Electrophile (H^+, Me^+)-Mediated Carbon−Carbon Bond Formation between η^3-Allyl and Alkynyl Groups Coordinated to "Cp*Ir"

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η^3-Allyliridium(III) complexes Cp*Ir(η^3-CHPhCHCH$_2$)(−C≡C-*t*-Bu) (**2**), Cp*Ir(η^3-CHPhCHCH−CH═CH(*t*-Bu))Cl (**3H**), Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))I (**3Me**), [Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(NCMe)]$^+$ (**4**), and Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(−C≡C-*t*-Bu′) (**5**) have been prepared from the reactions of [Cp*Ir(η^3-CHPhCHCH$_2$)(NCMe)]$^+$ (**1**) with H−C≡C-*t*-Bu (in the presence of NEt$_3$), HCl, and MeI. The crystal structures of **2** and **5** have been determined by X-ray diffraction data analyses. Reactions of **3** and **5** with HCl produce *trans*,*trans*-1,3-pentadienes, PhCH═CHCH═CHCH$_2$(*t*-Bu) (**6H**) and PhCH═CHCH═CHCHMe(*t*-Bu) (**6Me**), and *cis*,*trans*,*trans*-1,3,5-heptatriene, (*t*-Bu′)CH═CHC(Ph)═CHCH═CHCHMe(*t*-Bu) (**8**), respectively.

Introduction

Metal-mediated C−C bond formation is known to give polyenes such as dienes and trienes from the reactions of alkenes and alkynes.[1] Iridium−Cp* ($C_5Me_5^-$) complexes react with alkenes and alkynes to produce Ir−alkene,[2a−e] −allyl,[2d,e,3] −alkyne,[4,5d] and −alkynyl[4b] complexes. The η^3-allyl group, in particular, of Cp*M(η^3-allyl) (M = Rh, Ir) shows interesting reactivity such as regioselective nucleophilic addition at the central carbon and alkyne addition at the terminal carbons to produce metallacyclobutanes[5] and cyclopentadienes,[6] respectively. We now wish to report electrophile (Me^+, H^+)-mediated C−C bond formation between the α-carbon of the alkynyl group (Ir-*C*≡C-*t*-Bu) and the terminal carbons of the allyl group (η^3-*C*HPhCH*C*H$_2$) coordinated to Cp*Ir to produce conjugated polyenes, 1,3-pentadienes, and 1,3,5-heptatriene.

Results

Synthesis of Metal Complexes. Alkynyl η^3-allyl complex Cp*Ir(η^3-CHPhCHCH$_2$)(−C≡C-*t*-Bu) (**2**) is prepared by replacing MeCN with −C≡C-*t*-Bu from the reaction of H−C≡C-*t*-Bu with [Cp*Ir(η^3-CHPhCHCH$_2$)(NCMe)]$^+$ (**1**) in the presence of NEt$_3$ and characterized by spectral and elemental analysis data and also by crystal structure determination by X-ray diffraction analysis (Figure 1). The η^3-allyl group of **2** in the solid state is best described as a symmetric η^3-allyl ligand since the C−C distances (C(11)−C(12) 1.44(2) Å; C(12)−C(13) 1.38(2) Å) in the η^3-allyl group are not much different from each other. ^{1}H NMR spectrum of **2** in CDCl$_3$ shows typical signals due to an η^3-allyl lignd.[3a,7]

Complex **2** reacts with HCl and MeI to give the η^3-pentadienyl−iridium complexes Cp*Ir(η^3-CHPhCHCH−CH═CH(*t*-Bu))Cl (**3H**) and Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))I (**3Me**), respectively (see Scheme 1). The I$^-$ in **3Me** is readily replaced by MeCN to give [Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(NCMe)]$^+$ (**4**), which further undergoes substitution reaction of MeCN with another −C≡C-*t*-Bu′ group to produce Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(−C≡C-*t*-Bu′) (**5**) in the presence of NEt$_3$ (see Scheme 1).

These η^3-pentadienyl−iridium complexes **3**−**5** have been unambiguously characterized by spectral and elemental analysis data and also by crystal structure

