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Iridium Complexes Containing Four and Five Ir−C Bonds: Alkyl-Bis(alkenyl)-Alkynyl and Carbonyl-Alkyl-Bis(alkenyl)-Alkynyl Iridium

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Iridium complexes containing four Ir−C σ-bonds, *cis,cis*-$[Ir(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}CR)(PPh_3)_2]^+$ (**2**, R = *p*-$C_6H_4CH_3$ (**a**), cyclohex-1-enyl (**b**), $C(CH_3){=}CH_2$ (**c**)), are obtained from the reactions of *cis,trans*-$[Ir(CH_3)(-CH{=}CHPPh_3)_2(CO)(PPh_3)_2]^{2+}$ (**1**) with $HC{\equiv}CR$ in the presence of Me_3NO. One of the two PPh_3 in **2** is readily replaced to give complexes containing five Ir−C σ-bonds, *cis*-$[Ir(CO)(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}CR)(PPh_3)]^+$ (**3**, R = *p*-$C_6H_4CH_3$ (**a**), cyclohex-1-enyl (**b**), $C(CH_3){=}CH_2$ (**c**)). Complexes **3** are also obtained from the reactions of **2** with $CHCl_3$ in the presence of OH^- in H_2O. The reaction of *trans*-$[IrBr(CH_3)(-CH{=}CHPPh_3)_2(CO)(PPh_3)]^+$ (**4**) with Ag^+ and 4-ethynyltoluene in the presence of NEt_3 gives a mixture of geometric isomers, **3a** (where the CH_3 group is *cis* to $-C{\equiv}C$-*p*-$C_6H_4CH_3$ ligand) and **3′a** (where the CH_3 group is *trans* to $-C{\equiv}C$-*p*-$C_6H_4CH_3$ ligand). Addition of aqueous HCl to **2a** or **3a** causes a new carbon−carbon bond formation between the methyl and alkynyl groups to produce *cis*-$CH_3CH{=}CH$-*p*-$C_6H_4CH_3$ (**5**) exclusively and $[IrCl_2(-CH{=}CHPPh_3)_2(PPh_3)(L)]^+$ (L = PPh_3, CO).

Introduction

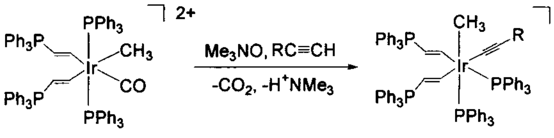
Metal-hydrocarbyls such as metal-alkyls, metal-alkenyls, and metal-alkynyls are useful precursors and key intermediates in C−C bond forming reactions.[1] Organometallic compounds with more than two hydrocarbyl ligands undergo C−C bond forming reactions between the hydrocarbyl ligands under appropriate reaction conditions.[2]

We recently reported several iridium complexes containing various hydrocarbyl ligands, some of which undergo C−C bond forming reactions between the hydrocarbyl ligands to produce interesting conjugated olefins.[3,4]

In this paper, we wish to report the synthesis of alkyl-bis(alkenyl)-alkynyl-iridium(III) compounds containing four and five Ir−C σ-bonds and their reactions with HCl to produce *cis*-olefin selectively.

Results and Discussion

Iridium(III) complexes containing four Ir−C σ-bonds, alkyl-bis(alkenyl)-alkynyl-iridium *cis,cis*-$[Ir(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}CR)(PPh_3)_2]^+$ (**2**), have been prepared from the reactions of *cis,trans*-$[Ir(CH_3)(-CH{=}CHPPh_3)_2(CO)(PPh_3)_2]^{2+}$ (**1**)[5] with $HC{\equiv}CR$ in the presence of Me_3NO (eq 1).[6,7]



(1)

1 2

R = *p*-$C_6H_4CH_3$ (**a**), cyclohex-1-enyl (**b**), $C(CH_3){=}CH_2$ (**c**)

It is somewhat surprising to obtain the *cis*-$(PPh_3)_2$ complexes **2** in eq 1. *cis*-$Ir(PPh_3)_2$ complexes are formed

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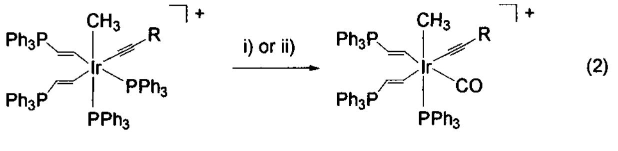
when RH (R = H, Cl) is oxidatively added to the *trans*-Ir(A)(CO)(PPh_3)$_2$ (A = halogen, RCN, $OClO_3$, carborane, −C≡CR) as the kinetic products.[8] The PPh_3 groups in Vaska's complex bend back to give the *cis*-Ir(PPh_3)$_2$ complex in the reaction with a bulky ligand such as a C_{70} group.[9] Complexes **2** may not be the kinetic products since no isomerization reaction of **2** (to the *trans*-(PPh_3)$_2$ complex) has been observed even at 70 °C. The abstraction of the CO ligand from **1** by Me_3NO (eq 1) would give a five-coordinate intermediate ($[Ir(CH_3)(-CH{=}CHPPh_3)_2(PPh_3)_2]^{2+}$) initially in a square pyramidal geometry that may undergo an intramolecular rearrangement probably to trigonal bipyramidal geometry before the alkynyl group (−C≡CR) then coordinates to the metal to give the *cis*-(PPh_3)$_2$ complexes **2**.

