Ammonia–Borane Dehydrogenation Catalyzed by Dual-Mode Proton-Responsive Ir-CNN\(^h\) Complexes

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Cite This: Inorg. Chem. 2021, 60, 18490–18502

ABSTRACT: Metal complexes incorporating proton-responsive ligands have been proved to be superior catalysts in reactions involving the H\(_2\) molecule. In this contribution, a series of Ir\(^{III}\) complexes based on lutidine-derived CNN\(^h\) pincers containing N-heterocyclic carbene and secondary amino NHR [R = Ph (4a), tBu (4b), benzyl (4c)] donors as flanking groups have been synthesized and tested in the dehydrogenation of ammonia–borane (NH\(_3\)BH\(_3\), AB) in the presence of substoichiometric amounts (2.5 equiv) of tBuOK. These preactivated derivatives are efficient catalysts in AB dehydrogenation in THF at room temperature, albeit significantly different reaction rates were observed. Thus, by using 0.4 mol % of 4a, 1.0 equiv of H\(_2\) per mole of AB was released in 8.5 min (turnover frequency (TOF\(_{50\%}\)) = 1875 h\(^{-1}\)), while complexes 4b and 4c (0.8 mol %) exhibited lower catalytic activities (TOF\(_{50\%}\) = 55–60 h\(^{-1}\)). 4a is currently the best performing Ir\(^{III}\) homogeneous catalyst for AB dehydrogenation. Kinetic rate measurements show a zero-order dependence with respect to AB, and first order with the catalyst in the dehydrogenation with \(4a \quad (t\text{d}[\text{AB}]/dt = k[4a])\). Conversely, the reaction with 4b is second order in AB and first order in the catalyst (\(-d[\text{AB}]/dt = k[4b][\text{AB}]\)). Moreover, the reactions of the derivatives 4a and 4b with an excess of tBuOK (2.5 equiv) have been analyzed through NMR spectroscopy. For the former precursor, formation of the iridate 5 was observed as a result of a double deprotonation at the amine and the NHC pincer arm. In marked contrast, in the case of 4b, a monodeprotonated (at the pincer NHC-arm) species 6 is observed upon reaction with tBuOK. Complex 6 is capable of activating H\(_2\) reversibly to yield the trihydride derivative 7. Finally, DFT calculations of the first AB dehydrogenation step catalyzed by 5 has been performed at the DFT//MN15 level of theory in order to get information on the predominant metal–ligand cooperation mode.

INTRODUCTION

The controlled release of H\(_2\) from high content hydrogen compounds used as H\(_2\)-storage systems is paramount to the use of this gas as an energy vector in the so-called Hydrogen Economy.\(^2,3\) In this context, ammonia–borane (NH\(_3\)BH\(_3\), AB) has received increasing attention as a hydrogen storage material because of its high available hydrogen content (19.6 wt % H\(_2\)), moisture kinetic stability and easy H\(_2\) thermal release.\(^3\) In addition, AB dehydrogenation renders B–N oligomers and polymers as byproducts that are suitable starting materials for the synthesis of boron nitride (BN) ceramics.\(^3\) Although AB dehydrogenation can be performed under simple thermal conditions,\(^3\) insufficient kinetic control of the process leads to the formation of ill-defined B–N containing solids. This is a serious drawback for the H\(_2\)-depleted material recycling. As a consequence, catalytic approaches to the H\(_2\) release from AB have been envisaged. The use of a catalyst allows for a fine control of the rate and extent of H\(_2\) production, as well as the nature of the H\(_2\)-depleted byproducts. In addition, the H\(_2\) release temperature is lowered, with respect to pure AB, and the process can be performed with a lower energetic impact.

Catalysts based on transition metals have provided fast kinetics and a large extent of H\(_2\) release under relatively mild reaction conditions.\(^6\) Particularly, metal complexes stabilized by pincer ligands have been widely investigated because of the enhanced catalyst stability provided by the \(k^3\)-tridentate ligand coordination.\(^7,16\) Moreover, since ammonia–borane is a polar molecule with hydridic (BH) and acidic (NH) hydrogen atoms, transition-metal complexes based on ligands containing Brønsted basic sites have been shown to be
particularly adequate to promote H₂ release from AB through the transfer of the hydridic BH to the acidic metal center and the NH proton to the basic ligand functionality (bifunctional catalysts). Prevalent examples of such systems are metal complexes based on ligands bearing secondary amine donors, which are capable of getting involved in reversible metal-amine/metal-amido interconversion (Figure 1a).

