

A Rare η^2 -Butadienyl Complex from an Alkyne Double Insertion with Double Vinylidene Rearrangement

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Rearrangement of η^2 -1-alkynes $\text{RC}\equiv\text{CH}$ to metal-bound vinylidenes, $\text{RHC}=\text{C}=\text{ML}_n$, is well known,¹ and the resulting carbenes can undergo vinyl,^{2a-c} alkyl,^{2d} alkynyl, or aryl insertion,^{2e-h} a reaction that can lead to useful C–C coupling products. Double insertions are sometimes only apparent: for example, the proposed double insertions of CO were subsequently shown to proceed via another pathway;³ true multiple insertions are known for isonitriles $\text{RN}=\text{C}=\text{ML}_n$.⁴ Here we report a double insertion of alkynes with the double alkyne to vinylidene rearrangement together with mechanistic studies that indicate each alkyne independently undergoes intramolecular rearrangement.

Starting material **1** was obtained (91%) by refluxing $[\text{IrH}_2(\text{acetone})_2(\text{PPh}_3)_2]\text{SbF}_6$ and 2 equiv of *trans*- $\text{PhCH}=\text{CHC}(\text{O})\text{Me}$ in acetone for 4 h.⁵ **1** then reacts (CH_2Cl_2 , 25 °C) with 2 equiv of $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Ph}$, PhCH_2) to give the title products **2** ($\text{X} = \text{H}$) (Scheme 1). Both crystallographic and spectroscopic data support the presence of a rare η^2 -butadienyl coordination in **2**. As shown in the crystal structure of **2** ($\text{R} = \text{Ph}$, $\text{X} = \text{H}$)^{6a} (Figure 1), C-12 is weakly bound^{2c} [$\text{Ir}\cdots\text{C}(12) = 2.509(9) \text{ \AA}$] to the metal, but C-11 [$\text{Ir}\cdots\text{C}(11) = 3.092(8) \text{ \AA}$, comparable to $\text{Ir}\cdots\text{C}(14) = 3.110(9) \text{ \AA}$] is outside the range of any coordinative interaction. Consistent with previous η^2 -allyl or benzyl complexes,^{7a,b,8} ¹³C NMR spectra of **2** show large (>30 ppm) chemical shift differences between C-11 and C-12.^{6b} The C-11, C-12 double bond is twisted (77.9°, $\text{R} = \text{Ph}$, $\text{X} = \text{H}$) and is almost deconjugated from the C-13, C-14 double bond. The $\text{Ir}\cdots\text{C}(12)$ bond, readily replaced by CO, is weak (<10 kcal/mol^{7a}): the VT ¹H NMR of **2** ($\text{R} = \text{PhCH}_2$, $\text{X} = \text{H}$) at –85 °C failed to decoalesce the diastereotopic protons in either CH_2 group. Such η^2 -allyl or benzyl complexes have mostly been reported for early transition metals,⁷ and only one is known for a late metal (Ru).⁸

The reaction between **1** and $\text{RC}\equiv\text{CD}$ ($\text{R} = \text{Ph}$ or PhCH_2) gives products exclusively labeled (>97%) at the terminal carbons C-11 and C-14. For **2** ($\text{R} = \text{Ph}$, $\text{X} = \text{H}$), the key assignment of the proton NMR peaks for H-11, H-12, and H-14 follows from the characteristic 16.2 Hz ³*J*(H-11, H-12) *trans* $\text{H}-\text{C}=\text{C}-\text{H}$ coupling constant and the 1.6 Hz ⁴*J*(H-12, H-14) coupling constant (acetone-*d*₆). Additional ³*J*(H, H) couplings between H-11, H-14 and their adjacent CH_2 groups in **2** ($\text{R} = \text{PhCH}_2$, $\text{X} = \text{H}$) confirmed this assignment, which is also consistent with prior work.^{7a,b}

Additional information was obtained from the α -tetralone series, where intermediates could be isolated (Scheme 2). A crystallographically and spectroscopically (VT NMR) characterized C–H agostic kinetic product **4**,⁹ initially isolated (91%), is a precursor to the η^2 -butadienyl complex **5**, the thermodynamic product (89% from **3**).

