# Kinetic Evidence for $\pi$ -Complex Formation Prior to Oxidative Addition of Propargyl Halides to Triphenylphosphine-Platinum(0) Complexes

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The mechanism of oxidative addition of phenylpropargyl halides to  $Pt(PPh_3)_4$  to give  $Pt-(\eta^1-CH_2C\equiv CPh)(X)(PPh_3)_2$  has been investigated on the basis of the kinetics of the reaction and stereomeric analysis of the products. The kinetic results of the reaction showed the contributions of two pathways involving  $Pt(PPh_3)_3$  and  $Pt(PPh_3)_2$  complexes as active species. The second-order rate constants for both pathways were on the order of  $10^3$  larger than the corresponding rate constants of the oxidative addition reaction of  $CH_3I$ . Moreover, both active species and the substrate halide gave, as the kinetic product, the isomer having two PPh\_3 groups located cis, which is also in sharp contrast to the case of the reaction of  $CH_3I$ . It is proposed that the rate-determining step in the reaction involving  $Pt(PPh_3)_2$  is the coordination of the  $C\equiv C$  bond to  $Pt(PPh_3)_2$  to form  $Pt(\eta^2-PhC\equiv CCH_2X)(PPh_3)_2$ , which subsequently undergoes rapid collapse to the  $\eta^3$ -propargyl complex  $[Pt(\eta^3-CH_2CCPh)(PPh_3)_2]X$  and eventually to *cis*- $Pt(\eta^1-CH_2C\equiv CPh)(X)(PPh_3)_2$ . The reaction of  $Pt(PPh_3)_3$  may also involve a rate-determining  $C\equiv C$  bond coordination step.

# Introduction

The oxidative addition reaction is one of the most fundamental steps constituting many homogeneous catalytic cycles. The oxidative addition of organic halides to zerovalent group 10 metal complexes containing more than 2 equiv of tertiary phosphine ligands gives trans isomers of organo halo bis-phosphine complexes, except for a limited few examples.<sup>1</sup> These exceptions involved the addition of sp<sup>2</sup>-carbon-halogen compounds, where the formation of cis product is a logical outcome of the proposed mechanistic pathway.<sup>2</sup> In this respect it appears of special interest that Wojcicki and co-workers reported that oxidative addition reaction of Pt(C<sub>2</sub>H<sub>4</sub>)-(PPh<sub>3</sub>)<sub>2</sub> with PhC=CCH<sub>2</sub>Br leads to the formation of cis- $Pt(\eta^1-CH_2C \equiv CPh)(Br)(PPh_3)_2$ , which isomerizes further to the more stable trans isomer.<sup>3</sup> However, these authors offered no mechanistic explanation for the cis product. We took interest in elucidating the reason for such unusual stereochemistry and, more generally, the mechanism of the oxidative addition reaction of propargyl halides to Pt(0) complexes in view of increasing attention paid to both inorganic and organic aspects of propargyl and allenyl complexes.<sup>4</sup> Moreover, there is a possibility that studying the above-mentioned reactions of Pt(0) complexes leads to a better understanding of the mechanisms of the related reactions involving palladium complexes important as intermediates in catalysis<sup>5</sup> or even closely related allylic substrates.

We report here intriguing kinetic behavior in the reaction of  $Pt(PPh_3)_4$  with phenylpropargyl halides, from which a very fundamental oxidative addition mechanism is offered that is consistent with the reported formation of the cis isomer from  $Pt(C_2H_4)(PPh_3)_2$  as the kinetic product.

