

Cationic Ir(III) alkyl and hydride complexes: stoichiometric and catalytic C–H activation by $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{R})(\text{X})$ in homogeneous solution

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Received 15 June 2001; accepted 4 September 2001

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 $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{R})(\text{X})$ (Cp^* is pentamethylcyclopentadienyl or $\eta^5\text{-C}_5\text{Me}_5$; R = alkyl, hydrido; X = OSO_2CF_3 , $\text{B}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3)_4$), 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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Keywords: C–H activation; Cationic Ir(III) complexes; H–D exchange; Ir(V) complexes; Methyl abstraction

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 (CH_4) functionalization because of the expense and danger involved in transporting the liquified 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 H_2), using a nickel based catalyst ($\text{Ni}/\text{Al}_2\text{O}_3/\text{CaO}$) at 700–900 °C and 10–40 bar [4]. The reaction between

1 mol of CH_4 and 1 mol of H_2O to form 1 mol of CO and 3 mol of H_2 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 CO_2 and H_2O . 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 CO_2 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

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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 C_nH_{2n+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 alkanes using a rhodium(I) catalyst [7].

Our research group has had an interest in the development of transition metal based systems that effect the controlled activation of C–H bonds for many years. This article concerns the C–H activation system we have been studying most recently, involving cationic iridium alkyl and hydrido complexes that react selectively with hydrocarbons under mild conditions. Here, we trace the development of a C–H activation system from its discovery through mechanistic studies, and we conclude with catalytic work that has developed as a result of what we have learned.

2. Experimental

Syntheses and/or characterization data for complexes **1–6** [8], **7** [9], **8** [9], **10–12** [10], **13** [11], **14** [12], **15** [13], **21** [14], **22** [14], **23** [8], **24** [15], **33** [16], **34** [17], and **38** [18] have been previously reported. Spectroscopic (1H and $^{31}P\{^1H\}$ NMR) identification of complexes **31**, **32**, **35**, **36**, **39**, and **40** was made possible by analogy to their corresponding triflate salts, and the identification of $Cp^*(PMe_3)Ir(CD_3)OTf$ (**28**) was made by comparison with $Cp^*(PMe_3)Ir(CH_3)OTf$ (**1**). $Cp^*(PMe_3)Ir(CD_3)OTf$ (**28**) was prepared by reaction of $Cp^*(PMe_3)Ir(CD_3)_2$ [12] with $Cp^*(PMe_3)Ir(OTf)_2$ [8].

Generation of $[Cp^*(PMe_3)IrMe(CICD_2Cl)][MeB(C_6F_5)_3]$ (**16**). In a typical experiment, a J. Young-style NMR tube was charged with 17 mg (0.0392 mmol)

of $Cp^*(PMe_3)IrMe_2$ and 24 mg (0.0468 mmol) of $B(C_6F_5)_3$. Dichloromethane- d_2 (0.75 ml) was added by static vacuum transfer at $-84^\circ C$ and the solid reactants dissolved by gentle agitation to produce a yellow–brown solution with the following NMR spectroscopic features. 1H NMR (400 MHz, CD_2Cl_2 , 258 K) δ 1.70 (d, $J_{P-H} = 1.5$ Hz, 15H, C_5Me_5), 1.56 (d, $J_{P-H} = 10.5$ Hz, 9H, PMe_3), 1.00 (d, $J_{P-H} = 6.5$ Hz, 3H, Ir–Me), 0.44 (s, br, 3H, B–Me). $^{31}P\{^1H\}$ NMR: δ -29.64 . $^{11}B\{^1H\}$: δ -15.75 . $^{13}C\{^1H\}$ NMR: (C–F resonances observed between 154 and 158 ppm but unassigned) δ 95.32 (C_5Me_5), 14.35 (d, $J_{P-C} = 39$ Hz, PMe_3), 10.0 (br, B– CH_3), 8.87 (s, C_5Me_5), -14.48 (s, Ir– CH_3). Literature [10] $[Cp^*(PMe_3)IrMe(CICD_2Cl)][B(3,5-C_6H_3(CF_3)_2)_4]$: 1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 1.68 (15H), 1.58 (9H), 1.23 (3H). Solution MS (electrospray) expected for $[Cp^*(PMe_3)IrMe]^+$: 419; found, 419. The yield of this compound was determined to be 98% by reaction with CO to produce $[Cp^*(PMe_3)Ir(Me)(CO)][MeB(C_6F_5)_3]$ in the following analogous synthesis. Solid $Cp^*(PMe_3)IrMe_2$ (100 mg, 0.231 mmol) and $B(C_6F_5)_3$ (125 mg, 0.244 mmol) were added to a Schlenk flask equipped with a stir bar. The flask was cooled to $-84^\circ C$, and CH_2Cl_2 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 \times 5 ml) portions of pentane. The solid was collected to yield 220 mg (98%, 0.226 mmol) of $[Cp^*(PMe_3)IrMe(CO)][MeB(C_6F_5)_3]$. 1H NMR (CD_2Cl_2 , 298 K): δ 1.97 (s, 15H, C_5Me_5), 1.63 (d, $J_{P-H} = 11$ Hz, 9H, PMe_3), 0.49 (d, $J_{P-H} = 5.9$ Hz, 3H, Ir– CH_3), 0.33 (s, br, 3H, B– CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , C–F resonances observed between 154 and 158 ppm but not assigned): δ 167.29 (s, Ir–CO), 102.37 (s, C_5Me_5), 15.45 (d, $J_{P-C} = 41.3$ Hz, PMe_3), 10.1 (br, s, B– CH_3), 9.17 (s, C_5Me_5), -24.92 (s, Ir– CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 298 K): δ -38.6 . MS (electrospray) expected for $[Cp^*(PMe_3)IrMe(CO)]^+$: 447. Found: 447. Analytically calculated for $C_{34}H_{30}BIrPF_{15}O$: C,

41.95; H, 3.11. Found: C, 41.69; H, 2.80. Literature for $[\text{Cp}^*(\text{PMe}_3)\text{IrMe}(\text{CO})][\text{OTf}]$ [19]: ^1H NMR: δ 1.97 (s, 15H), 1.69 (d, 9H), 0.51 (d, 3H).

