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SYNTHESIS AND PROPERTIES OF HYDRIDO(SELENOLATO)PLATINUM(II) COMPLEXES BEARING CHELATING PHOSPHINE LIGANDS

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The reactions of an overcrowded selenol, TripSeH (1, Trip = 9-triptycyl) with [PtCl₂L] (L = dppe, dppf), in the presence of NaBH₄ afforded the corresponding hydrido(selenolato) platinum(II) complexes [PtH(SeTrip)(L)] [2 (L = dppe), 3 (L = dppf)]. Complexes 2 and 3 were fully characterized by NMR and IR spectroscopies, and their molecular structures were determined by X-ray crystallography. Thermal reaction of 2 or treatment of 2 with an excess amount of HBF₄ produced five-membered selenaplatinacycle [Pt(η²-C,Se-Trip)(dppe)] 4 in moderate yields.

Keywords Hydrido complex; platinum; selenaplatinacycle; selenium; selenol; X-ray crystallography

INTRODUCTION

Hydrido(selenolato) platinum(II) complexes have been proposed as the key intermediate in the catalytic hydroselenation of alkynes employing selenols in the presence of platinum(0) complexes.^{1,2} Ananikov et al. previously described the spectroscopic detection of [*trans*-PtH(SePh)(PPh₃)₂] by ¹H NMR, but no isolation or characterization of the hydrido(selenolato) platinum(II) complexes as stable molecules had been reported until quite recently due to their thermal instability.^{2a} We recently succeeded in the synthesis and structure determination of the first stable hydrido(selenolato) platinum(II) complex [*cis*-PtH(SeTrip)(PPh₃)₂],³ kinetically stabilized with a 9-triptycyl (Trip) group.⁴ Furthermore, we found the unique reactions of selenoseleninate [TripSe(O)SeTrip] or selenenic acid [TripSeOH] with [Pt(η²-C₂H₄)(Ph₃P)₂] to form a five-membered selenaplatinacycle by an intramolecular C–H activation leading to the cyclometalation.³ Herein, we present the synthesis of hydrido(selenolato) platinum(II) complexes bearing a chelating phosphine ligand such as dppe [1,2-bis(diphenylphosphino)ethane] and dppf [1,1'-bis(diphenylphosphino)ferrocene] by the reactions of an overcrowded selenol,

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

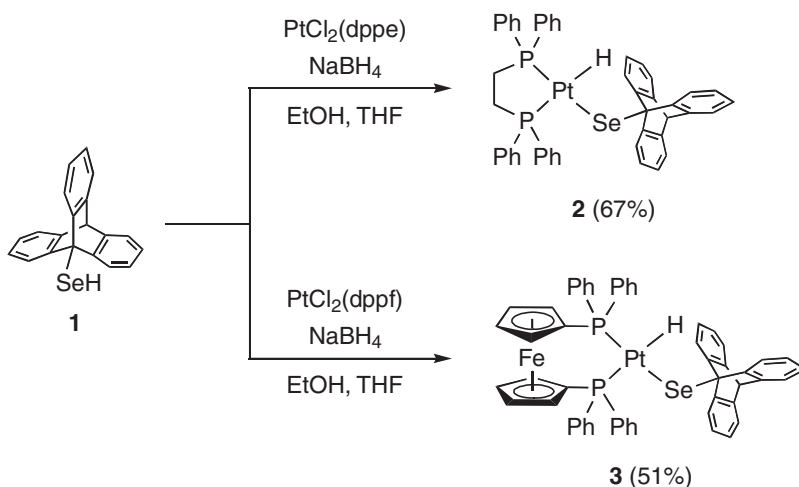
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TripSeH (**1**), with the corresponding platinum(0) complexes, and their characterization and properties.

RESULTS AND DISCUSSION

The reactions of TripSeH **1** with 1 equiv. of [Pt(dppe)] or [Pt(dppf)], which were generated in situ by the reduction of [PtCl₂(dppe)] or [PtCl₂(dppf)], with an excess amount of NaBH₄ in ethanol, afforded the corresponding hydrido(selenolato) platinum(II) complexes [PtH(SeTrip)L] [**2** (L = dppe), **3** (L = dppf)] in 67% or 51% yield, respectively (Scheme 1).



