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Mechanism of Hydrogenolysis of an Iridium−Methyl Bond: Evidence for a Methane Complex Intermediate

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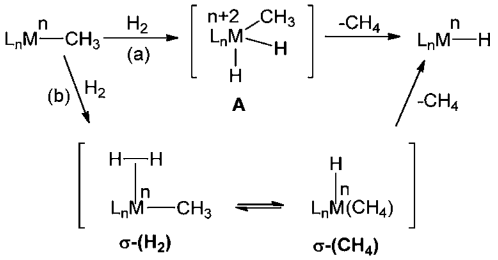
S *Supporting Information*

ABSTRACT: Evidence for key σ-complex intermediates in the hydrogenolysis of the iridium−methyl bond of (PONOP)Ir(H)(Me)$^+$ (**1**) [PONOP = 2,6-bis(di-*tert*-butylphosphinito)pyridine] has been obtained. The initially formed η^2-H_2 complex, **2**, was directly observed upon treatment of **1** with H_2, and evidence for reversible formation of a σ-methane complex, **5**, was obtained through deuterium scrambling from η^2-D_2 in **2-d_2** into the methyl group of **2** prior to methane loss. This sequence of reactions was modeled by density functional theory calculations. The transition state for formation of **5** from **2** showed significant shortening of the Ir−H bond for the hydrogen being transferred; no true Ir(V) trihydride intermediate could be located. Barriers to methane loss from **2** were compared to those of **1** and the six-coordinate species (PONOP)Ir(H)(Me)(CO)$^+$ and (PONOP)Ir(H)(Me)(Cl).

σ-Bond metathesis is a fundamental transformation exhibited by complexes of metals across the periodic table and plays an important role in many catalytic and stoichiometric processes.[1] Hydrogenolysis of metal−alkyl bonds is a particularly significant reaction for both early and late transition metal alkyls.[2] For example, hydrogenolysis of d^0 metal−alkyl bonds provides an important method for controlling polymer molecular weights in olefin polymerization reactions.[3] In both early- and late-metal systems, hydrogenolysis of metal−alkyl bonds releases the alkane in hydrogenation reactions in which the catalytic cycle involves olefin insertion into a metal monohydride.

In the case of d^0 metal−alkyl complexes, the σ-bond metathesis reaction cannot occur via an oxidative addition/reductive elimination process.[4] Density functional theory (DFT) calculations suggest that σ-complex intermediates intervene along the pathway, but such species are sufficiently high in energy that, to date, they have escaped observation. In the case of late-transition-metal systems, there are multiple possibilities for the exact pathways followed during σ-bond metathesis, as revealed by both DFT studies and experimental observations.[5] A simplified scheme is shown in Scheme 1 for the basic hydrogenolysis reaction, cleavage of a M−CH_3 bond by H_2. Pathway (a) involves the formation of oxidative addition intermediate **A** followed by reductive elimination of CH_4. Pathway (b) involves the formation of a σ-H_2 complex, conversion to a σ-methane (σ-CH_4) complex, and release of methane. While these are two "simplified" schemes, experimentally relevant pathways are certainly more complex. σ-Complex intermediates likely intervene in the formation and decay of **A** in pathway (a). In pathway (b), a higher-energy oxidative addition intermediate such as **A** may connect the σ-H_2 and σ-CH_4 intermediates or the interconversion of these species may be a concerted process. The latter case, in which there is no higher-oxidation-state intermediate along the pathway, has been termed σ-complex-assisted metathesis (σ-CAM).[6] The extent of the M−H interaction in this transition state may also vary substantially.

Scheme 1. Two Possible Pathways for Hydrogenolysis of a M−CH_3 Bond



Here we report the hydrogenolysis of the Ir−CH_3 bond of a cationic iridium complex wherein the σ-H_2 intermediate can be observed spectroscopically. Deuterium labeling experiments provided evidence for interconversion of the σ-H_2 complex with the σ-CH_4 complex prior to release of methane. DFT calculations revealed the energy difference between the σ-H_2 and σ-CH_4 complexes and the nature and structure of the transition state connecting these species.