### Results

**Stereochemistry of the Kinetic Product.** We previously reported<sup>6</sup> that the oxidative addition product  $Pt(\eta^{1}-CH_{2}C\equiv CPh)(X)(PPh_{3})_{2}$  (X = Cl, Br) from PhC $\equiv$  CCH<sub>2</sub>X and Pt(PPh\_{3})\_{4} after recrystallization at room temperature has two PPh\_3 ligands located trans to each other. We have now confirmed by NMR examinations that the kinetic product of the reaction of Pt(PPh\_{3})\_{4} with PhC $\equiv$ CCH<sub>2</sub>Cl in the presence of excess PPh\_3 (20 equiv) formed in toluene-*d*<sub>8</sub> at temperatures from -60 to 0 °C has the cis geometry (eq 1; L = PPh\_3, *n* = 2). The cis

$$PtL_{n}(PPh_{3})_{2} + Ph \xrightarrow{\qquad} CI \xrightarrow{\qquad} Ph \xrightarrow{\qquad} Pt \xrightarrow{$$

complex remained stable with respect to the cis-trans isomerization at 0  $^{\circ}$ C for 1 h, but the isomerization

<sup>(1)</sup> Casado, A. L.; Espinet, P. Organometallics **1998**, *17*, 954. Urata, H.; Tanaka, M.; Fuchikami, T. Chem. Lett. **1987**, 751. Addition of vinyl sulfides to  $Pt(C_2H_4)(PPh_3)_2$  also gave the cis products: Kuniyasu, H.; Otaka, A.; Nakazono, T.; Kurosawa, H. J. Am. Chem. Soc. **2000**, *122*, 2375.

<sup>(2)</sup> Portnoy, M.; Milstein, D. Organometallics 1993, 12, 1665.

<sup>(3)</sup> Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1992. Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164

<sup>(4)</sup> Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. Adv. Organomet. Chem. **1995**, 37, 39. Wojcicki, A. New J. Chem. **1994**, 18, 61.

<sup>(5)</sup> Tsuji, J.; Mandai, T. Angew. Chem., Int. Ed. Engl. 1995, 34, 2587.
(6) Ogoshi, S.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. Inorg. Chim. Acta 1997, 265, 9.

Table 1. Kinetic Results of the Reaction of **Pt(PPh<sub>3</sub>)<sub>4</sub> with PhC≡CCH<sub>2</sub>Cl** 

			$k_{obs}/[PhC \equiv CCH_2C]$
run	[PPh <sub>3</sub> ] (mol/L)	1/[PPh3] (L/mol)	(L/(mol s))
1	$2.49 imes10^{-3}$	$4.02 imes10^2$	5.10
2	$4.00 imes10^{-3}$	$2.50  imes 10^2$	3.92
3	$6.67 imes10^{-3}$	$1.50  imes 10^2$	3.21
4	$2.50 imes10^{-2}$	$4.00 \times 10$	2.20
5	$5.14 imes10^{-2}$	1.95  imes 10	2.14
6	$1.03 imes10^{-1}$	9.71	2.12
7	$2.51 imes10^{-1}$	3.98	2.09
	kobs/[PhC≡CCH <sub>2</sub> CI]		400-

Figure 1.  $1/[PPh_3]$  vs  $k_{obs}/[PhC \equiv CCH_2Cl]$ .

proceeded gradually at room temperature in the toluene $d_8$  solution to give 100% trans isomer after 17 h.

The kinetic product of the reaction of  $Pt(C_2H_4)(PPh_3)_2$ with PhC=CCH<sub>2</sub>Cl was also confirmed *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C= CPh)(Cl)(PPh<sub>3</sub>)<sub>2</sub> in toluene- $d_8$  at -30 °C (eq 1; L = C<sub>2</sub>H<sub>4</sub>, n = 1), as reported<sup>3</sup> in the corresponding reaction of the bromide.

