Carbene Ligands

An Electron-Deficient Iridium(III) Dihydride Complex Capable of Intramolecular C–H Activation**

*Natalie M. Scott, Vincent Pons, Edwin D. Stevens, D. Michael Heinekey, and Steven P. Nolan**

Coordinatively unsaturated late-transition-metal hydride complexes are of significant importance in light of their vital role in many stoichiometric and catalytic reactions.[1] In particular, unsaturated cationic iridium hydride complexes have been shown to mediate a range of catalytic transformations, including alkane C–H bond activation.[2] Unsaturated cationic complexes are stabilized in many cases through the coordination of solvent molecules and/or by agostic interactions.[3] It has always been postulated that complexes coordinated with only sigma-bonding interactions, including agostic interactions, possess weak metal binding.[4] Thus, well-defined and characterized examples of these interactions are rare because of their high reactivity/poor stability.[5,6]

We recently reported the interactions of *N,N'*-di(*tert*-butyl)imidazol-2-ylidene (I*t*Bu) with $[\{Ir(coe)]_2Cl\}_2]$ (coe = cyclooctene) leading to the formation of a doubly cyclometalated product $[Ir(ItBu')_2Cl]$ (**1**; Scheme 1). Simple halide abstraction in **1** with $AgPF_6$ allows the preparation of a four-coordinate 14-electron complex $[Ir(ItBu')_2](PF_6)$ (**2**) with a *cis* stereochemistry of the two vacant positions at the pseudooctahedral Ir center.[6]

The highly unsaturated nature of **2** led us to examine its reactivity with dihydrogen. Exposure of the deep-red solution of **2** in dichloromethane to H_2 gas resulted in the solution changing rapidly to pale yellow, and afforded a microcrystalline product **3** in excellent yield after work up in pentane [Eq. (1)].[7] The ^1H NMR spectrum of **3** at 298 K exhibits a single resonance in the hydride region at $\delta = -29.03$ ppm. A single sharp resonance at $\delta = 1.55$ ppm for the *t*butyl groups and a resonance at $\delta = 7.18$ ppm for the imidazole units were observed. The intensity ratio of the resonances for the hydride/*t*butyl/imidazole moieties is 2:36:4, which suggests **3** is a dihydride complex. Crystals of suitable quality for X-ray

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[*] Dr. N. M. Scott, Prof. Dr. E. D. Stevens, Prof. Dr. S. P. Nolan
Department of Chemistry
University of New Orleans
New Orleans, LA 70148 (USA)
Fax: (+1) 504-280-6860
E-mail: snolan@uno.edu

Dr. V. Pons, Prof. Dr. D. M. Heinekey
Department of Chemistry
Box 351700, University of Washington
Seattle WA 98195-1700 (USA)

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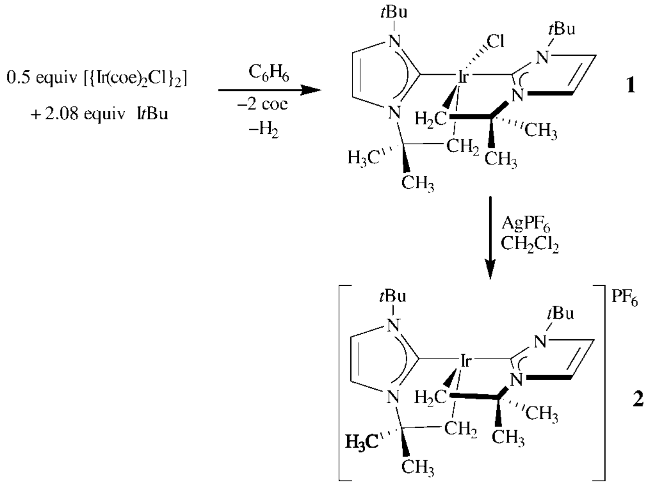
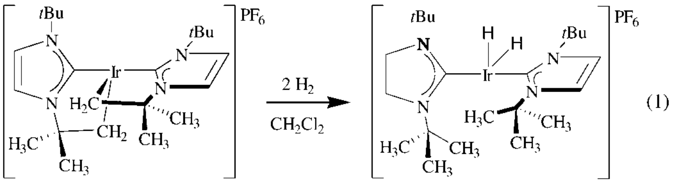


Scheme 1. Synthetic routes to **1** and **2**.



