Deprotonation of the Transition Metal Hydride $(\eta^{5}-C_{5}Me_{5})(PMe_{3})IrH_{2}$. Synthesis and Chemistry of the Strongly Basic Lithium Iridate $(\eta^5-C_5Me_5)(PMe_3)Ir(H)(Li)$

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Treatment of $(\eta^5$ -C₅Me₅)(PMe₃)IrH₂ (1) with *tert*-butyllithium gives $(\eta^5$ -C₅Me₅)(PMe₃)Ir-(H)(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-d₂ (3-syn-d₂) gave the alkylated hydridoiridium complex 4a-anti-d₂, which was converted to the corresponding chloride Cp*(PMe₃)Ir(CHDCHDCMe₃)(Cl) (4c-anti-d₂) by treatment with CCl₄. 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 $S_N 2$ displacement and not an outer-sphere electron-transfer reaction. Protonation studies carried out on iridate **2** with organic acids of varying pK_a allowed us to estimate that the pK_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 pK_a has been quantitatively estimated. Treatment of 2 with main group electrophiles allowed the preparation of several other hydridoiridium derivatives, including Cp*(PMe₃)Ir(SnPh₃)(H) (5a), Cp*(PMe₃)Ir(SnMe₃)(H) (5b), and Cp*(PMe₃)Ir(BR₂)(H) (6a, R = F; 6b, R = Ph). Reaction of 2 with acid chlorides and anhydrides leads to acyl hydrides Cp*(PMe₃)Ir(COR)(H), and fluorocarbons also react, giving products such as $Cp^*(PMe_3)Ir(C_6F_5)(H)$ 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

в L_nM B-H (1)L_nM-H +

numerous; many have been employed in organic synthesis as well as in the preparation of more highly functionalized organometallic species.^{1–14}

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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 pK_a 's for the hydride.^{15–20} The fewer non-CO-containing metal anions known are typically exceptionally reactive, 1-3,5,21-24 but little quantitative thermodynamic or kinetic information is available on these species.

Previously, we reported that successive treatment of $Cp^*(PMe_3)IrH_2$ ($Cp^* = C_5Me_5$) with *tert*-butyllithium followed by alkyl or silvl trifluoromethanesulfonates

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(triflates) in pentane solution afforded the corresponding alkyl and silyl hydrides in good yields.² We describe here the spectroscopic characterization of the putative Cp*-(PMe₃)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*(PMe₃)Ir(Li)(H). When a colorless C₆D₆ solution of $Cp^*(PMe_3)IrH_2$ (1) was treated at ambient temperature with *tert*-butyllithium, an intense yellow color developed immediately. Analysis of this solution by ¹H NMR spectroscopy showed complicated resonance patterns in each of the characteristic Cp*, PMe₃, 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 ¹H NMR spectrum could have resulted from deprotonation at several sites in the starting dihydride complex. However, integration of the Cp*, PMe₃, 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*-(PMe₃)Ir(Li)(H) (2) (eq 2).



Previous studies by Gladysz and co-workers demonstrated that the reaction of CpRe(PPh₃)(NO)(H) with *n*-BuLi at -78 °C resulted in abstraction of a Cp ring proton to form (C₅H₄Li)Re(PPh₃)(NO)(H).⁴ Subsequent warming to -32 °C resulted in rearrangement to the thermodynamically favored CpRe(PPh₃)(NO)(Li). To address the possibility that kinetic deprotonation could occur at a site other than the iridium center, Cp*(PMe₃)-IrD₂ was prepared. Treatment with *tert*-butyllithium produced Cp*(PMe₃)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).

$$Cp^{*}(PMe_{3})Ir \stackrel{D}{\searrow} \underbrace{tert-BuLi}_{C_{6}H_{6}}$$

$$1-d_{2}$$

$$Cp^{*}(PMe_{3})Ir \stackrel{D}{\swarrow} + \stackrel{D}{\swarrow} (3)$$

Removal of the volatile materials in vacuo from a benzene solution of $Cp^*(PMe_3)Ir(Li)(H)$ afforded a bright yellow microcrystalline solid in 90% yield. This material



Figure 1. ¹H NMR spectrum of **2** and residual **1** in THF $d_8 (\bullet 1; \triangle 2)$.

was sparingly soluble in THF- d_8 , but exhibited a much simpler NMR spectrum than that observed in benzene. At ambient temperature, single sharp resonances were observed for the Cp*, PMe₃, and hydride nuclei, in addition to resonances due to residual Cp*(PMe₃)IrH₂. Single resonances were also observed for **2** in the ³¹P and ⁷Li NMR spectra.²⁵ 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 ⁷Li 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.²⁶ The addition of 12crown-4 as a sequestering agent to a C_6D_6 solution of Cp*(PMe₃)Ir(Li)(H) produced no change in the ¹H 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 $Cp^*(PMe_3)Ir(Li)(H)$ suitable for study by X-ray diffraction were unsuccessful. Diffusion of THF or DME into a benzene solution of Cp^* -(PMe_3)Ir(Li)(H) led to precipitation of a yellow microcrystalline solid. Analysis of the DME adduct by ¹H NMR spectroscopy indicated a composition of [Cp*-(PMe_3)Ir(Li)(H)]₂(DME). The stoichiometry of the com-

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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 [Ru(OEP)(neopentyl)]₂(μ -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.²⁴

THF solutions of Cp*(PMe₃)Ir(Li)(H) were stable for several days at ambient temperature. Benzene solutions of Cp*(PMe₃)Ir(Li)(H) were similarly stable, but the aggregated complex began to precipitate after several hours at room temperature. Heating C₆D₆ solutions of Cp*(PMe₃)Ir(Li)(H) resulted in decomposition to Cp*-(PMe₃)IrH₂ with no detectable deuterium incorporation as determined by analysis by ²H NMR spectroscopy.²⁷ We have not investigated the source of the Ir-bound hydrogen in this reaction.²⁸

Stereochemistry of the Reaction of Cp*(PMe₃)-Ir(Li)(H) with 3,3-Dimethylbutane Trifluoromethanesulfonate-1,2-*syn-d*₂. Previous work performed in this laboratory demonstrated that reaction of Cp*(PMe₃)Ir(Li)(H) with certain organic triflates produced good yields of the complexes Cp*(PMe₃)Ir(R)-(H) (R = primary alkyl, trimethylsilyl).² We adopted this method for independent syntheses of compounds of this class to facilitate our studies of C-H activation by the 16e fragment Cp*(PMe₃)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 (S_N2) reaction of triflate anion by Cp*(PMe₃)Ir(Li)(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.²⁹ 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 CpFe-(CO)₂ salts by carrying out the alkylation with 1-bromo-3,3-dimethylbutane-1,2-*syn*- d_2 and 1-bromo-3,3-dimethylbutane-1,2-*anti*- d_2 , each of which proceeded with clean inversion of configuration in the iron system.⁶ We enlisted a similar strategy for our investigation of the reaction of Cp*(PMe₃)Ir(Li)(H) with alkyl triflates.³⁰

A benzene solution of $Cp^*(PMe_3)IrH_2$ (1) was treated with 1 equiv of *tert*-butyllithium at ambient temperature to give a solution of $Cp^*(PMe_3)Ir(Li)(H)$ (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 ¹H NMR spectroscopy showed $Cp^*(PMe_3)Ir(CH_2CH_2CMe_3)(H)$ (4a) and $Cp^*(PMe_3)IrH_2$ (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 CHBr₃ and subsequent chromatography on silica gel.