**Kinetics.** The rates of the reaction of Pt(PPh<sub>3</sub>)<sub>4</sub> with  $PhC \equiv CCH_2Cl$  were measured spectrophotometrically in benzene at 25 °C. The measurements employed [PhC= CCH<sub>2</sub>Cl] and [PPh<sub>3</sub>] in sufficient excess over the Pt complex, the initial concentration ranges being 6.99 imes $10^{-5}$  mol/L for Pt(PPh<sub>3</sub>)<sub>4</sub>, 2.66 ×  $10^{-3}$  to  $1.59 \times 10^{-2}$ mol/L for PhC=CCH<sub>2</sub>Cl and  $2.49 \times 10^{-3}$  to  $2.51 \times 10^{-1}$ mol/L for PPh<sub>3</sub>. In each run the pseudo-first-order rate constant  $k_{obs}$  was obtained by plots of ln A (absorbance of Pt(0) complex at 410 nm) vs time, and the  $k_{obs}$ / [PhC≡CCH<sub>2</sub>Cl] value at a given [PPh<sub>3</sub>] was obtained from slopes of plots of  $k_{obs}$  vs [PhC=CCH<sub>2</sub>Cl]. Then, plotting  $k_{obs}/[PhC \equiv CCH_2Cl]$  vs  $1/[PPh_3]$  gave a straight line (Table 1 and Figure 1) from which the following experimental kinetic equation is given:

$$\frac{k_{\rm obs}}{[\rm PhC=CCH_2Cl]} = 2.01 + 7.70 \times 10^{-3} \frac{1}{[\rm PPh_3]} \qquad (2)$$

# Discussion

It has been established7 that Pt(PPh<sub>3</sub>)<sub>4</sub> dissociates to the two active species Pt(PPh<sub>3</sub>)<sub>3</sub> and Pt(PPh<sub>3</sub>)<sub>2</sub> in solution. The concentration of Pt(PPh<sub>3</sub>)<sub>4</sub> can be neglected under the kinetic conditions, since the equilibrium constant for the dissociation of this species is

Table 2. Rate Constants for Reactions of Pt(PPh<sub>3</sub>)<sub>3</sub>  $(k_1)$  and Pt(PPh<sub>3</sub>)<sub>2</sub>  $(k_3)$ 

substrate	$k_1$ (L/(mol s))	<i>k</i> <sub>3</sub> (L/(mol s))
PhC≡CCH₂Cl CH₃I PhC≡CCH₃	$\begin{array}{c} 2.0\\ 3.5\times10^{-3}\\ 5.0\times10^{-2} \end{array}$	$\begin{array}{c} 4.8 \times 10 \\ 2.0 \times 10^{-2} \\ 2.0 \times 10 \end{array}$

greater than 10 mol/L.<sup>7</sup> The kinetic behavior observed in eq 2 can be accommodated by the mechanism, which includes the contributions of two simultaneous pathways to the reaction: (a) the pathway corresponding to eq 3 and (b) the pathway described by eqs 4 and 5.

$$Pt(PPh_{3})_{3} + Ph \underbrace{\qquad }_{CI} \underbrace{\qquad }_{Ph} \underbrace{\qquad }_{Ph_{3}P} \underbrace{\qquad }_{Ph_{3}P} \underbrace{\qquad }_{PPh_{3}} Ft + PPh_{3}$$
(3)

(4)

 $Pt(PPh_3)_3 \xrightarrow{K_2} Ph(PPh_3)_2 + PPh_3$ 

$$Pt(PPh_{3})_{2} + Ph \underbrace{\qquad }_{Cl} \underbrace{k_{3}}_{Ph} \underbrace{Ph}_{Ph_{3}P} \underbrace{Pt}_{PPh_{3}} (5)$$

Equations 3–5 give rise to the rate law shown in eq 6.8

$$-\frac{d[Pt(0)]}{dt} = k_{obs}[Pt(0)] = \frac{k_1[PPh_3] + k_3K_2}{K_2 + [PPh_3]} [PhC \equiv CCH_2Cl][Pt(0)] \quad (6)$$

