Synthesis and Chemistry of the Aryliridium(III) Fluorides $Cp'Ir(PMe_3)(Aryl)F$: High Reactivity due to Surprisingly Easy Ir−F Ionization

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Abstract: This paper reports the synthesis and chemistry of the unusual late metal fluoride complexes, $Cp'Ir(PMe_3)(Aryl)F$ [Cp′ = Cp* (C_5Me_5), Aryl = Ph (**1a**); Cp′ = Cp*, Aryl = *p*-tolyl (**1b**); Cp′ = Cp^{Et} (C_5Me_4Et), Aryl = Ph (**1c**)]. The solid-state structure of **1c** has been determined: crystals of **1c** are monoclinic, space group $P2_1/c$, with a = 9.235(2) Å, b = 12.667(2) Å, c = 17.129(3) Å, β = 104.547(16)°, and Z = 4; R = 3.98%, wR = 4.65% for 2859 data for $F^2 > 3\sigma(F^2)$. These complexes exhibit reactivity that is substantially different from that of related Cl, Br, and I species because of the greater propensity of fluoride ion to dissociate from the Ir center, even in nonpolar solvents. For example, in solution at room temperature, fluoride is slowly displaced from complexes **1** by Lewis bases such as pyridines and phosphines (L); the resulting salts $[Cp'Ir(PMe_3)(Aryl)(L)]F$ (**2**) exist in equilibrium with the covalent starting materials. This equilibrium lies well to the left for pyridines and phosphines under anhydrous conditions, but both the rate of establishment and the magnitude of K_{eq} are increased dramatically by the addition of H_2O. In aqueous THF the aquo species $[Cp^*Ir(PMe_3)(Ph)(OH_2)]F\cdot xH_2O$ (**2e**) is formed much more rapidly than the $[Cp'Ir(PMe_3)(Aryl)(L)]F$ salts. This, and the rapid further reactivity of **2e**, enables the aquo species to serve as an intermediate in the water-catalyzed substitution of fluoride by L. Treatment of **1a** with mixtures of water and other entering ligands and monitoring these reactions over time reveals that the kinetic affinity of these ligands for the Ir center is exactly the reverse of their thermodynamic affinity: kinetically, H_2O > pyridines > phosphines; thermodynamically, phosphines > pyridines > H_2O. Addition of BPh_3 to $[Cp'Ir(PMe_3)(Aryl)(L)]F$ (**2**) in nonaqueous media leads to irreversible formation of the borate complexes, $[Cp'Ir(PMe_3)(Aryl)(L)]BPh_3F$. The lability of the fluoride ligand in complexes **1** is also demonstrated by mixing $Cp^*Ir(PMe_3)(Ph)F$ with $Cp^*Ir(PMe_3)(p\text{-tolyl})X$ [X = Cl, Br, OTf, OPh] in C_6D_6, which leads to solutions containing four species identifiable as the two starting materials and the two exchange products $Cp^*Ir(PMe_3)(Ph)X$ and $Cp^*Ir(PMe_3)(p\text{-tolyl})F$. Organic halides participate in exchange as well; reaction of **1a** with $PhCH_2Br$, Me_3SiCl, MeCOCl, and even CH_2Cl_2 results in complete replacement of fluoride by bromide or chloride in **1a**. The labile fluoride ion also leads to other novel reactivity. For example, addition of dimethyl acetylenedicarboxylate to complexes **1** gives iridacyclopentadiene complexes (**5**) and reaction of **1a** and **1c** with (1-trimethylsilyl)imidazole provides $Cp'Ir(PMe_3)(Ph)$(imidazolate) complexes (**7**) and Me_3SiF. Treatment of **1** with silanes $HSiMe_2R$ [R = Ph, Me] leads to the formation of $Cp'Ir(PMe_3)(R)(SiMe_2F)$ complexes (**8**); excess HS-*p*-tolyl reacts with either **1a** or **1b** to provide $Cp^*Ir(PMe_3)(S\text{-}p\text{-tolyl})_2$ (**10**).

Introduction

Lanthanides, actinides, and metals located early in the transition series form exceptionally strong bonds to fluorine. Bond dissociation enthalpies approaching 160 kcal/mol can be rationalized using the Hard−Soft Acid−Base (HSAB) principle in which a strong interaction between the similarly hard metal and fluorine atoms would be expected.[1] Bonds between "softer" low-valent late-transition-metal centers and fluorine are expected to be much weaker. In this paper we describe a series of compounds having late transition metal−fluorine bonds that exhibit substantial reactivity. Specifically, we report the synthesis, characterization, exchange reactions, and other chemical reactivity of $Cp'Ir(PMe_3)(Aryl)F$ [Cp′ = Cp* (C_5Me_5), Aryl = Ph (**1a**); Cp′ = Cp*, Aryl = *p*-tolyl (**1b**); Cp′ = Cp^{Et} (C_5Me_4Et), Aryl = Ph (**1c**)]. While the synthesis and structural characterization of a number of transition-metal fluoride complexes has been reported,[2] the chemical reactivity of transition-metal fluoride bonds is virtually undocumented.[2,3]

Results and Discussion

Synthesis and Characterization of Iridium Fluoride Complexes. Substitution of triflate in $Cp'Ir(PMe_3)(Aryl)(OTf)$ (OTf = O_2SOCF_3) with TAS-F [$(Me_2N)_3S^+(Me_3SiF_2)^-$][4,5] yields the fluoride complexes $Cp^*Ir(PMe_3)(Ph)F$ (**1a**), $Cp^*Ir(PMe_3)(p\text{-tolyl})F$ (**1b**), and $Cp^{Et}Ir(PMe_3)(Ph)F$ (**1c**) in 80−90% isolated yields after crystallization from Et_2O at −40 °C (Scheme 1). These reactions proceed in a straightforward manner over the course of 10−24 h at room temperature with an observed color change of orange to pale yellow. While **1b** is sparingly soluble in hexanes, **1a** and **1c** are soluble only in more polar solvents such as benzene, THF, and Et_2O. All three fluoro complexes, while stable as solids, are thermally sensitive in solution above 50 °C.[6] They react with chromatographic materials and can only be filtered through Celite. In solution, the presence of Ir-bound fluorides is most apparent from the $^{31}P\{^1H\}$ spectra

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity,* 3rd ed.; Harper and Row: New York, 1983.

(2) Inorganic fluoride complexes containing carbonyl and phosphine ligands have been reviewed; see: Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553−573.

(3) Bennett, B. K.; Harrison, R. G.; Richmond, T. G. *J. Am. Chem. Soc.* **1994**, *116*, 11165−11166.

(4) $CpRe(NO)(PPh_3)F$ can be prepared by reaction of TAS-F and $CpRe(NO)(PPh_3)(OTf)$; see: Agbossou, S. K.; Roger, C.; Igau, A.; Gladysz, J. A. *Inorg. Chem.* **1992**, *31*, 419−424.

(5) Hoffman and Doherty have used [PPN]F to convert a Re−OTf complex to a Re−F complex, see: Hoffman, N. W.; Prokopuk, N.; Robbins, M. J.; Jones, C. M.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4177−4181.

(6) Thermolyses in benzene or THF give complicated mixtures of products.

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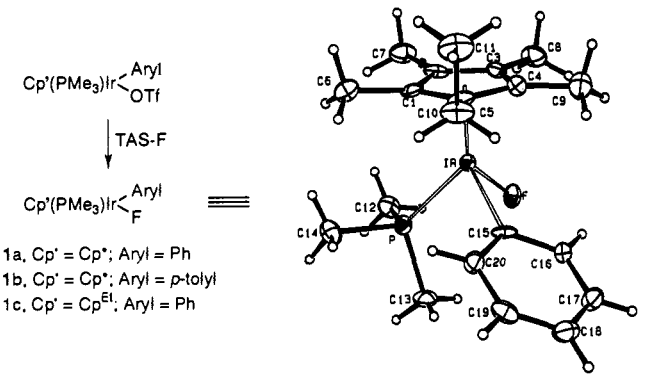
Scheme 1



of these compounds where doublet resonances at ≈−25 ppm ($^2J_{PF}$ ≈ 55 Hz) are observed. Analogously, the ^{19}F NMR spectra of these compounds show doublet resonances at very high field (≈−413 to −415 ppm) with the same two-bond coupling constants. The Cp^{Et} derivative (**1c**) shows four different ring methyl resonances (δ 1.49, 1.48, 1.44, 1.40 ppm) in its ^{1}H NMR spectrum suggesting that fluoride dissociation is slow on the NMR time scale in nonaqueous media (*vide infra*). This stands in contrast to Cp^{Et}Ir(PMe$_3$)(Ph)OTf whose NMR spectra show two equivalent pairs of Cp^{Et} methyl resonances which do not decoalesce until −80 °C in CD_2Cl_2. In all three fluoro complexes broad ^{1}H and ^{13}C aryl resonances are observed at room temperature indicating substantial barriers to Ir−aryl rotation.

In the solid state, a covalent Ir−F interaction is observed for complex **1c**[7] which we have structurally characterized. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The study showed that **1c** crystallizes in the space group $P2_1/c$: the structure refined to R = 0.0398 and wR = 0.0465. The molecular geometry of **1c** is shown in an ORTEP diagram in Scheme 1; crystallographic data and parameters are shown as Table 1 with positional parameters in Table 2 and selected bond distances and angles in Table 3. Cp^{Et}Ir(PMe$_3$)(Ph)F is a typical three-legged piano stool with a fairly long Ir−F bond length of 2.069(4) Å. While this compound is the first neutral Ir(III) fluoro complex to be structurally characterized, the Ir−F bond length can be compared to the two other known, but cationic, Ir(III) fluoro complexes. Specifically, [(Et$_3$P)$_2$(CO)$_2$(C{O}F)-Ir−F][BF$_4$] exhibits an Ir−F separation of 1.998(3) Å[8] and [(Ph$_3$P)$_2$(CO)(η^2-NH=NC$_6$H$_3$(*p*-CF$_3$))Ir−F][BF$_4$] shows an Ir−F distance of 2.21(4) Å.[9] This latter structure should be considered with some care due to the high degree of error and the overall quality of the structure determination (R = 8.5%).

Fluoride Dissociation Experiments (Nonaqueous Media). Fluoride is slowly displaced from complexes **1** by N- and P-donor Lewis bases (L) such as NCMe, pyridine (py), PEt$_3$, and PPh$_3$ (Scheme 2).[10] A typical experiment involves dissolving Cp*Ir(PMe$_3$)(Ph)F (**1a**) and L in C_6D_6 or THF-d_8, and then allowing the reaction mixture to stand at room temperature for about 1 week. Over this time an equilibrium between the salts [Cp*Ir(PMe$_3$)(Ph)(L)]F (**2a,** L = NCMe; **2b**, L = py; **2c**, L = PEt$_3$; **2d**, L = PPh$_3$) and the covalent starting material is established.[11] These equilibria always lie in favor of the neutral fluoro compound, even the presence of 100 or more equiv of L. The most obvious spectral feature of the ionization products is the loss of PF coupling in the ^{31}P{^{1}H} spectra of these materials as compared to the starting fluorides. For example,

Table 1. Crystal and Data Parameters for Cp^{Et}Ir(PMe$_3$)(Ph)F (**1c**)

Crystal Parameters	
formula	Ir P F C_{20} H_{31}
formula weight	513.6
cryst syst	monoclinic
space group	$P2_1/c$
Z	4
a, Å	9.235(2)
b, Å	12.667(2)
c, Å	17.129(3)
β, deg	104.547(16)
V, Å^3	1939.5(12)
d_{calc}, g cm^{-3}	1.76
cryst dimens, mm	0.13 × 0.25 × 0.28
T, °C[a]	−126
Measurement of Intensity Data	
radiation (monochrome)	Mo, 0.71073 Å (graphite)
scan type	θ-2θ
scan rate, deg/min	5.49
scan width	$\Delta\theta = 0.80 + 0.35 \tan\theta$
2θ range, deg	3−50
data collected	$+h, +k, \pm l$
no. of data collected	3575
no. of unique data ($F^2 > 3\sigma(F^2)$)	2859
no. of variables	209
μ_{calc}, cm^{-1}	69.5
R	3.98
wR	4.65
GOF	2.18

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 24° and 30°.

Table 2. Position Parameters and B (Esd's) for Cp^{Et}Ir(PMe$_3$)(Ph)F (**1c**)[a]

atom	x	y	z	B (Å^2)
Ir	0.10379(1)	0.17220(1)	0.28241(1)	1.099(5)
P	−0.0348(2)	0.2061(2)	0.1556(1)	1.42(4)
F	0.0040(5)	0.0264(3)	0.2531(3)	1.71(9)
C1	0.2961(8)	0.2764(6)	0.2934(5)	1.4(2)
C2	0.3483(8)	0.1710(6)	0.2794(5)	1.6(2)
C3	0.3308(8)	0.1063(6)	0.3430(5)	1.7(2)
C4	0.2734(9)	0.1671(6)	0.4002(5)	1.8(2)
C5	0.2523(8)	0.2738(6)	0.3670(6)	1.8(2)
C6	0.3115(9)	0.3726(7)	0.2476(6)	2.3(2)
C7	0.4200(9)	0.1420(8)	0.2127(5)	2.4(2)
C8	0.3660(9)	−0.0090(7)	0.3509(6)	2.3(2)
C9	0.251(1)	0.1310(7)	0.4780(6)	2.7(2)
C10	0.2118(9)	0.3679(7)	0.4101(6)	2.2(2)
C11	0.346(1)	0.4155(7)	0.4671(6)	2.8(2)
C12	0.0161(9)	0.1208(7)	0.0815(5)	2.1(2)
C13	−0.2340(9)	0.1815(7)	0.1375(6)	2.1(2)
C14	−0.029(1)	0.3377(7)	0.1150(5)	2.2(2)
C15	−0.0801(8)	0.2078(6)	0.3254(5)	1.3(1)
C16	−0.1476(8)	0.1299(6)	0.3639(5)	1.6(2)
C17	−0.2624(9)	0.1514(7)	0.3981(5)	2.1(2)
C18	−0.3173(9)	0.2535(8)	0.3978(6)	2.2(2)
C19	−0.2539(9)	0.3325(6)	0.3619(5)	1.9(2)
C20	−0.1379(9)	0.3104(6)	0.3251(5)	1.7(2)

[a] The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as (4/3)[$a^2\beta$(1,1) + $b^2\beta$(2,2) + $c^2\beta$(3,3) + ab(cos γ)β(1,2) + ac(cos β)β(1,3) + bc(cos α)(β(2,3)] where a, b, c are real cell parameters, and $\beta(i,j)$ are anisotropic β's.

