

# Mono- or Diplatinum Complexes Containing a $\pi$ -Conjugated Pentadiynyl Ligand

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The reaction of pentadiynyl halides  $XCH_2C\equiv CC\equiv CPh$  (**1**) with equimolar amounts of  $Pt(C_2H_4)(PPh_3)_2$  in  $C_6D_6$  produced *cis*-( $PPh_3$ )<sub>2</sub> $PtX(\eta^1-CH_2C\equiv CC\equiv CPh)$  (*cis*-**2**) as a kinetic product. Complex *cis*-**2** isomerized to *trans*-( $PPh_3$ )<sub>2</sub> $PtX(\eta^1-CH_2C\equiv CC\equiv CPh)$  (*trans*-**2**) or *trans*-( $PPh_3$ )<sub>2</sub> $PtX[\eta^1-C(C\equiv CPh)=C=CH_2]$  (*trans*-**3**) under some reaction conditions. In contrast to the reaction of  $Pt(C_2H_4)(PPh_3)_2$ , treatment of **1** with  $Pt(PPh_3)_4$  generated cationic platinumacyclobutene [( $PPh_3$ )<sub>2</sub>- $Pt\{\eta^2-CH_2C(PPh_3)=C(C\equiv CPh)\}]^+Cl^-$  (**5**) together with *cis*-**2** and *trans*-**2**. Moreover, 2 equiv. of  $Pt(C_2H_4)(PPh_3)_2$  and **1** provided  $\eta^1, \eta^2$ -coordinated diplatinum complex *cis*-( $PPh_3$ )<sub>2</sub>-

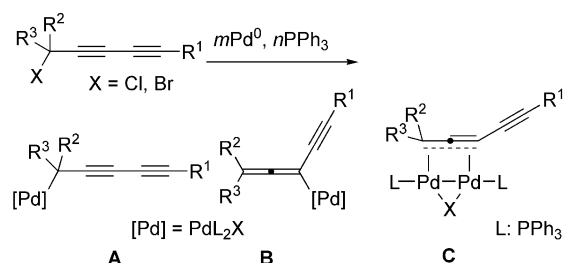
$PtCl[\eta^1-CH_2C\equiv C\{(PPh_3)_2Pt(\eta^2-C\equiv CPh)\}]$  (**7**) and/or metallacyclobutene diplatinum complex ( $PPh_3$ )<sub>2</sub> $Pt[\eta^2-CH_2C\{(PPh_3)_2PtCl\}=C(C\equiv CPh)]$  (**8**). The coordination modes of these complexes depend on the ratio of pentadiynyl halide, Pt, and  $PPh_3$ , as well as temperature and the nature of the solvents. Protonolysis of metallacyclobutene complexes **5** and **8** with HCl gave [*cis*-( $PPh_3$ )<sub>2</sub> $PtCl[\eta^1-C(C\equiv CPh)=C(PPh_3)CH_3]]^+Cl^-$  (**9**) and [( $PPh_3$ )<sub>2</sub> $Pt\{\eta^3-CH_2\{cis-(PPh_3)_2PtCl\}CCH(C\equiv CPh)\}]^+Cl^-$  (**10**). Single-crystal X-ray diffraction analysis of **12** showed  $\eta^3$ - and  $\eta^1$ -coordination structure.

## Introduction

Currently, there is increasing interest in highly  $\pi$ -conjugated carbon-rich compounds, such as polyyne, polyene-polyyne, and cumulene, because of their potentially wide applications in synthetic chemistry and materials science.<sup>[1]</sup> Although the elucidation of transition-metal complexes bearing expanded  $\pi$ -conjugated hydrocarbons promises new insights, little is understood about such complexes compared to metal complexes bearing a propargyl/allenyl unit as the shortest polyyne/cumulene.<sup>[2]</sup>

We have reported the synthesis of mono- and dinuclear palladium complexes containing a pentadiynyl unit.<sup>[3]</sup> The reaction of pentadiynyl halide with a (triphenylphosphanyl)palladium(0) complex produces monopalladium complexes  $\eta^1$ -pentadiynylpalladium **A**,  $\eta^1$ -(penta-1,2-dien-4-yn-3-yl)palladium **B**, and dinuclear complex **C**, revealing the unique  $\mu$ - $\eta^3$ -coordination of the Pd–Pd unit to three carbon atoms (Scheme 1). These complexes can be yielded selectively by treating pentadiynyl halide with  $Pd^0$  and  $PPh_3$  in a suitable ratio. Palladium and/or platinum complexes containing a propargyl/allenyl unit with similar coordination

modes **A'–C'** are generated from the reaction of propargyl halides with palladium(0)- or platinum(0)-triphenylphosphane complexes (Figure 1).<sup>[4–6]</sup> In some cases, the oxidative addition of  $Pd^0(PPh_3)_n$  or  $Pt^0(PPh_3)_2$  to the corresponding propargyl or allenyl halides gives cationic or neutral  $\eta^3$ -propargyl/allenyl palladium and/or platinum complexes **D'** and **E'**.<sup>[7,8]</sup> Although various propargyl/allenyl palladium and platinum complexes have been widely investigated, metal complexes containing pentadiynyl ligand have been limited to Mo and Fe complexes bearing  $\eta^1$ -pentadiynyl ligand (type **A**), with the exception of Pd complexes.<sup>[9]</sup> In an extension of these studies, we disclose here the synthesis of mono- or diplatinum complexes from simple reactions of pentadiynyl halide with  $Pt^0$  and  $PPh_3$ , and we discuss the coordination structures of the obtained platinum complexes and their stability under various reaction conditions.



Scheme 1. Reaction of pentadiynyl halides with  $Pd^0$  and  $PPh_3$ .

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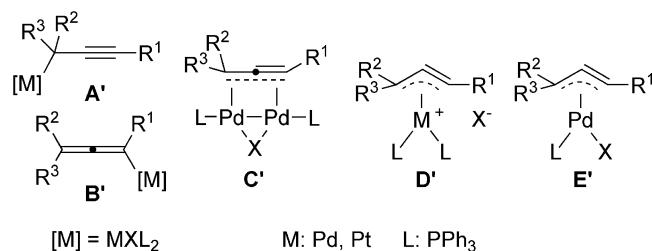
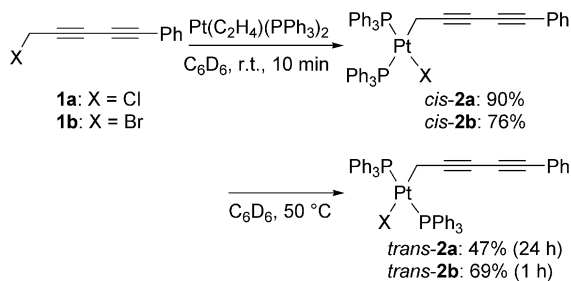


Figure 1. Structure of the propargyl/allenyl palladium and/or platinum complexes.

## Results and Discussion

### Reaction of Pentadiynyl Halides **1** with Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>

In the reaction of pentadiynyl halide **1a** or **1b** (X = Cl, Br) with equimolar amounts of Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at room temperature, *cis*-(PPh<sub>3</sub>)<sub>2</sub>PtX(η<sup>1</sup>-CH<sub>2</sub>C≡CC≡CPh) (*cis*-**2a** or *cis*-**2b**) was obtained as a sole product (Scheme 2). Each complex shows a <sup>1</sup>H NMR resonance of the methylene protons at δ = 2.64 ppm or δ = 2.79 ppm as a doublet of doublets on the basis of two phosphanes (*J*<sub>HP</sub> = 9.2, 6.1 Hz or *J*<sub>HP</sub> = 9.2, 6.7 Hz) with <sup>195</sup>Pt satellites (*J*<sub>HPt</sub> = 73.3 Hz or *J*<sub>HPt</sub> = 77.6 Hz), which indicates the η<sup>1</sup>-pentadiynyl structure with a *cis* arrangement of phosphane ligands on the Pt atom. In the <sup>31</sup>P NMR spectra, two doublet signals of these complexes also support the *cis* structure [*cis*-**2a**: δ = 18.2 (d, *J*<sub>PP</sub> = 16.7 Hz), 21.2 (d, *J*<sub>PP</sub> = 16.7 Hz) ppm; *cis*-**2b**: δ = 18.4 (d, *J*<sub>PP</sub> = 16.8 Hz), 19.1 (d, *J*<sub>PP</sub> = 16.8 Hz) ppm]. Elemental analyses of these complexes showed the expected composition.