Similarly, metal complexes incorporating picoline- or lutidine-derived pincer ligands are able to participate in ligand-assisted H−X (X = H, C, O, N, B) bond activation upon deprotonation of the (acidic) CH₂ pincer side-arms and concomitant dearomatization of the N-containing ring (Figure 1b). Although these derivatives have been found to be efficient catalysts in a plethora of hydrogenation reactions of polar organic substrates and alcohol dehydrogenation reactions, their application in AB dehydrogenation has been limitedly explored. Moreover, development of homogeneous catalytic systems based on lutidine-derived ligands has been mainly focused on phosphine-containing PNX (X = phosphine or N-donor) pincers, albeit substitution of the flanking PR₃ groups by another strong σ-donor such as N-heterocyclic carbenes (NHCs) has also been briefly addressed. Upon deprotonation of the methylene CH₂−NHC arms, these organometallics are catalytically active in ligand-assisted processes.

A step forward in catalyst design that has provided superior catalytic systems in hydrogenation and dehydrogenation reactions relies on the use of ligands containing two Brønsted acidic/basic sites, such as a lutidine fragment and a secondary amino group. Since two Brønsted functionalities are present in these ligands, the related complexes might participate in ligand-assisted processes through pyridine aromatization/dearomatization or amine-metal/amido-metal interconversion. Herein, we report on the synthesis of a series of Ir complexes based on lutidine-derived CNNH ligands bearing secondary amino and NHC side-arms and their catalytic performance in AB dehydrogenation. Detailed kinetic and NMR spectroscopy studies show that different species are formed under catalytic conditions, depending on the substituent of the secondary amino group. Moreover, DFT calculations have determined the preferred metal−ligand cooperation mode when a doubly deprotonated catalytic species is formed.

**RESULTS AND DISCUSSION**

**Synthesis and Structure of Ir-CNNH Complexes.** Following previously reported procedures for the synthesis of Ir complexes based on related NHC-containing lutidine-derived ligands, the diolfin derivatives 2a and 2b were prepared by the reactions of Ir(acac)(COD) and the N-heterocyclic carbene ligand precursors 1a and 1b, respectively (Scheme 1). These complexes were isolated as yellow solids in good yields (99% and 77%, respectively), and spectroscopically and analytically characterized. In the ¹H NMR spectrum of 2a, the olefinic hydrogens of one of the C=C moieties of the COD ligand appear as multiplets at δ 4.51 and
4.41 ppm, whereas the resonances corresponding to the other olefin fragment are shown at δ 2.95 and 2.82 ppm. Moreover, the $^1$H−$^1$H EXSY experiment of 2a recorded at 298 K exhibits intense cross-peaks corresponding to the pairwise exchange of the olefinic signals corresponding to different C=C moieties. The observed dynamic behavior can be assigned to alkene site exchange involving the decoordination of one of the olefin fragments to produce a distorted tetrahedral intermediate, and subsequent recooordination of the uncoordinated C=C group to the opposite side (see the Supporting Information).\(^{25}\) Meanwhile, the C-2 of the NHC ligand fragment produces a singlet at δc 181.0 ppm in the $^{13}$C($^1$H) NMR spectrum. Similar NMR data and fluxional behavior were shown by complex 2b.

Conversely, heating a CH$_2$Cl$_2$ solution of Ir(acac)(COD) and the imidazolium salt 1c to 50 °C produced the expected coordination of the lutidine-derived CNN$^+$ pincer ligand along with the activation of one ortho C−H bond of the benzyl substituent, yielding the $\kappa^2$-(CNN$^+$N$_{\text{H}}$N$_{\text{amine}}$) complex 3 (Scheme 1). The solid-state structure of this derivative was determined by single-crystal X-ray diffraction (Figure 2). The complex is comprised of a stereogenic Ir center in an octahedral coordination geometry, in which the carbene carbon and the nitrogen donors of the CNN$^+$ ligand are coordinated in the meridional positions, as defined by the C$_{\text{NHC}}$−Ir−N$_{\text{amine}}$ angle of 171.0°, and the metalated aryl fragment is located trans to the Br atom (C$_{\text{aryl}}$−Ir−Br = 169.1°).

