

# Proton Mediated Carbon-Carbon Bond Formation between the $\beta$ -Carbon of $\eta^1$ -Allyl and $\alpha$ -Carbon of Alkynyl Groups Coordinated to “IrBr(CO)(PPh<sub>3</sub>)<sub>2</sub>”

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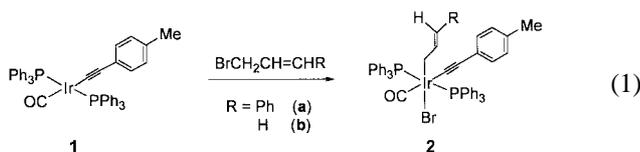
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Carbon-carbon bond formation mediated by transition metals has been investigated as an important step in organic synthesis.<sup>1</sup> Metal-alkynyls, in particular, are of interest due to the reactivity of the alkynyl group (M-C $\alpha$ ≡C $\beta$ R).<sup>2</sup> Addition of an electrophile to the  $\beta$ -carbon of the alkynyl group of alkynyl complexes is well-known to give metal-vinylidenes which consequently lead a carbon-carbon bond formation between the  $\alpha$ -carbon of the vinylidene and the  $\alpha$ -carbon of alkenyl<sup>2a</sup> or terminal carbon of the  $\pi$ -allyl<sup>2b</sup> groups adjacent to the vinylidene group.

In the course of our study on the electrophile-mediated carbon-carbon bond formation with alkynyliridium complexes,<sup>3</sup> we have unexpectedly found that proton initially attacks the  $\gamma$ -carbon of the  $\eta^1$ -allyl ligand in ( $\eta^1$ -allyl)(alkynyl)iridium(III) complexes and then a carbon-carbon bond is formed between the  $\beta$ -carbon of the protonated  $\eta^1$ -allyl group and the  $\alpha$ -carbon of the alkynyl group to produce 1,3-enynes.

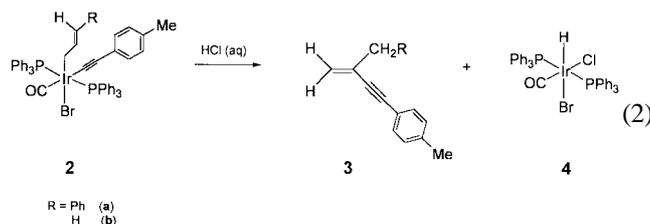
The ( $\eta^1$ -allyl)(alkynyl)iridium(III) complexes L<sub>3</sub>Ir( $\eta^1$ -CH<sub>2</sub>CH=CHR)(C≡C(*p*-C<sub>6</sub>H<sub>4</sub>Me))(Br) (**2**, R = Ph (**a**), H (**b**), L<sub>3</sub> = (CO)(PPh<sub>3</sub>)<sub>2</sub>)<sup>4</sup> have been prepared from the oxidative addition of allylic bromides (BrCH<sub>2</sub>CH=CHR) to the four coordinated alkynyliridium(I) complex L<sub>3</sub>Ir(C≡C(*p*-C<sub>6</sub>H<sub>4</sub>Me)) (**1**)<sup>5</sup> (eq. 1).



The complexes **2** have been unequivocally characterized by spectral data (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, and IR) and elemental analysis. It is well-known that *trans*-(alkyl)(bromo)iridium complexes are obtained from the oxidative addition of alkyl bromides to the related four coordinated iridium complexes.<sup>3b,6</sup> The  $\eta^1$ -type coordination (Ir-CH $\alpha$ 2CH $\beta$ =CH $\gamma$ R) of the allyl groups in **2** is also confirmed by comparing the data with those for the well-characterized  $\eta^1$ -allyl complexes (Ir,<sup>7a</sup> W,<sup>7b</sup> Pd<sup>7c</sup> and Os<sup>7d</sup>). The <sup>1</sup>H NMR spectra show multiplets at  $\delta$  2.88 for **2a** and 2.63 for **2b** due to the H $\alpha$  of Ir-CH $\alpha$ 2CH $\beta$ =CH $\gamma$ R with small coupling constants with two PPh<sub>3</sub> and the H $\beta$ . Relatively large coupling constant (J<sub>H $\beta$ -H $\gamma$</sub>  = 15.5 Hz) between H $\beta$  ( $\delta$  6.08) and H $\gamma$  ( $\delta$  5.12) in **2a** suggests these two protons being *trans* to each other. This *trans* configuration is also supported by NOE spectral measurement (Supplementary Information). The <sup>13</sup>C NMR spectra show

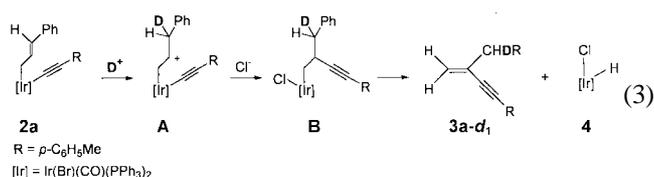
triplet-like signals at  $\delta$  6.05 for **2a** and 7.30 for **2b** due to the C $\alpha$  of  $\eta^1$ -C $\alpha$ H<sub>2</sub>C $\beta$ H = C $\gamma$ HR which seem to couple with the two equivalent PPh<sub>3</sub>. The coupling reaction between the allyl and alkynyl groups observed in the reaction of **2** with HCl (see below) also supports the allyl group being *cis* to alkynyl ligand.

