

Distinct Thermodynamics for the Formation and Cleavage of N–H Bonds in Aniline and Ammonia. Directly-Observed Reductive Elimination of Ammonia from an Isolated Amido Hydride Complex

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Metal-catalyzed reactions of ammonia or alkylamines that occur by oxidative addition or reductive elimination of N–H bonds are rare.¹ Even examples of stoichiometric oxidative addition or reductive elimination of ammonia or alkylamines are rare.^{2–5} Recently, anti-Markovnikov hydroamination and oxidative amination of vinylarenes with group 9 metal complexes have been reported,⁶ and these reactions could occur by N–H oxidative addition of an amine. To evaluate the potential of N–H activation and elimination to occur during catalytic processes, the relative thermodynamic stabilities and the kinetic barriers to interconversions of late metal amido hydride complexes and late metal amine complexes must be established experimentally.⁷

During the past 20 years, many examples of the formation and cleavage of C–H bonds by late metals have been discovered.^{8,9} Studies on the analogous reactions of N–H bonds with the same metal fragments would provide a context to interpret data on the reactivity of ammonia and amines. (PCP)Ir complexes (PCP = η^3 -C₆H₃-2,6-(CH₂PR₂)₂) readily cleave hydrocarbon C–H bonds,¹⁰ activate the OH bond in water,¹¹ and catalytically dehydrogenate alkanes,¹² alcohols,¹³ amines,^{14,15} ethers, and alkylarenes.¹² Herein we report studies on N–H bond formation and cleavage that have revealed clear differences between the thermodynamics for addition and elimination of ammonia and aniline and that have allowed the first direct observation of reductive elimination of ammonia from a monomeric amido hydride complex.

The reaction of (PCP)IrH₂ with norbornene or *tert*-butylethylene in benzene solvent is known to generate (PCP)Ir, which oxidatively adds C–H bonds to form alkyl and aryl hydride complexes.¹⁰ Reaction of (PCP)IrH₂ and norbornene with 1.2 equiv of aniline in *p*-xylene solvent at room temperature gave the anilide hydride (PCP)IrH(NHPh) (**1a**) in 95% yield by N–H oxidative addition. This product was characterized by standard NMR techniques and X-ray diffraction, as shown in Figure 1. In the ¹H NMR spectrum the hydride was detected as a triplet at –38.21 ppm, and the N–H proton, as a singlet at 4.90 ppm.

In contrast, reaction of (PCP)IrH₂ with norbornene and 2.0 equiv of ammonia at room temperature formed the ammonia complex (PCP)Ir(NH₃) (**2**) in 29% yield by ¹H NMR spectroscopy with an internal standard. The ammonia complex was also characterized by standard NMR methods and X-ray diffraction (Figure 1). In addition, the presence of an ammonia ligand was confirmed by ¹⁵N DEPT NMR spectroscopy. This spectrum contained a quartet at 75.1 ppm (¹J_{NH} = 67.2 Hz).

To determine whether the distinct reactivity of aniline and ammonia resulted from kinetic or thermodynamic factors, we independently synthesized the parent amido hydride (PCP)Ir(H)-

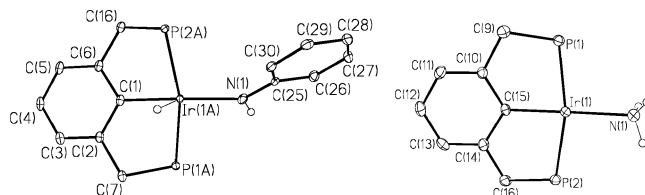
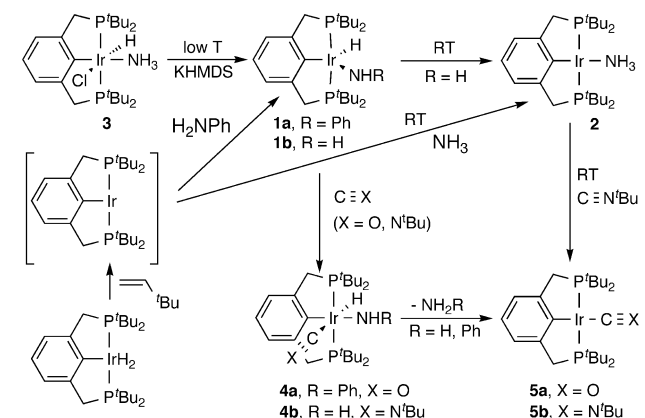


Figure 1. ORTEP diagrams of the products of reactions with “(PCP)Ir” (a) oxidative addition of the aniline N–H bond **1a** (left), (b) addition of ammonia **2** (right). (For clarity, *tert*-butyl groups are omitted).

