Organometallic Transformations from an η^3-Propargyl or η^3-Allenyl Ligand to η^3-Hydroxyallyl, η^3-Heterotrimethylenemethane, and η^6-Diallyl Ether Species

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Abstraction of bromide ion from the allenyl complex *trans*-Pt(η^1-CHCCH$_2$)(Br)(PPh$_3$)$_2$ (**1**) with AgBF$_4$ leads to the formation of the new cationic unsubstituted η^3-propargyl complex [Pt(η^3-CH$_2$CCH)(PPh$_3$)$_2$](BF$_4$) (**2**(BF$_4$)). Unlike **1**, which is stable to air, complex **2** is highly susceptible to regioselective addition of water at the propargyl central carbon to form the hydroxyallyl complex [Pt(η^3-CH$_2$C(OH)CH$_2$)(PPh$_3$)$_2$](BF$_4$) (**3**). Further addition of **3** to **2** gives the cationic η^6-diallyl ether dinuclear complex [(PPh$_3$)$_2$Pt(η^3-(CH$_2$)$_2$C)]$_2$(O)(BF$_4$)$_2$ (**4**(BF$_4$)$_2$). The reaction of ethylenediamine with **2** yields the η^3-azatrimethylenemethane complex [Pt(η^3-CH$_2$C(NHCH$_2$CH$_2$NH$_2$)CH$_2$)(PPh$_3$)$_2$](BF$_4$) (**6a**(BF$_4$)), but that with **1** yields [Pt(η^1-CHCCH$_2$)(en)(PPh$_3$)](Br) (**5**). Such reactions suggest that the η^3-propargyl ligand could be subjected to direct external attack at its central carbon by a nucleophile. The η^1-allenyl complex, however, requires preceding coordination of the nucleophile to first result in a π-allene intermediate that then undergoes nucleophilic addition. Treatment of complex **3** with base gives the neutral η^3-oxatrimethylenemethane complex Pt(η^3-CH$_2$C(O)CH$_2$)(PPh$_3$)$_2$ (**7**). Addition of acid to **7** reverts it to **3**. Complex **4** reacts with Et$_2$NH to produce **7** along with 1 equiv of [Pt(η^3-CH$_2$C(NEt$_2$)CH$_2$)(PPh$_3$)$_2$](BF$_4$) (**6b**), presumably via regioselective nucleophilic substitution at the allyl central carbon. The X-ray single-crystal structures of **1** and **3** are provided.

Introduction

There has been an extensive research effort toward developing the chemistry of the transition-metal allenyl and propargyl complexes. Such complexes have been known to consist of a three-carbon skeleton that is generally prone to nucleophilic addition at its central carbon atom, thus providing synthetic routes to other organometallic derivatives, including metallacycles, metal clusters, etc.[1] They are also useful as building blocks for the synthesis of a variety of organic cyclopentanoids.[2] Most of the previously investigated mononuclear allenyl and propargyl complexes are in the η^1 bonding mode. Recently, new propargyl or allenyl complexes in the η^3 mode have been attracting great attention.[3] Among the reported examples, only two of them (including the one that we reported in a prior communication) involve an unsubstituted propargyl ligand.[4] Preliminary studies of these new organometallic species nevertheless indicate that η^3-propargyl species are also susceptible to nucleophilic addition at the central carbon, with more remarkable reactivity and in a more versatile fashion than their η^1 relatives. The obvious structural and chemical differences between η^3-propargyl and η^1-allenyl or other C$_3$ ligands, such as the well-studied π-allyl and metallacyclic derivatives, have drawn us to investigate such species further. We reveal in this article the synthesis and characterization of a

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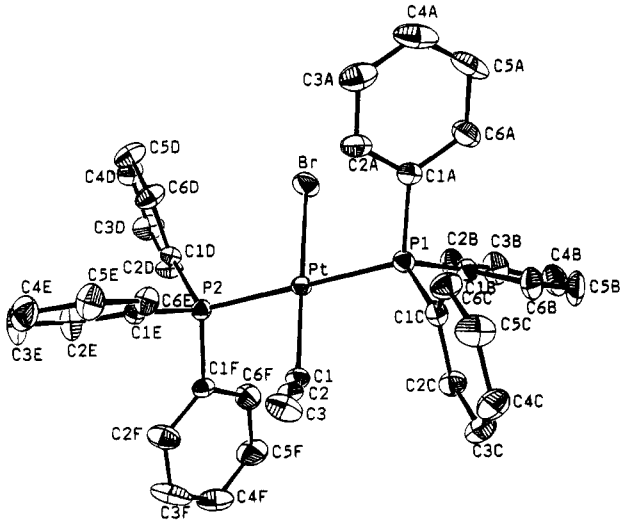
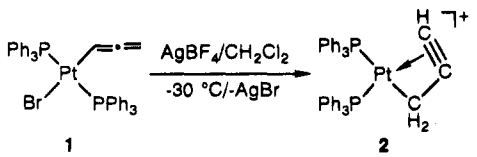


Figure 1. ORTEP drawing of *trans*-Pt(CHCCH$_2$)(Br)(PPh$_3$)$_2$ (**1**). All hydrogen atoms are omitted for clarity.

Scheme 1

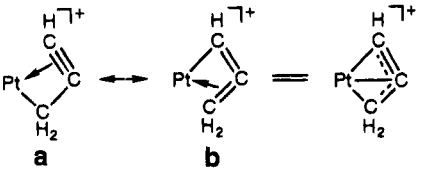


new cationic unsubstituted η^3-propargyl complex of platinum. Its susceptibility to water results in intriguing transformations, leading to η^3-hydroxyallyl and η^3-heterotrimethylenemethane species and a novel η^6-diallyl ether complex. In contrast with most of the other known π-allyl complexes, the β-substituted oxaallyl ligands tend to suffer regioselective nucleophilic attack at the central carbon instead of the terminal carbon. Relevant reaction mechanisms are discussed.

Results and Discussion

Synthesis and Characterization of the η^1-Allenyl Complex. Conventional oxidative addition of propargyl bromide to Pt(PPh$_3$)$_4$ provides *trans*-Pt(η^1-CHCCH$_2$)(Br)(PPh$_3$)$_2$ (**1**) in nearly quantitative yield. Characteristic ^{1}H NMR resonances due to the allenyl hydrogens are at δ 2.79 and 4.86 in a 2:1 ratio and are consistent with the literature data.[1a] The α-, β-, and γ-allenyl carbons of **1** were observed at δ 63.30, 204.75, and 75.55, respectively, in the ^{13}C NMR spectrum. The allenyl absorption in the infrared spectrum was found at 1922 cm^{-1}. These spectral data are typical of a linear η^1-allenyl ligand.[1] The X-ray structure of **1** is shown in Figure 1.[16] It possesses a square-planar trans geometry and indeed contains a linear allenyl ligand of which D(C1-C2) = 1.269 (8) Å, D(C2-C3) = 1.310 (8) Å and $\angle$(C1-C2-C3) = 178.7 (7)°. The angle of $\angle$(Pt-C1-C2) is 126.2 (5)° and the Pt-C1-C2 plane is perpendicular to the molecular plane, P1-C1-P2-Br, with the dihedral angle being 88 (2).°

