Cationic Ir(III) alkyl and hydride complexes: stoichiometric and catalytic C–H activation by Cp∗(PMMe3)Ir(R)(X) in homogeneous solution

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Abstract

This report details our work in the area of C–H activation by cationic Ir(III) complexes. We highlight the previously reported chemistry of transition metal complexes of the type Cp∗(PMMe3)Ir(R)(X) (Cp∗ is pentamethylcyclopentadienyl or η5-C5Me5; R = alkyl, hydrido; X = OSO2CF3, B(3,5-(CF3)2C6H3)4), and disclose new results concerning the production of these complexes using Lewis acids (LAs). Additionally, new work aimed at examining the mechanism of C–H activation by these complexes is presented.

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1. Introduction

The controlled functionalization of alkanes and alkyl groups has been a goal of researchers for a number of years [1–3]. There has been interest in methane (CH4) functionalization because of the expense and danger involved in transporting the liquefied material. The conventional method for converting methane into methanol involves an initial steam reforming step, in which methane is converted into synthesis gas (CO and H2), using a nickel based catalyst (Ni/Al2O3/CaO) at 700–900 °C and 10–40 bar [4]. The reaction between 1 mol of CH4 and 1 mol of H2O to form 1 mol of CO and 3 mol of H2 is highly endothermic and is entropy-driven at temperatures in excess of 1000 K. This step is so energy-intensive that it renders the overall process uneconomical, and is one reason for the extensive research that has been focused on developing catalysts for “direct methane conversion processes”. That is, partial oxidation of methane (to methanol) would allow its transportation, but leave value in the product, as opposed to complete oxidation to CO2 and H2O. The main obstacle to these oxidative conversions of methane appears to be the necessity of running the reactions at low single-pass conversions (because the production of CO and CO2 increases dramatically as methane conversion is increased) and of recycling the unreacted gas. A significant advance in the field of methane oxidation chemistry using homogeneous metal catalysis was made a few years ago by Periana et al. at Catalytica. They reported a...
platinum(II) catalyst capable of converting methane to methyl bisulfate, which could in turn be hydrolyzed to give methanol in >70% overall yield [5].

The challenge of selectivity also arises in the functionalization of higher alkanes (having the general formula CnH2n+2). These chemicals are traditionally only used as solvents and fuels, because reactions with alkane substrates are notoriously unselective. Most alkanes contain several different types of C–H bonds with similar steric and electronic properties, making it difficult to transform them into any one new compound in high yield. Solving this selectivity problem would have an impact not only in creating new industrial processes involving alkanes, but also creating new ways to construct complex molecules for organic chemists [6]. Toward this end, Hartwig and co-workers recently reported a highly selective borylation reaction of Cp∗(PMe3)Ir(CD3)OTf (15H), 1.58 (9H), 1.23 (3H). Solution MS (electrospray) expected for [Cp∗(PMe3)IrMe]+: 419; found, 419. The yield of this compound was determined to be 98% by reaction with CO to produce [Cp∗(PMe3)IrMe(CO)][MeB(C6F5)3] in the following analogous synthesis. Solid Cp∗(PMe3)IrMe2 (100 mg, 0.231 mmol) and B(C6F5)3 (125 mg, 0.244 mmol) were added to a Schlenk flask equipped with a stir bar. The flask was cooled to −84 °C, and CH2Cl2 was added by static vacuum transfer (5 ml). The tube was filled with 1 atm CO, and the reaction mixture was allowed to warm to room temperature with stirring. The solvent volume was reduced to 0.25 ml in vacuo and pentane was layered onto the concentrated solution via cannula transfer. An off-white precipitate was produced upon stirring. The mother liquor was removed by cannula transfer, and the resulting solid was washed with (2 × 5 ml) portions of pentane. The solid was collected to yield 220 mg (98%, 0.226 mmol) of [Cp∗(PMe3)IrMe(CO)][MeB(C6F5)3]. 1H NMR (400 MHz, CD2Cl2, 298 K): δ 1.70 (d, Jp–H1 = 1.5 Hz, 15H, C5Me5), 1.56 (d, Jp–H1 = 10.5 Hz, 9H, PMe3), 1.00 (d, Jp–H1 = 6.5 Hz, 3H, Ir–Me) 0.44 (s, br, 3H, B–Me). 13C[P−H] NMR: δ −29.64. 11B[P−H]: δ −15.75. 13C[P−H] NMR: C–F resonances observed between 154 and 158 ppm but unassigned) δ 55.32 (C5Me5), 14.35 (d, Jp–C = 39 Hz, PMe3), 10.0 (br, B–CH3), 8.87 (s, C5Me5), −14.48 (s, Ir–CH3). Literature [10] [Cp∗(PMe3)IrMe(CD3)(Cl)]][B(3,5-C6H3(CF3)2)4]: 1H NMR (400 MHz, CD2Cl2, 298 K): δ 1.68 (15H), 1.58 (9H), 1.23 (3H). Solution MS (electrospray) expected for [Cp∗(PMe3)IrMe]+: 419; found, 419. The yield of this compound was determined to be 98% by reaction with CO to produce [Cp∗(PMe3)IrMe(CO)][MeB(C6F5)3] in the following analogous synthesis. Solid Cp∗(PMe3)IrMe2 (100 mg, 0.231 mmol) and B(C6F5)3 (125 mg, 0.244 mmol) were added to a Schlenk flask equipped with a stir bar. 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The solid was collected to yield 220 mg (98%, 0.226 mmol) of [Cp∗(PMe3)IrMe(CO)][MeB(C6F5)3]. 1H NMR (CD2Cl2, 298 K): δ 1.97 (s, 15H, C5Me5), 1.63 (d, Jp–H1 = 11 Hz, 9H, PMe3), 0.49 (d, Jp–H1 = 5.9 Hz, 3H, Ir–CH3), 0.33 (s, br, 3H, B–CH3). 13C[P−H] NMR (CD2Cl2): C–F resonances observed between 154 and 158 ppm but not assigned) δ 167.29 (s, Ir–CO), 102.37 (s, C5Me5), 15.45 (d, Jp–C = 39 Hz, PMe3), 10.1 (br, s, B–CH3), 9.17 (s, C5Me5), −24.92 (s, Ir–CH3). 31P[P−H] NMR (CD2Cl2, 298 K): δ −38.6. MS (electrospray) expected for [Cp∗(PMe3)IrMe(CO)]+: 447. Found: 447. Analytically calculated for C34H30BIrPF15O: C, 14.35 (d, Jp–C = 39 Hz, PMe3), 10.0 (br, B–CH3), 8.87 (s, C5Me5), −14.48 (s, Ir–CH3). Literature [10] [Cp∗(PMe3)IrMe(CD3)(Cl)]][B(3,5-C6H3(CF3)2)4]: 1H NMR (400 MHz, CD2Cl2, 298 K): δ 1.68 (15H), 1.58 (9H), 1.23 (3H). Solution MS (electrospray) expected for [Cp∗(PMe3)IrMe]+: 419; found, 419. 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41.95; H, 3.11. Found: C, 41.69; H, 2.80. Literature for [Cp*(PMe)(IrMe(CO)OTf)][19]: 1H NMR: δ 1.97 (s, 15H, C5Me5), 1.69 (d, 9H, C5Me5), 0.51 (d, 3H).

