N−H Activation of Hydrazines by Iridium(I). Double N−H Activation To Form Iridium Aminonitrene Complexes

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Abstract: Iridium(I) complexes of aromatic (PCP) and aliphatic (D^{r}BPP) pincer ligands undergo single cleavage of the N−H bonds of hydrazine derivatives to form hydrazido complexes and geminal double cleavage to form unusual late transition metal aminonitrene complexes. In some cases, the cleavage of the N−N bond in the hydrazine is also observed. Oxidative additions of the N−H bonds of benzophenone hydrazone and 1-aminopiperidine to iridium(I) complexes give the corresponding hydridoiridium(III) hydrazido complexes within minutes. The complex containing an aromatic pincer ligand, (PCP)Ir(H)(NHNC$_5$H$_{10}$), slowly undergoes a second N−H bond cleavage at the α-N−H bond and elimination of hydrogen to generate an aminonitrene complex and dihydrogen in high yield. The reactions of the (PCP)Ir(I) fragment containing an aromatic pincer ligand with methyl-substituted hydrazines form a mixture of aminonitrene complexes, isocyanide iridium(III) dihydride complexes, and ammonia. The latter two products are likely formed by initial oxidative addition of the methyl C−H bond and the subsequent N−N bond cleavage. Reactions of the aminonitrene complex with CO or reagents that undergo oxidative addition (MeI and PhOH) lead to release of the "isodiazine" fragment to give tetrazene and tetrazine derivatives.

The oxidative addition of N−H bonds can lead to new catalytic chemistry,[1] but this reaction has been studied less than the oxidative addition of C−H or O−H bonds. The oxidative addition of amines and ammonia to complexes of late transition metals is rare, particular additions to a single metal center.[2] We recently showed that the iridium(I) complex of an electron-rich D^{r}BPP-pincer ligand undergoes oxidative addition of ammonia to form a monomeric amido hydride complex.[2c] Subsequent studies have led to the oxidative addition of amides and aromatic amines to related pincer complexes of iridium(I),[2d,e] and several groups have recently reported oxidative additions of ammonia to other late-metal systems.[2e,f,3]

α-Elimination of amido complexes by internal or external base is a second type of N−H bond cleavage, and this reaction is a common route by which amido complexes of the early and middle transition elements convert to metal−nitrene complexes.[4] In contrast, analogous α-eliminations of amido complexes of the late transition metals to form nitrene complexes are rare[5] and have been limited to examples triggered by addition of an external base.[5]

Because initial studies on the reactivity of (PCP)Ir(H)(NH$_2$) complexes were dominated by reductive elimination of ammonia,[2b] we began to investigate the oxidative addition of ammonia equivalents that could form more stable products. Our initial studies focused on the reactions of iridium(I) complexes with hydrazines. We show that the oxidative addition of hydrazines to the iridium(I) pincer complex occurs readily and that several products of this oxidative addition undergo a second N−H activation in the form of an α-elimination or abstraction to generate rare low valent, late transition metal aminonitrene or "isodiazene" complexes of the third row.

The oxidative addition of hydrazine derivatives to iridium(I) complexes of aromatic and aliphatic pincer ligands to form hydridoiridium hydrazido complexes **2a**, **2b**, **3a**, and **3b** is shown in Scheme 1. Addition of 1.1 equiv of benzophenone hydrazone to alkene complex **1a** containing an aliphatic pincer ligand, or phenyliridium hydride complex **1b** containing an aromatic pincer ligand, occurred within 5 min at room temperature. This N−H activation reaction occurred exclusively over potential competing C−H activation of the hydrazone aryl groups or N−N bond cleavage. The products of this addition, (D^{r}BPP)Ir(H)(NH−N=CPh$_2$) (**2a**) and (PCP)Ir(H)(NH−N=CPh$_2$) (**2b**), were stable at room temperature and fully characterized. Moreover, addition of 10 equiv of 1-pentene to **2a** or dissolution of **2b** in benzene did not regenerate **1a** or **1b**.