The labeling experiment suggests the following proposed mechanism (Scheme 3). This involves an alkyne to vinylidene rearrangement followed by a hydride insertion, another alkyne to vinylidene rearrangement, and a migratory insertion of the vinyl to the vinylidene. In our system, this migratory insertion is favored

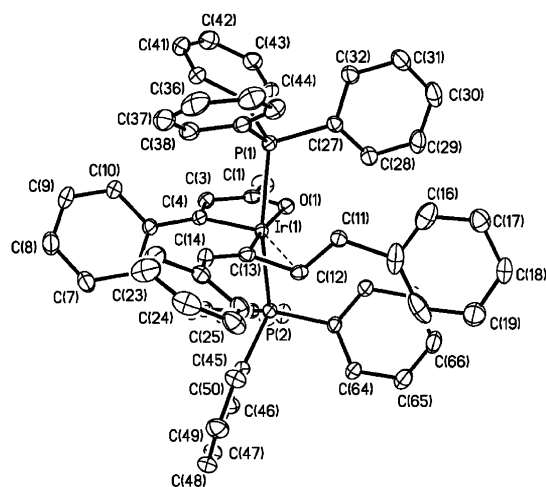
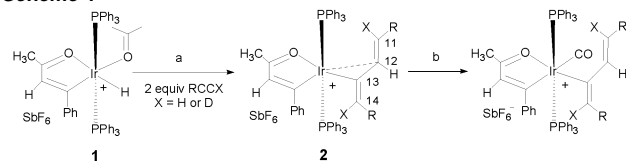


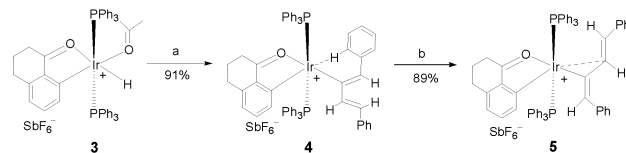
Figure 1. Crystal structure (ORTEP representation) of the cation part of **2** ($\text{R} = \text{Ph}$, $\text{X} = \text{H}$) with 50% thermal probability ellipsoids.^{6a} Hydrogen atoms are omitted for clarity. Selected (bond distances (Å): $\text{Ir}(1)-\text{O}(1) = 2.204(3)$; $\text{Ir}(1)-\text{C}(4) = 1.991(4)$; $\text{Ir}(1)-\text{C}(11) = 3.092(8)$; $\text{Ir}(1)-\text{C}(12) = 2.509(9)$; $\text{Ir}(1)-\text{C}(13) = 1.994(4)$; $\text{Ir}(1)-\text{C}(14) = 3.110(9)$; $\text{Ir}(1)-\text{P}(1) = 2.3788(12)$; $\text{Ir}(1)-\text{P}(2) = 2.3698(12)$; $\text{C}(11)-\text{C}(12) = 1.3494(10)$.

Scheme 1^a



^a (a) CH_2Cl_2 , 0 °C, 1 h, $\text{R} = \text{Ph}$, $\text{X} = \text{H}$, 88%; $\text{R} = \text{Ph}$, $\text{X} = \text{D}$, 86%; $\text{R} = \text{PhCH}_2$, $\text{X} = \text{H}$, 92%; $\text{R} = \text{PhCH}_2$, $\text{X} = \text{D}$, 89%. (b) 1 atm CO, CH_2Cl_2 , 25 °C, 5 min, $\text{R} = \text{Ph}$, $\text{X} = \text{H}$, 100%.

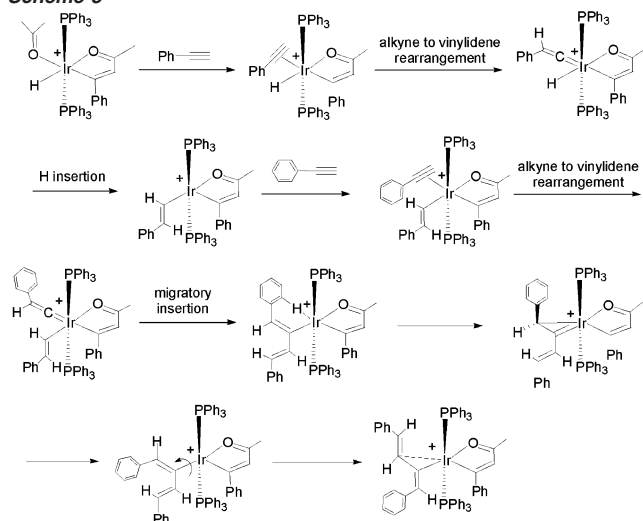
Scheme 2^a



^a (a) 2 equiv of PhCCH , CH_2Cl_2 , 25 °C, 15 min. (b) CH_2Cl_2 , 35 °C, 15 h.