Synthesis and characterization of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$ (**18**). A glass vessel sealed to a Kontes vacuum adapter was loaded with a suspension of $[\text{Cp}^*\text{IrCl}_2]_2$ (488 mg, 0.612 mmol) in approximately 10 ml of THF and 2 ml diethyl ether and cooled to -40°C . Then, 1.2 ml of a 0.82 M solution of 2-biphenylmagnesium bromide solution 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 PMe_3 were 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 CH_2Cl_2 (2×5 ml). The residue was then extracted with 15 ml of CH_2Cl_2 (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 \times 7 cm), and eluted with CH_2Cl_2 . The first band (pale yellow in color) was collected and the solvent removed in vacuo to give a yellow residue which was recrystallized from CH_2Cl_2 : diethyl ether (1:10) at -50°C to give 620 mg (1.11 mmol, 91%) of the desired complex. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) δ 7.41 (d, 2H, $J_{\text{H-H}} = 7.4$ Hz, H6), 7.41 (d, 2H, $J_{\text{H-H}} = 7.4$ Hz, H3), 6.92 (t, 2H, $J_{\text{H-H}} = 7.4$ Hz, H5), 6.77 (t, 2H, $J_{\text{H-H}} = 7.4$ Hz, H4), 1.79 (d, 15H, $J_{\text{P-H}} = 1.5$ Hz, C_5Me_5), 0.93 (d, 9H, $J_{\text{P-H}} = 10.2$ Hz, PMe_3); ^{13}C [^1H] NMR (101 MHz, CD_2Cl_2 , 298 K) δ 155.7 (s, C1), 152.3 (d, $J_{\text{P-C}} = 13.2$ Hz, C2), 136.8 (d, $J_{\text{P-C}} = 2.8$ Hz, C3), 125.7 (s, C4), 121.6 (s, C5), 120.0 (d, $J_{\text{P-C}} = 1.4$ Hz, C6), 94.1 (d, $J_{\text{P-C}} = 3$ Hz, C_5Me_5), 14.0 (d, $J_{\text{P-C}} = 39.6$ Hz, PMe_3), 9.6 (s, C_5Me_5); ^{31}P [^1H] NMR (162 MHz, CD_2Cl_2 , 298 K) δ -36.2 ; MS (EI) expected for $\text{M}^+\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$: 556. Found: 556. Analytically Calculated for $\text{C}_{25}\text{H}_{32}\text{IrP}$: C, 54.03; H, 5.80. Found: C, 53.95; H, 5.85.

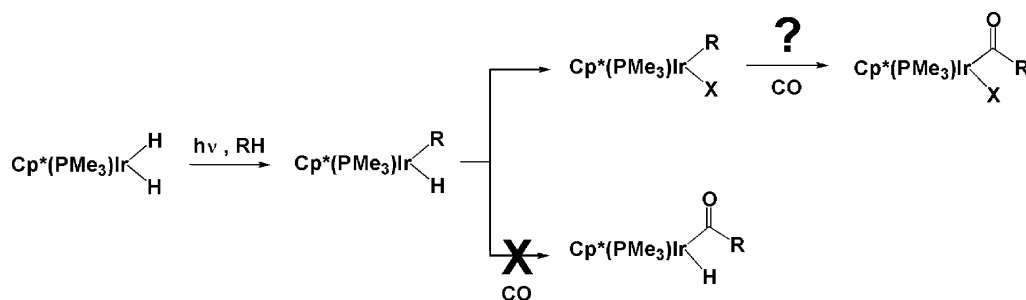
Protonation of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$ to yield either **19** or **20**. An NMR tube containing a 0.5 ml CD_2Cl_2 solution of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$ (11 mg, 0.019 mmol) was

cooled to -196°C and 2 μl HOSO_2CF_3 was added by syringe. The tube was then sealed under vacuum and thawed in a -95°C bath. The tube was manipulated to allow mixing of the reagents, resulting in an instantaneous color change to orange. At this temperature, the NMR tube was inserted into a pre-cooled (-88°C) NMR probe. ^1H NMR (400 MHz, CD_2Cl_2 , 184 K) δ 7.69 (m, 3H, biph), 7.49 (t, ^1H , $J_{\text{H-H}} = 7.3$ Hz, biph), 7.25 (m, 3H, biph), 7.15 (t, ^1H , $J_{\text{H-H}} = 7.3$ Hz, biph), 1.66 (s, 15H, C_5Me_5), 1.53 (d, 9H, $J_{\text{P-H}} = 10.9$ Hz, PMe_3), -5.37 (d, ^1H , $J_{\text{P-H}} = 19.8$ Hz, Ir-H, ($J_{\text{C-H}} = 67$ Hz); ^{31}P [^1H] NMR (162 MHz, CD_2Cl_2 , 184 K) δ -34.9 ; ^1H NMR (400 MHz, CD_2Cl_2 , 295 K) δ 7.60 (br s, 4H, biph), 7.21 (t, 4H, $J_{\text{H-H}} = 6.8$ Hz, biph), 1.61 (s, 15H, C_5Me_5), 1.49 (d, 9H, $J_{\text{P-H}} = 10.9$ Hz, PMe_3); ^{31}P [^1H] NMR (162 MHz, CD_2Cl_2 , 295 K) δ -35.40 . Repeated attempts to isolate this complex in analytically pure form failed.

3. Results and discussion

3.1. Stoichiometric C–H activation reactions involving $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})(\text{X})$ 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 derived 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 $\eta^5\text{-C}_5\text{H}_5$) and pentamethylcyclopentadienyl 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 $\text{Cp}^*(\text{CO})\text{Ir}(\text{R})(\text{H})$ system [21]. Although complexes of the general structure $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{R})(\text{H})$ 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



Scheme 1.