(7) The use of C$_5$Me$_4$Et ligands in place of Cp* ligands in this chemistry greatly facilitated isolation and crystallization of compounds.

(8) Blake, A. J.; Cockman, R. W.; Ebsworth, E. A. V.; Holloway, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 529−530.

(9) Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462−2469.

(10) It has been noted that MF(CO)(PPh$_3$)$_2$ [M = Rh, Ir] behave as weak electrolytes in methanol or THF; see: Vaska, L.; Peone, J. *J. Chem. Soc., Chem. Commun.* **1971**, 418−419.

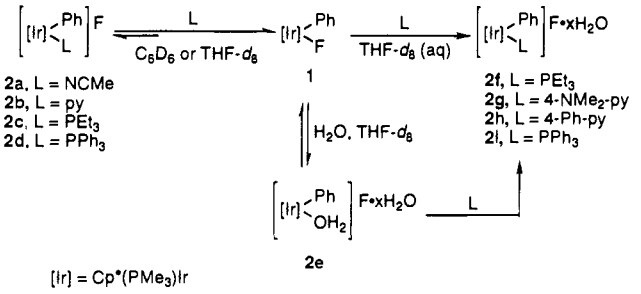
(11) In contrast to the behavior of the fluoro complexes, chloride displacement from Cp'Ir(PMe$_3$)(Aryl)Cl to [Cp'Ir(PMe$_3$)(Aryl)(L)]Cl does not occur at room temperature in benzene in the presence of excess L.

Table 3. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for $Cp^{Et}Ir(PMe_3)(Ph)F$ (**1c**)

Distances					
Ir–P	2.269(2)	Ir–C1	2.183(7)	Ir–C5	2.154(8)
Ir–F	2.069(4)	Ir–C2	2.271(8)	P–C12	1.815(9)
Ir–C15	2.063(7)	Ir–C3	2.253(8)	P–C13	1.814(9)
Ir–CP	1.849	Ir–C4	2.223(9)	P–C14	1.812(9)

Angles			
CP–Ir–P	133.82	F–Ir–C15	85.70(25)
CP–Ir–F	127.32	Ir–P–C12	112.0(3)
CP–Ir–C15	124.92	Ir–P–C12	115.8(3)
P–Ir–F	80.01(14)	Ir–P–C13	118.5(3)
P–Ir–C15	89.04(25)	Ir–C15–C16	120.8(6)
		Ir–C15–C20	123.1(6)

Scheme 2

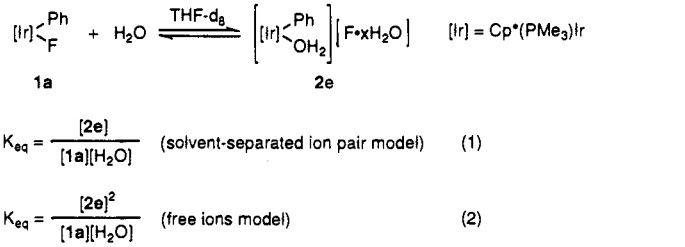


the $^{31}P\{^1H\}$ spectrum of an equilibrium mixture of $Cp^*Ir(PMe_3)(Ph)F$ and 8 equiv of NCMe shows two resonances: a doublet at −25.3 ppm for **1a** (J_{PF} = 54 Hz) and a singlet at −32.9 ppm for **2a** (no J_{PF}) in a 2:1 ratio. It is interesting to note the close parallels between the reactivity of $Cp^*Ir(PMe_3)(Ph)(OTf)$[12] and $Cp^*Ir(PMe_3)(Ph)(F)$. Both triflate and fluoride can be ionized (dissociated) from Ir to provide ionic Ir(III) complexes, but exposing $Cp^*Ir(PMe_3)(Ph)(OTf)$ to 8 equiv of NCMe causes a complete shift to $[Cp^*Ir(PMe_3)(Ph)(NCMe)]OTf$. This is consistent with OTf^- being a poorer base than F^-.[13]

Attempts to isolate compounds **2** in pure form were not very successful. For example, over the course of a month a benzene/Et_2O solution of **1a/2c** deposited white needles. A FAB mass spectrum of these needles gave the expected parent ion *m/z* of 599 for $[Cp^*Ir(PMe_3)(Ph)(PEt_3)]^+$, but combustion analysis was low on C and H (Calcd: C, 48.60; H, 7.18. Found: C, 46.32; H, 6.47). The cause of this may be partial loss of PEt_3 in vacuo while the sample was being dried since the elemental analysis lies between the expected value and that calculated for $Cp^*Ir(PMe_3)(Ph)F$ (C; 45.68; H, 5.85). Therefore, ionic compounds **2** were studied spectroscopically.[14] In the instances where salts **2** could be precipitated as solids redissolution in THF-d_8 caused equilibration with **1a** and free ligand, always in favor of the covalent fluoride materials since excess L is not present under these conditions.

The cationic complexes **2** show singlet resonances in their respective $^{31}P\{^1H\}$ spectra if the L donor atom is oxygen or nitrogen whereas P-based ligands show P–P coupling with the Ir–PMe_3 resulting in two doublet resonances typically coupled by 20 Hz ($^2J_{PP}$). While the ^{19}F NMR resonances for complexes **1** are doublets at ≈−414 ppm no new ^{19}F resonances are observed for ionic species **2** from −1000 to +1000 ppm. No

Scheme 3



detailed discussion of these equilibria is warranted since in "dry" solvents the results proved difficult to accurately reproduce. Reaction mixtures generally take considerable, and variable, time to come to equilibrium with the final apparent K_{eq} varying by as much as a factor of 5. For example, a small base such as NCMe results in the **1a/2a** equilibrium being established in less than 1 h. Addition of a larger base such as PPh_3 to a solution of **1a** initially has no effect, but over the course of 2 days (6 days in another instance) the equilibrium concentration of **2d** is fully established. On the note of irreproducibility, addition of 8 and 35 equiv of NCMe to **1a** in C_6D_6 led to values of K_{eq} that differed by a factor of 2.4; and addition of 3 equiv of PPh_3 to **1a** in C_6D_6 on different days led to K_{eq} values differing by a factor of 4.5. Water (*vide infra*) proved to be an effective agent for shifting the equilibria between compounds **1** and **2** in the presence of ligands L, and the presence of inevitable traces of H_2O was probably the cause of our erratic observations. More quantitative studies with known quantities of water are summarized below.

Fluoride Dissociation Experiments (Aqueous Media). In wet THF we observe a species consistent with the formulation of an aquo complex. This species, $[Cp^*Ir(PMe_3)(Ph)(OH_2)]F\cdot xH_2O$ (**2e**) exhibits a singlet $^{31}P\{^1H\}$ resonance at −28.5 ppm and appears to be indefinitely stable in THF solution. It is interesting that even in the presence of excess water, we never observe the formation of $Cp^*Ir(PMe_3)(Ph)(OH)$ which we have previously prepared.[12] Clearly, the ability of fluoride to deprotonate an Ir-bound ligand is severely attenuated by solvation since fluoride is able to deprotonate substantially less acidic ligands in nonaqueous media (*vide infra*). The simple ^1H NMR resonances for **2e** are easily assignable, but we were unable to locate distinct resonances for the Ir-bound H_2O molecule since it is presumably exchanging rapidly with free H_2O which is present in vast excess. In support of this hypothesis, a recent paper by Eisen and Fish has shown that the Rh-bound water molecules in $Cp^*Rh(OH_2)_3^{2+}$ exchange with the bulk aqueous solution with a rate constant greater than 8150 s^{-1}.[15] A 2-D NOESY experiment on a solution of **1a/2e** shows cross peaks between that of bulk water (δ 2.98) and both sets of Cp*, PMe_3, and aryl protons on the two Ir species in solution. This conclusively demonstrates that H_2O is bound to one species, namely $[Cp^*Ir(PMe_3)(Ph)(OH_2)]F\cdot xH_2O$ (**2e**), and that species is rapidly exchanging with $Cp^*Ir(PMe_3)(Ph)F$ (**1a**). A low-temperature NMR study was attempted in an effort to locate a resonance for Ir-bound water, but it was unsuccessful. Two other Ir(III) aquo complexes that we have been able to locate in the literature are $[IrH_2(THF)(PPh_3)_2(OH_2)]^+SbF_6^-$[16] and $Cp^*Ir(Cl)(OH_2)_2]^+PF_6^-$.[17] No NMR data have been reported for either compound so no comparisons can be made with **2e**.

The effect of water concentration on the equilibrium between **1a** and **2e** (Scheme 3) at room temperature was determined by

(12) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888–7889.

(13) This phenomenon has been reported for $(PPh_3)_2(CO)_3ReX$ [X = OTf, F], see ref 5.

(14) The exact nature of the fluoride counterion in these ionic compounds cannot be determined readily. One would not expect F^- to exist discretely without some interaction with other atoms, see: Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 292–293.

(15) Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806–2812.

(16) Luo, X.-L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682–686.

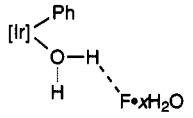
(17) Bodige, S.; Porter, L. C. *J. Organomet. Chem.* **1995**, *487*, 1–6.

Table 4. Data for Titration of Water against Cp*Ir(PMe$_3$)(Ph)F (**1a**)

[**1a**] (M)	[**2e**] (M)	[H_2O] (M)	K_{eq}(SSIP)[a]	K_{eq}(FI)[b]
0.01170	0	0		
0.01010	0.00151	0.17	0.88	0.0013
0.00942	0.00221	0.34	0.69	0.0015
0.00881	0.00278	0.51	0.62	0.0017
0.00809	0.00347	0.68	0.64	0.0022
0.00795	0.00357	0.84	0.54	0.0019
0.00735	0.00413	1.01	0.56	0.0023
0.00699	0.00447	1.17	0.55	0.0024
0.00651	0.00491	1.35	0.56	0.0027
0.00615	0.00524	1.50	0.57	0.0030
0.00602	0.00534	1.66	0.54	0.0029
0.00543	0.00588	1.82	0.60	0.0035
0.00472	0.00652	2.21	0.62	0.0041
0.00401	0.00713	2.60	0.68	0.0049
0.00343	0.00763	2.99	0.74	0.0057
0.00264	0.00836	3.37	0.94	0.0079
0.00229	0.00861	3.74	1.00	0.0087
0.00151	0.00928	4.47	1.37	0.0127

[a] SSIP = solvent-separated ion pair; K_{eq} = [**2e**]/[**1a**][H_2O]. [b] FI = free ions; K_{eq} = [2e]^2/[**1a**][H_2O].

titration of a solution of the fluoride **1a** with water to a maximum concentration of 4.5 M. The results of this titration are presented in Table 4 and depicted in Figure 1; added water increases the concentration of [Cp*Ir(PMe$_3$)(Ph)(OH_2)]F·xH_2O (**2e**). Apparent K_{eq} values for each point on Figure 1 were calculated using two models for the equilibrium, as shown in Scheme 3. The first model assumes that the aquo complex exists as one species, a solvent-separated ion pair, giving eq 1 as the formula for K_{eq}. Values of K_{eq} calculated in this way are relatively constant over the titration range (≈0.6 M^{-1}) with deviations observed only at very low and very high [H_2O]. The second model assumes that **2e** exists as dissociated ions, giving eq 2 as the formula for K_{eq}. Values of K_{eq} calculated using this model steadily increase (by as much as a factor of 10) as the concentration of water is increased. We therefore favor the solvent-separated ion pair model for complex **2e**. It may be that fluoride is hydrogen bound to the Ir-bound water molecule in addition to being solvated by other water molecules as shown below. Two solid-state structures of ion pairs with a single fluoride hydrogen bound to metal-bound water molecules can be found in the literature.[18,19]



2e

[Ir] = Cp*(PMe$_3$)Ir

It is not unreasonable to assume that in THF, which is a solvent of only moderate polarity, the product ions are likely to be predominantly associated in the form of solvent-separated ion pairs.[20]

Temperature Dependence of the 1a/2e Equilibrium. The equilibrium in Scheme 3 is established rapidly at all except the lowest temperatures examined (−30 °C and lower). To determine $\Delta H°$ and $\Delta S°$ for this reaction we measured K_{eq} over the temperature range −38 to 64 °C. The equilibrium ratio [Cp*Ir(PMe$_3$)(Ph)(OH_2)]$^+$/Cp*Ir(PMe$_3$)(Ph)F (**2e/1a**) was determined by integration and summation of resonances due to both the Cp* and PMe$_3$ protons in one-pulse ^{1}H{^{31}P} NMR spectra. Values of the apparent K_{eq} (solvent-separated ion pair model) were determined using initial concentrations of **1a** of 0.0132 M and H_2O of 0.755 M. Over the 102 degree temperature range, the observed **2e/1a** ratio changes from 2.59 (−38 °C) to 0.15 (64 °C)—that is, $\Delta G°$ undergoes an inversion in sign in going from low to high temperature.

