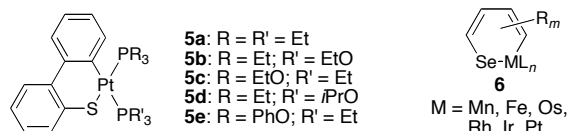# Reactions of *Se*-9-Triptycyl Triptycene-9-selenoseleninate (RSe(=O)-SeR; R = 9-triptycyl) and Related Compounds with a Platinum(0) Complex. Formation of Selenaplatinacycle and (Hydrido-selenolato)Platinum(II) Complexes**

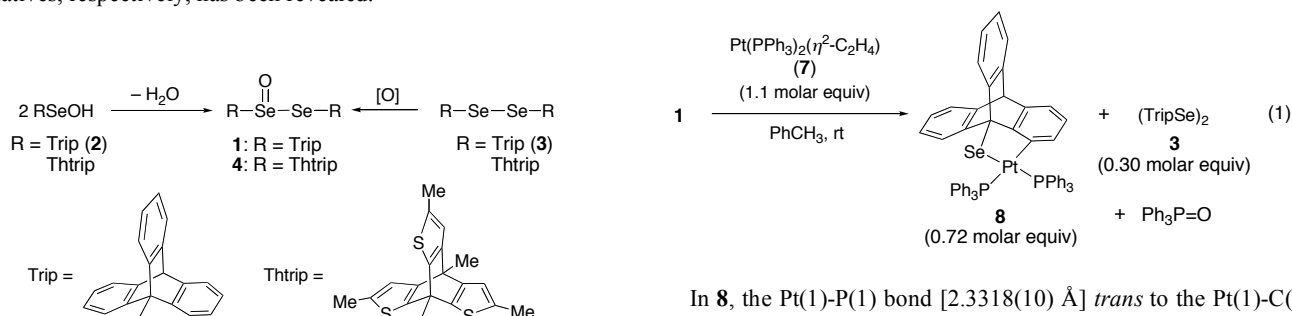*Akihiko Ishii,* Norio Nakata, Rei Uchiumi, and Keiko Murakami*

Dedicated to Professor Renji Okazaki on the occasion of his 70th birthday

Oxidative additions of cyclic and acyclic disulfides and their oxides to platinum(0) complexes are a topic of recent research.[1–3] However, analogous reactions of selenium compounds are limited only for diselenides.[3,4] For example, in the diselenation of terminal acetylenes with diselenides in the presence of Pd(0) or Pt(0) complexes,[5,6] diselenolato complexes have been proposed as the intermediates. As far as we know, there are no reports on analogous reactions for oxides of diselenides such as selenoseleninates [RSe(O)SeR], a major reason for which must be that only few isolable selenoseleninates are known.[7,8] It is important to investigate their reactivity toward low-valent transition metal complexes and the nature of the resulting selenium-metal complexes in relation to the corresponding chemistry of sulfur.

Previously we reported the preparation of selenoseleninate **1** by dehydration of selenenic acid **2** or oxidation of diselenide **3**.[7] Selenoseleninate **1** and another selenoseleninate **4** are the only ones isolable under ambient conditions. Here we report the reactions of selenoseleninate **1** and its related compounds with a platinum(0) complex, where we unexpectedly observed the formation of a five-membered selenaplatinacycle by an intramolecular C-H activation leading to the cyclometalation.[9] The chemistry of chalcogenametallacycles is also interesting in relation to the mechanistic study of homogeneous hydrodesulfurization process of crude oil distillates. The formation of thiaplatinacycles **5**[10] and selenametallacycles **6**[11] by insertion of low-valent transition metals into C-S and C-Se bonds of the thiophene and selenophene derivatives, respectively, has been revealed.

