Mechanistic Investigation of the Reaction of Iridium Dihydride Complexes with Organic Acid Chlorides

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Treatment of Cp*(PMe_3)IrH_2 (**1a**) with aromatic and hindered aliphatic acid chlorides ClC(O)R in benzene in the presence of an amine (*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (**7**), (−)-sparteine (**8**), or triethylamine (**9**)), results in the formation of Ir(III) acyl hydride complexes, Cp*(PMe_3)Ir(C(O)R)H (R = C_6H_5, **3a**; *p*-$CH_3C_6H_4$, **3b**; *p*-CNC_6H_4, **3c**; *p*-$NO_2C_6H_4$, **3d**; *p*-$CF_3C_6H_4$, **3e**; *p*-FC_6H_4, **3f**; *p*-$CH_3OC_6H_4$, **3g**; $CHMe_2$, **4**; $CHPh_2$, **5**; CMe_3, **6**) with the accompanying precipitation of the corresponding ammonium chloride salt. Kinetic studies revealed the formation of **3**−**6** to be first order in **1a** and acid chloride and zero order in amine. A Hammett correlation showed that the reaction rate is increased by electron-withdrawing groups on the aromatic ring of the aroyl chloride. Changing the substituent on the iridium-bound phosphine was found to have a significant steric effect along with an unexpected electronic effect. In contrast to the reaction seen with aroyl chlorides, the reaction of **1a** with monosubstituted acetyl chlorides in the presence of Proton Sponge results in the formation of vinyl chloride complexes, Cp*(PMe_3)Ir(CH=CHR)(Cl) (R = H, **15a**; CH_3, **15b**; C_6H_5, **15c**). On the basis of the kinetic results for the formation of **3**−**6**, the formation of both acyl hydride and vinyl chloride complexes is proposed to occur via nucleophilic attack of the metal center at the carbonyl carbon as the first step.

Introduction

Alkylation and acylation of organometallic anions via nucleophilic displacement is a common method for the formation of metal−carbon bonds.[1−10] In these reactions, the transition metal complex acts as the nucleophile. The kinetics and mechanisms of these reactions have received much attention since formal nucleophilic attack by a metal complex is a key step in many catalytic processes.[2,11−17]

The nucleophilicities of a number of organometallic complexes have been compiled, and large differences have been observed.[14,18−21] However, most of the complexes studied were metal carbonyl anions;[6−8,14,15,17−19,21] the nucleophilicity of only a few neutral, 18-electron, organometallic complexes have been evaluated quantitatively.[22−24] Previous work in our group has shown that Cp*(PMe_3)IrH_2 (**1a**) can be deprotonated using *tert*-butyllithium, and the resulting anion acts as a nucleophile in many types of reactions.[25,26] In this report we describe mechanistic studies of the reaction of this coordinatively saturated electron-rich iridium hydride with acid chlorides in the presence of amines. In light of our previous results, we were interested in whether this reaction occurs via the neutral complex or the deprotonated metal anion.

Results

Reactivity of 1 with Benzoyl and Substituted Acetyl Chlorides. Synthesis of Cp*(PMe_3)Ir(C(O)R)(H) Complexes. Previously, we reported the synthesis of the acyl hydride Cp*(PMe_3)Ir($C(O)C_6H_5$)(H) (**3a**) from

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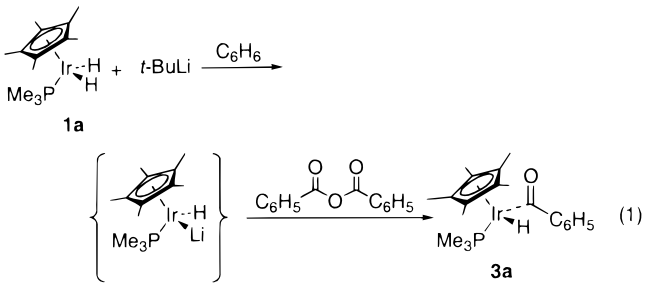
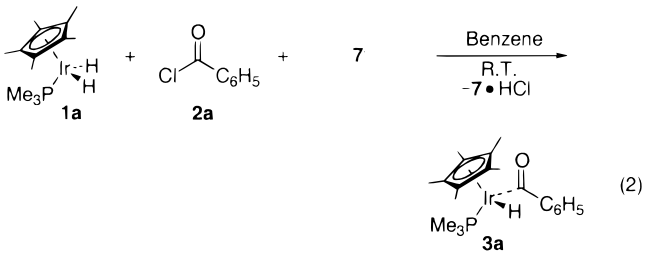
$\{Cp^*(PMe_3)Ir(Li)(H)\}_n$ (Cp^* = pentamethylcyclopentadienyl) and benzoic acid anhydride (eq 1).[25] The iridate was synthesized by deprotonation of $Cp^*(PMe_3)IrH_2$ (**1a**) with *t*-BuLi. This method, however, gave poor yields of compound **3a** due to the difficulty of isolating the product cleanly. To solve these problems with the synthetic route, a new method was developed.



(1)

Treatment of $Cp^*(PMe_3)IrH_2$ (**1a**)[27,28] with acid chlorides ClC(O)R ((R = C_6H_5, **2a**; *p*-$CH_3C_6H_4$, **2b**; *p*-CNC_6H_4, **2c**; *p*-$NO_2C_6H_4$, **2d**; *p*-$CF_3C_6H_4$, **2e**; *p*-FC_6H_4, **2f**; *p*-$CH_3OC_6H_4$, **2g**; $CHMe_2$, **2h**; $CHPh_2$, **2i**; CMe_3, **2j**) in benzene in the presence of an amine (*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (**7**), (−)-sparteine (**8**), or triethylamine (**9**)) results in the formation of yellow or orange complexes $Cp^*(PMe_3)Ir(C(O)R)H$ (R = C_6H_5, **3a**; *p*-$CH_3C_6H_4$, **3b**; *p*-CNC_6H_4, **3c**; *p*-$NO_2C_6H_4$, **3d**; *p*-$CF_3C_6H_4$, **3e**; *p*-FC_6H_4, **3f**; *p*-$CH_3OC_6H_4$, **3g**; $CHMe_2$, **4**; $CHPh_2$, **5**; CMe_3, **6**) with the precipitation of the corresponding ammonium chloride salt.[29] A representative example is shown in eq 2. All the products exhibit similar spectroscopic characteristics. The hydride resonances in the ^1H NMR spectra appear as doublets at ca. δ −16.5 ppm (depending on the acyl group). The resonance for the phosphine in the $^{31}P\{^1H\}$ NMR spectrum is at ca. δ −38 ppm for **3**−**6**.



(2)

X-ray Crystallographic Study of 3b. To investigate the solid-state structure of compounds **3a**−**g**, a single-crystal X-ray diffraction study of compound **3b**, R = *p*-tolyl, was performed. X-ray quality crystals of **3b** were obtained by crystallization from pentane at −40 °C. An ORTEP diagram is shown in Figure 1, selected bond lengths and angles are listed in Table 1, and the crystal and data collection parameters are listed in Table 2. Compound **3b** forms as an undisordered chiral crystal, and only one enantiomer is shown. The hydride ligand was located and refined isotropically; the Ir−H bond distance was determined to be 1.58 Å. The observed three-legged piano stool geometry is common for complexes of this type.

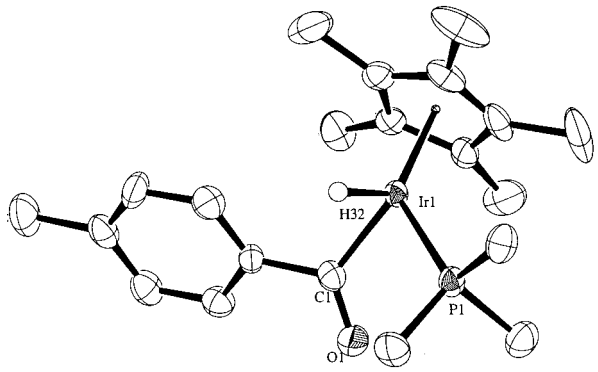


Figure 1. ORTEP diagram of $Cp^*(PMe_3)Ir(C(O)p\text{-}CH_3C_6H_4)(H)$ (**3b**). Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms (except H32) are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b

Bond Lengths	
Ir(1)−P(1)	2.239(1)
C(1)−Ir(1)	2.016(4)
C(1)−O(1)	1.238(5)
Ir(1)−C(101)	2.073(8)
Ir(1)−H(32)	1.58(5)
Bond Angles	
P(1)−Ir(1)−C(1)	87.4(1)
C(1)−Ir(1)−C(101)	126.2(1)
Ir(1)−C(1)−C(2)	120.0(3)
Ir(1)−C(1)−H(32)	127(1)

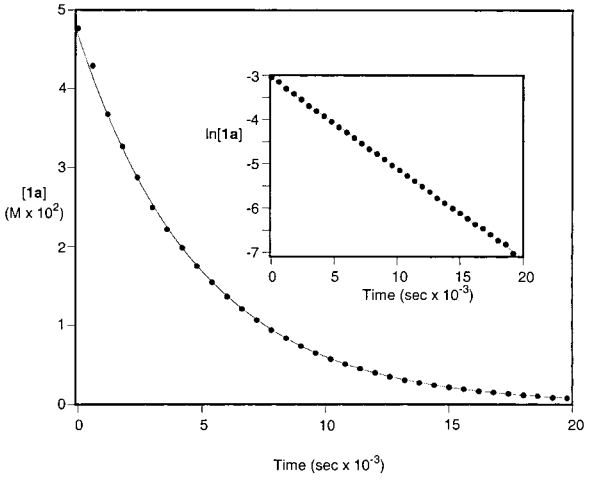


Figure 2. Plot of the disappearance of **1a** with time obtained using flooding conditions. Conditions: [**1a**] = 4.00 × 10^{-2} M, [**7**] = 0.242 M, [**2a**] = 0.408 M. Inset: Plot of ln[**1a**] vs time. The observed rate constant = (2.04 ± 0.1) × 10^{-4} s^{-1}.

Kinetic Studies of the Reaction of 1a with Benzoyl Chlorides. To gain further insight into the mechanism of the reaction, the concentration of reagent **1a** and products **3a**−**g** were monitored over the course of the reaction by ^1H NMR spectroscopy. The reaction was performed under pseudo-first-order conditions by employing a large excess of benzoyl chloride and **7**. A typical plot of the change in concentration of **1a** over time is shown in Figure 2, along with its corresponding ln [**1a**] versus time plot. These plots indicate a clean

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(29) One referee asked about the result of treating **1a** with **2a** in the absence of amine. This results in formation of a complex mixture of products, several of which we were unable to identify, but including a small amount of **3a**.