The *K*<sub>2</sub> value of eq 4 has been previously evaluated as  $1.6 \times 10^{-4}$  mol/L (benzene, 25 °C) by Halpern,<sup>9</sup> which can be neglected relative to [PPh<sub>3</sub>] (the minimum being  $2.5 \times 10^{-3}$  mol/L) in the denominator of eq 6, so that eq 6 can be simplified to eq 7. This equation conforms to the experimental rate law of eq 2.10a

$$\frac{k_{\text{obs}}}{[\text{PhC}=\text{CCCH}_2\text{Cl}]} = k_1 + k_3 K_2 \frac{1}{[\text{PPh}_3]}$$
(7)

Table 2 shows the rate constants  $k_1$  and  $k_3$ , calculated by comparing eqs 2 and 7, which represent the oxidative addition rates of  $Pt(PPh_3)_3$  and  $Pt(PPh_3)_2$  species with PhC≡CCH<sub>2</sub>Cl, respectively. For comparison, Table 2 also includes the rate of the reaction of the two Pt(0) active species with  $CH_3I^8$  and  $PhC \equiv CCH_3^{10b,11}$  measured under the same conditions. Interestingly, both  $k_1$ and  $k_3$  for the reaction with PhC=CCH<sub>2</sub>Cl were much larger (by an order of 10<sup>3</sup>) than the corresponding rate constants of the oxidative addition reaction of CH<sub>3</sub>I<sup>8</sup> (Table 2). The rates of the reaction of propargyl halides with a range of nucleophiles other than low-valent metal

<sup>(7)</sup> Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. J. Am. Chem. Soc. 1972, 94, 2669.

<sup>(8)</sup> Pearson, R. G.; Rajaram, J. *Inorg. Chem.* **1974**, *13*, 246.
(9) Birk, J. P.; Halpern, J.; Pickard, A. L. *Inorg. Chem.* **1968**, *7*, 2673.
(10) (a) Another kinetic treatment of eqs 3–5 assumes steady-state concentrations of active complexes,<sup>11</sup> giving the rate law  $k_{bb}/[PhC \equiv CCH_2-CI] = k_1 + k_2/[(k_{-2}/k_3)[PPh_3] + [PhC \equiv CCH_2CI]]$ , where  $K_2 = k_2/k_{-2}$ . In the denominator of the second term [PhC=CCH<sub>2</sub>Cl] (2.66  $\times$  10<sup>-3</sup> to  $1.59 \times 10^{-2}$  mol/L) could be neglected relative to  $(k_{-2}/k_3)$  [PPh<sub>3</sub>] under the kinetic conditions  $(k_{-2}/k_3 \text{ for PhC} = CCH_3 \text{ was observed}^{11} \text{ as } 2.5 \times$ 10<sup>2</sup>). This gives a kinetic law consistent with eq 7. (b) The  $k_{-2}$  value was estimated as 5.7  $\times$  10<sup>3</sup> L/(mol s) on the basis of the observed  $k_2$  $(0.91 \text{ s}^{-1})^{11}$  and the estimated value of  $K_2$ .<sup>9</sup> This, together with the known  $k_{-2}/k_3$ , leads us to estimate  $k_3$  for the reaction of PhC=CCH<sub>3</sub> shown in Table 2

<sup>(11)</sup> Halpern, J.; Weil, T. A. J. Chem. Soc., Chem. Commun. 1973, 63Ì.



species are normally rather slower than those of CH<sub>3</sub>I.<sup>12</sup> These results suggest the importance of the triple bond coordination to Pt(0) prior to or during the oxidative addition.