5a: R = R' = Et
5b: R = Et; R' = EtO
5c: R = EtO; R' = Et
5d: R = Et; R' = *i*PrO
5e: R = PhO; R' = Et

6
M = Mn, Fe, Os, Rh, Ir, Pt

In the beginning of the study, we examined the reaction of selenoseleninate **1** with [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (**7**) in the expectation of obtaining the corresponding (selenenato-selenolato)Pt^{II} complex [Pt(SeTrip)[Se(O)Trip](PPh$_3$)$_2$]. However, when **1** was treated with 1.1 molar equivalents of **7** in toluene at room temperature, we obtained an unexpected compound (**8**, 0.72 molar equiv) together with diselenide **3** (0.30 molar equiv, 30%) [Equation (1)]. In the ^{31}P NMR spectrum of the compound, two doublets accompanying satellite signals from the ^{195}Pt isotope are observed at δ=22.7 [d, ^2J(P,P)=20.4 Hz, ^1J(Pt,P)=1833 Hz] and 25.2 [d, ^2J(P,P)=20.4 Hz, ^1J(Pt,P)=3276 Hz]. In the ^{1}H NMR spectrum, a characteristic signal appears at δ=5.81–5.88 (m, 1H). The structure was finally disclosed by X-ray crystallography to be selenaplatinacycle **8** as depicted in Figure 1. The ^{31}P NMR signal at δ=25.3 with a ^1J(Pt,P) value of 3276 Hz was assigned to the P atom *trans* to the Se atom. The ^1J(Pt,P) value is comparable to those of the reported (selenolato)Pt^{II} complexes.[3,4] The other doublet assigned to the P atom *trans* to the C atom has 1833 Hz of the ^1J(Pt,P) value, which is very similar to those of thiaplatinacycles **5a** (1777 Hz), **5c** (1691 Hz), and **5e** (1645 Hz).[10e]

$$Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)$$

1 + (**7**) (1.1 molar equiv), PhCH$_3$, rt → **8** (0.72 molar equiv) + (TripSe)$_2$ **3** (0.30 molar equiv) + Ph$_3$P=O   (1)

In **8**, the Pt(1)-P(1) bond [2.3318(10) Å] *trans* to the Pt(1)-C(3) bond is longer than the Pt(1)-P(2) bond [2.2975(10) Å] *trans* to the Pt(1)-Se(1) bond. This observation, as well as the smaller ^1J(Pt,P) value of P(1) than that of P(2), indicates that the trans influence of the aromatic C atom is larger than that of the Se atom. The Pt atom maintains the planarity of tetracoordinated Pt(II) atoms; the sum of four angles around the Pt atom is 359.99°. The P(2)-Pt(1)-P(1) angle widens to 95.70(4)° and other three angles are less than 90°.

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Figure 1. ORTEP drawing of selenaplatinacycle **8** with 30% probability thermal ellipsoids (hydrogen atoms and the solvated molecule were omitted for clarity). Relevant bond lengths (Å) and bond angles (deg) data: Pt(1)-C(3) 2.099(4); Pt(1)-P(2) 2.2975(10); Pt(1)-P(1) 2.3318(10); Pt(1)-Se(1) 2.4097(4); C(3)-Pt(1)-P(2) 92.78(11); P(2)-Pt(1)-P(1) 95.70(4); C(3)-Pt(1)-Se(1) 85.65(10); P(1)-Pt(1)-Se(1) 85.86(3); C(3)-Pt(1)-P(1) 171.36(10); P(2)-Pt(1)-Se(1) 178.44(3).

A plausible formation mechanism for selenaplatinacycle **8** is depicted in Scheme 1. The attack of Pt(PPh$_3$)$_2$ at the divalent selenium atom in selenoseleninate **1** takes place first to give a cationic intermediate **9** and TripSe$^-$. An intramolecular substitution reaction of **9** leads to the selenaplatinacycle **8**, where TripSe$^-$ acts as a base to abstract a proton from **9** to be selenenic acid **2**. No formation of the presumed (selenenato-selenolato)Pt^{II} complex is probably due to the bulkiness of the 9-triptycyl group and triphenylphosphane ligands, which hinders the combination of **9** and TripSe$^-$ and permits reaction of the metal center in **9** toward the C-H bond of the 9-triptycyl group. Incidentally, diselenide **3** would be formed by deoxygenation of **1** with triphenylphosphane liberated under the reaction conditions. In a separate experiment, the deoxygenation of **1** with triphenylphosphane took place readily to give diselenide **3** and triphenylphosphane oxide quantitatively.

