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η^3-Propargyl/Allenyl Complexes of Platinum and Palladium of the Type $[(PPh_3)_2M(\eta^3\text{-}CH_2CCR)]^+$

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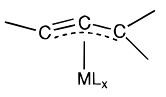
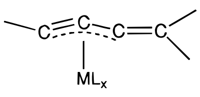
A study is reported on the synthesis, spectroscopic properties, molecular structure, and reaction chemistry of η^3-propargyl/allenyl complexes of platinum and palladium of the type $[(PPh_3)_2M(\eta^3\text{-}CH_2CCR)]^+$ (M = Pt, R = Ph (**1a**), Me (**1b**); M = Pd, R = Ph (**2a**), Me (**2b**)). Complexes **1a,b** were obtained by each of the following methods: (i) reaction of *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ with AgO_3SCF_3; (ii) treatment of $(PPh_3)_2Pt(\eta^2\text{-}PhC{\equiv}CCH_2OMe)$ with $BF_3{\cdot}OEt_2$; (iii) addition of $RC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p* to $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ in solution. Complexes **2a,b** resulted upon (i) abstraction of Br^- from *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CR)$/*trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(R){=}C{=}CH_2)$ with $AgBF_4$ and (ii) treatment of $Pd_2(dba)_3{\cdot}CHCl_3$ with PPh_3 and $RC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p*. The structures of **1a**(OTf)$\cdot CH_2Cl_2$ (Tf = O_2SCF_3) and **2a**(BF_4) were determined by X-ray diffraction techniques. Both cationic metal complexes show remarkably similar structures, the salient features being the attachment to the metal of all three propargyl/allenyl carbon atoms of the nonlinear C_3 fragment (C(1)−C(2)−C(3) bond angles: 152.2(9)° for **1a**, 154.7(5)° for **2a**) and the essentially coplanar arrangement of the three carbon, two phosphorus, and platinum or palladium atoms. **1a,b** react readily with MeOH and Et_2NH to afford the corresponding complexes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(X)CHR)]^+$ (X = OMe, NEt_2); **2a,b** behave analogously, except that the reaction with MeOH requires trace amounts of NaOMe or NEt_3. ^1H and ^{13}C NMR spectroscopic data suggest that the reaction products are best formulated as resonance hybrids of η^3-allyl and metallacyclic structures.

Introduction

In recent years there has been a considerable surge of interest in transition-metal η^3- (or π-) propargyl/allenyl complexes (**I**).[1] The propargyl and the allenyl ligands, like the allyl ligand, can coordinate to a metal center in a σ or π manner. In the latter, all three skeletal carbon atoms are ligated, and the two different C_3 groups become resonance representations of one and the same species. That mode of bonding was first realized for metal η^3-butenynyl complexes (**II**),[2] which are closely related to **I**. Subsequently, metal η^3-propargyl/allenyl complexes have been prepared for molybdenum,[3] tungsten,[4] rhenium,[4,5] zirconium,[6] platinum,[7−9] and palladium.[10,11]

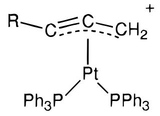


I

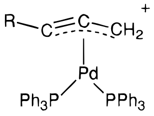


II

This paper focuses on cationic platinum and palladium η^3-propargyl/allenyl complexes of the type $[(PPh_3)_2M(\eta^3\text{-}CH_2CCR)]^+$ (M = Pt (**1**), Pd (**2**); R = Ph (**a**), Me (**b**)). Since analogous η^3-allyl complexes readily undergo addition of nucleophilic reagents to the allyl ligand, and since such reactions are of great synthetic[7] value for palladium,[12] it was of considerable interest to investigate related chemistry of the η^3-propargyl/allenyl complexes **1** and **2**. In fact, a number of organic transformations are known that involve use of propargylic and similar unsaturated compounds in conjunction



1a R = Ph
1b R = Me
1c R = H



2a R = Ph
2b R = Me

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with palladium complexes.[13] Some of these reactions may well proceed by intermediacy of palladium η^3-propargyl/allenyl species.

We describe herein a comparative study of the chemistry of **1** and **2**, with emphasis on methods of synthesis, spectroscopic properties, solid-state structure, and some reactions with nucleophiles. A more extensive investigation of the reaction chemistry of these complexes will be reported later.[14] Some aspects of our study have already been communicated.[15]

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry Ar by use of standard procedures.[16] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, and Atlantic Microlab, Inc., Norcross, GA. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared, NMR (^{1}H, ^{13}C, ^{19}F, and ^{31}P), and FAB mass spectra were obtained as previously described.[17,18]

Materials. All solvents were dried, distilled under an Ar atmosphere, and degassed before use.[19] Reagents were obtained from various commercial sources and used as received. Literature procedures were followed to synthesize $PhC\equiv CCH_2Br$,[20] $MeC\equiv CCH_2Br$,[21] $PhC\equiv CCH_2OMe$,[22] $PhC\equiv CCH_2OS(O)_2C_6H_4Me$-*p*,[23] $MeC\equiv CCH_2OS(O)_2C_6H_4Me$-*p*,[23] $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$,[24] $Pd(PPh_3)_4$,[25] and $Pd_2(dba)_3{\cdot}CHCl_3$[26] (dba = dibenzylideneacetone).

Preparation of *cis*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C\equiv CPh)$. Phenylpropargyl bromide (0.50 mL, 4.0 mmol) was added dropwise to a stirred suspension of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (2.05 g, 2.74 mmol) in 40 mL of hexane at 0 °C. After 20 min the ice bath was removed, and vigorous stirring continued for 2 h as the color of the suspended solid changed from white to yellow. The solid was then collected on a filter frit in air, washed twice with 30 mL of diethyl ether, and dried under vacuum: Yield 2.45 g (98%); ^{1}H NMR (CD_2Cl_2) δ 7.9−7.0 (m, Ph), 2.17 (dd, J_{PH} = 8.9, 6.3 Hz, J_{PtH} = 77 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 18.7 (d, J_{PP} = 16.4 Hz, J_{PtP} = 1906 Hz), 17.8 (d, J_{PP} = 16.4 Hz, J_{PtP} = 4493 Hz), 17.3 (d, J_{PP} = 16.7 Hz, J_{PtP} = 1928 Hz), 15.2 (d, J_{PP} = 16.7 Hz, J_{PtP} = 4351 Hz); IR (Nujol) ν(C≡C) 2160 cm^{-1}. Anal. Calcd for $C_{45}H_{37}BrP_2Pt$: C, 59.09; H, 4.08. Found: C, 59.29; H, 4.08.

Preparation of *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C\equiv CPh)$. A solution of *cis*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C\equiv CPh)$ (2.45 g, 2.68 mmol) in 200 mL of THF was stirred for 2 h at 55 °C under an Ar atmosphere. All solvent was then removed under vacuum, and the product was dried for 2 h. The yellow solid was triturated with 200 mL of hexane, collected on a filter frit in air, and dried overnight: Yield 2.35 g (96%); ^{1}H NMR (CD_2Cl_2) δ 8.0−7.0 (m, Ph), 1.39 (t, J_{PH} = 8.1 Hz, J_{PtH} = 103 Hz, CH_2); ^{13}C NMR (CD_2Cl_2) δ 135−126 (m, Ph), 95.7 (s, J_{PtC} = 96 Hz, *C*Ph), 81.7 (s, J_{PtC} = 42 Hz, CH_2*C*), −5.5 (tt, $^1J_{CH}$ = 140 Hz, J_{PC} = 3.9 Hz, J_{PtC} = 637 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 24.7 (s, J_{PtP} = 3144 Hz); IR (Nujol) ν(C≡C) 2175 cm^{-1}. Anal. Calcd for $C_{45}H_{37}BrP_2Pt$: C, 59.09; H, 4.08. Found: C, 58.96; H, 4.06.

Preparation of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SCF_3$ (1a(OTf)) from *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C\equiv CPh)$ and AgO_3SCF_3. A solution of AgO_3SCF_3 (0.634 g, 2.45 mmol) in 25 mL of THF was added to a solution of *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C\equiv CPh)$ (2.23 g, 2.44 mmol) in 225 mL of THF. A pale yellow precipitate began to form upon mixing. The slurry was vigorously stirred for 3 h and then filtered through a filter frit to remove the precipitated AgBr. The filtrate was evaporated to dryness under vacuum, and 30 mL of CH_2Cl_2 was added to the residue. The resulting slightly cloudy solution was filtered through a filter frit, and the clear brown filtrate was concentrated to ca. 5 mL. The addition of 100 mL of hexane induced precipitation of the beige product. The volume of the solution was reduced to 50 mL, and the product was collected on a filter frit and dried under vacuum for 3 days: Yield 2.30 g (96%); ^{1}H NMR (CD_2Cl_2) δ 7.5−6.5 (m, Ph), 2.74 (d, J_{PH} = 6.8 Hz, J_{PtH} = 29.9 Hz, CH_2); ^{13}C NMR (CD_2Cl_2) δ 135−128 (m, Ph), 102.1 (dd, J_{PC} = 47, 1.5 Hz, J_{PtC} = 93 Hz, *C*Ph), 97.3 (dd, J_{PC} = 4.8, 3.2 Hz, J_{PtC} = 63 Hz, CH_2*C*), 48.3 (td, $^1J_{CH}$ = 170 Hz, J_{PC} = 37 Hz, J_{PtC} =126 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 15.4 (d, J_{PP} = 18.7 Hz, J_{PtP} = 3785 Hz), δ 10.5 (d, J_{PP} = 18.7 Hz, J_{PtP} = 4285 Hz); $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ −78.9 (s). Anal. Calcd for $C_{46}H_{37}F_3O_3P_2PtS$: C, 56.16; H, 3.79. Found: C, 55.91; H, 4.02.

