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

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The thermal reaction of a (dibenzobarreleneselenolato)-(hydrido)platinum(II) complex gave two four-membered selenaplatinacycles, one of which is formed by hydroplatination of the Pt–H bond to the etheno bridge and the other is a vinylic C–H bond activation product, and a five-membered selenaplatinacycle formed by an aromatic C–H bond activation.

Activation of a C–H bond by transition metals accounts for a major part of organometallic chemistry,¹ and the C–H activation occurring on a ligand leads to cyclometalation, which is known before several decades.² We recently reported the reaction of selenoseleninate **1** having sterically demanding 9-triptycyl groups (hereafter abbreviated as Trip) with $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$ to give selenaplatinacycle **2** by a cyclometalation.³ In relation to this reaction, we synthesised the first isolable (hydrido)(selenolato)Pt^{II} complex **3** by the reaction of selenol TripSeH with $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$, which could lead to selenaplatinacycle **2** by heating or treatment with HBF₄³ (Scheme 1). In the course of our study on the generality of the above reactions, we have been investigating the effects of transition metals,⁴ substituents on selenium,⁵ and phosphine ligands⁶ in addition to the reactions of 9-triptycenethiol⁷ and 9-triptycylgermane with Pt⁰ complexes.⁸



Scheme 1 Formation of selenaplatinacycle 2.

One of our present interest is, when different types of $C(sp^2)$ -H bonds exist in a substituent on the selenium of (hydrido)(selenolato)Pt^{II} complexes, which $C(sp^2)$ -H bond is activated intramolecularly. As such a substituent with adequate steric demand, we chose 9,10-etheno-9,10-dihydroanthracen-9-yl group (dibenzobarrelenyl, hereafter abbreviated as Dbb) that has

two types of C(sp²)-H bonds, aromatic and vinylic C–H bonds. Cyclometalations by activation of these C–H bonds are expected to give five- and/or four-membered selenaplatinacycles, respectively, the latter of which is a hitherto unknown ring system.⁹ In addition, one can anticipate a competitive hydroplatination to the etheno bridge in Dbb, which is another common reaction for hydrido transition-metal complexes.^{10,11}

The reaction of DbbLi, prepared by treatment of DbbBr 4^{12} with *t*-BuLi, with elemental selenium gave (Dbb)₂Se_n, reduction of which with NaBH₄ provided DbbSeH 5 in 78% from 4 (Scheme 2).



Scheme 2 Reaction Conditions: (a) *t*-BuLi (2 equiv.), -78 °C, THF; (b) Se, -78 °C, and then reflux; (c) NaBH₄, THF, rt.

The reaction of selenol **5** with $[Pt(\eta^2-nb)(PPh_3)_2]$ (nb = norbornene) in toluene gave *cis*- $[PtH(SeDbb)(PPh_3)_2]$ **6** in 83% yield. In the ³¹P{¹H} NMR spectrum, two doublets accompanying satellites due to the ¹⁹⁵Pt isotope were observed at $\delta 20.2 ({}^2J_{P-P} 15, {}^1J_{Pt-P} 3265)$ and 29.9 (d, ${}^2J_{P-P} 15, {}^1J_{Pt-P} = 2086)$, which are assigned as phosphorus atoms *trans* to the selenolato and the hydrido ligands, respectively.³ The thermal reaction of (hydrido)(selenolato)Pt^{II} complex **6** was carried out in refluxing toluene, and we isolated three platinum(II) complexes **7–9**. The major product is the fourmembered selenaplatinacycle **7**, a hydroplatination product of the Pt–H bond to the etheno bridge. The minor products are another four-membered selenaplatinacycle **8** and five-membered selenaplatinacycle **9**, which are the products *via* vinylic and aromatic C–H bonds activation, respectively (Scheme 3). The



Scheme 3 Formation of three selenaplatinacycles 7, 8 and 9.

