Ammonia Activation

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Ammonia Activation by a Nickel NCN-Pincer Complex featuring a Non-Innocent N-Heterocyclic Carbene: Ammine and Amido Complexes in Equilibrium**

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In memory of Tom Ziegler

Abstract: *A Ni^0-NCN pincer complex featuring a six-membered N-heterocyclic carbene (NHC) central platform and amidine pendant arms was synthesized by deprotonation of its Ni^{II} precursor. It retained chloride in the square-planar coordination sphere of nickel and was expected to be highly susceptible to oxidative addition reactions. The Ni^0 complex rapidly activated ammonia at room temperature, in a ligand-assisted process where the carbene carbon atom played the unprecedented role of proton acceptor. For the first time, the coordinated (ammine) and activated (amido) species were observed together in solution, in a solvent-dependent equilibrium. A structural analysis of the Ni complexes provided insight into the highly unusual, non-innocent behavior of the NHC ligand.*

The activation of ammonia at metal centers is believed to play a crucial step in the catalytic functionalization of organic substrates, most notably olefins.[1] Unfortunately, conducting this reaction with a Lewis base as a substrate poses substantial difficulties related to the activation–coordination equilibrium, which in the vast majority of cases is completely shifted in favor of the latter. Early studies on ammonia activation involved Ti^{III} by Armor and Zr^{II} by Hillhouse and Bercaw,[2] as well as $[Os_3(CO)_{12}]$ by the research groups of Lewis and Süss-Fink.[3] Iridium took center stage in the activation of ammonia starting with the reports of Milstein and co-workers describing the oxidative addition of N−H bonds at Ir^I centers to yield dinuclear, bridging amido complexes $[L_n(H)Ir^{III}(\mu\text{-}NH_2)_2Ir^{III}(H)L_n]$.[4] Similar reactions were also investigated by Braun and co-workers.[5] Another significant development was the introduction of pincer complexes by Hartwig and co-workers and later by Turculet and co-workers, who described the activation of ammonia on Ir^I PCP and PSiP pincer complexes, respectively, to yield mononuclear, terminal $[L(H)Ir^{III}\text{-}NH_2]$ derivatives.[6] Also notable is the homolytic activation of ammonia by a dinuclear Pd^I PNP pincer complex, reported by Ozerov and co-workers, where a terminal $[LPd^{II}\text{-}NH_2]$ species was obtained along with $[LPd^{II}\text{-}H]$.[7]

Ammonia activation by metathesis, without formally changing the oxidation state of the metal, is well-documented on several metals including Ru and Ir,[8] but can pose problems in terms of catalysis because the hydrogen atom is removed from the catalytic site. The Milstein group showed evidence for heterolytic, deprotonative N−H bond activation of ammonia using a Ru^{II} complex incorporating non-innocent PNP pincer ligands, without observing the corresponding $[LRu^{II}\text{-}NH_2]$ species.[9a] A similar, ligand-assisted cleavage of the N−H bond in ammonia by an Ir^I complex featuring a pyridyl-based PNP pincer ligand, to give a terminal $[LIr^I\text{-}NH_2]$ species was described by Yoshizawa, Ozawa, and co-workers.[9b] A related ligand-assisted ammonia activation reaction was reported by Kuwata, Ikariya, and co-workers on a dinuclear $[LIr^{III}(\mu\text{-}H)(\mu\text{-}NH)Ir^{III}L]^-$ compound, which resulted in the formation of $[LIr^{III}(\mu\text{-}H)(\mu\text{-}NH_2)_2Ir^{III}L]^-$.[10] Piers and co-workers recently disclosed the use of a carbene-based Ni^0-PCP pincer complex for the ligand-assisted activation of ammonia to give a terminal $[LNi^{II}\text{-}NH_2]$ product.[11] The remarkable progress made in the activation of ammonia by main-group systems is also noteworthy.[12]

The activation of the N−H bond in ammonia proved to be highly sensitive to the nature of the catalyst,[13] with the ammine–amide equilibrium being completely shifted upon changing the metal from rhodium (ammine) to iridium (amide) with the same ligand system.[6b] Moreover, the nature of the phosphine ligand was shown to have similar effects in iridium complexes.[4d] Homogeneous catalytic hydroamination with ammonia remains a major challenge, and notable progress towards this goal was the stoichiometric, intramolecular hydroamination of the coordinated ligand in an iridium amide complex.[14]

