Modeling the Proposed Intermediate in Alkane Carbon−Hydrogen Bond Activation by Cp*(PMe$_3$)Ir(Me)OTf: Synthesis and Stability of Novel Organometallic Iridium(V) Complexes

Peter J. Alaimo and Robert G. Bergman*

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

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Addition of HX to CH_2Cl_2 solutions of Cp*IrMe$_4$ (Cp* = η^5-C_5Me_5) at low temperature provided Cp*Ir(Me)$_3$X (X = Cl, **5**; X = OSO_2CF_3 = OTf, **6**). Both complexes are very thermally sensitive yet proved to be useful precursors for novel cationic iridium(V) complexes. Treatment of **6** with a variety of trisubstituted phosphines, arsines, and stibines (L) afforded compounds **7**−**12**, [Cp*(L)IrMe$_3$][OTf] (L = PMe$_3$, **7**; L = PEt$_3$, **8**; L = PPh$_3$, **9;** L = AsEt$_3$, **10**; L = AsPh$_3$, **11**; L = SbPh$_3$, **12**). Metathesis of the triflate anion of antimony complex **12** for the tetraphenylborate anion afforded [Cp*(SbPh$_3$)IrMe$_3$][BPh$_4$] (**13**). The molecular structure of **13** was determined by single-crystal X-ray diffraction analysis. Complex **7** is a potential model for the proposed intermediate on the methane carbon−hydrogen bond activation reaction pathway by Cp*(PMe$_3$)Ir(Me)OTf, and its relevance to this reaction is discussed. Complex **7** decomposed by reductive elimination of MeCp*. The remaining iridium fragment was trapped by added phosphine to form [*cis*-{PMe$_3$}$_4$IrMe$_2$][OTf] (**14**) as an impure mixture. Reaction of **6** with excess dppm (dppm = $Ph_2PCH_2PPh_2$) afforded [*cis*-{η^2-Ph_2PCH_2-PPh_2}$_2$IrMe$_2$][OTf] (**15**). The molecular structure of **15** was determined by single-crystal X-ray structure analysis.

Introduction

Our research group and others have long been interested in understanding the mechanistic details of intermolecular carbon−hydrogen bond activation by well-defined homogeneous transition-metal complexes.[1−5] More specifically, we have recently been studying the scope and generality of reactions (eq 1) involving Cp*-

$$\text{Cp*(L)Ir(Me)X} + \text{R}-\text{H} \rightarrow \text{Cp*(L)Ir(R)X} + \text{CH}_4 \qquad (1)$$

(PMe$_3$)Ir(Me)X (Cp* = η^5-C_5Me_5; X = OTf = OSO_2CF_3 (**1**), X = BAr$_f$ = B(3,5-$C_6H_3(CF_3)_2$)$_4$ (**2**)).[6−11] Our interest in these compounds stems from their ability to activate a wide variety of C−H bonds under remarkably mild conditions. Although we have explored the reactivity of **1** and **2** extensively, the rapidity with which these reactions occur, especially with **2**, has made the mechanistic details of the C−H bond breaking step difficult to uncover.

On the basis of previous studies, we have postulated that the active species in these reactions is the cationic complex [Cp*(PMe$_3$)Ir(Me)]$^+$. Furthermore, we have proposed that there are two plausible mechanistic extremes worthy of serious consideration: the first is a two-step mechanism consisting of oxidative addition followed by rapid reductive elimination, and the second, a concerted σ-bond metathesis. These mechanistic extremes are illustrated in Scheme 1.

The first mechanism is supported by the fact that both C−H oxidative addition and C−H reductive elimination reactions are well-precedented with many different transition metals in a variety of oxidation states.[12] However, iridium(V) compounds such as **3** are rare, calling into question the likelihood of this mechanism. Although there are a number of reports that invoke the intermediacy of iridium(V) complexes along reaction pathways,[13−17] only a few organometallic iridium(V) complexes have been isolated to date.[13,18−31]

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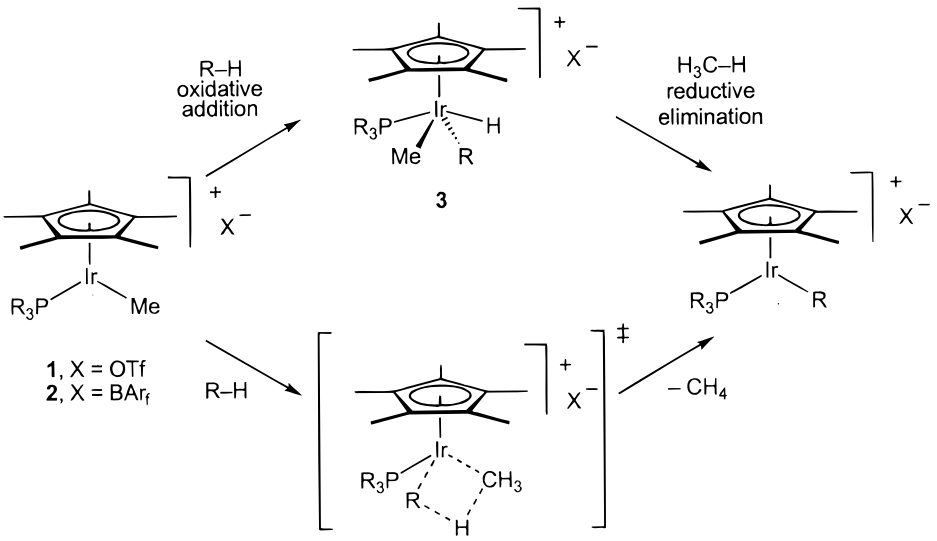
Scheme 1



For the following reasons, we felt that none of the previously reported Ir(V) complexes provided ample precedent for **3**. First, the complexes (mesityl)$_3$IrO,[18] [(mesityl)$_4$Ir][X] (X = BF_4, OTf),[19] Tp*IrH_4,[13,20,21] Cp*IrH_3X (X = H, $SiMe_3$, $SnMe_3$, $SnPh_3$),[22,23] and Cp*Ir(H)$_2$(MR_3)$_2$ (MR_3 = $SiMe_3$, $SnMe_3$, $SnBu_3$)[24−26] have few ligands in common with proposed intermediate **3**. Second, Cp*$IrMe_4$[27,28] is not cationic and does not contain a phosphine ligand, rendering it electronically very dissimilar to **3**. Third, the only reported *cationic* organometallic Ir(V) complexes are the trihydride salts [Cp(L)IrH_3]$^+$ [29,30] and [Cp*(PMe_3)IrH_3]$^+$,[31] prepared from protonation of Cp′(L)IrH_2 (Cp′ = Cp, Cp*) with HBF_4. Although these cationic iridium(V) complexes may appear similar to **3**, we were uncomfortable considering them as appropriate models for intermediate **3**, since they are polyhydrides. First, we consider the fact that the Pauling electronegativity of iridium (2.20) is more similar to that of hydrogen (2.20) than to that of carbon (2.55), suggesting that an iridium−hydride and an iridium−methide might be electronically very different. Additionally, the differences between the hydrogen 1s and the methide sp^3 orbitals have been suggested as explanations for differing H and Me ligand reactivities.[12] Because no suitable model for intermediate **3** had been reported, we felt that it was important to consider the possibility that a σ-bond metathesis mechanism might be operative.

It is well-established that C−H activation by high-valent early-metal systems occurs by σ-bond metathesis.[32,33] However, σ-bond metathesis at late-metal centers is rarely invoked, as these systems tend to undergo oxidative addition. In fact, we are aware of only one report of a late-metal system wherein σ-bond metathesis has been convincingly demonstrated by disproof of an alternative oxidative addition mechanism. That report involves B−H bond metathesis with the Ru−CH_3 bond of a coordinatively and electronically saturated ruthenium center.[34]

Further support for the oxidative addition/reductive elimination mechanism in our Ir(III) system comes from recent computational work performed by the research group of Hall. Density functional calculations (B3LYP) on the model cation Cp(PH_3)$IrMe^+$ have predicted that the oxidative addition/reductive elimination pathway is preferred over the σ-bond metathesis pathway. Furthermore, these authors were not able to locate a σ-bond metathesis transition state, leading them to suggest that σ-bond metathesis "is doubtful even at higher energies."[35] *Ab initio* MO calculations (MP2) on the same model cation have predicted the same result.[36]

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To gain evidence for the predicted iridium(V) intermediate on the oxidative addition/reductive elimination pathway, a number of seemingly straightforward experiments were undertaken; however, all attempts failed to identify such a species in these reactions. These efforts included low-temperature NMR spectroscopic experiments to (a) directly monitor C−H activation *in situ* and (b) spectroscopically characterize an iridium(V) intermediate generated by protonation (HOTf) or methylation (MeOTf) of $Cp^*(L)Ir(Me)_2$, $Cp^*(L)Ir(H)_2$, or $Cp^*(L)Ir(Me)(H)$.[37] We reasoned that if the C−H bond activation reaction by $Cp^*(PMe_3)Ir(Me)OTf$ (**1**) were indeed proceeding by oxidative addition, $[Cp^*(L)Ir(Me)_2(H)][OTf]$ (**3**) would likely be an extremely short-lived species, due to the fact that C−H reductive elimination from such an intermediate should be rapid. Hence, our lack of direct observation of **3** by no means rules out the oxidative addition pathway.