Spectral (^{1}H and ^{31}P NMR) data strongly support the *cis*-configuration between the two PPh_3 ligands and between the two CH=CHPPh$_3$ groups, respectively. Assignments of ^{1}H NMR signals due to Ir−C*H*=C*H*PPh$_3$ of **2** are rather straightforward by comparing the data with those for the related and well-characterized complexes containing Ir−CH=CHPPh$_3$,[10] *cis*-Ir(−CH=CHPPh$_3$)$_2$,[5] and *cis*-Re(−CH=CHPPh$_3$)$_2$.[11] The ^{1}H NMR spectra clearly show two sets of signals at δ 10.67−10.71 (dddd) and 10.00−10.06 (dddd) due to the α protons of the two Ir−C*H*=CHPPh$_3$ in **2a**−**c** (see Experimental Section for detailed coupling data). One of the β protons in the two alkenyl groups (Ir−$CH_{\alpha'}$=$CH_{\beta'}$PPh$_3$, *trans* to $P_{a'}Ph_3$) is seen at δ 5.96−6.00 (dd), while the other β proton (Ir−CH_α=CH_βPPh$_3$, *trans* to −C≡CR) seems to be obscured by large signals due to the phenyl protons in the region δ 6.7−8.0. The two PPh_3 groups in **2a**−**c** do not seem to be *trans* to each other since the Ir−C*H*$_3$ is seen as a doublet of doublets at δ 0.56−0.63 due to the two nonequivalent *P*Ph$_3$ ligands. (The Ir−C*H*$_3$ in **1** is seen as a triplet.[5])

The ^{31}P NMR spectra of **2a**−**c** show four signals, two for the nonequivalent CH=CH*P*Ph$_3$ groups (at δ 11.52−11.59 (dd) and 9.36−9.59 (t)) and two for the nonequivalent *P*Ph$_3$ ligands (at δ −8.67 to −9.34 (ddd) and −11.36 to −11.87 (ddd)) with coupling constants ca. 39 Hz between the *trans* CH=CH*P*Ph$_3$ and *P*Ph$_3$ and ca. 16 Hz between the two *cis* *P*Ph$_3$ ligands, respectively (see Experimental Section for detailed spectral data). The *trans* relationship between CH_3 and P_aPh_3 and between the alkenyl group ($CH_{\alpha'}$=$CH_{\beta'}$PPh$_3$) and $P_{a'}Ph_3$ is apparent according to the ^{13}C NMR spectra of **2a**−**c** that show a doublet at δ −0.13−0.14 for Ir−*C*H$_3$ with the large coupling (79−85 Hz due to the *trans* P_aPh_3) and another doublet at δ 193.9−194.1 for Ir−$CH_{\alpha'}$=$CH_{\beta'}$-PPh$_3$ with the large coupling (97−115 Hz due to the *trans* $P_{a'}Ph_3$) (see Experimental Section). The presence of the alkynyl ligands in **2a**−**c** is also unambiguously confirmed by the signals due to R groups of Ir−C≡CR in the ^{1}H NMR spectra and the absorption due to ν(C≡C) in the range 2080−2090 cm^{-1} in the IR spectra.

The PPh_3 *cis* to the CH_3 ligand of **2** is readily replaced by CO to give the metal complexes containing five Ir−C σ-bonds, *cis*-$[Ir(CO)(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}CR)(PPh_3)]^+$ (**3**), at room temperature under ambient pressure of CO (eq 2), while such replacement does not occur for the *trans*-bis(PPh_3)$_2$ complex **1** even under high pressure of CO. This facile replacement of PPh_3 by CO may be due to the two bulky PPh_3 being *cis* in **2**. These iridium complexes **3** containing five Ir−C σ-bonds are stable in the solid state and in solution for several days. To the best of our knowledge, no example has been reported thus far for an iridium complex with five Ir−C σ-bonds.



2 **3**

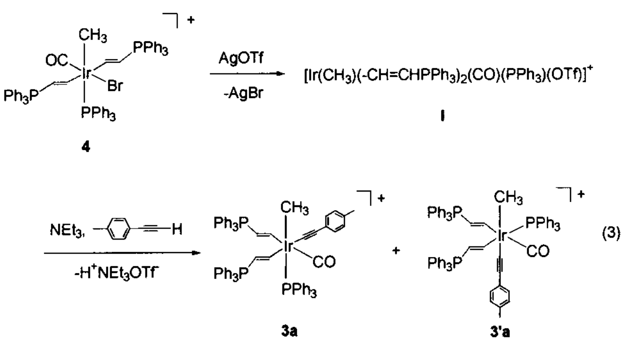
R = *p*-$C_6H_4CH_3$ (**a**), cyclohex-1-enyl (**b**), $C(CH_3){=}CH_2$ (**c**)

i) CO/-PPh$_3$

ii) CHCl$_3$, NaOH in H$_2$O/-PPh$_3$, -NaCl

Complexes **3** are also obtained in high yields from the reactions of **2** in CHCl$_3$ and OH$^-$ in H$_2$O at 50 °C (eq 2) (see Experimental Section). It is well-known that metal carbonyls are obtained by the hydrolysis of metal carbenes (M = CCl$_2$) generated by reactions of metals with CHCl$_3$ in the presence of OH$^-$ in H$_2$O.[12]

The ^{31}P NMR spectra of **3a**−**c** show two doublets for the two nonequivalent CH=CH*P*Ph$_3$ (at δ 14.49−14.67 and 13.54−13.69) and one doublet of doublets for the *P*Ph$_3$ (at δ −7.98 to −8.18). The ^{1}H NMR spectra of **3a**−**c** show two sets of signals (ddd) due to the α protons of the two Ir−C*H*=CHPPh$_3$ groups (as those observed for **2a**−**c**), suggesting that the two CH=CHPPh$_3$ groups are *cis* to each other. The doublets at δ −10.8 to −11.3 due to Ir−*C*H$_3$ with large *J*(CH$_3$−*P*Ph$_3$) = ca. 73 Hz indicate that the CH$_3$ and PPh$_3$ groups are *trans* to each other in **3a**−**c**.



4 **I** **3a** **3'a**

Complex **3a** can be also prepared from the reaction of *trans*-$[IrBr(CH_3)(-CH{=}CHPPh_3)_2(CO)(PPh_3)]^+$ (**4**)[5]

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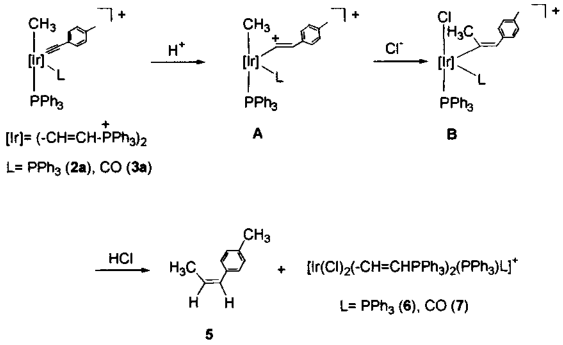
Scheme 1



with Ag^+ and 4-ethynyltoluene in the presence of NEt_3 according to eq 3. The isomer **3′a** is simultaneously produced. A mixture of many geometric isomers seems to be produced from the reaction of intermediates **I** (mixture of geometric isomers) with 1-ethynylcyclohexene and 2-methyl-1-buten-3-yne, respectively, in the presence of NEt_3, while only two isomers (**3a** and **3′a**) are obtained from the reaction of **I** with 4-ethynyltoluene in the presence of NEt_3. The two geometric isomers **3a** and **3′a** have been successfully separated by column chromatography on alumina.