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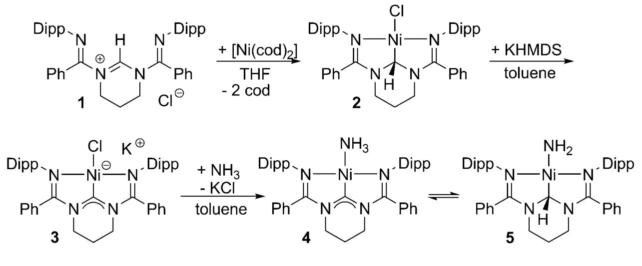
Continuing our investigations of ammonia activation on pincer complexes incorporating NHC scaffolds, we report herein the reversible, ligand-assisted activation of ammonia on a Ni^0–NCN pincer complex.

Proligand **1** is similar to those reported by the research groups of Byers and Lavoie and was prepared by stepwise functionalization of 1,4,5,6-tetrahydropyrimidine with N-Dipp-benzimidoyl chloride (Dipp = 2,6-diisopropylphenyl) using a modification of a reported procedure.[15] Its room-temperature reaction with [Ni(cod)$_2$] (cod = cycloocta-1,5-diene) produced a deep-red solution, from which complex **2** was isolated as an orange solid in 67 % yield (Scheme 1). The ^{1}H NMR spectrum of **2** revealed a C_s symmetry, instead of the C_{2v} symmetry expected for a Ni–NHC complex. The resonance corresponding to the N$_2$CH proton appeared at 5.82 ppm, substantially upfield shifted from 8.84 ppm in **1**. The crystal structure confirmed the distorted tetrahedral geometry of the N$_2$CH carbon atom on the NCN pincer complex, with the sum of the bond angles formed by the heavier elements at C1 measuring 332.5° (Figure 1). With 1.848(5) Å, the C1–Ni1 bond is short when compared to similar bonds in Ni^{II} pincer complexes featuring dialkylmethyl[16] or diarylmethyl[11] central platforms (av. Ni–C 1.98(2) and 1.986(3) Å, respectively). Although the preference for alkyl versus carbene coordination is common for complexes of dialkyl and diaryl carbenes, it is very rare for complexes of the more stable NHCs. Only a few such examples have been structurally characterized to date,[17] and we propose that the competitive delocalization of the nitrogen lone pairs of electrons onto the exocyclic amidine moieties is responsible for a reduced stabilization of the carbene structure.[18] In support of this theory, the two C–N bonds of each pendant amidine group in **2** are almost equal in length. Treatment of **2** with potassium hexamethyldisilazide in toluene nevertheless yielded the NHC complex **3**, with nickel retaining the chloride in its coordination sphere. The ^{1}H NMR spectrum of this Ni^0 complex confirmed the disappearance of the resonance corresponding to the N$_2$CH proton.



Scheme 1. Synthesis of derivatives **1**–**5**.

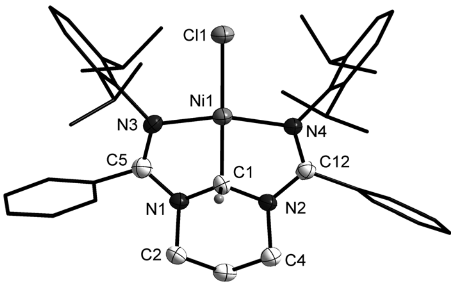


Figure 1. Structure of one of the two independent molecules of **2** in the solid state, with selected ellipsoids drawn at 50% probability. All hydrogen atoms except for the N$_2$CH proton are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1-C1 1.848(5), Ni1-Cl1 2.222(1), Ni1-N3 1.914(4), Ni1-N4 1.914(4), N1-C1 1.440(6), N2-C1 1.439(6), C5-N3 1.312(6), C12-N4 1.305(6), C5-N1 1.340(6), C12-N2 1.352(6); N1-C1-N2 111.3(4), C1-Ni1-Cl1 175.0(2), N3-Ni1-N4 159.2(2).

