

## New $\eta^3$ -Allyl-Alkenyl- and $\eta^3$ -Allyl-Alkynyl-Ir-Cp\* Compounds from Reactions of $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{NCMe})]^+$ with Alkynes

Chong Shik Chin,\* Daesung Chong, Mieock Kim, and Hyungeui Lee

Department of Chemistry, Sogang University, Seoul 121-742, Korea

Received May 16, 2001

Reactions of  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{NCMe})]\text{OTf}$  (**1**) with  $\text{HC}\equiv\text{CR}$  ( $\text{R} = \text{H}, \text{CH}_2\text{OH}$ ) in the presence of bases, B ( $\text{B} = \text{NEt}_3, \text{PPh}_3, \text{AsPh}_3$ ) produce stable  $\text{Cp}^*\text{Ir}-\eta^3$ -allyl-alkenyl compounds  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{CH}=\text{CH}^+\text{B})]\text{OTf}$  (**2**) and  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{C}(\text{CH}_2\text{OH})=\text{CH}^+\text{PPh}_3)]\text{OTf}$  (**3**), respectively in high yields.  $\text{Cp}^*\text{Ir}-\eta^3$ -allyl-alkynyl compounds  $\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{C}\equiv\text{C}-\text{R}')$  (**4**) and  $\text{Cp}^*(\eta^3\text{-CH}_2\text{CHCHPh})\text{Ir}-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}-\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})\text{Cp}^*$  (**5**) have been prepared from reactions of **1** with  $\text{HC}\equiv\text{CR}'$  ( $\text{R}' = \text{C}_6\text{H}_5, p\text{-C}_6\text{H}_4\text{CH}_3, \text{C}_3\text{H}_5, \text{C}_6\text{H}_9$ ) and  $\text{HC}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{CH}$  in the presence of  $\text{NEt}_3$ .

**Keywords:**  $\eta^3$ -Allyl-alkenyl. Mono- and di-nuclear  $\eta^3$ -allyl-alkynyls.

### Introduction

Nitriles coordinated to metal ( $\text{M}-\text{N}\equiv\text{C}-\text{R}$ ) are so labile that they are readily replaced by a variety of ligands.<sup>1,2a-c,3a,b</sup> In particular, coordinated nitriles are substituted by alkynes ( $\text{RC}\equiv\text{CR}'$ ) in the presence of bases, B ( $\text{NR}_3, \text{PR}_3, \text{AsR}_3$ ) to produce metal-alkenyls ( $\text{M}-\text{CR}=\text{CR}'^+\text{B}$ )<sup>2</sup> by the apparent alkyne insertion into metal and base (B) bonds and metal-alkynyls ( $\text{M}-\text{C}\equiv\text{C}-\text{R}$ )<sup>2a-c,3</sup> by the substitution of the nitriles with alkynyl groups.

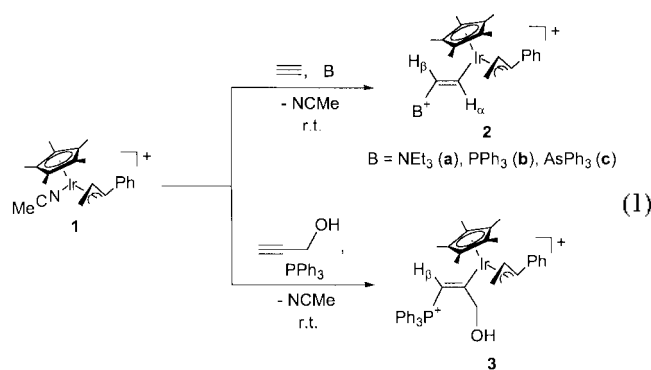
The apparent insertion of alkynes into the  $\text{M}-\text{B}$  bonds<sup>2</sup> and alkylation of metal<sup>2a-c,3</sup> have been of interest in synthetic chemistry since metal-alkenyls and -alkynyls are very useful precursors for metal-mediated C-C bond formation between adjacent hydrocarbyl ligands such as alkyl,<sup>2a,4</sup> allyl,<sup>3a,f,5</sup> alkyne,<sup>3d,e</sup> vinylidene<sup>3g,6</sup> and allenylidene<sup>7</sup> groups to form highly conjugated polyenes.

During our investigation on the reactivity of iridium-NCMe compound  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{NCMe})]\text{OTf}$  (**1**)<sup>8</sup> ( $\text{Cp}^* = \text{C}_5\text{Me}_5^-$ ,  $\text{OTf} = ^-\text{OSO}_2\text{CF}_3$ ) with alkynes, we have prepared new  $\text{Cp}^*\text{Ir}-\eta^3$ -allyl-alkenyl ( $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{CR}=\text{CH}^+\text{B})]\text{OTf}$  ( $\text{R} = \text{H}, \text{B} = \text{NEt}_3, \text{PPh}_3, \text{AsPh}_3; \text{R} = \text{CH}_2\text{OH}, \text{B} = \text{PPh}_3$ )) and  $\text{Cp}^*\text{Ir}-\eta^3$ -allyl-alkynyl compounds ( $\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{C}\equiv\text{C}-\text{R})$  ( $\text{R} = \text{C}_6\text{H}_5, p\text{-C}_6\text{H}_4\text{CH}_3, \text{C}_3\text{H}_5, \text{C}_6\text{H}_9$ ) and  $\text{Cp}^*(\eta^3\text{-CH}_2\text{CHCHPh})\text{Ir}-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}-\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})\text{Cp}^*$ ) from the reactions of **1** with alkynes.

