



Synthesis and thermal reaction of hydrido(selenolato) platinum(II) complex having a 9,10,11,12,14,15-hexahydro-9,10[3',4']-furanoanthracenyl group

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ABSTRACT

The oxidative addition of selenol, HhfSeH (**2**, Hhf = 9,10,11,12,14,15-hexahydro-9,10[3',4']-furanoanthracenyl) with $[\text{Pt}(\eta^2\text{-nb})(\text{Ph}_3\text{P})_2]$ (nb = norbornene) in toluene afforded the corresponding hydrido(selenolato) Pt(II) complex $[\text{cis-PtH}(\text{SeHhf})(\text{Ph}_3\text{P})_2]$ (**3**) as a stable compound. Refluxing a xylene solution of **3** produced two isomers of five-membered selenaplatinacycles **4** in moderate yield as an inseparable mixture. In addition, the molecular structures of HhfSeH **2** and the minor selenaplatinacycle **4a** were determined by X-ray crystallography.

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1. Introduction

There have been a number of studies on Pt-catalyzed reactions of organochalcogen compounds such as the hydroselenation [1,2] and thiocarbonylation [3,4] of alkynes. Most of these reactions are believed to involve hydrido(selenolato) and -(thiolato) Pt(II) intermediates. Although these complexes were readily prepared by the oxidative addition of selenol or thiol with Pt(0) complex, their full spectroscopic characterizations and crystal structure analyses have not been performed until recently due to their thermal instability [2a,4a,5]. Very recently, we succeeded in the synthesis and the first isolation of a stable hydrido(chalcogenolato) Pt(II) complex $[\text{cis-PtH}(\text{ETrip})(\text{PPh}_3)_2]$ (E = S, Se) by the oxidative addition reaction of a kinetically stabilized 9-triptyceneselenol or -thiol with Pt(0) complex [6,7]. Furthermore, we found a unique thermal reaction of $[\text{cis-PtH}(\text{ETrip})(\text{PPh}_3)_2]$ to produce a new type of five-membered chalcogenaplatinacycle $[\text{Pt}(\eta^2\text{-C,E-Trip})(\text{PPh}_3)_2]$ (E = S, Se) by an intramolecular C–H activation leading to the cyclometalation [6–8]. In order to elucidate the generality of substituent effect in the thermal reaction of $[\text{cis-PtH}(\text{SeTrip})(\text{PPh}_3)_2]$, we wish to report the synthesis and thermal reaction of stable hydrido(selenolato) Pt(II) complex having a 9,10,11,12,14,15-hexahydro-9,10[3',4']-furanoanthracenyl group (denoted as Hhf hereafter), which is a less hindered substituent than 9-triptycyl group.

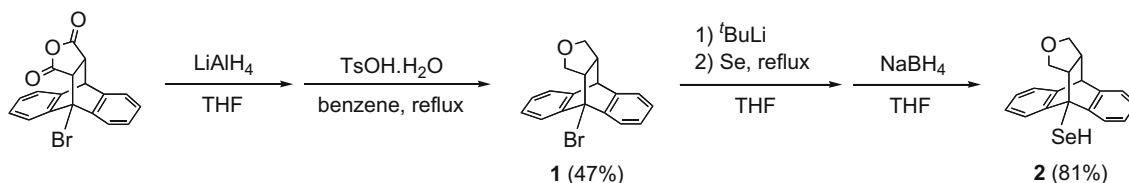
2. Results and discussion

2.1. Synthesis and structure of 9,10,11,12,14,15-hexahydro-9,10[3',4']-furanoanthraceneselenol **2**

According to the reported synthetic method [9], 9-bromo-9,10,11,12,14,15-hexahydro-9,10[3',4']-furanoanthracene (**1**, HhfBr) was prepared by the reduction of 9-bromo-9,10,11,15-tetrahydro-9,10[3',4']-furanoanthracene-12,14-dione with LiAlH_4 in THF, followed by treatment with $\text{TsOH}\cdot\text{H}_2\text{O}$ in benzene under reflux conditions. The starting material, HhfSeH **2** was synthesized by the reaction of in situ-generated HhfLi with an excess amount of elemental selenium in THF at -78°C , and following reduction with NaBH_4 in THF gave the corresponding selenol **2** in 81% yield as colorless crystals (Scheme 1).