Scheme 1

The structures of **2** and **3** were confirmed by NMR and IR spectroscopies and elemental analyses. In the ¹H NMR spectra of **2** and **3**, the hydride resonated as a doublet of doublets at δ -2.91 (²J_{P-H} = 197, 7, ¹J_{Pt-H} = 985 Hz) for **2** and -5.54 (²J_{P-H} = 187, 17, ¹J_{Pt-H} = 913 Hz) for **3**, which are shifted to downfield relative to those of reported [*trans*-PtH(SePh)(PPh₃)₂] [δ -8.77 (¹J_{Se-H} = 44.1, ¹J_{Pt-H} = 999.8 Hz)]^{2a} and [*cis*-PtH(SeTrip)(PPh₃)₂] [δ -6.10 (²J_{P-H} = 184, 16, ¹J_{Pt-H} = 1523 Hz)].³ This observation indicates that the hydride character of dppe derivative **2** is lower than that of dppf derivative **3** and [*cis*-PtH(SeTrip)(PPh₃)₂]. The ³¹P{¹H} NMR spectrum of **2** exhibited two singlets with ¹⁹⁵Pt satellites at δ 48.7 (¹J_{Pt-P} = 1764 Hz) and 49.9 (²J_{Se-P} = 38, ¹J_{Pt-P} = 3071 Hz), which were assigned to the phosphorus atoms lying *trans* to the hydride and the selenolato ligand, respectively. In contrast, the ³¹P{¹H} resonances for **3** were observed as two doublets at δ 17.9 (²J_{P-P} = 17, ²J_{Se-P} = 72, ¹J_{Pt-P} = 3334 Hz) and 26.4 (²J_{P-P} = 17, ¹J_{Pt-P} = 2029 Hz), where the observation of P-P coupling indicates a large deviation of the P-Pt-P angle from 90° of the ideal square planar geometry around the Pt(II) center (*vide infra*). In the IR spectrum, the Pt-H stretching vibrations (**2**: 2053 cm⁻¹, **3**: 2084 cm⁻¹) were observed at somewhat lower wave numbers than that of reported [*cis*-PtH(SeTrip)(PPh₃)₂] (2093 cm⁻¹).³ The molecular structures of **2** and **3** were determined by X-ray crystallography, as shown in Figures 1 and 2. Both of the Pt centers maintained the planarity. The P1-Pt1-P2 bond angle in **3** was widened by ca. 11° from 90° of the ideal square planar geometry

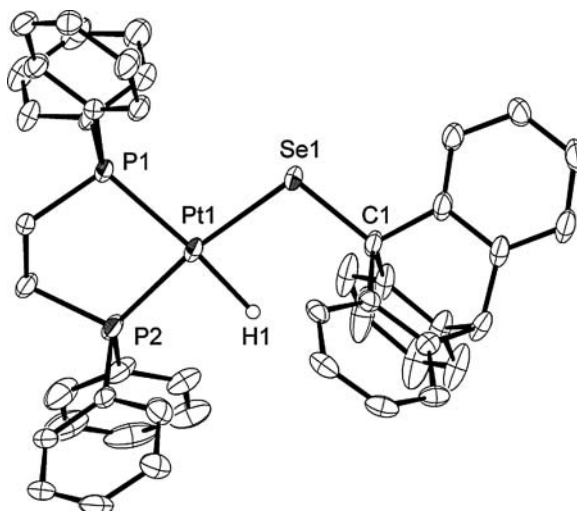


Figure 1 ORTEP drawing of $[\text{PtH}(\text{SeTrip})(\text{dppe})]$ **2** (30% thermal ellipsoids, a CH_2Cl_2 molecule and a CCl_4 molecule, and hydrogen atoms except H1 were omitted for clarity). Selected bond lengths (\AA): Pt1–Se1 = 2.4376(8), Pt1–P1 = 2.3093(16), Pt1–P2 = 2.2190(19), Pt1–H1 = 1.686(10), Se1–C1 = 1.982(6), Selected bond angles ($^\circ$): P1–Pt1–P2 = 86.39(6), Se1–Pt1–P1 = 101.42(5), Se1–Pt1–H1 = 85(3), P2–Pt1–H1 = 87(3), Se1–Pt1–P2 = 172.13(5), P1–Pt1–H1 = 172(3).

