Cycloiridation of α,β-Unsaturated Ketones, Esters, and Acetophenone

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C−H activation of acetophenone and cyclic and acyclic α,β-unsaturated ketones or esters occurs with $[IrH_2(acetone)_2(PPh_3)_2]^+$. In the case of acyclic α,β-unsaturated ketones or esters, the β-C−H bond was activated to afford iridafuran hydrides as cyclometalation products. For cyclopentenone, a cyclic α,β-unsaturated ketone, the C−H activation affords an η^5-hydroxycyclopentadienyl iridium hydride. The activation of the ortho C−H bonds in acetophenone affords orthometalated products structurally related to the iridafuran hydrides. Plausible mechanisms are proposed for reactions in each case. In particular, the formation of iridafurans is believed to proceed by a mechanism analogous to that previously proposed for the $RuH_2(CO)(PPh_3)_3$-catalyzed Murai reaction.

Introduction

Activation of C−H bonds through chelation assistance (cyclometalation) allows the synthesis of metal hydrides that have been of great interest recently.[1] These initially generated metal hydrides can be further elaborated by reaction with unsaturated molecules to afford synthetically useful C−C coupling products.[2−10] Catalytic reactions involving cyclometalation have been reported for various metals including ruthenium,[2,3] rhodium,[4−7] cobalt,[8] zirconium,[9] iridium,[10] and palladium.[11]

We recently reported the insertion of various terminal, internal, and nitro-functionalized alkynes into iridium hydrides, where mechanistic studies have shown that different alkynes react differently even with the same iridium hydride.[12] Furthermore, we also found that these iridium hydrides are stable and highly active catalysts for the cyclization of hydroxylaryl and aminoaryl alkynes to afford isochromenes and indoles, respectively, which will be published elsewhere. These iridium hydrides were synthesized through the cyclometalation of acetophenone and enones, as briefly mentioned previously.[12a] We now present a full report of the cycloiridation of cyclic and acyclic α,β-unsaturated ketones, esters, and acetophenones using $[IrH_2(acetone)_2(PPh_3)_2]^+$.

Results and Discussion

C−H Activation of Acyclic α,β-Unsaturated Ketones and Esters. Synthesis. Iridium readily gives cyclometalation,[13] and $[IrH_2(acetone)_2(PPh_3)_2]^+$ had proven effective in a number of other catalytic reactions involving C−H activation;[14] therefore, it seems to be a reasonable choice of starting material. Indeed, reflux of $[IrH_2(acetone)_2(PPh_3)_2]^+$ (**1**) in acetone with 2 equiv of α,β-unsaturated ketones or esters for 4−14 h leads to a color change to orange or yellow. Removal of the solvent under reduced pressure, followed by addition of diethyl ether, afforded off-white to yellow precipitates, which were then filtered to give the cyclometalated

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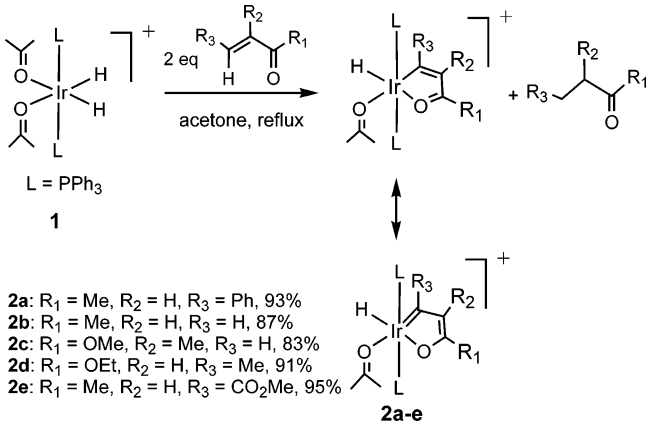
Scheme 1. Cyclometalation of α,β-Unsaturated Ketones or Esters

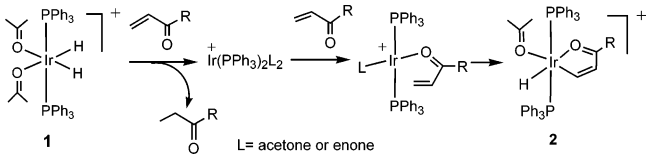


iridium hydrides **2a**−**e** in high yields (Scheme 1). These products are stable toward air and moisture in both solution and solid forms, and specially dry acetone solvent is not necessary. The same products were observed with excess (up to 6 equiv) α,β-unsaturated ketones or esters.

