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Synthesis of a β-diiminate iridium tetrahydride for arene C–H bond activation†

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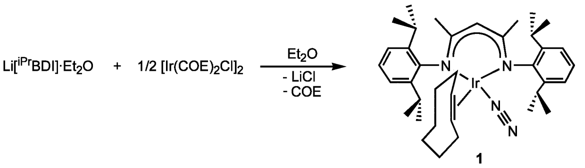
The preparation of the iridium tetrahydride (^{iPr}BDI)IrH$_4$ {BDI = ArNC(Me)CH(Me)CNAr, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$} and its activity in the catalytic C–H activation of arenes is described.

Organometallic complexes of iridium have shown considerable promise for the selective activation of carbon–hydrogen bonds.[1] Iridium 'pincer' complexes, (PCP)IrH$_2$ {PCP = η^3-2,6-(R$_2$PCH$_2$)$_2$C$_6$H$_3$}, are particularly noteworthy given their high thermal stability and efficiency in catalytic alkane[2] and amine[3] dehydrogenation. As part of our program aimed at developing synthetic methods involving both C–C and C–H cleavage,[4] we are developing new platforms for iridium hydride chemistry with the goal of discovering efficient and selective catalysts.

Monoanionic β-diiminate ligands are attractive ancillary ligands for catalytic C–H bond activation given their ease of synthesis, steric and electronic tunability and conceptual relationship to the well-studied pincer ligands.[5] Fekl and Goldberg have recently demonstrated the utility of β-diiminate platinum compounds for promoting facile H/D exchange in pentane,[6] as well as alkane dehydrogenation.[7] β-Diiminate iridium chemistry has been pioneered by Budzelaar *et al.*, who reported the synthesis of (^{Me}BDI)Ir(COE) {BDI = ArNC(Me)CH(Me)CNAr, Ar = 2,6-Me$_2$C$_6$H$_3$, COE = cyclooctene}, a molecule that adopts an Ir(III) allyl hydride ground-state structure.[8] Addition of dihydrogen to this complex yields a stable iridium(III) olefin dihydride that is unreactive toward excess alkene or H$_2$.[9]

We hypothesized that coordination of larger β-diiminate ligands to iridium may facilitate olefin dissociation, engendering more reactive iridium hydride species. The addition of one such example, Li[^{iPr}BDI]·Et$_2$O,[10] to [Ir(COE)$_2$Cl]$_2$ in the presence of N$_2$ afforded bright yellow crystals identified as (^{iPr}BDI)Ir(COE)N$_2$ (**1**; eqn. 1).[11] X-Ray diffraction studies‡ (Fig. 1) revealed a square-planar iridium center with the β-diiminate aryl groups and the disordered COE ligand oriented perpendicular to the square plane. The N–N bond length of 1.107(4) Å and the strong N–N stretch at 2126 cm^{-1} in the solid-state infrared spectrum are consistent with a weakly activated N$_2$ ligand. Curiously, no N–N stretch is observed in the solution IR spectrum in pentane, although a strong peak is observed at 2122 cm^{-1} in benzene. Both the ^{1}H and ^{13}C NMR spectra of **1** in benzene-d_6 indicate C_s symmetry, consistent with the solid-state structure.



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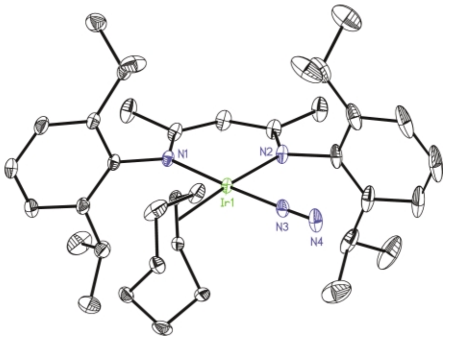


Fig. 1 Molecular structure of (^{iPr}BDI)Ir(COE)N$_2$ (**1**) plotted with 30% probability ellipsoids.

Treatment of a pentane solution of **1** with 4 atm of H$_2$ resulted in rapid hydrogenation of the COE ligand and allowed isolation of the iridium tetrahydride complex, (^{iPr}BDI)IrH$_4$ (**2**) as bright yellow blocks (eqn. 2). In toluene-d_8, **2** displays C_{2v} symmetry and a single hydride resonance centered at −16.99 ppm is observed in its ^{1}H NMR spectrum. This peak is unchanged upon cooling the solution to −80 °C. Whereas the smaller (^{Me}BDI)Ir(COE) complex oxidatively adds H$_2$ to form a relatively unreactive olefin dihydride complex,[8] incorporation of larger isopropyl aryl substituents allows synthesis of **2**, demonstrating the profound impact of subtle changes in the ligand architecture on the reactivity of iridium olefin complexes.