As previously reported, exposure of the cationic, coordinately unsaturated Ir(III) methyl hydride complex (PONOP)Ir(H)(Me)$^+$ (**1**) [PONOP = 2,6-bis(di-*tert*-butylphosphinito)-

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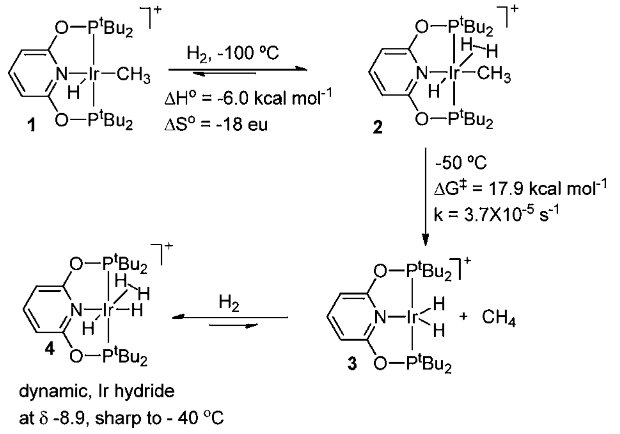
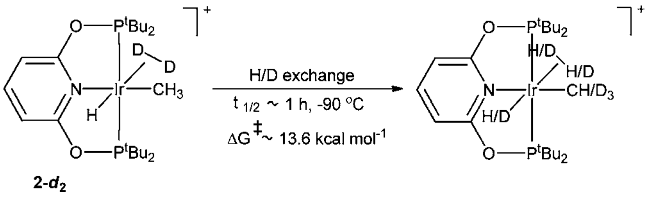
pyridine] to H_2 at −100 °C results in the formation of the η^2-H_2 complex **2** in equilibrium with **1**[7] (Scheme 2). The key ^1H NMR data for **2** show a 2H signal at −1.98 ppm for the σ^2-H_2 ligand (J_{HD} = 34 Hz for the HD complex) and a terminal hydride at −13.4 ppm. Warming to −50 °C results in loss of methane and formation of dihydride complex **3**, which under H_2 forms tetrahydride complex **4**.[8] The equilibrium ratio of **1** and **2** at known H_2 concentrations was examined over the temperature range from −110 to −60 °C. A van't Hoff plot revealed $\Delta H°$ = −6.0 kcal/mol and $\Delta S°$ = −18 eu.[9] With this correction for the equilibrium between **1** and **2**, we were able to determine the first-order rate constant for loss of methane from **2** as 3.7×10^{-5} s^{-1} at −50 °C, corresponding to $\Delta G^\ddagger \approx 17.9$ kcal/mol.

Scheme 2. Hydrogenolysis of Complex 1 at Low Temperature



Is a σ-CH_4 complex involved as an intermediate in the loss of methane from **2**? To probe this question, we prepared complex **2-*d*₂** possessing an η^2-D_2 ligand by exposure of **1** to a limited amount of D_2 at −120 °C in $CDCl_2F$. Monitoring of this solution at −90 °C showed deuterium scrambling into *both* the methyl group and the terminal hydride at *equal* rates. The results of this scrambling reaction are shown in Figure 1. The half-life of the scrambling reaction is ca. 1 h, corresponding to $\Delta G^\ddagger \approx 13.6$ kcal/mol.

These results point to a mechanism involving reversible formation of the σ-CH_4 complex **5** prior to methane loss, as shown in Scheme 3.[10,11] Rapid tumbling in the σ-CH_4 complex coupled with the equivalence of the two terminal hydride positions results in equal rates of deuterium scrambling into the two sites.