### Results and Discussion

**Synthesis of Alkenyl- and Alkynyl-Ir( $\eta^3$ -Allyl)-Cp\* Compounds from Reactions of  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{NCMe})]^+$  (**1**) with Alkynes.** Compound **1** reacts with acetylene in the presence of bases, B ( $\text{B} = \text{NEt}_3$  (**a**),  $\text{PPh}_3$  (**b**),  $\text{AsPh}_3$  (**c**)) at room temperature to give  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{CH}=\text{CH}^+\text{B})]\text{OTf}$  (**2**) which contain alkenyl group ( $\text{Ir}-\text{CH}=\text{CH}^+$ ) apparently inserted acetylene between iridium and bases (B) (eq. 1).

The new  $\text{Cp}^*\text{Ir}-\eta^3$ -allyl-alkenyl compounds, **2a-c**, have



been unambiguously characterized by detailed spectral ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR and IR) and elemental analysis data (see Experimental Section for detailed spectral data).

Those alkenyl compounds (**2**) are stable both in solution and in solid state at room temperature even in the air for several hours. While attempts to grow single crystals of the compounds **2a-c** for X-ray diffraction study have been unsuccessful, the crystal structures of the related alkenyl ( $\text{Ir}-\text{CH}=\text{CH}^+\text{B}$ ) iridium compounds  $[\text{Ir}-\text{CH}=\text{CH}-\text{CH}=\text{CH}(-\text{CH}=\text{CH}^+\text{NEt}_3)(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ <sup>2b</sup> and  $[\text{IrCl}(-\text{CH}=\text{CH}-\text{PPh}_3)_2(\text{CO})(\text{PPh}_3)_2](\text{ClO}_4)_2$ <sup>2d</sup> have been recently reported.

The  $\alpha$ - and  $\beta$ -protons of the alkenyl groups ( $\text{Ir}-\text{CH}_\alpha=\text{CH}_\beta^+\text{B}$ ) in **2** are measured at  $\delta$  7.94–9.96 ppm and  $\delta$  4.98–5.83 ppm, respectively. These observed chemical shifts in the  $^1\text{H}$  NMR spectra of **2** are very close to those of the well-known and related alkenyl-iridium compounds (apparent alkyne insertion products).<sup>2a-d</sup>

The relatively large coupling constants,  $^3J_{\text{H}_\alpha\text{H}_\beta}$  (15 Hz for **2a**, 18 Hz for **2b, c**) suggest  $\text{H}_\alpha$  being *trans* to  $\text{H}_\beta$  in **2** as shown in eq. 1. The  $^1\text{H}$  NMR spectrum of **2b**, unlike those of **2a** and **2c**, clearly exhibits two doublets of doublet for the two alkenyl protons ( $\text{Ir}-\text{CH}_\alpha=\text{CH}_\beta^+\text{P}$ ) at  $\delta$  5.70 ( $\text{H}_\beta$ ) and 9.96 ( $\text{H}_\alpha$ ) ppm due to  $\text{PPh}_3$  (see Experimental for the detailed couplings).

The reaction of  $\text{HC}\equiv\text{CCH}_2\text{OH}$  with **1** in the presence of  $\text{PPh}_3$  gives  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(-\text{C}(\text{CH}_2\text{OH})=\text{CH}^+\text{PPh}_3)]^+$

OTf (**3**) while mixtures of unidentified complexes were obtained from the reactions of  $\text{HC}\equiv\text{CCH}_2\text{OH}$  with **1** in the presence of  $\text{NEt}_3$  and  $\text{AsPh}_3$ .

The alkenyl proton ( $\text{Ir}-\text{C}_\alpha(\text{CH}_2\text{OH})=\text{C}_\beta\text{H}\beta^+\text{P}$ ) in **3** is clearly seen at  $\delta$  6.07 ppm with relatively large coupling constant,  $^2J_{\text{H-P}}$  (39.2 Hz). The assignment of the signal at  $\delta$  6.07 ppm to  $\text{Ir}-\text{C}(\text{CH}_2\text{OH})=\text{CH}\beta^-\text{PPh}_3$  of **3** is rather straightforward by comparing it with those for the related well-characterized compounds containing  $\text{Ir}-\text{CR}=\text{CH}^+\text{PPh}_3^{2c,d}$  moieties.

