4810 *Organometallics* **1999,** *18,* 4810−4816

Reaction of an (Alkyl)(alkenyl)(alkynyl)iridium(III) Complex with HCl: Intramolecular C−C Bond Formation from Alkyl, Alkenyl, and Alkynyl Groups Coordinated to "$Ir(CO)(PPh_3)_2$". H/D Exchange between CH_3 and DCl

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Received May 10, 1999

Reaction of the (alkyl)(alkenyl)(alkynyl)iridium(III) complex $[Ir(CH_3)(CH{=}CHNEt_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(CO)(PPh_3)_2]ClO_4$ (**3**) with aqueous HCl initiates an intramolecular coupling reaction between $-CH_3$ and $-C{\equiv}C(p\text{-}C_6H_4CH_3)$ groups to give $[Ir(C(CH_3){=}CH(p\text{-}C_6H_4CH_3)(CH{=}CHNEt_3)(Cl)(CO)(PPh_3)_2]ClO_4$ (**5**), which further reacts with aqueous HCl to produce $[Ir(CH{=}CHNEt_3)(Cl)_2(CO)(PPh_3)_2]ClO_4$ (**6**) and *cis*-$CH_3CH{=}CH(p\text{-}C_6H_4CH_3)$ (**7**). Complex **5** yields the C−C coupling product $[(p\text{-}C_6H_4CH_3)HC{=}C(CH_3)CH{=}CHNEt_3]ClO_4$ (**8**) when it is refluxed in $CHCl_3$. The (alkyl)bis(alkynyl)iridium(III) compound $Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))_2(CO)(PPh_3)_2$ (**4**) reacts with aqueous HCl to give $H_2C{=}C{=}CH(p\text{-}C_6H_4CH_3)$ (**9**). Complex **3** reacts with excess DCl to give the d_5 isotopomer $CD_3CD{=}CD(p\text{-}C_6H_4CH_3)$ (**7-*d*$_5$**), while the reaction of **4** with DCl gives the d_1 isotopomer $H_2C{=}C{=}CD(p\text{-}C_6H_4CH_3)$ (**9-*d*$_1$**). Plausible reaction pathways are discussed for the formation of **7** and **9** and for the H/D exchange to give the isotopomer **7-*d*$_5$**.

Introduction

The formation of a C−C bond mediated by a metal is an important step in organic synthesis, since it is one of the useful synthetic methods for the formation of polyenes such as dienes and trienes from the reactions of alkenes and alkynes.[1] These reactions involve the migratory insertion of an unsaturated organic group into a M−C bond, the coupling between adjacent carbons coordinated to a metal, and the direct attack of a reagent at an unsaturated organic ligand.[2]

Alkynes ($RC{\equiv}CH$, R = H, Ph) are known to insert into Ir−B (B = NEt_3, PPh_3, $AsPh_3$) bonds to give $Ir{-}CH{=}CR{-}B$.[3] The hydrido(alkenyl)(alkynyl)iridium(III) complex $[Ir(H)(C{=}CNEt_3)(C{\equiv}CPh)(CO)(PPh_3)_2]^+$ has been reported.[3d] We now wish to report the synthesis of the analogous complex (alkyl)(alkenyl)(alkynyl)iridium(III) and its reaction with aqueous HCl to produce olefins through the coupling reaction between those organic ligands, Ir−***CH$_3$***, Ir−***C=CNEt$_3$***, and Ir−***C≡C-(p-C$_6$H$_4$CH$_3$)***.

Results

Preparation of (Alkyl)(alkenyl)(alkynyl)- and (Alkyl)bis(alkynyl)iridium(III). The four-coordinated alkynyliridium(I) compound $L_3Ir(C{\equiv}C(p\text{-}C_6H_4CH_3))$ (L_3 = $(CO)(PPh_3)_2$)[4] readily undergoes the oxidative addition of CH_3I to give the methyl(alkynyl)iridium(III) species $L_3Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(I)$ (**1**). Reaction of **1** with $AgClO_4$ in the presence of CH_3CN gives $[L_3Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(NCCH_3)]ClO_4$ (**2**), which reacts with $HC{\equiv}CH$ and $HC{\equiv}C(p\text{-}C_6H_4CH_3)$ in the presence of NEt_3 to produce the (alkyl)(alkenyl)(alkynyl)iridium(III) complex $[L_3Ir(CH_3)(CH{=}CHNEt_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))]ClO_4$ (**3**) and the (alkyl)bis(alkynyl)iridium(III) species $L_3Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))_2$ (**4**), respectively (eq 1).

As the oxidative addition of an alkyl iodide (RI) to Vaska's complex and other metal complexes is well-known to give *trans* R−M−I complexes,[5] it is conceivable that the addition of CH_3I gives a *trans* $CH_3{-}Ir{-}I$

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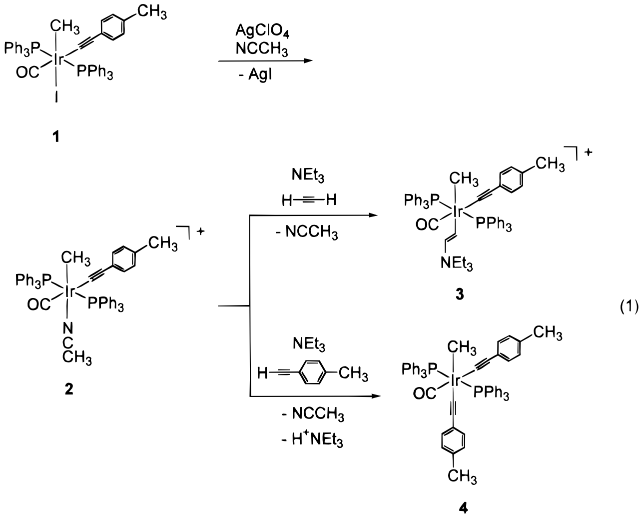
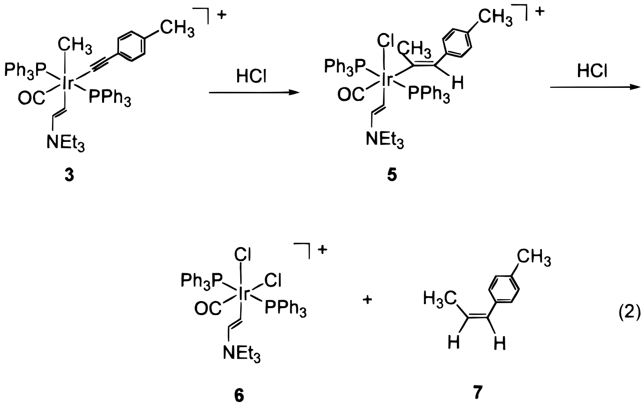