We therefore decided to synthesize $[Cp^*(PMe_3)IrMe_3][OTf]$ (**7**), a potential model compound that should be less reactive toward reductive elimination than hydride **3**, and explore its chemistry. We expected that complex **7** would undergo reductive elimination more sluggishly than the putative intermediate $[Cp^*(PMe_3)Ir(Me)_2(H)][OTf]$ (**3**), since C−C reductive elimination is known to have a higher kinetic barrier than C−H reductive elimination (eqs 2 and 3).[38] This paper describes the results of our investigation.

$$[Cp^*(L)Ir(Me)_2(H)][X] \xrightarrow[\text{fast}]{k_{\text{C-H red elim}}} Cp^*(L)Ir(Me)X + CH_4 \quad (2)$$

$$[Cp^*(L)IrMe_3][X] \xrightarrow[\text{slow?}]{k_{\text{C-C red elim}}} Cp^*(L)Ir(Me)X + C_2H_6 \quad (3)$$

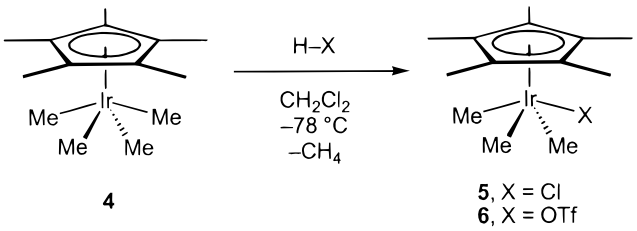
Results

Synthesis, Thermolysis, and Protonolysis of Cp^*IrMe_4 (4). The synthesis of Cp^*IrMe_4 (**4**) was reported by the Maitlis group in 1981.[27,28] Thermolysis of **4** at 75 °C in CD_2Cl_2 resulted in formation of hexamethylcyclopentadiene (MeCp*, 1 equiv, *vide infra*) and methane (1.3 equiv) as the only identified products (eq 4). Neither ethane nor ethylene was detected by ^1H NMR spectroscopy.

$$\underset{\mathbf{4}}{Cp^*IrMe_4} \rightarrow MeCp^* + CH_4 \quad (4)$$

The addition of either anhydrous HCl or HOTf to room-temperature solutions of tetramethyl complex **4** resulted in immediate formation of a complicated mixture of compounds (^1H NMR spectroscopy). A ^1H NMR spectrum of the hydrochloric acid reaction mixture indicated the formation of methane, but ethane, ethylene, ethyl chloride, and methyl chloride were not detected, nor was MeCp* observed. Instead, eight major unassigned resonances between δ 2.1 and 1.7 ppm were present. The ^1H NMR spectrum of the triflic acid reaction was more complicated, containing a resonance for methane and >20 unassigned resonances between δ 2.9 and −0.2 ppm. In this reaction too, neither ethane nor MeCp* was detected by ^1H NMR spectroscopy.

Scheme 2



The addition of anhydrous hydrochloric acid by vacuum transfer to frozen solutions of tetramethyl complex **4** (0.04 M in CD_2Cl_2, −196 °C) followed by warming to −78 °C resulted in the rapid formation of a bright yellow solution. Low-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra indicated that protonolysis of an Ir−CH_3 bond occurred to form the neutral complex $Cp^*Ir(Me)_3Cl$ (**5**) (Scheme 2). Likewise, dropwise addition of triflic acid (0.04 M in CD_2Cl_2) to a cold solution of **4** (0.04 M in CD_2Cl_2, −78 °C) resulted in formation of another bright yellow compound formulated as $Cp^*Ir(Me)_3OTf$ (**6**) on the basis of its low-temperature ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra (Scheme 2). Addition of excess acid (HX; X = Cl, OTf) did not provide a route into complexes $Cp^*Ir(Me)_2X_2$, $Cp^*Ir(Me)X_3$, and $Cp^*Ir(X)_4$ in detectable quantities by ^1H NMR spectroscopy; instead, no further reaction was observed.

The ^1H NMR spectrum of compound **5** exhibited resonances for the pentamethylcyclopentadienyl ligand at δ 1.35 (s, 15H), a single methyl group positioned *trans* to the chloride ligand at δ 0.98 (s, 3H), and the two chemically equivalent methyl groups *cis* to the chloride ligand at δ 1.62 (s, 6H). The ^1H NMR spectrum of compound **6** was similar. The $^{13}C\{^1H\}$ NMR spectra for complexes **5** and **6** were also similar, with resonances observed for the two types of carbon atoms of the Cp* rings as well as two resonances for the two types of metal-bound methyl groups. Both compounds **5** and **6** proved to be air- and temperature-sensitive. While solutions (CD_2Cl_2) of **5** or **6** were stable for weeks at −80 °C, complete decomposition occurred in minutes at 0 °C. The products resulting from thermal decomposition of **5** or **6** were not identified, but neither ethane nor MeCp* was detected by ^1H NMR spectroscopy. Due to the very high thermal instability of complexes **5** and **6**, characterization by low-temperature NMR spectroscopy was required. Weaker acids, including acetic acid, trifluoroacetic acid, and *p*-toluenesulfonic acid, did not react with **4** at room temperature.

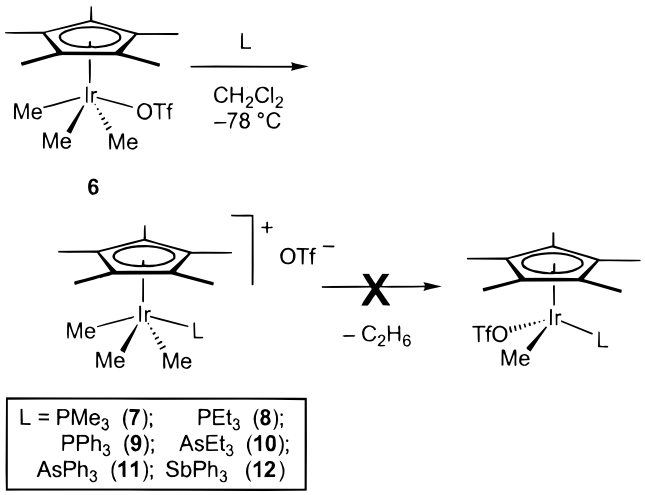
Attempted Substitution Reactions of $Cp^*Ir(Me)_3OTf$ (6) with Anionic Nucleophiles. A variety of anionic nucleophiles were introduced to solutions of triflate **6** at low temperature in order to assess the utility of **6** as a precursor for neutral iridium(V) complexes (eq 5). The potential ligands were added as

$$\underset{\mathbf{6}}{Cp^*Ir(Me)_3OTf} + Nu^- \not\rightarrow Cp^*Ir(Me)_3Nu + TfO^- \quad (5)$$

methylene chloride or THF solutions to methylene chloride or THF solutions of **6** at −78 °C, and the resulting mixtures were monitored by variable-temperature NMR spectroscopy. These reactions were moni-

(37) Burger, P.; Arndtsen, B. A.; Luecke, H. F.; Bergman, R. G. Unpublished results.
(38) See ref 12, p 330.

Scheme 3



L = PMe_3 (**7**); PEt_3 (**8**); PPh_3 (**9**); $AsEt_3$ (**10**); $AsPh_3$ (**11**); $SbPh_3$ (**12**)

tored by placing the cold (−78 °C), flame-sealed NMR tube into the precooled NMR probe (−80 to −30 °C, depending on the reaction), acquiring a low-temperature ^{1}H NMR spectrum, increasing the temperature (usually in 10 or 15 °C increments), and recording spectra at each successive temperature (−70, −60, −50 °C, etc.) until room temperature was attained. None of these reactions afforded isolable compounds. The anionic nucleophiles used included hydride sources (hydridoborates, hydridoboranes, aluminum hydrides, alkali-metal hydrides, alkaline-earth hydrides), carbon nucleophiles (alkali-metal reagents, Grignard reagents, dialkyl cuprate reagents, dialkyl zinc reagents; all performed in THF-d_8), oxygen anions (hydroxides, alkoxides, aryloxides, acetates, siloxides, peroxides), thiolates, cyanides, and sodium azide.

In some reactions, no shift in the ^{1}H NMR resonances for the free ligand or **6** was observed (aside from the temperature dependence of the chemical shift values). In many cases, though, a shift of the resonances was observed for both the incoming nucleophile and **6**, indicating some interaction between the two species (possibly substitution of the nucleophile for the triflate ligand). In runs where an excess of the nucleophile was added, resonances for both free and bound nucleophile were observed. Conversely, when a stoichiometric deficiency of the nucleophile was added, we observed resonances for both the iridium triflate starting material **6** and the iridium-containing product. However, in all cases decomposition occurred upon warming to room temperature, resulting in mixtures of unidentified products that appeared similar (by ^{1}H NMR spectroscopy) to the thermal decomposition products of triflate **6**. To determine the source of decomposition in these reactions, we allowed some of them to stand at −30 °C for up to 36 h before warming to room temperature. However, even in these runs, complicated product mixtures were obtained. Since none of the reactions with anionic nucleophiles resulted in the formation of a clean isolable material, they were not pursued further.

Substitution Reactions of Cp*Ir(Me)$_3$OTf (6) with Neutral Ligands. Addition of trimethylphosphine to a frozen methylene chloride solution of bright yellow triflate complex **6** resulted in formation of the colorless phosphine salt [Cp*(PMe_3)$IrMe_3$][OTf] (**7**) (Scheme 3). Substitution of the phosphine for triflate was very slow at low temperatures (−78 °C), and decomposition of **6** was rapid near 0 °C. To circumvent these difficulties, trimethylphosphine was vacuum-transferred onto a frozen solution (−196 °C) of **6** and then warmed to an intermediate temperature (−25 °C). This provided for efficient substitution with very little decomposition of **6**. Since the product (**7**) was moderately thermally sensitive in solution ($t_{1/2} \cong$ 18 h, room temperature), removal of the volatile materials *in vacuo* at −29 °C was performed to obtain **7** cleanly. Subsequent washing with pentane afforded air- and temperature-sensitive **7** in 87% isolated yield. The ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra were consistent with the given formulation. Additionally, the compound was characterized by FTIR and high-resolution mass spectrometry (FAB). Due to its thermal sensitivity, neither the melting point nor the elemental composition was determined for **7**.

