C−H Bond Activation Reactions with Ligand Adducts of a β-Diiminate Iridium Dihydride

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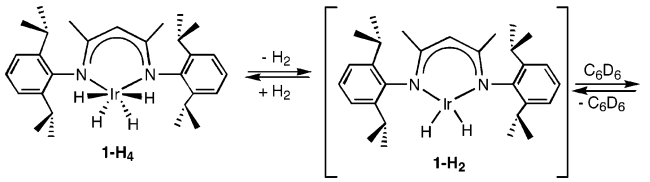
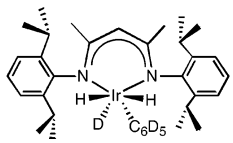
Addition of neutral ligands to the trigonal prismatic iridium tetrahydride (^{iPr}BDI)IrH_4 (BDI = ArNC(Me)CH(Me)CNAr, Ar = 2,6-$^{i}Pr_2C_6H_3$) induces reductive elimination of dihydrogen to afford (^{iPr}BDI)IrH_2(L) (L = phosphine, tetrahydrothiophene, cyclohexene) compounds. A combination of solution NMR data and infrared spectroscopic studies have established that the phosphine dihydride compounds and the cyclohexene adduct are best described as classical iridium(III) dihydride or "stretched dihydrogen" complexes. The corresponding tetrahydrothiophene adduct exhibits spectroscopic features and reactivity patterns consistent with increased iridium(I) dihydrogen character. In complexes containing large cone angle phosphines such as PCy_3 and P^iPr_3, ligand dissociation is facile and isotopic exchange in arene substrates is observed. The experimental data support an Ir(III)−Ir(V) oxidative addition−reductive elimination sequence for C−H bond activation, in contrast to more traditional coordinatively saturated precursors, where Ir(I)−Ir(III) couples are preferred.

Introduction

Organometallic and coordination complexes of iridium have attracted considerable interest, due to their role in hydrocarbon activation.[1,2] Traditionally this chemistry has been dominated by iridium(III) complexes with "L_2X-type" ancillary ligands such as cyclopentadienyl, tris(pyrazolyl)borate,[3] and pincer-type[4−6] ligands. Prototypical examples include Cp*Ir(PMe_3)(R)H[7] and (PCP)-IrH_2 (Cp* = η^5-C_5Me_5, R = alkyl, PCP = κ^3-2,6-$(R_2PCH_2)_2C_6H_3$),[8] which undergo reductive elimination of alkane or dihydrogen to afford formally 16-electron iridium(I) intermediates for oxidative addition of a C−H bond.

Introduction of lower electron count "LX-type" ligand architectures into iridium chemistry allows the synthesis of coordinatively unsaturated precursors that may open unique pathways for hydrocarbon activation. Periana has developed a family of iridium(III) acetylacetonate and related complexes that promote C−H activation in saturated alkanes[9] and are active for the hydroarylation of olefins.[10] With respect to the latter class of reactions, computational studies support C−H activation through an unusual "oxidative hydrogen migration" mechanism.[11] Substituted β-diiminate anions of the general formula ArNC(Me)CH(Me)CNAr (Ar = aryl group) are another class of LX ligand that has found widespread application in transition-metal chemistry owing to their ease of synthesis and steric and electronic modularity.[12] With respect to C−H activation chemistry, Fekl and Goldberg have reported β-diiminate platinum compounds that promote H/D exchange in pentane[13] as well as stoichiometric alkane dehydrogenation.[14] We recently reported the synthesis and crystallographic characterization of the 16-electron iridium(V) tetrahydride (^{iPr}BDI)IrH_4 (**1-H$_4$**; ^{iPr}BDI = ArNC(Me)-CH(Me)CNAr, Ar = 2,6-$^{i}Pr_2C_6H_3$).[15] At 23 °C, this





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molecule promotes H/D exchange in deuterated arene solvents such as benzene-d_6 and toluene-d_8. Preliminary mechanistic investigations support the intermediacy of an iridium(III) dihydride, **1-H$_2$**, consistent with an Ir(III)−Ir(V) oxidative addition−reductive elimination sequence for C−H activation and isotopic exchange. This pathway has been observed with several iridium(V)

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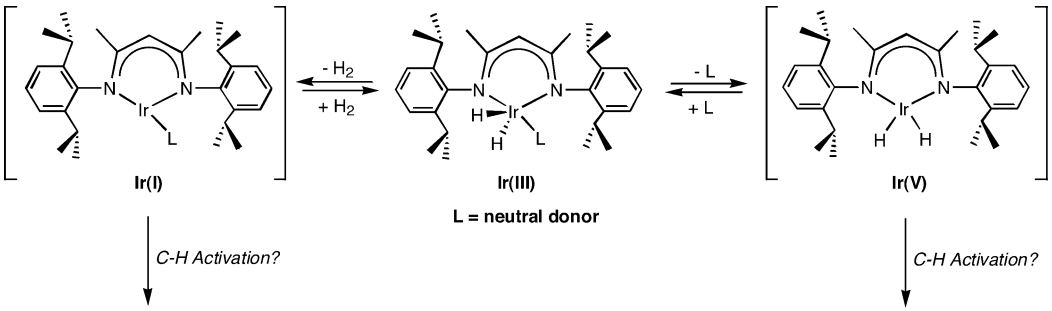


