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H−H and N−H Bond Cleavage of Dihydrogen and Ammonia with a Bifunctional Parent Imido (NH)-Bridged Diiridium Complex

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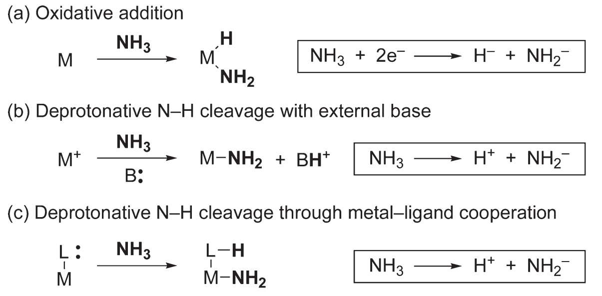
Supporting Information

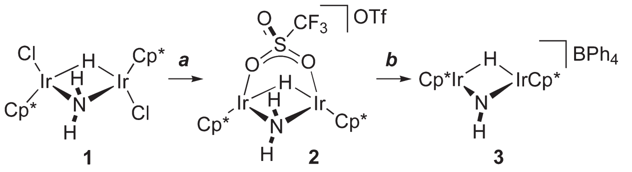
ABSTRACT: Hydrogenation and protonation of parent imido complexes have attracted much attention in relation to industrial and biological nitrogen fixation. The present study reports the structure and properties of the highly unsaturated diiridium parent imido complex $[(Cp^*Ir)_2(\mu_2\text{-H})(\mu_2\text{-NH})]^+$ derived from deprotonation of a parent amido complex. Because of the Lewis acid−Brønsted base bifunctional nature of the metal−NH bond, the parent imido complex promotes heterolysis of H_2 and deprotonative N−H cleavage of ammonia to afford the corresponding parent amido complexes under mild conditions.

Metal−parent imides (M−NH) and amides ($M{-}NH_2$) are key intermediates in industrial and biological nitrogen fixation performed on oxide-supported late transition metals and a $MoFe_7S_9$ cluster in nitrogenase.[1] Although the protonation and hydrogenation of parent imido complexes to form parent amido and ammine complexes have been extensively studied in this context,[2−4] most of such reductive transformations are associated with high-valent early transition metals. This is due in part to the $d\pi/p\pi$ repulsion between the low-valent late metal and nitrogen;[5] the resultant Brønsted basic and nucleophilic character of the nitrogen renders the compact NH ligand too reactive to be isolated or too much stabilized by triple or quadruple bridging without lone-pair electrons on the nitrogen.[6,7] Parent amido complexes also have close relevance to the use of ammonia as a substrate in homogeneous catalysis.[8,9] Recent progress in this area has focused on the oxidative addition of ammonia (Scheme 1a) as a N−H bond activation process.[10−12] An alternative and conventional access to parent amido complexes has been provided by salt elimination reactions (Scheme 1b), which in general require external strong bases such as sodium amides or alkoxides.[13] In contrast, deprotonative N−H bond cleavage promoted by an internal Brønsted basic cooperating ligand (Scheme 1c) remains much less explored. As an extension of our continuing studies of metal−amine/amido bifunctional catalysts,[14−19] we report here the synthesis of the highly unsaturated yet isolable diiridium(III) parent imido complex $[(Cp^*Ir)_2(\mu_2\text{-H})(\mu_2\text{-NH})][BPh_4]$ (**3**; $Cp^* = \eta^5\text{-}C_5Me_5$) by deprotonation of the parent amido complex $[(Cp^*IrCl)_2(\mu_2\text{-H})(\mu_2\text{-NH}_2)]$ (**1**). Facile heterolysis of dihydrogen and deprotonative N−H bond cleavage of ammonia at the Ir−NH bond in the dinuclear platform, leading to the formation of parent amido complexes, are described.

Scheme 1. Metal-Mediated N−H Bond Cleavage of Ammonia



Scheme 2. Synthesis of Parent Imido Complex 3[a]



[a] Reagents and Conditions: (a) AgOTf (2 equiv), THF, rt. (b) (i) NEt_3 (1 equiv), CH_2Cl_2, rt; (ii) $NaBPh_4$. OTf = OSO_2CF_3.

The parent imido complex **3** was obtained by stepwise dehydrochlorination of the parent amido complex **1**[17] through the intermediary triflate complex **2** (Scheme 2). X-ray analysis of **2**, which was generated by chloride abstraction of **1** in 61% isolated yield, revealed the dinuclear structure with a bridging triflate ligand (Figure S1 in the Supporting Information). The two amido protons as well as the two CF_3 groups in **2** are equivalent even at −40 °C in the ^1H and ^{19}F NMR spectra, indicating facile dissociation of the triflate ligand. Unlike the chloro complex **1**, the cationic triflate complex **2** smoothly reacted with an equimolar amount of triethylamine to afford the parent imido complex **3** in 24% overall yield after anion exchange with tetraphenylborate. The ^1H NMR spectrum of **3** exhibited a characteristic singlet due to the NH proton at δ 15.78, which was split into a doublet ($^1J_{NH}$ = 81.6 Hz) upon ^{15}N labeling, along with a hydrido resonance at δ −1.76. The NH stretching band appeared at

