

Proton Mediated Carbon-Carbon Bond Formation between the β -Carbon of η^1 -Allyl and α -Carbon of Alkynyl Groups Coordinated to "IrBr(CO)(PPh₃)₂"

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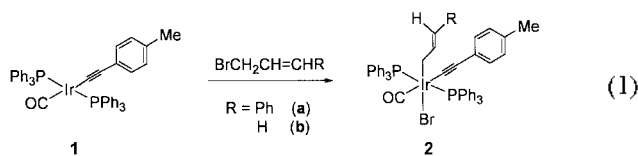
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Carbon-carbon bond formation mediated by transition metals has been investigated as an important step in organic synthesis.¹ Metal-alkynyls, in particular, are of interest due to the reactivity of the alkynyl group (M-C α ≡C β R).² Addition of an electrophile to the β -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 α -carbon of the vinylidene and the α -carbon of alkenyl^{2a} or terminal carbon of the π -allyl^{2b} groups adjacent to the vinylidene group.

In the course of our study on the electrophile-mediated carbon-carbon bond formation with alkynyliridium complexes,³ we have unexpectedly found that proton initially attacks the γ -carbon of the η^1 -allyl ligand in (η^1 -allyl)(alkynyl)iridium(III) complexes and then a carbon-carbon bond is formed between the β -carbon of the protonated η^1 -allyl group and the α -carbon of the alkynyl group to produce 1,3-enynes.

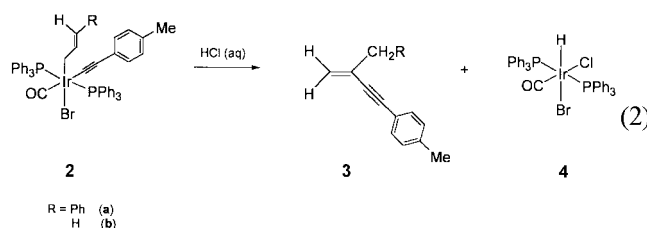
The (η^1 -allyl)(alkynyl)iridium(III) complexes L₃Ir(η^1 -CH₂CH=CHR)(C≡C(*p*-C₆H₄Me))(Br) (**2**, R = Ph (a), H (b), L₃ = (CO)(PPh₃)₂)⁴ have been prepared from the oxidative addition of allylic bromides (BrCH₂CH=CHR) to the four coordinated alkynyliridium(I) complex L₃Ir(C≡C(*p*-C₆H₄Me)) (**1**)⁵ (eq. 1).



The complexes **2** have been unequivocally characterized by spectral data (¹H, ¹³C and ³¹P 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.^{3b,6} The η^1 -type coordination (Ir-CH α C β H = CH γ R) of the allyl groups in **2** is also confirmed by comparing the data with those for the well-characterized η^1 -allyl complexes (Ir,^{7a} W,^{7b} Pd^{7c} and Os^{7d}). The ¹H NMR spectra show multiplets at δ 2.88 for **2a** and 2.63 for **2b** due to the H α of Ir-CH α C β H = CH γ R with small coupling constants with two PPh₃ and the H β . Relatively large coupling constant ($J_{H\beta, H\gamma}$ = 15.5 Hz) between H β (δ 6.08) and H γ (δ 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 ¹³C NMR spectra show

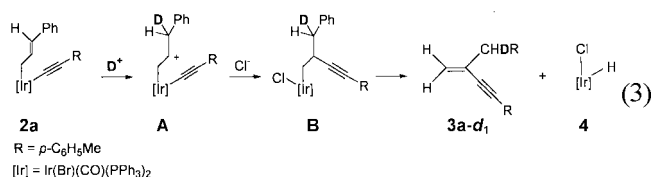
triplet-like signals at δ 6.05 for **2a** and 7.30 for **2b** due to the C α of η^1 -C α H₂C β H = CH γ R which seem to couple with the two equivalent PPh₃. The coupling reaction between the allyl and alkynyl groups observed in the reaction of **2** with HCl (see below) also supports the allyl group being *cis* to alkynyl ligand.

Reactions of **2** with HCl exclusively produce 1,3-enynes H₂C = C(CH₂R)C≡C(*p*-C₆H₄Me) (**3**) and the hydridochloro-iridium complex (**4**) (see eq. 2).⁸



The enynes H₂C = C(CH₂R)C≡C(*p*-C₆H₄Me) (**3**) have been identified by ¹H NMR and GC/mass spectral data analysis. The signals at δ 5.49 (s) and 5.29 (s) in the ¹H NMR spectrum for **3a** are due to the typical vinylidene protons (=CH₂), which agree well with the values reported for the related compounds.⁹ Complex **4**, L₃Ir(H)(Cl)(Br),¹⁰ is identified by ¹H NMR (δ -14.61(t)) in CDCl₃ and IR (ν (CO), 2024 cm⁻¹, 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*₁-isotopomer H₂C = C(CHDPh)C≡C(*p*-C₆H₄Me) (**3a-d**₁) which is identified by the smaller signal (half of that for **3a**) due to the methylene proton at δ 3.55 in the ¹H NMR spectrum and mass spectral data (M^+ 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⁺) initially attacks the γ -carbon of the allyl group in the reaction of **2a** with HCl while our recent studies showed that proton prefers to attack the β -carbon of alkynyl group in a (η^3 -allyl)(alkynyl)iridium^{3a} and (alkyl)(alkenyl)(alkynyl)iridium^{3b} 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.¹¹ The (η^1 -allyl)(alkynyl) copper complexes were suggested as the intermediates that undergo C-C coupling reaction between the α -carbons of the η^1 -allyl and alkynyl groups to give 1,4-enynes.¹¹ It should be also mentioned that an interesting C-C bond is formed in the



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

The intermediate **A** may undergo a carbon-carbon coupling between the β -carbon of the protonated η^1 -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^+ in particular) of the γ -carbon of the η^1 -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^1 -allyl group of $\text{L}_3\text{Ir}(\eta^1\text{-CH}_2\text{CH}=\text{CHR})(\text{C}\equiv\text{C}(p\text{-C}_6\text{H}_4\text{Me}))(\text{Br})$ (**2**) and then 1,3-enynes are produced through an intramolecular carbon-carbon coupling between the β -carbon of the protonated η^1 -allyl group and β -carbon of the alkynyl group.

