Iridabenzenes from Iridacyclopentadienes: Unusual C−C Bond Formation between Unsaturated Hydrocarbyl Ligands

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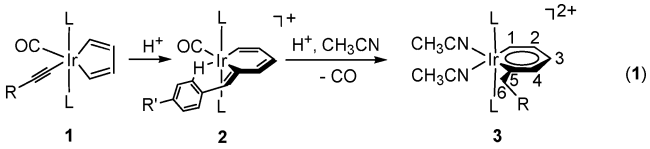
Received June 27, 2005

Summary: Iridabenzenes are produced by an unusual C−C coupling between the α-carbon of the alkynyl ligand and the δ-carbon of the neighboring 1,3-butadienyl ligand upon protonation of the β-carbon of the alkynyl ligand.

Introduction

Metallabenzenes are of interest to many chemists since these metal-containing aromatic compounds show some interesting reactivity compared with that of organic aromatics.[1] Metal-mediated carbon−carbon bond forming reactions between alkynes have been utilized to prepare metallabenzenes and related unsaturated six-membered metallacycles (metallabenzynes and isometallabenzenes).[1,2] We recently reported the synthesis of iridabenzenes from reactions of iridacyclopentadienes with alkynes (eq 1).[3] The C−C bond formation between the hydrocarbyl ligands is initiated by protonation of the β-carbon of the alkynyl ligand of **2**, and further protonation of the vinyl carbon in the presence of a base (CH_3CN) yields the stable iridabenzenes **3**. It may also be possible to prepare iridabenzenes via the intramolecular rearrangement of pent-2,4-dien-1-yl complexes, M−C(=CHR)−CH=CH−CH=CH_2, since a pent-1,3-dien-1-yl-iridium has been suggested as the transient species that undergoes C−H activation to produce iridabenzene.[4] One can expect pent-2,4-dien-1-yl complexes, M−C(=CHR)−CH=CH−CH=CH_2, as the products of the reaction of *cis*-(alkynyl)(but-1,3-dien-1-yl) complexes, M(−C≡CR)(−CH=CH−CH=CH_2), with proton through the C−C coupling reaction between the two unsaturated hydrocarbyl ligands since the β-carbon of the alkynyl ligand (M−C≡***C***R) is well-known to be so nucleophilic that it readily reacts with proton to initiate the C−C bond formation between the alkynyl and neighboring hydrocarbyl ligands.[5]



(1)

L = PPh_3; R = C_6H_5 (**a**), *p*-$C_6H_4CH_3$ (**b**); R' = H (**a**), CH_3 (**b**)

We now wish to report another synthetic synthesis of iridabenzenes via an unusual C−C bond forming reaction between the α-carbon of the alkynyl and the δ-carbon of the but-1,3-dien-1-yl ligands of *cis*-(alkynyl)-(but-1,3-dien-1-yl)iridium complexes.

Results and Discussion

Newly prepared (η^2-acetato)iridacyclopentadiene **4** reacts with alkynes (RC≡CH) to produce new *cis*-(alkynyl)(but-1,3-dien-1-yl)iridium **5**, which is readily protonated to give iridabenzenes **6** in high yields (eq 2). Iridabenzenes **6** are also obtained from ligand substitution reactions of *cis*-bis(acetonitrile)iridabenzenes **3**[3] with CH_3CO_2Na. It is likely that proton attacks the β-carbon of the alkynyl group of **5** to cause the C−C bond formation between the hydrocarbyl (alkynyl and but-1,3-dien-1yl) ligands to give iridabenzenes **6** (see below for the reaction mechanism). It is somewhat

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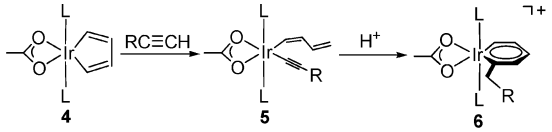
10.1021/om050529a CCC: $30.25
Publication on Web 08/30/2005

unusual not to observe the conjugate trienes (RCH=CH−CH=CH−CH=CH_2) from the reactions of **5** with H^+ (eq 2) since it is well-established that the reactions of alkynyl complexes with H^+ cause the C−C coupling reaction between the two α-carbons of the alkynyl and a neighboring unsaturated hydrocarbyl ligand to give conjugated polyenes and polyenynes.[5] Complexes **5** do not undergo the reductive elimination of the hydrocarbyl ligands to give conjugated dienynes (R−C≡C−CH=CH−CH=CH_2) even at 60 °C in $CHCl_3$ in the absence of H^+. 1,3-Butadiene is liberated from reactions of **5** with excess RC≡CH to give *cis*-bis(alkynyl)iridium (Ir(η^2-O_2CH_3)(−C≡CR)$_2$(PPh_3)$_2$) and with H^+ in the presence of RC≡CH to give unknown iridium complex(es).[6]