2 **3** (1)

studies were grown by slow evaporation from a dichloromethane/pentane solution. The structure determination confirmed that **3** was the stable electron-deficient iridium(III) dihydride complex [Ir(I*t*Bu)$_2$(H)$_2$](PF$_6$) (Figure 1).[8,9]

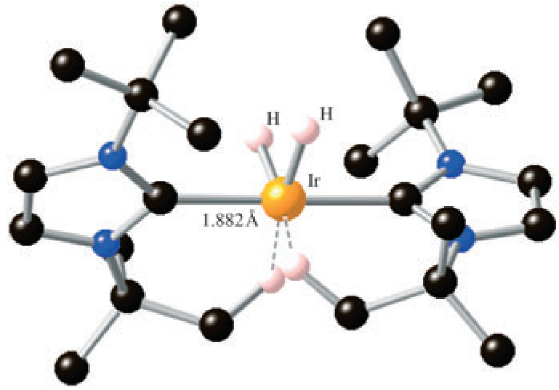


Figure 1. Ball-and-stick representation of [Ir(I*t*Bu)$_2$(H)$_2$](PF$_6$) (**3**). The PF$_6$ counterion is omitted for clarity.

The solid-state structure possesses a twofold rotation axis and clearly shows a double agostic interaction between the *t*butyl groups and the iridium center with distances of 2.653 and 1.882 Å for each agostic interaction (Ir–C9 and Ir–H9A, respectively). The four-coordinate Ir^{III} complex adopts a pseudooctahedral environment with two vacant sites in a *cis* arrangement with the carbenic carbon atoms *trans* to each other but *cis* to the two *cis* hydride ligands. Furthermore, the two *cis* vacant positions are sterically protected by two agostic interactions with the nearby *t*butyl group. The structure of **3** provides a rare example of a "proposed" intermediate for an intramolecular C–H activation process. The I*t*Bu ligand apparently provides a unique stabilizing effect in coordinatively unsaturated iridium complexes.[10]

The X-ray structure of **3** indicates the presence of a double agostic interaction, but the NMR spectrum at ambient temperature indicates a highly symmetrical structure. The ^{1}H NMR spectra that were recorded over a range of temperatures (175–300 K) to probe for agostic interactions in solution revealed interesting dynamic behavior (Figure 2).

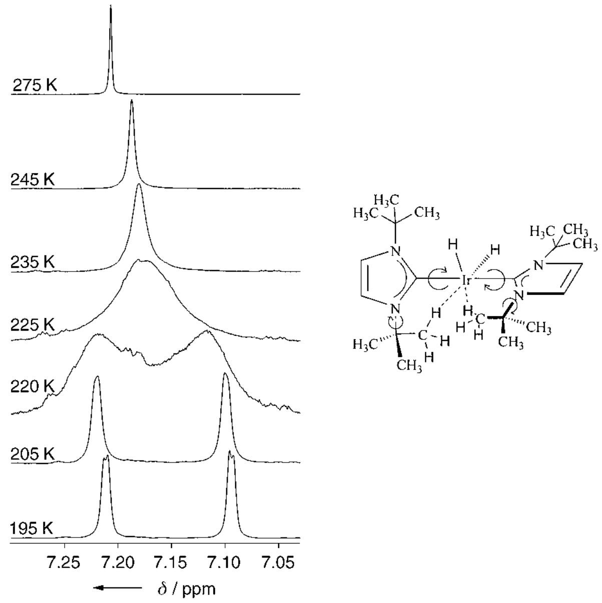


Figure 2. Imidazole region of the variable-temperature ^{1}H NMR spectra of **3** (500 MHz, CD$_2$Cl$_2$).

A dynamic process is frozen out at low temperature, which leads to two distinct environments for the *t*butyl and imidazole moieties. We attribute the appearance of the low-temperature spectra to a lower symmetry structure consistent with the solid-state structure. The switching of the *t*butyl groups between their free environments and undergoing agostic interactions is responsible for the changes in the NMR spectra with temperature (Figure 2). Lineshape analysis reveals that this process has $\Delta H^{\ddagger} = 7.68\,\text{kcal}\,\text{mol}^{-1}$, $\Delta S^{\ddagger} = -11\,\text{cal}\,\text{mol}^{-1}$ per degree, and $\Delta G^{\ddagger}_{215} = 10.0\,\text{kcal}\,\text{mol}^{-1}$ thermodynamic parameters.

