# New $\eta^3$ -Allyl-Alkenyl- and $\eta^3$ -Allyl-Alkynyl-Ir-Cp<sup>\*</sup> Compounds from Reactions of $[Cp^*Ir(\eta^3-CH_2CHCHPh)(NCMe)]^+$ with Alkynes

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Reactions of  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(NCMe)]OTf$  (1) with HC=CR (R = H, CH<sub>2</sub>OH) in the presence of bases, B (B=NEt<sub>3</sub>, PPh<sub>3</sub>, AsPh<sub>3</sub>) produce stable Cp\*Ir- $\eta^3$ -allyl-alkenyl compounds  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-CH=CH^+B)]OTf$  (2) and  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-C(CH_2OH)=CH^+PPh_3)]OTf$  (3), respectively in high yields. Cp\*Ir- $\eta^3$ -allyl-alkynyl compounds Cp\*Ir( $\eta^3-CH_2CHCHPh$ )(-C=C-R') (4) and Cp\*( $\eta^3-CH_2CHCHPh$ )Ir-C=C-p-C<sub>6</sub>H<sub>4</sub>-C=C-Ir( $\eta^3-CH_2CHCHPh$ )Cp\* (5) have been prepared from reactions of 1 with HC=CR' (R' = C<sub>6</sub>H<sub>5</sub>, p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, C<sub>3</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>9</sub>) and HC=C-p-C<sub>6</sub>H<sub>4</sub>-C=CH in the presence of NEt<sub>3</sub>.

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

# Introduction

Nitriles coordinated to metal (M-N=C-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 (RC=CR') in the presence of bases, B (NR<sub>3</sub>, PR<sub>3</sub>, AsR<sub>3</sub>) to produce metal-alkenyls (M-CR=CR'-<sup>+</sup>B)<sup>2</sup> by the apparent alkyne insertion into metal and base (B) bonds and metalalkynyls (M-C=C-R)<sup>2a-c,3</sup> by the substitution of the nitriles with alkynyl groups.

The apparent insertion of alkynes into the M-B bonds<sup>2</sup> and alkynylation 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 [Cp<sup>\*</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(NCMe)]OTf (1)<sup>8</sup> (Cp<sup>\*</sup>= C<sub>5</sub>Me<sub>5</sub><sup>-</sup>, OTf = <sup>-</sup>OSO<sub>2</sub>CF<sub>3</sub>) with alkynes, we have prepared new Cp<sup>\*</sup>-Ir- $\eta^3$ -allyl-alkenyl ([Cp<sup>\*</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)-(-CR=CH-<sup>+</sup>B)]OTf (R = H, B = NEt<sub>3</sub>, PPh<sub>3</sub>, AsPh<sub>3</sub>; R = CH<sub>2</sub>OH, B = PPh<sub>3</sub>)) and Cp<sup>\*</sup>-Ir- $\eta^3$ -allyl-alkynyl compounds (Cp<sup>\*</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-R) (R = C<sub>6</sub>H<sub>5</sub>, *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, C<sub>3</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>9</sub>) and Cp<sup>\*</sup>( $\eta^3$ -CH<sub>2</sub>CHCHPh)Ir-C≡C-*p*-C<sub>6</sub>H<sub>4</sub>-C≡C-Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)Cp<sup>\*</sup>)) from the reactions of 1 with alkynes.

### **Results and Discussion**

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

The new Cp<sup>\*</sup>Ir- $\eta^3$ -allyl-alkenyl compounds, **2a-c**, have



been unambiguously characterized by detailed spectral (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>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 (Ir-CH=CH-<sup>+</sup>B) iridium compounds [Ir-CH=CH-CH=CH(-CH= CH-<sup>+</sup>NEt<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub><sup>2b</sup> and [IrCl(-CH=CH-<sup>+</sup>PPh<sub>3</sub>)<sub>2</sub> (CO)(PPh<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub><sup>2d</sup> have been recently reported.

