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Oxidative Addition of Ammonia to Form a Stable Monomeric Amido Hydride Complex

Jing Zhao,[1] Alan S. Goldman,[2] John F. Hartwig[1]*

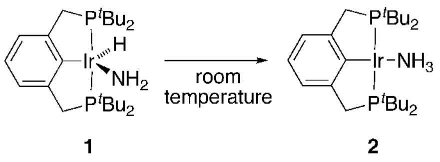
The insertion of an iridium complex into an N-H bond in ammonia leads to a stable monomeric amido hydride complex in solution at room temperature. This reaction advances the transition-metal coordination chemistry of ammonia beyond its role for more than a century as an ancillary ligand. The precursor for this insertion reaction is an iridium(I) olefin complex with an aliphatic ligand containing one carbon and two phosphorus donor atoms. Kinetic and isotopic labeling studies indicate that olefin dissociates to give a 14-electron iridium(I) fragment, which then reacts with ammonia. This cleavage of the N-H bond under neutral conditions provides a foundation on which to develop future mild catalytic transformations of ammonia, such as olefin hydroamination and arene oxidative amination.

The field of coordination chemistry began when Alfred Werner isolated and elucidated the structures of ammonia complexes of transition metals in the late 19th century (*1*). To this day, the reactions of ammonia with most transition-metal complexes generate simple Lewis acid-base complexes similar to Werner's. In contrast to this simple binding of ammonia, transition-metal complexes react with many other small molecules by inserting into otherwise generally unreactive X-H bonds. This insertion process, termed oxidative addition, is useful for chemical synthesis, because it enables the catalysis of reactions of H_2 (hydrogenation and hydroformylation), $H\text{-}SiR_3$ (hydrosilation), $H\text{-}BR_2$ (hydroboration), and H-C (hydroarylation and alkane dehydrogenation) that yield products ranging from chemical feedstocks to pharmaceuticals. Similarly, oxidative addition of the N-H bond of ammonia, if achieved, would have the potential to initiate valuable new catalytic reactions. For example, the catalytic addition of ammonia to olefins and the coupling of ammonia with arenes are considered to be two of the ten greatest current challenges for catalytic chemistry (*2*).

To accomplish the oxidative addition of ammonia, one must alter its classical transition-metal chemistry. An amido hydride complex formed by cleavage of the N-H bond must be favored over the isomeric ammonia coordination complexes of Werner (Fig. 1). Although no terminal amido complexes have previously been prepared by the oxidative addition of ammonia (*3–5*), several terminal amido complexes of the late transition metals have been prepared by other routes during the past several years (*6–9*). The reaction chemistry of these terminal amido complexes is beginning to unfold and, thus far, encompasses reactions with electrophiles, weak acids, nonpolar reagents such as hydrogen, and unsaturated reagents such as CO (*9–13*). Development of the reaction chemistry of these amido complexes, in combination with the ability to prepare these complexes directly from ammonia under neutral conditions, should give rise to new catalytic processes. We report making a long stride toward this end: the identification of an iridium complex that undergoes oxidative addition of ammonia rapidly at room temperature to form a monomeric terminal amido hydride complex.

To prepare a complex that would insert into the N-H bond of ammonia, we built upon existing iridium chemistry. Iridium complexes with tridentate "pincer" ligands can insert into a variety of X-H bonds under mild conditions (*14*, *15*). In past experiments, we showed that the hydridoiridium amido complex **1**, containing an aromatic pincer ligand, rapidly forms the N-H bond in ammonia complex **2** by reductive elimination, the opposite of oxidative addition (Scheme 1) (*16*). From these observations, we inferred that an appropriate modification of iridium complexes with pincer ligands might tip the thermodynamic balance from rapid formation to rapid cleavage of the N-H bond in ammonia.

Although many factors control the rates and thermodynamics of oxidative addition (*17*), the thermodynamics of oxidative addition tend to be favored by increasing electron density at the metal center. We reasoned that a pincer ligand with an aliphatic backbone (*18*) would be more electron donating than



Scheme 1.

