Selenium Metallacycles

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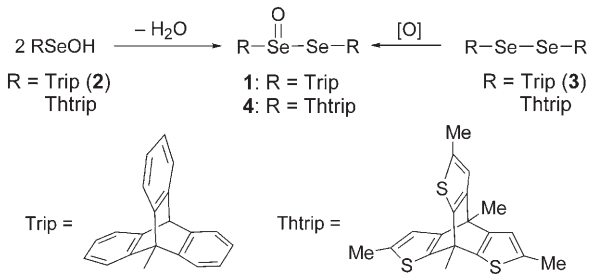
Reactions of a Ditriptycyl-Substituted Selenoseleninate and Related Compounds with a Platinum(0) Complex: Formation of Selenaplatinacycle and Hydrido Selenolato Platinum(II) Complexes**

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

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

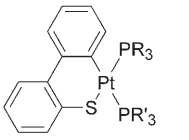
Oxidative additions of cyclic and acyclic disulfides and their oxides to platinum(0) complexes are a topic of recent research.[1–3] However, analogous reactions of selenium compounds are limited to diselenides.[3,4] For example, in the diselenation of terminal acetylenes with diselenides in the presence of palladium(0) and platinum(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** (Scheme 1).[7] Selenoseleninates **1** and **4** are the only such species isolable under ambient conditions. Herein

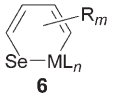


Scheme 1. Formation of selenoseleninates from selenenic acids and diselenides.

we report the reactions of **1** and its related compounds with a platinum(0) complex. We unexpectedly observed the formation of a five-membered selenaplatinacycle by intramolecular C–H activation.[9] The chemistry of chalcogenametallacycles is also interesting in relation to the mechanistic study of homogeneous hydrodesulfurization 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.

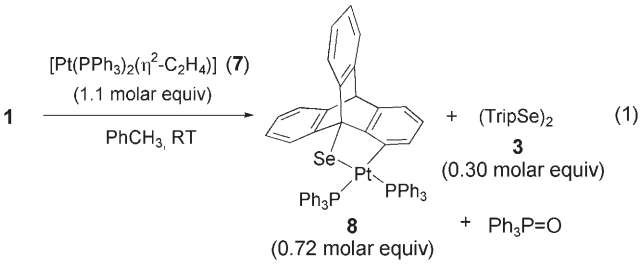


5a: R = R' = Et
5b: R = Et; R' = EtO
5c: R = EtO; R' = Et
5d: R = Et; R' = *i*PrO
5e: R = PhO; R' = Et



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

We first examined the reaction of selenoseleninate **1** with $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ (**7**) in the expectation of obtaining the corresponding selenenato selenolato platinum(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%) [Eq. (1)]. In the ^{31}P NMR spectrum of the compound,



(1)

two doublets with accompanying satellite signals from the ^{195}Pt isotope are observed at $\delta = 22.7$ (d, $^2J(P,P) = 20.4$ Hz, $^1J(Pt,P) = 1833$ Hz) and 25.3 ppm (d, $^2J(P,P) = 20.4$ Hz, $^1J(Pt,P) = 3276$ Hz). In the ^1H NMR spectrum, a characteristic signal appears at $\delta = 5.81$–5.88 ppm (m, 1H). The structure was finally shown by X-ray crystallography to be selenaplatinacycle **8** (Figure 1). The signal in the ^{31}P NMR spectrum at $\delta = 25.3$ ppm with $^1J(Pt,P) = 3276$ Hz was assigned to the

[*] Prof. Dr. A. Ishii, Dr. N. Nakata, R. Uchiumi, K. Murakami
Department of Chemistry
Graduate School of Science and Engineering, Saitama University
255 Shimo-okubo, Sakura-ku, Saitama 338-8570 (Japan)
Fax: (+81) 48-858-3700
E-mail: ishiiaki@chem.saitama-u.ac.jp
Homepage: http://www.chem.saitama-u.ac.jp/ishii-lab/index.files/slide0001.htm