Synthesis and Characterization of the η^3-Propargyl Complex. Abstraction of the bromide ion from **1** with 1 equiv of AgBF$_4$ in degassed anhydrous CH$_2$Cl$_2$ at −30 °C readily leads to the formation of the novel cationic unsubstituted η^3-propargyl complex [Pt(η^3-CH$_2$CCH)(PPh$_3$)$_2$](BF$_4$) (**2**(BF$_4$); Scheme 1). Recrystallization from CH$_2$Cl$_2$/Et$_2$O solutions at −20 °C gave whitish yellow solids. The isolated yields of **2** were around 90%. In various NMR spectra, all ^{1}H, ^{13}C, and ^{31}P resonances of **2** show coupling only to a single ^{195}Pt nucleus and to two ^{31}P nuclei, indicating that **2** is likely a mononuclear species with a novel η^3-propargyl ligand as shown by form **a**. The chemical shifts of propargyl hydrogens are



at δ 2.91 and 4.60 with an integration ratio of 2:1. The magnetic equivalency of the methylene hydrogens is probably due to rapid ligand fluxionality. In the ^{1}H-coupled ^{13}C NMR spectrum of **2**, a resonance at δ 101.6 with J_{C-P} = 2.7 and 4.7 Hz, $^2J_{C-H}$ = 29 Hz, and J_{C-Pt} = 58 Hz is assigned to the quaternary central carbon, a doublet at δ 90.8 with J_{C-H} = 246 Hz to the propargyl terminus CH, and a triplet of δ 51.8 with J_{C-H} = 171 Hz to the CH$_2$ group. The large J_{C-H} coupling constant corresponding to the methylene group suggests the possibility of a η^3-allenyl resonance structure as shown by form **b**. Such a highly strained C$_3$ feature also explains the unusually large values of J_{Pt-P} (which are 3810 and 4179 Hz) and the unusually small values of J_{Pt-C_t} (which are 105 and 137 Hz, respectively).[5-7] Our NMR data for **2** are reasonably consistent with those of its substituted analogues reported by Wojcicki and Stang, for which the planar structures of metal η^3-propargyl moieties were established by X-ray diffraction.[3j,l]

Reaction of the η^3-Propargyl Complex with Water. Our preliminary study on complex **2** has demonstrated that the reaction scope of **2** toward the nucleophiles is unique, and the η^1-allenyl derivatives are hardly competitive in activity with **2**.[4] In the solid state, **2** is reasonably stable under dry nitrogen but readily deteriorates in the air. It suffers slow thermal decomposition in anhydrous solutions at 20 °C, but it rapidly decays into many organometallic species in undried solutions. The stoichiometric reaction of **2** with water has been deliberately examined. At 25 °C, two products with comparable NMR data were observed. The prominent one designated as **3** resonated at δ 18.37 with J_{P-Pt} being 3634 Hz in the ^{31}P NMR spectrum. The minor product designated as **4** was shown at δ 15.96 with J_{P-Pt} being 3848 Hz. The yields of **3** were usually over 80% based on NMR integration, and a 78% yield was obtained after recrystallization from CH$_2$Cl$_2$/Et$_2$O.

When the reaction of complex **2** and water was carried out at 0 °C in CH$_2$Cl$_2$, the product **4** became most abundant. The relative yields of **4** to **3** were roughly 4:1 based on the ^{31}P NMR integration. An isolated sample of the mixture was redissolved in deliberately undried CDCl$_3$ and warmed to 50 °C. Both **3** and **4** were found to be stable, and their relative amounts were not changed at all. Compound **4** could be purified by

(5) The value of J_{P-Pt} for a P trans to a Pt−C(σ) bond is ~2000 Hz; the value of J_{C-Pt} for the carbon in the Pt−C(σ) bond is ~500 Hz.[6]

(6) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 39.

(7) For comparison: ^{1}H-coupled ^{13}C NMR data of [Pt(η^3-C$_3$H$_5$)(PPh$_3$)$_2$](BF$_4$) δ 119.1 (d, J_{C-H} = 163 Hz, J_{C-Pt} = 18.7 Hz, C$_c$), 69.8 (tdd, J_{C-H} = 161 Hz, J_{C-P} = 5.1, 32.2 Hz, J_{C-Pt} = 39.0 Hz, C$_t$); ^{31}P NMR δ 17.02 (J_{P-Pt} = 3989 Hz).

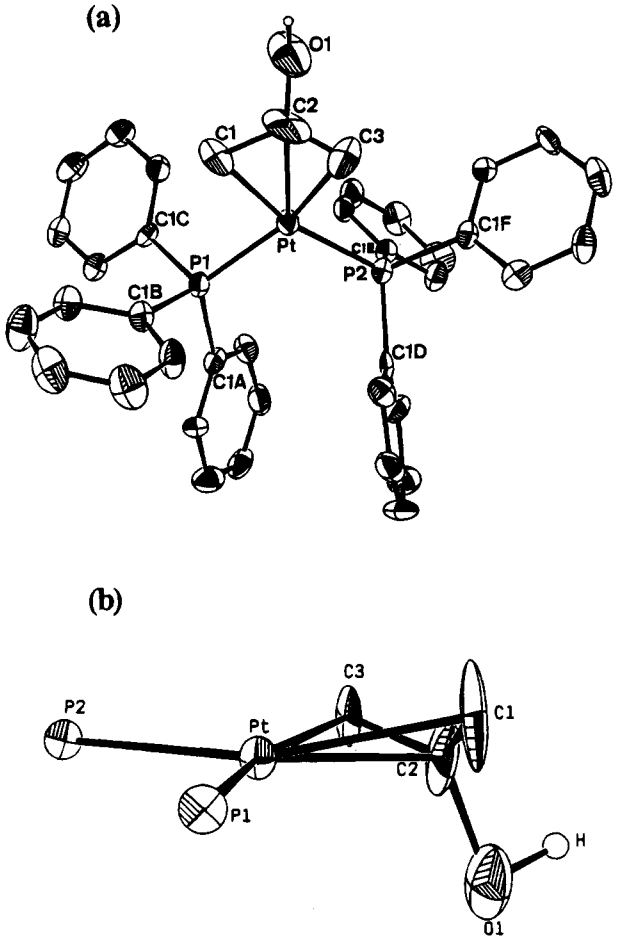
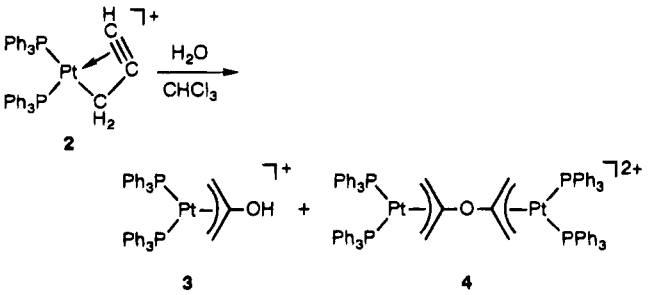


Figure 2. ORTEP drawing of $[Pt(\eta^3\text{-}CH_2C(OH)CH_2)(PPh_3)_2](BF_4)$ (**3**(BF_4)): (a) top view (the hydroxy hydrogen was located with a difference Fourier map and adjusted with a fixed O—H bond distance (0.95 Å); other hydrogen atoms are omitted for clarity); (b) side view (the phosphino phenyl groups are omitted for clarity).