The HhfSeH **2** was found to be quite stable toward air, moisture, and light. The structure of **2** was confirmed by NMR and IR spectroscopies and elemental analysis. In the ^1H NMR spectrum, the characteristic selenol proton appeared at δ 0.14, which was shifted upfield region relative to that of 9-triptycylselenol (δ 0.48) [10]. The $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of **2** showed a singlet at δ 28.6. The molecular structure of **2** was determined by X-ray crystallography, as shown in Fig. 1. The X-ray structural analysis of **2** revealed that the intermolecular interaction of the hydroseleno group with the oxygen atom results in the formation of hydrogen-bonding array (Se–H...O) leading to a chain structure (Fig. 2). The Se–H...O hydrogen-bonding [2.44(3) Å] is somewhat weaker than the S–H...O hydrogen bond of 12-crown-4-2[Ph₃CSH] complex [2.17(3) Å] [11].

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Scheme 1.

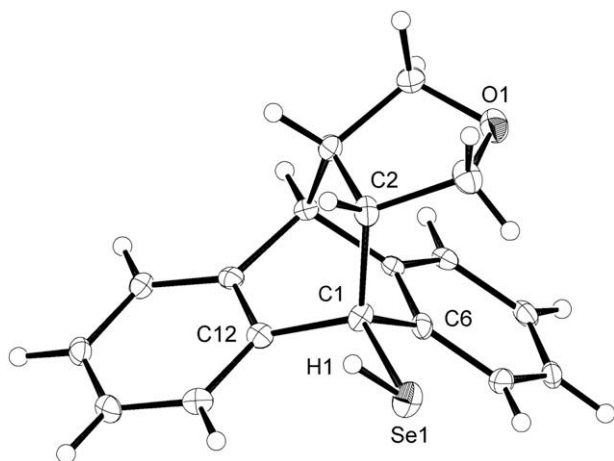


Fig. 1. ORTEP diagram of HhfSeH **2** with 30% thermal ellipsoids. Selected bond lengths (Å): Se1–C1 = 1.973(3), Se1–H1 = 1.12(3), C1–C2 = 1.573(5), C1–C6 = 1.529(4), C1–C12 = 1.518(5). Selected bond angles (°): C1–Se1–H1 = 84.5(16), Se1–C1–C2 = 110.6(2), Se1–C1–C6 = 110.6(2), Se1–C1–C12 = 114.7(2).

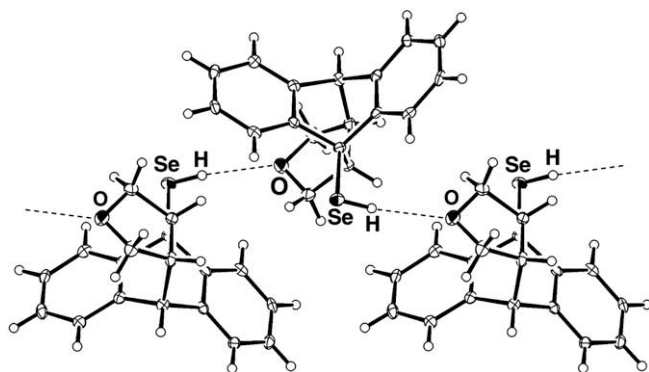
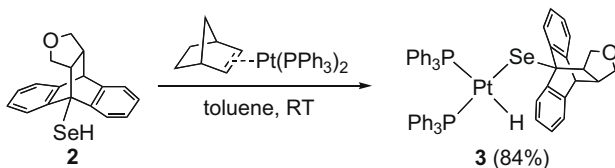


Fig. 2. A part of crystal structure of HhfSeH **2**, viewed along the *a* axis, showing the intermolecular Se–H...O hydrogen-bonding interaction (30% thermal ellipsoids). H...O = 2.44(3) Å, Se–H...O = 168.3(2)°.



Scheme 2.

2.2. Synthesis and thermal reaction of hydrido(selenolato) Pt(II) complex having a Hhf group

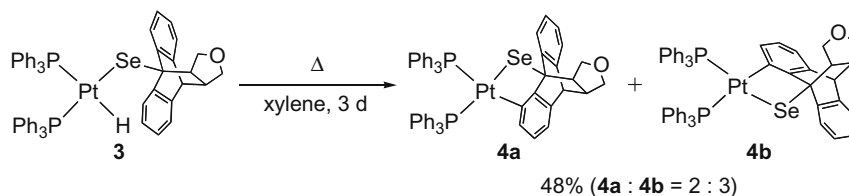
The reaction of HhfSeH **2** with $[\text{Pt}(\eta^2\text{-nb})(\text{Ph}_3\text{P})_2]$ in toluene at room temperature proceeded efficiently to form $[\text{cis-PtH}(\text{SeHhf})(\text{Ph}_3\text{P})_2]$ **3**