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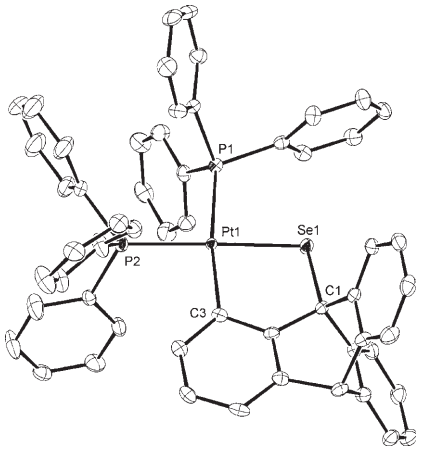
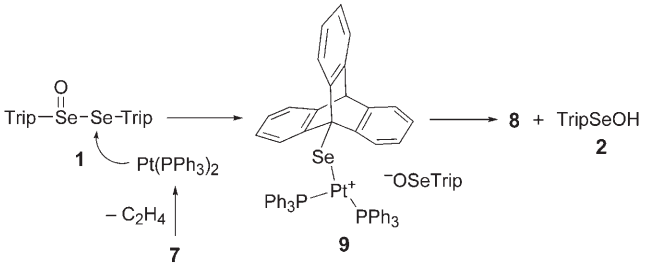


Figure 1. ORTEP drawing of **8**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms and the solvent molecule were omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–C3 2.099(4), Pt1–P2 2.2975(10), Pt1–P1 2.3318(10), Pt1–Se1 2.4097(4); C3-Pt1-P2 92.78(11), P2-Pt1-P1 95.70(4), C3-Pt1-Se1 85.65(10), P1-Pt1-Se1 85.86(3), C3-Pt1-P1 171.36(10), P2-Pt1-Se1 178.44(3).

P atom *trans* to the Se atom. The ^1J(Pt,P) value is comparable to those of reported (selenolato)Pt^{II} complexes.[3,4] The ^1J(Pt,P) value (1833 Hz) of the other doublet (assigned to the P atom *trans* to the C atom) is very similar to those of thiaplatinacycles **5a** (1777 Hz), **5c** (1691 Hz), and **5e** (1645 Hz).[10e]

In **8**, the Pt1–P1 bond (2.3318(10) Å) *trans* to the Pt1–C3 bond is longer than the Pt1–P2 bond (2.2975(10) Å) *trans* to the Pt1–Se1 bond. This observation, as well as the smaller ^1J(Pt,P) value of P1 than of P2, 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 the four angles around the Pt atom is 359.99°. The P2-Pt1-P1 angle widens to 95.70(4)°.

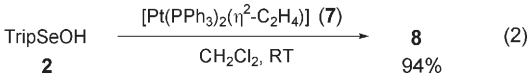
A plausible formation mechanism for selenaplatinacycle **8** is depicted in Scheme 2. The attack of $Pt(PPh_3)_2$ at the divalent selenium atom in selenoseleninate **1** takes place first to give a cationic intermediate **9** and TripSeO$^-$. An intramolecular substitution reaction of **9** leads to the selenaplatinacycle **8**, where TripSeO$^-$ acts as a base to abstract a proton from **9** to form selenenic acid **2**. The lack of formation of the presumed selenenato selenolato platinum(II) complex is probably due to the bulkiness of the 9-triptycyl group and



Scheme 2. 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**.

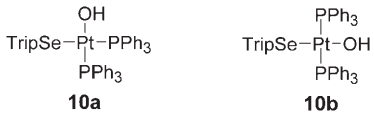
the triphenylphosphane ligands, which hinder the combination of **9** and TripSeO$^-$ and permit reaction of the metal center in **9** with the C–H bond of the 9-triptycyl group. Incidentally, diselenide **3** would be formed by deoxygenation of **1** with triphenylphosphane liberated under the reaction conditions. In a separate experiment, the deoxygenation of **1** with triphenylphosphane took place readily to give diselenide **3** and triphenylphosphane oxide quantitatively.

If the reaction mechanism in Scheme 2 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 confirmed by the reaction of **2** with **7** to give **8** in 94% yield [Eq. (2)]. This reaction would



proceed in a manner similar to that in Scheme 2, except that H_2O would be formed in this case. Thus two mole **8** should be formed from one mole **1**, and the yield of **8** in Equation (1) is 36%.

