

Four-Coordinate Iridium(I) Monohydrides: Reversible Dinitrogen Binding, Bond Activations, and Deprotonations

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Despite being implicated as reactive intermediates in important bond activation,¹ dehydrogenation,² and carbonylation³ processes, four-coordinate iridium(I) monohydrides of the formulation HIrL_3 have remained elusive toward isolation. Their existence has been inferred from formal trapping processes, either by transformation to five-coordinate HIrL_4 species or to stable Ir(III) complexes via oxidative addition reactions.^{1–3} However, the inability to isolate these Vaska-type Ir(I) monohydrides has prevented detailed elucidation of their reactivity patterns. Herein we report that judicious use of the monodentate phosphine $\text{P}(\text{CH}_2^1\text{Ad})(i\text{-Pr})_2$ (L^{mAd} ; mAd = methylene-1-adamantyl) allows for the isolation of the four-coordinate Ir(I)–hydride complex $\text{HIr}(\text{N}_2)(\text{L}^{\text{mAd}})_2$. The kinetic persistence of $\text{HIr}(\text{N}_2)(\text{L}^{\text{mAd}})_2$ has allowed us to probe both its reactivity toward small molecules and strong Brønsted bases. Importantly, the L^{mAd} ligand was targeted for the stabilization of a low-coordinate Ir(I) hydride because of the unfavorable strain associated with placement of a cyclometalated adamantane cage within a five-membered chelate ring.⁴

Treatment of a thawing Et_2O solution of the dihydride–chloride, $\text{H}_2\text{IrCl}(\text{L}^{\text{mAd}})_2$ (**1**), with PhMgBr under an N_2 atmosphere provided the four-coordinate monohydride complex $\text{HIr}(\text{N}_2)(\text{L}^{\text{mAd}})_2$ (**2**) as an orange solid (Scheme 1). X-ray crystallographic data obtained for square planar **2** was of sufficient quality to locate the hydride ligand, which occupies the position *trans* to the weakly σ -donating N_2 unit (Figure 1). Intramolecular contacts reflective of agostic interactions⁵ between the L^{mAd} ligands and the Ir center are not observed. FTIR analysis (KBr) of **2** revealed two intense features at 2127 and 2057 cm^{-1} , which are assigned to the $\nu(\text{N}\equiv\text{N})$ and $\nu(\text{Ir}–\text{H})$ bands. Attempts to definitively assign these bands by either ^2H or ^{15}N labeling were unsuccessful due to the concomitant L^{mAd} C–H activation and reversible N_2 -binding processes described below.⁶ However, the ^1H NMR spectrum (C_6D_{12}) of **2** features a triplet integrating to one proton at $\delta = -11$ ppm ($^2J_{\text{HP}} = 23$ Hz), which is indicative of a late metal hydride positioned *cis* to two phosphine ligands ($^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 30$ ppm).

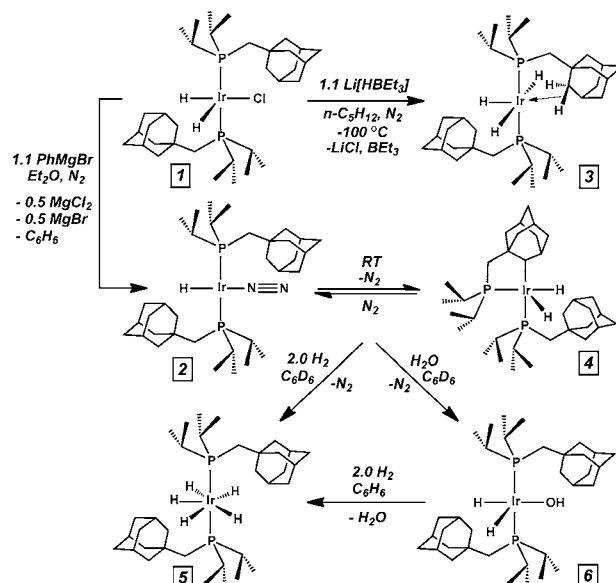
Given the difficulties identifying Ir–H units from X-ray crystallographic data, it is important to note that the trihydride complex, $\text{H}_3\text{Ir}(\text{L}^{\text{mAd}})_2$ (**3**), is also synthetically accessible (Scheme 1, $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 45$ ppm, $\nu(\text{Ir}–\text{H}) = 1721$ cm^{-1}). Structural characterization of **3** clearly revealed an agostic interaction between an adamantyl 2-position and the Ir center (Figure S3.4 (Supporting Information), $d(\text{Ir}–\text{H}20\text{A}) = 2.193$ Å, $d(\text{Ir}–\text{C}20) = 3.101$ Å). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy indicate that the interaction is fluxional at 20 °C as evidenced by the magnetic equivalence of all 12 2-position methylene groups of the L^{mAd} ligands.⁷ Such rapid exchange of agostic C–H units within **3** is significant since N_2 is seemingly blocked from binding to the Ir center at pressures ranging from 1–4 atm.⁸

With respect to the stability of the N_2 unit in four-coordinate **2**, like other iridium(I)–dinitrogen complexes,⁹ it is markedly labile.

