Synthesis of Iridium(III) Carboxamides via the Bimetallic Reaction between $Cp^*(PMe_3)IrPh(OH)$ and $[Cp^*(PMe_3)Ir(Ph)NCR]^+$

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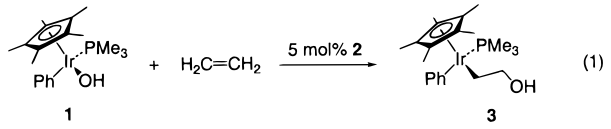
Reaction of $Cp^*(PMe_3)IrPh(OH)$ (**1**) with nitriles is undetectably slow in benzene solution at room temperature. However, in the presence of $Cp^*(PMe_3)IrPh(OTf)$ (**2**) ($OTf = O_3SCF_3$), the reaction is strongly catalyzed, leading to iridium(III) carboxamides $Cp^*(PMe_3)IrPh[NHC(O)R]$ (**6a**−**d**) [$R = C_6H_4CH_3$ (**6a**), C_6H_5 (**6b**), $C_6H_4CF_3$ (**6c**), CH_3 (**6d**)]. We propose that these transformations occur by initial displacement of the trifluoromethanesulfonate ("triflate") anion of **2** by a molecule of nitrile, leading to a nitrile-substituted iridium cation, $[Cp^*(PMe_3)IrPh(NCR)]^+$ (**10**). Following this, the nucleophilic hydroxide group of **1** attacks the (activated) nitrile molecule bound in **10**, leading (after proton transfer) to the iridium carboxamide complex. In the case of nitriles possessing hydrogens α to the cyano group, competitive loss of one of these protons is observed, leading to iridium C-bound cyanoenolates such as $Cp^*(PMe_3)(Ph)Ir(CH_2CN)$ (**7**). Protonolysis of carboxamides **6a**−**d** with HCl yields $Cp^*(PMe_3)IrPh(Cl)$ (**9**) and the free amides. A pronounced solvent effect is observed when the reaction between **1** and nitriles catalyzed by **2** is carried out in THF solution. The basic hydroxide ligand of **1** induces an overall dehydration/cyclization reaction of the coordinated aromatic nitrile. For example, the reaction of **1** with *p*-trifluorotolunitrile and a catalytic amount of **2** leads to the formation of **6c**, water, $[Ph(PMe_3)Ir[C_5Me_4CH_2C(C_6H_4CF_3)N]]$ (**12**), and $[Ph(PMe_3)Ir(C_5Me_4CH_2C(C_6H_4CF_3)NH)]OTf$ (**13**). A mechanism to explain the formation of both **12** and **13** and the role each compound plays in the formation of the iridium carboxamides is proposed.

Introduction

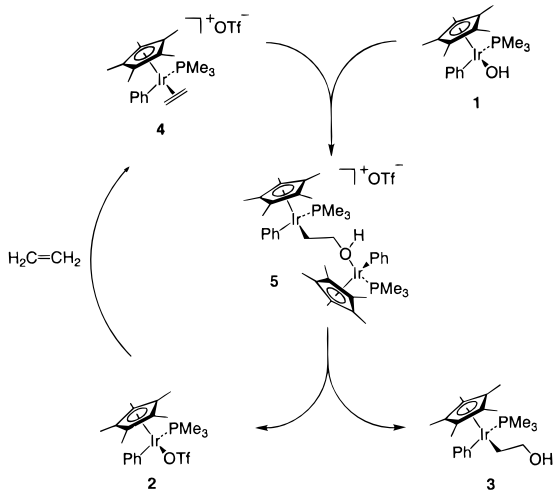
We recently demonstrated that the reaction of $Cp^*(PMe_3)Ir(Ph)OH$ (**1**) with ethylene to give hydroxyethyl complex **3**, involving formal insertion of ethylene into an iridium−oxygen bond, is catalyzed by $Cp^*(PMe_3)Ir(Ph)OTf$ (**2**) (eq 1).[1] In this



reaction, the ethylene and hydroxide ligands are activated and coupled by two individual $[Cp^*(PMe_3)Ir(Ph)]^+$ fragments (Scheme 1). This reaction is an unusual example of a tandem activation of two ligands by identical metal centers.

Other groups have also discovered and attempted to model similar reactivity patterns between two transition metals.[2] Jacobsen and co-workers have demonstrated that the chromium-catalyzed asymmetric ring opening of epoxides[3,4] and the cobalt-catalyzed kinetic resolution of chiral epoxides[5] proceed in a bimetallic fashion. Stanley and co-workers have developed homobimetallic rhodium complexes which serve as highly selective hydroformylation catalysts.[6] In attempts to mimic

Scheme 1



natural nucleases that possess two metal ions in their active sites, researchers have developed dinuclear metal complexes that exhibit markedly better catalytic behavior than their monomeric analogues.[7−17]

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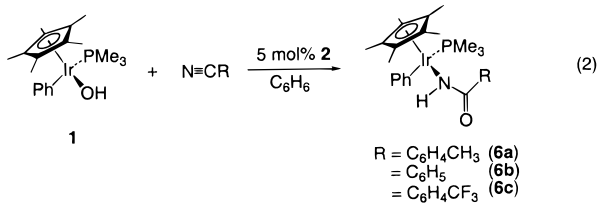
To extend the reaction manifold shown in Scheme 1 to other unsaturated organic compounds, we decided to explore the reaction of **1** with nitriles to generate iridium carboxamides. The conversion of nitriles to amides is a synthetically difficult reaction generally requiring harsh acidic or basic conditions.[18] The use of transition metal cations catalyzes this reaction.[19−22] We report the synthesis of a variety of iridium carboxamides, which are analogous to key intermediates in metal-catalyzed nitrile hydration reactions. These iridium carboxamides are generated by the addition of **1** to RCN in the presence of a catalytic amount of **2**. We believe that a critical step in this transformation is the transfer of the hydroxide ligand of **1** to an iridium-bound nitrile.[23]

Results and Discussion

Aromatic Nitriles. When a solution of equimolar amounts of **1** and *p*-tolunitrile was heated in benzene at 45 °C, no reaction was observed even after 14 d. However, upon treatment of an identical solution of **1** and *p*-tolunitrile with 0.02 equiv of Cp*(PMe$_3$)IrPh(OTf) (**2**), production of Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_4$CH$_3$] (**6a**) was observed in 4 d at 45 °C (eq 2).



(2)

Compound **6a** was isolated in 86% yield as tan, air-stable crystals. The N−*H* proton appears as a broad singlet at 4.79 ppm in the ^{1}H NMR spectrum (C$_6$D$_6$). In the ^{13}C{^{1}H} NMR spectrum, the carbonyl carbon resonance appears at 173 ppm. The carbonyl moiety on **6a** exhibits a strong infrared stretch at 1604 cm^{-1}. To confirm the connectivity of **6a**, a single-crystal X-ray diffraction study was performed. An ORTEP diagram of **6a** is shown in Figure 1. Data collection parameters for **6a** are given in Table 1, and selected bonding parameters for **6a** are presented in Table 2. As expected for the tautomer of **6a** illustrated in eq 2, the C(10)−N(1) bond length of 1.329(5) Å and the C(10)−O(1) bond length of 1.247(4) Å are consistent with free amide single and double bonds, respectively.[24]

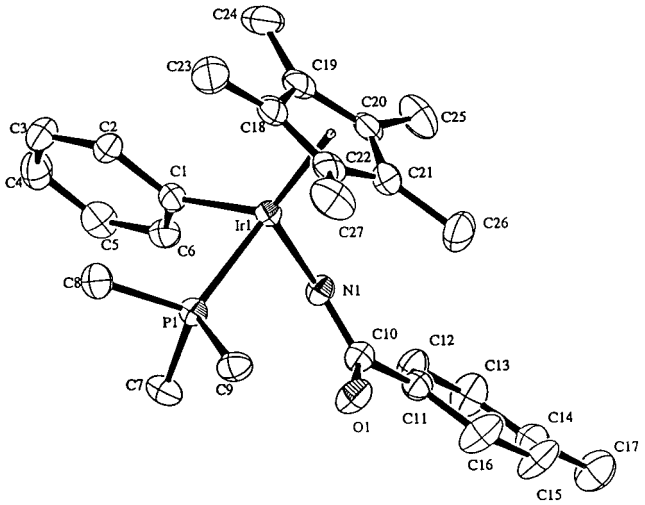


Figure 1. ORTEP diagram of Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_4$CH$_3$] (**6a**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 1. Crystal and Data Collection Parameters for Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_4$CH$_3$] (**6a**) and [Ph(PMe$_3$)Ir[C$_5$Me$_4$CH$_2$C(C$_6$H$_4$CF$_3$)N] (**12**)

formula	$C_{27}H_{37}IrNOP$	$C_{27}H_{32}NF_3PIr$
fw	614.79	650.75
cryst size	0.25 × 0.30 × 0.30 mm	0.33 × 0.10 × 0.05 mm
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a (Å)	25.2021(3)	22.9330(5)
b (Å)	13.4474(2)	12.2372(2)
c (Å)	15.0355(2)	19.0405(4)
Z	8	8
V (Å^3)	5011.6(1)	5222.4
T (K)	164	170
D_{calcd} (g/cm^3)	1.630	1.655
μ(Mo Kα, cm^{-1})	54.26	52.25
scan type (deg/frame)	ω (0.3)	ω (0.3)
scan rate (s/frame)	10.0	10.0
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite ($2\theta_{max}$ = 52.1°)	graphite ($2\theta_{max}$ = 52.2°)
2θ range (deg)	3−45	3−45
no. of reflns measd	11 716 (unique: 4651 (R_{int} = 0.029))	12553 (unique: 4885 (R_{int} = 0.056))
R^a	0.020	0 0.044
$R_w{}^b$	0.027	0.053
R_{all}	0.028	0.076
GOF	1.23	1.30
p-factor	0.030	0.030
no. of variables	280	298

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Table 2. Selected Intramolecular Distances and Angles for Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_4$CH$_3$] (**6a**)

	Distance (Å)		
Ir−N	2.099(3)	Ir−P(1)	2.273(1)
Ir−C(101)[a]	1.87950(10)	N−C(10)	1.329(5)
Ir−C(1)	2.086(4)	O−C(10)	1.247(4)
	Angles (deg)		
Ir−N−C(10)	128.7(2)	O−C(10)−C(11)	118.2(3)
O−C(10)−N	123.5(3)		

[a] C(101) is the centroid of cyclopentadienyl ring C(18)−C(22).