It is important to note that the  $k_3$  value for the reaction of PhC=CCH<sub>2</sub>Cl was similar to the rate of coordination of PhC=CCH<sub>3</sub> to Pt(PPh<sub>3</sub>) $_2^{10b}$  (Table 2). This result suggests that the rate-determining step of the oxidative addition of PhC=CCH<sub>2</sub>Cl to Pt(PPh<sub>3</sub>)<sub>2</sub> is the coordination of the triple bond. To gain further support for this notion, the competition between  $PhC \equiv$ CCH<sub>2</sub>Cl and PhC≡CCH<sub>2</sub>Br in the reaction with Pt- $(C_2H_4)(PPh_3)_2$  was attempted in toluene- $d_8$  at room temperature. The concentrations of the two halides were set equal to each other and were in excess relative to the Pt(0) complex. The yields of products, *cis*-Pt( $\eta^{1}$ - $CH_2C \equiv CPh)(X)(PPh_3)_2$ , obtained from a mixture of the two substrates were similar (1:1.5) for the chloride vs bromide. If the rate-determining step of the oxidative addition involved the C-halogen bond cleavage, the reactivity of the bromide would have been considerably greater than that of the chloride.

The rate-determining formation of  $Pt(\eta^2 - PhC \equiv CCH_2 -$ Cl)(PPh<sub>3</sub>)<sub>2</sub> from Pt(PPh<sub>3</sub>)<sub>2</sub> and PhC=CCH<sub>2</sub>Cl would be followed by rapid collapse of this complex to the ion pair  $[Pt(\eta^3-CH_2CCPh)(PPh_3)_2]Cl$ , which necessarily keeps two PPh<sub>3</sub> groups cis to each other (Scheme 1). It was also confirmed that the separately isolated cationic complex  $[Pt(\eta^3-CH_2CCPh)(PPh_3)_2](OTf)$  reacts readily with Cl<sup>-</sup> to give cis-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(Cl)(PPh\_3)<sub>2</sub>, as also reported<sup>3</sup> in the corresponding reaction with Br<sup>-</sup>.

With regard to the reaction of Pt(PPh<sub>3</sub>)<sub>3</sub>, it is remarkable that the rate constant  $k_1$  for the reaction with  $PhC \equiv CCH_2Cl$  is 40 times larger than that with  $PhC \equiv$  $CCH_3$  (Table 2). In the latter case, it is possible that the triple bond coordination to form an intermediate of the type  $Pt(\eta^2 - PhC \equiv CCH_3)(PPh_3)_3$  is not a rate-determining step. This intermediate, if formed as a discrete species, might have to overcome a subsequent higher barrier process, namely dissociation of PPh<sub>3</sub>. On the other hand, in the case of the reaction of PhC=CCH<sub>2</sub>Cl the C=C coordination complex  $Pt(\eta^2 - PhC = CCH_2Cl)$ -(PPh<sub>3</sub>)<sub>3</sub> formed first could undergo very facile ionization of the C-Cl bond to afford [Pt( $\eta^3$ -CH<sub>2</sub>CCPh)(PPh<sub>3</sub>)<sub>3</sub>]Cl (Scheme 2). In a search for further support, the competitive experiment was carried out by employing an equimolar mixture of PhC=CCH<sub>2</sub>Cl and PhC=CCH<sub>2</sub>-Br which are in excess relative to Pt(PPh<sub>3</sub>)<sub>4</sub> in the presence of a high concentration of PPh<sub>3</sub> (1.66  $\times$  10<sup>-1</sup> mol/L), where the contribution of Pt(PPh<sub>3</sub>)<sub>3</sub> species to the overall oxidative addition is expected to exceed Scheme 2



98%.<sup>13</sup> This reaction yielded *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(X)- $(PPh_3)_2$  in a 1:1.2 ratio for X = Cl vs X = Br, suggesting that the rate-determining step of the reaction does not involve a carbon-halogen bond cleavage.