Preparation of $(PPh_3)_2Pt(\eta^2\text{-}PhC\equiv CCH_2OMe)$. Methyl phenylpropargyl ether (0.18 mL, 1.1 mmol) was added dropwise to a stirred solution of $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ (0.75 g, 1.0 mmol) in 30 mL of THF at −78 °C. The resulting solution was slowly warmed to ambient temperature over 8 h, and all volatiles were removed under vacuum. The residue was washed twice with 50-mL portions of hexane, and the pale yellow solid was collected on a filter frit and dried overnight: Yield 0.82 g (94%). ^{1}H NMR (CD_2Cl_2) δ 7.6−7.1 (m, Ph), 4.06 (t, J_{PH} = 2.3 Hz, J_{PtH} = 14 Hz, CH_2), 3.16 (s, Me); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 28.0 (d, J_{PP} = 32 Hz, J_{PtP} = 3518 Hz), 24.6 (d, J_{PP} = 32 Hz, J_{PtP} = 3439 Hz); MS (FAB), ^{195}Pt isotope, *m/z* 866 (M^++1), 719 (M^+ − $PhCCCH_2OMe$).

Preparation of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]BF_3OMe$ (1a-(BF_3OMe)) from $(PPh_3)_2Pt(\eta^2\text{-}PhC\equiv CCH_2OMe)$ and $BF_3{\cdot}OEt_2$. To a mixture of $(PPh_3)_2Pt(\eta^2\text{-}PhC\equiv CCH_2OMe)$ (0.55 g, 0.64 mmol) in 50 mL of diethyl ether at 0 °C was added $BF_3{\cdot}OEt_2$ (0.06 mL, 0.7 mmol). After 15 min of stirring, the contents were warmed to room temperature and stirred for an additional 1 h. The pale yellow solid was filtered off, washed first with diethyl ether (50 mL) and then with hexane (50 mL), and dried under vacuum overnight: Yield 0.56 g (92%). The product was characterized by comparison of its ^{1}H and $^{31}P\{^1H\}$ NMR spectra with those of **1**(OTf).

***In Situ* Preparation of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SC_6H_4Me$-*p* (1a(OTs)) from $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ and $PhC\equiv CCH_2OS(O)_2C_6H_4Me$-*p*.** Solutions of $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ (0.050 g, 0.067 mmol) in 2 mL of CH_2Cl_2 and $PhC\equiv CCH_2$-

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$OS(O)_2C_6H_4$-*p* (0.019 g, 0.067 mmol) in 1 mL of CH_2Cl_2 were prepared in a drybox. The phenylpropargyl tosylate solution was added dropwise to the solution of $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ at −78 °C, and the contents were stirred for 3 h, during which time the temperature was allowed to rise slightly. The reaction solution was concentrated, and the $^{31}P\{^1H\}$ NMR spectrum was recorded and found to be essentially identical with that of **1a**(OTf). Attempts at isolation of **1a**(OTs), performed in the drybox, invariably resulted in decomposition to unidentified materials.

***In Situ* Preparation of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCMe)]O_3SC_6H_4Me$-*p* (1b(OTs)) from $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ and $MeC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p*.** The procedure was similar to that for **1a**(OTs). $^{31}P\{^1H\}$ NMR: δ 18.8 (d, J_{PP} = 17.4 Hz, J_{PtP} = 4240 Hz), 12.6 (d, J_{PP} = 17.4 Hz, J_{PtP} = 3754 Hz). The product decomposed during isolation workup.

Preparation of *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CPh)$/*trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(Ph){=}C{=}CH_2)$. $Pd(PPh_3)_4$ (3.0 g, 2.6 mmol) in 100 mL of THF was treated with $PhC{\equiv}CCH_2Br$ (0.53 g, 2.7 mmol). The resulting yellow solution was stirred at 25 °C for 30 min and concentrated to 50 mL under reduced pressure. The addition of 100 mL of hexane gave a yellow precipitate, which was collected on a filter frit and washed with 40 mL of diethyl ether. The product was dried under vacuum overnight: Yield 2.10 g (97%), with the approximate product ratio of 1:2, propargyl to allenyl; ^1H NMR (CD_2Cl_2) δ 7.8−6.6 (m, Ph), 3.62 (s, $CH_2{=}$), 1.71 (s, $PdCH_2$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 26.1 (br, propargyl complex), 22.9 (s, allenyl complex). Anal. Calcd for $C_{45}H_{37}BrP_2Pd$: C, 65.43; H, 4.51. Found: C, 65.28; H, 4.58.

Preparation of *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CMe)$/*trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(Me){=}C{=}CH_2)$. This mixture was prepared as described above for the Ph analogue from $Pd(PPh_3)_4$ (3.0 g, 2.6 mmol) and $MeC{\equiv}CCH_2Br$ (0.36 g, 2.7 mmol): Yield 1.88 g (95%) of a yellow solid, approximate product ratio 3:1, propargyl to allenyl; ^1H NMR (C_6D_6/CD_2Cl_2, 1:1) δ 7.8−7.0 (m, Ph), 3.44 (s, $CH_2{=}$), 1.59 (s, $PdCH_2$), 1.45 (s, Me); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 25.1 (br, propargyl complex), 22.7 (s, allenyl complex). Anal. Calcd for $C_{40}H_{35}BrP_2Pd$: C, 62.89; H, 4.62. Found: C, 62.73; H, 4.72.

Preparation of $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCPh)]BF_4$ (2a(BF_4)) from *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CPh)$/*trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(Ph){=}C{=}CH_2)$ and $AgBF_4$. A solution of $AgBF_4$ (0.118 g, 0.60 mmol) in 5 mL of THF was added to a stirred solution of *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CPh)$/*trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(Ph){=}C{=}CH_2)$ (0.50 g, 0.60 mmol) in 25 mL of CH_2Cl_2. A precipitate of AgBr formed almost immediately. The mixture was stirred for 15 min at room temperature, AgBr was removed by filtration, and the volume of the solution was reduced to ca. 5 mL. Slow addition of 25 mL of diethyl ether gave a pale yellow precipitate. The solid was collected on a filter frit, washed with 20 mL of diethyl ether, and dried under vacuum: Yield 0.45 g (90%); ^1H NMR (CD_2Cl_2) δ 7.5−6.8 (m, Ph), 3.19 (dd, J_{PH} = 7.8, 1.5 Hz, CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 135−120 (m, Ph), 105.4 (d, J_{PC} = 41.3 Hz, *C*Ph), 94.2 (m, CH_2*C*), 50.9 (d, J_{PC} = 41 Hz, CH_2; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 29.1 (d, J_{PP} = 46.6 Hz), 27.9 (d, J_{PP} = 46.6 Hz); MS (FAB), ^{106}Pd isotope, *m/z* 745 (M^+).

Preparation of $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCMe)]BF_4$ (2b(BF_4)) from *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CMe)$/*trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(Me){=}C{=}CH_2)$ and $AgBF_4$. This complex was prepared as above from *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CMe)$/*trans*$(PPh_3)_2PdBr(\eta^1\text{-}C(Me){=}C{=}CH_2)$ (0.50 g, 0.65 mmol) and $AgBF_4$ (0.126 g, 0.65 mmol) and isolated as a pale yellow solid: Yield 0.464 g (92%); ^1H NMR (CD_2Cl_2) δ 7.5−7.1 (m, Ph), 3.22 (m, CH_2), 1.33 (m, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 134−128 (m, Ph), 103.0 (d, J_{PC} = 43.9 Hz, *C*Ph), 91.2 (m, CH_2*C*), 53.1 (m, CH_2), 6.4 (s, Me); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 30.2 (d, J_{PP} = 43.9 Hz), 27.8 (d, J_{PP} = 43.9 Hz); MS (FAB), ^{106}Pd isotope, *m/z* 683 (M^+).

Preparation of $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCPh)]O_3SC_6H_4Me$-*p* (2a(OTs)) from $Pd_2(dba)_3{\cdot}CHCl_3$, PPh_3, and $PhC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p*. A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.250 g, 0.483 mmol of Pd) and PPh_3 (0.254 g, 0.968 mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature for 5 min and then treated with $PhC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p* (0.138 g, 0.483 mmol). Almost immediately the color of the solution changed from red-purple to orange. The reaction solution was stirred for 15 min at room temperature, concentrated to ca. 2 mL, and filtered through Celite. Addition of 20 mL of diethyl ether to the filtrate induced the precipitation of **2a**(OTs) as a pale yellow solid. The product was collected on a filter frit, washed with 20 mL of diethyl ether, and dried overnight under vacuum: Yield 0.334 g (81%). Characterization was effected by comparison of its ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and FAB mass spectra with those of **2a**(BF_4). Anal. Calcd for $C_{52}H_{44}O_3P_2PdS$: C, 68.09; H, 4.83. Found: C, 67.79; H, 4.98.

Preparation of $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCMe)]O_3SC_6H_4Me$-*p* (2b(OTs)) from $Pd_2(dba)_3{\cdot}CHCl_3$, PPh_3, and $MeC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p*. This complex was prepared similarly to **2a**(OTs) from $Pd_2(dba)_3{\cdot}CHCl_3$ (0.250 g, 0.483 mmol of Pd), PPh_3 (0.254 g, 0.968 mmol), and $MeC{\equiv}CCH_2OS(O)_2C_6H_4Me$ (0.108 g, 0.483 mmol) to give **2b**(OTs) as a white solid: Yield 0.343 g (83%). Characterization was effected by comparison of its ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and FAB mass spectra with those of **2b**(BF_4). Anal. Calcd for $C_{47}H_{42}O_3P_2PdS$: C, 66.01; H, 4.95. Found: C, 65.78; H, 5.03.

Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (1a) with MeOH. Methanol (1.5 mL, 3.7 mmol) was added to a stirred solution of **2a**(OTf) (0.200 g, 0.203 mmol) in 3 mL of CH_2Cl_2. After 5 min all solvent was removed under vacuum, and the residue was dissolved in 3 mL of CH_2Cl_2. A 30-mL portion of hexane was added to induce the precipitation of a beige product. After the volume of the solution had been reduced to 15 mL, the solid was collected on a filter frit and washed with 5 mL of hexane. The product $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OMe)CHPh)]O_3SCF_3$ (**3a**(OTf)) was dried under vacuum at 60 °C for 2 days: Yield 0.180 g (87%); ^1H NMR ($CDCl_3$) δ 7.5−6.6 (m, Ph), 4.41 (d, J_{PH} = 10.5 Hz, J_{PtH} = 39.8 Hz, C*H*Ph), 3.50 (s, OMe), 3.21 (dd, J_{PH} = 9.7 Hz, $^2J_{HH}$ = 6.6 Hz, J_{PtH} = 35 Hz, H_{anti} of CH_2), 2.86 (m, H_{syn} of CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.6 (s, *C*CH_2), 135−123 (m, Ph), 68.7 (d, J_{PC} = 36.8 Hz, J_{PtC} = 74.1 Hz, *C*HPh), 53.9 (s, OMe), 48.9 (d, J_{PC} = 34.7 Hz, J_{PtC} = 127 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 18.1 (d, J_{PP} = 9.5 Hz, J_{PtP} = 3824 Hz), δ 13.6 (d, J_{PP} = 9.5 Hz, J_{PtP} = 3783 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −79.0 (s). Anal. Calcd for $C_{47}H_{41}F_3O_4P_2PtS$: C, 55.57; H, 4.07. Found: C, 55.36; H, 4.30.

Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ (1a) with Et_2NH. Diethylamine (0.10 mL, 0.97 mmol) was added to a stirred solution of **1a**(OTf) (0.219 g, 0.223 mmol) in 3 mL of CH_2Cl_2. After 5 min, 30 mL of hexane was introduced to induce precipitation of the product. The volume of the solution was reduced to 15 mL, and the beige solid was collected on a filter frit and washed with 5 mL of hexane. The product $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(NEt_2)CHPh)]O_3SCF_3$ (**4a**(OTf)) was dried under vacuum at 60 °C for 2 days: Yield 0.203 g (86%); ^1H NMR ($CDCl_3$) δ 7.7−6.8 (m, Ph), 4.38 (m, C*H*Ph), 3.27 (m, NCH_2), 2.62 (m, H_{syn} of CH_2), 2.33 (dd, J_{PH} = 11.4 Hz, $^2J_{HH}$ = 7.7 Hz, J_{PtH} = 60 Hz, H_{anti} of CH_2), 1.07 (br, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 152.5 (s, J_{PtC} = 123 Hz, *C*CH_2), 136−124 (m, Ph), 57.0 (d, J_{PC} = 51.7 Hz, J_{PtC} = 236 Hz, *C*HPh), 41.7 (s, NCH_2), 35.0 (d, J_{PC} = 47.4 Hz, J_{PtC} =184 Hz, C*C*H_2), 10.7 (s, Me); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 17.2 (d, J_{PP} = 8.5 Hz, J_{PtP} = 3359 Hz), δ 14.5 (d, J_{PP} = 8.5 Hz, J_{PtP} = 3025 Hz); $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −79.1 (s). Anal. Calcd for $C_{50}H_{48}F_3NO_3P_2PtS$: C, 56.82; H, 4.58. Found: C, 56.57; H, 4.81.

4a was also obtained, as **4a**(OTs), by generating **1a**(OTs) *in situ*, from $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ (0.050 g, 0.067 mmol) and $PhC{\equiv}CCH_2OS(O)_2C_6H_4Me$-*p* (0.020 g, 1 equiv), in the presence of Et_2NH (0.030 mL, 0.020 g, 4 equiv) in CH_2Cl_2 at −78 °C. The temperature of the mixture was allowed to rise over 6 h, and the completion of the reaction was ascertained by $^{31}P\{^1H\}$ NMR spectroscopy. After evaporation of the solvent, the residue was dissolved in 2 mL of CH_2Cl_2. An off-white solid precipitated upon addition of 15 mL of hexane and was isolated by filtration and washed with 5-mL portions of hexane: Yield 0.045 g (61%). The product was characterized by comparison of its ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data with those of **4a**(OTf).

Reaction of [(PPh$_3$)$_2$Pt(η^3-CH$_2$CCMe)]$^+$ (1b) with MeOH. The procedure was analogous to that described above for the synthesis of **4a**(OTs). A solution of (PPh$_3$)$_2$Pt(η^2-C$_2$H$_4$) (0.050 g, 0.067 mmol) in 5 mL of CH$_2$Cl$_2$ at −78 °C was treated with MeOH (2.0 mL, 1.59 g, 49.0 mmol) and MeC≡CCH$_2$OS(O)$_2$C$_6$H$_4$Me-*p* (0.015 g, 1 equiv) in 1 mL of CH$_2$Cl$_2$. The mixture was allowed to warm to room temperature and was worked-up as in the immediately preceding reaction. [(PPh$_3$)$_2$Pt(η^3-CH$_2$C(OMe)CHMe]O$_3$SC$_6$H$_4$Me-*p* (**3b**(OTs)) was isolated in 61% yield (0.040 g) as an off-white solid: ^{1}H NMR (CDCl$_3$) δ 7.5−7.0 (m, Ph, C$_6$H$_4$), 3.49 (s, OMe), 3.48 (m, C*H*Me), 3.02 (dd, J_{PH} = 10.7 Hz, $^2J_{\mathrm{HH}}$ = 9.6 Hz, J_{PtH} = 33 Hz, H$_{\mathrm{anti}}$ of CH$_2$), 2.71 (br m, H$_{\mathrm{syn}}$ of CH$_2$), 2.28 (s, C$_6$H$_4$*Me*), 0.88 (m, CH*Me*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 152.6 (t, *C*CH$_2$), 145−126 (m, Ph, C$_6$H$_4$), 66.6 (d, J_{PC} = 37 Hz, J_{PtC} = 178 Hz, *C*HMe), 55.4 (s, OMe), 51.5 (d, J_{PC} = 35 Hz, J_{PtC} = 122 Hz, CH$_2$), 21.9 (s, C$_6$H$_4$*Me*), 10.0 (s, CH*Me*); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 20.6 (d, J_{PP} = 9.6 Hz, J_{PtP} = 3753 Hz), 15.2 (d, J_{PP} = 9.6 Hz, J_{PtP} = 3126 Hz).

Reaction of [(PPh$_3$)$_2$Pt(η^3-CH$_2$CCMe)]$^+$ (1b) with Et$_2$NH. A solution of (PPh$_3$)$_2$Pt(η^2-C$_2$H$_4$) (0.050 g, 0.067 mmol) in 5 mL of CH$_2$Cl$_2$ at 0 °C was treated with Et$_2$NH (0.015 mL, 0.011 g, 2.2 equiv) and MeC≡CCH$_2$OS(O)$_2$C$_6$H$_4$Me-*p* (0.015 g, 1 equiv) in 1 mL of CH$_2$Cl$_2$ to generate **1b**(OTs) in the presence of the amine. The mixture was stirred at 0 °C for 1 h, solvent was removed under reduced pressure, and CH$_2$Cl$_2$ (5 mL) and Et$_2$O (5 mL) were added with stirring. The resulting clear solution was separated from a yellow oil and pumped to dryness. The residue was recrystallized from benzene/hexane to yield 0.030 g (45%) of [(PPh$_3$)$_2$Pt(η^3-CH$_2$C(NEt$_2$)CHMe]O$_3$SC$_6$H$_4$Me-*p* (**4b**(OTs)) as an off-white solid: ^{1}H NMR (CDCl$_3$) δ 7.9−7.1 (m, Ph, C$_6$H$_4$), 3.15 (m, NCH$_2$), 2.92 (m, C*H*Me), 2.66 (m, H$_{\mathrm{syn}}$ of CH$_2$), 2.35 (m, H$_{\mathrm{anti}}$ of CH$_2$), 2.27 (s, C$_6$H$_4$*Me*), 1.14 (m, CH*Me*), 1.01 (t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CH$_2$*Me*); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 156.3 (t, J_{PC} = 8 Hz, J_{PtC} = 120 Hz, *C*CH$_2$), 145−126 (m, Ph, C$_6$H$_4$), 50.1 (d, J_{PC} = 52 Hz, J_{PtC} = 230 Hz, *C*HMe), 44.1 (s, NCH$_2$), 36.2 (d, J_{PC} = 47 Hz, J_{PtC} = 186 Hz, C*C*H$_2$), 21.2 (s, C$_6$H$_4$*Me*), 16.6 (d, J_{PC} = 6 Hz, J_{PtC} = 48 Hz, CH*Me*), 13.4 (br s, CH$_2$*Me*); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 18.2 (d, J_{PP} = 7 Hz, J_{PtP} = 3420 Hz), 15.4 (d, J_{PP} = 7 Hz, J_{PtP} = 2910 Hz).

Reaction of [(PPh$_3$)$_2$Pd(η^3-CH$_2$CCPh)]$^+$ (2a) with MeOH and Base. A solution of NaOMe (0.002 g, 0.037 mmol) in MeOH (1 mL, 27 mmol) was added to **2a**(BF$_4$) (0.250 g, 0.300 mmol) dissolved in 10 mL of CH$_2$Cl$_2$, and the resulting mixture was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure, the yellow residue was dissolved in a minimum amount of CH$_2$Cl$_2$, and 1 mL of THF was added. The solution was filtered through Celite and treated with 5 mL of Et$_2$O to induce the precipitation of a pale yellow solid. The product [(PPh$_3$)$_2$Pd(η^3-CH$_2$C(OMe)CHPh)]BF$_4$ (**5a**(BF$_4$)) was collected on a filter frit, washed with 5 mL of Et$_2$O, and dried under vacuum: Yield 0.240 g (92%); ^{1}H NMR (CD$_2$Cl$_2$) δ 7.6−6.6 (m, Ph), 4.51 (m, C*H*Ph), 3.55 (OMe), 3.20 (m, CH$_2$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 151.2 (t, J_{PC} = 5 Hz, *C*CH$_2$), 133−127 (m, Ph), 81.1 (dd, J_{PC} = 26, 10 Hz, *C*HPh), 58.9 (dd, J_{PC} = 24, 9 Hz, CH$_2$), 56.4 (s, OMe); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 25.8 (br); MS (FAB), ^{106}Pd isotope, *m/z* 777 (M$^+$).