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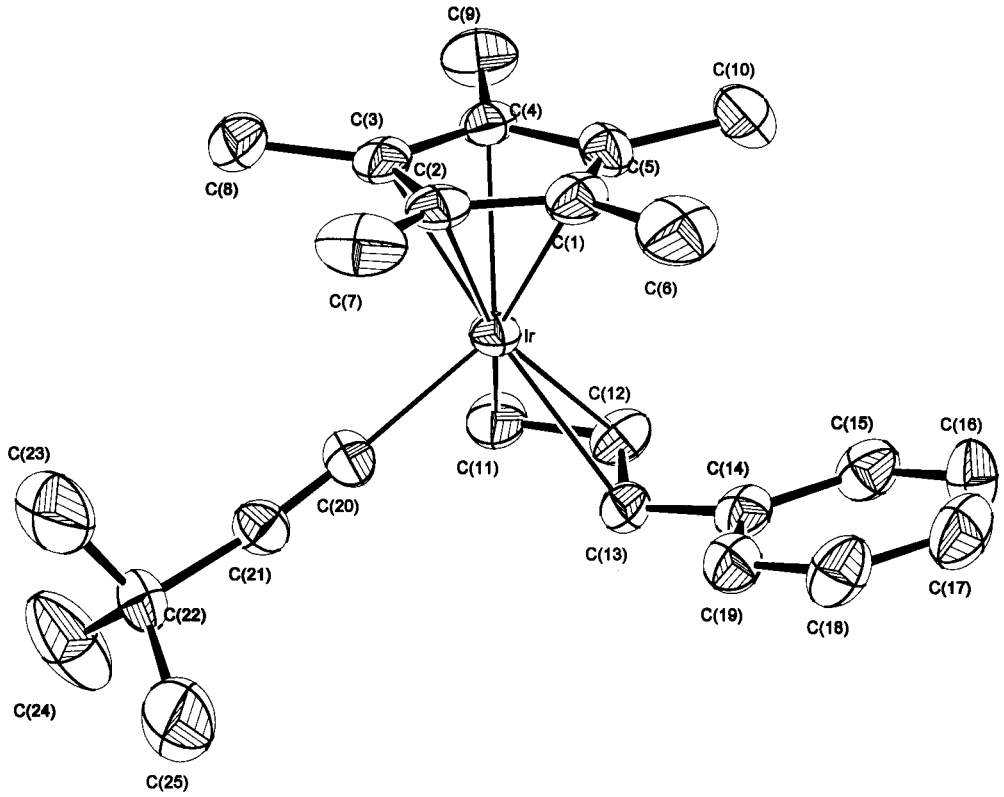
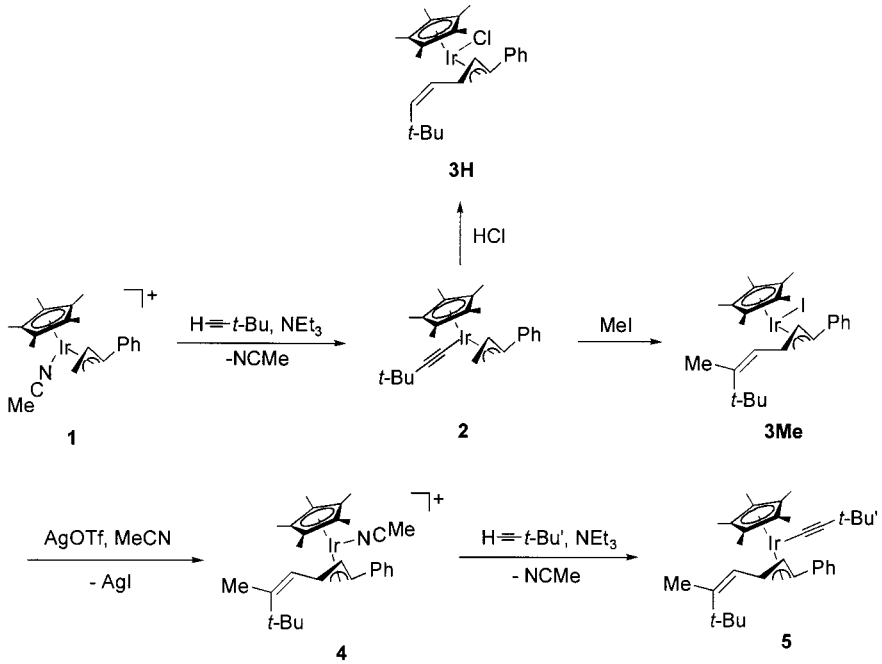


Figure 1. ORTEP drawing of Cp*Ir(η^3-CHPhCHCH$_2$)(−C≡C-*t*-Bu) (**2**) with 36% thermal ellipsoids probability. Selected bond distances (Å): Ir−C_{11} = 2.15(2); Ir−C_{12} = 2.08(14); Ir−C_{13} = 2.21(15); C_{11}−C_{12} = 1.44(2); C_{12}−C_{13} = 1.38(2); C_{20}−C_{21} = 1.18(2); C_{21}−C_{22} = 1.48(2); C_{11}−C_{20} = 2.85(19); C_{13}−C_{20} = 2.90(19). Selected bond angles (deg): Ir$C_{21}C_{20}$ = 177.6; $C_{20}C_{21}C_{22}$ = 173.6(18), $C_{11}C_{12}C_{13}$ = 120.1(15).

Scheme 1



determination for **5** by X-ray diffraction data analysis (Figure 2). The crystal structure reveals the *t*-Bu group being *cis* to the allyl group in complex **5**. ^{1}H and ^{13}C NMR spectra of **5** show no other isomers of **5** present in solution ($CDCl_3$). The η^3-pentadienyl moieties of **3** and **4** show practically the same types of signals in their ^{1}H and ^{13}C NMR spectra as those due to the η^3-pentadienyl moiety of **5**. Spectral data (^{1}H, ^{13}C NMR, NOE, ^{1}H, ^{1}H-2D COSY, and ^{1}H, ^{13}C-2D HETCOR, IR) and elemental analysis (see Supporting Information) confirm the structures of **3H**, **3Me**, and **4** as shown in Scheme 1. A relatively small coupling constant (J(−C*H*=C*H*−) = 11.5 Hz) between the olefinic protons suggests the *t*-Bu group being *cis* to the allyl group in **3H**, which is supported by NOE measurements (see Supporting Information). That the *t*-Bu group in **3Me** is *cis* to the