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo 255, Sakura-ku, Saitama, 338-8570, Japan. E-mail: ishiiaki@chem.saitama-u.ac.jp; Fax: +81-48-858-3394 † Electronic supplementary information (ESI) available: Synthetic procedures and spectral characterization of **5–9**. CCDC reference numbers 773881 (**7**) and 773882 (**8**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00483a

structures of **7** and **8** were unambiguously determined by X-ray crystallography (Fig. 1 and 2).¹³

Fig. 1 ORTEP drawing of 7 at the 30% ellipsoidal probability. Hydrogen atoms except those in the ethano bridge are omitted for clarity. Relevant bond length (Å) and bond angle (°) data: Pt1–C2 2.113(4); Pt1–Se1 2.4491(5); Se1–C1 1.970(4); C1–C2 1.559(6); Pt1–P1 2.3012(11); Pt1–P2 2.2532(11); C2–Pt1–Se1 72.47(12); C1–Se1–Pt1 78.89(13); C2–C1–Se1 99.7(3); C1–C2–Pt1 99.8(3); C2–Pt1–P2 94.31(13); C2–Pt1–P1 164.96(13); P2–Pt1–P1 99.87(4); P2–Pt1–Se1 166.18(3); P1–Pt1–Se1 93.67(3); sum of four bond angles around Pt1 360.32.



In the ¹H NMR spectrum of **8**, the bridgehead proton of the Dbb and the vinylic proton were observed at δ 4.46 (dd, J 5.6 and 2.0) and 5.26 (t, J 5.0, J_{Pt-H} 57), respectively. In the ³¹P{¹H} NMR spectrum, the phosphorus atom *trans* to the selenium atom resonated at δ 17.0 (d, ² J_{P-P} 13, ¹ J_{Pt-P} 3256) and that *trans* to the sp² carbon atom at δ 25.0 (d, ² J_{P-P} 13, ¹ J_{Pt-P} 2044), where ² J_{Se-P} satellite signals were observed for the doublet at δ 17.0.

Five-membered selenaplatinacycle **9** exhibited in the ¹H NMR spectrum the characteristic signal due to the aromatic proton neighboring the platinum atom at δ 5.80–5.86 as similar as **2**. The ³¹P{¹H} NMR exhibited two doublets with satellites due to the ¹⁹⁵Pt at δ 21.9 (d, ²J_{P-P} 21, ¹J_{Pt-P} 1831) and 24.2 (d, ²J_{P-P} 21, ¹J_{Pt-P} 3259), which are assigned to phosphorus atoms *trans* to the sp² carbon and the selenium atom, respectively, based on the ¹J_{Pt-P} values similarly to the cases of **7** and **8**.

In the crystalline state, the four-membered rings in 7 and 8 are puckered and the puckered angles along the Se1-C2 bonds are 31.79° and 9.25°, respectively. Thus, the four-membered ring in 7 is more puckered than that in 8, which is due to the presence of an sp³ carbon in the ring of 7. The Pt-Se and Se-C bond lenghts are 2.4491(5) and 1.970(4) Å for 7 and 2.4393(4) and 1.980(3) Å for 8, which are slightly larger than the corresponding bond lenghts in five-membered ring in 2 [2.4097(4) and 1.956(4) Å, respectively].³ The Pt1-C2(sp²) bond in 8 [2.046(3) Å] is shorter than the Pt1- $C2(sp^3)$ in 7 [2.113(4) Å] and the corresponding Pt–C(Ar) bond in 2 [2.099(4) Å]. The sums of bond angles around Pt1 in 7 and 8 are 360.32° and 361.05°, respectively, resulting from the distortion from planarity due to the strained four-membered rings (the sum for 2 is 359.99°) and the steric repulsion of the neighbouring PPh₃ ligands. The torsion angles between plane P1-Pt1-P2 and plane Se1-Pt1-C2 are 6.70° for 7 and 12.82° for 8 (1.62° for 2).

To verify that the intramolecular hydroplatination of **6** giving **7** occurs in the *syn* stereochemistry, deuterated selenol DbbSeD **5-d** was allowed to react with $[Pt(\eta^2-nb)(PPh_3)_2]$ to give the deuterido complex *cis*-[PtD(SeDbb)(PPh_3)_2] **6-d**. The thermal reaction of **6-d** gave **7-d** as the main product, and only the proton (δ 1.03–1.23) *cis* to the platinum atom was deuterated. However, the deuterium content was only 30%, which is probably due to fast D-H exchange with a trace amount of residual H₂O through reductive elimination of **6-d** giving **5-d** and [Pt(PPh_3)_2] on heating. When **6** or **6-d** was heated in toluene in the presence of D₂O, quantitatively-deuterated **7-d** was formed (eqn (1)). H-D exchange of **7** did not take place at all under similar conditions. Thus, the intramolecular *syn*-hydroplatination of **6** was evidenced experimentally.