Scheme 1. A plausible mechanism for the reaction of selenoseleninate **1** with [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (**7**) to give selenaplatinacycle **8**.

If the reaction mechanism in Scheme 1 is operative, selenenic acid **2**, which is stable in solution at room temperature,[7] should be formed. However, we did not obtain **2**, suggesting that **2** also reacts with **7** to give selenaplatinacycle **8**. This consideration was proved

by the reaction of **2** with **7** to give **8** in 94% yield [Equation (2)]. This reaction would proceed in a way similar to that in Scheme 1 with the formation of H$_2$O in this case. Thus, 2 moles of **8** should be formed from 1 mole of **1**, and the yield of **8** in Equation (1) is 36%.

$$\text{TripSeOH} \xrightarrow[\text{CH}_2\text{Cl}_2,\ \text{rt}]{\text{Pt(PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)\ \ (\textbf{7})} \quad \begin{matrix} \textbf{8} \\ 94\% \end{matrix} \qquad (2)$$

$$\textbf{2}$$

We observed occasionally two intermediates for **8** in ^{31}P NMR spectra of a reaction mixture of **1** and **7** and that of **2** and **7**. Though we have not succeeded in the isolation of them to date, we tentatively assigned the intermediates to be cis and trans hydroxo complex **10a** and **10b** based on the substrates employed and the comparison of the ^1J(Pt,P) values with those of reported hydroxo Pt^{II} complexes.[12] In the ^{31}P NMR spectrum, **10a** exhibited two doublets accompanying satellite signals from the ^{195}Pt isotope at δ=16.9 [d, ^2J(P,P)=19.5 Hz, ^1J(Pt,P)=3249 Hz] and 19.7 [d, ^2J(P,P)=19.5 Hz, ^1J(Pt,P)=3017 Hz], and **10b** showed a singlet at δ=8.6 [^1J(Pt,P)=3755 Hz]. These intermediates changed to **8** quantitatively in solution at room temperature within several hours.

The above two reactions are summarized as follows: TripSe-L reacts with Pt(0) complex **7** giving rise to selenaplatinacycle **8**, in which L is the leaving group in the initial nucleophilic attack of **7** toward TripSe-L and the resulting L$^-$ behaves as a base in the following cyclometalation. To investigate the generality of the present reaction, we next examined the reaction of diselenide **3** with **7**. The reaction of **3** with an equimolar amount of **7** was performed at room temperature, and we obtained **8** (42%), (hydrido-selenolato)Pt^{II} complex **12** (30%), and selenol **11** (9.7%) together with recovery of diselenide **3** (51%) [Equation (3)]. Conversion yields of **8**, **12**, and **11** were 85%, 61%, and 20%, respectively.

$$(3)$$

Thus, the reaction of diselenide **3** with **7** produced selenaplatinacycle **8** and selenol **11** as expected, and, interestingly, the selenol **11** reacted with **7** to give the hydrido Pt^{II} complex **12**. When a sufficient amount (two molar equivalents) of **7** was employed, **8** and **12** were obtained in 80% and 88% yields, respectively, together with a small amount of **3** (7%). The present result is in marked contrast to the previously reported reactions of other diselenides (RSeSeR) with smaller R groups to give the corresponding (diselenolato)Pt^{II} complexes.[3,4]

(Hydrido-selenolato)Pt^{II} complex **12** was obtained in the pure form by the reaction of selenol **11** with **7** (Scheme 2). The complex **12** is stable under ambient conditions, and the structure (*cis*-[Pt(H)(SeTrip)(PPh$_3$)$_2$]) was confirmed unambiguously by X-ray crystal analysis as depicted in Figure 2. The sum of four angles around the Pt atom is 365.4° and the planarity of the Pt atom is distorted. While the P(1)-Pt(1)-Se(1) bond angle [91.10(3)Å] is near 90°, the P(1)-Pt(1)-P(2) bond angle widens up to 100.87(4)° that is larger by about 5° than the corresponding angle in