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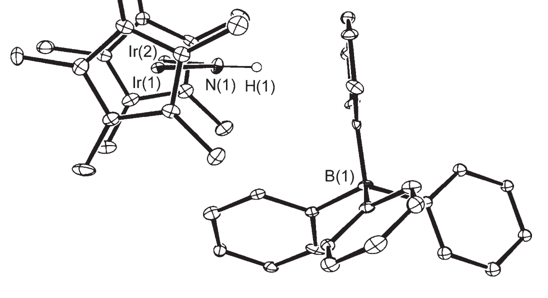
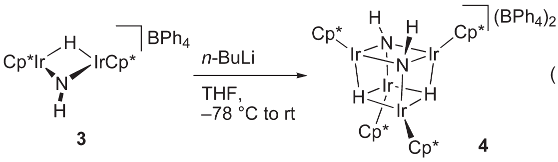


Figure 1. Structure of **3**. Hydrogen atoms except for the imido hydrogen have been omitted for clarity.

3272 cm^{-1} in the IR spectrum. The detailed structure of **3** was determined by X-ray crystallography, as shown in Figure 1. The Ir—N distances of 1.891(6) and 1.893(8) Å are much shorter than those in **1** and **2** [2.054(4)—2.069(6) Å], suggesting sizable π donation from the parent imido ligand to the unsaturated iridium centers.[18] The Ir—Ir distance of 2.6708(5) Å is also shorter than that in **2** [2.8188(3) Å]. The NH group points almost perpendicular to one of the phenyl rings in the tetraphenylborate anion, with a close NH···(Ph centroid) contact of 2.27 Å, indicating the presence of an NH···π interaction.[20] A related 30-electron, bulky imido-bridged dirhodium(II) complex without bridging hydride, $[(Cp^*Rh)_2(\mu_2\text{-}NC_6H_3Pr^i{}_2\text{-}2,6)]$, was recently isolated.[21]

The $Ir_2(\mu_2\text{-}NH)$ core in **3** features the potentially Lewis acidic iridium centers and the adjacent Brønsted basic imido nitrogen. This bifunctional nature led to base-assisted dimerization of **3**, possibly triggered by deprotonation of the imido ligand, to generate the bis(μ_3-NH)-bridged tetranuclear cluster **4** as the acid—base adduct in 72% yield (eq 1):



(1)

Figure 2 depicts the crystal structure of dicationic cluster **4**. The four iridium atoms form a butterfly-type core with five Ir—Ir contacts ranging from 2.9097(4) to 2.9484(4) Å, suggesting delocalized metal—metal bonding interactions in the 64-electron cluster, for which only four metal—metal bonds would be expected on the basis of the effective atomic number rule. Although the hydrido ligands could not be located in the X-ray analysis, the ^{1}H NMR spectrum of **4** was consistent with an approximately C_{2v}-symmetric structure with two μ_3-bridging hydrido ligands, as in the isoelectronic sulfido clusters.[22] The broad signal due to the NH protons at δ 2.87 disappeared upon treatment with D_2O. It is to be noted that few examples of isolable and fully characterized pairs of monomeric and dimeric imido complexes with the same empirical formula such as **3** and **4** have been reported to date.[23]

More importantly, hydrogenation of the Ir—NH group in **3** took place under mild conditions to produce the corresponding $IrH(NH_2)$ complex. When a solution of **3** was stirred under a H_2 atmosphere (1 atm) at room temperature, the parent amido complex **5** was isolated in 29% yield, as shown in Scheme 3. The ^{1}H NMR spectrum of **5** exhibited signals ascribed to the Cp*, hydrido, and amido protons in an intensity ratio of 15:1:1, consistent with the addition of 1 mol of H_2 across the unsaturated Ir—NH bond in **3** and the C_{2v}-symmetric structure of the product **5**. The crystal structure of **5** shown in Figure 3 again suggests the presence of NH···π interactions between the amido protons and the tetraphenylborate anion. The two crystallographically unlocated hydrido ligands most probably bridge the two iridium atoms, judging from the relative orientation of the two Cp* ligands with respect to the Ir_2N triangle. The Ir—NH_2 bond lengths of 2.063(9) and 2.114(10) Å, which are slightly longer than those in **1** and **2**, and the short Ir—Ir distance of 2.6138(5) Å might be explained by the reduction in electron donation from the nitrogen due to the Ir—Ir multiple-bond character. The reaction could be regarded as a dinuclear variant of H_2 heterolysis at mononuclear late transition metal—amido complexes, some of which have been used as effective hydrogenation catalysts.[15,19,24] The closest example in the literature is the hydrogenation of the saturated Ru—(μ_3-NH) bond in $[(Cp^*Ru)_3(\mu_2\text{-}H)_3(\mu_3\text{-}NH)]$ to give the parent amido complex $[(Cp^*Ru)_3(\mu_2\text{-}H)_4(\mu_2\text{-}NH_2)]$ through oxidative addition