Detailed spectral data (^1H, ^{13}C, and ^{31}P NMR) clearly suggest the structure of **3′a** having the CH_3 ligand *trans* to the alkynyl ligand as shown in eq 3. The *trans* relationship between PPh_3 and $CH_\alpha{=}CH_\beta PPh_3$ groups (see Experimental Section) is apparent according to ^{31}P NMR of **3′a**, which shows two doublets for the two nonequivalent $CH{=}CH\mathit{P}Ph_3$ groups, one of which shows a relatively large coupling (39.1 Hz) due to the *trans* $\mathit{P}Ph_3$ at δ 14.48, while the other shows a small coupling (3.9 Hz) due to the *cis* $\mathit{P}Ph_3$ at δ 14.02. The ^{13}C NMR spectrum of **3′a** shows a doublet at δ −17.4 due to Ir−$\mathit{C}H_3$ with a small coupling (4.0 Hz due to *cis* PPh_3) and a doublet at δ 187.0 due to Ir−$\mathit{C}H_\alpha{=}CH_\beta PPh_3$ with a large coupling (100.7 Hz due to *trans* PPh_3), which strongly indicates that the CH_3 ligand is not *trans* to PPh_3 any more and the alkenyl group ($CH_\alpha{=}CH_\beta PPh_3$) is *trans* to PPh_3 in complex **3′a**. The signal due to Ir−*C*O of **3′a** is a doublet of doublets due to *cis* $\mathit{P}Ph_3$ and *trans* $CH_{\alpha'}{=}CH_{\beta'}\mathit{P}Ph_3$ as observed for **3a**. The signal due to Ir−*C*≡CR of **3′a** is a doublet due to the *cis* $\mathit{P}Ph_3$, while that of **3a** is a triplet due to the *cis* $\mathit{P}Ph_3$ and *trans* $CH_\alpha{=}CH_\beta\mathit{P}Ph_3$. These observations show the CO ligand *trans* to the $CH_{\alpha'}{=}CH_{\beta'}PPh_3$ group and the alkynyl group *trans* to the CH_3 ligand. Addition of aqueous HCl to **2a** or **3a** results in a new carbon−carbon bond formation between the methyl and alkynyl groups to produce *cis*-$CH_3CH{=}CH(-\mathit{p}\text{-}C_6H_4CH_3)$ (**5**) exclusively and $[Ir(Cl)_2(-CH{=}CHPPh_3)_2(PPh_3)(L)]^+$ (L = PPh_3, CO) (see Scheme 1). Formation of **5** may be understood by the electrophilic attack of H^+ on the β carbon of the alkynyl ligand of **2a** or **3a** since it is well known that the proton attacks the electron-rich β carbon of an alkynyl ligand.[2a,13] The intermediate **A** then undergoes CH_3 group migration to the α carbon of the vinyl group to give another intermediate, **B**, which exclusively yields the *cis*-olefin, *cis*-$CH_3CH{=}CH(\mathit{p}\text{-}C_6H_4CH_3)$ (**5**). The C−C bond forming reaction between CH_3 and $-C{\equiv}C(\mathit{p}\text{-}C_6H_4\text{-}CH_3)$ ligands has not been observed in the reaction of **3′a** initiated by H^+ probably because those two ligands are *trans* to each other in **3′a**. Reactions of complexes **2b**/**3b** and **2c**/**3c** containing nonaromatic alkynyl ligands with H^+ give organic mixtures containing small amounts of expected *cis*-olefin and mixtures of unknown iridium complexes.

It is somewhat surprising not to observe C−C bond forming reactions involving the alkenyl ligand, Ir−$\mathit{CH}{=}\mathit{CHPPh}_3$, of **2a**, **3a**, and **3′a** in the reactions with H^+ since the ammonium ylide, Ir−$\mathit{CH}{=}\mathit{CHNEt}_3$, is involved in the C−C bond forming reactions between the hydrocarbyl ligands of $[(CO)(PPh_3)_2Ir(CH_3)(-C{\equiv}CR)(-CH{=}CHNEt_3)]^+$ initiated by H^+ to give 1,3-diene $[Et_3N-CH{=}CH-C(CH_3){=}CHR]^+$.[4] This inertness of the Ir−C bond of Ir−CH=$CHPPh_3$ may be understood by previous studies that predict the M−C bonds such as $\boldsymbol{M}^+{=}\mathit{C}H-CH{=}PR_3$ and $M-\mathit{C}H{=}CH-{}^+PR_3$ would be very much stabilized by the neighboring phosphonium ylides through various resonance forms.[11,14]

Complexes **6** and **7** have been unambiguously characterized by spectral data (^1H, ^{13}C, and ^{31}P NMR) by comparing the data with those for $[Ir(Br)_2(-CH{=}CHPPh_3)_2(CO)(PPh_3)]^+$.[5]

We have demonstrated ways of introducing alkynyl ligands to a metal and initiating carbon−carbon bond formation between the alkynyl and other hydrocarbyl ligands to produce *cis*-alkenes selectively. We hope these results to be useful information that may be further utilized in synthetic organic chemistry.

Experimental Section

General Information. A standard vacuum system and Schlenk type glassware were used in most of the experimental procedures in handling metal compounds, although most of the compounds seem to be stable enough to be handled without much precautions in air.

NMR spectra were recorded on either a Varian Gemini 300 or 500 spectrometer (^1H, 300 or 500 MHz; ^{13}C, 75.5 or 125.7 MHz; ^{31}P, 81.0 or 121.7 MHz). IR spectra were obtained on a Nicolet 205 spectrophotometer. Gas chromatography/mass spectra were determined by Hewlett-Packard HP5890A and VG-trio 2000 instruments. Elemental analyses were carried out by a Carlo Erba EA 1108 CHNS-O analyzer at the Organic Chemistry Research Center, Sogang University.