selenaplatinacycle **8** [95.70(4)°]. In hydroselenation of alkynes employing selenols in the presence of Pt(0) catalysts,[13,14] (hydrido-selenolato)Pt^{II} complexes were proposed as the key intermediate.[13a] Ananikov and coworkers succeeded in the observation of *trans*-[Pt(H)(SePh)(PPh$_3$)$_2$] by ^{1}H and ^{31}P NMR spectroscopies. The configuration of the two phosphane ligands in **12** is *cis* in contrast to Ananikov's *trans*-[Pt(H)(SePh)(PPh$_3$)$_2$]. In the ^{1}H NMR spectrum of **12**, the proton bound to the Pt atom resonates at $\delta=-6.10$ with 16 and 184 Hz of ^2J(P,H) couplings and with 1523 Hz of satellite signals from the ^{195}Pt isotope. In contrast, there observed no ^2J(P,H) coupling for *trans*-[Pt(PPh$_3$)$_2$(PhSe)(H)] (^{1}H NMR: $\delta=-8.77$, J(Pt,H)=999.8 Hz, J(Se,H)=44.1 Hz). Interestingly, treatment of **12** with HBF$_4$ provided selenaplatinacycle **8** in 60% yield (Scheme 2). Elimination of a hydride (H$^-$) from **12** under strongly acidic conditions would generate the cationic intermediate **9** to be led to **8**, which supports the mechanism in Scheme 1.

$$\text{TripSeH} \xrightarrow[\text{CH}_2\text{Cl}_2,\ \text{rt}]{\substack{\text{Pt(PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)\\ \textbf{(7)}}} \underset{\textbf{12} \ 78\%}{\text{TripSe}-\overset{\text{H}}{\underset{\text{PPh}_3}{\text{Pt}}}-\text{PPh}_3} \xrightarrow{\text{HBF}_4} \underset{60\%}{\textbf{8}}$$
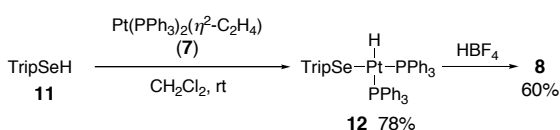
Scheme 2. The reaction of selenol **11** with **7** giving the (hydrido-selenolato)Pt^{II} complex **12** and the reaction of **12** with HBF$_4$ to give selenaplatinacycles **8**.
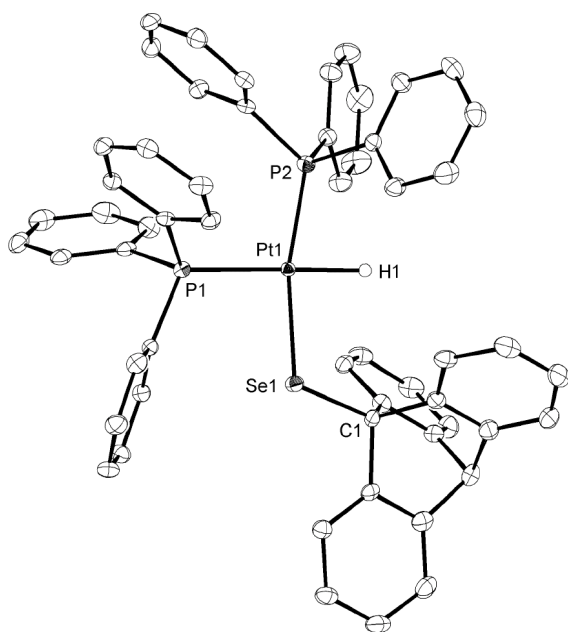
Figure 2. ORTEP drawing of *cis*-[Pt(H)(SeTrip)(PPh$_3$)$_2$] **12** with 30% probability thermal ellipsoids (hydrogen atoms except H1 were omitted for clarity). Relevant bond lengths (Å) and angles (deg): Pt(1)-P(2) 2.2474(12); Pt(1)-P(1) 2.3295(12); Pt(1)-Se(1) 2.4272(5); Pt(1)-H(1) 1.69(5); P(2)-Pt(1)-P(1) 100.87(4); P(1)-Pt(1)-Se(1) 91.10(3); P(2)-Pt(1)-H(55) 85.65(10); Se(1)-Pt(1)-H(55) 87.8(16); P(2)-Pt(1)-Se(1) 166.89(3); P(1)-Pt(1)-H(1) 178.9(16).