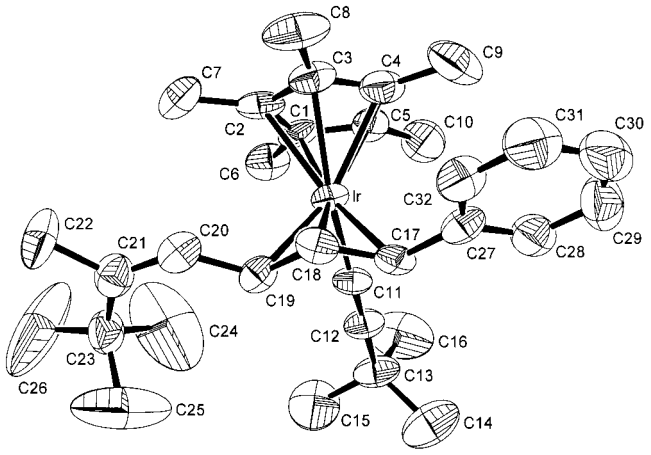
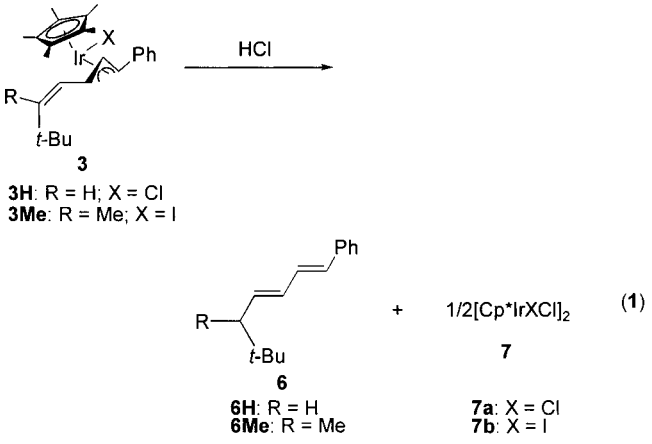


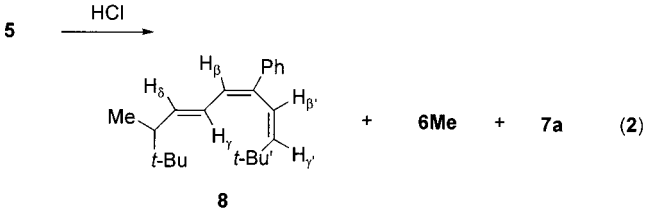
Figure 2. ORTEP drawing of Cp*(Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(−C≡C-*t*-Bu′) (**5**) with 40% thermal ellipsoids probability. Selected bond distances (Å): Ir−C_{17} = 2.20(11); Ir−C_{18} = 2.09(13); Ir−C_{19} = 2.18(14); C_{17}−C_{18} = 1.43(2); C_{18}−C_{19} = 1.41(2); C_{11}−C_{12} = 1.16(19); C_{12}−C_{13} = 1.48(19); C_{19}−C_{20} = 1.46(19); C_{20}−C_{21} = 1.35(2); C_{21}−C_{22} = 1.50(2); C_{21}−C_{23} = 1.51(2); C_{11}−C_{19} = 2.85(19); C_{11}−C_{17} = 2.83(19). Selected bond angles (deg): $IrC_{11}C_{12}$ = 175.1(12), $C_{17}C_{18}C_{19}$ = 119.6(13), $C_{18}C_{19}C_{20}$ = 117.9(13), $C_{19}C_{20}C_{21}$ = 132.4(14), $C_{20}C_{21}C_{22}$ = 117.0(16), $C_{20}C_{21}C_{23}$ = 127.5(14).

allyl group is deduced by the fact that it is so in **5** and supported by NOE measurements: Irradiation on δ 1.77 (Me) shows a positive NOE effect at δ 4.89 (−C*H*═CMe-(*t*-Bu)) (see Supporting Information).

Reactions of Metal Complexes with HCl. Complexes **3H** and **3Me** react with HCl to produce [Cp*-IrXCl]$_2$ (**7**) and, respectively, *trans*,*trans*-1,3-pentadienes PhCH═CHCH═$CHCH_2$(*t*-Bu) (**6H**) and PhCH═CHCH═CHCHMe(*t*-Bu) (**6Me**) (eq 1). ^{1}H, ^{13}C NMR, and GC/mass data analyses unambiguously identify the structures of **6H** and **6Me** shown in eq 1 (see Supporting Information for NOE and ^{1}H, ^{13}C-2D HETCOR spectra).



Complex **5** also readily reacts with HCl to give **6Me**, *cis*,*trans*,*trans*-1,3,5-heptatriene (*t*-Bu′)$CH_{\gamma'}$═$CH_{\beta'}C_\alpha$(Ph)═$CH_\beta CH_\gamma$═$CH_\delta CH_\epsilon$Me(*t*-Bu) (**8**), and [Cp*-$IrCl_2]_2$ (**7a**) (eq 2). ^{1}H, ^{13}C NMR, and GC/mass data analyses unambiguously identify the structure of compound **8** as shown in eq 2. The coupling between H(γ') and H(β') (J = 12.0 Hz) is evidently smaller than those observed between the olefinic *trans* protons (15.5−16.0 Hz for **6** and **8**) and suggests these two protons are *cis* to each other. This suggestion is supported by NOE measurements: The signal (δ 1.00) due to the newly added *t*-Bu′ shows a significant positive NOE effect on irradiation at the H(γ) signal (δ 6.38), and a significant effect on the latter is seen by irradiation at the former. The NOE effect of the *t*-Bu′ group is very small on the Ph group, suggesting the *t*-Bu′ group is far from the Ph group.



Discussion

Formation of Cp*Ir(η^3-CHPhCHCH−CH═CH(*t*-Bu))Cl (3H) and Cp*Ir(η^3-CHPhCHCH−CH═CMe-(*t*-Bu))I (3Me). Formation of **3** seems to be initiated by the attack of electrophiles H^+ and Me^+ on the β-carbon of the *tert*-butylethynyl group of **2**, which consequently makes the α-carbon of the alkynyl group more electrophilic to accept the nucleophilic terminal carbon of the allyl group to form a C−C bond. Addition of electrophiles to the β-carbon of metal−alkynyls is well-known to give metal−vinylidenes.[8] No direct evidence has been obtained for the Ir═C═CR(*t*-Bu) (R = H, Me) moiety during the reactions of **2** with HCl and MeI thus far. Metal−vinylidene, however, may not be excluded from the possible mechanisms for the formation of **3** (see Scheme 2).