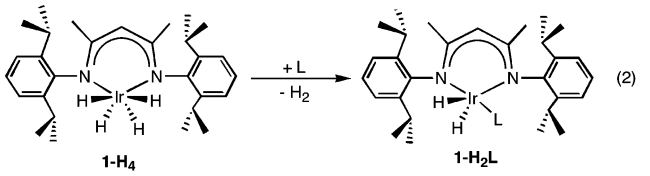
Figure 1. Possible pathways for C−H activation with β-diiminate iridium dihydride complexes.

tetrahydride precursors supported by monoanionic ligands.[16−19]

In this report, we describe the synthesis of a family of (^{iPr}BDI)IrH$_2$L complexes and examine their ground-state structures (e.g. classical iridium(III) dihydrides versus iridium(I) dihydrogen complexes) by NMR and IR spectroscopy and, in some cases, X-ray diffraction. These molecules were prepared to examine whether C−H activation occurs via an Ir(I)−Ir(III) couple accessed by reductive elimination or by an Ir(III)−Ir(V) pathway stemming from ligand dissociation (Figure 1). The relative rate of H/D exchange as a function of donor ligand has been determined, and preliminary mechanistic investigations into the preferred pathway for C−H activation have been explored.

Results and Discussion

As reported previously,[15] addition of PMe$_3$ to **1-H$_4$** results in loss of H$_2$ to yield (^{i}PrBDI)IrH$_2$(PMe$_3$) (**1-H$_2$(PMe$_3$)**). However, **1-H$_2$(PMe$_3$)** shows no propensity to participate in arene C−H activation reactions at ambient temperature, possibly due to the high affinity of the small, electron-rich phosphine for the iridium center. On the basis of these results, larger phosphines were explored with the goal of destabilizing the **1-H$_2$(PR$_3$)** ground state to facilitate generation of **1-H$_2$** in solution. Addition of PPh$_3$, P^{i}Pr$_3$, and PCy$_3$ to **1-H$_4$** in pentane at 23 °C induced reductive elimination of H$_2$ and furnished a series of (^{iPr}BDI)IrH$_2$(PR$_3$) complexes (eq 2).



1-H$_2$(PPh$_3$): L = PPh$_3$ (48 %)
1-H$_2$(P^{i}Pr$_3$): L = P^{i}Pr$_3$ (69 %)
1-H$_2$(PCy$_3$): L = PCy$_3$ (18 %)
1-H$_2$(THT): L = THT (97 %)
1-H$_2$(Cy): L = cyclohexene (40 %)

Each phosphine adduct was obtained as an orange powder in moderate yield. One exception, **1-H$_2$(PCy$_3$)**, was isolated in low yield, owing to the high lipophilicity of the compound. Attempts to prepare a similar adduct by addition of P^{t}Bu$_3$ to **1-H$_4$** produced no reaction.

Sulfur donors such as tetrahydrothiophene (THT) were also found to promote reductive elimination. Thus, (^{iPr}BDI)IrH$_2$(THT) (**1-H$_2$(THT)**) was isolated as a bright yellow powder in excellent yield (eq 2). Performing a similar procedure with THF produced no reaction. Addition of cyclohexene to **1-H$_4$** induced H$_2$ loss to afford the olefin dihydride adduct (^{iPr}BDI)IrH$_2$(η^2-C$_6$H$_{10}$) (**1-H$_2$(Cy)**). Cyclohexane has been observed as a byproduct of excess olefin addition. Regeneration of **1-H$_4$** can be achieved by addition of H$_2$. Consistent with this observation, both **1-H$_2$(Cy)** and **1-H$_4$** serve as hydrogenation catalysts for cyclohexene. While **1-H$_2$(Cy)** is structurally related to (^{Me}BDI)IrH$_2$(COE) (^{Me}BDI = ArNC(Me)CH(Me)CNAr, Ar = 2,6-Me$_2$C$_6$H$_3$, COE = cyclooctene),[20] the latter compound contains smaller β-diiminate aryl substituents and does not participate in hydrogenation chemistry. These results highlight the importance of the size of the aryl substituents in destabilizing the ground state of the olefin hydride complexes to impart catalytic activity.

Each of the β-diiminate iridium dihydride ligand adducts prepared in this study has been characterized by multinuclear NMR spectroscopy. Selected spectroscopic features are presented in Table 1. Also included are the Tolman cone angle and electronic parameters for the free phosphines.[21] In each case except for **1-H$_2$(THT)**, C_{2v}-symmetric compounds are observed by ^{1}H and ^{13}C NMR spectroscopy with equivalent β-diiminate substituents and iridium hydrides. The THT adduct is C_s symmetric in benzene-d_6 solution, exhibiting inequivalent methyl peaks along the ligand backbone as well as inequivalent aryl groups. All of the compounds display Ir−H resonances which are shifted substantially upfield of SiMe$_4$, appearing between −20 and −30 ppm. For the phosphine adducts, the hydrides appear as

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Table 1. Spectroscopic Characterization of 1-H_2(L) Complexes

compd	cone angle (deg)[a]	ν(CO) (cm^{-1})[a]	δ(Ir−*H*)[b] (ppm)	δ(Ir−*P*)[b] (ppm)	$^2J_{P-H}$ (Hz)	ν(Ir−H)[c] (cm^{-1})
1-H_2(PMe_3)	118	2064.1	−28.19	−48.33	40	2147
1-H_2(PPh_3)	145	2068.1	−26.38	1.81	33	2183
1-H_2(P^iPr_3)	160	2059.2	−27.28	22.79	32	2171
1-H_2(PCy_3)[d]	170	2056.4	−27.65	14.00	31	2178
1-H_2(THT)			−25.46			2168
1-H_2(Cy)			−23.09			2255