Complexes 2a and 2b reacted with H$_2$ (5 bar) in CH$_2$Cl$_2$, resulting in the formation of the bromodiydride complexes 4a and 4b, respectively (Scheme 1). Similarly, derivative 4c was obtained by exposing a CH$_2$Cl$_2$ solution of 3 at 60 °C to 4 bar of H$_2$. Complexes 4a−4c, which were isolated as air-stable yellow solids, were characterized analytically and spectroscopically. For example, in the $^1$H NMR spectrum of complex 4a, two mutually coupled doublets are detected in the hydride region, appearing at −19.05 and −23.25 ppm ($^3$J$_{\text{HH}}$ = 6.9 Hz), which are assigned to the IrH hydrogens located trans and cis to the pyridine fragment, respectively, as determined by $^1$H−$^1$H NOESY spectroscopy. In the same experiment, the NH hydrogen produces a broad doublet resonance at 6.15 ppm ($^3$J$_{\text{HH}}$ = 11.1 Hz). In the $^{13}$C($^1$H) NMR spectrum, diagnostic signals for complex 4a are shown at 153.5 ppm, caused by the carbene carbon, and at 62.2 and 55.3 ppm, corresponding to the methylene NH- and NHC-arms of the pincer, respectively. Analogous NMR data were observed in the case of complexes 4b and 4c, with the notable exception of the resonances due to the NH groups in the $^1$H NMR spectra, which are shifted upfield, with respect to that of 4a, appearing as a broad doublet of doublets at 4.03 ppm ($^3$J$_{\text{HH}}$ = 12.5 Hz, $^5$J$_{\text{HH}}$ = 3.2 Hz) for 4b, and 4.39 ppm ($^3$J$_{\text{HH}}$ = 9.2 Hz, $^5$J$_{\text{HH}}$ = 9.2 Hz) in the case of 4c.

The solid-state structure of 4b, as determined by single-crystal X-ray diffraction, exhibits an octahedral geometry with the CNN$^+$ pincer adopting a meridional coordination and the two hydride ligands in cis to each other (Figure 3). Moreover, the existence of a hydrogen bond between the bromine ligand and the amino hydrogen is evident from the H−Br distance of 2.76 Å, which is shorter than the sum of the van der Waals radii of H and Br (2.97 Å).\(^{27}\)

**AB Dehydrogenation.** Complexes 4a−4c were tested as catalysts in the dehydrogenation of ammonia borane after a preliminary activation with tBuOK (see the Supporting Information).
Information for the experimental setup). The initial treatment with a base is necessary to trigger the catalysis; bare complex 4a (without a base) was tested in AB dehydrogenation, and it was found to be a poor catalyst (initial turnover frequency (TOF) of <5 h\(^{-1}\)). Upon addition of a THF solution of 4a (0.4 mol %) and tBuOK (base: 4a = 2.5) to a stirred AB solution in the same solvent, instantaneous vigorous gas evolution was observed, followed by the immediate formation of an off-white precipitate. Follow-up of the reaction by measuring the pressure increase in the system showed that 1.0 equiv of H\(_2\) per AB molecule was released in ca. 8.5 min at room temperature (Figure 4a). To the best of our knowledge, the high-room-temperature catalytic activity of 4a (TOF = 1764 h\(^{-1}\)) is only surpassed by the cationic Pd complexes [Pd(allyl)][BF\(_4\)], [Pd(allyl)(2,4-hexadiene)][BF\(_4\)] and [Pd(MeCN)\(_4\)][BF\(_4\)]\(_2\) reported by the group of Michalak in 2010,\(^{28}\) and by the Ru-PNHP and RuCl\(_2\)(PN)\(_2\) derivatives reported by the Schneider group in 2009\(^{53}\) and the Fagnou group in 2008,\(^{17}\) respectively. Note that the catalytic activity of 4a is slightly superior to that of the most active Ir-based catalyst precursor reported to date: IrH\(_2\)(POCOP), published by Goldberg and colleagues in 2006.\(^{7}\) Thus, 4a is currently the best-performing iridium-containing homogeneous catalyst for AB dehydrogenation. On the other hand, reactions performed with complexes 4b and 4c, using 0.8 mol % of catalyst loading under the same reaction conditions, yielded ca. 0.75 equiv of H\(_2\) (Figure 4a). To the best of our knowledge, the high-room-temperature catalytic activity of 4a (TOF = 1764 h\(^{-1}\)) is only surpassed by the cationic Pd complexes [Pd(allyl)][BF\(_4\)], [Pd(allyl)(2,4-hexadiene)][BF\(_4\)] and [Pd(MeCN)\(_4\)][BF\(_4\)]\(_2\) reported by the group of Michalak in 2010,\(^{28}\) and by the Ru-PNHP and RuCl\(_2\)(PN)\(_2\) derivatives reported by the Schneider group in 2009\(^{53}\) and the Fagnou group in 2008,\(^{17}\) respectively. Note that the catalytic activity of 4a is slightly superior to that of the most active Ir-based catalyst precursor reported to date: IrH\(_2\)(POCOP), published by Goldberg and colleagues in 2006.\(^{7}\) Thus, 4a is currently the best-performing iridium-containing homogeneous catalyst for AB dehydrogenation. On the other hand, reactions performed with complexes 4b and 4c, using 0.8 mol % of catalyst loading under the same reaction conditions, yielded ca. 0.75–0.8 equiv of H\(_2\) in 5 h (for 4b, TOF\(_{50\%}\) = 55 h\(^{-1}\); for 4c, TOF\(_{50\%}\) = 60 h\(^{-1}\)); thus, both catalysts exhibit significantly lower catalytic activity than 4a (Figure 4b).

