Communication

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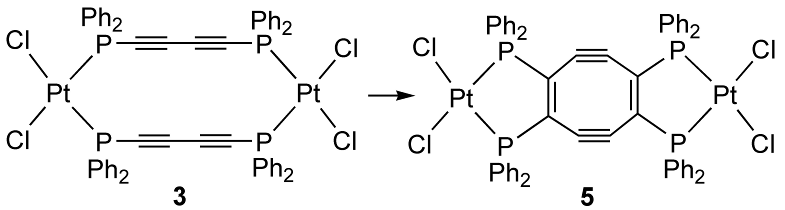

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Metal-Templated Diyne Cyclodimerization and Cyclotrimerization

Maria Paz Martin-Redondo,[†] Ludmila Scoles,[†] Brian T. Sterenberg,[†,§] Konstantin A. Udachin,[†] and
Arthur J. Carty*[,†,‡]

*Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, Canada K1A 0R6, Ottawa-Carleton Chemistry Research Institute, Department of Chemistry,
University of Ottawa, Ottawa, Ontario, Canada K1N 6N5, and the Department of Chemistry and Biochemistry,
University of Regina, 3737 Wascana Parkway, Regina, Saskatchewan, Canada S4S 0A2*

Received January 10, 2005; E-mail: acarty@pco-bcp.gc.ca

Inter- and intramolecular cycloaddition reactions of alkenes and alkynes constitute a powerful strategy for the synthesis of ring systems and often provide one-step syntheses of complex molecules with high atom efficiency.[1−3] Many of these reactions are catalyzed by transition-metal complexes.[2,3] Catalysis serves to overcome large kinetic barriers, resulting in milder reaction conditions, and to preorganize substrates, improving selectivity.[3] An alternative approach is a templated reaction, where reactive substrates are held together by a template molecule via interactions, such as metal coordination or hydrogen bonding, remote from the reactive site.[4] We have demonstrated the use of platinum coordination to template intramolecular coupling reactions of phosphino−alkynes.[5] In these reactions, metal coordination of the phosphine functionality holds the alkynes in close proximity, allowing facile coupling to form substituted naphthalenes. In this communication, we describe novel cycloaddition reactions of the phosphine-substituted diyne bis(diphenylphosphino)butadiyne, which are templated by coordination of the diyne to platinum via phosphorus.

Reaction of [Pt(CH$_3$)$_2$(COD)] with bis(diphenylphosphino)butadiyne, (Ph$_2$PC$_4$PPh$_2$), led to a mixture of the bridged dimer [{Pt(CH$_3$)$_2$}$_2$(μ-Ph$_2$PC$_4$PPh$_2$)$_2$] (**1**) and the trimer [{Pt(CH$_3$)$_2$}$_3$(μ-Ph$_2$PC$_4$PPh$_2$)$_3$] (**2**) in an 85:15 ratio (Scheme 1). The ratio is insensitive to concentration and temperature. Separation of the two compounds was achieved using thin-layer chromatography on cellulose, and both compounds have been characterized by X-ray crystallography (Figure 1).

Compound **1** consists of two cis square planar platinum centers bridged by two bisphosphino diyne units. The two square planes are close to perpendicular (86.09(8)°) as a result of a twist in the overall geometry of the complex, which is necessary to accommodate the square planar geometry at platinum and the tetrahedral geometry at phosphorus. This geometry results in a close approach of the alkyne units on adjacent phosphines, with center-to-center distances of 3.34 and 3.27 Å. The carbon−carbon distances within the alkyne chain clearly indicate localized bonding, with alternating long and short distances. Compound **2** consists of three cis square planar platinum centers bridged by three bisphosphino diyne ligands, forming a triangular complex. Each platinum square plane is almost perpendicular (73.4(3), 73.3(4), and 74.4(3)°) to the overall plane of the molecule in order to accommodate the 90° angles at platinum and the tetrahedral angles at phosphorus, resulting in a helical structure in which the phosphorus atoms alternate between positions above and below the plane formed by the three platinum atoms. The bonding within the alkyne chain is again clearly localized. Nearest alkyne center-to-center distances are 3.40, 3.42, and 3.33 Å.