[a] Values taken from ref 21. [b] Spectra recorded in toluene-d_8. [c] Spectra recorded in KBr. [d] Spectra recorded in cyclohexane-d_{12}.

doublets with $^2J_{P-H}$ coupling constants ranging between 31 and 40 Hz. These observations are consistent with iridium(III) dihydride complexes rather than iridium(I) η^2-dihydrogen compounds.[22] Mixtures of deuterated isotopologs have also been prepared, but reliable H−D coupling constants could not be discerned from the iridium hydride peaks, indicating that the coupling constants may be below the 0.6 Hz line width resolution. Further support for the iridium(III) dihydride descriptor was also provided by infrared spectroscopy, where strong Ir−H bands are observed between 2147 and 2255 cm^{-1}.[22]

T_1(min) values of the iridium dihydrides were also determined at 500 MHz for several representative adducts. For the tricyclohexylphosphine derivative **1-H_2(PCy_3)**, a value of 366 ms was measured at −20 °C, yielding a computed H−H distance of 1.85 Å,[23] consistent with the value of 1.83 Å measured from the solid-state structure (vide infra). A T_1(min) value of 487 ms was determined at −50 °C for **1-H_2(P^iPr_3)**, producing an approximate H−H distance of 2.14 Å, also in agreement with an iridium(III) dihydride structure. A shorter T_1(min) value of 117 ms was determined for **1-H_2(Cy)** at −35 °C, but this value is still within the range typically ascribed to metal hydride rather than η^2-dihydrogen character,[21] although classification as a "stretched dihydrogen complex" may be appropriate.[24] For **1-H_2(THT)**, the lowest measured T_1 value was 248 ms at −20 °C. However, this value is not a true T_1(min), as broadening of the iridium hydride at temperatures below −20 °C has made quantitation unreliable.

1-H_2(THT) also displays unique dynamic behavior with free dihydrogen. Exposure of a benzene-d_6 solution of **1-H_2(THT)** to even trace amounts of H_2 resulted in disappearance of the iridium hydride resonance, consistent with rapid exchange between the hydride ligands and free dihydrogen. Removal of the free gas regenerates the signal. To further investigate this behavior, a solution of **1-H_2(THT)** was exposed to 0.5 atm of D_2 for 30 min and the gas removed. Analysis by ^1H and ^2H NMR spectroscopy revealed complete conversion to **1-D_2(THT)**, consistent with rapid substitution. These observations, in conjunction with the observed C_s symmetry in solution, suggest increased η^2-dihydrogen character in the ground state of **1-H_2(THT)**.

Both **1-H_2(P^iPr_3)** and **1-H_2(PCy_3)** were characterized by single-crystal X-ray diffraction. The solid-state structures are presented in Figures 2 and 3, respectively, while selected metrical parameters are reported in Table 2. The data for **1-H_2(PCy_3)** were of sufficient quality such that the iridium hydrides were located and refined. The crystals of **1-H_2(P^iPr_3)** suffered from twinning and yielded weaker data, preventing definitive location of the iridium hydrides. In both structures, the isopropyl aryl groups are oriented perpendicular to the metal−ligand plane. The geometry of **1-H_2(PCy_3)** is distorted between the idealized trigonal-bipyramidal and square-pyramidal extremes. Unlike **1-H_4**, where statistically invariant iridium−nitrogen distances of 2.049(2) and 2.051(2) Å are observed, **1-H_2(PCy_3)** contains a long Ir(1)−N(1) distance of 2.159(2) Å and a shorter value of 2.067(2) Å for Ir(1)−N(2). These data are consistent with the known strong trans influence of the hydride ligand, producing an elongated iridium−nitrogen bond. This bond alternation is also present in **1-H_2(P^iPr_3)**, where iridium−nitrogen bond distances of 2.151(7) and 2.055(7) Å are observed. Although the hydride ligands were not found in the difference maps from the diffraction data for **1-H_2(P^iPr_3)**, the elongated Ir(1)−N(1) distance offers strong indirect evidence for its location trans to

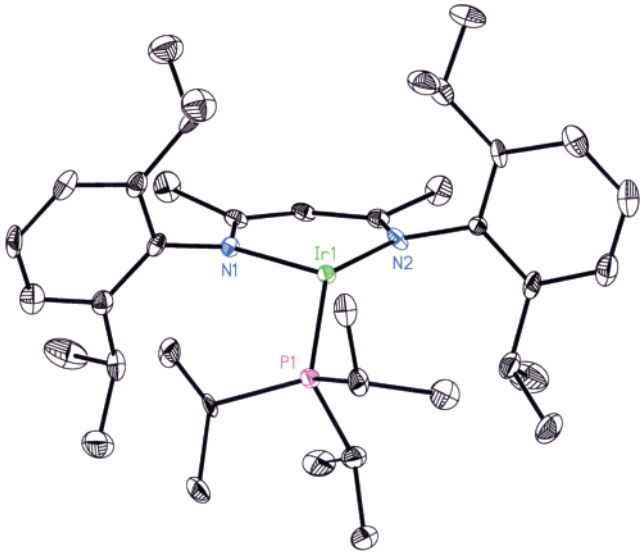

Figure 2. Partially labeled view of the molecular structure of **1-H_2(P^iPr_3)** with ellipsoids at the 30% probability level.

