in toluene to dry ammonia gas at room temperature leads to a clear colorless solution. According to NMR spectroscopy and ESI-MS measurements of the resulting clear solution, DMAP in **3** is completely released and one equimolar amount of ammonia has been added to the Si═O subunit, presumably via intermediate **A**. Furthermore, the ^{1}H NMR spectrum reveals that the expected adduct, sila-hemiaminal **4**, is in equilibrium with its striking tautomer, silanoic amide **5** (Scheme 1), owing to the pronounced basicity of the exocyclic methylene group on the C_3N_2 ligand backbone.[5a,11] The equilibrium between **4** and **5** depends both on the polarity of the solvent and on concentration. Although the amount of **5** increases in more concentrated solution (in both d_8-THF and C_6D_6), in all solutions the amount of **4** always dominates over **5** especially in polar solvents such as d_8-THF. While **4** shows only one set of resonances at room temperature, by cooling of the solutions to −60 °C, the signals of **4** split completely into two sets of signals, but the resonance signals of **5** remain as one set. The two sets of signals for **4** coalesce at 0 °C. This observation suggests the presence of a Si−O−H···O═Si hydrogen bond between **4** and **5**, which results in two different sets of resonances for **4** in the ^{1}H NMR spectrum: one set from the hydrogen-bonded **4**, the other set from “free” **4**. The coalescence of these two sets of signals above 0 °C can be rationalized by their rapid exchange (“free” vs hydrogen-bonded **4**) at the NMR time scale.

Scheme 1. DMAP Stabilized Silanone **3** and Its Reactivity Toward Ammonia



In fact, crystallization in benzene and THF solutions leads to single crystals of a 1:1 mixture of the tautomers **4** and **5**. Its molecular structure has been established by an X-ray diffraction analysis (Figure 1). Two independent molecules of tautomeric pairs are present in the asymmetric unit. In each pair the $Si(O)NH_2$ moieties of **4** and **5** prefer a *gauche* conformation and are connected by an OH···O hydrogen bridge with O···O distances of 2.570 and 2.589 Å, which fall in the common range for hydrogen bonds. This is in contrast to the structural features of the only known sila-

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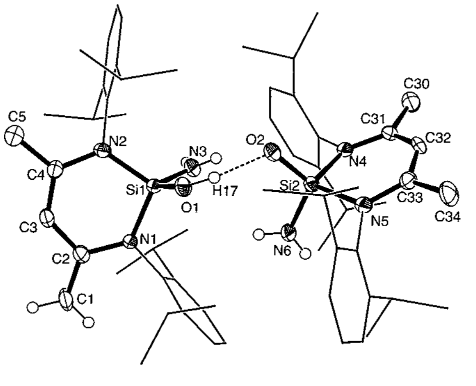


