Reversible Gas-Solid Ammonia N–H Bond Activation Mediated by an Organopalladium Complex

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ABSTRACT: N–H bond activation of gaseous ammonia is achieved at room temperature in a reversible solvent-free reaction using a solid dicyclopalladated azobenzene complex. Monitoring of the gas-solid reaction in real-time by in situ solid-state Raman spectroscopy enabled a detailed insight into the stepwise activation pathway proceeding to the final amido complex via a stable diammine intermediate. Gas-solid synthesis allowed for isolation and subsequent structural characterization of the intermediate and the final amido product, which presents the first dipalladated complex with the Pd$^{	ext{II}}$-(μ-NH$_2$)-Pd$^{	ext{II}}$ bridge. Gas-solid reaction is readily followed via color changes associated with conformational switching of the palladated azobenzene backbone. The reaction proceeds analogously in solution and has been characterized by UV-vis and NMR spectroscopies showing the same stepwise route to the amido complex. Combining the experimental data with DFT calculations we propose a stepwise mechanism of this heterolytic N–H bond activation assisted by exogenous ammonia.

INTRODUCTION

Metal-mediated N–H bond activation is studied as the first step on a route to catalytic transformation of inexpensive ammonia or amines into more precious nitrogen-containing compounds. Ammonia activation is hindered by the strong ammonia N–H bond and, in case of late-transition metals, preferential formation of ammine Werner-like adducts over amido complexes. Although amido species have an important role in catalytic reactions often performed with palladium catalysts in solution, synthetic and structural reports on palladium amido complexes are limited.

Preparation of metal complexes with ammonia and N–H bond activation are usually carried out in solution. Exploiting the solid-state techniques, such as accelerated aging (also known as vapor digestion) and mechanochemical milling, or even simpler gas-solid approach for reactions with ammonia is limited and thus far has yielded only ammine adducts. Controllable and reversible conversion of the ammine complex into the amido species, relevant in catalysis, is seldom observed in solution and has never been characterized in the solid state.

Widely accepted N–H bond activation routes, either metal-mediated or promoted by organic compounds, can be divided into two major groups: one with homolytic and the other with heterolytic cleavage of the N–H bond. Homolytic N–H bond cleavage yields amido and hydrido groups and results in oxidative addition of these ligands to the same atom that is changing its oxidation state. On the other hand, heterolytic cleavage of the N–H bond results in deprotonation of the ammonia either with an external base, or through metal-ligand cooperation. Deprotonation with the base is generally not reversible, sometimes requires a strong base (like sodium amides or alkoxides) and often leads to the net loss of the proton from the metal catalyst. This hampers the catalytic reaction resulting in poor reaction yields.

Cyclopalladated compounds are common intermediates in palladium-catalyzed reactions. These compounds, widely applied in areas from materials science to organic synthesis, are mostly prepared in solution using organic solvents. Following the green chemistry trends, our recent efforts have been oriented towards developing rapid and environmentally-friendly methods for synthesis of cyclopalladated compounds. In this context, solid-state
techniques have been employed for the C–H bond activation by palladium(II) acetate and ligand exchange in dicyclopalladated complexes showing the potential of these solvent-free methods as simple yet rapid and powerful means for the synthesis of organometallic compounds. These initial reports have been extended to systems and solid-state catalytic processes mediated by other transition metals.  