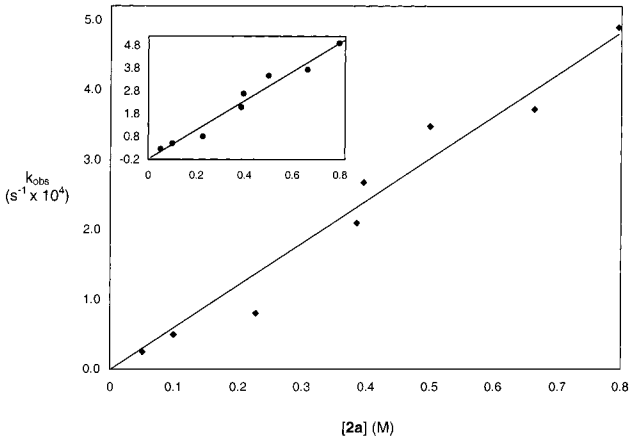


Figure 3. Rate dependence on [**2a**] using flooding conditions for the reaction with **1a** and **7** ($R^2 = 0.96$) with the intercept set at zero. Inset: Same rate dependence plot with intercept not set at zero ($R^2 = 0.97$).

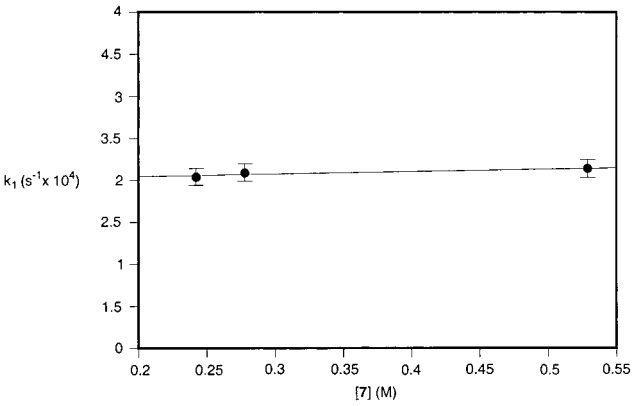


Figure 4. Rate dependence on [**7**] measured using flooding conditions for the reaction with **1a** and **2a**.

first-order dependence of the reaction rate on the concentration of **1a**.

By measuring the reaction rate with varied (excess) concentrations of benzoyl chloride, we found the reaction to be first order in benzoyl chloride as well. A plot of the pseudo-first-order rate constant versus [benzoyl chloride] is shown in Figure 3.[30] A similar study demonstrated that the reaction is zero order in the concentration of **7** (Figure 4). From the kinetic data, an experimental rate law was derived (eq 3). The rate constants derived from the kinetic runs are shown in Table 2.

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_1[\mathbf{1}][\text{acid chloride}] \qquad (3)$$

To test for radical intermediates, the reaction was run in the presence of 5 equiv of a radical scavenger, 9,10-dihydroanthracene (DHA). No changes in the product composition or the qualitative rates of reaction were observed.

Dependence of Reactivity on Acid Chloride Structure. In an effort to better understand the electronic effects in the reaction of **1** with acid chlorides, a Hammett correlation study was undertaken using four different *p*-substituted benzoyl chlorides. Rate constants were measured for the reaction of **1** and **7** with *p*-methoxybenzoyl, *p*-toluoyl, benzoyl, and *p*-fluoromethylbenzoyl chlorides. Qualitative $t_{1/2}$ values were measured for *p*-trifluoromethyl, *p*-cyano, and *p*-nitrobenzoyl chloride as the rates of reaction of **1a** with these substrates were too fast to measure conveniently by ^{1}H NMR spectroscopy.[31] The initial concentrations of **1**, acid chloride, and **7** were kept constant for all runs. Electron-withdrawing substituents on the acid chloride induced a dramatic increase in the reaction rate relative to the reaction with benzoyl chloride. A Hammett plot (Figure 5) of the results yielded a linear correlation with a ρ value of 2.42. The half-life decreased from 5 h for *p*-methoxybenzoyl chloride to 20 min for *p*-fluorobenzoyl chloride. The $t_{1/2}$ for *p*-nitrobenzoyl chloride was approximately 2 min.

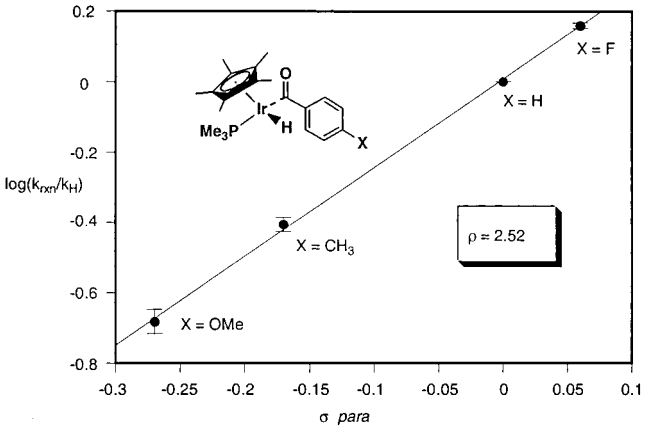


Figure 5. Hammett correlation for the reaction of **1a** with para-substituted benzoyl chlorides in the presence of **7**.

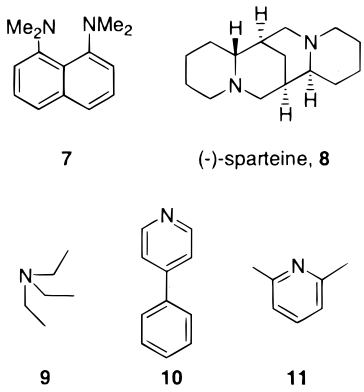


Figure 6. Amines used in the kinetic study.

Dependence on Amine Structure. The reaction rate was measured in the presence of several different amines to study the dependence on amine structure. The reaction conditions were the same as those used for the Hammett correlation. Five different amines were studied: *N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (**7**), (−) sparteine (**8**), *p*-phenylpyridine (**9**), 2,6-dimethylpyridine (**10**), and triethylamine (**11**) (Figure 6). Due to competitive formation of Cp*(PMe_3)$IrCl_2$ along with the acyl

(30) Data taken initially showed more scatter, leading to ambiguity with regard to the intercept and reaction order in [**2a**]. Redetermination of some of the kinetic data improved the error and the reliability of the order in [**2a**]. We are grateful to a referee for calling our attention to this problem.

(31) Due to the thermal sensitivity of the products, determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction with benzoyl chloride was unsuccessful. Running the reaction above room temperature results in side products, and the temperature could not be reduced enough to provide a temperature range large enough to ensure good accuracy in the derived activation parameters.

Table 2. Crystal and Data Collection Parameters for 3b and 15a

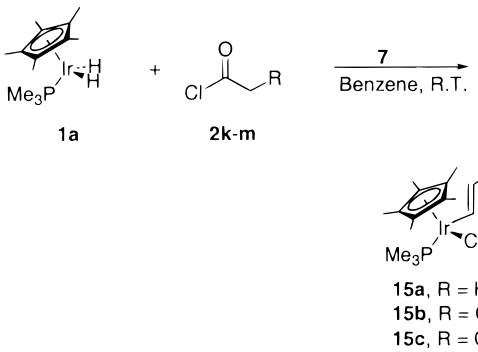
	3b	15a
empirical formula	$C_{15}H_{33}OPIr$	$C_{15}OPClIrH_{27}$
fw	523.68	482.02
cryst color, habit	pale yellow, blades	yellow, prism
cryst dimens	0.32 × 0.22 × 0.08 mm	0.20 × 0.21 × 0.07 mm
cryst syst	monoclinic	orthorhombic
lattice type	primitive	primitive
lattice params	a = 8.6780(1) Å	a = 11.9627(2) Å
	b = 11.76704(2) Å	b = 12.8214(1) Å
	c = 20.2744(1) Å	c = 11.2949(2) Å
	β = 91.472(1)°	V = 1732.40(4) Å^3
	V = 2069.62(4) Å^3	
space group	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)
Z value	4	4
D_{calc}	1.681 g/cm^3	1.848 g/cm^3
F_{000}	1032.00	936.00
μ(Mo Kα)	65.51 cm^{-1}	79.66 cm^{-1}
diffractometer	SMART CCD	SMART CCD
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
	graphite monochromated	graphite monochromated
detector position	60.00 mm	60.00 mm
temperature	−96 °C	10.0 s per frame
scan type	ω (0.30 deg/frame)	ω (0.30 deg/frame)
scan rate	10.0 s/frame	
$2\theta_{max}$	52.3°	51.9°
no. of reflns measd	total: 10 009	total: 8370
	unique: 3870 (R_{int} = 0.029)	unique: 1826 (R_{int} = 0.040)
corrections	Lorentz−polarization absorption	Lorentz−polarization absorption
	(T_{max} = 0.959, T_{min} = 0.441)	(T_{max} = 0.86, T_{min} = 0.62)
structure solution	direct methods (SIR92)	direct methods (SIR92)
refinement	full-matrix least-squares	full-matrix least-squares
p-factor	0.0300	0.03
anomalous dispersion	all non-hydrogen atoms	all non-hydrogen atoms
no. observations ($I > 3.00\sigma(I)$)	3074	2160
no. variables	226	162
reflection/param ratio	13.60	13.33
residuals: R; R_w; R_{all}	0.020; 0.028; 0.027	0.020; 0.023; 0.025
goodness of fit indicator	1.15	0.78
max shift/error in final cycle	0.02	0
max peak in final diff map	0.47 e/ Å^3	0.90 e/Å3
min peak in final diff map	−0.59 e/ Å^3	−1.50 e/Å3

hydride product with *p*-phenylpyridine and 2,6-dimethylpyridine, rate constants were not measured in these cases. In the case of the remaining three amines, the measured rate constants are shown in Table 2. They were, as expected, the same within error. This is consistent with the zero-order rate dependence of the amine determined previously in the kinetic studies.