Reactions of **2** with HCl exclusively produce 1,3-enynes H<sub>2</sub>C = C(CH<sub>2</sub>R)C≡C(*p*-C<sub>6</sub>H<sub>4</sub>Me) (**3**) and the hydridochloro-iridium complex (**4**) (see eq. 2).<sup>8</sup>



The enynes H<sub>2</sub>C = C(CH<sub>2</sub>R)C≡C(*p*-C<sub>6</sub>H<sub>4</sub>Me) (**3**) have been identified by <sup>1</sup>H NMR and GC/mass spectral data analysis. The signals at  $\delta$  5.49 (s) and 5.29 (s) in the <sup>1</sup>H NMR spectrum for **3a** are due to the typical vinylidene protons (=CH<sub>2</sub>), which agree well with the values reported for the related compounds.<sup>9</sup> Complex **4**, L<sub>3</sub>Ir(H)(Cl)(Br),<sup>10</sup> is identified by <sup>1</sup>H NMR ( $\delta$  -14.61(t)) in CDCl<sub>3</sub> and IR ( $\nu$ (CO), 2024 cm<sup>-1</sup>, KBr) spectral data.

To elucidate the mechanism for the reaction (eq 2), a deuterium labeling experiment was carried out. The treatment of **2a** with DCl yields only the *d*<sub>1</sub>-isotopomer H<sub>2</sub>C = C(CHDPh)C≡C(*p*-C<sub>6</sub>H<sub>4</sub>Me) (**3a-d<sub>1</sub>**) which is identified by the smaller signal (half of that for **3a**) due to the methylene proton at  $\delta$  3.55 in the <sup>1</sup>H NMR spectrum and mass spectral data (M<sup>+</sup> at *m/z* 233). This result suggests the reaction pathway as depicted by equation 3. It is very unusual to observe that the proton (H<sup>+</sup>) initially attacks the  $\gamma$ -carbon of the allyl group in the reaction of **2a** with HCl while our recent studies showed that proton prefers to attack the  $\beta$ -carbon of alkynyl group in a ( $\eta^3$ -allyl)(alkynyl)iridium<sup>3a</sup> and (alkyl)(alkenyl)(alkynyl)iridium<sup>3b</sup> rather than any other carbon in these complexes. An allylation of alkynes is catalyzed in the presence of copper chloride with allyl bromide and acetylenes.<sup>11</sup> The ( $\eta^1$ -allyl)(alkynyl) copper complexes were suggested as the intermediates that undergo C-C coupling reaction between the  $\alpha$ -carbons of the  $\eta^1$ -allyl and alkynyl groups to give 1,4-enynes.<sup>11</sup> It should be also mentioned that an interesting C-C bond is formed in the



absence of H<sup>+</sup> between the α-carbon of the η<sup>1</sup>-allyl and the β-carbon of alkynyl group coordinated to iridium in a binuclear complex<sup>7a</sup> while no such C-C coupling reaction has been found for **2** in the absence of H<sup>+</sup>.

The intermediate **A** may undergo a carbon-carbon coupling between the β-carbon of the protonated η<sup>1</sup>-allyl group and the adjacent α-carbon of the alkynyl group to form intermediate **B** which further undergoes the β-hydrogen elimination to give the enyne **3a** and complex **4**.

In summary, the reaction shown in eq 3 suggests that the nucleophilicity (for H<sup>+</sup> in particular) of the γ-carbon of the η<sup>1</sup>-allyl group is greater than that of the β-carbon of the alkynyl group in **2**. Proton initially attacks on the γ-carbon of the η<sup>1</sup>-allyl group of L<sub>3</sub>Ir(η<sup>1</sup>-CH<sub>2</sub>CH=CHR)(C≡C(*p*-C<sub>6</sub>H<sub>4</sub>Me))(Br) (**2**) and then 1,3-enynes are produced through an intramolecular carbon-carbon coupling between the β-carbon of the protonated η<sup>1</sup>-allyl group and β-carbon of the alkynyl group.

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- Synthesis of 2a:** A CHCl<sub>3</sub> (10 mL) solution of **1** (0.18 g, 0.20 mmol) and BrCH<sub>2</sub>CH=CHPh (0.05 mL, 0.33 mmol) was stirred at 25 °C under N<sub>2</sub>. The dark brown reaction mixture turned pale yellow within 10 min. Addition of Et<sub>2</sub>O (25 mL) to the CHCl<sub>3</sub> solution resulted in precipitation of the beige microcrystals of **2a** which were collected by filtration, washed with cold *n*-hexane (3 × 10 mL) and

cold acetone (10 mL), and dried under vacuum.