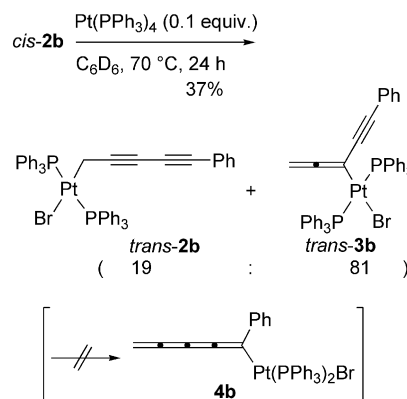


Scheme 2. Reaction of XCH<sub>2</sub>C≡CC≡CPh (**1**) with Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>.

Heating of *cis*-**2a** or *cis*-**2b** to 50 °C in C<sub>6</sub>D<sub>6</sub> produced *trans*-(PPh<sub>3</sub>)<sub>2</sub>PtX(η<sup>1</sup>-CH<sub>2</sub>C≡CC≡CPh) (*trans*-**2a** or *trans*-**2b**). In the <sup>1</sup>H NMR spectrum, a signal attributed to the methylene protons appears at δ = 1.64 ppm or δ = 1.72 ppm as a triplet. Other platinum complexes with metal shifted on a pentadiynyl ligand, such as, (PPh<sub>3</sub>)<sub>2</sub>PtX[η<sup>1</sup>-C(C≡CPh)=C=CH<sub>2</sub>], were not generated by prolonged heating. It turns out that *cis*-**2a** and *cis*-**2b** are kinetically preferred over *trans*-**2a** and *trans*-**2b**, which are similarly preferred in the case of propargylplatinum complexes.<sup>[6,10]</sup>

Although chloride complex *cis*-**2a** required 24 h for *cis*–*trans* isomerization, bromide analogue *cis*-**2b** isomerized to *trans*-**2b** within 1 h. The order of the reaction rates (Br > Cl) is similar to that of the mutual isomerization of η<sup>1</sup>-

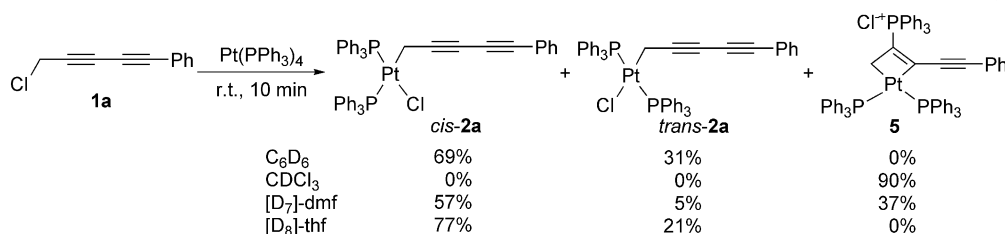
propargyl- and η<sup>1</sup>-allenylplatinum complexes.<sup>[11,12]</sup> In addition, Kurosawa and Ogoshi reported that Pt(PPh<sub>3</sub>)<sub>4</sub> accelerates the propargyl–allenyl isomerization reaction through an intermolecular redox transmetalation process; thus, a similar reaction was tested for complex *cis*-**2b**.<sup>[12]</sup> When *cis*-**2b** was heated in the presence of 0.1 equiv. of Pt(PPh<sub>3</sub>)<sub>4</sub> at 70 °C, *trans*-(PPh<sub>3</sub>)<sub>2</sub>PtBr[η<sup>1</sup>-C(C≡CPh)=C=CH<sub>2</sub>] (*trans*-**3b**) was formed along with *trans*-**2b** (Scheme 3). The <sup>1</sup>H NMR spectrum of *trans*-**3b** shows a triplet signal for the methylene protons at low field (δ = 3.28 ppm) with a smaller coupling constant (*J*<sub>HP</sub> = 4.0 Hz) compared to those of complexes **2**. Further isomerization to (PPh<sub>3</sub>)<sub>2</sub>PtBr[η<sup>1</sup>-C(Ph)=C=C=C=CH<sub>2</sub>] (**4b**) was not observed even under the reaction conditions. It is possible that the steric repulsion between the Ph group bonding to the terminal acetylene and PPh<sub>3</sub> prevent isomerization to **4b**. This behavior is similar to that of the corresponding palladium analogues.<sup>[3]</sup>



Scheme 3. Isomerization reaction of *cis*-**2b**.

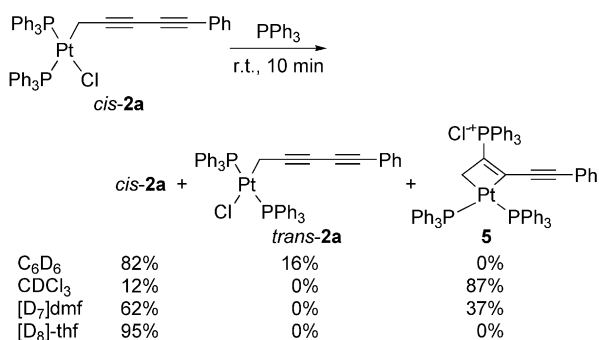
### Reaction of Pentadiynyl Halide **1a** with Pt(PPh<sub>3</sub>)<sub>4</sub>

The reaction of **1a** with Pt(PPh<sub>3</sub>)<sub>4</sub> in C<sub>6</sub>D<sub>6</sub> gave a mixture of *cis*-**2a** and *trans*-**2a** (Scheme 4). Excess amounts of PPh<sub>3</sub> may accelerate the *cis*–*trans* isomerization of the geometry around platinum. Interestingly, a similar reaction was conducted in CDCl<sub>3</sub> to give the phosphane adduct platina-cyclobutene complex [(PPh<sub>3</sub>)<sub>2</sub>Pt{η<sup>2</sup>-CH<sub>2</sub>C(PPh<sub>3</sub>)=C(C≡CPh)}]<sup>+</sup>Cl<sup>−</sup> (**5**) in 90% yield. In the <sup>1</sup>H NMR spectra, the resonance of methylene protons was found upfield (δ = −0.05 ppm) with a <sup>195</sup>Pt satellite (*J*<sub>HPt</sub> = 83.7 Hz). The <sup>31</sup>P NMR spectroscopic data, δ = 4.1 (dd, *J*<sub>PP</sub> = 26.9, 26.1 Hz), 21.0 (dd, *J*<sub>PP</sub> = 26.1, 9.3 Hz), and 22.3 (dd, *J*<sub>PP</sub> = 26.9, 9.3 Hz) ppm, indicate that three phosphane ligands exist in one *cis* and two *anti* arrangements as shown in Scheme 4. The phosphorus attached to carbon indicates smaller values for the <sup>195</sup>Pt satellite (*J*<sub>PPt</sub> = 606.6 Hz) compared to the phosphorus ligands attached to platinum (*J*<sub>PPt</sub> = 2521.3, 2169.6 Hz). These spectral features are almost similar to those of the other metallacyclobutene analogues.<sup>[13]</sup> In [D<sub>7</sub>]-dmf, **5** was generated together with *cis*-**2a** and *trans*-**2a**. However, **5** was not observed in [D<sub>8</sub>]thf, similarly to the reaction in C<sub>6</sub>D<sub>6</sub>. This is strong evidence of a crucial sol-

Scheme 4. Reaction of ClCH<sub>2</sub>C≡CC≡CPh (**1a**) with Pt(PPh<sub>3</sub>).

vent effect on the products. There are no reports of the corresponding platinacyclobutene analogues generated from a similar reaction of propargyl halides with Pt(PPh<sub>3</sub>)<sub>4</sub>.