The crystal structure of **3** revealed a dimeric arrangement with two anionic LNi^{0}Cl moieties bridged by the potassium counterions (Figure 2). In turn, the π coordination of the Dipp groups completes the distorted square-planar coordination geometry of the potassium ions. The carbene carbon atom C1 is close to planarity, with the sum of the bond angles being 350.8°. At 1.795(7) Å, the Ni1–C1 bond in **3** is shorter than in **2**, and in fact shorter than all reported Ni^0–C$_{NHC}$ bonds (1.827(6) to 2.021(4) Å, av. 1.91(4) Å).[19] The conversion into an NHC is accompanied by the expected shortening of the C–N bonds to the carbene carbon atom, from 1.44 Å in **2** to 1.39 Å in **3**. These bonds remain nevertheless a bit long compared to those observed in other NHC complexes (av. 1.36(2) Å),[17] thus supporting a contribution of resonance structure **3b** (Scheme 2).

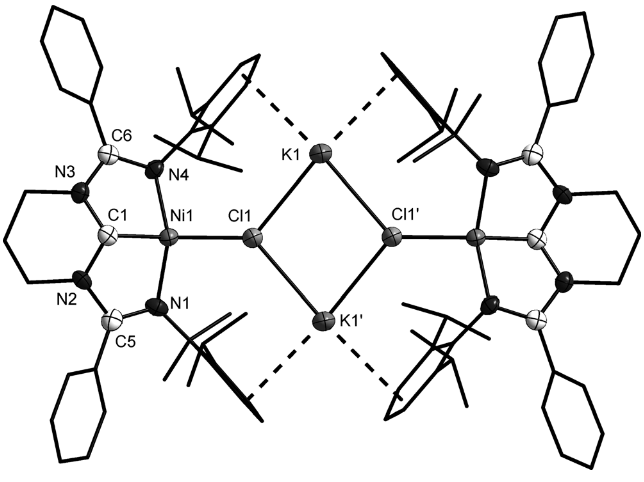
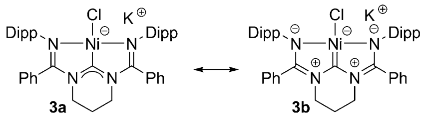


Figure 2. Structure of one of the two independent molecules of **3** in the solid state, with selected ellipsoids drawn at 50% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1-C1 1.795(7), Ni1-Cl1 2.296(2), Ni1-N1 1.913(6), Ni1-N4 1.903(6), N2-C1 1.395(9), N3-C1 1.392(9), C5-N1 1.361(10), C6-N4 1.364(9), C5-N2 1.380(10), C6-N3 1.355(10), Cl1-K1 2.948(3), Cl1-K1′ 2.977(3); Ni2-C1-N3 117.3(4), C1-Ni1-Cl1 166.2(2), N1-Ni1-N4 155.7(3).

Complex **3** was expected to be prone to oxidative addition reactions upon elimination of KCl. Exposure of **3** to ammonia gas at room temperature in either toluene or THF immediately yielded a dark solution. ^{1}H NMR spectroscopy indicated the presence of two compounds, one with C_{2v} and the other



Scheme 2. Resonance structures **3a** and **3b**.