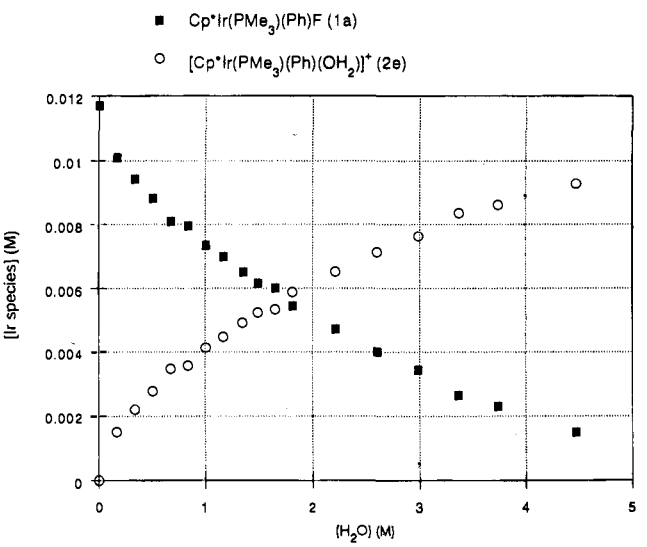


Figure 1. Titration of H_2O against Cp*Ir(PMe$_3$)(Ph)F (**1c**) in THF-d_8.

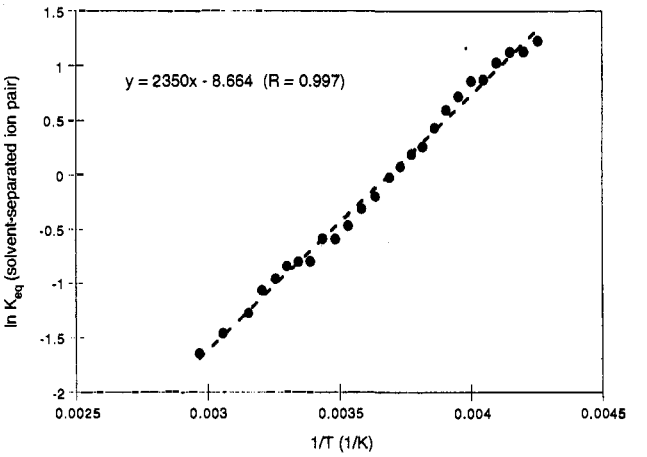


Figure 2. Plot of ln K_{eq} (for a solvent-separated ion pair) against 1/T.

Plotting ln K_{eq} vs 1/T (K^{-1}) provides a straight line (R = 0.997) from which values of $\Delta S°$ (−17.2 eu) and $\Delta H°$ (−4.7 kcal/mol) can be calculated (Figure 2). However, we caution against overinterpretation of these values because examining the equilibrium in Scheme 3 at different absolute concentrations shows that higher dilution does affect the value of the apparent K_{eq}. For example, starting with [**1a**]$_0$ = 0.0132 M and [H_2O]$_0$ = 0.755 M, the apparent K_{eq} at 279 K is 0.74 M^{-1}. Diluting the solution by a factor of 4 causes a change in K_{eq} to 1.13 M^{-1}. Similarly, at 235 K the observed values of K_{eq} are 3.43 (high concentration) and 2.34 (low concentration). This lack of constancy over wider concentration ranges could be due to changes in activity caused by the different concentration of the more polar solvent water in THF, the change in ionic strength caused by dilution, and/or the greater tendency for the ion pair **2e** to dissociate into free ions at lower absolute concentrations. Attempts to measure K_{eq} at constant ionic strength were frustrated by the complete shift of the equilibrium to the right when significant concentrations of an "innocent" salt such as

(18) Green, M. L. H.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1986**, 2227–2236.

(19) Jacobsen, R. A.; Jensen, W. P. *Inorg. Chim. Acta* **1981**, *52*, 205–209.

(20) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 185.

LiOTF of $NaBPh_4$ were added to the solution. This is perhaps the most dramatic piece of evidence that K_{eq} is strongly influenced by solution environmental factors.

Competition Reactions of 1a with H_2O and Other Ligands: Catalysis of 1a to 2f−i by H_2O via the Intermediate [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·xH$_2$O (2e). We next used NMR spectroscopy to monitor the competitive reaction of fluoride **1a** with water and other ligands L (Lewis bases). For **1a** in the presence of L and H_2O in THF-d_8, the aquo complex [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·xH$_2$O (**2e**) is the kinetic product and the ligand complex [Cp*Ir(PMe$_3$)(Ph)(L)]F·xH$_2$O is the thermodynamic product of fluoride dissociation (Scheme 2). For example, when a 1.4×10^{-5} M solution of Cp*Ir(PMe$_3$)(Ph)F is dissolved in THF-d_8 and treated with 6 equiv of PEt_3, no [Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]F is *initially* observed. Addition of 15 μL (46 equiv) of deaerated H_2O immediately leads to a kinetic mixture of starting material (**1a**) ($^{31}P\{^1H\}$ NMR δ -25.5 (d), $J_{PF} = 55$ Hz, 90%) and the aquo complex **2e** (δ −28.5 (s), 10%). Within 1 min, resonances are observed in the $^{31}P\{^1H\}$ NMR spectrum attributable to **1a** (23%), **2e** (41%), and [Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]F·xH$_2$O (**2f**) (δ −22.5 (d) and −47.6 (d), $^2J_{PP} = 24.9$ Hz, 36%). Allowing this mixture of products to stand for 24 h leads to complete conversion to PEt_3 complex **2f** which therefore must be the thermodynamic product.[21] A similar experiment was conducted using 4-(dimethylamino)pyridine. The behavior of the system was similar to that observed with L = PEt_3, and after 24 h only [Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$−NMe$_2$)]F·xH$_2$O (**2g**) could be spectroscopically observed ($^{31}P\{^1H\}$ NMR δ −34.1 (s)). Thus, in the presence of water (a) the equilibria between **1a** and various pyridine and phosphine-type ligands are established more rapidly, and (b) they lie completely to the right. This stands in marked contrast to the equilibria in "dry" nonaqueous media where the rates are slow and the equilibria lie far toward **1a**.

Precipitates could be obtained from solutions of **2** containing water. Drying these materials in vacuo followed by redissolution in THF-d_8 caused equilibration with **1a** and free ligand in favor of the covalent fluoride materials. The fact that the covalent complex Cp*Ir(PMe$_3$)(Ph)F (**1a**) can be recovered after extended exposure to water proves that while the fluoride ligand may be solvated in the equilibrium experiments the solvation is not irreversible. Stirring **1a** in 1:1 THF/water for 24 h, followed by extended exposure to vacuum, also gives back **1a** quantitatively.

Ligand Competition Reactions. To monitor the reactions of **1a** with several ligands simultaneously over time, and to determine the thermodynamic preference of the [Cp*Ir(PMe$_3$)(Ph)]$^+$ fragment for various ligands, we conducted the following experiment. A solution of fluoride **1a** (9.2 μmol, 1.0 equiv), 4-phenylpyridine (70.0 μmol, 8.3 equiv), PPh_3 (69.4 μmol, 7.5 equiv), and H_2O (499.0 μmol, 54.2 equiv) was prepared in an NMR tube using cannula techniques at −78 °C. The NMR tube was sealed and transferred to an NMR probe maintained at −55 °C. After allowing the tube to thermally equilibrate in the probe for 15 min an initial spectrum showed a pre-equilibrium situation with **1a** constituting about 80% of the Ir-containing species with the remaining 20% being aquo complex **2e**. No [Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$−Ph)]F·xH$_2$O (**2h**) or [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F·xH$_2$O (**2i**) were observed. The reaction mixture was then warmed to −31 °C where the growth of **2e** could be observed at the expense of **1a** (Figure 3). After 95 min the relative percentages of the two Ir species in solution were fluoride **1a** 43% and aquo complex **2e** 57%; no further change was observed at this temperature and neither ligand complex **2h** or **2i** was detected. Upon warming the reaction mixture to 25 °C, **1a** grew in to 59%, **2h** grew in to 23%, and **2e** dropped to 18%; still no [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F·xH$_2$O (**2i**) was observed. Continued evolution of the reaction at 25 °C is shown in Figure 4 (note that the time on the horizontal axis was reset to zero at 25 °C). Even at this temperature the growth of [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F·xH$_2$O (**2i**) is not observed for 74 min! At this point we can begin to detect a slow but steady growth to 74% (2946 min). Fluoride **1a** and pyridine complex **2h** are slowly consumed, while the concentration of [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·xH$_2$O (**2e**) remains at about 0.002 M until the latter parts of the reaction where its concentration finally starts to decay.[21] This shows the superior thermodynamic binding affinity of phosphorus-based ligands for what is formally [Cp*Ir(PMe$_3$)(Ph)]$^+$ as compared to F^-, H_2O, and N-based ligands, in spite of its slow rate of attack on all of the kinetically-formed products (Scheme 4).

Our conclusions from these experiments are that water and Cp*Ir(PMe$_3$)(Ph)F establish an equilibrium with [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·xH$_2$O quickly even at low temperatures. In the presence of more thermodynamically preferred ligands such as pyridines or phosphines [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·xH$_2$O acts

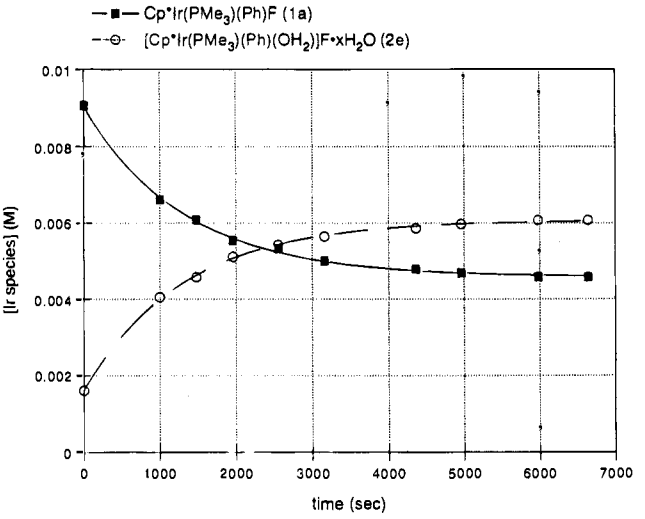


Figure 3. Plot of a mixture of complexes **1a/2e** coming to equilibrium at −31 °C in THF-d_8.

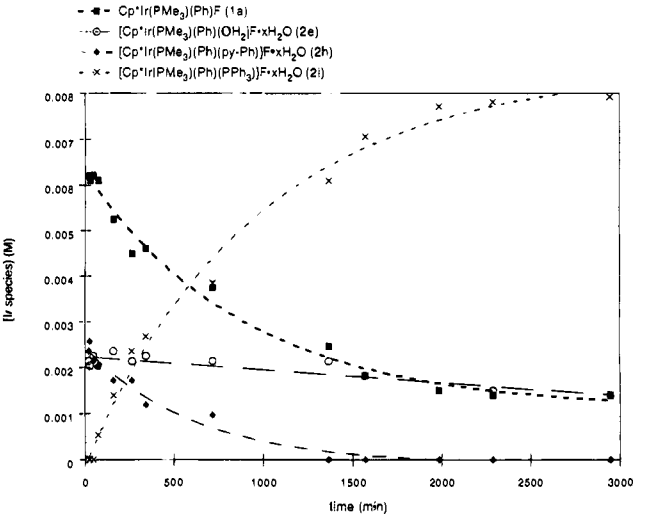
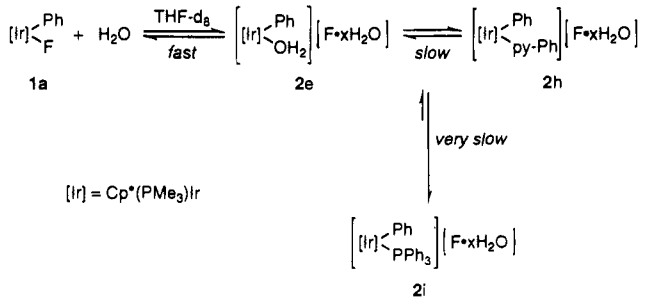


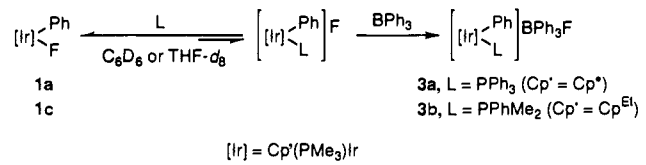
Figure 4. Evolution of a mixture of Cp*Ir(PMe$_3$)(Ph)F (**1c**), H_2O, 4-Ph-py, and PPh_3 over time at room temperature in THF-d_8.

(21) Over this time the ratio of **1a** to **2e** does not remain constant, even though we know that the two complexes interconvert rapidly at this temperature. We suggest that the changing ionic strength of the medium as the reaction progresses is responsible for shifting the apparent K_{eq} (vide infra).