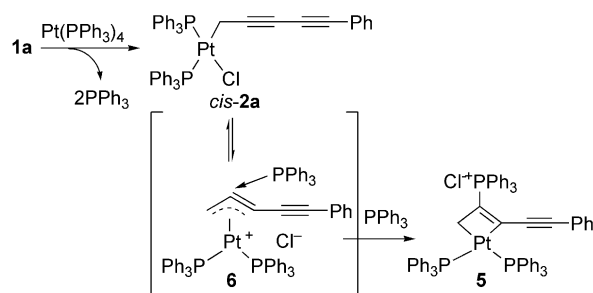
Treatment of **1a** with an equimolar amount of Pt<sup>0</sup> and 2 equiv. of PPh<sub>3</sub> from Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> generated *cis*-**2a** as a kinetic product. Thus, we examined the reaction of *cis*-**2a** with an equimolar amount of PPh<sub>3</sub> in various solvents (Scheme 5). Both <sup>1</sup>H and <sup>31</sup>P NMR analyses showed platinacyclobutene **5** in CDCl<sub>3</sub> and [D<sub>7</sub>]-dmf and not in C<sub>6</sub>D<sub>6</sub> and [D<sub>8</sub>]-thf. In particular, **5** was feasibly produced in CDCl<sub>3</sub> similarly to the reaction of **1a** with Pt(PPh<sub>3</sub>)<sub>4</sub>, as shown in Scheme 4, possible due to the stability of metallacyclobutene complexes in the solvents. Complex *trans*-**2a** was observed only in C<sub>6</sub>D<sub>6</sub> within 10 min, and thus the *cis*–*trans* isomerization may proceed more rapidly in C<sub>6</sub>D<sub>6</sub> than in other solvents, which is also supported by the results shown in Scheme 4. NMR spectroscopic monitoring of the reaction of *cis*-**2a** with PPh<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> at room temperature showed that *trans*-**2a** increased to 82% and *cis*-**2a** decreased to 10% after 1.5 h. In [D<sub>8</sub>]-thf, the *cis*–*trans* isomerization proceeded smoothly to give *cis*-**2a** and *trans*-**2a** in 38 and 59% yield, respectively, after 4 h. On the other hand, *trans*-**2a** was not observed in CDCl<sub>3</sub> or [D<sub>7</sub>]-dmf even after 2 h.

Scheme 5. Reaction of *cis*-**2a** with PPh<sub>3</sub>.

When a similar reaction was carried out in the presence of NaOTf (OTf=OSO<sub>3</sub>CF<sub>3</sub>), the platinacyclobutene complex [(PPh<sub>3</sub>)<sub>2</sub>Pt{η<sup>2</sup>-CH<sub>2</sub>C(PPh<sub>3</sub>)=C(C≡CPh)}]<sup>+</sup>OTf<sup>−</sup> (**5**-OTf) was obtained as the sole product in 98% yield. The NMR spectral features are similar to that of **5**, and the composition of **5**-OTf was also elucidated by elemental analysis.

### Mechanistic Aspects of the Transformation of Monoplatinum Complexes

Chen reported that treatment of PPh<sub>3</sub> with a cationic η<sup>3</sup>-allenyl/propargyl platinum complex [(PPh<sub>3</sub>)<sub>2</sub>Pt(η<sup>3</sup>-CH<sub>2</sub>-CCH)]<sup>+</sup> afforded a phosphane adduct platinacyclobutene complex [(PPh<sub>3</sub>)<sub>2</sub>PtBr{η<sup>2</sup>-CH<sub>2</sub>C(PPh<sub>3</sub>)=CH}]<sup>+</sup>.<sup>[13]</sup> Cationic η<sup>3</sup>-allenyl/propargyl platinum complexes easily react with nucleophiles at the central carbon of the η<sup>3</sup>-allenyl/propargyl ligand, which is in contrast to the reactivity of the neutral η<sup>1</sup>-propargyl- or η<sup>1</sup>-allenyl platinum complexes.<sup>[6,7,14]</sup> Therefore, complex **5** is probably formed via the corresponding cationic η<sup>3</sup>-type complex [(PPh<sub>3</sub>)<sub>2</sub>Pt{η<sup>3</sup>-CH<sub>2</sub>CC(C≡CPh)}]<sup>+</sup> (**6**), which could be produced as an equilibrium isomer of **2a** by the spontaneous dissociation of a chloride ion (Scheme 6). Although cationic η<sup>3</sup>-type complex **6** was not observed directly by NMR spectroscopic analysis of *cis*-**2a** in any solvent tested, complex **5** resulted from the addition of PPh<sub>3</sub> in both CDCl<sub>3</sub> and [D<sub>7</sub>]-dmf (Scheme 5). The equilibrium may lie in favor of cationic complex **6** in a polar solvent, similarly to the case of allenyl/propargyl palladium analogues.<sup>[15]</sup> Thus it is reasonable that **5** was not observed in the less-polar solvent C<sub>6</sub>D<sub>6</sub>. However, the fact that **5** was produced in the polar solvent [D<sub>8</sub>]-thf shows that such solvent effects may be related to the relative stability of the products in solution.

Scheme 6. Plausible mechanism for the generation of **5**.

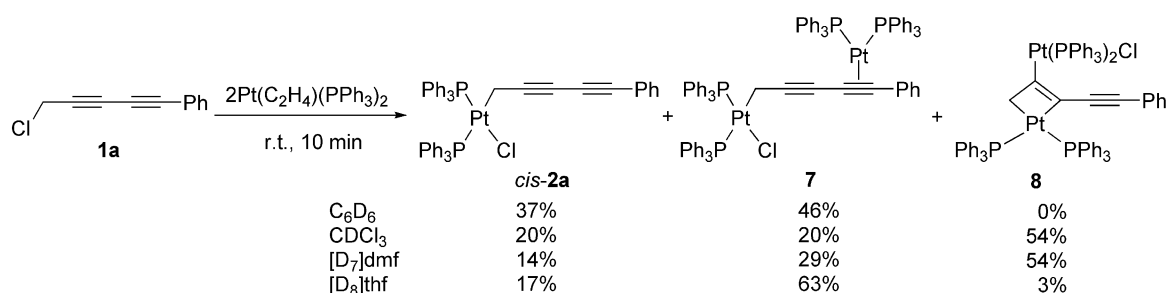
Wojcicki reported that the reactions of η<sup>1</sup>-propargylplatinum complex (PPh<sub>3</sub>)<sub>2</sub>PtBr(η<sup>1</sup>-CH<sub>2</sub>C≡CPh) or cationic η<sup>3</sup>-allenyl/propargylplatinum complex [(PPh<sub>3</sub>)<sub>2</sub>Pt(η<sup>3</sup>-CH<sub>2</sub>-CCH)]<sup>+</sup> with large excess amounts of PMe<sub>3</sub> in thf led to tautomerization product [(PMe<sub>3</sub>)<sub>3</sub>Pt{η<sup>1</sup>-C(Ph)=C=CH<sub>2</sub>}]<sup>+</sup>.<sup>[16]</sup> However, corresponding tris(triphenylphosphane)platinum products such as [(PPh<sub>3</sub>)<sub>3</sub>Pt(η<sup>1</sup>-CH<sub>2</sub>C≡CC≡CPh)]<sup>+</sup>Cl<sup>−</sup> and [(PPh<sub>3</sub>)<sub>3</sub>Pt{η<sup>1</sup>-C(C≡CPh)=C=CH<sub>2</sub>}]<sup>+</sup>

$\text{Cl}^-$  were not observed. The steric repulsion between  $\text{PPh}_3$  on the Pt atom, which is more bulky than  $\text{PMe}_3$ , may destabilize the tris(phosphane)-coordinated platinum complexes, so that the products are also related to the bulkiness of the phosphane ligand.