(1)

complex. Spectral data (^{1}H and ^{13}C NMR) also suggest *trans* CH_3−Ir−A moieties for **1**−**4** (A = I (**1**), $NCCH_3$ (**2**), $CH{=}CHNEt_3$ (**3**), $C{\equiv}C(p\text{-}C_6H_4CH_3)$ (**4**)). For example, the chemical shifts of the signals due to Ir−C***H***$_3$ and Ir−***C***H$_3$ shift significantly by varying the *trans* ligand A from 0.81 ppm for **1** to −0.33 ppm for **4** and from −14.9 ppm for **1** to −28.7 ppm for **3**, respectively. On the other hand, no significant shifts have been observed for those due to Ir−***C***O (from 169 ppm for **2** to 173 ppm for **3**) and Ir−***C***≡C (from 86 ppm for **1**−**3** to 87 ppm for **4**) that are *trans* to each other (see Experimental Section for detailed spectral data).

It is straightforward to assign the signals of ^{1}H and ^{13}C NMR spectra for **2**−**4**, since relevant spectral data are available for the analogous hydridoiridium complexes $[L_3Ir(H)(L')(C{\equiv}CR)]^{0,+}$ (L′ = $NCCH_3$, $CH{=}CHNEt_3$, C≡CR) from our previous studies[3a,d,6] and other reports of various metal alkyls[7] and metal alkynyls.[8] Signals due to the α- and β-protons of $IrC\boldsymbol{H}_\alpha{=}C\boldsymbol{H}_\beta NEt_3$ appear at 7.2−8.0 and 4.8−5.3 ppm, respectively, in related complexes such as $[L_3Ir(H)(CH{=}CHNEt_3)(C{\equiv}CPh)]^+$.[3d] The α- and β-protons have been observed at 7.52 and 4.86 ppm for **3**. The coupling constant (J_{H-H} = 15.9 Hz) between H_α and H_β in **3** suggests these two protons are *trans* to each other. The triplet at 0.30 ppm (J_{P-H} = 5.4 Hz) for **3** is apparently due to Ir−C***H***$_3$ being *cis* to both PPh_3 groups.

Reaction of $[L_3Ir(CH_3)(CH{=}CHNEt_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))]ClO_4$ (3) with Aqueous HCl. Complex **3** readily reacts with aqueous HCl to produce the bis(alkenyl)chloroiridium(III) complex $[L_3Ir(C(CH_3){=}CH(p\text{-}C_6H_4CH_3))(CH{=}CHNEt_3)(Cl)]ClO_4$ (**5**), which further reacts with HCl to give the (alkenyl)dichloroiridium(III) species $[L_3Ir(CH{=}CHNEt_3)(Cl)_2]ClO_4$ (**6**) and *cis*-$CH_3CH{=}CH(p\text{-}C_6H_4CH_3)$ (**7**) (eq 2).



(2)

Complexes **5** and **6** have been unambiguously characterized by spectral data (^{1}H, ^{13}C NMR) compared with those for related complexes containing $Ir(CH{=}CHNEt_3)$[3d] and various metal alkenyls.[9] We note in the ^{13}C NMR spectra of **5** and **6** that the signal due to Ir−***C***O *trans* to carbon is seen at lower field (173.6 ppm for **5**) than that (160.1 ppm for **6**) *trans* to Cl. Irradiation of the signal at 1.92 ppm (Ir−C(C***H***$_3$)=CH(p-$C_6H_4CH_3$)) shows no NOE effect on the signal at 6.41 ppm (Ir−C(CH_3)=C***H***(p-$C_6H_4CH_3$)), suggesting a *trans* relationship between ***CH***$_3$ and ***H*** (Ir−C(***CH***$_3$)=C***H***(p-$C_6H_4CH_3$)) in **5**.

The quantitative formation of **7** (*cis*-$CH_3CH{=}CH(p\text{-}C_6H_4CH_3)$) was verified by ^{1}H NMR and GC/mass spectral analysis (see Experimental Section). The relatively small coupling constant (J_{H-H} = 11.4 Hz) suggests the two olefinic protons ($CH_3C\boldsymbol{H}{=}C\boldsymbol{H}(p\text{-}C_6H_4CH_3)$) are *cis* to each other. This *cis* configuration is also confirmed by NOE measurement: irradiation of the signal at 5.74 ppm ($CH_3C\boldsymbol{H}{=}$) shows a positive NOE effect on the signal at 6.40 ppm ($=C\boldsymbol{H}(p\text{-}C_6H_4CH_3)$) (see Supporting Information).

Formation of 1,3-Diene by the Reductive Elimination between Two *cis*-Alkenyl Ligands of $[L_3Ir(C(CH_3){=}CH(p\text{-}C_6H_4CH_3))(CH{=}CHNEt_3)(Cl)]ClO_4$ (5). Complex **5** yields the *cis,trans*-1,3-diene $[HC(p\text{-}C_6H_4CH_3){=}C(CH_3)CH{=}CHNEt_3]ClO_4$ (**8**) and $IrCl(CO)(PPh_3)_2$ when it is refluxed in $CHCl_3$ (eq 3). Compound **8** has been unambiguously identified by ^{1}H and ^{13}C NMR, IR, and mass spectral data, and Vaska's complex, $IrCl(CO)(PPh_3)_2$, was confirmed by the three distinctive electronic absorption bands at 338, 388, and 440 nm in $CHCl_3$. Decoupling and NOE spectral data (Supporting Information) agree with the structure for **8** as shown in eq 3.

The three protons (see eq 3 for α, γ, and δ protons) for **8** are seen at 6.82 (s), 6.73 (d), and 5.95 (d) ppm. The coupling constant (J_{H-H} = 14.8 Hz) between H_γ and H_δ in **8** suggests these two protons are *trans* to each other, which is also supported by NOE spectral measurement (see Supporting Information).