Formation of **3** requires transfer of one hydrogen from the γ-carbon to the δ-carbon of **A**. This hydrogen transfer may occur through the β-hydrogen elimination to produce the Cp*Ir(V) intermediate **B**, which then undergoes reductive cleavage to give **3** (see Scheme 2). Cp*M (M = Ir, Rh) complexes with M in their high oxidation state (Ir(V), Rh(V)) have been observed,[9] suggested[10] as the products from reactions of Cp*Ir(III) complexes with HX (X = halogen, H, and Me), and supported by theoretical calculation.[11] Metallacyclopropanes such as **B** in Scheme 2 have been frequently suggested as the intermediates in the reactions of

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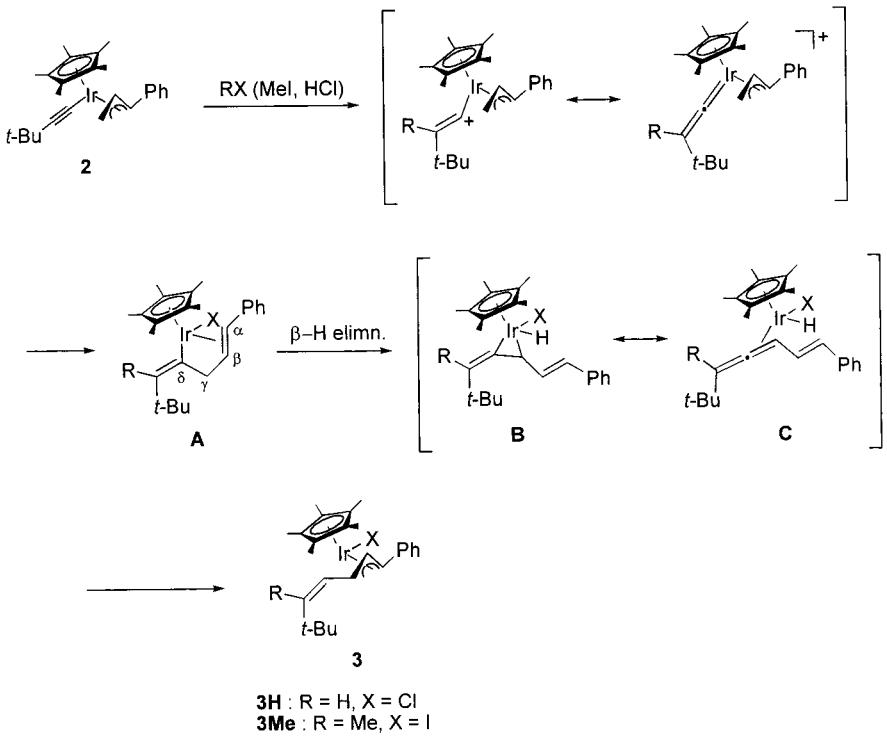
Scheme 2



metal−alkynyls and related compounds.[12] η^2-Allene complexes have been suggested as the products of β-hydrogen elimination of alkenyl complexes.[13] Therefore, the intermediate **B** may have an η^2-allene Ir(III) resonance structure, **C**.

Formation of *trans,trans*-1,3-Pentadienes PhCH=CHCH=CHCH$_2$(*t*-Bu) (6H) and PhCH=CHCH=CHCHMe(*t*-Bu) (6Me) from the Reactions of 3H and 3Me with HCl. There are two possible ways for **3** to give 1,3-pentadienes in the reactions with H^+: (i) H^+ attacks the terminal γ-carbon of the allylic group (η^3-CHPhCHCH−CH=CR(*t*-Bu)) (R = H, Me) to give 1,4-pentadienes, which then undergo isomerization to 1,3-pentadienes since it is well-known that electrophiles such as H^+ attack the terminal carbons of allyl ligand.[7a] (ii) H^+ attacks the terminal carbon of the olefinic group (η^3-CHPhCHCH−CH=*C*R(*t*-Bu)) (R = H, Me) to give 1,3-pentadienes since noncoordinated olefinic carbons may also be attacked by electrophiles such as H^+.[14] Attempts have been unsuccessfully made to obtain more information on the reaction pathways (i and/or ii) for the formation of 1,3-pentadienes. No conclusive evidence has been obtained for the formation of 1,4-pentadienes during the reactions of **3** with HCl.[15] Reactions of **3** with DCl produce deuterium-containing 1,3-pentadienes whose ^{1}H NMR and mass spectra are very complex.[16] A further investigation is currently being carried out for the formation of 1,3-pentadienes from the reaction of **3** with HCl.

Formation of *cis,trans,trans*-1,3,5-Heptatatriene (*t*-Bu′)CH=CHC(Ph)=CH−CH=CHCHMe(*t*-Bu) (8) and PhCH=CHCH=CHCHMe(*t*-Bu) (6Me) from Reaction of 5 with HCl. Heptatriene compound **8** is apparently the product of a H^+-mediated coupling reaction between the α-carbon of the allyl group and the α-carbon of the alkynyl group of **5**. It is somewhat surprising not to see the coupling reaction between the γ-carbon of the allyl group and the α-carbon of the alkynyl group in the reaction of **5** with HCl since it was observed in the reaction of **2** with HCl. It is most likely that this coupling reaction occurs through the similar reaction pathways as suggested for the formation of **6** from the reactions of **3** with HCl and MeI. It may be mentioned here again that the reaction of **5** with DCl gives many deuterium-containing heptatrienes whose spectral (^{1}H NMR and mass) data are very complex, and a further investigation is currently being carried out to obtain more information on the formation of **8**. Formation of **6Me** may be understood in the same way as discussed in the reaction of **3Me** with HCl.