Cp*(PMe₃)Ir(CH₂CH₂CMe₃)(Br) (4b) was isolated as a yellow crystalline solid. Determination of the stereochemistry of the reaction with labeled 3 (3-d₂) required prior knowledge of each of the ${}^{1}H-{}^{1}H$ coupling constants in the fully protiated complex Cp*(PMe₃)Ir(CH₂CH₂-CMe₃)(Br) (4b). The stereogenicity of the pseudotetrahedral iridium center in complex 4b results in a diastereotopic relationship between each pair of protons on the α - and β -carbons of the dimethylbutyl group (Scheme 1; Figure 2). In C_6D_6 , the two α -protons appear at 2.27 and 1.44 ppm with each resonance displaying a 16-line dddd pattern, while the two diastereotopic β -protons are manifest as two overlapping doublet of triplets (1.19 and 1.11 ppm). In C_6D_6 , the α -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 CDCl₃. In this solvent, both α -proton resonances were well-resolved; however slow conversion to the chloride complex Cp*-(PMe₃)Ir(CH₂CH₂CMe₃)(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 Cp*(PMe₃)IrLi₂. 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. ¹H{³¹P} NMR spectrum of complex 4b in CDCl₃.

Table 1. Coupling Constants for Complex 4b in Hz $(C_6D_6 \text{ Solvent})$

resonance (ppm)	$^{2}J_{lpha-lpha}$	$^{3}J_{lpha-eta}$ sy	$_{\gamma n}$ $^{3}J_{\alpha - \beta}$	$_{\rm Banti}$ $^3J_{ m \alpha-P}$
2.27	10.6	4.6	13.	6 4.8
1.44	10.7	4.4	13.	9 4.8
resonance (ppm)	$^{2}J_{eta-eta}$	$^{3}J_{lpha-eta ext{syn}}$	$^{3}J_{lpha-eta}$ anti	$^{3}J_{eta-\mathrm{P}}$
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 α -hydrogens, especially in the ³¹P-decoupled spectrum, where two 8-line ddd patterns are observed (Figure 2). The spectra are consistent with two-bond coupling of the α -protons with each other and threebond couplings to the diastereotopic β -hydrogen atoms and the bound phosphine. The individual ¹H-¹H coupling constants for the α - and β -hydrogen resonances were ascertained by comparison of the ¹H{³¹P} spectrum with the fully coupled ¹H NMR spectrum and are provided in Table 1.

The preparation of the labeled iridium complex 4a*d*₂ was effected by the reaction of triflate **3**-*syn*-*d*₂ 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 CDCl₃ solvent, prompted us to perform the coupling constant analysis on the analogous complex Cp*(PMe₃)Ir(CHDCHDCMe₃)-(Cl) $(4c-d_2)$. Therefore, $4a-d_2$ was converted to the chloride complex by reaction with CCl₄ (Scheme 1). The coupling constants for the deuterium-labeled complex **4c**-*d*₂ were determined analogously. However, the presence of two- and three-bond ${}^{1}H-{}^{2}H$ couplings complicated a straightforward interpretation and required that we obtain the ¹H{²H} spectrum as well.³¹ The deuteriumdecoupled spectrum of the product $4c - d_2$ in $C_6 D_6$ is shown in Figure 3. Once again, the downfield α -H resonance provides the clearest opportunity for analysis of the reaction stereochemistry. With one α - and one β -hydrogen replaced by deuterium, in the absence of ²H coupling a simple dd pattern for the downfield α -H is predicted, due to coupling to P and to the (now single) β -H. From these experiments, ${}^{3}J_{H-H}$ was found to be



Figure 3. ${}^{1}H{}^{2}H{}$ NMR spectrum of complex **4c**-*anti-d*₂ in C₆D₆.

14.1 Hz for the downfield α -hydrogen resonance (2.38 ppm in CDCl₃) and 14.1 Hz for the upfield α -hydrogen resonance (1.71 ppm in CDCl₃). By comparison with the coupling constants determined for the all-protio system, this assignment suggests that the α - and β -hydrogen atoms of each diastereomer³² exist in a relative anti relationship to one another (**4c**-*anti*-*d*₂, Figure 3).

The smaller H–H coupling predicted for **4c**-*syn*-*d*₂ would require that the presence of this material produce lines appearing between the two doublets seen for α -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 ²H decoupling in the experiment, or to the presence of some **4c**-*syn*-*d*₂. 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 S_N2 mechanism.³³

⁽³¹⁾ Details of the ²H 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).

⁽³²⁾ The presence of stereogenic centers on the α - and β -carbons of the dimethylbutyl group as a result of isotopic substitution in **3-dz** gives rise to four possible enantiomeric pairs of diasteromers in **4c-dz**. 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 Cp*(PMe₃)IrH₂. Data on the pK_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 pK_a data for transition metal hydrides.^{15–18,20} 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.³⁴ Other ligands attached to the metal center also have a strong effect on the pK_a , electron-donating ligands (e.g., phosphines) reducing acidities and electronaccepting ligands (e.g., CO) increasing them. Typical examples of measured pK_a values in acetonitrile solvent range from 8.4 for Co(CO)₄(H) to 26.6 for Cp(PMe₃)W- $(CO)_2(H)$. Substitution of Cp^{*} for Cp in the complex $CpMo(CO)_3(H)$ led to a increase in the p K_a from 13.9 to 17.1. A similar substitution in the complex $CpFe(CO)_2$ -(H) increased the pK_a from 19.4 to 26.3. Substitution of a phosphine for CO had an even larger effect. The acidity of CpW(CO)₃(H) ($pK_a = 16.1$) is 10.5 pK_a units lower than $CpW(CO)_2(PMe_3)(H)$ (p $K_a = 26.6$).

