

# Deprotonation of the Transition Metal Hydride $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrH}_2$ . Synthesis and Chemistry of the Strongly Basic Lithium Iridate $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}(\text{H})(\text{Li})$

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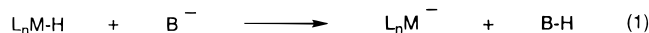
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Treatment of  $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{IrH}_2$  (**1**) with *tert*-butyllithium gives  $(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Ir}(\text{H})(\text{Li})$  (**2**) as a bright yellow solid. NMR evidence indicates that the lithium iridate **2** is aggregated in benzene, is converted to a single symmetrical species in THF, and is present as a dimer in DME. Treatment of **2** with 3,3-dimethylbutane trifluoromethanesulfonate-1,2-*syn-d*<sub>2</sub> (**3-syn-d**<sub>2</sub>) gave the alkylated hydridoiridium complex **4a-anti-d**<sub>2</sub>, which was converted to the corresponding chloride  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CHDCHDCMe}_3)(\text{Cl})$  (**4c-anti-d**<sub>2</sub>) by treatment with  $\text{CCl}_4$ . Analysis of this material by NMR spectroscopy showed that it was contaminated with  $\leq 15\%$  syn isomer. The alkylation therefore proceeds with predominant inversion of configuration at carbon, indicating that the major pathway is an  $\text{S}_{\text{N}}2$  displacement and not an outer-sphere electron-transfer reaction. Protonation studies carried out on iridate **2** with organic acids of varying  $\text{p}K_{\text{a}}$  allowed us to estimate that the  $\text{p}K_{\text{a}}$  of the dihydride **1** falls in the range 38–41, making it less acidic than DMSO and more acidic than toluene. This represents the least acidic transition metal hydride whose  $\text{p}K_{\text{a}}$  has been quantitatively estimated. Treatment of **2** with main group electrophiles allowed the preparation of several other hydridoiridium derivatives, including  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{SnPh}_3)(\text{H})$  (**5a**),  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{SnMe}_3)(\text{H})$  (**5b**), and  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{BR}_2)(\text{H})$  (**6a**, R = F; **6b**, R = Ph). Reaction of **2** with acid chlorides and anhydrides leads to acyl hydrides  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{COR})(\text{H})$ , and fluorocarbons also react, giving products such as  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{C}_6\text{F}_5)(\text{H})$  in the case of hexafluorobenzene as the electrophile.

## Introduction

Although complexes with transition metal–hydrogen bonds are traditionally referred to as “hydrides”, the chemical behavior of the hydrogen atom in these complexes can vary from hydridic to protic, allowing transition metal hydrides to function as Brønsted acids as well as reducing agents. When the former mode of reactivity is realized, deprotonation of a neutral transition metal hydride yields an anionic metal complex as shown in eq 1. Examples of low-valent organometallic anions are



numerous; many have been employed in organic synthesis as well as in the preparation of more highly functionalized organometallic species.<sup>1–14</sup>

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While examples of organometallic anions may be found that span the transition series, most examples incorporate one or more carbonyl groups in the ligand system to provide stabilization of the charged metal center and correspondingly modest  $\text{p}K_{\text{a}}$ 's for the hydride.<sup>15–20</sup> The fewer non-CO-containing metal anions known are typically exceptionally reactive,<sup>1–3,5,21–24</sup> but little quantitative thermodynamic or kinetic information is available on these species.

Previously, we reported that successive treatment of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) with *tert*-butyllithium followed by alkyl or silyl trifluoromethanesulfonates

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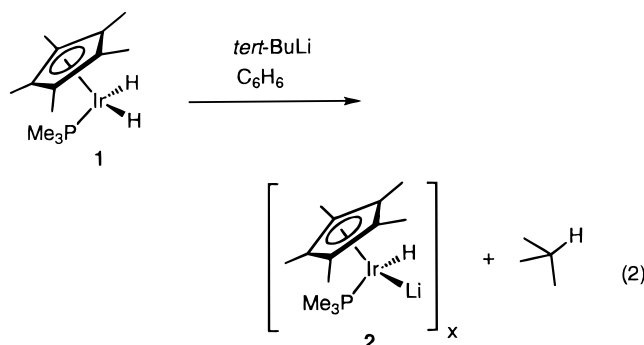
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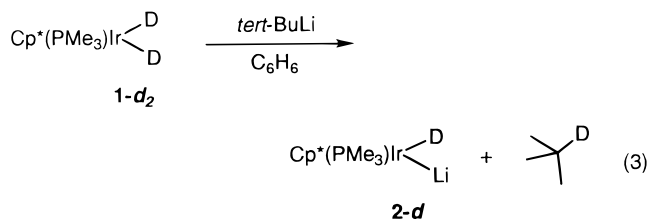
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(triflates) in pentane solution afforded the corresponding alkyl and silyl hydrides in good yields.<sup>2</sup> We describe here the spectroscopic characterization of the putative Cp\*(PMe<sub>3</sub>)Ir(Li)(H) intermediate, its expanded reactivity with organic and main group electrophiles, and a comprehensive study of its properties and chemistry.

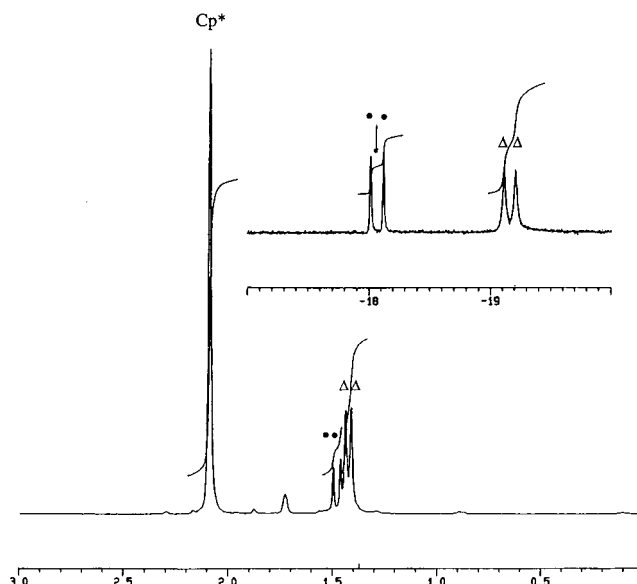
**Generation and Spectroscopic Characterization of Cp\*(PMe<sub>3</sub>)Ir(Li)(H).** When a colorless C<sub>6</sub>D<sub>6</sub> solution of Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> (**1**) was treated at ambient temperature with *tert*-butyllithium, an intense yellow color developed immediately. Analysis of this solution by <sup>1</sup>H NMR spectroscopy showed complicated resonance patterns in each of the characteristic Cp\*, PMe<sub>3</sub>, and hydride spectral regions as well as the expected signals for isobutane. Previous investigations have shown that protons bound to cyclopentadienyl and phosphine ligands are capable of being removed by potent bases and suggested to us that the complex <sup>1</sup>H NMR spectrum could have resulted from deprotonation at several sites in the starting dihydride complex. However, integration of the Cp\*, PMe<sub>3</sub>, and hydride regions gave a 15:9:1 ratio, suggesting instead that the Ir-bound hydrogen had been removed, as we hoped, but the observed spectrum was the result of extensive aggregation of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) (**2**) (eq 2).



Previous studies by Gladysz and co-workers demonstrated that the reaction of CpRe(PPh<sub>3</sub>)(NO)(H) with *n*-BuLi at -78 °C resulted in abstraction of a Cp ring proton to form (C<sub>5</sub>H<sub>4</sub>Li)Re(PPh<sub>3</sub>)(NO)(H).<sup>4</sup> Subsequent warming to -32 °C resulted in rearrangement to the thermodynamically favored CpRe(PPh<sub>3</sub>)(NO)(Li). To address the possibility that kinetic deprotonation could occur at a site other than the iridium center, Cp\*(PMe<sub>3</sub>)IrD<sub>2</sub> was prepared. Treatment with *tert*-butyllithium produced Cp\*(PMe<sub>3</sub>)Ir(Li)(D) (**2-d**), as expected. Analysis of the isobutane product by GC/MS showed that isobutane-*d* had been formed (>90% deuterium incorporation), indicating that it is indeed the Ir-bound hydrogen that reacts with *tert*-butyllithium (eq 3).



Removal of the volatile materials in vacuo from a benzene solution of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) afforded a bright yellow microcrystalline solid in 90% yield. This material



**Figure 1.** <sup>1</sup>H NMR spectrum of **2** and residual **1** in THF-*d*<sub>8</sub> (● **1**; △ **2**).

was sparingly soluble in THF-*d*<sub>8</sub>, but exhibited a much simpler NMR spectrum than that observed in benzene. At ambient temperature, single sharp resonances were observed for the Cp\*, PMe<sub>3</sub>, and hydride nuclei, in addition to resonances due to residual Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub>. Single resonances were also observed for **2** in the <sup>31</sup>P and <sup>7</sup>Li NMR spectra.<sup>25</sup> Our initial interpretation of these observations was that good donor solvents such as THF effected deaggregation to a single symmetrical species (Figure 1). When this solution was cooled to -101 °C, however, the <sup>7</sup>Li NMR spectrum decoalesced into multiple broad resonances. This result suggested instead that dissolution in THF effected rapid aggregate interconversion at 21 °C so that the observed spectra were the result of fast exchange.<sup>26</sup> The addition of 12-crown-4 as a sequestering agent to a C<sub>6</sub>D<sub>6</sub> solution of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) produced no change in the <sup>1</sup>H NMR spectrum even upon heating to 75 °C. This implied either that the barrier to lithium decoordination from the complex was slow (kinetic stability) at the reaction temperature or that the strength of the Li–Ir bonds in the aggregate made complexation by the crown ether energetically unfavorable (thermodynamic stability).

Attempts to grow crystals of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) suitable for study by X-ray diffraction were unsuccessful. Diffusion of THF or DME into a benzene solution of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) led to precipitation of a yellow microcrystalline solid. Analysis of the DME adduct by <sup>1</sup>H NMR spectroscopy indicated a composition of [Cp\*(PMe<sub>3</sub>)Ir(Li)(H)]<sub>2</sub>(DME). The stoichiometry of the com-

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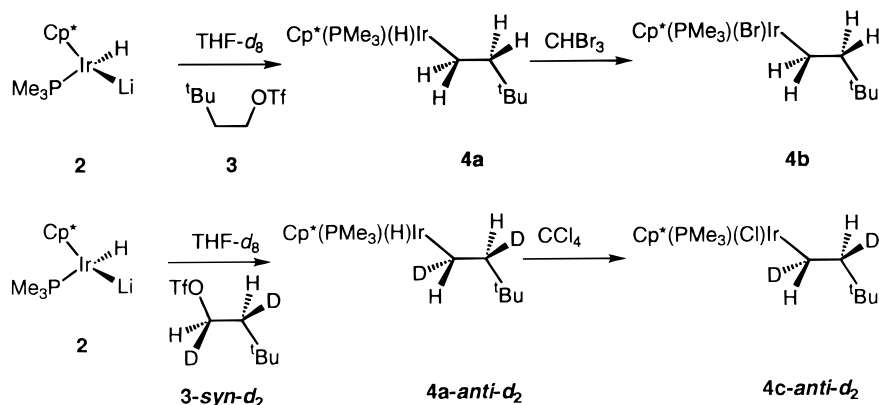
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(26) The possibility that aggregation is unfavored at ambient temperatures in THF solution but can be observed at lower temperatures in this solvent cannot be ruled out on the basis of these experiments.

Scheme 1



plex suggested that each lithium atom bridges to a second atom in addition to the two oxygen atoms of DME to maintain a preferred tetravalent coordination sphere. The dimeric  $[\text{Ru}(\text{OEP})(\text{neopentyl})_2(\mu\text{-Li})_2]$  (OEP = octaethylporphyrin) reported previously by James and co-workers was found to contain two bridging lithium centers and provides precedent for such a bridging structure.<sup>24</sup>

THF solutions of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  were stable for several days at ambient temperature. Benzene solutions of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  were similarly stable, but the aggregated complex began to precipitate after several hours at room temperature. Heating  $\text{C}_6\text{D}_6$  solutions of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  resulted in decomposition to  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  with no detectable deuterium incorporation as determined by analysis by  $^2\text{H}$  NMR spectroscopy.<sup>27</sup> We have not investigated the source of the Ir-bound hydrogen in this reaction.<sup>28</sup>

**Stereochemistry of the Reaction of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  with 3,3-Dimethylbutane Trifluoromethanesulfonate-1,2-*syn-d*<sub>2</sub>.** Previous work performed in this laboratory demonstrated that reaction of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  with certain organic triflates produced good yields of the complexes  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{R})(\text{H})$  (R = primary alkyl, trimethylsilyl).<sup>2</sup> We adopted this method for independent syntheses of compounds of this class to facilitate our studies of C–H activation by the 16e fragment  $\text{Cp}^*(\text{PMe}_3)\text{Ir}$ . However, these early studies did not include an investigation of the mechanism of the alkylation reactions.

An obvious candidate for the mechanism is a simple “inner-sphere” bimolecular nucleophilic displacement ( $\text{S}_{\text{N}}2$ ) reaction of triflate anion by  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$ . This should take place with inversion of stereochemical configuration at the reacting carbon atom of the alkyl triflate. Alternatively, the reaction could proceed by sequential “outer-sphere” electron transfer and triflate loss with products subsequently formed by collapse of the resulting radical pair.<sup>29</sup> This process should take place with significant loss of stereochemical integrity (racemization) at carbon. Whitesides and co-workers

distinguished these pathways in the alkylation of  $\text{CpFe}(\text{CO})_2$  salts by carrying out the alkylation with 1-bromo-3,3-dimethylbutane-1,2-*syn-d*<sub>2</sub> and 1-bromo-3,3-dimethylbutane-1,2-*anti-d*<sub>2</sub>, each of which proceeded with clean inversion of configuration in the iron system.<sup>6</sup> We enlisted a similar strategy for our investigation of the reaction of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  with alkyl triflates.<sup>30</sup>

A benzene solution of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (**1**) was treated with 1 equiv of *tert*-butyllithium at ambient temperature to give a solution of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  (**2**). The volatile materials were removed in vacuo, and the resulting oil was dissolved in THF. Dropwise addition of 1 equiv of 3,3-dimethylbutane-1-trifluoromethanesulfonate (**3**, Scheme 1) in THF solution produced a rapid reaction, as was evident from a deep yellow to yellow-gold color change. Removal of the solvent and analysis of the reaction mixture by  $^1\text{H}$  NMR spectroscopy showed  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_2\text{CH}_2\text{CMe}_3)(\text{H})$  (**4a**) and  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (**1**) in an 8:1 ratio. The alkylation product was isolated as the bromide by treatment of a benzene solution of the crude product mixture with  $\text{CHBr}_3$  and subsequent chromatography on silica gel.