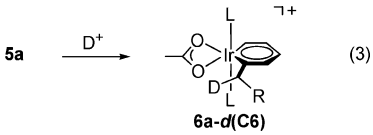


(2)

L = PPh_3, R = Ph (**a**), p-$C_6H_4CH_3$ (**b**)

To look into the reaction pathways of this C−C coupling in detail as well as the following intramolecular hydrogen transfer steps to give the final product iridabenzene, two different deuterium-labeling experiments have been carried out.

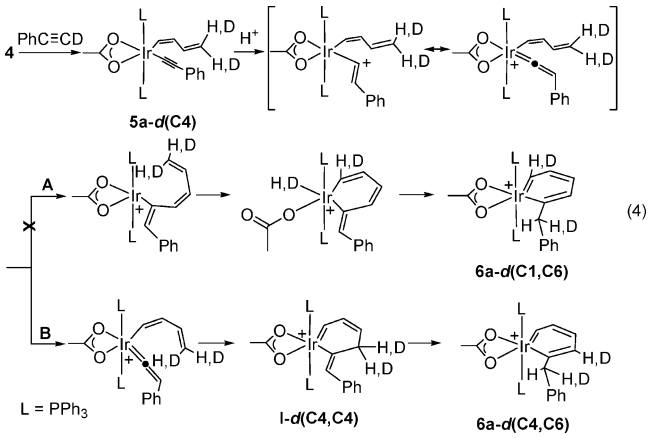
The reaction of **5a** with D^+ produces the iridabenzene **6a**-*d*(C6), containing deuterium only at the sixth carbon from the metal, the methylene carbon (−C(6)H*D*Ph) (eq 3), which confirms the C−C coupling reaction being initiated by the attack of D^+ on the *β*-carbon of the alkynyl ligand of **5a** and the deuterium staying at the same carbon during the following intramolecular rearrangements to give iridabenzene **6a**-*d*(C6).



(3)

Two different reaction pathways (A and B in eq 4) may be considered for the C−C bond formation between the hydrocarbyl ligands of **5** to produce iridabenzene **6**. Pathway A includes the well-established C−C coupling between the α-carbons of the two neighboring hydrocarbyl ligands initiated by the protonation of the *β*-carbon of the alkynyl ligand, whereas pathway B involves the somewhat unusual C−C bond formation between the α-carbon of the alkynyl ligand and the *δ*-carbon of the but-1,3-dien-1-yl ligand.

The reaction of **4** with PhC≡C*D* gives the isotopomer **5a**-*d*(C4), having deuterium only at the *δ*-carbon (the fourth carbon from the metal; 0.5 deuterium at the *cis*- and *trans*-position, respectively) of the but-1,3-dien-1-yl ligand according to the ^{1}H NMR spectral data (see eq 4 and Supporting Information). The iridabenzene **6a**-*d*(C4, C6), obtained from the reaction of **5a**-*d*(C4) with H^+, contains deuterium at the two carbons C4 and C6 (eq 4) and does not seem to have deuterium on the α-carbon (C1) at all. These results unambiguously exclude the possibility of the C−C bond formation



(4)

between the α-carbons of the alkynyl and but-1,3-dien-1-yl ligands (pathway A), but support pathway B as the main route in eq 4. The iridacyclohexadiene **I**-*d*(C4, C4) may then be aromatized through the well-known 1,3-shift reaction of hydrogen to produce iridabenzene **6a**-*d*(C4, C6)).

The sum of deuterium found at the two carbons C4 and C6 of **6a**-*d*(C4, C6) is somewhat less than 1.0 (ca. 0.7: ca. 0.4 at C4 and ca. 0.3 at C6) according to the integration of signals at *δ* 6.05 (Ir−CH=CH−CH=C(4)*H*-C(CH_2Ph) and 4.66 (Ir−CH=CH−CH=CH−C-(C(6)H_2Ph) ppm in the ^{1}H NMR spectrum of **6a**-*d*(C4, C6) (see Supporting Information). It may be conceivable that some of the deuterium is transferred during the 1,3-shift reaction of deuterium (or hydrogen) between the intermediate **I**-*d*(C4, C4) and the iridabenzene **6a**-*d*(C4, C6), possibly to the solvent $CHCl_3$ through the H/D exchange mediated by the conjugate anion OTf^- ($^-OSO_2CF_3$) present in the reaction mixture.