In light of these observations, we anticipated that $Cp^{*}(PMe_{3})IrH_{2}$ (1), by virtue of its relatively electronrich coordination sphere and position in the transition series, would exhibit an unusually high pK_1 . This prediction was substantiated semiquantitatively by quenching studies with various carbon acids. Benzene solutions of $Cp^*(PMe_3)IrH_2$ (1) were treated with 1 equiv of *tert*-butyllithium to generate Cp*(PMe₃)Ir(Li)(H) (2), and the volatile materials were removed in vacuo. The resulting yellow oil was dissolved in THF-d₈ and treated with 1 or more equiv of a carbon acid of known acidity (unfortunately, the reactivity of DMSO and CH₃CN 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 ($pK_a = 32.2$), CH₃CN $(pK_a = 31.3)$, and even DMSO $(pK_a = 35.1)^{35}$ afforded $Cp^{\ast}(PMe_{3})IrH_{2}$ and the corresponding lithium methide conjugate bases of the carbon acids in quantitative yield, as determined by $^1\!H$ NMR spectroscopy (eq 4a). While

$$Cp^{*}(PMe_{3})Ir < H \xrightarrow{H} H \xrightarrow{R-H} H \xrightarrow{H} H \xrightarrow{H}$$

H₂ is not often regarded as a Brønsted acid, we found that it underwent a clean reaction with **2**. When a C_6D_6 solution of Cp*(PMe₃)Ir(Li)(H) was placed under 720 Torr of hydrogen, heating at 45 °C for 18 h resulted in quantitative formation of Cp*(PMe₃)IrH₂ and was accompanied by the formation of a white precipitate (presumably polymeric LiH) (Scheme 2). In an analogous experiment, a C_6D_6 solution of $Cp^*(PMe_3)Ir(Li)$ -(H) was placed under 720 Torr of D_2 and a mixture of Cp*(PMe₃)IrH₂, Cp*(PMe₃)Ir(D)(H), and Cp*(PMe₃)IrD₂ was detected by ¹H and ²H NMR spectroscopy. No deuterium was detected in the Cp* or PMe₃ ligands (vide supra). The observation of the three isotopomeric complexes suggests not only that Cp*(PMe₃)Ir(Li)(H) is capable of deprotonating H₂ but that Cp*(PMe₃)Ir(Li)-(H) undergoes proton exchange with Cp*(PMe₃)IrH₂ to result in a statistical mixture of isotopomers (Scheme $2).^{36}$

In contrast, treatment of the yellow solution of **2** with toluene did not result in its deprotonation to form benzyllithium and Cp*(PMe₃)IrH₂. 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 THF- d_8 solution of Cp*(PMe₃)IrH₂ was treated with 1 equiv of benzyllithium, quantitative formation of toluene and Cp*(PMe₃)Ir(Li)(H) was observed (eq 4b). This demonstrates that the acidity of Cp*(PMe₃)IrH₂ in THF is bracketed by the acidities of DMSO and toluene.³⁵ To the extent that pK_a's in CH₃-

⁽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.

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⁽³⁵⁾ Bordwell, F. G. Acc. Chem. Res. 1988, 21, 456.

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

$$Cp^{*}(PMe_{3})Ir < \overset{H}{\underset{Li}{\overset{Li}{\overset{}}}} + \underbrace{ \begin{array}{c} & & \\ & \\ & & \\ & \\ & \\ & &$$

CN and/or DMSO can be extrapolated to THF,^{37,38} the first pK_a of Cp*(PMe₃)IrH₂ falls in the range 38–41. To our knowledge, this represents the highest pK_a of a transition metal hydride yet reported.

With the assistance of A. Streitwieser and J. Krom, we attempted to determine more precisely the pK_1 of Cp*(PMe₃)IrH₂. The use of cesium bases in THF solvent systems has been found to minimize ion-pairing effects on acidities and provide pK_a values comparable to those observed in other solvent systems.^{37,38} Unfortunately, the attempted reaction of cumylcesium with Cp*(PMe₃)-IrH₂ failed to provide a detectable concentration of hydridoiridate before the onset of decomposition of cumylcesium. That cumylcesium (p K_a cumene = 40.7)³⁷ failed to react while benzyllithium (p K_a toluene = 40.9)³⁷ gave quantitative deprotonation of Cp*(PMe₃)IrH₂ suggests that the 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 hydridoiridate 2 can also be generated by reaction with benzylpotassium 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 Cp*(PMe₃)IrH₂ with less basic agents were unsuccessful. Treatment of Cp*(PMe₃)IrH₂ with NaNH₂ (pK_a NH₃ = 38),³⁵ KH-18-crown-6 (pK_a H₂ = 35),³⁵ or LDA (p K_a diisopropylamine = 35.7)³⁹ failed to produce any detectable reaction. This supports our assertion that the pK_1 of $Cp^*(PMe_3)IrH_2$ lies above 38.

Reactions of Cp*(PMe₃)Ir(Li)(H) with Main Group and Organic Electrophiles. Organostannanes. Cp*(PMe₃)Ir(Li)(H) was found to undergo a variety of clean reactions with electrophilic main group compounds. Treatment of a benzene solution of Cp*-(PMe₃)Ir(Li)(H) with 1 equiv of Ph₃SnCl or Me₃SnCl resulted in formation of Cp*(PMe₃)Ir(SnPh₃)(H) (5a) and Cp*(PMe₃)Ir(SnMe₃)(H) (5b) in 71% and 91% yields, respectively (eq 5). Complex 5a was remarkably stable



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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 ¹H and ³¹P NMR spectroscopy revealed couplings between tin, hydrogen, and phosphorus. The observed coupling constants ($J_{P-Sn} = 167$ Hz and $J_{H-Sn} = 133$ 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 Cp*(PMe₃)Ir fragment. Typical values of ${}^{1}J_{\rm H-Sn}$ for alkyltin hydrides range from 1500 to 1800 Hz with ${}^{2}J_{\rm H-Sn}$ for alkyltin species in the range of 50– 70 Hz.⁴⁰ However, ${}^{2}J_{H-Sn}$ was found to be well below the value of 1895 Hz reported for ${}^{1}J_{H-Sn}$ in Ph₃SnH, which suggests the absence of any significant interaction between the hydridic hydrogen atom and the Sn center.^{41,42} 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 metalcatalyzed functionalization of organic substrates mediated by boranes has prompted much recent interest in the nature of transition metal-boryl complexes.⁴³⁻⁴⁵ 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;⁴³⁻⁵⁰ recently metalboryl complexes capable of alkane activation have been discovered.⁵¹ Though much of the work to date has focused on the use of catecholboranes, several examples involving boranes lacking oxygen donor groups are known.^{46,52-56} With the nucleophilicity of Cp*(PMe₃)Ir-(Li)(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 Cp*(PMe₃)Ir(Li)-(H) at -78 °C with 1 equiv of boron trifluoride-etherate led to immediate reaction and precipitation of LiBF₄.