Treatment of a methylene chloride solution of **6** with other trisubstituted phosphines, as well as arsine and antimony ligands (L), at −78 °C resulted in the formation of the complexes [Cp*(L)$IrMe_3$][OTf] (**8**−**12**; L = PEt_3, **8**; L = PPh_3, **9;** L = $AsEt_3$, **10**; L = $AsPh_3$, **11**; L = $SbPh_3$, **12**), which are analogous to **7** (Scheme 3). Spectral data for complexes **8**−**12** are consistent with the given formulations. The ^{1}H NMR spectrum of complex **9** displays broad resonances for the aryl protons of the triphenylphosphine ligand. The corresponding aryl carbon resonances for **9** in the ^{13}C{^{1}H} NMR spectrum are also broad. We presume that this is likely due to hindered Ir−P bond rotation on the NMR time scale.

Triflate salt **12** was converted to tetraphenylborate salt **13** by anion metathesis in CH_2Cl_2 (eq 6). Single

$$\underset{\mathbf{12}}{[Cp^*(SbPh_3)IrMe_3][OTf]} + NaBPh_4 \xrightarrow[CH_2Cl_2]{} \underset{\mathbf{13}}{[Cp^*(SbPh_3)IrMe_3][BPh_4]} + NaOTf\downarrow \quad (6)$$

crystals of [Cp*($SbPh_3$)$IrMe_3$][BPh_4] (**13**) suitable for X-ray diffraction study were grown by vapor diffusion of pentane into a methylene chloride solution at −30 °C over 3 days. The molecular structure of **13** is shown in Figure 1. The complex crystallizes with two methylene chloride molecules in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The iridium atom has an approximate four-legged piano-stool coordination geometry: coordinated by a Cp* ligand, three methyl ligands, and a $SbPh_3$ ligand. The Ir−C distances for the Cp* ligand range from 2.22 to 2.37 Å. The longest Ir−C distance corresponds to the carbon atom closest to the antimony ligand. The shortest Ir−C distances correspond to the carbon atoms furthest from the antimony ligand. Apparently, the large Sb atom is in close contact with one side of the Cp* ligand, causing the carbon atoms to be pushed away from the Sb atom. Crystal data and structure refinement details are given in Table 1. Selected bond lengths and angles are listed in Table 2.

To our knowledge, this crystal structure represents only the third crystallographically characterized complex containing an Ir−Sb bond.[39,40] In 1991, Balch and co-workers reported the complex [$Ir_2(SbF_2)(CO)_2Cl_2$(μ-dpma)$_2$][BF_4], in which the SbF_2^+ unit bridges two

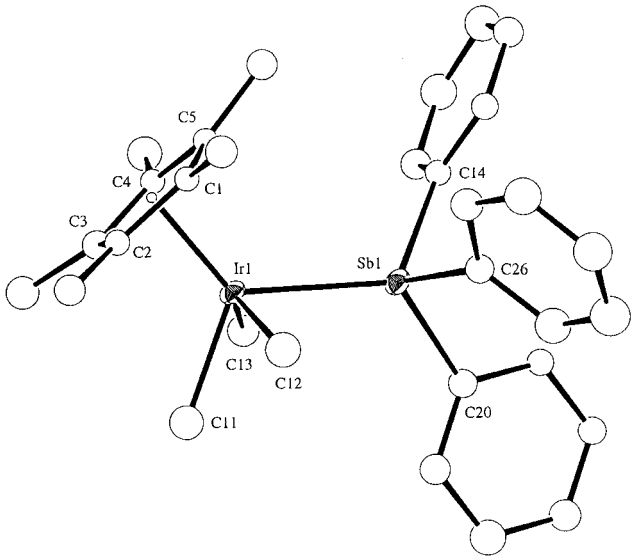


Figure 1. ORTEP diagram of the cationic portion of [Cp*-($SbPh_3$)$IrMe_3$][BPh_4]·$2CH_2Cl_2$ (**13**), with partial atom labeling scheme. The anion and the methylene chloride molecules were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

iridium atoms.[39] The Ir−Sb bond distances in this complex are 2.655(1) Å. In 1996, Werner and co-workers reported the crystal structure of [$IrCl(C_2H_4)_2$(Sb(*i*-Pr)$_3)_2$].[40] The Ir−Sb bond distances in this complex are 2.546(1) and 2.655(1) Å. In our complex (**13**), the Ir−Sb bond distance is 2.5848(8) Å.

Complexes **7**−**12** displayed a range of air and temperature sensitivities. Phosphine salts **7**−**9** were moderately air-sensitive and moderately temperature-sensitive. Methylene chloride solutions of **7**−**9** decomposed in a few minutes upon exposure to air to give unidentified products. Benzene or methylene chloride solutions of **7**−**9** stored in the dark eliminated MeCp* (*vide infra*) over the course of 2 days. Qualitative results suggest that the rate of the thermal decomposition of **7**−**9** is independent of added phosphine. When two equimolar CD_2Cl_2 solutions of **7**, **8**, or **9** were placed in NMR tubes and free phosphine was added to only one tube, the rate of disappearance of the iridium starting material and the rate of appearance of MeCp* were approximately the same in both tubes (^{1}H NMR). Additionally, the rate of elimination of MeCp* appears to be independent of solvent. When three equimolar solutions of **7** were prepared in C_6D_6, CD_2Cl_2, and CD_3-CN, respectively, placed in NMR tubes, and allowed to react at room temperature in the dark, the rate of appearance of MeCp* was approximately the same in all three tubes (^{1}H NMR). Finally, two solutions of **7** (CD_2Cl_2) at different concentrations (1.1 and 10 mM) formed MeCp* (room temperature, darkness) at the same approximate rate (^{1}H NMR), implying that the reaction proceeds unimolecularly.

Arsine salts **10** and **11** are mildly air- and temperature-sensitive. Methylene chloride solutions of **10** or **11** decompose over a few hours upon exposure to air giving unidentified decomposition products. Thermolysis (room temperature) of methylene chloride solutions of **10** or

Table 1. Crystal Data and Structure Refinement Details for Compounds 13 and 15

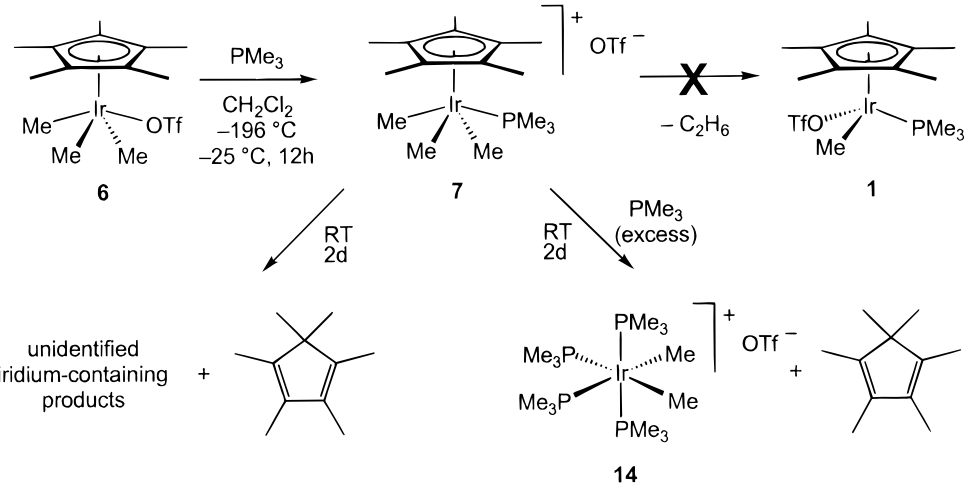
	13	**15**
empirical formula	$C_{57}H_{63}SbIrBCl_4$	$C_{55}H_{54}Cl_4IrP_4SO_3F_3$
fw	1214.72	1310.01
cryst color, habit	colorless, blades	clear, blades
cryst dimens, mm	0.35 × 0.27 × 0.09	0.43 × 0.09 × 0.07
cryst syst	triclinic	monoclinic
lattice type	primitive	primitive
lattice params		
a, Å	11.2311(7)	14.4780(3)
b, Å	14.5216(10)	20.9230(5)
c, Å	17.1433(11)	17.9432(4)
α, deg	76.863(1)	
β, deg	87.807(1)	93.128(1)
γ, deg	69.632(1)	
V, Å^3	2550.0	
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Z	2	4
D_{calcd}, g/cm^3	1.582	1.603
F_{000}	1212.00	2624.00
temp, °C	−155 ± 1	−147 ± 1
μ(Mo Kα), cm^{-1}	33.89	28.74
diffractometer	SMART CCD	
radiation	Mo Kα (λ = 0.710 69 Å), graphite monochromated	
detector position, mm	60.00	
exposure time, s/frame	10.0	
scan type	ω (0.3°/frame)	
$2\theta_{max}$, deg	52.2	52.4
no. of rflns measd		
total	13 970	26 113
unique	8703	9882
R_{int}	0.047	0.044
corrns	Lorentz−polarization	
structure soln	direct methods (SIR92)	
refinement	full-matrix least squares	
function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$	
least-squares weights	$w = (\sigma^2(F_o))^{-1} = [\sigma_c^2(F_o) + (p^2/4)F_o^2]^{-1}$	
p factor	0.0310	0.0300
anomalous dispersion	all non-hydrogen atoms	
no. of observns ($I > 3.00\sigma(I)$)	5031	6378
no. of variables	287	645
rfln/param ratio	17.53	9.89
residuals: *R*; R_w; *R*(all)	0.045; 0.044; 0.097	0.029; 0.031; 0.061
goodness-of-fit indicator	1.28	0.90
max shift/error in final cycle	0.00	0.02
final diff map		
max peak, e/Å^3	1.61	0.98
min peak, e/Å^3	−1.75	−0.64