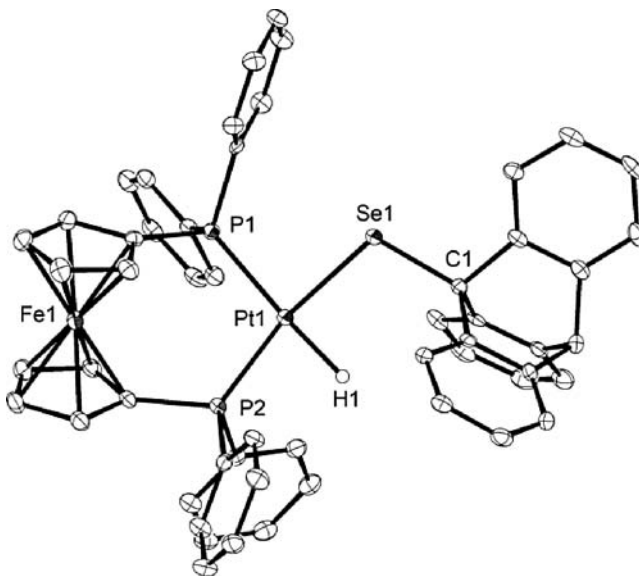
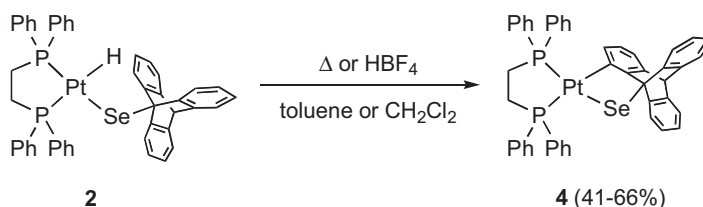


Figure 2 ORTEP drawing of $[\text{PtH}(\text{SeTrip})(\text{dppf})]$ **3** (30% thermal ellipsoids, a C_6H_6 molecule, and hydrogen atoms except H1 were omitted for clarity). Selected bond lengths (\AA): Pt1–Se1 = 2.4291(4), Pt1–P1 = 2.3175(11), Pt1–P2 = 2.2470(11), Pt1–H1 = 1.686(10), Se1–C1 = 1.985(4), Selected bond angles ($^\circ$): P1–Pt1–P2 = 100.96(4), Se1–Pt1–P1 = 90.04(3), Se1–Pt1–H1 = 87(3), P2–Pt1–H1 = 82(3), Se1–Pt1–P2 = 168.97(3), P1–Pt1–H1 = 177(3).

due to the structural requirement of dppe ligand, similarly to the case of reported [*cis*-PtH(SeTrip)(PPh₃)₂].³ The Pt–Se bond lengths [2.4376(8) Å for **2**, 2.4291(4) Å for **3**] were similar to that observed in [*cis*-PtH(SeTrip)(PPh₃)₂] [2.4272(5) Å]³ and the related diselenolato platinum(II) complex [*cis*-Pt(SePh)₂(PPh₃)₂] [2.4604(10), 2.4970(9) Å].⁵ The Pt1–P1 bond lengths [2.3093(16) Å for **2**, 2.3175 (11) Å for **3**] were slightly longer than the Pt1–P2 bond lengths [2.2190(19) Å for **2**, 2.2470(11) Å for **3**], suggesting the lower trans influence of the selenium atom than that of the hydride.