The cyclometalation of α,β-unsaturated ketones is relatively fast, and the reaction is complete within 5 h (**2a**,**b**), while the reaction of α,β-unsaturated ester is much slower and requires as long as 14 h for **2d**. The formation of **2e** is of interest; the organic starting material can be regarded as both an α,β-unsaturated ketone and an α,β-unsaturated ester. Since the cyclometalation of esters is much slower than that of ketones, we observed only **2e** as a result of the cyclometalation of the ketone moiety.

NMR Spectroscopy. Hydrides **2a**−**e** were fully characterized by ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H NMR spectra (acetone-d_6) of **2a**−**e** show a high-field triplet resonance at δ 20−23, assigned to the hydride due to its coupling to two equivalent phosphines. More interestingly, resonances were observed for **2b** (δ 10.22, 1H) and **2c** (δ 9.09, 1H) that appear at too low a field for assignment to vinyl protons, but are reasonably assigned to α-protons of metal carbenes. This is best explained by resonance between the two structures shown in Scheme 1, the five-membered iridacycle being essentially an iridafuran.[15−17] A contribution from the carbenoid form was also indicated by ^{13}C{^{1}H} NMR spectra of hydrides **2a**−**e**, where a low-field triplet resonance (δ 159−199) is observed for each complex. In general, the Ir-*C* of the products from α,β-unsaturated ketones (**2a**,**b**,**e**) appears to have more carbenoid character, because they give a lower field Ir-*C* resonance in ^{13}C NMR spectroscopy than those in esters **2c**,**d**. The ^{31}P{^{1}H} NMR spectrum of each of these hydrides simply shows a singlet, indicating a trans arrangement of the phosphines. In complexes **2a**, **2b**, and **2e**, a long-range coupling ($^5J_{PH}$ = 1.2 Hz) is observable between the phosphines and the C*H*$_3$ (R$_3$ group).

Scheme 2 Proposed Mechanism for the Formation of Hydrides 2a−e



Mechanistic Aspects. In the reaction between **1** and 2 equiv of *trans*-PhCH=CHC(O)Me, the saturated ketone PhCH$_2$CH$_2$C(O)Me was isolated (92%) together with complex **2a**. In a reaction of **1** with 1 equiv of *trans*-PhCH=CHC(O)Me in acetone-d_6 (70 °C, 4 h), ^{1}H NMR spectroscopy showed that the reaction mixture contains starting material **1**, product **2a**, and coproduct PhCH$_2$-CH$_2$C(O)Me in a ratio of 1:1:1, and only 50% of **1** was converted.

These results suggest that the role of the α,β-unsaturated ketone is twofold: 1 equiv acts as a hydrogen acceptor to generate the saturated ketone and an Ir(I) species, which reacts with the second equivalent of substrate to afford the cyclometalation product. If so, other hydrogen acceptors, such as *tert*-butylethylene (TBE), a hydrogen acceptor with very high driving force, should also dehydrogenate **1**. Indeed, 1 equiv of *trans*-PhCH=CHC(O)Me reacts (acetone, reflux) with a mixture of 15 equiv of TBE and **1** to afford **2a** in nearly quantitative yield.

To further understand the mechanism, we probed the reaction using 2 equiv of commercially available methyl methacrylate-d_5 [CD$_2$=C(CD$_3$)CO$_2$CH$_3$, MMA-d_5]. Both ^{1}H and ^{2}H NMR spectroscopy indicate that the organometallic product **2c**-d_5 contained >98% Ir-D. MMA-d_5 acts as a hydrogen acceptor, as indicated by the detection of free CD$_2$HCH(CD$_3$)CO$_2$CH$_3$ in ^{1}H NMR spectroscopy.

A plausible mechanism for this transformation is proposed in Scheme 2 based on these observations. Dihydride **1** is first dehydrogenated by the α,β-unsaturated ketone to generate an iridium(I) species. The carbonyl group of the α,β-unsaturated ketone coordinates to the iridium(I) to bring the β-C−H bond into the vicinity, where it may interact via agostic bonds.[18] Another possible intermediate, an η^4-π-species, was proposed in a closely related report.[17] C−H activation of this species and coordination of the solvent would lead to the formation of hydrides **2**. This mechanism is analogous to that proposed for RuH$_2$(CO)(PPh$_3$)$_3$-catalyzed C−C coupling reactions between acetophenone and alkenes (Murai-type catalysis).[1a] Syntheses of iridafurans through C−H activation have previously been reported.[16,17]

Failure of Murai-Type Catalysis. Hydrides **2a**−**e** (5 mol % loading) proved inactive as catalysts for the Murai-type coupling between the corresponding α,β-unsaturated ketones or esters and a variety of alkenes (styrene, 1-hexene, triethoxylvinylsilane, TBE, and allylbenzene). The failure is probably an indication of the high activation barrier of the final C−C coupling step, since the alkene insertion step is generally low in barrier and we did observe the isomerization of allyl-

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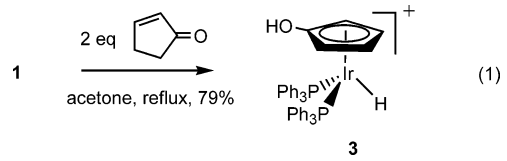
benzene to *trans*-MeCH=CHPh when allylbenzene was heated with a catalytic amount of **2a**, showing that insertion is possible. C−C reductive elimination from iridium centers is usually difficult, and only a few examples have been reported.[17,19] The barrier for this reductive elimination is expected to be even higher when it involves a carbon with carbenoid character.