### Reaction of Pentadiynyl Halides **1a** with Two Equivalents of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$

Reaction of **1a** with 2 equiv. of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  afforded *cis*-**2a** and a new  $\eta^1, \eta^2$ -coordinated diplatinum complex *cis*- $(\text{PPh}_3)_2\text{PtCl}[\eta^1\text{-CH}_2\text{C}\equiv\text{C}\{(\text{PPh}_3)_2\text{Pt}(\eta^2\text{-C}\equiv\text{CPh})\}]$  (**7**) in  $\text{C}_6\text{D}_6$  (Scheme 7). Complex **7** shows a  $^1\text{H}$  NMR signal at  $\delta = 2.84$  ppm as a broad singlet with a  $^{195}\text{Pt}$  satellite ( $J_{\text{HPt}} = 66.5$  Hz), which indicates that the methylene protons of the  $\eta^1$ -pentadiynyl ligand are bonded to the Pt atom. The chemical shift and the  $^{195}\text{Pt}$  satellites are almost identical to those of *cis*-**2a**. The  $^{31}\text{P}$  NMR spectrum of **7** consists of four nonequivalent signals, that is,  $\delta = 18.6$  (d,  $J_{\text{PP}} = 16.7$  Hz), 21.3 (dd,  $J_{\text{PP}} = 16.7, 5.6$  Hz), 26.9 (dd,  $J_{\text{PP}} = 31.6, 5.6$  Hz), and 27.8 (d,  $J_{\text{PP}} = 31.6$  Hz) ppm, which support the *cis* arrangements of four phosphane ligands, as shown in Scheme 7.  $\text{Pt}^0\text{-}\eta^2$ -alkyne complexes are well known,<sup>[17]</sup> and dimetal coordination to alkynes has been reported.<sup>[18]</sup>

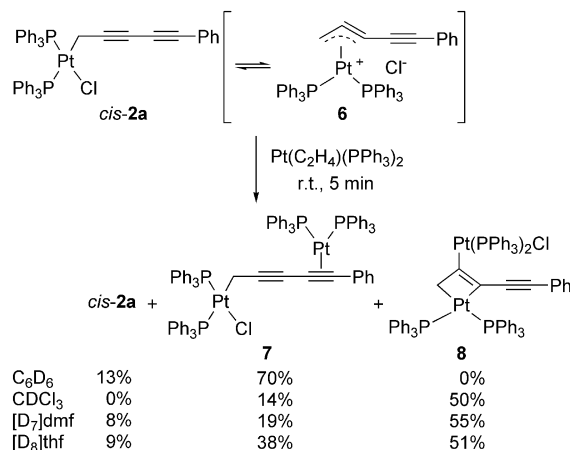
In contrast, a similar reaction was carried out in  $\text{CDCl}_3$  to generate a noble platinum adduct platinacyclobutene complex  $(\text{PPh}_3)_2\text{Pt}[\eta^2\text{-CH}_2\text{C}\{(\text{PPh}_3)_2\text{PtCl}\}\text{C}(\text{C}\equiv\text{CPh})]$  (**8**) together with *cis*-**2a** and **7**. The  $^1\text{H}$  NMR spectra of **8** show a broad singlet signal at  $\delta -0.42$  ppm with  $J_{\text{HPt}} = 82.5$  Hz, which is assigned to the methylene protons of the metallacyclic form, similar to complex **5**. Diplatinum complexes **7** and **8** were observed in both  $[\text{D}_7]\text{dmf}$  and  $[\text{D}_8]\text{thf}$ . The geometry of the  $\sigma$ -bonded  $\text{Pt}(\text{PPh}_3)_2\text{Cl}$  unit, attached to the platinacyclobutene ring, could not be clearly established, because complex **8** is less stable in solution and detectable only in the early stage of the reaction, but the perceived coordination and the composition of **8** are also supported by comparison with protonation product **10** as shown below (Scheme 9). It is interesting to note that complex **8** shows a different structure from the dipalladium complex prepared by treatment of **1a** with 2 equiv. of  $\text{Pd}^0(\text{PPh}_3)$  (Scheme 1, C).<sup>[3]</sup> To the best of our knowledge, this is the first example of metallacyclobutene coordination with another metal.



Scheme 7. Reaction of  $\text{ClCH}_2\text{C}\equiv\text{CC}\equiv\text{CPh}$  (**1a**) with 2 equiv. of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ .

### Mechanistic Aspect of the Coordination of Diplatinum to **1a**

Complex *cis*-**2a** reacted with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  to produce diplatinum complexes **7** and/or **8** in good-to-moderate yield in each solvent (Scheme 8). Hence, in the reaction of excess amounts of  $\text{Pt}^0(\text{PPh}_3)_2$ , *cis*-**2a** is first kinetically generated, after which the second  $\text{Pt}^0(\text{PPh}_3)_2$  may coordinate to *cis*-**2a**. Complex **8** was not observed in the less-polar solvent  $\text{C}_6\text{D}_6$ , which is in contrast to intermediate **7**, similarly to the formation of complex **5**. Dissociation of a  $\text{Cl}^-$  ion together with  $\eta^1\text{-}\eta^3$  rearrangement of the pentadiynyl ligand easily occurs to generate **6**, followed by the addition of the second platinum moiety to produce  $\eta^2\text{-}\eta^1$ -coordinating dimetal complex **8**. Therefore, a dimetal complex such as **8** including **7** should be explored as a new intermediate in metal-catalyzed reactions of polyyne compounds containing propargyl/allenyl compounds.



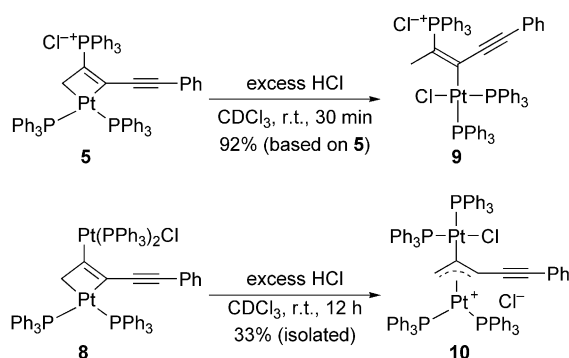
Scheme 8. Reaction of *cis*-**2a** with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ .

### Protonolysis of Platinacyclobutene **5** or **8**

Complex **5** did not react with nucleophiles such as  $\text{MeOH}$  and  $\text{HNet}_2$ . The methylene carbon atom of **5** may have high electron density because the  $^1\text{H}$  NMR signal of the methylene protons appears upfield; hence, the reactivity of electrophiles was examined. Treatment of **1a** with  $\text{Pt}(\text{PPh}_3)_4$  in  $\text{CDCl}_3$  resulted in complex **5** (Scheme 4), after which **5** reacted with the excess amounts of  $\text{HCl}$ , an electro-

phile generated from the reaction of  $\text{H}_2\text{O}$  with  $\text{Me}_3\text{SiCl}$  in situ, thus yielding the cationic platinum complex  $[(\text{PPh}_3)_2\text{-PtCl}\{\eta^1\text{-C}(\text{C}\equiv\text{CPh})=\text{C}(\text{PPh}_3)\text{CH}_3\}]^+\text{Cl}^-$  (**9**; Scheme 9). Complex **9** shows a  $^1\text{H}$  NMR signal at  $\delta = 2.14$  ppm as a broad singlet with a  $^{195}\text{Pt}$  satellite ( $J_{\text{HPt}} = 67.2$  Hz), which is indicated by the methylene protons of the  $\eta^1\text{-C}(\text{C}\equiv\text{CPh})=\text{C}(\text{PPh}_3)\text{CH}_3$  ligand.  $^{31}\text{P}$  NMR spectroscopic data,  $\delta = 19.0$  (d,  $J_{\text{PP}} = 31.6$  Hz),  $20.3$  (d,  $J_{\text{PP}} = 16.7$  Hz), and  $23.0$  (dd,  $J_{\text{PP}} = 31.6, 16.7$  Hz) ppm, indicate that three phosphane ligands exist in one *cis* and one *anti* arrangement. The phosphorus attached to carbon shows smaller values of the  $^{195}\text{Pt}$  satellite ( $J_{\text{PPt}} = 145.1$  Hz) compared to the phosphorus ligands coordinated to platinum ( $J_{\text{PPt}} = 4252.3$  Hz,  $1731.3$  Hz). Other isomers, such as,  $[(\text{PPh}_3)_2\text{-Pt}\{\eta^3\text{-CH}_2\text{C}(\text{PPh}_3)\text{CH}(\text{C}\equiv\text{CPh})\}]^+\text{Cl}^-$ , were not observed in situ.

