

Thermal reaction of a (hydrido)(selenolato)platinum(II) complex having a dibenzobarrelenyl group leading to three cyclometalations

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Experimental

General: The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ¹H, ¹³C{¹H}, ³¹P{¹H}, and ⁷⁷Se{¹H} NMR spectra were determined on Bruker AM400 or DRX400 (400, 100.7, 162, and 76.3 MHz, respectively) spectrometers using CDCl₃ as the solvent at 25 °C, unless otherwise noted. IR spectra were taken on a Perkin Elmer System 2000 FT-IR spectrometer. Mass spectra were determined on a JEOL JMS-700AM spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed at Molecular Analysis and Life Science Center of Saitama University. Column chromatography was performed with silica gel (70-230 mesh) and the eluent is shown in parentheses.

Preparation of 9-Dibenzobarreleneselenol (DbbSeH, 5)

t-BuLi (1.58 M, 12.5 mL, 19.75 mmol) was added to a solution of 9-bromodibenzobarrelene (**4**) (2.7981g, 9.88 mmol) in THF (50 mL) at -78 °C under argon. After stirring for 30 min at -78 °C, elemental selenium (1.9355 g, 24.5 mmol) was added. The mixture was warmed to room temperature, heated under reflux for 21 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 dichloromethane and water. The organic layer was separated, dried over anhydrous Na₂SO₄, and evaporated to dryness. The residue was subjected to column chromatography (hexane-dichloromethane 3/1) to give (Dbb)₂Se_{*n*} (2.4547 g) as an orange solid, which was treated with

NaBH₄ (729.2 mg, 19.3 mmol) in THF (70mL) at room temperature. The reaction was quenched by addition of dilute hydrochloric acid and the mixture was extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous Na₂SO₄, and the solvent was evaporated to dryness to give selenol DbbSeH (**5**) (2.19 g, 78% from DbbBr).

5: Colorless crystals, mp 139–140 °C (from CH₂Cl₂) (Found: C, 67.66; H, 4.26. Calc. for C₁₆H₁₂Se: C, 67.85; H, 4.27%); ν_{\max} (KBr)/cm⁻¹ 2299 (SeH); δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.51 (1 H, s, $J_{\text{Se-H}}$ 53), 5.09 (1 H, d, J 6.0), 6.84 (1 H, d, J 6.8), 6.95–7.02 (5 H, m), 7.25 (2 H, d, J 6.4), and 7.60 (2 H, d, J 6.8); δ_{C} (100.7 MHz; CDCl₃; Me₄Si) 51.0, 54.6, 122.6, 122.7, 124.4, 125.0, 140.3, 145.3, 145.5, and 146.8; δ_{Se} (76.3 MHz; CDCl₃ Me₂Se) 19.4.

Reaction of DbbSeH (**5**) with [Pt(nb)(PPh₃)₂]

A solution of selenol **5** (113 mg, 0.40 mmol) in toluene (5 mL) was added to a solution of [Pt(nb)(PPh₃)₂] (324 mg, 0.40 mmol) in toluene (5 mL) at 0 °C under argon. The mixture was stirred for 2 h at room temperature, and the solvent was removed under reduced pressure. The residue was recrystallized from a mixed solvent of CH₂Cl₂ and hexane to give [PtH(SeDbb)(PPh₃)₂] (**6**) (329 mg, 83%).

PtH(SeDbb)(PPh₃)₂ (**6**)