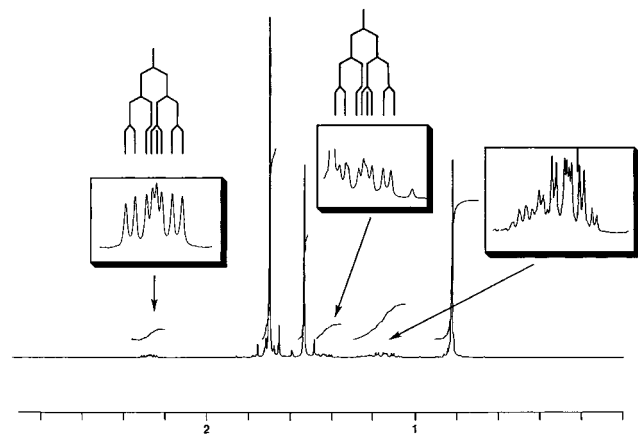
$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_2\text{CH}_2\text{CMe}_3)(\text{Br})$  (**4b**) was isolated as a yellow crystalline solid. Determination of the stereochemistry of the reaction with labeled **3** (**3-d**<sub>2</sub>) required prior knowledge of each of the  $^1\text{H}$ – $^1\text{H}$  coupling constants in the fully protiated complex  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_2\text{CH}_2\text{CMe}_3)(\text{Br})$  (**4b**). The stereogenicity of the pseudotetrahedral iridium center in complex **4b** results in a diastereotopic relationship between each pair of protons on the  $\alpha$ - and  $\beta$ -carbons of the dimethylbutyl group (Scheme 1; Figure 2). In  $\text{C}_6\text{D}_6$ , the two  $\alpha$ -protons appear at 2.27 and 1.44 ppm with each resonance displaying a 16-line dddd pattern, while the two diastereotopic  $\beta$ -protons are manifest as two overlapping doublet of triplets (1.19 and 1.11 ppm). In  $\text{C}_6\text{D}_6$ , the  $\alpha$ -proton resonance located at 1.44 ppm was partially obscured by an impurity which could not be removed by chromatography or recrystallization, and we attempted determination of the coupling constants in  $\text{CDCl}_3$ . In this solvent, both  $\alpha$ -proton resonances were well-resolved; however slow conversion to the chloride complex  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_2\text{CH}_2\text{CMe}_3)(\text{Cl})$  via halogen exchange was

(27) This indicated that the walls of glass vessels could serve as proton sources for the decomposition of the complex.

(28) A reviewer has suggested to us the interesting possibility that the formation of **1** upon heating solutions of complex **2** could result from disproportionation of **2** to **1** and  $\text{Cp}^*(\text{PMe}_3)\text{IrLi}_2$ . The fact that we have never been able to isolate **2** completely free from **1** as well as the observation of precipitates in standing benzene solutions of **2** lend additional support to this idea.

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**Figure 2.**  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of complex **4b** in  $\text{CDCl}_3$ .

**Table 1. Coupling Constants for Complex 4b in Hz ( $\text{C}_6\text{D}_6$  Solvent)**

resonance (ppm)	$^2J_{\alpha-\alpha}$	$^3J_{\alpha-\beta\text{syn}}$	$^3J_{\alpha-\beta\text{anti}}$	$^3J_{\alpha-\text{P}}$
2.27	10.6	4.6	13.6	4.8
1.44	10.7	4.4	13.9	4.8

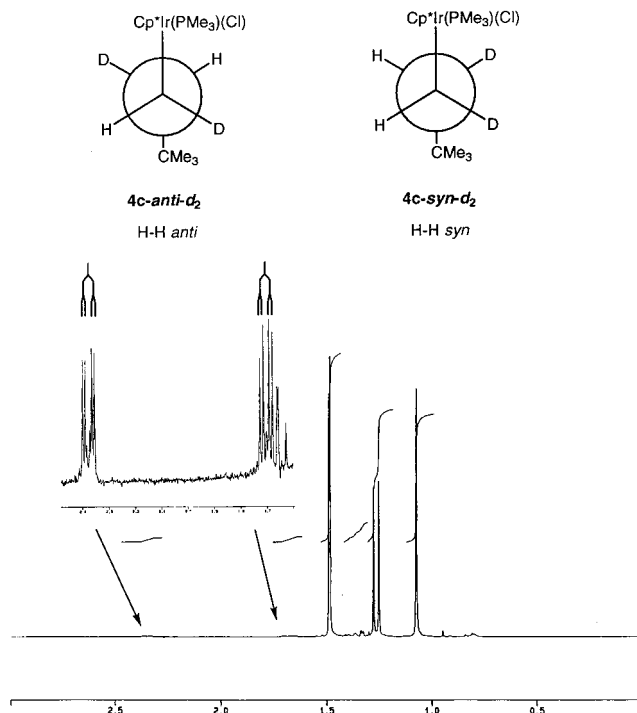
  

resonance (ppm)	$^2J_{\beta-\beta}$	$^3J_{\alpha-\beta\text{syn}}$	$^3J_{\alpha-\beta\text{anti}}$	$^3J_{\beta-\text{P}}$
1.19	13.6	4.9	13.6	not observed
1.11	13.5	4.9	13.5	not observed

observed. The splitting patterns are most easily resolved for the  $\alpha$ -hydrogens, especially in the  $^{31}\text{P}$ -decoupled spectrum, where two 8-line ddd patterns are observed (Figure 2). The spectra are consistent with two-bond coupling of the  $\alpha$ -protons with each other and three-bond couplings to the diastereotopic  $\beta$ -hydrogen atoms and the bound phosphine. The individual  $^1\text{H}$ - $^1\text{H}$  coupling constants for the  $\alpha$ - and  $\beta$ -hydrogen resonances were ascertained by comparison of the  $^1\text{H}\{^{31}\text{P}\}$  spectrum with the fully coupled  $^1\text{H}$  NMR spectrum and are provided in Table 1.

The preparation of the labeled iridium complex **4a-d<sub>2</sub>** was effected by the reaction of triflate **3-syn-d<sub>2</sub>** with **2** as described for the unlabeled complex. The presence of complexes with both *R* and *S* absolute configuration at the iridium stereocenter, and the observation of chloride for bromide exchange in **4b** in  $\text{CDCl}_3$  solvent, prompted us to perform the coupling constant analysis on the analogous complex  $\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{Ir}(\text{CHDCHDCMe}_3)(\text{Cl})$  (**4c-d<sub>2</sub>**). Therefore, **4a-d<sub>2</sub>** was converted to the chloride complex by reaction with  $\text{CCl}_4$  (Scheme 1). The coupling constants for the deuterium-labeled complex **4c-d<sub>2</sub>** were determined analogously. However, the presence of two- and three-bond  $^1\text{H}$ - $^2\text{H}$  couplings complicated a straightforward interpretation and required that we obtain the  $^1\text{H}\{^2\text{H}\}$  spectrum as well.<sup>31</sup> The deuterium-decoupled spectrum of the product **4c-d<sub>2</sub>** in  $\text{C}_6\text{D}_6$  is shown in Figure 3. Once again, the downfield  $\alpha$ -H resonance provides the clearest opportunity for analysis of the reaction stereochemistry. With one  $\alpha$ - and one  $\beta$ -hydrogen replaced by deuterium, in the absence of  $^2\text{H}$  coupling a simple dd pattern for the downfield  $\alpha$ -H is predicted, due to coupling to P and to the (now single)  $\beta$ -H. From these experiments,  $^3J_{\text{H-H}}$  was found to be

(31) Details of the  $^2\text{H}$  decoupling procedure as well as the coupled and uncoupled spectra are available at the UC Berkeley NMR facility website (<http://www.cchem.berkeley.edu/college/facilities/nmr/apps/misc/h2dec.html>).

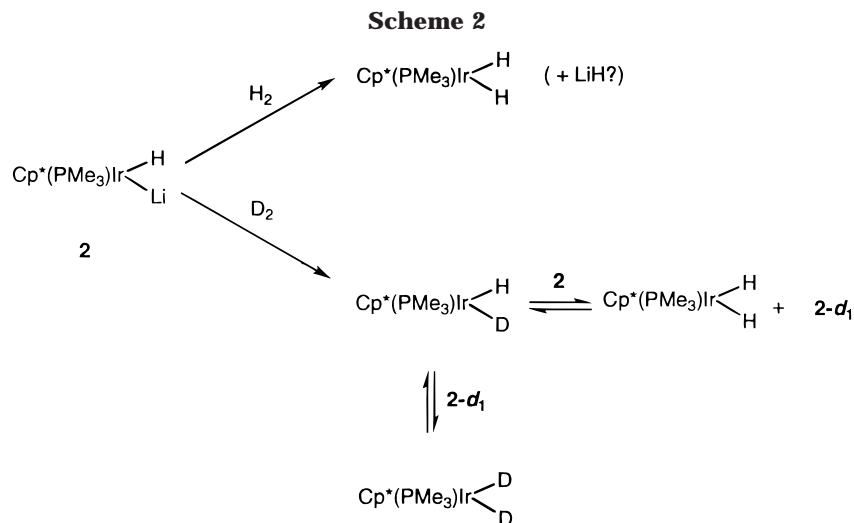


**Figure 3.**  $^1\text{H}\{^2\text{H}\}$  NMR spectrum of complex **4c-anti-d<sub>2</sub>** in  $\text{C}_6\text{D}_6$ .

14.1 Hz for the downfield  $\alpha$ -hydrogen resonance (2.38 ppm in  $\text{CDCl}_3$ ) and 14.1 Hz for the upfield  $\alpha$ -hydrogen resonance (1.71 ppm in  $\text{CDCl}_3$ ). By comparison with the coupling constants determined for the all-protio system, this assignment suggests that the  $\alpha$ - and  $\beta$ -hydrogen atoms of each diastereomer<sup>32</sup> exist in a relative anti relationship to one another (**4c-anti-d<sub>2</sub>**, Figure 3).

The smaller H-H coupling predicted for **4c-syn-d<sub>2</sub>** would require that the presence of this material produce lines appearing between the two doublets seen for  $\alpha$ -H of the anti isomer. Unfortunately, this section of the spectrum is not completely clean. Spectral simulations using the *J* values measured from the perprotio material predict that the pattern would look somewhat different from that shown in Figure 3. However, the simulations require a guess as to the isotope shift on the resonance positions, and so we cannot rigorously determine whether the small peaks between the two large doublets are due to an impurity, to insufficient power to effect complete  $^2\text{H}$  decoupling in the experiment, or to the presence of some **4c-syn-d<sub>2</sub>**. Even if the smaller lines are *all* due to the syn isomer, careful integration indicates that this would constitute a ratio of about 85:15 inversion/retention. We can therefore conservatively say that the reaction proceeds with at least 85% inversion of configuration at the reacting carbon center of 3,3-dimethylbutyl triflate and therefore occurs substantially, if not exclusively, by an  $\text{S}_{\text{N}}2$  mechanism.<sup>33</sup>

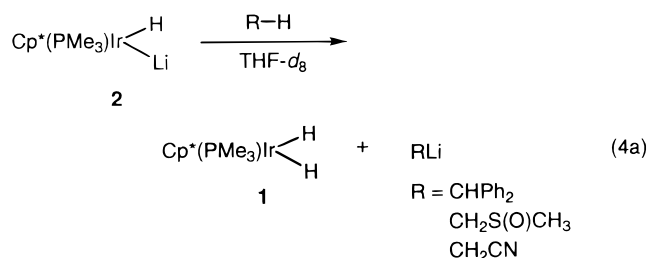
(32) The presence of stereogenic centers on the  $\alpha$ - and  $\beta$ -carbons of the dimethylbutyl group as a result of isotopic substitution in **3-d<sub>2</sub>** gives rise to four possible enantiomeric pairs of diastereomers in **4c-d<sub>2</sub>**. If a mixture of inversion and retention mechanisms was active in the present reaction, all four enantiomeric pairs could, in principle, be observed. Since the method of preparation of the labeled triflate has in essence "coupled" two of the enantiomeric pairs to each other, an exclusive inversion or retention mechanism can produce only two enantiomeric pairs of diastereomers.



**Estimation of the Acidity of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ .** Data on the  $\text{p}K_a$ 's of organometallic complexes are not as extensive as those available for organic compounds. However, in recent years several groups have begun to provide  $\text{p}K_a$  data for transition metal hydrides.<sup>15–18,20</sup> In general, it is found that thermodynamic acidities decrease in descending a metal triad and increase from left to right across the transition series in the periodic table.<sup>34</sup> Other ligands attached to the metal center also have a strong effect on the  $\text{p}K_a$ , electron-donating ligands (e.g., phosphines) reducing acidities and electron-accepting ligands (e.g., CO) increasing them. Typical examples of measured  $\text{p}K_a$  values in acetonitrile solvent range from 8.4 for  $\text{Co}(\text{CO})_4(\text{H})$  to 26.6 for  $\text{Cp}(\text{PMe}_3)\text{W}(\text{CO})_2(\text{H})$ . Substitution of  $\text{Cp}^*$  for  $\text{Cp}$  in the complex  $\text{CpMo}(\text{CO})_3(\text{H})$  led to an increase in the  $\text{p}K_a$  from 13.9 to 17.1. A similar substitution in the complex  $\text{CpFe}(\text{CO})_2(\text{H})$  increased the  $\text{p}K_a$  from 19.4 to 26.3. Substitution of a phosphine for CO had an even larger effect. The acidity of  $\text{CpW}(\text{CO})_3(\text{H})$  ( $\text{p}K_a = 16.1$ ) is 10.5  $\text{p}K_a$  units lower than  $\text{CpW}(\text{CO})_2(\text{PMe}_3)(\text{H})$  ( $\text{p}K_a = 26.6$ ).