While the complexes **2** and **3** are stable to air in the solid state [mp: 204–206°C (dec) for **2**, 195–196°C (dec) for **3**], refluxing a toluene solution of dppe derivative **2** for 12 h gave five-membered selenaplatinacycle [Pt(η^2 -C,Se-Trip)(dppe)] (**4**) in 66% yield, which is formed by an intramolecular C–H activation⁶ leading to the cyclometalation. In addition, treatment of **2** with an excess amount of HBF₄ in dichloromethane also provided **4** in 41% yield (Scheme 2). In the case of *cis*-PtH(SeTrip)(PPh₃)₂, the corresponding selenaplatinacycle [Pt(η^2 -C,Se-Trip)(PPh₃)₂] was formed in 60% yield by treatment with HBF₄.³ These results suggest that the reactivity of Pt–H of **2** as a hydride is lower than that of [*cis*-PtH(SeTrip)(PPh₃)₂], which is in harmony with the consideration based on their ¹H NMR data as mentioned above. In the ¹H NMR spectrum of **4**, a characteristic signal was observed at δ 6.18, which is assigned to the aromatic proton neighboring to the Pt atom. The ³¹P{¹H} NMR spectrum of **4** showed two doublets accompanying ¹⁹⁵Pt satellite signals at δ 46.3 (¹J_{Pt–P} = 1737 Hz) and 47.8 (¹J_{Pt–P} = 3167 Hz). The former signal (δ 46.3) is assigned to the phosphorus trans to the Pt-bonded carbon atom on the basis of similar Pt–P coupling constant values of selenaplatinacycle [Pt(η^2 -C,Se-Trip)(PPh₃)₂] (¹J_{Pt–P} = 1833 Hz)³ and thiaplatinacycles [Pt(η^2 -C,S-C₁₂H₈)(PEt₃)₂] (¹J_{Pt–P} = 1777 Hz) and {Pt(η^2 -C,S-C₁₂H₈)(PEt₃)[P(OEt)₃]} (¹J_{Pt–P} = 1691 Hz).⁷



Scheme 2

In the X-ray analysis of **4**, there observed two crystallographically independent molecules, having very similar structural parameters. The structure of one of them is depicted in Figure 3. The five-membered PtSeC₃ ring of **4** features a nearly planar geometry; the sum of the interior bond angles is 539.10°. The platinum atom maintains the planarity of tetracoordinated Pt(II) atoms; the sum of the four bond angles around the Pt atom is 360.02°. The Pt1–C3 bond length [2.081(6) Å] is close to that of selenaplatinacycle [Pt(η^2 -C,Se-Trip)(PPh₃)₂] [2.099(4) Å]³ and somewhat shorter than that of selenametalacycle {Pt[η^2 -C,Se-C₄H₄Mn(CO)₃](PPh₃)₂]⁺ [2.256(5) Å].⁸ The Pt1–P1 bond [2.2982(16) Å] trans to the Pt1–C3 bond is slightly longer than the Pt1–P2 bond [2.2606(17) Å] trans to the Pt1–Se1 bond. This observation, as well as the smaller ¹J_{Pt–P} value of P1 than that of P2, indicates that the trans influence of the aromatic carbon atom is larger than that of the selenium atom.