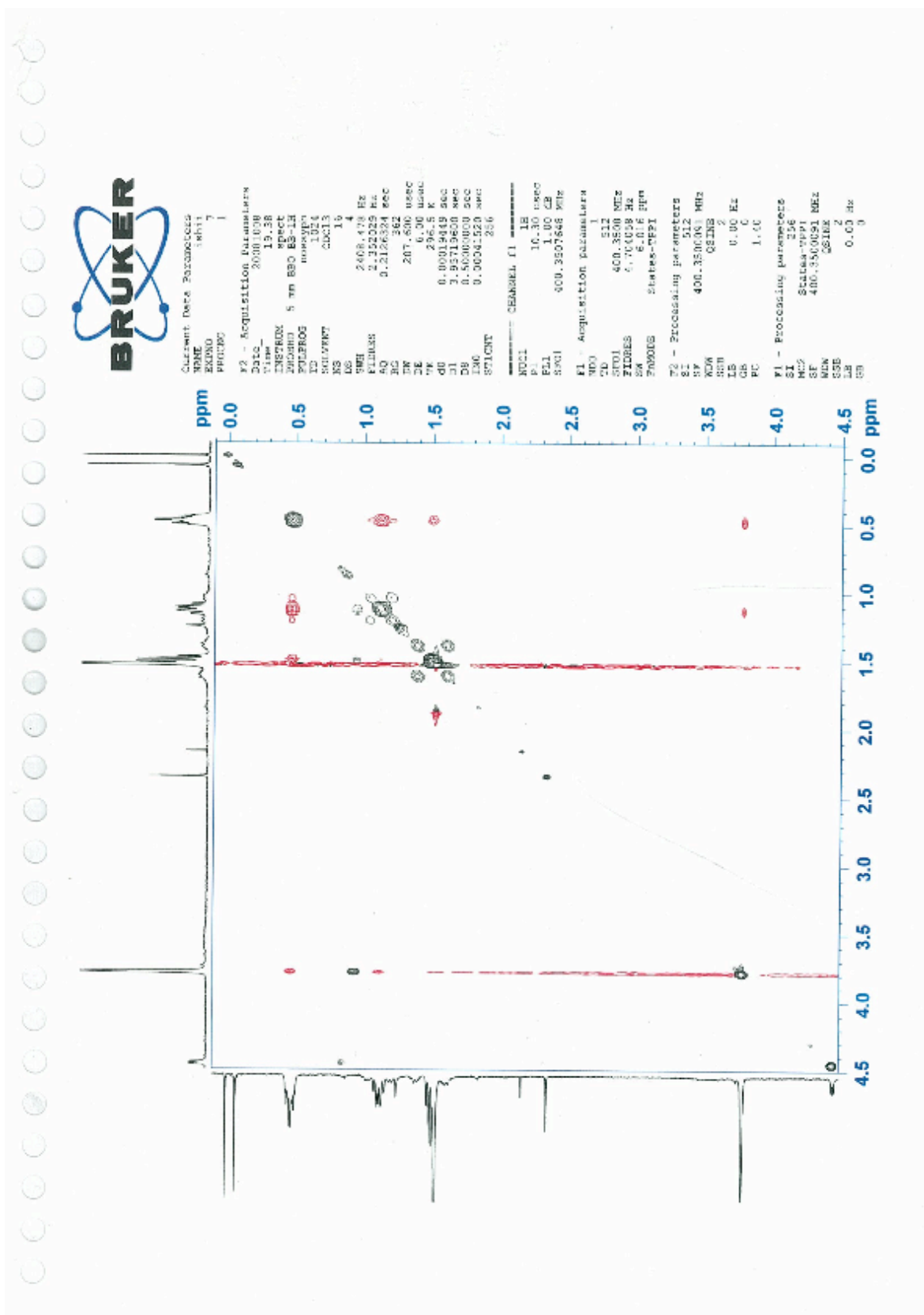
Coloreless crystals, mp 144–145 °C decomp (from CH₂Cl₂-hexane) (Found: C, 60.93; H, 4.17. Calc for C₅₂H₄₂P₂PtSe•H₂O: C, 61.17; H, 4.34%; one equivalent of H₂O was observed in the ¹H NMR spectrum measured in CDCl₃ dried by passing through a short column of active Al₂O₃); ν_{\max} (KBr)/cm⁻¹ 2096 (PtH); δ_{H} (400 MHz; CDCl₃; Me₄Si) -5.99 (1 H, dd, ² $J_{\text{P-H}}$ 182 and 16, ¹ $J_{\text{Pt-H}}$ 874), 4.95 (1 H, d, J 2.8), 6.78–6.88 (2 H, m), 6.93–7.01 (8 H, m), 7.12–7.28 (22 H, m), 7.51–7.56 (6 H, m), and 8.12 (2 H, d, J 6.8); δ_{P} (162 MHz; CDCl₃; 85% H₃PO₄) 20.2 (d, ² $J_{\text{P-P}}$ 15 Hz, ¹ $J_{\text{Pt-P}}$ 3265) and 29.9 (d, ² $J_{\text{P-P}}$ 15, ¹ $J_{\text{Pt-P}}$ 2086).

Thermal reaction of PtH(SeDbb)(PPh₃)₂ (**6**)

A solution of (hydrido)(selenolato)Pt^{II} complex **6** (419 mg, 0.418 mmol) in toluene (20 mL) was refluxed for 4 h, and then the solvent was removed under reduced pressure. The residue was chromatographed (hexane-CH₂Cl₂ 2/1) to give **7** (191 mg, 45%), **8** (50 mg, 12%), and **9** (20 mg, 5%) in this order.