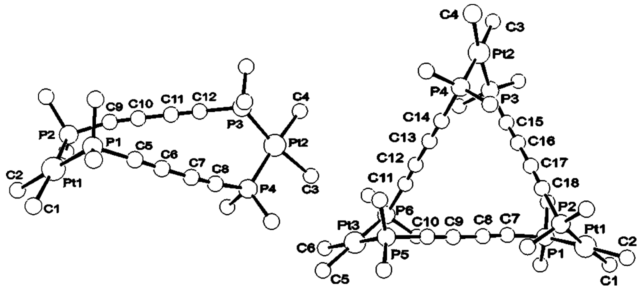
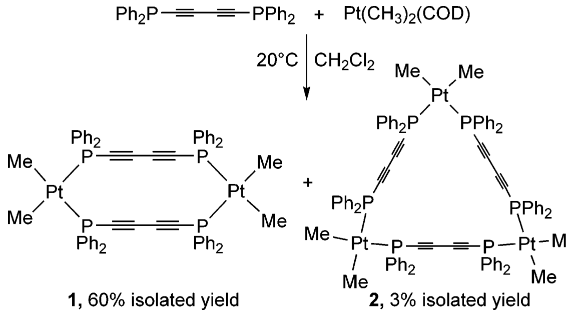


Figure 1. Molecular structure diagrams for **1** and **2**. For clarity, only the ipso carbons of the phenyl groups are shown. Selected distances (Å) and angles (deg) for **1**: P(2)−C(9) 1.776(5), C(9)−C(10) 1.198(6), C(10)−C(11) 1.376(7), C(11)−C(12) 1.203(6), P(3)−C(12) 1.776(5), P(1)−Pt(1)−P(2) 94.74(4), C(9)−P(2)−Pt(1) 117.41(16). For **2**: P(1)−C(7) 1.79(2), C(7)−C(8) 1.18(3), C(8)−C(9) 1.39(3), C(9)−C(10) 1.20(3), P(5)−C(10) 1.76(2), P(1)−Pt(1)−P(2) 94.7(2), C(7)−P(1)−Pt(1) 117.6(7).

Scheme 1



The ^{31}P NMR spectrum of **1** shows a singlet with platinum satellites at δ 5.54 (^1J(PtP) = 1799 Hz). The methyl groups appear as a doublet of doublets at δ 0.40 with *cis*- and *trans*-phosphorus couplings of 6.5 and 9.2 Hz and a PtH coupling of 72 Hz. Spectroscopic data for **2** are similar to those of **1**.

The synthesis of the analogous PtCl$_2$ complexes was also attempted. Reaction of [PtCl$_2$(COD)] with the diyne Ph$_2$PC$_4$PPh$_2$ led to the formation of compounds analogous to the methyl dimer and trimer, [{PtCl$_2$}$_2$(μ-Ph$_2$PC$_4$PPh$_2$)$_2$] (**3**) and [{PtCl$_2$}$_3$(μ-Ph$_2$PC$_4$-PPh$_2$)$_3$] (**4**) in a similar 85:15 ratio. However, in contrast to the thermally stable methyl complexes, the chloro complexes are unstable and spontaneously transform at room temperature into the 8- and 12-membered rings, [{PtCl$_2$}$_2${μ-C$_8$(PPh$_2$)$_4$}] (**5**) and [{PtCl$_2$}$_3${μ_3-C$_{12}$(PPh$_2$)$_6$}] (**6**), formally via [4 + 4] and [4 + 4 + 4] cycloadditions (Scheme 2). The transformations also occur in the solid state and in the dark. Mixtures of **5** and **6** were isolated in 70% yield. Pure samples of **5** can be made by reaction of **1** with HCl in 94% isolated yield, suggesting that the cycloaddition reactions are unimolecular and quantitative. Compounds **3** and **4**

[†] National Research Council of Canada.
[‡] University of Ottawa.
[§] University of Regina.

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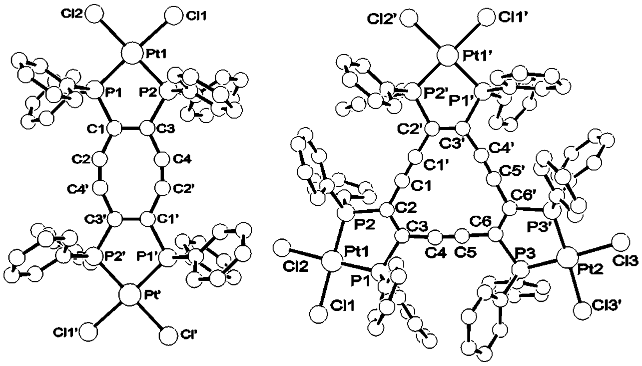
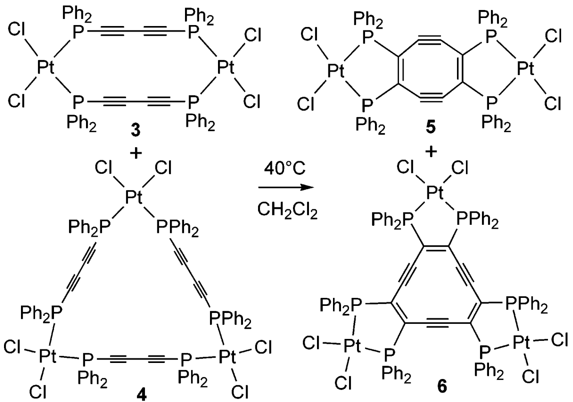