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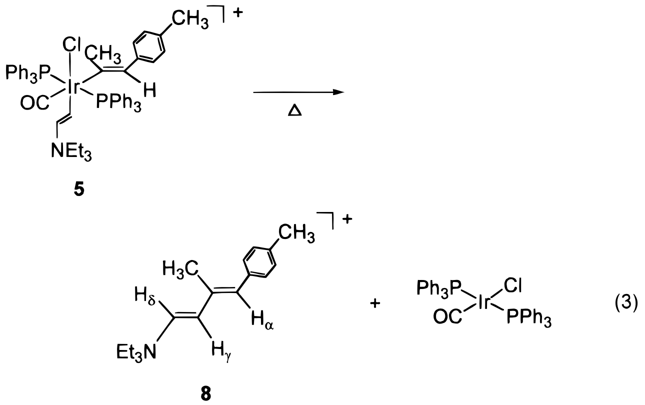
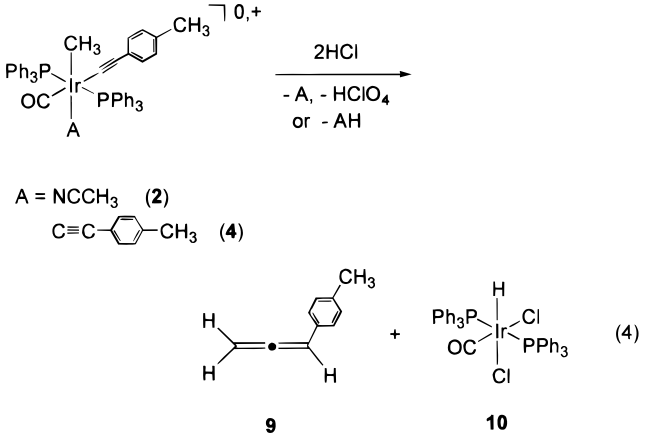


Reactions of (Alkyl)(alkynyl)iridium(III) Compounds 2 and 4 with Aqueous HCl: Formation of Allene. Reactions of **2** and **4** with aqueous HCl produce $L_3Ir(H)(Cl)_2$ (**10**) and $H_2C{=}C{=}CH(p\text{-}C_6H_4CH_3)$ (**9**) (eq 4), which have been identified by spectroscopic and GC/mass data. The signals at 6.14 (t) and 5.12 (d) ppm for **9** are due to the olefinic protons $H_2C{=}C{=}C\boldsymbol{H}(p\text{-}C_6H_4\text{-}CH_3)$ and $\boldsymbol{H_2}C{=}C{=}CH(p\text{-}C_6H_4CH_3)$, respectively. The small coupling constant ($J_{H-H} = 6.6$ Hz) between these protons unambiguously suggests that these protons are allenic ones, which agrees well with the values reported for the related compounds.[10] The strong ν(C=C) band at 1731.3 cm^{-1} in the IR spectrum and GC/mass data (M^+ at m/z 130) also support the identification of **9**.

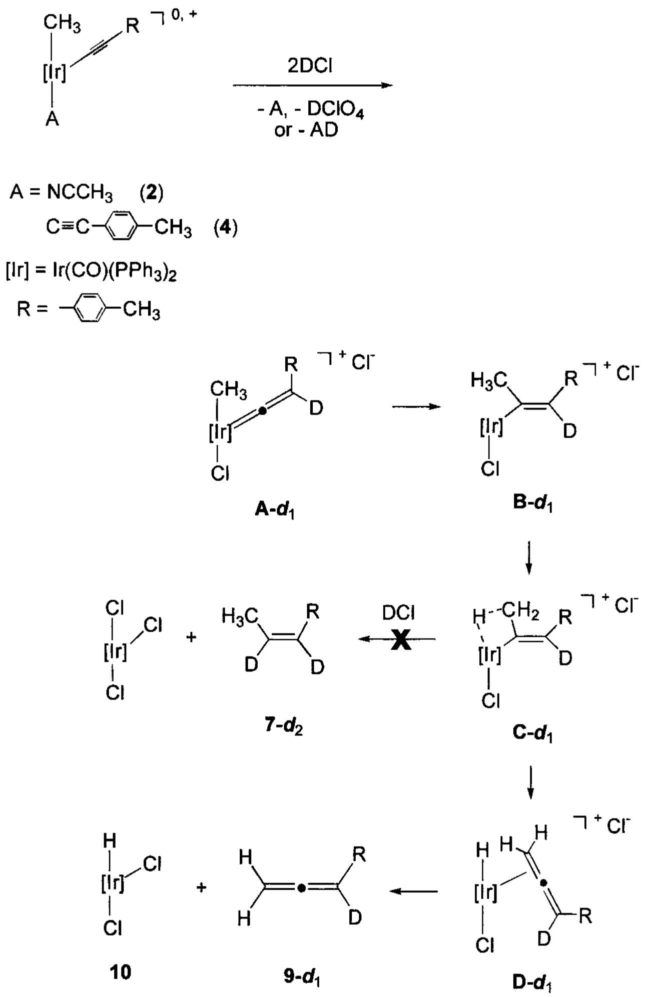


Compound **10**, $L_3Ir(H)(Cl)_2$,[11] has been identified by ^1H NMR (−15.4 (t) ppm) in $CDCl_3$ and IR (ν(C≡O), 2046 cm^{-1}, KBr) spectral data.

Discussion

Reaction Pathway for the Formation of $H_2C{=}C{=}CH(p\text{-}C_6H_4CH_3)$ (9). The treatment of **2** with aqueous DCl yields only the d_1 isotopomer $H_2C{=}C{=}CD(p\text{-}C_6H_4CH_3)$ (**9-d_1**), which is clearly confirmed by the absence of the signal at 6.14 ppm ($C{=}C\boldsymbol{H}(p\text{-}C_6H_4CH_3)$) while all other signals of **9** are seen in the ^1H NMR spectrum. No other isotopomers (such as $DHC{=}C{=}CD(p\text{-}C_6H_4CH_3)$ and $D_2C{=}C{=}CD(p\text{-}C_6H_4CH_3)$) have been found. The only isotopomer, **9-d_1**, is also verified by GC/mass (M^+ at m/z 131) data. The position of the deuterium atom in **9-d_1** suggests an electrophilic attack of D^+ at the β-carbon of the alkynyl ligand of **2** to give the iridium vinylidene (**A-d_1**) (see Scheme 1), as it is well-known that the proton attacks the β-carbon of an alkynyl ligand to give a metal vinylidene.[12] The intermediate **A-d_1** may undergo the CH_3 group migration to the α-carbon of the vinylidene group to give another intermediate **B-d_1**, as previously observed for the alkyl (R) group migration of $Re(C{=}CH_2)(R)$ to give $Re(CR{=}CH_2)$[12h] and the reaction of $Os(CH_2Ph)(C{\equiv}CPh)$ with H^+ to give $Os(C(CH_2Ph){=}CHPh)$.[13] It is most likely that **B-d_1** undergoes the β-hydrogen elimination to give the allene (**9-d_1**) and **10** as shown in Scheme 1. η^2-Allene

Scheme 1



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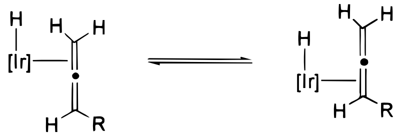
complexes[14] have been suggested as the products of the β-hydrogen elimination reaction of metal alkenyls.[14a–d] The same reaction pathway (Scheme 1) may be applicable for the formation of allene from the reaction of **4** with aqueous HCl.