When this reaction was conducted without added base (NaOMe or NEt$_3$ (1 drop)), no formation of **5a**(BF$_4$) was observed by ^{31}P{^{1}H} NMR spectroscopy.

5a was also obtained, in comparable yield, as the pale yellow **5a**(OTs), by reaction of **2a**(OTs) with MeOH and NaOMe under similar conditions and with a similar workup. Alternatively, **5a**(OTs) can be prepared by treatment of a solution of Pd$_2$(dba)$_3$·CHCl$_3$ (0.225 g, 0.435 mmol of Pd) and PPh$_3$ (0.228 g, 0.870 mmol) in 20 mL of CH$_2$Cl$_2$ with PhC≡CCH$_2$OS(O)$_2$C$_6$H$_4$-Me-*p* (0.125 g, 0.436 mmol), followed by addition of NaOMe (0.002 g, 0.037 mmol) in 1 mL of MeOH (27 mmol). Similar reaction time and workup led to the isolation of the product in 70% yield (0.291 g). Its spectroscopic properties agreed with those of **5a**(BF$_4$). Anal. Calcd for C$_{53}$H$_{48}$O$_4$P$_2$PdS: C, 67.05; H, 5.10. Found: C, 66.70; H, 5.34.

Reaction of [(PPh$_3$)$_2$Pd(η^3-CH$_2$CCMe)]$^+$ (2b) with MeOH and Base. All procedures were strictly analogous to those for the corresponding reactions of **2a**. By use of **2b**(BF$_4$) (0.250 g, 0.324 mmol), MeOH (1 mL), and NaOMe (0.002 g, 0.037 mmol) or NEt$_3$ (1 drop), 0.245 g (94% yield) of [(PPh$_3$)$_2$Pd(η^3-CH$_2$C(OMe)CHMe]BF$_4$ (**5b**(BF$_4$)), a beige solid, was isolated: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.6−7.0 (m, Ph), 3.55 (m, C*H*Me), 3.50 (s, OMe), 3.04 (m, CH$_2$), 0.81 (m, Me); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 153.8 (t, J_{PC} = 6 Hz, *C*CH$_2$), 134−128 (m, Ph), 76.5 (d, J_{PC} = 37 Hz, *C*HMe), 58.6 (d, J_{PC} = 33 Hz, CH$_2$), 56.2 (s, OMe), 11.0 (s, Me); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 27.2 (d, J_{PP} = 38 Hz), 24.2 (d, J_{PP} = 38 Hz); MS (FAB), ^{106}Pd isotope, *m/z* 715 (M$^+$). Anal. Calcd for C$_{41}$H$_{39}$BF$_4$OP$_2$Pd: C, 61.33; H, 4.90. Found: C, 61.37; H, 4.97.

5b(OTs) was prepared similarly to **5a**(OTs) either from **2b**(OTs), MeOH, and NaOMe (or NEt$_3$) or from Pd$_2$(dba)$_3$·CHCl$_3$, PPh$_3$, MeC≡CCH$_2$OS(O)$_2$C$_6$H$_4$Me-*p*, MeOH, and NaOMe (or NEt$_3$). Comparable yields were obtained, and spectroscopic properties of the product agreed with those of **5b**(BF$_4$).

No formation of **5b**(OTs) was observed in the absence of added base.

Reaction of [(PPh$_3$)$_2$Pd(η^3-CH$_2$CCPh)]$^+$ (2a) with Et$_2$NH. Excess Et$_2$NH (0.10 mL, 0.97 mmol) was added to a solution of **2a**(BF$_4$) (0.250 g, 0.300 mmol) in 10 mL of CH$_2$Cl$_2$, the resulting mixture was stirred for 10 min at room temperature, and the volatiles were removed under reduced pressure. The yellow residue was dissolved in minimum CH$_2$Cl$_2$, and 1 mL of THF was added. Slow addition of 10 mL of Et$_2$O induced the precipitation of a pale yellow solid, which was collected by filtration, washed with 10 mL of Et$_2$O, and dried under vacuum: Yield 0.251 g (92%) of [(PPh$_3$)$_2$Pd(η^3-CH$_2$C(NEt$_2$)CHPh)]BF$_4$ (**6a**(BF$_4$)); ^{1}H NMR (CD$_2$Cl$_2$) δ 7.7−6.9 (m, Ph), 4.98 (m, C*H*Ph), 3.16 (m, NCH$_2$), 2.80 (m, CH$_2$), 1.09 (t, Me); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 151.2 (t, J_{PC} = 5 Hz, *C*CH$_2$), 138−127 (m, Ph), 71.1 (d, J_{PC} = 44 Hz, *C*HPh), 47.8 (d, J_{PC} = 40 Hz, C*C*H$_2$), 44.6 (s, NCH$_2$), 13.4 (s, Me); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 24.4 (d, J_{PP} = 32 Hz), 23.5 (d, J_{PP} = 32 Hz); MS (FAB), ^{106}Pd isotope, *m/z* 818 (M$^+$).

6a was also prepared and isolated as **6a**(OTs) either from **2a**(OTs) and Et$_2$NH or from Pd$_2$(dba)$_3$·CHCl$_3$, PPh$_3$, PhC≡CCH$_2$OS(O)$_2$C$_6$H$_4$Me-*p*, and Et$_2$NH. The procedures were similar to those already described. The yields were ca. 92 and 72%, respectively. Spectroscopic properties of the product agreed with those of **6a**(BF$_4$). Anal. Calcd for C$_{56}$H$_{55}$NO$_3$P$_2$PdS: C, 67.91; H, 5.60; N, 1.41. Found: C, 67.34; H, 5.85; N, 1.52.

Reaction of [(PPh$_3$)$_2$Pd(η^3-CH$_2$CCMe)]$^+$ (2b) with Et$_2$NH. By using procedures strictly analogous to those for the preparation of **6a**, [(PPh$_3$)$_2$)Pd(η^3-CH$_2$C(NEt$_2$)CHMe)]$^+$ (**6b**) was isolated as the beige **6b**(BF$_4$) and the white **6b**(OTs) in similar yields. **6b**(BF$_4$): ^{1}NMR (CD$_2$Cl$_2$) δ 7.6−7.0 (m, Ph), 3.35 (m, C*H*Me), 3.02 (m, NCH$_2$), 2.80 (m, CCH$_2$), 1.16 (m, CH*Me*), 0.97 (t, CH$_2$*Me*); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 152.3 (t, J_{PC} = 5 Hz, *C*CH$_2$), 134−128 (m, Ph), 62.7 (d, J_{PC} = 46 Hz, *C*HMe), 45.9 (d, J_{PC} = 41 Hz, C*C*H$_2$), 44.0 (s, NCH$_2$), 16.3 (CH*Me*), 13.3 (CH$_2$*Me*); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ 24.4 (d, J_{PP} = 29 Hz), 22.6 (d, J_{PP} = 29 Hz); MS (FAB), ^{106}Pd isotope, *m/z* 756 (M$^+$). **6b**(OTs): Anal. Calcd for C$_{51}$H$_{53}$NO$_3$P$_2$PdS: C, 65.98; H, 5.75; N, 1.51. Found: C, 65.74; H, 5.80; N, 1.49.

Crystallographic Analysis of [(PPh$_3$)$_2$Pt(η^3-CH$_2$CCPh)]O$_3$SCF$_3$·CH$_2$Cl$_2$ (1a(OTf)·CH$_2$Cl$_2$) and [(PPh$_3$)$_2$Pd(η^3-CH$_2$CCPh)]BF$_4$ (2a(BF$_4$)). Crystals of **1a**(OTf)·CH$_2$Cl$_2$, pale gold rods, were grown from CH$_2$Cl$_2$/hexane, and those of **2a**(BF$_4$), pale yellow rods, from CH$_2$Cl$_2$/diethyl ether. Both data sets were measured on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation. The unit cell constants were obtained by a least-squares fit of the diffractometer setting angles using 25 reflections in the 2θ range 24

Table 1. Crystal Data and Data Collection and Refinement for 1a(OTf)·CH$_2$Cl$_2$ and 2a(BF$_4$)

	Crystal Data	
cmpd	**1a**(OTf)·CH$_2$Cl$_2$	**2a**(BF$_4$)
chem formula	$C_{47}H_{39}Cl_2F_3O_3P_2PtS$	$C_{45}H_{37}BF_4P_2Pd$
fw	1068.82	832.90
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	10.678(3)	10.547(1)
b, Å	19.633(4)	12.031(2)
c, Å	21.428(2)	16.125(1)
α, deg		101.570(7)
β, deg	92.68(1)	105.493(8)
γ, deg		92.355(7)
V, Å^3	4487(1)	1922.1(3)
Z	4	2
D_{calcd}, g cm^{-3}	1.58	1.44
μ(Mo Kα), cm^{-1}	34.44	6.07
cryst size, mm	0.17 × 0.21 × 0.38	0.15 × 0.19 × 0.19
	Data Collection and Refinement	
temp, °C	ambient	ambient
radiation	Mo Kα with graphite monochromator	
transm factors	0.75−1.0	0.890−0.920
2θ limits, deg	4−55	4−55
scan speed, deg min^{-1} (in ω)	4 with up to 3 rescans	4 with up to 3 rescans
scan type	ω	$\omega-2\theta$
scan range, deg (in ω)	$1.20 + 0.35 \tan \theta$	$1.30 + 0.35 \tan \theta$
data collcd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
unique data	10 613	8881
unique data used in refinement	5797[a]	8881
final no. of variables	484	483
$R(F)$[b]	0.047	0.102
$R_w(F)$[c]	0.056	
$R_w(F^2)$[d]		0.129
error in obsn of unit wt, e	1.79	1.02

[a] With $F_o^2 > 3\sigma(F_o^2)$. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$. [d] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 1.5355P]$ and $P = {}^1/_3(\text{maximum of } (0 \text{ or } F_o^2)) + {}^2/_3(F_c)^2$.

to 30° for **1a**(OTf)·CH$_2$Cl$_2$ and 25 reflections in the 2θ range 21 to 30° for **2a**(BF$_4$). The crystal data are given in Table 1.