In light of these observations, we anticipated that  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (**1**), by virtue of its relatively electron-rich coordination sphere and position in the transition series, would exhibit an unusually high  $\text{p}K_1$ . This prediction was substantiated semiquantitatively by quenching studies with various carbon acids. Benzene solutions of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (**1**) were treated with 1 equiv of *tert*-butyllithium to generate  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  (**2**), and the volatile materials were removed in vacuo. The resulting yellow oil was dissolved in  $\text{THF-}d_8$  and treated with 1 or more equiv of a carbon acid of known acidity (unfortunately, the reactivity of DMSO and  $\text{CH}_3\text{CN}$  toward **2** precluded their use as solvents for quenching studies, preventing exact comparisons to previously measured transition metal hydride acidities). These experiments demonstrated that **2** is exceptionally basic. Reaction with diphenylmethane ( $\text{p}K_a = 32.2$ ),  $\text{CH}_3\text{CN}$  ( $\text{p}K_a = 31.3$ ), and even DMSO ( $\text{p}K_a = 35.1$ )<sup>35</sup> afforded  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  and the corresponding lithium methide

conjugate bases of the carbon acids in quantitative yield, as determined by  $^1\text{H}$  NMR spectroscopy (eq 4a). While



$\text{H}_2$  is not often regarded as a Brønsted acid, we found that it underwent a clean reaction with **2**. When a  $\text{C}_6\text{D}_6$  solution of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  was placed under 720 Torr of hydrogen, heating at 45 °C for 18 h resulted in quantitative formation of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  and was accompanied by the formation of a white precipitate (presumably polymeric  $\text{LiH}$ ) (Scheme 2). In an analogous experiment, a  $\text{C}_6\text{D}_6$  solution of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  was placed under 720 Torr of  $\text{D}_2$  and a mixture of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ ,  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{D})(\text{H})$ , and  $\text{Cp}^*(\text{PMe}_3)\text{IrD}_2$  was detected by  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy. No deuterium was detected in the  $\text{Cp}^*$  or  $\text{PMe}_3$  ligands (vide supra). The observation of the three isotopomeric complexes suggests not only that  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  is capable of deprotonating  $\text{H}_2$  but that  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  undergoes proton exchange with  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  to result in a statistical mixture of isotopomers (Scheme 2).<sup>36</sup>

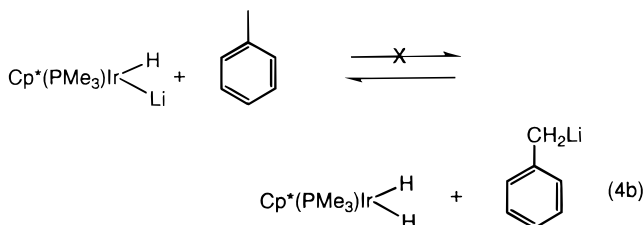
In contrast, treatment of the yellow solution of **2** with toluene did not result in its deprotonation to form benzyllithium and  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ . The possibility that toluene deprotonation was slow rather than thermodynamically unfavorable, as is often observed with lithium bases, prompted us to investigate the reverse of this reaction. When a  $\text{THF-}d_8$  solution of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  was treated with 1 equiv of benzyllithium, quantitative formation of toluene and  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  was observed (eq 4b). This demonstrates that the acidity of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  in THF is bracketed by the acidities of DMSO and toluene.<sup>35</sup> To the extent that  $\text{p}K_a$ 's in  $\text{CH}_3\text{-}$

(33) However, we cannot rule out a contribution to the reaction resulting from an electron-transfer mechanism that creates a geminal radical pair that collapses on the time scale of radical inversion.

(34) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Ch. 3, p 92.

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(36) Alternatively, reaction with hydrogen could be reversible and HD formed could scramble H/D into the iridium complex.

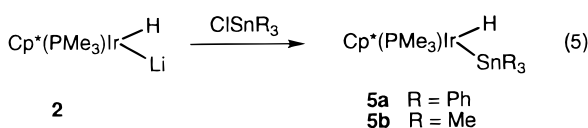


CN and/or DMSO can be extrapolated to THF,<sup>37,38</sup> the first  $\text{p}K_a$  of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  falls in the range 38–41. To our knowledge, this represents the highest  $\text{p}K_a$  of a transition metal hydride yet reported.

With the assistance of A. Streitwieser and J. Krom, we attempted to determine more precisely the  $\text{p}K_1$  of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ . The use of cesium bases in THF solvent systems has been found to minimize ion-pairing effects on acidities and provide  $\text{p}K_a$  values comparable to those observed in other solvent systems.<sup>37,38</sup> Unfortunately, the attempted reaction of cumylcesium with  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  failed to provide a detectable concentration of hydridoirdiate before the onset of decomposition of cumylcesium. That cumylcesium ( $\text{p}K_a$  cumene = 40.7)<sup>37</sup> failed to react while benzyllithium ( $\text{p}K_a$  toluene = 40.9)<sup>37</sup> gave quantitative deprotonation of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  suggests that the  $\text{p}K_1$  of **1** is less than that of cumene (i.e., proton transfer from **1** to cumylcesium is thermodynamically favorable), but steric congestion around the iridium center inhibits the approach of the tertiary aromatic base.

The potassium salt of hydridoirdiate **2** can also be generated by reaction with benzyllithium in benzene or benzene–THF mixtures. The resulting complex was found to be unstable at ambient temperature in pure THF, undergoing decomposition to a single unidentified iridium hydride product. Initial studies of the potassium iridate complex show that it possesses enhanced reactivity in comparison to its lithium congener in related reactions, though it reacts much less cleanly. Attempts to deprotonate  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  with less basic agents were unsuccessful. Treatment of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  with  $\text{NaNH}_2$  ( $\text{p}K_a$   $\text{NH}_3$  = 38),<sup>35</sup> KH-18-crown-6 ( $\text{p}K_a$   $\text{H}_2$  = 35),<sup>35</sup> or LDA ( $\text{p}K_a$  diisopropylamine = 35.7)<sup>39</sup> failed to produce any detectable reaction. This supports our assertion that the  $\text{p}K_1$  of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  lies above 38.

**Reactions of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  with Main Group and Organic Electrophiles. Organostannanes.**  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  was found to undergo a variety of clean reactions with electrophilic main group compounds. Treatment of a benzene solution of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  with 1 equiv of  $\text{Ph}_3\text{SnCl}$  or  $\text{Me}_3\text{SnCl}$  resulted in formation of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{SnPh}_3)(\text{H})$  (**5a**) and  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{SnMe}_3)(\text{H})$  (**5b**) in 71% and 91% yields, respectively (eq 5). Complex **5a** was remarkably stable



(37) Streitwieser, A.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074.

(38) Krom, J. A.; Petty, J. T.; Streitwieser, A. *J. Am. Chem. Soc.* **1993**, *115*, 8024.

(39) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442.

with respect to exposure to air and moisture and could even be recrystallized from an ethanol–water mixture. The trimethylstannyl analogue was less stable and decomposed rapidly in solution upon exposure to air or attempted purification by column chromatography. Analysis of complex **5a** by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy revealed couplings between tin, hydrogen, and phosphorus. The observed coupling constants ( $J_{\text{P-Sn}} = 167$  Hz and  $J_{\text{H-Sn}} = 133$  Hz) are consistent with two-bond coupling and support our assignment of a structure with an Ir–Sn bond. We anticipated that complexes **5a** and **5b** might show evidence of an agostic Sn–H interaction, providing an example of an arrested transition state for oxidative addition/reductive elimination of Sn–H bonds to/from the  $\text{Cp}^*(\text{PMe}_3)\text{Ir}$  fragment. Typical values of  $^1J_{\text{H-Sn}}$  for alkyltin hydrides range from 1500 to 1800 Hz with  $^2J_{\text{H-Sn}}$  for alkyltin species in the range of 50–70 Hz.<sup>40</sup> However,  $^2J_{\text{H-Sn}}$  was found to be well below the value of 1895 Hz reported for  $^1J_{\text{H-Sn}}$  in  $\text{Ph}_3\text{SnH}$ , which suggests the absence of any significant interaction between the hydridic hydrogen atom and the Sn center.<sup>41,42</sup> Further, complex **5a** was found to be exceptionally stable, showing no signs of decomposition even upon prolonged photolysis or heating for 20 h at 195 °C in benzene solution.

**Boryl Derivatives.** The discovery of transition metal-catalyzed functionalization of organic substrates mediated by boranes has prompted much recent interest in the nature of transition metal–boryl complexes.<sup>43–45</sup> These complexes are typically formed via oxidative addition of a borane to an electronically unsaturated transition metal center or by the reaction of a transition metal anion with a boron halide;<sup>43–50</sup> recently metal–boryl complexes capable of alkane activation have been discovered.<sup>51</sup> Though much of the work to date has focused on the use of catecholboranes, several examples involving boranes lacking oxygen donor groups are known.<sup>46,52–56</sup> With the nucleophilicity of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  being clearly defined in the present study, we sought to determine if its reaction with boron halides could provide entry into a novel class of iridium complexes.

Treatment of a toluene solution of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  at  $-78$  °C with 1 equiv of boron trifluoride-etherate led to immediate reaction and precipitation of  $\text{LiBF}_4$ .

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5155.

(50) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*,

4403.

(51) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211.

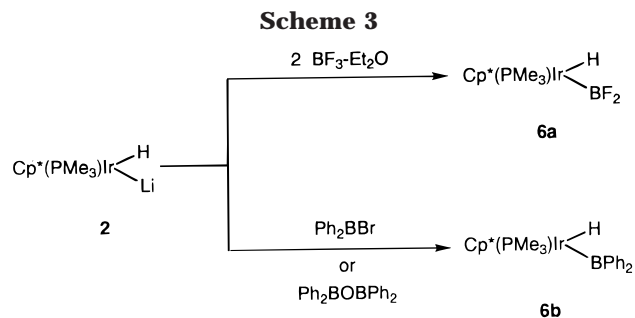
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(53) Cundy, C. S.; Nöth, H. *J. Organomet. Chem.* **1971**, *30*, 135.

(54) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 9399.

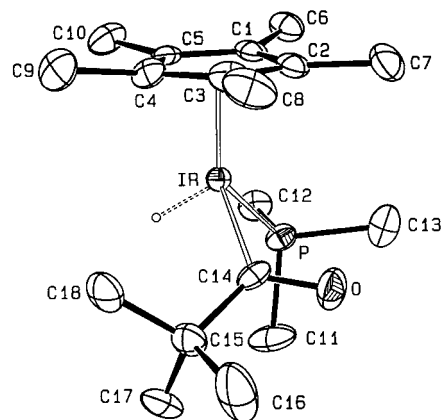
(55) Nöth, H.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 623.

(56) Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 819.



Analysis of the reaction mixture by <sup>1</sup>H NMR spectroscopy revealed that approximately 50% conversion to a new iridium complex had occurred. When the reaction was carried out using 2 equiv of boron trifluoride-etherate, greater than 90% conversion to the new complex was indicated by <sup>1</sup>H NMR analysis. The complex exhibited resonances at 1.95, 1.29, and -17.45 ppm in the <sup>1</sup>H NMR spectrum indicative of bound Cp\*, PMe<sub>3</sub>, and hydride ligands. The hydride resonance appeared as a doublet of triplets consistent with coupling to phosphorus and two equivalent fluorine atoms and suggested a structure involving a bound difluoroboryl ligand. Analysis of the complex by <sup>13</sup>C, <sup>31</sup>P, <sup>19</sup>F, and <sup>11</sup>B NMR spectroscopy supported a structural assignment of Cp\*(PMe<sub>3</sub>)Ir(BF<sub>2</sub>)(H) (**6a**) for the reaction product (Scheme 3). The <sup>19</sup>F NMR spectrum showed a 1:1:1 quartet (<sup>1</sup>J<sub>B-F</sub> = 154 Hz) located at -23.2 ppm. The <sup>11</sup>B NMR spectrum gave a 1:2:1 triplet at 23.9 ppm (<sup>1</sup>J<sub>B-F</sub> = 160 Hz) further supporting this assignment. The lack of observable coupling between <sup>11</sup>B and <sup>1</sup>H as well as the position of the hydride <sup>1</sup>H NMR resonance indicates minimal, if any, interaction between boron and the hydridic hydrogen. The spectroscopic equivalence of the two diastereotopic fluorine nuclei is consistent with a complex exhibiting free rotation about the Ir-B bond at ambient temperatures. Single crystals of **6a** for study by X-ray diffraction were grown by slow cooling of an acetonitrile solution to -40 °C. Unfortunately, preliminary data indicated long-range disorder in the crystal due to interchange of the BF<sub>2</sub> and H ligands in the crystal lattice, thus preventing a meaningful solution of the structure. Additionally, multiple attempts at recrystallization could not generate analytically pure samples of **6a** free from dihydride complex **1**. Complex **6a** was found to be thermally stable in toluene solution, exhibiting no signs of decomposition upon extended heating at 135 °C. Interestingly, at this temperature the complex was observed to undergo H-D exchange with toluene-*d*<sub>8</sub>.

In contrast to the reaction with boron trifluoride-etherate, Cp\*(PMe<sub>3</sub>)Ir(Li)(H) underwent complete reaction with just 1 equiv of Ph<sub>2</sub>BBr. The <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>11</sup>B NMR spectra support an analogous reaction product (**6b**) containing the diphenylboryl ligand with equivalent phenyl groups attached to boron (Scheme 3). Complex **6b** was obtained in analytically pure form with great difficulty. Reaction of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) with Ph<sub>2</sub>BBr to produce **6b** was also accompanied by the formation of Cp\*(PMe<sub>3</sub>)Ir(H)(Br) and Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub>, and so pure material was obtained only after partitioning the crude reaction mixture between pentane and acetonitrile, selective bromination of the dihydride complex by titration of the reaction mixture with bromoform, and



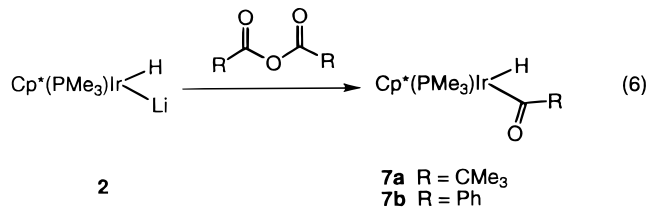
**Figure 4.** ORTEP diagram illustrating the structure of **7a** (hydride ligand not located).

multiple recrystallization of the resulting product from acetonitrile. Subsequently, we found that Cp\*(PMe<sub>3</sub>)Ir(Li)(H) underwent clean reaction with tetraphenylboronic anhydride (Ph<sub>2</sub>BOBPh<sub>2</sub>) (Scheme 3) to produce **6b** in 90% yield unaccompanied by the formation of the dihydride or other byproducts.

#### Reactions with Organic Carbonyl Compounds.

The ability of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) to undergo clean S<sub>N</sub>2-type reactions prompted us to investigate whether the iridate could also be used to generate novel iridium complexes with electrophilic reagents via nucleophilic acyl substitution reactions. To this end, we explored reactions with a variety of organic carbonyl compounds.