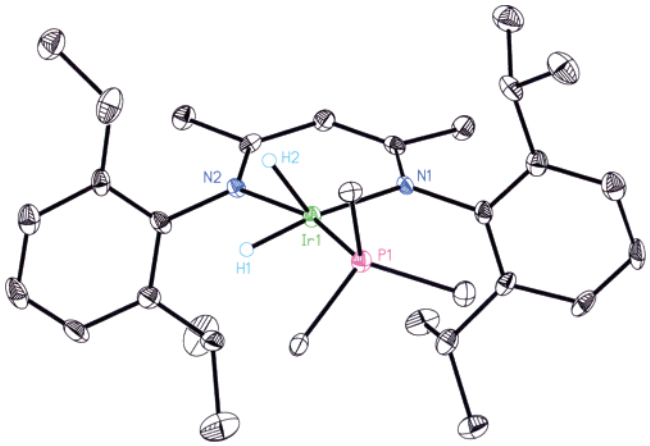

Figure 3. Partially labeled view of the molecular structure of **1-H_2(PCy_3)** with ellipsoids at the 30% probability level. Cyclohexyl substituents and hydrogens, except for the iridium hydrides, are omitted for clarity.

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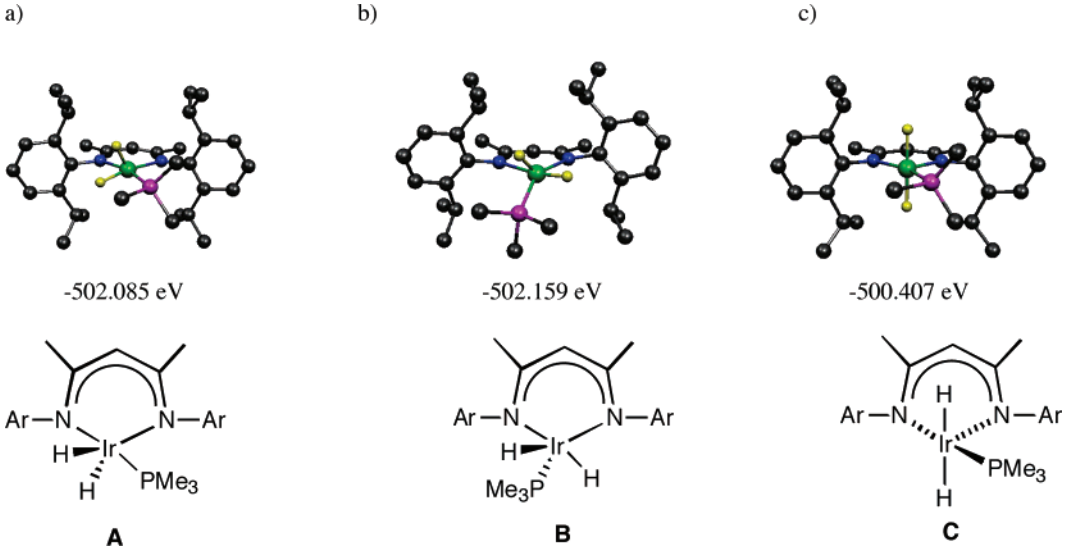


Figure 4. Optimized geometries for the isomers of **1-H$_2$(PMe$_3$)**.

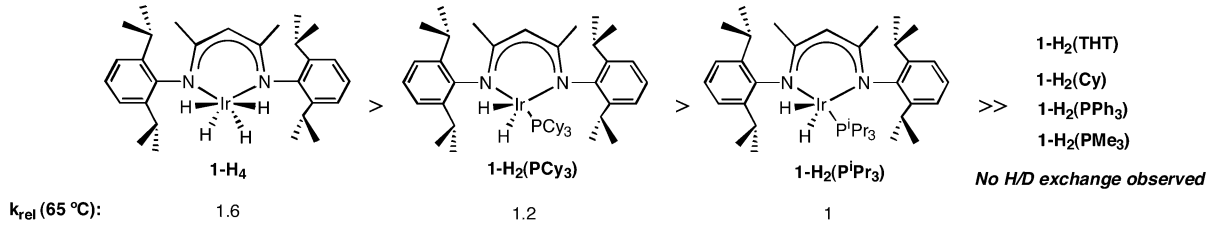


Figure 5. Relative activity of β-diiminate iridium dihydride ligand adducts for H/D exchange in benzene-d_6.

this position. Significantly, the solid-state structures of both **1-H$_2$(PCy$_3$)** and **1-H$_2$(P^{i}Pr$_3$)** do not match the high symmetry observed in solution, suggesting a dynamic process that renders both the ligand substituents and the iridium hydrides equivalent on the time scale of the NMR experiment.

To gain further insight into the relative energies of the different isomers of these five-coordinate structures, full-molecule computational studies were conducted on **1-H$_2$(PMe$_3$)**. Three idealized geometries were optimized and are presented in Figure 4. The lowest energy structure, **A**, where the β-diiminate nitrogens are essentially trans to a phosphine and a hydride, is in excellent agreement with the solid-state structure of **1-H$_2$(PCy$_3$)**. Interchanging the phosphine with one of the hydrides affords isomer **B**, with an energy approximately 2 kcal/mol higher than that of isomer **A**. This structure is in good agreement with the observed solid-state structure of **1-H$_2$(P^{i}Pr$_3$)**. While the kinetic barriers for isomer interconversion have not been computed, a fluxional process where **A** and **B** exchange through a turnstile-type mechanism seems likely. Support for such a dynamic process has been previously proposed by Budzelaar[20] with a related β-diiminate dihydride olefin complex. The computed kinetic barriers were in good agreement with a fluxional process on the time scale of ambient-temperature ^{1}H NMR spectroscopy.