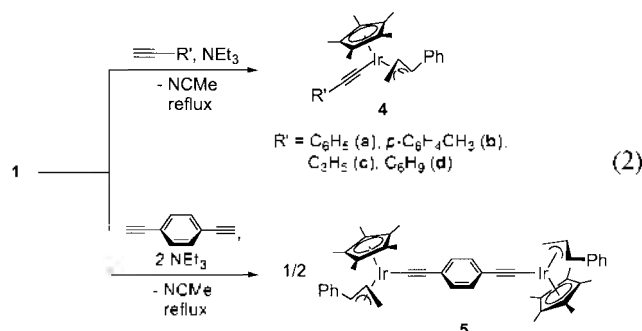
The apparent insertion of alkynes into M-B bonds has been suggested to occur by the nucleophilic attack of B on the coordinated alkynes.<sup>2</sup> The insertion of alkynes ( $\text{HC}\equiv\text{CR}$ ;  $\text{R} = \text{H}, \text{CH}_2\text{OH}$ ) between Ir-B bonds to form  $\text{Ir}-\text{CR}=\text{CH}^+\text{B}$  (**2** and **3**) in eq. 1 may also occur *via* the attack of B on the coordinated alkynes in place of the labile NCMe in 1.

It is somewhat surprising to find that alkyne inserted complexes such as **2** are not obtained with  $\text{HC}\equiv\text{CR}'$  ( $\text{R}' = \text{C}_6\text{H}_5, p\text{-C}_6\text{H}_4\text{CH}_3, \text{C}_3\text{H}_5, \text{C}_6\text{H}_9$ ) and  $\text{HC}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{CH}^9$  under the same experimental conditions. On the other hand, reactions of **1** with  $\text{HC}\equiv\text{CR}'$  and  $\text{HC}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{CH}$  in the presence of  $\text{NEt}_3$  under reflux conditions produce the mono-nuclear- $\eta^3$ -allyl-alkynyl compounds **4** ( $\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-C}\equiv\text{C-R}')$ ) and di-nuclear- $\eta^3$ -allyl-alkynyl compound **5** ( $\text{Cp}^*(\eta^3\text{-CH}_2\text{CHCHPh})\text{Ir}-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}-\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})\text{Cp}^*$ ) in high yields (> 83%) (eq. 2).

It may be understood in terms of the relative acidity of the acetylenic protons of terminal alkynes. Acetylenic protons ( $\text{-C}\equiv\text{C-H}$ ) of  $\text{H-C}\equiv\text{C-R}'$  ( $\text{R}' = \text{C}_6\text{H}_5, p\text{-C}_6\text{H}_4\text{CH}_3, \text{C}_3\text{H}_5, \text{C}_6\text{H}_9$ ) and  $\text{H-C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-H}$  are more acidic than those of  $\text{H-C}\equiv\text{C-R}$  ( $\text{R} = \text{H}, \text{CH}_2\text{OH}$ ). Therefore, the proton abstractions of  $\text{H-C}\equiv\text{C-R}'$  and  $\text{H-C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-H}$  by base ( $\text{NEt}_3$ ) readily occur to produce alkynyl compounds (**4** and **5**) from reactions of **1** with  $\text{HC}\equiv\text{CR}'$  and  $\text{HC}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{CH}$  in the presence of  $\text{NEt}_3$ , whereas alkenyl compounds ( $\text{HC}\equiv\text{CR}$  insertion products) **2** and **3** are the only products from reactions of **1** with  $\text{HC}\equiv\text{CR}$  in the presence of bases ( $\text{NEt}_3, \text{PPh}_3, \text{AsPh}_3$ ).

Compounds **4** and **5** have been unequivocally identified by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR, infrared spectral and elemental analysis data (see Experimental Section). The signal at  $\delta$  3.1 ppm due to the acetylenic proton of  $\text{H-C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-H}^9$  completely disappeared in the  $^1\text{H}$  NMR spectrum of **5** which clearly shows the ratio of the signals due to the methyl protons of  $\text{Cp}^*(\text{C}_5(\text{CH}_3)_5)$  to the aromatic protons ( $-\text{C}_6\text{H}_5$  and  $-\text{C}_6\text{H}_4-$ ) being 30 : 14. One set of alkynyl signals at  $\delta$  84.5 ppm ( $\text{Ir}-\text{C}\equiv\text{C}$ ) and  $\delta$  100.8 ppm ( $\text{Ir}-\text{C}\equiv\text{C}$ ) and one medium band ( $\nu(\text{C}\equiv\text{C})$ ) at  $2084.5\text{ cm}^{-1}$  due to the coordinated alkynyl group were observed in  $^{13}\text{C}$  NMR and infrared spectra of **5**, respectively. These spectral data observed for **5** are very similar to those of the well-characterized the  $\text{-C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}-$  bridged dinuclear metal compounds.<sup>10</sup> Recently, the crystal structure of a related dinuclear iridium compound  $(\text{PPh}_3)_2(\text{CO})(\text{CH}=\text{CHCH}=\text{CH})\text{Ir}-\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}-\text{Ir}(\text{-CH}=\text{CH}-\text{CH}=\text{CH})(\text{CO})(\text{PPh}_3)_2$  has been determined in our laboratory.<sup>11</sup> No dinuclear  $\text{Cp}^*\text{Ir}-\eta^3$ -allyl-alkynyl compound with a bridging  $\text{-C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}-$  ligand such as **5**

has been reported thus far while a related compound  $\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-C}\equiv\text{C}-t\text{-Bu})$  was previously reported.<sup>3a</sup>