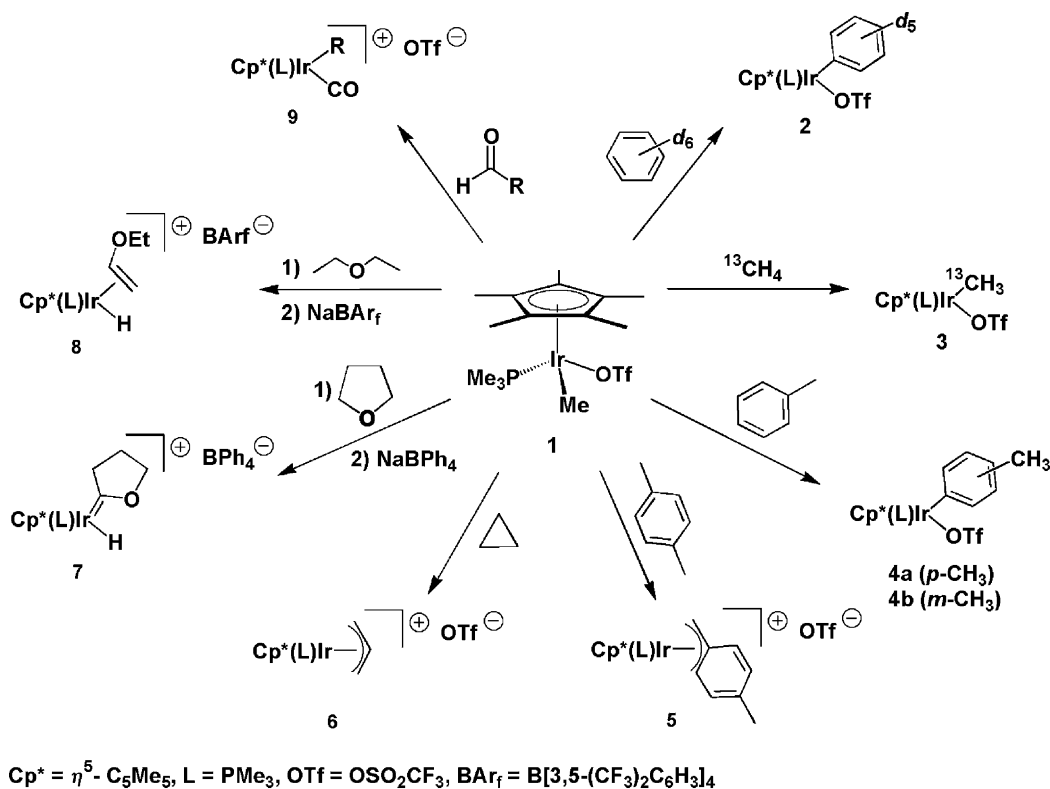
complexes with a better anionic leaving group to produce $\text{Cp}^*(\text{PMe}_3)\text{Ir(R)(X)}$ (Cp^* is pentamethylcyclopentadienyl; R = alkyl, hydrido; X = OSO_2CF_3 , $\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4$) was attempted. It was hoped that use of a weakly co-ordinating X group would 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 $\text{Cp}^*(\text{PMe}_3)\text{IrMeOTf}$ (**1**) from $\text{Cp}^*(\text{PMe}_3)\text{IrMe}_2$ and $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{OTf})_2$ in Et_2O solvent in 1993 [8]. However, upon removal of the solvent and dissolution of the residue in C_6D_6 for NMR spectroscopic study, only the phenyl derivative $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{C}_6\text{D}_5)\text{OTf}$ (**2**) was observed! It was soon found that this apparent σ -bond metathesis reaction could be extended to saturated hydrocarbons (Scheme 2).³ For example, exposing **1** to 2 atm of $^{13}\text{CH}_4$ afforded $\text{Cp}^*(\text{PMe}_3)\text{Ir}(^{13}\text{CH}_3)\text{OTf}$ (**3**) and CH_4 . 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 *para* and *meta*) rather than benzylic activation, to give a mixture of products (**4a** and **b**) in a 1.25:1 ratio statistically corrected). However, reaction with *p*-xylene affords $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_3)][\text{OTf}]$ (**5**) as the only observed product in a reaction that apparently disrupts the aromaticity of the organic starting material. The lack of attack at the *ortho* positions in toluene and *p*-xylene is presumably a result of steric shielding by the proximate methyl groups. Reaction

³ For a more detailed discussion of the C–H activation mechanism see Section 3.3.

of **1** with cyclopropane gives the π -allyl complex $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^3\text{-CH}_2\text{CHCH}_2)][\text{OTf}]$ (**6**), a product whose formation is explained in terms of an initial C–H activation, followed by β -alkyl elimination. Exposure of **1** to an atmosphere of ethane resulted in formation of the ethylene hydride complex $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{C}_2\text{H}_4)(\text{H})][\text{OTf}]$. 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 β -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 $[\text{Cp}^*(\text{PMe}_3)\text{Ir(R)(CO)}][\text{OTf}]$ (**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 $\text{Cp}^*(\text{PMe}_3)\text{Ir(COR)(OTf)}$. Using deuterium labelled $[1\text{-}d_1]\text{acetaldehyde}$, it was shown that the aldehydic proton is indeed the one being activated, by observing the quantitative production of CH_3D and no detectable CH_4 by ^1H NMR spectroscopy. These

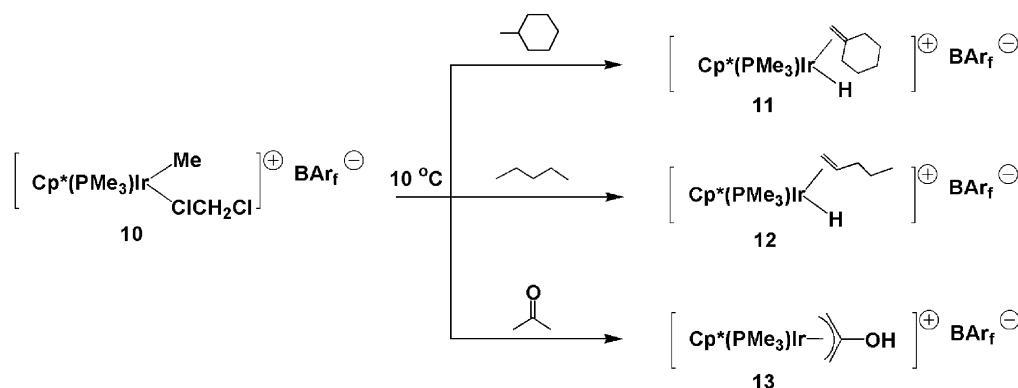


Scheme 2.

reactions demonstrated the ability of complex **1** to activate aldehydic as well as secondary sp^3 C–H bonds.