New iridium compounds, **4**, **5**, **6**, and (Ir(η^2-O_2CCH_3)(−C≡CR)$_2$ (PPh_3)$_2$) prepared in this study have been unambiguously characterized by detailed spectral ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR, ^{1}H,^{13}C-HETCOR, IR (see Supporting Information), and elemental analysis data. Straightforward assignments were possible for the signals in the NMR spectra of new compounds by comparing with those for related compounds previously reported.[3,5,7]

^{1}H NMR spectra of the isotopomers 5a-*d*(C4), **6a**-*d*(C6), and **6a**-*d*(C4, C6) clearly show decreases only in the integration of the corresponding hydrogens, i.e., at *δ* 4.82 for Ir−CH=CH−CH=C$H_{cis}$$H_{trans}$ and *δ* 4.68 for Ir−CH=CH−CH=C$H_{cis}$$H_{trans}$ of **5a**; at *δ* 4.66 for [Ir=CH−CH=CH−CH=C(CH_2Ph) of **6a**; at *δ* 6. 05 and 4.66 for the two hydrogens Ir=CH−CH=CH−C*H*=C(CH_2Ph) of **6a**, respectively (see Supporting Information).

In summary, iridabenzenes [Ir(CHCHCHCHC(CH_2R)-L_4)]$^+$ (L_4 = (η^2-O_2CCH_3)(PPh_3)$_2$; R = Ph, *p*-$C_6H_4CH_3$) are prepared from the reactions of *cis*-(alkynyl)(but-1,3-dien-1-yl)iridium [Ir(−C≡CR)(−CH=CHCH=CH_2)L_4]$^+$ with

(6) The reactions of **5** with H^+ in the presence of RC≡CH (3 equiv) produce a mixture of iridabenzene **6** and unknown iridium complex(es), and a small amount of 1,3-butadiene.

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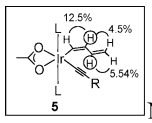
H^+. The plausible reaction mechanism involves (i) proton attack on the β-carbon of the alkynyl ligand (Ir−C≡*C*Ph) to form the vinylidene complex [Ir(=C=CHPh)(−CH=CH−CH=CH_2)L_4]$^+$ and (ii) an unusual C−C bond formation between the α-carbon of the vinylidene ligand (Ir$^+$=*C*=CHPh) and the δ-carbon of the *cis*-but-1,3-dien-1-yl ligand (Ir−CH=CH−CH=*C*H_2) to give the hexadienyl complex ([Ir=CHCH=CH*C*H_2-*C*(=CHPh)L_4]$^+$), which undergoes the well-known hydrogen 1,3-shift reaction to produce the iridabenzene [IrCHCHCHCHC(CH_2Ph)L_4]$^+$.

Experimental Section

General Procedures. A standard vacuum system and Schlenk type glassware were used in most of the experiments in handling metal complexes, although most of the compounds are stable enough to be handled in air. PhC≡CD, HOTf, and DOTf were purchased from Aldrich. [Ir(CH=CHCH=CH)(NCCH$_3$)(CO)(PPh_3)$_2$]OTf was prepared by literature methods.[4e] NMR spectra were measured using a Varian 200 or 500 MHz spectrometer for ^{1}H, 125.7 MHz for ^{13}C, and 81 or 121.3 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Elemental analyses were performed at the Organic Chemistry Research Center, Sogang University, using a Carlo Erba EA 1108.