with C_s symmetry, which were assigned to **4** and **5**, respectively. For the former compound, the ^{1}H NMR spectrum of the mixture displayed the two expected doublet resonances corresponding to the diastereotopic methyl groups of the ligand and a resonance corresponding to the coordinated ammonia at −0.11 ppm in [D$_8$]toluene and 0.45 in [D$_8$]THF. For the activation product **5**, the spectrum displayed four doublet resonances corresponding to the methyl groups of the ligand and a resonance for the amide protons at −2.97 ppm in [D$_8$]toluene and −3.63 ppm in [D$_8$]THF. Additionally, the signal corresponding to the N$_2$CH proton was observed at 5.13 ppm in [D$_8$]toluene and 5.22 ppm in [D$_8$]THF. The two structural isomers **4**/**5** were present in ratios of about 4:1 in [D$_8$]toluene and 2:3 in [D$_8$]THF, with intermediate ratios in mixed-solvent systems, thus indicating that an equilibrium was present in solution (Figure 3). This was further confirmed by EXSY NMR spectroscopy, which showed cross-peaks between the signals corresponding to the NH$_3$ protons in **4** and the NH$_2$ and N$_2$CH protons in **5** (see the Supporting Information). Exposure of a solution of **4** and **5** in [D$_8$]toluene to ND$_3$ resulted, as expected, in the rapid decrease in the intensity of the ^{1}H NMR signals corresponding to the N$_2$CH, NH$_3$, and NH$_2$ protons following the exchange with deuterium. Solvent removal from solutions containing **4** and **5** produced a highly sensitive microcrystalline dark-green solid that could be stored for several weeks at −38 °C in the absence of air and moisture. Its identity could not be confirmed because the single crystals were of insufficient quality. No distinctive IR bands corresponding to N-H stretching vibrations were observed. The solid redissolved in THF and toluene to give solutions that displayed properties identical to those observed for the solution of in situ prepared **4**/**5**.

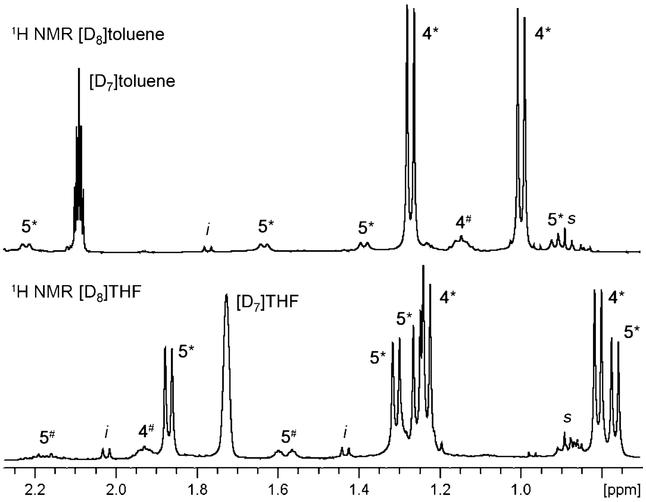


Figure 3. Selected range of the ^{1}H NMR spectra of the equilibrium mixture of **4** and **5** in [D$_8$]toluene (top) and [D$_8$]THF (bottom). The signs indicate: *: (C*H*$_3$)$_2$CH, #: NHC backbone, *i*: unidentified impurity, *s*: solvent.

Density functional theory calculations were performed on model compounds **4^{Ph}** and **5^{Ph}**, in which the Dipp substituents were replaced by phenyl groups. The gas-phase free energies of the optimized structures show that **4^{Ph}** is favored over **5^{Ph}** by 6 kJ mol^{-1} in low dielectric media, in good agreement with the value of 3.4 kJ mol^{-1} derived from the relative concentrations in [D$_8$]toluene solutions. When a continuum solvent model for THF was used, the calculations predicted **5^{Ph}** to be lower in energy than **4^{Ph}** by 21 kJ mol^{-1}. This matches less well the experimentally derived value of 1.0 kJ mol^{-1}, but it shows the same preference for **5^{Ph}**.

An equilibrium between coordinated (ammine) and activated (amido) ammonia complexes has been proposed before, mainly based on exchange experiments using ND$_3$.[9a,11] However, in some systems the incorporation of deuterium was likely to be a result of mechanisms other than the reversible oxidative addition of ammonia.[5c,6b] The **4**/**5** system represents the first instance where the thermodynamic stability of the two complexes is comparable, thus allowing the observation of both species in solution.

In conclusion, we report here a highly active Ni^0 pincer complex that is able to reversibly activate ammonia at room temperature in a ligand-assisted process. Both coordinated (ammine, **4**) and activated (amide, **5**) species coexist in solution in comparable, solvent-dependent proportions. The unprecedented ability of the six-membered NHC in **3** to assist N−H bond activation, accepting the proton at the carbene carbon atom, opens up a new page in the chemistry of this versatile family of compounds that have found widespread applications as ancillary ligands.

Keywords: ammonia · bond activation · N-heterocyclic carbenes · nickel · N ligands

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