C−H Activation of Cyclopentenone, a Cyclic α,β-Unsaturated Ketone. Synthesis and Spectroscopy. On the basis of the mechanism proposed in Scheme 2, the cyclometalation of enones is expected only when the carbonyl group is syn to the β-C−H bond, but not in an anti arrangement as in 2-cyclohexen-1-one.

Indeed, a different pathway was now observed. When 2 equiv of 2-cyclopenten-1-one and hydride **1** were heated under reflux in acetone for 10 h, hydride **3** was isolated (eq 1) and characterized by NMR spectroscopy and X-ray crystallography. In the ^{1}H NMR spectrum (CD_2Cl_2), a high-field triplet at δ −15.33 ($^2J_{PH}$ = 26.4 Hz) was assigned to the hydride. The CH protons in the Cp ring give two slightly broadened singlets at δ 5.01 (2H) and 4.69 (2H). Another broad singlet at δ 7.76, which disappeared upon addition of D_2O, was assigned to the −OH. Accordingly, the IR spectroscopy confirmed the presence of a hydroxyl group (ν_{OH} = 3293 cm^{-1}). In the ^{31}P{^{1}H} NMR spectrum, only a singlet was observed, indicating the phosphines were equivalent. ^{13}C{^{1}H} NMR spectroscopy showed no virtual coupling for the *ipso* aryl carbons of the phosphines, in contrast to those in hydrides **2a**−**e** (see Experimental Section). This result together with the relatively large *P*-Ir-*H* coupling constant (26.4 Hz) agrees well with the proposed structure of **3**, where the two phosphines and the hydride are cofacial.



(1)

Crystallographic Studies of Hydride 3. Single crystals of **3** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into its acetone solution. As shown in Figure 1, complex **3** has a distorted octahedral geometry assuming the Cp ring occupies three coordination positions. The pentahapticity of the functionalized Cp ring follows from the Ir(1)−C(1−5) distances ranging from 2.211 to 2.357 Å. The phosphines are in a cis arrangement (P(1)−Ir(1)−P(2) = 99.38(8)°), enforced by the Cp ring. Selected bond lengths and angles are displayed in Table 1.

This appears to be a remarkably simple synthesis of this functionalized Cp complex. Casey et al. recently studied a related ruthenium-substituted hydroxycyclopentadienyl hydride and proposed hydrogen transfer from this complex to ketones or aldehydes through a novel outer sphere concerted proton-hydride transfer mechanism.[20] In contrast, Bäckvall et al. has shown that the hydrogen transfer from the complex to an imine goes via a stepwise inner sphere mechanism.[21] A catalytic version of this type of hydrogen transfer was also reported by Bäckvall et al.[22] Complex **3**, however, fails to transfer any hydrogen to aldehydes. This is probably because (1) the Ir−H bond is stronger than the Ru−H bond and/or (2) the product from the hydrogen transfer would be an iridium(I) species and would need π-acidic ligands to be stable.

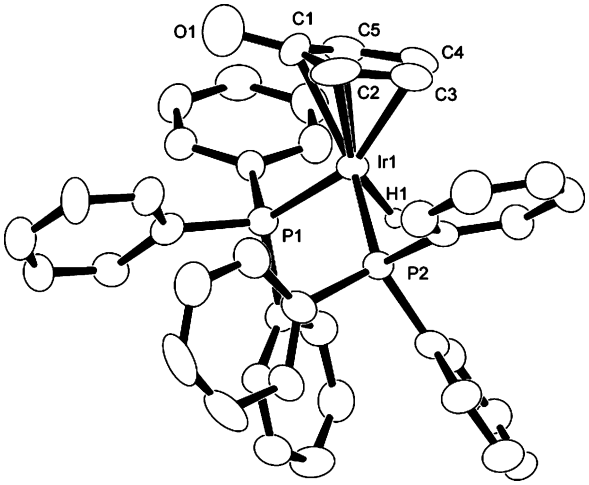


Figure 1. ORTEP diagram of the cation of **3** shown with 50% thermal ellipsoids. The hydride position is calculated.