When a benzene solution of **2** was treated with pivalic anhydride at room temperature, an immediate reaction occurred. Analysis of the product by <sup>1</sup>H NMR spectroscopy showed resonances at 1.82, 1.28, 1.19, and -17.02 ppm, corresponding to the Cp\*, PMe<sub>3</sub>, *tert*-butyl, and hydride functionalities along with resonances for Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub>. Removal of the volatile materials in vacuo, extraction of the crude solid with pentane, and slow cooling to -40 °C afforded an analytically pure compound identified as the 2,2-dimethylpropionyl hydride complex **7a** by a combination of spectroscopic techniques (eq 6). The identity of the reaction product was con-



firmed by X-ray diffraction. The ORTEP diagram and positional parameters are provided in Figure 4. In this structure, the hydride was not located but has been added to the diagram for clarity. The Ir-C<sub>14</sub> and C<sub>14</sub>-O bond distances were found to be 2.036 and 1.235 Å, respectively, in the range expected from comparison with other late metal acyl complexes.<sup>57-61</sup> The Ir atom

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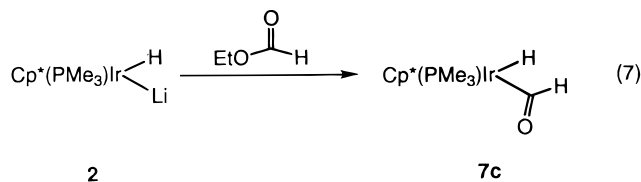
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is roughly in the C=C=O plane of the acyl group. The sum of angles around the carbonyl carbon atom was found to be 360°, indicating symmetric bonding of the acyl carbon to Ir.

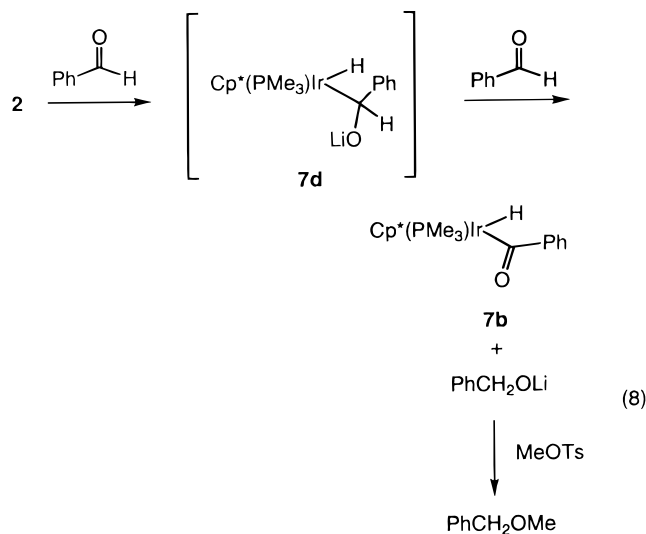
Reaction of **2** with benzoic anhydride provided the analogous phenacyl hydride **7b** in 45% yield after chromatographic purification and recrystallization. Both acyl hydride complexes were stable indefinitely in solution at room temperature under an inert nitrogen atmosphere, but decomposed quickly upon exposure to air. In contrast, reaction of **2** with acetic anhydride yielded Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> as the sole iridium-containing product. Although the organic product of this reaction was not characterized, we assume the dihydride was formed by proton abstraction from the α-carbon of the anhydride. The basicity of the iridate complex would thus appear to limit its use in the formation of acyl hydride derivatives to reactions with compounds lacking acidic hydrogens.

The parent formyl complex **7c** was obtained analogously in 28% purified yield by reaction of **2** with ethyl formate (eq 7).<sup>62</sup> The connectivity of **7c** was confirmed



by X-ray diffraction, but long-range disorder resulting from -CHO and -H interchange in the lattice unfortunately prevented an accurate determination of bond lengths and angles. Complex **7c** was found to be moderately stable in solution at ambient temperatures but showed signs of decomposition after several hours.

Somewhat surprisingly, complex **2** was also found to undergo reaction with benzaldehyde. In a NMR tube reaction, when a benzene solution of **2** was treated with 1 equiv of benzaldehyde at ambient temperature, conversion to phenacyl hydride **7b** and **1** was observed in a 1.25:1 ratio. When 2 equiv of benzaldehyde was utilized, **7b** and **1** were formed in a 3:1 ratio. The increased yield of **7b** observed when a second equiv of benzaldehyde was employed suggested that its formation was mediated by the formation of adduct **7d**, which underwent hydride transfer to benzaldehyde to give **7b** and lithium benzyloxide (eq 8). To test this hypothesis, we attempted to trap the benzyloxide ion via reaction with methyl *p*-toluenesulfonate. As expected, addition of benzaldehyde to a solution of **2**, followed by the addition of methyl *p*-toluenesulfonate to the reaction solution resulted in the formation of benzyl methyl ether in 66% yield (relative to **7b**), consistent with the intermediacy of the benzyloxide ion.



By analogy with the reactions of **2** with acid anhydrides, we anticipated that reactions of **2** with organic carbonates would provide access to the corresponding alkoxycarbonyl hydride complexes. However, when a benzene solution of **2** was treated with dimethyl carbonate at ambient temperature, the known complex Cp\*(PMe<sub>3</sub>)Ir(CO) (**8**) was obtained in a 1:2.2:1.4 ratio along with Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> and Cp\*(PMe<sub>3</sub>)Ir(Me)(H) (**9**) (Scheme 4). Similarly, reactions of **2** with di-*tert*-butyl dicarbonate or CO<sub>2</sub> both yielded the carbonyl complex **8**.

Acyl and alkoxycarbonyl hydrides are believed to be intermediates in a large number of industrially important processes including the Fischer-Tropsch reaction, the water-gas shift reaction, and olefin hydroformylation. Consequently, the study of such complexes has drawn considerable attention.<sup>57-61,63-72</sup> We anticipated that complexes **7a-c** would undergo thermal reductive elimination to produce the transient unsaturated 16e Cp\*(PMe<sub>3</sub>)Ir fragment and aldehyde products. While acyl hydride complexes **7a-c** were found to exhibit varying degrees of thermal stability, they gave complex mixtures of products, which by <sup>1</sup>H NMR analysis in each case included at least some of the carbonyl derivative Cp\*Ir(PMe<sub>3</sub>)(CO) (**8**). This pathway, which involved the unusual overall elimination of R-H across the Ir-C linkage, was especially evident in the case of the formyl hydride **7c**. In C<sub>6</sub>D<sub>6</sub> solution, the parent formyl complex **7c** underwent clean conversion to **8** via the apparent elimination of dihydrogen upon heating for 21 h at 45 °C (Scheme 5).

We considered the possibility that the targeted methoxycarbonyl hydride **10** might actually be an intermediate in the formation of **8** from **2** and dimethyl carbonate, but that this intermediate was unstable, undergoing an

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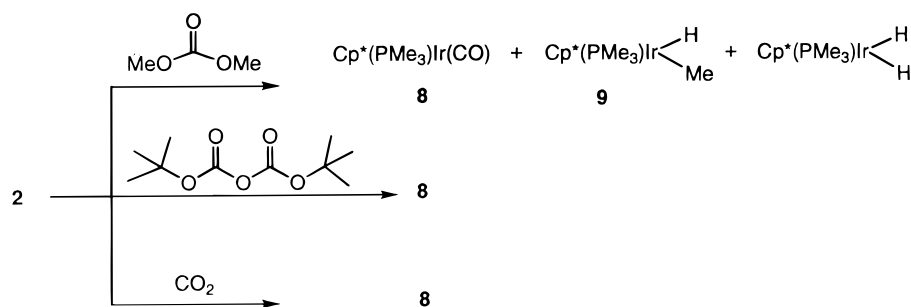
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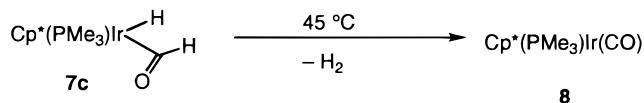
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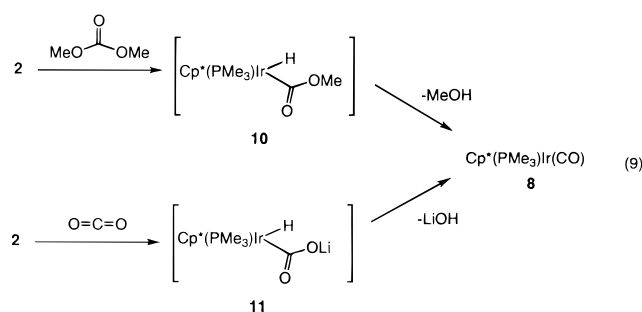
## Scheme 4



## Scheme 5



elimination similar to that observed in the thermolyses of **7a–c** (eq 9). We therefore attempted to observe this



intermediate in a low-temperature NMR experiment. A solution of **2** in toluene- $d_8$  was frozen in liquid nitrogen, and 2 equiv of dimethyl carbonate was transferred into the tube in vacuo. After warming the tube to  $-78\text{ }^\circ\text{C}$ , it was placed in an NMR probe at  $-66\text{ }^\circ\text{C}$  and a  $^1\text{H}$  NMR spectrum was recorded. No reaction was observed at this temperature. Gradual warming of the tube did not produce an observable reaction until it reached  $0\text{ }^\circ\text{C}$ . After 5 min at  $10\text{ }^\circ\text{C}$ , approximately 35% conversion to **8** and **9** was observed *without the detection of any intermediate species*. In a similar vein, we attempted direct observation of the postulated lithium salt of the iridium carboxylate hydride **11** formed by the reaction of **2** with carbon dioxide (eq 9). In this experiment,  $\text{CO}_2$  was condensed into an NMR tube containing a frozen toluene solution of **2**. After warming to  $-78\text{ }^\circ\text{C}$  for 5 min, the tube was placed in the NMR probe at  $-66\text{ }^\circ\text{C}$  and the  $^1\text{H}$  NMR spectrum was recorded. At this temperature, however, complete reaction to **8** had already occurred. If iridium acyl derivatives are intermediates in these reactions, these results require that they are formed in a rate-limiting step and rapidly decompose to **8**.

Two possible mechanisms that would account for these elimination reactions are illustrated in Scheme 6. In mechanism **a**, phosphine loss would generate a transient 16-electron  $\text{Cp}^*\text{Ir}(\text{COR})(\text{H})$  complex which undergoes subsequent CO deinsertion,<sup>73–78</sup> RH reductive elimination, and phosphine recoordination to give

the observed products. A similar mechanism has been proposed to account for reactions involving decarbonylation of aldehydes by Rh(I) and Ir(I) complexes.<sup>69,71</sup> In mechanism **b**, the acyl hydride complex undergoes a simple concerted elimination to provide the observed products. While the stepwise mechanism has precedent for late-metal systems, we believe that it can be ruled out in the present cases for two reasons. Previous studies of RH reductive eliminations from  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{R})(\text{H})$  conducted within our group have shown that  $\text{PMe}_3$  loss is not a thermally facile process.<sup>79</sup> Even if acyl-for-alkyl substitution facilitated phosphine loss, the different acyl substituents would not be expected to lead to the *range* of thermal stabilities observed in the present work. In addition, reductive elimination of RH from  $\text{Cp}^*(\text{CO})\text{Ir}(\text{R})(\text{H})$  would generate the 16e  $\text{Cp}^*\text{Ir}(\text{CO})$  fragment and would be expected to lead to C–H activation of the solvent, an outcome that was not observed.<sup>80</sup>

In contrast, support for the concerted elimination mechanism can be obtained by examining the relative rates for the elimination process. In theoretical studies of reductive elimination reactions from platinum phosphine complexes, Goddard and Low rationalized the relative rates of reductive elimination of X–Y ( $\text{X–Y} = \text{H–H} > \text{CH}_3\text{–H} > \text{CH}_3\text{–CH}_3$ ) on the basis of the spherical symmetry of the H 1s valence orbital, which can allow it to simultaneously form H–H and C–H bonds while breaking M–H bonds.<sup>81,82</sup> However, the directionality of the carbon  $\text{sp}^3$  hybrid requires that it adopt different orientations for the M–C and C–C or C–H bonds such that “in the transition state a compromise must be reached that is not optimal for either bond”. This concept of bond directionality can also be used to explain the relative ordering of elimination rates ( $\text{R} = \text{OCH}_3 \sim \text{OLi}$  (presumed; see below)  $> \text{H} \gg \text{Ph} > \text{tert-Bu}$ ) described above. The directionality of the  $\text{sp}^3$ -hybridized carbon of the *tert*-butyl group attached to the

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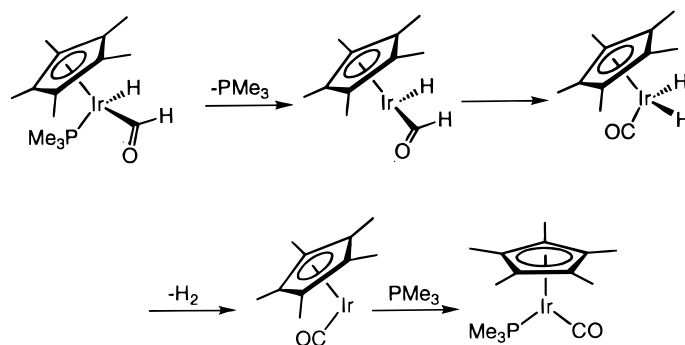
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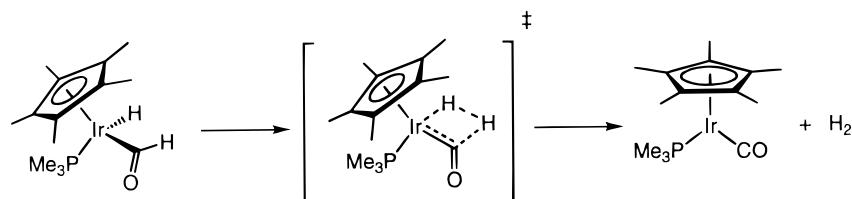
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Scheme 6

mechanism a:



mechanism b:



carbonyl carbon atom (as well as its steric bulk in an already sterically encumbered ligand sphere) would require that it undergo significant reorientation to achieve bonding with the hydride in the elimination transition state, thereby leading to low rates of elimination. The phenyl group, however, bonds to the acyl carbon via an  $sp^2$  hybrid and can utilize its unhybridized p orbital in transition-state bonding with the hydride and would be expected to demonstrate a reduced barrier to  $\alpha$ -elimination relative to alkyl derivatives. Following a similar argument for the formyl hydride complex **7c**, the spherically symmetric 1s orbital of the acyl-bound hydrogen would be anticipated to facilitate transition-state interactions and cause a further lowering of the activation barrier. Finally, our inability to directly observe alkoxy carbonyl and lithium carboxylate hydrides **10** and **11** could be rationalized on the basis of the ease with which the oxygen nonbonding pairs can interact with the hydride with minimal disruption of bonding to the acyl carbon, leading to even faster elimination rates.<sup>83,84</sup> We cannot, however, rule out the intervention of  $\eta^2$ -aldehyde or  $\eta^2$ -arene complexes.<sup>64,85</sup> Given the importance of acyl hydrides in numerous industrial processes, it would be interesting to determine the scope of this postulated mechanism as it relates to other metal complexes.