Scheme 4



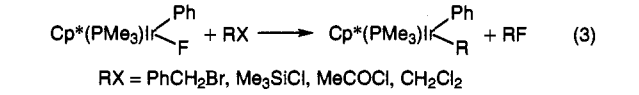
Scheme 5



as an intermediate on the way to [Cp*Ir(PMe$_3$)(Ph)(L)]F·xH$_2$O. We observe a strong steric bias in the kinetic products of these reactions. Water displaces fluoride very quickly, likely aided by hydrogen bonding, whereas 4-phenylpyridine is slower to coordinate to Ir. The thermodynamically preferred ligand for [Cp*Ir(PMe$_3$)(Ph)]$^+$ in the above experiment is PPh$_3$ which only very slowly displaces water and/or 4-phenylpyridine on the way to forming the ultimate product [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F·xH$_2$O (**2i**). We rationalize the preference of [Cp*Ir(PMe$_3$)(Ph)]$^+$ for phosphines on the basis of its being a very soft Lewis acid. It is interesting that water and pyridines can sterically access the iridium center more readily and can thus serve as transients in the overall formation of [Cp*Ir(PMe$_3$)(Ph)(PR$_3$)]F·xH$_2$O.

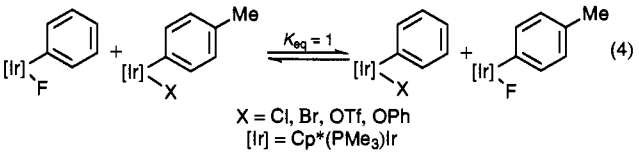
Sequestration of Fluoride by a Lewis Acid. In the instances where salts **2** could be precipitated as solids redissolution in THF-d_8 caused equilibration with **1a**−**c** and free ligand, always in favor of the covalent fluoride materials since excess L is not present under these conditions. This made it very difficult to characterize complexes **2** in the solid state. To prove that fluoride was still a part of these salts we added a stoichiometric amount of BPh$_3$ to selected equilibrium mixtures of **1** and **2** (Scheme 5). This action leads to irreversible formation of the borate complexes, [Cp'Ir(PMe$_3$)(Aryl)(L)]$^+$BPh$_3$F$^-$, in cases where formation of L·BPh$_3$ is unfavorable. For example, treating an equilibrium mixture of Cp*Ir(PMe$_3$)(Ph)F and PPh$_3$ in benzene-d_6 with a slight deficiency of BPh$_3$ causes the ^{31}P{^{1}H} NMR resonance for **1a** to decrease and the two doublet resonances for [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]$^+$ to increase in intensity. [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]$^+$BPh$_3$F$^-$ (**3a**) can be isolated as a yellow amorphous solid by repeated precipitations from benzene in 68% yield. Interestingly, while no ^{19}F NMR resonance can be observed for [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F, **3a** shows a broad (presumably due to boron coupling) resonance at −141 ppm in the ^{19}F NMR spectrum for its BPh$_3$F$^-$ counterion. Complex **3b**, [Cp^{Et}Ir(PMe$_3$)(Ph)(PPhMe$_2$)]$^+$BPh$_3$F$^-$, was similarly prepared except that the reaction was done in Et$_2$O.

Fluoride Exchange Experiments. Reactions of **1a** with organic halides such as PhCH$_2$Br, Me$_3$SiCl, MeCOCl, and even CH$_2$Cl$_2$[22] lead to complete halide exchange (eq 3), thus precluding any temperature-dependent equilibrium studies that might enable us to determine Ir−F bond strengths. The organic products of these exchange reactions were identified by ^{1}H NMR spectroscopy. Yields of Cp'Ir(PMe$_3$)(Aryl)X and RF were greater than 90%. The rates of these exchange reactions are



highly variable and somewhat irreproducible: some are complete in minutes (Me$_3$SiCl) and others require days (PhCH$_2$Br).[23] The driving force for reaction 3 is large—a combination of the energetically favorable ($D_{R-F} > D_{R-hal}$) change in C−halogen bond strengths (ca. −26 kcal/mol for R−Cl) and the undoubtedly reinforcing (but unknown magnitude) change in Ir−halogen bond strengths. Because the equilibrium for this reaction probably lies so far to the right, it does not seem reasonable to use it to estimate a limiting value for $D_{Ir-hal} - D_{Ir-F}$. Interestingly, Cp*(PMe$_3$)Rh(C$_6$F$_5$)F has been shown to react instantaneously with CHCl$_3$ to give Cp*(PMe$_3$)Rh(C$_6$F$_5$)Cl.[24] Additionally, the formation of Cp*(PMe$_3$)Rh(C$_6$F$_5$)F from Cp*(PMe$_3$)Rh(C$_2$H$_4$) and C$_6$F$_6$ (under photolytic conditions) is complicated by the formation of Cp*(PMe$_3$)Rh(C$_6$F$_5$)Cl presumably from minute quantities of C$_6$F$_5$Cl in commercial samples of 99.9% C$_6$F$_6$.

The fluoride complexes **1** also exchange ligands rapidly with other organometallic compounds. For instance, within minutes of dissolution in C$_6$D$_6$ an equimolar mixture of Cp*Ir(PMe$_3$)(Ph)F and Cp*Ir(PMe$_3$)(*p*-tolyl)X [X = Cl, Br, OTf, OPh] leads to a solution containing four species in a 1:1:1:1 ratio (eq 4).



These species[25] are identifiable (by both ^{1}H and ^{31}P NMR spectroscopy) as the two starting materials (left side of equilibrium) and the two exchange products Cp*Ir(PMe$_3$)(Ph)X and Cp*Ir(PMe$_3$)(*p*-tolyl)F (right side of equilibrium). Interestingly, there is no bias for fluoride to reside on Ir−Ph vs Ir−*p*-tolyl complexes (K_{eq} = 1). Apparently, the methyl substitution on the phenyl ring (**1b** vs **1a**) does not strongly affect the electronic nature of the iridium compounds. On this note, the ^{31}P{^{1}H} and ^{19}F chemical shifts for **1a**−**c** are virtually identical.

Other Reactivity Studies: Deprotonation and Desilylation. Olefins and unactivated acetylenes are unreactive with **1** at room temperature. In contrast, the activated alkyne dimethyl acetylenedicarboxylate (DMAD) reacts with the fluoro complexes in benzene over the course of minutes at room temperature to give metallacycles **5** in 55−80% isolated yields (Scheme 6).[26] A probable mechanism for the formation of these metallacycles involves coordination of the alkyne to iridium with concomitant dissociation of fluoride. Then attack of the bound alkyne at the ortho carbon of the phenyl group followed by deprotonation by fluoride would yield the final product. Attempted removal of the organic group from **5a** with (*p*-tolyl)SH, [PhNH$_3$]OTf,

(22) The recently reported [Cp$_2$Co]F (ref 3) is apparently stable in methylene chloride solution although it is remarkably reactive toward other organic chlorides. A referee has suggested that the Ir(III) cation may play a role in assisting halide metathesis, at least for the carbon-based systems.

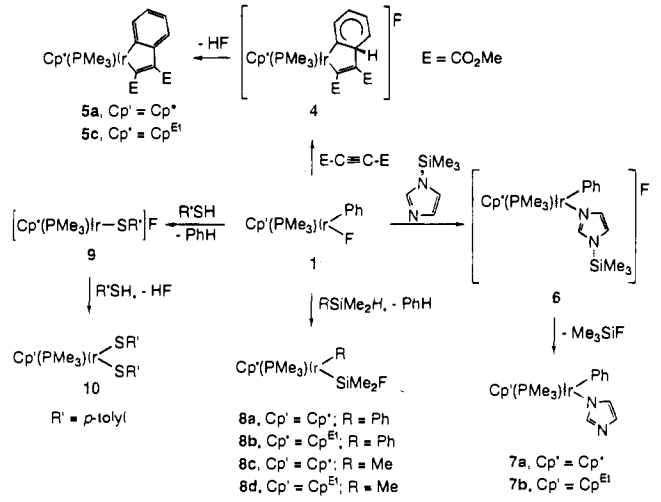
(23) Water has been shown to dramatically affect the position of (PPh$_3$)$_2$(CO)RhF/[PPN]Br:(PPh$_3$)$_2$(CO)RhBr/[PPN]F equilibria, see: Branan, D. M.; Hoffman, N. W.; McElroy, E. A.; Miller, N. C.; Ramage, D. L.; Schott, A. F.; Young, S. H. *Inorg. Chem.* **1987**, *26*, 2915−2917.

(24) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429−1440.

(25) All exchange products have been synthesized and characterized independently.

(26) **5a** can also be synthesized from Cp*Ir(PMe$_3$)(Ph)(OTf) and DMAD in the presence of base; see: Meyer, T. Y.; Woerpel, K. A.; Novak, B. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 10290−10291.

Scheme 6

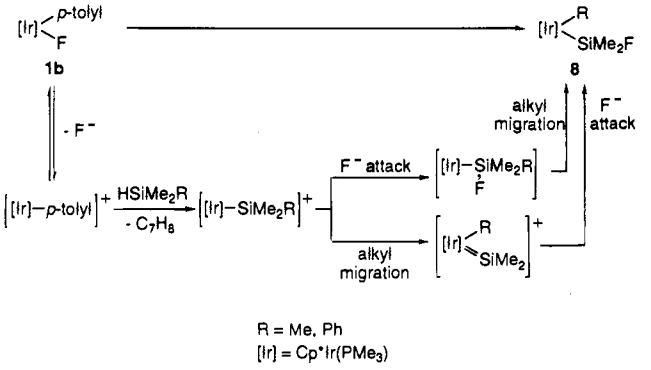


or HCl (aq) has so far been unsuccessful. While **5a** is inert to the former two reagents, extended exposure to HCl (aq) in the air does cause decomposition to a mixture of products. It is interesting to note that Cp*Ir(PMe$_3$)(Ph)OTf reacts with DMAD to give **5a**, but only after reaction with a base such as CsOH or *p*-tolylNH$_2$. Presumably triflate is not powerful enough to deprotonate the first-formed, and still protonated, metallacycle (cf. intermediate **4**).

Formal activation of Si−N and Si−H bonds by fluoro complexes **1** has been observed. Treatment of **1c** with 1-(trimethylsilyl)imidazole (Me$_3$Si-Im) presumably forms a transient cation (**6**) which is rapidly desilylated by fluoride to give the covalently bound imidazolate complex **7** in 60% yield (Scheme 6). A stoichiometric amount of Me$_3$SiF is detectable by NMR spectroscopy in C_6D_6 (^{1}H NMR δ 0.02 (d, J_{HF} = 7.2 Hz)) of representative reaction mixtures.[27]

Since deprotonation (HX reagents) *and* desilylation (Me$_3$SiX reagents) were effected by complexes **1** we wondered whether H−SiMe$_3$ would be deprotonated and/or desilylated by our Ir−fluoride complexes to give Cp*Ir(PMe$_3$)(Ph)(SiMe$_3$) or Cp*Ir(PMe$_3$)(Ph)H. In fact, neither reaction is observed to a substantial degree. Treatment of **1** with silanes such as HSiMe$_2$R [R= Ph, Me] leads instead to the formation of pentane-soluble Cp'Ir(PMe$_3$)(R)(SiMe$_2$F) complexes (**8**) (Scheme 6). The reactions to form complexes **8** are much cleaner when an excess of silane (>10 equiv) is used and the silane is added to the reaction mixture all at once. Surprisingly, both *phenyl* fluoride **1a** and *p-tolyl* fluoride **1b** react with HSiMe$_2$Ph to give the *identical* product Cp*Ir(PMe$_3$)(Ph)(SiMe$_2$F) (**8a**). One equivalent of toluene is observable (^{1}H NMR spectroscopy) in representative examples of the latter reaction. This result provides clear evidence that the first reaction with silanes involves removal of the aryl group from Ir.[28] Treatment of **1a** and **1c** with HSiMe$_3$ leads to the formation of **8c** and **8d** along with variable amounts of Cp'Ir(PMe$_3$)(Ph)(H) (15−45%) and Cp'Ir(PMe$_3$)(H)$_2$ (<5%). In order to purify complexes **8** we needed to treat the crude reaction mixtures with CCl_4 (>10 equiv) to convert any Ir-hydride coproducts to their respective chlorides which are markedly less soluble and thus removable by chromatography (silylated silica gel, pentane eluant). Ir−phenyl complexes **8a** and **8b** were isolated in 33 and 82% yields respectively after several chromatographic purifications followed

Scheme 7



by recrystallization from (Me$_3$Si)$_2$O. Ir−methyl derivatives **8c,d** are both extremely soluble and have resisted complete purification. However, the SiMe$_2$F groups in these compounds are clearly characterized by ^{1}H NMR spectroscopy. The diastereotopic Si−Me groups at ≈0.6 ppm are both coupled to ^{19}F ($^3J_{HF} \approx 8$ Hz, $^1J_{Si-F} \approx 310$ Hz). Compounds **8** exhibit singlet ^{31}P resonances near −45 ppm which is typical for related Cp*Ir(PMe$_3$)(Aryl)H complexes. The ^{19}F spectra for these complexes show singlet resonances at −139 to −143 ppm attributable to their −SiMe$_2$F ligands.

