Kinetic Evidence for π-Complex Formation Prior to Oxidative Addition of Propargyl Halides to Triphenylphosphine−Platinum(0) Complexes

Takuma Nishida, Sensuke Ogoshi, Ken Tsutsumi, Yoshiaki Fukunishi, and Hideo Kurosawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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The mechanism of oxidative addition of phenylpropargyl halides to $Pt(PPh_3)_4$ to give $Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$ 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≡C bond to $Pt(PPh_3)_2$ to form $Pt(\eta^2\text{-}PhC{\equiv}CCH_2X)(PPh_3)_2$, which subsequently undergoes rapid collapse to the η^3-propargyl complex $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]X$ and eventually to *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$. The reaction of $Pt(PPh_3)_3$ may also involve a rate-determining C≡C bond coordination step.

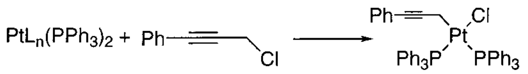
Introduction

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.[1] These exceptions involved the addition of sp^2-carbon−halogen compounds, where the formation of cis product is a logical outcome of the proposed mechanistic pathway.[2] In this respect it appears of special interest that Wojcicki and co-workers reported that oxidative addition reaction of $Pt(C_2H_4)(PPh_3)_2$ with $PhC{\equiv}CCH_2Br$ leads to the formation of *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Br)(PPh_3)_2$, which isomerizes further to the more stable trans isomer.[3] 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.[4] 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[5] 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[6] that the oxidative addition product $Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$ (X = Cl, Br) from $PhC{\equiv}CCH_2X$ 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 $PhC{\equiv}CCH_2Cl$ in the presence of excess PPh_3 (20 equiv) formed in toluene-d_8 at temperatures from −60 to 0 °C has the cis geometry (eq 1; $L = PPh_3$, $n = 2$). The cis



(1)

complex remained stable with respect to the cis−trans isomerization at 0 °C for 1 h, but the isomerization

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[1] 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.

[2] Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665.

[3] 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

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[5] 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.

10.1021/om000376l CCC: $19.00

Table 1. Kinetic Results of the Reaction of $Pt(PPh_3)_4$ with $PhC{\equiv}CCH_2Cl$

run	$[PPh_3]$ (mol/L)	$1/[PPh_3]$ (L/mol)	$k_{obs}/[PhC{\equiv}CCH_2Cl]$ (L/(mol s))
1	2.49×10^{-3}	4.02×10^{2}	5.10
2	4.00×10^{-3}	2.50×10^{2}	3.92
3	6.67×10^{-3}	1.50×10^{2}	3.21
4	2.50×10^{-2}	4.00×10	2.20
5	5.14×10^{-2}	1.95×10	2.14
6	1.03×10^{-1}	9.71	2.12
7	2.51×10^{-1}	3.98	2.09

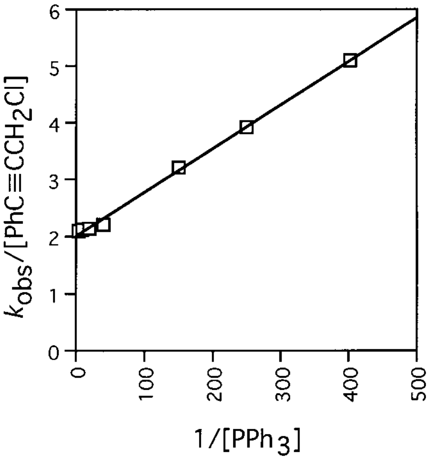


Figure 1. $1/[PPh_3]$ vs $k_{obs}/[PhC{\equiv}CCH_2Cl]$.

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 $PhC{\equiv}CCH_2Cl$ was also confirmed *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$ in toluene-d_8 at −30 °C (eq 1; $L = C_2H_4$, $n = 1$), as reported[3] in the corresponding reaction of the bromide.

Kinetics. The rates of the reaction of $Pt(PPh_3)_4$ with $PhC{\equiv}CCH_2Cl$ were measured spectrophotometrically in benzene at 25 °C. The measurements employed $[PhC{\equiv}CCH_2Cl]$ and $[PPh_3]$ in sufficient excess over the Pt complex, the initial concentration ranges being 6.99×10^{-5} mol/L for $Pt(PPh_3)_4$, 2.66×10^{-3} to 1.59×10^{-2} mol/L for $PhC{\equiv}CCH_2Cl$ and 2.49×10^{-3} to 2.51×10^{-1} mol/L for PPh_3. 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 $k_{obs}/[PhC{\equiv}CCH_2Cl]$ value at a given $[PPh_3]$ was obtained from slopes of plots of k_{obs} vs $[PhC{\equiv}CCH_2Cl]$. 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:

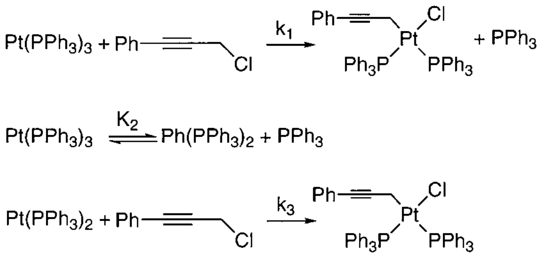
$$\frac{k_{obs}}{[PhC{\equiv}CCH_2Cl]} = 2.01 + 7.70 \times 10^{-3}\frac{1}{[PPh_3]} \qquad (2)$$

Discussion

It has been established[7] that $Pt(PPh_3)_4$ dissociates to the two active species $Pt(PPh_3)_3$ and $Pt(PPh_3)_2$ in solution. The concentration of $Pt(PPh_3)_4$ can be neglected under the kinetic conditions, since the equilibrium constant for the dissociation of this species is greater than 10 mol/L.[7] 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.

Table 2. Rate Constants for Reactions of $Pt(PPh_3)_3$ (k_1) and $Pt(PPh_3)_2$ (k_3)

substrate	k_1 (L/(mol s))	k_3 (L/(mol s))
$PhC{\equiv}CCH_2Cl$	2.0	4.8×10
CH_3I	3.5×10^{-3}	2.0×10^{-2}
$PhC{\equiv}CCH_3$	5.0×10^{-2}	2.0×10



(3)

(4)

(5)

Equations 3−5 give rise to the rate law shown in eq 6.[8]

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

The K_2 value of eq 4 has been previously evaluated as 1.6×10^{-4} mol/L (benzene, 25 °C) by Halpern,[9] which can be neglected relative to $[PPh_3]$ (the minimum being 2.5×10^{-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]

$$\frac{k_{obs}}{[PhC{\equiv}CCCH_2Cl]} = k_1 + k_3K_2\frac{1}{[PPh_3]} \qquad (7)$$

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 $PhC{\equiv}CCH_2Cl$, 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 $PhC{\equiv}CCH_2Cl$ were much larger (by an order of 10^3) than the corresponding rate constants of the oxidative addition reaction of CH_3I[8] (Table 2). The rates of the reaction of propargyl halides with a range of nucleophiles other than low-valent metal

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[7] Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

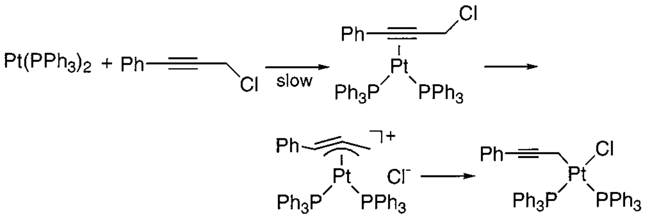
[8] Pearson, R. G.; Rajaram, J. *Inorg. Chem.* **1974**, *13*, 246.

[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,[11] giving the rate law $k_{obs}/[PhC{\equiv}CCH_2Cl] = k_1 + k_2/[(k_{-2}/k_3)[PPh_3] + [PhC{\equiv}CCH_2Cl]]$, where $K_2 = k_2/k_{-2}$. In the denominator of the second term $[PhC{\equiv}CCH_2Cl]$ (2.66×10^{-3} to 1.59×10^{-2} mol/L) could be neglected relative to $(k_{-2}/k_3)[PPh_3]$ under the kinetic conditions (k_{-2}/k_3 for $PhC{\equiv}CCH_3$ was observed[11] as 2.5×10^2). This gives a kinetic law consistent with eq 7. (b) The k_{-2} value was estimated as 5.7×10^3 L/(mol s) on the basis of the observed k_2 ($0.91\ s^{-1}$)[11] and the estimated value of K_2.[9] This, together with the known k_{-2}/k_3, leads us to estimate k_3 for the reaction of $PhC{\equiv}CCH_3$ shown in Table 2.

[11] Halpern, J.; Weil, T. A. *J. Chem. Soc., Chem. Commun.* **1973**, 631.

Scheme 1



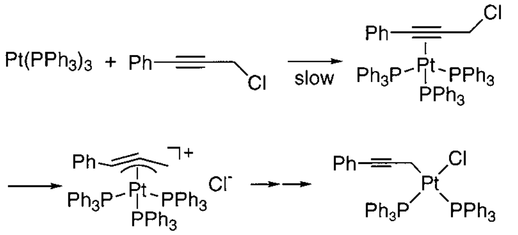
species are normally rather slower than those of CH_3I.[12] These results suggest the importance of the triple bond coordination to Pt(0) prior to or during the oxidative addition.