(Ph_3P)₂ (**3**) in 84% yield as colorless crystals (Scheme 2). In the ^1H NMR spectrum of **3**, the characteristic signals of the platinum hydride were observed centered at $\delta -6.08$, which involved 16 and 182 Hz of ^{31}P – ^1H couplings and 877 Hz of satellite signals from the ^{195}Pt isotope. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** exhibited two singlets with ^{195}Pt satellites at $\delta 19.6$ ($^1J_{\text{Pt-P}} = 3243$ Hz) and 29.9 ($^1J_{\text{Pt-P}} = 2070$ Hz), which were assigned to the phosphorus atoms lying *trans* to the selenolato ligand and the hydrogen, respectively. The IR spectrum for **3** showed Pt–H stretching vibration at 2096 cm^{-1} . The complex **3** was a stable compound under an air atmosphere, and no decomposition or disproportionation was observed.

While complex **3** is thermally stable in the solid state (M.p.: 140–141 °C), refluxing a xylene solution of **3** for 3 days gave the corresponding five-membered selenaplatinacycles **4a** and **4b** in 48% yield as an inseparable mixture of structural isomers (**4a**:**4b** = 2:3) (Scheme 3). The ^1H NMR spectrum of **4** exhibited characteristic signals due to the aromatic protons neighboring the Pt atom at $\delta 5.96$ – 6.01 and 6.52 – 6.58 . These values are slightly upfield-shifted in comparison to that of the reported selenaplatinacycle ($\delta 5.85$) [6]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** showed two sets of two doublets with the ^{195}Pt satellites at $\delta 21.8$ ($^2J_{\text{P-P}} = 15$, $^1J_{\text{Pt-P}} = 1827$ Hz) and 24.7 ($^2J_{\text{P-P}} = 15$, $^1J_{\text{Pt-P}} = 3257$ Hz) for **4a**, and 21.9 ($^2J_{\text{P-P}} = 17$, $^1J_{\text{Pt-P}} = 1824$ Hz) and 24.8 ($^2J_{\text{P-P}} = 17$, $^1J_{\text{Pt-P}} = 3256$ Hz) for **4b**. Fortunately, we could obtain single crystals of the minor product **4a** suitable for X-ray analysis by the slow evaporation of its saturated CH_2Cl_2 and hexane solution. In the X-ray analysis of **4a** (Fig. 3), the central five-membered PtSeC₃ ring of **4a** features a nearly planar geometry; the sum of the interior bond angles is 539.9°. The platinum atom maintains the planarity of tetracoordinated Pt(II) atoms; the sum of the four bond angles around the Pt atom is 359.91°. The Pt–C3 bond length [2.132(7) Å] is close to those of reported selenaplatinacycles $[\text{Pt}(\eta^2\text{-C,Se-Trip})(\text{PPh}_3)_2]$ [2.099(4) Å] [6] and $[\text{Pt}(\eta^2\text{-C,Se-Trip})(\text{dppe})]$ [2.081(6) Å] [8], and slightly shorter than that of selenametalacycle $\{\text{Pt}[\eta^2\text{-C,Se-C}_4\text{H}_4\text{Mn}(\text{CO})_3](\text{PPh}_3)_2\}^+$ [2.256(5) Å] [12]. The Pt–P1 bond [2.3443(19) Å] *trans* to the Pt–C3 bond is slightly longer than the Pt–P2 bond [2.296(2) Å] *trans* to the Pt–Se1 bond. This observation indicates that the *trans* influence of the aromatic carbon atom is larger than that of the selenium atom.

3. Conclusion

We prepared a novel selenol **2** having a 9,10,11,12,14,15-hexahydro-9,10[3',4']-furanoanthracenyl group, which was linked into chains by a Se–H...O hydrogen-bonding in the solid state. We also demonstrated that the reaction of **2** with $[\text{Pt}(\eta^2\text{-nb})(\text{Ph}_3\text{P})_2]$ resulted in the formation of $[\text{cis-PtH}(\text{SeHhf})(\text{Ph}_3\text{P})_2]$ **3** as a stable compound. The thermal reaction of complex **3** in xylene afforded two isomers of five-membered selenaplatinacycles **4a** and **4b** as an inseparable mixture (**4a**:**4b** = 2:3). Further investigations on the synthesis and reactivity of stable hydrido(selenolato) Pt(II) complexes having unique substituents are currently in progress.