A possible mechanistic sequence of events for the reaction of silanes (HSiMe$_2$R) and fluoride **1b** is shown in Scheme 7. Based on the observation in the preceding paragraph that toluene is produced early in the reaction between **1b** and HSiMe$_2$Ph we surmise that a σ-bond metathesis reaction between the dissociated fluoride species and silane produces a cationic Ir(III) silyl complex which can then proceed via two possible pathways to the observed product **8**. The first involves attack by fluoride at silicon, followed by alkyl migration to Ir. The second involves the reverse sequence of steps in which alkyl migration from silicon to Ir gives a cationic Ir(V) silylene complex which is rapidly trapped by fluoride. A recent paper indicates the reactions of Cp*Ir(PMe$_3$)(Me)(OTf) and silanes are thought to proceed via this latter pathway.[28]

Finally, reaction of excess HS-*p*-tolyl with either **1a** or **1b** at room temperature over the course of minutes provides the bisthiolate complex Cp*Ir(PMe$_3$)(S-*p*-tolyl)$_2$ (**10**) in 51% isolated yield (100% NMR yield) (Scheme 6). This again shows the relative ease with which the Ir−C$_{aryl}$ bond of the aryl fluoride complexes is cleaved. The thiocresolate complex is related to other thiolate complexes we have prepared from Cp*Ir(PMe$_3$)Cl$_2$ by direct metathesis reactions.[29] When the reaction of 1 equiv of HS-*p*-tolyl and **1b** is conducted at low temperature an unisolable species formulated as **9** can be observed.[30] As a control experiment we prepared Cp*Ir(PMe$_3$)(Ph)(S-*p*-tolyl) from Cp*Ir(PMe$_3$)(Ph)(OTf) and LiS-*p*-tolyl and then treated it with thiocresol in C_6D_6. After 1 day at 75 °C no formation of **10** was observed thus precluding Cp*Ir(PMe$_3$)(Ph)(S-*p*-tolyl) from being an intermediate in the formation of Cp*Ir(PMe$_3$)(S-*p*-tolyl)$_2$ from Cp*Ir(PMe$_3$)(Ph)F.

Conclusion

In summary, it is clear that stable iridium fluoride complexes can be prepared and that they exhibit reactivity that is substantially different from that of the related Cl, Br, and I complexes, but strikingly similar to that of the corresponding triflates.[28] Based on a comparison to the relative reactivities

(27) Complexes **7** are also formed when H-Im is treated with the aryl fluoride complexes. Presumably, in these cases HF (undetected) is the liberated byproduct.

(28) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462−10463.

(29) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022−2024.

(30) ^{1}H NMR (C_6D_6): δ 2.11 (s, 3H, *p*-Me), 1.47 (s, 15H, Cp*), 1.06 (s, 9H, PMe$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ −39.40 (s).

of carbon−fluorine and carbon−OTf bonds, this would not have been expected. It emphasizes the relatively poor affinity of F^- for the Ir^+ centers in Cp'Ir(PMe$_3$)(Aryl)F complexes, and by inference for other low-valent late-transition-metal centers as well.

Experimental Section

General Methods. Experimental details routinely employed in our laboratories are discussed in detail elsewhere.[31] Unless otherwise specified, reagents were purchased from commercial suppliers and used without further purification. Acetonitrile was distilled from CaH_2, then P_2O_5. $HSiMe_2Ph$ was degassed and stored over 4 Å molecular sieves. Cp*Ir(PMe$_3$)(*p*-tolyl)X and Cp^{Et}Ir(PMe$_3$)(Ph)Y complexes [X = Br, OTf; Y = Cl, OTf] were prepared in a manner analogous to the related Cp*Ir(PMe$_3$)(Ph)X compounds.[26,28,29] Cp*Ir(PMe$_3$)(Ph)(OPh) was prepared according to the literature procedure.[12] DMAD was distilled at ambient pressure under argon. (*p*-tolyl)SH was recrystallized from hexanes. $PhCH_2Br$ was freshly distilled in vacuo in the dark. Me_3SiCl was distilled from CaH_2 in vacuo.

Cp'Ir(PMe$_3$)(Aryl)F (1a−c). Since these compounds were prepared similarly, their syntheses are presented in a generalized manner. In a typical experiment, Cp'Ir(PMe$_3$)(Aryl)OTf (1 mmol) was dissolved in a minimum of Et_2O then the resulting orange solution was treated with a suspension of TAS-F $[(Me_2N)_3S^+(Me_3SiF_2)^-]$ (1.08 mmol) in Et_2O (5 mL). The reaction mixture was then stirred vigorously overnight causing a slow color change from orange to yellow. A gray precipitate was also observed. The yellow supernatant was filtered through a pad of Celite to remove the insoluble triflate byproduct. The filtrate was taken to dryness in vacuo and then recrystallized from Et_2O at −40 °C. Alternatively, crystallization could be effected by diffusing pentane into concentrated toluene solutions of the compounds at room temperature. Typical isolated yields were 80−90%.

Cp*Ir(PMe$_3$)(Ph)F (1a). Yellow needles; ^{1}H NMR (400 MHz, C_6D_6) δ 7.30 (m, 3H, C_6H_5), 7.19 (br m, 2H, C_6H_5), 1.41 (d, 15H, $^3J_{HP}$ = 2.0 Hz, $C_5(CH_3)_5$), 1.00 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 127.4, 122.5 (s, C_{aryl}), other aryl resonances not detected, 90.2 (d, $^2J_{CP}$ = 3.4 Hz, C_5Me_5), 12.7 (d, $^1J_{CP}$ = 36.6 Hz, $P(CH_3)_3$), 9.0 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −25.25 (d, $^2J_{PF}$ = 53.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ −24.46 (d, $^2J_{PF}$ = 53.3 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ −413.0 (d, $^2J_{PF}$ = 54 Hz); IR (CsI) 1890 (br m), 1570 (m), 1450 (br), 1286 (m), 1063 (m), 1022 (s), 953 (s), 858 (m), 736 (s), 704 (m) cm^{-1}; MS (EI) 500 (M^+, ^{193}Ir). Anal. Calcd for $C_{19}H_{29}FPIr$: C, 45.68; H, 5.85. Found: C, 45.64; H, 5.80.

Cp*Ir(PMe$_3$)(*p*-tolyl)F (1b). Yellow needles; ^{1}H NMR (400 MHz, C_6D_6) δ 7.4 (br, 4H, C_6H_4), 2.36 (s, 3H, *p*-CH_3), 1.40 (s, 15H, $C_5(CH_3)_5$), 1.02 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) aryl resonances not detected due to broadness, δ 89.99 (d, $^2J_{CP}$ = 3.2 Hz, C_5Me_5), 21.22 (s, *p*-CH_3), 12.73 (d, $^1J_{CP}$ = 36.6 Hz, $P(CH_3)_3$), 9.11 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −25.48 (d, $^2J_{PF}$ = 54.7 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ −413.97 (d, $^2J_{PF}$ = 54.7 Hz); IR (CsI) 1481 (m), 1452 (m, br), 1379 (m), 1302 (w), 1282 (m), 1030 (m), 1018 (m), 955 (vs), 854 (m), 802 (s), 737 (ms), 681 (m), 503 (mw) cm^{-1}; MS (EI) 514 (M^+, ^{193}Ir); MS (EI) 514 (M^+, ^{193}Ir); HRMS (EI) calcd for $C_{20}H_{31}PFIr$, 514.1777; found 514.1784. Anal. Calcd for $C_{20}H_{31}FPIr$: C, 46.77; H, 6.08. Found: C, 46.66; H, 6.16.

Cp^{Et}Ir(PMe$_3$)(Ph)F (1c). Yellow crystals; ^{1}H NMR (400 MHz, C_6D_6) δ 7.3 (br, 2H, C_6H_5), 7.18 (br d, 3H, C_6H_5), 1.87 (q, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2Me), 1.49, 1.48, 1.44, 1.40 (m, 3H each, $C_5(CH_3)_4Et$), 1.01 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$), 0.84 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 146.9 (dd, $^2J_{CP}$ = 15.6 Hz, $^2J_{CF}$ = 3.2 Hz, C_{ipso}), 137 (br), 127.3 (s), 122.38 (s), C_{aryl}, 91.8, 91.7, 91.7, 91.6, 91.5 (s, C_5Me_4Et), 18.3 (s, CH_2Me), 13.6 (s, CH_2CH_3), 12.8 (dd, $^1J_{CP}$ = 36.0 Hz, $^3J_{CF}$ = 1.2 Hz, $P(CH_3)_3$), 9.0, 8.9, 8.9, 8.9 (s, $C_5(CH_3)_4Et$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −25.71 (d, $^2J_{PF}$ = 55.4 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6) δ −415.10 (d, $^2J_{PF}$ = 55.4 Hz); IR (CsI) 1568 (mw), 1456 (m), 1434 (w), 1377 (w), 1282 (mw), 1061 (m), 958 (s), 856 (mw), 739 (s), 706 (m), 678 (mw) cm^{-1}; MS (EI) 514 (M^+, ^{193}Ir). Anal. Calcd for $C_{20}H_{31}FPIr$: C, 46.77; H, 6.08. Found: C, 47.05; H, 6.30.

Spectroscopic Data for [Cp*Ir(PMe$_3$)(Ph)(L)]F Complexes in Nonaqueous Media (2a−d). Since complexes **2a−d** could not be isolated in analytically pure form, what follows is mostly spectroscopic data obtained on equilibrium mixtures of **1** and **2**. ^{13}C NMR data are not reported since the concentrations of products **2** were not sufficiently high that their resonances could be unambigously assigned. For each NMR experiment the solvent for the experiment, the number of equivalents of added ligand, and the ratio of covalent Cp*Ir(PMe$_3$)(Ph)F species to ionic [Cp*Ir(PMe$_3$)(Ph)(L)]F species observed at 25 °C is provided.

[Cp*Ir(PMe$_3$)(Ph)(NCMe)]F (2a). C_6D_6 experiment: ratio of **1a**:NCMe = 1:8; observed ratio of **1a**:**2a** = 2:1. ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 (br, 5H, C_6H_5), 2.47 (s, 3H, Ir−NCCH_3), 1.31 (d, 15H, $^3J_{HP}$ = 2.0 Hz, $C_5(CH_3)_5$), 1.24 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −32.85 (s).

[Cp*Ir(PMe$_3$)(Ph)(py)]F (2b). THF-d_8 experiment: ratio of **1a**:py = 1:10; observed ratio of **1a**:**2b** = 1:1. ^{1}H NMR (400 MHz, THF-d_8) δ 8.54, 7.12, 6.99, 6.83, 6.77 (m, 1H each, Ir−NC_5H_5), 8.0 (br, 3H, C_6H_5), 7.4 (br, 2H, C_6H_5), 1.60 (d overlapping **1a** Cp* doublet), 1.47 (d, 9H, $^2J_{HP}$ = 10.4 Hz, $P(CH_3)_3$). C_6D_6 experiment: ratio of **1a**:py = 1:3.6; observed ratio of **1a**:**2b** = 2.2:1. ^{1}H NMR (400 MHz, C_6D_6) δ 8.62 (br, 1H) 7.19 (br, 2H), 7.00 (br, m, 6H), 6.81 (br, 1H) (Ir−C_6H_5 and Ir−NC_5H_5), 1.24 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$), 1.18 (s, 15H, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ −34.70 (s).

Complexes **2c** and **2d** precipitated from solution over the course of several months. The white solids were dried under vacuum and then subjected to FAB-MS. Pure by NMR, **2c** was reprecipitated and subjected to combustion analysis several times without obtaining data that agreed with calculated values.

[Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]F (2c). C_6D_6 experiment: ratio of **1a**:PEt_3 = 1:11; observed ratio of **1a**:**2c** = 1:2. ^{1}H NMR (400 MHz, C_6D_6) δ 7.09 (m, 2H, C_6H_5), 6.91 (m, 3H, C_6H_5), 1.86 (d, 9H, $^2J_{HP}$ = 10.4 Hz, $P(CH_3)_3$), 1.62 (pseudo pentet, 6H, Ir−$P(CH_2CH_3)_3$), 1.39 (br s, 15H, $C_5(CH_3)_5$), 0.82 (dt, 9H, Ir−$P(CH_2CH_3)_3$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −23.17 (d, $^2J_{PP}$ = 24.3 Hz, PEt_3), −47.27 (d, $^2J_{PP}$ = 24.3 Hz, PMe_3). MS (FAB − sulfolane) 599 ([Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]$^+$, ^{193}Ir).

[Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F (2d). C_6D_6 experiment: ratio of **1a**:PPh_3 = 1:1.7; observed ratio of **1a**:**2d** = 3:1. ^{1}H NMR (400 MHz, C_6D_6) δ complex aryl region obscured by excess PPh_3, 1.34 (br s, 15H, $C_5(CH_3)_5$), 1.23 (d, 9H, $^2J_{HP}$ = 10.8 Hz, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −4.47 (d, $^2J_{PP}$ = 21.1 Hz, PPh_3), −50.98 (d, $^2J_{PP}$ = 21.1 Hz, PMe_3). MS (FAB − sulfolane) 743 ([Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]$^+$, ^{193}Ir).

Treatment of 1a with Ligands in the Presence of H_2O: Preparation of Complexes 2e−i. Data for ligand complexes **2** in the presence of water are reported separately from the nonaqueous experiments above. All of these experiments were conducted similarly. A mixture of Cp*Ir(PMe$_3$)(Ph)F, ligand (excess), and water (excess) was transferred to an NMR tube which was then left to come to equilibrium. Reaction mixtures were then shown spectroscopically to contain only one Ir compound, namely [Cp*Ir(PMe$_3$)(Ph)L]F·*x*H_2O (except for **2e**).

[Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·*x*H_2O (2e). An NMR tube was charged with Cp*Ir(PMe$_3$)(Ph)F (12.0 mg), THF-d_8 (714 mg), and H_2O (50.0 μL, 116 equiv). The tube was sealed in vacuo and warmed to 45 °C for 1 min. After that time a ^{1}H NMR spectrum showed that the ratio of **1a**:**2e** was 1:2.64. ^{1}H NMR (400 MHz, THF-d_8) δ 7.16 (d, 2H, *J* = 8.0 Hz, C_6H_5), 6.86 (t, 2H, *J* = 8.0 Hz, C_6H_5), 6.73 (t, 1H, *J* = 8.0 Hz, C_6H_5), 1.56 (d 15H, $^4J_{HP}$ = 1.6 Hz, $C_5(CH_3)_5$), 1.38 (d, 9H, $^2J_{HP}$ = 10.4 Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ −27.68 (s). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ 137.96, 132.60, 128.15, 122.78 (C_{aryl}), 92.93 (s, C_5Me_5), 13.76 (d, *J* = 38.6 Hz, $P(CH_3)_3$), 9.16 (s, $C_5(CH_3)_5$).

[Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]F·*x*H_2O (2f). An NMR tube was charged with Cp*Ir(PMe$_3$)(Ph)F (4.5 mg), THF-d_8 (634 mg), and PEt_3 (6.8 mg, 6.4 equiv). An initial ^{1}H NMR spectrum showed that the only species in solution were the starting materials. Addition of 15 μL, H_2O (92 equiv) to the NMR tube led to a mixture of Cp*Ir(PMe$_3$)(Ph)F (84%), [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·*x*H_2O (16%), and [Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]F·*x*H_2O (trace). After 1 min the ratio of the three compounds was

(31) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974−985.

23:41:36. After 24 h at room temperature the originally yellow, now colorless solution was shown to contain [Cp*Ir(PMe$_3$)(Ph)(PEt$_3$)]F·xH$_2$O (**2f**) as the only observable iridium-containing species. ^{1}H NMR (400 MHz, THF-d_8) δ 7.28 (d, 2H, J = 6.9 Hz, C$_6H_5$), 6.88 (overlapping multiplets, 3H, C$_6H_5$), 2.13 (m, 6H, P(CH_2Me)$_3$), 1.82 (d, 9H, $^2J_{HP}$ = 10.4 Hz, P(CH_3)$_3$), 1.71 (t, 15H, $^4J_{HP}$ = 1.8 Hz, C$_5$(CH_3)$_5$), 1.09 (m, 9H, P(CH$_2$CH_3)$_3$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ −22.54 (d, $^2J_{PP}$ = 24.9 Hz, PEt$_3$), −47.55 (d, $^2J_{PP}$ = 24.9 Hz, PMe$_3$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) δ C_{ipso} not observed, 142.64 (t, J = 4.8 Hz, C_{ortho}), 128.93 (s, C_{meta}), 123.69 (s, C_{para}), 100.76 (br s, C_5Me$_5$), 20.54 (d, J = 33.8 Hz, P(CH_2Me)$_3$), 19.48 (d, J = 13.5 Hz, free PEt$_3$), 17.52 (d, J = 38.8 Hz, P(CH_3)$_3$), 10.40 (s, C$_5$(CH_3)$_5$), 9.90 (d, J = 13.7 Hz, free PEt$_3$), 9.58 (d, J = 5.6 Hz, P(CH$_2$(CH_3))$_3$).

[Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$-4-NMe$_2$)]F·xH$_2$O (2g). An NMR tube was charged with Cp*Ir(PMe$_3$)(Ph)F (4.5 mg) and THF-d_8 (656 mg) and NC$_5$H$_4$-4-NMe$_2$ (2.8 mg, 2.5 equiv). Then 15 μL of H$_2$O (46 equiv) was added to the NMR tube. After 1 h an NMR spectrum of the reaction mixture revealed that it contained a mixture of Cp*Ir(PMe$_3$)(Ph)F (26%), [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F (21%), and [Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$-4-NMe$_2$)]F·xH$_2$O (53%). After 1 day only [Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$-4-NMe$_2$)]F·xH$_2$O (**2g**) was observed. ^{1}H NMR (400 MHz, THF-d_8) δ 7.99 (d, 2H, J = 7.4 Hz, NC$_5H_4$-4-NMe$_2$), 7.14 (d, 2H, J = 7.6 Hz, C$_6H_5$), 6.91 (m, 3H, C$_6H_5$), 6.74 (d, 2H, J = 7.4 Hz, NC$_5H_4$-4-NMe$_2$), ≈3.1 (NMe$_2$ resonance is buried as a shoulder on H$_2$O resonance), 1.61 (d, 15H, $^4J_{HP}$ = 2.0 Hz, C$_5$(CH_3)$_5$), 1.45 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ −34.1 (s, PMe$_3$).

[Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$-4-Ph)]F·xH$_2$O (2h). An NMR tube was charged with Cp*Ir(PMe$_3$)(Ph)F (6.0 mg), THF-d_8 (771 mg), NC$_5$H$_4$-4-Ph (18.6 mg, 10.0 equiv), and H$_2$O (20.0 mg, 92.5 equiv). The tube was sealed in vacuo and heated to 45 °C for 20 min and then left at room temperature overnight. An NMR spectrum of the reaction mixture revealed it to contain mostly [Cp*Ir(PMe$_3$)(Ph)(NC$_5$H$_4$-4-Ph)]F·xH$_2$O (**2g**) and traces of Cp*Ir(PMe$_3$)(Ph)F and [Cp*Ir(PMe$_3$)(Ph)(OH$_2$)]F·xH$_2$O. ^{1}H NMR (400 MHz, THF-d_8) δ 7.2−6.6 complicated aryl region, 1.63 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$), 1.51 (d, 9H, $^2J_{HP}$ = 10.4 Hz, P(CH_3)$_3$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ −34.11 (s, PMe$_3$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) δ 131.1, 130.1, 128.4, 128.1, 125.2, 123.4 (6 of 11 expected aryl and pyridyl resonances), 89.4 (br s, C_5Me$_5$), 14.0 (d, J = 39.2 Hz, P(CH_3)$_3$), 9.34 (s, C$_5$(CH_3)$_5$).

[Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F·xH$_2$O (2i). An NMR tube was charged with Cp*Ir(PMe$_3$)(Ph)F (6.0 mg), THF-d_8 (0.8 mL), PPh$_3$ (24.0 mg, 7.6 equiv), and H$_2$O (20.0 mg, 92.5 equiv). The tube was sealed in vacuo and heated to 45 °C for 20 min. An observed color change from yellow to colorless was observed. An NMR spectrum of the reaction mixture revealed it to contain [Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]F·xH$_2$O as >98% of the Ir-containing species present. ^{1}H NMR (400 MHz, THF-d_8) δ 7.65 (br s), 7.51 (br s), 7.12 (br s), and 6.92 (br m, H_{aryl}), 1.52 (br s, C$_5$(CH_3)$_5$), 1.27 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ −4.14 (d, $^2J_{PP}$ = 20.3 Hz, PPh$_3$), −51.13 (d, $^2J_{PP}$ = 20.3 Hz, PMe$_3$). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) δ C_{aryl} obscured by excess PPh$_3$, 100.20 (br s, C_5Me$_5$), 17.52 (d, J = 39.2 Hz, P(CH_3)$_3$), 10.04 (s, C$_5$(CH_3)$_5$).

[Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]BPh$_3$F (3a). A solution of Cp*Ir(PMe$_3$)(Ph)F (186 mg, 372 μmol) in Et$_2$O (15 mL) was treated dropwise with PPh$_3$ (246 mg, 939 μmol, 2.52 equiv) in Et$_2$O (5 mL). The slighty cloudy reaction mixture was filtered through a small plug of Celite and then treated dropwise with BPh$_3$ (90 mg, 372 μmol, 1.00 equiv) dissolved in Et$_2$O (5 mL) over the course of 5 min. The yellow reaction mixture became cloudy and a white precipitate was observed. After addition of the borane was complete the reaction mixture was filtered through Celite (1 × 0.3 cm) and taken to dryness in vacuo. The resulting oily yellow solid was triturated exhaustively with Et$_2$O (5 × 5 mL). The still oily solid was dissolved in THF (2 mL), filtered through Celite (1 × 0.3 cm), and taken to dryness in vacuo. The yellow residue was then dissolved in benzene and layered with Et$_2$O (2 mL). The pale yellow solid of analytically pure **3a** (253 mg, 68% yield) that precipitated over the course of 15 min was isolated by decantation and drying in vacuo for 24 h. ^{1}H NMR (400 MHz, THF-d_8) δ 7.9−6.9 (complex series of m, 35H, B(C$_6H_5$)$_3$F, P(C$_6H_5$)$_3$, and Ir−C$_6H_5$), 1.59 (t, 15H, $^3J_{HP}$ = 2.0 Hz, C$_5$(CH_3)$_5$), 1.28 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, THF-d_8) δ 143.14, 143.10, 143.06, 133.95, 129.29, 129.03, 125.99, 124.42, 122.77 (s, 9 × C_{aryl}), 137.9, 134.9, 131.7 (br s, 3 × C_{ipso}), 102.11 (br s, C_5Me$_5$), 17.50 (d, $^1J_{CP}$ = 38.5 Hz, P(CH_3)$_3$), 10.05 (s, C$_5$(CH_3)$_5$); ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ 4.37 (d, $^2J_{PP}$ = 20.3 Hz, PPh$_3$), −51.43 (d, $^2J_{PP}$ = 20.3 Hz, PMe$_3$); ^{19}F NMR (376 MHz, THF-d_8) δ −195.3 (br s); IR (CsI) 1570 (mw), 1481 (ms), 1433 (s), 1379 (w), 1159 (mw), 1090 (m), 1018 (ms), 945 (s), 856 (m), 739 (vs), 704 (vs), 683 (m), 615 (m), 534 (s) cm^{-1}; MS (FAB − sulfolane) 744 ([Cp*Ir(PMe$_3$)(Ph)(PPh$_3$)]$^+$ + 1, ^{193}Ir). Anal. Calcd for C$_{55}$H$_{59}$P$_2$BFIr: C, 65.79; H, 5.92. Found: C, 65.95; H, 6.24.

[Cp^{Et}Ir(PMe$_3$)(Ph)(PPhMe$_2$)]BPh$_3$F (3b). A solution of Cp^{Et}Ir(PMe$_3$)(Ph)F (95 mg, 185 μmol) in Et$_2$O (15 mL) was treated with PPhMe$_2$ (198 mg, 1433 μmol, 7.75 equiv) and then a deficiency of BPh$_3$ (33 mg, 136 μmol, 0.74 equiv) dissolved in Et$_2$O (5 mL) over the course of 5 min. The yellow reaction mixture became cloudy and a yellow oil separated. The oil was seperated from the mother liquor and washed with Et$_2$O (3 × 5 mL) to remove excess starting material and phosphine. The oily residue was then dissolved in THF (1 mL), filtered through Celite (1 × 0.3 cm), and taken to dryness in vacuo. Repeated attempts to further purify, or crystallize, the resulting yellow oil were unsuccessful. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.46 (m, 8H), 7.36 (m, 3H), 7.20 (m, 2H), 7.1−7.0 (m, 9H), 6.95 (t, 3H, J = 7.2 Hz, B(C$_6H_5$)$_3$F, P−C$_6H_5$, and Ir−C$_6H_5$), 2.07 (q, 2H, $^3J_{HP}$ = 7.6 Hz, CH_2-Me), 1.87 (d, 3H, $^2J_{HP}$ = 9.6 Hz, P(CH_3)$_a$Me$_b$Ph), 1.71 (d, 3H, $^2J_{HP}$ = 10.0 Hz, PMe$_a$(CH_3)$_b$Ph), 1.69, 1.67, 1.58, 1.58 (s, 3H each, C$_5$(CH_3)$_4$-Et), 1.27 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$), 1.07 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$) δ 141.92 (t, J = 4.0 Hz, Ir−phenyl C_{ortho}), 132.90 (d, J = 5.0 Hz, P−phenyl C_{meta}), 131.55 (d, J = 2.0 Hz, Ir−phenyl C_{meta}), 130.91 (d, J = 9.1 Hz, P−phenyl C_{ortho}), 129.50 (d, J = 10.1 Hz, B−phenyl C_{ortho}), 129.04 (s, B−phenyl C_{meta}), 126.29 (s, B−phenyl C_{para}), 123.96, 123.19 (2 × s, Ir−phenyl and P−phenyl C_{para}), 103.90, 101.29, 100.77, 100.07, 99.42 (5 × br t, C_5-Me$_4$Et), 18.83 (d, $^1J_{CP}$ = 37.4 Hz, P(CH_3)$_a$Me$_b$Ph), 18.76 (s, CH_2-Me—assigned using a DEPT45 experiment), 17.19 (d, $^1J_{CP}$ = 38.2 Hz, P(CH_3)$_3$), 16.01 (d, $^1J_{CP}$ = 40.0 Hz, PMe$_a$(CH_3)$_b$Ph), 13.11 (s, CH$_2$CH_3), 10.08, 10.05, 10.02, 9.97 (4 × s, C$_5$(CH_3)$_4$Et); ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$) δ −39.5 (d, $^2J_{PP}$ = 22.9 Hz, PMe$_2$Ph), −47.1 (d, $^2J_{PP}$ = 22.9 Hz, PMe$_3$); ^{19}F NMR (376 MHz, CD$_2$Cl$_2$) δ −178 (br m); IR (CsI) 1572 (mw), 1475 (m), 1456 (m), 1427 (m), 1290 (w), 1157 (mw), 1065 (w), 1018 (mw), 955 (s), 941 (ms), 908 (ms), 854 (m), 742 (s), 704 (s), 617 (m) cm^{-1}; MS (FAB − sulfolane) 633 ([Cp^{Et}Ir(PMe$_3$)(Ph)(PPhMe$_2$)]$^+$, ^{193}Ir).