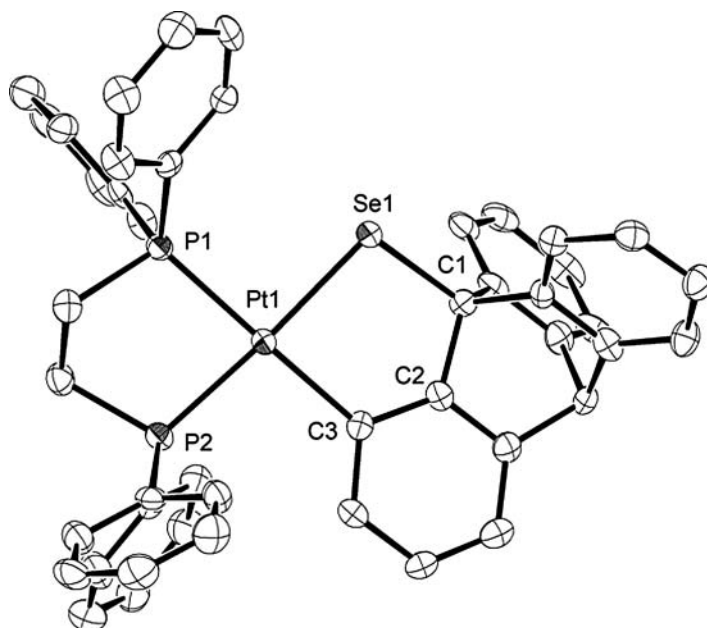


Figure 3 ORTEP drawing of one of the two independent molecules in the unit cell of selenaplatinacycle **4** (30% thermal ellipsoids, CH_2Cl_2 molecules, and hydrogen atoms were omitted for clarity). Selected bond lengths (Å): Pt1–Se1 = 2.4139(7), Pt1–C3 = 2.081(6), Pt1–P1 = 2.2982(16), Pt1–P2 = 2.2606(17), Se1–C1 = 1.959(6), C1–C2 = 1.535(9), C2–C3 = 1.396(9). Selected bond angles (°): P1–Pt1–P2 = 84.64(6), Se1–Pt1–P1 = 92.47(4), Se1–Pt1–C3 = 86.43(18), P2–Pt1–C3 = 96.48(18), Se1–Pt1–P2 = 175.99(5), P1–Pt1–C3 = 178.82(18), Pt1–Se1–C1 = 98.47(18), Se1–C1–C2 = 110.6(4), C1–C2–C3 = 124.2(6), Pt1–C3–C2 = 119.4(5).

EXPERIMENTAL

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Bruker DPX-400 or a DRX-400 (400, 100.7, and 162 MHz, respectively) spectrometers using CDCl_3 or CD_2Cl_2 as the solvent at room temperature. IR spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. All melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. Preparative gel permeation liquid chromatography (GPC) was performed on an LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: CHCl_3). 9-Triptyceneselenol **1** was prepared according to the reported procedure.^{4a}

[PtH(SeTrip)(dppe)] (**2**)

A solution of **1** (118.9 mg, 0.357 mmol) in dry THF (10 mL) was added to a solution of [Pt(dppe)] prepared by the reduction of [PtCl₂(dppe)] (231.5 mg, 0.348 mmol) with NaBH_4 (31.0 mg, 0.819 mmol) in ethanol (10 mL) at room temperature for 10 min. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered through

a pad of Celite and rinsed with CH_2Cl_2 . After removal of the solvent in vacuo, the residue was purified by column chromatography (SiO_2 , CH_2Cl_2) to give $[\text{PtH}(\text{SeTrip})(\text{dppe})]$ (**2**) (221.2 mg, 67%) as colorless crystals. Mp 204–206°C (dec.); ^1H NMR (CDCl_3 , δ) –2.91 (dd, 1 H, $^2J_{\text{H-P}(\text{trans})} = 197$, $^2J_{\text{H-P}(\text{cis})} = 7$, $^1J_{\text{Pt-H}} = 985$ Hz), 2.34–2.49 (m, 4 H), 5.39 (s, 1 H), 6.92–6.97 (m, 6 H), 7.26–7.33 (m, 12 H), 7.43–7.51 (m, 6 H), 7.61–7.67 (m, 4 H), 8.07–8.11 (m, 4 H); ^{13}C NMR (CDCl_3 , δ) 28.2 (dd, $^1J_{\text{C-P}} = 34$, $^2J_{\text{C-P}} = 17$ Hz), 28.9 (dd, $^1J_{\text{C-P}} = 34$, $^2J_{\text{C-P}} = 14$ Hz), 54.8, 59.2 (d, $^3J_{\text{C-P}} = 10$ Hz), 122.2, 123.6, 124.3, 128.6 (d, $^2J_{\text{C-P}} = 42$ Hz), 128.7 (d, $^2J_{\text{C-P}} = 42$ Hz), 130.7, 130.9 (d, $^1J_{\text{C-P}} = 93$ Hz), 131.8 (d, $^1J_{\text{C-P}} = 93$ Hz), 133.0 (d, $^3J_{\text{C-P}} = 16$ Hz), 133.2 (d, $^3J_{\text{C-P}} = 16$ Hz), 146.6, 149.2; ^{31}P NMR (CDCl_3 , δ) 48.7 (s, $^1J_{\text{P-Pt}} = 1764$ Hz), 49.9 (s, $^1J_{\text{P-Pt}} = 3071$, $^2J_{\text{P-Se}} = 38$ Hz); IR (KBr) (ν , cm^{-1}): 2053 (Pt–H); Anal. Calcd for $\text{C}_{46}\text{H}_{38}\text{P}_2\text{PtSe}$: C, 59.61; H, 4.13. Found: C, 58.69; H, 3.99.