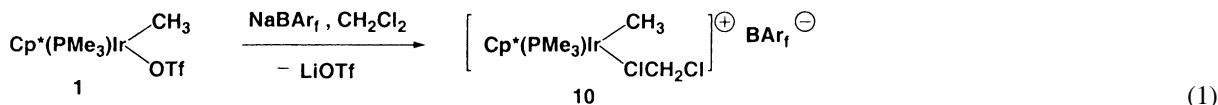
The C–H activation behavior of methyliridium complexes **1** allowed access to interesting classes of organometallic compounds. For example, the tandem C–H bond activation/decarbonylation reactions observed for aldehydes led to the isolation of the first tertiary alkyl complexes of iridium. In fact, 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 NaBAR_f (BAR_f = B[3,5-(CF₃)₂C₆H₃]₄) was found to afford the thermally sensitive dichloromethane complex Cp*(PMe₃)Ir(Me)(CH₂Cl₂)[BAR_f] (**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^3 -hydroxyallyl complex



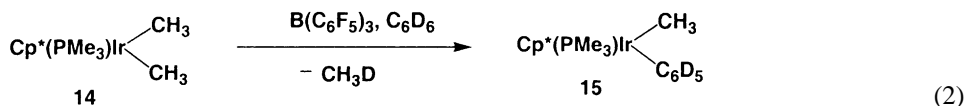
Scheme 3.

$[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\eta^3\text{-CH}_2\text{C}(\text{OH})\text{CH}_2)]^+ [\text{BAR}_f]^-$ (**13**) [11].



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 $\text{Cp}^*(\text{PMe}_3)_2\text{IrMe}_2$ with strong Lewis acids (LAs),

cation $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})(\text{CD}_2\text{Cl}_2)]^+ [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**16**) cleanly in CD_2Cl_2 solution by reaction of **14** with $\text{B}(\text{C}_6\text{F}_5)_3$ at -84°C . The reactivity of this abstracted methyl species in CD_2Cl_2 was shown to mirror the chemistry of methyliridium species **10** in reactions with carbon monoxide (Section 2), benzene, tetrahydrofuran, diethyl ether, and aldehydes [23].

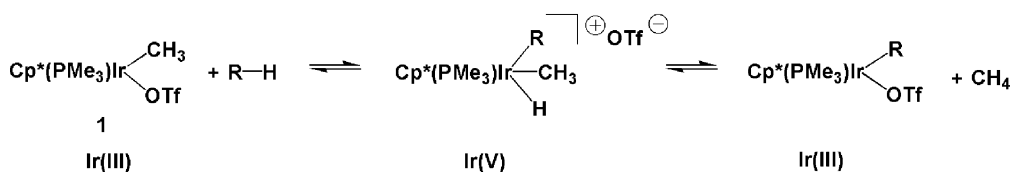


in hopes of partially or fully abstracting a methyl group to produce $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})][\text{MeLA}]$ [23]. This methodology provides a shorter route to the salts of this general formula. Addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to a solution of dimethyliridium species **14** in C_6D_6 at 25°C solution produced $\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})(\text{C}_6\text{D}_5)$ (**15**) over the course of a few seconds (Eq. (2)).⁴ The yield of the reaction was found to be extremely variable (43–94%) when performed at room temperature, and the reaction was found to be catalytic in $\text{B}(\text{C}_6\text{F}_5)_3$. In an experiment that provided information about how this process occurs, it was found possible to generate the methyl

3.2. Mechanistic study of C–H activation reactions by $\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})\text{OTf}$

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 $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})]^+$ (or its solvates) is a pre-requisite for C–H activation [24]. Molar conductivity experiments suggested that the triflate ligand of $\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})\text{OTf}$ (**1**) is slightly dissociated under the reaction conditions and more highly dissociated at lower initial concentrations [8]. In contrast, $\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})(\text{Cl})$ is completely stable in benzene- d_6 even at temperatures up to 100°C . This observation can be explained by the presence of

⁴ Experimental details concerning these previously unreported results can be found in the Section 2 of this paper.



Scheme 4.

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) σ -bond metathesis, (3) σ - π addition, and (4) electron transfer catalysis. Each of these is discussed in the following sections.

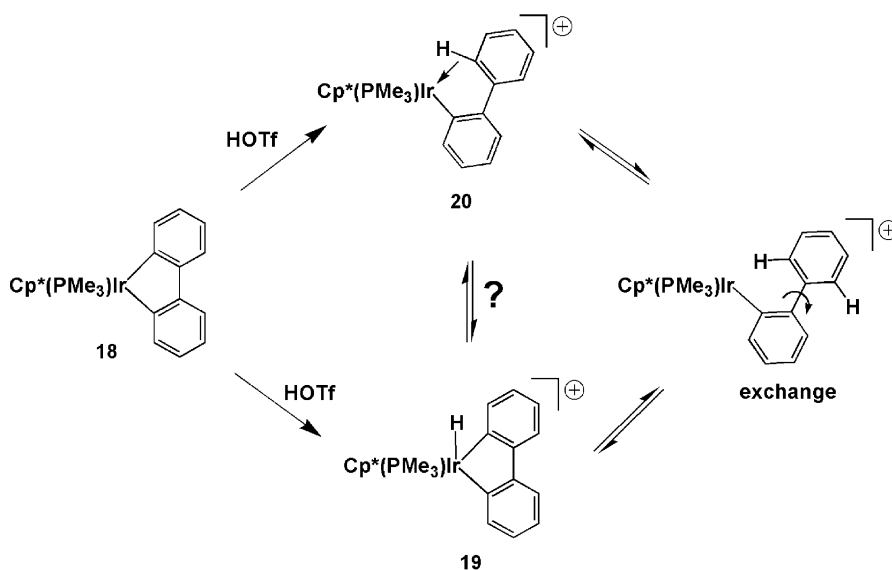
3.2.1. Oxidative addition–reductive elimination

One possible pathway for the C–H activation process involves C–H oxidative addition to give a discrete penta-coordinated 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 it as a reaction pathway would be synthetically straightforward.