In contrast to the straightforward course of the reaction from  $Pt(PPh_3)_2$  shown in Scheme 1, it is not certain at the moment how the proposed initial oxidative addition product [Pt(n<sup>3</sup>-CH<sub>2</sub>CCPh)(PPh<sub>3</sub>)<sub>3</sub>]Cl from Pt- $(PPh_3)_3$  is converted to the observable kinetic product, *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(Cl)(PPh<sub>3</sub>)<sub>2</sub>. The cationic 18-electron  $\eta^3$ -propargyl complex might undergo either dissociation of one PPh<sub>3</sub> to give  $[Pt(\eta^3-CH_2CCPh)(PPh_3)_2]Cl$ or  $\eta^3$  to  $\eta^1$  conversion, which gives [Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)- $(PPh_3)_3$ ]Cl. In fact, a separate treatment of  $[Pt(\eta^3-CH_2-$ CCPh)(PPh<sub>3</sub>)<sub>2</sub>]OTf with 1 equiv of PPh<sub>3</sub> resulted in the observation of NMR resonances attributable to the complex  $[Pt(\eta^1-CH_2C \equiv CPh)(PPh_3)_3](OTf)$  together with additional minor resonances possibly due to cis- $\{(PPh_3)_2 Pt[CH_2C(PPh_3)CPh]\}(OTf).^{14}$  When further

treated with Cl<sup>-</sup>, the mixture was completely converted to *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(Cl)(PPh<sub>3</sub>)<sub>2</sub>. It is likely that the cationic  $\eta^1$ -propargyl intermediate [Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)-(PPh<sub>3</sub>)<sub>3</sub>]Cl is formed before the observable cis product.<sup>15</sup>

#### Conclusions

The oxidative addition reaction of propargyl halides to Pt(PPh<sub>3</sub>)<sub>4</sub> proceeded via the two active species Pt- $(PPh_3)_2$  and  $Pt(PPh_3)_3$ . The rate-determining step of the reaction of Pt(PPh<sub>3</sub>)<sub>2</sub> is the coordination of the triple bond of PhC=CCH<sub>2</sub>X, which is followed by rapid collapse of  $Pt(\eta^2 - PhC \equiv CCH_2X)(PPh_3)_2$  to  $[Pt(\eta^3 - CH_2CCPh) (PPh_3)_2$ ]Cl and finally to *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(Cl)-(PPh<sub>3</sub>)<sub>2</sub>. The rate-determining step of the reaction of Pt(PPh<sub>3</sub>)<sub>3</sub> would also involve the coordination of the triple bond to form  $Pt(\eta^2 - PhC \equiv CCH_2X)(PPh_3)_3$ , which then undergoes C-Cl bond cleavage without dissociation of PPh<sub>3</sub> ligand. These reaction profiles must be also essential in the oxidative addition of allylic electrophiles with zerovalent group 10 metal complexes.

# **Experimental Section**

General Considerations. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. <sup>1</sup>H and <sup>31</sup>P nuclear magnetic resonance (NMR) spectra were recorded on a JEOL GSX-270 spectrometer. Kinetic measurements were carried out by using a

<sup>(13)</sup> The second term of eq 2 amounts to ca.  $4.64 \times 10^{-2}$ . (14) Cheng, Y.-C.; Chen, Y.-K.; Huang, T.-M.; Yu, C.-I.; Lee, G.-H.; Wang, Y.; Chen, J.-T. *Organometallics* **1998**, *17*, 2953.

<sup>(15)</sup> A similar cationic complex, [Pt(CH<sub>3</sub>)(PPh<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub>, was converted (13) A SIMILAL CAUGHIC COMPLEX,  $[Pt(CH_3)(PPh_3)_3]BF_4$ , was converted to the cis product *cis*-Pt(CH\_3)(Cl)(PPh\_3)\_2 when treated with Cl<sup>-</sup>, while *trans*-Pt(CH\_3)(I)(PPh\_3)\_2 was the only observable product when  $[Pt-(CH_3)(PPh_3)_3]BF_4$  was treated with  $I^{-,16}$ 

<sup>(16)</sup> Unpublished results.

