Platinum(0)−Enyne Complexes: The Platinum Analogue of an Intermediate in the Palladium(0)-Catalyzed Benzannulation of Conjugated Enynes

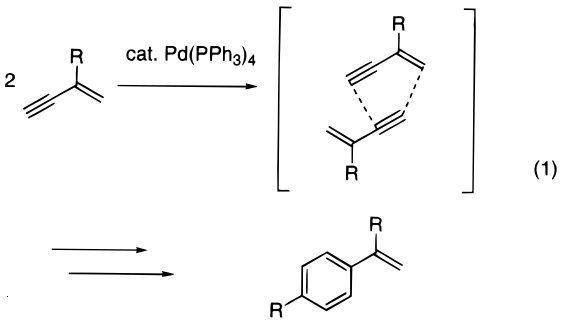
Shinichi Saito,*[,†] Kazushi Tando,[‡] Chizuko Kabuto,[‡] and Yoshinori Yamamoto*[,‡]

Institute for Chemical Reaction Science and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received April 18, 2000

Summary: Pt(0)−enyne π complexes, which could be the platinum analogues of an intermediate in the palladium-(0)-catalyzed benzannulation of conjugated enynes, were synthesized, and the structure and reactivity of the complexes were investigated.

For the mechanistic studies of synthetically important palladium catalyzed reactions, we frequently encounter difficulty in isolating and identifying the palladium intermediates, because they are highly reactive and unstable. In such cases, the corresponding platinum complexes are synthesized and employed for the mechanistic studies, since they are in general more stable and less reactive compared to the corresponding Pd complexes. This approach has been useful in elucidating the mechanism of the palladium-catalyzed reactions.[1] Recently we found a new Pd(0)-catalyzed *homo*-benzannulation of conjugated enynes (eq 1),[2] and the scope of



(1)

this reaction has been expanded significantly by the discovery of the *cross*-benzannulation reaction of enynes with diynes.[3,4] Though we initially assumed that the mechanism of the benzannulation reaction might be similar to that of the cyclotrimerization of alkynes, the reaction does not proceed in the presence of $CpCo(CO)_2$ or $RhCl(PPh_3)_2$ catalyst, which are efficient catalysts for the cyclotrimerization of alkynes.[2] In this paper we report the synthesis, structure, and reactivity of Pt(0)−enyne complexes, which provide further information for understanding the mechanism of the benzannulation of conjugated enynes in the presence of Pd(0) catalyst.

Results and Discussion

Conjugated enynes undergo cyclodimerization in the presence of $Pd(PPh_3)_4$.[2] Though it is clear that the conjugate enynes are initially activated by the formation of a complex between enynes and the Pd(0) species, it is not clear what kind of an intermediate is formed in the reaction and how such a complex activates the conjugated enynes. It is less likely that the insertion of the Pd(0) species into the acetylenic C−H bond becomes a key step for the benzannulation, since one result of our study indicated that the acetylenic C−H bond was not cleaved in the benzannulation,[2] and this assumption was confirmed by the fact that some 4-substituted enynes also cyclodimerized in the presence of Pd(0) catalyst.[4,6] We thought that the Pd(0)-enyne π complex, which should be a highly unstable compound, might be a possible intermediate.[7] Accordingly, we synthesized the corresponding Pt analogues and investigated their structure and reactivity.

Conjugated enynes **1a**,**b** reacted with Pt(0)-ethylene complexes **2a**,**b** in benzene at room temperature to give Pt(0)−enyne complexes **3a**−**d** in good yields (eq 2). The structures of **3a**−**d** were determined unambiguously by NMR and IR analysis. ^{1}H NMR spectrum of **1a** showed a signal integrated for one proton at 2.86 ppm (terminal acetylene). The signal at 2.86 ppm was not observed in the ^{1}H NMR spectrum of the complex **3a**, and instead a signal integrated for one proton appeared at 6.76 ppm, which was split into 12 peaks (4 strong peaks and 8 weak peaks). The coupling pattern could be explained in terms of the interaction of the proton with two nonequivalent ^{31}P nuclei (strong signals, $J(^{31}P-H)$ = 22.8, 11.0 Hz) and one ^{195}Pt nucleus (weak signals, $J(^{195}$-

† Institute for Chemical Reaction Science.
‡ Department of Chemistry, Graduate School of Science.

