Catalytic Alkane Dehydrogenation by $IrClH_2(PPr^i_3)_2$: Evidence for an Alkane Associative Mechanism

Jack Belli† and Craig M. Jensen*

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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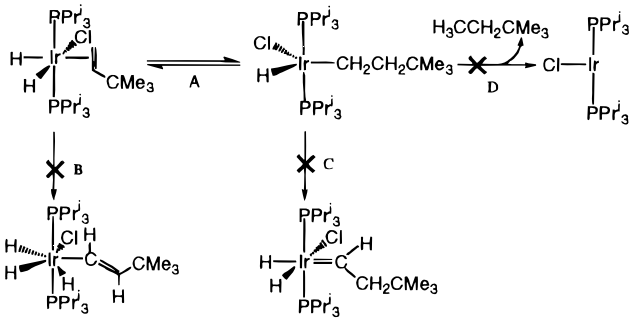
Summary: $IrClH_2(PPr^i_3)_2$ catalyzes the dehydrogenation of alkanes to alkenes in the presence of the hydrogen acceptor, tert-butylethylene at 150 °C. Mechanistic studies, including labeling experiments with $IrClD_2(PPr^i_3)_2$, indicate that reversible coordination and hydride migration to tert-butylethylene is facile and that the slower, subsequent elimination of tert-butylethane requires prior coordination of alkane.

Catalytic dehydrogenation of alkanes by soluble iridium and rhodium complexes has been extensively studied in recent years. Systems involving hydrogen transfer from alkane to hydrogen acceptors,[1−3] photoirradiation,[4−6] and, most recently, thermal hydrogen evolution,[7] have been identified. It is accepted that alkane activation in these systems occurs through oxidative addition to intermediate, 14-electron complexes which arise from catalyst precursors such as $IrH_5(PPr^i_3)_2$ (**1**).[2,3,5,6] A recent theoretical study by Cundari found markedly different reaction enthalpies for alkane C−H activation by $IrH(PH_3)_2$ vs $IrCl(PH_3)_2$.[8] The chloro complex $IrClH_2(PPr^i_3)_2$ (**2**) undergoes D/H exchange between the hydride ligands and deuterated solvents.[9] Therefore, it was of interest to explore **2** as a catalyst for alkane dehydrogenation and compare its activity to that of **1**. We have found that catalytic alkane dehydrogenation by **2** operates by a very different mechanism than has been found for previously studied systems.

A cyclooctane solution (2 mL, 14.86 mmol) of **2**[10] (56 mg, 0.10 mmol) and the hydrogen acceptor *tert*-butylethylene[11] (tbe) (0.5 mL, 3.99 mmol) was fully immersed for 2 days in a 150 °C oil bath. Analysis of the reaction mixture by gas chromatography[12] indicated that 4 turnovers of cyclooctane to cyclooctene had occurred. A nearly quantitative amount of **2** was recovered upon removal of the hydrocarbons in vacuo. An analogous experiment in which **2** was substituted with an equimolar amount of **1** resulted in 9 turnovers of cyclooctane to cyclooctene.

Scheme 1



Despite the similar levels of activity, deuterium labeling experiments show that **1** and **2** catalyze the dehydrogenation of alkanes through different mechanisms. The ^{2}H NMR spectrum (76.8 MHz) of a tbe solution (0.8 mL, 6.2 mmol) of $IrClD_2(PPr^i_3)_2$ (**2**-d_2)[9] (10 mg, 0.02 mmol) is seen in Figure 1a. The signal for the deuterides of **2**-d_2 are seen to have much greater intensity than those for the natural abundance deuterium in tbe. The tube was fully immersed in a 150 °C bath for 2 days and the ^{2}H NMR spectrum again obtained. As seen in Figure 1b, the deuterium label was exclusively incorporated into the β position of tbe. This result establishes the occurrence of reversible coordination of tbe and subsequent reversible migration of hydride as seen in reaction A of Scheme 1. The preference for formation of the linear alkyl is established by the exclusive incorporation of the deuterium into the tbe β position. The absence of deuterium label incorporation into the α position of tbe contrasts the preferential α incorporation found for $IrH_5(PPr^i_3)_2/C_6D_6$[13] and equal α and β incorparation observed with $IrD_2\{OC(O)CF_3\}(PPr^i_3)_2$.[14] Label incorporation into the α position has been proposed to occur through vinyl C−H activation[13] and α elimination of an alkyl hydrogen[14] as respectively seen in reactions B and C of Scheme 1. Both

† 1993 J. J. Zuckermann fellow.