The  $\alpha$ - and  $\beta$ -protons of the alkenyl groups (Ir-C $H_{\alpha}$ =C $H_{\beta}$ -<sup>+</sup>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 <sup>1</sup>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,  ${}^{3}J_{H\alpha \cdot H\beta}$  (15 Hz for **2a**, 18 Hz for **2b**, **c**) suggest H<sub> $\alpha$ </sub> being *trans* to H<sub> $\beta$ </sub> in **2** as shown in eq. 1. The <sup>1</sup>H NMR spectrum of **2b**, unlike those of **2a** and **2c**, clearly exhibits two doublets of doublet for the two alkenyl protons (Ir-C $H_{\alpha}$ =C $H_{\beta}$ -<sup>+</sup>P) at  $\delta$  5.70 (H<sub> $\beta$ </sub>) and 9.96 (H<sub> $\alpha$ </sub>) ppm due to PPh<sub>3</sub> (see Experimental for the detailed couplings).

The reaction of HC=CCH<sub>2</sub>OH with **1** in the presence of PPh<sub>3</sub> gives  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-C(CH_2OH)=CH^+PPh_3)]$ -

OTf (3) while mixtures of unidentified complexes were obtained from the reactions of HC=CCH<sub>2</sub>OH with 1 in the presence of NEt<sub>3</sub> and AsPh<sub>3</sub>.

The alkenyl proton (Ir- $C_{\alpha}(CH_2OH)=C_{\beta}H_{\beta}^{+P}P$ ) in **3** is clearly seen at  $\delta$  6.07 ppm with relatively large coupling constant,  ${}^{2}J_{H-P}$  (39.2 Hz). The assignment of the signal at  $\delta$  6.07 ppm to Ir-C(CH<sub>2</sub>OH)=C $H_{\beta}^{-+P}Ph_{3}$  of **3** is rather straightforward by comparing it with those for the related well-characterized compounds containing Ir-CR=CH-+PPh<sub>3</sub><sup>2c,d</sup> 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 (HC=CR: R = H, CH<sub>2</sub>OH) between Ir-B bonds to form Ir-CR=CH-<sup>+</sup>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 HC≡CR' (R' =  $C_6H_5$ , p- $C_6H_4CH_3$ ,  $C_3H_5$ ,  $C_6H_9$ ) and HC≡C-p- $C_6H_4$ -C≡CH<sup>9</sup> under the same experimental conditions. On the other hand, reactions of **1** with HC≡CR' and HC≡C-p- $C_6H_4$ -C≡CH in the presence of NEt<sub>3</sub> under reflux conditions produce the mono-nuclear- $\eta^3$ -allyl-alkynyl compounds **4** (Cp\*Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(-C≡C-R')) and di-nuclear- $\eta^3$ -allyl-alkynyl compound **5** (Cp\*( $\eta^3$ -CH<sub>2</sub>CHCHPh)Ir-C≡C-p-C<sub>6</sub>H<sub>4</sub>-C≡C-Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)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 (-C=C-*H*) of *H*-C=C-R' (R' = C<sub>6</sub>H<sub>5</sub>, *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, C<sub>3</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>9</sub>) and *H*-C=C-*p*-C<sub>6</sub>H<sub>4</sub>-C=C-*H* are more acidic than those of *H*-C=C-R (R = H, CH<sub>2</sub>OH). Therefore, the proton abstractions of *H*-C=C-R' and *H*-C=C-*p*-C<sub>6</sub>H<sub>4</sub>-C=C-*H* by base (NEt<sub>3</sub>) readily occur to produce alkynyl compounds (4 and 5) from reactions of 1 with HC=CR' and HC=C-*p*-C<sub>6</sub>H<sub>4</sub>-C=C+*H* in the presence of NEt<sub>3</sub>, whereas alkenyl compounds (HC=CR insertion products) 2 and 3 are the only products from reactions of 1 with HC=CR in the presence of bases (NEt<sub>3</sub>, PPh<sub>3</sub>, AsPh<sub>3</sub>).