It should be mentioned here that the attempts to prepare the alkynyl compounds  $\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-C}\equiv\text{C-R})$  ( $\text{R} = \text{H}, \text{CH}_2\text{OH}$ ) have been unsuccessful. As mentioned earlier, several unknown iridium compounds were obtained from the reactions of **1** with  $\text{HC}\equiv\text{CR}$  in the presence of  $\text{NEt}_3$  even under refluxing conditions. Reactions of **1** with  $\text{HC}\equiv\text{CR}'$  ( $\text{R}' = \text{C}_6\text{H}_5$  (a),  $p\text{-C}_6\text{H}_4\text{CH}_3$  (b)) in the presence of  $\text{PPh}_3$  under same reaction conditions give iridium-triphenylphosphine compound  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{PPh}_3)]^+$  which has been previously reported.<sup>12</sup>

The newly prepared  $\eta^3$ -allyl-alkenyl- and alkynyl- $\text{Cp}^*\text{Ir}$  compounds **2** - **5** may be useful for the intramolecular carbon-carbon bond formation between the alkenyl and  $\eta^3$ -allyl ligands, and alkynyl and  $\eta^3$ -allyl ligands to produce conjugated olefins. Further investigation is currently undertaken to obtain the polyenes from the reactions of **2** - **5** with electrophiles ( $\text{H}^+, ^{13}\text{Me}^-$ ).

## Experimental Section

**General Information.** All reactions were carried out under a dry  $\text{N}_2$  atmosphere. A standard vacuum system and Schlenk type glassware were used in handling metal complexes.

The NMR spectra were obtained on a Varian Gemini 200 or 300 MHz for  $^1\text{H}$  and 50.3 or 75.4 MHz for  $^{13}\text{C}$  and 121.3 MHz for  $^{31}\text{P}$ . Infrared spectra were obtained on Shimadzu IR-440 spectrophotometer. Elemental analysis was carried out by a Carlo Erba EA1108 at the Organic Chemistry Research Center, Sogang University.

$[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{NCMe})]\text{OTf}$  (**1**)<sup>8</sup> and 1,4-diethynyl benzene<sup>9</sup> ( $\text{HC}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-C}\equiv\text{CH}$ ) were prepared by literature methods.

**Synthesis of  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-CH}=\text{CH}^+\text{NEt}_3)]\text{-OTf}$  (**2a**),  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-CH}=\text{CH}^+\text{PPh}_3)]\text{OTf}$  (**2b**) and  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-CH}=\text{CH}^+\text{AsPh}_3)]\text{OTf}$  (**2c**).**

**Preparation of  $[\text{Cp}^*\text{Ir}(\eta^3\text{-CH}_2\text{CHCHPh})(\text{-CH}=\text{CH}^+\text{NEt}_3)]\text{OTf}$  (**2a**):** A solution of **1** (0.20 g, 0.32 mmol) in 10 mL of  $\text{CHCl}_3$  was stirred under  $\text{HC}\equiv\text{CH}$  (1 atm) in the presence of  $\text{NEt}_3$  (0.96 mmol, 0.13 mL) at room temperature for 18 h. A 10 mL portion of water was added to the reaction mixture and unreacted  $\text{NEt}_3$  in the aqueous layer was separated from

**2a** in the CHCl<sub>3</sub> layer. A beige-white solid was obtained by distillation of the solution under vacuum and recrystallized in CHCl<sub>3</sub>/Et<sub>2</sub>O to isolated beige microcrystals of **2a**. The yield was 0.21 g and 91% based on [Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-CH=CH-<sup>+</sup>NEt<sub>3</sub>)]OTf. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.32 (t, 9H, *J* = 7.3 Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.54 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 1.68 (d, 1H, *J* = 10 Hz, CHHCHCHPh), 2.89 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 3.13 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 3.41 (q, 6H, *J* = 7.3 Hz, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 4.44 (m, 1H, CH<sub>2</sub>-CHCHPh), 4.98 (d, 1H, *J* = 15 Hz, Ir-CH=CH-<sup>+</sup>N), 7.05-7.35 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 7.94 (d, 1H, *J* = 15 Hz, Ir-CH=CH-<sup>+</sup>N). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  7.9 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 8.4 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 36.2 (CH<sub>2</sub>CHCHPh), 54.2 (CH<sub>2</sub>CHCHPh), 55.4 (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 70.1 (CH<sub>2</sub>CHCHPh), 93.4 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 108.1 (Ir-CH=CH-<sup>+</sup>N), 131.8 (Ir-CH=CH-<sup>+</sup>N), 125, 126, 129 and 141 (C<sub>6</sub>H<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): 1026, 1140 and 1257 (br s, OTf). Anal. Calcd for C<sub>28</sub>H<sub>41</sub>O<sub>3</sub>NSF<sub>3</sub>Ir: C, 46.7; H, 5.73. Found: C, 46.6; H, 5.59.