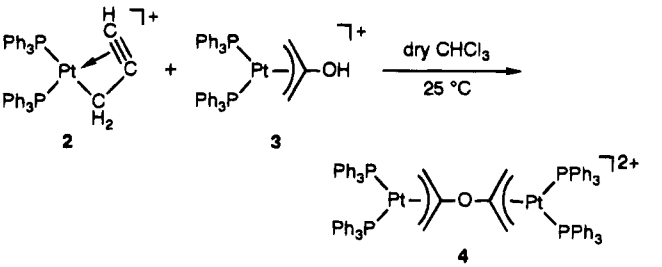
recrystallization from CH_2Cl_2/Et_2O cosolvents and a 50% final yield acquired.

Complex **3**(BF_4) is identified as the η^3-hydroxyallyl complex $[Pt(\eta^3\text{-}CH_2C(OH)CH_2)(PPh_3)_2](BF_4)$. In its ^1H NMR spectrum, a broad signal at δ 9.36 is assigned to the hydroxy proton, and the resonances of the allyl methylene appear at δ 2.32 and 3.25. The characteristic ^{13}C NMR data for the terminal carbons and the central allyl carbon was found at δ 53.0 and 155.3, respectively. Single crystals of **3** were grown from CH_2Cl_2/*n*-pentane. The X-ray analysis unequivocally confirms the η^3-hydroxyallyl skeleton as exhibited in Figure 2. Such a cationic complex is in a distorted square-planar configuration with ∠Cl—Pt—C3 = 65.5(7)° and ∠P1—Pt—P2 = 103.5(2)°. The three allyl carbon atoms are bonded to the metal center at roughly equal distances. $D(Pt—C_t)$ = 2.16(2), 2.18(2) Å; $D(Pt—C_c)$ = 2.16(2) Å. However, the central carbon of the unsubstituted η^3-allyl ligand in $[Pt(\eta^3\text{-}CH_2CHCH_2)(PPh_3)_2](BF_4)$ is drawn close to the metal with $D(Pt—C_t)$ = 2.16(2), 2.17(2) Å and $D(Pt—C_c)$ = 2.07 (2) Å)[8] and is inclined away from the metal in the η^3-oxatrimethylenemethane ligand (for instance in $Pt(\eta^3\text{-}CH_2C(O)CH_2)(PPh_3)_2$ (**7**, vide supra): $D(Pt—C_t)$ = 2.16(2), 2.17(2) Å; $D(Pt—C_c$ = 2.42(1) Å).[9] The length of the C2—O1 bond in **3**, evalulated as 1.52(3) Å, is surely a single-bond distance. The C1—C2 bond is 1.21(3) Å, and the C2—C3 bond is 1.41(3) Å. Such a difference is probably due to large anisotropic thermal motion of the allyl moiety. The dihedral angle between the C1—C2—C3 and C1—Pt—C3 planes is 61(3)°, which falls in the low range for π-allyl complexes (61—72°).[6] The corresponding angle is 63° in **7** and 95° in $[Pt(\eta^3\text{-}CH_2CHCH_2)(PPh_3)_2](BF_4)$. These data may be due to the fact that oxa substituents tend to impoverish the electron density of the central allyl carbon, so that the Pt—C_c bond will be weakened.

Scheme 2



Scheme 3



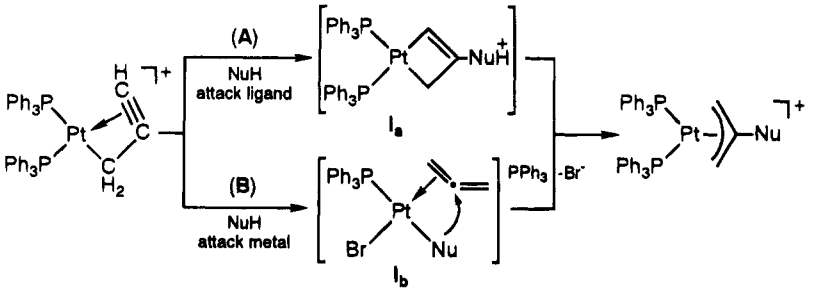
The NMR pattern of **4** is similar to that of β-substituted η^3-allyl complexes.[4b] It is certainly comparable to the data for **3**, although obviously distinguishable. Complex **4** is identified as an unprecedented diplatinum η^6-diallyl ether dication as illustrated in Scheme 2. Such a symmetric structure explains the simple NMR data and is strongly supported by FAB mass spectrometry. The slight discrepancy of the elemental analysis from the calculated values is probably the result of the solvent molecules trapped in the solid sample.

Reaction of the η^3-Propargyl Complex with the Hydroxyallyl Complex. In order to understand the mechanism of the formation of complex **4**, we have deliberately examined the reaction of the η^3-propargyl complex **2** with the hydroxyallyl complex **3** at 25 °C. Because water has been found in the microcrystalline sample of **3**, the solution of complex **3** was first dried with $MgSO_4$. It was then transferred to a deaerated solution of **2** through a cannula. The immediate product was indeed complex **4** in >80% yield (Scheme 3). When this reaction was carried out in undried solutions, **3** was again recovered as the major product. These experiments indicate that the reactivity of water with **2** has to be substantially higher than that with **3** at 25 °C. The mobility and solubility of water in $CHCl_3$ is markedly reduced below 0 °C. The first-formed complex **3**, therefore, gets a chance to react with the unreacted η^3-propargyl complex **2** to form **4**.

(8) (a) See supplementary material. (b) For the data of [(biphemp)-$Pt(\eta^3\text{-}C_3H_5)](ClO_4)$, see: *Helv. Chim. Acta* **1992**, *75*, 1211.

(9) (a) Fawcett, J.; Henderson, W.; Jones, M. D.; Kemmit, R. D.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991. (b) Jones, M. D.; Kemmit, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279.