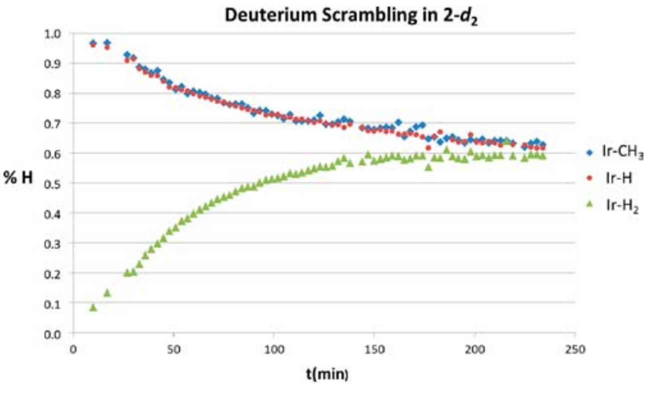
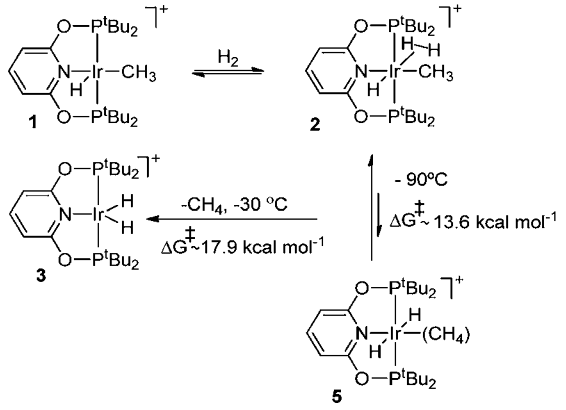


Figure 1. Deuterium scrambling in the σ-D_2 complex **2-*d*₂** at −90 °C.

Scheme 3. Hydrogenolysis of Complex 1 and Formation of σ-CH₄ Complex 5



To gain further insights into this σ-bond metathesis reaction, this transformation was investigated using DFT. We modeled our system using the PBE0 functional[12] with the Stuttgart basis set including an additional f polarization function with an exponent of 0.685 for Ir and the 6-311G** basis set[13] for all other elements. Recent publications on similar systems[7,14] have found success with this functional using basis sets of double-ζ quality. Calculations using the M06 functional were also examined [see the Supporting Information (SI)], but the PBE0 calculations were found to be in better agreement with experiment. All of the structures were optimized in the gas phase with a single-point solvent correction using the SMD solvation model[15] (solvent = CH_2Cl_2) as implemented in Gaussian 09.[16]

The DFT-computed structures of **2** and **5** are shown in Figure 2. The H−H distance of 0.84 Å in the σ^2-H_2 ligand is consistent with the observed J_{HD} value of 34 Hz,[17] and the Ir−H distances of 1.57 and 1.80 Å are in the expected ranges for a terminal Ir−H and an η^2-H_2, respectively. In the σ-CH_4 complex **5**, CH_4 is bound primarily through one C−H bond (M−H distance of 1.78 Å, in contrast to next-nearest geminal

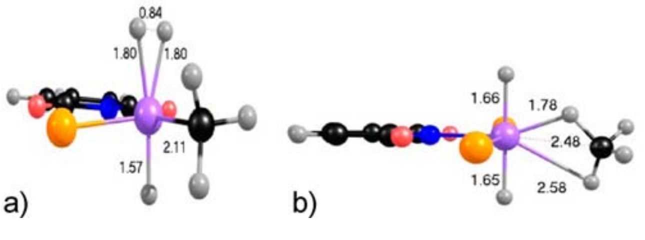
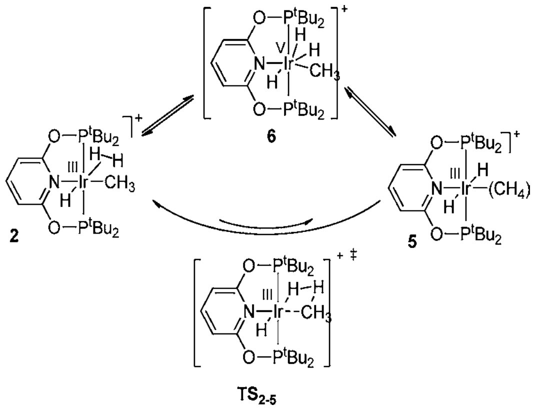


Figure 2. DFT-calculated structures of (a) (PONOP)Ir(H)(Me)(H_2)$^+$ (**2**) and (b) (PONOP)Ir(CH_4)(H)$_2$$^+$ (**5**). The *tert*-butyl substitutents have been omitted for clarity. Ir, purple; C, black; H, gray; O, red; P, orange; N, blue.