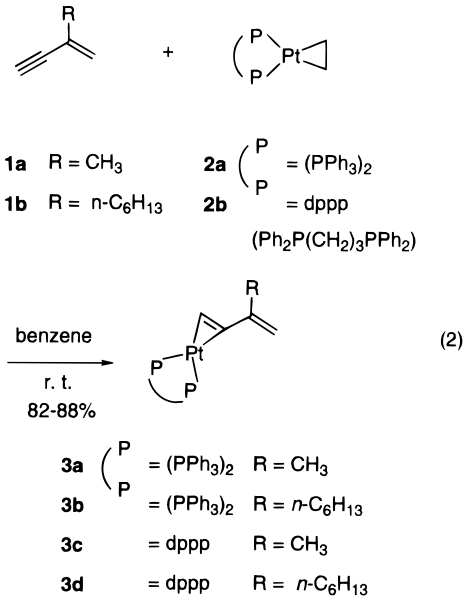
(1) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Able, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. VI, Chapter 39, pp 471−762.
(2) Saito, S.; Salter, M. M.; Gevorgyan, V.; Tsuboya, N.; Tando, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970−3971.
(3) (a) Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970−3971. (b) Gevorgyan, V.; Takeda, A.; Homma, M.; Sadayori, N.; Radhakrishnan, U.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 6391−6402.
(4) For reviews, see: Saito, S.; Yamamoto, Y. *Chem. Rev.*, in press. Gevorgyan, V.; Yamamoto, Y. *J. Organomet. Chem.* **1999**, *576*, 232−247.
(5) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−644. (b) Neeson, S. J.; Steverson, P. J. *Tetrahedron* **1989**, *45*, 6239−6248 and references therein.
(6) (a) Saito, S.; Tsuboya, N.; Chounan, Y.; Nogami, T.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7529−7532. (b) Gevorgyan, V.; Tando, K.; Uchiyama, N.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 7022−7025.
(7) Examples of Pd(0)−alkyne π complexes which contain internal alkynes have been reported. See ref 1, Vol. 6, Chapter 38.5 (Maitlis, P. M.; Espinet, P.; Russel, M. J. H.), pp 352−362. The first example of a Pd(0)−alkyne π complex to contain a terminal alkyne (ethyne) was recently reported by Pörschke et al. Pd(0)−ethyne π complexes are unstable at room temperature. See: Krause, J.; Bonrath, W.; Pörschke, K. R. *Organometallics* **1992**, *11*, 1158−1167.

10.1021/om000320r CCC: $19.00
Publication on Web 08/02/2000

Table 1. Selected ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt NMR Data for the Pt(0)−Enyne Complexes 3a−d[a]

compd	δ_H(≡CH)	J(HP)	J(HPt)	δ_C(≡CH)	J(CP)	J(CPt)	δ_P	J(PPt)	J(PP)	δ_{Pt}
1a	2.87			77.5						
3a	6.76	23, 11	25	131.7	67, 9	325	31.6	3580	37	−2601
							27.1	3460		
3c	*b*	*b*	*b*	115.6	70, 6	274	8.2	3330	30	−2734
							5.4	3190		
1b	2.87			77.5						
3b	6.72	23, 11	59	113.5	63, 8	260	31.7	3590	38	−2582
							27.1	3460		
3d	*b*	*b*	*b*	114.7	68, 6	274	8.2	3340	30	−2726
							5.2	3190		

[a] δ values are given in ppm and J values in Hz. [b] The signal overlapped with the signals of the aromatic protons.