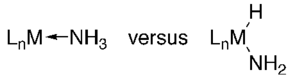
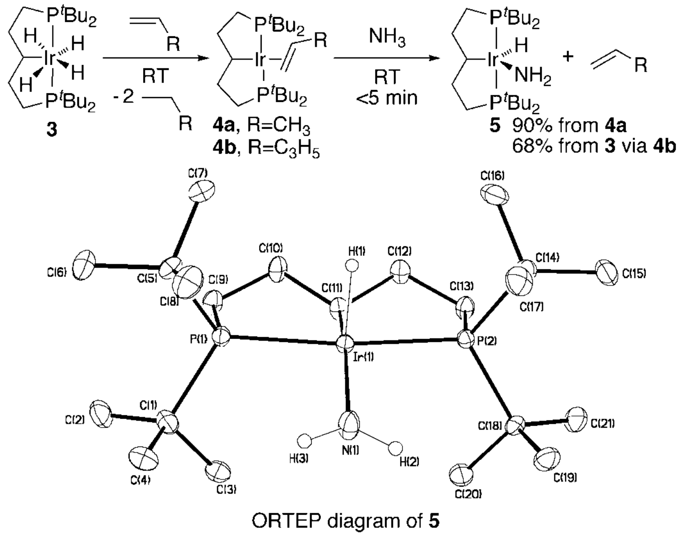


Fig. 1. Ammine versus amido hydride complexes.



Scheme 2.

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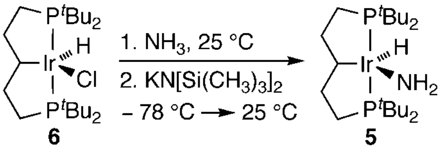
the aromatic ligand in **1** and would, therefore, favor N-H insertion over the coordination of ammonia; the coordination of ammonia would transfer substantial electron density to an already electron-rich metal center. To that end, we treated iridium tetrahydride complex **3** (*19*) with propene and pentene to prepare the olefin complexes **4a** and **4b** (Scheme 2) (*20*).

Treatment of propene complex **4a** with four equivalents of ammonia, at 25°C in cyclohexane, generated the monomeric amido hydride complex **5** in 90% yield within 5 min. Free propene (57%) was observed in the solution phase by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Similarly, addition of ammonia to the pentene complex **4b**, generated in situ from the precursor **4** and pentene, led to the amido hydride **5** in 68% yield for the two-step process.

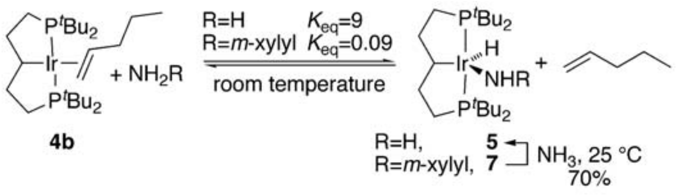
Complex **5** was characterized by standard NMR spectroscopic methods, combustion analysis, and x-ray diffraction. We further confirmed the identity of this amido hydride complex by an independent synthesis (Scheme 3). Reaction of the 16-electron hydrido chloride complex **6** with ammonia, followed by addition of the strong base $KN[Si(CH_3)_3]_2$ to deprotonate the coordinated ammonia and eliminate KCl, generated the 16-electron amido hydride complex **5**.



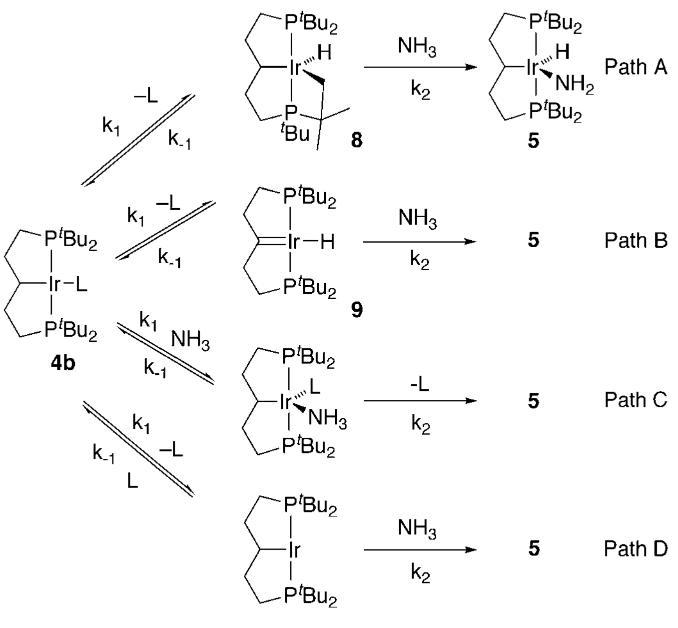
Scheme 3.