Table 1. Selected Bond Lengths and Angles for Complex 3

Bond Lengths (Å)	
Ir(1)−P(1)	2.286(2)
Ir(1)−P(2)	2.286(2)
Ir(1)−C(1)	2.348(10)
Ir(1)−C(2)	2.314(10)
Ir(1)−C(3)	2.213(10)
Ir(1)−C(4)	2.238(8)
Ir(1)−C(5)	2.216(10)
Bond Angles (deg)	
P(1)−Ir(1)−P(2)	99.36(7)
P(1)−Ir(1)−C(1)	99.5(2)
P(1)−Ir(1)−C(2)	127.9(3)
P(1)−Ir(1)−C(3)	158.2(3)
P(1)−Ir(1)−C(4)	131.5(3)
P(1)−Ir(1)−C(5)	99.5(2)

Mechanistic Aspects. In a proposed mechanism shown in Scheme 3, the first equivalent of cyclopentenone may be hydrogenated by the dihydride **1** to generate a reactive iridium(I) species. The cyclopentenone is proposed to undergo tautomerization to form a hydroxycyclopentadiene, which probably binds to the iridium in an η^4 mode to stabilize this iridium(I) species. Activation of the allylic C−H bonds of the hydroxycyclopentadiene finally leads to the formation of **3**. In closely related examples, Crabtree et al.[23] reported the C−H activation of unfunctionalized cyclopentadiene, cyclopentene, and indene using the same iridium dihy-

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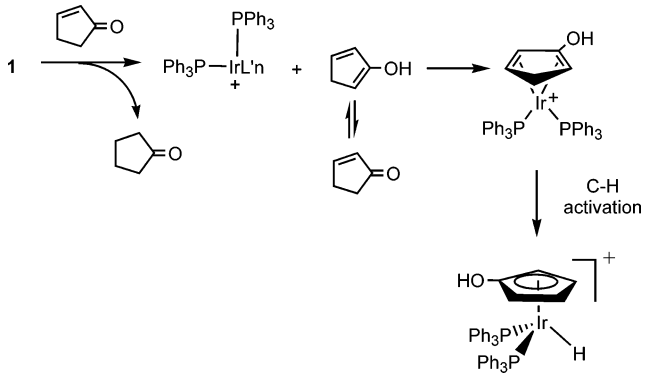
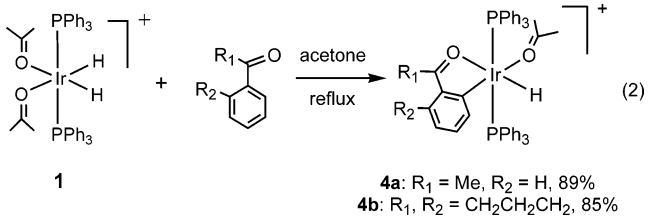
Scheme 3 Proposed Mechanism for the C−H Activation of Cyclopentenone

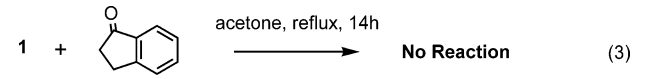


dride to give cyclopentadienyl or indenyl iridium hydrides, with aromatization being an obvious driving force.

C−H Activation of Acetophenone and Its Derivatives. Synthesis and Spectroscopy. Acetophenone, structurally related to α,β-unsaturated ketones, reacts with dihydride **1** in acetone under reflux to afford a greenish yellow solution. Upon addition of diethyl ether, **4a** was obtained as a yellow precipitate (eq 2). In contrast to the synthesis of **2a**−**e**, 1 equiv of acetophenone is enough to afford **4a** in nearly quantitative yield. Similarly, α-tetralone reacts with **1** to afford **4b** through a directly analogous synthesis. Both **4a** and **4b** are stable toward air and moisture in solid or solution form and were characterized spectroscopically. In particular, the ^{1}H NMR spectrum of **4a** gives the resonance of the hydride at δ −21.95 as a triplet ($^2J_{PH}$ = 14.6 Hz), the ^{13}C{^{1}H} NMR spectrum (acetone-d_6) shows a triplet ($^2J_{PC}$ = 8.2 Hz) at δ 149.0, assigned to the Ir-*C*, and the coordinated acetone gives resonances at δ 215.8 and 31.0. The ^{31}P{^{1}H} NMR spectrum gives a singlet. All these NMR data are similar to those observed in hydrides **2a**−**e**, except for the Ir-*C* resonance, which is simply an aryl carbon with little carbenenoid character. The stereochemistry of **4a**,**b**, together with **2a**−**e**, with H cis to the aryl or vinyl group, was assigned by analogy with the great number of Ir(III) derivatives having two high trans effect ligands mutually cis. These include a broad range of $[IrH_2(L)_2(PPh_3)_2]BF_4$ derivatives (L = acetone, 2,2′-dipyridyl, OH_2).[23,24]