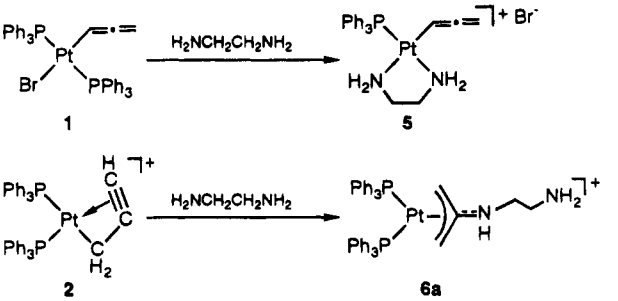
Scheme 4



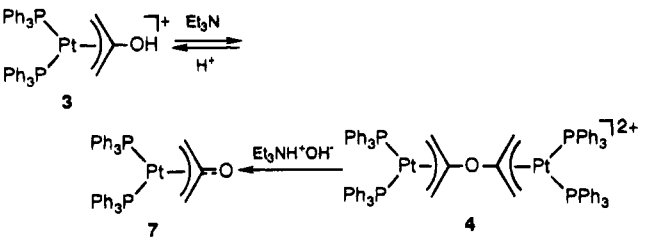
Mechanism of Nucleophilic Addition to the η^3-Propargyl and η^1-Allenyl Complexes. The reactivity of the η^3-propargyl complex **2** toward nucleophiles, particularly in comparison to that of the η^1-allenyl species, is peculiar and intriguing. It can be generally considered that there are two possible electrophilic sites in the cationic propargylplatinum(II) complex, which are the central carbon of the organic ligand and the platinum center. Therefore, two pathways may be considered for nucleophilic addition to the propargyl complexes as illustrated in Scheme 4. (A) Nucleophilic attack takes place directly at the central carbon of the propargyl ligand, first yielding the intermediate of metallacyclobutene $\mathbf{I_a}$. The ensuing protonation at the olefinic α-carbon of $\mathbf{I_a}$ then gives the product. (B) Coordination of a nucleophile to the metal center and protonation at the propargyl ligand first result in the η^2-allene intermediate $\mathbf{I_b}$.[10] The reaction is then accomplished by an intramolecular transfer of the nucleophile from the metal to the central carbon of π-allene. The facile reaction between complexes **2** and **3** suggests that the η^3-propargyl complex is likely to exploit path A. It should be difficult for the bulky **3** to penetrate the coordination sphere of **2**. Furthermore, formation of metallacyclobutene from nucleophilic attack at the highly strained η^3-propargyl ligand has been observed in the rhenium system.[3g]

The reactivity of a linear η^1-allenyl ligand (as in **1**) toward nucleophiles is perhaps too low to allow direct addition. On the other hand, coordinated π-olefins are known to be subject to nucleophilic attack.[14] Therefore, nucleophilic addition of complex **1** probably undergoes the substitution-controlled path B. As a result, good ligating compounds such as amines can react with **1**, at a much slower rate, however, than with **2**. Oxygen donor compounds such as alcohols and water which are known to be poor ligands for Pt(II) are unreactive to **1**. Further evidence is given by the distinct products obtained from analogous reactions of **1** and **2** with $H_2NCH_2CH_2NH_2$ (en). The former reaction affords the substituted product $[Pt(\eta^1\text{-}CHCCH_2)(PPh_3)(en)](Br)$ (**5**), which does not show any reactivity to en. In the latter reaction, the η^3-azatrimethylenemethane complex $[Pt(\eta^3\text{-}CH_2C(NHCH_2CH_2NH_2)CH_2)(PPh_3)_2](BF_4)$ (**6a**(BF_4)) is formed (Scheme 5).

Scheme 5



Scheme 6



Acid–Base Reactions between η^3-Hydroxyallyl and η^3-Oxatrimethylenemethane Complexes. The reaction of Scheme 3 indicates that the "allyl alcohol" in **3** contains an active hydrogen. Indeed, treatment of the η^3-hydroxyallyl complex **3** with 1 equiv of Et_3N instantaneously results in quantitative transformation of **3** to the neutral η^3-oxatrimethylenemethane complex $Pt(\eta^3\text{-}CH_2C(O)CH_2)(PPh_3)_2$ (**7**).[9] When the reaction of "wet" Et_3N with a mixture of **3** and **4** was monitored by ^{31}P NMR spectroscopy, it was found that complex **7** was immediately formed, mainly at the expense of **3**. After all of complex **3** disappeared, **7** continued to increase along with a continuing decrease of **4** prior to complete conversion. Addition of HBF_4 to **7** instantaneously reverts it to **3**. However, no recovery of **4** was ever observed. These reactions are summarized in Scheme 6.

The acid–base equilibrium between **3** and **7** is consistent with the independent results observed by Kurosawa and Ikeda.[11] Its facile reactivity is reasonably ascribed to direct intermolecular deprotonation and protonation. The formation of **7** from **4** with the assistance of Et_3N is unprecedented and may be rationalized by Scheme 7. The real nucleophile, which may be either amine or hydroxide ion (originating from trace water under basic conditions) first attacks at one of the central allyl carbons in the diallyl ether complex, presumably to cause a diplatina–allyl–cyclobutane intermediate, $\mathbf{I_c}$, which then decomposes to **3** and **7** via the cleavage of the C–O bond on the metallacyclobutane.[15] Such a mechanism is supported by an analogous reaction in which a secondary amine such as Et_2NH was

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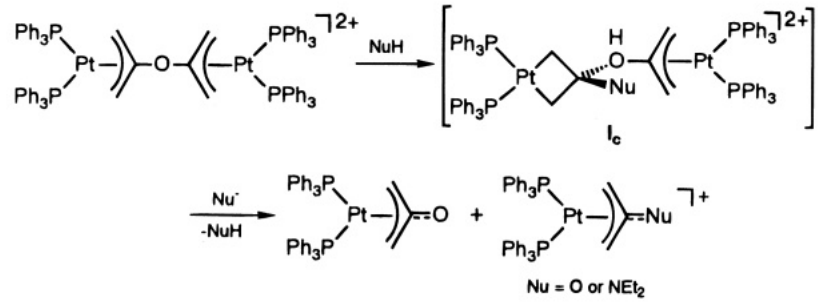
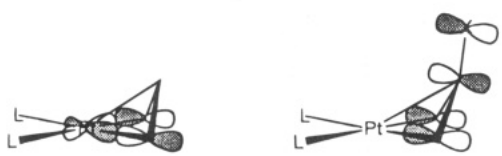
Scheme 7



employed to replace Et_3N. The reaction results in the formation of **7** along with $[Pt(\eta^3\text{-}CH_2C(NEt_2)CH_2)(PPh_3)_2](BF_4)$ (**6b**) in equimolar amounts. The complex **6b** has been reported in a previous communication.[1j] A detailed investigation of the chemistry of platina−azatrimethylenemethanes will be reported in a separate article.

The reactivity of the π-allyl complexes with nonhydrocarbyl substituents at the central carbon (C_c) has been rarely studied, mainly due to the paucity of such species. It is worthwhile to note that nucleophilic substituion on C_c in the diallyl ether ligand as shown in Scheme 7 is a chemical feature distinct from that of general allylplatinum complexes. It has been calculated that the coordinated π-allyl undergoes nucleophilic attack predominantly at the terminal carbons (C_t).[12] Such regioselectivity has been ascribed to electronic factors: first, the LUMO of the (π-allyl)platinum complexes (designated by $d_\pi - n_\pi^*$ as depicted in form **A**) is largely attributed to the p_π orbitals on C_t with a negligible contribution by C_c. Second, a cationic platinum(II) center would enhance the electrophilicity of C_t.[13]



On the other hand, the second LUMO (designated by π^* as depicted in form **B**) would be dependent on the substituent X. When X is H or an alkyl group, π^* will have higher energy than $d_\pi - n_\pi^*$. Nuclophilic attack at C_t as observed in most known examples of allyl ligands is expected. We assume that the strong electron-withdrawing substituent on C_c, particularly with available p_π orbitals, probably can stabilize π^* to the LUMO level and facilitate the formation of the C_c−Nu−bonded metallacyclobutane intermediate. In this case, regioselectivity of nucleophilic attack at C_c could become preferable. In order to more quantitatively describe the bonding of this system, theoretical calculation is necessary and will be carried out.