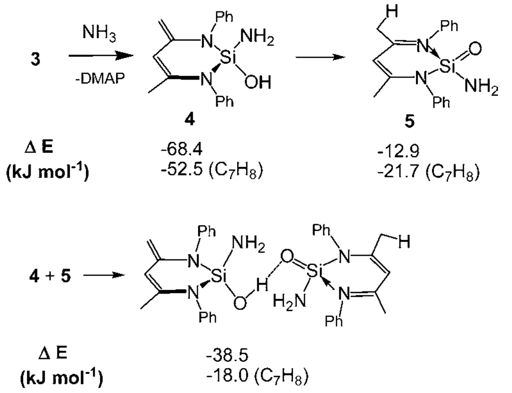
4 **5**

Figure 1. Molecular structure of the H-bonded adduct between **4** and **5**. Thermal ellipsoids are drawn at 50% probability level. H atoms (except those at C1, N3, N6, O1) and solvent benzene molecules are omitted for clarity. The H atoms at O1, N3, and N6 were located from the difference electron density map and refined. There are two pairs of molecules (see Supporting Information); only one tautomeric pair is shown here. Selected interatomic distances (Å) and angles (deg): **Pair 1**: Si1−O1 1.607(2), Si2−O2 1.545(2), C1−C2 1.383(3), C4−C5 1.463(3), C30−C31 1.499(4), C33−C34 1.516(4), Si1−N1 1.742(2), Si1−N2 1.736(2), Si1−N3 1.681(3), Si2−N6 1.677(2), Si2−N5 1.793(2), Si2−N4 1.817(2), O2···H17 1.721, O1−H17 0.872, O1−O2 2.570; O1−H17−O2 172.9; **Pair 2**: Si1−O1 1.607(2), Si2−O2 1.546(2), C1−C2 1.404(4), C4−C5 1.432(3), C30−C31 1.494(4), C33−C34 1.508(4), Si1−N11.746(2), Si1−N2 1.737(2), Si1−N3 1.677(2), Si2−N6 1.683(2), Si2−N5 1.795(2), Si2−N4 1.805(2), O2···H17 1.720, O1−H17 0.854, O1−O2 2.589; O1−H17−O2 173.2.

hemiaminal, tBu$_2$Si(OH)NH$_2$ characterized structurally which forms also a dimer but possesses NH···O and OH···N instead of OH···O bridges.[12] The Si atoms in the subunits **4** and **5** are tetrahedral coordinated and embedded in slightly puckered six-membered C_3N_2Si rings. The most noteworthy structural feature is the Si−O distance (1.607(2) Å) in **4** and the much shorter Si−O distance (1.545(2), 1.546(2) Å) in **5**, suggesting a Si−O single bond in **4** and significant Si=O double bond character in **5**.[13] Accordingly, one of the exocyclic C−C bonds in **4** [C1−C2 (1.383(3), 1.404(4) Å)] represents a C=C double bond, whereas both exocyclic C−C bonds in **5** [C30−C31 (1.499(4), 1.508(4) Å) and C33−C34 (1.516(4), 1.494(4) Å)] are C−C single bonds. All Si−NH$_2$ distances, ranging from 1.676(3) to 1.683(2) Å, are shorter than the endocyclic Si−N distances (1.736(2)−1.746(2) Å).

To gain insight into the thermodynamic features of these systems, DFT calculations (RI-BP86/def2-TZVP level of theory) have been performed for activation of ammonia by compound **3** (Scheme 2). In addition to the results in the gas phase, a continuum solvent model has been applied for the conversions in toluene. Consistent with the experimental observations, the calculations revealed that displacement of the DMAP donor and addition of ammonia to the Si=O double bond in **3** can lead to both tautomers **4** and **5** in different ratios and can be dependent on the presence of a solvent and on concentration (Scheme 2). Likewise, our calculations support the formation of the tautomer pair **4**−**5** via a hydrogen bond.

Scheme 2. Energies from Full Optimizations at the RI-BP86/def2-TZVP Level of Theory of the Reaction Products of Compound **3** with Ammonia To Give **4**, **5**, and Its Hydrogen-Bonded Pair



In summary, we reported here the unique reactivity of a Si=O double bond toward ammonia. In contrast to NHC-stabilized silanones, the DMAP-stabilized Si=O precursor **3** is capable undergoing addition of ammonia under mild conditions and extrusion of the DMAP ligand to give the sila-hemiaminal **4**. In accordance with DFT calculations, the latter can readily undergo tautomerization to furnish the unprecedented silanoic amide derivative **5**. Compounds **4** and **5** are in equilibrium in solution and can undergo intermolecular stabilization in solution and in the solid state via SiOH···O=Si interaction. The relatively weakly coordinated DMAP ligand in **4** calls for future studies of E−H bond activation of small molecules by Si=O double bonds.

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Supporting Information Available: Experimental details for the syntheses and spectroscopic data of starting materials **2** (precursors for **3**), **3**, **4**, and **5** (PDF) and crystallographic data for **2**, **3**, and the adduct **4**−**5** (CIF), respectively, as well as computational details and coordinates of DFT-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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