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 13

Ir(1)−Sb(1)	2.5848(8)	Ir(1)−C(13)	2.17(1)
Ir(1)−C(1)	2.29(1)	Sb(1)−C(14)	2.10(1)
Ir(1)−C(2)	2.23(1)	Sb(1)−C(20)	2.13(1)
Ir(1)−C(3)	2.22(1)	Sb(1)−C(26)	2.11(1)
Ir(1)−C(4)	2.27(1)	C(1)−C(2)	1.45(1)
Ir(1)−C(5)	2.37(1)	C(1)−C(5)	1.42(1)
Ir(1)−Cp Cent	1.9254(4)	C(2)−C(3)	1.43(1)
Ir(1)−C(11)	2.13(1)	C(3)−C(4)	1.44(1)
Ir(1)−C(12)	2.12(1)	C(4)−C(5)	1.41(1)
Sb(1)−Ir(1)−C(11)	112.4(3)	C(12)−Ir(1)−Cp Cent	115.4(3)
Sb(1)−Ir(1)−C(12)	79.0(3)	C(12)−Ir(1)−Cp Cent	113.2(3)
Sb(1)−Ir(1)−C(13)	77.1(3)	Ir(1)−Sb(1)−C(14)	115.4(3)
Sb(1)−Ir(1)−Cp Cent	127.31(3)	Ir(1)−Sb(1)−C(20)	119.9(3)
C(11)−Ir(1)−C(12)	75.2(4)	Ir(1)−Sb(1)−C(26)	117.0(3)
C(11)−Ir(1)−C(13)	75.7(4)	C(14)−Sb(1)−C(20)	100.8(4)
C(11)−Ir(1)−Cp Cent	120.3(3)	C(14)−Sb(1)−C(26)	99.8(4)
C(12)−Ir(1)−C(13)	131.0(4)	C(20)−Sb(1)−C(26)	100.7(4)

(39) Balch, A. L.; Catalano, V. J.; Chatfield, M. A.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E. *J. Am. Chem. Soc.* **1991**, *113*, 1252−1258 (dpma = bis((diphenylphosphino)methyl)phenylarsine).
(40) Werner, H.; Ortmann, D. A.; Gevert, O. *Chem. Ber.* **1996**, *129*, 411−417.

Scheme 4



11 in the dark induces elimination of MeCp* more slowly than for the phosphine analogues **7**−**9**. These reactions proceed over the course of 4 days, compared to 2 days for **7**−**9**.

Although triphenylantimony salt **12** is mildly sensitive to both air and temperature, it is the most stable of these complexes that we have found. Decomposition in air required >4 h, and decomposition from room-temperature thermolysis in the dark required >5 days. Neither the air- nor the thermal-decomposition products for complexes **7**−**12** were isolated.

Although thermolysis of a methylene chloride solution of **7** at room temperature in the dark resulted in the formation of MeCp* and unidentified iridium-containing products, repeating this experiment in the presence of a 3-fold (or greater) excess of trimethylphosphine gave a different result. This experiment resulted in the formation of MeCp* as the major organic product (97% yield by NMR integration vs Cp_2Fe internal standard), [*cis*-{PMe_3}$_4$$IrMe_2$][OTf] (**14**) as the major iridium-containing product, and several minor unidentified iridium−phosphine-containing products (Scheme 4). Complex **14**, formed in ∼60% yield (vs internal standard), could not be isolated in pure form, even by repeated recrystallization. It was therefore characterized by ^{1}H, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, as well as FABMS. The ^{1}H NMR spectrum of **14** included all the expected resonances for the *cis*-disposed complex, including one resonance for the chemically equivalent iridium-bound methyl groups and two resonances for the two inequivalent sets of trimethylphosphine ligands, as well as resonances for the unidentified iridium-containing products. The stereochemistry of the complex was assigned on the basis of the ^{31}P{^{1}H} NMR spectrum, which contained two triplets (δ −48.85, −61.02, $^2J_{PP}$ = 18.0 Hz) for the two coupled sets of two trimethylphosphine ligands, and by analogy to complex **15** (*vide infra*). The identity of hexamethylcyclopentadiene was confirmed by comparison of the volatile materials of the reaction mixture to independently synthesized material by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and GC-MS.[41]

In fact, all three phosphine salts **7**−**9** eliminated MeCp* thermally in the presence of added phosphine. Complex **7** appeared to form tetrakis(trimethylphosphine) complex **14** as the major iridium-containing product. Triethylphosphine complex **8** appeared to give a product ("[*cis*-{PEt_3}$_4$$IrMe_2$][OTf]") analogous to **14**, but triphenylphosphine complex **9** did not.

Room-temperature thermolysis of **8** in the presence of added triethylphosphine (5 equiv) gave a reaction mixture whose ^{31}P{^{1}H} NMR spectrum contained two triplets. However, room-temperature thermolysis of **9** in the presence of added triphenylphosphine (5 equiv) gave a reaction mixture whose ^{31}P{^{1}H} NMR spectrum contained only several singlets, not two triplets as would be predicted for cationic [*cis*-{PPh_3}$_4$$IrMe_2$]$^+$. Moreover, removal of the volatile materials *in vacuo*, followed by washing with ether and pentane to remove excess triphenylphosphine, showed that only three triphenylphosphine groups had been incorporated into the iridium-containing product. The major product of the thermolysis of **9** in the presence of triphenylphosphine was not isolated; however, it was assigned as a five-coordinate Ir(III) ("[{PPh_3}$_3$$IrMe_2$][OTf]") complex, based on the ^{1}H NMR integrations and the precedent[42−45] for five-coordinate d^6 complexes bearing three triphenylphosphine ligands. This type of structure has been rationalized on the basis of the greater steric requirements of the triphenylphosphine ligand relative to either trimethyl- or triethylphosphine ligands.

Although complexes **7** and **8** appeared to undergo reductive elimination of MeCp* to presumably generate the remaining iridium fragment "[{PR_3}$IrMe_2$]$^+$", trapping of this fragment by added phosphine ligand was relatively inefficient, since only intractable product mixtures were isolated. This prompted us to attempt to trap the iridium species in the reaction by using a chelating phosphine. Treatment of a methylene chloride solution of **6** with 2 equiv of bis(diphenylphosphino)-methane at −78 °C gave MeCp* and [*cis*-(η^2-Ph_2PCH_2-PPh_2)$_2$$IrMe_2$][OTf] (**15**) (Scheme 5). The ^{31}P{^{1}H} NMR signals at δ −61.31 (t, $^2J_{PP}$ = 14.5 Hz) and −63.33 (t, $^2J_{PP}$ = 14.4 Hz) indicated that the stereochemistry at

(41) Courtneidge, J. L.; Davies, A. G.; Shields, C. J.; Yazdi, S. N. *J. Chem. Soc. Perkin Trans. 2* **1988**, 799−805.

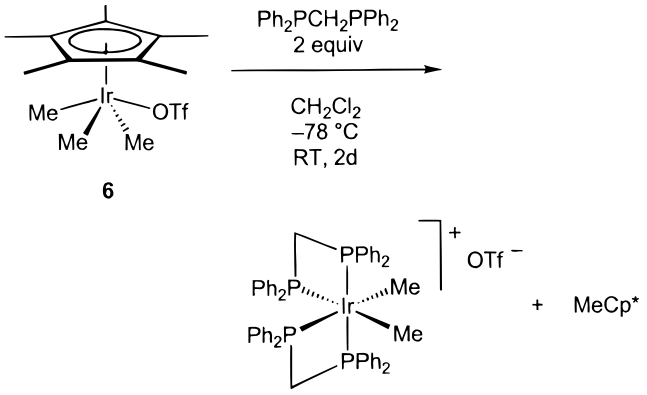
(42) Cotton, F. A.; Matusz, M. *Inorg. Chim. Acta* **1987**, *131*, 213-216.

(43) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Acta Crystallogr.* **1985**, *C41*, 698−699.

(44) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221−4228.

(45) La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778−783.

Scheme 5



iridium was *cis*. The ^{1}H NMR spectrum of this complex displayed a signal for the iridium-bound methyl groups (δ 0.74), two signals for the diastereotopic methylene protons of the diphosphine ligand spacer unit (δ 5.93, 5.24), and the expected number of aryl resonances. The ^{13}C{^{1}H} and the DEPT 135 NMR spectra of compound **15** displayed the expected upfield resonances but somewhat unusual aryl resonances. Three sets of four resonances appeared between 133 and 128 ppm. One set of four appeared as singlets, one set of four appeared as 1:2:1 triplets, and one set of four appeared as 1:1:1 triplets. All of these resonances were positive in the DEPT 135 spectrum, indicating that they correspond to the aryl methine carbon atoms. The ipso-carbon atoms were not observed in either the ^{13}C{^{1}H} or the DEPT 135 NMR spectrum. Additionally, the observed "coupling constants" were independent of spectrometer frequency (400 vs 500 MHz). These rather unusual patterns may be due to virtual P−C coupling.[46−48] In the interest of clarity, we have deposited a copy of a partial spectrum in the Supporting Information of this paper.

Single crystals of [*cis*-{η^2-$Ph_2PCH_2PPh_2$}$_2$$IrMe_2$][OTf] (**15**) suitable for X-ray diffraction analysis were grown by vapor diffusion of pentane into a concentrated solution of **15** in methylene chloride at −30 °C. The molecular structure of **15** is shown in Figure 2. The compound cocrystallizes with two methylene chloride molecules in the monoclinic space group $P2_1/n$ with four formula units in the unit cell. The iridium atom is pseudo-octahedrally coordinated by the two bidentate phosphine ligands and two methyl ligands. The methyl groups are *cis* to one another, and there is local, approximate C_2 symmetry in the molecule. Additionally, the chelation of the phosphorus ligands is not planar. The carbon atoms of the four-membered chelate rings are 0.34 (C(25)) and 0.24 Å (C(50)) from the planes defined by Ir(1)−P(1)−P(2) and Ir(1)−P(3)−P(4), respectively. One of the CH_2Cl_2 molecules is disordered. Crystal data and structure refinement details are given in Table 1. Selected bond lengths and angles are listed in Table 3.