Conclusions

A cationic unsubstituted η^3-propargyl complex of platinum(II) with the formula $[Pt(\eta^3\text{-}CH_2CCH)(PPh_3)_2]^+$ has been conveniently prepared by removal of halide ion from *trans*-$Pt(\eta^1\text{-}CHCCH_2)(Br)(PPh_3)_2$. Such a synthetic strategy has provided a feasible methodology for the synthesis of η^3-propargyl derivatives of platinum or other transition metals. This η^3-propargyl complex belongs to a new class of organometallic species containing a highly strained MC_3 skeleton with planarity, according to relevant X-ray structural studies. As a result, remarkable reactivity toward external nucleophilic attack with exclusive regioselectivity on the central propargyl carbon has been discovered in these η^3-propargyl complexes. Our investigation of such chemical reactivity in the platinum system has led to facile transformation of the η^3-propargyl species to a substituted MC_3 constitution such as η^3-hydroxyallyl, η^3-oxatrimethylenemethane, η^3-azatrimethylenemethane, and η^6-diallyl ether ligands. These new platinum species demonstrate intriguing structural and chemical features which are distinct from those of relevant π-allyl complexes. Specifically, an electron-withdrawing substituent on the central carbon of the C_3 component may compete with the metal for the bond interaction. Consequently, the M−C_c bond is substantially weakened and regioselectivity of nucleophilic attack shifts from C_t to C_c.

Experimental Section

General Considerations. Commercially available reagents were purchased and used without purification. Solvents were dried by means of standard procedures. The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were routinely measured on Bruker ACE-200 and Bruker ACE-300 spectrometers. A Bruker AMX-500 spectrometer was used for collecting ^1H-coupled ^{13}C NMR data. For the ^{31}P NMR spectra, spectrometer frequencies of 81.015 and 121.49 MHz were employed, respectively; chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in $CDCl_3$. The corresponding frequencies for ^{13}C NMR spectra were at 50.32, 75.47, and 125.76 MHz for the respective spectrometers. Mass spectrometric analyses were collected on a JEOL SX-102A spectrometer. Elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer.

Synthesis and Characterization. ***trans*-Pt(η^1-CHCCH$_2$)(Br)(PPh$_3$)$_2$ (1).** To 30 mL of benzene which contained 2.1 g of $Pt(PPh_3)_4$ was added 0.24 mL (1.2 equiv) of propargyl bromide under dry N_2. The reaction solution turned colorless immediately. Further stirring for 30 min caused precipitation of the white product **1**. The solution was then concentrated to 15 mL and was filtered. White crystalline product in 96% yield (1.26 g) was recovered after washing with Et_2O. IR (KBr): $\nu_{C=C=C}$ 1922 cm^{-1}. ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 22.8 (J_{P-Pt} = 2996 Hz). ^1H NMR ($CDCl_3$): δ 4.86 (1H, tt, J_{H-H} = 6.4 Hz, J_{P-H} = 4.3 Hz, J_{Pt-H} = 114.6 Hz, C*H*), 2.79 (2H, dt, J_{H-H} = 6.4 Hz, J_{P-H} = 3.8 Hz, J_{Pt-H} = 57.0 Hz, CH_2). ^{13}C NMR ($CDCl_3$; 75.469 MHz): δ 63.3 (t, $^1J_{C-H}$ = 165 Hz, $^3J_{Pt-C}$ = 70.2 Hz, CH_2), 75.55 (dt, $^1J_{C-H}$ = 180 Hz, J_{P-C} = 9.2 Hz, $^1J_{Pt-C}$ = 888.5 Hz, *C*H), 204.75 (t, J_{P-C} = 3.5 Hz, C_β). Anal. Calcd for $C_{39}H_{33}BrP_2Pt\cdot H_2O$: C, 54.63; H, 4.12. Found: C, 53.48; H, 3.77.

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[Pt(η^3-CH_2CCH)(PPh_3)$_2$](BF_4) (2(BF_4)). To a mixture containing **1** (400 mg, 0.48 mmol) and $AgBF_4$ (103 mg, 0.53 mmol) was added 15 mL of N_2-degassed dry CH_2Cl_2 at −20 °C. The reaction solution was stirred for 20 min to allow the complete precipitation of AgBr. After AgBr was removed by filtration, the reaction solution was concentrated to about 2 mL. The addition of degassed dry Et_2O to the solution resulted in a whitish yellow solid product. The isolated yield of **2** was 90% (362 mg) after recrystallization. ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 11.5 (d, J_{P-P} = 20.0 Hz, J_{P-Pt} = 4179 Hz), 13.0 (d, J_{P-P} = 20 Hz, J_{P-Pt} = 3810 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.91 (2H, dd with H−Pt doublet satellites, J_{H-H} = 2.4 Hz, J_{P-H} = 6.5 Hz, J_{Pt-H} = 30.8 Hz, CH_2), 4.60 (1H, ddt with H−Pt doublet satellites, J_{H-H} = 2.4 Hz, J_{P-H} = 1.4, 8.1 Hz, J_{Pt-H} = 27.2 Hz, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 268 K, 50.324 and 125.76 MHz): δ 51.8 (ddt with C−Pt doublet satellites, J_{C-P1} = 39 Hz, J_{C-P2} unresolved, $^2J_{C-H}$ = 171 Hz, J_{C-Pt} = 105 Hz, −*C*H_2-CCH), 90.8 (ddd with C−Pt doublet satellites, J_{C-P1} = 2.7 Hz, J_{C-P2} = 49 Hz, $^1J_{C-H}$ = 246 Hz, J_{C-Pt} = 137 Hz; −CH_2*C*CH), 101.6 (ddd with C−Pt doublet satellites, J_{C-P} = 2.7, 4.7 Hz, $^2J_{C-H}$ = 29 Hz, J_{C-Pt} = 58 Hz, −CH_2*C*CH).