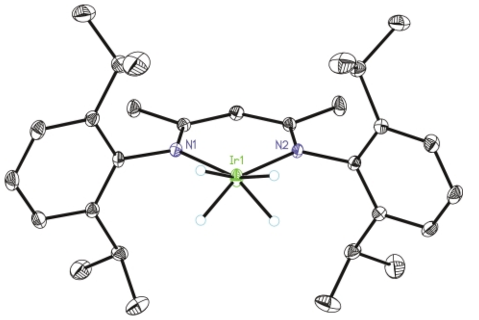
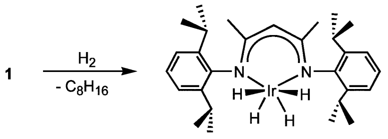


Fig. 2 Molecular structure of (^{iPr}BDI)IrH$_4$ (**2**) plotted with 30% probability ellipsoids.

A combination of X-ray diffraction, computational and solution spectroscopic studies were carried out to elucidate the ground-state structure of **2**. Possibilities include a classical iridium(V) tetrahydride or rapidly equilibrating Ir(III) or Ir(I) η^2-dihydrogen complexes.[12] Single crystal X-ray diffraction‡ on bright yellow crystals of **2** revealed a trigonal prismatic iridium tetrahydride in the solid state (Fig. 2). The data were of sufficient quality that each hydrogen atom, including the iridium hydrides, could be located in the difference map and isotropically refined. The iridium hydride distances are statistically invariant and range between 1.45–1.48 Å, slightly shorter, as expected, than typical Ir–H distances of 1.58–1.59 Å determined by neutron diffraction.[13] The closest H···H contacts are 1.25 and 1.30 Å, suggesting a classical iridium tetrahydride in the solid state.[13]



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† Electronic supplementary information (ESI) available: full experimental and computational details, plus X-ray crystallographic data for **1**-N$_2$ and **2**. See http://www.rsc.org/suppdata/cc/b3/b315817a/

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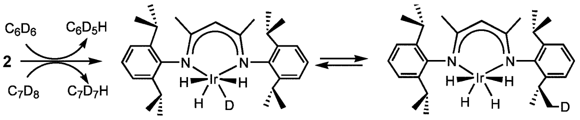
Geometry optimizations on **2** were carried out using the ADF program suite (TZ2P/ZORA).† The computational results are in good agreement with the solid-state structure, predicting a trigonal prismatic iridium tetrahydride with isopropyl aryl groups flanking the iridium–BDI plane. The computed Ir–H distances are slightly longer (~0.1 Å) than the solid-state structure, highlighting the underestimation of the Ir–H distances by the X-ray diffraction experiment.

A combination of NMR and IR spectroscopic studies were used to elucidate the structure of **2** in solution. The isotopomers $(^{iPr}BDI)IrD_4$ (**2**-d_4) and $(^{iPr}BDI)IrD_2H_2$ (**2**-d_2) were prepared by addition of D_2 and HD, respectively, to pentane solutions of **1**. In general, the iridium hydride (deuteride) resonance is unaffected by isotopic substitution (−16.86 ppm for **2**-d_4 and −16.96 ppm for **2**-d_2), consistent with a classical Ir(V) tetrahydride structure. The relatively low H–D coupling constant of 3.4 Hz measured for **2**-d_2 is also in accord with this structural assignment.[13] A T_1(min) value of 74 ms (500 MHz) was measured in toluene-d_8 for the hydride signal of **2**, consistent with the short H···H distances observed in the solid state.[14] Infrared spectra of **2** in both the solid state and in pentane solution display a single broad band centered at 2221 and 2236 cm^{-1}, respectively. These observations are similar to those recently described for the seven-coordinate Tp^*IrH_4 (Tp^* = $HB(3,5\text{-}Me_2pyrazol\text{-}1\text{-}yl)_3$, which adopts a classical Ir(V) tetrahydride structure similar in energy to a kinetically accessible Ir(III) dihydrogen complex.[15]