Here we report a unique reversible solvent-free activation of ammonia N–H bond conducted at room temperature in a reaction of gaseous ammonia with a solid dicyclopalladated azobenzene 1 (Figure 1). Solid-state synthesis allowed for isolation of the reaction intermediate, a diammine complex 2, and the amido product 3. Both have been fully structurally and spectroscopically characterized. Splitting of the ammonia N–H bond in the intermediate 2 yields a unique dipalladated amido complex 3 with a Pd₃(μ-Cl)(μ-NH₂)₃-Pd₃ bridge (Figure 2). In situ solid-state Raman monitoring shows that gas-solid reaction is stepwise, proceeding over the diammine intermediate 2. UV-vis kinetic data suggest an analogous reaction pathway in solution. Activation is reversible and can be tuned by ammonia and chloride concentrations. DFT calculations have rationalized the experimental data and suggested a metal-mediated heterolytic N–H bond cleavage assisted by exogenous ammonia. This study reveals a unique palladium amido compound that in spite of its formation in situ, the complex is efficiently isolated allowing for isolation of the reaction intermediate, a diammine complex 2 and amido product 3.

**Figure 1.** Gas-solid reaction of dicyclopalladated azobenzene (1) with ammonia.

**Figure 2.** Reaction of 2 with ammonia is accompanied by (a) structural switching from planar to bridged geometry; giving 3 whose crystal structure contains (b) chloride in two special positions involved in N–H–Cl interactions.
RESULTS AND DISCUSSION

Synthesis. Following a traditional approach, we have initially conducted reaction of the dicyclopalladated complex 1 with ammonia in solution. The solution rapidly changes color from orange to yellow. However, all attempts to isolate a product have resulted in poor yields of the obtained solid, which was a mixture of ammine and amido complexes.

At this point, we have turned to solvent-free methods and employed gas-solid reaction of solid reactant 1 in dry ammonia at room temperature. In a matter of minutes, the brown-red solid 1 changes to dark green diammine solid 2 that converts to the red amido product 3 in 1 to 12 hours depending on the layer thickness of the solid reactant (10-150 mg of solid in a vessel with a 2 cm diameter). The product 3 has been isolated by washing with a small amount of diluted aqueous ammonia. Apart from the gas-solid reaction using 1 and dry ammonia, 3 can be isolated also from the gas-solid reaction in moist ammonia at room temperature (Figure S1). PXRD confirmed that the by-product, ammonium chloride, is not present in the isolated product. If the complex 3 is not washed after its removal from the ammonia atmosphere, ammonia loss induces back-formation of 2 showing ready reversibility of the activation in the solid state.

Ammonium chloride originates from the reaction of ammonia present in excess with the HCl arising from the activation. It is interesting to note, that the red-ochre solid 3 in HCl vapor turns brown in matter of minutes and after 12 hours is orange. 1H NMR spectrum of the final reaction mixture in DMSO-d<sub>6</sub> shows signals of the azobenzene ligand, PhN=NPh (Ph = phenyl), indicating that HCl destroys the dipalladated complex. No black precipitate is observed in solution suggesting that Pd remains in a soluble form most likely as chloropalladate(II) species. Thus, an important role of ammonia excess during activation is to preserve the dipalladated core by removing HCl as ammonium chloride.

Role of the dipalladated core for N–H activation has been tested using mononyclopalladated azobenzene. This orange compound exposed to ammonia yields a stable yellow ammine complex. The N–H bond activation has not been observed even in large excess of NH<sub>3</sub> both in solution and in the solid state. This suggests an important role of the dipalladated system with two closely-positioned metal centers bonded to the same flexible ligand, azobenzene, working together to capture nascent amido anion in the Pd<sup>III</sup>-(μ-NH<sub>3</sub>)<sup>+</sup>-Pd<sup>III</sup> bridge.

Structural characterization. Once isolated, complexes 2 and 3 are air-stable crystalline solids that have been fully structurally characterized by powder X-ray diffraction (PXRD) (Table S1, Figures 3 and S3-S14). The determined planar molecular structure of 2 confirmed the isomerisation in the first metal coordination sphere after NH<sub>3</sub> bonding and positioning of chlorides in trans position to ortho phenyl carbons, in accordance with the trans choice concept and higher coordination affinity of Pd toward N-donor than O-donor ligands (Figures 1 and 2a).