Six standard reflections were measured after every 150 reflections during data collection and indicated some crystal decay for both structures. On the average the standards decreased in intensity by 10.9% for **1a**(OTf)·CH$_2$Cl$_2$ and 3.3% for **2a**(BF$_4$). Data reduction was done with the TEXSAN package,[27] and a linear decay correction was applied to both data sets. The data set for **1a**(OTf)·CH$_2$Cl$_2$ was corrected for absorption by the ψ scan method,[28] and an analytical absorption correction was applied to the data set for **2a**(BF$_4$).[29]

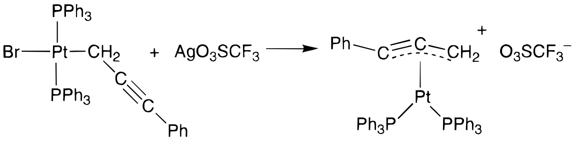
For **1a**(OTf)·CH$_2$Cl$_2$, the Pt atom was located by the Patterson method. The rest of the structure was elucidated by means of the DIRDIF procedure[30] and standard Fourier methods. There is a solvent molecule of CH$_2$Cl$_2$ in the asymmetric unit. Full-matrix least-squares refinements were performed in TEXSAN;[27] the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The triflate group was not well behaved. It was necessary to treat the CF$_3$ half as a rigid group, with each atom having its own isotropic thermal parameter. In the SO$_3$ portion, the oxygen atoms were refined isotropically and acquired large B values, which is an indication of disorder. The CH$_2$Cl$_2$ molecule also seemed to suffer from disorder and so was restricted to isotropic refinement too. Hydrogen atoms were included in the model as fixed contributions based on calculated positions at C−H = 0.98 Å and B(H) = 1.2B_{eq}(attached carbon atom). The two hydrogen atoms bonded to C(1) were refined isotropically. The final refinement cycle was based on the 5797 intensities with $I > 3\sigma(I)$ and 484 variables and resulted in agreement factors of $R = 0.047$ and $R_w = 0.056$. The final difference electron density map contains two large peaks of 1.86 and 1.45 e/Å^3 in the immediate vicinity of Cl(2). The next largest peak is 0.98 e/Å^3, and the minimum peak is −1.08 e/Å^3. Neutral atom scattering factors are used and include terms for anomalous scattering.[31]

The structure of **2a**(BF$_4$) was solved for the positions of the Pd and two P atoms by the Patterson method using SHELXS-86[32] in $P\bar{1}$. Phasing on these three atoms revealed the rest of the complex on an electron density map. However, the position of the BF$_4^-$ anion was not evident at this point. Full-matrix least-squares refinements on F^2 were performed in SHELXL-93;[33] the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$. The BF$_4$ group is disordered, and it was modeled in terms of two orientations sharing a common boron atom. The set of fluorine atoms belonging to one orientation is labeled as F(1), F(2), F(3), and F(4), while the set belonging to the second orientation is labeled F(1A), F(2A), F(3A), and F(4A). The occupancy factor for F(1) was refined, and the others were constrained accordingly. Its final value was 0.54(1). The fluorines were kept isotropic while the boron was refined anisotropically. The hydrogen atoms for the phenyl rings are included in the structure using a riding model with C−H = 0.98 Å and U(H) = 1.2U_{eq}(attached carbon atom). The two hydrogen atoms bonded to C(1) were located on a difference electron density map and refined isotropically. The final refinement cycle was based on all the 8881 unique intensities and 483 variables and resulted in agreement indices of $R(F) = 0.102$ and $R_w(F^2) = 0.129$. For the subset of intensities with $F_o^2 > 2\sigma(F_o^2)$ (6016 reflections) the $R(F)$ value is 0.048. The final difference electron density map contains maximum and minimum peak heights of 0.75 and −0.51 e/Å^3. Neutral atom scattering factors were used and included terms for anomalous dispersion.[34]

Final positional and equivalent thermal parameters for **1a**(OTf)·CH$_2$Cl$_2$ and **2a**(BF$_4$) are given in Tables 2 and 3, respectively. Other data are provided as Supporting Information; see the paragraph at the end of this paper.

Results and Discussion

Synthesis of [(PPh$_3$)$_2$M(η^3-CH$_2$CCR)]$^+$ (1, M = Pt; 2, M = Pd). Cationic platinum and palladium η^3-propargyl/allenyl complexes of general formula [(PPh$_3$)$_2$M(η^3-CH$_2$CCR)]$^+$ have been prepared by several methods. Thus, complex **1a** results upon treatment of *trans*-(PPh$_3$)$_2$Pt(Br)(η^1-CH$_2$C≡CPh) with 1 equiv of AgO$_3$SCF$_3$ in THF at room temperature (eq 1) and was



(1)

1a (OTf)

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[33] Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1993.

[34] *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

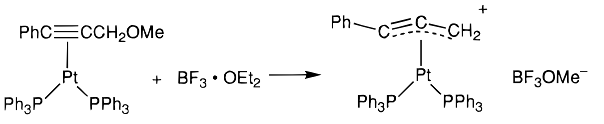
Table 2. Positional and Equivalent Isotropic Thermal Parameters for 1a(OTf)·CH_2Cl_2

atom	*x*	*y*	*z*	B_{eq}[a] or *B*, Å^2
Pt	0.23893(3)	0.05495(2)	0.23600(2)	3.21(1)
P(1)	0.2528(2)	−0.0546(1)	0.2733(1)	3.4(1)
P(2)	0.1605(2)	0.0349(1)	0.1378(1)	3.4(1)
C(1)	0.228(1)	0.1655(5)	0.2246(5)	5.1(6)
C(2)	0.276(1)	0.1493(5)	0.2844(5)	5.3(5)
C(3)	0.308(1)	0.1082(5)	0.3252(5)	4.6(5)
C(4)	0.360(1)	0.0967(4)	0.3885(5)	4.4(5)
C(5)	0.488(1)	0.0986(5)	0.4011(5)	5.2(6)
C(6)	0.534(1)	0.0914(6)	0.4617(7)	6.4(7)
C(7)	0.457(2)	0.0845(7)	0.5098(6)	7.1(8)
C(8)	0.335(2)	0.0816(8)	0.4977(6)	8.4(9)
C(9)	0.281(1)	0.0885(6)	0.4371(5)	6.3(7)
C(10)	0.4136(9)	−0.0830(5)	0.2901(4)	3.7(4)
C(11)	0.446(1)	−0.1512(5)	0.2985(5)	5.6(6)
C(12)	0.565(1)	−0.1720(7)	0.3151(6)	7.3(8)
C(13)	0.655(1)	−0.1222(8)	0.3242(5)	6.9(8)
C(14)	0.626(1)	−0.0538(6)	0.3170(5)	5.6(6)
C(15)	0.508(1)	−0.0351(5)	0.2983(4)	4.2(5)
C(16)	0.1740(9)	−0.0597(5)	0.3463(4)	3.9(4)
C(17)	0.211(1)	−0.1054(5)	0.3940(5)	5.0(5)
C(18)	0.142(1)	−0.1112(6)	0.4463(5)	6.5(7)
C(19)	0.032(1)	−0.0734(7)	0.4521(5)	6.4(7)
C(20)	−0.006(1)	−0.0278(6)	0.4053(5)	6.0(6)
C(21)	0.066(1)	−0.0212(5)	0.3530(5)	4.8(5)
C(22)	0.180(1)	−0.1239(4)	0.2282(4)	3.7(4)
C(23)	0.060(1)	−0.1457(5)	0.2392(5)	5.5(6)
C(24)	0.003(1)	−0.1958(7)	0.2024(6)	7.6(8)
C(25)	0.064(2)	−0.2257(6)	0.1551(7)	7.5(8)
C(26)	0.182(2)	−0.2060(6)	0.1434(5)	7.2(7)
C(27)	0.242(1)	−0.1551(5)	0.1803(5)	5.4(6)
C(28)	0.2603(9)	−0.0115(4)	0.0871(4)	3.5(4)
C(29)	0.222(1)	−0.0237(6)	0.0252(4)	5.0(5)
C(30)	0.299(1)	−0.0592(6)	−0.0137(5)	6.0(6)
C(31)	0.414(1)	−0.0815(6)	0.0083(6)	6.2(7)
C(32)	0.454(1)	−0.0678(6)	0.0699(6)	6.4(7)
C(33)	0.378(1)	−0.0325(5)	0.1081(5)	4.5(5)
C(34)	0.0087(9)	−0.0063(5)	0.1400(4)	3.9(4)
C(35)	−0.032(1)	−0.0618(5)	0.1038(5)	4.7(5)
C(36)	−0.148(1)	−0.0894(7)	0.1115(6)	6.8(7)
C(37)	−0.224(1)	−0.0640(9)	0.1552(8)	8(1)
C(38)	−0.188(1)	−0.0087(8)	0.1906(6)	6.8(7)
C(39)	−0.071(1)	0.0205(6)	0.1844(5)	5.2(6)
C(40)	0.130(1)	0.1122(5)	0.0918(4)	4.1(5)
C(41)	0.232(1)	0.1463(6)	0.0690(5)	6.0(6)
C(42)	0.215(2)	0.2047(7)	0.0338(6)	8(1)
C(43)	0.095(2)	0.2299(7)	0.0230(7)	10(1)
C(44)	−0.002(2)	0.1963(8)	0.0445(8)	9(1)
C(45)	0.012(1)	0.1375(6)	0.0802(6)	6.6(7)
S	0.8395(5)	0.1615(2)	0.3223(3)	11.1(3)
O(1)	0.724(2)	0.1926(8)	0.3118(8)	18.4(6)*
O(2)	0.923(2)	0.162(1)	0.2715(9)	20.8(7)*
O(3)	0.837(2)	0.101(1)	0.3479(9)	20.0(6)*
Cl(1)	0.5484(5)	0.1172(3)	0.1698(2)	12.1(1)*
Cl(2)	0.5945(8)	0.2419(4)	0.1105(4)	20.3(3)*
C(47)	0.635(2)	0.191(1)	0.169(1)	13.5(6)*
C(46)	0.922(1)	0.2191(5)	0.3728(5)	18.7(9)**
F(1)	0.937(1)	0.2786(7)	0.3465(6)	20.0(5)**
F(2)	0.847(1)	0.225(1)	0.4189(8)	28.3(8)**
F(3)	1.031(1)	0.1962(7)	0.3943(8)	26.2(7)**