Complex **1** also reacted with benzonitrile and *p*-trifluorotolunitrile in the presence of catalytic amounts of **2** (5 mol %) at 45 °C to yield Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_5$] (**6b**) ($t_{1/2}$ = 36

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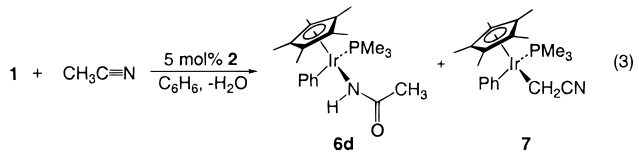
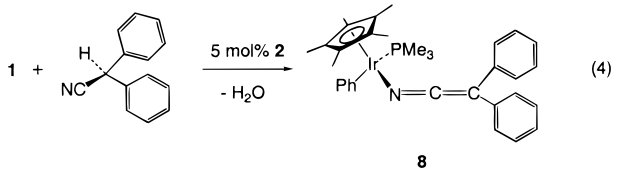
h) and Cp*(PMe_3)IrPh[NHC(O)$C_6H_4CF_3$] (**6c**) ($t_{1/2}$ = 4 h), respectively (eq 2). The yields were quantitative by ^{1}H NMR spectroscopy, and **6b**,**c** were isolated in 89% and 54% yields, respectively, following crystallization. Compounds **6b**,**c** exhibit spectroscopic properties similar to those of **6a**.

Aliphatic Nitriles. The reactions of aliphatic nitriles (R_2HCCN) with hydroxide complex **1** exhibit a similar dependence upon the presence of triflate **2**. However, an additional mode of reactivity is observed with these substrates. For example, treatment of a benzene solution containing equimolar amounts of **1** and acetonitrile with 0.02 equiv of **2** resulted in the generation of a 64:36 mixture of Cp*(PMe_3)IrPh[NHC(O)CH_3] (**6d**) and Cp*(PMe_3)Ir(CH_2CN)Ph (**7**) (eq 3).[25] Separation of these product mixtures was not attempted; instead the identities of **6d** (vide infra) and **7**[26] were confirmed via independent syntheses.



(3)

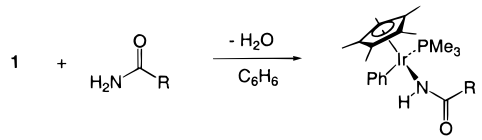
These results suggest that, in addition to activating CH_3CN toward nucleophilic attack (to give **6d**), **2** activates CH_3CN toward deprotonation at the α-carbon (to give **7**), a type of process that has previously been observed for other transition metal nitrile complexes.[27] These two competing modes of reactivity are seen with a variety of other nitriles. The ratio of the products from deprotonation and nucleophilic attack appears to depend on both the steric and electronic properties of the nitrile. In one example, treatment of **1** with diphenylacetonitrile and a catalytic amount of **2** (5 mol %) gave exclusively the deprotonation product Cp*(PMe_3)Ir[N═C═C($Ph)_2$]Ph (**8**) (eq 4). The keteniminate **8** was isolated in 75% yield as bright



(4)

orange crystals. This compound exhibits a strong infrared band at 2105 cm^{-1} assigned to the N═C═C stretching mode. The connectivity of this compound was confirmed crystallographically. An ORTEP diagram and structural information are provided as Supporting Information.[28] In contrast to our observations with acetonitrile, the deprotonation of diphenylacetonitrile does occur in the absence of **2**, but at a slower rate. This is consistent with our hypothesis that **2** functions to activate the nitrile moiety.

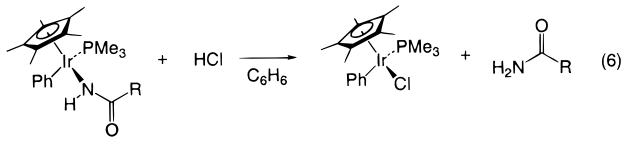
As illustrated in eq 5, the iridium carboxamides **6a**−**d** can be synthesized independently in 65−88% isolated yields by treatment of **1** with the appropriate organic amides. Cleavage of the Ir−N bond in **6a**−**d** would represent the final step in the overall metal-mediated conversion of a nitrile to an amide. Attempts to generate **1** and free amide by treatment of **6a**−**d** with water were unsuccessful even when the reactions were



(5)

R = $C_6H_4CH_3$ (**6a**)
= C_6H_5 (**6b**)
= $C_6H_4CF_3$ (**6c**)
= CH_3 (**6d**)

performed at elevated temperatures in the presence of a large excess of water (10 equiv). The free amide was produced, however, by treatment of **6a**−**d** with HCl. Addition of 1 equiv of HCl (diethyl ether solution) to a solution of **6a**−**d** in benzene resulted in the quantitative formation of Cp*(PMe_3)IrPh(Cl) (**9**),[29] as determined by NMR spectroscopy, and the free amide (eq 6). The free amides were isolated in 38−73% yields, and their identities were confirmed by gas chromatography and ^{1}H NMR spectroscopy.



(6)

Proposed Mechanism. Formation of carboxamides **6a**−**d** from the corresponding nitriles and **1** is proposed to occur by the mechanism outlined in Scheme 2. Precoordination of the nitrile to **2** generates [Cp*(PMe_3)IrPh(NCR)]$^+$OTf$^-$ (**10a**−**d**) (vide infra). The cationic iridium fragment "Cp*(PMe_3)Ir(Ph)$^+$" serves to activate the nitrile toward nucleophilic attack. Transfer of the hydroxide moiety from **1** to **10a**−**d**, in a manner similar to that reported in the reaction with ethylene,[1] produces **2** and the iminol **11**, which quickly rearranges to generate the observed carboxamide. For aliphatic nitriles, a second pathway is accessible. In addition to generation of the carboxamide **6d**, hydroxide **1** can deprotonate the α carbon of the cyano group on **10d**, leading to formation of **7** and regeneration of **2**.

Effect of Added Salts. To determine whether **2** exerts its effect in the formation of the carboxamides **6a**−**c** simply by increasing the ionic strength of the solution, we probed the effect of added salt on the rate of the reaction.[30,31] For example, a benzene solution containing equimolar amounts of hydroxide **1** and acetonitrile was treated with 5 mol % tetrahexylammonium tetra(3,5-bistrifluoromethyl)phenylborate, a benzene-soluble salt. Neither **6d** nor **7** was observed after prolonged heating of this solution at 45 °C. Thus, addition of the borate salt did not serve to promote formation of the carboxamide or deprotonation products.

Reactions in THF. Having explored the effect of added ammonium salts, we were interested in determining how changing the solvent would affect the reaction of **1** with nitriles. In particular, we were interested in increasing the concentration of **2** relative to hydroxide **1**, since the nitrile adducts **10a**−**d**, which are generated from **2** and the appropriate nitrile, are sparingly soluble in benzene. To access a range of concentrations wider than those available in benzene, we carried out the

(25) The ratio of **3d** to **4** was determined by ^{1}H NMR spectroscopy.
(26) Synthesis of compound **7** can be found in the Experimental Section.
(27) Buckingham, D. A.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, *95*, 5649−5652.
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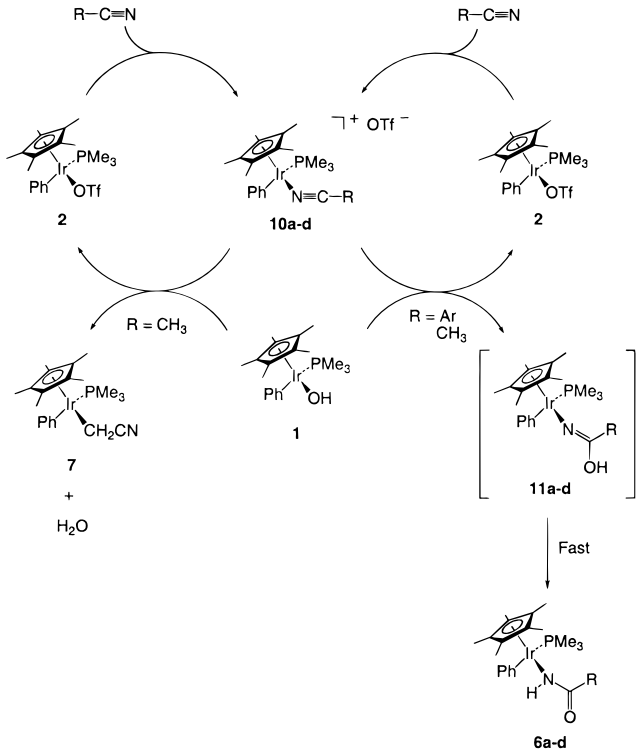
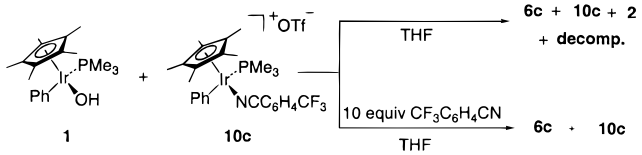
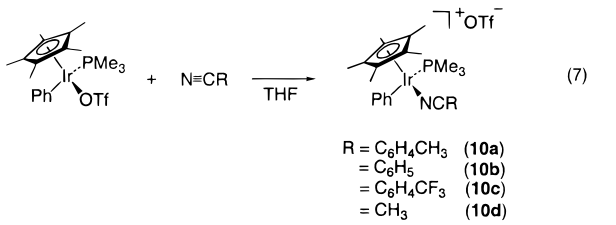
Scheme 2



Scheme 3



reactions of **1**, **2**, and nitrile in THF. Treatment of a THF-d_8 solution of **2** with 1 equiv of *p*-trifluorotolunitrile resulted in the quantitative formation of $[Cp^*(PMe_3)Ir(Ph)NCC_6H_4CF_3]^+OTf^-$ (**10c**) as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (eq 7). Addition of 1 equiv of hydroxide **1** to the