Synthesis and characterization of Cp*(PMe)(Ir(biph)) [18]. A glass vessel sealed to a Kontes vacuum adapter was loaded with a suspension of [Cp*IrCl2] (488 mg, 0.612 mmol) in approximately 10 ml of THF and 2 ml diethyl ether and cooled to −40°C. The tube was degassed with three freeze-pump-thaw cycles, 1.2 equivalent of PMe5 was condensed into the reaction vessel using a glass bulb and allowed to warm to room temperature during which time the vessel was stirred for 22 h and allowed to warm to room temperature overnight. After the vessel was degassed with three freeze-pump-thaw cycles, 1.2 equivalent of PMe5 was condensed into the reaction vessel using a glass bulb of known volume and a digital pressure gauge. The sealed reaction mixture was then heated at 45°C for 7 h, over which time the color of the reaction mixture changed from brown to orange. After allowing the reaction mixture to cool to room temperature overnight, the volatile materials were removed in vacuo and the residue was triturated with CH2Cl2 (2 × 5 ml). The residue was then extracted with 15 ml of CH2Cl2 (3 × 5 ml), producing a brown suspension which was filtered through a fritted glass funnel. The filtrate was evaporated to dryness to give a yellow residue which was recrystallized from CH2Cl2: diethyl ether and cooled to −40°C. Then, 1.2 ml of a 0.82 M solution of 2-biphenylmagnesium bromide (1:10) at −40°C was added. The mixture was stirred for 22 h and allowed to warm to room temperature during that time. After the vessel was degassed with three freeze-pump-thaw cycles, 1.2 equivalent of PMe5 was condensed into the reaction vessel using a glass bulb of known volume and a digital pressure gauge. The sealed reaction mixture was then heated at 45°C for 7 h, over which time the color of the reaction mixture changed from brown to orange. After allowing the reaction mixture to cool to room temperature overnight, the volatile materials were removed in vacuo, and the residue was triturated with CH2Cl2 (2 × 5 ml). The residue was then extracted with 15 ml of CH2Cl2 (3 × 5 ml), producing a brown suspension which was filtered through a fritted glass funnel. The filtrate was concentrated to approximately 5 ml, loaded onto a silica column (2 cm × 7 cm), and eluted with CH2Cl2. The first band (pale yellow in color) was collected and the solvent removed in vacuo to give a yellow residue which was recrystallized from CH2Cl2: diethyl ether (1:10) at −50°C to give 620 mg (1.11 mmol, 91%) of the desired complex. 1H NMR (400 MHz, CD2Cl2, 298 K): δ 7.41 (d, 2H, Jη-C5-H = 7.4 Hz, H6), 7.41 (d, 2H, Jη-C5-H = 7.4 Hz, H3), 6.92 (t, 2H, Jη-C5-H = 7.4 Hz, H4), 1.79 (d, 15H, C5Me5), 0.93 (d, 9H, Jη-C5-H = 10.2 Hz, PMe3), 13C[1H] NMR (101 MHz, CD2Cl2, 298 K): δ 155.7 (s, C1), 152.3 (d, Jη-C5-H = 13.2 Hz, C2), 136.8 (s, Jη-C5-H = 2.8 Hz, C3), 125.7 (s, C4), 121.6 (s, C5), 120.0 (d, Jη-C5-H = 1.4 Hz, C6), 94.1 (d, Jη-C5-H = 3 Hz, CMe5), 14.0 (d, Jη-C5-H = 39.6 Hz, PMe3), 9.6 (s, PMe3). 31P[1H] NMR (162 MHz, CD2Cl2, 298 K): δ −36.2; MS (EI) expected for [Cp*(PMMe3)Ir(R)(Me)(CO)(OTf)] [19]. 1H NMR (400 MHz, CD2Cl2, 298 K): δ 7.60 (6H, br s, 4H, biph), 7.21 (t, 4H, Jη-C5-H = 6.8 Hz, biph), 1.61 (s, 15H, C5Me5), 1.49 (d, 9H, Jη-C5-H = 10.9 Hz, PMe3). 13C[1H] NMR (162 MHz, CD2Cl2, 298 K): δ −35.40. Repeat attempts to isolate this complex in analytically pure form failed.