Reaction Pathway for the Formation of the d_5 Isotopomer *cis*-$(CD_3)CD{=}CD(p\text{-}C_6H_4CH_3)$ (7-d_5). To obtain information on the formation of the *cis*-alkene **7**, deuterium labeling experiments have been carried out. Both reactions of **3** and **5** with excess DCl (DCl/Ir $>$ 10) produce the d_5 isotopomer $(CD_3)CD{=}CD(p\text{-}C_6H_4\text{-}CH_3)$ (**7-d_5**), which is unequivocally identified by ^1H NMR and GC/mass data (see Experimental Section and Supporting Information). Partially deutrated isotopomers, **7-d_n** ($n = 1-5$) were obtained when 7 equiv of DCl (DCl/Ir = 7) was used to react with **5** (see Supporting Information for ^1H NMR and mass spectra). It is, therefore, conceivable that the H/D exchange observed for the reactions of **3** and **5** with DCl seems to occur one by one to give **5-d_n** and **7-d_5**.

Reactions of **7** with DCl in the absence and presence of **6** give no deuterium-containing isomers of **7**. The H/D exchange possibly occurs at the complex **5** before the dissociation of **7** from the metal. Scheme 2 is suggested for the formation of **5-d_1** and the H/D exchange between **C*H₃*** of **5-d_1** and ***D*Cl** to give **5-d_4** ($[L_3Ir(C(C\mathbf{D_3}){=}C\mathbf{D}(p\text{-}C_6H_4CH_3))(CH{=}CHNEt_3)]ClO_4$) and then **7-$d_5$**. Scheme 2 also involves the formation of the η^2-allene-d_1 complex **E-d_1** by the same type of β-hydrogen elimination reaction of **5-d_1** as suggested in Scheme 1.

The H/D exchange between **C*H₃*** of **5-d_1** and ***D*Cl** (conversion of CH_3 into CD_3) may be expressed by the exchange between Ir−***H*** of **E-d_1** and ***D***$^+$ (in DCl/D_2O) to give Ir-***D*** in **E′-d_1** and ***H***$^+$ ($Ir{-}H + D^+ \leftrightarrow Ir{-}D + H^+$). Bases such as Cl^- and H_2O may be able to abstract H^+ (or D^+) from Ir−H (or Ir−D) of **E-d_1** as observed for $L_3Ir(H)(OClO_3)_2$, which reacts with H_2O to give $L_3Ir(OClO_3)$.[15] The hydride of $H{-}Co(CO)_4$ undergoes the H/D exchange in D_2O to give $D{-}Co(CO)_4$.[16] The final product **7-d_5** would be produced when D^+ attacks the α-carbon of Ir−**C**$(CD_3){=}CD(p\text{-}C_6H_4CH_3)$ in **5-d_4**. Equation 5 is also suggested to explain the formation of **7-d_5** from the reaction of **5** (not **5-d_1**) with DCl.



(5)

Formation of Allene vs Formation of *cis*-Alkene with the Rapid H/D Exchange. It is interesting to notice that (i) the allene **9** is produced from the reactions of **2** and **4** with HCl (eq 4) while the reaction of **3** gives the *cis*-alkene **7** (eq 2) and (ii) H/D exchange occurs extensively during the formation of **7** but not during the formation of **9**. These differences seem to be due to the different ligands *trans* to CH_3. Since the ligands $NCCH_3$ (in **2**) and $C{\equiv}C(p\text{-}C_6H_4CH_3)$ (in **4**) are readily substituted by Cl^- (eq 4) while $CH{=}CHNEt_3$ (in **3**) remains to be coordinated to metal during the reactions with HCl (eq 2), it seems conceivable to discuss the differences between the two intermediates $[L_3Ir(H)(\eta^2\text{-}H_2C{=}C{=}CHR)(Cl)]ClO_4$ (**D**, see Scheme 1) and $[L_3Ir(H)(\eta^2\text{-}H_2C{=}C{=}CHR)(CH{=}CHNEt_3)][(ClO_4)(Cl)]$ (**E**, see Scheme 2).

The hydride (Ir−***H***) *trans* to Cl^- (in **D**) could be less protic than the hydride (Ir−***H***) *trans* to $-CH{=}CH{-}NEt_3$ (in **E**): the positive charge on $-CH{=}CHNEt_3$ may increase the protic property of Ir−***H*** in **E** while the π-donor property of the Cl^- ligand may decrease that of Ir−***H*** in **D**. In fact, Ir−***H*** *trans* to Cl^- appears at δ −15.33 ppm for $L_3Ir(H)(Cl)(C{\equiv}CPh)$,[17] while Ir−***H*** *trans* to $-CH{=}CHNEt_3$ is seen at lower field (−9.96 ppm) for $[L_3Ir(H)(CH{=}CHNEt_3)(C{\equiv}CPh)]^+$.[3d] It may be easier for base (H_2O and/or Cl^-) to abstract Ir−***H*** in **E** than that in **D**, which may explain the rapid H/D exchange between D^+ in solution and Ir−***H*** of **E** to give Ir−***D*** and H^+ (see Scheme 2).

It is also conceivable that the relative affinity of the metals for the allene **9** causes the differences in the reactivity of **2** (and **4**) and **3** observed in the H/D exchange. Those dicationic intermediates started from **3** in Scheme 2 may bind the allene ligand more strongly than do the monocationic ones derived from **2** and **4** in Scheme 1, which may explain extensive H/D exchange in the reaction of **3**. The difference in H/D exchange rates may also be explained by the relative rates of the hydride transfer of the hydrido η^2-allene complexes to give the alkenyl complexes (i.e., slower **D** → **C** in Scheme 1 and faster **E** → **5** in Scheme 2).

It may be said that more well-planned experiments should be carried out to obtain more conclusive results to explain the differences in H/D exchange observed with **2** and **4**, and **3**.