We occasionally observed two intermediates for **8** in the ^{31}P NMR spectra of reaction mixtures of **1** and **7** and of **2** and **7**. Though we have not yet succeeded in isolating these intermediates, we tentatively assigned them as *cis* and *trans* hydroxo complexes **10a** and **10b** on the basis of the substrates

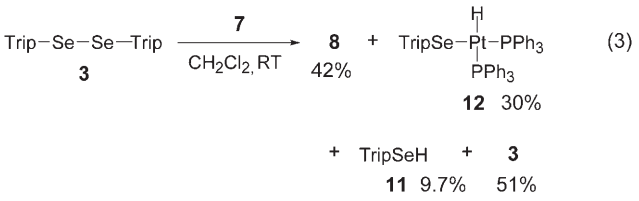


employed and the comparison of the ^1J(Pt,P) values with those of reported hydroxo Pt^{II} complexes.[12] In the ^{31}P NMR spectrum, **10a** exhibited two doublets with accompanying satellite signals from the ^{195}Pt isotope at $\delta = 16.9$ (d, ^2J(P,P) = 19.5 Hz, ^1J(Pt,P) = 3249 Hz) and 19.7 ppm (d, ^2J(P,P) = 19.5 Hz, ^1J(Pt,P) = 3017 Hz), and **10b** showed a singlet at $\delta = 8.6$ ppm (^1J(Pt,P) = 3755 Hz). These intermediates were transformed into **8** quantitatively in solution at room temperature within several hours.

The above two reactions are summarized as follows: TripSe-LG reacts with Pt^0 complex **7**, giving rise to selenaplatinacycle **8**, in which LG is the leaving group in the initial nucleophilic attack of **7** and the resulting LG$^-$ behaves as a base in the subsequent cyclometalation. To investigate the generality of this 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 platinum(II) complex **12** (30%), and selenol **11** (9.7%); diselenide **3** (51%) was also recovered [Eq. (3)]. Conversion yields of **8**, **12**, and **11** were 85%, 61%, and 20%, respectively.

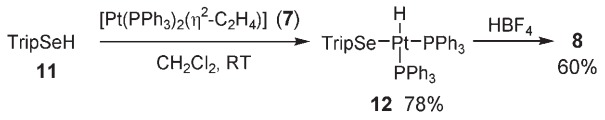
Thus, the reaction of diselenide **3** with **7** produced selenaplatinacycle **8** and selenol **11** as expected, and, inter-

estingly, the selenol **11** reacted with **7** to give the hydrido Pt^{II} complex **12**. When a sufficient amount (two molar equiv-



alents) of **7** was employed, **8** and **12** were obtained in 80% and 88% yields, respectively, together with a small amount of **3** (7%). This 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 platinum(II) complex **12** was obtained in pure form by the reaction of selenol **11** with **7** (Scheme 3). Complex **12** is stable under ambient conditions, and the



Scheme 3. The reaction of selenol **11** with **7** giving the hydrido selenolate platinum(II) complex **12** and the reaction of **12** with HBF_4 to give selenaplatinacycle **8**.

structure was confirmed unambiguously by X-ray crystallographic analysis (Figure 2). The sum of the four angles around the Pt atom is 365.4°, and the planarity of the Pt atom is

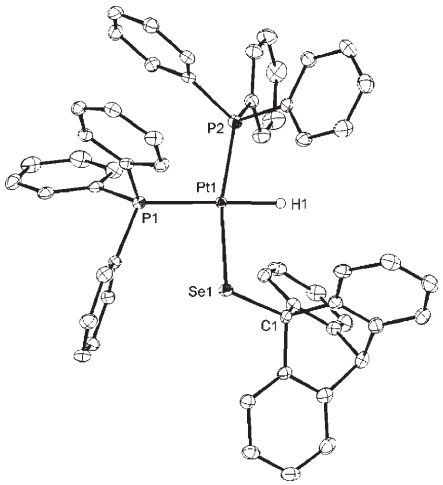


Figure 2. ORTEP drawing of *cis*-[Pt(H)(SeTrip)(PPh_3)$_2$] **12**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms except H1 and the solvent molecules were omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P2 2.2474(12), Pt1–P1 2.3295(12), Pt1–Se1 2.4272(5), Pt1–H1 1.69(5); P2-Pt1-P1 100.87(4), P1-Pt1-Se1 91.10(3), P2-Pt1-H1 85.65(10), Se1-Pt1-H1 87.8(16), P2-Pt1-Se1 166.89(3), P1-Pt1-H1 178.9(16).