**Fluorocarbons: C–F Bond Activation.** The chemistry of perfluoroalkyl and perfluorovinyl transition metal complexes has long been of interest due to the

vastly different chemical properties observed in these complexes in comparison to their protioalkyl analogues.<sup>86–93</sup> Vinyl fluorides are normally quite inert, but in some cases undergo substitution reactions with strongly nucleophilic agents via addition–elimination mechanisms to afford substituted vinyl derivatives.<sup>94</sup> The reactivity we observed in nucleophilic substitution at carbon–oxygen multiple bonds prompted us to investigate the possibility of substitution at activated carbon–carbon multiple bonds, especially those that might lead to overall C–F activation reactions.

Complex **2** underwent a clean instantaneous reaction with hexafluorobenzene to generate the pentafluorophenyl iridium hydride complex **12** in 74% yield (Scheme 7). Complex **12** was purified by column chromatography and recrystallization. Analysis of **12** by  $^{19}\text{F}$  NMR spectroscopy showed five inequivalent fluorine nuclei indicating slow rotation about the iridium–phenyl bond on the time scale of the NMR measurement. Complex **12** was found to be extremely stable, undergoing no detectable decomposition upon heating for 20 h at 195 °C. Reaction of **2** was also observed with fluorobenzene, albeit much more slowly than with perfluorobenzene, to give the known compound  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Ph})(\text{H})$  (**13**) in 20% NMR yield along with **1**.<sup>95</sup>

(83) Preliminary studies of the perfluoroacyl hydride complex  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{COC}_3\text{F}_7)(\text{H})$  indicate that it undergoes  $\alpha$ -elimination at a temperature intermediate between that of the formyl and phenacyl complexes **7c** and **7b**. This observation is consistent with a concerted mechanism on the basis of the increased s-character on carbon fragments bearing strongly electron-withdrawing substituents (see following reference).

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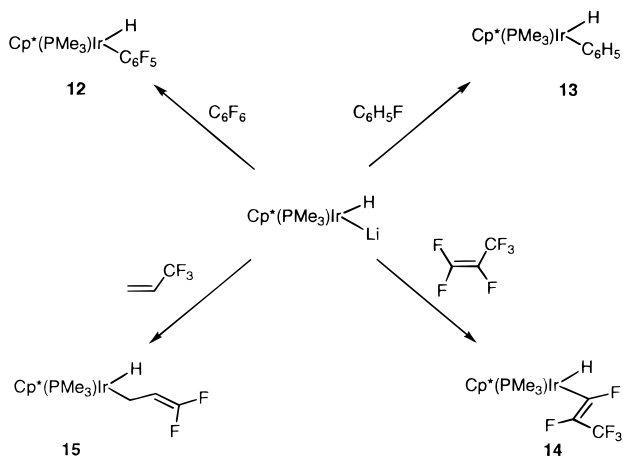
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(95) The slow rate observed for the reaction of **2** with fluorobenzene allowed for significant decomposition of **2** to the dihydride complex **1**, the major product of the reaction.

Scheme 7



When  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  was treated with  $\text{CF}_2=\text{CF}_2$  in benzene solution at ambient temperature, an immediate reaction occurred to provide numerous products. In contrast, reaction of **2** with hexafluoropropene occurred cleanly to give the perfluoropropenyl complex **14** in 78% yield. Complex **14** showed  $^1\text{H}$  NMR resonances at 1.76, 1.12, and  $-17.01$  with coupling constants supporting a trans orientation of the trifluoromethyl group with respect to the iridium center. The iridate was also found to react with 3,3,3-trifluoropropene to give  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CH}_2\text{CH}=\text{CF}_2)$  (**15**). The identity of this reaction product was readily deduced from the one-proton dddd signal located at 4.56 ppm in its  $^1\text{H}$  NMR spectrum and its characteristic resonances in the  $^{19}\text{F}$  NMR spectrum. Unfortunately, attempts to isolate **15** from unreacted dihydride by crystallization or column chromatography were unsuccessful. Further, attempts to derivatize **15** by conversion to its chloride with  $\text{CCl}_4$  to facilitate purification resulted in decomposition to unknown products. The perfluoropropenyl and difluoroallyl hydrides were found to be thermally stable, the former undergoing no detectable decomposition upon heating in benzene solution at  $160^\circ\text{C}$  for 60 h and the latter showing no signs of reaction after heating for 48 h at  $75^\circ\text{C}$ . Photolysis of the perfluoropropenyl hydride (**14**) for 12 h in  $\text{C}_6\text{D}_6$  solution resulted in 30% conversion to **13-d<sub>6</sub>**.

We believe that reactions of **2** with unsaturated fluorocarbons proceed via addition–elimination mechanisms involving carbanionic intermediates. The relative rates of the above reactions and regiochemistry observed in the reaction products are consistent with this mechanism. The mechanism is illustrated in Scheme 8 and involves the addition of **2** to the double bond of the fluoroolefin (e.g., hexafluoropropene) to give intermediate **16** followed by the elimination of  $\text{LiF}$  to give the observed products. For the reactions of hexafluorobenzene, fluorobenzene, and tetrafluoroethylene with **2**, attack at any reactive position in the molecule gives the same intermediate. However, for reactions of **2** with hexafluoropropene and 1,1,1-trifluoropropene, the observed products are consistent with only one regiochemistry of addition. This attack occurs at the least hindered carbon atom, giving the most highly substituted carbanionic intermediate. Nucleophilic additions to fluoroolefins have been studied extensively by a number of investigators, and this regiochemistry of addition has

been postulated to be favorable due to the better ability of a fluoroalkyl substituent to stabilize a negative charge compared with that of a fluorine atom. In the reaction with 1,1,1-trifluoropropene, the only possible mode of elimination occurs at the 3-position to give the  $\eta^1$ -difluoroallyl complex. However, in the reaction with hexafluoropropene, elimination can occur at either the 1- or the 3-position, with elimination at the 1-position being exclusively observed, leading to the vinyl derivative. In contrast, complex **2** was found to be completely unreactive toward (trifluoromethyl)cyclohexane and  $\alpha,\alpha,\alpha$ -trifluorotoluene, supporting the proposed addition–elimination mechanism.

## Summary

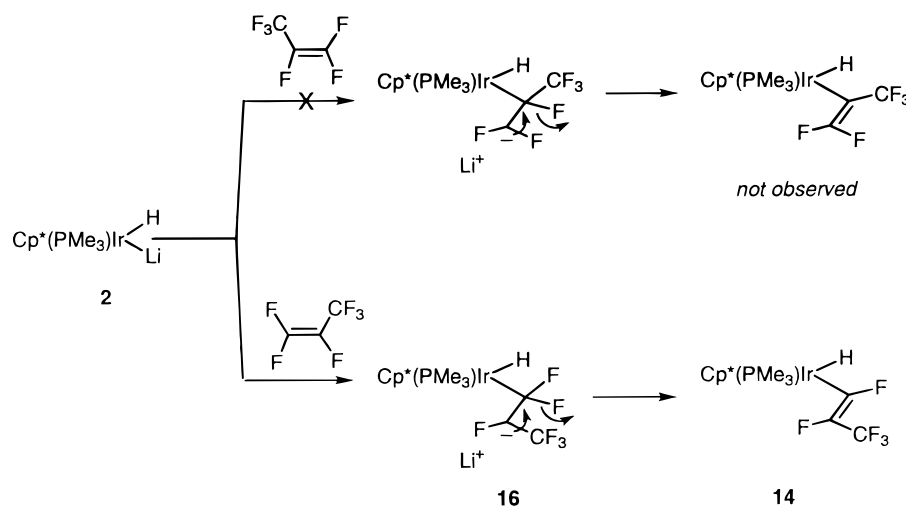
This paper has outlined the preparation, solution characterization, and reactivity of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  (**2**). This complex can be prepared by deprotonation of  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  with only the most basic reagents, and we have estimated the  $\text{p}K_1$  for the dihydride to be in the range 38–41. In aromatic solvents, **2** appears to be highly aggregated, giving complex spectra, but it reacts cleanly with a number of electrophilic agents, leading to the formation of novel stannyl, boryl, fluorocarbyl, and acyl hydrides. The latter have been shown to decompose thermally via reductive  $\alpha$ -elimination, and we have proposed a concerted mechanism to account for the observed products. We are currently pursuing the  $\alpha$ -elimination as a synthetic method directed toward generating novel complexes of iridium with compounds of aluminum, magnesium and other Lewis acidic elements.

## Experimental Section

**General Comments.** Unless indicated otherwise, all manipulations were conducted in a Vacuum Atmospheres 553-2 drybox containing nitrogen purified by a MO-40-2 Dritrain or on vacuum lines using standard Schlenk techniques.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{19}\text{F}$ ,  $^7\text{Li}$ , and  $^{11}\text{B}$  NMR spectra were obtained at the University of California, Berkeley (UCB), NMR facility on Bruker AMX series 300 and 400 MHz spectrometers. Infrared spectra were obtained in KBr matrixes on a Mattson Galaxy series FT-IR 3000 spectrometer and are referenced to a polystyrene standard. Elemental analyses were performed at the UCB Microanalytical Laboratory. Mass spectrometric analyses were conducted at the UCB Mass Spectrometry Facility on Kratos MS-50 and AEI MS-12 mass spectrometers.

NMR spectra were obtained in Wilmad series 505-PP tubes. Flame-sealing of NMR tubes was effected under vacuum by connection of the tube to a Kontes stopcock equipped with a ground glass joint and connected via a Cajon Ultratorr adapter. Known-volume gas transfers were conducted with calibrated glass vessels with pressure measurements determined by an MKS Baratron gauge attached to a high-vacuum line. Pentane, hexanes, benzene, toluene, diethyl ether, and tetrahydrofuran and their deuterated analogues were distilled under nitrogen from sodium benzophenone ketyl prior to use. Methylene chloride, chloroform, carbon tetrachloride, acetonitrile, and boron trifluoride-etherate were distilled from calcium hydride. *tert*-Butyllithium (Aldrich) was obtained as a solution and was filtered, concentrated in vacuo, and recrystallized from pentane prior to use. All other reagents and solvents were obtained from commercial suppliers and were degassed (liquids) and used as received unless otherwise noted.  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  was prepared by known literature methods.<sup>96</sup>

## Scheme 8



**$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  (2).** In a typical procedure,  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (100 mg, 0.25 mmol) was dissolved in 5 mL of  $\text{C}_6\text{H}_6$ , and a solution of *tert*-butyllithium (16 mg, 0.25 mmol) in  $\text{C}_6\text{H}_6$  (1 mL) was added via pipet. After allowing the solution to stir for 15 min at ambient temperature, the volatile materials were removed in vacuo to give a yellow oil. Trituration with a small amount of pentane and washing of the resulting solid with additional pentane provided  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Li})(\text{H})$  as a yellow microcrystalline solid free from residual  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ . Complex 2 could also be generated as described above and manipulated as a solution without its isolation.  $^1\text{H}$  NMR analysis of these solutions indicated yields typically exceeding 80%, with small amounts of residual dihydride present. Alternatively, the oil thus obtained could be treated with an ethereal solvent (e.g., THF or DME) to generate an adduct that was sparingly soluble in that solvent. Filtration of the solid adduct and washing with benzene produced a yellow microcrystalline solid that was stable for weeks at  $-30^\circ\text{C}$ .  $^1\text{H}$  NMR (THF- $d_6$ ):  $\delta$  2.08 (s, 15 H), 1.27 (9 H, d, 10 Hz),  $-19.16$  (d,  $J_{\text{H-P}} = 28.3$  Hz) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_6$ ):  $\delta$   $-43.17$  ppm.  $^7\text{Li}$  NMR (THF- $d_6$ ):  $\delta$   $-7.32$  ppm. MS (EI):  $m/z$  404 (M -  $\text{Li}^+$ ).

**$\text{Cp}^*(\text{PMe}_3)\text{IrD}_2$  (1- $d_2$ ).** In a glass reaction vessel equipped with a vacuum stopcock was placed  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (100 mg, 0.25 mmol), 100 mg of dry silica gel, and a stir bar. The vessel was evacuated on a Schlenk manifold, and degassed EtOD (3 mL) was added via vacuum transfer. After warming to ambient temperature, the resulting slurry was stirred for 16 h. The volatile materials were then removed in vacuo, and a second 3 mL portion of EtOD was added via vacuum transfer. After stirring for an additional 16 h, the reaction mixture was pumped to dryness and taken into a glovebox. The crude reaction product was suspended in pentane (5 mL) and was filtered through Celite. The tan-colored supernatant was concentrated in vacuo to afford 90 mg of an off-white solid. Analysis of the solid by a single-pulse  $^1\text{H}$  NMR experiment showed  $\text{Cp}^*(\text{PMe}_3)\text{IrD}_2$  as the sole product in 90% yield with greater than 93% deuterium incorporation based upon integration.

**Determination of the Kinetic Deprotonation Site in  $\text{Cp}^*(\text{PMe}_3)\text{IrD}_2$ .** A solid mixture of  $\text{Cp}^*(\text{PMe}_3)\text{IrD}_2$  (10 mg, 0.025 mmol) and *crystallized tert*-butyllithium (2.0 mg, 0.031 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (2 mL) at ambient temperature. The bright yellow solution was then quenched with acetone (70 mL), and the pale yellow solution was analyzed for isobutane by GC/MS spectrometry. GC/MS analysis revealed the presence of isobutane with greater than 90% deuterium incorporation.