Scheme 1



(NH₂) (**1b**), as shown in Scheme 1. Treatment of (PCP)Ir(H)(Cl) with ammonia generated the ammonia complex (PCP)Ir(H)(Cl)(NH₃) (**3**). Reaction of this species with 2.0 equiv of KN(SiMe₃)₂ at –78 °C in THF formed **1b** in 100% yield, along with HN(SiMe₃)₂ and KCl (Scheme 1). Amido hydride **1b** was stable below –10 °C. It was, therefore, characterized in THF-*d*₃ at –30 °C. A triplet resonance at δ –26.66 ppm was observed for the hydride in the ¹H NMR spectrum, along with a broad singlet at δ 4.66 ppm for the amide. ¹⁵N NMR DEPT spectroscopy showed a triplet of doublet of triplet resonance at 48.9 ppm (¹J_{NH} = 70.9 Hz, ²J_{NH} = 8.0 Hz, ²J_{NP} = 4.0 Hz).

Warming of amido hydride **1b** to room temperature generated the ammonia complex **2** in 91% yield within 10 min at room temperature by a rare N–H bond-forming reductive elimination of an amido hydride complex. Thus, the formation of **2** instead of **1b** upon reaction of ammonia with the (PCP)Ir intermediate most likely results from a thermodynamic stability of the ammonia complex that is greater than that of amide hydride **1b**. The contrast in stability of the products from the reactions of aniline and ammonia¹⁶ can be rationalized by two factors. The dative bond in an aniline complex should be weaker than that in an ammonia complex because of lower basicity, and an M–N bond in an anilide complex

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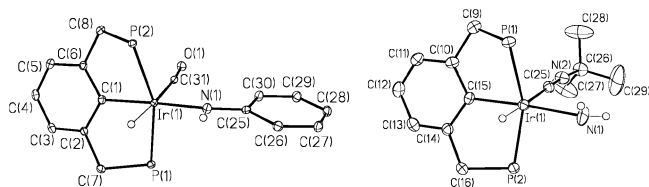


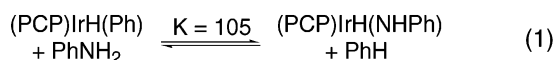
Figure 2. ORTEP diagrams of (PCP)Ir(H)(NHPH)(CO) (**4a**, left) and (PCP)Ir(H)(NH₂)(CN^tBu) (**4b**, right) (*tert*-butyl groups omitted for clarity).

should be stronger (relative to the respective H–N bonds) than the M–N bond in an amido complex because of a greater ionic interaction.¹⁷

Addition of CO to the 16-electron anilide hydride **1a** and amido hydride **1b** gave 18-electron adducts. The CO adduct of **1b** was unstable at room temperature, but addition of ^tBuNC to **1b** formed the isolable 18-electron amido hydride **4b** (Scheme 1) in 56% yield. The hydride of **4b** was observed as a triplet at δ –10.82, and the protons of the NH₂ were observed as a broad singlet at δ –2.39 (–15 °C in THF-*d*₈). The hydride of anilide carbonyl **4a** appeared as a triplet of doublets at δ –7.75, and the NHPH proton appeared as a singlet at δ 1.95 (*p*-xylene-*d*₁₀, 22 °C).

Isocyanide complex **4b** underwent reductive elimination of NH₃ at room temperature, in this case to generate the Ir(I) isocyanide complex **5b** (*t*_{1/2} ≈ 80 min) and free ammonia in 90% yield by ¹H NMR spectroscopy (Scheme 1). The anilide hydride **4a** likewise underwent reductive elimination to give the Ir(I) carbonyl complex, **5a**. Elimination of aniline from **4a** was much slower (*t*_{1/2} ≈ 4 h at 90 °C) than elimination of ammonia from **4b**.

The structures of complexes **4a** and **4b** were determined by X-ray crystallography (Figure 2). A comparison of the solid-state structures of ammonia complex **2** and amide **4b** shows little difference between the length of the dative Ir–N bond in **2** (2.215(5) Å) and that of the covalent Ir–N bond of amide **4b** (2.193(4) Å). The Ir–N bond in the six-coordinate anilide CO adduct **4a** (2.142(2) Å) is slightly shorter than that in **4b**, despite the larger size of the anilide group. The Ir–N bond distance of the five-coordinate anilide **1a**, however, is significantly shorter than the Ir–N distances in the other complexes; two disordered components (88:12) were found with Ir–N bond lengths of 2.082(2) and 2.000(3) Å, respectively. These very short distances may reflect $p\pi-d\pi$ donation¹⁸ in the Ir–N bonding of the 16-electron complex **1a**.



