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Hydroselenation and Carboselenation of Electron-Deficient Alkynes with Isolable (Hydrido)(selenolato)platinum(II) Complexes and a Selenaplatinacycle Bearing a Triptycene Skeleton

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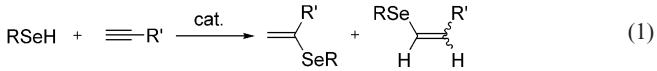
Keywords: Platinum / Insertion / Hydride ligands / Phosphane ligands / Selenium

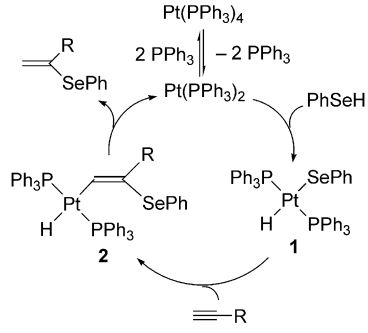
The reaction of [PtH(SeTrip)(PPh_3)$_2$] (Trip = 9-triptycyl) (**3**) with dimethyl acetylenedicarboxylate (DMAD) or methyl propiolate gave hydroselenation *syn* adducts. The reaction of [PtH(SeTrip)(dppe)] [dppe = 1,2-bis(diphenylphosphanyl)-ethane], which has a stronger phosphane σ-donor ligand than **3**, with DMAD gave both *syn* and *anti* adducts. The reaction of **3** and DMAD in the presence of PPh_3 yielded no adducts. These observations indicate that, in the hydroselenation, the dissociation of a PPh_3 ligand from **3** is a key step. The selenaplatinacycle **6**, which is a thermal reaction product of **3**, reacted with DMAD to give the carboselenation product, 1*H*-2-benzoselenin **7**, which was also formed by the reaction of TripSeH with DMAD.

Introduction

Regioselective and/or stereoselective, transition-metal-catalyzed hydroselenation of terminal alkynes,[1–3] as well as other chalcogenation reactions of alkynes,[4–6] are important reactions that provide synthetically useful vinyl selenides [Equation (1)]. Carboselenation and carbothiolation[7] are also important synthetic reactions from the point of view of providing C–Se and C–C bonds in one step.[8] Concerning the mechanism for hydroselenation catalyzed by group 10 metals, Ogawa proposed a possible mechanism involving ligand exchange of [Pd(SePh)$_2$L$_n$] (L = pyridine), formed by the reaction of [Pd(OAc)$_2$] with 2 PhSeH and 2 L, with a terminal alkyne, followed by insertion of the alkyne into the Pd–Se bond to give [(*Z*)-2-selenovinyl]palladium(II) complexes.[1b] The protonolysis of the vinyl Pd^{II} complexes with PhSeH gives the Markovnikov-type adduct (1,1-disubstituted alkene) accompanying the regeneration of the catalyst.[1b] Ananikov proposed a similar mechanism for the Pd(PPh_3)$_4$-catalyzed hydroselenation that involved both *trans*-[PdH(SePh)(PPh_3)$_2$] and dinuclear Pd^{II} complexes, *cis*- and *trans*-[{Pd(SePh)(PPh_3)}$_2$(μ-SePh)$_2$], instead of mononuclear diselenolato complexes.[2a] In the case of the Pt(PPh_3)$_4$-catalyzed hydroselenation with PhSeH, Ananikov observed a key intermediate, *trans*-[PtH(SePh)(PPh_3)$_2$] (**1**), by ^{1}H NMR spectroscopy and proposed the catalytic cycle shown in Scheme 1.[2a] (Hydrido)-platinum(II) complex **1** undergoes insertion of the alkyne into the Pt–Se bond to give **2** (*syn*-selenoplatination), the reductive elimination from which yields the vinyl selenide and [Pt(PPh_3)$_2$].[2a,9] As far as we know, however, there have been no reports on a direct, stoichiometric reaction between (hydrido)(selenolato)palladium(II) or -platinum(II) complexes with alkynes.