***cis,cis*-$\mathbf{[Ir(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}CR)(PPh_3)_2]OTf}$ (2, R = *p*-$\mathbf{C_6H_4CH_3}$ (a), cyclohex-1-enyl (b), $\mathbf{C(CH_3){=}CH_2}$ (c)).** Complexes **2a**−**c** were prepared in the same manner as described below for **2a**. The reaction mixture of *cis,trans*-$[Ir(CH_3)(-CH{=}CHPPh_3)_2(CO)(PPh_3)_2](OTf)_2$ (**1**)[5] (0.2 g, 0.13 mmol) and $HC{\equiv}C(\mathit{p}\text{-}C_6H_4CH_3)$ (0.023 mL, 0.18 mmol) in $CHCl_3$ (15 mL) was stirred in the presence of Me_3NO (0.02 g, 0.27 mmol) at 25 °C for 3 h under nitrogen before the colorless solution turned reddish brown. Excess Me_3NO and $[HNMe_3]OTf$ were removed by extraction with H_2O (3 × 10 mL). Addition of *n*-pentane (10 mL) to the $CHCl_3$ solution resulted in precipitation of beige microcrystals of **2a**, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.18 g and 93% based on **2a**.

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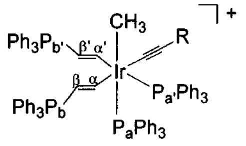


2

R= *p*-C$_6$H$_4$CH$_3$ (**a**), cyclohex-1-enyl (**b**), C(CH$_3$)=CH$_2$ (**c**)

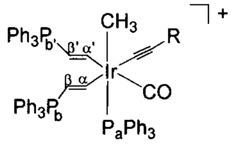
***cis,cis*-[Ir(CH$_3$)(−CH=CHPPh$_3$)$_2$(−C≡C(*p*-C$_6$H$_4$CH$_3$))(PPh$_3$)$_2$]OTf (2a).** ^{1}H NMR (500 MHz, CDCl$_3$): δ 10.70 (dddd, *J*(H$_\alpha$−P$_b$) = 33.3 Hz, *J*(H$_\alpha$−H$_\beta$) = 18.0 Hz, *J*(H$_\alpha$−P$_a$) = 8.7 Hz, *J*(H$_\alpha$−P$_{a'}$) = 7.0 Hz, H_α), δ 10.00 (dddd, *J*(H$_{\alpha'}$−P$_{b'}$) = 29.4 Hz, *J*(H$_{\alpha'}$−H$_{\beta'}$) = 17.0 Hz, *J*(H$_{\alpha'}$−P$_{a'}$) = 4.0 Hz, *J*(H$_{\alpha'}$−P$_a$) = 2.0 Hz, $H_{\alpha'}$), δ 6.00 (dd, *J*(H$_\beta$−P$_b$) = 38.5 Hz, *J*(H$_\alpha$−H$_\beta$) = 18.0 Hz, H_β), δ 2.31 (s, *p*-C$_6$H$_4$CH_3), δ 0.62 (dd, *J*(H−P$_a$) = 8.3 Hz, *J*(H−P$_{a'}$) = 5.0 Hz, Ir−CH_3), δ 6.7−8.0 ($H_{\beta'}$ and the phenyl protons of PPh$_3$). The pair of signals for H$_\alpha$−H$_\beta$ and H$_{\alpha'}$−H$_{\beta'}$ was assigned by decoupling experiments. ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 204.5 (br s, C_α), δ 193.9 (dm, *J*(C$_{\alpha'}$−P$_{a'}$) = 97.0 Hz, $C_{\alpha'}$), δ 109.3 (br s, Ir−C≡*C*), δ 103.6 (d, *J*(C$_{\beta'}$−P$_{b'}$) = 69.4 Hz, $C_{\beta'}$), δ 97.1 (d, *J*(C$_\beta$−P$_b$) = 73.8 Hz, C_β), δ 77.5 (m, Ir−*C*≡C), δ 21.1 (s, *p*-C$_6$H$_4$*C*H$_3$), δ 0.14 (d, *J*(C−P$_a$) = 79.1 Hz, Ir−*C*H$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 10.70 → 204.5; δ 10.00 → 193.9; δ 6.00 → 97.1; δ 2.31 → 21.1; δ 0.62 → 0.14. ^{31}P NMR (81.0 MHz, CDCl$_3$): δ 11.59 (dd, *J*(P$_{a'}$−P$_{b'}$) = 39.0 Hz, *J*(P$_a$−P$_{b'}$) = 5.5 Hz, $P_{b'}$), δ 9.59 (t, *J*(P$_a$−P$_b$) and *J*(P$_{a'}$−P$_b$) = 2.5 Hz, P_b), δ −8.71 (ddd, *J*(P$_{a'}$−P$_{b'}$) = 39.0 Hz, *J*(P$_a$−P$_{a'}$) = 16.6 Hz, *J*(P$_{a'}$−P$_b$) = 2.5 Hz, $P_{a'}$), δ −11.37 (ddd, *J*(P$_a$−P$_{a'}$) = 16.6 Hz, *J*(P$_a$−P$_{b'}$) = 5.5 Hz, *J*(P$_a$−P$_b$) = 2.5 Hz, P_a). IR (KBr, cm^{-1}): 2088 (s, $\nu_{C≡C}$), 1271, 1150, and 1035 (br s, due to uncoordinated triflate[15]). Anal. Calcd for IrP$_4$O$_3$S$_1$F$_3$C$_{87}$H$_{74}$: C, 66.44; H, 4.74. Found: C, 66.72; H, 4.77.

