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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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. [4,5] For example, in the diselenation of terminal acetylenes with diselenides in the presence of Pd(0) or Pt(0) complexes, [6,7] 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 selenolates [RSe(=O)SeR], a major reason for which must be that only few isolable selenolates 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 selenolatenuclete 1 by dehydration of selenenic acid 2 or oxidation of diselenide 3. [7] Selenolatenuclete 1 and another selenolatenuclete 4 are the only ones isolable under ambient conditions. Here we report the reactions of selenolatenuclete 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 chalcogenometallacycles is also interesting in relation to the mechanistic study of homogeneous hydrodesulfurization process of crude oil distillates. The formation of thiaplatinacycles [10] and selenametallacycles [11] by insertion of low-valent transition metals into C-S and C-Se bonds of the thioephene and selenophene derivatives, respectively, has been revealed.

In the beginning of the study, we examined the reaction of selenolatenuclete 1 with [Pt2(PPh3)20(μ2-C2H4)] (7) in the expectation of obtaining the corresponding (selenenate-selenolato)PtII complex [Pt2SeTriplet(μ3-SeTriplet)(μ3-PPh3)]. 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 31P NMR spectrum of the compound, two doublets accompanying satellite signals from the 195Pt isotope are observed at δ = 22.7 [d, 2J(Pt,P) = 20.4 Hz, 1J(Pt,P) = 1833 Hz] and 25.2 [d, 2J(Pt,P) = 20.4 Hz, 1J(Pt,P) = 3276 Hz]. In the 1H 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 31P NMR signal at δ = 25.3 with a 2J(Pt,P) value, which is very similar to those of the reported (selenolato)Pt0 complexes [12,13]. The other doublet assigned to the P atom trans to the Se atom. The 1J(Pt,P) value is comparable to those of the reported (selenolato)PtII complexes [12]. 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). 

In 8, the Pt(1)-(P) bond [2.3318(10) Å] trans to the Pt(1)-(C) bond is longer than the Pt(1)-(P) bond [2.2975(10) Å] trans to the Pt(1)-(Se) 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 PtII 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°. 

\[ \text{Se-Pt-C Cycle} \]

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A plausible formation mechanism for selenaplatinacycle 8 is depicted in Scheme 1. The attack of Pt(PPh3)2 at the divalent selenium atom in selenoselenenate 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 (selenenate-selenolato)PtII complex is probably due to the bulkiness of the 9-tripryl group and triphenylphosphate 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-tripryl group. Incidentally, diselenide 3 would be formed by deoxygenation of 1 with triphenylphosphate liberated under the reaction conditions. In a separate experiment, the deoxygenation of 1 with triphenylphosphate took place readily to give diselenide 3 and triphenylphosphate oxide quantitatively.

If the reaction mechanism in Scheme 1 is operative, selenenic acid 2, which is stable in solution at room temperature[17] 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 H2O 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%.

We observed occasionally two intermediates for 8 in 31P 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 PtII complexes.[12] In the 31P NMR spectrum, 10a exhibited two doublets accompanying satellite signals from the 31Pt isotope at δ=16.9 [d, 1J(Pt,P)=19.5 Hz, 1J(Pt,P)=3249 Hz] and 19.7 [d, 1J(Pt,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 equivmolar amount of 7 was performed at room temperature, and we obtained 8 (42%), (hydrido-selenolato)PtII 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.

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 PtII 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)PtII complexes.[13,14]

(Hydrido-selenolato)PtII 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)(TripSe)(PPh3)]) 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 P1(1)-P1(1)-Se(1) bond angle [91.10(3)°] is near 90°, the P1(1)-Pt1-P1(2) bond angle widens up to 100.87(4)° that is larger by about 5° than the corresponding angle in

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)-Pt(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); Pt(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).

Scheme 1. A plausible mechanism for the reaction of selenoselenenate 1 with [Pt(PPh3)2(η2-C2H4)] (7) to give selenaplatinacycle 8.