Since, protonation of $\text{Cp}^*(\text{PMe}_3)\text{IrMe}_2$ with HOTf gives $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})\text{OTf}$ (**1**), we hoped to observe a pentavalent iridium intermediate $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{CH}_3)(\text{CH}_3)]^+[\text{OTf}]^-$ (**17**) by low temperature NMR spectroscopy. However, even when this reaction was carried out at -80°C , only the protonolysis product $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})\text{OTf}$ (**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 $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$ (**18**) was sought. This complex was prepared by the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ with 2-biphenylmagnesium bromide followed by reaction with PMe_3 , 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

$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$ at -80°C resulted in an immediate color change from colorless to orange. The $^{31}\text{P}\{^1\text{H}\}$ 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 PMe_3 ligand signals remained unchanged. This process was reversed when the reaction mixture was cooled again to -90°C . In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at -90°C , resonances for two independent PMe_3 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 ^{13}C – ^1H NMR coupling constant [25] of ca. 70 Hz was measured for this unique proton resonance (observed at -5.1 ppm at -80°C).

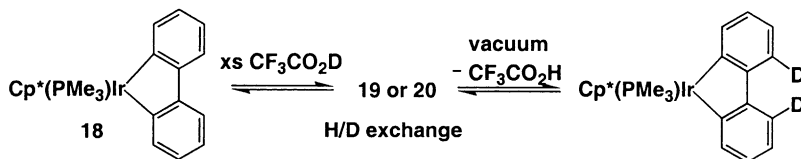
The above observations can be explained by the processes depicted in Scheme 5. Data from the above spin saturation transfer experiment suggests that there is rapid exchange between two species even at temperatures as low as -63°C . Unfortunately, the available NMR data did not allow us to distinguish 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 $J_{\text{P-H}}$ and $J_{\text{C-H}}$ coupling constants of 18 and 70 Hz, respectively, can be explained with a *static* agostic and also a “fluxional” iridium hydride structure. The observed



Scheme 5.

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 ^1H 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 ^1H NMR spectrum only coupling to phosphorus is observed, although it is also possible that additional coupling is obscured by the broadness

the protonation reaction was re-investigated using deuterated acid. The reaction of $\text{CF}_3\text{CO}_2\text{D}$ with $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})$ is reversible, and upon removal of the acid in vacuo the neutral iridium complex is obtained again (Eq. (3)). ^1H , ^2H , ^{13}C NMR and MS data unequivocally demonstrated that two deuterium atoms were incorporated "exclusively" into the *ortho* positions of the biphenyl linkage.⁵ 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, $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{biph})(\text{D}, \text{H})][\text{OTf}]$, since electrophilic attack of the deuterium may have occurred directly at the Ir–C bond rather than the metal center.



(3)

of the resonance. It is also certainly possible that an interconverting mixture of **19** and **20** might be present, as shown in Scheme 5.

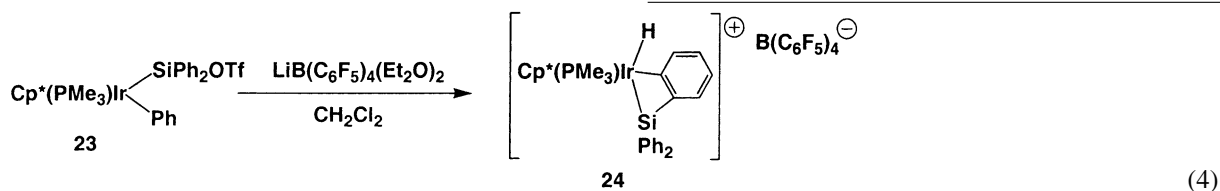
Given that the above observations precluded definitive assignment of a pentavalent iridium complex,

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

⁵ Note that excess deuterotrifluoroacetic acid is required to shift the equilibrium completely towards the deuterated complex.

C–H activation reactions discussed. The synthesis of the thermally sensitive Ir(V) compound Cp*IrMe₃OTf (**21**) from HOTf and Cp*IrMe₄ was possible, and addition of PMe₃ to this triflate led to the model complex [Cp*(PMe₃)IrMe₃][OTf] (**22**). This complex was not decomposed by the elimination of ethane (as was hoped), but rather by loss of Cp*Me [14]. 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]. As shown in Eq. (4), treatment of Cp*(PMe₃)Ir(SiPh₂OTf)(Ph) (**23**) with LiB(C₆F₅)₄(Et₂O)₂ led to the formation of the crystallographically characterized, cyclometallated 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**.



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 for C–H activation by Cp(PH₃)IrMe⁺. The authors were unable to locate a σ -bond metathesis transition state and concluded that the existence of such a pathway “is doubtful even at higher energies” [27]. Similar results were found using ab

initio calculations (MP2) on the same model cation [28].