The registered ATR-IR spectrum of the insoluble H\(_2\)-depleted material produced in the AB dehydrogenation reactions with 4a (amounting to >95% of the total BN byproducts, as estimated by mass balance) contains corresponding to the N–H (3299 and 3248 cm\(^{-1}\)) and B–H (2384 and 2313 cm\(^{-1}\)) stretching modes (see Figure S7 in the Supporting Information). These absorptions, as well as the spectrum fingerprint, closely resemble those described for the mainly linear poly(aminoboranes), [NH\(_2\)BH\(_2\)]\(_{as}\), isolated from the dehydrogenation of AB with Brookharts Ir-POCOP complex,\(^{56}\) and Ru- and Fe-PNHP complexes.\(^{13,14}\) The \(^{11}\)B NMR spectrum of the soluble part of the reaction with 4a exhibits broad signals between \(\delta_B \approx 17–31\) ppm, in agreement with the formation of species resulting from the release of more than 1 equiv of H\(_2\) (see Figure S8 in the Supporting Information). However, the small fraction of these products is not enough to account for an overall H\(_2\) yield exceeding 1.0 equiv.

The observed differences in the catalytic activity provided by 4a and complexes 4b and 4c led us to determine the reaction kinetic laws. For 4a, plotting of [AB] versus time gave a straight line (\(k_{obs} = 3.4 \times 10^{-3} \text{ M s}^{-1}\)), indicative of a pseudo-zero order relationship in AB (see Figures S10 and S11 in the Supporting Information). Initial rate experiments performed at different catalyst concentrations showed that hydrogen release has a first-order rate dependence in 4a (Figure S12 in the Supporting Information). The observed lack of dependence on AB concentration is in agreement with its rapid reaction with the catalyst and, therefore, with a rate-determining step that does not involve AB activation.

Next, kinetic isotope effects (KIE) values were determined using the deuterated AB isotopologues (NH\(_3\)BD\(_3\), ND\(_3\)BH\(_3\), and ND\(_3\)BD\(_3\)). A pronounced decrease in the reaction rate was observed with the N-deuterated substrate [ND\(_3\)BH\(_4\), \(k_{H}/k_{D} = 8.4\)], while deuteration at boron produces a somewhat lower rate [NH\(_3\)BD\(_3\)], \(k_{H}/k_{D} = 1.4\)]. In the case of full AB deuteration, within the experimental error, the KIE is the product of the individual isotope effects measured with ND\(_3\)BH\(_4\) and NH\(_3\)BD\(_3\), [ND\(_3\)BD\(_3\)], \(k_{H}/k_{D} = 13.4\)]. This suggests a concerted, asynchronous transition state in the cleavage of the N–H and B–H bonds. However, this conclusion is tentative, since the observed KIEs should reflect the contributions of all the multiple steps of the catalytic cycle. We must bear in mind that AB activation does not seem to be the rate-determining step.\(^{30}\)

The kinetic law was also inferred for the reaction with the catalyst precursor 4b. From the initial rate experiments performed at different AB and catalyst concentrations, a kinetic law [AB] / dt = \(k_{obs}[AB] = k[4b][AB]^{2} (k_{obs} = 1.3 \times 10^{-4} \text{ M s}^{-1})\) was revealed, evidencing different rate laws for the reactions with complexes 4a and 4b (see Figures S14 and S15 in the Supporting Information). For the latter catalyst, the KIE values using deuterated NH\(_3\)BD\(_3\), ND\(_3\)BH\(_3\), and ND\(_3\)BD\(_3\) were found to be 2.5, 2.8, and 7.7, respectively. These data suggest a mechanism where two AB molecules are involved in the rate-limiting step,\(^{12}\) with the N–H and B–H bonds splitting occurring in a concerted manner.

Mechanistic Insights. Taking into account previous studies with catalysts based on proton-responsive ligands,\(^{13,14,16,17}\) a plausible mechanism for AB dehydrogenation catalyzed by complexes 4 in the presence of an auxiliary base should involve initial hydrogen transfer from AB to the deprotonated form of the Ir-CNNH\(_4\) catalyst precursors with the concomitant formation of the “inorganic ethylene analogue” BH\(_4\) = NH\(_2\), followed by ligand-assisted H\(_2\) elimination. Therefore, to gain insight into the species formed upon
Treatment of complexes 4 with a base, derivative 4a was initially reacted with tBuOK (2.5 equiv) in THF-d₈ (Scheme 2).