Exchange Reactions: (A) Organic Halides. In a typical experiment, an NMR tube was charged with a few milligrams of Cp*Ir(PMe$_3$)(Ph)F in 0.7 mL of C$_6$D$_6$. Then 3−10 equiv of the appropriate organic halide was added to the tube by vacuum transfer. Monitoring of the reaction was then effected at regular intervals until completion of the reaction (minutes to days). The products of the reaction, both organometallic and organic, were identified by comparison to authentic samples.

(B) Organometallic Complexes. In a typical experiment, an NMR tube was charged with 1 equiv each of Cp*Ir(PMe$_3$)(Ph)F and Cp*Ir(PMe$_3$)(p-tolyl)X (X = Cl, Br, OTf, OPh) in 0.7 mL of C$_6$D$_6$. By the time the first NMR spectrum could be obtained equilibrium between the four possible organometallic products was observed. All organometallic products were compared to independently synthesized authentic samples.

Iridacyclopentadiene Complexes 5a−c. Because these compounds were prepared similarly their syntheses are presented in a generalized manner. In a typical experiment, Cp'Ir(PMe$_3$)(Aryl)F (0.1 mmol) was dissolved in benzene (2 mL) and treated with DMAD (0.5 mmol, 5 equiv) at room temperature. Although no color change was observed, spectroscopic monitoring of the reactions indicated completion within seconds. The yellow reaction mixture was then taken to dryness and washed with pentane (2 × 2 mL). The resulting pale yellow solid was then recrystallized by diffusing pentane into a concentrated toluene solution of the compound.

Cp*Ir(PMe$_3$)(η^2-C$_6$H$_4$(CO$_2$Me)C=C(CO$_2$Me)) (5a). Yellow solid, 55% yield; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 8.35 (dd, 1H, J = 1.6, 7.6 Hz, C_{aryl}), 7.36 (br d, 1H, J ≈ 8 Hz, C_{aryl}), 7.23 (br t, 1H, J = 7.6 Hz, C_{aryl}), 7.02 (dt, 1H, J = 1.6, 7.6 Hz, C_{aryl}), 3.66 (s, 3H, CO$_2$CH_3), 3.56 (s, 3H, CO$_2$CH_3), 1.55 (d, 15H, $^3J_{HP}$ = 1.2 Hz, C$_5$(CH_3)$_5$), 0.89 (d, 9H, $^2J_{HP}$ = 10.8 Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 175.9

(s, CO_2Me), 165.8 (d, $^2J_{CP}$ = 11.5 Hz, C_{ipso}), 165.6 (s, CO_2Me), 154.4 (s, Ir−C=C), 151.0 (d, $^2J_{CP}$ = 13.0 Hz, Ir−C=C), 141.0 (s, C_{quat}), 135.1 (d, $^3J_{CP}$ = 2.6 Hz, C_{ortho}), 124.4, 124.4, 121.6 (3 × C_{aryl}), 94.6 (d, $^3J_{CP}$ = 2.6 Hz, C_5Me$_5$), 51.0 (s, CO_2CH_3), 50.5 (s, CO_2CH_3), 13.6 (d, $^1J_{CP}$ = 40.2 Hz, P(CH_3)$_3$), 9.0 (s, C_5(CH_3)$_5$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −39.23 (s); MS (EI) 622 (M^+, ^{193}Ir); HRMS (EI) calcd for $C_{25}H_{34}PO_4Ir$ 622.1824, found 622.1818.

Cp*Ir(PMe$_3$)(η^2-C$_6$H$_3$-4-Me(CO$_2$Me)C=C(CO$_2$Me)) (5b). Yellow bricks, 80% yield; ^{1}H NMR (400 MHz, C_6D_6) δ 8.25 (1H, d, J = 7.6 Hz, C_{aryl}), 7.24 (1H, s, C_{aryl}), 7.04 (1H, d, J = 7.6 Hz, C_{aryl}), 3.67 (s, 3H, CO_2CH_3), 3.56 (s, 3H, CO_2CH_3), 1.58 (d, 15H, $^3J_{HP}$ = 1.2 Hz, C_5(CH_3)$_5$), 0.93 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 175.42 (s, CO_2Me), 165.79 (s, CO_2Me), 162.54 (s), 162.43 (s), 152.83 (d, $^3J_{CP}$ = 2.6 Hz), 151.72 (s), 151.59 (s) (5 × C_{quat}), 136.25 (d, $^3J_{CP}$ = 2.0 Hz, C_{ortho}), 125.32, 123.24 (s, 2 × C_{aryl}), 94.35 (d, $^3J_{CP}$ = 2.5 Hz, C_5Me$_5$), 50.64 (s, CO_2CH_3), 50.22 (s, CO_2CH_3), 21.59 (s, p-CH_3), 13.42 (d, $^1J_{CP}$ = 40.4 Hz, P(CH_3)$_3$), 9.01 (s, C_5(CH_3)$_5$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −38.95 (s); IR (CsI) 1695 (vs, $\nu_{C=C}$) 1525 (m), 1433 (ms), 1377 (mw), 1329 (ms), 1282 (m), 1200 (vs), 1034 (m), 1016 (ms), 960 (vs), 943 (s), 820 (m), 733 (m), 690 (ms), 679 (m), 650 (m) cm^{-1}; MS (EI) 636 (M^+, ^{193}Ir). The yellow bricks of **5b** are solvated by one-half molecule of toluene. Anal. Calcd for $C_{26}H_{36}PO_4Ir$·0.5(C_7H_8): C, 51.97; H, 5.91. Found: C, 51.63; H, 5.87. Dissolution of **5b** in benzene followed by lyophilization provided unsolvated **5b**. Anal. Calcd for $C_{26}H_{36}PO_4Ir$: C, 49.12; H, 5.71. Found: C, 49.18; H, 5.79.

Cp^{Et}Ir(PMe$_3$)(η^2-C$_6$H$_4$(CO$_2$Me)C=C(CO$_2$Me)) (5c). Yellow needles in 62% yield; ^{1}H NMR (400 MHz, C_6D_6) δ 8.37 (dd, 1H, J = 1.6, 8.0 Hz, C_{aryl}), 7.38 (d, 1H, J = 7.6 Hz, C_{aryl}), 7.24 (tq, 1H, J = <1, 7.6 Hz, C_{aryl}), 7.03 (dt, 1H, J = 1.6, 7.6 Hz, C_{aryl}), 3.67 (s, 3H, CO_2CH_3), 3.57 (s, 3H, CO_2CH_3), 2.04 (dq, 2H, J = 1.6, 7.6 Hz, CH_2Me), 1.64, 1.61, 1.57, 1.56 (d, 3H each, J = 1.6 Hz, C_5(CH_3)$_4$Et), 0.91 (d, 9H, $^2J_{HP}$ = 10.8 Hz, P(CH_3)$_3$), 0.83 (t, 3H, J = 7.6 Hz, CH_2CH_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 175.45, 165.78, 163.77, 155.22, 151.09, 142.80 (s, 6 × C_{qual}), 135.52 (d, J = 3.2 Hz, C_{aryl}), 125.61, 124.87, 122.56 (s, 3 × C_{aryl}, assigned by DEPT-135 experiment), 98.74, 95.05, 94.57, 94.31, 94.10 (d, $J \approx$ 3 Hz, C_5Me$_4$Et), 50.69, 50.24 (s, 2 × CO_2CH_3), 17.84 (s, CH_2Me, assigned by DEPT-135 experiment), 14.03 (d, $^1J_{CP}$ = 16 Hz, P(CH_3)$_3$), 13.71 (CH_2CH_3), 8.97, 8.90, 8.81, 8.76 (s, C_5(CH_3)$_4$Et); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −39.46 (s); IR (CsI) 1695 (s, $\nu_{C=C}$), 1527 (m), 1444 (m), 1432 (m), 1379 (mw), 1329 (m), 1302 (w), 1284 (m), 1211 (s), 1024 (sh), 1014 (m), 956 (s), 858 (mw), 792 (mw), 733 (m), 681 (mw), 669 (mw) cm^{-1}; MS (EI) 636 (M^+, ^{193}Ir). Anal. Calcd for $C_{26}H_{36}PO_4Ir$: C, 49.12; H, 5.71. Found: C, 49.19; H, 5.63.

Imidazolate Complexes 7a,b. The preparation of **7b** was as follows. A solution of Cp^{Et}Ir(PMe$_3$)(Ph)F (105 mg, 204 μmol) in C_6H_6 (5 mL) was transferred to a vial containing Me$_3$Si-Im (549 mg, 3914 μmol, 19.2 equiv) dissolved in C_6H_6 (5 mL). The reaction mixture was allowed to stand at ambient temperature for 30 min and then one-fourth of the solvent and any Me$_3$SiF that had formed were removed in vacuo. The reaction mixture was allowed to stand for a further 2 h at which time the light amber reaction mixture was taken to dryness in vacuo. The amber oil that resulted was suspended in pentane (5 mL). Cooling of this suspension to −40 °C for 2 h gave an oil which was separated from the mother liquor. The oil was exposed to dynamic vacuum for several hours and then dissolved in 1:1 pentane/Et$_2$O (8 mL). After 2 weeks at −40 °C off-white lumps of **7b** (69 mg, 60% yield) formed and were isolated by decanting away the mother liquor. ^{1}H NMR (400 MHz, C_6D_6) δ 7.62 (s, 1H, Im-H), 7.52 (m, 3H, H_{aryl}), 7.48 (s, 1H, H_{aryl}), 7.10 (d, 1H, $^3J_{HH}$ = 2.0 Hz, Im-H), 7.09 (d, 1H, $^3J_{HH}$ = 2.0 Hz, Im-H), 6.95 (s, 1H, Im-H), 1.69 (complex m, 2H, CH_2Me), 1.27, 1.24, 1.21, 1.21 (d, 3H each, J = 2.0 Hz, C_5(CH_3)$_4$Et), 0.87 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$), 0.71 (t, 3H, $^3J_{HH}$ = 8.0 Hz, CH_2CH_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 147.54, 141.55, 141.52, 136.13, 135.99, 127.51, 122.80 (s, 7 × C_{aryl} and Im-methine), 96.64, 94.28, 94.19, 94.16, 93.50 (d, $^2J_{CP} \approx$ 2.6 - 3.3 Hz, C_5Me$_4$Et), 18.12 (s, CH_2Me), 14.30 (d, $^1J_{CP}$ = 37.6 Hz, P(CH_3)$_3$), 13.24, 13.21, 9.12, 9.00 (s, C_5(CH_3)$_4$Et), 2.00 (s, CH_2CH_3); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −36.55 (s); IR (CsI) 1568 (m), 1458 (s), 1377 (w), 1283 (mw), 1229 (w), 1028 (w), 1075 (s), 1020 (ms), 968 (s), 947 (s), 733 (s), 705 (m), 679 (mw) cm^{-1}; MS (EI) 562 (M^+, ^{193}Ir). HRMS (EI) calcd for $C_{23}H_{34}PN_2Ir$ 562.2089, found 562.2091. Anal. Calcd for $C_{23}H_{34}PN_2Ir$: C, 49.18; H, 6.10; N, 4.99. Found: C, 48.95; H, 6.37; N, 5.11.

Compound **7a** was prepared in a similar manner except that the compound could not be crystallized. The white solid was purified by repeated dissolutions in diethyl ether and precipitation with pentane. ^{1}H NMR (400 MHz, C_6D_6) δ 7.68 (s, 1H, Im-H), 7.50, 7.09 (m, 3H each, Im-H and H_{aryl}), 6.95 (s, 1H, m-H), (m, 2H, C_6H_5), 1.19 (d, 15H, $^3J_{HP}$ = 2.0 Hz, C_5(CH_3)$_5$), 0.84 (d, 9H, $^2J_{HP}$ = 10.2 Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 147.3 (s, Im-methine), 141.5 (d, $^3J_{PC}$ = 3.5 Hz, C_{ortho}), 137.0 (d, $^2J_{PC}$ = 14.0 Hz, C_{ipso}), 128.7, 127.4, 127.1, 122.3 (s, remaining 4 methine carbons); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −36.28 (s); IR (KBr) 2926 (m), 1670 (m), 1581 (s), 1466 (vs), 1086 (s), 962 (vs), 750 (vs) cm^{-1}; MS (EI) 548 (M^+, ^{193}Ir).