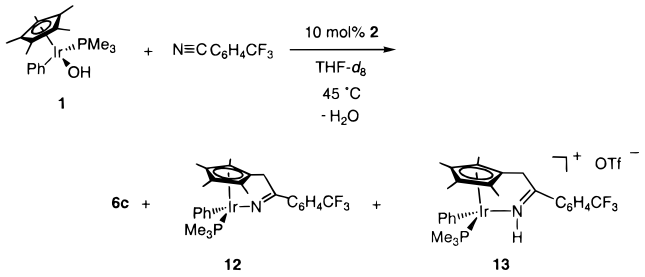


nitrile adduct **10c** (Scheme 3) led to the formation of carboxamide **6c** in 60% yield after 2 d, along with triflate **2**, nitrile adduct **10c**, and an unidentified, insoluble black precipitate. In contrast, when a THF-d_8 solution of triflate **2** was treated with 10 equiv of *p*-trifluorotolunitrile, followed by 1 equiv of **1**, clean formation of carboxamide **6c** was observed in 5 h (Scheme 3). The concentration of nitrile adduct **10c** remained constant in this reaction, as expected. It is therefore necessary to run these reactions in the presence of excess nitrile to favor formation of **6c** and prevent competing side reactions.[32]

An interesting change in the reactivity of **1** in THF is observed as the amount of **2** is decreased below 1 equiv relative to **1**

(32) Presumably, the cation derived from **2** which is generated during the reaction is responsible for this decomposition.

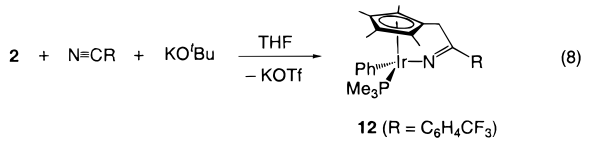
Scheme 4



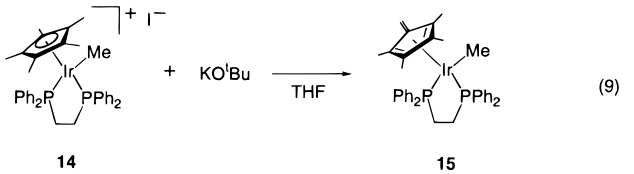
while excess nitrile is maintained. As shown in Scheme 4, reactions run in the presence of 10 mol % **2** at 45 °C in THF result in the formation of not only **6c** (30% NMR yield), but also $[Ph(PMe_3)Ir[C_5Me_4CH_2C(C_6H_4CF_3)N]]$ (**12**) (60% NMR yield), small amounts of $[Ph(PMe_3)Ir(C_5Me_4CH_2C(C_6H_4CF_3)-NH)]OTf$ (**13**), and water.[33]

The structure of the cyclometalated compound **12**, a product resulting from the formal addition of nitrile followed by dehydration of **1**, was initially assigned using NMR spectroscopy. The ^1H NMR spectrum (THF-d_8) of compound **12** contains four cyclopentadienyl methyl signals on the cyclopentadienyl ligand at δ 2.19, 2.02, 1.68, and 1.53. The methylene protons on the cyclopentadienyl ligand are diastereotopic and appear as two doublets centered at 3.66 and 3.59 ppm ($^2J_{H-H}$ = 17 Hz). Consistent with incorporation of *p*-trifluorotolunitrile, **12** exhibits a resonance in the ^{19}F NMR spectrum (THF-d_8) at −59.4 ppm.

Cyclometalated compound **12** was independently synthesized by treatment of triflate **2** with an excess of *p*-trifluorotolunitrile followed by addition of KO^{t}Bu (eq 8). Compound **12** was



isolated in 35% yield following crystallization. This methodology was previously employed for the deprotonation of $[Cp^*(Ph_2P(CH_2)_2PPh_2)IrMe]^+I^-$ (**14**) with KO^{t}Bu leading to formation of the iridium(I) fulvene $(C_5Me_4CH_2)(Ph_2P(CH_2)_2-PPh_2)IrMe$ (**15**) (eq 9).[34]



The structural assignment of **12** was confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram (Figure 2) confirms the connectivity. The data collection parameters are presented in Table 1, and selected bonding parameters are displayed in Table 3. The metallacycle causes the cyclopentadienyl ligand to tilt such that the bridging Cp carbon C(3) is only 2.153 Å from iridium. The remaining Cp carbon to iridium

(33) Treatment of **10c** with a slurry of CsOH (1 equiv) in THF-d_8 results in immediate formation of **1** and free nitrile. Subsequently, consumption of **1** and nitrile is observed, generating a product mixture similar to that illustrated in Scheme 4. Presumably the presence of small amounts of **2** catalyzes this reaction, but the heterogeneous nature of this mixture makes analysis difficult.

(34) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862−2863.

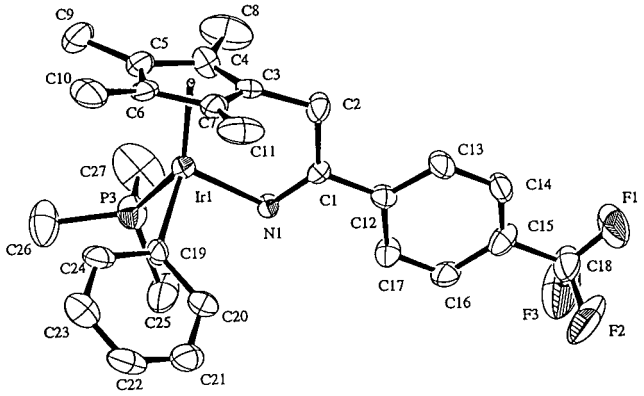


Figure 2. ORTEP diagram of $Ph(PMe_3)Ir[C_5Me_4CH_2C(C_6H_4CF_3)N]$ (**12**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 3. Selected Intramolecular Distances and Angles for $[Ph(PMe_3)Ir[C_5Me_4CH_2C(C_6H_4CF_3)N]$ (**12**)

	Distance (Å)		
Ir−N	2.038(7)	Ir−C(7)	2.20(1)
Ir−C(101)[a]	1.8684(4)	N−C(1)	1.27(1)
Ir−C(3)	2.153(10)	C(1)−C(2)	1.53(1)
Ir−C(5)	2.29(1)	C(2)−C(3)	1.50(1)
	Angles (deg)		
Ir−N−C(1)	115.3(6)	N−C(1)−C(12)	119.5(8)
N−C(1)−C(2)	122.7(8)	C(2)−C(1)−C(12)	117.8(8)
C(1)−C(2)−C(3)	109.6(8)		

[a] C(101) is the centroid of cyclopentadienyl ring C(3)−C(7).

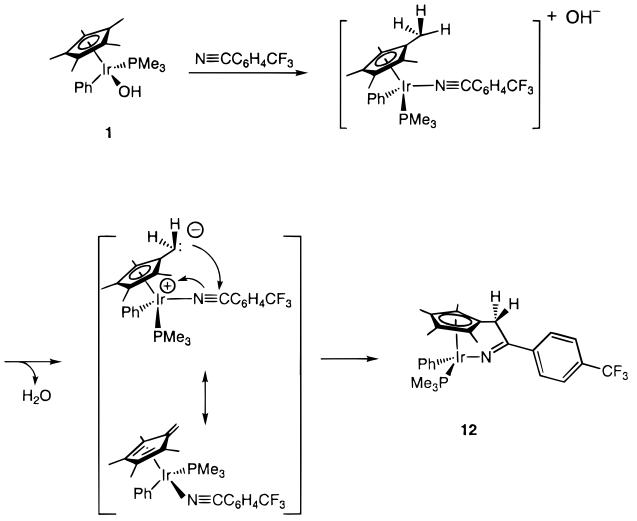
distances are longer: C(4)−Ir(1) = 2.22(1) Å, C(5)−Ir(1) = 2.29(1) Å, C(6)−Ir(1) = 2.29(1) Å and C(7)−Ir(1) = 2.20(1) Å.

Complex **13**, the *N*-protonated analogue of **12** (see Scheme 4), was independently synthesized by treatment of a methylene chloride solution of **12** with trifluoromethanesulfonic acid. Following crystallization metallacyle **13** was isolated in 62% yield. Compound **13** exhibits a broad resonance at δ 10.74 ppm in the ^{1}H NMR spectrum consistent with the N−*H* proton. Analogous to **12**, a set of doublets attributable to the diastereotopic methylene protons are observed at 3.99 and 3.78 ($^2J_{H-H}$ = 19 Hz).

We propose the mechanism outlined in Scheme 5 to explain the formation of **12**. The presence of excess nitrile promotes dissociation of the hydroxide ion, generating an iridium/hydroxide ion pair. The hydroxide then rapidly deprotonates the Cp* methyl group. The resulting anion attacks the nitrile carbon to generate **12**. Analogous to the hydroxide dissocation above, the displacement of anilide by a dative ligand to generate an outer-sphere anion has been postulated in the formation of a similar iridium fulvene complex.[34] While we cannot rule out dissociation of hydroxide followed by nucleophilic attack upon the nitrile adduct to generate carboxamide **6c** in THF, the reaction which generates **12** appears to involve only one metal. This is based upon the observation that the rate of formation of the cyclometalated compound **12** is independent of added triflate **2**. In addition, as illustrated in Scheme 3, under high concentrations of triflate **2** in THF, carboxamide **6c** is formed and no metallacyle **12** is observed.