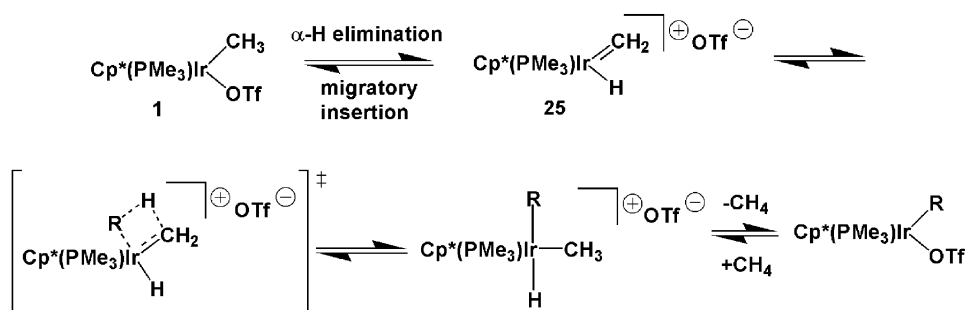
3.2.2. σ -Bond metathesis

The overall C–H activation reactions of methyliridium species **1** resembles the σ -bond metathesis reactions that are more characteristic of d⁰ 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-ordinatively 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

intermediacy of an Ir=C double bond is worth consideration. The mechanism depicted in Scheme 6 involves formation of a (hydrido)(methylidene)iridium 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



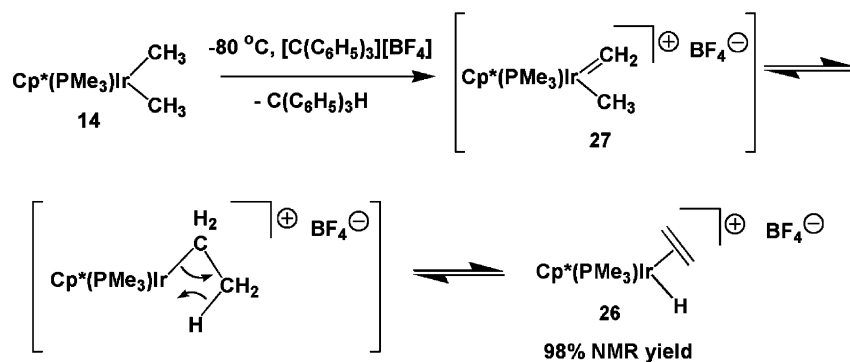
Scheme 6.

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 α -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 α -H elimination step.

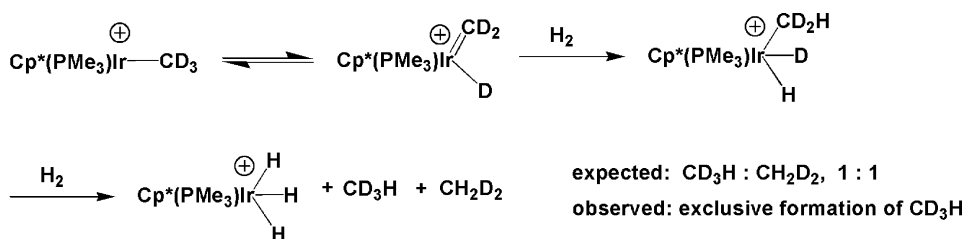
Further support for possible carbene intermediates in this iridium system was provided by the outcome of the reaction of $\text{Cp}^*(\text{PMe}_3)\text{IrMe}_2$ (**11**) with $[\text{C}(\text{C}_6\text{H}_5)_3][\text{BF}_4]$, which leads to $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{C}_2\text{H}_4)(\text{H})][\text{BF}_4]$ (**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 $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{PPh}_3)(\text{Me})_2$ was shown to produce the corresponding cationic ethylene complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{PPh}_3)(\text{C}_2\text{H}_4)(\text{H})][\text{BF}_4]$ upon treatment with $[\text{C}(\text{C}_6\text{H}_5)_3][\text{BF}_4]$ [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 Cp_2WMe_2 [43].

In order to experimentally test the viability of this σ - π addition mechanism, the reaction of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CD}_3)(\text{OTf})$ (**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 CD_3H and CH_2D_2 . Using NMR detection methods, however, exclusive formation of CD_3H along with $[\text{Cp}^*(\text{PMe}_3)\text{IrH}_3][\text{OTf}]$ was observed, providing evidence against the σ - π addition pathway. Further evidence against this mechanism was obtained in



Scheme 7.

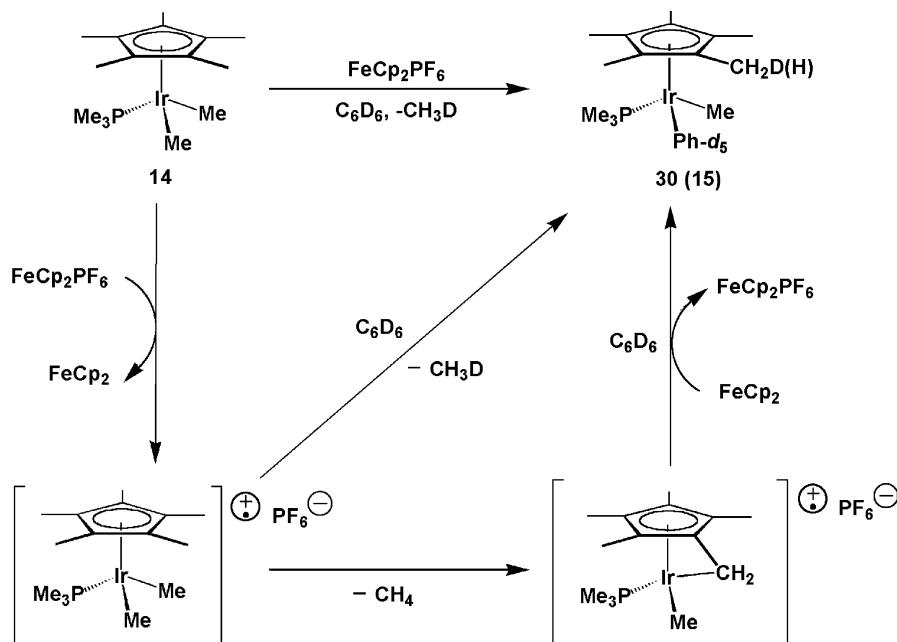


Scheme 8.