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Analysis of the reaction mixture by ¹H 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 trifluorideetherate, greater than 90% conversion to the new complex was indicated by ¹H NMR analysis. The complex exhibited resonances at 1.95, 1.29, and -17.45 ppm in the ¹H NMR spectrum indicative of bound Cp*, PMe₃, 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 ¹³C, ³¹P, ¹⁹F, and ¹¹B NMR spectroscopy supported a structural assignment of $Cp^*(PMe_3)Ir(BF_2)(H)$ (6a) for the reaction product (Scheme 3). The ¹⁹F NMR spectrum showed a 1:1:1:1 quartet (${}^{1}J_{B-F} = 154$ Hz) located at -23.2 ppm. The ¹¹B NMR spectrum gave a 1:2:1 triplet at 23.9 ppm $(^{1}J_{B-F} = 160 \text{ Hz})$ further supporting this assignment. The lack of observable coupling between ¹¹B and ¹H as well as the position of the hydride ¹H 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_2 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-d₈.

In contrast to the reaction with boron trifluorideetherate, Cp*(PMe₃)Ir(Li)(H) underwent complete reaction with just 1 equiv of Ph₂BBr. The ¹H, ¹³C, ³¹P, and ¹¹B 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*(PMe₃)Ir(Li)(H) with Ph₂BBr to produce **6b** was also accompanied by the formation of Cp*(PMe₃)Ir(H)(Br) and Cp*(PMe₃)IrH₂, 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 $Cp^*(PMe_3)$ -Ir(Li)(H) underwent clean reaction with tetraphenylborinic anhydride (Ph₂BOBPh₂) (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 $Cp^*(PMe_3)Ir(Li)(H)$ to undergo clean S_N2 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 ¹H NMR spectroscopy showed resonances at 1.82, 1.28, 1.19, and -17.02ppm, corresponding to the Cp*, PMe₃, *tert*-butyl, and hydride functionalities along with resonances for Cp*-(PMe₃)IrH₂. 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 $Ir-C_{14}$ and $C_{14}-O$ 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.^{57–61} The Ir atom

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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*(PMe₃)IrH₂ 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).⁶² 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 vield 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 benzaldhyde 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.

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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*-(PMe₃)Ir(CO) (8) was obtained in a 1:2.2:1.4 ratio along with Cp*(PMe₃)IrH₂ and Cp*(PMe₃)Ir(Me)(H) (9) (Scheme 4). Similarly, reactions of 2 with di-tert-butyl dicarbonate or CO₂ 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.^{57-61,63-72} We anticipated that complexes 7a - c would undergo thermal reductive elimination to produce the transient unsaturated 16e Cp*(PMe₃)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 ¹H NMR analysis in each case included at least some of the carbonyl derivative Cp*Ir(PMe₃)(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 C₆D₆ 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

- 198 C7
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Scheme 4

Cp*(PMe₃)Ir<

observed.80



elimination similar to that observed in the thermolyses of $7\mathbf{a}-\mathbf{c}$ (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 °C, it was placed in an NMR probe at -66 °C and a ¹H 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 °C. After 5 min at 10 °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, CO₂ was condensed into an NMR tube containing a frozen toluene solution of **2**. After warming to -78 °C for 5 min, the tube was placed in the NMR probe at -66°C and the ¹H 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 Cp*Ir(COR)(H) complex which undergoes subsequent CO deinsertion,^{73–78} RH reductive elimination, and phosphine recoordination to give



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 (X-Y = $H-H > CH_3-H > CH_3-CH_3$) 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.^{81,82} However, the directionality of the carbon sp³ 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 $(R = OCH_3 \sim OLi \text{ (presumed; see below)} > H \gg Ph >$ *tert*-Bu) described above. The directionality of the sp³hybridized carbon of the *tert*-butyl group attached to the

activation of the solvent, an outcome that was not

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Scheme 6



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 sp² 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 α -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 transitionstate interactions and cause a further lowering of the activation barrier. Finally, our inability to directly observe alkoxycarbonyl 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.^{83,84} We cannot, however, rule out the intervention of η^2 -aldehyde or η^2 -arene complexes.^{64,85} 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.^{86–93} 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.⁹⁴ 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 ¹⁹F 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 Cp*(PMe₃)Ir(Ph)(H) (13) in 20% NMR yield along with 1.⁹⁵

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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.

⁽⁸³⁾ Preliminary studies of the perfluoroacyl hydride complex Cp*-(PMe₃)Ir(COC₃F₇)(H) indicate that it undergoes α -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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⁽⁸⁵⁾ We believe that a bimolecular mechanism as has been suggested by Norton for osmium alkyl complexes can be ruled out in the present system, as this mechanism requires that at least one metal center in the reacting pair possess an open coordination site (see ref 72).



When $Cp^{*}(PMe_{3})Ir(Li)(H)$ was treated with $CF_{2}=CF_{2}$ 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 ¹H 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 Cp*(PMe₃)Ir(CH₂CH=CF₂) (15). The identity of this reaction product was readily deduced from the oneproton dddd signal located at 4.56 ppm in its ¹H NMR spectrum and its characteristic resonances in the ¹⁹F 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 CCl₄ 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 °C for 60 h and the latter showing no signs of reaction after heating for 48 h at 75 °C. Photolysis of the perfluoropropenyl hydride (14) for 12 h in C₆D₆ solution resulted in 30% conversion to 13-d₆.

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 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 η^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 α,α,α -trifluorotoluene, supporting the proposed addition-elimination mechanism.