[a] The form of the equivalent isotropic displacement parameter is $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$. Asterisks designate *B* values for atoms refined isotropically. Double asterisks designate *B* values for atoms refined as part of a rigid group.

isolated as the triflate salt **1a**(OTf) in 96% yield. Similarly, **1c**(BF_4) was obtained from *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH{=}C{=}CH_2)$ and $AgBF_4$ in CH_2Cl_2 at −30 °C by Chen and co-workers.[8] This methodology has the advantage of simplicity and high yield of the product; however, it does require the availability of the appropriate halogeno−η^1-propargyl or −η^1-allenyl complex of platinum(II) as the immediate precursor. The latter are generally accessible from platinum(0) phosphine complexes and propargyl or allenyl halides.[35]

An alternative preparation of **1a** entails acid cleavage of a phenylpropargyl ether complex of platinum(0). The reaction presented in eq 2 also affords **1a** in excellent

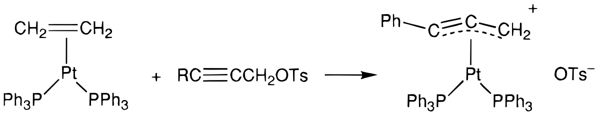


(2)

1a (BF_3OMe)

yield and is simple to carry out. The precursor $(PPh_3)_2Pt(\eta^2\text{-}PhC{\equiv}CCH_2OMe)$ can be obtained by treatment of $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ with $PhC{\equiv}CCH_2OMe$.

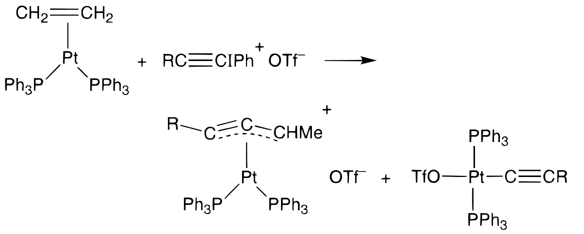
In an attempt to develop a "one-pot" synthesis of **1** from a non-propargyl or -allenyl compound of platinum, $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ was treated with each of $PhC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$ and $MeC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$. It was thought that the presence of a relatively poor coordinating ligand, tosylate (OTs), may lead to the formation of **1** by oxidative addition of $RC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$ at the platinum center (eq 3). Examination of solutions of $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ and $RC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$ in CH_2Cl_2 by NMR spectroscopy revealed that the expected η^3-propargyl/allenyl product had indeed formed. This was further corroborated by addition to these solutions of MeOH or Et_2NH, which resulted in the formation of the appropriate η^3-allyl complexes with the OMe or NEt_2 substituents at C(2) (**3** or **4**, respectively; vide infra). However, attempts at isolation of the η^3-propargyl/allenyl complexes **1a**(OTs) and **1b**(OTs) invariably led to the formation of unidentified decomposition products. It would appear that the decomposition is caused by the presence of the tosylate counterion, but we do not know whether this anion triggers it by coordinating to platinum or to the η^3-propargyl/allenyl ligand or by reacting in some other manner.



(3)

1a-b (OTs)

Finally, a rather unusual method of synthesis of methyl-substituted derivatives of **1**, $[(PPh_3)_2Pt(\eta^3\text{-}MeCHCCR)]^+$, was recently reported by Stang and co-workers.[9] These complexes were obtained by reaction of $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ with $[RC{\equiv}CIPh]O_3SCF_3$ where R = *t*-Bu, *n*-Bu, SiMe$_3$, or Me (eq 4). Generally, *trans*-$(PPh_3)_2Pt(OS(O)_2CF_3)(C{\equiv}CR)$ was a coproduct.



(4)

The palladium complexes **2a,b** were synthesized similarly to the platinum complexes **1a,c**[10,11] (cf. eq 1).

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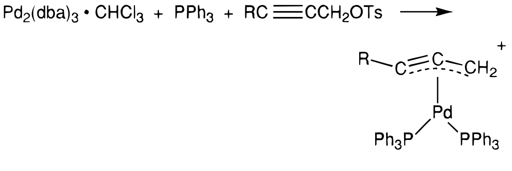
Table 3. Positional and Equivalent Isotropic Displacement Parameters for 2a(BF_4)

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Pd	0.20997(3)	0.35147(3)	0.32506(2)	0.0316(1)
P(1)	0.09152(10)	0.40833(9)	0.19872(7)	0.0324(2)
P(2)	0.06406(10)	0.21964(9)	0.34484(7)	0.0335(2)
C(1)	0.3642(5)	0.3271(5)	0.4370(4)	0.052(1)
C(2)	0.4101(4)	0.4097(4)	0.4005(3)	0.047(1)
C(3)	0.4019(4)	0.4700(4)	0.3462(3)	0.046(1)
C(4)	0.4558(5)	0.5462(4)	0.3028(3)	0.050(1)
C(5)	0.5452(5)	0.5084(5)	0.2565(3)	0.061(1)
C(6)	0.6004(6)	0.5812(7)	0.2166(4)	0.079(2)
C(7)	0.5665(7)	0.6894(7)	0.2202(4)	0.085(2)
C(8)	0.4768(7)	0.7286(6)	0.2651(5)	0.087(2)
C(9)	0.4229(6)	0.6570(5)	0.3080(4)	0.068(2)
C(10)	0.2007(4)	0.4048(4)	0.1279(3)	0.035(1)
C(11)	0.2639(4)	0.3077(4)	0.1133(3)	0.043(1)
C(12)	0.3466(5)	0.2965(5)	0.0588(3)	0.051(1)
C(13)	0.3694(5)	0.3854(5)	0.0210(3)	0.054(1)
C(14)	0.3106(5)	0.4842(5)	0.0371(3)	0.056(1)
C(15)	0.2255(4)	0.4952(4)	0.0898(3)	0.044(1)
C(16)	0.0476(4)	0.5541(3)	0.2225(3)	0.035(1)
C(17)	0.0936(5)	0.6215(4)	0.3072(3)	0.045(1)
C(18)	0.0628(6)	0.7337(4)	0.3242(4)	0.059(1)
C(19)	−0.0167(6)	0.7769(4)	0.2570(4)	0.060(1)
C(20)	−0.0650(5)	0.7088(4)	0.1743(4)	0.058(1)
C(21)	−0.0344(5)	0.5983(4)	0.1566(3)	0.047(1)
C(22)	−0.0639(4)	0.3319(4)	0.1245(3)	0.036(1)
C(23)	−0.0783(5)	0.2804(4)	0.0379(3)	0.052(1)
C(24)	−0.1994(6)	0.2246(5)	−0.0153(4)	0.067(2)
C(25)	−0.3065(5)	0.2212(5)	0.0178(4)	0.068(2)
C(26)	−0.2933(5)	0.2731(5)	0.1037(4)	0.066(2)
C(27)	−0.1731(5)	0.3292(5)	0.1565(3)	0.054(1)
C(28)	−0.0646(4)	0.2844(4)	0.3875(3)	0.038(1)
C(29)	−0.1542(5)	0.2205(4)	0.4129(3)	0.052(1)
C(30)	−0.2543(5)	0.2729(5)	0.4424(4)	0.062(2)
C(31)	−0.2615(5)	0.3869(5)	0.4501(3)	0.059(1)
C(32)	−0.1723(5)	0.4503(5)	0.4264(3)	0.055(1)
C(33)	−0.0737(4)	0.4004(4)	0.3952(3)	0.043(1)
C(34)	−0.0130(4)	0.1139(3)	0.2439(3)	0.036(1)
C(35)	0.0665(5)	0.0755(4)	0.1906(3)	0.046(1)
C(36)	0.0149(6)	−0.0024(4)	0.1123(3)	0.058(1)
C(37)	−0.1167(7)	−0.0404(4)	0.0849(4)	0.066(2)
C(38)	−0.1979(6)	−0.0030(5)	0.1362(4)	0.064(2)
C(39)	−0.1464(5)	0.0748(4)	0.2167(3)	0.051(1)
C(40)	0.1436(4)	0.1373(4)	0.4250(3)	0.042(1)
C(41)	0.2169(5)	0.0501(4)	0.4004(4)	0.058(1)
C(42)	0.2974(6)	0.0005(5)	0.4640(4)	0.070(2)
C(43)	0.3005(6)	0.0366(6)	0.5513(4)	0.076(2)
C(44)	0.2249(6)	0.1205(6)	0.5761(4)	0.073(2)
C(45)	0.1487(5)	0.1725(5)	0.5134(3)	0.059(1)
B	0.4629(9)	0.0664(10)	0.2243(7)	0.094(3)
F(1)	0.5454(12)	−0.0218(11)	0.2152(9)	0.138(4)*
F(2)	0.3606(10)	0.0487(8)	0.1512(6)	0.113(4)*
F(3)	0.5370(10)	0.1678(9)	0.2242(7)	0.131(4)*
F(4)	0.4418(13)	0.0814(12)	0.3047(9)	0.166(5)*
F(1A)	0.3584(14)	−0.0220(12)	0.2176(9)	0.152(6)**
F(2A)	0.4142(14)	0.1533(13)	0.2711(10)	0.153(6)**
F(3A)	0.452(2)	0.076(2)	0.1410(13)	0.201(8)**
F(4A)	0.5710(11)	0.0222(10)	0.2588(8)	0.097(3)**

[a] The form of the equivalent isotropic displacement parameter is $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$. Asterisks designate isotropic refinement with occupancy factor of 0.54(1). Double asterisks designate isotropic refinement with occupancy factor of 0.46(1).