2-Platinaselenetane 7: Colorless crystals, m.p. 304-305 °C decomp (from CH₂Cl₂) (Found: C, 62.29; H, 4.12. Calc for C₅₂H₄₂P₂PtSe: C, 62.28; H, 4.22%.); δ_H(400 MHz; CDCl₃; Me₄Si) 0.45–0.51 (1 H, m), 1.03–1.23 (1 H, m), 1.39–1.63 (1 H, m, *J*_{Pt-H} 90 Hz), 3.79 (1 H, s), 6.79–7.00 (16 H, m), 7.03–7.14 (3 H, m), 7.17–7.33 (11 H, m), 7.44–7.48 (6 H, m), 7.59–7.72 (1 H, m), and 8.13 (1 H, d, *J* 7.2); δ_C (100.7 MHz; CDCl₃; Me₄Si) 17.0 (d, ¹*J*_{P-C} 97), 35.0, 45.5, 60.6, 121.0, 121.3, 123.0, 123.3, 124.8, 124.9, 125.0, 127.5 (d, ²*J*_{P-C} 10), 127.8 (d, ²*J*_{P-C} 10), 127.9, 129.6, 129.7, 132.3 (d, ¹*J*_{P-C} 6.0), 132.8 (d, ¹*J*_{P-C} 14), 134.1 (d, ³*J*_{P-C} 6.0), 134.2 (d, ³*J*_{P-C} 6.0), 139.1, 145.3, 148.9, and 154.2; δ_P(162 MHz; CDCl₃; 85% H₃PO₄) 18.4 (d, ²*J*_{P-P} 9.7, ¹*J*_{Pt-P} 3530) and 26.4 (d, ²*J*_{P-P} 9.7, ¹*J*_{Pt-P} 1920).

NOESY spectrum of 7



3-Methylene-2-platinaselentane 8: Colorless crystals, mp 304–305 °C (from CH₂Cl₂) (Found: C, 62.18; H, 3.89. Calc for C₅₂H₄₀P₂PtSe: C, 62.40; H, 4.03%); δ_{H} (400 MHz; CDCl₃; Me₄Si) 4.46 (1 H, dd, *J* 5.6 and 2.0), 5.26 (1 H, t, *J* 5.0, *J*_{Pt-H} 57), 6.80–6.90 (8 H, m), 6.95–6.99 (3 H, m), 7.05–7.30 (17 H, m), 7.42–7.47 (8 H, m), and 7.66 (2 H, d, *J* 7.2 Hz); δ_{C} (100.7 MHz; CDCl₃; Me₄Si) 51.2 (d, ⁴*J*_{P-C} 6.0), 68.8 (dd, ³*J*_{P-C} 11 and 3.0), 120.6, 122.7 (2C), 123.2, 127.3 (d, ²*J*_{P-C} 10), 127.6 (d, ¹*J*_{P-C} 10), 129.7, 129.9, 131.7 (d, ¹*J*_{P-C} 47), 133.1 (d, ¹*J*_{P-C} 37), 134.3 (d, ³*J*_{P-C} 11), 135.0 (d, ³*J*_{P-C} 11), 145.0, and 149.5; δ_{P} (162 MHz; CDCl₃; 85% H₃PO₄) 17.0 (d, ²*J*_{P-P} 13, ¹*J*_{Pt-P} 3256) and 25.0 (d, ²*J*_{P-P} 13, ¹*J*_{Pt-P} 2044).

Selenaplinationcyclopentene 9: Colorless crystals, m.p. 212–213 °C decomp (from hexane-CH₂Cl₂) (Found: C, 62.14; H, 4.01. Calc for C₅₂H₄₀P₂PtSe: C, 62.40; H, 4.03%); δ_{H} (400 MHz; CDCl₃; Me₄Si) 4.88 (1 H, d, *J* 5.6), 5.80–5.86 (1 H, m), 6.58–7.76 (38 H, m), and 7.97 (1 H, d, *J* 6.4); δ_{P} (162 MHz; CDCl₃; 85% H₃PO₄) 21.9 (d, ²*J*_{P-P} 21, ¹*J*_{Pt-P} 1831) and 24.2 (d, ²*J*_{P-P} 21, ¹*J*_{Pt-P} 3259).

Thermal reaction of [PtH(SeDbb)(PPh₃)₂] (6) in the presence of PPh₃

A mixture of **6** (34 mg, 0.037 mmol) and PPh₃ (97 mg, 0.371 mmol) in toluene (2 mL) was heated under reflux for 13 h. The solvent was removed under reduced pressure and the residue was subjected to chromatography (hexane-CH₂Cl₂ 1/2) to give **8** (24 mg, 67%) and **9** (5 mg, 13%) in this order.