Experimental Section

Safety Note. *Extensive precautions should be taken since perchlorate salts of transition-metal complexes are potentially explosive.*[18]

General Procedures. All reactions were carried out under nitrogen with the use of standard Schlenk glassware. DCl (37 wt % in D_2O) and HCl (32 wt % in H_2O) were purchased from Aldrich and Merck, respectively. Triethylamine (Aldrich) was dried over $CaSO_4$ and distilled from CaH_2 under N_2 prior to use. $Ir(C{\equiv}C(p\text{-}C_6H_4CH_3))(CO)(PPh_3)_2$ was prepared by the literature method.[4]

Physical Measurements. 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, 121.7 MHz). IR spectra were obtained on Shimadzu IR-440 and Nicolet 205 spectrophotometers. Gas chromatography/mass spectra were determined by Hewlett-Packard HP5890A and VG-trio 2000 instruments. Electronic absorption spectra were obtained by a Hewlett-Packard 8452A diode array spectrophotometer. Elemental analyses were carried out by a Carlo Erba EA1108 CHNS-O analyzer at Organic Chemistry Research Center, Sogang University.

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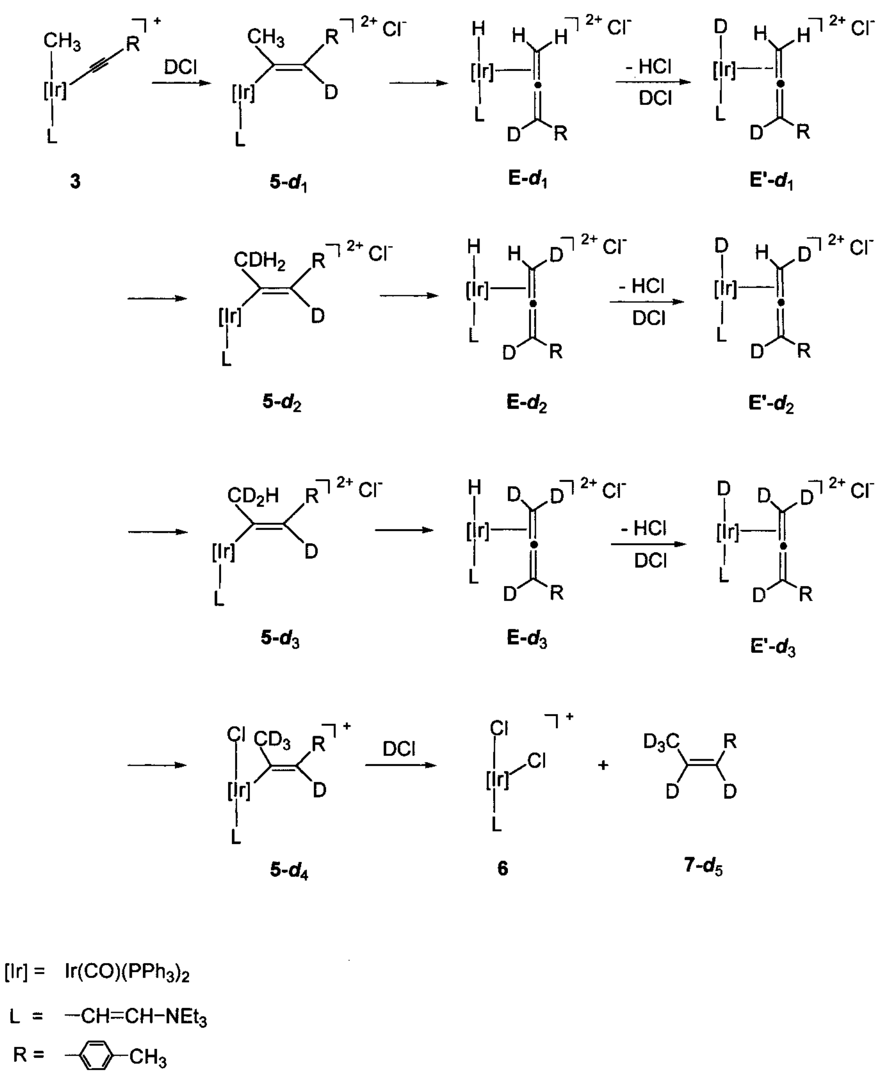
Scheme 2



Preparation of $Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(I)(CO)(PPh_3)_2$ (1). A $CHCl_3$ (10 mL) solution of $[Ir(NCCH_3)(CO)(PPh_3)_2]ClO_4$[19] (0.18 g, 0.20 mmol) and $HC{\equiv}C(p\text{-}C_6H_4CH_3)$ 0.03 mL, 0.24 mmol) was stirred in the presence of NEt_3 (0.03 mL, 0.22 mmol) for 5 min to produce $Ir(C{\equiv}C(p\text{-}C_6H_4CH_3))(CO)(PPh_3)_2$,[4] and then excess CH_3I (0.02 mL, 0.32 mmol) was added to the dark brown reaction mixture. The reaction mixture turned pale yellow within 3 min. A 10 mL portion of water was added to the solution, and excess NEt_3 and $HNEt_3^+ClO_4^-$ in the aqueous layer were separated from reaction mixture. Addition of *n*-hexane (25 mL) to the $CHCl_3$ solution resulted in precipitation of the beige microcrystals of **1**, which were collected by filtration, washed with cold *n*-hexane (3 × 10 mL), and dried under vacuum. The yield was 0.17 g (85%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.93–7.04 (AB quartet with $\Delta\nu/J = 2.3$, 4H, $J_{H_A-H_B} = 8.0$ Hz, $p\text{-}C_6H_4CH_3$), 2.33 (s, 3H, $p\text{-}C_6H_4CH_3$), 0.81 (t, 3H, $J_{P-H} = 5.3$ Hz, Ir-CH_3). ^{13}C NMR ($CDCl_3$): δ 169.8 (t, $J_{P-C} =$ 6.5 Hz, Ir–*C*O), 113.7 (s, Ir–C≡*C*), 85.8 (t, $J_{P-C} = 18.2$ Hz, Ir–*C*≡C), 21.2 (s, $p\text{-}C_6H_4CH_3$), –14.9 (br, Ir–CH_3). ^{31}P NMR ($CDCl_3$): δ 8.1 (s). IR (KBr, cm^{-1}): ν(C≡C) 2106.0 (w), ν(CO) 2026.5 (s). Anal. Calcd for $IrP_2C_{47}H_{40}IO$: C, 56.37; H, 4.03. Found: C, 56.56; H, 4.00.