Pt−H) = 24.8 Hz). It is also noteworthy that the signal of C≡C stretching (2104 cm^{-1} in **1a**) was not observed in the IR spectra of **3a**. Compounds **3b−d** also showed similar spectral features (Table 1). These results strongly indicate that the acetylenic moiety of the enyne reacted with the Pt(0) species, and we concluded that **1a**,**b** reacted with Pt(0)−ethylene complexes **2a,b** to give Pt(0)-enyne π-complexes **3a−d**. This result is in contrast to the results reported by Pörshke et al., who observed the formation of a mixture of Pd^0\{(1,2-η^2)-H_2C=CHC≡CH\} and Pd^0\{(3,4-η^2)-H_2C=CHC≡CH\} in the reaction of the Pd(0)−ethylene complex with vinylacetylene.[8] We assume that the observed difference was caused by the steric hindrance of the 2-alkyl group attached to the enyne.

The structure of **3c** was confirmed by an X-ray analysis (Figure 1).[9] The structure of **3c** was similar to those of the well-known Pt(0)−alkyne (Pt(0)−monoyne) complexes.[10] The C(1)−C(2) distance (1.297(6) Å) is close to the length of a standard C=C double bond.[11] It is noteworthy that the platinum atom, phosphorus atoms, and carbon atoms of the enyne moiety lie in a plane: the enyne moiety of **3c** could further interact with another enyne molecule without strong steric repulsion. It is reasonable to assume that the structure of the Pd(0)−enyne complex, which might be formed in the initial stage of the benzannulation reaction, is quite similar to the structure of this complex.

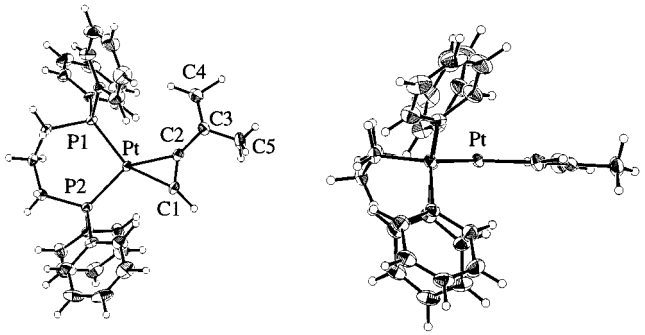


Figure 1. ORTEP drawings of **3c**. Ellipsoids are drawn at the 30% probability level.

In order to examine the stability of the π-complex, we carried out the ligand exchange experiments. Thus, complex **3b** was treated with **1** in toluene-d_8, and the reaction was monitored by NMR. The ligand exchange reaction took place at room temperature, and the reaction reached equilibrium in 2 h (eq 3). Since we observed the dissociation of a small amount of the ligand in the solutions of π-complex by NMR, we assume that the reaction proceeds via a dissociative pathway.

We examined the reactivity of the Pt(0)−enyne complexes **3** and found that the nucleophilicity of **3** was much higher compared to that of the corresponding conjugated enynes. Conjugated enynes only react with strong electrophiles such as HBr and acylium ion.[12] On the other hand, complex **3b** reacted with *hydrazine monohydrochloride*, a weaker electrophile, as well as

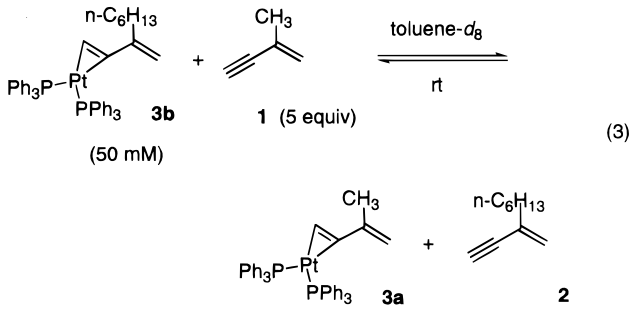
(8) Schager, F.; Bonrath, W.; Pörschke, K. R.; Kessler, M.; Krüger, C.; Seevogel, K. *Organometallics* **1997**, *16*, 4276−4286.