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(11) In order circumvent analytical problems arising from the presence of small amounts of *tert*-butylethane present in most commercially available *tert*-butylethylene, 99.98% *tert*-butylethylene from API Standard Reference Materials, Carnegie Mellon University, Pittsburgh, PA 15213, was used in this study.

(12) GC−MS analysis was performed on a temperature-programmed (35 °C isothermo for 3 min; 2 °C/min to 60 °C) Hewlett Packard 5890 gas chromatograph using a 250 μm × 25 m OV-1 capillary column coupled to a VG 70SE dual sector high-resolution mass spectrometer.

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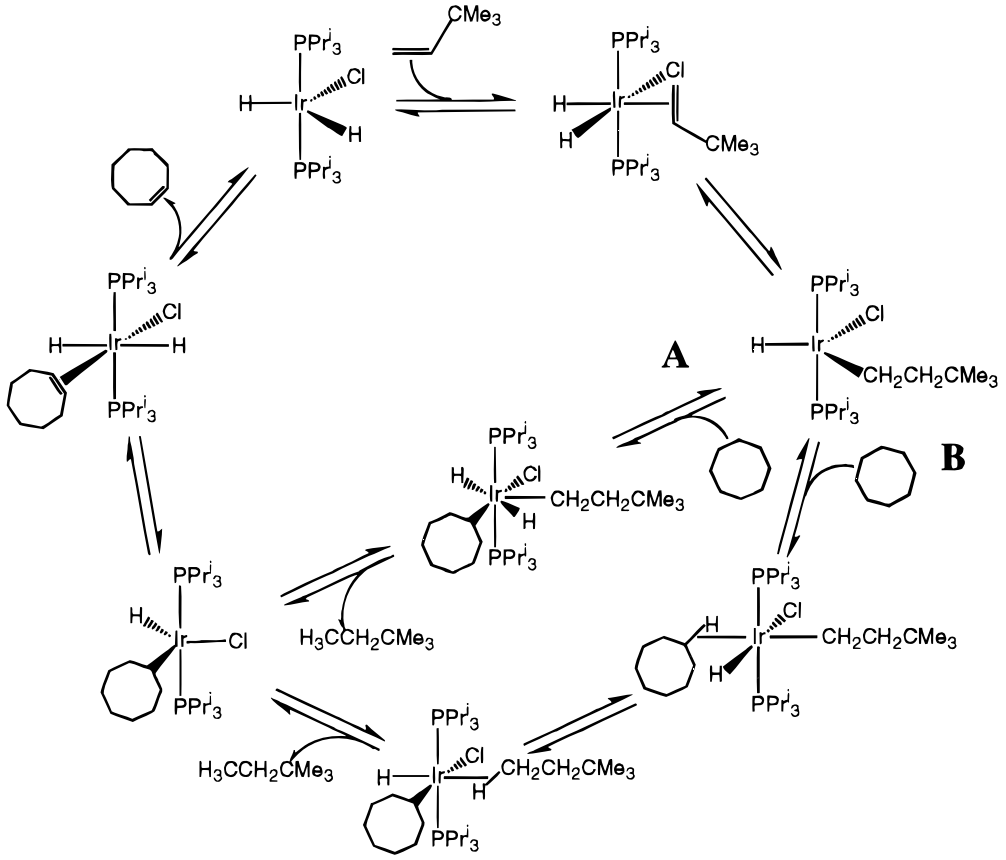
Scheme 2