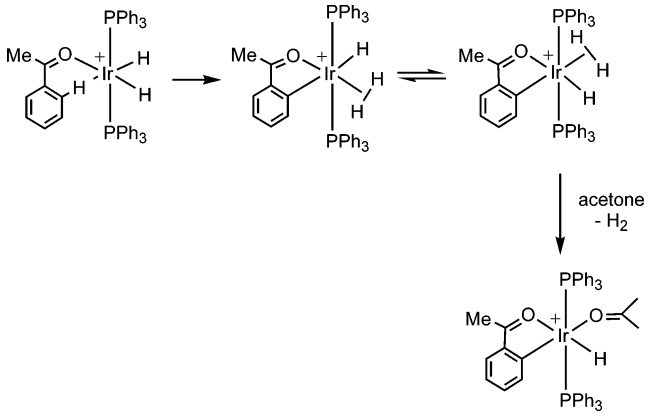


Interestingly, complex **1** failed to react with 1-indanone (acetone, reflux, 14 h), the five-membered ring analogue of α-tetralone, and only starting materials were returned (eq 3).



Since this reaction proceeds without any hydrogen acceptor, the mechanism must be different from that proposed in Scheme 3, and molecular hydrogen should be a coproduct. In a plausible mechanism (Scheme 4), the acetophenone coordinates at the carbonyl group when the acetone ligand is substituted. The carbonyl coordination guides the ortho C−H bonds to interact with the iridium, probably via a C−H agostic intermediate. C−H activation is then proposed to generate an iridium(III) aryl hydride dihydrogen species; loss of dihydrogen and substitution by acetone affords the final orthometalation product. Although this iridium(III) aryl hydride dihydrogen species was not detected, a related iridium(III) alkyl hydride dihydrogen species was previously proposed.[24] The driving force of this acceptorless C−H activation is probably the formation of a strong Ir−aryl bond that favors C−H over H−H bond metathesis.[24b]

Scheme 4 Proposed Mechanism for the Formation of 4a



Conclusions

Various iridium hydrides can be synthesized from the C−H activation of acetophenone and both cyclic and acyclic α,β-unsaturated ketones or esters. In the case of acyclic α,β-unsaturated ketones or esters, the β-C−H bond was activated to afford iridafuran hydrides as cyclometalation products, in which case 2 equiv of such α,β-unsaturated ketones are necessary. For cyclopentenone, a cyclic α,β-unsaturated ketone, the C−H activation affords a hydroxycyclopentadienyl hydride. The activation of the ortho C−H bonds in acetophenone affords orthometalated products structurally related to the iridafuran hydrides, but only 1 equiv of acetophenone is needed. Plausible mechanisms are proposed for reactions in each case. In particular, the formation of iridafurans is believed to go by a mechanism analogous to that previously proposed for the $RuH_2(CO)(PPh_3)_3$-catalyzed Murai reaction.

Experimental Section

General Considerations. All reactions were carried out under argon, although all the products proved to be air stable. Acetone was used without any treatment. All α,β-unsaturated ketones and esters, acetophenone, and *tert*-butylethylene were purchased from Aldrich and used without purification. α-Tetralone was distilled before use. ^{1}H and ^{13}C NMR spectra

(24) (a) Lee, D.-H.; Chen, J.; Faller, J. W., Crabtree, R. H. *Chem. Commun*. **2001**, 213. (b) Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242.

were recorded on Bruker 400 or 500 spectrometers. $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker 400 spectrometers with external 85% H_3PO_4 standard. Elemental analyses were performed at the Atlantic Microlab.