Compounds 4 and 5 have been unequivocally identified by <sup>1</sup>H-, <sup>13</sup>C-NMR, infrared spectral and elemental analysis data (see Experimental Section). The signal at  $\delta$  3.1 ppm due to the acetylenic proton of  $H-C=C-p-C_6H_4-C=C-H^9$  completely disappeared in the <sup>1</sup>H NMR spectrum of 5 which clearly shows the ratio of the signals due to the methyl protons of  $\operatorname{Cp}^*(\operatorname{C}_5(\operatorname{CH}_3)_5)$  to the aromatic protons  $(-\operatorname{C}_6H_5)$ and  $-C_6H_{4-}$ ) being 30 : 14. One set of alkynyl signals at  $\delta$ 84.5 ppm (Ir-C=C-) and  $\delta$  100.8 ppm (Ir-C=C-) and one medium band ( $\nu$ (C=C)) at 2084.5 cm<sup>-1</sup> due to the coordinated alkynyl group were observed in <sup>13</sup>C NMR and infrared spectra of 5, respectively. These spectral data observed for 5 are very similar to those of the well-characterized the -C=C*p*-C<sub>6</sub>H<sub>4</sub>-C=C- bridged dinuclear metal compounds.<sup>10</sup> Recently, the crystal structure of a related dinuclear iridium compound (PPh<sub>3</sub>)<sub>2</sub>(CO)(CH=CHCH=CH-)Ir-C=C-p-C<sub>6</sub>H<sub>4</sub>-C=C-Ir(-CH=CH-CH=CH)(CO)(PPh<sub>3</sub>)<sub>2</sub> has been determined in our laboratory.<sup>11</sup> No dinuclear Cp\*Ir- $\eta^3$ -allyl-alkynyl compound with a bridging  $-C \equiv C - p - C_6 H_4 - C \equiv C$ - ligand such as 5

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has been reported thus far while a related compound Cp<sup>\*</sup>Ir  $(\eta^3$ -CH<sub>2</sub>CHCHPh)(-C=C-*t*-Bu) was previously reported.<sup>3a</sup>



It should be mentioned here that the attempts to prepare the alkynyl compounds  $Cp^*Ir(\eta^3-CH_2CHCHPh)(-C\equiv C-R)$ (R = H, CH<sub>2</sub>OH) have been unsuccessful. As mentioned earlier, several unknown iridium compounds were obtained from the reactions of **1** with HC=CR in the presence of NEt<sub>3</sub> even under refluxing conditions. Reactions of **1** with HC= CR' (R' = C<sub>6</sub>H<sub>5</sub> (**a**), *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (**b**)) in the presence of PPh<sub>3</sub> under same reaction conditions give iridium-tripheylphosphine compound [Cp<sup>\*</sup>Ir( $\eta^3$ -CH<sub>2</sub>CHCHPh)(PPh<sub>3</sub>)]<sup>+</sup> which has been previously reported.<sup>12</sup>

The newly prepared  $\eta^3$ -allyl-alkenyl- and alkynyl-Cp<sup>\*</sup>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 elecetophiles (H<sup>+</sup>, <sup>13</sup> Me<sup>+</sup>).

#### **Experimental Section**

General Information. All reactions were carried out under a dry  $N_2$  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 <sup>1</sup>H and 50.3 or 75.4 MHz for <sup>13</sup>C and 121.3 MHz for <sup>31</sup>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.

 $[Cp^*Ir(\eta^3-CH_2CHCHPh)(NCMe)]OTf (1)^8$  and 1,4-diethynyl benzene<sup>9</sup> (HC=C-*p*-C<sub>6</sub>H<sub>4</sub>-C=CH) were prepared by literature methods.

Synthesis of  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-CH=CH-^+NEt_3)]$ -OTf (2a),  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-CH=CH-^+PPh_3)]$ OTf (2b) and  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-CH=CH-^+AsPh_3)]$ OTf (2c).

**Preparation of [Cp\*Ir**( $\eta$ <sup>3</sup>-CH<sub>2</sub>CHCHPh)(-CH=CH-\*NEt<sub>3</sub>)] OTf (2a): A solution of 1 (0.20 g, 0.32 mmol) in 10 mL of CHCl<sub>3</sub> was stirred under HC=CH (1 atm) in the presence of NEt<sub>3</sub> (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 NEt<sub>3</sub> in the aqueous layer was separated from

# *New* $\eta^3$ *-Allyl-Alkenyl- and* $\eta^3$ *-Allyl-Alkynyl-Ir-Cp*<sup>\*</sup> *Compounds*

**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>CHCH-Ph)(-CH=CH-<sup>+</sup>NEt<sub>3</sub>)]OTf. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 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> $H_5$ ), 7.94 (d, 1H, J = 15 Hz, Ir-CH=CH-<sup>+</sup>N). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C): δ7.9 (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 ( $C_6$ 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**.