Figure 2. Molecular structure diagrams of **5** and **6**. Selected distances (Å) and angles (deg) for **5**: C(1)−C(2) 1.436(9), C(1)−C(3) 1.377(9), C(2)−C(4′) 1.200(9), C(3)−C(4) 1.455(9), C(3)−C(1)−C(2) 115.7(5), C(4′)−C(2)−C(1) 153.4(6), C(1)−C(3)−C(4) 114.9(6), C(2′)−C(4)−C(3) 155.9(7). For **6**: C(1)−C(1′) 1.15(2), C(2)−C(1) 1.43(1), C(3)−C(2) 1.36(2), C(3)−C(4) 1.43(2), C(4)−C(5) 1.16(2), C(5)−C(6) 1.45(2), C(6)−C(6′) 1.31(2), C(2)−C(3)−C(4) 123.2(10), C(3)−C(2)−C(1) 120.7(10), C(1′)−C(1)−C(2) 177.9(17), C(5)−C(4)−C(3) 175.3(13), C(4)−C(5)−C(6) 179.4(15), C(6′)−C(6)−C(5) 121.3(7).

Scheme 2



70% isolated yield of mixture

can be observed by ^{31}P NMR at low temperature; however, limited solubility prevents a detailed study of their transformation to **5** and **6**. Separation of **3** and **4** was impossible because of their instability. Attempts to isolate crystals of **3** at low temperature led only to crystals of **5**. Compound **4** appears to be slightly more stable, and a structure determination has been carried out. The structure of **4** is analogous to that of the methyl complex **2**.

The molecular structures of **5** and **6** are shown in Figure 2. Compound **5** consists of a cycloocta-1,5-diene-3,7-diyne ring with diphenylphosphino substituents on each alkene carbon. The two phosphino groups on each alkene chelate $PtCl_2$ units. The 8-membered ring is essentially planar, consistent with computational predictions,[6] and the two square planar platinum units deviate only slightly from this plane. The distances indicate strictly localized multiple bonding with no aromaticity. Cyclooctadiene−diynes have not previously been isolated,[7] although the related compounds, *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne[8] and 5,6,9,10-tetradehydrobenzocyclooctene,[9] are known. A previous example of metal-mediated coupling of two tetraynes to form a [12]dehydroanulene ring containing four carbon−carbon triple bonds has been described.[10]

Compound **6** consists of a 12-membered ring of carbon atoms containing three alternating double and three triple bonds. The carbon−carbon distances clearly indicate localized bonding, and the ring is planar. Each alkene unit has two diphenylphosphino substituents. Each phosphine pair is coordinated to a square planar platinum center. Compound **6** is analogous to several known rings, including the parent molecule cyclododeca-2,6,10-triene-1,5,9-triyne,[11] tribenzocyclyne,[12] and other substituted rings.[13]

The facile diyne coupling reaction in the chloro complexes led us to study the related reactions of the methyl complexes. The methyl dimer **1** is thermodynamically very stable and shows no change when heated to moderate temperatures. Coupling of the trimer **2** occurs more readily, and heating of a sample to 80 °C in the presence of CuCl resulted in the formation of $[\{PtMe_2\}_3\{C_{12}(PPh_2)_6\}]$ (**7**). Compound **7** has been structurally characterized and is analogous to **6**.

A comparison of the two trimer structures **2** and **4** reveals that the alkyne−alkyne distance in the chloro trimer **4** is 3.24 Å, compared with an average distance of 3.38 Å in the methyl trimer **2**. The smaller alkyne center-to-center distance in the chloro complex suggests that the reactivity difference may result from a steric effect of the platinum substituents, likely resulting from the longer Pt−Cl bond (Pt−C = 2.09 Å average in **2**; Pt−Cl = 2.327(4) Å in **4**) since the steric size of the two moieties are very similar. The steric effects of the Pt substituents are transferred to the alkyne chain via interactions of the phenyl groups on phosphorus. Favorable positioning of the phenyl groups with respect to the platinum substituents results in rotation about the Pt−P bond, moving the diyne chains closer together or further apart, depending on the substituents. We are carrying out further studies on the effects of different metal and ligand substituents on the cyclization reactions.

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Supporting Information Available: Complete experimental data for all compounds, and details of structure determinations compounds **1**, **2**, **5**, **6**, and **7** (cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

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