Scheme 3.

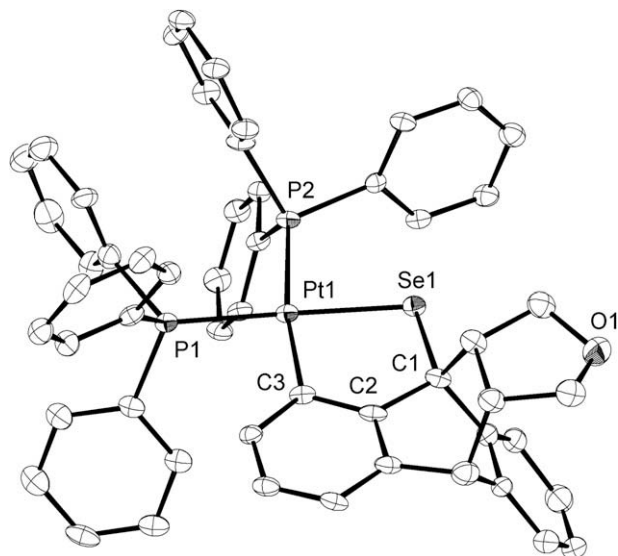


Fig. 3. ORTEP diagram of selenaplatinacycle **4a** with 30% thermal ellipsoids. A solvated CH_2Cl_2 molecule and hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Pt1–Se1 = 2.4172(9), Pt1–C3 = 2.132(7), Pt1–P1 = 2.296(2), Pt1–P2 = 2.3443(19), Se1–C1 = 1.971(8), C1–C2 = 1.495(12), C2–C3 = 1.424(12). Selected bond angles ($^\circ$): P1–Pt1–P2 = 95.57(7), Se1–Pt1–P2 = 85.74(6), Se1–Pt1–C3 = 85.6(2), P1–Pt1–C3 = 93.0(2), Se1–Pt1–P1 = 178.68(5), P2–Pt1–C3 = 171.2(2), Pt1–Se1–C1 = 99.8(3), Se1–C1–C2 = 110.6(6), C1–C2–C3 = 125.7(7), Pt1–C3–C2 = 118.2(5).

4. Experimental

4.1. General procedures

All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra were recorded on Bruker DPX-400 or DRX-400 (400, 100.7, 162.1, and 76.3 MHz, respectively) spectrometers using CDCl_3 as the solvent at room temperature. 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. 9-bromo-9,10,11,15-tetrahydro-9,10[3',4']-furananthracene-12,14-dione [**13**] and $[\text{Pt}(\eta^2\text{-nb})(\text{Ph}_3\text{P})_2]$ [**14**] were prepared according to the reported procedures.

4.2. Preparation of 9-bromo-9,10,11,12,14,15-hexahydro-9,10[3',4']-furananthracene (HhfBr) **1**

A solution of 9-bromo-9,10,11,15-tetrahydro-9,10[3',4']-furananthracene-12,14-dione (1.25 g, 3.53 mmol) in THF (40 mL) was added slowly to a suspension of LiAlH_4 (686 mg, 18.10 mmol) in THF (20 mL) at 0°C , and the mixture was stirred for 3 h at room temperature. The reaction was quenched by addition of dilute hydrochloric acid and the mixture was extracted with CH_2Cl_2 .

The organic layer was washed with water and dried over anhydrous MgSO_4 , and the solvent was evaporated to dryness to give a colorless solid, which was dissolved in benzene (50 mL) with $\text{TsOH}\cdot\text{H}_2\text{O}$ (1.05 g, 5.52 mmol) and the mixture was refluxed for 3 h. To the mixture was added aqueous NaHCO_3 . The organic layer was washed with water and dried over anhydrous MgSO_4 , and the solvent was evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2) to give HhfBr **1** (548 mg, 47%) as colorless crystals. M.p. $144\text{--}145^\circ\text{C}$ (CH_2Cl_2). ^1H NMR (CDCl_3): δ 2.85–2.92 (m, 1H), 3.12–3.18 (m, 1H), 3.30–3.34 (m, 1H), 3.42–3.46 (m, 1H), 3.74–3.82 (m, 2H), 4.16 (d, $J = 3.1$ Hz, 1H), 7.05–7.25 (m, 6H), 7.70–7.74 (m, 2H). ^{13}C NMR (CDCl_3): δ 47.0 (CH), 48.3 (CH), 56.2 (CH), 70.6 (C), 70.9 (CH_2), 71.5 (CH_2), 123.0 (CH), 124.5 (CH), 124.6 (CH), 126.0 (CH), 126.2 (CH), 126.5 (CH), 127.0 (CH), 127.2 (CH), 139.3 (C), 139.7 (C), 142.2 (C), 142.8 (C). Anal. Calc. for $\text{C}_{18}\text{H}_{15}\text{OBr}$: C, 66.07; H, 4.62. Found: C, 65.90; H, 4.49%.