The structures of **2a** and **2b** were determined by X-ray diffraction (Figure 1). The two complexes have similar distorted square-pyramidal structures with an apical hydride. In both cases, the lone pair of the amido nitrogen is oriented to allow π-donation into the empty d-orbital that lies in the plane of the iridium(III) centers containing the ipso carbon, the hydride, and the Ir-bound nitrogen. The Ir−N bond distances in **2a** and **2b** are short (2.018(7) and 2.022(3) Å, respectively), reflecting a partial double-bond character between Ir and N.[2b,6]

Scheme 1. Formation of Hydridoiridium Hydrazido Complexes via N−H Bond Addition
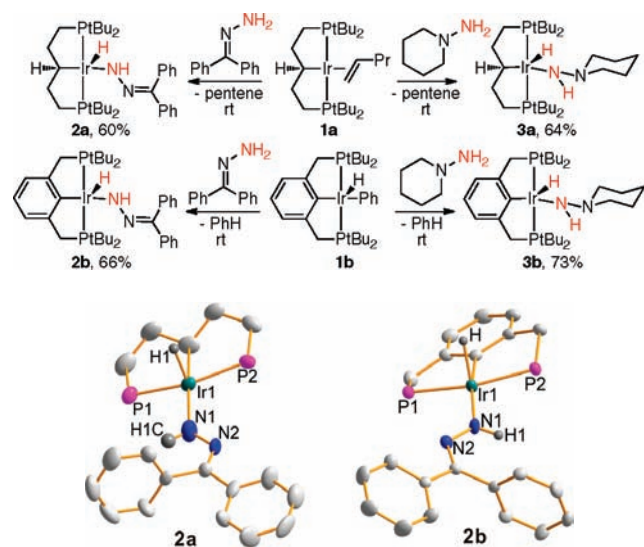

Figure 1. ORTEP diagrams of (D^{r}BPP)Ir(H)(NH−N=CPh$_2$) (**2a**, left, Ir−N = 2.018(7) Å, N−N = 1.397(9) Å, <H−Ir−C = 83.8(14)°, <C−Ir−N = 163.2(4)°, <Ir−N−N = 132.6(6)°) and (PCP)Ir(H)(NH−N=CPh$_2$) (**2b**, right, Ir−N = 2.022(3) Å, N−N = 1.356(4) Å, <H−Ir−C = 75.1(11)°, <C−Ir−N = 164.79(13)°, <Ir−N−N = 130.2(2)°) (*tert*-butyl groups and most H atoms omitted for clarity).
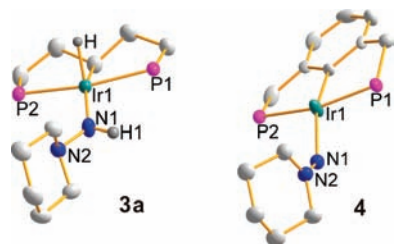
Figure 2. ORTEP diagrams of (D′BPP)Ir(H)(NHNC$_5$H$_{10}$) (**3a**, left, Ir−N = 1.9875(18) Å, N−N = 1.435(2) Å, <H−Ir−C = 73.9(8)°, <C−Ir−N = 154.47(9)°, <Ir−N−N = 132.53(14)°, <N−N−C = 108.83(17)° and 108.61(17)°, <C−N−C = 109.37(17)°) and (PCP)IrN≡NC$_5$H$_{10}$ (**4**, right, Ir−N = 2.008(11) Å, N−N = 1.244(16) Å, <C−Ir−N = 154.9(4)°, <Ir−N−N = 135.1(12)° <N−N−C = 128.4(16)° and 118.8(15)°, <C−N−C = 112.8(14)°) (*tert*-butyl groups and most H atoms omitted for clarity).

1-Aminopiperidine (C$_5$H$_{10}$NNH$_2$, 1.1 equiv) also reacted at room temperature with **1a** and **1b** to give the products of oxidative addition (D′BPP)Ir(H)(NHNC$_5$H$_{10}$) (**3a**) and (PCP)Ir(H)(NHNC$_5$H$_{10}$) (**3b**) (Scheme 1). Structural characterization (Figure 2) of **3a** showed that this complex also adopts a structure that is consistent with an interaction of the nitrogen electron pair with the metal center, resulting in a short Ir−N bond distance of 1.9875(18) Å.[2b,6] The C−Ir−N angle in **3a** (154.47(9)°) is more acute than those in **2a** and **2b** (163.2(4)° and 164.79(13)°, respectively), and the structure of **3a** is best described as a distorted trigonal bipyramid.
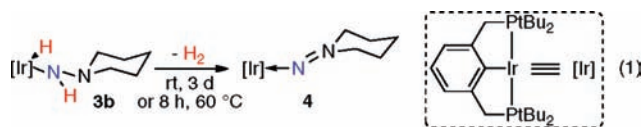
Complex **3a** was stable at room temperature, but complex **3b** underwent *a second N−H bond cleavage* at room temperature over several days or at 60 °C over 8 h to form an aminonitrene complex, **4** (eq 1). The identity of this species was determined by NMR spectroscopy and X-ray diffraction. The reaction formed dihydrogen as the byproduct, and the H$_2$ was observed as a broad signal in the ^{1}H NMR spectrum between 4.0 and 4.4 ppm due to a reversible interaction with iridium.[7] The conversion of hydrido hydrazido complex **3b** to nitrene **4** was cleanly first-order (k_{obs} = 8.3 × 10^{-6} s^{-1} at 23 °C; $\Delta G^{\ddagger}$ = 24.2 kcal/mol; see Supporting Information for the raw data).