Compounds **2b**, **c** have been prepared in the similar manner as described for **2b** below using the same amounts of **1**.

[Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-CH=CH-<sup>+</sup>PPh<sub>3</sub>)]OTf (**2b**): The yield was 0.25 g and 90% based on [Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-CH=CH-<sup>+</sup>PPh<sub>3</sub>)]OTf. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.42 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 1.67 (d, 1H, *J* = 10 Hz, CHHCHCHPh), 3.08 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 3.36 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 4.57 (m, 1H, CH<sub>2</sub>CHCHPh), 5.70 (dd, 1H, *J* = 18 Hz, *J* = 32.2 Hz, Ir-CH=CH-<sup>+</sup>P), 7.00-7.90 (m, 20H, C<sub>6</sub>H<sub>5</sub> and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 9.96 (dd, 1H, *J* = 18 Hz, *J* = 30.4 Hz, Ir-CH=CH-<sup>+</sup>P). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  8.1 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 40.5 (CH<sub>2</sub>CHCHPh), 60.7 (CH<sub>2</sub>CHCHPh), 70.3 (CH<sub>2</sub>CHCHPh), 93.4 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 101.1 (d, *J* = 78.7 Hz, Ir-CH=CH-<sup>+</sup>P), 125, 126, 127, 129, 130, 131, 133, 135 and 140 (C<sub>6</sub>H<sub>5</sub> and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 179.7 (d, *J* = 7.25 Hz, Ir-CH=CH-<sup>+</sup>P). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  15.2 (PPh<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 1026, 1143 and 1267 (br s, OTf). Anal. Calcd for C<sub>40</sub>H<sub>41</sub>O<sub>3</sub>-F<sub>3</sub>SP<sub>3</sub>Ir: C, 54.47; H, 4.69. Found: C, 54.40; H, 4.59.

[Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-CH=CH-<sup>+</sup>AsPh<sub>3</sub>)]OTf (**2c**): The yield was 0.27 g and 93% based on [Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-CH=CH-<sup>+</sup>AsPh<sub>3</sub>)]OTf. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.43 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 1.68 (d, 1H, *J* = 10 Hz, CHHCHCHPh), 3.06 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 3.34 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 4.54 (m, 1H, CH<sub>2</sub>CHCHPh), 5.83 (d, 1H, *J* = 18 Hz, Ir-CH=CH-<sup>+</sup>As), 7.00-7.90 (m, 20H, C<sub>6</sub>H<sub>5</sub> and As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 9.61 (d, 1H, *J* = 18 Hz, Ir-CH=CH-<sup>+</sup>As). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  8.1 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 39.4 (CH<sub>2</sub>CHCHPh), 59.5 (CH<sub>2</sub>CHCHPh), 70.2 (CH<sub>2</sub>CHCHPh), 95.0 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 102.0 (Ir-CH=CH-<sup>+</sup>As), 125, 126, 128, 131, 133, 134 and 141 (C<sub>6</sub>H<sub>5</sub> and As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 172.2 (Ir-CH=CH-<sup>+</sup>As). IR (KBr, cm<sup>-1</sup>): 1027, 1142 and 1261 (br s, OTf). Anal. Calcd for C<sub>40</sub>H<sub>41</sub>O<sub>3</sub>F<sub>3</sub>SA<sub>3</sub>Ir: C, 51.89; H, 4.46. Found: C, 51.92; H, 4.40.

**Synthesis of [Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C(CH<sub>2</sub>OH)=CH-<sup>+</sup>PPh<sub>3</sub>)]OTf (**3**):** A reaction mixture of **1** (0.16 g, 0.25 mmol), HC≡CCH<sub>2</sub>OH (0.045 mL, 0.75 mmol) and PPh<sub>3</sub> (0.07 g, 0.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred for 19 h at room temperature and distilled under vacuum to about 2 mL