![Figure 3](image-url)

Figure 3. a) Molecular structure and Rietveld plot for a) 2 and b) 3. High-angle part of the pattern is enlarged to reveal more detail. Sample 2 contained small amount of an unidentified impurity, two low-angle peaks of which are designated with black circles. Chloride of 3 that is positioned in two crystallographic special positions and hydrogen atoms (except for the amido group) are omitted for clarity. Symmetry operator i is [-1-x, 1-y, 3-z].
For the structure of complex 2, the symmetry and unit cell volume suggested that half of the molecule should be in the asymmetric unit which was included in simulated annealing (SA) with one chlorine atom and one ammonia molecule refining freely. Final Rietveld plot is shown on Figure 3a. The crystal structure of 2 is stabilized by N–H–Cl hydrogen bonds (Figures S4-S6). Packing in 2 viewed almost along ac diagonal shows one-dimensional infinite zig-zag chain of molecules assembled via N–H–Cl hydrogen bonds. The chains are further connected by N–H–Cl bonds to form a layered structure (Figure S5).

In addition to being a stable amido complex, compound 3 is remarkable as the first monomeric compound with a structurally characterized Pd\(_{\text{II}}\)-(μ-NH\(_2\))\(_3\)-Pd\(_{\text{II}}\) bridge that also features the bridging dipalladated azobenzene ligand with two almost perpendicular square-planar coordinate planes analogous to those in Pd\(_{\text{II}}\)-(μ-Cl)-Pd\(_{\text{II}}\) complexes\(^{16,18}\) (Figure 2 and Table S2). The amido motif is similar to previously reported mixed-metal amido bridges. Chloride is located in two different special crystallographic positions in the vicinity of NH\(_2\) ligands and is involved in several H-bonding interactions with the amido group and NH\(_3\) (Figure 2b). Two NH\(_2\) ligands on the same Pd center found in trans position to the phenyl carbon or amido group are expected to be weakly coordinated due to the trans influence.

For the structure solution of complex 3, we have found by SA, which included the torsion angle around the azo group, that both palladium atoms are on the same side of the azobenzene fragment. This is confirmed by the Fourier map calculated using observed reflection intensities (Figure S7). SA also found positions of two independent chlorine atoms. Both are not coordinated to palladium and lie on centers of symmetry satisfying charge neutrality. Occupancies of ammonia molecules refined below full occupancy of 1 (Figure S8). We do not exclude the possibility that an exchange between ammonia molecules and chlorides could be taking place in the crystals. Final refinement of the crystal structure of 3, which was performed using restraints on bond distances and angles as well as planarity restraints, led to a featureless difference Fourier map (Figure S9) and a satisfactory agreement between the observed and calculated patterns (Figure 3b).

Crystal packing of 3 shows columns of molecules stabilized by N–H–Cl hydrogen bonds. The columns are further connected along b-axis by N–H–Cl interactions (Figures S1-S3).

Described molecular structures show that the activation which readily occurs both in solid state and in solution includes cleavage of the strong ammonia N–H bond as well as one Pd–N bond with the azobenzene accompanied by rotation of the palladated phenyl group (Figure 2a). This ammonia-induced structural switching places both Pd centers on the same side of the azobenzene ligand. Described substantial alterations in geometry of the azobenzene ligand and coordination environment around Pd centers are associated with the observed color change of the dipalladated complexes 1 and 2 to red in presence of ammonia.

**Solid-state Raman spectra and monitoring.** Ex situ Raman spectra of the reactant and isolated products have been assigned using DFT results and literature data\(^{29}\) and agree with their molecular structures (Figure S15). Spectra of pure planar complexes 1 and 2 are similar and contain bands at 1225 (ν(C–N\(_{\text{amido}}\)) and 1308 (ν(N=N)) cm\(^{-1}\) which agree with a highly delocalized dicyclopalladated azobenzene core. In spectrum of the amido complex 3 bands found at 1196 (ν(C–N\(_{\text{amido}}\)) and 1380 (ν(N=N)) cm\(^{-1}\) are shifted to lower and higher energies, respectively, comparing to the planar complex 2 indicating only one five-membered cyclopalladated ring. Similar observations were obtained for mono- and dicyclopalladated azobenzene acetates.\(^{17}\)