3. Results and discussion

3.1. Stoichiometric C–H activation reactions involving Cp*(PMe)(IrMe(R)(X)) complexes

Our studies of 16-electron cationic iridium alkyl complexes were motivated by the desire to functionalize the metal alkyl hydride species produced from photochemical C–H activation (Scheme 1) [20]. Although there are a significant number of isolable metal alkyl hydrides discovered from alkane oxidative addition, efforts aimed at functionalizing these materials have been frustrated by the propensity of these compounds to regenerate alkane by reductive elimination in preference to other reaction pathways. Cyclopentadienyl (Cp or Cp*), and pentamethycyclpentadienyl iridium complexes provide a particularly dramatic example of this problem. For example, migration of the alkyl or hydrido fragment to co-ordinated CO has never been observed in the Cp*(CO)Ir(H)(H) system [21]. Although complexes of the general structure Cp*(PMe)(IrMe(R)(H)) are some of the most thermally stable alkyl hydrides discovered, their reluctance to open a new co-ordination site at the metal renders them resistant to reaction with added unsaturated dative ligands (L is CO, alkyne or alkene) without the loss of alkane. It was with this property in mind that replacement of the hydrogen of these
complexes with a better anionic leaving group to produce \( \text{Cp}^*\text{(PMe}_3\text{)}\text{Ir}(\text{R})(\text{X}) \) (\( \text{Cp}^* \) is pentamethylcyclopentadienyl; \( \text{R} = \text{alkyl, hydrido} \); \( \text{X} = \text{OSO}_2\text{CF}_3, \text{B}(\text{3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3)_4 \) ) was attempted. It was hoped that use of a weakly co-ordinating \( \text{X} \) group would allow generation of an unsaturated iridium center which would more readily incorporate additional ligands (Scheme 1).

In pursuit of this goal, Burger and Bergman reported the synthesis of \( \text{Cp}^*\text{(PMe}_3\text{)}\text{IrMeOTf} \) (1) from \( \text{Cp}^*\text{(PMe}_3\text{)}\text{IrMe}_2 \) and \( \text{Cp}^*\text{(PMe}_3\text{)}\text{Ir(OTf)}_2 \) in \( \text{Et}_2\text{O} \) solvent in 1993 [8]. However, upon removal of the solvent and dissolution of the residue in \( \text{C}_6\text{D}_6 \) for NMR spectroscopic study, only the phenyl derivative \( \text{Cp}^*\text{(PMe}_3\text{)}\text{Ir(C}_6\text{D}_5\text{)}\text{OTf} \) (2) was observed! It was soon found that this apparent \( \pi \)-bond metathesis reaction could be extended to saturated hydrocarbons (Scheme 2). For example, exposing 1 to 2 atm of \( ^{13}\text{CH}_4 \) afforded \( \text{Cp}^*\text{(PMe}_3\text{)}\text{Ir(^{13}\text{CH}_3)}\text{OTf} \) (3). In fact, complex 1 was shown to react selectively to cleave the C–H bonds of a variety of organic molecules (Scheme 2). Toluene reacts with 1 by aromatic (both \( \text{para} \) and \( \text{meta} \)) rather than benzyl activation, to give a mixture of products (4a and b in a 1.25:1 ratio statistically corrected). However, reaction with \( \text{p-xylene} \) affords \( \text{Cp}^*(\text{PMe}_3\text{)}\text{Ir(}^{13}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3\text{)}\text{OTf} \) (5) as the only observed product in a reaction that apparently disrupts the aromaticity of the starting material. The lack of attack at the \( \text{ortho} \) positions in toluene and \( \text{p-xylene} \) is presumably a result of steric shielding by the proximate methyl groups. Reaction of 1 with cyclopropane gives the \( \sigma \)-allyl complex \( [\text{Cp}^*(\text{PMe}_3\text{)}\text{Ir(}^{13}\text{CH}_2\text{CHCH}_2\text{)}]\text{OTf} \) (6), a product whose formation is explained in terms of an initial C–H activation, followed by \( \beta \)-alkyl elimination. Exposure of 1 to an atmosphere of ethane resulted in formation of the ethylene hydride complex \( [\text{Cp}^*(\text{PMe}_3\text{)}\text{Ir(C}_2\text{H}_4\text{)}\text{H}\text{OTf}] \). No reaction could be observed with cyclohexane or neopentane, presumably for steric reasons.

The C–H activation reactions of methyliridium species 1 demonstrate high selectivity toward a number of substrates. Reaction with tetrahydrofuran followed by anion metathesis with NaBPh\(_4\) led to the isolation of only the cyclic carbene complex 7 (Scheme 2) [9]. Methyl triflate complex 1 reacts with diethyl ether also, but selectively affords the cationic hydrido (ethyl vinyl ether) complex 8 instead of the analogous carbene complex (Scheme 2). The simplest explanation for the formation of this product (over formation of a carbene similar to 7) involves C–H activation at the terminal position (for steric reasons), followed by rapid \( \beta \)-H elimination (footnote 3). Later it was reported that reactions of methyl complex 1 with aldehydes (RCHO) occur rapidly with decarbonylation at room temperature to produce methane and iridium salts of the general formula \( [\text{Cp}^*(\text{PMe}_3\text{)}\text{Ir(R)(CO)}]\text{OTf} \) (9) (Scheme 2) [22]. It is believed that the formation of these iridium complexes proceeds by initial C–H activation of the aldehydic proton to afford acyl intermediate \( \text{Cp}^*(\text{PMe}_3\text{)}\text{Ir(}^{13}\text{CH}_2\text{CHC(O)OTf}) \). Using deuterium labelled [1-\( ^{1}$$D_2\text{]acetaldheyde} \), it was shown that the aldehydic proton is indeed the one being activated, by observing the quantitative production of CH\(_3\)D and no detectable CH\(_4\) by \( ^1\text{H} \) NMR spectroscopy. These
Scheme 2.

reactions demonstrated the ability of complex 1 to activate aldehydic as well as secondary sp³ C–H bonds.