A variety of additional neutral ligands (L′; carbon monoxide, nitriles, isonitriles, olefins, dienes, allene, alkynes, amines, anilines, pyridines, amine oxides, alcohols, ethers, phosphine oxides, dimethyl sulfoxide, and triphenylbismuth) were added to cold methylene chloride solutions of **6** in the method described above for anionic nucleophiles. None of these reactions yielded isolable iridium(V) salts (eq 7).

$$\underset{\mathbf{6}}{Cp^*Ir(Me)_3OTf} + L' \not\rightarrow [Cp^*(L')Ir(Me)_3][OTf] \quad (7)$$

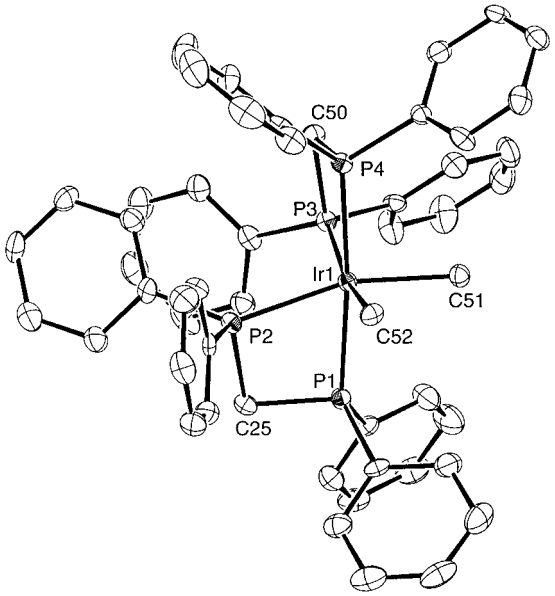


Figure 2. ORTEP diagram of the cationic portion of [*cis*-{η^2-$Ph_2PCH_2PPh_2$}$_2$$IrMe_2$][OTf] (**15**), with partial atom labeling scheme. The anion and the methylene chloride molecules were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 15

Ir(1)−P(1)	2.331(1)	Ir(1)−P(4)	2.339(1)
Ir(1)−P(2)	2.382(1)	Ir(1)−C(51)	2.148(5)
Ir(1)−P(3)	2.357(1)	Ir(1)−C(52)	2.135(5)
P(1)−Ir(1)−P(2)	71.44(5)	P(2)−Ir(1)−C(51)	163.8(1)
P(1)−Ir(1)−P(3)	102.41(5)	P(2)−Ir(1)−C(52)	88.2(1)
P(1)−Ir(1)−P(4)	172.71(5)	P(3)−Ir(1)−C(51)	92.7(1)
P(2)−Ir(1)−P(3)	97.61(5)	P(3)−Ir(1)−C(52)	167.0(1)
P(2)−Ir(1)−P(4)	104.18(5)	P(4)−Ir(1)−C(51)	90.9(1)
P(3)−Ir(1)−P(4)	72.06(4)	P(4)−Ir(1)−C(52)	95.3(1)
P(1)−Ir(1)−C(51)	94.2(1)	C(51)−Ir(1)−C(52)	84.4(2)
P(1)−Ir(1)−C(52)	90.4(1)		

Discussion

Thermal Decomposition of 5 and 6. The initial goal of this work was to synthesize several new iridium(V) neutral and cationic complexes and to explore their stability and reactivity. The protonolysis reactions of **4** provided two new neutral compounds of this type, **5** and **6**. Due presumably to the inherent instability of iridium in the +5 formal oxidation state and the high lability of chloride and triflate ligands, complexes **5** and **6** are very thermally sensitive. In fact, **5** and **6** were stable for weeks at −80 °C in methylene chloride solution but for only 1−2 min at 0 °C. Aside from methane, the decomposition products resulting from warming solutions of **5** or **6** to room temperature were not identified.

Attempted Synthesis of Neutral Iridium(V) Species. Since compounds **5** and **6** were so thermally

(46) For leading references, see refs 47 and 48.
(47) Pregosin, P. S.; Kunz, R. *Helv. Chim. Acta* **1975**, *58*, 423−431.
(48) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727−733.

unstable, we sought to derivatize them further and isolate other neutral high-valent iridium species. For most of these derivatization reactions we used triflate **6**, as we expected substitution to be more facile with this complex. Since triflate **6** was not isolable, all reactions utilizing **6** as a starting material required its *in situ* generation at −78 °C. Unfortunately, no neutral iridium(V) complexes were successfully synthesized by this route. On the basis of NMR spectroscopic evidence, we believe that some interaction between the anionic ligand and the metal complex occurred in many of these reactions. However, it is unclear whether the observed change in the ^{1}H NMR chemical shift values resulted from a true substitution of the anionic ligand for the triflate or from some other weak interaction. Although it is possible that there is an unusually high barrier for substitution of the anionic ligand for the iridium-bound triflate, we believe that the decomposition of the reaction mixtures to intractable products is best explained by inherent instability of the target complexes.

Stability of [Cp*(PMe$_3$)IrMe$_3$][OTf] and Its Relevance to C−H Bond Activation. Careful addition of trimethylphosphine to triflate complex **6** results in the formation of the (trimethylphosphine)iridium salt **7**. The trimethylphosphine salt **7** is a potential model for the proposed oxidative addition intermediate **3** in the methane C−H bond activation reaction.[6−11] We initially hypothesized that complex **7** would be more stable than presumed intermediate **3**, since reductive elimination of two sp^3-hybridized carbon ligands is relatively rare.[49−64] This is especially true for third-row transition metals. Furthermore, C−H reductive elimination is much more common, as proposed in eq 2 for complex **3**.[65] It was our hope that upon thermolysis **7** would undergo a carbon−carbon reductive elimination reaction in order to form ethane and Cp*(PMe$_3$)Ir(Me)-OTf **1** (eq 3); this would render the reactivity of model complex **7** analogous to that which we hypothesize for **3**.

However, we detected no ethane in these reaction mixtures by ^{1}H NMR spectroscopy. Rather than undergoing reductive elimination of ethane, methylene chloride solutions of **7** reacted to give MeCp* and unidentified iridium-containing products. Complex **7** also lost MeCp* in the presence of added phosphine (>3 equiv), and the remaining iridium fragment "[(PMe$_3$)IrMe$_2$]$^+$" formed in the reaction was trapped, in part, as [*cis*-{PMe$_3$}$_4$IrMe$_2$][OTf] (**14**). We can rationalize the absence of H$_3$C−CH$_3$ reductive elimination in our system. Carbon−carbon reductive elimination reactions in other systems are most commonly observed when at least one group involved is an sp^2-hybridized carbon. The scarcity of systems which couple two sp^3 centers has been explained by a high kinetic barrier for these types of reactions, relative to those involving sp^2 centers.[66,67]

The migration of alkyl or hydride groups between a transition metal and a cyclopentadienyl ligand has been observed in other laboratories. Examples include (a) the migration of an alkyl group from a transition metal to a cyclopentadienyl ligand,[68−71] (b) the migration of a hydride group from a metal to a cyclopentadienyl ligand,[72−77] (c) oxidative C−C bond cleavage of a functionalized cyclopentadienyl ligand (the reverse process of (a)),[78−82] and (d) the *reversible* migration of an ethyl group between a metal center and a Cp ligand.[83]

Addition of other Neutral Ligands to Complex 6. Other phosphines (PR$_3$, R = Et, Ph), as well as arsines (AsR$_3$, R = Et, Ph) and triphenylantimony, reacted with complex **6** to displace the triflate ligand and form the corresponding trimethyliridium salts (**8**−**12**). These

(49) For examples of reductive elimination reactions involving two sp^3 carbon centers, see refs 50−64.
(50) There are many more examples of C−C reductive elimination not involving two sp^3 carbon atoms. For leading references, see ref 12.
(51) From Au(III): Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140−6148.
(52) From Au(III): Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255−7265.
(53) From Ni(II): Yamamoto, T.; Abla, M. *J. Organomet. Chem.* **1997**, *535*, 209−211.
(54) From Pd(II): Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182−4186.
(55) From Pd(II): Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933−4941.
(56) From Pd(II): Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319−1327.
(57) From Pd(IV): Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2053−2058.
(58) From Pd(IV): Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363−1367.
(59) From Pt(II): DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601−3607.
(60) From Pt(II): Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713−6725.
(61) From Pt(IV): Goldberg, K. I.; Yan, J.; Winter, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 1573−1574.
(62) From Pt(IV): Goldberg, K. I.; Yang, J.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889−6896.
(63) (a) From Pt(IV): Hill, G. S.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 4522−4524. (b) Hill, G. S.; Yap, G. P. A.; Puddephatt, P. J. *Organometallics* **1999**, *18*, 1408−1418.
(64) From Pt(IV): Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457−2465.
(65) Theoreticians have rationalized the relative difficulty of C−C reductive elimination, compared to C−H or H−H reductive elimination: Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115−6128.
(66) Churchill, M. R.; Fettinger, J. C.; Janik, T. S.; Rees, W. M.; Thompson, J. S.; Tomaszewski, S.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *323*, 233−246.
(67) A reveiwer has commented that "all indications...indicate that such reductive eliminations require prior ligand dissociation to a 16-electron intermediate". We agree that, in some systems, prior ligand dissociation is required to effect reductive elimination, but this does not seem to be universally true (see, for example: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537). We therefore do not see a need to postulate its occurrence here, although we obviously cannot determine from our data whether Cp "slippage" occurs prior to the reductive elimination step.
(68) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, *118*, 5508−5509.
(69) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818−825.
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(75) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870−2876.
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(77) Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951−953.
(78) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789−805.
(79) Barretta, A.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H.; Gourdon, A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1981**, 156−158.
(80) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260−1261.
(81) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222−7227.
(82) Eilbracht, P.; Mayser, U. *Chem. Ber.* **1980**, *113*, 2211−2220.
(83) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324−1331.

reactions proceeded cleanly at −25 °C, and the products are air- and temperature-sensitive, as is trimethylphosphine complex **7**. To our knowledge, complexes **7**−**12** represent the only characterized cationic iridium(V) organometallic complexes that are not polyhydrides. The stability of complexes **7**−**12** lends credence to the postulate that cationic Ir(V) organometallic complexes are reasonable intermediates on reaction pathways.

