



Supporting Information

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Supporting Information

Reactions of *Se*-9-Triptycyl Triptycene-9-selenoseleninate (RSe(=O)-SeR; R = 9-triptycyl) and Related Compounds with a Platinum(0) Complex. Formation of Selenaplatinacycle and (Hydrido-selenolato)Platinum(II) Complexes

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Experimental Section

Reaction of *Se*-9-Triptycyl Triptycene-9-selenoseleninate (1) with [Pt(PPh₃)₂(η^2 -C₂H₄)] (7). A solution of 7 (58.3 mg, 0.0780 mmol) in toluene (5 mL) was added dropwise at room temperature to a solution of 1 (47.9 mg, 0.0704 mmol) in toluene (5 mL) under argon. The mixture was stirred for 1 h at room temperature and then the solvent was removed in vacuo. The mixture was subjected to column chromatography (silica gel). Di-9-triptycyl diselenide (3) (14.0 mg, 0.021 mmol, 30%) was first eluted with a mixed solvent of hexane and dichloromethane (1:1), and then the column was eluted with dichloromethane to give selenaplatinacycle 8 (53.4 mg, 0.0508 mmol, 36%). 8: colorless crystals, m.p. 286–288 °C decomp. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ =5.22 (s, 1H), 5.81–5.88 (m, 1H), 6.65–6.71 (m, 2H), 6.90–6.98 (m, 10H), 7.13 (pseudo t, J =6.9 Hz, 3H), 7.21 (d of t, J =7.7, 1.9 Hz, 6H), 7.25–7.36 (m, 11H), 7.62–7.68 (m, 6H), 7.98 ppm (pseudo d, J =7.6 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃, 25 °C, TMS): δ =56.0 (CH \times 1), 63.6 [C \times 1, dd, J (P,C)=17.5, 2.2 Hz], 117.6 (CH \times 1), 121.9 (CH \times 2), 122.2 [CH \times 1, dd, J (P,C)=7.3, 3.3 Hz], 124.1 (CH \times 2), 124.2 (CH \times 2), 124.7 (CH \times 2), 127.29 [CH \times 6, d, J (P,C)=10 Hz], 127.53 [CH \times 6, d, J (P,C)=10.1 Hz], 129.6 [CH \times 3, J (P,C)=1.4 Hz], 129.9 [CH \times 3, J (P,C)=2.9 Hz], 132.6

[C×3, dd, $J(\text{P,C})=50.2, 2.9$ Hz], 132.9 [C×3, d, $J(\text{P,C})=45.8$ Hz], 134.6 [CH×3, d, $J(\text{P,C})=11.7$ Hz], 135.4 [CH×3, d, $J(\text{P,C})=11.7$ Hz], 139.5 [CH×1, dd, $J(\text{P,C})=13.1, 3.6$ Hz], 143.1 [C×1, d, $J(\text{P,C})=2.9$ Hz], 146.4 (C×2), 150.5 (C×2), 166.8 ppm (C×1) (signals from the carbon atom directly bonded to the Pt atom could not be assigned probably because of broadening or overlapping with other signals.); ^{31}P NMR (162 MHz, CDCl_3 , 25 °C, external 85% H_3PO_4): $\delta=22.7$ [d, $^2J(\text{P,P})=20.4$ Hz, $^1J(\text{Pt,P})=1833$ Hz], 25.2 ppm [d, $^2J(\text{P,P})=20.4$ Hz, $^1J(\text{Pt,P})=3276$ Hz]. We tried to measure ^{77}Se NMR signals using a saturated solution of **8** in CDCl_3 only to observe a small, weak signal at around $\delta=340$. It was difficult to obtain clear ^{77}Se NMR signals probably because of collapse by couplings with the two P atoms and the ^{195}Pt atom. Anal. Calcd for $\text{C}_{57}\text{H}_{44}\text{Cl}_2\text{P}_2\text{PtSe}$ ($\text{C}_{56}\text{H}_{42}\text{P}_2\text{PtSe}\cdot\text{CH}_2\text{Cl}_2$): C, 60.27; H, 3.86. Found: C, 60.74; H, 3.90.