The C–H activation behavior of methyliridium complexes 1 allowed access to interesting classes of organometallic compounds. For example, the tandem C–H bond activation/decarbonylation reactions observed for aldehydes led to the isolation of the first tertiary alkyl complexes of iridium. In fact, very few tertiary alkyl complexes of any of the transition metals have been described[19]. Such complexes have been difficult to isolate because of their high propensity to decompose to stable transition-metal hydrides via further reactions such as β-H elimination. This reaction also adds to the methodology known for preparation of cyclopropyl-substituted transition-metal complexes, which previously consisted of Grignard (or Grignard-like) substitutions of metal halides and photolytic C–H activation [19].

A significant synthetic advance in our work with Ir(III) C–H activation was accomplished when anion metathesis of methyliridium complex 1 with NaBARf (BARf = B[3,5-(CF₃)₂C₆H₃]₄) was found to afford the thermally sensitive dichloromethane complex Cp′(L)(Ir(Me)(CH₂Cl₂))[BARf] (10) (Eq. (1)) [10]. This complex underwent reaction with methane and terminal alkanes at unprecedented low temperatures (10 °C), and its reactions with all comparable substrates were noticeably faster than the analogous reactions with triflate complex 1. Alkanes such as n-pentane and methylcyclohexane could be dehydrogenated stoichiometrically in only few minutes at room temperature to ultimately generate terminal olefin complexes 11 and 12 (Scheme 3). Reactions with functionalized organics again showed high selectivity, as treatment of complex 10 with acetone resulted in overall double C–H activation, cleanly generating the cationic η⁳-hydroxyallyl complex.
The interesting chemistry of methylene chloride complex 10 led us to explore the other potential synthetic routes to complexes of this type. In particular, we were interested in learning whether species similar to 1 and 10 could be accessed by interaction of Cp∗(PMe3)IrMe2 with strong Lewis acids (LAs), in hopes of partially or fully abstracting a methyl group to produce [Cp∗(PMe3)Ir(Me)OTf] (16) cleanly in CD2Cl2 solution by reaction of 14 with B(C6F5)3 at −84 °C. The reactivity of this abstracted methyl species in CD2Cl2 was shown to mirror the chemistry of methyliridium species 10 in reactions with carbon monoxide (Section 2), benzene, tetrahydrofuran, diethyl ether, and aldehydes.

3.2. Mechanistic study of C–H activation reactions by Cp∗(PMe3)Ir(Me)OTf

We have carried out detailed mechanistic studies of these hydrocarbon activation reactions. Kinetic and labelling experiments suggest that formation of the 16-electron methyl cation ([Cp∗(PMe3)Ir(Me)])+(or its solvates) is a pre-requisite for C–H activation [24]. Molar conductivity experiments suggested that the triflate ligand of Cp∗(PMe3)Ir(Me)OTf (1) is slightly dissociated under the reaction conditions and more highly dissociated at lower initial concentrations [8]. In contrast, Cp∗(PMe3)Ir(Me)(Cl) is completely stable in benzene-d6 even at temperatures up to 100 °C. This observation can be explained by the presence of...
the strong iridium–chlorine bond, which is presumably not ionized under the reaction conditions and prevents the formation of an open coordination site.

In evaluating how C–H activation takes place at the cationic Ir center, once it is generated, we have considered four mechanisms: (1) oxidative addition–reductive elimination via a discrete Ir(V) intermediate, (2) H9268–H9266 bond metathesis, (3) H9268–H9266 addition, and (4) electron transfer catalysis. Each of these is discussed in the following sections.

3.2.1. Oxidative addition–reductive elimination

One possible pathway for the C–H activation process involves C–H oxidative addition to give a discrete pentacoordinated Ir(V) intermediate that reductively eliminates methane (Scheme 4). Given the fundamental and common nature of oxidative addition in organometallic chemistry, it seemed likely that establishing this as a reaction pathway would be synthetically straightforward.

Since, protonation of Cp∗(PM3)IrMe2 with HOTf gives Cp∗(PM3)Ir(Me)OTf (1), we hoped to observe a pentavalent iridium intermediate [Cp∗(PM3)Ir(H)(CH3)(CH3)OTf] (17) by low temperature NMR spectroscopy. However, even when this reaction was carried out at −80 °C, only the protonolysis product Cp∗(PM3)IrMe2OTf (1) and methane could be detected in the 1H NMR spectrum. The release of methane essentially renders this reaction irreversible, a feature that could potentially be modified through the use of a chelating ligand. Hence, protonation of the tethered biphenyl complex Cp∗(PM3)Ir(biph) (18) was sought. This complex was prepared by the reaction of [Cp∗IrCl2]2 with 2-biphenylmagnesium bromide followed by reaction with PM3, a synthetic process that involves substitution followed by intramolecular C–H activation of the ortho position of the biphenyl linkage (Section 2). Addition of one equivalent of HOTf to Cp∗(PM3)Ir(biph) at −80 °C resulted in an immediate color change from colorless to orange. The 31P[1H] NMR spectrum of the reaction mixture displayed just one peak (at temperatures between −90 and 25 °C), which suggested the product had been formed cleanly. In the 1H NMR spectrum at −90 °C, a broad doublet with a rather small phosphorus coupling constant of 18 Hz was observed at −5.3 ppm.