X-ray diffraction showed that amido hydride **5** [Oak Ridge thermal ellipsoid plot (ORTEP) diagram in Scheme 2] possesses a geometry between trigonal bipyramidal and square pyramidal. The three angles of the equatorial plane (±estimated standard deviation) are 139.4°(13°) for H-Ir-N, 153.69°(17°) for C-Ir-N, and 66.8°(13°) for C-Ir-H. According to earlier calculations on related iridium complexes (*21*), this geometry results from π bonding between the electron pair on nitrogen and the lowest unoccupied molecular orbital on the metal, which lies in the equatorial plane. The nitrogen in compound **5** could be either cis or trans to the hydrogen on the methine carbon of the ligand backbone. We detected only one isomer by NMR spectroscopy in solution. In the solid state, the nitrogen was cis to this hydrogen.

To investigate the thermodynamics of the oxidative addition, we determined the stability of the amido hydride **5**, relative to the olefin complex **4b**. We combined ammonia, pentene, and the complex **4b** (0.03 M in diethyl ether-d_{10}) in a 15:30:1 ratio. The resulting equilibrium distribution was a 3.9:1 ratio of amido hydride **5** to pentene complex **4b** (Scheme 4) and a 1:2.3 ratio of dissolved ammonia to pentene. Addition of the same ratio of ammonia and pentene to a 0.03 M solution of amido hydride **5** led to the same ratio of **5a** and **4b**. These experiments yield an equilibrium constant of 9 for the conversion of olefin complex **4b** to amido hydride **5**.



Scheme 4.



Scheme 5.

We also compared the oxidative addition of ammonia to **4b** with the oxidative addition of aromatic amines, which are typically more reactive toward cleavage of the N-H bond by transition metals (*22–24*). Like ammonia, 3,5-dimethylaniline underwent rapid oxidative addition to **4a** and **4b** at room temperature (71% from **4a** with an excess of arylamine), in this case to form arylamido hydride **7** (Scheme 4). However, the conversion of the olefin complex to the hydrido arylamide **7** was thermodynamically less favorable than the reaction with ammonia. Despite the lower N-H bond strength and greater acidity of the aromatic amine, the equilibrium constant for the oxidative addition of 3,5-dimethylaniline to **4b** was only 0.09. In accordance with the more favorable oxidative addition of ammonia, the reaction of **7** with ammonia fully consumed the arylamide and generated free 3,5-dimethylaniline and amido hydride **5** in 70% yield (Scheme 4). These results contrast with the typically greater stability of adducts generated from more acidic protic reagents (*25*). The smaller size of the parent amide ligand relative to the arylamido ligand, the greater π donation by the parent amide ligand, or both may account for the unusual stability of **5** relative to that of **7**.

The formation of **5** from the reaction of ammonia with the olefin complexes **4a** and **4b** need not occur by a simple insertion of the iridium into an N-H bond. For example, insertion of iridium(I) into the C-H bonds of alkyl ligands (*26*) and the α elimination from related pincer ligands in related iridium compounds (*27*, *28*) are precedented. If these reactions occur with **4b**, then the overall oxidative addition of ammonia might occur by addition of ammonia's N-H bond across the iridium-carbon single bond in **8** or the iridium-carbon double bond in **9** of Scheme 5. To investigate whether these mechanisms are operating, we treated **4b** with isotopically labeled ammonia-d_3. In the product of this reaction, **5**-d_3, there was no evidence by ^{2}H NMR spectroscopy for the presence of deuterium in the pincer ligand (*29*). We thereby ruled out reaction through potential intermediates **8** and **9**; all data are consistent with insertion of an iridium(I) complex into the N-H bond of ammonia.