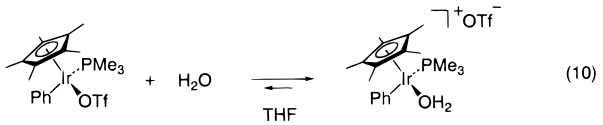
Consistent with dissociation of the hydroxide to generate an ionic intermediate, the reaction between complex **1** and *p*-trifluorotolunitrile to produce metallacyle **12** exhibits a dependence on solvent polarity. Treatment of a benzene solution of hydroxide **1** and a catalytic amount of triflate **2** with 10 equiv of *p*-trifluorotolunitrile results in formation of carboxamide **6c**

Scheme 5



(>90%) and small amounts of **12** (<5%). The formation of larger amounts of **12** is presumably not observed because dissociation of the hydroxide, as proposed in THF, is unfavorable in benzene, a less polar solvent. Hughes and co-workers have observed a similar solvent effect in the coupling of a Cp* ligand and a perfluorobenzyl ligand on cobalt, which proceeds in THF and not in benzene.[35]

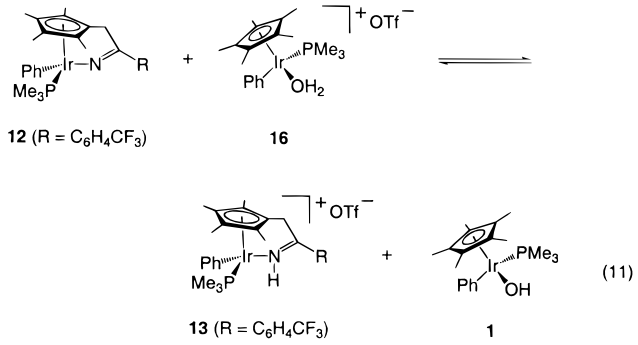
Reactivity of 12 and 13. Attempts to perform a kinetic analysis on the triflate-catalyzed reaction of hydroxide **1** with nitriles in THF at constant ionic strength were complicated by formation of **12** and **13**. In an attempt to gain a better understanding of what roles, if any, **12** and **13** might play during the reaction illustrated in Scheme 4, we subjected the independently synthesized metallacycle **12** to conditions similar to those of the original reaction. First, approximately 1 equiv of water was added to a THF-d_8 solution of **12**. No reaction was observed between these two complexes even after prolonged heating. In a separate experiment, approximately 1 equiv of water was added to a THF-d_8 solution of triflate **2**. The formation of the aquo adduct $[Cp^*(PMe_3)Ir(Ph)OH_2]OTf$ (**16**) was observed (eq 10). Subsequent addition of 1 equiv of **12** to



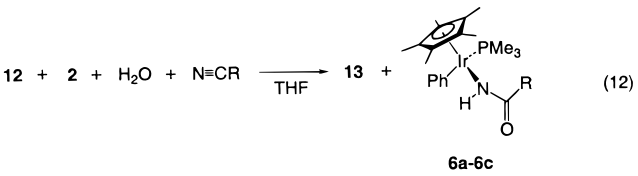
the THF-d_8 solution containing triflate **2** and water generated a mixture containing four compounds, as determined by NMR spectroscopy (eq 11). Along with **12** and aquo adduct **16**, hydroxide **1** and $[Ph(PMe_3)Ir(C_5Me_4CH_2C(C_6H_4CF_3)NH)]OTf$ (**13**) were observed. The equilibrium depicted in eq 11 is suggested to account for these observations.[36] In this transformation, metallacycle **13** and hydroxide **1** are generated by deprotonation of **16** by **12**. Compound **12** is incapable of deprotonating water in the absence of triflate **2**. It is only when water is bound to the iridium cation "$Cp^*(PMe_3)Ir(Ph)^+$" (i.e., the aquo adduct **16**) that it is sufficiently acidic to be deprotonated by **12**.

(35) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678−5686.

(36) Attempts to quantitatively determine the equilibrium constant were unsuccessful because the mixture slowly decomposes to unidentified products.



Formal addition of water or hydroxide to **12** and **13**, respectively, would result in formation of carboxamide **6c**. We were interested in exploring the possible intermediacy of either **12** or **13** in the formation of **6c**. As mentioned previously, no reaction was observed between **12** and water. Furthermore, heating the reaction mixture shown in eq 11 does not lead to generation of carboxamide **6c**, demonstrating that neither **12** nor **13** is an intermediate in the formation of **6c**. Consistent with this, treatment of the solution shown in eq 10 with nitrile leads only to formation of the carboxamide derived from the added nitrile (eq 12). For example, addition of 10 equiv of



p-tolunitrile to a solution containing equimolar amounts of **2**, water, and **12** in THF-d_8 leads to formation of carboxamide **6a** (*not* **6c**) and **13** after heating at 45 °C for 2 d (eq 12). Carboxamide **6a** is generated from the reaction of triflate **2**, hydroxide **1**, and *p*-tolunitrile and not from either **12** or **13**.

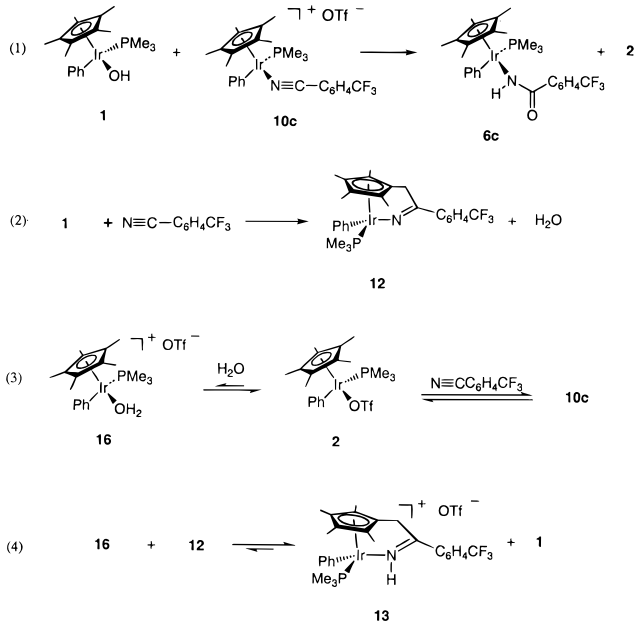
The reactivity of **1** and **2** in the presence of *p*-trifluorotolunitrile in THF is summarized in Scheme 6. The bimetallic reaction between hydroxide **1** and the nitrile adduct **10c** produces **6c** and triflate **2** (Scheme 6, eq 1). In contrast, hydroxide **1** reacts with free *p*-trifluorotolunitrile to generate **12** and water (Scheme 6, eq 2). This primarily occurs in the initial stages of the reaction. As the concentration of water increases, the generation of aquo adduct **16** becomes competitive with the formation of **10c** (Scheme 6, eq 3). As independently demonstrated, compound **16** can then be deprotonated by **12** to generate **13** and hydroxide **1** (Scheme 6, eq 4).

Conclusion

In summary, we have reported an unusual example of bimetallic reactivity that results in the synthesis of a series of iridium(III) carboxamides by the formal addition of an iridium hydroxide to an iridium−nitrile complex. This reaction is catalyzed by the cationic iridium Lewis acid **2**, which activates the nitrile toward nucleophilic attack. Transfer of a hydroxide moiety from **1** to [Ir−NCR]$^+$ results in the regeneration of **2**. In the case of aliphatic nitriles, deprotonation of the carbon α to the nitrile moiety is possible. The iridium carboxamides **6a**−**c** react with HCl to quantitatively generate Cp*(PMe$_3$)IrPh(Cl) (**9**) and the free amides.

In addition to formation of the expected carboxamides, an alternate mode of reactivity for hydroxide **1** is observed in THF, where complex **1** reacts with *p*-trifluorotolunitrile to generate the cyclometalated compound **12**. Compound **12** is neither a

Scheme 6



side product nor an intermediate in the generation of carboxamide **6c**, but acts as a base in the regeneration of hydroxide **1**.

The reactivity demonstrated in this paper illustrates an example of an organometallic reaction which utilizes two metal centers to effect a transformation. We hope that our results will be helpful in understanding related processes that have recently been observed in the fields of bioinorganic and organic chemistry and ultimately in the development of new organometallic reactions utilizing two metal centers.[37]

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed at ambient temperature in a recirculating Vacuum Atmospheres inert atmosphere glovebox (N_2) or using standard Schlenk and vacuum techniques. Glassware was dried in an oven at 160 °C before use.

The ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C{^{1}H} NMR spectra were recorded at 100 MHz (or, if specified, 125 MHz), ^{31}P{^{1}H} NMR spectra were recorded at 161.9 MHz, and ^{19}F NMR spectra were recorded at 376.5 MHz. ^{31}P and ^{19}F NMR spectra were referenced externally to 85% phosphoric acid in water and trichlorofluoromethane, respectively. In cases where assignments of ^{13}C{^{1}H} resonances were ambiguous, resonances were assigned by using DEPT 45, 90, and 135 pulse sequences. All chemical shifts are reported in parts per million (ppm). Elemental analyses were performed by the University of California−Berkeley Microanalytical facility. X-ray structural analyses were performed at the University of California−Berkeley CHEXRAY facility.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Hexanes, pentane, diethyl ether, tetrahydrofuran, benzene, and toluene were distilled from sodium/benzophenone ketyl under N_2 prior to use. Methylene chloride and acetonitrile were distilled from CaH_2 under N_2. Deuterated solvents were purified by the same method as their protiated analogues and vacuum-transferred prior to use. Cp*(PMe$_3$)Ir(Ph)Cl (**9**) and Cp*(PMe$_3$)-IrPh(OH) (**1**) were prepared by literature methods.[29] KO^{t}Bu was sublimed prior to use. Acetamide was recrystallized from hot benzene prior to use. Benzamide was crystallized twice from ethanol and dried in vacuo for 24 h.

Cp*(PMe$_3$)Ir(Ph)OTf (2). Modification of a literature procedure was employed.[38] To a stirred solution of Cp*(PMe$_3$)IrPh(Cl) (1.1 g,

(37) See refs 2−17.

2.2 mmol) in methylene chloride (15 mL) at −40 °C was added a slurry of AgOTf (0.63 g, 2.4 mmol, 1.1 equiv) in methylene chloride (10 mL). The mixture was allowed to warm to 20 °C and was protected from light. After 1 h, the solvent was evaporated under reduced pressure, and the residual orange solid was dissolved in C_6H_6 and filtered through silylated silica gel (5 × 2 cm). The solvent was lyophilized to yield an orange powder. Yield: 1.4 g, 97% (lit. yield: 94%). Spectroscopic data were in accord with literature values.[38]

Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_4$CH$_3$] (6a). Method 1. A glass vessel sealed to a Kontes vacuum adapter was charged with **1** (23 mg, 0.045 mmol), **2** (1.0 mg, 0.0013 mmol), *p*-tolunitrile (5.3 mg, 0.045 mmol), and benzene (10 mL). The vessel was heated for 4.5 d at 45 °C. The tan solution was filtered, and the solvent was removed under reduced pressure. The oily residue was dissolved in a minimum of ether (6 mL). The solution was filtered and concentrated (4 mL). Crystals of **6a** were obtained by slow evaporation of the solvent at −40 °C. Yield: 24 mg, 86%.