Upon warming to −50 °C, this resonance broadened while shifting downfield and flattened out into the baseline at temperatures above −40 °C. While dramatic changes were observed for the biphenyl resonances also, the Cp∗ and PM3 ligand signals remained unchanged. This process was reversed when the reaction mixture was cooled again to −90 °C. The 13C[1H] NMR spectrum at −90 °C, resonances for two independent PM3 and Cp∗ methyl groups indicated the presence of two different metal species in solution. Spin saturation transfer experiments, carried out at −63 °C, demonstrated that exchange occurs between the proton located at −4.8 ppm and a proton located in the aromatic region. At −80 °C, a remarkably low 13C–1H NMR coupling constant [25] of ca. 70 Hz was measured for this unique proton resonance (observed at −5.1 ppm at −80 °C).

The above observations can be explained by the processes depicted in Scheme 5. Data from the above spin saturation transfer experiment suggests that there is rapid exchange between two species even at temperatures as low as −63 °C. Unfortunately, the available NMR data did not allow us to distinguish between the two different possible equilibria as shown in Scheme 5, since unambiguous assignment of the high field NMR resonance at −5.3 ppm (at −90 °C) to either the iridium(V) hydride species 19 or the agostic iridium(III) complex 20 is not possible. The low Jp–H and Jc–H coupling constants of 18 and 70 Hz, respectively, can be explained by a static agostic and also a “fluxional” iridium hydride structure. The observed...
The chemical shift of this resonance seems more indicative of an agostic structure, since known chemical shifts of static iridium(III) hydride complexes of this type are typically in the range from $-13$ to $-19$ ppm [9,17]. However, the chemical shift for the fluxional hydride complex 19 would be (1) due to a hydride bound to Ir(V) and not to Ir(III), and (2) averaged between the static iridium hydride and the aromatic biphenyl resonance. Some evidence against an agostic complex is provided by the $^1$H NMR spectrum, since coupling of the unique proton to the ortho-biphenyl proton would be expected in this agostic structure; however, this is not observed. In the $^1$H NMR spectrum only coupling to phosphorus is observed, although it is also possible that additional coupling is obscured by the broadness of the resonance. It is also certainly possible that an interconverting mixture of 19 and 20 might be present, as shown in Scheme 5.

Given that the above observations precluded definitive assignment of a pentavalent iridium complex, the protonation reaction was re-investigated using deuterated acid. The reaction of CF$_3$CO$_2$D with Cp'(PMe$_3$)Ir(biph) is reversible, and upon removal of the acid in vacuo the neutral iridium complex is obtained again (Eq. (3)). $^1$H, $^2$H, $^{13}$C NMR and MS data unequivocally demonstrated that two deuterium atoms were incorporated “exclusively” into the ortho positions of the biphenyl linkage. This observation provided compelling evidence that reaction of the deuterons had occurred selectively at the metal biphenyl carbon bond. However, this provides only circumstantial evidence for the formation of an iridium(V) hydride intermediate, [Cp'(PMe$_3$)Ir(biph)(D, H)][OTf], since electrophilic attack of the deuteron may have occurred directly at the Ir-C bond rather than the metal center.

Additional protonation reactions have been performed to model the proposed intermediate in the

Note that excess deuterotrifluoroacetic acid is required to shift the equilibrium completely towards the deuterated complex. 

\[\text{(3)}\]
C–H activation reactions discussed. The synthesis of the thermally sensitive Ir(V) compound \( \text{Cp}^*\text{IrMe}_3\text{OTf} \) (21) from HOTf and \( \text{Cp}^*\text{IrMe}_4 \) was possible, and addition of PMe3 to this triflate led to the model complex \( \text{[Cp}^*(\text{PMe}_3)\text{IrMe}_3]\text{[OTf]} \) (22). This complex was not decomposed by the elimination of ethane (as was hoped), but rather by loss of \( \text{Cp}^*\text{Me} \). It has been previously observed that C–C reductive elimination reactions occur most readily when at least one group involved is an sp2-hybridized carbon, and the reluctant coupling of sp3 centers has; therefore, been attributed to a high kinetic barrier [26].

It is worthy noting that many of the Ir(V) species that have been synthesized have hydride and/or silyl ligands bound to the Ir center. Considering the Pauling electronegativities of iridium (2.20), hydrogen (2.20), silicon (1.90), and carbon (2.55), it is evident that a bond to carbon should render an iridium center relatively electron-deficient compared to those with Ir–H or Ir–Si bonds. This may explain the reactive nature of the iridium(V) intermediates in the C–H activation system, and also why the investigations of silyliridium complexes allowed us to observe the first stable Ir(V) products formed by oxidative addition to Ir(III) centers [15].

In support of our mechanistic conclusion, density functional theory calculations at the B3LYP level demonstrated that Ir(III) to Ir(V) oxidative addition is a lower energy pathway than σ-bond metathesis to Ir(III) centers [15]. As shown in Eq. (4), treatment of \( \text{Cp}^*(\text{PMe}_3)\text{IrSiPh}_2\text{OTf}(\text{Ph}) \) (23) with LiB\(_6\text{C}_6\text{F}_{5,6}\text{H}_2\text{O}_2\) led to the formation of the crystallographically characterized, cyclometalated species 24 by intramolecular C–H activation. This is our most convincing experimental evidence that Ir(V) species are involved in chemistry involving methyliridium species 1.

\[ \text{Cp}^*(\text{PMe}_3)\text{IrSiPh}_2\text{OTf}(\text{Ph}) \rightarrow \text{Cp}^*(\text{PMe}_3)\text{IrSiPh}_2\text{OTf} + \text{LiB}\(_6\text{C}_6\text{F}_{5,6}\text{H}_2\text{O}_2} \]

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3.2.2. σ-Bond metathesis

The overall C–H activation reactions of methyliridium species 1 resemble the σ-bond metathesis reactions that are more characteristic of d4 early transition metal, lanthanide, and actinide complexes [29–33]. In contrast to the oxidative addition–reductive elimination scenario discussed previously, concerted σ-bond metathesis requires no formal change in the oxidation state at iridium during the C–H activation process. This alternative to oxidative addition was considered because of the low number of isolable “cationic” iridium(V) complexes known. We are only aware of one report of σ-bond metathesis occurring in a late transition metal system (by offering disproof of the alternative oxidative-addition mechanism), involving B–H bond metathesis with a Ru–CH3 bond of a co-ordinately and electronically saturated ruthenium center [34]. Collecting experimental evidence that completely rules out σ-bond metathesis in C–H activation reactions involving methyl iridium complex 1 is challenging, although the experimental and theoretical evidence cited above make us favor the oxidative addition–reductive elimination pathway.

