

A Metal-Templated 4 + 2 Cycloaddition Reaction of an Alkyne and a Diyne To Form a 1,2-Aryne

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Summary: Coordination of bis-phosphino diyne substrates to mixed platinum and tungsten metal templates results in a templated 4 + 2 alkyne–diyne cycloaddition reaction to form an aryne intermediate, which abstracts two H atoms to form an arene ring. The aryne intermediate can also be trapped via a Diels–Alder reaction with furan.

Templated reactions are those in which substrates are held into a specific geometry via interaction with a template such that they react in a controlled fashion.¹ Substrate–template interactions can involve many types of bonds; examples include covalent bonds, coordinative bonds to metals, hydrogen bonds, and π – π interactions.² Our research is focused on transition-metal templates, which provide well-defined geometries, tunable bond lengths, easy substrate–template complex formation, and straightforward template removal. Metal templates have been used extensively in the synthesis of macrocycles, catenanes, and rotaxanes.^{2,3} We are using transition metals to template alkene and alkyne cycloaddition reactions. In these reactions, the template–substrate interaction is remote from the reactive alkynes. The cycloadditions are not metal-catalyzed, nor do the alkynes interact directly with the metals. Such metal templation has been used to control regioselectivity and stereochemistry of

alkene cycloaddition reactions, including Diels–Alder reactions⁴ and alkene photodimerization.⁵ However, applications to alkyne cycloaddition are limited.⁶ Previously, Martin-Redondo et al. showed that coordination of the phosphine-substituted diyne Ph₂PC₄PPh₂ to PtCl₂ fragments effectively templates diyne cycloaddition reactions to form cyclooctadienediyne and cyclododecatrienyne rings.⁷ Later, by using W(CO)₄ templates, we showed that the critical parameter controlling cycloaddition is distance between the diyne terminal carbons (α to P) and that the threshold for reactivity is about 3.2 Å. This carbon–carbon distance is in turn controlled by the M–P distance.⁸ The small Pt–P bond lengths of the PtCl₂ complex bring the diynes into close proximity, inducing reaction. In contrast, the longer M–P bond lengths in the W(CO)₄ complexes hold the substrates far enough apart that the diynes are unreactive. Here we describe mixed tungsten–platinum template complexes, in which two diynes are held in close proximity at one end by PtX₂, while the other ends are held further apart by W(CO)₄, and we show how careful choice of the metal template fragment allows us to control the nature of the cycloaddition reaction.

The mixed template complexes are formed via sequential addition of the W(CO)₄ precursor followed by the PtX₂ precursor. The compound [$\{W(CO)_4\}(Ph_2PC_4PPh_2-\kappa^1P)_2$] (**1**) is first prepared by reaction of [W(CO)₄(2-pic)₂] with excess Ph₂PC₄PPh₂.⁸ In **1**, two substrates are coordinated to one tungsten center, and the other end of each bis-phosphine dangles. Compound **1** was first combined with Pt(CH₃)₂(COD) (COD = cyclooctadiene) and reacts to form [$\{W(CO)_4\}-\{Pt(CH_3)_2\}(\mu-Ph_2PC_4PPh_2)_2$] (**2**) (Scheme 1). This complex was not expected to be reactive toward cycloaddition, on the basis of the fact that the templated complex with two Pt(CH₃)₂ templates is unreactive.⁷ This prediction was borne out, and **2** does not react, even when heated. An ORTEP diagram of **2** is shown in Figure 1.

Reaction of **1** with PtCl₂(COD) also leads to the rapid formation of the mixed template complex [$\{W(CO)_4\}-\{PtCl_2\}(\mu-Ph_2PC_4PPh_2)_2$] (**3**), which has been characterized spectroscopically.⁹ In CH₂Cl₂ solution, **3** starts turning black within minutes and decomposes within 24 h to a complex mixture. However, if **3** is formed in THF rather than CH₂Cl₂,

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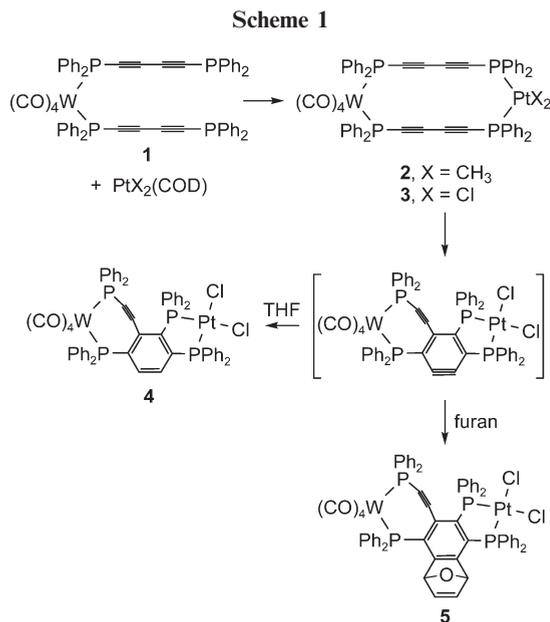
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(9) Spectroscopic data for **3**: ¹H NMR δ 7.0–8.0 (m, Ph); ³¹P NMR δ 1.5 (s, ¹J_{WP} = 241 Hz, WP), –10.8 (s, ¹J_{PP} = 3710 Hz, PtP); IR (cast, cm^{–1}) ν (C=C) 2089 w, ν (CO) 2024 s, 1930 s, 1904 vs.