Synthesis of Ir(CH=CHCH=CH)(η^2-O_2CCH$_3$)(PPh_3)$_2$, 4. To a solution of [Ir(CH=CHCH=CH)(NCCH$_3$)(CO)(PPh_3)$_2$]OTf (0.098 g, 0.1 mmol) in $CHCl_3$ (10 mL) were added Me_3NO (0.019 g, 0.25 mmol) and CH_3CN (0.012 g, 0.3 mmol), and the reaction mixture was stirred at 25 °C under N_2 for 30 min before the pale yellow solution turned light brown. Excess Me_3NO and NMe_3 were removed by extraction with H_2O (2 × 10 mL). A light brown solution of $CHCl_3$ was stirred in the presence of CH_3CO_2Na (0.15 mmol) at 25 °C for 3 h before MeOH (30 mL) was added to precipitate beige microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.097 g and 98% based on **4**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.5 (m, P(C_6H_5)$_3$, 30H), 6.86 (m, Ir−C*H*=CHCH=C*H*, 2H), 5.63 (m, Ir−CH=C*HC*H=CH, 2H), 0.48 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.5 (s, Ir-η^2-O_2*C*CH$_3$), 143.6 (s, Ir−CH=*C*HCH=CH), 132.9 (t, J(C−P) = 8.0 Hz, Ir−*C*H=CHCH=*C*H), 24.1 (s, Ir-η^2-O_2C*C*H$_3$), 135.05, 129.81, 129.79, and 127.48 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 0.48 → 24.1; 5.63 → 143.6; 6.86 → 132.9. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 13.36 (s, *P*Ph$_3$). Anal. Calcd for $Ir_1P_2O_2C_{42}H_{37}$: C, 60.93; H, 4.50. Found: C, 60.90; H, 4.49.

Synthesis of Ir(−CH=CHCH=CH_2)(C≡CPh)(η^2-O_2CCH$_3$)(PPh_3)$_2$, 5a. Both **5a** and **5b** were synthesized in the same manner as described below for **5a**. A $CHCl_3$ (10 mL) solution of **4** (0.084 g, 0.1 mmol) and C_6H_5C≡CH (0.010 g, 0.10 mmol) was stirred at 25 °C for 10 min before *n*-pentane (20 mL) was added to precipitate light yellow microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.096 g and 98% based on **5a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.6 (m, P(C_6H_5)$_3$, 30H), 7.44 (d, J(H−H) = 10 Hz, Ir−C*H*=CHCH=CH_2, 1H), 6.86−6.97 (m, *metha*- and *para*-protons of C_6H_5 and Ir−CH=CHC*H*=CH_2, 4H), 6.36 (d, J(H−H) = 7 Hz, *ortho*-protons of C_6H_5, 2H), 5.60 (t, J(H−H) = 10 Hz, Ir−CH=C*H*CH=CH_2, 1H), 4.82 (d, J(H−H) = 10 Hz, Ir−CH=CHCH=C$H_{cis}H_{trans}$, 1H), 4.68 (d, J(H−H) = 17 Hz, Ir−CH=CHCH=C$H_{cis}H_{trans}$, 1H), 0.65 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.98 (s, Ir-η^2-O_2*C*CH$_3$), 138.15 (s, Ir−CH=CH*C*H=CH_2), 130.99, 127.14, and 123.92 (s, CH carbons of C_6H_5), 130.19 (s, Ir−CH=*C*HCH=CH_2), 129.52 (s, C_{ipso} carbons of C_6H_5), 116.08 (br s, Ir−*C*H=CHCH=CH_2), 111.14 (s, Ir−CH=CHCH=*C*H_2), 104.78 (s, Ph−*C*≡C−Ir), 70.97 (t, J(C−P) = 14 Hz, Ph−C≡*C*−Ir), 23.58 (s, Ir-η^2-O_2C*C*H$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 7.44 → 116.08; ca. 6.9 → 138.15; 5.60 → 130.19; 4.82 and 4.68 → 111.14; 0.65 → 23.58. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 10.17 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 2113.4 (s, $\nu_{C\equiv C}$). Anal. Calcd for $Ir_1P_2O_2C_{50}H_{43}$: C, 64.57; H, 4.66. Found: C, 64.55; H, 4.68.