Solid-state N–H activation has been studied by modified in situ solid-state Raman technique, developed recently for mechanistic studies of mechanochemical reactions and additive effects.\(^{17a,30}\) Real-time monitoring (Figure 4) shows that the DMF/NH\(_3\) exchange in 1 occurs in less than 3 minutes. Rapid formation of 2 is followed by its direct transformation to 3 without other observable intermediate. Raman band of 2 at 1308 cm\(^{-1}\) gradually loses intensity whereas simultaneously the band of 3 at 1380 cm\(^{-1}\) increases in intensity. In 90 minutes complex 2 is completely converted into the red amido product 3 which is stable in ammonia vapor, but reverts back to 2 in around 25 minutes if the reaction vessel is unsealed and ammonia vapor is removed. After the vessel is sealed again, 2 transforms to 3 and the cycle can be repeated with reaction time close to the first activation-deactivation cycle. Reverse reaction can be prevented by washing the bulk amido product with diluted aqueous ammonia to remove the ammonium chloride by-product.

**Spectroscopic characterization.** Spectroscopic characterization of complexes 2 and 3 in solution suggests that planar and amido-bridged dipalladated core of 2 and 3, respectively, are maintained in solution (Table S3). We note that two DMF ligands in the complex 1 exchange with DMSO upon dissolution in DMSO giving [Pd\(_2\)Cl\(_2\)(L–2H)(O–DMSO)\(_2\)] (1').\(^{29}\) H NMR spectrum of the diammine...
intermediate \(2 \) (Figure 5b) shows marked differences with regard to the spectrum of the dicyclopalladated reactant \(1 \) (Figure 5a).\(^{1,20}\) Indicative broadening and shifts for protons located in the neighborhood of Pd centers, downfield for H-6 (\(\Delta \delta \approx 1.7 \) ppm) and upfield for H-3 (\(\Delta \delta \approx 1.5 \) ppm), suggest that H-6 is positioned close and H-3 is away from the coordinated chlorides which is in agreement with structural data. Coordinated ammonia ligands give one broad \(^1\)H NMR signal at \(\delta \approx 3.8 \) ppm (Figure S17). \(^1\)H NMR spectrum of the amido complex \(3 \) (Figure 5c) shows marked differences with regard to the spectrum of the dicyclopalladated diammine intermediate \(2 \) (Figure 5b). The spectrum contains two doublets at \(\delta \approx 0.94 \) and \(-0.40 \) ppm assigned to amido protons according to the literature data.\(^{5,9,12}\) Eight azobenzene protons appear in distinct positions confirming that the symmetry of the dipalladated azobenzene core is broken upon activation. Significant upfield shift of proton H-6 (\(\Delta \delta \approx 1.55 \) ppm) if compared to the H-6 shift of complex \(2 \) suggests that the environment of this proton is significantly changed which is attributed to loss of the interaction with the coordinated chloride in \(2 \). Three broad singlets in the \(\delta \approx 2-4 \) ppm region of \(^1\)H NMR spectrum of \(3 \) suggest three distinct ammonia ligands (Figure S7). H/D exchange in DMSO-\(d_6\) for amido protons is slower than for ammonia ligands and is complete in about three days whereas ammonia ligands are exchanged in matter of minutes.

**Figure 5.** Selected parts of \(^1\)H NMR spectra of \(1 \) in DMSO-\(d_6\) a) without NH\(_2\)OH, and upon addition of b) ca. 2 \(\mu\)L of NH\(_2\)OH (2), and c) ca. 5 \(\mu\)L of NH\(_2\)OH (3); d) \(^1\)H spectrum of the sample shown in (c) after three weeks (2); e) \(^1\)H spectrum of the sample shown in (d) upon addition of ca. 1 \(\mu\)L of NH\(_2\)OH (regenerated 3).