Experimental Section

General Information. A standard vacuum system and Schlenk type glassware were used in handling metal complexes, although most of metal complexes investigated in this study seemed to be stable enough to be handled without much precautions against air and moisture.

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(15) ^{1}H NMR spectra were measured for the reaction mixture of **2** and HCl (H_2O solution, HCl/Ir = *ca.* 2.0) in $CDCl_3$ at 0 °C at intervals. Two sets of new signals appeared at the expense of the signals due to **2** and slowly disappeared as the signals due to the products **3H** and **6H** (1,3-pentadiene) increased. It may be possible that those two sets of signals are probably those due to 1,4-pentadiene (*t*-BuCH=CHCH$_2$-CH=CHPh) and the geometric isomer of **3H**, respectively.

(16) ^{1}H NMR spectra showed that the products contained deuterium at five different carbons of **6H** with different % of D, and mass spectra also showed various isotopomers.

The NMR spectra were obtained on a Varian Gemini 300 or 500 MHz for ^{1}H and 75 or 125 MHz for ^{13}C. Infrared spectra were obtained on Nicolet 205 and Shimadzu IR-440 spectrophotometers. Gas chromatography/mass spectra were measured by Hewlett-Packard HP 5890A and VG-trio 2000 instruments. Elemental analysis was performed with a Carlo Erba EA1108 at the Organic Chemistry Research Center, Sogang University, Korea.

Complex **1**, [Cp*Ir(η^3-CHPhCHCH$_2$)(NCMe)]OTf, was prepared by the literature method.[17]

Preparation of Cp*Ir(η^3-CHPhCHCH$_2$)(−C≡C-*t*-Bu) (2). Triethylamine (0.96 mmol) and *tert*-butylacetylene (0.96 mmol) were added to a benzene (10 mL) solution of **1** (0.32 mmol) under N_2. The yellow solution was refluxed for 1 h, cooled to room temperature, and distilled under vacuum to obtain a yellowish residue, which was washed with H_2O (5 mL) and dissolved in diethyl ether (100 mL). The orange-yellow solution obtained by filtration was distilled under vacuum to dryness to obtain a yellow-orange solid, which was washed with methanol (1 mL) and dried under vacuum. The yield was 93% (0.16 g) based on Cp*Ir(η^3-CHPhCHCH$_2$)(−C≡C-*t*-Bu). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 1.24 (s, 9H, C(CH_3)$_3$), 1.60 (s, 15H, CH_3 of Cp*), 2.17 (d, 1H, J(HH) = 9.0 Hz, CHPhCHC*H*), 2.78 (d, 1H, J(HH) = 6.3 Hz, CHPhCHCH*H*), 3.96 (d, 1H, J(HH) = 9.6 Hz, C*H*PhCHCH$_2$), 4.25 (m, 1H, CHPhC*H*CH$_2$), 7.02−7.30 (m, 5H, C$_6$H$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 8.4, 92.7 (Cp*), 29.0 (*C*(CH$_3$)$_3$), 33.4 (CHPhCH*C*H$_2$), 33.8 (C(*C*H$_3$)$_3$), 55.2 (*C*HPhCHCH$_2$), 67.3 (Ir−*C*≡C), 69.6 (CHPh*C*HCH$_2$), 107.1 (Ir−C≡*C*), 124.4, 125.3, 128.4 and 141.9 (*C*$_6$H$_5$). IR (KBr, cm^{-1}): 2098 (m, $\nu_{C\equiv C}$). Anal. Calcd for $C_{25}H_{38}Ir$: C, 57.12; H, 6.33. Found: C, 57.12; H, 6.34.

Preparation of Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))I (3Me). MeI (0.073 mL, 1.2 mmol) was added to an acetone (5 mL) solution of **2** (0.59 mmol), and the resulting solution was stirred at 70 °C for 4 h under N_2 in a bomb reactor (Parr 4701, 22 mL). The reaction mixture was cooled to room temperature, and the solvent was removed by blowing N_2 into the solution to obtain an orange solid, which was stirred in pentane (50 mL) and filtered. The clear orange filtrate was concentrated in a stream of dry N_2 to obtain an orange solid, which was recrystallized in $CHCl_3$/(cold)MeOH. The yield was 0.20 g (51% based on Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))I). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 1.20 (s, 9H, C(CH_3)$_3$), 1.48 (s, 15H, CH_3 of Cp*), 1.77 (d, 3H, J(HH) = 0.9 Hz, CH═CCH_3), 4.21 (dd, 1H, J(HH) = 9.8 Hz, J(HH) = 8.3 Hz, CHPhC*H*CH), 4.89 (dd, 1H, J(HH) = 11.5 Hz, J(HH) = 0.9 Hz, C*H*═CCH$_3$), 4.99 (dd, 1H, J(HH) = 8.3 Hz, J(HH) = 11.5 Hz, CHPhCHC*H*), 5.46 (d, 1H, J(HH) = 9.8 Hz, C*H*PhCHCH), 7.10−7.30 (m, 5H, C$_6$H$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 8.8, 92.0 (Cp*), 24.8 (CH═C*C*H$_3$), 29.7 (C(*C*H$_3$)$_3$), 35.6 (*C*(CH$_3$)$_3$), 52.1 (CHPhCH*C*H), 53.2 (*C*HPhCHCH), 77.5 (CHPh*C*HCH), 128 (*C*H═CCH$_3$), 140.8 (CH═*C*CH$_3$), 125.4, 126.0, 128.7 and 142.2 (*C*$_6$H$_5$). HETCOR (^{1}H (300 MHz) → ^{13}C (75 MHz)): δ 1.77 → 24.8; δ 4.21 → 77.5; δ 4.89 → 128; δ 4.99 → 52.1; δ 5.46 → 53.2. NOE ($CDCl_3$, 300 MHz): irradiation at δ 1.77, positive effect at δ 1.20, 4.89. Anal. Calcd for $C_{26}H_{36}IIr$: C, 46.77; H, 5.43. Found: C, 46.68; H, 5.24.