with the vinylidene moiety, one of the strongest π -acceptors,¹⁰ receiving minimal back-donation when *trans* to a high *trans*-effect ligand in a cationic metal complex (Scheme 3). The kinetic product (**4**) is formed from the migratory insertion of the vinyl group anti to the β -Ph of the vinylidene ligand, which has a free rotation around the metal–vinylidene bond,^{10a} but **5** is more thermodynamically stable, having the iridium *trans* to the terminal Ph– group. Analogues of **4** have been previously seen as stable products,¹¹ and rearrangement of **4** to **5** very likely goes through an η^2 -vinyl or a zwitterionic carbene intermediate.¹²

Scheme 3



Previously proposed mechanisms for alkyne to vinylidene rearrangement go by (i) $\text{RC}\equiv\text{C}-\text{H}$ oxidative addition¹³ followed by either a 1,3-hydrogen shift^{13f} or a bimolecular proton shift,^{13b} (ii) an α -hydrogen elimination of the metal–vinyl intermediate (from $\text{C}\equiv\text{C}$ insertion into $\text{M}-\text{H}$),¹⁴ or (iii) a concerted intraligand 1,2-hydrogen shift.¹⁵ No definitive experimental evidence for path (iii) has previously been obtained. Our $\text{M}-\text{H}$ does not scramble but appears (>97%) as H-12 in **2** (Scheme 1). This eliminates path (ii) and makes path (i) unlikely because any oxidative addition should give either a fluxional seven-coordinate $\text{Ir}^{\text{V}}(\text{H})(\text{D})$ species or, more likely,^{13f,16} an $\text{Ir}^{\text{III}}(\text{H}-\text{D})$ complex, both leading to H/D exchange. We carried out two crossover studies, one with $\text{PhCH}_2\text{C}\equiv\text{CH}/\text{PhC}\equiv\text{CD}$, the other with $\text{PhCH}_2\text{C}\equiv\text{CD}/\text{PhC}\equiv\text{CH}$. To compensate for their different reactivities, we used a 0.8:1.2 ratio of $\text{PhCH}_2\text{C}\equiv\text{CH}(\text{D})/\text{PhC}\equiv\text{CD}(\text{H})$. All four possible products were obtained (^1H and ^2H NMR), but there is essentially no (<5%) proton scrambling between $\text{RC}\equiv\text{CH}$ and $\text{R}'\text{C}\equiv\text{CD}$ in both experiments. This was concluded by identifying the separately distinguishable H-11 and H-14 ^1H NMR signals associated with R or R' and measuring the D/H ratio. This result is consistent with path (iii), where each η^2 -alkyne independently rearranges to a C–H agostic η^2 -alkyne, followed by intraligand 1,2-hydrogen shift.

In summary, a rare η^2 -butadienyl Ir(III) complex is formed via a concerted alkyne to vinylidene rearrangement. A reaction intermediate was isolated, and isotope labeling indicates that the alkyne to vinylidene rearrangements are concerted intramolecular processes without crossover.

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Supporting Information Available: Experimental procedure for the synthesis of all of the complexes, ^1H and ^{13}C NMR spectra, and X-ray crystal structure data for **2** (R = Ph, X = H) and **4** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) (a) Crystal structure data for **2** (R = Ph, X = H): orange block, monoclinic, space group $P2_1/n$, $a = 14.507(3)$ Å, $b = 18.091(4)$ Å, $c = 20.457(4)$ Å, $\beta = 90.48(3)^\circ$, $Z = 4$; $R[I > 2\sigma(I)] = 0.0414$, $wR(\text{all data}) = 0.1042$, $\text{GOF} = 1.083$; 296 K. C(11) and C(12) are positionally disordered and were refined with alternative positions (60/40). Only the major component (60%) is shown. See Supporting Information for details. (b) ^{13}C NMR chemical shifts (125 MHz, CD_2Cl_2 , 298 K) of C-14, C-13, C-12, and C-11 are δ 128.3 (br s), 132.7 (t, 6.8 Hz), 100.3 (s), and 133.7 (s), respectively, for **2** (R = Ph, X = H) and 124.6 (br s), 126.4 (t, 5.9 Hz), 99.4 (s), and 129.6 (s), respectively, for **2** (R = PhCH_2 , X = H).
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