In the lowest energy structure **A**, an H−H distance of 1.86 Å is computed and is in excellent agreement with both the value determined from the T_1(min) measurement (1.85 Å) and the solid-state structure (1.83 Å) of **1-H$_2$(PCy$_3$)**. A third isomer, **C**, with trans hydride ligands was also considered and found to be significantly higher in energy (~40 kcal/mol) than **A** and is not believed to be accessible in solution.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1-H$_2$(P^{i}Pr$_3$) and 1-H$_2$(PCy$_3$)

	1-H$_2$(P^{i}Pr$_3$)	1-H$_2$(PCy$_3$)
Ir(1)−H(1)		1.71(4)
Ir(1)−H(2)		1.50(3)
Ir(1)−N(1)	2.151(7)	2.159(2)
Ir(1)−N(2)	2.055(7)	2.067(2)
Ir(1)−P(1)	2.189(2)	2.2706(7)
H(1)−Ir(1)−P(1)		78.1(14)
H(2)−Ir(1)−P(1)		74.5(12)
H(2)−Ir(1)−N(1)		170.9(120
N(1)−Ir(1)−P(1)	112.9(2)	109.83(6)
N(2)−Ir(1)−P(1)	136.7(2)	162.49(6)
N(2)−Ir(1)−N(1)	89.8(3)	87.47(8)

With a series of β-diiminate iridium dihydride ligand adducts in hand, each complex was assayed for C−H activation and isotopic exchange reactions with deuterated arenes. In a typical experiment, a 2.0 mM solution of the desired iridium complex was prepared in benzene-d_6 and the disappearance of the iridium hydride resonance monitored as a function of time by ^{1}H NMR spectroscopy. The relative rates of benzene H/D exchange (statistically corrected) as a function of the donor are presented in Figure 5. Relative rates were measured in parallel NMR experiments at 65 °C. The complex containing the largest cone angle and most reducing phosphine, **1-H$_2$(PCy$_3$)**, promotes arene H/D exchange over the course of hours at 23 °C. Decreasing the size and nucleophilicity of the phosphine, as in the case of **1-H$_2$(P^{i}Pr$_3$)**, reduces the rate of C−H activation, as only

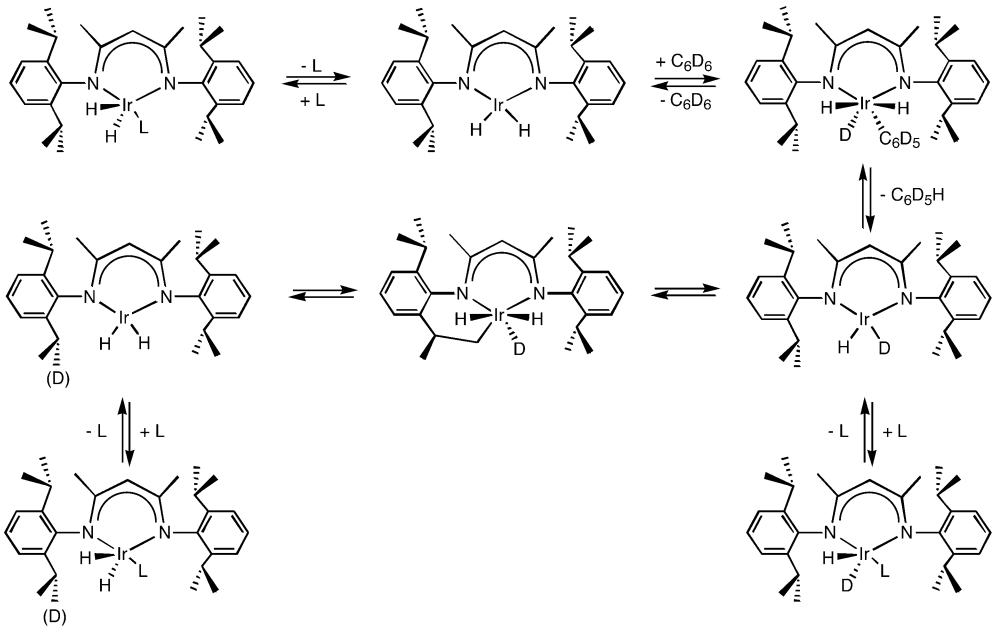
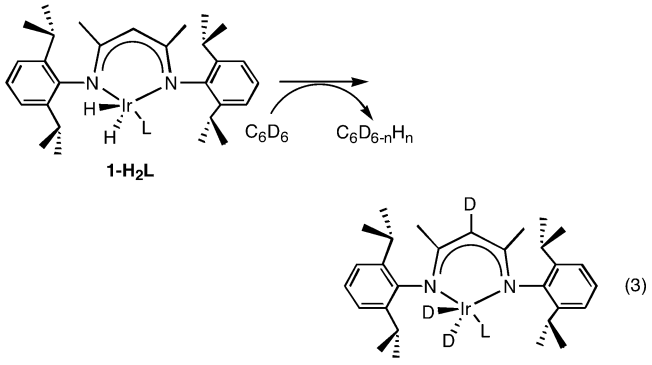


Figure 6. Proposed mechanism for C−H activation and H/D exchange with **1-H$_2$(L)** complexes.

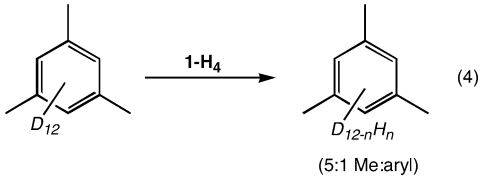
minimal isotopic exchange is observed after several days at ambient temperature. Rates comparable to those for **1-H$_2$(PCy$_3$)** can be achieved by heating the reaction mixture to 50 °C. All of the other adducts prepared in this study are inactive for H/D exchange, even after heating for several days at 50 °C.