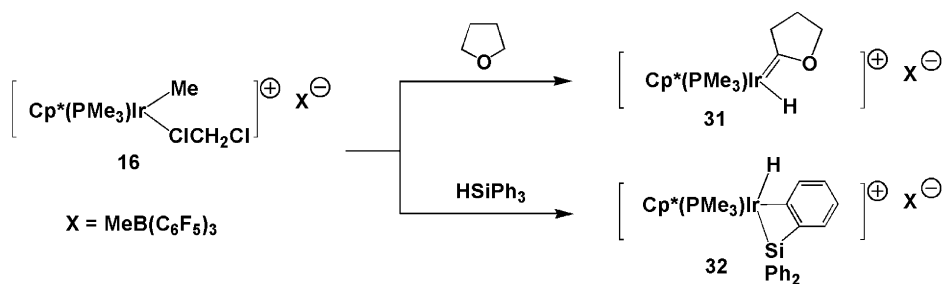
the “inverse” reaction of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})(\text{OTf})$ (**1**) with D_2 , which yields (within NMR detection limits) exclusively $[\text{Cp}^*(\text{PMe}_3)\text{IrD}_3][\text{OTf}]$ (**29**) and CH_3D , instead of the mixture of CH_3D and CH_2D_2 predicted for the carbene mechanism. Additional arguments against this mechanism arise from kinetic isotope effect measurements. For the carbene type mechanism, a primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} > 2$) would be expected for a rate determining $\alpha\text{-C-H}$ elimination step. In kinetic measurements for the reaction of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CD}_3)(\text{OTf})$ (**28**) with C_6H_6 ; however, a kinetic isotope effect of close to 1 was observed ($k_{\text{H}}/k_{\text{D}} = 1 \pm 0.1$).

3.2.4. Electron transfer catalysis

The C–H activation reactions that occur on treatment of dimethyl complex **14** with $\text{B}(\text{C}_6\text{F}_5)_3$ (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 $[\text{FeCp}_2][\text{PF}_6]$ or AgBF_4 to dimethyliridium complex **14** in C_6D_6 produces $\text{Cp}^*(\text{PMe}_3)\text{IrMe}(\text{C}_6\text{D}_5)$ (**15**), $(\text{Cp}^*-\text{d}_1)(\text{PMe}_3)\text{Ir}(\text{Me})(\text{C}_6\text{D}_5)$ (**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 9.



Scheme 10.

directly or abstracts a hydrogen atom from the Cp^* ligand to produce both CH_4 and CH_3D as byproducts of the reaction.⁶ Noting these similarities, we elected to investigate whether one-electron processes were operative in the reaction between $\text{Cp}^*(\text{PMe}_3)_2\text{IrMe}_2$ (**14**) and $\text{B}(\text{C}_6\text{F}_5)_3$ in the presence of C_6D_6 . In contrast to Diversi et al.'s result, we observed exclusive formation of CH_3D . It was also shown that $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})(\text{CH}_2\text{Cl}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ reacted with THF to produce the expected iridium carbene species $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{H})(\text{C}_4\text{H}_6\text{O})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**31**), and with triphenylsilane to yield $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{H})(\text{SiPh}_2(\text{C}_6\text{H}_4))][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**32**) (Scheme 10). Attempts to perform the analogous reactions with $[\text{FeCp}_2][\text{PF}_6]$ 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 $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{Me})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**16**).

3.3. Catalytic chemistry involving

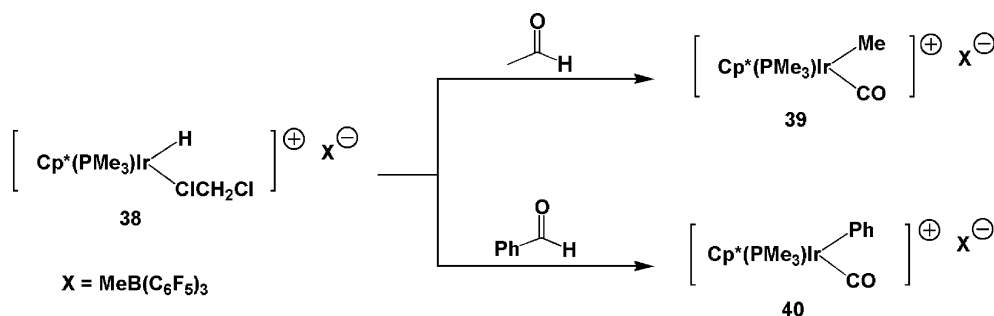
$[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{H})(\text{CH}_2\text{Cl}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$

In order to compare their reactivity to that of methyliridium complexes **1** and **10**, we attempted the synthesis of the analogous cationic hydrido-iridium species $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{H})(\text{CH}_2\text{Cl}_2)][\text{X}]$. Despite previous attempts, until now it has not been

⁶ The step that neutralizes the charged intermediates, leading to **12**, is not made clear; presumably electron transfer from Cp_2Fe generated in the first or another molecule of **14** step plays this role.

possible to prepare or detect such hydrides; reasonable synthetic approaches nearly always led to $[\text{Cp}^*(\text{PMe}_3)_2\text{IrH}_3][\text{OTf}]$ (**33**) and/or $[\text{Cp}^*(\text{PMe}_3)_2(\text{H})\text{Ir}(\mu\text{-H})\text{Ir}(\text{H})(\text{PMe}_3)\text{Cp}^*][\text{OTf}]$ (**34**) [47]. The anion abstraction method described (vide supra) for generating $[\text{Cp}^*(\text{PMe}_3)_2\text{IrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**16**) raised the possibility of avoiding this problem. Unfortunately, the addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to $\text{Cp}^*(\text{PMe}_3)_2\text{IrH}_2$ in CD_2Cl_2 even at low temperatures (-84°C) produced trihydrido cations $[\text{Cp}^*(\text{PMe}_3)_2\text{IrH}_3][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**35**) and $[\text{Cp}^*(\text{PMe}_3)_2(\text{H})\text{Ir}(\mu\text{-H})\text{Ir}(\text{H})(\text{PMe}_3)\text{Cp}^*][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**36**) by an unknown mechanism, although a very small amount of monohydrido salt $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{H})(\text{CH}_2\text{Cl}_2)][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**37**) was occasionally observed by the low temperature ^1H NMR spectroscopy. However, addition of one atmosphere of H_2 at -84°C to solutions of monomethyl complex **16** in CD_2Cl_2 was more successful, resulting in the formation of the thermally sensitive monohydrido-iridium product $[\text{Cp}^*(\text{PMe}_3)_2\text{Ir}(\text{H})(\text{CH}_2\text{Cl}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**38**) in >90% yield, along with the production of some (3–10%) $[\text{Cp}^*(\text{PMe}_3)_2\text{IrH}_3]^+$ [18]. The low solubility of dihydrogen in CD_2Cl_2 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