Crystallographic data for 8: $\text{C}_{63}\text{H}_{50}\text{P}_2\text{PtSe}$ ($\text{C}_{56}\text{H}_{42}\text{P}_2\text{PtSe}\cdot\text{C}_7\text{H}_8$), $M_s = 1143.02$, colorless prism, $0.25 \times 0.25 \times 0.20$ mm³, monoclinic, $P2_1/c$. $a = 13.9733(8)$, $b = 16.8802(10)$, $c = 20.5325(13)$ Å, $\beta = 91.374^\circ$, $V = 4841.7(5)$ Å³, $r_{\text{calcd}} = 1.568$ g cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 3.758$ cm⁻¹. Intensity data of 9503 unique reflections were collected in the range of $-16 \leq h \leq 17$, $-20 \leq k \leq 20$, $-16 \leq l \leq 25$ at 183 K. $R_1 = 0.0346$ ($I \geq 2\sigma I$, 7858 reflections), $wR_2 = 0.0846$ (for all), and GOF = 1.025, 688 parameters; max/min residual electron density = 1.474/-0.594 e Å⁻³.

Reaction of Triptycene-9-selenenic Acid (2) with $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ (7). To a mixture of **2** (11.6 mg, 0.033 mmol) and **7** (25.2 mg, 0.034 mmol) under argon was added dichloromethane (0.5 mL) at room temperature. The mixture was stirred for 1 h at room temperature, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography and then GPC to give selenaplatinacycle **8** (34.1 mg, 94%).

Reaction of Di-9-triptycyl Diselenide (3) with $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ (7). A solution of **3** (52.2 mg, 0.0785 mmol) in dichloromethane (6 mL) was added to a solution of **7** (56.5 mg, 0.0756 mmol) in dichloromethane (5 mL) under argon. 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 (hexane/dichloromethane 1:1 and then dichloromethane) to give first an 84:16 mixture (29.2 mg) of diselenide **3** (0.0401 mmol, 51%) and selenol **11** (0.0076 mmol, 9.7%) and

then a 58:42 mixture (59.3 mg) of selenaplatinacycle **8** (0.0328 mmol, 42%) and (hydrido-selenolato)Pt(II) complex **12** (0.0235 mmol, 30%). The mixture of **8** and **12** complex could not be separated.

Reaction of 9-Triptyceneselenol (11) with [Pt(PPh₃)₂(η^2 -C₂H₄)] (7). A solution of **11** (14.2 mg, 0.0429 mmol) in toluene (5 mL) was added to a solution of **7** (35.3 mg, 0.0472 mmol) in toluene (5 mL) under argon. The mixture was stirred for 1.5 h at room temperature, and the solvent was removed in vacuo. The residue was subjected to column chromatography (acidic SiO₂, hexane/dichloromethane 1:1) to give the (hydrido-selenolato)Pt^{II} complex **12** (35.1 g, 78%): colorless crystals, m.p. 158–160 °C decomp (toluene-hexane). ¹H NMR: δ =-6.10 [dd, ²*J*(P,H)=184, 16 Hz, and satellite signals with ¹*J*(H, Pt)=1523 Hz], 5.29 (s, 1H), 6.88–7.01 (m, 12H), 7.12–7.32 (m, 21H), 7.58–7.63 (m, 6H), 8.38 ppm (br s, 3H); ³¹P NMR: δ =21.3 [d, ²*J*(P,P)=14.0 Hz, ¹*J*(Pt,P)= 3281 Hz], 30.9 ppm [d, ²*J*(P,P)=14 Hz, ¹*J*(Pt,P)=2028 Hz]; IR (KBr): $\tilde{\nu}$ =2093 cm⁻¹ (Pt-H). Anal. Calcd for C₅₆H₄₄P₂PtSe: C, 63.88; H, 4.21. Found: C, 63.33; H, 4.13.

Crystallographic data for 12: C₆₃H₅₀P₂PtSe (C₅₆H₄₂P₂PtSe·1.5C₇H₈), *M_s*=1190.62, colorless prism, 0.25 × 0.25 × 0.20 mm³, triclinic, *P*-1. *a* = 12.4546(6), *b* = 14.5548(7), *c* = 16.8369(8) Å, α = 93.8360(10), β = 102.4290(10), γ = 115.0090(10)°, *V* = 2657.8(2) Å³, *r*_{calcd} = 1.488 g cm⁻³, *Z* = 2, μ (Mo-*K* α) = 3.426 cm⁻¹. Intensity data of 9880 unique reflections were collected in the range of -15 ≤ *h* ≤ 14, -17 ≤ *k* ≤ 14, -20 ≤ *l* ≤ 20 at 123 K. *R*₁ = 0.0360 (*I* ≥ 2 σ *I*, 8664 reflections), *wR*₂ = 0.0840 (for all), and GOF = 1.009, 647 parameters; max/min residual electron density = 1.566/-0.566 e Å⁻³.

CCDC-666761 (**8**) and 666762 (**12**) contain the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.