NOE enhancements

Ir(−CH=CHCH=CH_2)(−C≡C-*p*-$C_6H_4CH_3$)(η^2-O_2CCH$_3$)(PPh_3)$_2$, 5b. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.3−7.6 (m, P(C_6H_5)$_3$ and Ir−C*H*=CHCH=CH_2, 31H), 6.90 (dt, J(H−H) = 16.5 Hz, J(H−H) = 10.3 Hz, Ir−CH=CHC*H*=CH_2, 1H), 6.27−6.79 (AB system, *p*-$C_6H_4CH_3$, 4H), 5.59 (t, J(H−H) = 10.3 Hz, Ir−CH=C*H*CH=CH_2, 1H), 4.82 (d, J(H−H) = 10.3 Hz, Ir−CH=CHCH=C$H_{cis}H_{trans}$, 1H), 4.68 (d, J(H−H) = 16.5 Hz, Ir−CH=CHCH=C$H_{cis}H_{trans}$, 1H), 2.22 (s, *p*-C_6H_4CH_3, 3H), 0.66 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 185.93 (s, Ir-η^2-O_2*C*CH$_3$), 138.22 (s, Ir−CH=CH*C*H=CH_2), 129.94 (s, Ir−CH=*C*HCH=CH_2), 130.80 and 127.90 (s, CH carbons of *p*-$C_6H_4CH_3$), 127.83 (s, C_{ipso} carbons of *p*-$C_6H_4CH_3$), 116.18 (br s, Ir−*C*H=CHCH=CH_2), 110.05 (s, Ir−CH=CHCH=*C*H_2), 104.50 (s, *p*-tolyl-*C*≡C−Ir), 68.95 (br s, *p*-tolyl-C≡*C*-Ir), 23.57 (s, Ir-η^2-O_2C*C*H$_3$), 21.08 (s, *p*-$C_6H_4CH_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ ca. 7.4 → 116.18; 6.90 → 138.22; 5.59 → 129.94; 4.82 and 4.68 → 110.05; 2.22 → 21.08; 0.66 → 23.57. ^{1}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ 10.11 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 2117 ($\nu_{C\equiv C}$). Anal. Calcd for $Ir_1P_2O_2C_{51}H_{45}$: C, 64.88; H, 4.80. Found: C, 64.93; H, 4.81.

Synthesis of [Ir(CHCHCHCHC(CH_2Ph))(η^2-O_2CCH$_3$)(PPh_3)$_2$](OTf), 6a. Both **6a** and **6b** were synthesized in the same manner as described below for **6a**. HOTf (11 μL, 0.12 mmol) was added to a solution of **5a** (0.093 g, 0.1 mmol) in $CHCl_3$ (15 mL) at 25 °C, and the reaction mixture was stirred for 5 min. Excess HOTf was removed by extraction with H_2O. Addition of *n*-pentane (10 mL) to the $CHCl_3$ solution resulted in beige microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.08 g and 79% based on **6a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.13 (d, J(H−H) = 7.5 Hz, H1), 7.2−7.9 (m, P(C_6H_5)$_3$, H2 and H3, 32H), 6.28 (d, J(H−H) = 7 Hz, C_6H_5, 2H), 6.02 (d, J(H−H) = 8.5 Hz, H4, 1H), 4.63 (s, H6, 2H), 0.486 (s, Ir-$\eta^2$$O_2CCH_3$, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 241.0 (br s, *C*5), 208.63 (br, *C*1), 187.4 (s, Ir-$\eta^2$$O_2$*C*CH$_3$), 162.36 and 129.36 (both s, *C*2 and *C*3), 27.27 (s, *C*4), 56.65 (s, *C*6), 23.30 (s, Ir-$\eta^2$$O_2$C*C*H$_3$), 134.5, 132.5, 128.9, and 124.7 (P(C_6H_5)$_3$), 120.98 (q, J(C−F) = 320.79 Hz, CF_3SO_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 13.13 → 208.63; ca. 7.6 → 162.36; ca. 7.3 → 129.36; 6.02 → 127.27; 4.63 → 56.65; 0.486 → 23.30. ^{31}P{^{1}H} NMR ($CDCl_3$; 81 MHz): δ 10.76 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 1263.6, 1155.6, and 1031.5 (s, ν_{OTf^-}). Anal. Calcd for $Ir_1P_2O_5S_1F_3C_{51}H_{44}$: C, 56.71; H, 4.11; S, 2.97. Found: C, 56.75; H, 3.97; S, 2.89.