Method 2. A glass vessel attached to a Kontes vacuum adapter was charged with **1** (84 mg, 0.17 mmol), *p*-toluamide (23 mg, 0.017 mmol), and benzene (5 mL). The vessel was then heated for 12 h at 45 °C. The vessel was brought into a drybox, and the solvent was removed under reduced pressure. The tan solid was crystallized by slow evaporation of a concentrated diethyl ether of **6a** at −40 °C. Yield: 77 mg, 74%.

^{1}H NMR (C_6D_6): δ 8.11 (d, J = 8 Hz, 2H, NHC(O)C$_6$*H*$_4$CH$_3$), 7.45 (d, J = 7 Hz, 2H, NHC(O)C$_6$*H*$_4$CH$_3$), 7.20 (m, 2H, *o*-C$_6$*H*$_5$), 7.01 (m, 2H, *m*-C$_6$*H*$_5$), 6.95 (m, 1H, *p*-C$_6$*H*$_5$), 4.79 (br, 1H, N*H*), 2.08 (s, 3H, NHC(O)C$_6$H$_4$C*H*$_3$), 1.56 (d, $^4J_{P-H}$ = 2 Hz, 15H, C$_5$*Me*$_5$), 1.20 (d, $^2J_{P-H}$ = 11 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 172.9 (s, *C*═O), 140.2 (d, $^2J_{P-C}$ = 12 Hz, *i*-*C*$_6$H$_5$), 138.8 (d, $^3J_{P-C}$ = 3 Hz, *o*-*C*$_6$H$_5$), 138.5 (s, *i*-NHC(O) *C*$_6$H$_5$), 129.1 (s, *o* to NHC(O)*C*$_6$H$_5$), 128.0 (s, *m*-*C*$_6$H$_5$), 127.2 (s, *p*-*C*$_6$H$_5$), 122.5 (s, *m* to NHC(O)*C*$_6$H$_5$), 92.9 (d, $^2J_{P-C}$ = 3 Hz, *C*$_5$Me$_5$), 21.1 (s, NHC(O)C$_6$H$_4$*C*H$_3$), 15.1 (d, $^1J_{P-C}$ = 37 Hz, P*Me*$_3$), 9.5 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ −37.9. IR (CH_2Cl_2): 3345 (s, N−H), 3128 (m), 2910 (s), 2306 (s), 2194 (s), 2094 (w), 2007 (w), 1756 (w), 1604 (s), 1444 (m), 1384 (m), 962 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{37}IrNOP$: C, 52.70; H, 6.07; N, 2.30. Found: C, 52.64; H, 6.12; N, 2.28.

Cp*(PMe$_3$)IrPh[NHC(O)C$_6$H$_5$] (6b). Method 1. The procedure for the synthesis of **6a** (method 1) was followed using 65 mg of **1**, 3.0 mg of **2**, and 13 mg of benzonitrile. The product was isolated as a light tan solid after crystallization from ether. Yield: 71 mg, 89%.

Method 2. The procedure for the synthesis of **6a** (method 2) was followed using 78 mg of **1** and 19 mg of benzamide. Yield: 62 mg, 69%.

^{1}H NMR (C_6D_6): δ 8.15 (d, J = 9 Hz, 2H, *o*-NHC(O)C$_6$*H*$_5$), 7.43 (d, J = 7 Hz, 2H, *o*-C$_6$*H*$_5$), 7.20 (m, 2H, *m*-NHC(O)C$_6$*H*$_5$), 7.19 (m, 2H, *o*-C$_6$*H*$_5$), 7.17 (m, 1H, *p*-NHC(O)C$_6$*H*$_5$), 7.13 (m, 1H, *p*-C$_6$H$_5$), 4.79 (s, 1H, N-*H*), 1.54 (d, $^4J_{P-H}$ = 2 Hz, 15H, C$_5$*Me*$_5$), 1.19 (d, $^2J_{P-C}$ = 11 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 172.9 (s, *C*═O), 141.0 (s, *i*-NHC(O)*C*$_6$H$_5$), 140.2 (d, $^2J_{P-C}$ = 12 Hz, *i*-*C*$_6$H$_5$), 138.8 ($^3J_{P-C}$ = 3 Hz, *o*-*C*$_6$H$_5$), 128.9 (s, *m*-*C*$_6$H$_5$), 128.5 (s, *p*-*C*$_6$H$_5$), 128.2 (s, *o*-NHC-(O)*C*$_6$H$_5$), 127.3 (s, *m*-NHC(O)*C*$_6$H$_5$), 122.5 (s, *p*-NHC(O)*C*$_6$H$_5$), 93.0 (d, $^2J_{P-C}$ = 4 Hz,*C*$_5$Me$_5$), 15.3 (d, $^1J_{P-C}$ = 37 Hz, P*Me*$_3$), 9.5 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ −37.9. IR (KBr): 3381 (s), 3059 (s), 2972 (s), 2910 (s), 1620 (s), 1564 (s), 1428 (s), 1279 (m), 1242 (w), 1018 (w), 956 (s), 739 (m), 696 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{35}IrNOP$: C, 51.98; H, 5.87; N, 2.33. Found: C, 52.13; H, 6.07; N, 2.28.

Cp*(PMe$_3$)Ir[NHC(O)C$_6$H$_3$CF$_3$]Ph (6c). Method 1. The procedure for the synthesis of **6a** (method 1) was followed using 26 mg of **1**, 1.0 mg of **2**, and 9.1 mg of *p*-CF$_3$C$_6$H$_4$CN. The product was obtained as a light tan solid after crystallization from ether. Yield: 19 mg, 54%.

Method 2. The procedure for the synthesis of **6a** (method 2) was followed using 150 mg of **1** and 57 mg of *p*-trifluorotoluamide. Yield: 130 mg, 65%.

^{1}H NMR (C_6D_6): δ 7.91 (d, J = 8 Hz, 2H, C(O)C$_6$*H*$_4$CF$_3$), 7.37 (d, J = 7 Hz, 2H, *o*-C$_6$*H*$_5$), 7.31 (d, J = 8 Hz, 2H, C(O)C$_6$*H*$_4$CF$_3$), 7.21 (m, 2H, *m*-C$_6$*H*$_5$), 7.15 (m, 1H, *p*-C$_6$*H*$_5$), 4.70 (br s, 1H, N*H*), 1.52 (d, $^4J_{P-H}$ = 1 Hz, 15H, C$_5$*Me*$_5$), 1.16 (d, $^2J_{P-H}$ = 11 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 171.2 (s, *C*═O), 143.6 (s, NHC(O)*C*$_6$H$_4$CF$_3$), 139.6 (d, $^3J_{P-C}$ = 13 Hz, *i*-*C*$_6$H$_5$), 138.3 (d, $^3J_{P-C}$ = 3 Hz, *o*-*C*$_6$H$_5$), 130.1 (q, $^2J_{F-C}$ = 31 Hz, NHC(O)C$_6$H$_4$*C*F$_3$), 127.9 (s, NHC(O)*C*$_6$H$_4$CF$_3$), 127.2 (s, *m*-*C*$_6$H$_5$), 124.9 (q, $^3J_{F-C}$ = 3.6 Hz, NHC(O)*C*$_6$H$_4$CF$_3$), 122.3 (s, *p*-*C*$_6$H$_5$), 92.7 (d, $^2J_{P-C}$ = 3 Hz, *C*$_5$Me$_5$), 14.8 (d, $^1J_{P-C}$ = 37 Hz, P*Me*$_3$), 9.1 (s, C$_5$*Me*$_5$), *C*F$_3$ not observed.^{31}P{^{1}H} NMR (C_6D_6): δ −37.9. ^{19}F NMR (C_6D_6): δ −62.1. IR (KBr): 3392 (s, N−H), 3056 (m), 2989 (m), 2910 (s), 2366 (w), 1619, 1569 (s), 1432 (s), 1326 (s), 1122 (s), 954 (s), 840 (s), 736 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{34}IrNOPF_3$: C, 48.50; H, 5.12; N, 2.09. Found: C, 48.20; H, 5.08; N, 2.07.

Cp*(PMe$_3$)IrPh[NHC(O)CH$_3$] (6d). The procedure for the synthesis of **6a** (method 2) was followed using 80 mg of **1** and 10 mg of acetamide. Amide **6d** was crystallized at −40 °C by layering a saturated toluene solution with pentane to afford tan, needlelike crystals of **6d**. Yield: 80 mg, 88%. ^{1}H NMR (C_6D_6): δ 7.29 (d, J = 7 Hz, 2H, *o*-C$_6$*H*$_5$), 7.11 (m, 2H, *m*-C$_6$*H*$_5$), 7.10 (m, 1H, *p*-C$_6$*H*$_5$), 3.59 (br s, 1H, N*H*), 2.09 (s, 3H, NHC(O)C*H*$_3$), 1.49 (d, $^4J_{P-H}$ = 2 Hz, 15H, C$_5$*Me*$_5$), 0.81 (d, $^2J_{P-H}$ = 13 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.5 (s, *C*═O), 138.8 (d, $^3J_{P-C}$ = 3.4 Hz, *o*-*C*$_6$H$_5$), 127.9 (s, *m*-*C*$_6$H$_5$), 122.4 (s, *p*-*C*$_6$H$_5$), 92.8 (d, $^2J_{P-C}$ = 3 Hz, *C*$_5$Me$_5$), 27.1 (s, NHC(O)*C*H$_3$), 15.2 (d, $^1J_{P-C}$ = 37 Hz, P*Me*$_3$), 9.5 (s, C$_5$*Me*$_5$), *i*-*C*$_6$H$_5$ not observed.^{31}P{^{1}H} NMR (C_6D_6): δ −38.2. IR (C_6D_6): 3373 (m, N−H), 2950 (m), 2909 (m), 2868 (m), 1628 (s), 1571 (s), 1422 (m), 1281 (m), 944 (m), 574 (w) cm^{-1}. MS (EI): *m*/*z* 539 (M$^+$). Anal. Calcd for $C_{21}H_{33}IrNOP$: C, 46.82; H, 6.18; N, 2.66. Found: C, 46.92; H, 6.24; N, 2.45.