(9) Crystal data for **3c**: $C_{32}H_{32}P_2Pt$, yellow prism, 0.10 × 0.07 × 0.3 mm, monoclinic, $P2_1/c$, a = 10.732(1) Å, b = 15.706(1) Å, c = 16.871(1) Å, β = 101.081(7)°, V = 2790.8(7) Å^3, Z = 4, ρ_{calcd} = 1.603 g/cm^3, $2\theta_{max}$ = 125.4°, Cu Kα (λ = 1.541 78 Å), ω−2θ scans, T = 286 K. A total of 4936 reflections ((sin θ)/λ < 0.52) was measured, of which 4292 reflections with $I_o > 3\sigma(I_o)$ were used in the refinement. Data were corrected for Lorentz and polarization factors, and an empirical absorption correction using DIFABS method was applied by using the TEXSAN program package: μ(Cu Kα) = 102.57 cm^{-1}; minimum/maximum transition factors 0.7498−1.0000. The structure was solved by direct methods (SIR92). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The number of parameters was 317. The final R factor was 0.023 (R_w = 0.025). The final difference peaks were ρ_{max} = 0.89 and ρ_{min} = −1.09 e/Å^3. See the Supporting Information for the details of the crystallographic data.

(10) (a) Barlex, D. M.; Kemmitt, R. D. W.; Littlecott, G. W. *J. Chem. Soc. D* **1969**, 613−614. (b) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. D* **1970**, 1333−1335. (c) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667−2673. (d) Tripathy, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 3825−3826. (e) Tripathy, P. B.; Renoe, B. W.; Adzamli, K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 4406−4410.

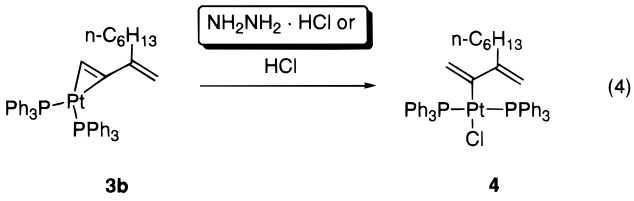
(11) Reference 1, pp 696−700.

(12) (a) Santelli-Rouvier, C.; Lefrere, S.; Mamai, M.; Santelli, M. *Tetrahedron Lett.* **1995**, *36*, 2459−2460. (b) Taylor, D. A. *Chem. Rev.* **1967**, *67*, 317−359.



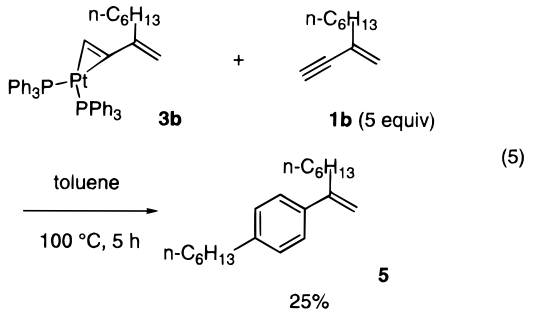
time (min)	ratio **3b** : **3a**	
5	0.81	0.19
40	0.24	0.76
120	0.13	0.87
24 h	0.13	0.87

HCl, to yield the corresponding Pt(II) σ-dienyl complex **4** (eq 4). The result can be explained by the increased



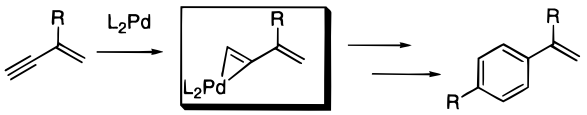
nucleophilicity of the enyne moiety on complexation. This result also indicates that the reactivity of the Pt(0)−enyne complex **3b** is even higher than that of the Pt(0)−monoyne complexes, since Pt(0)−monoyne complexes reacted only with strong acids such as HCl and trifluoroacetic acid to give Pt(II)−σ-alkenyl complexes,[13] while it did not react with a weak acid such as hydrazine hydrochloride.[10,14] Obviously, the reactivity (nucleophilicity) of the π complex is enhanced to a significant extent by attachment of an additional vinyl group. On the basis of these results, we assume that the nucleophilic reactivity of the corresponding Pd(0)−enyne complex is very high, which may play an imoprtant role in the benzannulation of the conjugated enynes.