It is important to note that the k_3 value for the reaction of $PhC{\equiv}CCH_2Cl$ was similar to the rate of coordination of $PhC{\equiv}CCH_3$ to $Pt(PPh_3)_2$[10b] (Table 2). This result suggests that the rate-determining step of the oxidative addition of $PhC{\equiv}CCH_2Cl$ to $Pt(PPh_3)_2$ is the coordination of the triple bond. To gain further support for this notion, the competition between $PhC{\equiv}CCH_2Cl$ and $PhC{\equiv}CCH_2Br$ 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*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$, 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 $Pt(\eta^2\text{-}PhC{\equiv}CCH_2Cl)(PPh_3)_2$ from $Pt(PPh_3)_2$ and $PhC{\equiv}CCH_2Cl$ would be followed by rapid collapse of this complex to the ion pair $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]Cl$, which necessarily keeps two PPh_3 groups cis to each other (Scheme 1). It was also confirmed that the separately isolated cationic complex $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2](OTf)$ reacts readily with Cl^- to give *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$, as also reported[3] in the corresponding reaction with Br^-.

With regard to the reaction of $Pt(PPh_3)_3$, 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 $Pt(\eta^2\text{-}PhC{\equiv}CCH_3)(PPh_3)_3$ 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_3. On the other hand, in the case of the reaction of $PhC{\equiv}CCH_2Cl$ the $C{\equiv}C$ coordination complex $Pt(\eta^2\text{-}PhC{\equiv}CCH_2Cl)(PPh_3)_3$ formed first could undergo very facile ionization of the C−Cl bond to afford $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_3]Cl$ (Scheme 2). In a search for further support, the competitive experiment was carried out by employing an equimolar mixture of $PhC{\equiv}CCH_2Cl$ and $PhC{\equiv}CCH_2Br$ which are in excess relative to $Pt(PPh_3)_4$ in the presence of a high concentration of PPh_3 (1.66×10^{-1} mol/L), where the contribution of $Pt(PPh_3)_3$ species to the overall oxidative addition is expected to exceed 98%.[13] This reaction yielded *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$ 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.

Scheme 2



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 $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_3]Cl$ from $Pt(PPh_3)_3$ is converted to the observable kinetic product, *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$. The cationic 18-electron η^3-propargyl complex might undergo either dissociation of one PPh_3 to give $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]Cl$ or η^3 to η^1 conversion, which gives $[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(PPh_3)_3]Cl$. In fact, a separate treatment of $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]OTf$ with 1 equiv of PPh_3 resulted in the observation of NMR resonances attributable to the complex $[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(PPh_3)_3](OTf)$ together with additional minor resonances possibly due to *cis*-$\{(PPh_3)_2\overline{Pt[CH_2C(PPh_3)C}Ph]\}(OTf)$.[14] When further treated with Cl^-, the mixture was completely converted to *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$. It is likely that the cationic η^1-propargyl intermediate $[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(PPh_3)_3]Cl$ is formed before the observable cis product.[15]

Conclusions

The oxidative addition reaction of propargyl halides to $Pt(PPh_3)_4$ proceeded via the two active species $Pt(PPh_3)_2$ and $Pt(PPh_3)_3$. The rate-determining step of the reaction of $Pt(PPh_3)_2$ is the coordination of the triple bond of $PhC{\equiv}CCH_2X$, which is followed by rapid collapse of $Pt(\eta^2\text{-}PhC{\equiv}CCH_2X)(PPh_3)_2$ to $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2]Cl$ and finally to *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$. The rate-determining step of the reaction of $Pt(PPh_3)_3$ would also involve the coordination of the triple bond to form $Pt(\eta^2\text{-}PhC{\equiv}CCH_2X)(PPh_3)_3$, which then undergoes C−Cl bond cleavage without dissociation of PPh_3 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. ^1H and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a JEOL GSX-270 spectrometer. Kinetic measurements were carried out by using a

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[12] (a) Vernon, C. A. *J. Chem. Soc.* **1954**, 4462. (b) de la More, P. B. D. *J. Chem. Soc.* **1955**, 3169. (c) Hughes, E. D.; Ingold. C. K.; Mackie, J. D. H. *J. Chem. Soc.* **1955**, 3177.

[13] The second term of eq 2 amounts to ca. 4.64×10^{-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.

[15] A similar cationic 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^-, 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]

[16] Unpublished results.