Cp*(PMe$_3$)Ir(CH$_2$CN)Ph (7). To a solution of **2** (420 mg, 0.67 mmol) in THF (10 mL) was added CH_3CN (3.8 g, 93 mmol). The light green-yellow solution was cooled to −40 °C, and a slurry of KO^{t}Bu (75 mg, 0.67 mmol) in THF (2 mL) was added. The solution immediately turned orange-yellow upon mixing. After being stirred for 30 min at −40 °C, the solution was warmed to room temperature and the solvent was removed under reduced pressure. The residual solid was extracted with ether (3 × 5 mL). The ether extracts were collected, filtered through glass fiber filter paper, and concentrated under reduced pressure. Hexanes were allowed to slowly diffuse into the ether solution at −40 °C. A yellow-brown precipitate containing two unidentified products formed. The remaining solution was separated from this mixture, concentrated under reduced pressure, and layered with pentane to yield yellow microcrystals of **7**. Yield: 30 mg, 9%. Material suitable for elemental analysis was obtained by recrystallizing this material in an identical manner. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.12 (m, 2H, C$_6$*H*$_5$), 7.03 (m, 3H, C$_6$*H*$_5$), 1.64 (dd, $^2J_{Hb-Ha}$ = 15 Hz, $^3J_{P-Ha}$ = 4 Hz, 1H, IrC*H*$_a$H$_b$CN), 1.55 (dd, $^2J_{Ha-Hb}$ = 15 Hz, $^2J_{P-Hb}$ = 8 Hz, 1H, IrCH$_a$*H*$_b$-CN), 1.36 (d, $^4J_{P-H}$ = 2 Hz, 15H, C$_5$*Me*$_5$), 1.02 (d, $^2J_{P-H}$ = 10 Hz, 9 H, P*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 139.3 (d, $^4J_{P-C}$ = 4 Hz, *m*-*C*$_6$H$_5$), 135.9 (d, $^2J_{P-C}$ = 12 Hz, *i*-*C*$_6$H$_5$), 129.5 (d, $^3J_{P-C}$ = 5 Hz, *o*-*C*$_6$H$_5$), 122.1 (s, *p*-*C*$_6$H$_5$), 92.9 (d, $^2J_{P-C}$ = 3 Hz, *C*$_5$Me$_5$), 13.9 (d, $^1J_{P-C}$ = 37 Hz, P*Me*$_3$), 8.6 (d, $^3J_{P-C}$ = 1 Hz, C$_5$*Me*$_5$), −29.6 (d, $^2J_{P-C}$ = 8 Hz, *C*H$_2$CN). ^{31}P{^{1}H} NMR (C_6D_6): δ −44.2 ppm. IR (KBr): 3052 (w), 2973 (w), 2956 (w), 2913 (s), 2357 (w), 2194 (s), 1733 (w), 1568 (m), 1474 (m), 1458 (m), 1422 (m), 1401 (m), 1379 (m), 1283 (m), 1020 (m), 952 (s), 735 (m), 704 (m), 678 (w) cm^{-1}. MS (EI): *m*/*z* 673 (M$^+$). Anal. Calcd for $C_{21}H_{31}NIrP$: C, 48.44; H, 6.00; N, 2.70. Found: C, 48.80; H, 6.33; N, 2.75.

Cp*(PMe$_3$)Ir[N═C═C(Ph)$_2$]Ph (8). A glass vessel attached to a Kontes vacuum adapter was charged with **1** (77 mg, 0.15 mmol), diphenylacetonitrile (30.0 mg, 0.15 mmol), and benzene (5 mL). The solution was heated at 45 °C for 2 h, over which time it turned a bright orange color. After 2 h, the solvent was lyophilized, and the orange solid was redissolved in a minimum of pentane/benzene (9:1), filtered through Celite, and evaporated under reduced pressure to yield **8**. The orange solid was crystallized by allowing pentane to diffuse into a saturated toluene solution of **8** at room temperature. Yield: 78 mg, 75%. ^{1}H NMR (C_6D_6): δ 7.80 (d, 4H, J = 8 Hz, N═C═C(*o*-C$_6$H$_5$)$_2$), 7.33 (t, 4H, J = 7 Hz, N═C═C(*m*-C$_6$H$_5$)$_2$), 7.31 (m, 2H, *o*-C$_6$*H*$_5$), 7.20 (m, 2H, *m*-C$_6$*H*$_5$), 7.13 (m, 1H, *p*-C$_6$*H*$_5$), 6.93 (t, 2H, J = 7 Hz, N═C═C(*p*-C$_6$H$_5$)$_2$), 1.27 (d, 15H, $^4J_{P-H}$ = 2 Hz, C$_5$*Me*$_5$), 0.89 (d, 9H, $^2J_{P-H}$ = 11 Hz, P*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 142.6 (s, N═C═*C*(C$_6$H$_5$)$_2$), 139.7 (d, $^3J_{P-C}$ = 4 Hz, *o*-C$_6$H$_5$), 138.3 (d, $^2J_{P-C}$ = 14 Hz, *i*-*C*$_6$H$_5$), 129.7 (d, $^3J_{P-C}$ = 5 Hz, N═*C*═C(C$_6$H$_5$)$_2$), 128.8 (s, N═C═

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C(*i*-C_6H_5)$_2$), 128.6 (N═C═C(*o*-C_6H_5)$_2$), 128.2 (d, J = 3 Hz, *m*-C_6H_5), 123.6 (N═C═C(*m*-C_6H_5)$_2$), 122.9 (s, *p*-C_6H_5), 119.4 (s, N═C═C(*p*-C_6H_5)$_2$), 94.4 (d, $^2J_{P-C}$ = 3 Hz, C_5Me_5), 14.6 (d, $^1J_{P-C}$ = 38 Hz, P*Me*$_3$), 9.4 (s, C_5*Me*$_5$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −35.5. IR (KBr): 3048 (m), 2908 (m), 2105 (s), 1587 (s), 1376 (w), 1307 (m), 1255 (m), 1178 (m), 944 (s), 752 (s), 692 (s) cm^{-1}. MS (EI): *m*/*z* 673 (M^+). Anal. Calcd for $C_{32}H_{39}IrNP$: C, 58.91; H, 5.84; N, 2.08. Found: C, 59.01; H, 6.01; N, 2.07.

[Cp*(PMe$_3$)Ir(Ph)NCC$_6$H$_4$CH$_3$]$^+$OTF$^-$ (10a). To a stirred solution of **2** (110 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was added a solution of *p*-tolunitrile (21 mg, 0.18 mmol) in CH_2Cl_2 (1 mL). Upon addition, the initally orange solution turned light green. After 15 min, the solution was filtered through glass fiber filter paper, and the solvent was removed under reduced pressure to yield a light green solid. The product was isolated as a light green solid after crystallization from a concentrated methylene chloride solution layered with diethyl ether. Yield: 90 mg, 67%. ^1H NMR (CD_2Cl_2): δ 7.67 (d, 2H, J = 8 Hz, NC$_6$*H*$_4$CH$_3$), 7.46 (d, 2H, J = 8 Hz, NC$_6$*H*$_4$CH$_3$), δ 7.23 (m, 2H, *o*-C_6H_5), 7.07 (m, 2H, *m*-C_6H_5), 7.01 (m, 1H, *p*-C_6H_5), 2.51 (s, 3H, NC$_6$H$_4$C*H*$_3$), 1.74 (d, 15H, $^4J_{P-H}$ = 2 Hz, C_5*Me*$_5$), 1.52 (d, 9H, $^2J_{P-H}$ = 11 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.0 (s, NC*C*$_6$H$_4$CH$_3$ (*i* to CH$_3$)), 138.0 (s, *p*-C_6H_5), 134.3 (d, $^2J_{P-C}$ = 10 Hz, *i*-C_6H_5), 133.7 (s, NC$_6$*H*$_4$CH$_3$ (*o* to CN)), 131.2 (s, *m*-C_6H_5), 129.3 (s, NC$_6$*H*$_4$CH$_3$ (*o* to CH$_3$)), 124.0 (s, *o*−C_6H_5), 120.3 (s, N*C*C$_6$H$_4$CH$_3$), 106.9 (s, NC*C*$_6$H$_4$CH$_3$ (*i* to CN)), 96.7 (s, C_5Me$_5$), 22.5 (s, NCC$_6$H$_4$*C*H$_3$), 14.6 (d, $^1J_{P-C}$ = 30 Hz, P*Me*$_3$), 9.3 (s, C_5*Me*$_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −34.1. ^{19}F NMR (CD_2Cl_2): δ −77.0. IR (KBr): 3054 (s), 2980 (s), 2918 (s), 2247 (w), 1603 (s), 1571 (s), 1503 (m), 1460 (s), 1261 (s), 1148 (s), 1065 (m), 1030 (s), 956 (s), 856 (w), 819 (m), 740 (s), 638 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{36}NF_3IrPO_3S$: C, 45.03; H, 4.86; N, 1.88. Found: C, 44.68; H, 4.94; N, 1.84.