distorted. While the P1-Pt1-Se1 bond angle (91.10(3) Å) is near 90°, the P1-Pt1-P2 bond angle widens to 100.87(4)°; this value 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 platinum(II) complexes were proposed as key intermediates.[13a] Ananikov et al. succeeded in the observation of *trans*-[Pt(H)(SePh)(PPh_3)$_2$] by ^{1}H and ^{31}P NMR spectroscopy. The configuration of the two phosphane ligands in **12** is *cis*, in contrast to *trans*-[Pt(H)(SePh)-(PPh_3)$_2$] of Ananikov et al. In the ^{1}H NMR spectrum of **12**, the proton bound to the Pt atom resonates at $\delta = -6.10$ ppm with ^2J(P,H) couplings of 16 and 184 Hz and with satellite signals from the ^{195}Pt isotope separated by 1523 Hz. In contrast, no ^2J(P,H) coupling was observed for *trans*-[Pt-(PPh_3)$_2$(PhSe)(H)] (^{1}H NMR: $\delta = -8.77$ ppm, 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 3). Elimination of a hydride (H^-) from **12** under strongly acidic conditions would generate the cationic intermediate **9**, which then proceeds to form **8**, thus supporting the mechanism in Scheme 2.

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_2H_4)] **7** gave selenaplatinacycle **8** by intramolecular C–H bond activation. We also succeeded for the first time in the full characterization of a hydrido selenolato platinum(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** play an important role. The generality of this reaction is under investigation, focusing both on the substituents of the organic selenium compounds and on the phosphane ligands and metals of low-valent transition metal-complexes.

Experimental Section

Reaction of **1** with **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-triptycyldiselenide (**3**, 14.0 mg, 0.021 mmol, 30%) was first eluted with hexane/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 (dt, $J = 7.7$, 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). Elemental analysis calcd (%) for $C_{57}H_{44}Cl_2P_2PtSe$ ($C_{56}H_{42}P_2PtSe{\cdot}CH_2Cl_2$): C 60.27, H 3.86; found: C 60.74, H 3.90. Crystallographic data: $C_{63}H_{50}P_2PtSe$ ($C_{56}H_{42}P_2PtSe{\cdot}C_7H_8$), $M_s = 1143.02$, colorless prism, $0.25 \times 0.25 \times 0.20$ mm^3, monoclinic, space group $P2_1/c$, $a = 13.9733(8)$, $b = 16.8802(10)$, $c = 20.5325(13)$ Å, $\beta = 91.374(2)°$, $V = 4841.7(5)$ Å^3, $\rho_{calcd} = 1.568$ g cm^{-3}, $Z = 4$, $\mu(Mo_{K\alpha}) = 3.758$ cm^{-1}. Intensity data of 9503 unique reflections were collected in the range of $-16 \le h \le 17$, $-20 \le k \le 20$, $-16 \le l \le 25$ at 183 K. $R_1 = 0.0346$ ($I \ge 2\sigma I$, 7858 reflec-

tions), $wR_2 = 0.0846$ (all data), GOF = 1.025, 688 parameters, max/min residual electron density = 1.474/−0.594 e Å^{-3}.

12: colorless crystals, m.p. 158–160 °C (decomp), recrystallized from a toluene/hexane solution. ^{1}H NMR: $\delta = -6.10$ (dd, ^2J(P,H) = 184, 16 Hz, ^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): $\tilde{\nu}$ = 2093 cm^{-1} (Pt–H). Elemental analysis calcd (%) for $C_{56}H_{44}P_2PtSe$: C 63.88, H 4.21; found: C 63.33, H 4.13. Crystallographic data: $C_{63}H_{50}P_2PtSe$ ($C_{56}H_{42}P_2PtSe \cdot 1.5\,C_7H_8$), $M_s = 1190.62$, colorless prism, $0.25 \times 0.25 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$. $a = 12.4546(6)$, $b = 14.5548(7)$, $c = 16.8369(8)$ Å, $\alpha = 93.8360(10)$, $\beta = 102.4290(10)$, $\gamma = 115.0090(10)$°, $V = 2657.8(2)$ Å^3, $\rho_{calcd} = 1.488$ 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 $-15 \le h \le 14$, $-17 \le k \le 14$, $-20 \le l \le 20$ at 123 K. $R_1 = 0.0360$ ($I \ge 2\sigma I$, 8664 reflections), $wR_2 = 0.0840$ (all data), GOF = 1.009, 647 parameters, max/min residual electron density = 1.566/−0.566 e Å^{-3}.

CCDC-666761 (**8**) and CCDC-666762 (**12**) contain the supplementary crystallographic data for this paper. These data 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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