(1)



Scheme 1. Catalytic cycle for the hydroselenation proposed by Ananikov.[4b]

We recently succeeded in the isolation of stable (hydrido)(selenolato)platinum(II) complexes with *cis* configuration of two phosphane ligands by the reaction of 9-triptyceneselenol (TripSeH, Trip = 9-triptycyl) with [Pt(C_2H_4)(PPh_3)$_2$][10a] [Equation (2)] or [Pt(dppe or dppf)][10b] [dppe = 1,2-bis(diphenylphosphanyl)ethane; dppf = 1,1′-bis(diphenylphosphanyl)ferrocene] (Figure 1).[11] The investigation of the stoichiometric reaction of (hydrido)-(selenolato)platinum(II) complexes with alkynes is quite in-

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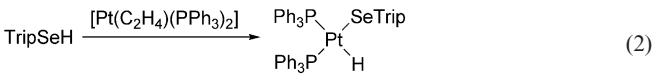
formative for clarifying the course of the hydroselenation. Here, we report the reaction of two (hydrido)(selenolato)-platinum(II) complexes, [PtH(SeTrip)(PPh_3)$_2$] (**3**) and [PtH(SeTrip)(dppe)] (**4**), with electron-deficient alkynes and the related carboselenation reactions.



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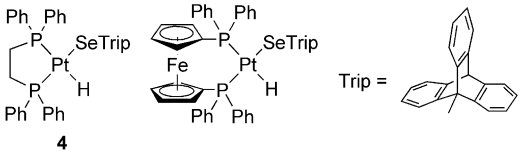


Figure 1. [PtH(SeTrip)(dppe)] (left, **4**) and [PtH(SeTrip)(dppf)] (right).

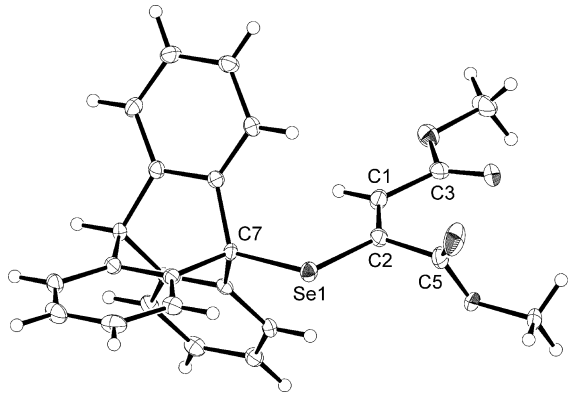
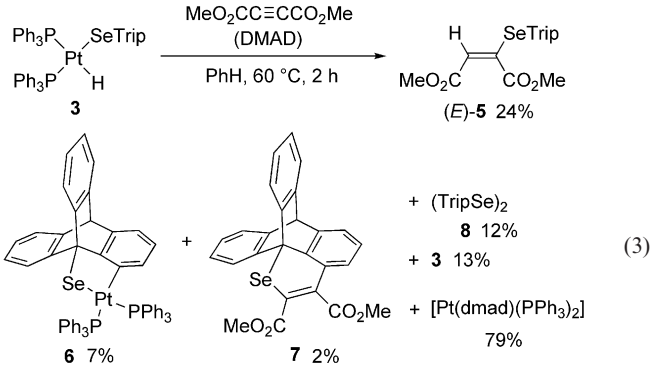


Figure 2. ORTEP drawing of (*E*)-**5** at the 30% probability level. Selected bond lengths [Å] and angles [°]: Se1–C2 1.890(3), Se1–C7 1.953(3), C1–C2 1.335(5), C1–C3 1.468(5), C2–C5 1.506(5); C2–Se1–C7 106.15(14), Se1–C2–C1 130.0(3), Se1–C2–C5 106.9(2), C1–C2–C5 123.1(3), C2–C1–C3 120.8(3).