[Cp*(PMe$_3$)Ir(Ph)NCC$_6$H$_5$]$^+$OTF$^-$ (10b). The procedure for the synthesis of **10a** was followed using 76.0 mg of **2** and 12.4 mg of benzonitrile. The product was isolated as a light green solid after crystallization from a concentrated methylene chloride solution layered with diethyl ether. Yield: 47 mg, 53%. ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.83 (m, 2H, NC$_6$*H*$_5$), 7.68 (m, 2H, NC$_6$*H*$_5$), 7.52 (m, 1H, NC$_6$*H*$_5$), 7.27 (m, 2H, *o*-C_6H_5), 7.10 (m, 2H, *m*-C_6H_5), 7.04 (m, 1H, *p*-C_6H_5), 1.77 (d, 3H, $^5J_{P-H}$ = 2 Hz, C*H*$_3$CN), 1.69 (d, 15H, $^4J_{P-H}$ = 2 Hz, C_5*Me*$_5$), 1.56 (d, 9H, $^2J_{P-H}$ = 11 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 137.4 (s, *p*-C_6H_5), 135.2 (s, *p*-NC$_6$*H*$_5$) 133.7 (d, $^2J_{P-C}$ = 14 Hz, *i*-C_6H_5), 133.2 (s, *o*-NC$_6$*H*$_5$), 129.9 (s, *m*-C_6H_5), 128.7 (s, *m*-NC$_6$*H*$_5$), 123.3 (s, *o*-C_6H_5), 119.4 (s, N*C*C$_6$H$_5$), 109.6 (s, *i*-NC$_6$H$_5$), 96.1 (d, $^2J_{P-C}$ = 3 Hz, C_5Me$_5$), 14.0 (d, $^1J_{P-C}$ = 40 Hz, P*Me*$_3$), 8.70 (s, C_5*Me*$_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −34.0. ^{19}F NMR (CD_2Cl_2): δ −77.0. IR (KBr): 3066 (m), 2990 (m), 2970 (m), 2918 (m), 2291 (w), 2228 (w), 1571 (m), 1464 (m), 1428 (m), 1386 (m), 1272 (s), 1224 (s), 1151 (s), 1031 (s), 961 (m), 763 (s), 686 (m), 638 (m), 572 (m), 517 (m) cm^{-1}. HRMS (FAB, nitrobenzyl alcohol) *m*/*z* for $[C_{26}H_{34}NPIr]^+$: calcd 584.2058, obsd 584.2045. Anal. Calcd for $C_{26}H_{34}NF_3IrPO_3S$: C, 44.25; H, 4.59; N, 1.91. Found: C, 43.76; H, 4.90; N, 1.78.

[Cp*(PMe$_3$)Ir(Ph)NCC$_6$H$_4$CF$_3$]$^+$OTF$^-$ (10c). The procedure for the synthesis of **10a** was followed using 120 mg of **2** and 33 mg of *p*-trifluorotolunitrile. Nitrile adduct **10c** was crystallized by layering a concentrated methylene chloride solution with pentane to afford clear, light green crystals. Yield: 60 mg, 40%. ^1H NMR (CD_2Cl_2, 500 MHz): δ 8.07 (d, 2H, J_{H-H} = 9 Hz, NC$_6$*H*$_4$CF$_3$), 7.93 (d, 2H, J_{H-H} = 8 Hz, NC$_6$*H*$_4$CF$_3$), 7.26 (m, 2H, *o*-C_6H_5), 7.12 (m, 2H, *m*-C_6H_5), 7.05 (m, 1H, *p*-C_6H_5), 1.78 (d, 15H, $^4J_{P-H}$ = 2 Hz, C_5*Me*$_5$), 1.58 (d, 9H, $^2J_{P-H}$ = 11 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 137.9 (s, *p*-C_6H_5), 136.4 (q, $^2J_{F-C}$ = 34 Hz, NC$_6$H$_4$CF$_3$ (*i* to CF$_3$)), 134.9 (s, NC$_6$H$_4$CF$_3$ (*o* to CN)), 134.2 (d, *i*-C_6H_5, 13 Hz), 129.1 (s, *o*-C_6H_5), 127.3 (q, $^3J_{F-C}$ = 4 Hz, NC$_6$H$_4$CF$_3$ (*o* to CF$_3$)), 123.6 (s, *m*-C_6H_5), 123.5 (q, $^1J_{F-C}$ = 270 Hz, NC$_6$H$_4$CF$_3$), 118.6 (s, N*C*C$_6$H$_4$CF$_3$), 114.1 (s, NC$_6$H$_4$CF$_3$ (*i* to CN)), 97.0 (d, $^2J_{P-C}$ = 3 Hz, C_5Me$_5$), 14.6 ($^1J_{P-C}$ = 40 Hz, P*Me*$_3$), 9.23 (s, C_5*Me*$_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −34.2. ^{19}F NMR (CD_2Cl_2): δ −62.1 (NCC$_6$H$_4$C*F*$_3$), −77.0 (OSO$_3$C*F*$_3$). IR (KBr): 3102 (w), 3060 (s), 2992 (s), 2919 (s), 2249 (w), 1613 (m), 1570 (s), 1503 (m), 1461 (m), 1409 (m), 1384 (s), 1321 (s), 1268 (s), 1147 (s), 1064 (s), 1031 (s), 952 (s), 853 (s), 742 (s), 637 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{33}NF_6IrO_3PS$: C, 42.00; H, 4.15; N, 1.75. Found: C, 42.01; H, 4.48; N, 1.64.

[Cp*(PMe$_3$)Ir(Ph)NCCH$_3$]$^+$OTF$^-$ (10d). The procedure for the synthesis of **10a** was followed using 72 mg of **2** and 4.7 mg of acetonitrile. Nitrile adduct **10d** was purified by precipitation from a concentrated methylene chloride solution with diethyl ether to afford an off-white powder. Yield: 45 mg, 60%. ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.17 (m, 2H, *o*-C$_6$*H*$_5$), 7.03 (m, 2H, *m*-C$_6$*H*$_5$), 6.97 (m, 1H, *p*-C$_6$*H*$_5$), 2.80 (d, $^4J_{P-C}$ = 2 Hz, 3H, C*H*$_3$CN), 1.69 (d, $^4J_{P-C}$ = 2 Hz, 15H, C_5*Me*$_5$), 1.48 (d, $^2J_{P-H}$ = 11 Hz, 9H, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 137.5 (s, *p*-C_6H_5), 134.2 (d, $^2J_{P-C}$ = 14 Hz, *i*-C_6H_5), 128.5 (s, *m*-C_6H_5), 123.2 (s, *o*-C$_6$H$_5$), 116.9 (s, N*C*CH$_3$), 95.5 (d, $^2J_{P-C}$ = 3 Hz, C_5Me$_5$), 13.9 (d, $^1J_{P-C}$ = 39 Hz, P*Me*$_3$), 8.6 (s, C_5*Me*$_5$), 4.2 (s, *C*H$_3$CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −34.2. ^{19}F NMR (CD_2Cl_2): δ −77.0. IR (KBr): 3059 (m), 2988 (s), 2924 (s), 2294 (w), 1571 (s), 1502 (m), 1465 (s), 1427 (s), 1384 (s), 1257 (s), 1156 (s), 1031 (s), 961 (s), 862 (m), 747 (s), 707 (s), 682 (w), 638 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{32}NF_3IrO_3PS$: C, 39.4; H, 4.81; N, 2.10. Found: C, 39.28; H, 5.10; N, 1.99.

[Ph(PMe$_3$)Ir[C$_5$Me$_4$CH$_2$C(C$_6$H$_4$CF$_3$)N]] (12). To a solution of **2** (105 mg, 0.17 mmol) in THF (10 mL) was added *p*-$CF_3C_6H_4CN$ (720 mg, 4.2 mmol). It was found that an excess of *p*-trifluorotolunitrile is necessary to drive the equilibrium toward formation of the adduct [Cp*(PMe$_3$)IrPh(NC$_6$H$_4$CF$_3$)]OTf (**10c**). Reactions run in the presence of only 1 equiv of *p*-trifluorotolunitrile led to the formation of **12** and a variety of unidentified products. The light green-yellow solution was cooled to −40 °C, and a slurry of K^{t}OBu (20 mg, 0.17 mmol) in THF (2 mL) was added. The solution immediately turned red upon mixing and became a darker red color as it warmed to room temperature. After the solution was stirred for 30 min at room temperature, the solvent was removed under reduced pressure. The residual solid was extracted with benzene (15 mL) and filtered through glass fiber filter paper directly into a glass vessel attached to a vacuum Kontes adapter. The solvent was lyophilized and the residual material left under full vacuum (25 °C, 0.01 Torr) for 24 h to remove the remaining *p*-$CF_3C_6H_4CN$. The remaining material was crystallized at −40 °C from a concentrated toluene solution layered with pentane to yield **12** as bright red-orange crystals. Yield: 38 mg, 35% yield. ^1H NMR (THF-d_8): δ 7.87 (d, J = 8 Hz, 2H, C$_6$*H*$_4$CF$_3$), 7.52 (d, J = 8 Hz, 2H, C$_6$*H*$_4$CF$_3$), 7.28 (m, 2H, C$_6$*H*$_5$), 6.79 (m, 3H, C$_6$*H*$_5$), 3.66 (d, J = 17 Hz, 1H, C$_5$Me$_4$C*H*$_a$H$_b$), 3.59 (d, J = 17 Hz, 1H, C$_5$Me$_4$CH$_a$*H*$_b$), 2.19 (s, 3H, C$_5$*Me*$_4$CH$_2$), 2.02 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.68 (d, J = 4 Hz, 3H, C$_5$*Me*$_4$CH$_2$), 1.53 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.37 (d, J = 10 Hz, 9H, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 368.5 (d, $^3J_{P-C}$ = 7 Hz, *C*═N), 143.1 (s, $C_6H_4CF_3$), 139.5 (m, $C_6H_4CF_3$), 138.7 (d, $^2J_{P-C}$ = 13 Hz, *i*-C$_6$H$_5$), 128.3 (s, *o*-C_6H_5), 127.0 (s, *m*-C_6H_5), 126.1 (s, $C_6H_4CF_3$), 125.3 (q, $^3J_{F-C}$ = 3 Hz, $C_6H_4CF_3$), 122.4 (s, *p*-C_6H_5), 109.2 (d, $^2J_{P-C}$ = 2 Hz, C_5Me$_4$CH$_2$), 97.3 (s, C_5Me$_4$CH$_2$), 93.3 (s, C_5Me$_4$CH$_2$), 87.0 (d, $^2J_{P-C}$ = 12 Hz, C_5Me$_4$CH$_2$), 83.4 (s, C_5Me$_4$CH$_2$), 36.6 (d, $^3J_{P-C}$ = 1 Hz, C$_5$Me$_4$*C*H$_2$), 13.8 (d, $^1J_{P-C}$ = 30 Hz, P*Me*$_3$), 10.4 (s, C$_5$*Me*$_4$CH$_2$), 10.0 (s, C$_5$*Me*$_4$CH$_2$), 9.5 (s, C$_5$*Me*$_4$-CH$_2$), 8.3 (d, $^3J_{P-C}$ = 2 Hz, C$_5$*Me*$_4$CH$_2$), *C*F$_3$ not observed. $^{31}P\{^1H\}$ NMR (THF-d_8): δ −33.72. ^{19}F NMR (THF-d_8): δ −59.4. IR (KBr): 3044 (m), 2974 (m), 2905 (m), 2868 (w), 1611 (m), 1568 (m), 1528 (m), 1404 (w), 1325 (s), 1308 (s), 1281 (m), 1157 (s), 1117 (s), 1065 (s), 1018 (m), 952 (m), 847 (m), 737 (m), 705 (m) cm^{-1}. MS (EI): *m*/*z* 651 (M^+). Anal. Calcd for $C_{27}H_{32}NF_3PIr$: C, 49.83; H, 4.96; N, 2.15. Found: C, 50.12; H, 5.14; N, 2.02.