C−H···Ir distance of 2.58 Å). The σ^2-H_2 complex **2** was calculated to be 8.6 kcal/mol more stable than the σ-CH_4 isomer **5** in a continuum CH_2Cl_2 solution. This value provides an estimate of 17.9 − 8.6 = 9.3 kcal/mol for $\Delta G^\ddagger$ for dissociation of methane from **5**.

We considered that σ-H_2 complex **2** could be converted into σ-CH_4 complex **5** by either a two-step or a one-step mechanism (Scheme 4). In the two-step mechanism, the H_2 ligand would undergo oxidative addition to give a seven-coordinate trihydride complex, **6**, which in turn would undergo reductive elimination to form the CH_4 adduct. The one-step concerted mechanism would involve a direct hydrogen transfer from the H_2 ligand to the CH_3 ligand to form the CH_4 adduct. The single hydrogen-transfer step could proceed via transition state $\mathbf{TS_{2-5}}$ with either substantial or little involvement of the metal.

Scheme 4. Two Potential Mechanisms for Interconversion of 2 and 5



We were not able to locate a minimum on the potential energy surface corresponding to **6**. All attempts to locate this trihydride complex optimized to the σ-H_2 complex **2**. The lack of a stable iridium trihydride complex is strong evidence against an oxidative addition/reductive elimination pathway for the interconversion of the σ-H_2 and σ-CH_4 complexes.

The free energy of the transition state for the one-step conversion of H_2 to CH_4 was calculated to be $\Delta G^\ddagger$ = 13.3 kcal/mol in CH_2Cl_2, which is in close agreement with the experimental free energy barrier of 13.6 kcal/mol derived from the H/D scrambling experiments. In the transition state, the Ir−H distance for the hydrogen being transferred is 1.60 Å (Figure 3). This short metal−hydride distance (which can be compared to the distances of 1.80 Å for the η^2-H_2 ligand in **2**) indicates a very significant interaction of the metal with the hydrogen being transferred in the transition state, which therefore seems closer to a trihydride structure. To determine whether this interaction with the metal was necessary for reactivity, we searched for a transition state with a reduced Ir−H interaction. This was accomplished by freezing the distance between the Ir center and the H being transferred and optimizing the rest of structure. With this procedure, a second transition state with a frozen Ir−H distance of 2.00 Å was located (Figure 3b). This structure does not represent a true saddle point on the potential energy surface because one coordinate was not allowed to optimize, and therefore, the energy of this structure is not physically meaningful. When the constraint was removed and the full system was allowed to optimize, a structure with an Ir−H distance of ~2.0 Å was not obtained. Instead, the optimized structure had an Ir−H distance of 1.6 Å, similar to the structure discussed previously. This preference for the shorter Ir−H distance suggests that the Ir−H interaction is important in stabilizing the transition state and is thus consistent with a σ-CAM mechanism. The reactivities of other isomers of **2** were considered, but the reaction pathways required to access those intermediates were deemed too high in energy to be chemically significant (see the SI).

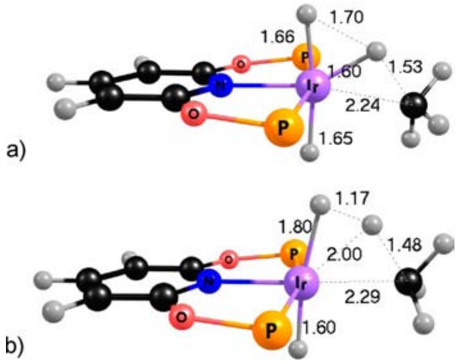


Figure 3. (a) Transition state for hydrogen transfer with an Ir−H bond length of 1.6 Å. (b) Transition state for hydrogen transfer with a restricted Ir−H distance of 2.0 Å. The *tert*-butyl substitutents have been omitted for clarity.