Preparation of Cp*Ir(η^3-CHPhCHCH−CH═CH(*t*-Bu))Cl (3H). HCl (32 wt % H_2O solution, 14 μL, 0.14 mmol) was added to a pale yellow solution of **2** (0.095 mmol) in $CHCl_3$ (2 mL), and the reaction mixture was stirred for 5 min at 0 °C, during which time the reaction mixture turned more yellowish. After solvents were removed by vacuum distillation, pentane (20 mL) was added to dissolve **3H** and **6H**, and the reaction mixture was filtered to obtain insoluble **7a** (0.017 g, 23% based on [Cp*IrCl$_2$]$_2$[18]). The filtrate was eluted through a silica gel column using hexane/diethyl ether to separate **3H** (0.011 g, 12%) from unreacted **2** and a small amount of **6H**. **3H**: ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 1.16 (s, 9H, C(CH_3)$_3$), 1.36 (s, 15H, Cp*), 4.39 (dd, 1H, J(HH) = 10.5 Hz, J(HH) = 9.5 Hz, CHPhCHC*H*), 4.64 (d, 1H, J(HH) = 10.5 Hz, C*H*PhCHCH), 4.91 (dd, 1H, J(HH) = 10.5 Hz, J(HH) = 9.5 Hz, CHPhC*H*CH), 4.99 (dd, 1H, J(HH) = 11.5 Hz, J(HH) = 9.5 Hz, C*H*═CH(*t*-Bu)), 5.69 (dd, 1H, J(HH) = 11.5 Hz, J(HH) = 1.0 Hz, CH═C*H*(*t*-Bu)), 7.12−7.30 (m, 5H, C$_6$H$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 7.7, 91.6 (Cp*), 30.6 (C(*C*H$_3$)$_3$), 33.4 (*C*(CH$_3$)$_3$), 58.4 (CHPhCH*C*H), 61.7 (*C*HPhCHCH), 79.7 (CHPh*C*HCH), 129.3 (*C*H═CH(*t*-Bu)), 138.6 (CH═*C*H(*t*-Bu)), 125.4, 125.8, 128.6 and 140.8 (*C*$_6$H$_5$). 2D ^{1}H NMR ($CDCl_3$, 500 MHz, ^{1}H ↔ ^{1}H): δ 4.39 ↔ 4.91, 4.99; δ 4.64 ↔ 4.91; δ 4.91 ↔ 4.39, 4.64; δ 4.99 ↔ 4.39, 5.69; δ 5.69 ↔ 4.99. NOE ($CDCl_3$, 500 MHz): irradiation at δ 5.69, positive effect at δ 4.99, 1.16. Anal. Calcd for $C_{25}H_{34}ClIr$: C, 53.41; H, 6.10. Found: C, 53.39; H, 5.73.

Preparation of [Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(NCMe)]OTf (4). A 0.09 g (0.36 mmol) sample of AgOTf was added to a MeCN (10 mL) solution of **3Me** (0.19 g, 0.29 mmol), and the reaction mixture was stirred for 1 h at room temperature. AgI was removed by filtration, and the filtrate was vacuum distilled to obtain a pale yellow solid, which was recrystallized in $CHCl_3$/(C$_2$H$_5$)$_2$O to obtain pale yellow microcrystals of [Cp*Ir(η^3-CHPhCHCH−CH═CHCMe(*t*-Bu))(NCMe)]OTf, (**4**, 0.195 g, 96%). ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 1.18 (s, 9H, C(CH_3)$_3$), 1.41 (s, 15H, CH_3 of Cp*), 1.85 (s, 3H, CH═CCH_3), 2.90 (s, 3H, NCCH_3), 4.01 (dd, 1H, J(HH) = 9.6 Hz, J(HH) = 11.5 Hz, CHPhCHC*H*), 4.22 (d, 1H, J(HH) = 10.5 Hz, C*H*PhCHCH), 4.74 (dd, 1H, J(HH) = 10.5 Hz, J(HH) = 9.6 Hz, CHPhC*H*CH), 4.99 (d, 1H, J(HH) = 11.5 Hz, C*H*═CMe), 7.09−7.39 (m, 5H, C$_6$H$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 3.76 (NC*C*H$_3$), 7.5, 94.1 (Cp*), 24.2 (CH═C*C*H$_3$), 29.5 (C(*C*H$_3$)$_3$), 35.8 (*C*(CH$_3$)$_3$), 61.0 (CHPhCH*C*H), 61.2 (*C*HPhCHCH), 79.9 (CHPh*C*HCH), 121.4 (N*C*CH$_3$), 126.5 (*C*H═CMe), 146.7 (CH═*C*Me), 124.7, 126.1, 129.5 and 137.5 (*C*$_6$H$_5$). HETCOR (^{1}H (500 MHz) → ^{13}C (125 MHz)): δ 1.85 → 24.2; δ 4.01 → 61.0; δ 2.90 → 3.76; δ 4.22 → 61.2; δ 4.74 → 79.9; δ 4.99 → 126.5. IR (KBr, cm^{-1}): 1030, 1140 and 1254 (br. s, ν_{OTf}). Anal. Calcd for $C_{29}H_{39}NO_3SF_3Ir$: C, 47.66; H, 5.38; N, 1.92. Found: C, 47.65; H, 5.48; N, 1.94.