![Diagram](image-url)

TripSeOH + [Pt(PPh3)2(η2-C2H4)] (7) → 8 + TripletSeOH (2)
selenenolactacycles 8 [95.70(4)°]. In hydroselenation of alkynes employing selenols in the presence of Pt(0) catalysts,\textsuperscript{13,14} (hydrido-selenolato)Pt\textsuperscript{II} complexes were proposed as the key intermediate.\textsuperscript{13}\textsuperscript{a} Ananikov and coworkers succeeded in the observation of trans-[Pt(H)(SePh)(PPh\textsubscript{3})\textsubscript{2}] by \textsuperscript{1}H and \textsuperscript{31}P NMR spectroscopies. The configuration of the two phosphine ligands in 12 is cis in contrast to Ananikov’s trans-[Pt(H)(SePh)(PPh\textsubscript{3})\textsubscript{2}]. In the \textsuperscript{1}H NMR spectrum of 12, the proton bound to the Pt atom resonates at δ=−6.10 with 16 and 184 Hz of \textsuperscript{2}J(P,H) couplings and with 1523 Hz of satellite signals from the \textsuperscript{195}Pt isotope. In contrast, there observed no \textsuperscript{2}J(P,H) coupling for trans-[Pt(PPh\textsubscript{3})\textsubscript{2}(PhSe)(H)] \textsuperscript{(1)}\textsuperscript{1}H NMR: δ=−8.77, \textsuperscript{3}J(Pt,H)=999.8 Hz, \textsuperscript{4}J(Se,H)=44.1 Hz. Interestingly, treatment of 12 with HBF\textsubscript{4} provided selenenolactacycle 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.

**Scheme 2.** The reaction of selenol 11 with 7 giving the (hydrido-selenolato)Pt\textsuperscript{II} complex 12 and the reaction of 12 with HBF\textsubscript{4} to give selenenolactacycles 8.

\[
\text{Scheme 2.}
\]

In conclusion, we found that the reactions of selenenolactinate 1, selenenic acid 2, and diselenide 3, which have a 9-tritylpyridine group, with [Pt(PPh\textsubscript{3})\textsubscript{2}(η\textsuperscript{2}-C\textsubscript{4}H\textsubscript{4}Cl\textsubscript{2})]\textsubscript{7} gave selenenolactacycle 8 by an intramolecular C-H bond activation. We also succeeded for the first time in the full characterization of a (hydrido-selenolato)Pt\textsuperscript{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-selenenolactane (1) with [Pt(PPh\textsubscript{3})\textsubscript{2}(η\textsuperscript{2}-C\textsubscript{4}H\textsubscript{4}Cl\textsubscript{2})\textsubscript{7}] (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-tritylpyridine diselenide (3) (14.0 mg, 0.021 mmol, 30%) was first eluted with a mixed solvent of hexane and dichloromethane (1:1). Then, the column was eluted with dichloromethane to give selenenolactane 8 (53.4 mg, 0.0508 mmol, 36%). 8: colorless crystals, m.p. 286–288 °C decomp. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 25 °C, TMS): δ=−5.22 (s, 1H), 4.81–5.88 (m, 1H), 6.65–6.71 (m, 2H), 6.90–6.98 (m, 10H), 7.13 (pseudo t, \textit{J}=6.9 Hz, 3H), 7.21 (d of t, \textit{J}=7.7, 1.9 Hz, 6H), 7.25–7.36 (m, 11H), 7.62–7.68 (m, 6H), 7.98 ppm (pseudo d, \textit{J}=7.6 Hz, 2H). Anal. Calcd for C\textsubscript{56}H\textsubscript{42}PtSe: C, 60.27; H, 4.44%. Found: C, 60.74; H, 3.86. 

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Crystallographic data:

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\begin{align*}
&\text{C}_{56}\text{H}_{42}\text{PtSe} \quad (\text{C}_{56}\text{H}_{42}\text{PtSe} \cdot \text{CHCl}_{3}) \\
&M_s=1190.62, \text{colorless prism, } P2_1/c \\
&a=13.973(8), b=16.8082(10), c=20.5325(13) \text{ Å}, \beta=91.374^\circ, V=4841.7(5) \text{ Å}^3; \\
&r_{\text{calc}}=1.568 \text{ g cm}^{-3}, Z=4, \mu(\text{Mo-K\textalpha})=3.758 \text{ cm}^{-1}. \\
\end{align*}
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Intensity data of 9503 unique reflections were collected in the range of −16 ≤ \( l ≤ 17, −20 ≤ h ≤ 20, −16 ≤ k ≤ 25 \) at 183 K. \textit{R}_1 = 0.0346 (\textit{I} ≥ 2\textit{sigma} \( I \)), 7858 reflections, \textit{wR}_2 = 0.0846 (for all), and GOF = 1.025, 688 parameters; max/min residual electron density = 1.474/−0.594 e Å\(^{-3}\).

**Figure 2.** ORTEP drawing of cis-[Pt(H)(HSeTri)(PPh\textsubscript{3})\textsubscript{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).

\[
\text{Figure 2. ORTEP drawing of cis-[Pt(H)(HSeTri)(PPh\textsubscript{3})\textsubscript{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).}
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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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