Cp'Ir(PMe$_3$)(R)(SiMe$_2$F) (8a−d). Because these compounds were prepared similarly their syntheses are presented in a generalized manner. In a typical experiment, Cp'Ir(PMe$_3$)(Aryl)F (0.1 mmol) was dissolved in benzene (2 mL) and treated with a single aliquot of silane (HSiMe$_2$R) (2 mmol, 20 equiv) at room temperature either by syringe (HSiMe$_2$Ph) or vacuum transfer (HSiMe$_3$). Over the course of 1 to 2 min the yellow reaction mixture faded to colorless (or slightly yellow) and the solvent and excess silane were removed in vacuo. The residue was then dissolved in pentane and filtered through silylated silica gel (0.3 × 4 cm). The colorless filtrate was then treated with 10 drops of CCl_4 and allowed to stand at room temperature overnight. Any Cp'Ir(PMe$_3$)(Aryl)H or Cp'Ir(PMe$_3$)H$_2$ formed in the original reaction were converted quantitatively to Cp'Ir(PMe$_3$)(Aryl)Cl and Cp'Ir(PMe$_3$)Cl$_2$ by this method. The now yellow reaction mixture was taken to dryness in vacuo and extracted into pentane. The pentane extracts were filtered three times through columns of silylated silica gel (0.3 × 6 cm). Compound **8c** (a colorless oil) was isolated in about 95% purity (as judged by ^{1}H NMR spectroscopy) by removal of the pentane solvent. Compound **8d** (a colorless oily solid) was isolated in about 98% purity (as judged by ^{1}H NMR spectroscopy) by removal of the pentane solvent. Compounds **8a** and **8b** (33% and 82% yield, respectively) were crystallized from (Me$_3$Si)$_2$O at −40 °C as a white solid and colorless blocks, respectively.

Cp*Ir(PMe$_3$)(Ph)(SiMe$_2$F) (8a). ^{1}H NMR (400 MHz, C_6D_6) δ 7.59 (m, 2H, C_6H_5), 7.04 (m, 3H, C_6H_5), 1.54 (d, 15H, $^3J_{HP}$ = 1.6 Hz, C_5(CH_3)$_5$), 1.15 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$), 0.73 (d, 3H, $^3J_{HF}$ = 8.0 Hz, Ir−Si(CH_3)$_2$F), 0.72 (d, 3H, $^3J_{HF}$ = 8.4 Hz, Ir−Si(CH_3)$_2$F) (these two methyl resonances were assigned by collecting spectra at different field strengths); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ C_{ipso} not observed, 143.69 (d, J = 4.0 Hz, C_{ortho}), 127.55 (s, C_{meta}), 121.76 (s, C_{para}), 96.64 (d, $^2J_{CP}$ = 2.9 Hz, C_5Me$_5$), 18.55 (d, $^1J_{CP}$ = 37.6 Hz, P(CH_3)$_3$), 9.93 (s, C_5(CH_3)$_5$), 8.78 (d, $^2J_{CF}$ = 17.3 Hz, Si(CH_3)), 8.73 (d, $^2J_{CF}$ = 17.3 Hz, Si(CH_3)); ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ −47.77 (s); ^{19}F NMR (376 MHz, C_6D_6) δ −139.97 (br m, $^1J_{SiF}$ = 309.6 Hz); IR (CsI) 1568 (m), 1473 (m), 1458 (mw), 1425 (m), 1377 (m), 1304 (mw), 1284 (ms), 1240 (ms), 1020 (ms), 953 (vs), 825 (s, sh), 808 (vs), 750 (m), 737 (s), 723 (m), 715 (m), 704 (ms), 679 (mw), 661 (mw), 651 (m), 644 (mw) cm^{-1}; MS (EI) 558 (M^+, ^{193}Ir); HRMS (EI) calcd for $C_{21}H_{35}FPSiIr$ 558.1859, found 558.1855.

Cp^{Et}Ir(PMe$_3$)(Ph)(SiMe$_2$F) (8b). ^{1}H NMR (400 MHz, C_6D_6) δ 7.61 (m, 2H, C_6H_5), 7.04 (m, 3H, C_6H_5), 2.06 (complex nonet, 2H, CH_2-Me), 1.64, 1.59, 1.55, 1.50 (d, 3H each, $^4J_{HP}$ = 1.6 Hz, C_5(CH_3)$_4$Et), 1.16 (d, 9H, $^2J_{HP}$ = 9.6 Hz, P(CH_3)$_3$), 0.82 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3), 0.74 (d, 3H, $^3J_{HF}$ = 8.0 Hz, Si−CH_3), 0.71 (d, 3H, $^3J_{HF}$ = 7.6 Hz, Si−CH_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 143.82 (d, $^3J_{CP}$ = 3.0 Hz, C_{ortho}), 131.71 (d, $^2J_{CP}$ = 10.3 Hz, C_{ipso}), 127.50 (C_{meta}), 121.78 (C_{para}), 100.66, 97.56, 96.92, 96.82, 95.86 (d, $^2J_{CP} \approx$ 1.6−4 Hz, C_5Me$_4$Et), 18.79 (s, CH_2Me), 18.69 (d, $^1J_{CP}$ = 37.6 Hz, P(CH_3)$_3$), 14.09 (CH_2CH_3), 9.80, 9.80, 9.75, 9.70 (C_5(CH_3)$_4$Et), 8.95 (d, $^2J_{CF}$ = 17.0 Hz, Si(CH_3)), 8.78 (d, $^2J_{CF}$ = 17.0 Hz, Si(CH_3)); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −44.60 (d, $^3J_{PF}$ = 3.2 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ −139.66 (br t, $^1J_{SiF}$ = 309 Hz); IR (CsI) 1568 (m), 1470 (ms), 1460 (ms), 1424 (mw), 1303 (mw), 1284 (m), 1236 (ms), 1020 (m), 954 (s), 937 (ms, sh), 852 (ms), 827 (s), 814 (s), 746 (ms), 735 (ms), 721 (ms) cm^{-1}; MS (EI) 572 (M^+, ^{193}Ir). Anal. Calcd for $C_{22}H_{37}$-FPSiIr: C, 46.21; H, 6.52. Found: C, 46.32; H, 6.38.

Cp*Ir(PMe$_3$)(Me)(SiMe$_2$F) (8c). ^{1}H NMR (400 MHz, C_6D_6) δ 1.59 (d, 15H, $^3J_{HP}$ = 1.6 Hz, C_5(CH_3)$_5$), 1.17 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$), 0.66 (d, 3H, $^3J_{HF}$ = 8.4 Hz, Ir−Si(CH_3)$_2$F), 0.61 (d, 3H, $^3J_{HF}$

= 8.8 Hz, Ir−Si(CH_3)$_2$F), 0.49 (d, 3H, $^3J_{HP}$ = 5.6 Hz, Ir−CH_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 94.50 (d, $^2J_{CP}$ = 2.4 Hz, C_5Me_5), 17.97 (dd, $^1J_{CP}$ = 37.6 Hz, $^4J_{CF}$ = 3.2 Hz, P(CH_3)$_3$), 9.53 (C_5(CH_3)$_5$), 8.21 (d, $^2J_{CF}$ = 16.9 Hz, Si(CH_3)), 5.47 (d, $^2J_{CF}$ = 18.5 Hz, Si(CH_3)), −33.00 (d, $^2J_{CP}$ = 6.4 Hz, Ir−CH_3); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −43.45 (s); ^{19}F NMR (376 MHz, C_6D_6) δ −143.18 (br m); IR (CsI) 1423 (br, mw), 1379 (mw), 1282 (m), 1261 (m), 1234 (ms), 1093 (ms), 1068 (ms), 1026 (s), 955 (s), 857 (m), 810 (vs), 748 (m), 723 (m), 679 (w), 646 (m) cm^{-1}; MS (EI) 496 (M$^+$, ^{193}Ir); HRMS (EI) calcd for $C_{16}H_{33}$FPSiIr 496.1703, found 496.1704.

Cp^{Et}Ir(PMe$_3$)(Me)(SiMe$_2$F) (8d). ^{1}H NMR (400 MHz, C_6D_6) δ 2.06 (q, 2H, CH_2Me), 1.66, 1.65, 1.57, 1.56 (d, 3H each, $^3J_{HP}$ = 1.6 Hz, C_5(CH_3)$_4$Et), 1.19 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$), 0.89 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH$_2$CH_3), 0.66 (d, 3H, $^3J_{HF}$ = 8.4 Hz, Ir−Si(CH_3)$_2$F), 0.61 (d, 3H, $^3J_{HF}$ = 8.8 Hz, Ir−Si(CH_3)$_2$F), 0.50 (d, 3H, $^3J_{HP}$ = 6.4 Hz, Ir−CH_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 99.35, 95.09, 94.63, 94.60, 93.61 (d, $^2J_{CP} \approx$ 2.6−3.1 Hz, C_5Me$_4$Et), 18.44 (d, $^1J_{CP}$ = 27.2 Hz, P(CH_3)$_3$), 18.32 (s, CH_2Me), 17.95, 17.92, 14.53, 14.51 (s, C_5(CH_3)$_4$Et), 9.38 (s, CH$_2$CH_3), 8.33 (d, $^2J_{CF}$ = 17.1 Hz, Si(CH_3)), 5.54 (d, $^2J_{CF}$ = 18.7 Hz, Si(CH_3)), −33.48 (d, $^2J_{CP}$ = 7.6 Hz, Ir−CH_3); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −43.90 (s); ^{19}F NMR (376 MHz, C_6D_6) δ −143.07 (br septet, $^3J_{HF} \approx$ 8Hz, $^1J_{SiF}$ = 297.4 Hz); IR (CsI) 1456 (br, w), 1427 (br, w), 1379 (w), 1282 (mw), 1236 (m), 955 (s), 856 (m), 816 (vs), 748 (m), 721 (ms), 681 (m), 646 (m) cm^{-1}; MS (EI) 510 (M$^+$, ^{193}Ir); HRMS (EI) calcd for $C_{17}H_{35}$FPSiIr 510.1859, found 510.1858.

Cp*Ir(PMe$_3$)(S-*p*-tolyl)$_2$ (10). A solution of Cp*Ir(PMe$_3$)(Ph)F (30 mg, 60 μmol) in C_6H_6 (3 mL) was treated dropwise with a solution (1 mL, C_6H_6) of HS-*p*-tolyl (31 mg, 248 μmol, 4.1 equiv) over the course of 1 min. The originally yellow solution turned orange and deposited an insoluble white precipitate over the course of 2 h. The orange supernatant was separated by filtation (Celite, 0.3 × 1 cm). After removal of the solvent in vacuo the resulting orange oil was extracted with Et_2O (2 × 1 mL). The combined extracts were filtered through silylated silica gel (0.3 × 1 cm) and the column was rinsed with an additional 1 mL of Et_2O. The filtrate was reduced in volume by 50% and transferred to a −40 °C freezer. Overnight, orange crystals (20 mg, 51% yield) formed which were isolated by discarding the mother liquor and washing the crystals with pentane (2 × 2 mL). ^{1}H NMR (400 MHz, C_6D_6) δ 7.62 (d, 4H, $^3J_{HH}$ = 8.0 Hz, aryl H), 6.88 (d, 4H, $^3J_{HH}$ = 8.0 Hz, aryl H), 2.13 (s, 6H, 2 × *p*-CH_3), 1.51 (d, 15H, $^3J_{HP}$ = 1.6 Hz, C_5(CH_3)$_5$), 1.31 (d, 9H, $^2J_{HP}$ = 10.4 Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 140.64 (d, $^2J_{CP}$ = 4.0 Hz, C_{ipso}), 133.14, 131.60 (s, C_{aryl}), 128.31 (s, C_{para}), 94.77 (d, $^2J_{CP}$ = 4.0 Hz, C_5Me$_5$), 20.94 (s, *p*-CH_3), 14.18 (d, $^1J_{CP}$ = 40.6 Hz, P(CH_3)$_3$), 9.06 (s, C_5(CH_3)$_5$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ −38.74 (s); IR (CsI) 1597 (w), 1485 (s), 1375 (mw), 1300 (w), 1281 (mw), 1080 (ms), 1022 (m), 955 (s), 854 (w), 808 (s), 733 (mw), 679 (mw), 496 (m) cm^{-1}; MS (EI) 650 (M$^+$, ^{193}Ir). Anal. Calcd for $C_{27}H_{38}PS_2Ir$: C, 49.90; H, 5.89. Found: C, 49.95; H, 5.95.

X-ray Structure Determination of Cp^{Et}Ir(PMe$_3$)(Ph)F (1c). Clusters of clear yellow prismatic crystals of the compound were obtained by slow crystallization from Et_2O at −35 °C. A fragment cut from one of these crystals was mounted on a glass fiber using Paratone N hydrocarbon oil. The crystal was then transferred to our Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to −126 °C by a nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. Crystal quality was evaluated via measurement of intensities and inspection of peak scans. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The final cell parameters and specific data collection parameters for this data set are given in Table 1.

The 3575 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Calculations were performed on DEC MicroVax computers using locally modified versions of the Enraf-Nonius MolEN structure solution and refinement package and other programs. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a variation I_{min}/I_{max} = 0.66 for the average curve. However, the curves showed an effect of apparent misorientation. Therefore an empirical correction was made to the data based on the combined differences of F_{obs} and F_{clc} following refinement of all atoms with isotropic thermal parameters (T_{max} = 1.50, T_{min} = 0.74, no θ dependence). Inspection of the systematic absences indicated uniquely space group $P2_1/c$. Removal of systematically absent data left 3398 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.15 times the B_{eqv} of the atoms to which they were attached. They were included in structure factor calculations, but not refined.

The final residuals for 209 variables refined against the 2859 data for which $F^2 > 3\sigma(F^2)$ were R = 3.98%, wR = 4.65%, and GOF = 2.18. The R value for all 3398 data was 4.89%. In the final cycles of refinement a secondary extinction parameter was included (maximum correction was 8% on F).

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Supporting Information Available: Experimental details of X-ray structure determination and tables of positional and thermal parameters for H atoms, root-mean-square amplitudes of anisotropic displacement, and complete intramolecular distances and angles for **1c** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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