Treatment of the isomeric mixtures of *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}CH_2C{\equiv}CR)$ and *trans*-$(PPh_3)_2PdBr(\eta^1\text{-}C(R){=}C{=}CH_2)$ (R = Ph, Me), prepared by the general method of Boersma,[36] with $AgBF_4$ in CH_2Cl_2 solution led to the isolation of **2a,b** in 90−92% yield. **2a,b** were also prepared by addition of $RC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$ to a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ and PPh_3 in CH_2Cl_2 followed by stirring at room temperature (eq 5). This method afforded the η^3-propargyl/allenyl complexes in 81−83% yield. It is noteworthy that the use of $RC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$ with $Pd_2(dba)_3{\cdot}CHCl_3$ and PPH_3 gives the tosylate salts of **2** that are stable toward isolation. In contrast, as mentioned earlier, use of $RC{\equiv}CCH_2OS(O)_2C_6H_4Me\text{-}p$ with $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ yields the corresponding platinum complexes that decompose during workup. The difference in behavior may be a result of the observed greater tendency of **1** than of **2** to undergo reaction with nucleophilic reagents. This aspect of the relative chemistry of **1** and **2** will be considered later in the paper.



(5)

2a-b (OTs)

Spectroscopic Properties of Platinum and Palladium η^3-Propargyl/Allenyl Complexes. The palladium complexes **2a,b** are pale yellow solids when isolated as **2**(BF_4) and off-white solids when obtained as the tosylates. The platinum complex **1a** is a beige to pale yellow solid with the various counterions used. All are stable to air in the solid. **2a,b** do not appear to be affected by moisture, whereas **1a** slowly reacts with water in the air.[37]

NMR spectroscopic properties of **1** and **2** (cf. Experimental Section) serve to characterize these products as η^3-propargyl/allenyl complexes and rule out possible η^1-propargyl and -allenyl modes of attachment of the organic ligand to the metal. Thus, the ^{1}H NMR spectra of **1a** and **2a,b** show that the CH_2 protons are equivalent and coupled differently to the two phosphorus nuclei. The different coupling is in agreement with the two PPh_3 ligands appearing inequivalent in the $^{31}P\{^1H\}$ NMR spectra. The chemical shift of the CH_2 protons is comparable to that for metal η^1-allenyl complexes but is appreciably downfield (0.6−1.9 ppm) from that for analogous metal η^1-propargyl complexes.[1] In the $^{13}C\{H\}$ NMR spectra, signals of the η^3-propargyl/allenyl ligand are observed at δ 105.4−102.1, 97.3−91.2, and 53.1−48.3. All of them show coupling to the phosphorus nuclei, with additional coupling to ^{195}Pt for **1a**. Those of the terminal carbon atoms CH_2 at δ 53.1−48.3 and *C*R at δ 105.4−102.1 display much stronger coupling to one phosphorus (37−47 Hz) than to the other (<1.5 Hz), in agreement with a distorted square-planar disposition of the *C*H_2, *C*R, and two P atoms around the metal (vide infra). The central carbon atom is only weakly coupled to the phosphorus nuclei. The resonance of the CH_2 carbon atom for **1** and **2** at δ 53.1−48.3 appears downfield from that for metal η^1-propargyl complexes at $\delta \leq 8$, whereas the resonance of the central carbon atom of **1** and **2** at δ 97.3−91.2 occurs much farther upfield than that for metal η^1-allenyl complexes at $\delta \geq 194$.[1,14,35,38] Furthermore, for **1a**, each of the CH_2 and *C*R carbon atoms is quite strongly coupled to ^{195}Pt (J_{PtC} = 126 and 93 Hz, respectively), as expected for an η^3 mode of attachment of the propargyl/allenyl ligand.

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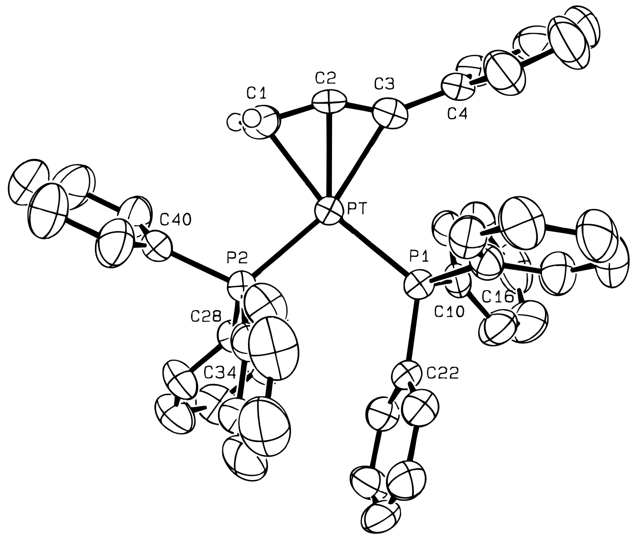


Figure 1. ORTEP drawing of **1a** in **1a**(OTf)·CH_2Cl_2 showing the atom-numbering scheme. Only the ipso carbon atoms have been numbered for the phenyl rings. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The CH_2 hydrogen atoms are drawn with artificial radii, and the phenyl hydrogen atoms are omitted.

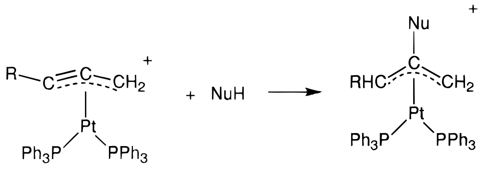
In the proton-coupled ^{13}C NMR spectrum of **1a**, the coupling constant $^1J_{CH} = 170$ Hz for the CH_2 moiety shows sp^2 hybridization at carbon,[39] also consistent with this type of ligation. In contrast, the corresponding $^1J_{CH} = 140$ Hz for *trans*-$(PPh_3)_2PtBr(\eta^1\text{-}CH_2C{\equiv}CPh)$ indicates sp^3 hybridization.[39]

Structural Characterization of $[(PPh_3)_2M(\eta^3\text{-}CH_2CCPh)]^+$ (1a, M = Pt; 2a, M = Pd). The structure of the cationic platinum complex **1a** (in **1a**(OTf)·CH_2Cl_2) is shown in Figure 1; that of the palladium analogue **2a** (in **2a**(BF_4)) is virtually identical and was given the same atom-numbering scheme. Selected bond distances, bond angles, and dihedral angles for both complexes are presented in Table 4.

The CH_2CCPh ligand is bent and attached to the metal in an η^3 mode. The degree of bending (152.2(9)° for **1a**, 154.7(5)° for **2a**) is comparable to that found in other transition-metal η^3-propargyl/allenyl and related η^3-butenynyl complexes.[2,3,6,9] Interestingly, the value of this angle is approximately halfway between that for an unperturbed allenyl or propargyl fragment (180°) and the η^3-allyl ligand in metal complexes (120°).[40] For both cations **1a** and **2a**, the M−C bond distances follow the order $M-C(2) \leq M-C(1) < M-C(3)$. The M−C(1) distance is essentially identical for the two complexes, as is also the M−C(2) distance. However, the M−C(3) distance is somewhat longer for **2a** than for **1a**. These relative bond distances are consistent with the angle C(1)−C(2)−C(3) being slightly more obtuse for the Pd complex compared to the Pt complex. The C(1)−C(2) and C(2)−C(3) bond lengths are respectively 1.395(14) and 1.227(13) Å for **1a** and 1.385(7) and 1.233(7) Å for **2a**. They indicate substantial contributions of both η^3-allenyl and η^3-propargyl resonance structures to the bonding description of these complexes.

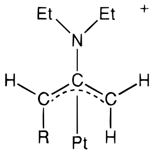
Rotation of the cationic complex by 90° about the M−C(2) axis generates a structure which is shown in Figure 2 for **2a**. The atoms C(1), C(2), C(3), Pd (or Pt, for **1a**), P(1), and P(2) essentially lie in one plane, as evidenced by the dihedral angles listed in Table 4. (The respective displacements of the atoms M, P(1), and P(2) from the C(1)C(2)C(3) plane are −0.0362, 0.1129, and −0.0514 Å for **1a** and −0.0908, −0.0742, and −0.1788 Å for **2a**.) The coordination environments of C(1), C(3), P(1), and P(2) around the metal center in **1a** and **2a** are thus planar but appreciably distorted from square-planar because of the differences in the bond angles as depicted in Figure 3A,B. The observed distortion is similar to that recently reported for the η^3-trimethylenemethane complex $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)\text{-}CHPh)$[41] (Figure 3C). In contrast, the platinacyclobutane complex $(PEt_3)_2Pt(\eta^2\text{-}CH_2CMe_2CH_2)$ shows a much more regular square-planar coordination environment[42] (Figure 3D).

Reactions of Platinum and Palladium η^3-Propargyl/Allenyl Complexes. The platinum complexes **1a,b** react with nucleophilic reagents of the type NuH (NuH = MeOH, Et_2NH) to afford the corresponding η^3-allyl complexes **3a,b** and **4a,b**, respectively, with the nucleophile Nu^- adding to the central carbon atom (eq 6). The palladium complexes **2a,b** react similarly with Et_2NH to give **6a,b**, but they add MeOH only in the presence of trace amounts of OMe^- or NEt_3 to yield **5a,b**.

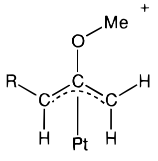


3 - 4 (6)

The addition of Et_2NH to the η^3-propargyl/allenyl ligand of **1a,b** proceeds stereospecifically to give η^3-allyl products in which the groups R and NEt_2 are anti (**III**).



III



IV

This orientation has been determined with the aid of the ^1H NMR spectra. The spectra show three equal-intensity η^3-allyl proton signals at δ 4.38−2.92, 2.66−2.62, and 2.35−2.33, which are assigned respectively to C*H*R and the inequivalent protons of CH_2. Selective proton decoupling experiments for **4a** showed that the hydrogens resonating at δ 4.38 and 2.62 are weakly coupled. Such small long-range coupling ($^4J_{HH}$)—the so-called W-effect—is known to occur between syn protons in metal η^3-allyl complexes.[43] The similar appearance of the three resonances in the spectra of **4a,b** (cf. Experimental Section) indicates that these products have the same orientation of R and NEt_2.