**(*E*)-1,2-Dideuterio-3,3-dimethyl-1-butene.** In a Parr high-pressure reactor was placed a solution of 3,3-dimethylbutyne (5.00 g, 60.9 mmol) and quinoline (300 mL, 2.5 mmol) in toluene (15 mL). The solution was charged with 100 mg of 5% Pd on carbon (deactivated with  $\text{Pb}(\text{OAc})_2$ ), and the reactor was pressurized to 200 psi with  $\text{D}_2$  and then vented. After repeating the pressurization/vent procedure a second time, the reactor was pressurized to 260 psi and was maintained at ambient temperature for 90 min. The Parr reactor was then vented, and the crude reaction mixture was filtered through Celite. The filtrate was subjected to distillation at atmospheric pressure through a 10 cm Vigreux column. (*E*)-1,2-Dideuterio-3,3-dimethyl-1-butene (2.66 g) was collected (bp  $42-44^\circ\text{C}$ ) in an ice-cooled glass reaction vessel equipped with a vacuum stopcock. Analysis of the product by  $^1\text{H}$  NMR spectroscopy demonstrated greater than 90% purity with no detectable hydrogen atoms in the 1-(*E*)- or 2-positions.  $^2\text{H}$  NMR analysis indicated detectable deuterium incorporation (approximately 40%) in the 1-(*Z*)-position.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.92 (br s, 0.6 H), 1.00 (s, 9 H) ppm.  $^2\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  5.81, 4.92, 4.81 ppm. Lit.<sup>30</sup>  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.91 (s), 0.95 (s).

**3,3-Dimethyl-1-butanol-1,2-*syn-d*<sub>2</sub>.** 3,3-Dimethyl-1-butanol-1,2-*syn-d*<sub>2</sub> was prepared following a modified procedure of Bergbreiter and Rainville.<sup>97</sup> In an oven-dried 100 mL round-bottom flask was placed 40 mL of freshly distilled THF and a magnetic stir bar. The flask was fitted with a septum and purged with nitrogen for 5 min. (*E*)-1,2-Dideuterio-3,3-dimethyl-1-butene (3.06 mL) was added via syringe, and the stirred solution was cooled to  $0^\circ\text{C}$  under nitrogen. Borane-THF complex (9.3 mL of a 1 M solution in THF) was added dropwise via syringe over a 3 min period. The solution was stirred for 40 min at  $0^\circ\text{C}$  and 4 h at room temperature. Methanol (1.15 mL) was then added, and the solution was recooled to  $0^\circ\text{C}$ . The solution was then treated with 2.55 mL of 3 N aqueous NaOH solution and 2.8 mL of 30%  $\text{H}_2\text{O}_2$  solution in succession. After refluxing for 1 h, the reaction mixture was partitioned between 100 mL of ice/water and 50 mL of  $\text{Et}_2\text{O}$ . The ethereal layer was separated, and the aqueous phase was washed with four 50 mL portions of  $\text{Et}_2\text{O}$ . The combined ethereal extracts were washed with two 20 mL portions of saturated aqueous sodium thiosulfate, and the thiosulfate extracts were extracted with  $\text{Et}_2\text{O}$ . After drying the combined ethereal extracts over  $\text{MgSO}_4$ , the solvent was removed by distillation through a Vigreux column and the residue was short-path distilled (bp  $140^\circ\text{C}$ , lit.<sup>97</sup> bp  $140-145^\circ\text{C}$ ) to provide 1.80 g of pure 3,3-dimethyl-1-butanol-1,2-*syn-d*<sub>2</sub> in 74% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.63 (m, 0.7 H), 1.45 (br d, 1 H), 0.89 (s, 9 H) ppm.  $^1\text{H}\{^2\text{H}\}$  NMR lit.<sup>97</sup> ( $\text{CDCl}_3$ ):  $\delta$  3.65

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(d 1 H), 3.47 (s, 1 H), 1.49 (d 1 H), 0.93 (s, 9 H) ppm. MS (EI): *m/z* 104.06 (M<sup>+</sup>, 100), 105.06 (M + 1, 29.46).

**3,3-Dimethylbutane-1-trifluoromethanesulfonate-1,2-syn-d<sub>2</sub> (3-syn-d<sub>2</sub>).** 3,3-Dimethylbutane-1-trifluoromethanesulfonate-1,2-syn-d<sub>2</sub> was prepared according to the method of Baum for organic triflates.<sup>98</sup> In a 25 mL round-bottom flask was placed CH<sub>2</sub>Cl<sub>2</sub> (10 mL), 3,3-dimethyl-1-butanol-1,2-syn-d<sub>2</sub> (200 mg, 1.92 mmol), and pyridine (155 mL, 1.92 mmol). The flask was fitted with a septum and was purged with N<sub>2</sub> for 10 min. The stirred solution was cooled to 0 °C and was treated with triflic anhydride (380 mL, 2.25 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min. The crude mixture was then poured into a separatory funnel, diluted with 10 mL of pentane, and washed with three 10 mL portions of saturated aqueous sodium bicarbonate and a 10 mL portion of saturated aqueous sodium chloride. The organic layer was then dried over MgSO<sub>4</sub> and concentrated in vacuo to afford 249 mg of a pale yellow oil. Analysis of the product by <sup>1</sup>H NMR spectroscopy indicated formation of the desired product in 55% yield. The triflate shows signs of decomposition to unknown products upon concentration and therefore could not be purified. However, it can be stored indefinitely at -78 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.56 (br d, 0.7 H), 1.74 (br d, 1 H), 0.95 (s, 9 H) ppm.

**Cp\*(PMe<sub>3</sub>)Ir[1-(3,3-dimethyl)butyl]Br.** The undeuterated bromide was prepared for determination of the coupling constants in the NMR analysis. As described in the text, the analysis of the deuterated complex was carried out for the chloride (**4b**). A solution of **2** was prepared by dissolving Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> (114 mg, 0.281 mmol) in 20 mL of THF and adding *tert*-butyllithium (0.28 mmol, 1.7 M/Et<sub>2</sub>O, 165 μL) via syringe. After stirring for 30 min **3** (68 mg, 0.290 mmol) was added via syringe. The resulting reaction mixture was stirred for 30 min and the volatile materials removed under vacuum. The reaction mixture was extracted with toluene (10 mL) and then filtered via filterstick cannula. The filtrate was treated with 200 μL of CHBr<sub>3</sub>, producing an immediate color change from gold to bright orange. After stirring for 1 h the volatile materials were removed under vacuum. The crude product was dissolved in diethyl ether and purified by chromatography through a 1 × 25 cm silica gel column. The leading orange band (15 mL fraction) was collected and solvent volume reduced under vacuum. The bromide was then chromatographed again using pentane as the eluent. The leading orange band was collected (10 mL fraction), and the volatile materials were removed in a vacuum to yield an orange microcrystalline product. The product was crystallized from pentane and dried in vacuo to afford Cp\*(PMe<sub>3</sub>)Ir[1-(3,3-dimethyl)butyl]Br in 37% yield. Mp: 129.5–131 °C. IR (NaCl): 2946, 2928, 2909, 2861, 1462, 1418, 1376, 1359, 1300, 1280, 1143, 1028, 953, 851, 831, 812, 730, 703, 677, 572 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.27 (dddd, *J*<sub>H-H</sub> = 4.8 Hz, *J*<sub>H-H</sub> = 10.6 Hz, *J*<sub>H-H</sub> = 13.6 Hz, *J*<sub>H-P</sub> = 4.8 Hz, 1H), 1.70 (d, *J*<sub>H-P</sub> = 2.0 Hz, 15 H), 1.53 (d, *J*<sub>H-P</sub> = 10.0 Hz 9H), 1.44 (dddd, *J*<sub>H-H</sub> = 4.4 Hz, *J*<sub>H-H</sub> = 10.7 Hz, *J*<sub>H-H</sub> = 13.9 Hz, *J*<sub>H-P</sub> = 4.8 Hz, 1H), 1.19 (ddd, *J*<sub>H-H</sub> = 4.9 Hz, *J*<sub>H-H</sub> = 13.6 Hz, *J*<sub>H-H</sub> = 13.6 Hz, 1H), 1.11 (ddd, *J*<sub>H-H</sub> = 4.9 Hz, *J*<sub>H-H</sub> = 13.5 Hz, *J*<sub>H-H</sub> = 13.5 Hz, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 92.0 (C) 52.5 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 30.2 (CH<sub>3</sub>), 15.3 (CH<sub>3</sub>, *J*<sub>P-C</sub> = 37.0 Hz), 9.3 (CH<sub>3</sub>), -3.4 (C) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 39.3 ppm. MS (EI): *m/z* 568 (M<sup>+</sup>). HRMS calcd for C<sub>19</sub>H<sub>37</sub>IrPBr: 568.143390. Found: 568.144568.

**4c-anti-d<sub>2</sub>.** A solution of **2** was prepared by dissolving a solid mixture of Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> (50 mg, 0.123 mmol) and *tert*-butyllithium (8 mg, 0.125 mmol) in C<sub>6</sub>H<sub>6</sub> (8 mL). After stirring for 15 min at ambient temperature, the Cp\*(PMe<sub>3</sub>)Ir(Li)(H) solution was evaporated to dryness and dissolved in 10 mL of THF. A solution of **3-syn-d<sub>2</sub>** (30 mg, 0.127 mmol) in THF (3 mL) was added to the iridate solution, and the resulting yellow

mixture was stirred at ambient temperature for 15 min. The volatile materials were removed in vacuo, and the brown residue was dissolved in C<sub>6</sub>H<sub>6</sub> (5 mL). To the benzene solution was added CCl<sub>4</sub> (100 mg, 0.65 mmol), and the resulting mixture was stirred for 2 h at ambient temperature. After removal of the volatile materials under vacuum, the crude chloride was chromatographed on a 10 mm × 200 mm silica gel column employing 25% diethyl ether in pentane as the eluent. The leading yellow band was collected and evaporated to dryness to give 16 mg of **4c-anti-d<sub>2</sub>** in 24% isolated yield. <sup>1</sup>H{<sup>2</sup>H} NMR (CDCl<sub>3</sub>): δ 2.38 (dd, *J*<sub>H-P</sub> = 3.9 Hz, *J*<sub>H-H</sub> = 14.1 Hz, 0.5 H), 1.71 (dd, *J*<sub>H-P</sub> = 5.3 Hz, *J*<sub>H-H</sub> = 14.1 Hz, 0.5 H), 1.50 (d, *J*<sub>H-P</sub> = 1.8 Hz, 15 H), 1.28 (d, *J*<sub>H-P</sub> = 10.2 Hz, 9 H) (the diastereotopic β-protons were partially obscured by the PMe<sub>3</sub> resonance in CDCl<sub>3</sub> solvent). <sup>2</sup>H NMR (CDCl<sub>3</sub>): δ 2.36 (br s), 1.66 (br s), 1.34 (br s), 1.27 (br s) ppm.

**Reaction of 2 with H<sub>2</sub> and D<sub>2</sub>.** A solution of **2** (10 mg, 0.025 mmol) in C<sub>6</sub>D<sub>6</sub> (0.55 mL) was placed in a J. Young NMR tube. The solution was frozen in liquid N<sub>2</sub>, evacuated under full vacuum, and pressurized with 720 Torr of hydrogen gas. The tube was sealed, thawed, and maintained at room temperature for 45 min. Analysis of the solution by <sup>1</sup>H NMR indicated no reaction had occurred. The tube was then heated at 45 °C for 18 h, during which the formation of a fine white precipitate was observed. Analysis of the tube contents at this time indicated complete and clean conversion to Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> (**1**). The reaction of Cp\*(PMe<sub>3</sub>)Ir(Li)(H) with deuterium gas was effected analogously to the reaction with hydrogen as described above. After 18 h at 45 °C, the tube contents were analyzed by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum indicated the presence of a statistical mixture of Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub>, Cp\*(PMe<sub>3</sub>)Ir(H)(D), and Cp\*(PMe<sub>3</sub>)IrD<sub>2</sub> along with approximately 20% unreacted **2**. Removal of the volatile materials in vacuo and dissolution in C<sub>6</sub>H<sub>6</sub> with addition of 5 mL of C<sub>6</sub>D<sub>6</sub> as an internal standard allowed for quantitative analysis of the <sup>2</sup>H NMR spectrum. This spectrum indicated that deuterium incorporation had occurred exclusively at the hydride position of **1** with the extent of conversion from **2** being 80%.

**Reactions of 2 with Carbon Acids.** In a typical reaction, a solution of **2** (8–15 mmol) in 0.5 mL of THF-*d*<sub>8</sub> was placed in an NMR tube. Subsequently, a solution of a carbon acid (diphenylmethane, DMSO, or CH<sub>3</sub>CN, 2–16 equiv) in THF-*d*<sub>8</sub> was added via syringe. Analysis of the <sup>1</sup>H NMR spectrum indicated complete conversion of **2** to Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub>.

**Reaction of 1 with Benzylpotassium.** Benzylpotassium (6.7 mg, 52 mmol) was suspended in C<sub>6</sub>D<sub>6</sub> (200 mL), and THF-*d*<sub>8</sub> (100 mL) was added to effect dissolution. To this solution was added a solution of **1** (21 mg, 52 mmol) in C<sub>6</sub>D<sub>6</sub> (800 mL). A 360 mL aliquot of the red-orange solution was transferred to an NMR tube and analyzed by <sup>1</sup>H NMR and <sup>31</sup>P NMR spectroscopy. The spectrum showed a 90:10 ratio of Cp\*(PMe<sub>3</sub>)Ir(K)(H) and **1** based upon average integrations of the Cp\*, PMe<sub>3</sub>, and hydride resonances. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>-THF-*d*<sub>8</sub>): δ 2.17 (s, 15 H), 1.49 (d, *J*<sub>H-P</sub> = 8.0 Hz, 9 H), -19.0 (d, *J*<sub>H-P</sub> = 30.7 Hz, 1 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>-THF-*d*<sub>8</sub>): δ -63.4 ppm.

**Reaction of 1 with Benzyl lithium.** To a solution of **1** (14 mg, 35 mmol) in 0.5 mL C<sub>6</sub>D<sub>6</sub> was added benzyl lithium·2THF<sup>99</sup> (7.3 mg, 31 mmol). The yellow solution was placed in an NMR tube, and the contents were subjected to <sup>1</sup>H NMR analysis. The <sup>1</sup>H NMR spectrum showed complete conversion of benzyl lithium to toluene and **2** as a mixture of oligomers.

