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The Mechanism of Silicon−Hydrogen and Carbon−Hydrogen Bond Activation by Iridium(III): Production of a Silylene Complex and the First Direct Observation of Ir(III)/Ir(V) C−H Bond Oxidative Addition and Reductive Elimination

Steven R. Klei, T. Don Tilley,* and Robert G. Bergman*

Department of Chemistry, University of California
and Chemical Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, California 94720

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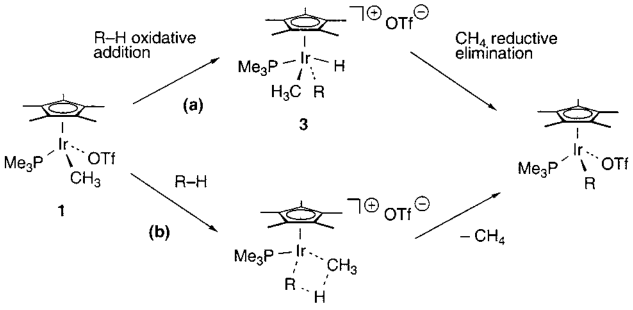
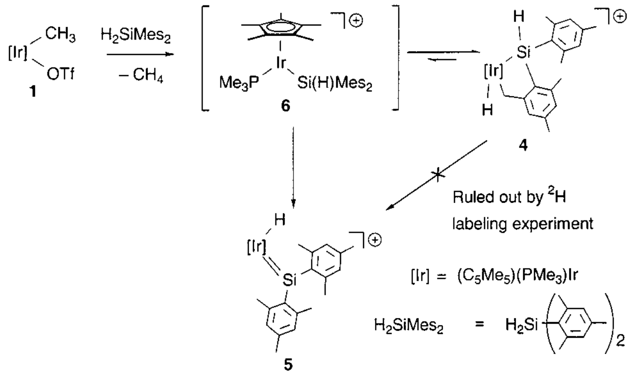
The complexes Cp*(PMe$_3$)Ir(Me)OTf (Me = CH$_3$, OTf = OSO$_2$CF$_3$) (**1**) and [Cp*(PMe$_3$)Ir(Me)(CH$_2$Cl$_2$)][BAr$_f$] (BAr$_f^-$ = [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B]$^-$) (**2**), which contain iridium in oxidation state +3, were recently shown to undergo C−H activation reactions with alkanes under mild thermal conditions.[1−3] Complex **1** also undergoes rapid Si−H activation reactions with silanes.[4] Although theoretical studies[5] support an oxidative addition mechanism, proceeding through Ir(V) intermediate **3** (path a in Scheme 1), no such species has been detected during this reaction.[6] Furthermore, compared with the large number of known Ir(I) and Ir(III) complexes, many fewer stable examples of organometallic Ir(V) complexes have been prepared.[7,8] Because of this, a concerted "σ-bond metathesis" pathway has been considered as one mechanistic alternative for the C−H activation process (path b).

Maitlis' groundbreaking work in the 1980s established that charge-neutral methyliridium complexes can react with benzene to release methane and give phenyliridium complexes.[9,10] Diversi later found that such transformations can be catalyzed by one-electron oxidants.[11] Ir(III) to Ir(V) C−H activation steps were proposed to intervene in some of these reactions, but to our knowledge they have not been observed directly. We now wish to report a series of observations, including the first conversion of Ir(III) precursors to an *isolable*, structurally characterized Ir(V) aryl-hydride and a spectroscopically observable Ir(V) alkyl-hydride, that lends convincing experimental support to the Ir(III) → Ir(V) → Ir(III) mechanism.

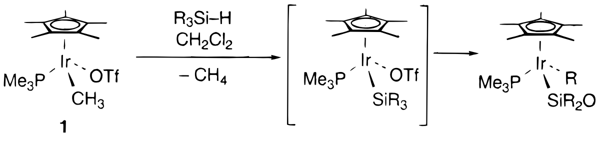
Scheme 1



Scheme 2



The complex Cp*(PMe$_3$)Ir(Me)OTf (**1**) reacts rapidly with alkanes (H-CR$_3$) to produce 1 equiv of methane (CH$_4$) and rearranged products derived from Cp*(PMe$_3$)Ir(CR$_3$)OTf, which form as a consequence of the β-hydride elimination pathway.[2] When **1** is added to silanes (H-SiR$_3$, R = Me, Ph), products of a structural rearrangement type unobserved in C−H activation reactions are isolated along with 1 equiv of methane. These products, Cp*(PMe$_3$)Ir(SiR$_2$OTf)(R), are presumably derived from a 1,2-migration in Cp*(PMe$_3$)Ir(SiR$_3$)OTf, wherein one of the groups initially bound to silicon migrates to iridium (eq 1).[2] We