Similarly, subsequent addition of HCl to diplatinum complex **8**, which was generated in situ by the reaction of **1a** with 2 equiv. of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  in  $\text{CHCl}_3$ , gave new diplatinum complex  $[(\text{PPh}_3)_2\text{Pt}\{\eta^3\text{-CH}_2\text{C}\{cis\text{-}(\text{PPh}_3)_2\text{-PtCl}\}\text{CH}(\text{C}\equiv\text{CPh})\}]^+\text{Cl}^-$  (**10**). The  $^1\text{H}$  NMR spectrum indicates that three different  $\pi$ -allyl protons exist in complex **10** ( $\delta = 2.23, 3.20$ , and  $3.58$  ppm) and that the  $^{31}\text{P}$  NMR spectrum consists of four nonequivalent signals, that is,  $\delta = 17.7$  (d,  $J_{\text{PP}} = 18.6$  Hz,  $J_{\text{PPt}} = 4182.8, 48.3$  Hz),  $16.4$  (d,  $J_{\text{PP}} = 11.2$  Hz,  $J_{\text{PPt}} = 4004.6$  Hz),  $15.2$  (d,  $J_{\text{PP}} = 11.2$  Hz,  $J_{\text{PPt}} = 3995.2$  Hz),  $14.6$  (d,  $J_{\text{PP}} = 18.6$  Hz,  $J_{\text{PPt}} = 1787.8, 39.0$  Hz) ppm, in accordance with a  $\eta^3, \eta^1$ -allyl diplatinum structure, as shown in Scheme 9. Although **5** and **8** have similar platinacyclobutene frameworks, the regioselectivity of their protonation was different. The reason for the difference in regioselectivity is not clear.



Scheme 9. Reaction of **5** or **8** with HCl.

Single crystals of complex **10** were grown by slow diffusion of hexane into dichloromethane solution, and the structure was confirmed by X-ray crystallography (Figure 2). Platinum atoms coordinate as  $\eta^1$  and  $\eta^3$  modes. The bond lengths of C1–C2 and C2–C3 are between those of single and double bonds, and hence, the three-carbon moiety reveals a  $\pi$ -allyl structure derived from diplatinum coordination.  $(\text{PPh}_3)_2\text{PtCl}$  and  $\text{PhC}\equiv\text{C}$  moieties attached to the allyl group show *syn* geometry.  $^1\text{H}$  NMR analysis of the obtained crystals shows spectra similar to those of **10** generated from the reaction of **8** with HCl in situ. In addition,

variable-temperature (VT) NMR experiments indicate that no equilibration of *syn* and *anti* configurations of the allyl moiety or *cis* and *trans* environments of phosphorus occur on the NMR timescale up to  $50^\circ\text{C}$  in  $\text{CDCl}_3$ . Several  $\eta^1, \eta^3$ -coordinated dimetal complexes have been reported.<sup>[19]</sup>

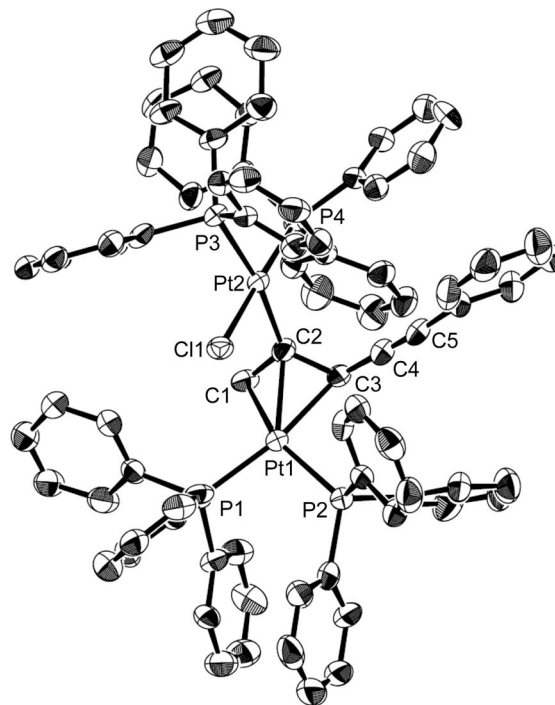


Figure 2. The molecular structure of the  $(\text{PPh}_3)_2\text{Pt}\{\eta^3\text{-CH}_2\text{C}\{cis\text{-}(\text{PPh}_3)_2\text{PtCl}\}\text{CH}(syn\text{-C}\equiv\text{CPh})\}^+$  cation (**10**) is drawn with thermal ellipsoids at the 50% probability level. All hydrogen atoms and a counteranion are omitted for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: C1–C2 1.396(13), C2–C3 1.439(16), C3–C4 1.449(14), C4–C5 1.179(15), C1–Pt1 2.172(11), C2–Pt1 2.227(12), C3–Pt1 2.186(9), C2–Pt2 2.083(13), Pt1–P1 2.265(2), Pt1–P2 2.302(3), Pt2–P3 2.355(3), Pt2–Pt4 2.248(2), Pt2–C11 2.356(2); C1–C2–C3  $115.4(11)$ , Pt1–C2–Pt2  $122.5(4)$ .

## Conclusions

The reactions of pentadiynyl halides  $\text{XCH}_2\text{C}\equiv\text{CC}\equiv\text{CPh}$  (**1**) with  $m\text{Pt}^0$  and  $n\text{PPh}_3$  afforded various mono- or diplatinum complexes  $(\text{PPh}_3)_n\text{Pt}_m\text{X}(\text{CH}_2\text{CCCCPh})$  (**2**, **3**, **5**, **7**, **8**). The coordination mode of pentadiynyl species on platinum crucially depended on the following factors: (i) the ratio of pentadiynyl halide, phosphane ligand, and  $\text{Pt}^0$ ; (ii) the solvent; and (iii) the temperature.  $\eta^1$ -Pentadiynylplatinum complex **2** was selectively generated in the reactions of **1** with an equimolar amount of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  or  $\text{Pt}(\text{PPh}_3)_4$  in  $\text{C}_6\text{D}_6$ . Complex **2** isomerized into  $\eta^1$ -(penta-1,2-dien-4-yn-3-yl)platinum **3** in the presence of catalytic amounts of  $\text{Pt}(\text{PPh}_3)_4$  under heating. Platinacyclobutene **5** was easily generated by treatment of  $\text{Pt}(\text{PPh}_3)_4$  with **1a** in  $\text{CDCl}_3$  or  $[\text{D}_7]\text{dmf}$ . We also found that excess amounts of  $\text{Pt}(\text{PPh}_3)_2$  resulted in the  $\eta^2, \eta^1$ -coordinating diplatinum complex **8**. Furthermore, complex **8** has a novel dinuclear structure, which was easily generated by the reaction of **1a**

with excess amounts of  $\text{Pt}(\text{PPh}_3)_2$  in  $\text{CDCl}_3$ ,  $[\text{D}_7]\text{dmf}$ , or  $[\text{D}_8]\text{thf}$ . Therefore, these complexes may be intermediates in the catalytic reactions of polyynyl, especially propargyl/allenyl, compounds. Metallacyclobutene complexes **5** and **8** reacted with HCl to give novel mono- or diplatinum complexes **9** and **10**, respectively.

## Experimental Section

**Materials and Measurements:** Mostly commercially available reagents were used without further purification. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry nitrogen by using standard vacuum line techniques.  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$  NMR were recorded with a JEOL JNM-ECP500 or a JNM-ECP600NK spectrometer. Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br. s = broad singlet, m = multiplet), coupling constant [Hz], and integration. The H and C contents were determined by elemental analysis by using a Perkin–Elmer 2900II CHNS/O analyzer. Melting points were determined with a Yanaco MP-500D micro melting point apparatus.