Preparation of Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(−C≡C-*t*-Bu′) (5). This compound (yellow microcrystals) was prepared in the same manner as described for **2** using 0.27 mmol of **4**, 1.62 mmol of H−C≡C-*t*-Bu′, and 0.81 mmol of NEt$_3$. The yield was 0.14 g (84% based on **5**, [Cp*Ir(η^3-CHPhCHCH−CH═CMe(*t*-Bu))(−C≡C-*t*-Bu′)]). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 1.19 (s, 9H, C(CH_3)$_3$), 1.20 (s, 9H, C(CH_3)$_3$), 1.46 (s, 15H, CH_3 of Cp*), 1.72 (d, 3H, J(HH) = 0.9 Hz, CH═CCH_3), 3.86 (dd, 1H, J(HH) = 8.1 Hz, J(HH) = 11.1 Hz, CHPhCHC*H*), 4.05 (d, 1H, J(HH) = 9.6 Hz, C*H*PhCHCH), 4.17 (dd, 1H, J(HH) = 9.6 Hz, J(HH) = 8.1 Hz, CHPhC*H*CH), 4.79 (dd, 1H, J(HH) = 11.1 Hz, J(HH) = 0.9 Hz, C*H*═CMe), 7.01−7.29 (m, 5H, C$_6$H$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ 8.1, 92.4 (Cp*), 24.6 (CH═C*C*H$_3$), 28.8 (*C*(CH$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$), 33.8 (C(*C*H$_3$)$_3$), 35.5 (*C*(CH$_3$)$_3$), 51.4 (CHPhCH*C*H), 51.6 (*C*HPhCHCH), 68.9 (Ir−*C*≡C), 73.3 (CHPh*C*HCH), 105.9 (Ir−C≡*C*), 129.3 (*C*H═CMe), 142.4 (CH═*C*Me), 124.2, 125.4, 128.3 and 139.9 (*C*$_6$H$_5$). HETCOR (^{1}H (300 MHz) → ^{13}C (75 MHz)): δ 1.72 → 24.6; δ 1.19 → 29.8; δ 1.20 → 33.8; δ 3.86 → 51.4; δ 4.05 → 51.6; δ 4.17 → 73.3; δ 4.79 → 129.3. IR (KBr, cm^{-1}): 2101 (m, $\nu_{C\equiv C}$). Anal. Calcd for $C_{32}H_{45}Ir$: C, 61.80; H, 7.29. Found: C, 61.75; H, 7.20.

Reaction of 3H with HCl. A 0.123 mL sample of HCl (32 wt % solution in H_2O, 1.27 mmol) was added to a $CHCl_3$ (5 mL) solution of **2** (0.165 g, 0.314 mmol), and the reaction mixture was stirred at room temperature for 10 min, during which time the yellow solution turned red. After solvents were removed by vacuum distillation, pentane (20 mL) was added to dissolve **6H**, and the reaction mixture was filtered to obtain insoluble **7a** (0.11 g, 0.27 mmol, 86% based on [Cp*IrCl$_2$]$_2$). The filtrate was eluted through a silica gel column using

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hexane/diethyl ether to obtain 0.25 mmol of **6H** (80% based on PhCH=CHCH=CHCH$_2$(*t*-Bu) measured by ^{1}H NMR). **7a**: ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ 1.59 (lit. δ 1.59).[18] **6H**: ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 0.94 (s, 9H, C(C*H*$_3$)$_3$), 2.05 (d, 2H, *J*(HH) = 7.5 Hz, CH=CHC*H*$_2$), 5.88 (dt, 1H, *J*(HH) = 7.5 Hz, *J*(HH) = 15.5 Hz, CH=C*H*CH$_2$), 6.20 (dd, 1H, *J*(HH) = 11.0 Hz, *J*(HH) = 15.5 Hz, C*H*=CHCH$_2$), 6.47 (d, 1H, *J*(HH) = 15.5 Hz, PhC*H*=CH), 6.80 (dd, 1H, *J*(HH) = 11.0 Hz, *J*(HH) = 15.5 Hz, PhCH=C*H*), 7.19−7.43 (m, 5H, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 29.4 (C(*C*H$_3$)$_3$), 31.4 (*C*(CH$_3$)$_3$), 47.5 (CH=CH*C*H$_2$), 129.4 (PhCH=*C*H), 130.1 (Ph*C*H=CH), 132.6 (*C*H=CHCH$_2$), 133.0 (CH=*C*HCH$_2$), 126.1, 127.0, 128.5 and 137.7 (*C*$_6$H$_5$). HETCOR (^{1}H (500 MHz) → ^{13}C (125 MHz)): δ 0.94 → 29.4; δ 2.05 → 47.5; δ 5.88 → 133.0; δ 6.20 → 132.6; δ 6.47 → 130.1; δ 6.80 → 129.4. NOE ($CDCl_3$, 500 MHz): irradiation at δ 6.80, positive effect at δ 5.88, 7.42. MS, *m*/*z*: M^+ = 200.