**Cp\*(PMe<sub>3</sub>)Ir(SnPh<sub>3</sub>)(H) (5a).** A solution was prepared by dissolving **2** (76.8 mg isolated as a solid, 187 mmol) in THF (4 mL). To this solution was added, with vigorous stirring, a solution of Ph<sub>3</sub>SnCl (65 mg, 169 mmol) in THF (2 mL). After 1 h at ambient temperature, the solvent was removed in vacuo, and the resulting yellow oil was dissolved in pentane (10 mL) and filtered through Celite. The pale yellow filtrate was concentrated in vacuo to a volume of 7 mL and was slowly

cooled to  $-40\text{ }^{\circ}\text{C}$  to produce fine clumps of a white crystalline material. The supernatant was decanted and the product was dried under vacuum to afford **5a** (89.4 mg) in 71% yield. IR (KBr): 3054, 2854, 2114, 2096, 1425, 953, 702,  $461\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.95 (6 H, d,  $J_{\text{Sn-H}} = 36\text{ Hz}$ ), 7.28 (6 H, m), 7.20 (3 H, m), 1.77 (15 H, d,  $J_{\text{P-H}} = 1.9\text{ Hz}$ ), 1.12 (9 H, d,  $J_{\text{P-H}} = 9.8\text{ Hz}$ ),  $-17.40$  (1 H, d,  $J_{\text{P-H}} = 30.2\text{ Hz}$ ,  $J_{\text{Sn-H}} = 133\text{ Hz}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  147.3 (CH), 138.1 (CH,  $J_{\text{Sn-C}} = 35.2\text{ Hz}$ ), 127.8 (CH), 127.2 (C), 92.4 (C), 23.3 ( $\text{CH}_3$ , d,  $J_{\text{P-C}} = 38.3\text{ Hz}$ ), 10.99 ( $\text{CH}_3$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-54.6$  ( $J_{\text{Sn-P}} = 167\text{ Hz}$ ) ppm. MS (EI):  $m/z$  754 ( $\text{M}^+$ ). HRMS calcd for  $\text{C}_{31}\text{H}_{40}\text{P}\text{SnIr}$ : 754.151314. Found: 754.151705.

**$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{SnMe}_3)(\text{H})$  (**5b**).** To a solution of **1** (100 mg, 247  $\mu\text{mol}$ ) in  $\text{C}_6\text{H}_6$  (7 mL) was added a solution of *tert*-butyllithium (18 mg, 281  $\mu\text{mol}$ ) in  $\text{C}_6\text{D}_6$  (3 mL). The bright yellow solution was stirred at ambient temperature for 5 min and a solution of  $\text{Me}_3\text{SnCl}$  (56 mg, 281  $\mu\text{mol}$ ) in  $\text{C}_6\text{H}_6$  (2 mL) was added via pipet. Reaction was observed over a period of 20 min as indicated by a lightening of the yellow color concomitant with the precipitation of LiCl. The solution was filtered through Celite and concentrated in vacuo to afford 132 mg of a yellow-gold oil. Analysis of the crude product by  $^1\text{H}$  NMR spectroscopy indicated 91% conversion to **5b**. Multiple attempts to purify this material by recrystallization from pentane at  $-40\text{ }^{\circ}\text{C}$  were unsuccessful, as no solid material could be obtained. Attempts to purify the complex by chromatography on silica gel resulted in complete decomposition to **1**. IR (KBr): 2976, 2913, 2092, 1419, 950,  $489\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.90 (15 H, s), 1.29 (9 H, d,  $J_{\text{P-H}} = 10.0\text{ Hz}$ ), 0.53 (9 H, s,  $J_{\text{Sn-H}} = 37.8\text{ Hz}$ ),  $-18.08$  (1 H, d,  $J_{\text{P-H}} = 30\text{ Hz}$ ,  $J_{\text{Sn-H}} = 137\text{ Hz}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  92.2 (C), 23.4 ( $\text{CH}_3$ , d,  $J_{\text{P-C}} = 28.6\text{ Hz}$ ), 11.24 ( $\text{CH}_3$ ),  $-5.2$  ( $\text{CH}_3$ ,  $J_{\text{Sn-C}} = 187\text{ Hz}$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-51.2$  ( $J_{\text{Sn-P}} = 162\text{ Hz}$ ) ppm. MS (EI):  $m/z$  570 ( $\text{M}^+$ ). HRMS calcd for  $\text{C}_{16}\text{H}_{34}\text{P}\text{SnIr}$ : 570.104956. Found: 570.106435.

**$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{BF}_2)(\text{H})$  (**6a**).** A solid mixture of **1** (152 mg, 375  $\mu\text{mol}$ ) and *tert*-butyllithium (27.5 mg, 430  $\mu\text{mol}$ , 1.15 equiv) was dissolved in  $\text{C}_6\text{H}_6$  (5 mL). After stirring for 10 min at room temperature, a solution of boron trifluoride-etherate (108 mg, 124  $\mu\text{mol}$ , 2 equiv) in  $\text{C}_6\text{H}_6$  (2 mL) was added dropwise over a 2 min period. The solution became dark brown during the addition of the first equiv of boron reagent and lightened to a yellow color with the addition of the second equivalent. After stirring for 30 min at ambient temperature, the solution was filtered through Celite to remove  $\text{LiBF}_4$  and was concentrated in vacuo to afford a dark brown oil. The oil was dissolved in 1:1 hexanes–benzene (approximately 10 mL) and was refiltered through Celite to provide a pale yellow filtrate. Removal of the volatile materials under vacuum gave a pale yellow oil (119 mg) which slowly crystallized upon standing at room temperature.  $^1\text{H}$  NMR analysis of the oil showed it to be a mixture of **6a** and **1** in an 84:16 ratio. Recrystallization of the crude product from hexamethyldisiloxane ( $-40\text{ }^{\circ}\text{C}$ ) afforded 40 mg of **6a** as a white crystalline solid in a 23% yield containing approximately 10% **2** as an impurity. Mp:  $73\text{--}75\text{ }^{\circ}\text{C}$ . IR (KBr): 2972, 2906, 2088,  $954\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.95 (15 H, s), 1.29 (9 H, d,  $J_{\text{P-H}} = 9.9\text{ Hz}$ ),  $-17.45$  (1 H, dt,  $J_{\text{P-H}} = 27.0\text{ Hz}$ ,  $J_{\text{H-F}} = 12.0\text{ Hz}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  95.2 (C), 21.9 ( $\text{CH}_3$ , d,  $J_{\text{P-C}} = 38.9\text{ Hz}$ ), 10.5 ( $\text{CH}_3$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-42.6$  ppm.  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ): (22  $^{\circ}\text{C}$ )  $\delta$   $-29.6$  ppm (br d with unresolved coupling).  $^{19}\text{F}$  NMR ( $\text{C}_7\text{D}_8$ ) (90  $^{\circ}\text{C}$ ):  $\delta$   $-23.2$  ppm (q,  $J_{\text{B-F}} = 154.4\text{ Hz}$ ).  $^{11}\text{B}$  NMR ( $\text{C}_7\text{D}_8$ ) (22  $^{\circ}\text{C}$ ):  $\delta$  23.9 ppm (t,  $J_{\text{B-F}} = 159.6\text{ Hz}$ ) MS (EI):  $m/z$  454 ( $\text{M}^+$ ). HRMS calcd for  $\text{C}_{13}\text{H}_{25}\text{BF}_2\text{PIr}$ : 454.138443. Found: 454.138992.

**$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{BPh}_2)(\text{H})$  (**6b**).** **Method A. Reaction of **2** with  $\text{Ph}_2\text{BBr}$ .** A solid mixture of **1** (150 mg, 370  $\mu\text{mol}$ ) and *tert*-butyllithium (25 mg, 390  $\mu\text{mol}$ , 1.05 equiv) was dissolved in  $\text{C}_6\text{H}_6$  (10 mL). After stirring for 15 min at room temperature, a  $\text{C}_6\text{H}_6$  solution of  $\text{Ph}_2\text{BBr}$  (100 mg, 407  $\mu\text{mol}$ , 1.1 equiv) was added via pipet. After stirring for 1 h, the reaction mixture

was filtered through Celite and concentrated in vacuo. The crude product was then partitioned between pentane (2 mL) and  $\text{CH}_3\text{CN}$  (2 mL). The pentane layer was decanted and set aside, and the  $\text{CH}_3\text{CN}$  layer was extracted with a fresh portion of pentane. The extraction process was repeated a total of five times, and the pentane extracts were combined and concentrated under vacuum to afford a bright yellow oil.  $^1\text{H}$  NMR analysis of the oil showed it to be a mixture of **6b** and **1** in a 4:1 ratio. The oil was then dissolved in  $\text{C}_6\text{D}_6$  and titrated with portions of  $\text{CHBr}_3$  to convert **1** to  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{Br})$  and  $\text{Cp}^*(\text{PMe}_3)\text{IrBr}_2$ . The titration was monitored by  $^1\text{H}$  NMR spectroscopy to determine the extent of conversion of **1** to  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{Br})$  and  $\text{Cp}^*(\text{PMe}_3)\text{IrBr}_2$ . Complete conversion was observed after a total of 6.3 mL of  $\text{CHBr}_3$  had been added. The volatile materials were then removed under vacuum and the residue was extracted with pentane. The pentane extract was pumped to dryness, and the crude complex was twice recrystallized from  $\text{CH}_3\text{CN}$  to afford 40 mg of  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{BPh}_2)(\text{H})$  as a yellow crystalline solid. The purified yield for the procedure was calculated to be 24% based on recovered **1**, though  $^1\text{H}$  NMR analysis of the crude reaction product suggests that the product is formed in an approximate 80% yield in the reaction.

**Method B. Reaction of **2** with  $\text{Ph}_2\text{BOBPh}_2$ .** A solid mixture of **1** (90 mg, 220  $\mu\text{mol}$ ) and *tert*-butyllithium (18 mg, 280  $\mu\text{mol}$ , 1.25 equiv) was dissolved in  $\text{C}_6\text{H}_6$  (5 mL), and the resulting solution was stirred for 5 min at room temperature. A solution of  $\text{Ph}_2\text{BOBPh}_2$  (90 mg, 260  $\mu\text{mol}$ , 1.18 equiv) in  $\text{C}_6\text{H}_6$  (2 mL) was added dropwise over a 1 min period. After stirring for 30 min at ambient temperature, the crude reaction mixture was pumped to dryness and the residue was suspended in hexanes (5 mL) and filtered through Celite. The filtrate was then concentrated under vacuum to a volume of 2 mL, resulting in the precipitation of a white solid, and after a second filtration through Celite, the filtrate was pumped to dryness and the crude reaction product was recrystallized from  $\text{CH}_3\text{CN}$  (1.5 mL) to afford pure **6b** (40 mg) as a bright yellow crystalline solid in 32% yield (first crop). Analysis of the crude product by  $^1\text{H}$  NMR spectroscopy indicated unisolated yields are greater than 90%. IR (KBr): 2971, 2904, 2088, 1297, 952,  $701\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.66 (d, 4 H), 7.34 (t, 4 H), 7.25 (t, 2 H), 1.77 (15 H, s), 1.02 (9 H, d,  $J_{\text{P-H}} = 9.6\text{ Hz}$ ),  $-16.53$  (1 H, d,  $J_{\text{P-H}} = 32.8\text{ Hz}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  161.2, 133.9, 127.4, 126.6, 95.3, 22.0 ppm (d,  $J_{\text{C-P}} = 38.5\text{ Hz}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-42.6$  ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  93 ppm (v. broad) Anal. Calcd for  $\text{C}_{25}\text{H}_{35}\text{BPIr}$ : C, 52.72; H, 6.19. Found: C, 52.73; H, 6.28.

**$\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{CO}^i\text{Bu})(\text{H})$  (**7a**).** To a stirred suspension of **2** (104 mg, 252  $\mu\text{mol}$ ) in THF (10 mL) at room temperature was added a solution of pivalic anhydride (47 mg, 252  $\mu\text{mol}$ ) in THF (5 mL). Within 5 min, the solution had become homogeneous, turning from bright yellow to yellow-gold in color. After continued stirring for 1 h, the volatile materials were removed under vacuum, and the crude product was extracted into pentane. The pentane extract was filtered through Celite and concentrated in vacuo to afford a golden yellow oil. Analysis by  $^1\text{H}$  NMR spectroscopy indicated an 83% yield of **7a** with **1** as a minor impurity. The crude product was purified by column chromatography on alumina III employing 10%  $\text{Et}_2\text{O}$  in pentane as the eluent. The product eluted as a yellow band, which was collected, pumped to dryness, and recrystallized from pentane ( $-40\text{ }^{\circ}\text{C}$ ). The recrystallization provided pure **7a** as very large ( $>20\text{ mg}$ ) yellow blocklike crystals. IR (KBr): 2085,  $1574\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.82 (15 H, s), 1.28 (9 H, s), 1.19 (9 H, d,  $J_{\text{P-H}} = 10.3\text{ Hz}$ ),  $-17.02$  (1 H, d,  $J_{\text{P-H}} = 34.8\text{ Hz}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  233.1 (C, d,  $J_{\text{P-C}} = 10.5\text{ Hz}$ ), 94.0 (C), 29.5 (C), 19.6 ( $\text{CH}_3$ , d,  $J_{\text{P-C}} = 37.6\text{ Hz}$ ), 10.8 ( $\text{CH}_3$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-35.5$  ppm. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{OPIr}$ : C, 44.20; H, 7.00. Found: C, 44.21; H, 7.24.

**Cp\*(PMe<sub>3</sub>)Ir(COPh)(H) (7b).** To a vigorously stirred suspension of **2** (80 mg, 195 mmol) in THF (10 mL) was added a solution of benzoic anhydride (44 mg, 195 mmol) in THF (5 mL). After stirring for 1 h at ambient temperature, the deep orange solution was concentrated in vacuo and the crude reaction product was dissolved in C<sub>6</sub>H<sub>6</sub> (5 mL). After filtration through Celite, the solvent was removed under vacuum to provide an orange oil. <sup>1</sup>H NMR analysis of the oil indicated a mixture of **7b** and **1** in a 5:1 ratio. The crude product was purified on a 4 cm alumina III column utilizing 25 mL of pentane (to elute the dihydride) followed by 10% Et<sub>2</sub>O in pentane to elute the phenacyl hydride. Concentration of the leading yellow band under vacuum provided a yellow oil, which was crystallized from hexamethyldisiloxane (−40 °C) to provide 45 mg of **7b** as a yellow crystalline solid. The yield after chromatography and recrystallization was 45%. IR (KBr): 2096, 1558 cm<sup>−1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.24 (2 H, d, J<sub>H-H</sub> = 7.2 Hz), 7.29 (2 H, m), 7.20 (1 H, m), 1.77 (15 H, d, J<sub>P-H</sub> = 1.9 Hz), 1.23 (9 H, d, J<sub>P-H</sub> = 10.4 Hz), −16.35 (1 H, d, J<sub>P-H</sub> = 36.0 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 223.1 (C, d, J<sub>P-C</sub> = 11.6 Hz), 154.3 (CH), 129.2 (C), 129.1 (CH), 127.1 (CH), 93.7 (C), 18.5 (CH<sub>3</sub>, d, J<sub>P-C</sub> = 38.4 Hz), 10.1 (CH<sub>3</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ −38.2 ppm. MS (EI): *m/z* 510 (M<sup>+</sup>). Anal. Calcd for C<sub>20</sub>H<sub>30</sub>OPIr: C, 47.13; H, 5.93. Found: C, 47.30; H, 5.96.