The importance of the π-complex as an intermediate in the benzannulation is also shown in the reaction of Pt(0)−enyne complex **3b** with conjugated enynes. Complex **3b** reacted with **1b** to give the 1,4-disubstituted benzene **5** (eq 5). Though the reaction did not proceed catalytically and the yield was low (25%), it is clear that **3b** can become a partner for the cyclodimerization of conjugated enynes.[15] It is noteworthy that this reaction was inhibited by the addition of PPh_3 (1 equiv) to a



mixture of **1a** and **3b**, indicating that the dissociation of the ligand (PPh_3) or the coordination of **1a** with **3b** is essential for the reaction to proceed.

In summary, we isolated novel Pt(0)−enyne complexes **3** and showed the high reactivity of **3**. The activation of the acetylenic moiety of the conjugated enynes by the coordination of the Pt(0) species has been confirmed. The corresponding Pd(0)−enyne complex may be a possible reactive intermediate in the benzannulation of conjugated enynes (eq 6).



Experimental Section

Materials. Enyne **1a** was commercially available (Aldrich) and was purified by distillation (bp 32 °C). Enyne **1b** was synthesized by the reaction of dilithiated **1a** with 1-bromopentane.[16] The ethylene complexes **2a**,**b** were prepared by the reduction of the corresponding dichlorides in the presence of ethene.[17] ^{31}P NMR and ^{195}Pt NMR chemical shifts were referenced to H_2PO_4/D_2O and H_2PtCl_4/D_2O, respectively.

Praparation of Pt(0)−Enyne complexes 3a−d. General Procedure. To a solution of **2** (1 mmol) in dry benzene (15 mL) was added **1** (1.5−5 mmol) in dry benzene (15 mL) at room temperature under Ar. The solution was stirred at room temperature for 2 h. The solvent was removed by evaporation, and the residue was treated with pentane to give a pale yellow powder, which was separated by centrifuge separator. The Pt(0)−enyne complexes **3a**−**d** partially dissociated in $CDCl_3$, and the spectra were complicated due to the dissociation of the enyne and the weakness of some signals, which were coupled with other nuclei. Some signals are therefore missing.

[CH$_2$=CH(CH$_3$)C≡CH]Pt(PPh$_3$)$_2$ (3a). Yield: 82%. Mp: 111−115 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.4−7.1 (m, 30H), 6.76 (dd, $J(^{31}P-H) = 23$ Hz, 11.0 Hz, $J(^{195}Pt-H) = 25$ Hz, 1H), 4.71 (s, 1H), 4.37 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 136.9 (dd, $J(^{31}P-C) = 41$, 3 Hz, $J(^{195}Pt-C) = 26$ Hz), 136.4 (dd, $J(^{31}P-C) = 42$, 3 Hz, $J(^{195}Pt-C) = 26$ Hz), 134.1 (m), 133.8 (d, $J(^{31}P-C) = 13$ Hz, $J(^{195}Pt-C) = 19$ Hz), 131.7 (dd, $J(^{31}P-C) = 67$, 9 Hz, $J(^{195}Pt-C) = 325$ Hz), 128.9 (m), 127.6 (m), 118.1 (d, $J(^{31}P-C) = 4$ Hz, $J(^{195}Pt-C) = 32$ Hz), 114.6 (dd, $J(^{31}P-C) = 64$, 8 Hz, $J(^{195}Pt-C) = 260$ Hz), 25.1 (d, $J(^{31}P-C) = 6$ Hz, $J(^{195}Pt-C) = 46$ Hz). ^{31}P NMR (109 MHz, C_6D_6): δ 31.6 (d, $J(^{31}P-^{31}P) = 37$ Hz, $J(^{195}Pt-^{31}P) = 3580$ Hz), 27.1 (d, $J(^{31}P-^{31}P) = 37$ Hz, $J(^{195}Pt-^{31}P) = 3460$ Hz). ^{195}Pt NMR (57.9 MHz, C_6D_6): δ −2601 (dd, $J(^{195}Pt-^{31}P) = 3580$, 3460 Hz). IR (KBr): 3049 (m), 1684 (w), 1477 (m), 1435 (s), 1182 (w), 1094 (s), 1028 (w), 999 (w), 945 (m), 696 (s), 538 (w),