Reaction of 3Me with HCl. This reaction was carried out in the same manner as described above for the reaction of **3H** with HCl using 0.29 mmol (0.15 g) of **3Me** in $CHCl_3$ (5 mL) and HCl (32 wt %, 0.11 mL, 1.14 mmol). A 0.11 g (93% based on [Cp*IrClI]$_2$) sample of **7b** was obtained, and 0.24 mmol of **6Me** (82% based on PhCH=CHCH=CHCHMe(*t*-Bu)) was measured by ^{1}H NMR. **6Me**: ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 0.92 (s, 9H, C(C*H*$_3$)$_3$), 1.03 (d, 3H, *J*(HH) = 6.9 Hz, CH=CHCHC*H*$_3$), 2.04 (m, 1H, CH=CHC*H*Me), 5.83 (dd, 1H *J*(HH) = 15.1 Hz, *J*(HH) = 9.0 Hz, CH=C*H*CHMe), 6.18 (dd, 1H, *J*(HH) = 15.1 Hz, *J*(HH) = 10.4 Hz, C*H*=CHCHMe), 6.48 (d, 1H, *J*(HH) = 15.7 Hz, PhC*H*=CH), 6.80 (dd, 1H, *J*(HH) = 15.7 Hz, *J*(HH) = 10.4 Hz, PhCH=C*H*), 7.19−7.43 (m, 5H, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 15.4 (*C*H$_3$), 27.5 (C(*C*H$_3$)$_3$), 33.3 (*C*(CH$_3$)$_3$), 47.5 (CH=CH*C*HMe), 129.7 (*C*H=CHCHMe), 129.9 (PhCH=*C*H), 130.1 (Ph*C*H=CH), 139.4 (CH=*C*HCHMe), 126.1, 127.0, 128.5 and 137.7 (*C*$_6$H$_5$). HETCOR (^{1}H (500 MHz) → ^{13}C (125 MHz)): δ 0.92 → 27.5; δ 1.03 → 15.4; δ 2.04 → 47.5; δ 5.83 → 139.4; δ 6.18 → 129.7; δ 6.48 → 130.1; δ 6.80 → 129.9. MS, *m*/*z*: M^+ = 214.

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Reaction of 5 with HCl. This reaction was carried out in the same manner as described above for the reaction of **3H** with HCl except that the reaction mixture was stirred for 10 min at 0 °C. A 0.29 mmol (0.18 g) sample of **5** in $CHCl_3$ (5 mL) and HCl (32 wt %, 0.071 mL, 0.72 mmol) were used to obtain 0.097 g of **7a** (84% based on [Cp*IrCl$_2$]$_2$), 0.19 mmol of **8** (58% based on (*t*-Bu′)CH=CHC(Ph)=CHCH=CHCHMe(*t*-Bu)), and 0.081 mmol of **6Me** (28% based on PhCH=CHCH=CHCHMe-(*t*-Bu)), which were measured by ^{1}H NMR. The ratio of **8**/**6Me** ≈ 2/1 has also been confirmed by GC measurements. **8**: ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz): δ 0.89 (s, 9H, CHCHMeC-(C*H*$_3$)$_3$)), 0.99 (d, 3H, *J*(HH) = 6.5 Hz, CHCHC*H*$_3$(*t*-Bu)), 1.00 (s, 9H, (C*H*$_3$)$_3$CCH=CH), 2.04 (m, 1H, CHC*H*Me(*t*-Bu)), 5.68 (d, 1H, *J*(HH) = 12.0 Hz, (*t*-Bu′)C*H*=CH), 5.80 (dd, 1H, *J*(HH) = 15.5 Hz, *J*(HH) = 9.5 Hz, C*H*CHMe(*t*-Bu)), 5.88 (dd, 1H, *J*(HH) = 12.0 Hz, *J*(HH) = 1.5 Hz, (*t*-Bu′)CH=C*H*), 6.38 (dd, 1H, *J*(HH) = 11.0 Hz, *J*(HH) = 15.5 Hz, C(Ph)=CHC*H*), 6.57 (dd, 1H, *J*(HH) = 11.0 Hz, *J*(HH) = 1.5 Hz, C(Ph)=C*H*CH), 7.21−7.50 (m, 5H, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz): δ 15.5 (*C*H$_3$), 27.6 (CHCHMeC(*C*H$_3$)$_3$), 29.8 ((*C*H$_3$)$_3$CCH=CH), 33.3 (CHCHMe*C*(CH$_3$)$_3$), 34.7 ((CH$_3$)$_3$*C*CH=CH), 47.8 (CH*C*H-Me(*t*-Bu)), 122.8 ((*t*-Bu′)CH=*C*H), 127.0 (C(Ph)=*C*HCH), 129.1 (C(Ph)=CH*C*H), 139.3 (*C*HCHMe(*t*-Bu)), 143.8 ((*t*-Bu′)*C*H=CH), 126.0, 126.8, 128.2 and 136.4 (*C*$_6$H$_5$), 140.7 (*C*(Ph)). HETCOR (^{1}H (500 MHz) → ^{13}C (125 MHz)): δ 0.99 → 15.5; δ 2.04 → 47.8; δ 5.68 → 143.8; δ 5.80 → 139.3; δ 5.88 → 122.8; δ 6.38 → 129.1; δ 6.57 → 127.0. NOE ($CDCl_3$, 500 MHz): irradiation at δ 5.68, positive effect at δ 5.88; irradiation at δ 6.38, positive effect at δ 1.00. MS, *m*/*z*: M^+ = 296.

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Supporting Information Available: Tables giving details of the X-ray structure determination, including tables of crystal data, bond distances and angles, and positional and thermal parameters for **2** and **5**. ^{1}H, ^{1}H-2D COSY (for **3H**), ^{1}H, ^{13}C-2D HETCOR (for **3Me**, **4**, **5**, **6H**, **6Me**, and **8**), and NOE (for **3H**, **3Me**, **6H**, and **8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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