The thermodynamics of addition of the aniline N–H bond to the (PCP)Ir fragment are more favorable than those of addition of arene C–H bonds. Monitoring of the equilibrium in eq 1 by ³¹P NMR spectroscopy at 22 °C showed the value of *K*_{eq} to be 105. Thus, addition of the aniline N–H bond is much more favorable than addition of the benzene C–H bond. The difference between addition of the N–H bond of aniline and the more closely analogous benzylic C–H bond of toluene is even greater; addition of toluene occurs exclusively at the aryl C–H bonds, and reaction of a 0.01 M solution of benzene in mesitylene occurs only at the benzene C–H bond.¹⁰ The preference for N–H over C–H addition to (PCP)Ir is likely due to a stronger ionic component in the Ir–N bond and to $p\pi-d\pi$ bonding.

The rates of the reductive eliminations of aniline from **1a**, and of ammonia from **1b** are much slower than elimination of benzene

from (PCP)IrPhH. The elimination of benzene from (PCP)IrPhH occurs on the NMR time scale, even at –20 °C.¹⁰ Formation of the ammonia complex from the 16-electron amido hydride **1b** required at least 2 h at –10 °C. The anilide complex **1a** showed no evidence of exchange with free aniline on the NMR time scale (¹H NMR, hydride resonance), even at 85 °C, although exchange of the anilide in **1a** with *p*-trifluoromethylaniline occurred at room temperature within several minutes after mixing.

In conclusion, a monomeric iridium terminal amido complex has been prepared, and the reductive elimination of ammonia from this complex has been observed directly. In contrast, aniline adds to the same metal fragment from which ammonia eliminated. The products from N–H addition, especially from addition of aniline, are more stable kinetically and thermodynamically than products of C–H addition to the same (PCP)Ir fragment. Studies designed to elucidate the reactivity, mechanism of addition and elimination, and factors that control the thermodynamics of N-coordination and N–H addition are in progress.

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Supporting Information Available: Preparative procedures and spectroscopic data for new compounds (PDF); crystallographic data for **1a**, **2**, **4a**, **4b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) A Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (c) Cowan, R. L.; Troglor, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750.
- (2) For addition of ammonia to form a bridging amide, see: Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.
- (3) Sussfink, G. *Z. Naturforsch. (B)* **1980**, *35*, 454.
- (4) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972.
- (5) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.
- (6) (a) Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608. (b) Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Herwig, J.; Muller, T. E.; Thiel, O. R. *Chem. Eur. J.* **1999**, *5*, 1306.
- (7) For a theoretical treatment, see: (a) Macgregor, S. A. *Organometallics* **2001**, *20*, 1860. (b) Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 799.
- (8) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
- (9) Crabtree, R. H. *Chem. Commun.* **2001**, 2437.
- (10) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.
- (11) Morales-Morales, D.; Lee, D. W.; Wang, Z. H.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144.
- (12) Jensen, C. M. *Chem. Commun.* **1999**, 2443.
- (13) Morales-Morales, D.; Redon, R.; Wang, Z. H.; Lee, D. W.; Yung, C.; Magnuson, K.; Jensen, C. M. *Can. J. Chem.* **2001**, *79*, 823.
- (14) Gu, X. Q.; Chen, W.; Morales-Morales, D.; Jensen, C. M. *J. Mol. Catal. A: Chem.* **2002**, *189*, 119.
- (15) Zhang, X.; Fried, A.; Knapp, S.; Goldman, A. S. *Chem. Commun.* **2003**, (16), 2060.
- (16) In principle, formation of **1a** instead of the analogue of ammonia complex **2** containing a coordinated arylamine could result from kinetic, rather than thermodynamic, effects, and the aniline analogue of **2** could be more stable than anilide hydride **1a**. However, formation of Lewis acid–base complexes is typically fast; we therefore expect that the aniline analogue of **2** should be kinetically accessible, particularly at temperatures at which **1a** undergoes rapid exchange with anilines. Attempts to prepare the aniline analogue of **2** at –35 °C gave a major product that appears to result from the coordination of aniline and cyclometalation of the aniline phenyl group. Upon warming to room temperature, the complex undergoes conversion to **1a**. This preliminary observation is consistent with the expectation that coordination of the aniline nitrogen lone pair is kinetically facile.
- (17) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J. K.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800.
- (18) Riehl, J. F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729.

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