The solid-state structure of complex **4** is shown in Figure 2. This complex contains a distorted square planar geometry with a C−Ir−N angle of 154.9(4)°. The N−N bond (1.244(16) Å) in **4** is considerably shorter than the N−N bonds in complexes **2a**, **2b**, and **3a** (1.356(4)−1.435(2) Å), and this difference indicates that **4** contains N−N multiple bond character. The β-N atom (N2) in the hydrazido hydride complex **3a** is pyramidal, whereas the β-N atom in **4** is nearly planar, more akin to the geometry of aminonitrene or isodiazene complexes.[8] The Ir−N bond distance (2.008(11) Å) in **4** is similar to those in complexes **2a**, **2b**, and **3a**. The NNC$_5$H$_{10}$ ligand in **4** is bent with an Ir−N−N angle of 135.1(12)°.
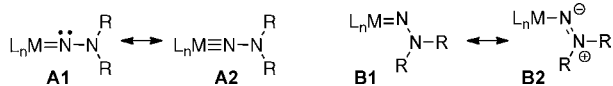
**Figure 3.** Two limiting resonance structures of bent aminonitrene complexes.

Limiting structures of M−N−NR$_2$ species are shown in Figure 3. Most complexes of :NNR$_2$ ligands have linear M−N−N linkages (structure **A**),[8b,9] but a few contain bent M−N−NR$_2$ units (**B**) that are resonance hybrids of structures **B1** and **B2**.[8a,10] The two tung-

sten complexes [Cp$_2$WH(NNHC$_6$H$_4$F)] PF$_6$ (W−N = 1.837(7) Å, N−N = 1.315(9) Å, W−N−N = 146.4(5)°)[10b] and *fac*-(CO)$_3$(DPPE)WNNMe$_2$ (W−N = 2.12(1) Å, N−N = 1.21(2) Å, W−N−N = 139(1)°)[8a] have bent M−N−N angles but very different M−N and N−N distances. The high-valent tungsten complex contains a shorter W−N bond and a longer N−N bond than the low-valent compound, suggesting that it adopts a structure more like resonance structure **B1**, whereas the low-valent tungsten complex adopts a structure more like **B2**. The short N−N distance of our iridium complex **4** suggests that resonance form **B2** contributes most to its structure, and after correcting for the covalent radii of Ir (1.41 Å) and W (1.62 Å),[11] the M−N bond distance in **4** (2.008(11) Å) is comparable to that in the W(0) species *fac*-(CO)$_3$(DPPE)-WNNMe$_2$. Finally, the Ir−N distance is much longer than that in the closest iridium analog, imido complex Cp*IrN*t*Bu containing an Ir−N distance of 1.712(7) Å and Ir−N triple bond character.[5a]

DFT calculations of the structure and bonding of **4** were conducted. The geometry of the calculated structure (see Supporting Information) resembles that of the experimental one. The C−Ir−N angle in the computed structure is bent, but this angle in a derivative containing methyl groups at phosphorus was computed to be more linear, implying that steric effects control this feature.[12] The computed natural bond order[13] implies that the N−N bond has multiple bond character (bond order: 1.76). In this case, the dominant Ir−N interaction results from donation of the nitrogen electron pair to iridium with little backbonding. Thus, both experimental and computational results imply that **4** is a 16-electron iridium(I) species containing a neutral aminonitrene ligand like that in structure **B2**.

Pincer-ligated iridium complexes are well-known to add the C−H bonds of aromatic groups[14] and methyl groups α-to heteroatoms.[15] To determine the relative rates for addition of N−H bonds versus addition of these types of C−H bonds, we studied the reactions of PCP-iridium complex **1b** with 1-methyl-1-phenylhydrazine (Me-PhNNH$_2$) and 1,1-dimethylhydrazine (Scheme 2). These reactions of **1b** with MePhNNH$_2$ and Me$_2$NNH$_2$ indicate that both double N−H activation and a combination of α-methyl C−H activation and subsequent N−N bond cleavage occur readily.