Scheme 2. Formation of Iridate Complex 5

Reaction of the Ir-CN₃ derivatives with a strong base could induce deprotonation of the pincer ligand at its methylene carbon in the side arm and/or at the secondary amino group. Analysis of the deuterated solution through NMR spectroscopy showed the formation of a major species (ca. 90%), which was characterized as the highly air-sensitive amido iridate(III) 5, confirming the deprotonation of both the NH and the NHC−methylene arm of 4a. The ¹H NMR spectrum of 5 features two mutually coupled doublets at δ −16.35 ppm and δ −18.61 ppm (JHH = 5.5 Hz), corresponding to the hydride ligands. In the same experiment, the methylene CH₂NPH hydrogens appear as doublets at δ 5.62 ppm. In the ¹H DOSY experiment of 5 afforded a diffusion coefficient D = 7.2 × 10⁻¹⁰ m²/s (log D = −9.14) from which a value of its hydrodynamic radius (rH) was estimated using the Stokes–Einstein equation. The radius for the dimeric structure calculated from its X-ray volume was rH = 5.5 Å. This further supports the existence of a monomeric form of 5 in solution.

In marked contrast, under the conditions used for the formation of 5, reaction of 4b with tBuOK (2.5 equiv) in THF-d₈ gave rise to complex 6 (75%−80% NMR yield), which is selectively deprotonated at the NHC-bridge, as determined through NMR spectroscopy (Scheme 3). The ¹H NMR experiment of 6 shows, in the hydride region, two mutually coupled doublets appearing at −16.49 and −18.41 ppm (JHH = 5.6 Hz). Moreover, in the same spectrum, a doublet of

Figure 5. ORTEP drawing at 30% ellipsoid probability of the dimeric form of complex 5. Hydrogen atoms (except for the hydride ligands) have been omitted for clarity. Selected bond lengths: Ir(1)−C(1), 1.999(19) Å; Ir(1)−N(3), 2.033(13) Å; Ir(1)−N(4), 2.115(15) Å; and Ir(1)−C(13), 2.215(17) Å. Selected bond angles: C(1)−Ir(1)−N(3), 165.9(7)°; C(1)−Ir(1)−N(4), 90.4(7)°; N(3)−Ir(1)−N(4), 78.5(6)°; C(1)−Ir(1)−C(13), 98.9(6)°; and N(4)−Ir(1)−C(13), 90.6(6)°.
doublets at 3.88 ppm ($^2J_{HH} = 13.6$ Hz, $^3J_{HH} = 2.8$ Hz) and a multiplet at 3.39 ppm, corresponding to the CH$_2$N hydrogens, and a broad doublet at $\delta$ 2.97 ppm ($^2J_{HH} = 10.9$ Hz) due to the NH, are also observed; whereas, the proton of the deprotonated methine-NHC arm produces a singlet at 5.48 ppm.

In the $^{13}$C{1H} NMR spectrum of 6, the carbene carbon appears as a singlet at 150.0 ppm, while the N- and NHC-linkers of the pincer produce singlet resonances at 56.1 and 54.9 ppm, respectively. Further attempts to perform the deprotonation of the amino group of 4b were unsuccessful, likely due to the reduced NH acidity, in comparison to 4a.

Because of the fast kinetics, attempts to detect metallic intermediates through NMR spectroscopy during the dehydrogenation reaction catalyzed by 4a at room temperature were unsuccessful. However, at the end of the catalytic process, the main metal-containing species present in solution (>90%, from $^1$H NMR analysis) is the amido iridate(III) 5. Moreover, pressurization of a THF-$d_8$ solution of 5 with H$_2$ (4 bar, 48 h) produced the selective formation of trihydride derivative 7, which is only stable under a hydrogen atmosphere (Scheme 3). Complex 7 gives rise in the hydride region of the $^1$H NMR spectrum to a multiplet signal integrating for 2H at $-8.92$ ppm, corresponding to the apical IrH hydrogens, and a doublet of doublets at $-18.24$ ppm ($^2J_{HH} = 5.2$, $^2J_{HH} = 5.2$ Hz) that integrates for 1H, ascribed to the meridional hydride ligand. Moreover, the reprotonation of the pincer ligand side arm was confirmed from the presence of two mutually coupled doublets appearing at 5.02 and 5.10 ppm ($^2J_{HH} = 13.5$ Hz), corresponding to the methylene–NHC pincer arm.