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- Synthesis of 2a:** A CHCl_3 (10 mL) solution of **1** (0.18 g, 0.20 mmol) and $\text{BrCH}_2\text{CH}=\text{CHPh}$ (0.05 mL, 0.33 mmol) was stirred at 25 °C under N_2 . The dark brown reaction mixture turned pale yellow within 10 min. Addition of Et_2O (25 mL) to the CHCl_3 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%): ^1H NMR (500 MHz, CDCl_3): 6.08 (dt, 1H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$, $J_{\text{H}\beta\text{H}\alpha} = 15.5$ Hz, $J_{\text{H}\beta\text{H}\alpha} = 8.5$ Hz), 5.12 (d, 1H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$, $J_{\text{H}\beta\text{H}\alpha} = 15.5$ Hz), 2.88 (m, 2H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$), 137.71 (s, $\text{Ir-C}\equiv\text{C}$), 140.78 (s, $\text{Ir-C}_\alpha\text{H}_2\text{C}_\beta\text{H} = \text{C}_2\text{HPh}$), 137.71 (s, $\text{Ir-C}_\alpha\text{H}_2\text{C}_\beta\text{H} = \text{C}_2\text{HPh}$), 114.30 (s, $\text{Ir-C}\equiv\text{C}$), 86.89 (t, $J_{\text{P-C}} = 18.2$ Hz, $\text{Ir-C}\equiv\text{C}$), 6.05 (br, $\text{Ir-C}_\alpha\text{H}_2\text{C}_\beta\text{H} = \text{C}_2\text{HPh}$). ^{31}P NMR (CDCl_3): δ -15.30 (s). IR (KBr, cm^{-1}): 2122.1w [$\nu(\text{C}\equiv\text{C})$] 2046.6s [$\nu(\text{CO})$]. Anal. Calcd for $\text{IrP}_2\text{C}_{55}\text{H}_{46}\text{BrO}$: C, 62.50; H, 4.39. Found: C, 62.56; H, 4.24.

For 2b (yield: 0.15 g, 73%): ^1H NMR (500 MHz, CDCl_3): 5.67 (ddt, 1H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$, $J_{\text{H}\beta\text{H}\alpha} = 16.6$ Hz, $J_{\text{H}\beta\text{H}\alpha} = 10.0$ Hz, $J_{\text{H}\beta\text{H}\alpha} = 8.5$ Hz), 4.28 (dd, 1H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$, $J_{\text{H}\beta\text{H}\alpha} = 10.0$ Hz, $J_{\text{H}\beta\text{H}\alpha} = 2.3$ Hz), 3.96 (dd, 1H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$, $J_{\text{H}\beta\text{H}\alpha} = 16.6$ Hz, $J_{\text{H}\beta\text{H}\alpha} = 2.3$ Hz), 2.63 (m, 2H, $\text{Ir-CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}$, $J_{\text{H}\beta\text{H}\alpha} = 10.0$ Hz, $J_{\text{H}\beta\text{H}\alpha} = 2.3$ Hz), 137.21 (s, $\text{Ir-C}\equiv\text{C}$), 147.83 (s, $\text{Ir-C}_\alpha\text{H}_2\text{C}_\beta\text{H} = \text{C}_2\text{H}_2$), 130.43 (s, $\text{Ir-C}_\alpha\text{H}_2\text{C}_\beta\text{H} = \text{C}_2\text{H}_2$), 113.77 (s, $\text{Ir-C}\equiv\text{C}$), 87.41 (t, $J_{\text{P-C}} = 18.9$ Hz, $\text{Ir-C}\equiv\text{C}$), 7.30 (br, $\text{Ir-C}_\alpha\text{H}_2\text{C}_\beta\text{H} = \text{C}_2\text{H}_2$). ^{31}P NMR (CDCl_3): δ -14.47 (s). IR (KBr, cm^{-1}): 2124.8w [$\nu(\text{C}\equiv\text{C})$], 2050.5s [$\nu(\text{CO})$]. Anal. Calcd for $\text{IrP}_2\text{C}_{49}\text{H}_{42}\text{BrO}$: 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_2O containing 32 wt % HCl) was added to a solution of **2a** (0.21 g, 0.2 mmol) in CHCl_3 (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_2O using a separatory funnel. Complex **4** (beige microcrystals)⁸ 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 $\text{Ir}(\text{H})(\text{Cl})(\text{Br})(\text{CO})(\text{PPh}_3)_2$). 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:** ^1H NMR (300 MHz, CDCl_3): 5.49, 5.29 (both s, $=\text{CH}_2$), 3.55 (s, 2H, CH_2Ph), 2.33 (s, 3H, *p*- $\text{C}_6\text{H}_4\text{Me}$). Mass: M^- at *m/z* 232. For **3b**: ^1H NMR (300 MHz, CDCl_3): 5.42, 5.32 (both s, $=\text{CH}_2$), 2.37 (s, 3H, *p*- $\text{C}_6\text{H}_4\text{Me}$), 1.99 (s, 3H, CH_3). Mass: M^+ at *m/z* 156.
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