Results and Discussion

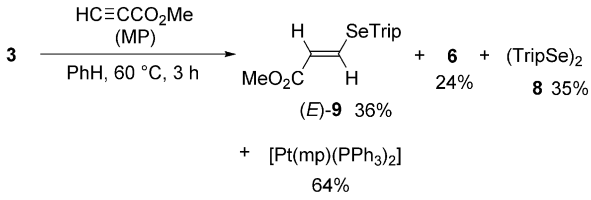
Hydroselenation

The reaction of [PtH(SeTrip)(PPh_3)$_2$] (**3**) with dimethyl acetylenedicarboxylate (DMAD) in benzene at 60 °C for 2 h gave *syn* adduct (*E*)-**5** in 24% yield, together with selenaplatinacycle **6** (7%), 1*H*-2-benzoselenin derivative **7** (2%), diselenide **8** (12%), **3** (13%), and [Pt(dmad)(Ph_3P)$_2$] (79%) [Equation (3)]. The structure of (*E*)-**5** was determined unambiguously by X-ray crystallography (Figure 2).[12] The selenaplatinacycle **6** is formed as a thermal reaction product of **3** as reported previously.[10a] 1*H*-2-Benzoselenin **7** is a carboselenation product of DMAD with **6** or TripSeH, as discussed in the next section.



(3)

Similarly, the reaction of **3** with methyl propiolate was carried out in benzene at 60 °C for 3 h to produce *syn* adduct (*E*)-**9** in 36% yield, together with [Pt(mp)(PPh_3)$_2$] (64%), selenaplatinacycle **6** (24%), and diselenide **8** (35%) [Equation (4)]. In the ^{1}H NMR spectrum of (*E*)-**9**, a large coupling constant (16 Hz) between the two vinylic protons (δ = 5.43 and 6.27 ppm) indicated the *trans* stereochemistry. The structure of (*E*)-**9** was finally confirmed by X-ray crystallography (Figure 3).[12] The stereoselectivity found here contrasts with that reported by Ananikov and co-workers for the reaction between methyl propiolate and PhSeH in the presence of $Pt(PPh_3)_4$ in toluene at 80 °C, which gave a 1:7 (*E*)/(*Z*) mixture of **9** through a noncatalytic reaction.[2a] They also reported that reactions of terminal alkynes with PhSeH under similar conditions gave Markovnikov-type products [H_2C=C(SePh)R] regioselectively in the case of 2-propyn-1-ol, 1-hexyne, 3-dimethylaminopropyne, and 1-ethynylcyclohexanol, and anti-Markovnikov-type products, (*E*) and (*Z*) isomers, in the case of phenylacetylene.[2a] The reaction of **3** with 1-hexyne, phenylacetylene, diphenylacetylene, or methyl 2-butynoate, did not yield hydroselenation adducts, which is probably due to the steric hindrance of the bulky 9-triptycyl group and to the strong coordinating ability of this alkaneselenolato ligand compared with the benzeneselenolato ligand.



(4)

The regio- and stereoselective formation of (*E*)-**5** and (*E*)-**9** supports the *syn* insertion of DMAD or methyl propiolate into the Pt–Se bond of **3** to give the [(*Z*)-2-selenovinyl]platinum(II) complex, followed by reductive elimination. On the other hand, the reaction of [PtH(SeTrip)(dppe)] (**4**) with DMAD in benzene proceeded sluggishly at 60 °C, and heating in refluxing benzene for 38 h was necessary to bring about complete consumption of **4**

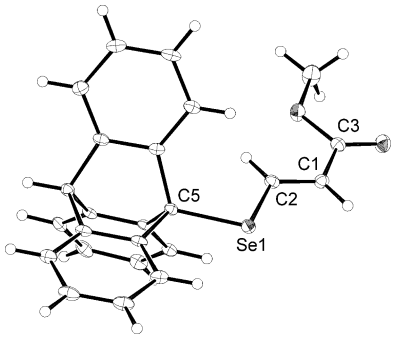
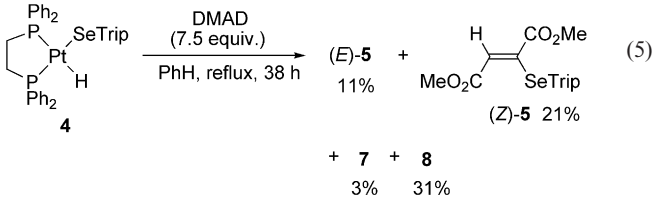