**Reaction of  $\text{ClCH}_2\text{C}\equiv\text{CC}\equiv\text{CPh}$  (**1a**) with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ :** To a solution of  $\text{ClCH}_2\text{C}\equiv\text{CC}\equiv\text{CPh}$  (**1a**; 1.6 mg, 0.0092 mmol) and an appropriate amount of trioxane as an internal standard dissolved in dry  $\text{C}_6\text{D}_6$  (0.6 mL) in an NMR tube under an atmosphere of dry nitrogen was added  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  (6.9 mg, 0.0092 mmol). The NMR tube was sealed under a nitrogen atmosphere, and the reaction was followed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. *cis*-( $\text{PPh}_3$ )<sub>2</sub>- $\text{PtCl}(\eta^1\text{-CH}_2\text{C}\equiv\text{CC}\equiv\text{CPh})$  (*cis*-**2a**) was obtained after 10 min (90%). Then the NMR tube was heated at 50 °C in an oil bath. *trans*-( $\text{PPh}_3$ )<sub>2</sub>- $\text{PtCl}(\eta^1\text{-CH}_2\text{C}\equiv\text{CC}\equiv\text{CPh})$  (*trans*-**2a**) was produced in 47% yield after 24 h. Data for *trans*-**2a**:  $^1\text{H}$  NMR (500.16 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.64 (t,  $J_{\text{HPt}}$  = 7.6 Hz,  $J_{\text{HPt}}$  = 103.3 Hz, 2 H,  $\text{CH}_2$ ), 6.89–7.11 (m, 21 H, Ph), 7.36–7.38 (m, 2 H, Ph), 8.01–8.06 (m, 12 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 25.4 (s,  $J_{\text{PPt}}$  = 3100.0 Hz,  $\text{PPh}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 14.3 ( $\text{CH}_2$ ), 66.3 (C), 75.1 (C), 77.9 (C), 91.7 (C), 124.1 (Ph), 128.3–128.6 (m, Ph), 130.5 (Ph), 130.6 (d,  $J_{\text{CP}}$  = 54.7 Hz, Ph), 132.5 (Ph), 135.5–135.6 (m, Ph) ppm.

**Reaction of  $\text{BrCH}_2\text{C}\equiv\text{CC}\equiv\text{CPh}$  (**1b**) with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ :** The reaction of  $\text{BrCH}_2\text{C}\equiv\text{CC}\equiv\text{CPh}$  (**1b**) was carried out similarly to that of **1a**. *cis*-( $\text{PPh}_3$ )<sub>2</sub>- $\text{PtBr}(\eta^1\text{-CH}_2\text{C}\equiv\text{CC}\equiv\text{CPh})$  (*cis*-**2b**) was obtained after 10 min (76%). *trans*-( $\text{PPh}_3$ )<sub>2</sub>- $\text{PtBr}(\eta^1\text{-CH}_2\text{C}\equiv\text{CC}\equiv\text{CPh})$  (*trans*-**2b**) was produced in 69% yield after heating for 1 h. Data for *trans*-**2b**:  $^1\text{H}$  NMR (500.16 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.72 (t,  $J_{\text{HPt}}$  = 7.6 Hz,  $J_{\text{HPt}}$  = 101.4 Hz, 2 H), 6.91–7.12 (m, 21 H), 7.38–7.41 (m, 2 H), 8.00–8.05 (m, 12 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 25.1 (s,  $J_{\text{PPt}}$  = 3067.1 Hz,  $\text{PPh}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 14.3 ( $\text{CH}_2$ ), 66.9 (C), 75.5 (C), 77.9 (C), 91.0 (C), 124.0 (Ph), 128.1–128.6 (m, Ph), 130.5 (Ph), 130.9 (d,  $J_{\text{CP}}$  = 55.7 Hz, Ph), 132.5 (Ph), 135.5–135.7 (m, Ph) ppm.

***cis*-2a:**  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  (244 mg, 0.326 mmol) was added to a dry benzene solution (7 mL) of **1a** (67.9 mg, 0.389 mmol) under an atmosphere of dry nitrogen. After 30 min at room temperature, the volume of the solvent was reduced to half by rotary evaporation. After the addition of hexane (200 mL), the yellow precipitate was collected on a glass filter and washed with diethyl ether and pentane to give an off-white solid of *cis*-**2a** (250 mg, 86%).  $^1\text{H}$  NMR (500.16 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.64 (dd,  $J_{\text{HPt}}$  = 9.2, 6.1 Hz,  $J_{\text{HPt}}$  = 73.3 Hz, 2 H,  $\text{CH}_2$ ), 6.80–6.96 (m, 21 H, Ph), 7.45 (d,  $J$  = 6.7 Hz,

2 H, Ph), 7.55–7.60 (m, 6 H, Ph), 7.65–7.69 (m, 6 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 18.2 (d,  $J_{\text{PP}}$  = 16.7 Hz,  $J_{\text{PPt}}$  = 4336.5 Hz,  $\text{PPh}_3$ ), 21.2 (d,  $J_{\text{PP}}$  = 16.7 Hz,  $J_{\text{PPt}}$  = 1936.1 Hz,  $\text{PPh}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 13.3 (dd,  $J_{\text{CP}}$  = 91.2, 3.8 Hz,  $\text{CH}_2$ ), 67.6 (d,  $J_{\text{CP}}$  = 6.7 Hz, 1 C), 75.2 (d,  $J_{\text{CP}}$  = 2.9 Hz, 1 C), 79.0 (d,  $J_{\text{CP}}$  = 4.8 Hz, 1 C), 93.6 (d,  $J_{\text{CP}}$  = 11.5 Hz, 1 C), 124.6 (Ph), 127.8–128.5 (m, Ph), 129.8 (Ph), 130.7 (Ph), 130.8 (d,  $J_{\text{CP}}$  = 60.5 Hz, Ph), 132.3 (d,  $J_{\text{CP}}$  = 46.1 Hz, Ph), 132.5 (Ph), 134.8 (d,  $J_{\text{CP}}$  = 10.6 Hz, Ph), 135.5 (d,  $J_{\text{CP}}$  = 10.6 Hz, Ph) ppm. M.p. 131.0–134.1 °C (decomp.).  $\text{C}_{47}\text{H}_{37}\text{ClP}_2\text{Pt}$  (894.28): calcd. C 63.12, H 4.17; found C 63.16, H 4.13.

***cis*-2b:** Prepared by a method similar to that for *cis*-**2a** (off-white solid, 65%).  $^1\text{H}$  NMR (500.16 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 2.79 (dd,  $J_{\text{HPt}}$  = 9.2, 6.7 Hz,  $J_{\text{HPt}}$  = 77.6 Hz, 2 H,  $\text{CH}_2$ ), 6.79–6.97 (m, 21 H, Ph), 7.44 (dd,  $J$  = 8.0, 1.9 Hz, 2 H, Ph), 7.53–5.58 (m, 6 H, Ph), 7.64–7.69 (m, 6 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 18.4 (d,  $J_{\text{PP}}$  = 16.8 Hz,  $J_{\text{PPt}}$  = 4330.0 Hz,  $\text{PPh}_3$ ), 19.1 (d,  $J_{\text{PP}}$  = 16.8 Hz,  $J_{\text{PPt}}$  = 1955.7 Hz,  $\text{PPh}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 10.9 (dd,  $J_{\text{CP}}$  = 91.2, 2.9 Hz,  $\text{CH}_2$ ), 68.0 (d,  $J_{\text{CP}}$  = 6.7 Hz, 1 C), 75.3 (d,  $J_{\text{CP}}$  = 2.9 Hz, 1 C), 79.0 (d,  $J_{\text{CP}}$  = 4.8 Hz, 1 C), 93.2 (d,  $J_{\text{CP}}$  = 11.5 Hz, 1 C), 124.6 (Ph), 127.7–128.5 (m, Ph), 129.8 (d,  $J_{\text{CP}}$  = 2.7 Hz, Ph), 130.7 (d,  $J_{\text{CP}}$  = 2.9 Hz, Ph), 130.8 (d,  $J_{\text{CP}}$  = 59.5 Hz, Ph), 132.5 (Ph), 132.8 (d,  $J_{\text{CP}}$  = 47.0 Hz, Ph), 134.8 (d,  $J_{\text{CP}}$  = 10.6 Hz, Ph), 135.7 (d,  $J_{\text{CP}}$  = 10.6 Hz, Ph) ppm. M.p. 123.5–126.0 °C (decomp.).  $\text{C}_{47}\text{H}_{37}\text{BrP}_2\text{Pt}$  (938.73): calcd. C 60.13, H 3.97; found C 59.92, H 3.92.