Thus, when **2** is dissolved in C_6D_{12} or Et_2O under an N_2 atmosphere, it establishes an equilibrium mixture with the cyclometalated complex $\text{H}_2\text{Ir}(\kappa^2\text{-P,C-L}^{\text{mAd}})(\text{L}^{\text{mAd}})$ (**4**) within 0.5 h as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Scheme 1). As may be expected, **2** is favored in this mixture at low temperature and constitutes 90% of the iridium-containing species present at -45 °C, as assayed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Application of prolonged vacuum is sufficient to fully convert the mixture to **4**. Importantly, exposure of isolated **4** to an N_2 atmosphere re-establishes its equilibrium with **2**, thus confirming that equilibrium can be reached from both species independently. These observations suggest that N_2 either promotes coordinatively induced C–H bond reductive elimination of the cyclometalated L^{mAd} unit or efficiently traps the reactive intermediate, $[\text{HIr}(\text{L}^{\text{mAd}})_2]$, if C–H bond reductive elimination is not assisted by coordination of an exogenous ligand.

Whereas C–H bond reductive elimination concomitant with N_2 binding has been observed previously,¹⁰ we are unaware of reports demonstrating the reversibility of such a process. We suggest that the reversibility observed here is derived from the interplay of two unfavorable phenomena, namely the strain associated with Ad cage cyclometalation⁴ and the generation of a reactive low-coordinate Ir(I) center. Lending credence to this suggestion is the fact that structural determination of **4** from crystals grown under argon revealed relevant C–C–Ir angles that are significantly perturbed from 109° (Figure 1). Indeed, while the C2–C1–Ir angle of **4** is typical for an intra-ring angle in a saturated iridacycle (115.7(4)°), the corresponding C4–C1–Ir angle (117.6(4)°) is significantly expanded from those normally found for cyclometalated iridium

Scheme 1



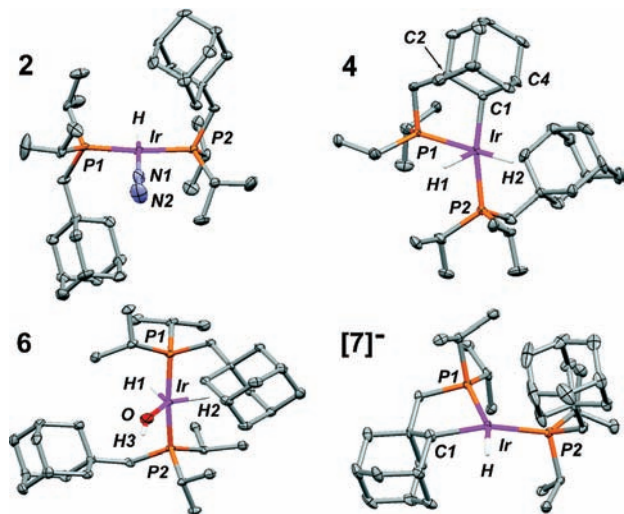
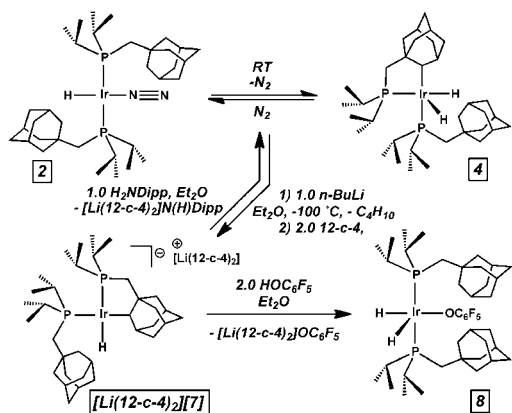


Figure 1. Molecular structures of complexes **2**, **4**, **6**, and the anionic component of $[\text{Li}(12\text{-c-}4)_2][\mathbf{7}]$.

Scheme 2



alkyls.¹¹ Accordingly, these large angles are reflective of strain on the metalated carbon atom as a consequence of its incorporation in the Ad cage system.⁴ We believe that alleviation of this strain provides sufficient driving force to promote C–H reductive elimination, irrespective of the fact that the product contains a reactive monovalent $[\text{Ir}–\text{H}]$ unit.

Despite the equilibrium between **2** and **4**, addition of certain substrates results in the clean formation of a single product. For example, treatment of a **2/4** mixture with 2.0 equiv of H_2 forms the pentahydride complex $\text{H}_3\text{Ir}(\text{L}^{\text{mAd}})_2$ (**5**, $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 14$ ppm, $\nu(\text{Ir}–\text{H}) = 1966\text{ cm}^{-1}$). Notably, addition of 1.0 equiv of H_2 results in a 1:1:2 mixture of **2/4** to **5** to **3**, thereby suggesting that trihydride **3** reacts with H_2 at a rate comparable to either **2** or **4**.