Analysis of **1-H$_4$**, **1-H$_2$(PCy$_3$),** and **1-H$_2$(P^{i}Pr$_3$)** by ^{2}H NMR spectroscopy in C_6H_6 after isotopic exchange revealed deuterium incorporation into the methyl substituents on the isopropyl aryl groups. Trace amounts of deuterium were also observed in the methine positions after prolonged reaction times. Evidence for reversible cyclometalation of the isopropyl aryl substituents has been observed previously during isotopic exchange reactions with **1-H$_4$** and by Goldberg with related platinum compounds.[13] In the present cases, experiments with more concentrated (∼30 mmol) samples resulted in deuterium incorporation in the backbone of the β-diiminate ligand, arising from a bimetallic C−H activation event (eq 3).[25]



(3)

The observation of H/D exchange along the β-diiminate backbone suggested that **1-H$_4$** may effect C−H activation in sterically hindered aromatic substrates. Stirring a 15 mM solution of **1-H$_4$** in mesitylene-d_{12} for several days at 23 °C induced isotopic exchange in both the methyl and aryl C−D bonds (eq 4). An approximate



(4)

5:1 preference (statistically corrected) for sp^3 methyl activation over sp^2 aryl activation is observed and is most likely a result of the relative steric accessibility of the two sites.

Several possible mechanistic pathways for isotopic exchange involving arene C−H bond activation were considered. The preferred mechanism that accounts for the experimental observations is presented in Figure 6. Dissociation of the neutral donor generates a formally 14-electron iridium(III) dihydride, which promotes the oxidative addition of the aromatic C−H bond. This pathway is analogous to that proposed for the isotopic exchange reactions involving **1-H$_4$**.[15] Reductive elimination of an arene C−H bond followed by coordination of the neutral donor (or oxidative addition of H_2 in the case of **1-H$_4$**) furnishes the iridium deuteride product.

Competitive with the oxidative addition of the arene is cyclometalation of an isopropyl aryl substituent. As in the arene cases, C−H bond reductive elimination followed by ligand complexation affords the experimentally observed isotopologue. Other pathways involving initial ligand dissociation followed by σ-bond metathesis as well as reductive elimination of dihydrogen followed by oxidative addition of the arene were also considered but are believed to be less likely, on the basis of the experimental data presented below.

If ligand dissociation to afford **1-H$_2$** were operative, the rate of isotopic exchange should be inhibited by added phosphine. Experimentally, these studies have been complicated by secondary reactions between **1-H$_2$-**

(25) Deuteration of the ligand backbone could also occur by transfer of an iridium deuteride, forming a tautomer of the β-diiminate ligand. For examples of such behavior, see ref 12. The observed concentration dependence seems to argue against this possibility.

(PCy_3) and excess PCy_3. Over the course of hours at 23 °C, approximately half of the **1-H_2(PCy_3)** in solution converts to a new iridium species that exhibits no iridium hydride resonance and a new singlet in the ^{31}P NMR spectrum. Complete conversion to this new compound is observed after several days. While definitive characterization has not been accomplished, we tentatively assign this species as the iridium(I) bis(phosphine) complex **1-(PCy_3)$_2$**. Despite these limitations, ligand exchange studies could be performed at low concentrations of added phosphine. Addition of small quantities of PCy_3 to **1-H_2(P^iPr_3)** resulted in phosphine exchange over the course of days at 23 °C, demonstrating the lability of the phosphine ligands.

Additional support for the pathway proposed in Figure 5 is derived from the relative rates of H/D exchange as a function of donor ligand. Larger and more basic phosphines such as PCy_3 and P^iPr_3 produce iridium complexes that are more active for isotopic exchange than their smaller counterparts such as PMe_3. These data, in combination with the isolability of **1-H_4** and computational studies by Hall[17] that favor oxidative addition to Ir(V) over concerted Ir(III) pathways, also support the proposed mechanism.

In addition, the effect of excess dihydrogen on the rate of isotopic exchange with benzene-d_6 was also explored. A side-by-side experiment was conducted whereby solutions of **1-H_2(P^iPr_3)** were heated to 50 °C in benzene-d_6 with and without excess hydrogen. The rates of isotopic exchange were nearly identical in both tubes, suggesting that reductive elimination of dihydrogen to form the transient, 14-electron iridium(I) species **1-(P^iPr_3)** is not a productive pathway for C−H activation and isotopic exchange.

Because **1-H_4** was the most active species for H/D exchange in arene solvents, this compound was also investigated for isotopic exchange with saturated hydrocarbons. Unfortunately, heating **1-H_4** to 85 °C in cyclohexane-d_{12} for 36 h produced no reaction. Likewise, thermolysis of **1-D_4** at 65 °C for 60 h in the presence of a large excess (∼10 equiv) of either methane or butane in benzene-d_6 solution produced no observable change. Extending the reaction time in all cases leads to decomposition of the iridium complex.