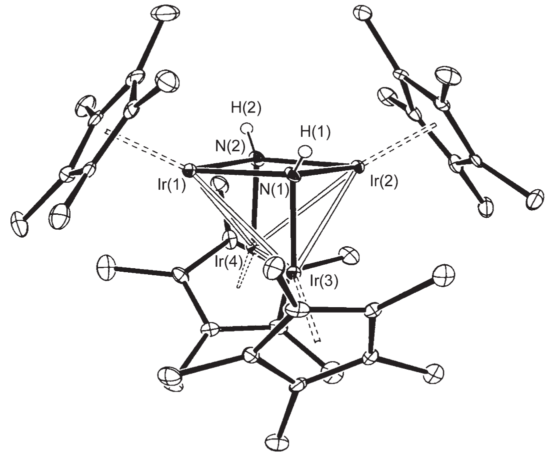
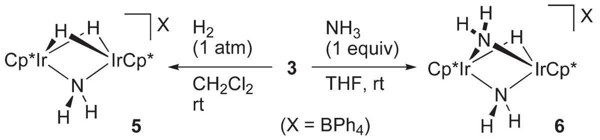


Figure 2. Structure of the cationic part of **4**·2THF. Hydrogen atoms except for the imido hydrogens have been omitted for clarity.

Scheme 3. H—H and N—H Cleavage with Parent Imido Complex 3



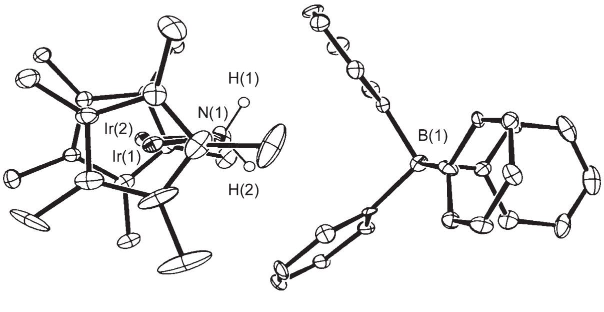


Figure 3. Structure of **5**. Hydrogen atoms except for the amido hydrogens have been omitted for clarity. The NH···(Ph centroid) distances are 2.60 and 2.69 Å.

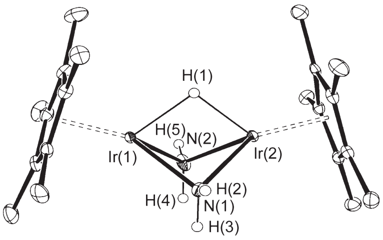


Figure 4. Structure of the cationic part of **6**. Hydrogen atoms in the Cp* ligands have been omitted for clarity.

of H_2,[4] which is less probable for the iridium(III) complex **3**. Such heterolytic cleavage of dihydrogen in dinuclear complexes is also attractive in relation to hydrogenase enzymes.[16]

The bifunctional metal—NH moiety in the dinuclear parent imido complex **3** also facilitates N—H bond cleavage of ammonia in the manner illustrated in Scheme 1c. As shown in Scheme 3, treatment of **3** with an equimolar amount of ammonia at room temperature afforded the parent bis(amido) complex **6** in 44% isolated yield. The ^{1}H NMR spectrum of **6** displayed two broad signals at δ −0.50 and 0.64 with a 2H intensity, which are ascribed to the exo and endo amido protons. The structure of **6** was determined by X-ray crystallography (Figure 4). The Ir—N distances [2.077(2)−2.104(2) Å] are consistent with coordinative saturation of the metal centers. Related deprotonative N—H cleavage of ammonia without formal redox of the metal has been documented for some hydroxo,[11] oxo,[12] and alkyl[25] complexes; however, the subsequent dissociation of the protonated cooperating ligands (LH in Scheme 1c) has prevented the catalytic application of such metal—ligand bifunctional activation. Quite recently, Milstein and co-workers[26] demonstrated the deprotonative and reversible N—H cleavage of ammonia through metal—ligand cooperation, wherein the parent amido intermediate was not directly observed. In solid-surface organometallic chemistry, formation of a parent amido species from a parent imido ligand and ammonia on a silica-supported tantalum complex has been reported.[27] The formation of **6** represents the first example of metal—ligand bifunctional activation of ammonia in which the produced parent amido complex has been unambiguously characterized and the cooperating ligand stays in the coordination sphere throughout the transformation.

In conclusion, the parent imido-bridged diiridium complex **3** featuring the Lewis acid—Brønsted base bifunctionality of the sterically encumbered M—NH bonds promotes heterolysis of dihydrogen and N—H bond cleavage of ammonia to give the corresponding parent amido complexes under mild conditions. The facile proton shifts between the reduced nitrogenous ligands and the dihydrogen molecule observed for the late metal complexes provide insights into the mechanism of nitrogen fixation as well as the organometallic transformation of ammonia. Further studies aimed at catalytic reactions of dihydrogen and ammonia on multimetallic centers furnished with metal—ligand bifunctionality are in progress.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental procedures and X-ray crystallographic data for **2**, **3**·CH_2Cl_2, **4**·2THF, **5**, and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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