In conclusion, we found that the reactions of selenoseleninate **1**, selenenic acid **2**, and diselenide **3**, which have a 9-triptycyl group, with [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] **7** gave selenaplatinacycle **8** by an intramolecular C-H bond activation. We also succeeded for the first time in the full characterization of a (hydrido-selenolato)Pt^{II} complex (**12**). These results will give a new insight into the reaction of selenium compounds with low-valent transition metal complexes.

In the formation of **8**, bulkiness of the substituents both on the selenium atom in **1** and on the platinum atoms in **7** would play an important role. The generality of the present reaction is under investigation, focusing from both sides of the kind of substituents of organic selenium compounds and of kinds of phosphane ligands and metals of low-valent transition metal complexes.

Experimental Section

Reaction of *Se*-9-Triptycyl Triptycene-9-selenoseleninate (1) with [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (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. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta=5.22$ (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). Anal. Calcd for C$_{57}$H$_{44}$Cl$_2$P$_2$PtSe (C$_{56}$H$_{42}$P$_2$PtSe•CH$_2$Cl$_2$): C, 60.27; H, 3.86. Found: C, 60.74; H, 3.90. *Crystallographic data:* C$_{63}$H$_{50}$P$_2$PtSe (C$_{56}$H$_{42}$P$_2$PtSe · C$_7$H$_8$), $Ms = 1143.02$, colorless prism, $0.25 \times 0.25 \times 0.20$ mm^3, monoclinic, $P2_1/c$. $a = 13.9733(8)$, $b = 16.8802(10)$, $c = 20.5325(13)$ Å, $\beta = 91.374°$, $V = 4841.7(5)$ Å^3, $r_{calcd} = 1.568$ g cm^{-3}, $Z = 4$, μ(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), w$R_2 = 0.0846$ (for all), and GOF = 1.025, 688 parameters; max/min residual electron density = 1.474/–0.594 e Å^{-3}.

(Hydrido-selenolato)Pt^{II} complex 12: colorless crystals, m.p. 158–160 °C decomp (toluene-hexane). ^{1}H NMR: $\delta=-6.10$ [dd, ^2J(P,H)=184, 16 Hz, and satellite signals with ^1J(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); ^{31}P NMR: $\delta=21.3$ [d, ^2J(P,P)=14.0 Hz, ^1J(Pt,P)= 3281 Hz], 30.9 ppm [d, ^2J(P,P)=14 Hz, ^1J(Pt,P)=2028 Hz]; IR (KBr): $\tilde{v}=2093$ cm^{-1} (Pt-H). Anal. Calcd for C$_{56}$H$_{44}$P$_2$PtSe: C, 63.88; H, 4.21. Found: C, 63.33; H, 4.13. *Crystallographic data:* C$_{63}$H$_{50}$P$_2$PtSe (C$_{56}$H$_{42}$P$_2$PtSe · 1.5C$_7$H$_8$), $Ms=1190.62$, colorless prism, $0.25 \times 0.25 \times 0.20$ mm^3, triclinic, P-1. $a = 12.4546(6)$, $b = 14.5548(7)$, $c = 16.8369(8)$ Å, $\alpha = 93.8360(10)$, $\beta = 102.4290(10)$, $\gamma = 115.0090(10)°$, $V = 2657.8(2)$ Å^3, $r_{calcd} = 1.488$ g cm^{-3}, $Z = 2$, μ(Mo-$K\alpha$) = 3.426 cm^{-1}. Intensity data of 9880 unique reflections were collected in the range of $-15 \leq h \leq 14$, $-17 \leq k \leq 14$, $-20 \leq l \leq 20$ at 123 K. $R_1 = 0.0360$ ($I \geq 2\sigma I$, 8664 reflections), w$R_2 = 0.0840$ (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.

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