UV-vis spectrum of 3 in DMSO shows a maximum at 365 nm (Figure S9). Band is blue-shifted in comparison to the bands of the planar dicyclopalladated complex \(1 \) (404 nm).\(^{20}\) This kind of shift has been previously described for Cl-bridged dipalladated complexes\(^{10,28}\) and supports isomerization of a planar complex to a bridged molecular structure with two metals on the same side of the azobenzene ligand.

**UV-vis kinetic study.** Ammonia N-H bond activation by \(1 \) in solution has been studied by NMR (Figure 5) and UV-vis (Figure 6) spectrosocopies. After addition of aqueous ammonia, dicyclopalladated reactant in DMSO-\(d_6\) shows \(^1\)H signals of aromatic protons in the isomerized planar diammine intermediate \(2 \) at about \(\delta \approx 9.5 \) ppm. These signals disappear and signals of the amido complex \(3 \) simultaneously appear upon further addition of NH\(_2\)OH (Figure 5). No other intermediates could be detected by \(^1\)H NMR. This nicely correlates with the UV-vis spectroscopic data that show that the reaction of \(1 \) with ammonia in DMSO has to be followed by stopped-flow UV-vis spectroscopy. The first fast ligand exchange of DMSO in \(1 \) to NH\(_2\)H in \(2 \) is complete before the first measurements could be made. This is further corroborated by time-resolved UV-vis spectral data analysis that suggests that only two absorbing species (2 and 3) have been observed during data acquisition. Fast diammine formation is followed by the activation step for which the observed pseudo-first-order rate constant \((k_{obs}(1))\) is linearly dependent on the ammonia concentration with a small non-zero intercept (Figure 6). If both NH\(_2\)Cl and NH\(_2\)OH are added in excess to the solution of \(1 \), increasing the NH\(_2\)Cl/NH\(_2\)OH molar ratio gradually blocks the forward reaction (Figure S23).

![Figure 6](image)

Reversibility of the N–H activation relevant for the potential application of the studied palladated azobenzenes has been confirmed in solution by NMR spectra of the in situ formed 3 in ammonia-rich DMSO-\(d_6\) (Figure 5). If ammonia is allowed to gradually evaporate from this solution, \(^1\)H spectrum shows full conversion of 3 into 2. Upon addition of NH\(_2\)OH, \(^1\)H spectrum shows signals of the regenerated amido complex.

UV-vis kinetics for the reaction of 3 with NH\(_2\)Cl in DMSO (Figure 7) shows that the observed pseudo-first-order rate constant of the conversion of 3 to the ammine complex \((k_{obs}(2))\) is directly proportional to concentration of the added NH\(_2\)Cl, but there is a significant intercept \((k')\) indicating that the back-reaction occurs even without the chlorides but is slow.
Computational study. Experimental data suggest that the described N–H bond activation can be classified as a metal-mediated heterolytic process. Hydrodor species were not observed in 1H NMR spectra of the complex 1 in the presence of ammonia. Moreover, 1H spectra stayed nicely resolved during the reaction suggesting no detectable paramagnetic Pd species. These data disfavor a metal-mediated homolytic N–H bond cleavage of ammonia as the operating mechanism. Metal-ligand cooperation mechanism can also be excluded as the spectroscopic and structural data showed no change of the azobenzene structure during reaction except the loss of planarity by rotation of one phenyl ring (Figure 2a). Thus, heterolytic cleavage of ammonia has been considered further and studied in detail using DFT calculations. The computational study revealed that three reaction steps, previously reported for N–H bond activation by various metals, are needed for conversion of the complex 1 into the amido product 3: (i) the coordination of additional ammonia ligand(s), (ii) chloride elimination, and (iii) the N–H bond cleavage.