Rate Dependence on Phosphine Structure. The reaction of **1a**−**f** (Cp*(PR$_3$)IrH$_2$: P(CH$_3$)$_3$, **1a**; P(CH$_2$CH$_2$CH$_3$)$_3$, **1b**; P(C$_6$H$_5$)(CH$_3$)$_2$, **1c**; P(*p*-CH$_3$OC$_6$H$_4$)(CH$_3$)$_2$, **1d**; P(*p*-CF$_3$C$_6$H$_4$)(CH$_3$)$_2$, **1e**; P(C$_6$H$_5$)$_3$, **1f**) with benzoyl chloride and **7** was studied to determine the effect on the reaction caused by changing the steric and electronic properties of the phosphine. Compounds **1b**−**f** were synthesized using a method analogous to that used to prepare the previously reported trimethylphosphine complex **1a** (**1c**−**e** from Cp*(L)IrCl$_2$, L = P(C$_6$H$_5$)(CH$_3$)$_2$ (**28**); P(*p*-CH$_3$OC$_6$H$_4$)(CH$_3$)$_2$ (**29**); P(*p*-CF$_3$C$_6$H$_4$)(CH$_3$)$_2$ (**30**), respectively).[27,28]

The reactions were monitored by ^{1}H NMR spectroscopy and carried out under conditions identical to those used in the Hammett study. Compounds **1f** and **1b** were unreactive toward benzoyl chloride in the presence of **7**. Upon heating the reaction mixture, several products were observed in both cases; the only easily identifiable species was Cp*(PMe$_3$)IrCl$_2$. As a result, rate constants were not determined in these two cases. The compounds **1c**−**e** yielded the corresponding acyl hydrides (Cp*(RP(CH$_3$)$_2$)Ir(C(O)Ph)(H), R = C$_6$H$_5$, **12**; *p*-CH$_3$OC$_6$H$_4$, **13**; *p*-CF$_3$C$_6$H$_4$, **14**). To separate phosphine steric and electronic effects, the rates of reaction of **1d** and **1e** were determined. Electron-donating groups were found to accelerate the rate of the reaction. However, the sensitivity of the rate to changes in the substituent was substantially weaker than that observed with the acid chlorides, and so a full Hammett study was not carried out.

Reaction of 1 with Monosubstituted Acyl Chlorides. Synthesis of Cp*(PMe$_3$)Ir(CH=CHR)Cl Complexes. Treatment of **1** with three monosubstituted acyl chlorides (ClC(O)CH$_2$R, R = H, **2k**; Me, **2l**; Ph, **2m**) in the presence of **7** resulted in the formation of Cp*(PMe$_3$)Ir(CH=CHR)(Cl) (H, **15a**; CH$_3$, **15b**; C$_6$H$_5$, **15c**) (eq 4). Compounds **15a**−**c** have been characterized using



(4)

^{1}H NMR, ^{31}P{^{1}H} NMR, ^{13}C{^{1}H} NMR, IR spectroscopy, elemental analysis, and in the case of the parent vinyl chloride complex, **15a**, X-ray crystallography.

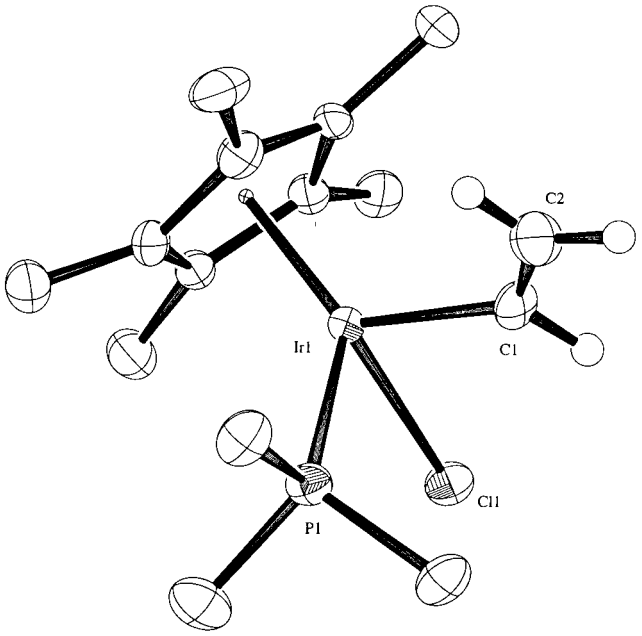


Figure 7. ORTEP diagram of Cp*(PMe_3)Ir($CH{=}CH_2$)Cl. Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms (except on the vinyl moiety) are omitted for clarity.

Complex **15a** exhibits three vinyl resonances in the ^{1}H NMR spectrum at 5.3, 6.7, and 9.1 ppm. Each proton is split by the two other neighboring protons as well as by the phosphorus atom at iridium. The substituted vinyl chlorides (**15b**, **15c**) exhibit one resonance at δ 8.5 ppm for the proton α to iridium and one resonance in the 6 ppm region for the proton β to iridium. In the ^{31}P-{^{1}H} NMR spectrum the vinyl chloride complexes show a singlet at −30 ppm. Compounds **15b** and **15c** form only the trans product, as shown by a coupling constant of 15 Hz between the α- and β-vinylic protons. In solution **15b** and **15c** exist as a mixture of rotational isomers. A similar observation was made previously with a (bromo)(vinyl)iridium complex.[32,33]

X-ray quality crystals of Cp*(PMe_3)Ir($CH{=}CH_2$)(Cl) were obtained by crystallization from pentane at −40 °C. An ORTEP diagram is shown in Figure 7, selected bond lengths and angles are given in Table 4, and crystal and data collection parameters are given in Table 2. The hydrogen atoms were observed on a difference Fourier map and included calculated positions but were not refined. There were no unusual bond lengths or angles in the molecule.

Deuterium Incorporation Studies. Reaction of **1** with acetyl chloride-d_3 resulted in 40% deuterium incorporation into the α-hydrogen position of **15a** and 70% deuterium incorporation in the β-hydrogen positions (as determined by ^{1}H NMR spectroscopy). In the reaction of **1**-d_2 with acetyl chloride, deuterium incorporation was determined to be 65% in the α-hydrogen position and 30% in the β-hydrogen positions. The reaction of **1**-d_2 with acetyl chloride-d_3 resulted in **15a** having 100% deuterium incorporation in all three vinyl positions.

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Discussion

Mechanism of Formation of Iridium Acyl Hydride. Three possible mechanisms for the formation of **3**−**6** are shown in Scheme 1. The two-electron mechanisms (A and B) will be discussed first. The difference between these two possible pathways hinges on whether nucleophilic attack by iridium on the acid chloride occurs as the rate-determining step (mechanism A) (eq 5), or deprotonation of **1** by the amine is the rate-determining step (mechanism B) (eq 6, 7). If the initial step involves deprotonation of **1** by the amine, followed by nucleophilic attack of the resulting anion **17** on the acid chloride, the rate law must include the amine concentration. If, however, the initial step involves nucleophilic attack of neutral **1** on the acid chloride to form a cationic intermediate, then the amine concentration need not be part of the rate law. The observed first-order rate dependence on [**1a**] is consistent with both mechanisms A (eq 5) and B (eq 6, i.e., $k_4 \gg k_{-3}$).

$$\text{mechanism A} \quad \text{rate} = k_1[\mathbf{1}][\text{ClC(O)R}] \text{ if } k_2 \gg k_{-1} \tag{5}$$

$$\text{mechanism B} \quad \text{rate} = k_3[\mathbf{1}][\text{NR}_3] \text{ if } k_4 \gg k_{-3} \tag{6}$$

$$\text{rate} = \frac{k_3[\mathbf{1}][\text{NR}_3]}{k_{-3} + k_4[\text{ClC(O)R}]} \text{ if } k_4 \text{ not} \gg k^{-3} \tag{7}$$

The absence of any change in the observed rate constant with varying amine concentrations demonstrates that the amine is *not* involved in the rate-determining step. This rules out deprotonation as the first step. This conclusion is also supported by the lack of noticeable change in the observed rate upon changing the nature of the amine. Therefore, unless electron transfer is involved (see below), we propose that the first step is most likely nucleophilic attack by **1** on the acid chloride followed by fast deprotonation of the cationic iridium intermediate by the amine (mechanism A).

Mechanism A is further supported by the observed Hammett correlation derived from the rate constants. A ρ value of 2.4 indicates substantial charge development in the rate-determining transition state, and this suggests that there is a charge-separated intermediate on the reaction pathway. Electron-withdrawing *p*-substituents on the acid chlorides increase the electrophilicity at the carbonyl carbon, increasing their rate of reaction with nucleophiles. This is consistent with an addition−elimination type of mechanism for this reaction.

Electron-Transfer Mechanism. It is possible that the overall formation of a metal−carbon bond between the iridium center of **1** and the acyl group of the acid chloride takes place by an outer-sphere electron-transfer mechanism. This alternative is illustrated as mechanism C in Scheme 2. Here it is proposed that transfer of an electron between the starting materials is the first step, leading to dihydride radical cation **19** and acid chloride radical anion **20**, initially as partners in a solvent cage. At this point several reaction pathways are possible. One is loss of Cl^- from **20**, followed by collapse of the resulting radical pair to acyl dihydride cation **23**, followed by proton transfer to give **3**−**6**. A related alternative would involve escape from the initial solvent cage, giving the free (presumably solvated)

Table 3. Kinetic Data[a]

iridium complex (× 10^2 M)		amine (M)		acid chloride (M)		k_{obs} (× 10^4 s^{-1})	k_1[b] (× 10^4 M^{-1} s^{-1})	σ_{para}
Acid Chloride Rate Dependence								
1a	1.04	**7**	0.083	**2a**	0.051	0.250 ± 0.02	4.83	
1a	0.962	**7**	0.109	**2a**	0.100	0.500 ± 0.03	4.85	
1a	3.95	**7**	0.225	**2a**	0.227	0.905 ± 0.04	4.02	
1a	3.87	**7**	0.278	**2a**	0.386	2.09 ± 0.1	5.40	
1a	2.00	**7**	0.134	**2a**	0.396	2.68 ± 0.1	6.76	
1a	2.66	**7**	0.271	**2a**	0.500	3.00 ± 0.2	6.00	
1a	4.07	**7**	0.285	**2a**	0.633	3.73 ± 0.2	5.89	
1a	5.03	**7**	0.280	**2a**	0.792	4.89 ± 0.3	6.17	
							av 5.49 ± 1.2	
Amine Rate Dependence								
1a	4.00	**7**	0.242	**2a**	0.408	2.04 ± 0.1	5.00	
1a	3.87	**7**	0.529	**2a**	0.396	2.24 ± 0.1	5.66	
1a	3.90	**7**	0.230	**2a**	0.400	2.09 ± 0.1	5.40	
1a	4.00	**7**	0.225	**2a**	0.227	0.905 ± 0.04	4.02	
1a	3.70	**8**	0.223	**2a**	0.280	1.44 ± 0.07	5.13	
1a	3.94	**9**	0.258	**2a**	0.263	1.09 ± 0.05	4.14	
							av 4.89 ± 0.8	
Hammett Correlation								
1a	4.00	**7**	0.277	**2g**	0.389	0.411 ± 0.02	1.04 ± 0.05	−0.27
1a	4.07	**7**	0.280	**2b**	0.288	0.565 ± 0.03	1.96 ± 0.1	−0.17
1a	4.00	**7**	0.242	**2a**	0.408	2.04 ± 0.1	5.00 ± 0.2	0
1a	4.04	**7**	0.292	**2f**	0.423	3.06 ± 0.2	7.23 ± 0.4	0.06
Phosphine Rate Dependence								
1d	4.05	**7**	0.289	**2a**	0.396	1.06 ± 0.05	2.68 ± 0.1	−0.27
1c	3.90	**7**	0.332	**2a**	0.362	0.830 ± 0.04	2.29 ± 0.1	0
1e	3.83	**7**	0.260	**2a**	0.392	0.340 ± 0.02	0.868 ± 0.04	0.54