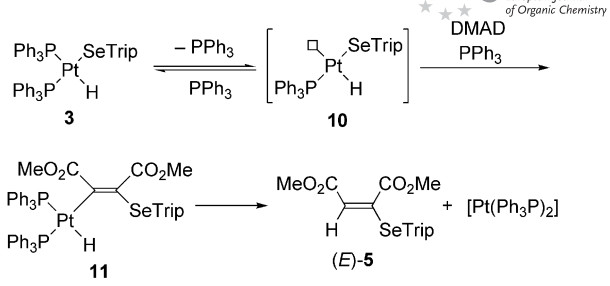
Figure 3. ORTEP drawing of (*E*)-**9** at the 30% probability level. The hexane solvent molecule is omitted. Selected bond lengths [Å] and angles [°]: Se1–C2 1.888(2), Se1–C5 1.959(2), C1–C2 1.326(3), C1–C3 1.468(3); C2–Se1–C5 97.08(9), Se1–C2–C1 125.26(18), C2–C1–C3 122.8(2).

to yield (*E*)-**5** (11%), (*Z*)-**5** (21%), 1*H*-2-benzoselenin **7** (3%), and diselenide **8** (31%) [Equation (5)]. These products are considered to form by the reaction of TripSeH and DMAD as described in the next section.



(5)

The difference in reactivities between [PtH(SeTrip)-$(PPh_3)_2$] (**3**) and [PtH(SeTrip)(dppe)] (**4**) toward DMAD is attributed to the weaker coordination ability of PPh_3 compared to dppe, that is, the dissociation of one phosphane ligand (PPh_3) from **3** is essential for the hydroselention reaction. The dissociation of PPh_3 from **3** should be depressed by the addition of PPh_3, which was evidenced by the reaction of **3** with DMAD in the presence of additional PPh_3 (2 equiv.); this impeded the formation of (*E*)-**5** to give diselenide **8** (39%), **3** (35%), and [Pt(dmad)$(PPh_3)_2$] (53%). Thus, as depicted in Scheme 2, dissociation of one of the PPh_3 ligands from **3** occurs first to give coordination-unsaturated intermediate **10**, where the ligand *trans* to H would be detached owing to the stronger *trans* effect of the H ligand than that of the selenolato ligand. The larger *trans* influence of hydrido ligands compared to the selenolato ligands in **3** and **4** has been discussed on the basis of NMR spectroscopic data in solution and X-ray structures in the crystalline state.[10] Then, **10** undergoes insertion of DMAD and re-coordination of PPh_3 to yield the (hydrido)(2-selenoalkenyl)platinum(II) intermediate **11**, from which reductive elimination provides the *syn* adduct (*E*)-**5** and [Pt$(PPh_3)_2$].



Scheme 2. Proposed mechanism for the reaction of [PtH-(SeTrip)$(PPh_3)_2$] (**3**) with DMAD to give the *syn* adduct (*E*)-**5**.

Figure 4 summarizes the bond lengths around the Pt atoms of **3**[10a] and **4**[10b] obtained from X-ray crystallographic data. The Pt–P bonds in **3** [2.2474(12) and 2.3295(12) Å] are longer than those in **4** [2.2190(19) and 2.3093(16) Å], indicating the weaker coordination of PPh_3 to the Pt atom compared to that of dppe, due to the weaker σ-donor ability and larger steric hindrance. This consideration is based on the structures of **3** and **4** in the crystalline state and is in agreement with their reactivities in solution. In both complexes, the Pt–P bonds *trans* to the H ligand are longer by 0.08–0.09 Å than those *trans* to the TripSe ligand, which is probably due to the P(1) ligands, suffering large steric repulsion from both *cis* ligands, in addition to a stronger *trans* influence of the H ligand. This would lead to a stronger *trans* effect of the H ligand observed for the PPh_3 dissociation step. Incidentally, the Pt–Se bond [2.4376(8) Å] in **4** is only slightly longer (0.01 Å) than that in **3** [2.4272(5) Å]. If the insertion of DMAD into the Pt–Se bonds of **3** and **4** occurred in the four-coordinate states, almost similar reactivity of both complexes toward DMAD might be observed.