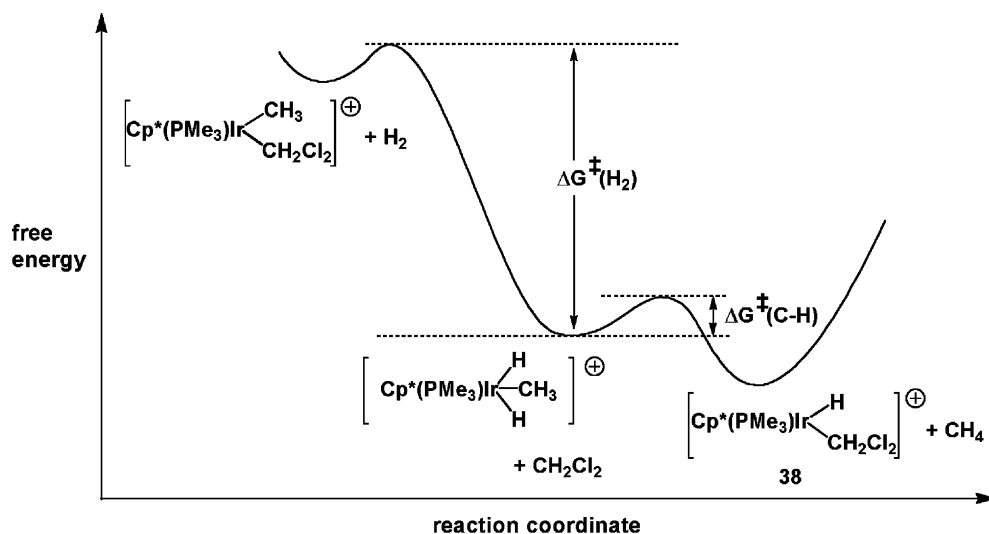


Scheme 11.

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 $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{THF})][\text{MeB}(\text{C}_6\text{F}_5)_3]$, 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°C . Interest in understanding this thermal decomposition of monohydride **38**, which as noted above leads to the trihydride complex $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})_3][\text{MeB}(\text{C}_6\text{F}_5)_3]$ and/or $[\text{Cp}^*(\text{PMe}_3)(\text{H})\text{Ir}(\mu\text{-H})\text{Ir}(\text{H})(\text{PMe}_3)\text{Cp}^*][\text{MeB}(\text{C}_6\text{F}_5)_3]$, prompted us to carry out the decomposition of **2** in the presence of deuterated hydrocarbons. This resulted in

the exclusive production of $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{D})_3][\text{MeB}(\text{C}_6\text{F}_5)_3]$, indicating that the alkane was the source of the iridium-bound deuterium in the product. Monitoring the reaction at temperatures below -20°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 H_2 , HD, or D_2 and the corresponding $[\text{Cp}^*(\text{L})\text{M-R}]^{\oplus}$ complex has never been observed,



Scheme 12.

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 hydrido-iridium 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)₃]⁺ (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], use 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 pincer complexes [51,55] most likely takes place using Ir(I)/Ir(III) chemistry (i.e. not associatively through an Ir(V) 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 hydride 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*(PMe₃)Ir(H)][MeB(C₆F₅)₃] is 16 electrons, each is able to mediate H/D exchange with methane. Several parallels and contrasts between these systems are worth considering. In the case of scandium, tetramethylsilane is deuterated at a rate comparable to that of methane while **38** deuterates tetramethylsilane much more slowly than methane. The scandium system deuterates only the methyl groups of propane, while hydrido cation **38** deuterates both the methyl and methylene groups with

preferential activation of the methyl groups. Cyclopropane 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 exchanged 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 observed exclusively). While olefins react only with **38** by co-ordination, the scandium system produces polyolefins. 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 temperatures, 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, similar 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 cations are catalysts for living alternating copolymerization 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*(PMe₃)Ir(R)₂(H)]⁺ and [Cp*(PMe₃)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/ σ -bond metathesis issue in related late transition metal systems. Tilset and co-workers [64] recently provided experimental evidence for the existence of $[(N-N)Pt(Me)_2(H)(L)]^+$ ($N-N = ArN=CMe-CMe=NAr$, $Ar = 3,5-(CF_3)_2C_6H_3$) 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 σ -bond metathesis starting from $[(N-N)Pt(Me)(CH_4)]^+$. Furthermore, using the aquo adduct $[(N-N)Pt(Me)(CH_4)(H_2O)]^+$ 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 σ -bond metathesis can occur, depending on whether the active species is $[(bipyrimidine)PtCl]^+$ or $[(bipyrimidine)Pt(OSO_3H)]^+$, 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.

Acknowledgements

Professors Richard A. Andersen, T. Don Tilley, and Dr. David Tellers are acknowledged for informative conversations. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the US Department of Energy under Contract no. DE-AC03-7600098, and also by a National Science Foundation Pre-doctoral Fellowship to Steven R. Klei. CNDOS is supported by Bristol-Myers Squibb as founding member. We are very grateful to the Boulder Scientific Company for their generous gift of lithium tetrakis(pentafluorophenyl)borate etherate complex.

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