Solid-state Raman monitoring and UV-vis data in solution have shown that the first step in the studied reaction with ammonia is the exchange of both weakly bound O-ligands from the planar dicyclopalladated azobenzene, i.e. [Pd3Cl4(L–2H)(O–DMF)2] (L = azobenzene) in the solid state or [Pd3Cl4(L–2H)(O–DMF)2] in DMSO solution, by two ammonia ligands. According to DFT results, each DMSO/NH3 exchange stabilizes the dicyclopalladated complex by ca. 20 kJ mol−1 (Scheme 1) and yields the planar diammine complex 2. Calculations support the experimental data and show that the most stable [Pd3Cl4(L–2H)(NH3)2] species has ammonia ligands positioned trans to azo nitrogens (Figure S28). The most stable Cl-bridged species [Pd3Cl4(μ–Cl)(L–2H)(NH3)2], similar to previously described Cl-bridged dipalladated azobenzenes, is 12.6 kJ mol−1 less stable than the complex 2 and is not expected to occur.

Activation starts with the neutral diammine complex 2 [Pd3Cl4(L–2H)(NH3)2] when an additional ammonia ligand coordinates to a metal center in planar reactant R1N via a trigonal-bipyramidal transition state TS1N (step i, Figure 8 and S30). This process requires 28.4 kJ mol−1. Introducing the fifth ligand at the metal center induces breaking of one Pd–N(azo) bond and rotation of the Pd-phenyl part resulting in P1N with two Pd centers on the same side of the azobenzene ligand. In this intramolecular rotation, one NH ligand at Pd(2) is positioned close to the chloride weakly coordinated to Pd(1) center due to trans influence of the phenyl carbon. These geometry changes are also evident from the Wiberg indices calculated for Pd(2)–N(azo) bond which decreases from 0.43 in R1N through 0.33 in TS1N to 0.27 in P1N, whereas the indices for the Pd(2) bond to the incoming NH ligand increase from 0.03 through 0.27 to 0.44 (Table S7). Calculations show that after a small structural rearrangement of P1N to R2N, the coordinated chloride at Pd(1) is easily eliminated in the next step giving P2N. The energy barrier for the step ii is quite low. Transition state associated with this process requires 14.2 kJ mol−1. At this point, planarity of the azobenzene ligand is almost restored (Figure S30). The NH3 ligand at Pd(2) in P2N is positioned closer to Pd(i), H-bonded to the uncoordinated chloride ion and thus ready for the chloride-assisted N–H bond activation (step iii). Breaking of the N–H bond occurs simultaneously with the formation of an unsymmetrical N–H bond activation (step iii). The N–H bond in P2N is positioned closer to Pd(i), H-bonded to the uncoordinated chloride ion and thus ready for the chloride-assisted N–H bond activation (step iii). The energy barrier for this reaction is 14.2 kJ mol−1. At this point, planarity of the azobenzene ligand is almost restored (Figure S30). The NH3 ligand at Pd(2) in P2N is positioned closer to Pd(i), H-bonded to the uncoordinated chloride ion and thus ready for the chloride-assisted N–H bond activation (step iii).
We also explored the reaction starting with the cationic triammine reactant \([\text{Pd}_2\text{Cl}(\text{L}-2\text{H})(\text{NH}_3)_3]^+\) which might also be engaged in the activation process. This species could originate from the complex \(2\) as each chloride in \(2\) is loosely bound. The experimental Pd–Cl bond length is 2.44 Å. This is considerably longer than Pd–Cl bonds in dicyclopalladated azobenzenes in which the chloride is in \textit{trans} position to the azo nitrogen that have bond lengths around 2.30 Å.\(^9\) Wiberg indices for the Pd–Cl bonds of 0.62 and 0.46 in \(1\) and \(2\), respectively, support these observations (Table S5). Calculated species for the reaction route from \([\text{Pd}_2\text{Cl}(\text{L}-2\text{H})(\text{NH}_3)_3]^+\) are analogous to those presented in Figure 8 but have ammonia ligand instead of the chloride on Pd(2) in \textit{trans} position to phenyl carbon (Figure S33). Calculations show that three activation steps require 26.1, 32.8 and 122.5 kJ mol\(^{-1}\) (Figure S32a) revealing a considerably higher energy barrier for the chloride elimination step (step ii) from the cationic species than from the neutral species \(R_2\text{a}_N\) (14.2 kJ mol\(^{-1}\)). The difference could be rationalized by more energy-demanding charge separation in the cationic reactant. This also suggests that the chloride elimination from the neutral complex might be prevailing.