Preparation of $[Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (2). The reaction mixture of $AgClO_4$ (0.03 g, 0.15 mmol) and **1** (0.1 g, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred at 25 °C for 30 min, during which time the reaction mixture turned brown. After AgI was removed by filtration, CH_3CN (0.01 mL, 0.19 mmol) was added to the reaction mixture, which was stirred for 15 min. Addition of cold *n*-hexane (20 mL) gave the beige microcrystals of **2**. The yield was 0.09 g (89%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.80–7.04 (AB quartet with $\Delta\nu/J = 6.7$, 4H, $J_{H_A-H_B} = 8.1$ Hz, $p\text{-}C_6H_4CH_3$), 2.32 (s, 3H, $p\text{-}C_6H_4CH_3$), 1.80 (s, 3H, Ir–$NCCH_3$), 0.66 (t, 3H, $J_{P-H} = 5.4$ Hz, Ir–CH_3). ^{13}C NMR ($CDCl_3$): δ 168.9 (br, Ir–*C*O), 121.3 (br, Ir–N*C*CH3), 111.9 (br, Ir–C≡*C*), 85.6 (br, Ir–*C*≡C), 21.3 (s, $p\text{-}C_6H_4CH_3$), 2.7 (s, Ir–NCCH_3), –26.0 (t, $J_{P-C} = 5.5$ Hz, Ir–CH_3). ^{31}P NMR ($CDCl_3$): δ 2.8 (s). IR (KBr, cm^{-1}): ν(C≡N) 2322.4 (w), ν(C≡C) 2121.8 (w), ν(CO) 2051.2 (s), $\nu(ClO_4^-)$ 1080.0 (s, br, due to noncoordinated tetrahedral ClO_4^-). Anal. Calcd for $IrP_2C_{49}H_{43}NClO_5$: C, 57.95; H, 4.28; N, 1.38. Found: C, 57.78; H, 4.33; N, 1.39.

Preparation of $[Ir(CH_3)(CH{=}CHNEt_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(CO)(PPh_3)_2]ClO_4$ (3). A solution of **2** (0.1 g, 0.1 mmol) in $CHCl_3$ (15 mL) was stirred under HC≡CH (1 atm) in the presence of NEt_3 (0.11 mmol) at 25 °C for 10 min, during which time the light beige solution turned slightly darker. A 10 mL portion of water was added to the reaction mixture, and excess NEt_3 and $HNEt_3^+ClO_4^-$ in the aqueous layer were separated from **3** in the $CHCl_3$ layer. Addition of *n*-hexane (25 mL) to the $CHCl_3$ solution resulted in precipitation of the beige-pink microcrystals of **3**, which were collected by filtration, washed with cold hexane (3 × 10 mL), and dried under vacuum. The yield was 0.10 g (91%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, 1H, $J_{H-H} = 15.9$ Hz, Ir–C*H*=CH), 6.88–7.05 (AB quartet with $\Delta\nu/J = 4.2$, 4H, $J_{H_A-H_B} = 7.8$ Hz, $p\text{-}C_6H_4CH_3$), 4.86 (d, 1H, $J_{H-H} = 15.9$ Hz, Ir–CH=C*H*), 2.81 (q, 6H, $J_{H-H} = 7.2$ Hz, $N(CH_2CH_3)_3$), 2.32 (s, 3H, $p\text{-}C_6H_4CH_3$), 0.74 (t, 9H, $J_{H-H} = 7.2$ Hz, $N(CH_2CH_3)_3$), 0.30 (t, 3H, $J_{P-H} = 5.4$ Hz, Ir–CH_3). ^{13}C NMR

($CDCl_3$): δ 173.0 (t, J_{P-C} = 6.5 Hz, Ir−*C*O), 131.3 (s, Ir−CH═*C*H), 129.6 (t, Ir−*C*H═CH, J_{P-C} = 7.8 Hz), 112.3 (s, Ir−C≡*C*), 85.8 (t, J_{P-C} = 18.2 Hz, Ir−*C*≡C), 53.5 (s, $N(CH_2CH_3)_3$), 20.9 (s, p-$C_6H_4CH_3$), 6.8 (s, $N(CH_2CH_3)_3$), −28.7 (t, J_{P-C} = 5.7 Hz, Ir−CH_3). ^{31}P NMR ($CDCl_3$): δ −16.1 (s). IR (KBr, cm^{-1}): ν(C≡C) 2115.5 (s), ν(CO) 2018.5 (s), $\nu(ClO_4^-)$ 1080.0 (s, br, due to noncoordinated tetrahedral ClO_4^-). Anal. Calcd for $IrP_2C_{55}H_{57}NClO_5$: C, 59.96; H, 5.23; N, 1.27. Found: C, 59.51; H, 5.27; N, 1.27.

Preparation of *cis,trans*-$Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))_2(CO)(PPh_3)_2$ (4). This compound was prepared by the same manner as described for **3** using **2** (0.1 g, 0.1 mmol), HC≡C(p-$C_6H_4CH_3$) (0.15 mmol), and NEt_3 (0.11 mmol), except that the reaction mixture was stirred at 0 °C for 30 min. The yield was 0.07 g (71%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.59−6.92 (a couple of an AB quartet with $\Delta\nu/J$ = 7.3 and 7.5, 8H, $J_{H_A-H_B}$ = 8.2 and 8.0 Hz, (p-$C_6H_4CH_3)_2$), 2.26, 2.25 (both singlet, total 6H, (p-$C_6H_4CH_3)_2$), −0.33 (t, 3H, J_{P-H} = 5.0 Hz, Ir−CH_3). ^{13}C NMR ($CDCl_3$): δ 171.3 (t, J_{P-C} = 6.6 Hz, Ir−*C*O), 110.9, 108.3 (s, (Ir−C≡*C*)$_2$), 87.1, 81.3, (t, J_{P-C} = 18.2, 13.1 Hz, (Ir−*C*≡C)$_2$), 21.2, 21.1 (s, (p-$C_6H_4CH_3)_2$), −21.5 (t, J_{P-C} = 4.5 Hz, Ir−CH_3). ^{31}P NMR ($CDCl_3$): δ −10.9 (s). IR (KBr, cm^{-1}): ν(C≡C) 2104.0 (s), ν(CO) 2024.0 (s). Anal. Calcd for $IrP_2C_{56}H_{47}O$: C, 67.92; H, 4.79. Found: C, 68.56; H, 4.75.