(13) (a) Chatt, J.; Rowe, G. A.; Williams, A. A. *Proc. Chem. Soc.* **1957**, 208−209. (b) Cook, C. D.; Allen, A. D. *Can. J. Chem.* **1964**, *42*, 1603−1068. (c) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879−3891.

(14) Pt(0)−cyclohexyne π complexes are more reactive than the Pt(0)−enyne π complexes we isolated. See: Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028−3030. Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750−1759.

(15) Though we expected to isolate another intermediate which may provide valuable information concerning a formal 1,3-hydride migration in the Pd(0)-catalyzed benzannulation reaction,[3,4] we could not characterize any Pt products we isolated from the reaction mixture. When we monitored the reaction by NMR, we observed the decomposition of the Pt complex in addition to the formation of **5**.

(16) Klusener, P. A. A.; Kulik, W.; Brandsma, L. *J. Org. Chem.* **1987**, *52*, 5261−5266.

(17) (a) Stang, P. J.; Song, L.; Halton, B. *J. Organomet. Chem.* **1990**, *388*, 215−220. (b) Appleton, T. G.; Bennett, M. A.; Tomkins, B. *J. Chem. Soc., Dalton Trans.* **1976**, 439−446.

519 (s), 511 (w), 500 (w) cm^{-1}. Anal. Calcd for $C_{46}H_{47}ClP_2Pt$: C, 61.92; H, 5.31; Cl, 3.97. Found: C, 62.09; H, 5.47; Cl, 3.95. A single crystal of this compound was obtained by recrystallization from hexane−CH_2Cl_2.

[CH_2=CH(*n*-C_6H_{13})C≡CH]Pt(PPh_3)$_2$ (3b). Yield: 82%. Mp: 61−63 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.4−7.1 (m, 30H), 6.72 (dd, $J(^{31}P-H)$ = 23, 11 Hz, $J(^{195}Pt-H)$ = 59 Hz), 4.66 (s, 1H), 4.37 (d, 1H, J = 2.6 Hz), 2.28 (t, 2H, J = 7.5 Hz), 1.52 (m, 2H), 1.23 (M, 6H), 0.88 (m, 3H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 138.9 (m), 136−138 (m), 134−135 (m), 128.9 (d, $J(^{31}P-C)$ = 4 Hz), 127.6 (d, $J(^{31}P-C)$ = 10 Hz), 117.1 (d, $J(^{31}P-C)$ = 4 Hz, $J(^{195}Pt-C)$ = 33 Hz), 113.5 (dd, $J(^{31}P-C)$ = 63, 8 Hz, $J(^{195}Pt-C)$ = 260 Hz), 38.9 (d, $J(^{31}P-C)$ = 6 Hz, $J(^{195}Pt-C)$ = 41 Hz), 31.8, 29.1, 28.5, 22.7, 14.1. ^{31}P NMR (109 MHz, C_6D_6): δ 31.7 (d, $J(^{31}P-^{31}P)$ = 38 Hz, $J(^{195}Pt-^{31}P)$ = 3590 Hz), 27.1 (d, $J(^{31}P-^{31}P)$ = 38 Hz, $J(^{195}Pt-C)$ = 3460 Hz). ^{195}Pt NMR (57.9 MHz, C_6D_6): δ −2582 (dd, $J(^{195}Pt-P)$ = 3590, 3460 Hz). IR (KBr): 3053 (w), 2928 (m), 2856 (w), 1684 (w), 1479 (m), 1435 (s), 1182 (w), 1094 (s), 1028 (w), 887 (w), 742 (m), 696 (s), 538 (m), 519 (s), 511 (s), 498 (w) cm^{-1}. Anal. Calcd for $C_{46}H_{46}P_2Pt$: C, 64.55; H, 5.42. Found: C, 64.58; H, 5.75.