Hitachi U3500 UV−vis spectrometer. Solvents and reagents were purchased from commercial vendors and distilled and degassed prior to use. Benzene, tetrahydrofuran, and hexane were purified by distillation from sodium benzophenone ketyl. CH_2Cl_2 and $CHCl_3$ were purified by distillation from CaH_2. Acetone was purified by distillation from sodium sulfate. Literature procedures were followed to synthesize $Pt(PPh_3)_4$, $Pt(PPh_3)_2(C_2H_4)$, *cis*-$Pt(CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$,[6] and $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2](OTf)$.[3]

Reaction of Ph≡CCH₂Cl with Pt(PPh₃)₄ in the Presence of a Large Excess of PPh₃. To a solution of $Pt(PPh_3)_4$ (4.9 mg, 3.9×10^{-3} mmol) and PPh_3 (19.1 mg, 7.3×10^{-2} mmol) in toluene-d_8 (0.6 mL) was added $PhC{\equiv}CCH_2Cl$ (1.1 mg, 7.3×10^{-3} mmol) at −78 °C. The reaction mixture was analyzed by ^1H and ^{31}P NMR at temperatures from −60 to 0 °C. The initial product was confirmed to be formed at −40 °C, whose ^{31}P NMR data coincided with those of *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$. Then the product began to isomerize to *trans*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$ at about 0 °C.

Reaction of PhC≡CCH₂Cl and PhC≡CCH₂Br with Pt(C₂H₄)(PPh₃)₂. To a solution of $Pt(C_2H_4)(PPh_3)_2$ (10.5 mg, 1.4×10^{-2} mmol) in toluene-d_8 (0.6 mL) were added $PhC{\equiv}CCH_2Cl$ (21.1 mg, 1.4×10^{-1} mmol) and $PhC{\equiv}CCH_2Br$ (27.4 mg, 1.4×10^{-1} mmol) at −78 °C. The reaction mixture was analyzed by ^1H and ^{31}P NMR at −30 °C. This reaction yielded *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$ in 1:1.5 ratio for X = Cl vs X = Br.

Reaction of PhC≡CCH₂Cl and PhC≡CCH₂Br with Pt(PPh₃)₄ in the Presence of a Large Excess of PPh₃. To a solution of $Pt(PPh_3)_4$ (12.1 mg, 1.0×10^{-2} mmol) and PPh_3 (26.6 mg, 1.0×10^{-1} mmol) in C_6D_6 (0.6 mL) were added $PhC{\equiv}CCH_2Cl$ (15.0 mg, 1.0×10^{-1} mmol) and $PhC{\equiv}CCH_2Br$ (20.0 mg, 1.0×10^{-1} mmol) at −20 °C. The reaction mixture was analyzed by ^1H and ^{31}P NMR at room temperature. The reaction yielded *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$ 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(η³-CH₂CCPh)(PPh₃)₂](OTf) with ⁿBu₄NCl. To a solution of $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2](OTf)$ (4.8 mg, 4.9×10^{-3} mmol) in CD_2Cl_2 (0.6 mL) was added $^nBu_4NCl$ (2.4 mg, 8.8×10^{-3} mmol) at −78 °C. The reaction mixture was analyzed by ^1H and ^{31}P NMR at −60 °C to room temperature to show the formation of *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$.

Reaction of [Pt(η³-CH₂CCPh)(PPh₃)₂](OTf) with ⁿBu₄NCl in the Presence of PPh₃. $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2](OTf)$ (13.8 mg, 1.4×10^{-2} mmol) and PPh_3 (3.7 mg, 1.4×10^{-2} mmol) in CD_2Cl_2 (0.6 mL) were added in an NMR tube at room temperature. The reaction mixture was analyzed by ^1H and ^{31}P NMR after 10 min. $[Pt(\eta^3\text{-}CH_2CCPh)(PPh_3)_2](OTf)$ disappeared almost completely, and instead two products (3:1 ratio) were visible. We assume the major product to be $[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(PPh_3)_3](OTf)$: ^1H NMR δ 1.18 (t, $J_{PH} = 6.5$ Hz, 2H); ^{31}P NMR δ 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*-$\{(PPh_3)_2\overline{Pt[CH_2C(PPh_3)C}Ph]\}(OTf)$: ^1H NMR δ 0.7 (s, 2H); ^{31}P NMR δ 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*-$\{(PPh_3)_2\overline{Pt[CH_2C(PPh_3)C}H]\}(BF_4)$.[14]

Then $^nBu_4NCl$ (20.6 mg, 7.4×10^{-2} mmol) was added in the tube containing the above mixture at room temperature. *cis*-$Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$ 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 ± 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 $[PPh_3]$ and $[PhC{\equiv}CCH_2Cl]$ in sufficient excess over $[Pt(PPh_3)_4]$. In each experiment, sample solutions were prepared under an N_2 atmosphere. The initial concentration ranges of PPh_3 and other species were as follows: 6.69×10^{-5} mol/L, $Pt(PPh_3)_4$; 2.66×10^{-3} to 1.59×10^{-2} mol/L, $PhC{\equiv}CCH_2Cl$; 2.49×10^{-3} to 2.51×10^{-1} mol/L, PPh_3.

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Supporting Information Available: Figures giving plots of k_{obs} vs $[PhC{\equiv}CCH_2Cl]$ in each run at a given $[PPh_3]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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