(1)

have used two methods to investigate the course of the silane rearrangement reactions: increasing the steric bulk of the substituents attached to silicon, and replacing the triflate ligand in **1** with a "noncoordinating" tetraarylborate anion. In the first approach, we treated **1** with the sterically hindered silane H$_2$SiMes$_2$ (Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$). The kinetic reaction product observed after 5 min is the Ir(V) cyclometalated complex **4**, whose structure was determined using ^{1}H, ^{13}C (including DEPT 90 and DEPT 135 pulse sequences), ^{29}Si, ^{31}P, and ^{19}F NMR spectroscopy (Scheme 2). The formation of **4** requires oxidative addition of a C−H bond of one of the mesityl methyl groups to the Ir(III) center to produce an unprecedented Ir(V) alkyl hydride. This is the first observed C−H oxidative addition that proceeds from Ir(III) to Ir(V). Interestingly, complex **4** isomerizes to an iridium silylene complex [Cp*(PMe$_3$)Ir=SiMes$_2$(H)][OTf] (**5**) over 9 h.

The conversion of cyclometalated **4** to silylene complex **5** could be envisioned as proceeding via C−H reductive elimination to an Ir(III) silyl cation intermediate (**6**), followed by 1,2-migration of hydride from silicon to iridium, or by direct 1,3-hydride transfer

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(1) For recent reviews of C−H activation see: (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A., Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Sen, A. *New Approaches in C−H Activation of Alkanes* in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: New York, 1996; pp 1081−1092. (c) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879. Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2181.

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(4) Oxidative addition of a Si−H bond to an Ir(III) center has been reported: Fernandez, M. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, *3*, 2063.

(5) Strout, D. L.; Zari'c, S.; Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6068.

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(7) For literature citations for stable Ir(V) species see ref 6, footnotes 13 and 18−31.

(8) For literature precedent for postulated Ir(V) species see ref 6, footnotes 13−17.

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(10) Gómez, M.; Kisenyi, J. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *296*, 197.

(11) Diversi, P.; Iacoponi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Pinzino, C.; Uccello-Barretta, G.; Zanello, P. *Organometallics* **1995**, *14*, 4, 3275. **Note added in proof:** These studies have recently been extended to the reactions of dialkyliridium complexes with silanes in the presence of one-electron oxidants: Diversi, P.; Marchetti, F.; Ermini, V.; Matteoni, S. *J. Organomet. Chem.* **2000**, *593−594*, 154.

10.1021/ja992954z CCC: $19.00

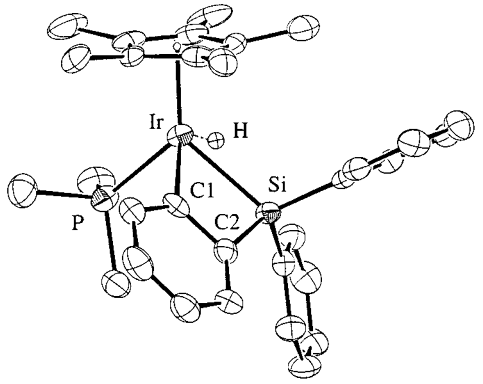
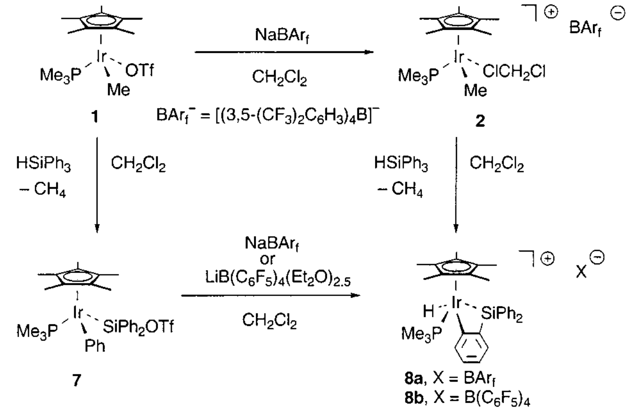


Figure 1. An ORTEP diagram of complex **8b** (iridium-bound hydrogen observed by IR and ^{1}H NMR spectroscopy not located; borate counterion not shown for clarity). Selected bond lengths and angles: Ir−P 2.290(2) Å; Ir−C1 2.086(8) Å; Ir−Si 2.479(2) Å; C1−C2 1.42(1) Å; Si−C2 1.828(8) Å; Ir−C1−C2 113.4(5)°; C1−C2−Si 96.8(5)°; C2−Si−Ir 85.3(3)°; Si−Ir−C1 64.2(2)°.