[Ir(CHCHCHCHC(CH_2-*p*-$C_6H_4CH_3$))(η^2-O_2CCH$_3$)(PPh_3)$_2$](OTf), 6b. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 13.12 (d, J(HH) = 7.0 Hz, H1), 7.1−7.7 (m, P(C_6H_5)$_3$, H2 and H3, 32H), 6.15−7.00 (AB type, *p*-$C_6H_4CH_3$, 4H), 6.04 (d, J(HH) = 8.5 Hz, H4, 1H), 4.62 (s, H6, 2H), 2.31 (s, *p*-C_6H_4CH_3, 3H), 0.50 (s, Ir-$\eta^2$$O_2CCH_3$, 3H). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ 241.96 (br s, *C*5), 208.3 (br, *C*1), 187.47 (s, Ir-$\eta^2$$O_2$*C*CH$_3$), 162.40 and 130.76 (both s, *C*2 and *C*3), 129.74 and 129.53 (both s, CH carbons of $C_6H_4CH_3$), 127.43 (s, *C*4), 56.48 (s, *C*6), 23.44 (s, Ir-$\eta^2$$O_2$C*C*H$_3$), 21.32 (s, C_6H_4*C*H$_3$), 134.6, 132.6, 129.0 and

124.8 (P(C_6H_5)$_3$), 121.2 (q, J(CF) = 321.4 Hz, CF_3SO_3). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 13.12 → 208.3; ca. 7.6 → 162.40; ca. 7.3 → 130.76; 6.04 → 127.43; 4.62 → 56.48; 2.31 → 21.32; 0.50 → 23.44. ^{31}P NMR ($CDCl_3$, 81 MHz): δ 10.73 (s, PPh$_3$). IR (KBr, cm^{-1}): 1262, 1155, and 1032 (ν_{OTf^-}). Anal. Calcd for $Ir_1P_2O_5S_1F_3C_{52}H_{46}$: C, 57.08; H, 4.24; S, 2.93. Found: C, 56.97; H, 4.01; S, 2.83.

Synthesis of Isotopomers Ir(−CH=CHCH=CHD)(C≡CPh)(η^2-O_2CCH_3)(PPh_3)$_2$, 5a-*d*(C4), [Ir=CH−CH=CH−CH=C(CH*D*Ph)(η^2-O_2CCH_3)(PPh_3)$_2$]$^+$, 6a-*d*(C6), and [Ir=CH−CH=CH−CH$_{1-y}$D$_y$=C(CH$_{2-x}$D$_x$Ph)(η^2-O_2CCH_3)(PPh_3)$_2$]$^+$, 6a-*d*(C4, C6) (0.5 < $x + y$ < 1). These isotopomers were prepared in the same manner as described above for **5a** and **6a** except that deuterium-containing reagents, DOTf and PhC≡CD, were used.

Synthesis of Ir (η^2-O_2CCH_3)(−C≡CC_6H_5)$_2$(PPh_3)$_2$. A $CHCl_3$ (10 mL) solution of **5a** (0.10 g, 0.093 mmol) and C_6H_5C≡CH (0.010 g, 0.10 mmol) was stirred at 25 °C for 10 min before n-pentane (20 mL) was added to precipitate light yellow microcrystals, which were collected by filtration, washed with n-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.11 g and 98% based on Ir(−C≡CPh)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$. ^{1}H NMR (500 MHz; $CDCl_3$): δ 7.18−7.77 (m, P(C_6H_5)$_3$, 30H), 6.84−6.93 (m, *meta*- and *para*-protons of C≡CC_6H_5, 6H), 6.14 (d, *ortho*-protons of C≡CC_6H_5, 4H), 0.62 (s, Ir-η^2-O_2CCH_3, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 188.1 (s, Ir-η^2-O_2CCH_3), 131.3, 126.9, and 124.2 (s, CH carbons of Ir−C≡CC_6H_5), 128.8 (s, *ipso*-carbons of Ir−C≡CC_6H_5), 103.9 (s, Ir−C≡*C*), 60.8 (t, J(C−P) = 13.0 Hz, Ir−*C*≡C), 23.3 (s, Ir-η^2-O_2CCH_3), 135.2, 130.2, 130.0, and 127.9 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.91 → 126.9; 6.86 → 124.2; 6.14 → 131.3; 0.62 → 23.3. ^{31}P{^{1}H} NMR (81 MHz; $CDCl_3$): δ 10.43 (s, PPh$_3$). IR (KBr, cm^{-1}): 2118.4 (s, C≡C). Anal. Calcd for $Ir_1P_2O_2C_{54}H_{43}$: C, 66.31; H, 4.43. Found: C, 66.25; H, 4.38.

Acknowledgment. The authors wish to thank the Korea Research Foundation (KRF) for their financial support of this study through the Basic Science Research Institute program (Grant No. KRF-2004-015-C00251).

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of complexes **4**, **5a**, **5a-***d*(C4), **6a**, **6a-***d*(C6), **6a-***d*(C4, C6), and Ir(−C≡CC_6H_5)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050529A