The reactivity of **2** with σ-donor and aromatic hydrocarbons has been explored. Addition of one equivalent of PMe_3 to **2** resulted in loss of one equivalent of dihydrogen, forming $(^{iPr}BDI)IrH_2(PMe_3)$ (**3**) as an orange solid. Performing the reaction under four atmospheres of H_2 has no effect on the rate of substitution. A single iridium hydride resonance is observed in benzene-d_6 solution as a doublet ($^2J_{P-H}$ = 40 Hz) centered at −28.19 ppm. Likewise, a singlet centered at −48.33 ppm is also observed by $\{^1H\}^{31}P$ NMR spectroscopy. This peak expands to a triplet, arising from coupling to two equivalent iridium hydrides, upon selective decoupling of the PMe_3 ligand. The equivalent hydride resonances, along with a C_{2v} symmetric BDI ligand environment, are consistent with either a fluxional five-coordinate molecule or a trigonal bipyramidal iridium dihydride.

Monitoring benzene-d_6 solutions of **2** over the course of 3 days at ambient temperature revealed complete disappearance of the iridium hydride signal with concomitant growth of the C_6D_5H resonance. Analysis of **2** by ^{2}H NMR spectroscopy after complete isotopic exchange demonstrated deuterium incorporation into the iridium–hydride (deuteride) position as well as into the isopropyl methyl groups of the BDI ligand (eqn. 3). Presumably, isotopic exchange in the iridium hydride arises from oxidative addition of an aromatic C–D bond, followed by reductive elimination of benzene-d_5.[16] Consistent with this hypothesis, the rate of the isotopic exchange reaction is inhibited by approximately 50% by excess dihydrogen, suggesting an Ir(III) dihydride is the catalytically active species.



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The deuterium present in the β-diiminate ligand may be accounted for by reversible cyclometalation, similar to that previously observed in the corresponding platinum system.[6] In the present case, no deuterium incorporation is observed in the isopropyl methine position, suggesting cyclometalation only occurs with the more accessible methyl groups.

Isotopic exchange reactions were also conducted with toluene-d_8. Proton incorporation is observed in all positions, with a preference for activation of the aromatic C–D bonds over the methyl group (2 : 1 statistically corrected), consistent with precoordination of the arene.[17] Within the aromatic positions, a slight preference for the *meta* over the *ortho*/*para* sites is observed. This lack of selectivity contrasts with previously observed rhodium arene activitations, where metal–carbon bond strengths dictate the position of C–H activation,[17] although deviation from this trend with iridium complexes has been reported.[18]

The increased reactivity of formally 16-electron **2** toward exogeneous ligands and arene activation contrasts with the forcing conditions required for ligand-induced reductive elimination reported for the 18-electron piano stool complexes Cp^*IrH_4[19] (Cp^* = $\eta^5\text{-}C_5Me_5$) and Tp^*IrH_4.[20] These initial investigations demonstrate the rich and potentially unique chemistry associated with β-diiminate iridium hydride complexes. Access to these molecules was made possible by subtle manipulation of the ligand architecture, leading to facile olefin hydrogenation. Further exploration of these molecules in carbon–hydrogen bond activation processes and other catalytic reactions is currently under investigation in our laboratory.

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Notes and references

‡ *Crystal data* for **1**: $C_{40}H_{62}IrN_4$, M = 791.14, triclinic, a = 8.8311(3), b = 12.1110(4), c = 18.4635(5) Å, α = 84.6470(10), β = 84.4850(10), γ = 84.6470(10)°, V = 1893.95(10) Å^3, T = 173(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-K$_\alpha$) = 3.556 mm^{-1}, 40 861 reflections measured, 13 735 unique (R_{int} = 0.0519), which were used in all calculations; the final R_1 was 0.0394. For **2**: $C_{29}H_{45}IrN_2$, M = 613.87, monoclinic, a = 12.6062(7), b = 15.9992(9), c = 14.2536(8) Å, β = 105.309(2)°, V = 2772.8(3) Å^3, T = 173(2) K, space group $P21_n$, Z = 4, μ(Mo-K$_\alpha$) = 4.833 mm^{-1}, 47 442 reflections measured, 9822 unique (R_{int} = 0.0516), which were used in all calculations; the final R_1 was 0.0332. CCDC 225948 and 225949. See http://www.rsc.org/suppdata/cc/b3/b315817a/ for crystallographic data in CIF or other electronic format.

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