Fig. 2 ORTEP drawing of 8 at the 30% ellipsoidal probability. Hydrogen atoms and a solvated molecule (CH_2Cl_2) are omitted for clarity. Relevant bond lengths (Å) and bond angles (°) data: Pt1–C2 2.046(3); Pt1–Se1 2.4393(4); Se1–C1 1.980(3); C1–C2 1.543(5); Pt1–P1 2.3083(9); Pt1–P2 2.2596(9); C2–Pt1–Se1 73.45(10); C1–Se1–Pt1 80.62(10); C2–C1–Se1 99.3(2); C1–C2–Pt1 105.9(2); C2–Pt1–P2 92.17(10); C2–Pt1–P1 167.39(10); P2–Pt1–P1 99.70(3); P2–Pt1–Se1 161.42(3); P1–Pt1–Se1 95.73(2); sum of four bond angles around Pt1 361.05.

In the ³¹P{¹H} NMR spectrum of 7, two doublets accompanying ¹⁹⁵Pt satellites appeared at δ 18.4 (d, ²J_{P-P} 9.7, ¹J_{Pt-P} 3530) and 26.4 (d, ²J_{P-P} 9.7, ¹J_{Pt-P} 1920), which are assigned as the phosphorus atoms *trans* to the selenium atom and the sp³ carbon atom,



The thermal reaction of hydrido complex **6** was carried out in the presence of 10 molar equivs of PPh₃ as the additive. Interestingly, hydroplatination product **7** was not formed and **8** was obtained in 67% yield together with **9** in 13% yield (eqn (2)). This result suggests that the equilibrium between **6** and {[PtH(SeDbb)(PPh₃)] (**10**) + PPh₃} (Scheme 4) was inclined largely to the left side by the addition of PPh₃ to inhibit the formation of **7**, that is, the dissociation of a PPh₃ ligand from **6** is necessary to form **7**. It is reasonable to consider that the coordination-unsaturated platinum center in **10** coordinates on the etheno bridge intramolecularly followed by the *syn*-hydroplatination and re-ligation of a PPh₃ to give **7**, and that **8** and **9** are formed directly from **6** involving an evolution of H₂.



Scheme 4 A plausible formation pathway for selenaplatinacycles 7, 8 and 9.

In conclusion, cyclometalation to the Dbb group in (hydrido)(DbbSe)Pt^{II} complex 6 takes place in three ways to give two, novel four-membered selenaplatinacycles 7 and 8 and a five-membered one 9. The hydroplatination of the Pt–H to the etheno bridge to give 7 occurs in the *syn* manner, which is precedented by the dissociation of a PPh₃ ligand. Although the ring sizes are different, the vinylic C–H bond activation to give 8 is preferred over the aromatic C–H bond activation to give 9. Efforts are currently directed towards carboselenation of 7–9 with alkynes¹⁴ to synthesise functional selenium-containing heterocycles incorporated in the Dbb skeleton.

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- 13 *Crystallographic data for* **7** and **8**. **7**: (C₃₂H₄₂P₂PtSe·CH₂Cl₂); colourless prism, Mo-Kα radiation ($\lambda = 0.71073$), 103 K, $M_r = 1087.77$, triclinic, $P\bar{1}, a = 10.5381(8), b = 12.8984(10), c = 17.2005(14)$ Å, $\alpha = 84.159(2)$, $\beta = 87.716(2), \gamma = 78.702(2)^{\circ}, V = 2256.7(3)$ Å³, $Z = 2, \mu = 4.141 \text{ mm}^{-1}, d_c = 1.601 \text{ g cm}^{-3}, R_1 (I > 2\sigma(I)) = 0.0340, wR_2 = 0.0801$ (all data) for 8294 reflections, 532 parameters, GOF 1.001. **8**: (C₅₂H₄₀P₂PtSe·CH₂Cl₂); colourless prism, Mo-Kα radiation ($\lambda = 0.71073$), 103 K, $M_r = 1085.76$, triclinic, $P\bar{1}, a = 12.9249(5), b = 13.1578(5), c = 15.7079(6)$ Å, $\alpha = 74.7340(10), \beta = 69.4590(10), \gamma = 61.9440(10)^{\circ}, V = 2191.88(15)$ Å³, $Z = 2, \mu = 4.263 \text{ mm}^{-1}, d_c = 1.645 \text{ g cm}^{-3}, R_1 (I > 2\sigma(I)) = 0.0286, wR_2 = 0.0706$ (all data) for 8123 reflections, 560 parameters, GOF = 1.050.
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