Summary

This paper has outlined the preparation, solution characterization, and reactivity of Cp*(PMe₃)Ir(Li)(H) (2). This complex can be prepared by deprotonation of Cp*(PMe₃)IrH₂ with only the most basic reagents, and we have estimated the pK_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 α -elimination, and we have proposed a concerted mechanism to account for the observed products. We are currently pursuing the α -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. ¹H, ¹³C, ³¹P, ¹⁹F, ⁷Li, and ¹¹B 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. Cp*(PMe₃)IrH₂ was prepared by known literature methods.⁹⁶



Cp*(PMe₃)Ir(Li)(H) (2). In a typical procedure, Cp*(PMe₃)- IrH_2 (100 mg, 0.25 mmol) was dissolved in 5 mL of C_6H_6 , and a solution of *tert*-butyllithium (16 mg, 0.25 mmol) in C_6H_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 Cp*(PMe₃)Ir(Li)(H) as a yellow microcrystalline solid free from residual Cp*(PMe₃)IrH₂. Complex 2 could also be generated as described above and manipulated as a solution without its isolation. ¹H 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 °C. ¹H NMR (THF-d₈): δ 2.08 (s, 15 H), 1.27 (9 H, d, 10 Hz), -19.16 (d, $J_{\rm H-P} = 28.3 \text{ Hz}$) ppm. ³¹P{¹H} NMR (THF-*d*₈): δ -43.17 ppm. ⁷Li NMR (THF- d_8): δ -7.32 ppm. MS (EI): m/z 404 (M - Li⁺).

Cp*(PMe₃)IrD₂ (1-d₂). In a glass reaction vessel equipped with a vacuum stopcock was placed Cp*(PMe₃)IrH₂ (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 ¹H NMR experiment showed Cp*(PMe₃)IrD₂ as the sole product in 90% yield with greater than 93% deuterium incorporation based upon integration.

Determination of the Kinetic Deprotonation Site in Cp*(PMe₃)IrD₂. A solid mixture of Cp*(PMe₃)IrD₂ (10 mg, 0.025 mmol) and *crystallized tert*-butyllithium (2.0 mg, 0.031 mmol) was dissolved in C₆H₆ (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 highpressure 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 Pb(OAc)₂), and the reactor was pressurized to 200 psi with D₂ 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 Vigreaux column. (E)-1,2-Dideuterio-3,3-dimethyl-1-butene (2.66 g) was collected (bp 42-44 °C) in an ice-cooled glass reaction vessel equipped with a vacuum stopcock. Analysis of the product by ¹H NMR spectroscopy demonstrated greater than 90% purity with no detectable hydrogen atoms in the 1-(*E*)- or 2-positions. ²H NMR analysis indicated detectable deuterium incorporation (approximately 40%) in the 1-(Z)-position. ¹H NMR (C₆D₆): δ 4.92 (br s, 0.6 H), 1.00 (s, 9 H) ppm. ²H NMR (C₆D₆): δ 5.81, 4.92, 4.81 ppm. Lit.³⁰ ¹H NMR (C₆D₆): δ 4.91 (s), 0.95 (s).

3,3-Dimethyl-1-butanol-1,2-syn-d2. 3,3-Dimethyl-1-butanol-1.2-syn-d₂ was prepared following a modified procedure of Bergbreiter and Rainville.⁹⁷ In an oven-dried 100 mL roundbottom 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 °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 °C and 4 h at room temperature. Methanol (1.15 mL) was then added, and the solution was recooled to 0 °C. The solution was then treated with 2.55 mL of 3 N aqueous NaOH solution and 2.8 mL of 30% H₂O₂ solution in succession. After refluxing for 1 h, the reaction mixture was partitioned between 100 mL of ice/water and 50 mL of Et₂O. The ethereal layer was separated, and the aqueous phase was washed with four 50 mL portions of Et₂O. The combined ethereal extracts were washed with two 20 mL portions of saturated aqueous sodium thiosulfate, and the thiosulfate extracts were extracted with Et₂O. After drying the combined ethereal extracts over MgSO₄, the solvent was removed by distillation through a Vigreaux column and the residue was short-path distilled (bp 140 °C, lit.⁹⁷ bp 140-145 °C) to provide 1.80 g of pure 3,3-dimethyl-1-butanol-1,2-syn d_2 in 74% yield. ¹H NMR (CDCl₃): δ 3.63 (m, 0.7 H), 1.45 (br d, 1 H), 0.89 (s, 9 H) ppm. ${}^{1}H{}^{2}H{}$ NMR lit.⁹⁷ (CDCl₃): δ 3.65

⁽⁹⁶⁾ Janowicz, A. H.; Bergman, R. G. J. Am. Chem. Soc. 1983, 105, 3929.

(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⁺, 100), 105.06 (M + 1, 29.46).

3,3-Dimethylbutane-1-trifluoromethanesulfonate-1,2syn-d₂ (3-syn-d₂). 3,3-Dimethylbutane-1-trifluoromethanesulfonate-1,2-syn-d₂ was prepared according to the method of Baum for organic triflates.98 In a 25 mL round-bottom flask was placed CH₂Cl₂ (10 mL), 3,3-dimethyl-1-butanol-1,2-synd₂ (200 mg, 1.92 mmol), and pyridine (155 mL, 1.92 mmol). The flask was fitted with a septum and was purged with N₂ 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 MgSO4 and concentrated in vacuo to afford 249 mg of a pale yellow oil. Analysis of the product by ¹H 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. ¹H NMR (CDCl₃): δ 4.56 (br d, 0.7 H), 1.74 (br d, 1 H), 0.95 (s, 9 H) ppm.

Cp*(PMe₃)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*-(PMe₃)IrH₂ (114 mg, 0.281 mmol) in 20 mL of THF and adding tert-butyllithium (0.28 mmol, 1.7 M/Et₂O, 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 μ L of CHBr₃, 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 \times 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*(PMe₃)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⁻¹. ¹H NMR (CDCl₃): δ 2.27 (dddd, $J_{\text{H-H}} = 4.8 \text{ Hz}, J_{\text{H-H}} = 10.6 \text{ Hz}, J_{\text{H-H}} = 13.6 \text{ Hz}, J_{\text{H-P}} = 4.8 \text{ Hz},$ 1H), 1.70 (d, $J_{\rm H-P} =$ 2.0 Hz, 15 H), 1.53 (d, $J_{\rm H-P} =$ 10.0 Hz 9H), 1.44 (dddd, $J_{\rm H-H} = 4.4$ Hz, $J_{\rm H-H} = 10.7$ Hz, $J_{\rm H-H} = 13.9$ Hz, $J_{H-P} = 4.8$ Hz, 1H), 1.19 (ddd, $J_{H-H} = 4.9$ Hz, $J_{H-H} = 13.6$ Hz, $J_{H-H} = 13.6$ Hz, 1H), 1.11 (ddd, $J_{H-H} = 4.9$ Hz, $J_{H-H} =$ 13.5 Hz, $J_{H-H} = 13.5$ Hz, 1H) ppm. ¹³C{¹H} NMR (C₆D₆): δ 92.0 (C) 52.5 (CH₂), 33.3 (CH₂), 30.2 (CH₃), 15.3 (CH₃, $J_{P-C} =$ 37.0 Hz), 9.3 (CH₃), -3.4 (C) ppm. ${}^{31}P{}^{1}H{}$ NMR (C₆D₆): 39.3 ppm. MS (EI): *m*/*z* 568 (M⁺). HRMS calcd for C₁₉H₃₇IrPBr: 568.143390. Found: 568.144568.