CH<sub>2</sub>CCPh)(PPh<sub>3</sub>)<sub>2</sub>](OTf).<sup>3</sup> **Reaction of Ph=CCH<sub>2</sub>Cl with Pt(PPh<sub>3</sub>)<sub>4</sub> in the Presence of a Large Excess of PPh<sub>3</sub>. To a solution of Pt(PPh<sub>3</sub>)<sub>4</sub> (4.9 mg, 3.9 \times 10^{-3} mmol) and PPh<sub>3</sub> (19.1 mg, 7.3 \times 10^{-2} mmol) in toluene-d\_8 (0.6 mL) was added PhC=CCH<sub>2</sub>Cl (1.1 mg, 7.3 \times 10^{-3} mmol) at -78 °C. The reaction mixture was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR at temperatures from -60 to 0 °C. The initial product was confirmed to be formed at -40 °C, whose <sup>31</sup>P NMR data coincided with those of** *cis***-Pt(\eta^1-CH<sub>2</sub>C=CPh)-(Cl)(PPh<sub>3</sub>)<sub>2</sub>. Then the product began to isomerize to** *trans***-Pt-(\eta^1-CH<sub>2</sub>C=CPh)(Cl)(PPh<sub>3</sub>)<sub>2</sub> at about 0 °C.** 

**Reaction of PhC=CCH<sub>2</sub>Cl and PhC=CCH<sub>2</sub>Br with Pt-(C<sub>2</sub>H<sub>4</sub>)(<b>PPh**<sub>3</sub>)<sub>2</sub>. To a solution of Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> (10.5 mg, 1.4  $\times$  10<sup>-2</sup> mmol) in toluene-*d*<sub>8</sub> (0.6 mL) were added PhC=CCH<sub>2</sub>-Cl (21.1 mg, 1.4  $\times$  10<sup>-1</sup> mmol) and PhC=CCH<sub>2</sub>Br (27.4 mg, 1.4  $\times$  10<sup>-1</sup> mmol) at -78 °C. The reaction mixture was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR at -30 °C. This reaction yielded *cis*-Pt( $\eta$ <sup>1</sup>-CH<sub>2</sub>C=CPh)(X)(PPh<sub>3</sub>)<sub>2</sub> in 1:1.5 ratio for X = Cl vs X = Br.

**Reaction of PhC=CCH<sub>2</sub>Cl and PhC=CCH<sub>2</sub>Br with Pt-(PPh<sub>3</sub>)<sub>4</sub> in the Presence of a Large Excess of PPh<sub>3</sub>. To a solution of Pt(PPh<sub>3</sub>)<sub>4</sub> (12.1 mg, 1.0 \times 10^{-2} mmol) and PPh<sub>3</sub> (26.6 mg, 1.0 \times 10^{-1} mmol) in C<sub>6</sub>D<sub>6</sub> (0.6 mL) were added PhC=CCH<sub>2</sub>-Cl (15.0 mg, 1.0 \times 10^{-1} mmol) and PhC=CCH<sub>2</sub>Br (20.0 mg, 1.0 \times 10^{-1} mmol) at -20 °C. The reaction mixture was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR at room temperature. The reaction yielded** *cis***-Pt(\eta^1-CH<sub>2</sub>C=CPh)(X)(PPh<sub>3</sub>)<sub>2</sub> in a 1:1.2 ratio for X = Cl vs X = Br after 10 min. Then the products began to isomerize to trans isomers.** 

**Reaction of** [Pt( $\eta^3$ -CH<sub>2</sub>CCPh)(PPh<sub>3</sub>)<sub>2</sub>](OTf) with "Bu<sub>4</sub>-NCl. To a solution of [Pt( $\eta^3$ -CH<sub>2</sub>CCPh)(PPh<sub>3</sub>)<sub>2</sub>](OTf) (4.8 mg, 4.9 × 10<sup>-3</sup> mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL) was added "Bu<sub>4</sub>NCl (2.4 mg, 8.8 × 10<sup>-3</sup> mmol) at -78 °C. The reaction mixture was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR at -60 °C to room temperature to show the formation of *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(Cl)(PPh<sub>3</sub>)<sub>2</sub>.