[a] A detailed explanation of the kinetic runs is given in the Experimental Section. [b] Standard deviation based on mean value.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 15a

Bond Lengths	
Ir(1)−Cl(1)	2.4256(16)
C(1)−Ir(1)	2.064(8)
Ir(1)−C(101)	1.86300(10)
Ir(1)−P(1)	2.2619(17)
C(1)−C(2)	1.312(12)
Bond Angles	
P(1)−Ir(1)−Cl(1)	86.32(6)
C(1)−Ir(1)−C(101)	122.36(4)
Ir(1)−C(1)−C(2)	127.0(7)
Cl(1)−Ir(1)−C(1)	88.0(3)
P(1)−Ir(1)−C(101)	122.36(4)

radical cation and anion. Earlier work on one-electron reduction of acid halides[34] indicates that the acid chloride radical anion should undergo rapid loss of chloride ion, leading to acyl radical **22**. This species can then either return to the cage or undergo decarbonylation to CO and the corresponding alkyl or aryl radical. With R = Ph, this process is relatively slow ($k_{CO} = 1.5 \times 10^{-7}$ s^{-1} (gas-phase data)),[35] but when R is a tertiary or phenyl-substituted alkyl group, it is much faster (e.g., for R = *t*-Bu $k_{CO} = 7 \times 10^5$ s^{-1} and for R = $CHPh_2$ $k_{CO} = 5.3 \times 10^6$ s^{-1}).[36−38]

To test for the presence of acyl or alkyl free radicals, the reaction was run in the presence of excess radical scavenger, 9,10-dihydroanthracene (DHA). No alkanes or aldehydes were detected by ^{1}H NMR spectroscopy under these conditions, nor did the rate or product distribution change. In the absence of DHA, no R−R products (<5% detectable) were observed. It therefore seems unlikely that *free* radicals are involved in this reaction. It is more difficult to rule out a completely solvent-caged electron-transfer process. However, we believe that in the cases of pivaldehyde and 2,2-diphenylacetaldehyde decarbonylation of the acyl radicals derived from these acid chlorides would be fast enough (see rate constants in previous paragraph) that this process would compete at least to some extent with C−M bond formation in the caged radical pair. The fact that we see good yields of iridium acyl hydrides in these cases argues against the involvement of an outer-sphere electron-transfer process.

Rate Dependence on the Phosphine. The effects on the rate caused by changing the substituents on the iridium-bound phosphine appear to be more complicated than those caused by changing the substituents on the acid chloride. Increasing the size of the alkyl group, as in $Cp^*(P(CH_2CH_2CH_3)_3)IrH_2$ (**1b**), or changing to three aryl groups, as in $Cp^*(P(C_6H_5)_3)IrH_2$ (**1f**), slowed the rate to such an extent that no reaction detectable by ^{1}H NMR spectroscopy occurred over a period of 5 days at 25 °C. When only one methyl group in the PMe_3 ligand was replaced by phenyl, as in $Cp^*(P(C_6H_5)(CH_3)_2)IrH_2$ (**1c**), conversion to acyl hydride product was observed, but the rate was significantly slower than that of the parent compound **1a**. Because of the substantially different electronic properties of alkyl and aryl groups, these results are most reasonably interpreted as a significant steric effect. That is, attaching groups larger than methyl to the phosphorus atom makes the iridium center sufficiently crowded that it is difficult for it to attack the carbonyl carbon atom of the acid chloride.

To investigate the effect of changing the electron density at Ir without simultaneously modifying its steric environment, we examined the rates of reaction of **1d** and **1e**, the complexes with $PMe_2(p\text{-}OMeC_6H_4)$ and

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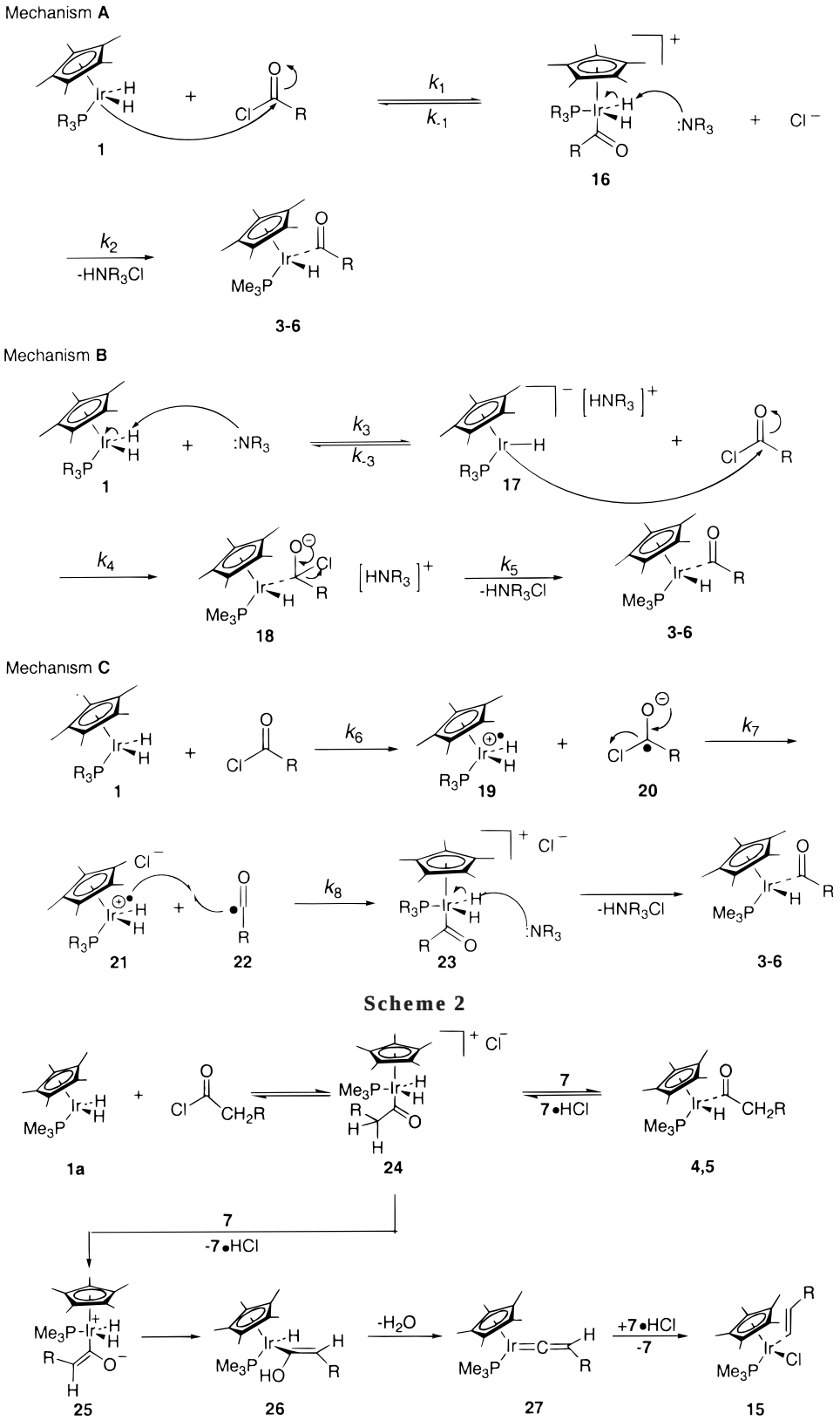
Scheme 1



Scheme 2

$PMe_2(p\text{-}CF_3C_6H_4)$ ligands, respectively, and compared them with that of the PMe_2Ph complex **1c**. Although the *p*-methoxy group is resonance-donating and inductively electron-withdrawing, this phosphine has been shown to accelerate the S_N2-type reactions of other iridium complexes, and so the donating effect dominates. In Vaska's complex, replacing the para H of the triphenylphosphine ligands with electron-donating para substituents was found to result in a large increase in rate of oxidative addition.[39] The rate constants measured for the reaction of **1d** and **1e** with benzoyl chloride showed that electron-donating groups on the phosphine increased the rate of reaction. Although a full Hammett study was not carried out, it was clear from the two

substituents examined that, qualitatively, the sensitivity to *p*-substituents on the phosphine-aryl group is substantially weaker than that observed with the *p*-substituted acid chlorides (i.e., a low apparent ρ value). In view of the effect observed in other systems, this is a surprising result. We suggest that the iridium center may be "soft" enough to provide sufficient polarizability for fast S_N2 substitution even when modestly electron-withdrawing (or donating) groups are present. The "harder" acyl carbon of the acid chloride may not be able to adjust its electron density distribution as readily, and so responds more strongly to substitution changes. To our knowledge, this type of effect has not been explicitly observed or commented upon previously. Examples of this behavior in other systems would therefore be of interest. Alternatively, it is possible that the small ρ value is due to the physical distance between the para substituent and the iridium center such that it has only a small effect on the rate of reaction of **1c**−**e**.

The proposed mechanism is quite different from that observed in many amine-catalyzed reactions of carbonyl compounds[40,41] for which it is thought that the amine attacks the carbonyl carbon first, forming a transient tetrahedral intermediate. Upon displacement of the leaving group, a quaternary acylammonium salt is thought to form. This salt is then susceptible to attack by a nucleophile to form the product. Once again, the lack of rate dependence on the amine makes this an unlikely mechanism for our system.

Johnson[42] has described the factors that determine whether a reaction follows a nucleophilic versus a base-catalyzed pathway. Nucleophilic attack mechanisms are favored by good leaving groups, highly electrophilic acyl groups, and strongly basic nucleophiles. The formation of **3**−**6** seems to follow this pattern. That $Cp^*(P(CH_3)_3)IrH_2$ (**1a**) can act as a Lewis base has been demonstrated elsewhere as well. Golden, Bergman and Anderson have shown that **1a** reacts with organoaluminum complexes to form an adduct of the form $(Cp^*(P(CH_3)_3)Ir(H)_2(AlPh_3)$.[43] This observation supports the first step in our mechanism. In contrast, Jones has found that $Cp^*(PMe_3)RhH_2$ reacts with C_6F_6 by a pathway postulated to involve initial deprotonation of the dihydride by F^- at elevated temperatures.[44] The iridium and rhodium systems are therefore isoelectronic and isostructural dihydrides that exhibit alternative reactivity patterns.