The order of stability of salts **7**−**12** [Cp*(L)Ir(Me)$_3$][OTf] toward loss of MeCp* is phosphines < arsines < antimony. This order seemed counterintuitive to us.[84] Assuming that the cationic iridium(V) center is a "hard" Lewis acid, we expected that the phosphine salts **7**−**9** would be most stable, and the antimony salt **12** would be least stable. At the present time, we have no explanation for the observed stability trend. Calculations on this series of complexes might offer some insight into this problem.

Conclusions

The synthesis and solution characterization of two new neutral iridium(V) complexes has been achieved. These compounds have served as convenient precursors for a variety of fully characterized cationic iridium(V) species. These results support the notion that the paucity of iridium(V) complexes in the literature may not preclude the intermediacy of such a species along the reaction pathway for C−H bond activation by Cp*(PMe$_3$)Ir(Me)OTf (**1**). Compound **7**, which so far is our best structural model of the proposed intermediate (**3**) on the methane C−H bond activation pathway, decomposes by reductive elimination of MeCp*. In the presence of added phosphine, the iridium fragment is trapped as [*cis*-{L}$_4$IrMe$_2$][OTf]. We plan to continue our search for iridium(V) species (e.g., alkyl hydrides) that will undergo simple reductive elimination reactions.

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed at 23 °C in an inert-atmosphere (N_2) glovebox, or using standard Schlenk and high-vacuum-line techniques. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using Bruker AM-400 or DRX-500 MHz spectrometers. Except where noted, all NMR spectra were acquired at room temperature. In cases where assignment of $^{13}C\{^1H\}$ NMR resonances from the initial $^{13}C\{^1H\}$ NMR spectrum was ambiguous, resonances were assigned using standard DEPT 45, 90, and/or 135 pulse sequences. Infrared (IR) spectra were recorded using samples prepared as KBr pellets, and spectral data are reported in wavenumbers (cm^{-1}). Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility on VT ProSpec, ZAB2-EQ, and 70-FE mass spectrometers. Unless otherwise noted, all FAB MS data were acquired from samples in a methylene chloride/3-nitrobenzyl alcohol matrix. Elemental analyses were performed at the University of California, Berkeley Microanalytical facility, on a Perkin-Elmer 2400 Series II CHNO/S Analyzer.

Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock *via* a Cajon Ultra-Torr reducing union and then flame-sealing on a vacuum line. Reactions with gases and low-boiling liquids involved condensation of a calculated pressure of gas from a bulb of known volume into the reaction vessel at −196 °C. Known-volume bulb vacuum transfers were accomplished with a digital MKS Baratron gauge attached to a high-vacuum line.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Potassium bromide (Aldrich), Celite (Aldrich), silica gel (Merck 60, 230−400) and alumina (Brockman I, Aldrich) were dried *in vacuo* at 250 °C for 48 h. Toluene (Fisher) was either distilled from sodium metal under N_2 or passed through a column of activated alumina (type A2, size 12 × 32, Purifry Co.) under nitrogen pressure and sparged with N_2 prior to use. Pentane, hexanes, and benzene (Fisher) were either distilled from purple sodium/benzophenone ketyl under N_2 or passed through a column of activated alumina (type A2, size 12 × 32, Purifry Co.) under nitrogen pressure and sparged with N_2 prior to use. Diethyl ether and tetrahydrofuran (Fisher) were distilled from purple sodium/benzophenone ketyl under N_2 prior to use. Methylene chloride (Fisher) was either distilled from CaH_2 (Aldrich) under N_2 or passed through a column of activated alumina (type A2, size 12 × 32, Purifry Co.) under nitrogen pressure and sparged with N_2 prior to use. Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum transfer from the appropriate drying agent (Na/Ph_2CO or CaH_2) prior to use. Trimethylphosphine (Aldrich) and triethylphosphine (Aldrich) were vacuum-transferred from sodium metal prior to use.

Cp*IrMe$_4$ (4). Synthesis of **4** was performed according to literature methods,[27,28] except that the scale was increased by a factor of 10.[85] ^1H NMR (C_6D_6): δ 1.03 (s, 15H, $C_5(CH_3)_5$); 0.96 (s, 12H, Ir(CH_3)$_4$) (lit.[28] ^1H NMR (C_6D_6): δ 1.03 (s, 15H, $C_5(CH_3)_5$); 0.92 (s, 12H, Ir(CH_3)$_4$)).

Cp*Ir(Me)$_3$Cl (5). In the glovebox, an NMR tube was charged with **4** (4.8 mg, 0.012 mmol) and 0.5 mL of CD_2Cl_2. The tube was then fitted with a Cajon adapter. On a vacuum line, the tube was freeze−pump−thaw degassed three times, and HCl(g) (0.013 mmol) was added to the frozen (−196 °C) solution by vacuum transfer. The solution was thawed to −78 °C to allow mixing. The solution was then freeze−pump−thaw degassed three times to remove the methane generated, carefully warming the solution only to −78 °C in the thaw cycles. The tube was then flame-sealed under vacuum. In this way, the complex was obtained in >95% purity by NMR. Repeating this reaction in the presence of a ferrocene internal standard provided an NMR yield of 94%. ^1H NMR (CD_2Cl_2, −21 °C): δ 1.62 (s, 6H, *cis*-Ir(CH_3)$_2$); 1.35 (s, 15H, $C_5(CH_3)_5$); 0.98 (s, 3H, *trans*-Ir(CH_3)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −21 °C): δ 100.9 (s, $C_5(CH_3)_5$); 6.81 (s, $C_5(CH_3)_5$); 4.43 (s, *cis*-Ir(CH_3)$_2$); −1.31 (s, *trans*-IrCH_3). This compound decomposes above 0 °C in about 1 min. Due to its high thermal sensitivity, compound **5** could not be isolated.

Cp*Ir(Me)$_3$OTf (6). In the glovebox, an NMR tube was charged with **4** (23.0 mg, 0.0594 mmol) and 0.3 mL of CD_2Cl_2. The tube was then fitted with a Cajon adapter. On a vacuum line, the tube was cooled to −78 °C. Triflic acid (10.7 mg, 0.0713 mmol) in 0.200 mL of CD_2Cl_2 was added slowly to the cold solution by gastight syringe, turning the solution bright yellow. The solution was freeze−pump−thaw degassed three times to remove the generated methane, carefully allowing the solution to warm only to −78 °C during the thawing procedure. The tube was then flame-sealed under vacuum. In this way, the complex was obtained in >96% purity by NMR. Repeating this reaction in the presence of a ferrocene internal standard provided an NMR yield of 95%. ^1H NMR (CD_2Cl_2, −80 °C): δ 1.80 (s, 6H, *cis*-Ir(CH_3)$_2$); 1.42 (s, 15H, $C_5(CH_3)_5$); 1.13 (s, 3H, *trans*-Ir(CH_3)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ 100.4 (s, $C_5(CH_3)_5$); 13.4 (s, $C_5(CH_3)_5$); 7.6 (s, *cis*-Ir(CH_3)$_2$); 4.0 (s, *trans*-IrCH_3). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ −77.0. This

(84) Elschenbroich, A. S. *Organometallics, A Concise Introduction*, 2nd ed.; VCH: New York, 1992; p 154.

(85) For safety concerns, see ref 28.

compound decomposes above 0 °C in about 1 min. Due to its high thermal sensitivity, compound **6** was not characterized further.

General Procedure for the Synthesis of Complexes 7−12. In the glovebox, a 50 mL Schlenk flask was charged with **4**, CH_2Cl_2, and a Teflon stirbar. The flask was fitted with a septum, attached to a vacuum line, and cooled to −78 °C. To the cold, stirred solution was added a CH_2Cl_2 solution of CF_3SO_3H by gastight syringe over 1 min. The resulting bright yellow solution of **6** was stirred at −78 °C for 5 min. Trialkylphosphine, -arsine, or -antimony was then added as a CH_2Cl_2 solution by gastight syringe over 1 min. The resulting reaction mixture was allowed to stand in a −25 °C freezer overnight. The volatile materials were then removed *in vacuo* while the reaction mixture was maintained at −29 °C (dry ice/*o*-xylene bath). The remaining residue was warmed to room temperature, quickly brought into the glovebox, and rapidly triturated at room temperature with pentane (5 × 2 mL) and Et_2O (5 × 2 mL). The remaining residue was dissolved in CH_2Cl_2 (5 mL) and the solution filtered through Celite. The volatile materials were removed *in vacuo* to give compounds **7−12** as powders that were stored as solids in the glovebox freezer at −30 °C. Since air-sensitive complexes **7−12** are also relatively thermally sensitive, they were handled at room temperature only for brief periods of time. Combustion analyses were not obtained for complexes **7−9** due to their high thermal sensitivity and their similarity to compounds **10−12**. Although many NMR spectra for complexes **7−12** were acquired at low temperature, the short-term thermal stability of these complexes allowed for rapid spectrum acquisition at ambient temperature. The reported NMR data for **7−12** are for spectra acquired at room temperature.