***cis,cis*-[Ir(CH$_3$)(−CH=CHPPh$_3$)$_2$(−C≡C$\overline{\text{C=CH(CH}_2\text{)}_3\text{C}}H_2$)(PPh$_3$)$_2$]OTf (2b).** ^{1}H NMR (500 MHz, CDCl$_3$): δ 10.71 (dddd, *J* = 33.3, 18.0, 8.7, 7.0 Hz, H_α,), δ 10.06 (dddd, *J* = 30.0, 17.0, 4.0, 2.0 Hz, $H_{\alpha'}$), δ 6.00 (dd, *J* = 38.3, 18.0 Hz, H_β), δ 5.57, 2.12, 1.96, 1.57 (Ir−C≡C$\overline{\text{C=C}H\text{(C}H_2\text{)}_3\text{C}}H_2$), δ 0.63 (dd, Ir−CH_3, *J* = 8.0, 5.0 Hz). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 205.2 (br s, C_α), δ 194.1 (dm, *J* = 100.5 Hz, $C_{\alpha'}$), δ 111.6 (br s, Ir−C≡*C*), δ 103.5 (d, *J* = 72.0 Hz, $C_{\beta'}$), δ 96.8 (d, *J* = 74.4 Hz, C_β), δ 77.5 (m, Ir−*C*≡C), δ 126.1, 124.3, 30.9, 25.5, 20.0, 22.3 (Ir−C≡C$\overline{C\text{=CH(CH}_2\text{)}_3C}H_2$), δ 0.01 (d, *J* = 81.2 Hz, Ir−*C*H$_3$). ^{31}P NMR (81.0 MHz, CDCl$_3$): δ 11.52 (dd, *J* = 39.1, 5.5 Hz, $P_{b'}$), δ 9.36 (t, *J* = 2.4 Hz, P_b), δ −9.34 (ddd, *J* = 39.1, 16.5, 2.4 Hz, $P_{a'}$), δ −11.87 (ddd, *J* = 16.5, 5.5, 2.4 Hz, P_a). IR (KBr, cm^{-1}): 2080 (s, $\nu_{C≡C}$), 1269, 1149, and 1031.[15] Anal. Calcd for IrP$_4$O$_3$S$_1$F$_3$C$_{86}$H$_{76}$: C, 66.10; H, 4.90. Found: C, 66.15; H, 4.89.

***cis,cis*-[Ir(CH$_3$)(−CH=CHPPh$_3$)$_2$(−C≡C−C(CH$_3$)=CH$_2$)(PPh$_3$)$_2$]OTf (2c).** ^{1}H NMR (500 MHz, CDCl$_3$): δ 10.67 (dddd, *J* = 33.1, 18.0, 8.5, 6.5 Hz, H_α), δ 10.00 (dddd, *J* = 29.6, 16.9, 4.2, 2.0 Hz, $H_{\alpha'}$), δ 5.96 (dd, *J* = 38.3, 18.0 Hz, H_β), δ 4.68, 1.66 (Ir−C≡C−C(CH_3)=CH_2), δ 0.56 (dd, *J* = 8.3, 5.0 Hz, Ir−CH_3). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 204.7 (br s, C_α), δ 194.0 (dm, *J* = 115.5 Hz, $C_{\alpha'}$), δ 111.3 (br s, Ir−C≡*C*), δ 103.6 (d, *J* = 71.4 Hz, $C_{\beta'}$), δ 97.0 (d, *J* = 71.4 Hz, C_β), δ 77.6 (m, Ir−*C*≡C), δ 113.3, 25.2 (s, Ir−C≡C−C(*C*H$_3$)=*C*H$_2$), δ −0.13 (d, *J* = 84.9 Hz, Ir-*C*H$_3$). ^{31}P NMR (81.0 MHz, CDCl$_3$): δ 11.58 (dd, *J* = 39.1, 5.5 Hz, $P_{b'}$), δ 9.49 (t, *J* = 2.5 Hz, P_b), δ −8.67 (ddd, *J* = 39.1, 16.5, 2.5 Hz, $P_{a'}$), δ −11.36 (ddd, *J* = 16.5, 5.5, 2.5 Hz, P_a). IR (KBr, cm^{-1}): 2088 (s, $\nu_{C≡C}$), 1272, 1154, and 1031.[15] Anal. Calcd for IrP$_4$O$_3$S$_1$F$_3$C$_{83}$H$_{72}$: C, 65.47; H, 4.77. Found: C, 65.35; H, 4.64.

***cis*-[Ir(CO)(CH$_3$)(−CH=CHPPh$_3$)$_2$(−C≡CR)(PPh$_3$)]OTf (3, R = *p*-C$_6$H$_4$CH$_3$ (a), cyclohex-1-enyl (b), C(CH$_3$)=CH$_2$ (c)). Method I.** Complexes **3a**−**c** were prepared in the same manner as described below for **3a**. A solution of **2a** (0.2 g, 0.13 mmol) in CHCl$_3$ (10 mL) was stirred at room temperature for 6 h under CO (1 atm). Beige microcrystals of **3a** were precipitated by addition of diethyl ether (20 mL) to the solution, collected by filtration, washed with *n*-pentane (2 × 20 mL), and dried under vacuum. The yield was 0.16 g and 94% based on **3a**.

Method II. Complexes **3a**−**c** were also obtained in the same manner as described below for **3a**. An aqueous solution of NaOH (1.0 g, 25 mmol) in H$_2$O (5 mL) was added to a solution of **2a** (0.2 g, 0.13 mmol) in CHCl$_3$ (10 mL). After being stirred at 50 °C for 12 h, the CHCl$_3$ layer of the reaction mixture was separated. Addition of diethyl ether to the CHCl$_3$ solution resulted in beige microcrystals of **3a**, which were collected by filtration, washed with *n*-pentane (2 × 20 mL), and dried under vacuum. The yield was 0.15 g and 88% based on **3a**.



3

R= *p*-C$_6$H$_4$CH$_3$ (**a**), cyclohex-1-enyl (**b**), C(CH$_3$)=CH$_2$ (**c**)