Synthesis of 2a (BF_4^-). To a flask charged with **1** (BF_4^-, 0.490 g, 0.532 mmol) and acetone (9 mL) was added *trans*-4-phenyl-3-buten-2-one (0.156 g, 1.067 mmol). This mixture was heated under reflux for 4 h, during which time the solution changed from light yellow to orange. The solution was then cooled to room temperature and concentrated to ca. 0.5 mL under reduced pressure, followed by slow precipitation using diethyl ether (15 mL). The bright yellow powder was filtered, washed with diethyl ether (15 mL), and dried in vacuo. Yield: 0.496 g (0.492 mmol, 93%). ^1H NMR (acetone-d_6, 400 MHz, 296 K): δ 7.59 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.40−7.52 (m, 30H, PPh_3), 7.19 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.03 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 6.50 (s, 1H, iridafuran C-*H*), 2.09 (s, 6H, overlapping with solvent signal, C*H*$_3$COC*H*$_3$), 1.90 (t, $^5J_{PH}$ = 1.5 Hz, 3H, CH_3), −20.82 (t, $^2J_{PH}$ = 14.1 Hz, Ir−H, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 211.1 (s, CO), 198.8 (t, 6.5 Hz, Ir-*C*), 145.05 (s), 135.55 (virtual t, 5.5 Hz, PPh_3), 132.8 (s), 132.4 (s), 132.2 (s), 132.0 (s), 129.7 (virtual t, 5.1 Hz, PPh_3), 128.9 (s), 128.6 (virtual t, 27.3 Hz, ipso-PPh_3), 31.09 (s, *C*H_3CO*C*H_3), 26.04(s, *C*H_3). The signal for coordinated CH_3COCH_3 may well be obscured by the solvent signal. $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 20.85 (s). Anal. Calcd for $C_{49}H_{46}BF_4IrO_2P_2$: C, 58.39; H, 4.60. Found: C, 58.03; H, 4.63. Evaporation of ether from the ethereal solution afforded $PhCH_2CH_2C(O)Me$ (72 mg, 0.486 mmol, 92%).

Complex 2b (BF_4^-). Complex **2b** was synthesized through a method directly analogous to that for **2a**, using **1** (BF_4^-, 300 mg, 0.326 mmol) and methyl vinyl ketone (68 mg, 0.971 mmol). Yield: 264 mg (0.283 mmol, 87%). ^1H NMR (acetone-d_6, 400 MHz, 296 K): δ 10.21 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ir-CH), 7.50−7.64 (m, 30 H, PPh_3), 6.15 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ir-CH=C*H*), 2.10 (s, 6H, C*H*$_3$COC*H*$_3$), 1.64 (t, $^5J_{PH}$ = 1.5 Hz, 3H, CH_3), −20.77 (t, $^2J_{PH}$ = 14.8 Hz, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 211.6 (s, CO), 184.1 (t, 8.8 Hz, Ir-C), 136.3 (s, CH), 135.3 (virtual t, 6.0 Hz, PPh_3), 132.4 (s), 130.0 (virtual t, 5.1 Hz, PPh_3), 129.8 (virtual t, 27.5 Hz, ipso-PPh_3), 31.0 (s, *C*H_3CO*C*H_3), 25.4 (s, CH_3). The signal for coordinated CH_3COCH_3 may well be obscured by the solvent signal. $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 23.79 (s). Anal. Calcd for $C_{43}H_{42}BF_4IrO_2P_2$: C, 55.43; H, 4.54. Found: C, 55.34; H, 4.67.

Complex 2c (BF_4^-). Complex **2c** was synthesized through a method directly analogous to that for **2a**, using **1** (BF_4^-, 300 mg, 0.326 mmol) and methyl methacrylate (82 mg, 0.975 mmol). Yield: 255 mg (0.270 mmol, 83%). ^1H NMR (acetone-d_6, 400 MHz, 296 K): δ 9.09 (s, 1H, Ir-CH), 7.50−7.65 (m, 30H, PPh_3), 3.45 (s, 3H, OMe), 2.11 (s, 6H, C*H*$_3$COC*H*$_3$), 1.04 (s, 3H, CH_3), −22.83 (t, $^2J_{PH}$ = 14.1 Hz, Ir-H, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 206.3 (s, CO), 182.3 (CO), 159.6 (t, 9.0 Hz, Ir−C), 135.2 (virtual t, 5.8 Hz, PPh_3), 132.3 (s, PPh_3), 130.0 (virtual t, 26.7 Hz, *ipso*-PPh_3), 129.9 (virtual t, 5.1 Hz, PPh_3), 129.3 (s), 54.3 (s, OMe), 31.0 (s, *C*H_3CO*C*H_3), 18.5 (s, CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 23.49 (s). Anal. Calcd for $C_{44}H_{44}BF_4IrO_3P_2$: C, 54.95; H, 4.61. Found: C, 54.50; H, 4.59.