[CH_2=CH(CH_3)C≡CH]Pt(dppp) (3c). Yield: 88%. Mp: 141−150 °C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.8−7.6 (m, 9H), 7.4−7.2 (m, 11H), 4.84 (s, 1H), 4.61 (s, 1H), 2.5 (m, 4H), 2.13 (s, 1H), 1.9 (m, 3H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 137 (m), 133 (m), 129.3 (d, $J(^{31}P-C)$ = 17 Hz), 128 (m), 118.1 (d, $J(^{31}P-C)$ = 4 Hz, $J(^{195}Pt-C)$ = 33 Hz), 115.6 (dd, $J(^{31}P-C)$ = 70, 6 Hz, $J(^{195}Pt-C)$ = 274 Hz), 28.9 (d, $J(^{31}P-C)$ = 100 Hz), 28.5 (d, $J(^{31}P-C)$ = 102 Hz), 24.8 (d, $J(^{31}P-C)$ = 6 Hz, $J(^{195}Pt-C)$ = 45 Hz), 21.0. ^{31}P NMR (109 MHz, C_6D_6): δ 8.2 (d, $J(^{31}P-^{31}P)$ = 30 Hz, $J(^{195}Pt-^{31}P)$ = 3330 Hz), 5.4 (d, $J(^{31}P-^{31}P)$ = 30 Hz, $J(^{195}Pt-^{31}P)$ = 3190 Hz). ^{195}Pt NMR (57.9 MHz, C_6D_6): δ −2734 (dd, $J(^{195}Pt-^{31}P)$ = 3330, 3190 Hz). IR (KBr): 3053 (m), 1668 (m), 1481 (m), 1435 (s), 1184 (w), 1153 (w), 1097 (m), 1028 (w), 966 (w), 895 (w), 827 (w), 789 (w), 743 (m), 696 (s), 665 (w), 513 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{32}P_2Pt$: C, 57.06; H, 4.79. Found: C, 56.95; H, 4.76.

[CH_2=CH(*n*-C_6H_{13})C≡CH]Pt(dppp) (3d). Yield: 87%. Yellow amorphous solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.7−7.5 (m, 9H), 7.1−7.3 (m, 12H), 4.74 (s, 1H), 4.56 (d, J = 2.6 Hz, 1H), 2.4 (m, 4H), 1.9 (m, 2H), 1.49 (m, 2H), 1.19 (m, 4H), 0.81 (m, 3H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 140.5 (m), 137 (m), 133 (m), 129.3 (d, J(^{31}P−C) = 16 Hz), 128 (m), 117.1 (d, $J(^{31}P-C)$ = 6 Hz, $J(^{195}Pt-C)$ = 33 Hz), 114.7 (dd, $J(^{31}P-C)$ = 68, 6 Hz, $J(^{195}Pt-C)$ = 274 Hz), 38.7 (d, $J(^{31}P-C)$ = 6 Hz, $J(^{195}Pt-C)$ = 40 Hz), 31.8, 29.2, 28.9 (d, $J(^{31}P-C)$ = 104 Hz), 28.7, 28.5 (d, $J(^{31}P-C)$ = 106 Hz), 22.7, 20.9, 14.1. ^{31}P NMR (109 MHz, C_6D_6): δ 8.2 (d, $J(^{31}P-^{31}P)$ = 30 Hz, $J(^{195}Pt-^{31}P)$ = 3340 Hz), 5.2 (d, $J(^{31}P-^{31}P)$ = 30 Hz, $J(^{195}Pt-^{31}P)$ = 3190 Hz). ^{195}Pt NMR (57.9 MHz, C_6D_6): δ −2726 (dd, $J(^{195}Pt-^{31}P)$ = 3340, 3190 Hz). IR (KBr): 3049 (w), 2926 (m), 2855 (w), 1665 (m), 1481 (w), 1435 (s), 1184 (w), 1153 (w), 1097 (s), 1028 (w), 999 (w), 966 (w), 893 (w), 831 (w), 792.7 (w), 742.5 (m), 694 (s), 664 (w), 513 (s) cm^{-1}.