**Cp\*(PMe<sub>3</sub>)Ir(CHO)(H) (7c).** A solid mixture of **1** (100 mg, 250 mmol) and *tert*-butyllithium (20 mg, 310 mmol, 1.2 equiv) was dissolved in C<sub>6</sub>H<sub>6</sub> (5 mL), and the yellow solution was stirred for 5 min at ambient temperature. A solution of ethyl formate (22 mg, 310 mmol) in C<sub>6</sub>H<sub>6</sub> (2 mL) was then added via pipet. After stirring for 10 min, the volatile materials were removed under vacuum and the residue was dissolved in pentane and filtered through Celite. After removal of the solvent, the crude reaction mixture was subjected to <sup>1</sup>H NMR analysis. The spectrum indicated a mixture of the desired formyl hydride complex **7c** and **1** in a 1.7:1 ratio. Recrystallization from hexamethyldisiloxane (−40 °C) provided 30.2 mg of pure **7c** as a white crystalline solid in 28% isolated yield. The complex may also be purified by chromatography on alumina III utilizing 25% Et<sub>2</sub>O in pentane as the eluent. Typical yields of unisolated material are greater than 75%. Mp: 93 °C (dec). IR (KBr): 2713, 2694, 2505, 2138, 1891, 1591, 958 cm<sup>−1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 15.25 (1 H, d, J<sub>P-H</sub> = 4 Hz), 1.73 (15 H, s), 1.36 (9 H, d, J<sub>P-H</sub> = 10.8 Hz), −17.33 (1 H, d, J<sub>P-H</sub> = 32.0 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 219.2 (C, d, J<sub>P-C</sub> = 11.6 Hz), 95.9 (C), 19.1 (CH<sub>3</sub>, d, J<sub>P-C</sub> = 40 Hz), 9.7 (CH<sub>3</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ −37.94 ppm. MS (EI): *m/z* 432 (M − 2<sup>+</sup>). MS (FAB): *m/z* 433 (M − 2 + H<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>25</sub>OPIr: C, 38.79; H, 6.04. Found: C, 38.97; H, 6.17.

**Reaction of 2 with Benzaldehyde.** A solution of **2** (10 mg, 24 mmol) in C<sub>6</sub>D<sub>6</sub> (400 mL) was placed in an NMR tube. Benzaldehyde (5.4 mg, 5 mL, 50 mmol, 2.08 equiv) was then added via microliter syringe, and the tube was capped and inverted to mix the reactants. Reaction occurred instantaneously as was evident from a yellow to gold color change. Analysis of the tube contents by <sup>1</sup>H NMR spectroscopy indicated a mixture of **7b** and **1** in a 3:1 ratio. A solution of methyl *p*-toluenesulfonate (10 mg, 54 mmol, 2.25 equiv) in C<sub>6</sub>D<sub>6</sub> (200 mL) was then added to the tube. After 65 min at ambient temperature, no reaction could be detected by NMR analysis. After 20 h at room temperature, formation of benzyl methyl ether was detected by comparison of the NMR spectrum of the reaction mixture with that of an authentic sample. The yield of benzyl methyl ether was 67% based upon the yield of **7b**.

**NMR Tube Studies of Reactions of 2 with CO<sub>2</sub> and Carbonates.** In a typical example, a solution of **2** (6.3 mg, 15.6 mmol) in toluene-*d*<sub>8</sub> (400 mL) was placed in an NMR tube, and the tube was connected to a vacuum manifold via a Cajon Ultratorr adapter. After freezing the tube contents in liquid N<sub>2</sub>, the tube was evacuated and dimethyl carbonate (14.4 mmol) was condensed via vacuum transfer from a calibrated

gas bulb (6.6 mL volume) pressurized to 40 Torr. The tube was then flame-sealed and maintained at −196 °C until the time of NMR analysis. The tube was then quickly warmed to −78 °C in a dry ice–acetone bath, and the contents were analyzed by <sup>1</sup>H NMR spectroscopy at −66 °C. No reaction at this temperature was observed. The NMR probe was warmed to −30 °C, and after 30 min at this temperature, no reaction could be detected. Further warming to 10 °C for 5 min resulted in 38% conversion to a 1.3:1 mixture of Cp\*(PMe<sub>3</sub>)Ir(Me)(H) and Cp\*(PMe<sub>3</sub>)Ir(CO). After 10 min at 23 °C, complete conversion to the aforementioned products was observed. No intermediate species could be detected. Similarly, a solution of **2** (6.3 mg, 15.6 mmol) in toluene-*d*<sub>8</sub> (400 mL) was treated with CO<sub>2</sub> (26 mmol) condensed into the tube at −196 °C via vacuum transfer from a calibrated gas bulb (6.6 mL volume) pressurized to 80 Torr. The tube was quickly warmed to −78 °C in a dry ice–acetone bath and the <sup>1</sup>H NMR spectrum was recorded at −66 °C after a reaction time of 5 min. The NMR spectrum indicated quantitative conversion to the previously characterized complex Cp\*(PMe<sub>3</sub>)Ir(CO). In an analogous reaction, a solution of **2** (6.9 mg, 16.8 mmol) in THF (0.5 mL) was added dropwise to a solution of di-*tert*-butyl dicarbonate (4 mg, 18 mmol) in THF (2 mL). The resulting yellow-gold solution was concentrated under vacuum to afford a gold-yellow oil. <sup>1</sup>H NMR analysis of the oil indicated a mixture of **1** and Cp\*(PMe<sub>3</sub>)Ir(CO) in a 2:1 ratio based upon <sup>1</sup>H NMR integrations.

**Thermolyses of Acyl Hydrides 7a–c.** In a representative example, a solution of **7a** (9 mg, 18.4 mmol) and **1** (2.76 mmol as an internal standard) in C<sub>6</sub>D<sub>6</sub> (500 mL) was placed in a medium-walled NMR tube. The tube was attached to a vacuum line via a Cajon Ultratorr adapter, and the contents were frozen in liquid N<sub>2</sub>. After evacuating to 30 mTorr, the tube was flame-sealed, thawed, and then heated for 6 h at 75 °C. <sup>1</sup>H NMR analysis showed no observable reaction. Further heating of the tube for 18 h at 105 °C and subsequently at 135 °C for 18 h similarly showed no detectable reaction. Continued thermolysis at 195 °C for 48 h showed 66% conversion to complex **8**. In an analogous experiment, a solution of **7b** (2 mg, 4 mmol) and **1** (0.48 mmol as an internal standard) in C<sub>6</sub>D<sub>6</sub> (500 mL) was prepared and heated at 135 °C for 18 h to achieve 15% conversion to complex **8**. Similarly, a solution of **7c** (7.2 mg, 16.6 mmol) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) showed a mixture of **7c** and **8** in 2.2:1 ratio, indicating observable thermal decomposition between the time of sample preparation and room-temperature NMR analysis. The tube was then heated for 21 h at 45 °C. Analysis by <sup>1</sup>H NMR indicated quantitative conversion to complex **8**.

**Cp\*(PMe<sub>3</sub>)Ir(C<sub>6</sub>F<sub>5</sub>)(H) (12).** To a solution of **1** (106 mg, 262 mmol) in C<sub>6</sub>H<sub>6</sub> (4 mL) was added a solution of *tert*-butyllithium (17 mg, 265 mmol) in C<sub>6</sub>H<sub>6</sub> (1 mL). After stirring for 5 min at room temperature, a solution of C<sub>6</sub>F<sub>6</sub> (102 mg, 548 mmol, 2.07 equiv) in C<sub>6</sub>H<sub>6</sub> (1 mL) was added, resulting in an instantaneous color change from yellow to gold. After 3 h at ambient temperature, the volatile materials were removed in vacuo, and the residue was dissolved in pentane (10 mL). Filtration of the solution through Celite and removal of the solvent under reduced pressure afforded a gold oil which crystallized spontaneously upon cooling to −40 °C. The crude product was recrystallized twice from pentane (−40 °C) to afford 111 mg of **12** as a pale gold-colored crystalline solid in 74% yield. Mp: 88.5–91 °C (dec). IR (KBr): 2912, 2113, 1498, 1427, 948 cm<sup>−1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.70 (15 H, s), 0.95 (9 H, d, J<sub>P-H</sub> = 10.0 Hz), −16.47 (1 H, dd, J<sub>P-H</sub> = 37.1 Hz, J<sub>H-F</sub> = 11.4 Hz) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 92.9 (C), 19.60 (CH<sub>3</sub>, d, J<sub>P-C</sub> = 38.4 Hz), 10.0 (CH<sub>3</sub>) ppm. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): δ −107.2 (d, J<sub>F-F</sub> = 31.6 Hz), −111.4 (d, J<sub>F-F</sub> = 35.1 Hz), −163.7 (t, J<sub>F-F</sub> = 20.6 Hz), −164.07 (ddd), −165.1 (ddd). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ −44.5 ppm. MS (EI): *m/z* 572 (M<sup>+</sup>). HRMS calcd for C<sub>19</sub>H<sub>25</sub>F<sub>5</sub>PIr: 572.124348. Found: 572.124514.

**Reaction of 2 with C<sub>6</sub>H<sub>5</sub>F To Give Cp\*(PMe<sub>3</sub>)Ir(C<sub>6</sub>H<sub>5</sub>)(H) (13).** A solution of **2** (7.42 mg, 18 mmol) in C<sub>6</sub>D<sub>6</sub> (350 mL)

was placed in a NMR tube. To the solution was added fluorobenzene (3.47 mg, 3.4 mL, 36 mmol, 2 equiv) via microliter syringe. The  $^1\text{H}$  NMR spectrum was recorded after a reaction time of 60 min, indicating no detectable reaction had occurred. The tube was then flame-sealed in vacuo and was heated at 75 °C for 22 h. Analysis of the contents by  $^1\text{H}$  NMR showed a mixture of **13** and **1** in a 1:4 ratio. We have not investigated the origin of **1** in this reaction, though we have observed that heating solutions of **2** at 75 °C leads to formation of **1** via an unknown mechanism (vide supra).

**Cp\*(PMe<sub>3</sub>)Ir(CF=CF<sub>2</sub>)**(H)** (**14**).** A solid mixture of **1** (152 mg, 375 mmol) and *tert*-butyllithium (25.2 mg, 393 mmol, 1.05 equiv) was dissolved in toluene (10 mL) in a Schlenk flask. The solution was frozen in liquid N<sub>2</sub>, and hexafluoropropene (5.36 mmol, 14 equiv) was condensed into the reaction flask via vacuum transfer from a known-volume bulb. The reaction flask was warmed to -78 °C and was stirred vigorously at that temperature for a period of 90 min. The reaction mixture was then warmed to ambient temperature, and the volatile materials were removed under reduced pressure. The crude reaction product was extracted with two 10 mL portions of C<sub>6</sub>H<sub>6</sub>, and the combined extracts were filtered through Celite. Removal of the solvent in vacuo afforded 146 mg of a dark brown oil identified by  $^1\text{H}$  NMR analysis as a 71:29 mixture of **14** and **1**, indicating a 78% yield based on recovered **1**. Crude **14** was purified by chromatography on alumina III employing pentane as the eluent and was subsequently recrystallized twice from pentane at -40 °C to provide 40 mg (20% yield) of analytically pure **14** as a yellow crystalline solid. IR (KBr): 2908, 2117, 1625, 1319, 1176, 692 cm<sup>-1</sup>.  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.76 (15 H, s), 1.12 (9 H, d,  $J_{\text{P-H}} = 10.4$  Hz), -17.01 (1 H, ddd,  $J_{\text{H-F}} = 6.0$  Hz,  $J_{\text{H-P}} = 14.0$  Hz,  $J_{\text{P-H}} = 34.5$  Hz) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  94.5 (C), 19.5 (CH<sub>3</sub>, d), 10.0 (CH<sub>3</sub>) ppm.  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -107.2 (d,  $J_{\text{F-F}} = 31.6$  Hz), -111.4 (d,  $J_{\text{F-F}} = 35.1$  Hz), -163.7 (t,  $J_{\text{F-F}} = 20.6$  Hz), -164.07 (ddd), -165.1 (ddd).  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -41.5 ppm. MS (EI): *m/z* 536 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>25</sub>F<sub>5</sub>PIr: C, 35.88; H, 4.70. Found: C, 36.10; H, 4.91.

**Reaction of 2 with 3,3,3-Trifluoropropene.** To a solution of **1** (122 mg, 301 mmol) in C<sub>6</sub>H<sub>6</sub> (25 mL) was added a solution of *tert*-butyllithium (25 mg, 390 mmol, 1.3 equiv) in C<sub>6</sub>H<sub>6</sub> (1 mL). The bright yellow solution was transferred to a 100 mL glass reaction vessel equipped with a Teflon stopcock and

frozen in liquid N<sub>2</sub>. After evacuating the reaction vessel, 3,3,3-trifluoropropene (4.2 mmol, 14 equiv) was condensed into the vessel via vacuum transfer from a known-volume bulb. The reaction vessel was warmed to ambient temperature and was stirred vigorously for a period of 3 h. During this time, the solution changed from yellow to gold in color, accompanied by the formation of a fine white precipitate. The volatile materials were then removed under reduced pressure, and the crude reaction product was extracted with three 2 mL portions of pentane. The hydrocarbon extracts were combined and filtered through Celite. The filtrate was concentrated in vacuo to afford 98.8 mg of a golden oil.  $^1\text{H}$  NMR analysis of the oil showed it to be a mixture of **15** and **1** in a 76:24 ratio. Multiple attempts to isolate complex **15** free from **1** by column chromatography (decomposition) or recrystallization were unsuccessful. Data for **15**:  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.56 (dddd, 1 H), 2.26 (m, 1 H), 1.98 (m 1 H), 1.76 (s, 15 H), 1.17 (d,  $J_{\text{P-H}} = 9.72$  Hz, 9 H), -17.75 (d,  $J_{\text{P-H}} = 40$  Hz, 1 H) ppm.  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -98.9 (d,  $J_{\text{F-F}} = 113$  Hz), -99.2 (dd,  $J_{\text{F-F}} = 110$  Hz,  $J_{\text{H-F}} = 42$  Hz) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -43.25 ppm.

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**Supporting Information Available:** Structural data for **7a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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