***cis*-[Ir(CO)(CH$_3$)(−CH=CHPPh$_3$)$_2$(−C≡C(*p*-C$_6$H$_4$CH$_3$))(PPh$_3$)]OTf (3a).** ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.12 (ddd, *J*(H$_\alpha$−P$_b$) = 33.0 Hz, *J*(H$_\alpha$−H$_\beta$) = 18.5 Hz, *J*(H$_\alpha$−P$_a$) = 3.0 Hz, H_α), δ 9.07 (ddd, *J*(H$_{\alpha'}$−P$_{b'}$) = 32.4 Hz, *J*(H$_{\alpha'}$−H$_{\beta'}$) = 18.0 Hz, *J*(H$_{\alpha'}$−P$_a$) = 6.5 Hz, $H_{\alpha'}$), δ 6.19 (ddd, *J*(H$_\beta$−P$_b$) = 37.5 Hz, *J*(H$_\alpha$−H$_\beta$) = 18.5 Hz, *J*(H$_\beta$−P$_a$) = 1.0 Hz, H_β), δ 2.30 (s, *p*-C$_6$H$_4$CH_3), δ 0.61 (d, *J*(H−P$_a$) = 5.5 Hz, Ir−CH_3), δ 7.0−8.0 ($H_{\beta'}$ and the phenyl protons of PPh$_3$). The pair of signals for H$_\alpha$−H$_\beta$ and H$_{\alpha'}$−H$_{\beta'}$ was assigned by decoupling experiments. ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 192.7 (t, *J*(C−P) = 10.0 Hz, *J*(C−P$_a$) = 10.0 Hz) and 192.5 (t, *J*(C−P) = 6.0 Hz, *J*(C−P$_a$) = 6.0 Hz) (C_α and $C_{\alpha'}$), 176.6 (dd, *J*(C−P$_{b'}$) = 12.6 Hz, *J*(C−P$_a$) = 5.0 Hz, Ir−*C*O), δ 107.1 (dd, *J*(C$_{\beta'}$−P$_{b'}$) = 70.0 Hz, *J*(C$_{\beta'}$−P$_a$) = 5.0 Hz, $C_{\beta'}$), δ 106.4 (s, Ir−C≡*C*), δ 104.8 (dd, *J*(C$_\beta$−P$_b$) = 70.5 Hz, *J*(C$_\beta$−P$_a$) = 2.5 Hz, C_β), δ 95.20 (td, *J*(C−P$_a$) = 12.0 Hz, *J*(C−P$_{b'}$) =12.0 Hz, *J*(C−P$_b$) = 2.5 Hz, Ir−*C*≡C), δ 21.0 (s, *p*-C$_6$H$_4$*C*H$_3$), δ −11.3 (d, *J*(C−P$_a$) = 73.0 Hz, Ir−*C*H$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 9.12, 9.07 → 192.7, 192.5; δ 6.19 → 104.8; δ 2.30 → 21.0; δ 0.61 → −11.3. ^{31}P NMR (81.0 MHz, CDCl$_3$): δ 14.67 (d, *J*(P−P$_a$) = 4.0 Hz) and 13.64 (d, *J*(P$_a$−P$_{b'}$) = 5.8 Hz) (P_b and $P_{b'}$), δ −8.18 (dd, *J*(P$_a$−P$_{b'}$) = 5.8 Hz, *J*(P$_a$−P$_b$) = 4.0 Hz, P_a). IR (KBr, cm^{-1}): 2106 (s, $\nu_{C≡C}$), 2007 (s, ν_{CO}), 1271, 1151, and 1037 (br s, due to uncoordinated triflate[15]). Anal. Calcd for IrP$_3$O$_4$S$_1$F$_3$C$_{70}$H$_{59}$: C, 62.82; H, 4.44. Found: C, 63.08; H, 4.30.

***cis*-[Ir(CO)(CH$_3$)(−CH=CHPPh$_3$)$_2$(−C≡C$\overline{\text{C=CH(CH}_2\text{)}_3\text{C}}H_2$)(PPh$_3$)$_2$]OTf (3b).** ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.09 (ddd, *J* = 33.0, 18.5, 3.0 Hz, H_α), δ 9.04 (ddd, *J* = 32.5, 18.0, 6.5 Hz, $H_{\alpha'}$), δ 6.19 (ddd, *J* = 37.5, 18.5, 1.0 Hz, H_β,), δ 5.68, 2.04, 1.99, 1.53 (Ir−C≡C$\overline{\text{C=C}H\text{(C}H_2\text{)}_3\text{C}}H_2$), δ 0.53 (d, *J* = 5.5 Hz, Ir−CH_3). ^{13}C NMR (75.5 MHz, CDCl$_3$,): δ 193.8 (m, C_α and $C_{\alpha'}$), 177.2 (dd, *J* = 12.8, 5.0 Hz, Ir-*C*O), δ 109.0 (s, Ir−C≡*C*), δ 107.4 (dd, *J* = 68.3, 5.0 Hz, $C_{\beta'}$), δ 105.0 (dd, *J* = 70.6, 2.5 Hz, C_β), δ 95.20 (t, *J* = 12.1 Hz, Ir−*C*≡C), δ 125.0, 122.2, 31.7, 25.8, 23.3, 22.5 (Ir−C≡C$\overline{C\text{=}C\text{H(}C\text{H}_2\text{)}_3C}H_2$), δ −10.8 (d, *J* = 73.0 Hz, Ir−*C*H$_3$). ^{31}P NMR (81.0 MHz, CDCl$_3$): δ 14.49 (d, *J* = 3.0 Hz) and 13.54 (d, *J* = 5.5 Hz) (P_b and $P_{b'}$), δ −8.18 (dd, *J* = 5.5, 3.0 Hz, P_a). IR (KBr, cm^{-1}): 2106 (s, $\nu_{C≡C}$), 2007 (s, ν_{CO}), 1272, 1151, and 1032.[15] Anal. Calcd for

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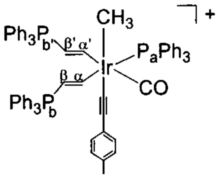
[15] Johnston, D. H.; Shriver, D. F. *Inorg. Chem.* **1993**, *32*, 1045.

$IrP_3O_4S_1F_3C_{69}H_{61}$: C, 62.39; H, 4.63. Found: C, 62.47; H, 4.63.