[Pt(η^3-$CH_2C(OH)CH_2$)(PPh_3)$_2$](BF_4) (3(BF_4)). The complex **2** was prepared from 300 mg (0.36 mmol) of **1** and 78 mg (0.4 mmol) of $AgBF_4$ in CH_2Cl_2 in situ. After removal of AgBr precipitate, the filtrate was warmed to 25 °C and was charged with 20 μL (1.11 mmol) of water. The reaction was allowed to last for another 1 h. The solution then was filtered again and concentration to about 5 mL in vacuo. Addition of 40 mL of Et_2O gave a whitish product in 78% isolated yield (240 mg). Single crystals suitable for X-ray diffraction were grown by slowly diffusing *n*-pentane into a CH_2Cl_2 solution of complex **3** at 5 °C. ^{31}P NMR ($CDCl_3$): δ 18.37 (J_{P-Pt} = 3634 Hz). ^1H NMR ($CDCl_3$): δ 2.32 (2H, dd, J_{H-H} = 4.3 Hz, J_{P-H} = 9.1 Hz, J_{Pt-H} ≈ 45 Hz, H_{anti}), 3.25 (2H, d, J_{H-H} = 4.3 Hz, H_{syn}), 9.36 (1H, br, O*H*). ^{13}C NMR ($CDCl_3$): δ 53.0 (dd, J_{P-C} = 4.8, 36.4 Hz, J_{Pt-C} = 120 Hz, C_t), 127−135 (phenyl carbons), 155.3 (t, J_{Pt-C} = 3.3 Hz, C_c). Anal. Calcd for $C_{39}H_{35}OP_2PtBF_4{\cdot}H_2O$: C, 53.09; H, 4.23. Found: C, 52.63; H, 3.74.

[(Ph_3P)$_2$Pt(η^3-$(CH_2)_2C$)]$_2$(O)(BF_4)$_2$ (4(BF_4)$_2$). Method I. A procedure similar to that used for the preparation of **4** was followed, except that water was added at 0 °C and the reaction was allowed to last for 12 h. The final yield for the diallyl ether complex was 50%.

Method II. In an alternative synthesis, 100 mg (0.12 mmol) of the allenyl complex **1** and 30 mg (0.15 mmol) of $AgBF_4$ were dissolved in 15 mL of anhydrous CH_2Cl_2 at −20 °C. After 20 min, the AgBr precipitate was removed by filtration. The filtrate was transferred to an anhydrous CH_2Cl_2 solution containing 115 mg (0.13 mmol) of complex **3** under dry nitrogen. The reaction mixture was warmed to room temperature and allowed to continue for 10 h. Addition of Et_2O to the concentrated solution gave white product in 83% isolated yield (170 mg). ^{31}P NMR ($CDCl_3$): δ 15.96 (J_{P-Pt} = 3848 Hz). ^1H NMR ($CDCl_3$): δ 3.22 (2H, br, H_{syn}), 3.55 (2H, dd, J_{H-H} = 6.5 Hz, J_{P-H} = 8.0 Hz, J_{Pt-H} = 37 ± 3 Hz, H_{anti}). ^{13}C NMR ($CDCl_3$): δ 58.6 (d, J_{P-C} = 33.4 Hz, J_{Pt-C} = 85 Hz, C_t), 128−134 (phenyl carbons), 145.8 (s, J_{Pt-C} = 17 Hz, C_c). Anal. Calcd for $C_{78}H_{68}OP_4Pt_2B_2F_8{\cdot}H_2O$: C, 54.19; H, 4.08. Found: C, 53.31; H, 3.88; MS (FAB): $M^+ - BF_4$, *m/z* 1622.

[Pt(η^1-$CHCCH_2$)($H_2NCH_2CH_2NH_2$)(PPh_3)](Br) (5(Br)). To 20 mL of a chloroform solution containing 80 mg (0.095 mmol) of **1** was added 7.01 μL (1.1 equiv) of ethylenediamine. The reaction solution was stirred for 25 min. A white precipitate of **5** was obtained. The solution was then concentrated to 4 mL. White crystalline product was recovered by filtration. The isolated yield was 68% (42 mg) after washing with Et_2O. IR (KBr pellet): $\nu_{C=C=C}$ 1903 cm^{-1}. ^{31}P NMR (CD_3OD): δ 17.9 (J_{P-Pt} = 3968 Hz). ^1H NMR (CD_3OD): δ 7.19, 7.36, 7.48 (15H, m, m, m, phenyl hydrogens), 5.02 (1H, td, J_{H-H} = 6.6 Hz, J_{H-P} = 9.5 Hz, J_{H-Pt} = 82.8 Hz, C*H*CCH$_2$), 3.86 (2H, dd, J_{H-H} = 6.6 Hz, J_{H-P} = 0.6 Hz, J_{H-Pt} = 45.1 Hz, CHCCH_2), 2.82 (4H, m, CH_2 (en)). ^{13}C NMR (CD_3OD): δ 205.9 (t, J_{P-C} = 24.2 Hz, CH*C*CH$_2$), 127−134 (phenyl carbons), 65.8 (t, J_{C-Pt} = 50.5 Hz, CHC*C*H$_2$), 63.7 (dt, J_{C-P} = 10.1 Hz, J_{C-Pt} = 875 Hz, *C*HCCH$_2$), 46.4, 45.8 (*C*H$_2$ (en)). Anal. Calcd for $C_{23}H_{26}N_2$-BrPPt: C, 43.41; H, 4.11. Found: C, 43.30; H, 3.82.

[Pt(η^3-$CH_2C(NHCH_2CH_2NH_2)CH_2$)($PPh_3$)$_2$]($BF_4$) (6a($BF_4$)). To a dry $CDCl_3$ solution containing 90 mg of **2** (0.11 mmol) was added 6.05 μL (0.85 equiv) of ethylenediamine under dry N_2 at 0 °C. The yellow solution was stirred for 10 min and then concentrated. Addition of Et_2O gave the yellow solid product. The primary isolated yield of **6a** was 62%. **6a** is subject to decomposition, which causes difficulties in purification. Spectral data thus were used for identification. IR (KBr pellet): ν_{N-H} 3450 cm^{-1}, $\nu_{C=N}$ 1557 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 17.6 (J_{P-Pt} = 3302 Hz), 18.5 (J_{P-Pt} = 3433 Hz). ^1H NMR ($CDCl_3$): δ 7.19, 7.36, 7.48 (30H, m, m, m, phenyl hydrogens), 6.51 (1H, m, N*H*), 3.96 (2H, br, H_{syn}), 3.14 (2H, br, H_{anti}), 2.86 (4H, br, CH_2 (en)), 2.68 (2H, br, NH_2). ^{13}C NMR ($CDCl_3$): δ 154.0 (J_{Pt-C} = 94.3 Hz, C_c), 125−134 (phenyl carbons), 46.5, 41.2 (*C*H$_2$ (en)), 44.4, 44.5 (C_t).

[Pt(η^3-$CH_2C(NEt_2)CH_2$)(PPh_3)$_2$](BF_4) (6b(BF_4)). To a dry $CDCl_3$ solution containing 20 mg of **4** was added 2 equiv of Et_2NH at 25 °C. The product **6b** was identified by comparing the spectral data with those of an authentic sample.[1j] IR (KBr): $\nu_{C=N}$ 1609, 1585 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 18.1 (d, J_{P-Pt} = 3252 Hz). ^1H NMR ($CDCl_3$): δ 3.08 (4H, q, J_{H-H} = 7.1 Hz, J_{P-H} = 6.6 Hz, CH_3CH_2), 2.28 (4H, br, CH_2), 0.99 (6H, t, J_{H-H} = 7.1 Hz, CH_3CH$_2$). ^{13}C NMR ($CDCl_3$): δ 157.55 (dd, *C*N), 43.89 (t, J_{Pt-C} = 6.5 Hz, CH_3CH_2), 39.91 (dd, J_{P-C} = 4.6 Hz, J_{Pt-C} = 50.9 Hz, *C*H$_2$), 12.82 (t, J_{Pt-C} = 5.2 Hz, *C*H$_3$CH$_2$).