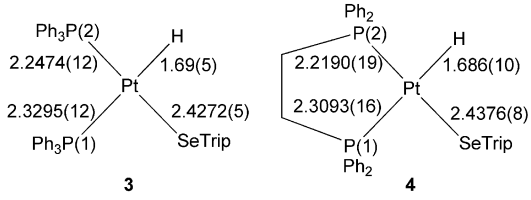
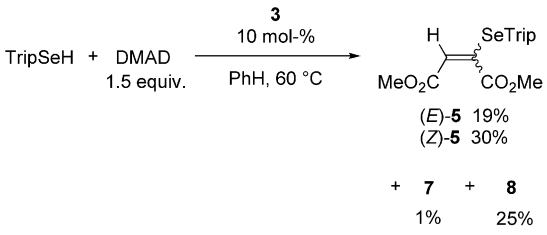


Figure 4. Bond lengths [Å] around the Pt atoms of [PtH-(SeTrip)$(PPh_3)_2$] (**3**)[10a] and [PtH(SeTrip)(dppe)] (**4**).[10b]

Similar prior dissociation of a phosphane ligand was reported for the insertion of an alkyne into the Pt–S bond in *trans*-[Pt$(SAr)_2(PPh_3)_2$][13] and the Pt–Si bond in *cis*-[Pt$(SiR_3)_2(PMe_2Ph)_2$].[14] Kuniyasu and Kambe succeeded in the isolation of (selenolato)(2-selenovinyl)platinum(II)[15a] and -palladium(II) complexes[15b] corresponding to **2** and **11**. In the present hydroselenation, we have neither isolated nor observed **11**.

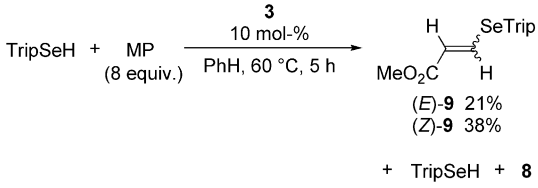
We examined whether hydrido complex **3** serves as a catalyst for the hydroselenation of DMAD with TripSeH. Thus, when TripSeH and DMAD were heated at 60 °C in benzene in the presence of 10 mol-% of **3**, both (*E*)-**5** (19%)

and (*Z*)-**5** (30%) were obtained, together with **7** (1%) and diselenide **8** (25%) [Equation (6)]. This result can largely be explained by the thermal reaction between TripSeH and DMAD. [$Pt(PPh_3)_2$], generated during the reductive elimination step, does not work as a catalyst, because it would undergo coordination of DMAD, preferentially furnishing [$Pt(dmad)(Ph_3P)_2$], which is persistent under the reaction conditions.



(6)

The catalytic ability of **3** in the reaction of TripSeH with methyl propiolate was also examined. When the reaction was carried out in benzene at 60 °C for 5 h, both (*E*)-**9** (21%) and (*Z*)-**9** (38%) were obtained [Equation (7)]. The structure of (*Z*)-**9** was determined from the spectroscopic data; in the ^1H NMR spectrum, signals of two *cis*-vinyl protons in (*Z*)-**9** appeared at δ = 6.53 and 7.72 ppm with a coupling constant of 9.6 Hz. Because the reaction of TripSeH with methyl propiolate in the absence of **3** proceeded very slowly under similar conditions to give a mixture of (*E*)-**9**, (*Z*)-**9** and recovered TripSeH in a ratio of 7:5:88, an alternative catalytic process promoting the addition of TripSeH to methyl propiolate is presumably operating here; however, the details are unclear.