***cis*-$[Ir(CO)(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}C-C(CH_3){=}CH_2)(PPh_3)]OTf$ (3c).** ^1H NMR (500 MHz, $CDCl_3$): δ 9.08 (ddd, J = 33.0, 18.5, 2.5 Hz, H_α), δ 9.02 (ddd, J = 32.3, 18.0, 6.0 Hz, $H_{\alpha'}$), δ 6.15 (ddd, J = 37.3, 18.5, 1.0 Hz, H_β), δ 4.84, 4.75 ($Ir-C{\equiv}C-C(CH_3){=}CH_2$), δ 0.53 (d, $J(H-P_a)$ = 5.5 Hz, $Ir-CH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$,): δ 193. 4 (m, C_α and $C_{\alpha'}$), 176.5 (dd, J = 13.0, 5.0 Hz, $Ir-CO$), δ 108.7 (s, $Ir-C{\equiv}C$), δ 108.2 (dd, J = 64.9, 3.0 Hz, $C_{\beta'}$), δ 105.7 (dd, J = 68.1, 2.0 Hz, C_β), δ 95.2 (t, J = 12.0, $Ir-C{\equiv}C$), δ 114.0, 25.8 ($Ir-C{\equiv}C-C(CH_3){=}CH_2$), δ −11.1 (d, J = 73.4 Hz, $Ir-CH_3$). ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 14.55 (d, J = 3.6 Hz) and 13.69 (d, J = 5.4 Hz) (P_b and $P_{b'}$), δ −7.98 (dd, J = 5.2, 3.6 Hz, P_a). IR (KBr, cm^{-1}): 2102 (s, $\nu_{C\equiv C}$), 2007 (s, ν_{CO}), 1270, 1150, and 1032.[15] Anal. Calcd for $IrP_3O_4S_1F_3C_{66}H_{57}$: C, 61.53; H, 4.46. Found: C, 61.50; H, 4.32.

***cis*-$[Ir(CO)(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}C(p\text{-}C_6H_4CH_3))(PPh_3)]OTf$ (3′a).** The reaction mixture of AgOTf (0.12 g, 0.47 mmol) and *trans*-$[IrBr(CH_3)(-CH{=}CHPPh_3)_2(CO)(PPh_3)]OTf$ (**4**)[5] (0.5 g, 0.38 mmol) in $CHCl_3$ (15 mL) was stirred at 25 °C for 1 h. After AgBr was removed by filtration from the reaction mixture, NEt_3 (0.08 mL, 0.57 mmol) and $HC{\equiv}C(p\text{-}C_6H_4CH_3)$ (0.07 mL, 0.55 mmol) were added, and the resulting solution was stirred for 1 h before 10 mL of water was added to the reaction mixture. Excess NEt_3 and $[HNEt_3]OTf$ in the aqueous layer were separated from **3a** and **3′a** in the $CHCl_3$ layer. The $CHCl_3$ solution of **3a** and **3′a** was chromatographed over neutral alumina with CH_2Cl_2 to separate **3′a** (late yellow elution band) from **3a** (early yellow elution band). The first and the second yellow solutions were collected, and removal of solvent afforded beige microcrystals of **3a** (0.28 g, 55%) and **3a′** (0.07 g, 14%) based on **3a** and **3′a**, respectively.



3'a

^1H NMR (500 MHz, $CDCl_3$): δ 9.36 (ddd, $J(H_\alpha-P_b)$ = 30.5 Hz, $J(H_\alpha-H_\beta)$ = 18.0 Hz, $J(H_\alpha-P_a)$ = 2.5 Hz, H_α), δ 9.04 (ddd, $J(H_{\alpha'}-P_{b'})$ = 32.0 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 18.0 Hz, $J(H_{\alpha'}-P_a)$ = 7.5 Hz, $H_{\alpha'}$), δ 6.90 (ddd, $J(H_{\beta'}-P_b)$ = 38.6 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 18.0 Hz, $J(H_{\beta'}-P_a)$ = 1.0 Hz, $H_{\beta'}$), δ 2.35 (s, $p\text{-}C_6H_4CH_3$), δ −0.55 (d, $J(H-P_a)$ = 5.0 Hz, $Ir-CH_3$), δ 7.0−8.0 (H_β and the phenyl protons of PPh_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 193.3 (t, $J(C_{\alpha'}-P_b)$ = 10.2 Hz, $J(C_{\alpha'}-P_a)$ = 10.2 Hz, $C_{\alpha'}$), δ 187.0 (dd, $J(C_\alpha-P_a)$ = 100.7 Hz, $J(C_\alpha-P_{b'})$ = 10.7 Hz, C_α), δ 176.8 (dd, $J(C-P_{b'})$ = 12.9 Hz, $J(C-P_a)$ = 7.2 Hz, $Ir-CO$), δ 107.0 (dd, $J(C_\beta-P_b)$ = 70.3 Hz, $J(C_\beta-P_a)$ = 3.1 Hz, C_β), δ 106.8 (dd, $J(C_{\beta'}-P_b)$ = 70.3 Hz, $J(C_{\beta'}-P_a)$ = 4.5 Hz, $C_{\beta'}$), δ 105.6 (s, $Ir-C{\equiv}C$), δ 99.2 (d, $J(C-P_a)$ = 10.4 Hz, $Ir-C{\equiv}C$), δ 21.5 (s, $Ir-C{\equiv}C-C_6H_4-CH_3$), δ −17.4 (d, $J(C-P_a)$ = 4.0 Hz, $Ir-CH_3$). HETCOR (^1H (500 MHz) → ^{13}C (125.7 MHz)): δ 9.36 → 187.0; δ 9.04 → 193.4; δ 7.3→ 107.0; δ 6.90 → 106.8; δ 2.35 → 21.5; δ −0.55 → −17.4. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 14.48 (d, P_b, $J(P_a-P_b)$ = 39.1 Hz), δ 14.02 (d, $P_{b'}$, $J(P_a-P_{b'})$ = 3.9 Hz), δ −8.71 (dd, P_a, $J(P_a-P_b)$ = 39.1 Hz, $J(P_a-P_{b'})$ = 3.9 Hz). IR (KBr, cm^{-1}): 2100 (s, $\nu_{C\equiv C}$), 2003 (s, ν_{CO}), 1272, 1151, and 1031 (br s, due to uncoordinated triflate[15]). Anal. Calcd for $IrP_3O_4S_1F_3C_{70}H_{59}$: C, 62.81; H, 4.44. Found: C, 63.01; H, 4.38.