one major product, $[\{\text{W}(\text{CO})_4\}\{\text{PtCl}_2\}\{\mu\text{-C}_6\text{H}_2(\text{PPh}_2)_3\text{-}(\text{CCPPH}_2)\}]$ (**4**), can be isolated in 92% yield (Scheme 1 and Figure 2). The compound consists of a *cis*- $\text{W}(\text{CO})_4\text{P}_2$ unit and a *cis*- PtCl_2P_2 unit bridged by a phosphine-substituted phenylacetylene. The arene ring is substituted in the 1-, 2-, and 5-positions by PPh_2 units and by $\text{C}\equiv\text{C}(\text{PPh}_2)_2$ in the 4-position. The PPh_2 units in the 1- and 2-positions are coordinated to platinum, while the 5- PPh_2 and $\text{C}\equiv\text{C}(\text{PPh}_2)_2$ phosphines coordinate to tungsten. All distances and angles are as expected, with the exception of alkyne angles of $151.0(7)$ and $157.0(8)^\circ$ (C11 and C12 in Figure 2), which indicate significant strain in the ring formed by coordination of the ligand to tungsten.

We propose that the arene ring in **4** results from cycloaddition of three of four alkynes, formally a $4 + 2$ cycloaddition of an alkyne with a diyne (a dehydro-Diels–Alder reaction).¹⁰ This cycloaddition reaction leads to a 1,2-aryne intermediate, which abstracts two hydrogen atoms. If the reaction is carried out in d_8 -THF, the deuterium NMR spectrum of the product shows two broad peaks at δ 7.87 and 7.6, supporting THF as the source for the hydrogen atoms in **4**. The corresponding peaks in the ^1H spectrum are obscured by the diphenylphosphino hydrogen resonances.

Further evidence for the proposed aryne intermediate was obtained by carrying out the reaction in furan, which is known to trap benzyne intermediates via a Diels–Alder reaction.¹¹ Compound **3** can be formed by dissolving **1** and $\text{PtCl}_2(\text{COD})$ in furan and can be identified by ^{31}P NMR in furan. If the resulting solution is stirred for 24 h, the new product **5** is formed, which is the Diels–Alder adduct of the proposed benzyne intermediate with the furan (Scheme 1). In contrast to the reaction in THF, formation of the furan adduct is essentially quantitative by ^{31}P NMR, and minor side products are not observed. The structure of **5** has been confirmed by X-ray crystallography. An ORTEP diagram is shown in Figure 3.

Unlike the well-known $4 + 2$ cycloaddition of a diene with an alkene or an alkyne (the Diels–Alder reaction), $4 + 2$

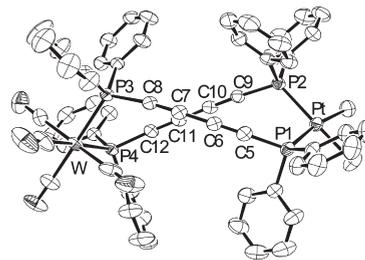


Figure 1. ORTEP diagram showing the crystal structure of compound **2**. Hydrogen atoms and cocrystallized solvent have been omitted. Selected distances (Å) and angles (deg): C5–C6 = 1.192(6), C6–C7 = 1.390(6), C7–C8 = 1.192(6), P1–Pt = 2.282(1), P2–Pt = 2.281(1), P3–W = 2.493(1), P4–W = 2.496(1), C5–C9 = 3.358, C8–C12 = 3.549; P2–Pt–P1 = 97.30(4), P3–W–P4 = 93.03(3).

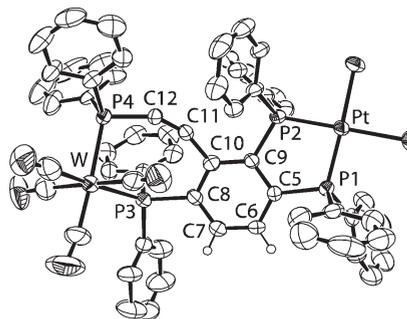


Figure 2. ORTEP diagram showing the crystal structure of compound **4**. Cocrystallized solvent and hydrogen atoms, except for those on the newly formed phenyl ring, have been omitted. Selected distances (Å) and angles (deg): Pt–P1 = 2.210(2), Pt–P2 = 2.210(2), W–P3 = 2.598(2), W–P4 = 2.512(2), C11–C12 = 1.201(1); P1–Pt–P2 = 88.32(7), P3–W–P4 = 87.39(7), P4–C12–C11 = 151.0(7), C12–C11–C10 = 157.0(8).