Complex 2d (BF_4^-). Complex **2d** was synthesized through a method directly analogous to that for **2a**, using **1** (BF_4^-, 200 mg, 0.217 mmol) and *trans*-CHMe=$CHCO_2Et$ (42.6 mg, 0.434 mmol). Yield: 189 mg (0.197 mmol, 91%). ^1H NMR (acetone-d_6, 400 MHz, 296 K): δ 7.50−7.63 (m, 30H, PPh_3), 5.47 (s, 1H, iridafuran CH), 4.13 (q, $^3J_{HH}$ = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 2.10 (s, 6H, C*H*$_3$COC*H*$_3$), 1.67 (s, 3H, CH_3), 1.10 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), −23.58 (t, $^2J_{PH}$ = 14.3 Hz, Ir-H, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 188.1 (t, 8.4 Hz, Ir-C), 183.4 (CO), 135.6 (virtual t, 5.5 Hz, PPh_3), 132.6 (s, PPh_3), 129.9 (virtual t, 4.9 Hz, PPh_3), 128.8 (virtual t, 26.7 Hz, ipso-PPh_3), 120.7 (s), 63.6 (s, O*C*H_2CH$_3$), 36.3 (s, CH_3), 31.1 (s, *C*H_3CO*C*H_3), 14.9 (s, OCH_2CH_3). The signal for coordinated CH_3COCH_3 may well be obscured by the solvent signal. $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 20.83 (s). Anal. Calcd for $C_{45}H_{46}BF_4IrO_3P_2$: C, 55.39; H, 4.75. Found: C, 55.17; H, 4.64.

Complex 2e (SbF_6^-). Complex **2e** (SbF_6^-) was synthesized through a method directly analogous to that for **2a**, using **1** (SbF_6^-, 200 mg, 0.187 mmol) and *trans*-MeC(O)CH=$CHCO_2Me$ (42 mg, 0.375 mmol). Yield: 200 mg (0.178 mmol, 95%). ^1H NMR (acetone-d_6, 500 MHz, 296 K): δ 7.49−7.61 (m, 30H, PPh_3), 6.48 (s, 1H, iridafuran CH), 3.38 (s, 3H, OCH_3), 2.10 (s, 6H, C*H*$_3$COC*H*$_3$), 1.85 (t, $^5J_{PH}$ = 1.2 Hz, 3H, CH_3), −21.78 (t, $^2J_{PH}$ = 14.0 Hz, Ir-H, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 214.8 (s, CO), 180.3 (t, 8.0 Hz, Ir-C), 172.2 (CO), 139.8 (s, CH), 135.7 (virtual t, 5.6 Hz, PPh_3), 132.5 (s, PPh_3), 129.8 (virtual t, 5.3 Hz, PPh_3), 128.6 (virtual t, 26.4 Hz, *ipso*-PPh_3), 52.6 (s, OCH_3), 36.3 (s, CH_3), 31.0 (s, *C*H_3-CO*C*H_3), 26.6 (s, CH_3). The signal for coordinated CH_3COCH_3 may well be obscured by the solvent signal. $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 22.91 (s). Anal. Calcd for $C_{45}H_{44}F_6IrO_4P_2Sb$: C, 47.46; H, 3.89. Found: C, 47.57; H, 3.93.

Complex 3 (BF_4^-). To an acetone solution (8 mL) of **1** (BF_4^-, 370 mg, 4.01 mmol) was added 2-cyclopenten-1-one (66 mg, 8.04 mmol) via syringe. The solution was heated under reflux for 12 h, followed by concentration of the solution to ca. 0.5 mL. Diethyl ether (20 mL) was added, and a light yellow precipitate formed, which was filtered and washed with diethyl ether (10 mL). The yellow precipitate was recrystallized using acetone−ether (1:4). Yield: 0.280 g (0.316 mmol, 79%). ^1H NMR (CD_2Cl_2, 400 MHz, 296 K): δ 7.76 (br s, 1H, exchangeable with D_2O, OH), 7.22−7.40 (m, 30H, PPh_3), 5.01 (br s, 2H, Cp ring C-H), 4.69 (br s, 2H, Cp ring C-H), −15.33 (t, $^2J_{PH}$ = 26.4 Hz, 1H, Ir-H). ^{13}C NMR (CD_2Cl_2, 125.8 MHz, 300 K): δ 149.0 (s, C−OH), 134.4 (virtual t, 5.5 Hz, PPh_3), 133.2 (d, 60.0 Hz, *ipso*-PPh_3), 131.4 (s), 128.9 (virtual t, 5.3 Hz, PPh_3), 82.8 (s, Cp ring C), 70.4 (s, Cp ring C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.9 MHz, 296 K): δ 6.51 (s). IR (CH_2Cl_2 film): 3293 cm^{-1} (br, ν_{OH}), 2173 cm^{-1} (w, ν_{Ir-H}). Anal. Calcd for $C_{41}H_{36}BF_4IrOP_2$: C, 55.60; H, 4.10. Found: C, 55.72; H, 4.12.