 $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-CH=CH^+PPh_3)]OTf(2b)$ : The yield was 0.25 g and 90% based on  $[Cp^*Ir(\eta^3-CH_2CH_2)]$ CHPh)(-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,  $C_5(CH_3)_5^{-}$ ), 1.67 (d, 1H, J = 10 Hz, CHHCH-CHPh), 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,  $C_6H_5$  and  $P(C_6H_5)_3$ ), 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): δ 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  $(CH_2CHCHPh)$ , 93.4  $(C_5(CH_3)_5)$ , 101.1 (d, J = 78.7 Hz, Ir-CH=CH-<sup>+</sup>P), 125, 126, 127, 129, 130, 131, 133, 135 and 140  $(C_6H_5 \text{ and } P(C_6H_5)_3)$ , 179.7 (d,  $J = 7.25 \text{ Hz Ir-}CH=CH-^+P)$ . <sup>31</sup>P NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  15.2 (*P*Ph<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>SPIr: 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>CH-CHPh)(-CH=CH-<sup>+</sup>AsPh<sub>3</sub>)]OTf. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 1.43 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 1.68 (d, 1H, *J* = 10 Hz, CHHCH-CHPh), 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): δ 8.1 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 39.4 (CH<sub>2</sub>CH-CHPh), 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>SAsIr: C, 51.89; H, 4.46. Found: C, 51.92; H, 4.40.

Synthesis of  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-C(CH_2OH)=CH^+PPh_3)]OTf$  (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  $[Cp^*Ir(\eta^3-CH_2CHCHPh)(-C(CH_2OH)=CH^+PPh_3)]OTf.$  <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, CHH-CHCHPh), 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,  $C_6H_5$  and  $P(C_6H_5)_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C): δ 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 = 9.4Hz, Ir-C(CH<sub>2</sub>OH)=CH<sup>+</sup>P), 93.8 ( $C_5$ (CH<sub>3</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 ( $C_6H_5$  and  $P(C_6H_5)_3$ ), 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): δ7.29 (PPh<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3340 (br m, v(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>SPIr: 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.

 $Cp^*Ir(\eta^3-CH_2CHCHPh)(-C\equiv C-Ph)$  (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): δ 1.68 (s, 15H,  $C_5(CH_3)_5$ ), 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>), 100.4 (Ir-C=C), 124.4, 125.0, 125.8, 127.8, 128.6, 129.3, 131.8 and 141.4 ( $C_6H_5$  and Ir-C=C- $C_6H_5$ ). IR (KBr, cm<sup>-1</sup>): 2088 (m, v(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\*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\*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<sup>-1</sup>): 2092 (m,  $\nu$ (C=C)). Anal. Calcd for C<sub>28</sub>H<sub>31</sub>Ir: C, 60.0; H, 5.58. Found: C, 59.9; H, 5.68.

**Cp**<sup>\*</sup>**Ir**( $\eta^3$ -**CH**<sub>2</sub>**CHCHPh**)(-**C≡C**-**C**(=**CH**<sub>2</sub>)**CH**<sub>3</sub>) (4c): The yield was 0.14 g and 85% based on Cp<sup>\*</sup>**I**r( $\eta^3$ -CH<sub>2</sub>CHCHPh) (-C≡C-C(=CH<sub>2</sub>)CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.65 (s, 15H, C<sub>5</sub>(*CH*<sub>3</sub>)<sub>5</sub><sup>-</sup>), 1.92 (dd, 3H, *J* = 1.4 and 1.6 Hz, *CH*<sub>3</sub>), 2.29 (d, 1H, *J* = 10 Hz, *CH*HCHCHPh), 2.74 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 4.04 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 4.32 (m, 1H, CH<sub>2</sub>CHCHPh), 4.77 (m, 1H, C(=CHH)), 4.90 (m, 1H, C(=CHH)), 7.05-7.32 (m, 5H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  8.6 (C<sub>5</sub>(*C*H<sub>3</sub>)<sub>5</sub><sup>-</sup>), 26.3 (-C(*C*H<sub>3</sub>)), 34.8 (*C*H<sub>2</sub>CHCHPh), 55.0 (CH<sub>2</sub>CHCHPh), 70.4 (CH<sub>2</sub>CHCHPh), 87.3 (Ir-*C*≡*C*-), 93.4 (*C*<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 101.8 (Ir-*C*≡*C*-), 114.3 (C(=*C*H<sub>2</sub>)), 131.1 (*C*(CH<sub>3</sub>)), 124.6, 125.4, 128.5 and 141.4 (*C*<sub>6</sub>H<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): 2089 (m, *v*(C≡*C*)). Anal. Calcd for C<sub>24</sub>H<sub>29</sub>Ir: C, 56.6; H, 5.01. Found: C, 56.4; H, 5.01.