**Isomerization Reaction of *cis*-2b in the Presence of  $\text{Pt}(\text{PPh}_3)_4$ :** To a solution of *cis*-**2b** (9.4 mg, 0.010 mmol) and an appropriate amount of trioxane as an internal standard dissolved in degassed dry  $\text{C}_6\text{D}_6$  (0.6 mL) in an NMR tube was added  $\text{Pt}(\text{PPh}_3)_4$  (1.2 mg, 0.00096 mmol). The NMR tube was sealed under a nitrogen atmosphere and heated at 50 °C in an oil bath. The reaction was followed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. After 24 h, a mixture of *trans*-**2b** and *trans*-( $\text{PPh}_3$ )<sub>2</sub>- $\text{PtBr}[\eta^1\text{-C}(\text{C}\equiv\text{CPh})=\text{C}=\text{CH}_2]$  (*trans*-**3b**) was observed in 37% yield (*trans*-**2b**/*trans*-**3b** = 19:81). Data for *trans*-**3b**:  $^1\text{H}$  NMR (500.16 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 3.28 (t,  $J_{\text{HPt}}$  = 4.0 Hz,  $J_{\text{HPt}}$  = 56.2 Hz, 2 H,  $\text{CH}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 21.5 (s,  $J_{\text{PPt}}$  = 3018.2 Hz,  $\text{PPh}_3$ ) ppm.

**Reaction of **1a** with  $\text{Pt}(\text{PPh}_3)_4$ :** The reactions were carried out in each solvent similarly to the reaction of **1a** with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ . The results are summarized in Scheme 4. Data for  $[(\text{PPh}_3)_2\text{Pt}\{\eta^2\text{-CH}_2\text{C}(\text{PPh}_3)=\text{C}(\text{C}\equiv\text{CPh})\}]^+\text{Cl}^-$  (**5**):  $^1\text{H}$  NMR (500.16 MHz,  $\text{CDCl}_3$ ):  $\delta$  = −0.05 (dd,  $J_{\text{HPt}}$  = 6.7, 3.7 Hz,  $J_{\text{HPt}}$  = 83.7 Hz, 2 H,  $\text{CH}_2$ ), 5.68 (d,  $J$  = 6.7 Hz, 2 H, Ph), 6.83 (dd,  $J$  = 7.3, 6.7 Hz, 2 H, Ph), 6.98 (t,  $J$  = 7.3 Hz, 1 H, Ph), 7.07–7.11 (m, 6 H, Ph), 7.16–7.39 (m, 24 H, Ph), 7.42–7.47 (m, 6 H, Ph), 7.52–7.57 (m, 6 H, Ph), 7.68–7.72 (m, 3 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.1 (dd,  $J_{\text{PP}}$  = 26.9, 26.1 Hz,  $J_{\text{PPt}}$  = 606.6 Hz,  $\text{CPPh}_3$ ), 21.0 (dd,  $J_{\text{PP}}$  = 26.1, 9.3 Hz,  $J_{\text{PPt}}$  = 2521.3 Hz,  $\text{PtPPh}_3$ ), 22.3 (dd,  $J_{\text{PP}}$  = 26.9, 9.3 Hz,  $J_{\text{PPt}}$  = 2169.6 Hz,  $\text{PtPPh}_3$ ) ppm.

**$[(\text{PPh}_3)_2\text{Pt}\{\eta^2\text{-CH}_2\text{C}(\text{PPh}_3)=\text{C}(\text{C}\equiv\text{CPh})\}]^+\text{OTf}^-$  (**5-OTf**):** To a solution of *cis*-**2a** (100 mg, 0.112 mmol) dissolved in degassed dry  $\text{CHCl}_3$  (10 mL) was added  $\text{PPh}_3$  (28.9 mg, 0.110 mmol) and  $\text{NaOTf}$  (37.4 mg, 0.217 mmol) under an atmosphere of nitrogen. The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was concentrated under vacuum, and the obtained residue was dissolved in dry  $\text{CH}_2\text{Cl}_2$ . After filtration, the filtrate was concentrated under vacuum again, and the residue was washed with benzene. Recrystallization from  $\text{CHCl}_3$  and hexane gave a yellow solid of **5-OTf** (137.4 mg, 98%).  $^1\text{H}$  NMR (600.18 MHz,  $\text{CDCl}_3$ ):  $\delta$  = −0.03 (dd,  $J_{\text{HPt}}$  = 6.6, 4.2 Hz,  $J_{\text{HPt}}$  = 85.0 Hz, 2 H,  $\text{CH}_2$ ), 5.78 (d,  $J$  = 8.4 Hz, 2 H, Ph), 6.84 (dd,  $J$  = 7.8, 7.2 Hz, 2 H, Ph), 6.97

(dd,  $J = 8.4, 7.2$  Hz, 1 H, Ph), 7.08–7.12 (m, 6 H, Ph), 7.17–7.41 (m, 24 H, Ph), 7.44–7.49 (m, 6 H, Ph), 7.53–7.57 (m, 6 H, Ph), 7.70 (t,  $J = 7.2$  Hz, 3 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.95 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.2$  (t,  $J_{\text{PP}} = 26.6$  Hz,  $J_{\text{PPt}} = 604.6$  Hz,  $\text{CPPH}_3$ ), 21.0 (dd,  $J_{\text{PP}} = 26.6$ , 8.7 Hz,  $J_{\text{PPt}} = 2517.8$  Hz,  $\text{PtPPH}_3$ ), 22.3 (dd,  $J_{\text{PP}} = 26.6$ , 8.7 Hz,  $J_{\text{PPt}} = 2156.7$  Hz,  $\text{PtPPH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CDCl}_3$ ):  $\delta = -5.5$  (dd,  $J_{\text{CP}} = 76.3$ , 4.8 Hz,  $J_{\text{PPt}} = 365.4$  Hz,  $\text{CH}_2$ ), 89.1 (q,  $J_{\text{CP}} = 5.6$  Hz, 1 C), 115.9 (d,  $J_{\text{CP}} = 5.8$  Hz,  $J_{\text{Cpt}} = 37.6$  Hz, 1 C), 120.9 (q,  $J_{\text{CF}} = 319.5$  Hz,  $\text{CF}_3$ ), 122.3 (s, Ph), 127.1–130.0 (m, Ph), 130.1 (dd,  $J_{\text{CP}} = 22.0$ , 1.9 Hz, 1 C), 149.3 (d,  $J_{\text{CP}} = 115.4$  Hz,  $J_{\text{Cpt}} = 598.0$  Hz, 1 C) ppm. M.p. 161.4–165.5 °C (decomp.).  $\text{C}_{66}\text{H}_{52}\text{F}_3\text{O}_3\text{P}_3\text{PtS}$  (1270.18): calcd. C 62.41, H 3.78; found C 62.29, H 4.04.