Pt(η^3-$CH_2C(O)CH_2$)(PPh_3)$_2$ (7). To 1 mL of $CDCl_3$ containing 30 mg of **3** was added 5 μL of Et_3N. The reactant complex that was monitored by NMR spectroscopy turned to **4** exclusively within 10 min. White crystalline product in 71% yield (19 mg) was recovered by recrystallization. A similar reaction from complex **4** took about 12 h to complete. The NMR data for **7** are in good agreement with those reported by Kemmit and his co-workers.[9] ^{31}P NMR ($CDCl_3$): δ 22.3 (J_{P-Pt} = 3103 Hz). ^1H NMR ($CDCl_3$): δ 2.31 (4H, d, J_{P-H} = 3.2 Hz, J_{Pt-H} = 44 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 177.5 (*s*, C_c), 127−135 (phenyl carbons), 50.8 (dd, J_{P-C} = 5, 51 Hz, J_{Pt-C} = 217 Hz, C_t).

X-ray Crystallographic Analysis. Diffraction data were measured at 298 K on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo K_α radiation. Cell parameters were determined by a least-squares fit of 25 reflections.

Table 1. X-ray Crystal Parameters and Data Collection Details for *trans*-Pt(η^1-$CHCCH_2$)(Br)(PPh_3)$_2$ (1) and [Pt(η^3-$CH_2C(OH)CH_2$)(PPh_3)$_2$](BF_4) (3(BF_4))

	1	3
formula	$C_{39}H_{33}P_2BrPt$	$C_{39}H_{36}OP_2PtBF_4{\cdot}H_2O$
fw	837.61	882.56
cryst dimens, mm	0.13 × 0.25 × 0.4	0.2 × 0.2 × 0.25
space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	10.826(3)	11.674(2)
b, Å	9.593(2)	20.829(3)
c, Å	32.320(6)	15.019(3)
β, deg	91.64(2)	92.69(2)
V, Å^3	3355(1)	3648(1)
Z	4	4
ϱ(calcd), Mg m^{-3}	1.658	1.607
F(000)	1640	1704
Mo Kα radiation, λ, Å	0.7107	0.7107
T, K	300	300
μ, mm^{-1}	5.52	4.02
transmission	0.69−1.0	0.92−1.0
max, 2θ, deg	50	45
hkl	±12,11,38	±12,22,16
no. of rflns measd	5895	4753
no. of rflns obsd	4201 (>2.0σ)	3058 (>2.0σ)
no. of variables	389	398
R(*F*)	0.030	0.049
$R_w(F)$	0.023	0.047
S	1.38	2.15
$(\Delta/\sigma)_{max}$	0.015	0.061

Table 2. Selected Bond Distances (Å) and Angles (deg) for *trans*-Pt(η^1-CHCCH$_2$)(Br)(PPh$_3$)$_2$ (1)

Pt–P1	2.313(2)	Pt–P2	2.307(2)	Pt–Br	2.4914(8)
Pt–C1	2.040(5)	C1–C2	1.269(8)	C2–C3	1.310(8)
P1–Pt–P2	176.44(6)	P1–Pt–C1	92.5(2)	P1–Pt–Br	89.36(5)
P2–Pt–C1	85.7(2)	P2–Pt–Br	92.68(4)	C1–Pt–Br	176.0(2)
Pt–C1–C2	126.2(5)	C1–C2–C3	178.7(7)		

Table 3. Atomic Coordinates and Isothermal Data for Non-Hydrogen Atoms of Complex 1 with Esd's in Parentheses

	x	*y*	*z*	B_{eq}, Å^2
Pt	0.130651(23)	0.228233(24)	0.132474(7)	2.360(10)
Br	0.27907(7)	0.10605(8)	0.180344(21)	4.55(4)
P1	0.25935(15)	0.18203(17)	0.07823(5)	2.73(7)
P2	−0.00749(14)	0.26769(17)	0.18424(4)	2.59(7)
C1	0.0115(5)	0.3408(6)	0.09559(17)	2.7(3)
C2	−0.0594(6)	0.2926(6)	0.06707(18)	3.2(3)
C3	−0.1304(6)	0.2430(7)	0.03703(19)	4.5(3)
C1A	0.3067(6)	−0.0006(6)	0.07736(17)	3.0(3)
C2A	0.2222(6)	−0.1003(7)	0.08653(20)	4.2(4)
C3A	0.2505(7)	−0.2398(7)	0.08442(20)	5.4(4)
C4A	0.3669(8)	−0.2800(8)	0.07372(21)	6.3(4)
C5A	0.4554(7)	−0.1806(8)	0.06590(22)	6.1(4)
C6A	0.4249(6)	−0.0409(7)	0.06701(20)	4.3(4)
C1B	0.4019(5)	0.2854(6)	0.07913(16)	2.9(3)
C2B	0.4503(6)	0.3336(7)	0.11562(18)	3.6(3)
C3B	0.5573(6)	0.4107(8)	0.11648(21)	4.8(4)
C4B	0.6181(6)	0.4386(8)	0.08136(22)	5.1(4)
C5B	0.5714(6)	0.3910(8)	0.04431(21)	5.3(4)
C6B	0.4630(6)	0.3138(7)	0.04289(18)	4.3(4)
C1C	0.1976(5)	0.2099(6)	0.02566(16)	2.8(3)
C2C	0.1743(6)	0.3459(6)	0.01230(19)	3.4(3)
C3C	0.1281(6)	0.3712(7)	−0.02720(20)	4.4(3)
C4C	0.1043(6)	0.2612(8)	−0.05319(17)	4.9(4)
C5C	0.1246(7)	0.1262(7)	−0.04024(20)	5.2(4)
C6C	0.1709(6)	0.1008(7)	−0.00063(18)	3.9(4)
C1D	0.0373(5)	0.2117(6)	0.23591(16)	2.6(3)
C2D	0.0734(6)	0.3011(6)	0.26739(18)	3.7(3)
C3D	0.1100(6)	0.2486(7)	0.30567(17)	4.6(4)
C4D	0.1128(6)	0.1085(7)	0.31274(18)	4.3(4)
C5D	0.0773(7)	0.0176(7)	0.28183(19)	4.7(4)
C6D	0.0398(7)	0.0686(6)	0.24394(19)	4.3(4)
C1E	−0.1548(5)	0.1768(6)	0.17645(17)	2.9(3)
C2E	−0.2353(6)	0.1844(7)	0.20606(19)	4.7(4)
C3E	−0.3558(6)	0.1151(9)	0.19971(22)	5.7(4)
C4E	−0.3759(6)	0.0354(8)	0.16508(23)	5.3(4)
C5E	−0.2865(6)	0.0268(7)	0.13593(20)	4.6(4)
C6E	−0.1752(6)	0.0963(6)	0.14133(18)	3.4(3)
C1F	−0.0426(6)	0.4548(6)	0.18715(17)	2.8(3)
C2F	−0.1611(6)	0.5052(7)	0.18271(22)	4.8(4)
C3F	−0.1824(7)	0.6472(8)	0.1815(3)	6.7(5)
C4F	−0.0862(7)	0.7381(7)	0.18592(21)	5.9(4)
C5F	0.0323(7)	0.6892(7)	0.19082(24)	5.8(5)
C6F	0.0548(6)	0.5468(7)	0.19079(21)	4.4(4)