3.2.3. σ–π Addition

Additions of H–H and C–H bonds to M = X double bonds (where X is NR, CR2) have been reported for several transition metals [33,35–39]. Due to these reports, a C–H activation mechanism involving the intermedicy of an Ir=C double bond is worth consideration. The mechanism depicted in Scheme 6 involves formation of a (hydrido)methyleneiridium species, 25, in the first reaction step by migration of hydride from carbon to iridium in the initial methyliridium cation, followed by C–H bond addition across the metal carbene fragment. Recalling the reaction of methyliridium complex 1 with THF, formation...
of the cyclic carbene product \(7\) is the evidence for the possibility of such a process, although it may not be operating with other substrates. Theoretical studies suggest that \(\alpha\)-hydrogen migrations can be kinetically favorable if a co-ordinatively unsaturated species can be accessed \[40,41\]. Although the proposed hydrido methylidene species \(25\) would be expected to be less stable than the Fischer-type carbene complex \(7\), and energetically uphill from the starting complex \(1\), this species could be formed on the C–H activation pathway in an \(\alpha\)-H elimination step.

Further support for possible carbene intermediates in this iridium system was provided by the outcome of the reaction of \(\mathrm{Cp}^*\)(PMe\(_3\))IrMe\(_2\) (11) with \([\mathrm{C(C_6H_5)_3}]\)[BF\(_4\)], which leads to \([\mathrm{Cp}^*(\mathrm{PMe}_3)\mathrm{Ir}(\mathrm{C}_2\mathrm{H}_4)(\mathrm{H})][\mathrm{BF}_4]\) (26), identical to that formed from 1 and ethane (Scheme 7). This reaction is instantaneous at room temperature, and no intermediates could be identified by low temperature NMR spectroscopy. A mechanism analogous to the one shown in Scheme 7 has been proposed by Werner and co-workers in a similar reaction in which \((6^\mathrm{\circ}\mathrm{C_6Me_6})\mathrm{Ru}(\mathrm{PPh}_3)(\mathrm{Me})_2\) was shown to produce the corresponding cationic ethylene complex \([((6^\mathrm{\circ}\mathrm{C_6Me_6})\mathrm{Ru}(\mathrm{PPh}_3)(\mathrm{C}_2\mathrm{H}_4)(\mathrm{H})][\mathrm{BF}_4]\) upon treatment with \([\mathrm{C(C_6H_5)_3}]\)[BF\(_4\)] \[42\]. Production of the cationic methyl methylidene complex \(27\) may also take place in two steps by an electron transfer process, as previous work by Cooper and Hayes demonstrated this to be an operative pathway for \(\mathrm{Cp}_2\mathrm{WMe}_2\) \[43\].

In order to experimentally test the viability of this \(\sigma-\pi\) addition mechanism, the reaction of \(\mathrm{Cp}^*(\mathrm{PMMe}_3)\mathrm{Ir}(\mathrm{CD}_3)(\mathrm{OTf})\) (28) with H\(_2\) was carried out (Scheme 8). Neglecting kinetic isotope effects for the reductive elimination of methane, this mechanism would predict the formation of a 1:1 ratio of \(\mathrm{CD}_3\mathrm{H}\) and \(\mathrm{CH}_2\mathrm{D}_2\). Using NMR detection methods, however, exclusive formation of \(\mathrm{CD}_3\mathrm{H}\) along with \([\mathrm{Cp}^*(\mathrm{PMMe}_3)\mathrm{Ir}\mathrm{H}_3][\mathrm{OTf}]\) was observed, providing evidence against the \(\sigma-\pi\) addition pathway. Further evidence against this mechanism was obtained in
the “inverse” reaction of \( \text{Cp}^*\text{(PMe}_3\text{)Ir(Me)(OTf)} \) (1) with \( \text{D}_2 \), which yields (within NMR detection limits) exclusively \( \text{[Cp}^*\text{(PMe}_3\text{)IrD}_3\text{][OTf]} \) (29) and \( \text{CH}_3\text{D} \), instead of the mixture of \( \text{CH}_3\text{D} \) and \( \text{CH}_2\text{D}_2 \) predicted for the carbene mechanism. Additional arguments against this mechanism arise from kinetic isotope effect measurements. For the carbene type mechanism, a primary kinetic isotope effect (\( k_H / k_D > 2 \)) would be expected for a rate determining \( \alpha\)–C–H elimination step. In kinetic measurements for the reaction of \( \text{Cp}^*\text{(PMe}_3\text{)Ir(CD}_3\text{)(OTf)} \) (28) with \( \text{C}_6\text{H}_6 \), however, a kinetic isotope effect of close to 1 was observed (\( k_H / k_D = 1 \pm 0.1 \)).