Described routes could not rationalize the observed reaction rates as it displays high activation barrier for the N–H bond cleavage (step iii) and low stability of the amido product. At this point, we have turned to other available species that could assist the activation. The proton originating from the N–H bond cleavage is most likely stabilized by basic ammonia molecule(s) rather than the solvent or water. Thus, we employed external ammonia molecules aiding the chloride release process (step ii) and the N–H bond activation (step iii). Two reaction paths with analogous geometries of the involved neutral and cationic species are proposed (Figure 9, S31 and S34). Calculated free energies of activation for the chloride loss from \(R_2\text{a}_N\) (4.4 kJ mol\(^{-1}\)) and \(R_2\text{a}_C\) (38.5 kJ mol\(^{-1}\)) indicate that the reaction most likely proceeds from \(R_2\text{a}_N\). The product of the release step \((P_2\text{a}_N)\) which has the chloride coordinated \textit{trans} to the phenyl carbon is close in energy to its analog that has ammonia ligand at this place \((P_2\text{a}_C, \text{Figure 9})\). Both have one NH\(_3\) molecule positioned between two Pd atoms ready for the activation step analogous to the previously described reaction (Figure 8). Species that will react in the step iii, \(R_3\text{a}_N\) or \(R_3\text{a}_C\), are formed after a small rearrangement of non-coordinated ammonia and chlorides in \(P_2\text{a}_N\) or \(P_2\text{a}_C\). The N–H bond activation requires 71.8 and 59.2 kJ mol\(^{-1}\) for \(R_3\text{a}_N\) or \(R_3\text{a}_C\), respectively, suggesting that the more stable reactant \(R_3\text{a}_C\) undergoes the N–H cleavage via the less energy-demanding route. We note that calculations exclude the complex \(3\) with a terminal amido group as the cation present in the isolated complex \(3\), \([\text{Pd}_2(\mu-\text{NH}_2)(\text{L}-2\text{H})(\text{NH}_3)_3]^+\), is by 66.5 kJ mol\(^{-1}\) more stable than its planar isomer, \([\text{Pd}_2(\text{NH}_2)(\text{L}-2\text{H})(\text{NH}_3)_3]^+\) (Figure S29). Wiberg indices for three Pd–N bonds of ammonia to Pd centers, i.e. 0.42 for NH\(_3\) at Pd(1) bonded \textit{trans} to azo nitrogen, 0.39 for NH\(_3\) at Pd(2) bonded \textit{trans} to amido bridge and 0.32 for NH\(_3\) at Pd(2) bonded \textit{trans} to phenyl carbon (Table S6), rationalize the structural data which give occupancies lower than one for two NH\(_3\) ligands at Pd(2) center.