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Pt(η^3-CH$_2$C(OH)CH$_2$)(PPh$_3$)$_2$](BF$_4$) (3(BF$_4$))

Pt–P1	2.281(4)	Pt–P2	2.288(4)	Pt–C1	2.16(2)
Pt–C2	2.16(2)	Pt–C3	2.18(2)	C1–C2	1.21(3)
C2–C3	1.41(3)	C2–O1	1.52(3)		
P1–Pt–P2	103.5(2)	P1–Pt–P1	97.7(6)	P1–Pt–C2	126.1(6)
P1–Pt–C3	163.1(4)	P2–Pt–C1	155.7(7)	P2–Pt–C2	130.2(6)
P2–Pt–C3	93.2(4)	C1–Pt–C2	32.5(8)	C1–Pt–C3	65.5(7)
C2–Pt–C3	37.8(7)	Pt–C1–C2	74(1)	Pt–C2–C1	74(1)
Pt–C2–C3	72(9)	Pt–C3–C2	71(1)	Pt–C2–O1	116(1)
C1–C2–C3	127(2)	C1–C2–O1	119(2)	C3–C2–O1	112(2)

Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at an ideal geometry and a C–H distance of 1.0 Å; their isotropic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from ref 17a.

Table 5. Atomic Coordinates and Isothermal Data for Non-Hydrogen Atoms of Complex 3 with Esd's in Parentheses

	x	*y*	*z*	B_{eq}, Å^2
Pt	0.04512(6)	0.13029(3)	0.16776(4)	2.89(3)
P1	0.0490(4)	0.23862(19)	0.1898(3)	2.93(20)
P2	0.0534(4)	0.08953(20)	0.3094(3)	2.92(21)
C1	−0.0022(21)	0.1314(10)	0.0267(10)	9.5(15)
C2	0.0499(20)	0.0818(11)	0.0406(11)	8.8(15)
C3	0.0301(17)	0.0358(8)	0.1066(9)	5.4(10)
C1A	−0.0658(13)	0.2650(7)	0.2580(9)	3.1(7)
C2A	−0.1756(13)	0.2427(8)	0.2315(10)	3.8(8)
C3A	−0.2689(13)	0.2636(9)	0.2746(11)	5.0(10)
C4A	−0.2516(15)	0.3057(9)	0.3469(11)	5.7(10)
C5A	−0.1460(15)	0.3270(9)	0.3737(11)	5.2(10)
C6A	−0.0522(15)	0.3067(7)	0.3275(11)	3.9(8)
C1B	0.1851(12)	0.2697(7)	0.2341(9)	2.7(7)
C2B	0.1996(13)	0.3354(7)	0.2514(11)	4.2(9)
C3B	0.3044(14)	0.3583(9)	0.2814(12)	5.9(10)
C4B	0.3977(13)	0.3191(9)	0.2902(11)	5.2(10)
C5B	0.3844(14)	0.2559(9)	0.2714(12)	5.3(10)
C6B	0.2767(13)	0.2297(7)	0.2429(10)	3.5(8)
C1C	0.0331(12)	0.2858(7)	0.0857(9)	3.0(8)
C2C	−0.0686(13)	0.3194(8)	0.0612(10)	3.8(8)
C3C	−0.0737(13)	0.3550(8)	−0.0167(10)	4.4(9)
C4C	0.0174(15)	0.3565(8)	−0.0686(10)	4.8(9)
C5C	0.1150(14)	0.3237(8)	−0.0464(10)	4.2(9)
C6C	0.1215(13)	0.2884(7)	0.0304(10)	3.7(8)
C1D	0.0357(12)	0.1410(7)	0.4064(9)	3.3(8)
C2D	−0.0566(12)	0.1380(8)	0.4591(9)	3.8(8)
C3D	−0.0654(15)	0.1774(9)	0.5321(11)	5.5(10)
C4D	0.0191(17)	0.2207(8)	0.5495(10)	5.6(11)
C5D	0.1149(15)	0.2253(8)	0.4979(11)	4.9(10)
C6D	0.1222(14)	0.1840(8)	0.4264(10)	4.0(9)
C1E	−0.0646(13)	0.0320(7)	0.3118(10)	3.5(8)
C2E	−0.1728(13)	0.0541(8)	0.2875(12)	4.6(9)
C3E	−0.2631(15)	0.0135(9)	0.2867(12)	6.2(11)
C4E	−0.2474(16)	−0.0505(9)	0.3093(12)	6.3(11)
C5E	−0.1416(16)	−0.0721(8)	0.3354(13)	6.3(12)
C6E	−0.0507(15)	−0.0312(7)	0.3375(12)	4.1(8)
C1F	0.1843(12)	0.0460(7)	0.3408(9)	2.8(7)
C2F	0.1987(13)	0.0193(7)	0.4269(10)	3.6(8)
C3F	0.2951(14)	−0.0149(7)	0.4507(11)	4.1(9)
C4F	0.3796(14)	−0.0206(8)	0.3904(12)	5.1(10)
C5F	0.3685(13)	0.0041(8)	0.3038(11)	4.3(9)
C6F	0.2704(14)	0.0382(7)	0.2833(10)	3.8(9)
O1	0.1672(14)	0.0738(7)	0.0028(8)	9.3(10)
O2	0.3169(14)	0.9838(9)	0.0500(12)	13.1(13)
B	0.54796	0.10622	0.11588	11.84
F1	0.52949	0.03568	0.12519	11.84
F2	0.56250	0.12898	0.19274	11.84
F3	0.43308	0.12543	0.09600	11.84
F4	0.58151	0.11728	0.03641	11.84

Computing programs are from the NRC VAX package.[17b] Crystallographic data and selected atomic coordinates and bond parameters are collected in Tables 1–5. The rest of the data for **1** and **3**, and the data for [Pt(η^3-C$_3$H$_5$)(PPh$_3$)$_2$](BF$_4$), are supplied in the supplementary material.

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Supplementary Material Available: Fully labeled ORTEP drawings and tables giving complete crystal data, complete bond lengths and angles, atomic coordinates, and thermal parameters for **1**, **3**, and [Pt(η^3-C$_3$H$_5$)(PPh$_3$)$_2$](BF$_4$) (24 pages). Ordering information is given on any current masthead page.

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