4.3. Preparation of 9,10,11,12,14,15-hexahydro-9,10[3',4']-furananthracene-9-selenol (HhfSeH) **2**

$^t\text{BuLi}$ (1.58 M, 7.8 mL, 12.3 mmol) was added slowly to a solution of HhfBr **1** (2.03 g, 6.19 mmol) in THF (40 mL) at -78°C . After stirring for 30 min at -78°C , elemental selenium (1.25 g, 15.92 mmol) was added using a bent tube. The mixture was warmed to room temperature, heated under reflux for 14 h, and subjected to oxidation by exposure to air for 1 h. The precipitates were removed through a pad of Celite[®] and the filtrate was shaken with CH_2Cl_2 and water. The organic layer was separated, dried over anhydrous MgSO_4 , and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2) to give polyselelenides Hhf_2Se_n (1.84 g) as an orange solid. A part of Hhf_2Se_n (102 mg) was treated with NaBH_4 (22 mg, 0.57 mmol) in THF (10 mL) at room temperature for 3 h. The reaction was quenched by addition of dilute hydrochloric acid and the mixture was extracted with CH_2Cl_2 . The organic layer was washed with water and dried over anhydrous MgSO_4 , and the solvent was evaporated to dryness to give HhfSeH **2** (91.5 mg, 81% from HhfBr **1**) as colorless crystals. M.p. $144\text{--}145^\circ\text{C}$ (CH_2Cl_2). ^1H NMR (CDCl_3): δ 0.14 (s, 1H), 2.83–2.95 (m, 2H), 3.23–3.32 (m, 2H), 3.77–3.86 (m, 2H), 4.15 (d, $J = 2.7$ Hz, 1H), 7.11–7.26 (m, 6H), 7.54–7.56 (m, 1H), 7.71–7.73 (m, 1H). ^{13}C NMR (CDCl_3): δ 47.0 (CH), 48.7 (CH), 55.1 (C), 55.9 (CH), 71.1 (CH_2), 71.4 (CH_2), 123.2 (CH), 124.9 (CH), 125.0 (CH), 125.8 (CH), 125.9 (CH), 126.2 (CH), 126.6 (CH), 126.8 (CH), 140.5 (C), 141.2 (C), 143.4 (C), 144.9 (C). ^{77}Se NMR (CDCl_3): δ 28.6. IR (KBr): ν 2262 cm^{-1} (br, Se–H). Anal. Calc. for $\text{C}_{18}\text{H}_{16}\text{OSe}$: C, 66.06; H, 4.93. Found: C, 65.92; H, 4.88%.

4.4. Preparation of [cis-PtH(SeHhf)(PPh₃)₂] **3**

A solution of selenol **2** (62 mg, 0.19 mmol) in toluene (5 mL) was added to a solution of $[\text{Pt}(\eta^2\text{-nb})(\text{Ph}_3\text{P})_2]$ (170 mg, 0.21 mmol) in toluene (5 mL) at 0°C . The mixture was stirred for 2 h at room temperature, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (Et_2O) to give [cis-PtH(SeHhf)(PPh₃)₂] **3** (165 mg, 84%) as colorless

crystals. M.p. 140–141 °C (decomp.). ^1H NMR (CDCl_3): δ –6.08 (dd, $^2J_{\text{P-H}} = 182$, 16 Hz, $^1J_{\text{Pt-H}} = 877$ Hz, 1H), 2.79–2.83 (m, 1H), 3.12–3.23 (m, 3H), 3.75–3.82 (m, 2H), 4.02 (d, $J = 2.4$ Hz, 1H), 6.99–7.30 (m, 30H), 7.49–7.54 (m, 6H), 8.18 (br s, 1H), 8.50 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (CDCl_3): δ 47.4 (CH), 49.8 (CH), 52.7 (C), 56.0 (CH), 71.3 (CH_2), 71.6 (CH_2), 122.0 (CH), 124.0 (CH), 124.3 (CH), 124.6 (CH), 124.9 (CH), 125.0 (CH), 127.5 (d, $J = 9.1$ Hz, CH), 129.1 (CH), 129.6 (d, $J = 9.1$ Hz, CH), 131.2 (C), 131.6 (C), 134.2 (m, CH), 141.4 (C), 144.3 (C), 144.4 (C), 147.9 (C). ^{31}P NMR (CDCl_3): δ 19.6 (br s, $^1J_{\text{Pt-P}} = 3243$ Hz), 29.9 (br s, $^1J_{\text{Pt-P}} = 2070$ Hz). IR (KBr): ν 2096 cm^{-1} (br, Pt–H). Anal. Calc. for $\text{C}_{54}\text{H}_{46}\text{OP}_2\text{PtSe}$: C, 61.95; H, 4.43. Found: C, 61.90; H, 4.42%.