Reaction of  $[Pt(\eta^3-CH_2CCPh)(PPh_3)_2](OTf)$  with <sup>n</sup>Bu<sub>4</sub>-NCl in the Presence of PPh<sub>3</sub>.  $[Pt(\eta^3-CH_2CCPh)(PPh_3)_2](OTf)$  (13.8 mg,  $1.4 \times 10^{-2}$  mmol) and PPh<sub>3</sub> (3.7 mg,  $1.4 \times 10^{-2}$  mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL) were added in an NMR tube at room temperature. The reaction mixture was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR after 10 min. [Pt( $\eta^3$ -CH<sub>2</sub>CCPh)(PPh<sub>3</sub>)<sub>2</sub>](OTf) disappeared almost completely, and instead two products (3:1 ratio) were visible. We assume the major product to be [Pt( $\eta^1$ -CH<sub>2</sub>C≡ CPh)(PPh<sub>3</sub>)<sub>3</sub>](OTf): <sup>1</sup>H NMR  $\delta$  1.18 (t,  $J_{PH}$  = 6.5 Hz, 2H); <sup>31</sup>P NMR  $\delta$  23.79 (d,  $J_{PP}$  = 23.3 Hz,  $J_{PtP}$  = 2989 Hz), 16.98 (t,  $J_{PP}$  = 22.0 Hz,  $J_{PtP}$  = 2018 Hz). We assume the minor to be *cis*-

{(PPh<sub>3</sub>)<sub>2</sub>Pt[CH<sub>2</sub>C(PPh<sub>3</sub>)CPh]}(OTf): <sup>1</sup>H NMR  $\delta$  0.7 (s, 2H); <sup>31</sup>P NMR  $\delta$  5.20 (dd,  $J_{PP}$  = 37, 28 Hz), 19.5 (dd,  $J_{PP}$  = 33.0, 11 Hz), 20.0 (dd,  $J_{PP}$  = 28.1, 11 Hz). The data for the latter are

analogous to the spectral data of cis-{(PPh<sub>3</sub>)<sub>2</sub> $Pt[CH_2C(PPh_3)-$ <sup>7</sup>CH]}(BF<sub>4</sub>).<sup>14</sup>

Then <sup>n</sup>Bu<sub>4</sub>NCl (20.6 mg,  $7.4 \times 10^{-2}$  mmol) was added in the

tube containing the above mixture at room temperature. *cis*-Pt( $\eta^1$ -CH<sub>2</sub>C=CPh)(Cl)(PPh<sub>3</sub>)<sub>2</sub> was observed after 10 min in 91% yield, which isomerized to the trans isomer after 14 h at room temperature.

**Kinetic Measurements.** The oxidative addition reactions were followed spectrophotometrically using a U3500 recording spectrophotometer with the cell compartment thermostated to  $25 \pm 0.1$  °C. The rates of the reactions were measured by following the disappearance of the absorption due to the reactant Pt(0) complex at 410 nm. The measurements employed [PPh<sub>3</sub>] and [PhC=CCH<sub>2</sub>Cl] in sufficient excess over [Pt-(PPh<sub>3</sub>)<sub>4</sub>]. In each experiment, sample solutions were prepared under an N<sub>2</sub> atmosphere. The initial concentration ranges of PPh<sub>3</sub> and other species were as follows:  $6.69 \times 10^{-5}$  mol/L, Pt(PPh<sub>3</sub>)<sub>4</sub>;  $2.66 \times 10^{-3}$  to  $1.59 \times 10^{-2}$  mol/L, PhC=CCH<sub>2</sub>Cl;  $2.49 \times 10^{-3}$  to  $2.51 \times 10^{-1}$  mol/L, PPh<sub>3</sub>.

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**Supporting Information Available:** Figures giving plots of  $k_{obs}$  vs [PhC=CCH<sub>2</sub>Cl] in each run at a given [PPh<sub>3</sub>]. This material is available free of charge via the Internet at http://pubs.acs.org.

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