**Selected data for 2a** (yield: 0.17 g, 77%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 6.08 (dt, 1H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>Ph, J<sub>Hβ-Hγ</sub> = 15.5 Hz, J<sub>Hβ-Hα</sub> = 8.5 Hz), 5.12 (d, 1H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>Ph, J<sub>Hβ-Hγ</sub> = 15.5 Hz), 2.88 (m, 2H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 170.38 (t, J<sub>P-C</sub> = 6.9 Hz, Ir-CO), 140.78 (s, Ir-C<sub>α</sub>H<sub>2</sub>C<sub>β</sub>H = C<sub>γ</sub>HPh), 137.71 (s, Ir-C<sub>α</sub>H<sub>2</sub>C<sub>β</sub>H = C<sub>γ</sub>HPh), 114.30 (s, Ir-C≡C), 86.89 (t, J<sub>P-C</sub> = 18.2 Hz, Ir-C≡C), 6.05 (br, Ir-C<sub>α</sub>H<sub>2</sub>C<sub>β</sub>H = C<sub>γ</sub>HPh). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -15.30 (s). IR (KBr, cm<sup>-1</sup>): 2122.1w [ν(C≡C)] 2046.6s [ν(CO)]. Anal. Calcd for IrP<sub>2</sub>C<sub>55</sub>H<sub>46</sub>BrO: C, 62.50; H, 4.39. Found: C, 62.56; H, 4.24.

**For 2b** (yield: 0.15 g, 73%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 5.67 (ddt, 1H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>cisH<sub>γ</sub>trans, J<sub>Hβ-Hγ</sub>trans = 16.6 Hz, J<sub>Hβ-Hγ</sub>cis = 10.0 Hz, J<sub>Hβ-Hα</sub> = 8.5 Hz), 4.28 (dd, 1H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>cisH<sub>γ</sub>trans, J<sub>Hβ-Hγ</sub>cis = 10.0 Hz, J<sub>Hγ</sub>trans-H<sub>γ</sub>cis = 2.3 Hz), 3.96 (dd, 1H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>cisH<sub>γ</sub>trans, J<sub>Hβ-Hγ</sub>trans = 16.6 Hz, J<sub>Hγ</sub>trans-H<sub>γ</sub>cis = 2.3 Hz), 2.63 (m, 2H, Ir-CH<sub>α</sub>CH<sub>β</sub>=CH<sub>γ</sub>cisH<sub>γ</sub>trans). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 171.21 (t, J<sub>P-C</sub> = 6.3 Hz, Ir-CO), 147.83 (s, Ir-C<sub>α</sub>H<sub>2</sub>C<sub>β</sub>H = C<sub>γ</sub>H<sub>2</sub>), 130.43 (s, Ir-C<sub>α</sub>H<sub>2</sub>C<sub>β</sub>H = C<sub>γ</sub>H<sub>2</sub>), 113.77 (s, Ir-C≡C), 87.41 (t, J<sub>P-C</sub> = 18.9 Hz, Ir-C≡C), 7.30 (br, Ir-C<sub>α</sub>H<sub>2</sub>C<sub>β</sub>H = C<sub>γ</sub>H<sub>2</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -14.47 (s). IR (KBr, cm<sup>-1</sup>): 2124.8w [ν(C≡C)], 2050.5s [ν(CO)]. Anal. Calcd for IrP<sub>2</sub>C<sub>49</sub>H<sub>42</sub>BrO: C, 60.00; H, 4.32. Found: C, 59.00; H, 4.23.

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- Reaction of 2a with HCl:** HCl (2.0 mmol, 0.19 mL of H<sub>2</sub>O containing 32 wt % HCl) was added to a solution of **2a** (0.21 g, 0.2 mmol) in CHCl<sub>3</sub> (5 mL) at 25 °C, and the reaction mixture was stirred for 12 h during which time the beige microcrystals were precipitated. Excess HCl was removed by washing with H<sub>2</sub>O using a separatory funnel. Complex **4** (beige microcrystals)<sup>8</sup> was collected by centrifugal separation, washed with *n*-hexane, dried under vacuum, and identified by spectral data (see text). The yield was 0.15 g (88% based on Ir(H)(Cl)(Br)(CO)(PPh<sub>3</sub>)<sub>2</sub>). The supernatant was distilled under vacuum and compound **3a** was isolated by column chromatography on silica gel (hexane). The isolated yield of **3a** was 60%.  
**Selected data for 3a:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.49, 5.29 (both s, =CH<sub>2</sub>), 3.55 (s, 2H, CH<sub>2</sub>Ph), 2.33 (s, 3H, *p*-C<sub>6</sub>H<sub>4</sub>Me). Mass: M<sup>+</sup> at *m/z* 232. For **3b:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.42, 5.32 (both s, =CH<sub>2</sub>), 2.37 (s, 3H, *p*-C<sub>6</sub>H<sub>4</sub>Me), 1.99 (s, 3H, CH<sub>3</sub>). Mass: M<sup>+</sup> at *m/z* 156.
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