before pentane (10 mL) was added to obtain pale-yellow microcrystals of **3** which were collected by filtration and dried under vacuum. The yield was 0.19 g and 87% based on [Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C(CH<sub>2</sub>OH)=CH-<sup>+</sup>PPh<sub>3</sub>)]OTf. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.57 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 1.82 (d, 1H, *J* = 10 Hz, CHHCHCHPh), 3.50 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 3.53 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 4.41 (br m, 2H, CH<sub>2</sub>OH), 4.45 (m, 1H, CH<sub>2</sub>CHCHPh), 4.63 (t, 1H, *J* = 2.9 Hz, CH<sub>2</sub>OH), 6.07 (d, 1H, *J* = 39.2 Hz, Ir-C(CH<sub>2</sub>OH)=CH-<sup>+</sup>P), 7.00-7.80 (m, 20H, C<sub>6</sub>H<sub>5</sub> and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  8.5 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 35.9 (CH<sub>2</sub>CHCHPh), 56.2 (CH<sub>2</sub>CHCHPh), 71.3 (CH<sub>2</sub>CHCHPh), 73.8 (d, *J* = 9.4 Hz, Ir-C(CH<sub>2</sub>OH)=CH-<sup>+</sup>P), 93.8 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 105.6 (d, *J* = 65.8 Hz, Ir-C(CH<sub>2</sub>OH)=CH-<sup>+</sup>P), 124, 125, 128, 129, 133 and 144 (C<sub>6</sub>H<sub>5</sub> and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>), 202 (d, *J* = 14.5 Hz, Ir-C(CH<sub>2</sub>OH)=CH-<sup>+</sup>P). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  7.29 (PPh<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3340 (br m,  $\nu$ (OH)), 1022, 1138 and 1241 (br s, OTf). Anal. Calcd for C<sub>41</sub>H<sub>43</sub>O<sub>4</sub>F<sub>3</sub>SP<sub>3</sub>Ir: C, 55.8; H, 4.92. Found: C, 55.6; H, 4.84.

**Synthesis of Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-Ph) (**4a**), Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-*p*-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>) (**4b**), Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-C(=CH<sub>2</sub>)CH<sub>3</sub>) (**4c**), Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-C(=CH-CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>) (**4d**):** All compounds **4a-d** have been prepared in the similar manner as described for **4a** below.

**Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-Ph) (**4a**):** Triethylamine (0.13 mL, 0.96 mmol) and phenylacetylene (0.11 mL, 0.96 mmol) were added to a benzene (10 mL) solution of **1** (0.20 g, 0.32 mmol) under N<sub>2</sub>. The resulting 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<sub>2</sub>O (5 mL) and dissolved in Et<sub>2</sub>O (100 mL). The yellow solution obtained by filtration was distilled under vacuum to dryness to obtain a yellow solid which was washed with cold methanol (1 mL) and dried under vacuum. The yields was 0.17 g and 95% based on Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-Ph). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.68 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 2.38 (d, 1H, *J* = 9 Hz, CHHCHCHPh), 2.88 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 4.15 (d, 1H, *J* = 9 Hz, CH<sub>2</sub>CHCHPh), 4.34 (m, 1H, CH<sub>2</sub>CHCHPh), 7.02-7.43 (m, 10H, C<sub>6</sub>H<sub>5</sub> and Ir-C≡C-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  8.3 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 34.0 (CH<sub>2</sub>CHCHPh), 55.0 (CH<sub>2</sub>CHCHPh), 70.3 (CH<sub>2</sub>CHCHPh), 86.6 (Ir-C≡C), 99.5 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 100.4 (Ir-C≡C), 124.4, 125.0, 125.8, 127.8, 128.6, 129.3, 131.8 and 141.4 (C<sub>6</sub>H<sub>5</sub> and Ir-C≡C-C<sub>6</sub>H<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): 2088 (m,  $\nu$ (C≡C)). Anal. Calcd for C<sub>27</sub>H<sub>29</sub>Ir: C, 58.9; H, 5.31. Found: C, 59.1; H, 5.15.

**Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-*p*-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>) (**4b**):** The yield was 0.17 g and 96% based on Cp<sup>+</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-*p*-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.67 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 2.31 (s, 3H, CH<sub>3</sub>), 2.37 (d, 1H, *J* = 10 Hz, CHHCHCHPh), 2.88 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 4.14 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 4.34 (m, 1H, CH<sub>2</sub>CHCHPh), 6.70-7.30 (m, 9H, C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  8.6 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 21.2 (CH<sub>3</sub>), 34.3 (CH<sub>2</sub>CHCHPh), 55.2 (CH<sub>2</sub>CHCHPh), 70.5 (CH<sub>2</sub>CHCHPh), 86.8 (Ir-C≡C), 93.5 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 100.0 (Ir-C≡C), 124.8, 125.8, 126.3, 128.4,

128.5, 131.6, 133.8 and 141.4 ( $C_6H_5$  and  $C_6H_4$ ). IR (KBr,  $cm^{-1}$ ): 2092 (m,  $\nu(C\equiv C)$ ). Anal. Calcd for  $C_{28}H_{31}Ir$ : C, 60.0; H, 5.58. Found: C, 59.9; H, 5.68.