Scheme 2. Reactions of **1b** with MePhNNH$_2$ and Me$_2$NNH$_2$
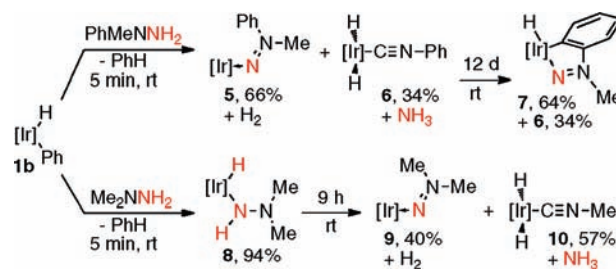
The reaction of **1b** with 1.1 equiv of MePhNNH$_2$ at room temperature rapidly formed a mixture of two products in a *ca*. 2:1 ratio. The major product was (PCP)IrN≡NPhMe (**5**) from double N−H activation;[16] the minor product was the phenyl isocyanide *trans*-dihydride complex (PCP)Ir(H)$_2$C≡NPh (**6**) resulting from N−N bond cleavage. A broad singlet at 0.2 ppm for NH$_3$ was observed in the ^{1}H NMR spectrum of the reaction mixture.[17] Aminonitrene complex **5** was isolated and fully characterized. This complex is thermally unstable at 23 °C over days and decayed quantitatively to a metallacyclic aminonitrene complex **7**, the crystal structure of which is provided in the Supporting Information.

Isocyanide complex **6** was characterized by NMR spectrscopy and X-ray diffraction. The ^{1}H NMR spectrum of **6** contained a triplet at −9.85 ppm ($^2J_{P-H}$ = 14.0 Hz) for two hydrogens, and the infrared

spectrum contained a $\nu_{C\equiv N}$ band at 2073 cm^{-1}. The structure of **6** determined by X-ray diffraction (see Supporting Information) consists of an octahedral geometry with two apical hydrides. The length of the C–N bond (1.172(5) Å) corresponds to that of a C–N triple bond.

Treatment of **1b** with 1.1 equiv of Me$_2$NNH$_2$ formed an analogous mixture of two products (PCP)IrN=NMe$_2$ (**9**) and (PCP)Ir(H)$_2$C≡NMe (**10**). The formation of ammonia again accompanied the formation of the isocyanide complex. At the early stage of this reaction (5 min), the hydrido hydrazido complex **8** that had formed from the first N–H bond addition of Me$_2$NNH$_2$ was observed in 94% yield. Like complex **3b**, monohydride **8** underwent a second N–H activation to form the aminonitrene complex (PCP)IrN=NMe$_2$ (**9**). The reaction was complete after 9 h, and a mixture of complex **9** and the isocyanide *trans*-dihydride complex **10** was formed in a *ca.* 2:3 ratio.

The proposed mechanism for the reactions of the phenyliridium hydride complex **1b** with MePhNNH$_2$ and Me$_2$NNH$_2$ is shown in Scheme 3. Like the aminonitrene complex **4**, the nitrene complexes **5** and **9** result from double N–H bond cleavages and elimination of H$_2$. The formation of the isocyanide complexes likely proceeds by initial oxidative addition of the methyl C–H bonds, followed by N–N bond cleavage via β-NH$_2$ elimination to generate ammonia and the imine. Addition of the C–H bond of the resulting imine and the subsequent deinsertion of the isocyanide unit[18] would form the final iridium product. Because the reaction of **1b** with Me$_2$NNH$_2$ initially formed the monohydride **8** in >90% yield, but the nitrene complex **9** derived from **8** was formed in 40% yield with a 57% yield of isocyanide complex **10**, the first N–H bond activation is likely reversible.

Scheme 3. Proposed Mechanism of the Reactions of **1b** with MePhNNH$_2$ and Me$_2$NNH$_2$
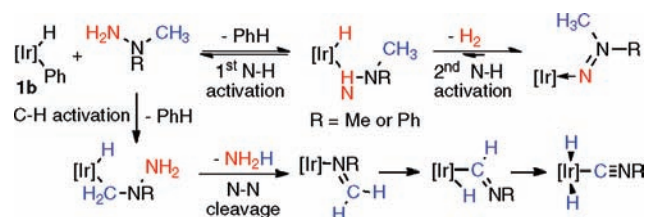
Preliminary studies of the reactivity of aminonitrene complex **4** are summarized in Scheme 4. In the presence of excess CO, the iridium(I) carbonyl complex was formed within minutes, along with the azopiperidine **11**. It is likely that this reaction occurs by coordination of CO, followed by release of the free isodiazene, which is known to undergo dimerization to form tetrazene **11**.[19] Treatment of **4** with MeI immediately formed the iridium(III) methyl iodide and the tetrazene **11**. The reaction of **4** with phenol formed the hydrido iridium(III) phenoxide complex after 7 days at room temperature. In this reaction dipyridododecahydro-s-tetrazine (**12**) was formed exclusively over the azopiperidine **11**. Tetrazine **12** is known to form over **11** in protic media.[20] Finally, addition of 4 atm of H$_2$ to the aminonitrene led to the formation of the iridium tetrahydride and 1-aminopiperidine, indicating that both of the N–H bond activation steps are reversible.