cycloaddition of an alkyne and a diyne to form a 1,2-aryne is very rare.^{10,12} 1,2-Aryne rings are more typically formed via elimination reactions from appropriately substituted arenes.¹³ The first clear example of a $[4 + 2]$ diyne–alkyne cycloaddition was reported as recently as 1997, when the pyrolysis of 1,3,8-nonatriyne was shown to lead to indane via a 1,2-benzyne intermediate.¹² The intermediacy of a 1,2-benzyne was proven using labeling studies. Ueda has also described reactions in which tetraacetylenes cyclize via intramolecular $[4 + 2]$ diyne–alkyne additions to form fluorene derivatives.¹⁴ In this case, the intermediacy of the 1,2-aryne was demonstrated by characterization of their Diels–Alder adducts with anthracene. Diyne–alkyne cycloaddition is also thought to be involved in the pyrolysis of acetylene to form benzene (the Berthelot reaction).¹⁵ The reverse reaction, a retro-Diels–Alder reaction of 1,2-benzyne to form acetylene and butadiyne, has been observed in the gas phase by mass spectrometry.¹⁶

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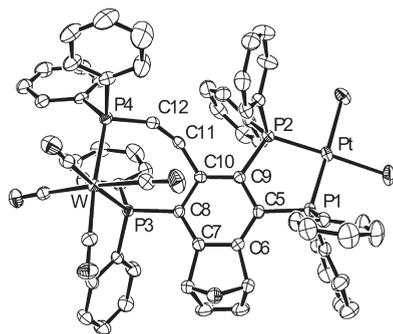


Figure 3. ORTEP diagram showing the crystal structure of compound **5**. Hydrogen atoms and cocrystallized solvent have been omitted. Selected distances and angles: Pt–P1 = 2.2074(8), Pt–P2 = 2.2139(8), W–P3 = 2.5444(8), W–P4 = 2.5078(8), C11–C12 = 1.201(4); P1–Pt–P2 = 87.95(3), P3–W–P4 = 88.02(3), P4–C12–C11 = 149.4(3), C12–C11–C10 = 155.8(3).

In the reaction described here, we have used metal coordination to induce the [4 + 2] alkyne–diyne cycloaddition between the two diyne substrates. The observed reactivity is a direct result of the geometry imposed on the diyne substrates by the Pt and W templates. Although it was impossible to obtain crystal structure of the template complex **3** prior to cycloaddition, the structure of the unreactive Pt(CH₃)₂ analogue **2** (Figure 1) can be used as a model. The smaller Pt radius results in shorter M–P bonds and thus holds the Pt ends of the diynes in close proximity (3.358 Å). The larger W radius means that the W ends of the diynes are further apart at 3.549 Å. Both ends are well above the reactivity threshold of 3.2 Å,⁸ consistent with the unreactivity of this complex. In the W(CO)₄–PtCl₂ templated complex **3**, the weaker trans influence of Cl versus CH₃ leads to shorter Pt–P bonds, which in turn bring the Pt ends of the diynes closer than 3.2 Å, leading to reaction. The greater distance at the W end of the diynes prevents formation of the cyclooctadienediyne ring observed in the homometallic bis-PtCl₂ complex and instead results in cycloaddition of three of the four triple bonds, leading to the 1,2-aryne intermediate.

The reactions described here, along with those described by Ueda, are also remarkable in that they occur at room temperature. A concerted 4 + 2 alkyne–diyne cycloaddition is expected to have a large activation barrier as a result of the large distortion required for the diyne to reach the transition state.¹¹ The facile room-temperature reactivity suggests that the reaction is not concerted but stepwise. The fact that the cycloaddition reaction is induced by holding only one end of the diynes in close proximity is consistent with a reaction initiated by σ -bond formation between the α -carbons on the Pt end.

In addition to its theoretical interest, the reaction described here has potential synthetic utility in the formation of complex and highly functionalized ring systems. The aryne formed has a sufficient lifetime to react intermolecularly and thus can potentially undergo a wide variety of addition and cycloaddition reactions, allowing other functional groups or rings to be added. The unreacted fourth alkyne may also be susceptible to facile addition reactions because of its significant ring strain. We are currently exploring these reactions.

In summary, we have demonstrated an unambiguous example of a rare 4 + 2 cycloaddition of a diyne with an alkyne to form a 1,2-aryne. This is the first example of a templated 4 + 2 alkyne–diyne cycloaddition between two separate substrates. We have also shown that, through careful choice of metal template size, we can control the nature of the cycloaddition reaction occurring between diyne substrates in metal templated reactions by controlling the relative geometries of the two reactive substrates.

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Supporting Information Available: Text, a table, and CIF files giving full experimental procedures, spectroscopic characterization data, and X-ray crystallographic data for **2–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.