$[\text{PtH}(\text{SeTrip})(\text{dppf})]$ (3**)**

A solution of **1** (53.3 mg, 0.160 mmol) in dry THF (8 mL) was added to a solution of $[\text{Pt}(\text{dppf})]$ prepared by the reduction of $[\text{PtCl}_2(\text{dppf})]$ (131.1 mg, 0.160 mmol) with NaBH_4 (19.1 mg, 0.505 mmol) in ethanol (8 mL) at room temperature for 10 min. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered through a pad of Celite and rinsed with CH_2Cl_2 . After removal of the solvent in vacuo, the yellow residue was purified by column chromatography (acidic SiO_2 , CH_2Cl_2) to give $[\text{PtH}(\text{SeTrip})(\text{dppf})]$ (**3**) (88.9 mg, 51%) as yellow crystals. Mp 195–196°C (dec.); ^1H NMR (CDCl_3 , δ) –5.54 (dd, 1 H, $^2J_{\text{H-P}(\text{trans})} = 187$, $^2J_{\text{H-P}(\text{cis})} = 17$, $^1J_{\text{Pt-H}} = 913$ Hz), 3.72 (s, 2 H), 4.15 (s, 2 H), 4.44 (s, 2 H), 4.76 (s, 2 H), 5.28 (s, 1 H), 6.86–6.94 (m, 6 H), 7.22–7.40 (m, 18 H), 7.59–7.63 (m, 4 H), 7.78–7.82 (m, 4 H); ^{13}C NMR (CDCl_3 , δ) 54.7, 58.0 (dd, $^3J_{\text{C-P}} = 13$, 3 Hz), 71.3 (d, $^3J_{\text{C-P}} = 7$ Hz), 73.0 (d, $^3J_{\text{C-P}} = 7$ Hz), 74.6 (d, $^2J_{\text{C-P}} = 9$ Hz), 76.0 (d, $^2J_{\text{C-P}} = 12$ Hz), 79.3 (d, $^1J_{\text{C-P}} = 54$ Hz), 79.4 (d, $^1J_{\text{C-P}} = 54$ Hz), 122.0, 123.8, 124.1, 127.7 (d, $^3J_{\text{C-P}} = 24$ Hz), 127.8 (d, $^3J_{\text{C-P}} = 24$ Hz), 130.1, 130.3, 133.3 (d, $^1J_{\text{C-P}} = 47$ Hz), 134.5 (d, $^2J_{\text{C-P}} = 31$ Hz), 134.6 (d, $^2J_{\text{C-P}} = 31$ Hz), 135.1 (d, $^1J_{\text{C-P}} = 50$ Hz), 146.0, 149.1; ^{31}P NMR (CDCl_3 , δ) 17.9 (d, $^2J_{\text{P-P}} = 17$, $^1J_{\text{P-Pt}} = 3334$, $^2J_{\text{P-Se}} = 72$ Hz), 26.4 (d, $^2J_{\text{P-P}} = 17$, $^1J_{\text{P-Pt}} = 2029$ Hz); IR (KBr) (ν , cm^{-1}): 2084 (Pt–H); Anal. Calcd for $\text{C}_{54}\text{H}_{42}\text{FeP}_2\text{PtSe}$: C, 59.90; H, 3.91. Found: C, 60.44; H, 4.10.