**DFT Calculations of the First AB Dehydrogenation Step.** To get further insight into the reaction catalyzed by 4a, DFT calculations on the first step of the AB dehydrogenation mechanism were performed at the DFT//MN15 level of theory on the real structure of the supposed active catalytic species 5, dimeric in the solid state (as found in the crystal structure determined from X-ray data collection) but monomeric in THF solution (as confirmed by DOSY NMR experiments). In this structure, possibly in the form of a THF...
adduct with general formula \( [(\text{CNN})\text{IrH}_2(\text{thf})]^- \), the solvent O atom occupies the empty coordination site \( \text{trans} \) to one of the hydride ligands, with the Ir\(^{III} \) ion in an octahedral coordination geometry. Successive THF/AB exchange in the metal coordination sphere is thermodynamically favored, leading to the complex \( [(\text{CNN})\text{IrH}_2(\text{AB})]^- \) (I, Figure 6). For this complex, two different isomeric forms are conceivable, depending on the interaction site of AB NH\(_3\) end. While the BH\(_3\) end is always directly bound to the metal center in a \( \eta^1 \)-fashion, the NH\(_3\) end may be interacting either with the carbanionic C atom on the pincer skeleton (“C-path”) or with the negative N atom of the NPh\(^-\)amido side arm (“N-path”). In principle, both sites are nucleophilic and both interactions are possible. No interaction with the central pyridine N atom or with the carbene arm was found. This is the typical example of “bifunctional catalyst” bearing an acidic (Ir\(^{III} \)) and a basic (C\(^-\)/NPh\(^-\)) reactive site at the same time, where the metal center and the pincer ligand act cooperatively to extract hydrogen from AB. This class of compound is widespread in the literature, and it has been frequently exploited in the dehydrogenation of BN lightweight inorganic hydrides.\(^{13,14,16-19}\) The analysis of the relative stability of the two isomers I\(_a\) (HC···H−N interaction, Figure 6a) and I\(_b\) (PhN···H−N interaction, Figure 6b) revealed that the latter is slightly more stable \( \Delta G^{\text{THF}}(\text{Ia}/\text{Ib}) = -2.9 \text{ kcal/mol} \). Given the small Gibbs energy difference between the two isomers, both forms were taken into account for the calculation of the reaction profiles. Consistent with the kinetic data from the KIE experiments, a simultaneous BH/NH bond activation occurs and the B−H bond activation is less difficult than that of the N−H bond, since AB coordination to the metal ion through its BH\(_3\) end is responsible for a B−H bond “preliminary” weakening. Indeed, in I, the B−H bond is already partially

![Figure 8](image1.png)

Figure 8. Optimized structures of (a) TS\(_{\text{SC}}\) (from I\(_a\)) and (b) TS\(_{\text{SN}}\) (from I\(_b\)). Selected optimized bond lengths are reported in Ångstroms. H atoms on the pincer ligand not relevant for the discussion are omitted for clarity. Bonds involved in the TS transformation depicted in red dotted lines. See Figure 6 for the atom color code.

![Figure 9](image2.png)

Figure 9. Gibbs energy (THF) vs. reaction coordinate profiles for the first AB dehydrogenation step mediated by I\(_a\) (blue line) and I\(_b\) (red line).
broken, as witnessed by the longer B–H distance on the coordinated bond if compared with the other two.

From this initial geometry, a transition state TS_{SC}/TS_{SN} of the CH\(^{-}\)/NPh\(^{-}\) protonation by NH\(_4\) could be found at \(\Delta G\_\text{TS}^{\text{HF}} = 3.9/5.9\) kcal/mol along the d(N–H–C/CH)/d(N–H–N/Ph) reaction coordinate (Figure 7), with related “inorganic ethylene analogue” (BH\(_2\) = NH\(_2\)) evolution and formation of the trihydride complex [(CNN)IrH\(_4\)]\(^-\) (II). Thermodynamics for this step is favorable in both cases, with \(\Delta G\_\text{TS}^{\text{HF}} = -9.5\) and \(-2.4\) kcal/mol for CH\(^-\) and NPh\(^-\) protonation, respectively.

From II (again, in two isomeric forms IIa and IIb, depending on the protonated group of choice), different reaction paths were then considered. No H\(_2\) formation (nonclassical hydride) from the (classical) hydride ligands with concomitant Ir\textsuperscript{III} \(\rightarrow\) Ir\textsuperscript{I} reduction could be observed, at the computational level used in this study. The same can be said for a direct interaction of the hydride ligands of II with BH\(_2\) = NH\(_2\); all the plausible geometries built in silico led to repulsive interactions and no maxima could be located on the corresponding reaction energy scan. The only mechanism featured by the presence of a maximum along the examined reaction coordinate is the direct H\(_2\) elimination from one hydride ligand on iridium and from the methylene –CH\(_2\)– side arm (IIa) or from the NPh group (IIb), to regenerate the starting active species S and close the catalytic cycle. The corresponding transition states TS\(_{SC}\) and TS\(_{SN}\) are located at 17.6 and 8.5 kcal/mol above IIa and IIb, respectively (Figure 8). The overall G versus reaction coordinate profiles at comparison are reported in Figure 9. From the inspection of the two profiles, we can conclude that for this complex the “N path” (red trace) is to be preferred to the “C path” (blue trace), from both a kinetic (\(\Delta G\)) and a thermodynamic (\(\Delta G\)) viewpoint. In addition, the rate-determining step in both cases is H\(_2\) elimination from the trihydride intermediate II rather than the easy AB activation by the bifunctional complex I. This result is consistent with the zero-order dependence of the reaction rate from AB concentration found experimentally, since AB is not involved in the rate-determining step.