Kinetic studies allowed us to distinguish between an associative path C, in which ammonia would react directly with compounds **4a** and **4b**, and a dissociative path D, in which ammonia would react with a 14-electron complex formed after dissociation of olefin (Scheme 5). The rates of decay of the pentene complex **4b** were measured by ^{31}P NMR spectroscopy with varied amounts of olefin and ratios of ammonia to olefin (data and plot are shown in figs. S1 and S2 and table S1). The observable rate constants, k_{obs}, predicted for reaction by associative path C (Eq. 1) and dissociative path D (Eq. 2), were derived with the steady state approximation. For path C, the observed rate constant would be independent of the concentration of olefin, but for path D, a plot of $1/k_{obs}$ versus the ratio of olefin to ammonia is predicted to be linear with a nonzero intercept. The reactions were clearly slower at higher concentrations of olefin, and a plot of $1/k_{obs}$ versus the ratio of olefin to ammonia was found to be linear with a positive slope ($0.20 \times 10^{-4} \pm 0.01 \times 10^{-4}$ s^{-1}) and a nonzero y intercept ($0.65 \times 10^{-4} \pm 0.16 \times 10^{-4}$ s). These data suggest that olefin dissociation is the first step in the reaction, and, if so, the y intercept of this double reciprocal plot would correspond to the inverse of the rate constant for dissociation of olefin.

$$\frac{1}{k_{obs}} = \frac{k_{-1}}{k_1 k_2[\text{ammonia}]} + \frac{1}{k_1[\text{ammonia}]} \quad (1)$$

$$\frac{1}{k_{obs}} = \frac{k_{-1}[\text{pentene}]}{k_1 k_2[\text{ammonia}]} + \frac{1}{k_1} \quad (2)$$

Because substitution reaction of square-planar d^8 complexes typically proceed associatively, and because the reactions could occur by more complex pathways with multiple equilibria preceding N-H bond cleavage, we conducted further experiments to test whether the reaction was initiated by dissociation of olefin. The pentene in complex **4b** is displaced by ethylene to form ethylene complex **4c**. If the reactions of **4b** occur dissociatively, then the rate constants for dissociation of pentene obtained from the reaction of **4b** with ethylene and from the reaction of **4b** with ammonia should be the same.

Consistent with dissociative reactions of **4b**, the reaction of **4b** with ethylene was independent of the concentration of ethylene or 0.03 to 0.3 M added pentene; all reactions occurred with rate constants within 3% of the mean value of 1.6×10^{-3}. Moreover, this mean value is well within experimental error of the value of k_1 (1.5×10^{-3}) measured for the reaction of ammonia with **4b**.

The identification of an iridium complex that undergoes oxidative addition of ammonia and the elucidation of key thermodynamic and mechanistic aspects of the reaction advance our understanding of how to cleave N-H bonds under mild conditions. We anticipate that this understanding will accelerate the development of catalytic chemistry that parallels the existing reactions of hydrogen, hydrocarbons, silanes, and boranes but begins with oxidative addition of the N-H bond of abundant and inexpensive ammonia.

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Materials and Methods
Figs. S1 to S5
Tables S1 to S6
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Efficient Bipedal Robots Based on Passive-Dynamic Walkers

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Passive-dynamic walkers are simple mechanical devices, composed of solid parts connected by joints, that walk stably down a slope. They have no motors or controllers, yet can have remarkably humanlike motions. This suggests that these machines are useful models of human locomotion; however, they cannot walk on level ground. Here we present three robots based on passive-dynamics, with small active power sources substituted for gravity, which can walk on level ground. These robots use less control and less energy than other powered robots, yet walk more naturally, further suggesting the importance of passive-dynamics in human locomotion.

Most researchers study human locomotion by observing people as they walk, measuring joint angles and ground reaction forces (*1*). Our approach is different: We study human locomotion by designing and testing walking machines that we compare to humans in terms of morphology, gait appearance, energy use, and control.

Previous bipedal robots with humanlike forms have demonstrated smooth, versatile motions (*2*–*5*). These impressive robots are based on the mainstream control paradigm, namely, precise joint-angle control. For the study of human walking, this control paradigm is unsatisfactory, because it requires actuators with higher precision and frequen-