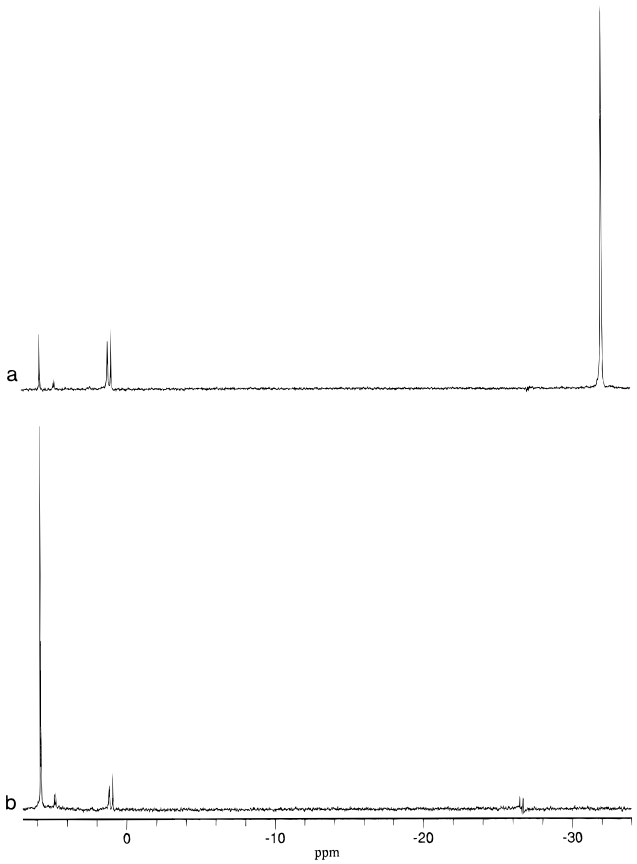


Figure 1. ^{2}H NMR spectra (76.8 MHz): (a) Solution of **2**-d_2 in tbe solution at 25 °C; (b) reaction mixture after 2 days of heating at 150 °C.

of these processes require formation of Ir(V) intermediates. Apparently the presence of the electronegative chloride ligand prevents the formation of an Ir(V) intermediate in our system. GC−MS analysis[12] of the reaction mixture showed no *tert*-butylethane (tba) was produced. We conclude that reductive elimination of tba from the alkyl hydride complex to form the 14-electron $IrCl(PPr^i_3)_2$ complex, as seen in reaction D of Scheme 1, does not occur at 150 °C.

In order to determine if alkane coordination is required to effect the reductive elimination of tba, solutions of **2** (56 mg, 0.10 mmol) in tbe (0.5 mL, 4.0 mmol) and 2 mL of a variety of alkanes were fully immersed in a 150 °C bath for 2 days. Production of tba was established by gas chromatographic analysis of the reaction mixtures. The solutions containing cyclooctane, cyclohexane, *n*-pentane, and *n*-nonane produced 3.9, 1.3, 0.4, and 1.2 equiv of tba, respectively. These results clearly demonstrate that alkanes are generally effective at inducing tba elimination. As expected for an associative process, the amount of tba produced in a 12 h period was found to increase with increasing alkane. Immersing solutions of **2** (70 mg, 0.13 mmol) in tbe (2.0 mL, 16 mmol) containing 0.15, 0.30, and 0.60 mL of cyclooctane in a 150 °C bath for 12 h resulted in the production of 0.8, 1.1, and 1.5 turnovers of tba, respectively. The lack of a linear relationship between cyclooctane concentration and tba production may be due to complications associated with catalyst decomposition. A full kinetic study of this system is in progress. In a second deuterium labeling experiment, a tbe solution (0.5 mL, 4.0 mmol) of **2**-d_2 (10 mg, 0.02 mmol) and cyclooctane (0.125 mL, 0.93 mmol) was fully immersed in a 150 °C bath for 2 days. Production of 2.1 turnovers of tba was detected by gas chromatographic analysis of the reaction mixture. The ^{2}H NMR spectrum

of the reaction mixture showed the deuterium label was exclusively incorporated into the β position of tbe. Apparently, the coordination of cyclooctane and subsequent elimination of tba is much slower than the hydride migration/β elimination equilibrium.

Our results demonstrate that the mechanism of dehydrogenation of cyclooctane by **2** does not involve an intermediate 14-electron complex but rather association of cyclooctane to an intermediate alkyl hydride complex as seen in Scheme 2. This may entail an initial oxidative addition of the cyclooctane C−H bond to give an Ir(V) intermediate as seen in pathway A. However, our labeling experiments indicate the that Ir(V) oxidation state is inaccessible to complexes with the $IrCl(PPr^i)_2$ framework. Alternatively, the key alkane activation step may occur through concerted pairwise coupling−decoupling as seen in pathway B. This process may be related to the rapid, pairwise interconversion of dihydrogen and hydride ligands in $IrClH_2(H_2)(PPr^i{}_3)_2$.[15,16] We hope to establish whether these H−H and C−H σ bond activations involve the same general mechanistic features.

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