As for 4b, the adduct of the activated neutral species 6 with two AB molecules is thermodynamically favored: \(\Delta G\_\text{TS}^{\text{HF}}\) for the mono- and bis(AB) adducts add up \(-1.4\) and \(-0.7\) kcal/mol, respectively. The result is in agreement with the experimental evidence of a second-order kinetic dependence from AB concentration. This interaction leads to the geometry III (Figure S49), where the first AB molecule sits in the empty coordination site of the five-coordinated 6 interacting through its BH and NH ends with iridium and the deprotonated side arm, respectively [optimized d(Ir–H–B) = 1.88 \AA; optimized d(H–C\textsuperscript{phen}–H–N) = 2.21 \AA]. The second AB molecule weakly interacts with the two hydrides on the metal center to the opposite side of the Ir(CNN) plane [optimized d(Ir–H\textsubscript{phen}–H–B) = 2.86 \AA; optimized d(Ir–H\textsubscript{quart}–H–N) = 1.74 \AA]. No interaction between AB and the NH\(_2\)Bu\(_2\) group is observed. Therefore, this part of the complex is not involved in the catalytic process and no “N path” can be conceived, at odds with its phenyl-substituted analogue. Unfortunately, no plausible reaction mechanism involving two AB molecules in the rate-determining step could be found, at the computational level used (see the Supporting Information).

### CONCLUSIONS

The results reported herein show that highly active Ir\textsuperscript{III} catalysts have been developed by using the same lutidine-derived CNN\(_2\) ligand scaffold with NH amino groups of different basicity. The phenyl-substituted amino complex 4a in particular is the most active iridium-based catalyst in AB dehydrogenation to date, to the best of our knowledge. The excellent catalytic activity of 4a is attributed to the formation of a doubly deprotonated species (the amido iridate S) upon reaction with a 2-fold excess of tBuOK under catalytic conditions. Meanwhile, double deprotonation of Ir-CNN\(_2\) complexes based on N-alkyl substituted ligands like 4b cannot be achieved, likely due to the reduced acidity of their amino group. Finally, density functional theory (DFT) calculations of the mechanisms of the first H\(_2\) release from AB catalyzed by S reveal that, despite the presence of two Bronsted basic sites (the amido fragment and the methine-NHC arm), the most favorable metal–ligand cooperation mode is based on reversible metal-amine/metal-amido interconversion. Given the widespread use of metal complexes containing proton-responsive ligands in many catalytic processes, this approach, based on the use of ligands with two proton-responsive sites, could lead to improved catalytic systems. Further applications in catalysis of metal complexes incorporating more than one Bronsted acidic/basic sites are currently being explored in our laboratories.

### EXPERIMENTAL SECTION

#### General Procedures.

All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen with the following desiccants: sodium-benzophenone-ketyl for diethyl ether (Et\(_2\)O) and tetrahydrofuran (THF); sodium for pentane and toluene; Ca\(_2\)H\(_2\) for dichloromethane and acetonitrile. Imidazolium salts 1a–1c\textsuperscript{15} and Ir(acac)(COD)\textsuperscript{35} were prepared as previously described. Deuterated ammonia borane adducts (NH\(_3\)BD\(_3\), D\(_3\)BH\(_3\), D\(_3\)BD\(_3\)) were synthesized by known methods.\textsuperscript{36} All other reagents were purchased from commercial suppliers and used as received. NMR spectra were obtained on Bruker DRX-400 and AVANCEIII/ASCEND 400R spectrometers.\textsuperscript{13}B{\textsuperscript{1}H} NMR shifts were referenced to external BF\(_3\)Et\(_2\)O, while \textsuperscript{13}C{\textsuperscript{1}H} and \textsuperscript{1}H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me\(_2\)Si. All NMR measurements were performed at 25 °C, unless otherwise stated. NMR signal assignments were confirmed by 2D NMR spectroscopy (\textsuperscript{1}H–\textsuperscript{1}H COSY, \textsuperscript{1}H–\textsuperscript{13}C NOESY, \textsuperscript{1}H–\textsuperscript{13}C HSQC and \textsuperscript{1}H–\textsuperscript{13}C HMBC) for all the complexes. Elemental analyses were run by the Analytical Service of the Instituto de Investigaciones Químicas in a Leco TrueSpec CHN elemental analyzer. IR spectra were acquired on a Thermo Scientific Nicolet iS5 iD7 ATR instrument.