[Cp*(PMe$_3$)IrMe$_3$][OTf] (7). Compound **7** was synthesized as described above using 19.1 mg (0.049 mmol) of **4** in 25 mL of CH_2Cl_2, 8.1 mg (0.054 mmol) of CF_3SO_3H in 5 mL of CH_2Cl_2, and 4.9 mg (0.064 mmol) of trimethylphosphine in 10 mL of CH_2Cl_2. Compound **7** was obtained as a colorless powder (25 mg, 0.043 mmol) in 87% yield. ^{1}H NMR (CD_2Cl_2): δ 1.60 (d, J = 1.4 Hz, 15H, $C_5(CH_3)_5$); 1.51 (d, J = 10.3 Hz, 9H, $P(CH_3)_3$); 0.92 (d, J = 8.7 Hz, 6H, *cis*-$Ir(CH_3)_2$); 0.48 (s, 3H, *trans*-$IrCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 104.1 (s, $C_5(CH_3)_5$); 11.4 (d, J = 44 Hz, $P(CH_3)_3$); 7.6 (s, $C_5(CH_3)_5$); 3.3 (d, J = 6 Hz, *cis*-$Ir(CH_3)_2$); 2.7 (d, J = 13 Hz, *trans*-$IrCH_3$). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.2 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −27.6 (s). IR: 2998 (s), 2983 (s), 2968 (s), 2938 (s), 2917 (s), 2907 (s), 2292 (w), 1493 (m), 1481 (m), 1460 (m), 1436 (m), 1420 (m), 1375 (m), 1317 (m), 1297 (s), 1262 (s), 1222 (s), 1146 (s), 1076 (w), 1030 (s), 953 (s), 887 (w), 843 (m), 751 (m), 733 (m), 678 (m), 637 (s), 571 (m), 516 (m) cm^{-1}. FABMS (*m*/*z*): calcd for $C_{16}H_{33}IrP$ 449.1949 (M^+ − OTf); found 449.1949.

[Cp*(PEt$_3$)IrMe$_3$][OTf] (8). Compound **8** was synthesized as described above using 101.3 mg (0.262 mmol) of **4** in 30 mL of CH_2Cl_2, 43.2 mg (0.288 mmol) of CF_3SO_3H in 10 mL of CH_2Cl_2, and 155 mg (1.31 mmol) of triethylphosphine in 10 mL of CH_2Cl_2. Compound **8** was isolated as a colorless powder (136 mg, 0.212 mmol) in 81% yield. ^{1}H NMR (CD_2Cl_2): δ 1.88 (m, 6H, $P(CH_2CH_3)_3$); 1.55 (d, J = 1.8 Hz, 15H, $C_5(CH_3)_5$); 1.07 (m, 9H, $P(CH_2CH_3)_3$); 0.91 (d, J = 10.8 Hz, 6H, *cis*-$Ir(CH_3)_2$); 0.52 (s, 3H, *trans*-$IrCH_3$).$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 104.8 (d, J = 3.8 Hz, $C_5(CH_3)_5$); 15.0 (d, J = 36.3 Hz, $P(CH_2CH_3)_3$); 9.8 (s, $P(CH_2CH_3)_3$); 8.9 (d, J = 4.5 Hz, *trans*-$IrCH_3$); 7.9 (s, $C_5(CH_3)_5$); −4.7 (d, J = 11.6 Hz, *cis*-$Ir(CH_3)_2$). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.4. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.0. Due to the thermal sensitivity of this compound, **8** was not characterized further.

[Cp*(PPh$_3$)IrMe$_3$][OTf] (9). Compound **9** was synthesized as described above using 218 mg (0.563 mmol) of **4** in 20 mL of CH_2Cl_2, 88.7 mg (0.591 mmol) of CF_3SO_3H in 10 mL of CH_2Cl_2, and 155 mg (0.591 mmol) of triphenylphosphine in 10 mL of CH_2Cl_2. Compound **9** was obtained as a red powder (401 mg, 0.512 mmol) in 91% yield. ^{1}H NMR (CD_2Cl_2): δ 7.51 (br m, 9H, aryl); 7.20 (br m, 6H, aryl); 1.66 (d, J = 1.8 Hz, 15H, $C_5(CH_3)_5$); 0.92 (d, J = 9.1 Hz, 6H, *cis*-$Ir(CH_3)_2$); 0.34 (s, 3H, *trans*-$IrCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.2 (d, J = 9.3 Hz, aryl); 133.7 (br s, aryl); 132.0 (br s, aryl); 129.4 (d, J = 10.6 Hz, aryl); 129.1 (d, J = 10.5 Hz, aryl); 105.6 (d, J = 2.8 Hz, $C_5(CH_3)_5$); 8.0 (s, $C_5(CH_3)_5$); 7.6 (d, J = 5.6 Hz, *trans*-$IrCH_3$); 1.3 (d, J = 10.7 Hz, *cis*-$Ir(CH_3)_2$). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.2 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 5.46 (s). IR: 3410 (m), 2920 (m), 2335 (w), 1483 (m), 1436 (s), 1380 (m), 1292 (s), 1260 (s), 1165 (s), 1146 (s), 1093 (s), 1027 (s), 843 (w), 749 (s), 702 (s) cm^{-1}. FABMS (*m*/*z*): 635.3 (M^+ − OTf).

[Cp*(AsEt$_3$)IrMe$_3$][OTf] (10). Compound **10** was synthesized as described above using 99.6 mg (0.257 mmol) of **4** in 30 mL of CH_2Cl_2, 42.5 mg (0.283 mmol) of CF_3SO_3H in 10 mL of CH_2Cl_2, and 208 mg (1.29 mmol) of triethylarsine in 10 mL of CH_2Cl_2. Compound **10** was obtained as a red powder (144 mg, 0.211 mmol) in 82% yield. ^{1}H NMR (CD_2Cl_2): δ 1.94 (q, J = 7.8 Hz, 6H, $As(CH_2CH_3)_3$); 1.56 (s, 15H, $C_5(CH_3)_5$); 1.47 (t, J = 7.7 Hz, 9H, $As(CH_2CH_3)_3$); 0.97 (s, 6H, *cis*-$Ir(CH_3)_2$); 0.56 (s, 3H, *trans*-$IrCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 103.3 (s, $C_5(CH_3)_5$); 12.66 (s, $As(CH_2CH_3)_3$); 9.6 (s, $As(CH_2CH_3)_3$); 7.6 (s, $C_5(CH_3)_5$); 1.8 (s, *trans*-$IrCH_3$); −8.9 (s, *cis*-$Ir(CH_3)_2$). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.3. IR: 2978 (s), 2934 (s), 2924 (s), 2878 (s), 2850 (m), 2292 (w), 1730 (w), 1632 (w), 1460 (m), 1383 (m), 1271 (s), 1223 (s), 1142 (s), 1072 (w), 1030 (s), 837 (w), 803 (w), 749 (m), 708 (m), 636 (s), 570 (m), 552 (w), 515 (m) cm^{-1}. FABMS (*m*/*z*): 535 (M^+ − OTf). Anal. Calcd for $C_{20}H_{39}AsF_3IrO_3S$: C, 35.13; H, 5.75. Found: C, 34.87; H, 5.90.

[Cp*(AsPh$_3$)IrMe$_3$][OTf] (11). Compound **11** was synthesized as described above using 73.1 mg (0.189 mmol) of **4** in 30 mL of CH_2Cl_2, 31.2 mg (0.208 mmol) of CF_3SO_3H in 10 mL of CH_2Cl_2, and 289 mg (0.944 mmol) of triphenylarsine in 10 mL of CH_2Cl_2. Compound **11** was obtained as a red powder (152 mg, 0.183 mmol) in 97% yield. ^{1}H NMR (CD_2Cl_2): δ 7.51 (m, 9H, aryl); 7.25 (m, 6H, aryl); 1.62 (s, 15H, $C_5(CH_3)_5$); 1.13 (s, 6H, *cis*-$Ir(CH_3)_2$); 0.65 (s, 3H, *trans*-$IrCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 133.3 (s, aryl); 131.8 (s, aryl); 129.7 (s, aryl); 127.7 (s, aryl); 104.6 (s, $C_5(CH_3)_5$); 7.7 (s, $C_5(CH_3)_5$); 4.8 (s, *trans*-$IrCH_3$); −3.6 (s, *cis*-$Ir(CH_3)_2$). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.0 (s). IR: 3053 (m), 2987 (s), 2922 (s), 2294 (w), 1977 (w), 1895 (w), 1824 (w), 1580 (m), 1481 (s), 1437 (s), 1380 (s), 1264 (br s), 1224 (s), 1186 (m), 1180 (s), 1075 (s), 1028 (s), 1000 (s), 841 (m), 803 (w), 740 (s), 696 (s), 635 (s), 571 (m), 516 (m), 479 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{39}AsF_3IrO_3S$: C, 46.37; H, 4.75. Found: C, 46.12; H, 4.79.

[Cp*(SbPh$_3$)IrMe$_3$][OTf] (12). Compound **12** was synthesized as described above using 52.8 mg (0.136 mmol) of **4** in 10 mL of CH_2Cl_2, 22.5 mg (0.150 mmol) of CF_3SO_3H in 10 mL of CH_2Cl_2, and 57.8 mg (0.164 mmol) of triphenylantimony in 5 mL of CH_2Cl_2. Compound **12** was obtained as a colorless powder (108 mg, 0.124 mmol) in 91% yield. ^{1}H NMR (CD_2Cl_2): δ 7.60 (m, 3H, aryl); 7.51 (m, 6H, aryl); 7.34 (m, 6H, aryl); 1.60 (s, 15H, $C_5(CH_3)_5$); 1.17 (s, 6H, *cis*-$Ir(CH_3)_2$); 0.81 (s, 3H, *trans*-$IrCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135.9 (s, aryl); 132.1 (s, aryl); 130.5 (s, aryl); 124.2 (aryl); 104.1 (s, $C_5(CH_3)_5$); 7.6 (s, $C_5(CH_3)_5$); 2.2 (s, *trans*-$IrCH_3$); −13.6 (s, *cis*-$Ir(CH_3)_2$). The $^{13}C\{^1H\}$ NMR resonance of the triflate ligand was not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −77.3 (s). IR: 3065 (m), 2982 (s), 2916 (s), 2836 (m), 2294 (w), 1973 (w), 1892 (w), 1820 (w), 1725 (w), 1630 (w), 1576 (m), 1480 (s), 1453 (sh), 1433 (s), 1379 (m), 1333 (w), 1262 (s), 1222 (s), 1183 (m), 1148 (s), 1066 (m), 1030 (s), 997 (m), 919 (w), 843 (w), 800 (w), 737 (s), 696 (s), 637 (s), 571 (m), 517 (m), 460 (m) cm^{-1}. FABMS (*m*/*z*): 725 (M^+ − OTf). Anal. Calcd for $C_{32}H_{39}F_3IrO_3SSb$: C, 43.94; H, 4.49. Found: C, 44.14; H, 4.75.