Proposed Mechanism for the Formation of Alkenyl Complexes 15a−c. We have less experimental information about the mechanism of formation of alkenyl complexes **15a**−**c**. However, a possible pathway for their formation is outlined in Scheme 2. We suggest that the first step is similar to that in the formation of **3**, resulting in the charge-separated intermediate **24**. From this intermediate two possible pathways can be imagined. The Proton Sponge can either remove an iridium-bound hydrogen to form an acyl hydride complex (**4**, **5**), a process that might be reversible when the RCH_2 group is relatively electron-rich, or remove a proton from the α-carbon of the acyl group to form a vinyl enolate intermediate (**25**).[45] The enolate can then rearrange to enol **26**, which upon loss of water, gives a vinylidene intermediate, **27**.[46] Addition of HCl from the ammonium chloride salt across the iridium−carbon double bond results in formation of **15a**−**c**.

The hydride resonance in the ^{1}H NMR spectrum at δ −16 ppm observed during the formation of **15c** has a chemical shift similar to those of acyl complexes **3**−**6**. This suggests that acyl hydride formation is a side pathway in the formation of the vinyl chloride species. This first step is apparently reversible, as no iridium acyl hydride product is observed in the final reaction mixture by ^{1}H NMR spectroscopy. Compounds **15a** and **15b** are likely to form by the same pathway as that which gives **15c**.

Conclusions

We have found that in the presence of tertiary amines $Cp^*(PMe_3)IrH_2$ reacts cleanly with aroyl and sterically hindered aliphatic chlorides to give a series of stable acyliridium hyrides **3**−**6**. A detailed investigation of the mechanism of this reaction, involving kinetics and substituent effect studies, has been carried out. These establish that the reaction rate is zero order in amine concentration and so does not proceed by initial deprotonation of the hydride. Instead, it involves direct nucleophilic attack of the iridium center at the carbon atom of the acyl chloride, followed by rapid chloride loss and subsequent deprotonation of the resulting intermediate by amine. Hammett studies showed that large changes in rate are caused by changing substituents at the para position of substituted benzoyl chlorides, but relatively small changes in rate are induced by modifying the substituents on the iridium-bound phosphine aryl groups. We suggest that, despite its formal +3 oxidation state, the iridium center appears to be polarizable ("soft") enough to be relatively unaffected in S_N2 reactions by electron-withdrawing or -donating groups on the attached phosphine substituent.

With monosubstituted acetyl chlorides, the reaction takes a different overall course, leading to vinyl iridium chloride complexes **15a**−**c**. We have obtained less quantitative information about this reaction, but we believe that it also proceeds by initial nucleophilic attack of Ir on the acid chloride. In this case, however, the product-forming step involves deprotonation at the α-carbon of the acyl fragment, rather than at the Ir center, leading to an Ir-substituted enolate. Proton shift, loss of water, and addition of HCl then leads to the final product.

Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were performed in a Vacuum Atmospheres

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(45) A question raised by a referee was the method by which it was determined that **4** or **5** reacted with **7**·HCl to yield **24** and then eventually **1**5. This was determined by following the formation of **15c** via ^{1}H NMR spectroscopy. Initially a hydride resonance at ca. −16 ppm, which is suggestive of an acyl hydride complex, grows in. This resonance subsequently disappears as the reaction goes to completion. These observations support our mechanism.
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recirculating inert atmosphere glovebox or using standard Schlenk and vacuum techniques. Glassware was dried in an oven at 150 °C before use. All $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were obtained using a Bruker AMX-400 MHz spectrometer (162.1 MHz for $^{31}P\{^1H\}$ spectra, 376.5 MHz for $^{19}F\{^1H\}$ spectra). All ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained using a Bruker DRX 500 MHz spectrometer (500.1 MHz for ^1H NMR spectra, 125.8 MHz for $^{13}C\{^1H\}$ NMR spectra). Unless otherwise indicated, NMR spectra were recorded as C_6D_6 solutions. Coupling patterns are reported as the number of lines observed for a particular resonance (e.g., "t" refers to an observed three-line 1:2:1 pattern) even in cases where other (usually smaller) coupling might have been expected to appear. IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer as benzene solutions in a NaCl-plated solution cell or as KBr pellets. IR frequencies are reported in cm^{-1}. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer 2400 Series II CHNO/S analyzer.

Sealed NMR tubes were prepared by attaching an NMR tube directly to a Kontes vacuum stopcock with a Cajon adapter and flame sealing. Reactions with gases involved condensation of a known pressure of a gas from a bulb of known volume into the reaction vessel at −196 °C. The pressure was determined with an MKS Baratron gauge attached to a high-vacuum line.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Silica gel (Merck, 60A, 230−400 mesh, grade 9385) was dried in vacuo at 200 °C for 48 h. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl under N_2. Pentane, hexanes, benzene, and toluene were either distilled from purple sodium/benzophenone ketyl under N_2 or passed through a column of activated alumina collected under and sparged with N_2 prior to use. Methylene chloride was either distilled from CaH_2 or passed through a column of activated alumina collected under and sparged with N_2 prior to use. Deuterated benzene and tetrahydrofuran were distilled from sodium/benzophenone ketyl under N_2 and degassed with three freeze−pump−thaw cycles. Deuterated methylene chloride and chloroform were distilled from CaH_2 and degassed with three freeze−pump−thaw cycles. Trimethylphosphine and tris-(*n*-propyl)phosphine were vacuum transferred from sodium. The compounds $(p\text{-}MeOC_6H_4)P(CH_3)_2$ and $(p\text{-}CF_3C_6H_4)P(CH_3)_2$ were synthesized according to a modified literature procedure. (−)-Sparteine was dried over 4 Å molecular sieves and degassed with three freeze−pump−thaw cycles. Triethylamine was dried over sodium and vacuum distilled. All acid chlorides were distilled under N_2 prior to use.

Kinetics. The reactions were analyzed by ^1H NMR spectroscopy in benzene-d_6 solution by integration of the Cp* resonance of **1** versus the Cp* resonance of **3**. All data were collected at 301 K (standardized using ethylene glycol). One equivalent of trimethoxybenzene relative to **1** was used as an internal standard in all runs. Reaction progress was followed to greater than three half-lives. The initial concentrations of **1**, aryl acid chloride, and **7** were set at concentrations near 0.04, 0.4, and 0.4 M, respectively, for all runs except where stated otherwise.

A series of reactions were conducted increasing the concentration of [**2a**] from 0.05 to 0.8 M acid chloride to determine the order in acid chloride. A third series of reactions were done in which [**1a**] and [**2a**] were kept constant and the concentration of [**7**] was increased from 0.2 to 0.5 M.

Rate constants were also measured for the reaction of **1a** and Proton Sponge with *p*-methoxybenzoyl, *p*-toluoyl, benzoyl, and *p*-fluoromethylbenzoyl chlorides. Qualitative $t_{1/2}$ values were measured for *p*-trifluoromethyl, *p*-cyano, and *p*-nitrobenzoyl chloride, as they were too fast to measure conveniently by ^1H NMR at the same temperature.

In a typical run, **1a** (15.7 mg, 0.0387 mmol), the internal standard (59.6 mg, 0.278 mmol), and **7** (9.2 mg, 0.0547 mmol) were weighed into a 1.0 mL volumetric flask. The solids were dissolved in approximately 0.5 mL of benzene-d_6, and to this solution benzoyl chloride (44.8 μL, 0.386 mmol) was added via syringe. The volumetric flask was quickly filled to the 1.0 mL line with more benzene-d_6, and a sample was transferred to a thick-walled Pyrex NMR tube. This tube was taken out of the glovebox, frozen in liquid N_2, and sealed under vacuum. The sealed tube was kept frozen until it was placed in the NMR probe, after which a timed run with (in this case) a 600 s delay between pulses was begun.

Compounds **1a**−**f** were synthesized from $IrCl_3 \cdot 3H_2O$ according to the literature procedure.[28] The synthesis of **3a** is used as a representative example for the synthesis of **3**−**6**, and the synthesis of **15a** is used as a representative example for the synthesis of **15a**−**c**.

Cp*(PMe$_3$)Ir[C(O)C$_6$H$_5$]H (3a). A solution of **1a** (97 mg, 0.25 mmol) in benzene (2 mL) was added to a solution of **2a** (40 mg, 0.28 mmol) and **7** (65 mg, 0.30 mmol) in benzene (5 mL). The solution immediately turned a pale yellow. After stirring for 18 h, the bright yellow solution was filtered to remove the amine hydrochloride salt and the solvent was removed in vacuo to give a yellow oil. The yellow oil was dissolved in pentane (10 mL) (or Et_2O) and filtered through SiO_2 (100 mg). Removal of the solvent in vacuo afforded a yellow powder, which was recrystallized from pentane to give 63 mg (33%) of **3a** as yellow crystals. In the presence 5 equiv of 9,10-dihydroanthracene (DHA), no changes were observed in the yields of **3a** as observed by ^1H NMR spectroscopy. IR (C_6H_6): 3101, 3058, 3054, 2972, 1964, 1670, 1507, 1393, 1172, 1033, 978, 849, 651, 647, 475, 433, 412 cm^{-1}. ^1H NMR: δ −16.28 (d, 1 H, J_{P-H} = 36 Hz), 1.24 (d, 9 H, J_{P-H} = 10 Hz), 1.76 (d, 15 H, J_{P-H} = 2 Hz), 7.23 (t, 1 H, J_{H-H} = 14 Hz), 7.29 (t, 2 H, J_{H-H} = 15 Hz), 8.26 (d, 2 H, J_{H-H} = 7 Hz). $^{13}C\{^1H\}$ NMR: δ 10.04, 18.5 (d, J_{C-P} = 37 Hz), 93.7, 127.1, 128.0, 129.1, 129.8, 131.1. $^{31}P\{^1H\}$ NMR: δ −37.9. Anal. Calcd for $C_{20}H_{30}IrOP$: C, 47.12; H, 6.0. Found: C, 47.13; H, 5.93.

Cp*(PMe$_3$)Ir[C(O)-*p*-CH$_3$C$_6$H$_4$]H (3b). Complex **1** (147 mg, 0.390 mmol), **2b** (70 mg, 0.45 mmol), and **7** (97 mg, 0.45 mmol) were dissolved in benzene (6 mL). Stirring for 72 h and workup as described above resulted in 78 mg (39%) of **3b** as yellow crystals. Using **8**, yield = 42%; using **9**, yield = 39%. IR (KBr): 2977, 2890, 1552, 1397, 1279, 1245, 1031, 961, 876, 650, 612 cm^{-1}. ^1H NMR: δ −16.26 (d, 1 H, J_{P-H} = 36 Hz), 1.26 (d, 9 H, J_{P-H} = 10 Hz), 1.80 (d, 15 H, J_{P-H} = 2 Hz), 2.11 (s, 3 H), 7.12 (d, 2 H, J_{H-H} = 8 Hz), 8.25 (d, 2 H, J_{H-H} = 8 Hz). $^{13}C\{^1H\}$ NMR: δ 10.1, 18.5 (d, J_{C-P} = 37 Hz), 20.9, 93.6, 114.5, 127.8, 128.0, 138.9, 151.8. $^{31}P\{^1H\}$ NMR: δ −37.8. Anal. Calcd for $C_{21}H_{32}IrOP$: C, 48.17; H, 6.16. Found: C, 47.92; H, 6.22.