Scheme 3

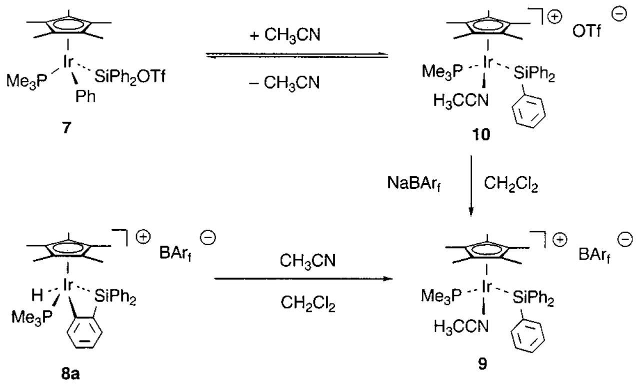


from silicon to the iridium-bound mesityl carbon (Scheme 2). To distinguish these possibilities, the reaction between D_2SiMes_2 and **1** was monitored by ^{1}H and ^{2}H NMR spectroscopy. The kinetic product was found to be analogous to **4**, except for the presence of a silicon−deuteride (Si−D) bond. Exclusive formation of CH_3D was also observed.[12] The iridium kinetic product isomerized exclusively to [Cp*(PMe$_3$)Ir═SiMes$_2$(D)][OTf]. This rules out 1,3-transfer and provides evidence that Ir(III)/Ir(V) C−H reductive elimination can occur in the conversion of **4** to **5**.

Further support for the viability of the Ir(III) to Ir(V) C−H oxidative addition reaction was obtained by replacing the triflate (TfO$^-$) group in **1** with a less strongly coordinating anion. This was accomplished by treating Cp*(PMe$_3$)Ir(SiPh$_2$OTf)(Ph) (**7**) with NaBAr$_f$[13] in an anion-exchange reaction, or alternatively by reacting the more potent C−H bond activating complex[3] [Cp*(PMe$_3$)Ir(Me)(CH$_2$Cl$_2$)][BAr$_f$] (**2**) with the tertiary silane HSiPh$_3$. Experimentally, either reaction gives as its major product the four-membered iridium(V) metallacycle **8a** (Scheme 3), the first reported spectroscopically observable Ir(V) aryl hydride. Isolation and full characterization of this Ir(V) cation was found to be possible only when the B(C$_6$F$_5$)$_4^-$ counteranion was used. This synthesis was accomplished by performing an anion-exchange reaction of **7** with LiB(C$_6$F$_5$)$_4$(Et$_2$O)$_{2.5}$, which afforded **8b** in 81% yield. Pale yellow single crystals of **8b** were grown from a mixture of CH$_2$Cl$_2$ and pentane, and an X-ray diffraction study confirmed its solid-state structure (Figure 1).

Additional experiments indicated a high degree of reversibility in the reactions that lead to these cyclometalated products (Scheme 4). The addition of 1 equiv of acetonitrile to **8a** afforded [Cp*(PMe$_3$)Ir(SiPh$_3$)(CH$_3$CN)][BAr$_f$] (**9**). This is a rare example of an observable Ir(V) to Ir(III) C−H reductive elimination reaction. Similarly, addition of CH$_3$CN to the triflate product Cp*(PMe$_3$)Ir(SiPh$_2$OTf)(Ph) (**7**) produces [Cp*(PMe$_3$)Ir(SiPh$_3$)-(CH$_3$CN)][OTf] (**10**), but the reaction does not proceed to completion. That is, there is competition between triflate and acetonitrile for coordination to the complex and an equilibrium mixture ($K_{eq} = 31 \pm 3$ at 25 °C) of **7** and **10** is observed by ^{1}H NMR spectroscopy. Complete conversion of this equilibrium mixture to the Ir(III) species **9** can be effected by anion metathesis using NaBAr$_f$.

Scheme 4



The isolation of base-free silylene complex **5** provides strong evidence that more highly transient analogues of these intermediates are present on the reaction pathway to the rearranged products shown in eq 1. Although it is not uncommon for silylene units to bridge two metal atoms, terminal silylene complexes are rare.[14] The other reactions detailed in this paper offer the best experimental evidence to date for an oxidative addition mechanism in C−H bond activation reactions by **1**. It is likely that the presence of the silyl ligands in both cyclometalated species **4** and **8** contributes to the stability of the Ir(V) oxidation state, as several of the few known organometallic Ir(V) species contain silyl ligands.[4,15,16] The added stability that silyl ligands appear to offer Ir(V) complexes may provide a clue to the development of an alkane functionalization catalyst that utilizes high metal oxidation states.

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Supporting Information Available: Characterization data and crystallographic information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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