Equilibrium mixtures of **2** and **4** also exhibit clean reactivity with water. Thus, treatment of the mixture with 1.0 equiv of H_2O in C_6H_6 results in N_2 loss and generation of the mononuclear complex $\text{H}_2\text{Ir}(\text{OH})(\text{L}^{\text{mAd}})_2$ (**6**, Figure 1). Interestingly, **6** represents a unique example of a transition metal dihydride–hydroxide complex, which is surprising given the large number of low-valent, metal monohydrides that may be expected to undergo water oxidative addition. While seemingly straightforward, formation of hydride–hydroxo complexes via oxidative addition of H_2O to a single metal center is limited to only a few examples.¹² Furthermore, such complexes are in many cases thermally unstable with respect to H_2O loss or other decomposition pathways.¹³ However, despite the presence of two hydride units, **6** is markedly resistant to H_2O ejection. Thus **6** retains its integrity in C_6D_6 solution at 90°C for

one week, yet rapidly loses H_2O en route to pentahydride **5** when treated with H_2 (2.0 equiv, 25°C).

The persistence of monohydride **2** also allowed for a survey of its reactivity toward strong Brønsted bases. Accordingly, addition of $n\text{-BuLi}$ to a thawing Et_2O mixture of **2/4** readily afforded the cyclometalated salt $\text{Li}[\text{H}(\text{Ir}(\kappa^2\text{-P,C-L}^{\text{mAd}})(\text{L}^{\text{mAd}}))]$ (**Li[7]**, Scheme 2). $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated that this reaction is complete upon mixing at -20°C , thus signifying that monohydride **2** is present in substantial concentration upon introduction of the base. This observation is significant in that deprotonation of **2** potentially generates the d^{10} anion, $[\text{Ir}(\text{N}_2)(\text{L}^{\text{mAd}})_2]^-$, which would be expected to easily cleave an adamantane cage C–H bond. However, it is important to note that direct deprotonation of cyclometalated **4** represents a competing process that may lead to **Li[7]**. Structural characterization of the latter revealed a contact ion-pair wherein the Li^+ ion interacts with both the Ir–C and Ir–H units. Correspondingly, addition of 2.0 equiv of 12-crown-4 to **Li[7]** results in discrete ions, with the anionic component featuring a slightly distorted square planar Ir(I) monohydride (Figure 1).

Neither **Li[7]** nor $[\text{Li}(12\text{-c-}4)_2][\mathbf{7}]$ react with additional $n\text{-BuLi}$. However, the protic reagents 2,6-diisopropyl aniline (H_2NDipp) and pentafluorophenol readily react with $[\text{Li}(12\text{-c-}4)_2][\mathbf{7}]$ under N_2 to regenerate **2/4** mixtures. We believe that $[\text{Li}(12\text{-c-}4)_2][\mathbf{7}]$ serves to deprotonate the H–X unit of these substrates to produce the corresponding lithium amide or phenoxide and **4**. Accordingly, the latter readily binds N_2 concomitant with C–H reductive elimination. This mechanistic scenario finds support from the reaction between $[\text{Li}(12\text{-c-}4)_2][\mathbf{7}]$ and D_2NDipp in Et_2O , which results in deuterium incorporation into L^{mAd} -adamantyl positions as assayed by ^2H NMR spectroscopy. Furthermore, addition of 2.0 equiv of pentafluorophenol to $[\text{Li}(12\text{-c-}4)_2][\mathbf{7}]$ at room temperature cleanly provides the phenoxide complex, $\text{H}_2\text{Ir}(\text{OC}_6\text{F}_5)(\text{L}^{\text{mAd}})_2$ (**8**), in a reaction mirroring that between **2/4** mixtures and H_2O (Scheme 2).

Given the reversibility of C–H activation processes for the L^{mAd} ligand, it is interesting to speculate that conditions may be found in which **Li[7]** functions as a reliable source of the two-coordinate d^{10} anion $[\text{Ir}(\text{L}^{\text{mAd}})_2]^-$. Experiments aimed at probing this ability, in addition to further defining the reactivity accessible to monohydride **2**, are in progress.

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Supporting Information Available: Synthetic procedures, spectroscopic and crystallographic data (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) The closest intramolecular Ir–C_{Ligand} distance observed in **2** is 3.485 Å, resulting in an Ir–H_{Ligand} distance of 2.609 Å.
- (6) Because of reversible cyclometalation, preparation of the monodeuteride $\text{D}[\text{Ir}(\text{N}_2)(\text{L}^{\text{mAd}})_2]$ from $\text{D}_2\text{IrCl}(\text{L}^{\text{mAd}})_2$ resulted in FTIR signatures for **2** in accord with the preference of deuterium to reside on carbon. See Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403–1420. ^{15}N -labeling of **2** was technically impeded by $^{15}\text{N}_2/^{14}\text{N}_2$ exchange (under $^{14}\text{N}_2$) and loss of the $^{15}\text{N}_2$ -label in vacuum or under argon.

- (7) See the Supporting Information for NMR and FTIR spectroscopic evidence supporting the agostic interaction in trihydride **3**.
- (8) To our knowledge, definitive examples of five-coordinate IrH₃L₂ complexes have not been reported. For an early preparation of [H₃Ir(PPh₃)₂], which has not been unequivocally confirmed, see Malatesta, L.; Caglio, G.; Angoletta, M. *J. Chem. Soc.* **1965**, 6974–6983.
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