Thermal Reaction of 2

A toluene (5 mL) solution of complex **2** (31.0 mg, 0.033 mmol) was refluxed for 12 h. After removal of the solvent in vacuo, the residual colorless solid was purified by PTLC (CH_2Cl_2) to give selenaplatinacycle **4** (15.5 mg, 66%) as colorless crystals. Mp 255°C (dec.); ^1H NMR (CD_2Cl_2 , δ) 2.27–2.35 (m, 4 H), 5.32 (s, 1 H), 6.19 (m, 1 H), 6.83–6.85 (m, 1 H), 6.94–7.04 (m, 5 H), 7.29–7.55 (m, 14 H), 7.82–7.87 (m, 4 H), 7.96–8.02 (m, 6 H); ^{13}C NMR (CD_2Cl_2 , δ) 28.5 (dd, $^1J_{\text{C-P}} = 33$, $^2J_{\text{C-P}} = 11$ Hz), 31.7 (dd, $^1J_{\text{C-P}} = 39$, $^2J_{\text{C-P}} = 17$ Hz), 56.1, 65.7 (dd, $^3J_{\text{C-P}} = 18$, 2 Hz), 68.1, 118.3, 122.2, 124.0 (d, $^4J_{\text{C-P}} = 7$ Hz), 124.4, 124.7, 124.9, 128.7 (d, $^3J_{\text{C-P}} = 17$ Hz), 128.8 (d, $^3J_{\text{C-P}} = 17$ Hz), 131.1, 131.2, 133.9 (d, $^2J_{\text{C-P}} = 19$ Hz), 134.0 (d, $^2J_{\text{C-P}} = 19$ Hz), 140.0 (d, $^3J_{\text{C-P}} = 12$ Hz), 143.5, 146.2, 150.4, 166.6; ^{31}P NMR (CD_2Cl_2 , δ) 46.3 (d, $^2J_{\text{P-P}} = 6$, $^1J_{\text{P-Pt}} = 1737$ Hz), 49.9 (d, $^2J_{\text{P-P}} = 6$, $^1J_{\text{P-Pt}} = 3167$, $^2J_{\text{P-Se}} = 72$ Hz); Anal. Calcd for $\text{C}_{46}\text{H}_{36}\text{P}_2\text{PtSe}$: C, 59.75; H, 3.92. Found: C, 60.15; H, 3.81.

Reaction of **2** with HBF₄

HBF₄ (52.9% w/v, ether, 28 μ L, 0.169 mmol) was added to a solution of **2** (31.0 mg, 0.033 mmol) in CH₂Cl₂ (5 mL) at 0°C. Then the reaction mixture was allowed to warm to room temperature and was stirred for 4 h. After quenching with aqueous solution of –NaHCO₃, the reaction mixture was extracted with CH₂Cl₂, and the organic layers were dried over Na₂SO₄. The solvents were evaporated, and the residual yellow solid was purified by PTLC (CH₂Cl₂) and then GPC to give **4** (12.5 mg, 41%) as colorless crystals.

X-Ray Crystallographic Analyses of Complexes **2–4**

Colorless single crystals of **2** were grown by the slow evaporation of its saturated CH₂Cl₂, CCl₄, and hexane solution. Yellow single crystals of **3** were grown by the slow evaporation of its saturated benzene and hexane solution. Colorless single crystals of **4** were grown by the slow evaporation of its saturated CH₂Cl₂ and hexane solution. The intensity data were collected at 103 K for **2–4** on a Bruker AXS SMART diffractometer employing graphite-monochromated MoK α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).⁹ Hydrogen atoms, except for PtH hydrogen of **2** and **3**, were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystal data for **2**: C₄₈H₄₀Cl₆P₂PtSe (**2**·CH₂Cl₂·CCl₄), MW = 1165.49, monoclinic, space group $P2_1/c$ (no. 14), a = 10.9618(5), b = 17.1160(7), c = 24.0864(10) Å, β = 96.7790(10)°, V = 4487.5(3) Å³, Z = 4, D_{calc} = 1.725 g cm^{–3}, R_1 (I > $2\sigma(I)$) = 0.0515, wR_2 (all data) = 0.1166 for 8363 reflections, 601 parameters, and 6 restraints, GOF = 1.082. Crystal data for **3**: C₆₀H₄₈FeP₂PtSe (**3**·C₆H₆), MW = 1160.82, monoclinic, space group $P2_1/n$ (no. 14), a = 21.8015(10), b = 12.3409(6), c = 18.9330(9) Å, β = 113.1900(10)°, V = 4682.4(4) Å³, Z = 4, D_{calc} = 1.647 g cm^{–3}, R_1 (I > $2\sigma(I)$) = 0.0348, wR_2 (all data) = 0.0820 for 9191 reflections, 590 parameters, and 1 restraint, GOF = 1.120. Crystal data for **4**: C₄₇H₃₇Cl_{1.5}P₂PtSe (**4**·0.75CH₂Cl₂), MW = 990.93, triclinic, space group $P1$ (no. 2), a = 14.2155(6), b = 17.7760(8), c = 18.6070(8) Å, α = 61.8940(10), β = 77.4580(10), γ = 67.1790(10)°, V = 3819.3(3) Å³, Z = 4, D_{calc} = 1.723 g cm^{–3}, R_1 (I > $2\sigma(I)$) = 0.0468, wR_2 (all data) = 0.1145 for 14959 reflections and 946 parameters, GOF = 1.003. CCDC Nos. 710510 for **2**, 710511 for **3**, and 71052 for **4** contain the supplementary crystallographic data for this article. These data can be obtained free of charge via the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