3.2.4. Electron transfer catalysis

The \( \text{C–H} \) activation reactions that occur on treatment of dimethyl complex 14 with \( \text{B(C}_6\text{F}_5\text{)}_3 \) (Eq. (2)) are superficially similar to those recently reported by Diversi et al. [13,44] involving electron transfer catalysis [45,46]. They reported that the addition of catalytic amounts of \( \text{[FeCp}_2\text{][PF}_6\text{]} \) or \( \text{AgBF}_4 \) to \( \text{C}_6\text{D}_6 \) produces \( \text{Cp}^*\text{(PMe}_3\text{)IrMe(C}_6\text{D}_5\text{)} \) (15), \( \text{(Cp}^*\text{–d}_1\text{)(PMe}_3\text{)IrMe} \)–\( \text{(C}_6\text{D}_5\text{)} \) (30), and an oily dark colored precipitate. Their proposed mechanism (Scheme 9) relies upon oxidation of 14 by ferrocenium to produce an iridium(IV) radical cation which attacks the solvent.

Scheme 8.

Scheme 9.
directly or abstracts a hydrogen atom from the Cp∗ ligand to produce both CH₄ and CH₃D as byproducts of the reaction. Noting these similarities, we elected to investigate whether one-electron processes were operative in the reaction between Cp∗(PMe₃)IrMe₂ (14) and B(C₆F₅)₃ in the presence of C₆D₆. In contrast to Diversi et al.’s result, we observed exclusive formation of CH₃D. It was also shown that [Cp∗(PMe₃)Ir(Me(CH₂Cl₂))][MeB(C₆F₅)₃] reacted with THF to produce the expected iridium carbene species [Cp∗(PMe₃)Ir(H)C₄H₆O][MeB(C₆F₅)₃] (31), and with triphenylsilane to yield [Cp∗(PMe₃)Ir(H)SiPh₂(C₆H₄)][MeB(C₆F₅)₃] (32) (Scheme 10). Attempts to perform the analogous reactions with [FeCp₂][PF₆] instead of borane always produced complex reaction mixtures. These combined results support the hypothesis that one-electron transfer processes are not involved. Our alternative mechanism is similar to that proposed for C–H activation by methyl complex 1 (vide infra), most likely involving oxidative addition and reductive elimination steps following the formation of the cationic species [Cp∗(PMe₃)IrMe][MeB(C₆F₅)₃] (16).

3.3. Catalytic chemistry involving [Cp′(PMe₃)Ir(H)](CH₂Cl₂)][MeB(C₆F₅)₃]

In order to compare their reactivity to that of methyliridium complexes 1 and 10, we attempted the synthesis of the analogous cationic hydridoiridium species [Cp′(PMe₃)Ir(H)CH₂Cl₂][MeB(C₆F₅)₃] (38) in >90% yield, along with the production of some (3–10%) [Cp′(PMe₃)IrH]⁺ [18]. The low solubility of dihydrogen in CD₂Cl₂ was more successful, resulting in the formation of the thermally sensitive monohydridoiridium product [Cp′(PMe₃)Ir(H)CH₂Cl₂][(MeB(C₆F₅)₃)] (38) in >90% yield, along with the production of some (3–10%) [Cp′(PMe₃)IrH]⁺ [18]. The low solubility of dihydrogen in CD₂Cl₂ is likely responsible for preventing conversion of 38 to monomeric or dimeric polyhydride complexes at −84 °C. Warming a solution of complex 38 above −20 °C lead immediately to the formation of these polyhydride species, and mechanical agitation of solutions of 38 lead to accelerated decomposition even at lower temperatures.

Carbon–hydrogen bond activation reactions involving monohydride complex 38 occur at the lowest temperatures yet observed for such a process. For example, reactions with acetaldehyde and benzaldehyde produced the expected alkyl-carbonyl cationic products 39 and 40 at −84 °C (Scheme 11). However, the products observed in reactions with other types of C–H bonds...
bonds are not strictly analogous to those seen with the corresponding methyl complex. For example, addition of THF to complex 38 resulted in the formation of the adduct \( [\text{Cp'PMe}_3\text{Ir(H)(THF)}][\text{MeB(C}_6\text{F}_5\text{)}_3] \), but this adduct never engaged in any observable C–H activation reaction.

The hydrido cation 38 exhibited no net reaction with hydrocarbon substrates below its decomposition temperature of \(-20^\circ\text{C}\). Interest in understanding this thermal decomposition of monohydride 38, which as noted above leads to the trihydride complex \([\text{Cp'PMe}_3\text{Ir(H)}_3][\text{MeB(C}_6\text{F}_5\text{)}_3]\) and/or \([\text{Cp'PMe}_3\text{Ir}(\mu-H)\text{Ir(H)}\text{PMe}_3][\text{PMe}_3\text{Ir}(\mu-H)\text{Ir(H)}\text{PMe}_3][\text{Cp'PMe}_3\text{Ir(H)}_2]\), prompted us to carry out the decomposition of 2 in the presence of deuterated hydrocarbons. This resulted in the exclusive production of \([\text{Cp'PMe}_3\text{Ir(D)}_3][\text{MeB(C}_6\text{F}_5\text{)}_3]\), indicating that the alkane was the source of the iridium-bound deuterium in the product. Monitoring the reaction at temperatures below \(-20^\circ\text{C}\) revealed that the iridium-bound hydrogen in 38 underwent H/D exchange with cyclohexane-\(d_12\) before thermal decomposition occurred. Indeed, hydrocarbon activation reactions involving hydridoiridium complex 38 were found to be highly reversible, allowing the use of the complex as a homogeneous catalyst for low temperature H/D exchange [18]. The substrates that were studied in these catalyses included ferrocene, tetrahydrofuran, toluene, methane, and ethane. The formation of \(\text{H}_2\), HD, or \(\text{D}_2\) and the corresponding \([\text{Cp'P}(\text{L})(\text{M-R})]^{+}\) complex has never been observed,
leading us to postulate the free-energy diagram as shown in Scheme 12 for the catalysis. The lowest minimum in the potential energy diagram is for that of hydridoiridium complex 38, as this is the observed resting state of the catalyst (observed in solution by NMR spectroscopy during the reaction). Considering relative bond strengths, we suggest that elimination of R–H (loss of one weaker Ir–C and one stronger Ir–H bond) is favored energetically, compared to loss of two (stronger) Ir–H bonds as H₂ [48]. The great stability of [Cp*]+(PMe₃)Ir(H)(H₂) [56] (which also does not lose H₂ easily) supports this as well. Interestingly, a similar energy profile was previously calculated in a theoretical study of alkane dehydrogenation by [CpIr(PH₃)H]⁺ [49], although CH₂Cl₂ solvates of this cation were not included in the calculations.