Complex 4a (BF_4^-). Complex **4a** was synthesized through a method directly analogous to that for **2a**, using **1** (BF_4^-, 250 mg, 0.271 mmol) and acetophenone (33 mg, 0.275 mmol). Yield: 236 mg (0.241 mmol, 89%). ^1H NMR (acetone-d_6, 400 MHz, 296 K): δ 7.49 (t, $^3J_{HH}$ = 7.4 Hz, 6H, PPh_3), 7.30−7.41 (m, 24H, PPh_3), 7.17 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.10 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 6.79 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.66 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 2.10 (s, 3H, CH_3), 2.09 (s, 6H, C*H*$_3$COC*H*$_3$), −21.95 (t, $^2J_{PH}$ = 14.6 Hz, Ir-H, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 215.8 (s, CO), 149.0 (t, 8.2 Hz, Ir-C), 145.3 (s), 141.9 (s), 136.0 (s), 135.2 (virtual t, 5.5 Hz, PPh_3), 133.8 (s), 132.1 (s, PPh_3), 129.8 (virtual t, 5.0 Hz, PPh_3), 128.8 (virtual t, 26.8 Hz, ipso-PPh_3), 122.2 (s), 31.0 (s, *C*H_3CO*C*H_3), 24.5 (s, CH_3). The signal for coordinated CH_3COCH_3 may well be obscured by the solvent signal. $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 22.12 (s). Anal. Calcd for $C_{47}H_{44}BF_4IrO_2P_2$: C, 57.50; H, 4.52. Found: C, 57.26; H, 4.77.

Complex 4b (BF_4^-). Complex **4b** was synthesized through a method directly analogous to that for **2a**, using **1** (BF_4^-, 250 mg, 0.271 mmol) and α-tetralone (40 mg, 0.274 mmol). Yield: 232 mg (0.230 mmol, 85%). ^1H NMR (acetone-d_6, 400 MHz, 296 K): δ 7.48−7.55 (m, 6H, PPh_3), 7.30−7.43 (m, 24H, PPh_3), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.79 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.67 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.58 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 2.36 (t, $^3J_{HH}$ = 6.0 Hz 2H, CH_2), 2.20 (t, $^3J_{HH}$ = 6.2 Hz 2H, CH_2), 2.09 (s, 6H, C*H*$_3$COC*H*$_3$), 1.34 (quintet, $^3J_{HH}$ = 6.2 Hz, CH_2CH_2-CH_2), −22.25 (t, $^2J_{PH}$ = 14.2 Hz, Ir−H, 1H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 100.6 MHz, 296 K): δ 215.8 (s, CO), 150.0 (s), 148.6 (t, 8.1 Hz, Ir-C), 143.1 (s), 139.5 (s), 136.5 (s), 135.2 (virtual t, 5.8 Hz, PPh_3), 132.1 (s, PPh_3), 129.7 (virtual t, 5.0 Hz, PPh_3), 129.0 (virtual t, 26.9 Hz, ipso-PPh_3), 121.8 (s), 38.0

Table 2. Crystallographic Data for Complex 3

empirical formula	$C_{41}H_{36}BF_4IrP_2O$
molecular weight (g mol^{-1})	885.71
radiation, λ (Å)	Mo Kα (monochr), 0.71073
T (°C)	−90
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	14.5538(6)
b (Å)	14.2109(7)
c (Å)	17.5636(8)
β (deg)	101.834(3)
V (Å^3)	3555.3(3)
Z	4
D_{calcd} (g cm^{-3})	1.655
μ (Mo Kα) (cm^{-1})	39.1
cryst size (mm)	0.07 × 0.12 × 0.12
total, unique no. of rflns	21 196, 8382
R_{int}	0.058
no. of observations used	4650
no. of variables	417
R^a, $R_w{}^b$	0.051, 0.060
GOF	1.39
min., max. resid dens (e Å^{-3})	−2.11, 4.35

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$

(s, CH_2), 31.0 (s, CH_3COCH_3), 29.2 (s, CH_2), 24.2 (s, CH_2). The signal for coordinated CH_3COCH_3 may well be obscured by the solvent signal. $^{31}P\{^1H\}$ NMR (acetone-d_6, 161.9 MHz, 296 K): δ 21.84 (s). Anal. Calcd for $C_{49}H_{46}BF_4IrO_2P_2$: C, 58.39; H, 4.60. Found: C, 58.46; H, 4.59.

Crystallography. Single crystals of **3** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into an acetone solution of **3**. X-ray diffraction for single crystals was measured on a Nonius Kappa CCD diffractometer. Data collection was carried out at −90 °C. The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms in the cation were refined anisotropically, while owing to disorder, the tetrafluoroborate atoms were refined isotropically as a rigid group. Hydrogen atoms (with the exception of the hydroxyl hydrogen atom, which could not be located) were included in calculated positions but not refined. The Ir−H distance was fixed at 1.60 Å and the vector oriented on the basis of residual density observed in the difference Fourier. The crystal parameters and other experimental details of the data collection are summarized in Table 2.

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Supporting Information Available: Tables providing atomic positional parameters, bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions for complex **3**. A CIF file is also available. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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