4c-*anti*-*d*₂. A solution of **2** was prepared by dissolving a solid mixture of Cp*(PMe₃)IrH₂ (50 mg, 0.123 mmol) and *tert*-butyllithium (8 mg, 0.125 mmol) in C₆H₆ (8 mL). After stirring for 15 min at ambient temperature, the Cp*(PMe₃)Ir(Li)(H) solution was evaporated to dryness and dissolved in 10 mL of THF. A solution of **3**-*syn*-*d*₂ (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 C₆H₆ (5 mL). To the benzene solution was added CCl₄ (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 \times 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-d2 in 24% isolated yield. ¹H{²H} NMR (CDCl₃): δ 2.38 (dd, $J_{H-P} = 3.9$ Hz, $J_{H-H} = 14.1$ Hz, 0.5 H), 1.71 (dd, $J_{H-P} = 5.3$ Hz, $J_{H-H} = 14.1$ Hz, 0.5 H), 1.50 (d, $J_{H-P} = 1.8$ Hz, 15 H), 1.28 (d, $J_{H-P} = 10.2$ Hz, 9 H) (the diastereotopic β -protons were partially obscured by the PMe₃ resonance in CDCl₃ solvent). ²H NMR (CDCl₃): δ 2.36 (br s), 1.66 (br s), 1.34 (br s), 1.27 (br s) ppm.

Reaction of 2 with H₂ and D₂. A solution of 2 (10 mg, 0.025 mmol) in C₆D₆ (0.55 mL) was placed in a J. Young NMR tube. The solution was frozen in liquid N2, evacuted under full vaccum, 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 ¹H 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 precipiate was observed. Analysis of the tube contents at this time indicated complete and clean conversion to Cp*(PMe₃)IrH₂ (1). The reaction of Cp*(PMe₃)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 ¹H NMR spectroscopy. The ¹H NMR spectrum indicated the presence of a statistical mixture of Cp*(PMe₃)IrH₂, Cp*-(PMe₃)Ir(H)(D), and Cp*(PMe₃)IrD₂ along with approximately 20% unreacted 2. Removal of the volatile materials in vacuo and dissolution in C_6H_6 with addition of 5 mL of C_6D_6 as an internal standard allowed for quantitative analysis of the ²H NMR spectrum. This spectrum indicated that deuterium incorporation had occurred exclusively at the hydride position of 1 with the exent 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_8 was placed in an NMR tube. Subsequently, a solution of a carbon acid (diphenylmethane, DMSO, or CH₃CN, 2–16 equiv) in THF- d_8 was added via syringe. Analysis of the ¹H NMR spectrum indicated complete conversion of **2** to Cp*(PMe₃)IrH₂.

Reaction of 1 with Benzylpotassium. Benzylpotassium (6.7 mg, 52 mmol) was suspended in C_6D_6 (200 mL), and THFd₈ (100 mL) was added to effect dissolution. To this solution was added a solution of **1** (21 mg, 52 mmol) in C_6D_6 (800 mL). A 360 mL aliquot of the red-orange solution was transferred to an NMR tube and analyzed by ¹H NMR and ³¹P NMR spectroscopy. The spectrum showed a 90:10 ratio of Cp*(PMe₃)-Ir(K)(H) and **1** based upon average integrations of the Cp*, PMe₃, and hydride resonances. ¹H NMR (C_6D_6 -THF-d₈): δ 2.17 (s, 15 H), 1.49 (d, $J_{H-P} = 8.0$ Hz, 9 H), -19.0 (d, $J_{H-P} = 30.7$ Hz, 1 H) ppm. ³¹P{¹H} NMR (C_6D_6 -THF-d₈): δ -63.4 ppm.

Reaction of 1 with Benzyllithium. To a solution of **1** (14 mg, 35 mmol) in 0.5 mL C_6D_6 was added benzyllithium·2THF⁹⁹ (7.3 mg, 31 mmol). The yellow solution was placed in an NMR tube, and the contents were subjected to ¹H NMR analysis. The ¹H NMR spectrum showed complete conversion of benzyllithium to toluene and **2** as a mixture of oligomers.

 $Cp^*(PMe_3)Ir(SnPh_3)(H)$ (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 Ph₃SnCl (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

⁽⁹⁸⁾ Beard, C. D.; Baum, K.; Grakauskas, V. J. Org. Chem. 1973, 38, 367.

cooled to -40 °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 cm⁻¹. ¹H NMR (C₆D₆): δ 7.95 (6 H, d, $J_{Sn-H} = 36$ Hz), 7.28 (6 H, m), 7.20 (3 H, m), 1.77 (15 H, d, $J_{P-H} = 1.9$ Hz), 1.12 (9 H, d, $J_{P-H} = 9.8$ Hz), -17.40 (1 H, d, $J_{P-H} = 30.2$ Hz, $J_{Sn-H} = 133$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆): δ 147.3 (CH), 138.1 (CH, $J_{Sn-C} = 35.2$ Hz) 127.8 (CH), 127.2 (C), 92.4 (C), 23.3 (CH₃, d, $J_{P-C} = 38.3$ Hz), 10.99 (CH₃) ppm. ³¹P{¹H} NMR (C₆D₆): δ -54.6 ($J_{Sn-P} = 167$ Hz) ppm. MS (EI): m/z 754 (M⁺). HRMS calcd for C₃₁H₄₀PSnIr: 754.151314. Found: 754.151705.

Cp*(PMe₃)Ir(SnMe₃)(H) (5b). To a solution of 1 (100 mg, 247 mmol) in C₆H₆ (7 mL) was added a solution of tertbutyllithium (18 mg, 281 mmol) in C₆D₆ (3 mL). The bright yellow solution was stirred at ambient temperature for 5 min and a solution of Me₃SnCl (56 mg, 281 mmol) in C₆H₆ (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 ¹H NMR spectroscopy indicated 91% conversion to 5b. Multiple attempts to purify this material by recrystallization from pentane at -40 °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 cm⁻¹. ¹H NMR (C₆D₆): δ 1.90 (15 H, s), 1.29 (9 H, d, J_{P-H} = 10.0 Hz), 0.53 (9 H, s, $J_{Sn-H} = 37.8$ Hz), -18.08 (1 H, d, $J_{P-H} = 30$ Hz, $J_{Sn-H} =$ 137 Hz) ppm. $^{13}\text{C}\{^{1}\text{H}\}$ NMR (C₆D₆): δ 92.2 (C), 23.4 (CH₃, d, $J_{P-C} = 28.6 \text{ Hz}$) 11.24 (CH₃), -5.2 (CH₃, $J_{Sn-C} = 187 \text{ Hz}$) ppm. ³¹P{¹H} NMR (C₆D₆): δ -51.2 (J_{Sn-P} = 162 Hz) ppm. MS (EI): m/z 570 (M⁺). HRMS calcd for C₁₆H₃₄PSnIr: 570.104956. Found: 570.106435.