Catalysis involving bond activation by Ir(III) complexes is extremely rare [49]. Other reported catalyses involving Ir(III) postulate either initial formation of active Ir(I) species [50,51] as a LA catalyst in which the oxidation state presumably stays constant [52], or cycles involving Ir(III) to Ir(IV) conversions, where electron transfer catalysis [13,53] is believed to be involved. Recent theoretical results [54] suggest that alkane dehydrogenation by iridium PCP pin-
cer complexes [51,55] most likely takes place using Ir(I)/Ir(III) chemistry (i.e. not associatively through an Ir(ν) intermediate, on which separate calculations have been performed [49]).

An interesting comparison can be drawn between the chemistry carried out by Bercaw and co-workers using Cp*₂SCH [31] and the reactivity of cationic hy-
dride complex 38 [56]. The scandium system promotes H/D exchange most likely via a σ-bond metathesis mechanism while an oxidative-addition mechanism is more probable for H/D exchange catalyzed by 38. Although the d-electron count for the scandocene hydride is 14 electrons while that for the presumed active species [Cp*⁺(PMe₂)Ir(H)][MeB(C₆F₅)₃] is 16 electrons, each is able to mediate H/D exchange with methanol. Several parallels and contrasts between these systems are worth considering. In the case of scandium, tetrathylsilane is deuterated at a rate comparable to that of methane while 38 deuterates tetramethylethylene much more slowly than methane. The scandium system deuterates only the methyl groups of propane, while hydrido cation 38 deuter-
ates both the methyl and methylene groups with preferential activation of the methyl groups. Cyclo-
propane is deuterated by the scandium system at a rate comparable to that of methane, while exposure to cyclopropane results in the decomposition of catalyst 38 to multiple products. Benzene is activated more rapidly than methane and the aryl hydrogens are ex-
changed faster than the methyl group in toluene in each system. Both systems can be used to deuterate ferrocene and decamethylferrocene. It is unknown whether the scandocene system will deuterate Et₂O, but both systems activate the α-hydrogens of THF preferentially (with scandium, α-deuteration is ob-
served exclusively). While olefins react only with 38 by co-ordination, the scandium system produces poly-
olefins. Pyridine is methylated in the ortho position by the scandium system; pyridine and CO stop all H/D exchange with 38. Despite the many similarities between these H/D exchange catalysis systems, the most important difference is the temperature regime where the catalysis takes place. Exchange catalyzed by the scandium system takes place at elevated tem-
peratures, while exchange promoted by 38 must be performed at temperatures less than ~20°C, once again emphasizing the mild conditions which can be used with monohydride catalyst 38.

4. Conclusion

This investigation of the synthesis and reactivity of iridium complexes 1, 10, and 38 was motivated by an interest in the chemistry of 16-electron cationic iridium complexes. The mild conditions under which these compounds display efficient intermolecular C–H activation chemistry gave us incentive to study them in detail. A comparison to other cationic late metal alkyl systems is informative. Whereas, sim-
ilar reactivity of cationic platinum(II) [57–59] and palladium [60] methyl complexes has been reported, related cobalt(III) alkyl complexes have shown activity in ethylene polymerization [61], palladium methyl cata-
lations are catalysts for living alternating copoly-
merization of olefins and carbon monoxide [62], and cationic rhodium(III) complexes have been used for the catalytic dimerization of methyl acrylate [63].

Providing incontrovertible proof that iridium(V) complexes of the type [Cp*⁺(PMe₂)IrR₂(H)]⁺ and [Cp⁺(PMe₂)Ir(R)(H₂)]⁺ are on the C–H activation
pathway is difficult, although essentially all of the theoretical and experimental evidence that is now available has led us to favor it. Other research groups have made important contributions toward resolving the oxidative addition/H-bond metathesis issue in related late transition metal systems. Tilset and co-workers [64] recently provided experimental evidence for the existence of (N–N)Pt(Me)2(H)(L)⁺ (N–N = ArN=CMe–CMe=NAr, Ar = 3,5-(CF3)2C6H3) by low temperature NMR spectroscopy. Theoretical calculations (DFT) indicated that, for the C–H activation reactions of [(N–N)Pt(Me)(L)]⁺, the oxidative addition pathway was favored by 12 kJ/mol over H-bond metathesis starting from [(N–N)Pt(Me)(CH4)]⁺. Furthermore, using the aquo adduct [(N–N)Pt(Me)(CH4)(H2O)]⁺ as the starting complex led to a predicted 20 kJ/mol preference for oxidative addition. Calculations[65] on Periana’s oxidation of methane by platinum(II) [5] predicted that both oxidative addition–reductive elimination and H-bond metathesis can occur, depending on whether the active species is [(bipyrimidine)PtCl]+ or [(bipyrimidine)[Pt(OSO3H)]²⁺, respectively.

The recently discovered catalytic C–H activation reactions discussed here arose as a result of a study of stoichiometric reaction chemistry. This offers hope that future catalytic systems will result from the growing body of C–H activation research. We are currently investigating the possibilities of using what we have learned to develop other types of catalytic reactions (such as oxidations) that will lead to more highly functionalized molecules.

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