Preparation of $[Ir(C(CH_3){=}CH(p\text{-}C_6H_4CH_3))(CH{=}CHNEt_3)(Cl)(CO)(PPh_3)_2]ClO_4$ (5). HCl (0.25 mmol, 0.024 mL of H_2O containing 32 wt % HCl) was added to a solution of **3** (0.22 g, 0.2 mmol) in $CHCl_3$ (15 mL) at 25 °C, and the reaction mixture was stirred for 1 h until it turned brown. Excess HCl was removed from the reaction mixture by washing with H_2O (10 mL) using a separatory funnel. Addition of n-hexane (25 mL) to the $CHCl_3$ solution resulted in orange microcrystals of **5**, which were collected by filtration, washed with cold hexane (3 × 10 mL), and dried under vacuum. The yield of **5** was 0.11 g (47%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.10 (d, 1H, J_{H-H} = 15.6 Hz, Ir−C*H*═CH), 7.04 (br, 2H, p-$C_6H_4CH_3$ (*meta* protons)), 6.62 (br, 2H, p-$C_6H_4CH_3$ (*ortho* protons)), 6.41 (br, 1H, Ir−C(CH_3)═C*H*), 4.87 (d, 1H, J_{H-H} = 15.6 Hz, Ir−CH═C*H*), 2.70 (q, 6H, J_{H-H} = 6.9 Hz, $N(CH_2CH_3)_3$), 2.31 (s, 3H, p-$C_6H_4CH_3$), 1.92 (s, 3H, Ir−C(CH_3)═CH), 0.96 (t, 9H, J_{H-H} = 6.9 Hz, $N(CH_2CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 173.6 (br, Ir−*C*O), 138.2 (s, Ir−C(CH_3)═CH_2), 129.5 (s, Ir−CH═*C*H), 128.5 (br, Ir−*C*H═CH), 121.1 (br, Ir−*C*(CH_3)═CH), 54.4 (s, $N(CH_2CH_3)_3$), 26.3 (br, Ir−C(CH_3)═CH), 21.0 (s, p-$C_6H_4CH_3$), 8.0 (s, $N(CH_2CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ −17.7 (s). IR (KBr, cm^{-1}): ν(CO) 2044.7 (s), $\nu(ClO_4^-)$ 1093.1 (s, br, due to noncoordinated tetrahedral ClO_4^-). Anal. Calcd for $IrP_2C_{55}H_{58}NCl_2O_5$: C, 58.03; H, 5.15; N, 1.23. Found: C, 57.62; H, 5.20; N, 1.25.

Reactions of $[Ir(CH_3)(CH{=}CHNEt_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(CO)(PPh_3)_2)]ClO_4$ (3) and $[Ir(C(CH_3){=}CH(p\text{-}C_6H_4CH_3))(CH{=}CHNEt_3)(Cl)(CO)(PPh_3)_2]ClO_4$ (5) with HCl: Formation of $[Ir(CH{=}CHNEt_3)(Cl)_2(CO)(PPh_3)_2]ClO_4$ (6) and *cis*-$CH_3CH{=}CH(p\text{-}C_6H_4CH_3)$ (7). HCl (0.25 mmol, 0.024 mL of H_2O containing 32 wt % HCl) was added to a solution of **3** (0.22 g, 0.2 mmol) in $CHCl_3$ (15 mL) at 25 °C; the reaction mixture was stirred for 6 h. Excess HCl was removed by washing with H_2O. Addition of n-hexane (10 mL) to the $CHCl_3$ solution resulted in beige microcrystals of **6**, which were collected by filtration, washed with $CHCl_3$ (3 mL), and dried under vacuum. The yield of **6** was 0.09 g (45%). The filtrate was distilled under vacuum to collect **7** in the cold trap of a dry ice/isopropyl alcohol bath. The yield of **7** was ca. 40%, measured by ^1H NMR in $CDCl_3$.

Data for **6** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, 1H, J_{H-H} = 15.3 Hz, Ir−C*H*═CH), 5.56 (d, 1H, J_{H-H} = 15.3 Hz, Ir−CH═C*H*), 2.96 (q, 6H, J_{H-H} = 7.2 Hz, $N(CH_2CH_3)_3$), 0.88 (t, 9H, J_{H-H} = 7.2 Hz, $N(CH_2CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 160.1 (t, J_{P-C} = 6.5 Hz, Ir−*C*O), 133.1 (s, Ir−CH═*C*H), 123.3 (br, Ir−*C*H═CH), 56.0 (s, $N(CH_2CH_3)_3$), 8.5 (s, $N(CH_2CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ −16.7 (s). IR (KBr, cm^{-1}): ν(CO) 2060.4 (s), $\nu(ClO_4^-)$ 1093.1 (s, br, due to noncoordinated tetrahedral ClO_4^-). Anal. Calcd for $IrP_2C_{45}H_{47}NCl_3O_5$: C, 51.84; H, 4.55; N, 1.34. Found: C, 51.59; H, 4.58; N, 1.41.

Data for **7** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ 7.12−7.22 (AB quartet with $\Delta\nu/J$ = 2.3, 4H, $J_{H_A-H_B}$ = 8.0 Hz, p-$C_6H_4CH_3$), 6.40 (dd, 1H, J_{H-H} = 11.4 Hz, 1.5 Hz, CH_3CH═C*H*), 5.74 (dq, 1H, J_{H-H} = 11.4, 7.2 Hz, CH_3C*H*═CH), 2.36 (s, 3H, p-$C_6H_4CH_3$), 1.89 (dd, 3H, J_{H-H} = 7.2, 1.5 Hz, CH_3CH═CH). ^{13}C NMR (MHz, $CDCl_3$): δ 14.6 (s, CH_3CH═CH), 21.1 (s, p-$C_6H_4CH_3$), 136.1, 134.8, 129.7, 128.8, 128.7, 126.0 (s, olefinic carbons and p-$C_6H_4CH_3$). Mass: M^+ at m/z 132. Reaction of **5** with HCl was carried out in the same manner as described for the formation of **6** and **7** from the reaction of **3** with aqueous HCl using **5** (0.2 g, 0.17 mmol). The yield of **6** was 0.11 g (62%).