In summary, a series of β-diiminate iridium(III) dihydride ligand adducts have been prepared and characterized. These molecules are best characterized as classical iridium(III) dihydrides or as "stretched dihydrogen" complexes. Preliminary findings suggest that ligand dissociation provides access to a reactive iridium(III) dihydride species that promotes oxidative addition of arene C−H bonds, even in hindered substrates such as mesitylene and the β-diiminate ligand backbone. This proposed mechanistic pathway is in contrast to observations in coordinatively saturated iridium(III) dihydride precursors supported by L_2X-type ligands, where reductive elimination of dihydrogen to form an Ir(I) species is preferred.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high-vacuum-line, Schlenk, or cannula techniques or in an M. Braun inert-atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[26] Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Hydrogen and argon gas were purchased from Airgas Inc. and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high-vacuum line. **1-H_4** and **1-H_2(PMe_3)** were prepared as described previously.[15] PPh_3, PCy_3, and P^iPr_3 were purchased from Acros and used as received. THT and cyclohexene were purchased from Acros and distilled from CaH_2 before use. Mesitylene-d_{12} was purchased from Acros and passed over alumina before use.

^1H spectra were recorded on Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.763, 399.780, and 500.62 MHz, respectively. ^{13}C NMR spectra were obtained on Varian Mercury 300 and Inova 500 spectrometers operating at 75.37 and 100.52 MHz, respectively. All chemical shifts are reported relative to $SiMe_4$ using ^1H (residual) chemical shifts of the solvent as a secondary standard. ^2H NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 76.851 MHz, and the spectra were referenced using an internal benzene-d_6 standard. ^{31}P NMR spectroscopy was carried out on a Varian Inova 400 spectrometer operating at 161.83 MHz, and spectra were referenced to an external H_3PO_4 standard. Infrared spectroscopy was conducted on a Mattson RS-10500 Research Series FT-IR spectrometer calibrated with a polystyrene standard.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD area detector system equipped with a molybdenum X-ray tube (λ = 0.710 73 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

All calculations were performed with the Amsterdam Density Functional Theory (ADF2003.01) suite of programs.[27−29] The calculations included scalar relativistic effects (ZORA)[30] for all atoms. The Vosko, Wilk, and Nusair (VWM) local density approximation,[31] Becke's exchange,[32] and Perdew's correlation[33] were used. The cores of the atoms were frozen

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up to 1s for C and N, 2p for P, and 4s for Ir. Uncontracted Slater-type orbitals (STOs) of triple-ζ quality with one polarization were employed. This basis set is denoted as TZP in the ADF program. Each geometry optimization was carried out without symmetry constraints.

Preparation of (^{iPr}BDI)IrH$_2$(PPh$_3$) (1-H$_2$(PPh$_3$)). A 20 mL scintillation vial was charged with 0.012 g (0.020 mmol) of **1-H$_4$** and approximately 10 mL of pentane. To the vial was added 0.005 g (0.019 mmol) of PPh_3, resulting in effervescence of dihydrogen and an immediate color change from yellow to orange. The resulting reaction mixture was stirred at ambient temperature for 16 h, after which time the solution was concentrated and chilled to −35 °C to yield 0.008 (48%) of **1-H$_2$(PPh$_3$)** as an orange powder. Anal. Calcd for $C_{47}H_{58}IrN_2P$: C, 64.58; H, 6.69; N, 3.20. Found: C, 64.37; H, 6.42; N, 2.93. ^{1}H NMR (toluene-d_8): δ 1.01 (d, 12H, 7 Hz, CHMe_2), 1.16 (d, 12H, 7 Hz, CHMe_2), 1.75 (s, 6H, CH_3), 3.45 (sept, 4H, 7 Hz, CHMe$_2$), 5.43 (s, 1H, CH), 6.84−7.21 (Ar H), −26.30 (d, 2H, 30 Hz, Ir−H). ^{31}P{^{1}H} NMR (toluene-d_8): δ 1.81 (s, Ir−PPh$_3$). ^{31}P NMR (toluene-d_8): δ 1.87 (t, 32 Hz). ^{13}C NMR (benzene-d_6): δ 24.34, 24.90 (CHMe_2), 28.83 (CMe), 102.30 (CH), 123.94 (Ar p-C), 125.82 (Ar m-C), 128.92, 129.24, 134.35 (PPh$_3$), 140.72 (Ar o-C). IR (KBr): ν_{Ir-H} 2183 cm^{-1}.

Preparation of (^{iPr}BDI)IrH$_2$(P^{i}Pr$_3$) (1-H$_2$(P^{i}Pr$_3$)). A 20 mL scintillation vial was charged with 0.065 g (0.105 mmol) of **1-H$_4$** and approximately 10 mL of pentane. Via microsyringe, 22 μL (0.115 mmol) of P^{i}Pr$_3$ was added and an immediate color change from yellow to orange was observed. The resulting orange reaction mixture was stirred at ambient temperature for 16 h, after which time the solution was concentrated and chilled to −35 °C to yield 0.056 g (69%) of **1-H$_2$(P^{i}Pr$_3$)** as orange crystals. Anal. Calcd for $C_{38}H_{64}IrN_2P$: C, 59.11; H, 8.35; N, 3.63. Found: C, 58.91; H, 8.53; N, 3.38. ^{1}H NMR (benzene-d_6): δ 0.77 (m, 21H, P^{i}Pr$_3$), 1.95 (d, 12H, 7 Hz, CHMe_2), 1.41 (d, 12H, 7 Hz, CHMe_2), 1.75 (s, 6H, CH_3), 3.56 (sept, 4H, 7 Hz, CHMe$_2$), 5.37 (s, 1H, CH), 7.09 (br s, 4H, Ar m-H), 7.16 (br s, 2H, Ar p-H), −27.28 (d, 2H, 32 Hz, Ir−H). ^{31}P{^{1}H} NMR (benzene-d_6): δ 22.79 (s, Ir−PMe$_3$). ^{13}C NMR (benzene-d_6): δ 20.19, 28.71 (PCHMe_2), 24.83, 25.15 (CHMe_2), 25.45 (CHMe$_2$), 27.96 (PCHMe$_2$) 101.66 (CH), 123.87 (p-Ar), 125.58 (m-Ar), 140.72 (o-Ar). IR (KBr): ν_{Ir-H} 2171 cm^{-1}.