1. For a recent review on the catalytic hydrochalcogenations, see: I. P. Beletskaya and V. P. Ananikov, *Eur. J. Org. Chem.*, 3431 (2007).
2. (a) V. P. Ananikov, D. A. Malyshev, I. P. Beletskaya, G. G. Aleksandrov, and I. L. Eremenko, *J. Organomet. Chem.*, **679**, 162 (2003); (b) V. P. Ananikov, N. V. Orlov, and I. P. Beletskaya, *Organometallics*, **26**, 740 (2007).
3. A. Ishii, N. Nakata, R. Uchiumi, and K. Murakami, *Angew. Chem., Int. Ed. Engl.*, **47**, 2661 (2008).
4. For applications of Trip group, see: (a) A. Ishii, S. Matsubayashi, T. Takahashi, and J. Nakayama, *J. Org. Chem.*, **64**, 1084 (1999); (b) A. Ishii, T. Takahashi, and J. Nakayama, *Heteroatom Chem.*, **12**, 198 (2001); (c) A. Ishii, T. Takahashi, A. Tawata, A. Furukawa, H. Oshida, and J. Nakayama, *Chem. Commun.*, 2810 (2002); (d) A. Ishii, Y. Mori, and R. Uchiumi, *Heteroatom Chem.*, **16**, 525

- (2005); (e) N. Nakata, S. Fukazawa, and A. Ishii, *Organometallics*, **28**, 534 (2009); (f) N. Nakata, R. Uchiumi, T. Yoshino, T. Ikeda, H. Kamon, and A. Ishii, *Organometallics*, **28**, 1981 (2009); (g) N. Nakata, S. Yamamoto, W. Hashima, and A. Ishii, *Chem. Lett.*, **38**, 400 (2009); (h) A. Ishii, H. Kamon, K. Murakami, and N. Nakata, *Eur. J. Org. Chem.*, **9**, 1653 (2010).
5. V. P. Ananikov, I. P. Beletskaya, G. G. Aleksandrov, and I. L. Eremenko, *Organometallics*, **22**, 1414 (2003).
 6. For reviews on the C–H activations with transition metal complexes, see: (a) A. S. Goldman, and K. I. Goldberg, ACS Symposium Series 855, *Activation and Functionalization of CH Bonds*, 1–43 (2004). (b) S. M. Hubig, S. V. Lindeman, and J. K. Kochi, *Coord. Chem. Rev.*, **200–202**, 831 (2000).
 7. G. Picazo, A. Arévalo, S. Bernès, and J. J. García, *Organometallics*, **22**, 4734 (2003).
 8. K. Yu, H. Li, E. J. Watson, K. L. Virkaitis, G. B. Carpenter, and D. A. Sweigart, *Organometallics*, **20**, 3550 (2001).
 9. G. M. Sheldrick, SHELX-97, Program for the Refinement of Crystal Structures, University of Göttingen: Göttingen, Germany, 1997.