Cp*(PMe₃)Ir(BF₂)(H) (6a). A solid mixture of 1 (152 mg, 375 mmol) and tert-butyllithium (27.5 mg, 430 mmol, 1.15 equiv) was dissolved in C_6H_6 (5 mL). After stirring for 10 min at room temperature, a solution of boron trifluoride-etherate (108 mg, 124 mL, 760 mmol, 2 equiv) in C_6H_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 LiBF₄ 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. ¹H 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 °C) afforded 40 mg of 6a as a white crystalline solid in a 23% yield containing approximately 10% 2 as an impurity. Mp: 73-75 °C. IR (KBr): 2972, 2906, 2088, 954 cm⁻¹. ¹H NMR (C₆D₆): δ 1.95 (15 H, s), 1.29 (9 H, d, $J_{P-H} = 9.9$ Hz), -17.45 (1 H, dt, $J_{P-H} = 27.0$ Hz, $J_{H-F} = 12.0$ Hz) ppm. ¹³C-{¹H} NMR (C₆D₆): δ 95.2 (C), 21.9 (CH₃, d, $J_{P-C} = 38.9$ Hz), 10.5 (CH₃) ppm. ³¹P{¹H} NMR (C₆D₆): δ -42.6 ppm. ¹⁹F NMR (C₆D₆): (22 °C) δ –29.6 ppm (br d with unresolved coupling). ¹⁹F NMR (C₇D₈) (90 °C): δ –23.2 ppm (q, J_{B-F} = 154.4 Hz). ¹¹B NMR (C₇D₈) (22 °C): δ 23.9 ppm (t, $J_{B-F} = 159.6$ Hz) MS (EI): m/z 454 (M⁺). HRMS calcd for C₁₃H₂₅BF₂PIr: 454.138443. Found: 454.138992.

Cp*(PMe₃)Ir(BPh₂)(H) (6b). Method A. Reaction of 2 with Ph₂BBr. A solid mixture of **1** (150 mg, 370 mmol) and *tert*-butyllithium (25 mg, 390 mmol, 1.05 equiv) was dissolved in C₆H₆ (10 mL). After stirring for 15 min at room temperature, a C₆H₆ solution of Ph₂BBr (100 mg, 407 mmol, 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 CH₃CN (2 mL). The pentane layer was decanted and set aside, and the CH₃CN 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. ¹H 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 C₆D₆ and titrated with portions of CHBr3 to convert 1 to Cp*(PMe3)Ir(H)(Br) and Cp*-(PMe₃)IrBr₂. The titration was monitored by ¹H NMR spectroscopy to determine the extent of conversion of 1 to Cp*-(PMe₃)Ir(H)(Br) and Cp*(PMe₃)IrBr₂. Complete conversion was observed after a total of 6.3 mL of CHBr3 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 CH₃CN to afford 40 mg of Cp*(PMe₃)Ir(BPh₂)-(H) as a yellow crystalline solid. The purified yield for the procedure was calculated to be 24% based on recovered 1, though ¹H 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 Ph₂BOBPh₂. A solid mixture of 1 (90 mg, 220 mmol) and tert-butyllithium (18 mg, 280 mmol, 1.25 equiv) was dissolved in C_6H_6 (5 mL), and the resulting solution was stirred for 5 min at room temperature. A solution of Ph₂BOBPh₂ (90 mg, 260 mmol, 1.18 equiv) in C₆H₆ (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 CH₃CN (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 ¹H NMR spectroscopy indicated unisolated yields are greater than 90%. IR (KBr): 2971, 2904, 2088, 1297, 952, 701 cm⁻¹. ¹H NMR (C₆D₆): δ 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, $J_{P-H} = 9.6$ Hz), -16.53 (1 H, d, $J_{P-H} = 32.8$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆): δ 161.2, 133.9, 127.4, 126.6, 95.3, 22.0 ppm (d, $J_{C-P} = 38.5$ Hz). ³¹P-{¹H} NMR (C₆D₆): δ -42.6 ppm. ¹¹B NMR (C₆D₆): δ 93 ppm (v. broad) Anal. Calcd for C₂₅H_{35B}PIr: C, 52.72; H, 6.19. Found: C, 52.73; H, 6.28.

Cp*(PMe₃)Ir(CO^tBu)(H) (7a). To a stirred suspension of 2 (104 mg, 252 mmol) in THF (10 mL) at room temperature was added a solution of pivalic anhydride (47 mg, 252 mmol) 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 ¹H NMR spectrscopy 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% Et₂O in pentane as the eluent. The product eluted as a yellow band, which was collected, pumped to dryness, and recrystallized from pentane (-40 °C). The recrystallization provided pure 7a as very large (>20 mg) yellow blocklike crystals. IR (KBr): 2085, 1574 cm⁻¹. ¹H NMR (C₆D₆): δ 1.82 (15 H, s), 1.28 (9 H, s), 1.19 (9 H, d, $J_{P-H} = 10.3$ Hz), -17.02 (1 H, d, $J_{P-H} = 34.8$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆): δ 233.1 (C, d, $J_{P-C} = 10.5$ Hz), 94.0 (C), 29.5 (C), 19.6 (CH₃, d, $J_{P-C} =$ 37.6 Hz), 10.8 (CH₃) ppm. ${}^{31}P{}^{1}H$ NMR (C₆D₆): δ -35.5 ppm. Anal. Calcd for C₂₀H₃₀OPIr: C, 44.20; H, 7.00. Found: C, 44.21; H, 7.24.