In summary, we have shown that one or two N–H bond cleavages of hydrazines occur to form a hydrido hydrazido or an aminonitrene complex, depending on the ligand at iridium and the substituents on the hydrazine. The reactions with methyl-substituted hydrazines formed a mixture of aminonitrene complexes and the combination of isocyanide iridium(III) dihydrides and ammonia by initial oxidative addition of the methyl C–H bond and subsequent N–N bond cleavage. Studies to generate additional nitrene derivatives on this metal–ligand framework are in progress.

Scheme 4. Preliminary Reactivity of Complex **4**
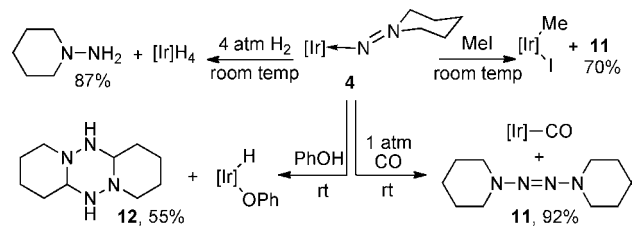
Supporting Information Available: Experimental procedures, spectra data for all compounds, and crystallographic data for **2a**, **2b**, **3a**, **4**, **6**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (b) Hartwig, J. F. *Organotransition metal chemistry: from bonding to catalysis*; University of Science Books: Sausalito, CA, 2010.

(2) (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13644. (c) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080. (d) Sykes, A. C.; White, P.; Brookhart, M. *Organometallics* **2006**, *25*, 1664. (e) Morgan, E.; MacLean, D. F.; McDonald, R.; Turculet, L. *J. Am. Chem. Soc.* **2009**, *131*, 14234. (f) Khaskin, E.; Iron, M. A.; Shimon, L. J. W.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 8542.

(3) (a) Nakajima, Y.; Kameo, H.; Suzuki, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 950. (b) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 10318.

(4) (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (c) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (d) Michelman, R. I.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1993**, *12*, 2741. (e) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839.

(5) (a) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. (b) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.

(6) (a) Riehl, J. F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729. (b) Yuan, J.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **2009**, *28*, 4646.

(7) H$_2$ apparently interacts weakly with the iridium aminonitrene complex, resulting in the broad signal in the ^{1}H NMR spectrum. This signal was absent after removal of the volatile materials but was regenerated by addition of H$_2$ to the solution of the aminonitrene complex **4**.

(8) (a) Arndtsen, B. A.; Schoch, T. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 7041. (b) Danopoulos, A. A.; Wilkinson, G.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1994**, 907.

(9) (a) Chatt, J.; Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P.; Gutkoska, R.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 2383. (b) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luongthi, N. T. *J. Chem. Soc., Dalton Trans.* **1982**, 345. (c) Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6343. (d) Li, Y.; Shi, Y.; Odom, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 1794.

(10) (a) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578. (b) Einstein, F. W. B.; Jones, T.; Hanlan, A. J. L.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2585.

(11) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(12) Hydrazido complex **3a** bearing the piperidine group contains a similarly bent C–Ir–N angle.

(13) Weinhold, F.; Landis, C. R. *Chem. Educ.: Res. Pract.* **2001**, *2*, 91.

(14) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.

(15) Choi, J.; Choliy, Y.; Zhang, X.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2009**, *131*, 15627.

(16) The monohydride from the first N–H activation was not observed.

(17) This signal was absent after removal of the volatile materials but was regenerated by adding NH$_3$.

(18) Zhang, X.; Emge, T. J.; Ghosh, R.; Goldman, A. S. *J. Am. Chem. Soc.* **2005**, *127*, 8250.

(19) (a) Back, T. G. *J. Chem. Soc., Chem. Commun.* **1981**, 530. (b) Hwu, J. R.; Wang, N.; Yung, R. T. *J. Org. Chem.* **1989**, *54*, 1070.

(20) Lemal, D. M.; Rave, T. W. *J. Am. Chem. Soc.* **1965**, *87*, 393.

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