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Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Dihedral Angles (deg) for 1a(OTf)·CH$_2$Cl$_2$ and 2a(BF$_4$)

	1a(OTf)·CH$_2$Cl$_2$	**2a**(BF$_4$)
Bond Distances		
M−P(1)	2.297(2)	2.3342(11)
M−P(2)	2.262(2)	2.2913(11)
M−C(1)	2.186(11)	2.162(5)
M−C(2)	2.150(8)	2.143(4)
M−C(3)	2.273(9)	2.334(5)
C(1)−C(2)	1.395(14)	1.385(7)
C(2)−C(3)	1.227(13)	1.233(7)
C(3)−C(4)	1.46(1)	1.442(7)
Bond Angles		
P(1)−M−P(2)	100.16(8)	103.77(4)
C(1)−M−P(2)	93.0(3)	92.1(1)
C(3)−M−P(1)	97.2(3)	95.0(1)
C(1)−M−P(1)	166.0(3)	164.0(1)
C(3)−M−P(2)	162.6(3)	161.2(1)
C(1)−M−C(3)	69.6(4)	69.1(2)
C(1)−C(2)−C(3)	152.2(9)	154.7(5)
C(2)−C(3)−C(4)	148(1)	153.7(5)
Dihedral Angles		
C(1)C(2)C(3), MC(1)C(3)	1.1	2.8
MC(1)C(3), MP(1)P(2)	4.6	2.3
C(1)C(2)C(3), MP(1)P(2)	3.7	2.2

In contrast, similar decoupling experiments for the methoxy analogue of **4a**, **3a**, revealed the absence of long-range coupling ($^4J_{HH}$) in the ^{1}H NMR spectrum. The three allylic proton signals of **3a,b** are also similar in appearance but differ from those of **4a,b**. The complexes **3a,b** are assigned structures in which the substituents R and OMe adopt a syn orientation (**IV**). This same orientation was also inferred from the ^{1}H NMR spectra for the groups Ph and C(CO$_2$Me)$_2$ in (PPh$_3$)$_2$Pt(η^3-CH$_2$C(C(CO$_2$Me)$_2$)CHPh)[7] and was later corroborated by an X-ray diffraction analysis.[41]

The palladium complexes **5a,b** and **6a,b** appear to have the same stereochemistry of the η^3-allyl ligand as their platinum counterparts, **3a,b** and **4a,b**, respectively. However, a detailed analysis of their ^{1}H NMR spectra is complicated by the overlap of the signals of the syn and anti CH$_2$ protons.[44]

The different stereochemistry of the addition of MeOH and Et$_2$NH to the η^3-propargyl/allenyl ligand of **1** is intriguing. The addition of NEt$_2$ anti to R suggests that this reaction may proceed by nucleophilic attack of Et$_2$NH at the central carbon atom of η^3-CH$_2$CCR, with an essentially synchronous proton transfer to the *C*R carbon (Scheme 1). The source of this proton would be either the attacking Et$_2$NH molecule or one attached to it by hydrogen-bonding. Methanol probably also attacks the central carbon atom of **1** but may give an uncharged methoxy-substituted metallacyclobutene intermediate. Protonation at metal and transfer of the proton to the *C*R carbon atom away from the OMe group would then afford the syn orientation of OMe and R in the product. Steric effects associated with the nucleophile apparently do not influence the stereochemistry of the product, since other alcohols (R′OH), including Me$_3$CCH$_2$OH, also give platinum η^3-allyl complexes in which the OR′ and R groups are syn.[14]

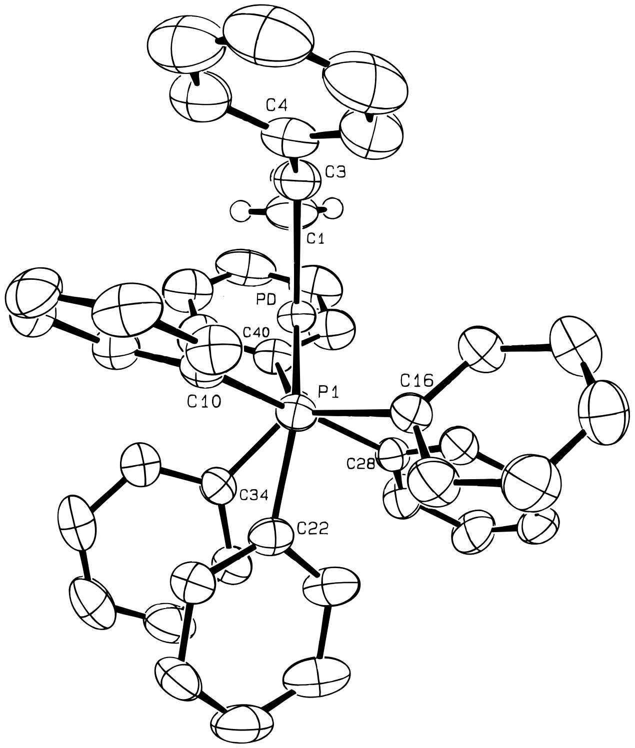
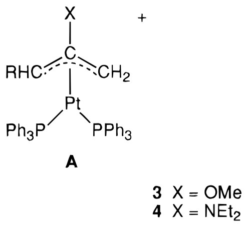


Figure 2. ORTEP drawing of **2a** in **2a**(BF$_4$) showing the atom-numbering scheme. Only the ipso carbon atoms have been numbered for the phenyl rings. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The CH$_2$ hydrogen atoms are drawn with artificial radii, and the phenyl hydrogen atoms are omitted. The atoms C(2) and P(2) are hidden behind C(3) and P(1), respectively.

The ^{1}H NMR spectra of **3** and **4** display a large geminal coupling constant of 6.6−9.6 Hz for the CH$_2$ group. This value of $^2J_{HH}$ suggests a considerable contribution from the metallacyclic resonance form **B**



to the overall bonding description of **3** and **4**. The ^{13}C{^{1}H} NMR spectra of **3**−**6** reveal two resonances at δ 81.1−50.1 and 58.9−35.0 which show substantial coupling to one phosphorus nucleus (24−52 Hz) and small, usually indiscernible, coupling to the other. These signals are assigned to the *C*HR and CH$_2$ carbon atoms, respectively. In addition, there is a resonance at δ 156.3−148.6, assigned to the central carbon atom, which appears as a singlet or a narrow triplet, with weak coupling (≤8 Hz) to both phosphorus nuclei. For the platinum complexes **3** and **4**, the former two signals show large J_{PtC} coupling constants (up to 236 Hz), and the latter signal shows a smaller coupling constant (up to 123 Hz). These ^{13}C NMR chemical shifts and coupling constants suggest a major contribution to the bonding of the η^3-allyl resonance form **A**.[45]

Finally, the regiochemistry of the addition of nucleophilic reagents to the central carbon atom of the η^3-CH$_2$-

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[44] The other possible explanation, viz., that these protons are involved in a fluxional process, appears unlikely, since the NMe$_2$ analogue of **6a** shows separate signals for the syn and anti CH$_2$ protons. These signals do not approach coalescence with decrease in temperature.

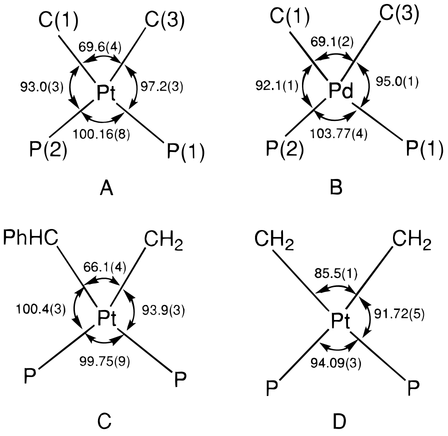
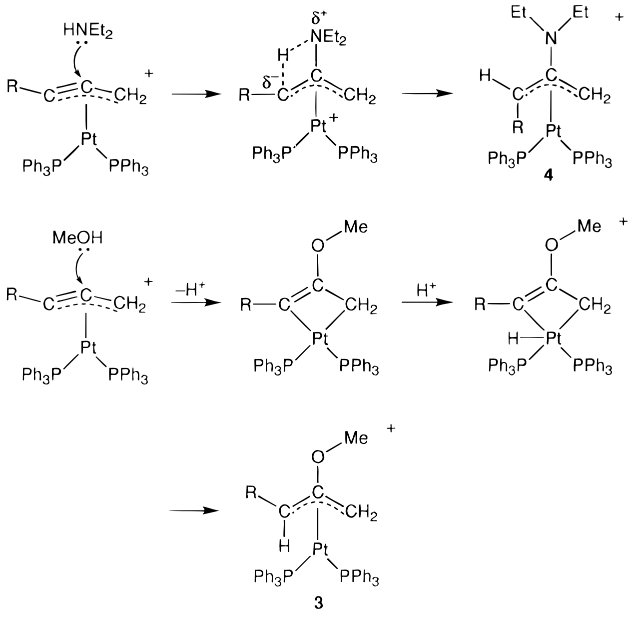


Figure 3. Coordination environment including the bond angles (deg) around the metal center: A, in **1a**; B, in **2a**; C, in the η^3-trimethylenemethane complex $(PPh_3)_2Pt(\eta^3$-$CH_2C(C(CO_2Me)_2)CHPh)$; D, in the platinacyclobutane complex $(PEt_3)_2Pt(\eta^2$-$CH_2CMe_2CH_2)$. The bond angles in C are average values.

CCR ligand merits brief comment. According to the rules of Green, Davies, and Mingos,[46] open π-polyenyl ligands undergo attack by nucleophiles at one of the terminal carbon atoms, unless the ML_x fragment is electron-donating. Thus, η^3-allyl complexes of palladium add nucleophiles in terminal position.[12] Complexes **1** and **2** represent the only open π-systems where nucleophilic addition to the organic ligand is exclusively nonterminal.[47] Recent calculations suggest that such reactions of **1** and **2** are charge controlled,[48] and that study will be reported later together with our further synthetic and mechanistic investigations.[14]

Scheme 1



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Supporting Information Available: Tables of hydrogen atom positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles for complexes **1a**(OTf)·CH_2Cl_2 and **2a**(BF_4) (16 pages). Ordering information is given on any current masthead page.

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