Cp*(PMe₃)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 C₆H₆ (5 mL). After filtration through Celite, the solvent was removed under vacuum to provide an orange oil. ¹H 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% Et₂O 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⁻¹. ¹H NMR (C₆D₆): δ 8.24 (2 H, d, $J_{H-H} = 7.2$ Hz), 7.29 (2 H, m), 7.20 (1 H, m), 1.77 (15 H, d, $J_{P-H} = 1.9$ Hz), 1.23 (9 H, d, $J_{\rm P-H}$ = 10.4 Hz), -16.35 (1 H, d, $J_{\rm P-H}$ = 36.0 Hz) ppm. ¹³C{¹H} NMR (C₆D₆): δ 223.1 (C, d, $J_{P-C} = 11.6$ Hz), 154.3 (CH), 129.2 (C), 129.1 (CH), 127.1 (CH), 93.7 (C), 18.5 (CH₃, d, $J_{P-C} = 38.4$ Hz), 10.1 (CH₃) ppm. ³¹P{¹H} NMR (C₆D₆): δ -38.2 ppm. MS (EI): m/z 510 (M^+). Anal. Calcd for C₂₀H₃₀OPIr: C, 47.13; H, 5.93. Found: C, 47.30; H, 5.96.

Cp*(PMe₃)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_6H_6 (5 mL), and the yellow solution was stirred for 5 min at ambient temperature. A solution of ethyl formate (22 mg, 310 mmol) in C₆H₆ (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 ¹H 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% Et₂O 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⁻¹. ¹H NMR (C₆D₆): δ 15.25 (1 H, d, $J_{P-H} = 4$ Hz), 1.73 (15 H, s), 1.36 (9 H, d, $J_{P-H} = 10.8$ Hz), -17.33 (1 H, d, J_{P-H} = 32.0 Hz) ppm. ¹³C{¹H} NMR (C₆D₆): δ 219.2 (C, d, J_{P-C} = 11.6 Hz), 95.9 (C), 19.1 (CH₃, d, $J_{P-C} = 40$ Hz), 9.7 (CH₃) ppm. ³¹P{¹H} NMR (C₆D₆): δ -37.94 ppm. MS (EI): m/z 432 (M -2⁺). MS (FAB): m/z 433 (M – 2 + H⁺). Anal. Calcd for C₁₄H_{25⁻} 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_6D_6 (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 ¹H 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_6D_6 (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_2 and Carbonates. In a typical example, a solution of 2 (6.3 mg, 15.6 mmol) in toluene- d_8 (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 N₂, 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 ¹H 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*(PMe₃)Ir(Me)(H) and Cp*(PMe₃)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_8 (400 mL) was treated with CO_2 (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 ¹H 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*(PMe₃)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. ¹H NMR analysis of the oil indicated a mixture of 1 and Cp*(PMe₃)Ir-(CO) in a 2:1 ratio based upon ¹H 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 C₆D₆ (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 N₂. After evacuating to 30 mTorr, the tube was flame-sealed, thawed, and then heated for 6 h at 75 °C. ¹H 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 C₆D₆ (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 C₆D₆ (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 ¹H NMR indicated quantitative conversion to complex 8.

Cp*(PMe₃)Ir(C₆F₅)(H) (12). To a solution of 1 (106 mg, 262 mmol) in C₆H₆ (4 mL) was added a solution of tert-butyllithium (17 mg, 265 mmol) in C_6H_6 (1 mL). After stirring for 5 min at room temperature, a solution of C₆F₆ (102 mg, 548 mmol, 2.07 equiv) in C₆H₆ (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 though 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⁻¹. ¹H NMR (C₆D₆): δ 1.70 (15 H, s), 0.95 (9 H, d, $J_{P-H} = 10.0$ Hz), -16.47 (1 H, dd, $J_{P-H} = 37.1$ Hz, $J_{H-F} = 11.4$ Hz) ppm. ¹³C{1H} NMR (C₆D₆): δ 92.9 (C), 19.60 (CH₃, d, $J_{P-C} = 38.4$ Hz), 10.0 (CH₃) ppm.¹⁹F NMR (C₆D₆): δ –107.2 (d, J_{F-F} = 31.6 Hz), -111.4 (d, $J_{F-F} = 35.1$ Hz), -163.7 (t, $J_{F-F} = 20.6$ Hz), -164.07 (ddd), -165.1 (ddd). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆): $\delta -44.5$ ppm. MS (EI): m/z 572 (M⁺). HRMS calcd for C₁₉H₂₅F₅PIr: 572.124348. Found: 572.124514.

Reaction of 2 with C₆H₅F To Give Cp*(PMe₃)Ir(C₆H₅)-(H) (13). A solution of 2 (7.42 mg, 18 mmol) in C₆D₆ (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 syring. The ¹H 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 ¹H 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*(PMe₃)Ir(CF=CFCF₃)(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 N₂, 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 C₆H₆, and the combined extracts were filtered through Celite. Removal of the solvent in vacuo afforded 146 mg of a dark brown oil identified by ¹H 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⁻¹. ¹H NMR (C₆D₆): δ 1.76 (15 H, s), 1.12 (9 H, d, $J_{P-H} = 10.4$ Hz), -17.01 (1 H, ddd, $J_{H-F} = 6.0$ Hz, $J_{H-F} = 14.0$ Hz, $J_{P-H} = 34.5$ Hz) ppm. ¹³C{¹H} NMR (C₆D₆): δ 94.5.(C), 19.5 (CH₃, d), 10.0 (CH₃) ppm.¹⁹F NMR (C₆D₆): δ -107.2 (d, J_{F-F} = 31.6 Hz), -111.4 (d, J_{F-F} = 35.1 Hz), -163.7 (t, $J_{F-F} = 20.6$ Hz), -164.07 (ddd), -165.1 (ddd). $^{31}P{^{1}H} NMR$ (C₆D₆): δ -41.5 ppm. MS (EI): m/z 536 (M⁺). Anal. Calcd for C₁₆H₂₅F₅PIr: 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_6H_6 (25 mL) was added a solution of *tert*-butyllithium (25 mg, 390 mmol, 1.3 equiv) in C_6H_6 (1 mL). The bright yellow solution was transferred to a 100 mL glass reaction vessel equipped with a Teflon stopcock and

frozen in liquid N₂. After evacuating the reaction vessel, 3,3,3trifluoropropene (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. ¹H 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: ¹H NMR (C₆D₆): δ 4.56 (dddd, 1 H), 2.26 (m, 1 H), 1.98 (m 1 H), 1.76 (s, 15 H), 1.17 (d, $J_{P-H} = 9.72$ Hz, 9 H), -17.75 (d, $J_{P-H} = 40$ Hz, 1 H) ppm. ¹⁹F NMR (C₆D₆): δ -98.9 (d, $J_{F-F} = 113$ Hz), -99.2 (dd, $J_{F-F} = 110$ Hz, $J_{H-F} = 42$ Hz) ppm. ³¹P{¹H} NMR (C₆D₆): δ -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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