**Cp\*Ir**( $\eta^3$ -**CH**<sub>2</sub>**CHCHPh**)(-**C≡C-C=CH-(CH**<sub>2</sub>)<sub>3</sub>-**CH**<sub>2</sub>) (4d): The yield was 0.15 g and 88% based on Cp\*Ir( $\eta^3$ -CH<sub>2</sub>CH-CHPh)(-C≡C-C=CH-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.64 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 2.05-2.21 (br m, 8H, (-CH<sub>2</sub>-)<sub>4</sub>), 2.30 (d, 1H, *J* = 9 Hz, C*H*HCHCHPh), 2.82 (d, 1H, *J* = 6 Hz, CHHCHCHPh), 4.30 (d, 1H, *J* = 10 Hz, CH<sub>2</sub>CHC*H*Ph), 4.32 (m, 1H, CH<sub>2</sub>CHCHPh), 5.71 (m, 1H, -C=CH-), 7.05-7.32 (m, 5H, C<sub>6</sub>H<sub>5</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>), 22.2, 23.2, 25.6 and 32.2 ((-CH<sub>2</sub>-)<sub>4</sub>), 34.5 (CH<sub>2</sub>CHCHPh), 54.9 (CH<sub>2</sub>CHCHPh), 70.4 (CH<sub>2</sub>CHCHPh), 83.2 (Ir-C≡C-), 93.3 (*C*<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 102 (Ir-C≡C-), 117 (-C=CH-), 127 (-C= CH-), 125, 126, 128, and 142 (*C*<sub>6</sub>H<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): 2081 (m,  $\nu$  (C≡C)). Anal. Calcd for C<sub>27</sub>H<sub>33</sub>Ir: C, 58.9; H, 6.05. Found: C, 58.8; H, 5.95.

**Cp**<sup>\*</sup>( $\eta^3$ -**CH<sub>2</sub>CHCHPh**)**Ir**-**C**≡**C**-*p*-**C**<sub>6</sub>**H**<sub>4</sub>-**C**≡**C**-**Ir**( $\eta^3$ -**CH<sub>2</sub>**-**CHCHPh**)**Cp**<sup>\*</sup> (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<sup>\*</sup>( $\eta^3$ -CH<sub>2</sub>CHCHPh)Ir-C≡C-*p*-C<sub>6</sub>H<sub>4</sub>-C≡C-Ir( $\eta^3$ -CH<sub>2</sub>CH-CHPh)Cp<sup>\*</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  1.68 (s, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 2.36 (d, 2H, *J* = 9 Hz, C*H*HCHCHPh), 2.87 (d, 2H, *J* = 6 Hz, CH*H*CHCHPh), 4.13 (d, 2H, *J* = 10 Hz, CH<sub>2</sub>CHCHPh), 4.35 (m, 2H, CH<sub>2</sub>CHCHPh), 7.08-7.40 (m, 14H, 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>), 34.4 (CH<sub>2</sub>CHCHPh), 55.4 (CH<sub>2</sub>CHCHPh), 70.7 (CH<sub>2</sub>CHCHPh), 84.5 (Ir-C≡C), 93.7 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub><sup>-</sup>), 100.8 (Ir-C≡C), 117, 125, 126, 129, 132 and 141 (C<sub>6</sub>H<sub>5</sub> and -C<sub>6</sub>H<sub>4</sub>-). IR (KBr, cm<sup>-1</sup>): 2084.5 (m, *v*(C≡C)). Anal. Calcd for C<sub>48</sub>H<sub>52</sub>Ir<sub>2</sub>: C, 70.2; H, 6.38. Found: C, 70.2; H, 6.32.

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