Reaction of **2** with D$_2$ gas was expected to lead to [D$_4$]**3** with D atoms incorporated in the hydride ligand and cyclometalated alkyl positions, in a manner analogous to the reaction of **2** with H$_2$ gas. Interestingly, rapid incorporation of D atoms into other *t*butyl C–H bonds was also observed. Extended exposure of **2** to D$_2$ gas led to complete deuteration in both the hydride ligands and the *t*butyl groups. Complex **3** can be completely regenerated by treatment with H$_2$ gas, which demonstrates that this D-atom exchange is fully reversible. A partially deuterated sample showed a very interesting range of 18 distinct resonances in the hydride region of the NMR spectrum from $\delta = -29.0$ to -29.15 ppm (an approximate span of 80 ppb; Figure 3).

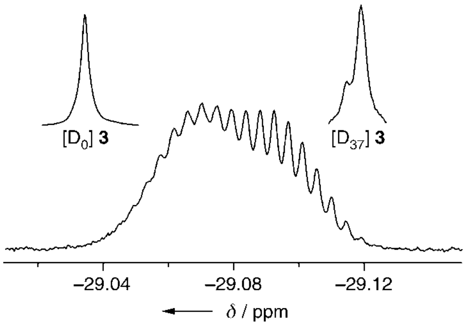
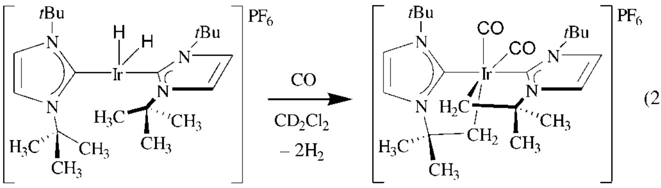


Figure 3. Partial ^{1}H NMR spectrum of [D$_n$]**3** (750 MHz, 298 K, CD_2Cl_2).

Experiments at different fields confirmed that none of these splittings arise from H–D coupling. We surmise that the 18 different resonances result from all the possible isotopomers of the two different deuterated *t*butyl groups. Two agostic interactions in **3**, with rapid equilibration of all C–H (C–D) bonds, are necessary for this conclusion to be correct. Our observations also require an unusual secondary-isotope effect on the chemical shift of a hydride ligand; however, the result of this isotope effect depends on whether the agostic interaction *trans* to the hydride ligand involves a C–H bond or a C–D bond. These interactions are rapidly averaged over all 18 C–H (C–D) bonds, thus leading to the resonance pattern in the NMR spectrum, with upfield shifts of approximately 5 ppb per deuterium center. These observations provide conclusive evidence that the double agostic interaction in the solid state is maintained in solution.

The highly unsaturated nature of **3** results in its rapid reaction with CO to form the previously reported dicarbonyl complex [Ir(I*t*Bu′)$_2$(CO)$_2$](PF$_6$).[6] Presumably, this complex is formed through intramolecular C–H activation and elimination of two equivalents of dihydrogen [Eq. (2)].[11]



(2)

3

The reactivity of the presented iridium/N-heterocyclic carbene (NHC) system is unique[12] as its behavior is in stark contrast to that displayed by the iridium/phosphine system [IrH(η^2-P*t*Bu$_2$Ph)(P*t*Bu$_2$Ph)][BAr′$_4$] (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$),[10] The iridium/phosphine system does not simply react with dihydrogen to form a dihydride complex but further reacts with H_2 gas to yield the 16-electron complex [Ir(H)$_2$(H$_2$)(P*t*Bu$_2$Ph)$_2$][BAr′$_4$], which is observed at low temperature but is easily converted into [Ir(H)$_2$(H$_2$)$_2$(P*t*Bu$_2$Ph)$_2$][BAr′$_4$] at higher temperature. No such dihydrogen binding is observed when **3** is subjected to atmospheric, or higher, pressures of H_2 gas. This lack of reactivity with excess H_2 gas to form a dihydrogen complex is further evidence of the strength of the agostic interactions within this electron-deficient Ir^{III} system in solution.

We performed a similar hydrogenation reaction with the related 14-electron rhodium(III) complex [Rh(I*t*Bu′)$_2$](PF$_6$).[13] Low-temperature NMR spectroscopic studies revealed the formation of a new hydride species; however, unlike **3**, the new hydride species has proven elusive and decomposes during attempted isolation. This instability may be associated with weaker M–H bonds in the case of rhodium complexes and nonoptimal positioning of the *t*butyl groups in the coordination sphere of the metal center, thus leading to weak agostic stabilization of the complex. Further exploration of the stabilization effects in this Rh system and other related Rh systems is ongoing.