Reactions of *cis,cis*-$[Ir(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}C(p\text{-}C_6H_4CH_3))(PPh_3)_2]OTf$ (2a) and *cis*-$[Ir(CO)(CH_3)(-CH{=}CHPPh_3)_2(-C{\equiv}C(p\text{-}C_6H_4CH_3))(PPh_3)]OTf$ (3a) with HCl: Formation of *cis*-$CH_3CH{=}CH(p\text{-}C_6H_4CH_3)$ (5) and $[Ir(Cl)_2(-CH{=}CHPPh_3)_2(PPh_3)(L)]OTf$ (L = PPh_3 for 6, CO for 7). Reactions of **2a** and **3a** with HCl were carried out by the same manner. Aqueous HCl (0.024 mL, 0.25 mmol of H_2O containing 32 wt % HCl) was added to a solution of **2a** (0.2 g, 0.13 mmol) in $CHCl_3$ (15 mL) at 25 °C, and the reaction mixture was stirred for 6 h. Excess HCl was removed by washing with H_2O. Addition of *n*-pentane (10 mL) to the $CHCl_3$ solution resulted in white microcrystals of **6**, which were collected by filtration, washed with *n*-pentane (2 × 20 mL), and dried under vacuum. The yields of **6** and **7** were 0.14 g (72%) and 0.15 g (92%), respectively. The filtrate was distilled at 25 °C under vacuum to less than 1.0 mL, and the residue was eluted with *n*-pentane on a column packed with silica gel to obtain **5**. The yield of **5** was ca. 70% in the reaction of **2** with HCl and ca. 87% in the reaction of **3** with HCl, respectively, based on ^1H NMR measurements in $CDCl_3$.

***cis*-$CH_3CH{=}CH(p\text{-}C_6H_4CH_3)$ (5).** ^1H NMR (500 MHz, $CDCl_3$): δ 7.20 and 7.14 (both d, J = 8.1 Hz, $C_6H_4CH_3$), δ 6.40 (dd, J = 11.4 Hz, J = 1.5 Hz, $CH_3CH{=}CH$), δ 5.74 (dq, J = 11.4, 7.2 Hz, $CH_3CH{=}CH$), δ 2.36 (s, $p\text{-}C_6H_4CH_3$), δ 1.89 (dd, J = 7.2, 1.5 Hz, $CH_3CH{=}CH$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.6 (s, $CH_3CH{=}CH$), δ 21.1 (s, $p\text{-}C_6H_4CH_3$), δ 136.1, 134.8, 129.7, 128.8, 128.7, 126.0 (olefinic carbons and $p\text{-}C_6H_4CH_3$). Mass: M^+ = 132.

$[Ir(Cl)_2(-CH_\alpha{=}CH_\beta P_bPh_3)_2(P_aPh_3)_2]OTf$ (6). ^1H NMR (300 MHz, $CDCl_3$): δ 10.23 (dd, $J(H_\alpha-P_b)$ = 28.5 Hz, $J(H_\alpha-H_\beta)$ = 16.0 Hz, H_α), δ 8.22 (dd, $J(H_\beta-P_b)$ = 32.3 Hz, $J(H_\alpha-H_\beta)$ = 16.0 Hz, H_β). ^{31}P NMR ($CDCl_3$): δ 11.60 (t, $J(P_a-P_b)$ = 2.0 Hz, P_b), δ −9.75 (t, (P_a-P_b) = 2.0 Hz, P_a). IR (KBr, cm^{-1}): 1270, 1150, and 1032.[15] Anal. Calcd for $IrP_4O_3S_1F_3Cl_2C_{77}H_{64}$: C, 61.11; H, 4.26. Found: C, 61.48; H, 4.30.

***cis,cis*-$[Ir(Cl)_2(-CH{=}CHPPh_3)_2(CO)(PPh_3)]OTf$ (7).** ^1H NMR (300 MHz, $CDCl_3$): δ 8.73 (ddd, $J(H_\alpha-P_b)$ = 30.7 Hz, $J(H_\alpha-H_\beta)$ = 17.5 Hz, $J(H_\alpha-P_a)$ = 6.5 Hz, $Ir-CH_\alpha{=}CHPPh_3$), δ 8.22 (ddd, $J(H_{\alpha'}-P_{b'})$ = 26.5 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 17.0 Hz, $J(H_{\alpha'}-P_a)$ = 3.0 Hz, $Ir-CH_{\alpha'}{=}CHPPh_3$). δ 6.43 (dd, $J(H_{\beta'}-P_{b'})$ = 30.0 Hz, $J(H_{\alpha'}-H_{\beta'})$ = 17.0 Hz, $Ir-CH{=}CH_{\beta'}PPh_3$). ^{13}C NMR ($CDCl_3$): δ 185.2 (t, $J(C_\alpha-P_a)$ and $J(C_\alpha-P_b)$ = 10.3 Hz, $Ir-C_\alpha H{=}CHPPh_3$), δ 172.9 (dd, $J(C-P_a)$ = 14.3 Hz, $J(C-P_b)$ = 5.0 Hz, $Ir-CO$), δ 166.3 (t, $J(C_\alpha-P_a)$ and $J(C_\alpha-P_b)$ = 5.7 Hz, $Ir-C_{\alpha'}H{=}CHPPh_3$), δ 110.5 (d, $J(C_\beta-P_b)$ = 71.0 Hz, $Ir-CH{=}C_\beta HPPh_3$), δ 109.1 (d, $J(C_{\beta'}-P_{b'})$ = 76.8 Hz, $Ir-CH{=}C_{\beta'}HPPh_3$). ^{31}P NMR ($CDCl_3$): δ 14.70 (d, $J(P_a-P_b)$ = 2.7 Hz, $Ir-CH{=}CHP_bPh_3$), δ 13.76 (d, $J(P_a-P_{b'})$ = 3.0 Hz, $Ir-CH{=}CHP_{b'}Ph_3$), δ −5.69 (br t, $J(P_a-P_{b'})$ and $J(P_a-P_b)$ = 3.0 Hz, $Ir-P_aPh_3$). IR (KBr, cm^{-1}): 2052 (s, ν_{CO}), 1266, 1152, and 1032.[15] Anal. Calcd for $IrP_3O_4S_1F_3Cl_2C_{60}H_{49}$: C, 56.34; H, 3.86. Found: C, 55.94; H, 3.95.

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Supporting Information Available: ^1H, ^{13}C, ^{31}P NMR and HETCOR ($^1H-^{13}C$) spectra of complexes **2a**, **3a**, and **3′a**. ^1H and ^{31}P NMR spectra of complexes **6** and **7**. ^1H NMR and mass spectra of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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