**$Cp^*Ir(\eta^3-CH_2CHCHPh)(-C\equiv C-C(=CH_2)CH_3)$  (4c):** The yield was 0.14 g and 85% based on  $Cp^*Ir(\eta^3-CH_2CHCHPh)(-C\equiv C-C(=CH_2)CH_3)$ .  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  1.65 (s, 15H,  $C_5(CH_3)_5^-$ ), 1.92 (dd, 3H,  $J = 1.4$  and 1.6 Hz,  $CH_3$ ), 2.29 (d, 1H,  $J = 10$  Hz,  $CHHCHCHPh$ ), 2.74 (d, 1H,  $J = 6$  Hz,  $CHHCHCHPh$ ), 4.04 (d, 1H,  $J = 10$  Hz,  $CH_2CHCHPh$ ), 4.32 (m, 1H,  $CH_2CHCHPh$ ), 4.77 (m, 1H,  $C(=CHH)$ ), 4.90 (m, 1H,  $C(=CHH)$ ), 7.05-7.32 (m, 5H,  $C_6H_5$ ).  $^{13}C$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  8.6 ( $C_5(CH_3)_5^-$ ), 26.3 ( $-C(CH_3)$ ), 34.8 ( $CH_2CHCHPh$ ), 55.0 ( $CH_2CHCHPh$ ), 70.4 ( $CH_2CHCHPh$ ), 87.3 ( $Ir-C\equiv C-$ ), 93.4 ( $C_5(CH_3)_5^-$ ), 101.8 ( $Ir-C\equiv C-$ ), 114.3 ( $C(=CH_2)$ ), 131.1 ( $C(CH_3)$ ), 124.6, 125.4, 128.5 and 141.4 ( $C_6H_5$ ). IR (KBr,  $cm^{-1}$ ): 2089 (m,  $\nu(C\equiv C)$ ). Anal. Calcd for  $C_{24}H_{29}Ir$ : C, 56.6; H, 5.01. Found: C, 56.4; H, 5.01.

**$Cp^*Ir(\eta^3-CH_2CHCHPh)(-C\equiv C-C(=CH-(CH_2)_3-CH_2))$  (4d):** The yield was 0.15 g and 88% based on  $Cp^*Ir(\eta^3-CH_2CHCHPh)(-C\equiv C-C(=CH-(CH_2)_3-CH_2))$ .  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  1.64 (s, 15H,  $C_5(CH_3)_5^-$ ), 2.05-2.21 (br m, 8H,  $-(CH_2)_4$ ), 2.30 (d, 1H,  $J = 9$  Hz,  $CHHCHCHPh$ ), 2.82 (d, 1H,  $J = 6$  Hz,  $CHHCHCHPh$ ), 4.30 (d, 1H,  $J = 10$  Hz,  $CH_2CHCHPh$ ), 4.32 (m, 1H,  $CH_2CHCHPh$ ), 5.71 (m, 1H,  $-C=CH-$ ), 7.05-7.32 (m, 5H,  $C_6H_5$ ).  $^{13}C$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  8.6 ( $C_5(CH_3)_5^-$ ), 22.2, 23.2, 25.6 and 32.2 ( $-(CH_2)_4$ ), 34.5 ( $CH_2CHCHPh$ ), 54.9 ( $CH_2CHCHPh$ ), 70.4 ( $CH_2CHCHPh$ ), 83.2 ( $Ir-C\equiv C-$ ), 93.3 ( $C_5(CH_3)_5^-$ ), 102 ( $Ir-C\equiv C-$ ), 117 ( $-C=CH-$ ), 127 ( $-C=CH-$ ), 125, 126, 128, and 142 ( $C_6H_5$ ). IR (KBr,  $cm^{-1}$ ): 2081 (m,  $\nu(C\equiv C)$ ). Anal. Calcd for  $C_{27}H_{33}Ir$ : C, 58.9; H, 6.05. Found: C, 58.8; H, 5.95.

**$Cp^*(\eta^3-CH_2CHCHPh)Ir-C\equiv C-p-C_6H_4-C\equiv C-Ir(\eta^3-CH_2CHCHPh)Cp^*$  (5):** This compound was prepared in the same manner as described above for **4** using 0.36 g (0.57 mmol) of **1**. The yields was 0.24 g and 83% based on  $Cp^*(\eta^3-CH_2CHCHPh)Ir-C\equiv C-p-C_6H_4-C\equiv C-Ir(\eta^3-CH_2CHCHPh)Cp^*$ .  $^1H$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  1.68 (s, 30H,  $C_5(CH_3)_5^-$ ), 2.36 (d, 2H,  $J = 9$  Hz,  $CHHCHCHPh$ ), 2.87 (d, 2H,  $J = 6$  Hz,  $CHHCHCHPh$ ), 4.13 (d, 2H,  $J = 10$  Hz,  $CH_2CHCHPh$ ), 4.35 (m, 2H,  $CH_2CHCHPh$ ), 7.08-7.40 (m, 14H,  $C_6H_5$  and  $-C_6H_4-$ ).  $^{13}C$  NMR ( $CDCl_3$ , 25 °C):  $\delta$  8.6 ( $C_5(CH_3)_5^-$ ), 34.4 ( $CH_2CHCHPh$ ), 55.4 ( $CH_2CHCHPh$ ), 70.7 ( $CH_2CHCHPh$ ), 84.5 ( $Ir-C\equiv C$ ), 93.7 ( $C_5(CH_3)_5^-$ ), 100.8 ( $Ir-C\equiv C$ ), 117, 125, 126, 129, 132 and 141 ( $C_6H_5$  and  $-C_6H_4-$ ). IR (KBr,  $cm^{-1}$ ): 2084.5 (m,  $\nu(C\equiv C)$ ). Anal. Calcd for  $C_{48}H_{52}Ir_2$ : C, 70.2; H, 6.38. Found: C, 70.2; H, 6.32.