**Reaction of 1a with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ :** The reactions were carried out in each solvent similarly to the reaction of 1a with  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ . The results are summarized in Scheme 7. *cis*-( $\text{PPh}_3$ )<sub>2</sub> $\text{PtCl}[\eta^1\text{-CH}_2\text{C}\equiv\text{C}\{(\text{PPh}_3)_2\text{Pt}(\eta^2\text{-C}\equiv\text{CPh})\}]$  (7) and ( $\text{PPh}_3$ )<sub>2</sub>- $\text{Pt}[\eta^2\text{-CH}_2\text{C}\{(\text{PPh}_3)_2\text{PtCl}\}(\text{C}\equiv\text{CPh})]$  (8) gradually decomposed in solution. Thus they cannot be isolated. Data for 7:  $^1\text{H}$  NMR (500.16 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.84$  (br. s,  $J_{\text{HPt}} = 66.5$  Hz, 2 H,  $\text{CH}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 18.6$  (d,  $J_{\text{PP}} = 16.7$  Hz,  $J_{\text{PPt}} = 4529.1$  Hz,  $\text{PPh}_3$ ), 21.3 (dd,  $J_{\text{PP}} = 16.7$ , 5.6 Hz,  $J_{\text{PPt}} = 1790.1$  Hz,  $\text{PPh}_3$ ), 26.9 (dd,  $J_{\text{PP}} = 31.6$ , 5.6 Hz,  $J_{\text{PPt}} = 3490.7$  Hz,  $\text{PPh}_3$ ), 27.8 (d,  $J_{\text{PP}} = 31.6$  Hz,  $J_{\text{PPt}} = 3449.8$  Hz,  $\text{PPh}_3$ ) ppm. Data for 8:  $^1\text{H}$  NMR (500.16 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.42$  (br. s,  $J_{\text{HPt}} = 82.5$  Hz, 2 H,  $\text{CH}_2$ ), 6.35 (d,  $J_{\text{HH}} = 7.4$  Hz, 2 H, Ph), 6.73 (dd,  $J_{\text{HH}} = 7.4$ , 7.3 Hz, 2 H, Ph), 6.83 (t,  $J_{\text{HH}} = 7.3$  Hz, 1 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta = 22.4$  (d,  $J_{\text{PP}} = 3.7$  Hz,  $J_{\text{PPt}} = 1953.8$  Hz,  $\text{PPh}_3$ ), 24.4 (d,  $J_{\text{PP}} = 3.7$  Hz,  $J_{\text{PPt}} = 2318.5$  Hz,  $\text{PPh}_3$ ), 25.6 (br. s,  $J_{\text{PPt}} = 3648.9$ , 63.3 Hz,  $\text{PPh}_3$ ) ppm.

**Reaction of 5 with HCl:**  $\text{Pt}(\text{PPh}_3)_4$  (74.7 mg, 0.060 mmol) was added to a dry solution of 1a (10.5 mg, 0.060 mmol) in  $\text{CDCl}_3$  (0.6 mL) at room temperature. After 10 min, 5 was observed in 90% NMR yield. Then,  $\text{Me}_3\text{SiCl}$  (7.8 mg, 0.072 mmol) and  $\text{H}_2\text{O}$  (ca. 1  $\mu\text{L}$ ) were added to the NMR tube. After 3.0 min,  $[(\text{PPh}_3)_2\text{-PtCl}\{\eta^1\text{-C}(\text{C}\equiv\text{CPh})=\text{C}(\text{PPh}_3)\text{CH}_3\}]^+\text{Cl}^-$  (9) was generated in 92% NMR yield based on 5. Complex 9 was not isolated because of the low stability in solution.  $^1\text{H}$  NMR (500.16 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.14$  (br. s,  $J_{\text{HPt}} = 67.2$  Hz, 3 H,  $\text{CH}_3$ ), 6.57 (d,  $J = 7.3$  Hz, 2 H, Ph), 7.05–7.75 (m, 48 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta = 19.0$  (d,  $J_{\text{PP}} = 31.6$  Hz,  $J_{\text{PPt}} = 145.1$  Hz,  $\text{CPPH}_3$ ), 20.3 (d,  $J_{\text{PP}} = 16.7$  Hz,  $J_{\text{PPt}} = 4252.3$  Hz,  $\text{PtPPH}_3$ ), 23.0 (dd,  $J_{\text{PP}} = 31.6$ , 16.7 Hz,  $J_{\text{PPt}} = 1731.3$  Hz,  $\text{PtPPH}_3$ ) ppm.

**Reaction of 8 with HCl:**  $\text{Pt}(\text{C}_2\text{H}_2)(\text{PPh}_3)_2$  (59.9 mg, 0.0801 mmol) was added to a solution of diynylchloride 1a (7.0 mg, 0.040 mmol) in degassed dry  $\text{CDCl}_3$  (0.6 mL) at room temperature. After 10 min, 8 was observed in 54% NMR yield. Then,  $\text{Me}_3\text{SiCl}$  (5.2 mg, 0.048 mmol) and  $\text{H}_2\text{O}$  (ca. 1  $\mu\text{L}$ ) were added to the NMR tube. After 30 min,  $[(\text{PPh}_3)_2\text{Pt}\{\eta^3\text{-CH}_2\text{C}\{cis\text{-(PPh}_3)_2\text{PtCl}\}(\text{C}\equiv\text{CPh})\}]^+\text{Cl}^-$  (10) was generated in 70% NMR yield based on 8. The volatiles were removed under vacuum, yielding a yellow oil. This material was washed with hexane and  $\text{Et}_2\text{O}$  and then recrystallized from  $\text{CH}_2\text{Cl}_2$  and hexane to give an off-white solid of 10 (21.7 mg, 33%).  $^1\text{H}$  NMR (500.16 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.23$  (m,  $J_{\text{HPt}} = 41.5$  Hz, 1 H, CH), 3.20 (m,  $J_{\text{HPt}} = 53.0$  Hz, 1 H, CH), 3.58 (br. s, 1 H, CH), 6.95–7.12 (m, 20 H, Ph), 7.19–7.48 (m, 15 H, Ph) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.6$  (d,  $J_{\text{PP}} = 18.6$  Hz,  $J_{\text{PPt}} = 1787.8$ , 39.0 Hz,  $\text{PPh}_3$ ), 15.2 (d,  $J_{\text{PP}} = 11.2$  Hz,  $J_{\text{PPt}} = 3995.2$  Hz,  $\text{PPh}_3$ ), 16.4 (d,  $J_{\text{PP}} = 11.2$  Hz,  $J_{\text{PPt}} = 4004.6$  Hz,  $\text{PPh}_3$ ), 17.7 (d,  $J_{\text{PP}} = 18.6$  Hz,  $J_{\text{PPt}} = 4182.8$ , 48.3 Hz,  $\text{PPh}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CDCl}_3$ ):  $\delta = 67.6$  (d,  $J_{\text{CP}} = 35.4$  Hz,  $J_{\text{Cpt}} = 95.0$  Hz, 1 C), 77.6 (s,  $\text{CH}_2$ ), 86.6 (s, 1 C), 93.6 (s, 1 C), 123.7 (s, 1

C), 127.8–132.0 (m, Ph), 133.7–135.0 (m, Ph) ppm. M.p. 147.9–149.3 °C (decomp.).  $\text{C}_{83}\text{H}_{68}\text{Cl}_2\text{P}_4\text{Pt}_2$  (1650.40): calcd. C 60.40, H 4.15; found C 60.40, H 4.40. Single crystals of 10 for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated  $\text{CH}_2\text{Cl}_2$  solution of 10.

**Crystal Data for 10:**  $\text{C}_{83}\text{H}_{68}\text{Cl}_2\text{P}_4\text{Pt}_2$ ,  $M = 1650.43$ , colorless, triclinic,  $a = 13.6897(7)$  Å,  $b = 16.8795(9)$  Å,  $c = 20.2072(12)$  Å,  $\alpha = 70.8631(16)^\circ$ ,  $\beta = 78.6225(15)^\circ$ ,  $\gamma = 81.8964(15)^\circ$ ,  $V = 4309.9(4)$  Å<sup>3</sup>,  $T = 153 \pm 1$  K, space group  $P\bar{1}$  (#2),  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 34.019$  cm<sup>-1</sup>, 33945 reflections measured, 15498 independent reflections ( $R_{\text{int}} = 0.058$ ). The final  $R_1$  values were 0.0719 [ $I > 2\sigma(I)$ ]. The final  $wR(F^2)$  values were 0.0896 [ $I > 2\sigma(I)$ ]. The goodness of fit on  $F^2$  was 0.979. CCDC-690680 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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