[Ph(PMe$_3$)Ir(C$_5$Me$_4$CH$_2$C(C$_6$H$_4$CF$_3$)NH)]$^+$OTf$^-$ (13). To a stirred solution of **12** (70.0 mg, 0.11 mmol) in methylene chloride (5 mL) at −40 °C was added a solution of HOTf (16.1 mg, 0.11 mmol) in methylene chloride (0.5 mL). Upon warming, the clear solution turned from orange to yellow. The solvent was removed under reduced pressure. The yellow solid was redissolved in methylene chloride, filtered, concentrated, layered with pentane, and cooled to −40 °C. Compound **12**, isolated as a microcrystalline yellow solid, was rinsed with pentane (3 × 5 mL) and dried in vacuo. Yield: 53 mg, 62%. ^1H NMR (CD_2Cl_2): δ 10.74 (s, 1H, N−*H*), 8.02 (d, J = 8 Hz, 2H, C$_6$*H*$_4$-CF$_3$), 7.77 (d, J = 8 Hz, 2H, C$_6$*H*$_4$CF$_3$), 7.03 (m, 5H, C$_6$*H*$_5$), 3.99 (d, J = 20 Hz, 1H, C$_5$Me$_4$C*H*$_a$H$_b$), 3.78 (d, J = 19 Hz, 1H, C$_5$Me$_4$*H*$_a$H$_b$), 2.16 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.92 (d, $^4J_{P-H}$ = 2 Hz, 3H, C$_5$*Me*$_4$CH$_2$), 1.68 (d, $^4J_{P-H}$ = 4 Hz, 3H, C$_5$*Me*$_4$CH$_2$), 1.51 (d, $^2J_{P-H}$ = 10 Hz, 9H, P*Me*$_3$),

1.41 (s, 3H, $C_5Me_4CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 199.4 (d, $^3J_{P-C}$ = 6 Hz, *C*═N), 138.1 (s, $C_6H_4CF_3$), 137.5 (s, $C_6H_4CF_3$), 135.1 (d, $^2J_{P-C}$ = 15 Hz, *i*-C_6H_5), 134.0 (q, $^2J_{F-C}$ = 32 Hz, $C_6H_4CF_3$), 128.7 (s, *o*-C_6H_5), 128.5 (s, *m*-C_6H_5), 126.7 (q, $^3J_{F-C}$ = 4 Hz, $C_6H_4CF_3$), 123.5 (s, *p*-C_6H_5), 103.2 (d, $^2J_{P-C}$ = 3 Hz, $C_5Me_4CH_2$), 99. 7 (s, $C_5Me_4CH_2$), 95.2 (d, $^2J_{P-C}$ = 12 Hz, $C_5Me_4CH_2$), 86.8 (s, $C_5Me_4CH_2$), 85.6 (s, $C_5Me_4CH_2$), 34.5 (s, $C_5Me_4CH_2$), 15.8 (d, $^1J_{P-C}$ = 40 Hz, P*Me*$_3$), 10.3 (s, $C_5Me_4CH_2$), 9.3 (s, $C_5Me_4CH_2$), 9.2 (s, $C_5Me_4CH_2$), 8.05 (d, $^3J_{P-C}$ = 2 Hz, $C_5Me_4CH_2$), *C*F_3 not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −37.9. ^{19}F NMR (CD_2Cl_2): δ −61.5 ($C_6H_4CF_3$), −77.0 (OSO_3CF_3). IR (KBr): 3495 (m), 3186 (m), 3055 (m), 2974 (m), 2916 (m), 1619 (w), 1570 (m), 1524 (m), 1422 (m), 1325 (s), 1281 (s), 1251 (s), 1224 (m), 1162 (s), 1131 (s), 1068 (s), 1030 (m), 955 (m), 737 (m), 637 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{33}F_6IrNO_3PS$: C, 42.00; H, 4.15; N, 1.75. Found: C, 41.81; H, 4.09; N, 1.54.

[Cp*(PMe$_3$)Ir(Ph)OH$_2$]OTf (16). Complex **16** could not be isolated. A procedure similar to that reported for the synthesis of Cp*(PMe$_3$)Ir(Ph)OH$_2$]F*nH_2O was followed.[39] An NMR tube was charged with **2** (31 mg, 0.049 mmol), THF-d_8 (452 mg), and H_2O (180 μL, 200 equiv). The tube was sealed in vacuo. Spectroscopic data were recorded after 24 h at ambient temperature. ^1H NMR (THF-d_8, 500 MHz): δ 7.14 (d, *J* = 7 Hz, 2H, *o*-C_6H_5), 6.93 (t, *J* = 8 Hz, 2H, *m*-C_6H_5), 6.79 (t, *J* = 7 Hz, 1H, *p*-C_6H_5), 4.39 (s, H_2O), 1.56 (d, $^4J_{P-C}$ = 2 Hz, 15H, C_5Me_5), 1.42 (d, $^2J_{P-C}$ = 11 Hz, 9H, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 144.4 (d, $^2J_{P-C}$ = 14 Hz, *i*-C_6H_5), 137.6 (s, *o*-C_6H_5), 128.4 (s, *m*-C_6H_5), 123.0 (s, *p*-C_6H_5), 93.4 (d, $^2J_{P-C}$ = 3 Hz, C_5Me_5), 13.9 (d, $^1J_{P-C}$ = 39 Hz, P*Me*$_3$), 9.1 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −26.7. ^{19}F NMR (THF-d_8): δ −75.5.

Reaction of Iridium Carboxamides 6a−d with HCl. In a typical reaction, HCl (1 equiv, 1 M in Et_2O) was added dropwise to a stirred solution of the iridium carboxamide in benzene (3 mL) at room temperature. Upon addition, the solution turned from tan to orange, and a white precipitate formed. The orange solution was decanted, and the remaining solid was rinsed with cold toluene (3 × 1 mL). The identity of the free amides was confirmed by comparison with authentic samples using gas chromatography and ^1H NMR spectroscopy. Yield from **6a**: 10.6 mg, 73%. Yield from **6b**: 7.9 mg, 61%. Yield from **6c**: 10.5 mg, 57%. Yield from **6d**: 2.6 mg, 38%.

X-ray Structure Determinations. X-ray diffraction measurements were made on a Siemens SMART diffractometer[40] with a CCD area detector. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range 3.00° < 2θ < 45.00°. Data were integrated using the program SAINT[41] with box parameters of 1.6 × 1.6 × 0.6 to a maximum 2θ value of 52.1°. No decay correction was applied. An empirical absorption correction based on comparison of redundant and equivalent data and an ellipsoidal model of the absorption surface was applied using the program XPREP[42] or SADABS.[43] The structures were solved using methods described previously.[44] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but not refined. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Data collection and refinement parameters for **6a** and **12** can be found in Table 1, while those for **8** can be found in the Supporting Information. The positional and thermal parameters for the non-hydrogen atoms and the complete list of intramolecular distances and angles for all structurally characterizated compounds are given in the Supporting Information.[45]

6a. Crystals of **6a** were obtained by slow evaporation of a diethyl ether solution at −40 °C. On the basis of the systematic absences of *hkl*, $h + k \neq 2n$, and *h*0*l*, $l \neq 2n$, packing considerations, a statisical analysis of intensity distribution, and the successful solution and refinement of the struture, the space group was determined to be *C*2/*c* (no. 15). No decay correction was applied. An empirical absorption correction (T_{max} = 0.920, T_{min} = 0.798) was applied using XPREP.[42]

8. Crystals of **8** were obtained by slow diffusion of pentane into a concentrated solution of **8** at room temperature. On the basis of the systematic absence of *h*0*l*, $h + 1 \neq 2n$, and 0*k*0, $k \neq 2n$, the space group was uniquely determined to be $P2_1/n$ (no. 14). No decay correction was applied. An empirical absorption correction (T_{max} = 0.862, T_{min} = 0.554) was applied using SADABS.[43]

12. Crystals of **12** were obtained from a concentrated toluene solution of **12** after 7 d. On the basis of the systematic absences of *hkl*, $h + k \neq 2n$, and *h*0*l*, $l \neq 2n$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be *C*2/*c* (no. 15). No decay correction was applied. An empirical absorption correction (T_{max} = 0.862, T_{min} = 0.375) was applied using SADABS.[43]

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Supporting Information Available: ORTEP diagrams and tables giving positional and thermal parameters for the non-hydrogen atoms and the complete list of intramolecular distances and angles for Cp*(PMe$_3$)IrPh[NHC(O)$C_6H_4CH_3$] (**6a**), Cp*(PMe$_3$)Ir[N═C═C(Ph)$_2$]-Ph (**8**), and [Ph(PMe$_3$)Ir[$C_5Me_4CH_2C(C_6H_4CF_3)N$]] (**12**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) Selected intramolecular bond angles and distances for compounds **6a** and **12** can be found in Tables 2 and 3, respectively.