**Acknowledgment.** We thank the Korea Research Foundation (KRF) for supporting this work through the Basic Science Research Institute program (No. 1999-015-DI0055).

## References

- Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.
- (a) Chin, C. S.; Cho, H.; Won, G.; Oh, M.; Ok, K. M. *Organometallics* **1999**, *18*, 4810. (b) Chin, C. S.; Lee, H.; Oh, M. *Organometallics* **1997**, *16*, 816. (c) Chin, C. S.; Park, Y.; Kim, J.; Lee, B. *J. Chem. Soc., Chem. Commun.* **1995**, 1495. (d) Chin, C. S.; Lee, M.; Oh, M.; Won, G.; Kim, M.; Park, Y. *J. Organometallics* **2000**, *19*, 1572. (e) Allen, A.; Lin, W. *Organometallics* **1999**, *18*, 2922. (f) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1994**, *13*, 3767. (g) Takats, J.; Washington, J.; Santarsiero, B. D. *Organometallics* **1994**, *13*, 1078. (h) Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wierda, D. A. *Organometallics* **1993**, *12*, 4312. (i) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134. (j) Nubel, P. O.; Brown, T. L. *Organometallics* **1984**, *3*, 29. (k) Fairhurst, S. A.; Hughes, D. L.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1998**, 1899.
- (a) Chin, C. S.; Maeng, W.; Chong, D.; Won, G.; Lee, B.; Park, Y. *J. Organometallics* **1999**, *18*, 2210, and references therein. (b) Chin, C. S.; Yoon, J.; Song, J. *Inorg. Chem.* **1993**, *32*, 5901. (c) Ara, I.; Berenguer, J. R.; Egui-zabal, E.; Fornies, J.; Lalinde, E.; Martin, A.; Martinez, F. *Organometallics* **1998**, *17*, 4578. (d) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698. (e) Comstock, M. C.; Shapley, J. R. *Organometallics* **1997**, *16*, 4816. (f) Ipaktschi, J.; Mirzaei, F.; Demuth-Eberle, G. J.; Beck, J.; Serafin, M. *Organometallics* **1997**, *16*, 3965. (g) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272.
- (a) Torkelson, J. R.; McDonald, R.; Cowie, M. *Organometallics* **1999**, *18*, 4134. (b) Torkelson, J. R.; McDonald, R.; Cowie, M. *J. Am. Chem. Soc.* **1998**, *120*, 4047.
- (a) George, D. S. A.; Hilt, R. W.; McDonald, R.; Cowie, M. *Organometallics* **1999**, *18*, 5330. (b) Grushin, V. V.; Alper, H. *J. Org. Chem.* **1992**, *57*, 2188. (c) Chin, C. S.; Won, G.; Kim, M. *Bull. Korean Chem. Soc.* **2001**, *22*, 255.
- Gil-Rubio, J.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 1365.
- Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1996**, *118*, 2495.
- Jeong, H.; Joo, K.-S.; Chin, C. S. *Bull. Korean Chem. Soc.* **1997**, *18*, 402.
- Jung, J. K.; Kim, D. K.; Cho, D. H.; Yoon, B. I.; Kim, K. S. *Polymer (Korea)* **1993**, *17*, 67.
- (a) Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; Younus, M.; White, A. J. P.; Williams, D. J.; Payne, N. N.; Yellowlees, L.; Beljonne, D.; Chawdhury, N.; Friend, R. H. *Organometallics* **1998**, *17*, 3034. (b) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184. (c) Narvor, N. L.; Lapinte, C. *Organometallics* **1995**, *14*, 634. (d) Santos, A.; Lopez, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. *Organometallics* **1994**, *13*, 3605.
- Detailed data of the crystal structure will be reported somewhere else.
- Chin, C. S.; Chong, D.; Lee, B.; Jeong, H.; Won, G.; Do, Y.; Park, Y. *J. Organometallics* **2000**, *19*, 638.
- Chin, C. S.; Maeng, W. Reaction of **4a** with  $H^+$  (4 equiv) produces the 1,3-diene,  $Ph-CH=CH-CH=CH-CH_2-Ph$ . Detailed results will be reported elsewhere.