[Cp*(SbPh$_3$)IrMe$_3$][BPh$_4$] (13). In the glovebox, a 20 mL scintillation vial was charged with **12** (100 mg, 0.114 mmol), $NaBPh_4$ (59 mg, 0.173 mmol), CH_2Cl_2 (10 mL), and a Teflon stirbar and sealed with a cap. The reaction mixture was stirred for 10 min at room temperature and stored in the glovebox freezer (−30 °C) overnight. The mixture was then filtered through Celite (1 cm) on a medium-porosity fritted glass filter, and the volatile materials were removed from the filtrate *in vacuo*. The remaining residue was crystallized from CH_2Cl_2/pentane at −30 °C. Compound **13** was obtained as colorless crystals (116 mg, 0.111 mmol) in 97% yield. ^{1}H NMR (CD_2Cl_2): δ 7.63 (t, J = 7.4 Hz, 3H, aryl); 7.56 (t, J = 7.7 Hz, 6H, aryl); 7.37 (m, 14H, aryl); 7.06 (t, J = 7.3 Hz, 8H, aryl); 6.91 (t, J = 7.7 Hz, 5H, aryl); 1.53 (s, 15H, $C_5(CH_3)_5$); 1.20 (s, 6H, *cis*-Ir(CH_3)$_2$); 0.85 (s, 3H, *trans*-IrCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.4 (1:1:1:1 q, J_{CB} = 49 Hz, ipso-aryl); 136.3 (t, J_{CB} = 2 Hz, aryl); 136.0 (s, aryl); 132.3 (s, aryl); 130.6 (s, aryl); 126.0 (1:1:1:1 q, J_{CB} = 3 Hz, aryl); 124.1 (s, ipso-aryl); 122.0 (s, aryl); 104.0 (s, $C_5(CH_3)_5$); 7.7 (s, $C_5(CH_3)_5$); 2.5 (s, *trans*-IrCH_3); −13.4 (s, *cis*-Ir(CH_3)$_2$). IR: 3053 (s), 3033 (s), 2982 (s), 2917 (m), 2834 (w), 1960 (w), 1883 (w), 1818 (w), 1725 (w), 1652 (w), 1578 (m), 1478 (s), 1478 (s), 1432 (s), 1377 (m), 1332 (w), 1304 (w), 1261 (m), 1233 (w), 1183 (w), 1135 (w), 1065 (m), 1019 (m), 997 (m), 843 (w), 732 (s), 704 (s), 612 (m), 457 (m) cm^{-1}. Elemental analysis was not obtained for this complex due to its similarity to complex **12**.

[*cis*-{PMe$_3$}$_4$IrMe$_2$][OTf] (14). In the glovebox, a 50 mL Schlenk flask was charged with **7** (60.2 mg, 0.100 mmol), CH_2Cl_2 (20 mL), and a Teflon stirbar and then fitted with a glass stopper. The flask was placed on a vacuum line, where it was degassed by three freeze−pump−thaw cycles. To the frozen solution (−196 °C) of **7** was added trimethylphosphine (0.35 mmol) by vacuum transfer. The resulting mixture was thawed and stirred at room temperature overnight. (In a separate NMR experiment, the yield of **14** was calculated to be ∼60%, based on 1,3,5-trimethoxybenzene internal standard.) The volatile materials were removed from the reaction mixture *in vacuo*, giving a pale yellow residue. In the glovebox, the mildly air-sensitive solids were triturated with pentane (5 × 2 mL) and Et_2O (5 × 2 mL). The remaining residue was dissolved in CH_2Cl_2 (5 mL) and the solution filtered through Celite. Removal of the volatile materials *in vacuo* afforded complex **14** as a slightly yellow powder as an impure mixture with other unidentified compounds. A yield was not determined for this reaction, since the product could not be isolated cleanly. Major component: ^{1}H NMR (CD_2Cl_2) δ 1.53 (d, J = 9.7 Hz, 18H, (P(CH_3)$_3$)$_2$), 1.46 (t, J = 4.6 Hz, 18H, (P(CH_3)$_3$)$_2$), −0.12 (m, 6H, Ir(CH_3)$_2$); ^{19}F{^{1}H} NMR (CD_2Cl_2) δ −76.9 (s); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −48.85 (t, $^2J_{PP}$ = 18 Hz), −61.02 (t, $^2J_{PP}$ = 18 Hz); FABMS (m/z) 527 (M^+ − OTf).

[*cis*-{Ph$_2$PCH$_2$PPh$_2$}$_2$IrMe$_2$][OTf] (15). In the glovebox, a 50 mL Schlenk flask was charged with **4** (85.6 mg, 0.221 mmol), CH_2Cl_2 (20 mL), and a Teflon stirbar and fitted with a rubber septum. The flask was placed on a vacuum line. The solution was cooled to −78 °C, and HOTf (36.5 mg, 0.243 mmol) was added as a CH_2Cl_2 solution (10 mL). The resulting bright yellow solution of **7** was stirred for 15 min at −78 °C. To the stirred solution of **7** was added a CH_2Cl_2 (10 mL) solution of bis(diphenylphosphino)methane (424 mg, 1.10 mmol) by gastight syringe. The resulting reaction mixture was stirred at room temperature overnight. The volatile materials were removed from the reaction mixture *in vacuo*, giving a pale yellow residue. In the glovebox, the mildly air-sensitive solids were triturated with pentane (10 × 2 mL) and Et_2O (10 × 2 mL). The remaining residue was dissolved in CH_2Cl_2 (10 mL) and the solution filtered through Celite. Removal of the volatile materials *in vacuo* afforded complex **15** (104 mg, 0.154 mmol) as a yellow powder in 93% yield. ^{1}H NMR (CD_2Cl_2): δ 7.62−7.13 (m, 28H, aryl); 6.96 (t, J = 6.3 Hz, 4H, aryl); 6.87 (t, J = 10.2 Hz, 4H, aryl); 6.77 (t, J = 8.6 Hz, 4H, aryl); 5.93 (m, 2H, P−CH_2−P); 5.24 (m, 2H, P−CH_2−P); 0.74 (m, 6H, Ir(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 132.6 (virtual 1:1:1 t, J = 4.9 Hz, aryl); 132.0 (virtual 1:2:1 t, J = 5.3 Hz, aryl); 131.8 (br s, aryl); 131.4 (br s, aryl); 131.3 (virtual 1:1:1 t, J = 6.0 Hz, aryl); 131.2 (virtual 1:2:1 t, J = 6.0 Hz, aryl); 131.0 (br s, aryl); 130.4 (br s, aryl); 129.8 (virtual 1:2:1 t, J = 5.2 Hz, aryl); 129.4 (virtual 1:2:1 t, J = 5.2 Hz, aryl); 129.0 (virtual 1:1:1 t, J = 5.0 Hz, aryl); 128.4 (virtual 1:1:1 t, J = 4.9 Hz, aryl); 45.8 (m, (P−CH_2−P)$_2$); −13.8 (m, Ir−(CH_3)$_2$). The ^{13}C{^{1}H} NMR resonances for the triflate ligand and the ipso-carbon atoms of the phenyl groups were not observed. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −77.3 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −61.31 (t, J = 14.5 Hz); −63.33 (t, J = 14.4 Hz). IR: 3053 (m), 2952 (m), 2902 (m), 2829 (m), 2355 (w), 1971 (w), 1888 (w), 1810 (w), 1573 (m), 1484 (s), 1435 (s), 1362 (w), 1276 (s), 1257 (s), 1223 (s), 1149 (s), 1136 (s), 1099 (s), 1030 (s), 999 (m), 918 (w), 845 (w), 723 (s), 696 (s) cm^{-1}. FABMS (m/z): 991.2 (M^+ − OTf). Anal. Calcd for $C_{53}H_{50}F_3IrO_3P_4S$: C, 55.83; H, 4.42. Found: C, 55.48; H, 4.64.

Crystal Structure Determinations of 13 and 15. Single crystals of **13** and **15** were grown by vapor diffusion of pentane into methylene chloride solutions of each complex at −30 °C over 3 days. Crystals were mounted on a quartz fiber using Paratone N hydrocarbon oil. Data were analyzed for agreement and possible absorption using XPREP.[86] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[87] (**13**, T_{max} = 0.75, T_{min} = 0.51; **15**, T_{max} = 0.87, T_{min} = 0.67). The structures were solved by direct methods and expanded using Fourier techniques. Hydrogen atoms were included in calculated idealized positions but not refined. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. All calculations were performed using the teXsan[88] crystallographic software package of Molecular Structure Corp.

For complex **13**, the Ir, Sb, and Cl atoms were refined anisotropically, while the remaining atoms were refined isotropically. Attempts to refine the carbon atoms anisotropically led to nonpositive values for some components of the anisotropic displacement parameters. The large residual peaks near the Ir and Sb atoms can be attributed to Fourier ripple near these heavy atoms. It is not unusual to see residual peaks of this magnitude in structures containing heavy atoms such as Ir and Sb.

For complex **15**, the non-hydrogen atoms were refined anisotropically, except for Cl(5), which was refined isotropically. This Cl atom is the minor component of a disordered molecule of CH_2Cl_2. Its occupancy was constrained so that the sum of the occupancies of Cl(5) and Cl(3) was equal to 1.0. The occupancy of Cl(3) was refined to 0.941(5). Cl(4) had full occupancy because this site was common to both components of the disordered CH_2Cl_2.

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Supporting Information Available: Listings of X-ray structural data for complexes **13** and **15** and a partial ^{13}C{^{1}H} NMR spectrum of complex **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(86) XPREP, v. 5.03 (part of the SHELXTL Crystal Structure Determination Package); Siemens Industrial Automation, Inc., 1995.
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