Cp*(PMe$_3$)Ir[C(O)-*p*-CNC$_6$H$_4$]H (3c). Complex **1** (52.1 mg, 0.0138 mmol), **2c** (23.2 mg, 0.140 mmol), and **7** (30.0 mg, 0.140 mmol) were dissolved in benzene (6 mL). Stirring for 1 h and workup as described above resulted in the formation of 36 mg (51%) of **3c** as orange crystals. IR (C_6H_6): 3074, 3070, 2954, 2890, 2226, 2098, 1960, 1572, 1532, 1282, 1002, 957, 885, 760, 753, 487 cm^{-1}. ^1H NMR: δ −16.5 (d, 1 H, J_{P-H} = 36 Hz), 1.23 (d, 9 H, J_{P-H} = 10 Hz), 1.62 (d, 15 H, J_{P-H} = 2 Hz), 7.25 (d, 1 H, J_{H-H} = 8 Hz), 7.85 (d, 1 H, J_{H-H} = 8 Hz). $^{13}C\{^1H\}$ NMR: δ 10.5, 19.0 (d, J_{C-P} = 37 Hz,), 94.5, 113.3, 119.6, 128.7, 129.2, 131.8, CN not observed. $^{31}P\{^1H\}$ NMR: δ −37.5. Anal. Calcd for $C_{21}H_{29}IrNOP$: C, 47.18; H, 5.49. Found: C, 47.16; H, 5.47.

Cp*(PMe$_3$)Ir[C(O)-*p*-NO$_2$C$_6$H$_4$]H (3d). Complex **1** (78.8 mg, 0.208 mmol), **2d** (40.3 mg, 0.217 mmol), and **7** (49.9 mg, 0.233 mmol) were dissolved in benzene (6 mL). Stirring for 1 h and workup as above resulted in the formation of 52.7 mg (46%) of **3d** as orange crystals. IR (C_6H_6): 3089, 3066, 2950, 2098, 1950, 1830, 1564, 1497, 1344, 1212, 1010, 995, 876, 790, 650, 634, 498, 430 cm^{-1}. ^1H NMR: δ −16.45 (d, 1 H, J_{P-H} = 36 Hz), 1.14 (d, 9 H, J_{P-H} = 10 Hz), 1.59 (s, 15 H, J_{P-H} = 2 Hz), 7.84 (d, 2 H, J_{H-H} = 8 Hz), 7.97 (d, 2 H, J_{H-H} = 8 Hz).

$^{13}C\{^1H\}$ NMR: δ 10.5, 19.1 (d, J_{C-P} = 37 Hz), 94.5, 123.2, 128.7, 132.4, 148.7, 158.4. $^{31}P\{^1H\}$ NMR: δ −37.9. Anal. Calcd for $C_{20}H_{29}IrNO_3P$: C, 43.31; H, 5.27. Found: C, 43.56; H, 5.55.

Cp*(PMe$_3$)Ir[C(O)-*p*-CF$_3$C$_6$H$_4$]H (3e). Complex **1** (72.2 mg, 0.191 mmol), **2e** (47.1 mg, 0.225 mmol), and **7** (59.8 mg, 0.279 mmol) were dissolved in benzene (6 mL). Stirring for 48 h and workup as above resulted in the formation of 72.2 mg (65%) of **3e** as yellow crystals. IR (C_6H_6): 3058, 2905, 2096, 1564, 1482, 1322, 1124, 1002, 980, 860, 720, 490 cm^{-1}. ^1H NMR: δ −16.35 (d, 1 H, J_{P-H} = 36 Hz), 1.25 (d, 6 H, J_{P-H} = 10 Hz), 1.67 (s, 15 H, J_{P-H} = 1 Hz), 7.52 (d, 1 H, J_{H-H} = 8 Hz), 8.08 (d, 1 H, J_{H-H} = 8 Hz). $^{13}C\{^1H\}$ NMR: δ 9.9, 18.4 (d, J_{C-P} = 37 Hz), 93.7, 113.5, 124.2, 124.5, 127.5, 128.8, 131.1. $^{31}P\{^1H\}$ NMR: δ −37.8. $^{19}F\{^1H\}$ NMR: δ −61.8. Anal. Calcd for $C_{21}H_{29}IrOPF_3$: C, 43.67; H, 5.06. Found: C, 43.71; H, 5.28.

Cp*(PMe$_3$)Ir[C(O)-*p*-FC$_6$H$_4$]H (3f). Complex **1** (93.1 mg, 0.247 mmol), **2f** (45.3 mg, 0.286 mmol), and **7** (58.4 mg, 0.273 mmol) were dissolved in benzene (6 mL). Stirring for 72 h and workup as above resulted in the formation of 69.8 mg (54%) of **3f** as yellow crystals. IR (C_6H_6): 3117 (s), 3058 (s), 2902 (w), 2101 (w), 1822 (d), 1594 (s), 1561 (s), 1488 (s), 1095, 987, 964, 896, 653, 627, 598, 483 (s) cm^{-1}. ^1H NMR: δ −16.36 (d, 1 H, J_{P-H} = 36 Hz), 1.22 (d, 9 H, J_{P-H} = 11 Hz), 1.74 (s, 15 H, J_{P-H} = 1 Hz), 6.92 (t, 2 H, J_{H-H} = 17 Hz), 8.17 (t, 2 H, J_{H-H} = 14 Hz). $^{13}C\{^1H\}$ NMR: δ 10.0, 18.4 (d, J_{C-P} = 37 Hz), 93.5, 113.5, 127.5, 128.0, 129.5, 131.1. $^{31}P\{^1H\}$ NMR: δ −37.8. $^{19}F\{^1H\}$ NMR: δ −113. Anal. Calcd for $C_{20}H_{29}IrOPF$: C, 45.53; H, 5.54. Found: C, 45.20; H, 5.74.

Cp*(PMe$_3$)Ir[C(O)-*p*-OCH$_3$ C$_6$H$_4$]H (3g). Complex **1** (72.3 mg, 0.192 mmol), **2g** (34.9 mg, 0.205 mmol), and **7** (44.9 mg, 0.210 mmol) were dissolved in benzene (6 mL). Stirring for 5 days and workup as above resulted in the formation of 72.3 mg (70%) of **3g** as yellow crystals. IR (C_6H_6): 2977, 2901, 2101, 1829, 1581, 1552, 1522, 1495, 1182, 1002, 879, 728, 708, 654, 598, 476 cm^{-1}. ^1H NMR: δ −16.29 (d, 1 H, J_{P-H} =36 Hz), 1.27 (d, 9 H, J_{P-H} = 10 Hz), 1.82 (s, 15 H, J_{P-H} = 2 Hz), 3.30 (s, 3 H), 6.37 (d, 2 H, J_{H-H} = 9 Hz), 7.85 (d, 2 H, J_{H-H} = 9 Hz). $^{13}C\{^1H\}$ NMR: δ 10.7, 19.2 (d, J_{C-P} = 37 Hz), 55.1, 94.2, 112.8, 128.7, 131.8, 148.0, 161.9. $^{31}P\{^1H\}$ NMR: δ −37.7. Anal. Calcd for $C_{21}H_{32}IrO_2P$: C, 46.74; H, 5.98. Found: C, 47.13; H, 6.23.

Cp*(PMe$_3$)Ir[C(O)CHMe$_2$]H (4). Complex **1** (80.9 mg, 0.199 mmol), **2h** (19.8 mg, 0.186 mmol), and **7** (45.7 mg, 0.213 mmol) were dissolved in benzene (6 mL). Stirring for 48 h and workup as above resulted in the formation of 52.5 mg (59%) of **4** as yellow crystals. Compounds **4** decomposed at ambient temperature over 24 h. IR (KBr): 2959, 2909, 2857, 2093, 1591, 1459, 1419, 1378, 1277, 1069, 1029, 959, 927, 841, 769, 728, 679, 637 cm^{-1}. ^1H NMR: δ −17.0 (d, 1 H, J_{P-H} = 36 Hz), 1.17 (d, 3 H, J_{H-H} = 7 Hz), 1.21 (d, 9 H, J_{P-H} = 10 Hz), 1.25 (d, 3 H, J_{H-H} = 7 Hz), 1.85 (d, 15 H, J_{P-H} = 2 Hz), 3.00 (m, 1 H). $^{13}C\{^1H\}$ NMR: δ 10.9, 19.2 (d, J_{C-P} = 37 Hz), 19.5, 19.8, 64.9, 94.6, 226.6. $^{31}P\{^1H\}$ NMR: δ −39.4. FAB ES MS Calcd for $C_{17}H_{32}OP^{193}Ir+^7Li$: 481.1962. Found: 481.1957.

Cp*(PMe$_3$)Ir[C(O)CHPh$_2$]H (5). Complex **1** (99.0 mg, 0.244 mmol), **2i** (56.8 mg, 0.246 mmol), and **7** (54.2 mg, 0.253 mmol) were dissolved in benzene (5 mL). Stirring for 24 h and workup as above resulted in the formation of 99.1 mg (68%) of **5** as yellow crystals. IR: 2096, 1602, 1498, 1447, 1419, 1203, 1169, 1084, 1030, 939, 852, 797, 730, 703, 678, 607 cm^{-1}. ^1H NMR: δ −16.7 (d, 1 H, J_{P-H} = 36 Hz), 1.07 (d, 9 H, J_{P-H} = 10 Hz), 1.70 (d, 15 H, J_{P-H} = 2 Hz), 5.95 (s, 1 H). $^{13}C\{^1H\}$ NMR: δ 10.8, 20.7 (d, J_{C-P} = 37 Hz), 90.4, 93.6, 125.5, 125.8, 128.9, 129.4, 142.3. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −39.75. Anal. Calcd for $C_{23}H_{36}PIrO$: C, 54.16; H, 5.89. Found: C, 53.93; H, 6.23.

Cp*(PMe$_3$)Ir[C(O)-*tert*-C$_4$H$_9$]H (6). Complex **1** (101 mg, 0.248 mmol), **2j** (35.9 mg, 0.297 mmol), and **7** (65.4 mg, 0.305 mmol) were dissolved in benzene (6 mL). Stirring for 18 h and workup as above resulted in the formation of 61.3 mg (51%) of **6** as yellow crystals. IR: 2975, 2943, 2902, 2085, 1573, 1479, 1453, 1418, 1375, 1349, 1280, 1027, 955, 938, 888, 855, 800, 762, 728, 681, 668, 612 cm^{-1}. ^1H NMR: δ −17.00 (d, 1 H, J_{P-H} = 36 Hz), 1.19 (d, 9 H, J_{P-H} = 5 Hz), 1.274 (s, 9 H), 1.82 (d, 15 H, J_{P-H} = 2 Hz). $^{13}C\{^1H\}$ NMR: δ 11.2, 19.8 (d, J_{C-P} = 37 Hz), 29.9, 57.1, 94.4, 248.0. $^{31}P\{^1H\}$ NMR: δ 39.46 ppm. Anal. Calcd for $C_{18}H_{34}IrOP$: C, 44.15; H, 7.00. Found: C, 44.17; H, 7.40.