Reactions of $[Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (2) and $[Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))_2(CO)(PPh_3)_2]ClO_4$ (4) with HCl: Formation of $CH_2{=}C{=}CH(p\text{-}C_6H_4CH_3)$ (9). HCl (2.0 mmol, 0.19 mL of H_2O containing 32 wt % HCl) was added to a solution of **2** (0.2 g, 0.2 mmol) in $CHCl_3$ (5 mL) at 25 °C, and the reaction mixture was stirred for 12 h, during which time white microcrystals precipitated. Excess HCl was removed by washing with H_2O using a separatory funnel. Compound **10** (white microcrystals) was collected by centrifugal separation, washed with n-hexane, dried under vacuum, and identified by spectral data (see text). The yield was 0.13 g (76% based on $Ir(H)(Cl)_2(CO)(PPh_3)_2$). The supernatant was distilled under vacuum to collect **9** in the cold trap of a dry ice/isopropyl alcohol bath. The yield of **9** was ca. 30%, measured by ^1H NMR in $CDCl_3$. The reaction of **4** (0.2 g, 0.2 mmol) with HCl was carried out in the same manner as described for the reaction of **2**. Spectral data for **9** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ 7.09−7.21 (AB quartet with $\Delta\nu/J$ = 1.5, 4H, $J_{H_A-H_B}$ = 8.1 Hz, CH(p-$C_6H_4CH_3$)), 6.14 (t, 1H, J_{H-H} = 6.6 Hz, C*H*(p-$C_6H_4CH_3$)), 5.12 (d, 2H, J_{H-H} = 6.6 Hz, CH_2═C), 2.32 (s, 3H, CH(p-$C_6H_4CH_3$)). ^{13}C NMR ($CDCl_3$): δ 93.7, 78.6, 77.4 (s, *C*═*C*═*C*), 21.1 (s, p-$C_6H_4CH_3$). IR (KBr, cm^{-1}): ν(C═C) 1731.3 (s). Mass: M^+ at m/z 130.

Reductive Elimination of $[H(p\text{-}C_6H_4CH_3)C{=}C(CH_3)CH{=}CHNEt_3]ClO_4$ (8) from $[Ir(C(CH_3){=}CH(p\text{-}C_6H_4CH_3))(CH{=}CHNEt_3)(Cl)(CO)(PPh_3)_2]ClO_4$ (5). Compound **5** (0.23 g, 0.2 mmol) was dissolved in $CHCl_3$ (10 mL), and the solution was refluxed for 2 h. Reducing the solution by distillation under vacuum to 1 mL resulted in precipitation of the white microcrystals of **8**, which were collected by filtration, washed with cold $CHCl_3$ (3 mL), and dried under vacuum. The yield was 0.04 g (56%). The electronic absorption spectrum of the filtrate ($CHCl_3$ solution) showed three distinctive absorption bands at 338, 388, and 440 nm of Vaska's compound, $IrCl(CO)(PPh_3)_2$.[11] Spectral data for **8** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ 7.20−7.29 (AB quartet with $\Delta\nu/J$ = 2.2, 4H, $J_{H_A-H_B}$ = 8.2 Hz, CH(p-$C_6H_4CH_3$)), 6.82 (s, 1H, H_α), 6.73 (d, 1H, J_{H-H} = 14.8 Hz, H_γ), 5.95 (d, 1H, J_{H-H} = 14.8 Hz, H_δ), 3.56 (q, 6H, J_{H-H} = 7.1 Hz, $N(CH_2CH_3)_3$), 2.38 (s, 3H, CH(p-$C_6H_4CH_3$)), 2.08 (d, 3H, J_{H-H} = 0.9 Hz, (CH_3)C═C), 1.36 (t, 9H, J_{H-H} = 7.1 Hz, $N(CH_2CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 139.2, 138.9, 137.2, 134.0, 130.7, 130.1, 129.9, 123.0 (s, olefinic carbons and p-$C_6H_4CH_3$), 56.3 (s, $N(CH_2CH_3)_3$), 21.7 (s, CH(p-$C_6H_4CH_3$)), 14.5 (s, (CH_3)C═C), 8.5 (s, $N(CH_2CH_3)_3$). IR (KBr, cm^{-1}): $\nu(ClO_4^-)$ 1094.5 (s, br). Mp: 196 °C. Electronic absorption: λ_{max} 228, 292 nm. Mass: m/z 229 ($M^+ - C_2H_5ClO_4$).

Reactions of $[Ir(CH_3)(C{\equiv}C(p\text{-}C_6H_4CH_3))(NCCH_3)(CO)(PPh_3)_2]ClO_4$ (2) with DCl: Formation of $CH_2{=}C{=}CD(p\text{-}C_6H_4CH_3)$ (9-d_1). This reaction was carried out using aqueous DCl (37 wt % in D_2O) in the same manner as described for the reaction of **2** with HCl. The isotopomer **9-d_1** was identified by ^1H NMR and mass spectral measurements. ^1H NMR (500 MHz, $CDCl_3$): δ 7.09−7.21 (AB quartet with $\Delta\nu/J$ = 1.5, 4H, $J_{H_A-H_B}$ = 8.1 Hz, CH(p-$C_6H_4CH_3$)), 5.12 (s, 2H, CH_2═C═CD(p-$C_6H_4CH_3$), 2.32 (s, 3H, p-$C_6H_4CH_3$). Mass: M^+ at m/z 131.

Reactions of [Ir(CH_3)(C≡C(p-$C_6H_4CH_3$))(CH=CHNEt$_3$)(CO)(PPh_3)$_2$]ClO_4 (3) and [Ir(C(CH_3)=CH(p-$C_6H_4CH_3$))(CH=CHNEt$_3$)(Cl)(CO)(PPh_3)$_2$]ClO_4 (5) with DCl: Formation of *cis*-CD_3CD=CD(p-$C_6H_4CH_3$)) (7-*d*$_5$). These reactions were carried out using aqueous DCl (37 wt % in D_2O) in the same manner as described for the reactions of **3** and **5** with HCl. Isotopomers **7-*d*$_5$** and **7-*d*$_n$** were identified by ^{1}H NMR and mass spectral measurements (also see Supporting Information). Data for **7-*d*$_5$** are as follows. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12−7.22 (AB quartet with $\Delta\nu/J = 2.3$, 4H, $J_{H_A-H_B} = 8.0$ Hz, p-C_6*H*$_4CH_3$), 2.36 (s, 3H, p-C_6H_4C*H*$_3$). Mass: M$^+$ at *m*/*z* 137. Data for **7-*d*$_n$** are as follows. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12−7.22 (AB quartet with $\Delta\nu/J = 2.3$, 4H, $J_{H_A-H_B} = 8.0$ Hz, p-C_6*H*$_4CH_3$), 6.40 (br, 0.46H, CH_3CH=C*H*), 5.74 (br, 0.73H, CH_3C*H*=CH), 2.36 (s, 3H, p-C_6H_4C*H*$_3$), 1.89 (br, 1.6H, C*H*$_3$CH=CH). Mass: M$^+$ (relative intensity) at *m*/*z* 137 (43), 136 (100), 135 (98), 134 (62), 133 (35).

Acknowledgment. We wish to thank the Ministry of Education (Grant No. BSRI-1998-015-D00168) and Korea Science and Engineering Foundation (Grant No. 97-05-01-05-01-3) for their financial support of this study.

Supporting Information Available: ^{1}H NMR and mass spectra of **7**, **7-*d*$_5$**, and **7-*d*$_n$** and NOE spectra of **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9903442