![Figure 9](image_url). Ammonia-assisted chloride elimination (step ii) and N–H bond activation (step iii) in \([\text{Pd}_2\text{Cl}(\text{L}-2\text{H})(\text{NH}_3)_3]^+\) and \([\text{Pd}_2\text{Cl}(\text{L}-2\text{H})(\text{NH}_3)_3]^+\) species. Free energies are reported relative to the free energy of \(R_2\text{a}_N\). Azobenzene protons are omitted for clarity.
Furthermore, Wiberg bond indices suggest that the facile ammonia-assisted chloride elimination (step ii, Figure 9) and the N–H bond activation (step iii) induce only a slight change for the metal-ligand bonds apart from Pd(1)–Cl(1) and Pd(1)–N(amido) bonds directly involved in the reaction (Table S8). The Pd(1)…Pd(2) bond index slightly increases in the step ii as a consequence of two metals coming closer whereas the opposite happens during the step iii. Decrease of the indices for Pd(1)–Cl(1) from 0.47 and 0.46 in R2aN or R2Ac to zero (i.e. 0.05 and 0.01) in P2aN or P2Ac confirms the chloride exit from the Pd coordination sphere in step ii. Indices for the Pd(1)–N(amido) bond increase from 0.03 to 0.40 in step iii indicating formation of the PdII(μ-NH3)–PdII bridge. Only small changes are observed for the remainder of the coordinate bonds.

Computational results agree with the presented kinetic data that show a fast reaction at room temperature with only one detectable reaction step. Comparison of the free energies of activation for three steps, ca. 28, 5 and 60 kJ mol⁻¹, shows that step iii, the N–H bond cleavage, is the rate-determining step. Computational results also suggest that reactants entering the first two steps, i.e. ammonia coordination and chloride elimination, most likely have two chlorides coordinated at two metal centers, whereas the last and rate-determining step might prefer the ammonia ligand coordinated trans to the phenyl carbon yielding the complex 3 and ammonium chloride as observed experimentally. Furthermore, rather low calculated stability of the amido product could rationalize the reversibility of the activation.

Much lower activation energy and greater product stability of the ammonia-assisted mechanism depend on the H-bonding interaction network involving chlorides and ammonia around the reaction site. This effect might be even more pronounced if more ammonia or even solvent molecules, DMSO or water, would be involved. Thus, a role of the ammonia excess, which has been found crucial for the reaction, can be rationalized by the presented theoretical study. Calculations suggest that ammonia loss from the reaction mixture would likely destabilize the amido species and enable a back-reaction that ultimately leads to the complex 2 in accordance with the experimental observations. Taking the presented results in account, we propose several roles for the ammonia which are necessary for a successful activation: (i) shift of two coordinated chlorides into trans position to the phenyl carbon as a consequence of two DMSO/NH3 exchanges in 1 forming 2, (ii) breaking the planar structure of 2 by coordination of additional ammonia, (iii) assisting the N–H bond cleavage by capturing the released proton, and (iv) stabilization of the amido product via participation in numerous interactions at the reaction site.

CONCLUSION

We have successfully performed the gas-solid reaction for the first Pd-mediated gas-solid activation of the strong ammonia N–H bond. Reversible activation by dicyclopalladated azobenzenes via the diammine intermediate at room temperature yields the monomeric amido complex with the PdII(μ-NH3)–PdII bridge. This reaction course has been confirmed both in the solid state by in situ Raman monitoring as well as in solution by UV-vis and NMR spectroscopies. According to experimental and computational results, the described reaction is a heterolytic metal-mediated N–H bond activation assisted by exogenous ammonia. The activation is facile and easily followed by a naked eye that makes it highly applicable in a common laboratory. We are currently pursuing this ammonia activation reaction for preparation of organic amines. Our kinetic and mechanistic study of the reversible ammonia N–H bond cleavage by the cyclopalladated complex should lead to better understanding of behavior of palladium compounds in presence of ammonia highly relevant in catalysis. This report opens a new course in the application of solid-state methods for important metal-mediated reactions, many of which are widely applied and yield valuable compounds from readily accessible materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information including experimental and computational details, as well as additional spectra and coordinates of calculated species is available free of charge on the ACS Publications Website at DOI: ___________. CCDC 1510288 and 1510289 contain the supplementary crystallographic data for this paper.

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Notes

The authors declare no competing financial interests.

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