Cp*(PMe$_3$)Ir(Cl)(CHCH$_2$) (15a). Complex **1** (99.3 mg, 0.245 mmol), **2k** (22.1 mg, 0.281 mmol), and **7** (62.3 mg, 0.291 mmol) were dissolved in benzene (6 mL). Upon stirring for 18 h the solvent was removed in vacuo to give a yellow oil. The yellow oil was dissolved in pentane (10 mL) and filtered through SiO_2 (100 mg). Removal of the solvent in vacuo afforded a yellow powder, which was recrystallized from pentane. This resulted in the formation of 69.6 mg (61%) of **15a** as yellow crystals. IR: 2903, 2099, 1603, 1573, 1555, 1455, 1414, 1278, 1144 cm^{-1}. ^1H NMR: δ 1.19 (d, 9 H, J_{P-H} = 11 Hz), 1.48 (d, 15 H, J_{P-H} = 2 Hz), 5.36 (ddd, 1 H, J_{H-H} = 15 Hz, J_{H-H} = 10 Hz, J_{H-P} = 2 Hz), 6.68 (ddd, J_{H-H} = 15 Hz, J_{H-H} = 10 Hz, J_{H-P} = 2 Hz), 9.11 (ddd, J_{H-H} = 15 Hz, J_{H-H} = 10 Hz, J_{H-P} = 1 Hz). $^{13}C\{^1H\}$ NMR: δ 9.3, 13.9 (d, J_{C-P} = 37 Hz), 92.6, 118.4, 145.4. $^{31}P\{^1H\}$ NMR: δ −30.8. Anal. Calcd for $C_{15}H_{27}ClIrP$: C, 38.66; H, 5.84. Found: C, 38.82; H, 6.09.

Cp*(PMe$_3$)Ir(Cl)(CHCHCH$_3$) (15b). Complex **1** (80.6 mg, 0.199 mmol), **2l** (23.4 mg, 0.253 mmol), and **7** (46.5 mg, 0.217 mmol) were dissolved in benzene (5 mL). Stirring for 18 h and workup as above resulted in the formation of 44.9 mg (47%) of rotational isomers of **15b** as yellow crystals (major:minor, 4:1). IR (both isomers): 2959, 2914, 2844, 1584, 1446, 1377, 1278, 1210, 1152, 1073, 1209, 957, 855, 734, 681, 616 cm^{-1}. ^1H NMR major isomer: δ 1.19 (d, 9 H, J_{P-H} = 11 Hz), 1.49 (d, 15 H, J_{P-H} = 2 Hz), 2.06 (d, 3 H, J_{H-H} = 6 Hz), 5.43 (m, 1 H), 8.25 (d, 1 H, J_{H-H} = 12 Hz); minor isomer: δ 1.25 (d, 9 H, J_{P-H} = 11 Hz), 1.51 (d, 15 H, J_{P-H} = 2 Hz), 1.75 (d, 3 H, J_{H-H} = 5 Hz), 6.81 (m, 1 H), 8.35 (m, 1 H). $^{13}C\{^1H\}$ NMR δ major and minor isomers: 9.3, 9.5, 14.0 (d, J_{C-P} = 37 Hz), 14.3 (d, J_{C-P} = 37 Hz), 25.39, 25.40 92.40, 92.53, 126.6, 132.8 ppm. $^{31}P\{^1H\}$ NMR major isomer: δ −30.7; minor isomer: δ −34.6 ppm. Anal. Calcd for $C_{11}H_{29}IrPCl$: C, 40.03; H, 6.09. Found: C, 39.93; H, 6.22.

Cp*(PMe$_3$)Ir(Cl)(CHCHC$_6$H$_5$) (15c). Complex **1** (89.0 mg, 0.219 mmol), **2m** (44.1 mg, 0.285 mmol), and **7** (51.7 mg, 0.241 mmol) were dissolved in benzene (7 mL). Stirring for 18 h and workup as above resulted in the formation of 77.1 mg (65%) of **15c** as yellow crystals. IR: 2959, 2917, 1594, 1579, 1552, 1483, 1441, 1373, 1278, 1168, 1071, 1028, 973, 953, 849, 814, 746, 733, 695, 677, 610, 543, 502, 467 cm^{-1}. ^1H NMR: δ 1.14 (d, 9 H, J_{P-H} = 11 Hz), 1.49 (d, 15 H, J_{P-H} = 2 Hz), 6.63 (dd, 1 H, J_{H-H} = 17 Hz, J_{P-H} = 3 Hz), 7.04 (t, 1 H, J_{H-H} = 7 Hz), 7.23 (t, 2 H, J_{H-H} = 7.5 Hz), 7.46 (d, 2H, J_{H-H} = 7 Hz), 9.63 (dd, 1 H, J_{H-H} = 17 Hz, J_{P-H} = 2 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.3, 14.1 (d, J_{C-P} = 37 Hz), 92.9, 125.2, 125.4, 129.1, 134.7, 139.6, 143.7. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −30.17. Anal. Calcd for $C_{16}H_{31}PIrCl$: C, 46.53; H, 5.76. Found: C, 46.21; H, 6.12.

Cp*(PPhMe$_2$)IrCl$_2$ (28). To a red/orange solution of $[Cp^*IrCl_2]_2$ (1.01 g, 1.26 mmol) in CH_2Cl_2 (75 mL, sparged with N_2) was added $P(C_6H_5)(CH_3)_2$ (0.21 mL, 1.47 mmol) via syringe to give a bright orange solution. After stirring for 18 h, the solvent was removed in vacuo to give an orange powder. This powder was passed through a SiO_2 column with Et_2O/CH_2Cl_2 (3:1) as the eluent. The solvent was removed in vacuo to give 1.13 g (83%) of the product as an orange powder. IR: 2983, 2914, 1434, 1106, 1034, 951, 912, 847, 760, 720, 701, 492, 438 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.42 (d, 15 H, J_{P-H} = 2 Hz), 1.86 (d, 6 H, J_{P-H} = 11 Hz), 7.44 (m, 3 H; meta and para positions are overlapped), 7.65 (m, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.6, 12.86 (d, J_{C-P} = 40 Hz), 91.3, 130.5, 131.0, 131.6, 131.7. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −19.66. Anal. Calcd for $C_{13}H_{26}PIrCl_2$: C, 40.30; H, 4.88. Found: C, 40.42; H, 5.17.

Cp*(PPhMe$_2$)IrH$_2$ (1c). $Cp^*PhMe_2IrCl_2$ (1.02 g, 1.80 mmol) was treated with Zn powder (3.20 g, 48.9 mmol) and acetic acid (2.5 mL, 43.4 mol) in methanol (100 mL, N_2 sparged) as described previously for the preparation for **1a** to give 852 mg

(96%) of **1c** as a tan oil. IR: 2972, 2905, 2089, 1476, 1434, 1379, 1277, 1101, 937, 909, 842, 720, 696, 493, 461 cm^{-1}. ^1H NMR: δ −17.14 (d, 1 H, J_{P-H} = 32 Hz), 1.64 (d, 6 H, J_{P-H} = 10 Hz), 1.99, (d, 15 H, J_{P-H} = 1 Hz), 7.05 (t, 1 H, J_{H-H} = 7 Hz), 7.15 (t, 2 H, J_{H-H} = 7 Hz), 7.59 (dd, 2 H, J_{H-H} = 8 Hz, J_{P-H} = 8 Hz). $^{13}C\{^1H\}$ NMR: δ 11.6, 24.7 (d, J_{C-P} = 40 Hz), 92.0, 129.4, 130.1, 131.6, 131.7 ppm. $^{31}P\{^1H\}$ NMR: δ −25.83 ppm. Anal. Calcd for $C_{18}H_{28}PIr$: C, 46.23; H, 6.04. Found: C, 46.32; H, 6.31.

Cp*(PPhMe$_2$)Ir(C(O)Ph)(H) (12). Cp*(PPhMe$_2$)IrH$_2$ (91.4 mg, 0.195 mmol), benzoyl chloride (23.0 uL, 0.198 mmol), and **7** (41.8 mg, 0.195 mmol) were dissolved in benzene (5 mL). Stirring for 4 days and workup as described for the acyl hydrides above resulted in 43 mg (39%) of **12** as yellow crystals. IR (C_6H_6): 2968, 2907, 2156, 2096, 1540, 1477, 1432, 1379, 1105, 1071, 1027, 942, 914, 879, 744, 693, 494, 439 cm^{-1}. ^1H NMR: δ −15.85, (1 H, d, J_{P-H} = 40 Hz), 1.40 (3 H, d, J_{P-H} = 11 Hz), 1.61 (15 H, d, J_{P-H} = 2 Hz), 1.71 (3 H, d, J_{P-H} = 11 Hz), 7.02 (1 H, td, J_{H-H} = 8 Hz, J_{P-H} = 2 Hz), 7.11 (2 Hz, td, J_{H-H} = 8 Hz, J_{P-H} = 2 Hz), 7.213 (1 H, t, J_{H-H} = 8 Hz), 7.31 (2 H, t, J_{H-H} = 8 Hz), 7.53 (2 H, td, J_{H-H} = 7 Hz, J_{P-H} = 3 Hz), 8.29 (2 H, d, J_{H-H} = 7 Hz). $^{13}C\{^1H\}$ NMR: δ 10.2, 14.6 (d, J_{C-P} = 37 Hz), 22.4 (d, J_{C-P} = 39 Hz), 94.5, 127.8, 129.7 (d, J_{C-P} = 3 Hz), 129.9, 130.0, 131.5 (d, J_{C-P} = 10 Hz), 132.5, 138.0, 138.4, 155.3. $^{31}P\{^1H\}$ NMR: δ −21.90. Anal. Calcd for $C_{25}H_{32}IrOP$: C, 52.52; H, 5.64. Found: C, 52.40; H, 5.60.