Preparation of 4. (a) A solution of 10% (w/w) hydrogen chloride in MeOH (46 μL, 1 equiv) was added to a solution of **3b** in EtOH (2.8 mL) at 45 °C under Ar. The suspension was stirred at 45 °C for 10 min, cooled to room temperature, and stirred for 1 night at room temperature. The colorless powder that formed was collected by centrifuge and washed with EtOH to yield pure **4** (41 mg, 47%).

(b) A suspension of hydrazine hydrochloride (14 mg, 2 equiv) in dry EtOH (1.6 mL) was added to a solution of **3b** in dry EtOH (2.4 mL) at 45 °C under Ar. The suspension was stirred at 45 °C for 10 min, cooled to room temperature, and stirred for 1 day at room temperature. The colorless powder that formed was collected by centrifuge and washed with EtOH and water and then again with EtOH. Yield: 29 mg (33%). The same product was obtained when a mixture of hydrazine hydrochloride (14 mg, 2 equiv) and hydrazine hydrate (50 μL) was used instead of hydrazine hydrochloride (yield 39 mg, 44%).

***trans*-(PPh_3)$_2$PtCl[C(=CH_2)C(*n*-C_6H_{13})=CH_2] (4).** Mp: 218−221 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.7−7.8 (m, 12H), 7.3−7.4 (m, 18H), 6.07 (d, J = 2.6 Hz, 1H), 5.30 (s, $J(^{195}Pt-H)$ = 131 Hz, 1H), 4.78 (s, $J(^{195}Pt-H)$ = 71 Hz, 1H), 4.58 (s, 1H), 0.8−1.3 (m, 13H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 153.5, 147.9, 135.2 (d, $J(^{31}P-C)$ = 6.1 Hz), 131.0 (t, $J(^{31}P-C)$ = 27.4 Hz), 129.9, 127.6 (d, $J(^{31}P-C)$ = 5.4 Hz), 117.1, 116.1, 32.5, 31.8, 29.5, 28.2, 22.6, 14.1. ^{31}P NMR (109 MHz, $CDCl_3$): δ 24.1 (s, $J(^{195}Pt-^{31}P)$ = 3240 Hz). ^{195}Pt NMR (57.9 MHz, $CDCl_3$): δ −6470 (d, $J(^{195}Pt-^{31}P)$ = 3240 Hz). IR (KBr): 3055 (m), 2951 (w), 2926 (m), 2866 (w), 1556 (w), 1481 (m), 1435 (s), 1188 (m), 1096 (s), 866 (m), 758 (m), 743 (s), 704 (s), 692 (s), 519 (s), 500 (s) cm^{-1}. Anal. Calcd for $C_{46}H_{47}ClP_2Pt$: C, 61.92; H, 5.31; Cl, 3.97. Found: C, 62.09; H, 5.47; Cl, 3.95.

Reaction of 3b with 1b. A solution of **3b** (43 mg, 50 μmol), hexadecane (2 μL, internal standard), and **1b** (44 μL, 5 equiv) in dry toluene (0.5 mL) was heated at 100 °C under Ar. Five hours later, a part of the solution was analyzed by GC. The yield of **5**[2] was determined by an NMR analysis using hexadecane as an internal standard.

Supporting Information Available: Text and tables giving details of the X-ray crystallographic analysis of **3c** and figures giving ^{1}H and ^{13}C NMR spectra of **3a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000320R