4.5. Thermal reaction of $[\text{cis-PtH}(\text{SeHf})(\text{Ph}_3\text{P})_2]$ **3**

A solution of complex **3** (65 mg, 0.062 mmol) in xylene (17 mL) was heated under reflux for 3 days, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (Et_2O) to give two isomers of selenaplating cycles **4a** and **4b** (31 mg, 48%) as an inseparable mixture. The ratio of **4a** (minor) and **4b** (major) (2:3) was judged from ^1H NMR spectroscopy. M.p. 213–214 °C (decomp.). ^1H NMR (CDCl_3): δ 2.70–3.24 (m, 3H), 3.66–3.73 (m, 1H), 3.87–3.96 (m, 2H), 4.12–4.17 (m, 1H), 5.96–6.01 (m, 1H), 6.52–6.58 (m, 1H), 6.81–6.90 (m, 1H), 6.96–7.08 (m, 7H), 7.09–7.20 (m, 10H), 7.23–7.30 (m, 4H), 7.38–7.45 (m, 6H), 7.54–7.59 (m, 6H), 7.75 (d, $J = 7.2$ Hz, **4b**), 7.84 (d, $J = 7.2$ Hz, **4a**). ^{31}P NMR (CDCl_3): δ 21.8 (d, $^2J_{\text{P-P}} = 15$ Hz, $^1J_{\text{Pt-P}} = 1827$ Hz, **4a**), 21.9 (d, $^2J_{\text{P-P}} = 17$ Hz, $^1J_{\text{Pt-P}} = 1824$ Hz, **4b**), 24.7 (d, $^2J_{\text{P-P}} = 15$ Hz, $^1J_{\text{Pt-P}} = 3257$ Hz, **4a**), 24.8 (d, $^2J_{\text{P-P}} = 17$ Hz, $^1J_{\text{Pt-P}} = 3256$ Hz, **4b**). Anal. Calc. for $\text{C}_{54}\text{H}_{44}\text{OP}_2\text{PtSe}$: C, 62.07; H, 4.24. Found: C, 61.79; H, 4.23%.

4.6. Crystallographic data for **2** and **4a**

Colorless single crystals of **2** and **4a** were grown by the slow evaporation of its saturated CH_2Cl_2 and hexane solution. The intensity data were collected at 103 K for **2** and **4a** on a Bruker AXS SMART diffractometer employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file [15]. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97) [16]. Hydrogen atoms except for the SeH hydrogen of **2** were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystal data for **2**: $\text{C}_{18}\text{H}_{16}\text{OSe}$, MW = 327.27, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 7.7595(5)$ Å, $b = 10.2448(7)$ Å, $c = 17.3797(11)$ Å, $V = 1391.59(16)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.573$ g cm^{-3} , R_1 ($I > 2\sigma I$) = 0.0343, wR_2 (all data) = 0.0786 for 2709 reflections and 185 parameters, GOF = 1.003. Crystal data for **4a**:

$\text{C}_{55}\text{H}_{46}\text{Cl}_2\text{OP}_2\text{PtSe}$ (**4a-CH}_2\text{Cl}_2), MW = 1129.81, monoclinic, space group $P2_1/n$ (no. 14), $a = 18.132(2)$ Å, $b = 11.1076(13)$ Å, $c = 22.667(3)$ Å, $\beta = 98.072(2)^\circ$, $V = 4520.0(10)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.660$ g cm^{-3} , R_1 ($I > 2\sigma I$) = 0.0499, wR_2 (all data) = 0.1285 for 8404 reflections and 559 parameters, GOF = 1.003.**

Supplementary material

CCDC 748260 and 748261 contain the supplementary crystallographic data for **2** and **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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