Cp*[(*p*-MeOC$_6$H$_4$)P(CH$_3$)$_2$]IrCl$_2$ (29). To a red/orange solution of [Cp*IrCl$_2$]$_2$ (505 mg, 0.634 mmol) in CH_2Cl_2 (80 mL, sparged with N_2) was added (*p*-MeOC$_6$H$_4$)P(CH$_3$)$_2$ (242 mg, 1.44 mmol) via syringe to give a bright orange solution. After stirring for 18 h, the solvent was removed in vacuo to give an orange powder. This powder was passed through a SiO_2 column with Et_2O/CH_2Cl_2 (3:1) as the eluent. The solvent was removed in vacuo to give 551 mg (77%) of the product as an orange powder. IR: 2980, 2915, 1593, 1506, 1462, 1412, 1376, 1290, 1250, 1194, 1110, 1023, 942, 913, 844, 704, 620, 538, 494, 425 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.43 (d, 15 H, J_{P-H} = 2 Hz), 1.80 (d, 6 H, J_{P-H} = 16 Hz), 3.81 (s, 3 H), 6.95 (dd, 2 H, J_{H-H} = 7 Hz, J_{P-H} = 2 Hz), 7.67 (dd, 2 H, J_{H-H} = 11 Hz, J_{P-H} = 9 Hz). $^{13}C\{^1H\}$ NMR: δ 8.1, 12.6 (d, J_{C-P} = 40 Hz), 55.2, 91.2, 113.7, 125.4, 132.5, 161.4 ppm. $^{31}P\{^1H\}$ NMR: δ −17.80. Anal. Calcd for $C_{19}H_{28}Cl_2IrOP$: C, 20.28; H, 4.98. Found: C, 40.46; H, 5.26.

Cp*[(*p*-MeOC$_6$H$_4$)P(CH$_3$)$_2$]IrH$_2$ (1d). Cp*[(*p*-MeOC$_6$H$_4$)P(CH$_3$)$_2$]IrCl$_2$ (566 mg, 0.876 mmol) was treated with Zn powder (1.60 g, 24.5 mmol) and acetic acid (1.2 mL, 20.8 mol) in methanol (60 mL, sparged) using the same procedure as described previously for the preparation of **1a** to give 425 mg (97%) of **1d** as a tan oil. IR: 3426, 2919, 2081, 1595, 1499, 1289, 1250, 1179, 1100, 1031, 910, 826, 710, 527, 440, 404 cm^{-1}. ^1H NMR: δ −17. 13 (d, 1 H, J_{P-H} = 40 Hz), 1.68 (d, 6 H, J_{P-H} = 16 Hz), 2.05 (d, 15 H, J_{P-H} = 2 Hz), 3.25 (s, 3 H), 6.80 (dd, 2 H, J_{H-H} = 8 Hz, J_{P-H} = 2 Hz), 7.60 (dd, 2 H, J_{H-H} = 12 Hz, J_{P-H} = 8 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 10.9, 24.4 (d, J_{C-P} = 40 Hz), 54.3, 91.2, 112.9, 132.5, 132.6, 160.5 ppm. $^{31}P\{^1H\}$ NMR: δ −27.3 ppm. Anal. Calcd for $C_{19}H_{30}IrOP$: C, 45.86; H, 6.08. Found: C, 46.09; H, 6.28.

Cp*[(*p*-MeOC$_6$H$_4$)P(CH$_3$)$_2$]Ir[C(O)Ph](H) (13). Cp*[(*p*-MeOC$_6$H$_4$)P(CH$_3$)$_2$]IrH$_2$ (102 mg, 0.204 mmol), benzoyl chloride (30.1 mg, 0.214 mmol), and **7** (44.2 mg, 0.206 mmol) were dissolved in benzene (6 mL). Stirring for 7 days and workup as described above resulted in the formation of 82.1 mg (67%) of **13** as yellow crystals. IR: 3449, 3070, 2972, 2909, 2081, 1593, 1555, 1498, 1289, 1247, 1180, 1145, 1105, 1026, 940, 915, 878, 830, 799, 755, 688, 646, 529, 493, 433 cm^{-1}. ^1H NMR: δ −15.80 (d, 1 H, J_{P-H}= 40 Hz), 1.40 (3 H, d, J_{P-H} = 11 Hz), 1.63 (15 H, d, J_{P-H} = 2 Hz), 1.68 (3 H, d, J_{P-H} = 11 Hz), 3.23 (3 H, s), 6.74 (dd, 2 H, J_{H-H} = 9 Hz, J_{P-H} = 1 Hz), 7.18 (1 H, t, J_{H-H} = 8 Hz), 7.28 (2 H, t, J_{H-H} = 8 Hz), 7.50 (2 H, td, J_{H-H} = 9 Hz, J_{P-H} = 2 Hz), 8.27 (2 H, d, J_{H-H} = 7 Hz). $^{13}C\{^1H\}$ NMR: δ 10.3, 15.6 (d, J_{C-P} = 37 Hz), 22.8 (d, J_{C-P} = 44 Hz), 55.1, 94.5, 113.4, 114.1, 127.8, 129.9, 130.0, 133.2, 134.5, 155.5, 161.5. $^{31}P\{^1H\}$ NMR: δ −23.62. Anal. Calcd for $C_{26}H_{34}IrOP$: C, 51.90; H, 5.69. Found: C, 51.62; H, 5.74.

Cp*[(*p*-CF$_3$C$_6$H$_4$)P(CH$_3$)$_2$]IrCl$_2$ (30). To a red/orange solution of [Cp*IrCl$_2$]$_2$ (523 mg, 0.657 mmol) in CH_2Cl_2 (80 mL, sparged with N_2) was added (*p*-CF$_3$C$_6$H$_4$)P(CH$_3$)$_2$ (289 mg, 1.40 mmol) via syringe to give a bright orange solution. After stirring for 18 h, the solvent was removed in vacuo to give an orange powder. This powder was passed through a column with Et_2O/CH_2Cl_2 (3:1) as the eluent. The solvent was removed in vacuo to give 559 mg (70%) of the product as an orange powder. IR: 3056, 2982, 2920, 1609, 1503, 1450, 1397, 1377, 1325, 1280, 1167, 1128, 1061, 1029, 1016, 948, 918, 842, 747, 712, 691, 600, 506, 492, 450, 418 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.45 (d, 15 H, J_{P-H} = 3 Hz), 1.91 (d, 9 H, J_{P-H} = 12 Hz), 7.72 (d, 2 H, J_{H-H} = 8 Hz), 7.95 (t, 2 H, J_{P-H} = 18.5 Hz, J_{H-H} = 8 Hz). $^{13}C\{^1H\}$ NMR: δ 8.7, 12.7 (J_{C-P} = 40 Hz), 92.1, 125.6, 131.9, 132.0, 134.3, 140.1. $^{31}P\{^1H\}$ NMR: δ −16.4. $^{19}F\{^1H\}$ NMR: δ −61.7. Anal. Calcd for $C_{19}H_{25}F_3PCl_2Ir$: C, 37.75; H, 4.17. Found: C, 37.78; H, 4.16.

Cp*[(*p*- CF$_3$C$_6$H$_4$)P(CH$_3$)$_2$]IrH$_2$ (1e). Cp*[(*p*-CF$_3$C$_6$H$_4$)P(CH$_3$)$_2$]IrCl$_2$ (539 mg, 0.893 mmol) was treated with Zn powder (1.77 g, 26.6 mmol) and acetic acid (1.2 mL, 20.8 mol) in methanol (60 mL, sparged) using the same procedure as described previously for the preparation of **1a** to give 308 mg (65%) of **1e** as a tan powder. IR: 2964, 2905, 2096, 1609, 1471, 1394, 1325, 1165, 1121, 1061, 1016, 944, 916, 848, 824, 715, 691, 598, 505, 494, 431, 415 cm^{-1}. ^1H NMR: δ −17.13 (d, 1 H, J_{P-H} = 32 Hz), 1.55 (d, 9 H, J_{P-H} = 10 hz), 7.38 (d, 2 H, J_{H-H} = 8 Hz), 7.45 (t, 2 H, J_{P-H} = 18 Hz, J_{H-H} = 9 Hz). $^{13}C\{^1H\}$ NMR: δ 11.5, 24.2 (d, J_{C-P} = 49 Hz), 92.2 (d, J_{C-P} = 5 Hz), 124.8, 131.7, 132.1, 142.1, 146.3. $^{31}P\{^1H\}$ NMR: δ −25.2. $^{19}F-\{^1H\}$ NMR: δ −62.2. Anal. Calcd for $C_{19}H_{27}F3IrP$: C, 42.61; H, 5.08. Found: C, 42.99; H, 5.32.

Cp*[(*p*- CF$_3$C$_6$H$_4$)P(CH$_3$)$_2$]Ir[C(O)Ph](H) (14). Cp*[(*p*-CF$_3$C$_6$H$_4$)P(CH$_3$)$_2$]IrH$_2$ (97.8 mg, 0.183 mmol), benzoyl chloride (30.1 μL, 0.258 mmol), and **7** (49.0 mg, 0.229 mmol) were dissolved in benzene (6 mL). After stirring for 4 days, 68 mg (57%) of **14** as yellow crystals was observed. IR (KBr): 3468, 3072, 2975, 2911, 2085, 1593, 1555, 1440, 1394, 1288, 1169, 1147, 1124, 1061, 1014, 940, 915, 878, 843, 825, 747, 730, 712, 692, 667, 625, 598, 506, 488, 407 cm^{-1}. ^1H NMR: δ −15.90 (1H, d, J_{P-H} = 40 Hz), 1.33 (3H, d, J_{P-H} = 10 Hz), 1.53 (15H, d, J_{P-H} = 2 Hz), 1.60 (3H, d, J_{P-H} = 11 Hz), 7.21 (1H, tt, J_{H-H} = 7 Hz, J_{P-H} = 2 Hz), 7.303 1H, (td, J_{H-H} = 8 Hz, J_{P-H} = 2 Hz), 7.37 (1H, d, J_{H-H} = 8 Hz), 7.46 (1H, t, J_{H-H} = 9 Hz), 8.23 (1H, dd, J_{H-H} = 9 Hz, J_{P-H} = 2 Hz). $^{13}C\{^1H\}$ NMR: δ 10.1, 14.9 (d, J_{C-P} = 37 Hz), 22.1 (d, J_{C-P} = 38 Hz), 94.6, 124.9 (m), 125.0, 127.9, 129.8, 130.2 (d, J_{C-P} = 13 Hz), 131.8 (d, J_{C-P} = 40 Hz), 131.9 (d, J_{C-F} = 64 Hz), 142.6, 143.0, 154.9. $^{31}P\{^1H\}$ NMR: δ −21.6, $^{19}F\{^1H\}$ NMR: δ −62.3. Anal. Calcd for $C_{26}H_{31}F_3IrOP$: C, 48.82; H, 4.88. Found: C, 48.60; H, 4.99.

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Supporting Information Available: Data collection and refinement details and listings of atomic coordinates, thermal parameters, bond lengths, and bond angles of both crystallographically characterized complexes and assignments of $^{13}C-\{^1H\}$ NMR spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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