We have described a remarkable electron-deficient cationic dihydride complex [Ir(I*t*Bu)$_2$(H)$_2$](PF$_6$) (**3**) generated in high yield from reaction of a 14-electron complex [Ir(I*t*Bu′)$_2$](PF$_6$) (**2**) and H_2 gas. The reaction illustrates the reversibility of a double, intramolecular C–H activation process. Solid-state structural and low-temperature NMR spectroscopic studies involving **3** show a rare double agostic interaction present in a dihydride complex. Furthermore, reaction of **2** with D_2 gas did not lead to the expected [D$_4$]**3** compound but rather to complete deuteration of the hydride ligands and *t*butyl groups. Work is currently underway to exploit this specific reaction and invesitgate the action of **3** and its precursors in intermolecular substrate activation and functionalization.

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Keywords: agostic interactions · C–H activation · carbene ligands · coordination modes · iridium

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[7] **3**: A 500-mL Fischer–Porter vessel was charged with [Ir(I*t*Bu′)$_2$](PF$_6$) (200 mg, 0.280 mmol) and dichloromethane (20 mL) in a glovebox. The vessel was taken out of the box, connected to a Schlenk line, and pressurized with H_2 gas (2.5 atm). The solution was then stirred for 3 days. The solvent volume was reduced to 3 mL and then pentane (10 mL) was added, which resulted in the immediate precipitation of a pale-yellow solid. The supernatant solution was decanted and the solid washed with pentane (3 × 5 mL) and dried in vacuo (186 mg, 95 % yield). ^{1}H NMR (750 MHz, CD_2Cl_2): $\delta = 7.18$ (s, 4H, CH-imidazole), 1.55 (s, 36H, (CH$_3$)$_3$), −29.03 ppm (s, 2H, H); ^{31}P NMR (161.90 MHz, CD_2Cl_2): $\delta = -138.67$ ppm (sept, $J = 710.4$ Hz); ^{19}F NMR (376.28 MHz, CD_2Cl_2): $\delta = -72.51$, −74.39 ppm ($J = 710.8$ Hz); ^{13}C NMR (100.56 MHz, CD_2Cl_2): $\delta = 168.14$ (C-carbene), 118.45 (C-imidazole), 58.68 (*C*(CH$_3$)$_3$), 29.66 ppm (C(*C*H$_3$)$_3$). Elemental analysis (%) calcd for $C_{22}H_{42}N_4F_6PIr$ (699.78): C 37.76, H 6.05, N 8.01; found: C 37.85, H 6.02, N 7.94.

[8] The number of electrons in **3** allows it to be described as a "14-electron" complex if the two M···H agostic interactions are simply considered as occupying the vacant sites in an ideal octahedral-metal environment. This observation is a matter of formalism and the words "electron deficient" are used to eliminate any ambiguity. For a 14-electron ruthenium complex, see: L. Watson, O. V. Ozerov, M. Pink, K. G. Caulton, *J. Am. Chem. Soc.* **2003**, *125*, 8426–8427.

[9] Crystal data for **3**: $C_{22}H_{42}F_6IrN_4P$, $M_r = 699.77$, orthorhombic *Pbcn*, $a = 9.8783(5)$, $b = 22.0515(12)$, $c = 12.4453(7)$ Å, 2711.0(3) Å^3, $T = 150(2)$ K, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.711\ \mathrm{mm^{-1}}$, 23556 reflections collected (1779 independent), $R1$ [$I > 2\sigma(I)$ = 0.0334, $wR2$ (all data) = 0.0608. Towards the end of the refinement, the Fourier difference map showed all the hydrogen atoms associated with the I*t*Bu unit, as well as two peaks in positions consistent with the presence of two hydride ligands, which was in accordance with the NMR spectroscopic analysis. Therefore, the position of all the hydrogen atoms and hydride ligands were refined in the final least-squares cycles without constraints by using an isotropic temperature factor. The refined positional parameters gave an acceptable geometry and were left without correction. CCDC-255338 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[11] Identical ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectroscopic characterization to that already reported for [Ir(I*t*Bu′)$_2$(CO)$_2$](PF$_6$)[6] was obtained.

[12] A T-shaped 14-electron monohydride/platinum system stabilized by one agostic interaction has recently been reported: W. Barrata, S. Stoccoro, A. Doppiu, E. Herdweck, A. Zucca, P. Rigo, *Angew. Chem.* **2003**, *115*, 105–108; *Angew. Chem. Int. Ed.* **2003**, *42*, 105–108. The Pt(II) center preferentially adopted a 16-electron configuration, which is not the case for the Ir(III) center as it prefers an 18-electron environment.

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