#### Computational Details.

Calculations were performed on the real structures of the Ir\textsuperscript{III} anionic complex 5 and the Ir\textsuperscript{II} neutral complex 6 with the Gaussian16\textsuperscript{16} package at the DFT/MM15\textsuperscript{16} level. Effective core potentials (ECP) and associated SDD basis set\textsuperscript{39} supplemented with \(j\)-polarization functions (SDD(\(j\)))\textsuperscript{40} were used to describe the inner electronic shells and the d valence electrons of the Ir atom. All the other atoms were described with a 6-31+G(dp) basis set.\textsuperscript{41} The structures of the reactants and complexes were fully optimized with this basis set without any symmetry restrictions in THF (\(\varepsilon = 7.42\)), which was introduced within the SMD solvation model.\textsuperscript{42} In these optimizations, individual solvation spheres were placed on the H atoms of AB and on the hydride ligands on Ir. The full geometry optimization was followed by the thermochemistry calculations. The nature of all the stationary points on the potential energy surface was confirmed by vibrational analysis. No scaling factors were applied to the calculated frequencies. The transition-state structures showed only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.\textsuperscript{43}
Synthesis of Ir-CN(B) Complexes. Complex 2a. A solution of 1a (0.105 g, 0.23 mmol) and Ir(acac)(COD) (0.090 g, 0.23 mmol) in CH₂Cl₂ (10 mL) was stirred for 2 days at room temperature. Volatiles were removed under reduced pressure, and the residue was successively washed with pentane (3 × 8 mL) and Et₂O (8 mL), and dried under vacuum. Yellow solid (0.179 g, 99%). Anal. Calcld (%) for C30H36BrIrN4: C, 47.39; H, 4.66; N, 9.00. Found: C, 47.26; H, 4.72; N, 9.00.

A solution of 1b (0.176 g, 0.40 mmol) and [Ir(pincer)NCl](COD) (0.159 g, 0.40 mmol) in CH₂Cl₂ (15 mL) was stirred for 24 h at room temperature. Volatiles were removed under reduced pressure, and the residue was washed with pentane (3 × 10 mL) and dried under vacuum. Yellow solid (0.229 g, 77%). Anal. Calcld (%) for C26H30BrIrN4: C, 46.56; H, 4.51; N, 8.35. Found: C, 46.46; H, 4.50; N, 8.34.

Complex 2b. A solution of 1b (0.176 g, 0.40 mmol) and [Ir(pincer)NCl](COD) (0.159 g, 0.40 mmol) in CH₂Cl₂ (15 mL) was stirred for 2 days at room temperature. Volatiles were removed under reduced pressure, and the residue was washed with pentane (3 × 10 mL) and dried under vacuum. Yellow solid (0.229 g, 77%). Anal. Calcld (%) for C26H30BrIrN4: C, 46.56; H, 4.51; N, 8.35. Found: C, 46.46; H, 4.50; N, 8.34.
Ammonia-Borane Dehydrogenation. Experimental Setup for H₂ Production. H₂ generation was followed up using a Fisher-Porter vessel (25 mL) that was connected to a vacuum line and coupled to an ESI pressure gauge model GS5200-USB (0–6 bar) that was connected to a computer (see the Supporting Information for details).

**Supporting Information**

Representative Procedure for AB Dehydrogenation. A solution of complex 4a (4.3 mg, 6.5 μmol) and tBuOK (1.8 mg, 0.016 mmol) in THF (0.5 mL) was added to a freshly prepared, stirred (750 rpm) solution of AB (50.0 mg, 0.162 mmol) in THF (0.5 mL) at room temperature. H₂ generation was monitored by registering the increase of pressure in the system. At the end of the reaction, the supernatant was transferred to an NMR tube and analyzed via ¹B NMR spectroscopy, to identify the soluble reaction byproducts. The insoluble residue was washed subsequently with THF and Et₂O, and then dried under vacuum before recording the IR spectrum.

**ASSOCIATED CONTENT**

Experimental setup details, kinetic studies, selected NMR spectra, and X-ray diffraction data (PDF).

**Cartesian coordinates, absolute Gibbs energies (THF) and imaginary frequencies (TSs) of the DFT-optimized structures (XYZ).**

**Accession Codes**

CCDC 2113023–2113025 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, 90 Cambridge CB2 1EZ, UK; fax: + 44 1223 363063.

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https://doi.org/10.1021/acs.inorgchem.1c03056

Inorg. Chem. 2021, 60, 18490–18502

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ACKNOWLEDGMENTS

The authors declare no competing financial interest.

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