Trapping of **1** by CO yields the six-coordinate Ir(III) cation $(PONOP)Ir(CO)(CH_3)(H)^+$ (**9**), while treatment of $(PONOP)IrCH_3$ with HCl yields the neutral, six-coordinate Ir(III) complex $(PONOP)Ir(H)(CH_3)Cl$ (**8**).[11b] When these species are warmed, they cleanly eliminate CH_4. The measured first-order rate constants for elimination at 80 °C are 1.6×10^{-4} s^{-1} ($\Delta G^\ddagger$ = 26.9 kcal/mol) for **8** and 7.1×10^{-4} s^{-1} ($\Delta G^\ddagger$ = 27.5 kcal/mol) for **9**. The elimination of CH_4 from **9** is not inhibited by CO, indicating that reductive elimination occurs from the six-coordinate complex. In the case of **8**, examination of deuterium-labeled $(PONOP)Ir(H)(CD_3)Cl$ showed scrambling into the iridium hydride site, indicating reversible formation of a CH_4 complex ($t_{1/2} \approx$ 90 min at 55 °C) prior to loss of CH_4. These data allow an interesting comparison of the barriers to methane loss for the series of complexes **1**,[11b] **2**, **8**, and **9**, as summarized in Figure 4.

Consistent with numerous previous studies, reductive elimination from the five-coordinate complex has a significantly lower barrier (by ca. 5 kcal/mol) relative to reductive

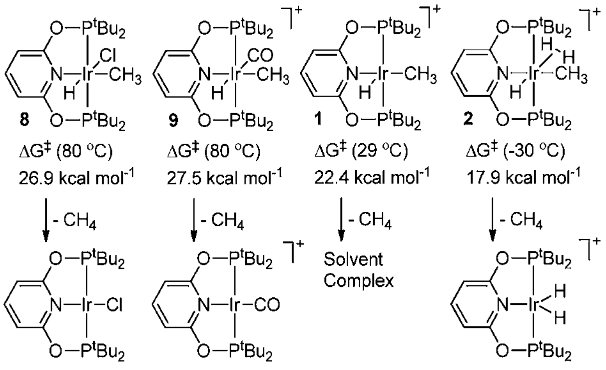


Figure 4. Experimentally determined $\Delta G^\ddagger$ values for CH_4 elimination from Ir complexes **1**, **2**, **8**, and **9**.

elimination from the six-coordinate complexes **8** and **9**.[18] The barrier for reductive elimination from cationic **9** possessing a π-acidic carbonyl ligand differs little from that for neutral **8** in which the CO ligand has been replaced by a chloride ligand. The barrier for release of CH_4 from six-coordinate **2** is ~9 kcal/mol lower than those from the six-coordinate complexes **8** and **9**. This is clearly the result of the operation of a σ-bond metathesis mechanism in the case of **2** wherein the oxidation state of Ir is unchanged.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, kinetic experiments, computations, complete ref 16 (as ref S14), and the crystal structure of **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) Complex **4** exhibits a 4H signal at −8.9 ppm. The structure is likely a highly fluxional η^2-H_2 dihydride, as shown.

(9) See the Supporting Information for details.

(10) An alternate explanation for scrambling would involve deprotonation/reprotonation of **2** coupled with reversible loss of H_2 from **2**. Under the conditions for generation of **2-d_2**, a small excess of **1** remained. No deuterium scrambling into **1** was observed during the scrambling described in Scheme 3, ruling out the involvement of **1**.

(11) A Rh−CH_4 complex, (PONOP)Rh$(CH_4)^+$, has been directly observed by low-temperature NMR spectroscopy, and the iridium analogue (PONOP)Ir$(CH_4)^+$ was proposed as the intermediate responsible for ^{1}H site exchange between the iridium hydride and the methyl hydrogens in (PONOP)Ir(H)$(CH_4)^+$. These methane complexes are square-planar Rh(I) and Ir(I) species, in contrast to **5**, which is a six-coordinate Ir(III)−CH_4 complex. See: (a) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553. (b) Bernskoetter, W. H.; Hanson, S. K.; Buzak, S. K.; Davis, Z.; White, P. S.; Swartz, R.; Goldberg, K. I.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131*, 8603. (c) Walter, M. D.; White, P. S.; Schauer, C. K.; Brookhart, M. *New J. Chem.* **2011**, *35*, 2884.

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