Preparation of (^{i}PrBDI)IrH$_2$(PCy$_3$) (1-H$_2$(PCy$_3$)). This molecule was prepared in a manner similar to that for **1-H$_2$(PPh$_3$)** with 0.030 g (0.049 mmol) of **1-H$_4$** and 0.016 g (0.057 mmol) of PCy$_3$, yielding 0.008 g (18%) of **1-H$_2$(PCy$_3$)** as red crystals. ^{1}H NMR (cyclohexane-d_{12}): δ 0.99 (m, PCy$_3$), 1.13 (d, 12H, 7 Hz, CHMe_2), 1.28 (d, 12H, 7 Hz, CHMe_2), 1.56 (m, PCy$_3$) 1.66 (s, 6H, CH_3), 3.38 (sept, 4H, 7 Hz, CHMe$_2$), 5.21 (s, 1H, CH), 7.03 (br s, 4H, Ar m-H), 7.21 (br s, 2H, Ar p-H), −27.65 (d, 2H, 32 Hz, Ir−H). ^{31}P{^{1}H} NMR (benzene-d_6): δ 14.00 (s, Ir−PCy$_3$). ^{13}C NMR (cyclohexane-d_{12}): δ 24.97, 27.90, 28.24 (PCy$_3$), 25.17, (CHMe_2), 28.62 (CMe), 31.38 (CHMe$_2$), 101.25 (CH), 123.65 (Ar p-C), 125.49 (Ar m-C), 140.74 (Ar o-C). IR (KBr): ν_{Ir-H} 2178 cm^{-1}.

Preparation of (^{iPr}BDI)IrH$_2$(η^2-C$_6$H$_{10}$) (1-H$_2$(Cy)). A 25 mL round-bottom flask was charged with 0.035 g (0.057 mmol) of **1-H$_4$** and approximately 10 mL of pentane. A 180° needle valve was attached, and 1.1 equiv of dry cyclohexene was vacuum-transferred onto the solution on the high-vacuum line using a calibrated gas bulb. The yellow reaction solution was stirred overnight, and pentane was removed in vacuo to yield 0.024 g (40%) of **1-H$_2$(Cy)** as a dark yellow solid. Anal. Calcd for $C_{35}H_{53}IrN_2$: C, 60.57; H, 7.70; N, 4.04. Found: C, 60.86; H, 7.53; N, 3.75. ^{1}H NMR (benzene-d_6): δ 1.12 (d, 12H, 6 Hz, CHMe_2), 1.49 (br d, 12H, 6 Hz, CHMe_2), 1.79 (s, 6H, CH_3), 2.23 (m, 4H, Cy H), 3.35 (br, 4H, CHMe$_2$), 3.55 (br, 2H, Cy H), 5.40 (s, 1H, CH), 7.07−7.19 (Ar H), −23.09 (s, 2H, Ir−H). ^{13}C NMR (benzene-d_6): δ 21.69, 24.74, 59.64 (cyclohexene), 24.14, 24.58 (CHMe_2), 28.16 (CMe), 32.54 (CHMe$_2$), 101.14 (CH), 123.93 (Ar p-C), 126.56 (Ar m-C), 141.98 (Ar o-C). IR (KBr): ν_{Ir-H} 2255 cm^{-1}.

Preparation of (^{iPr}BDI)IrH$_2$(SC$_4$H$_4$) (1-H$_2$(THT)). This molecule was prepared in a manner similar to that for **1-H$_2$(Cy)** with 0.037 g (0.060 mmol) of **1-H$_4$** and 1.2 equiv of dry THT, yielding 0.041 g (97%) of **1-H$_2$(THT)** as a bright yellow powder. Anal. Calcd for $C_{33}H_{51}IrN_2S$: C, 56.62; H, 7.34; N, 4.00. Found: C, 56.28; H, 6.97; N, 3.97. ^{1}H NMR (benzene-d_6): δ 1.17 (dd, 12H, 7 Hz, CHMe_2), 1.21 (m, 4H, α-H THT), 1.35 (d, 6H, 7 Hz, CHMe_2), 1.57 (d, 6H, 7 Hz, CHMe_2), 1.74 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.19 (br t, 4H, β-H THT), 3.48 (m, 4H, CHMe$_2$), 5.38 (s, 1H, CH), 7.09 (br s, 2H, Ar m-H), 7.11 (br s, 2H, Ar m-H), 7.18 (br s, 1H, Ar p-H), 7.20 (br s, 1H, Ar p-H), −25.46 (s, 2H, Ir−H). ^{13}C NMR (benzene-d_8): δ 24.00 (β-C THT), 24.45, 24.48, 24.70, 24.77 (CHMe_2), 24.90, 28.16 (CMe), 29.28 (CHMe$_2$), 47.13 (α-C THT), 101.01 (CH), 123.48, 123.74 (Ar p-C), 125.81, 126.13 (Ar m-C), 140.91, 141.90 (Ar o-C). IR (KBr): ν_{Ir-H} 2168 cm^{-1}.

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Supporting Information Available: Crystal structure data for **1-H$_2$(P^{i}Pr$_3$)** and **1-H$_2$(PCy$_3$)** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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