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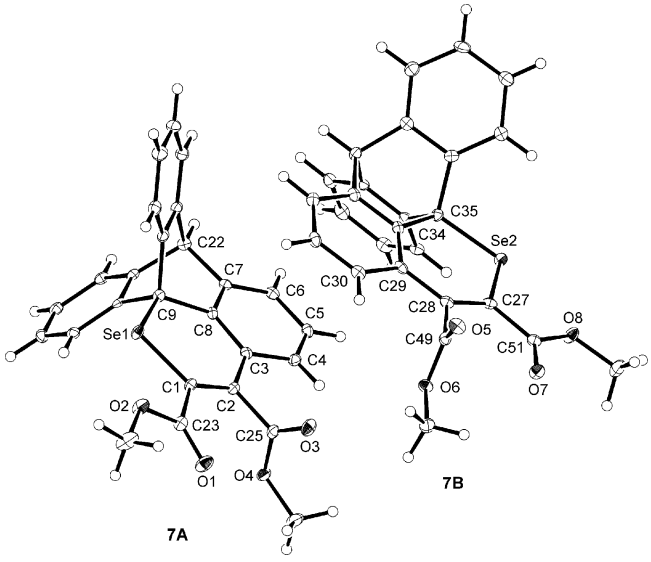
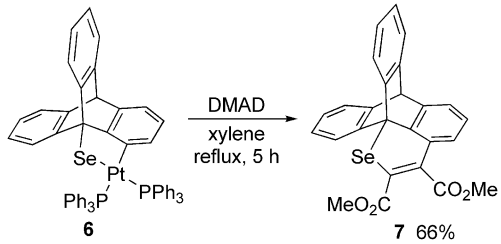


Figure 5. ORTEP drawing of **7** at the 30% probability level. Selected bond lengths [Å], angles [°], and torsion angles [°]. **7A**: Se1–C1 1.896(4), Se1–C9 1.961(3), C1–C2 1.344(6), C1–C23 1.483(4), C2–C3 1.467(4), C2–C25 1.508(6), C3–C4 1.411(6), C3–C8 1.400(5), C4–C5 1.373(4), C5–C6 1.392(6), C6–C7 1.385(6), C7–C8 1.391(4), C7–C22 1.524(6), C8–C9 1.543(5), C23–O1 1.197(5), C23–O2 1.342(5), O2–C24 1.447(4), C25–O3 1.192(5), C25–O4 1.342(5), O4–C26 1.444(5); C1–Se1–C9 101.1(1), Se1–C1–C2 125.4(3), Se1–C1–C23 113.0(3), C2–C1–C23 121.5(3), C1–C2–C3 125.6(3), C1–C2–C25 118.2(3), C3–C2–C25 116.3(3), C2–C3–C4 118.8(3), C2–C3–C8 123.8(3), C4–C3–C8 117.5(3), C3–C4–C5 121.9(3), C4–C5–C6 120.0(3), C5–C6–C7 119.0(3), C6–C7–C8 121.4(3), C6–C7–C22 123.9(3), C8–C7–C22 114.7(3), C3–C8–C7 120.1(3), C3–C8–C9 128.1(3), C7–C8–C9 111.8(3), Se1–C9–C8 115.3(2), C1–C23–O1 125.6(4), C1–C23–O2 110.5(3), O1–C23–O2 124.0(4), C23–O2–C24 116.0(3), C2–C25–O3 124.1(3), C2–C25–O4 111.0(3), O3–C25–O4 124.8(4), C25–O4–C26 114.3(3); C2–C1–C23–O2 –10.6(6), C1–C2–C25–O3 –87.2(5), C3–C8–C9–Se1 3.4(4). **7B**: C28–C27–C51–O7 –1.5(6), C27–C28–C49–O5 96.3(4), C29–C34–C35–Se2 –0.4(5).

Carboselenation

As mentioned above, we observed the formation of 1*H*-2-benzoselenin derivative **7**, which is an anticipated carboselenation product of DMAD with selenaplatinacycle **6**. Indeed, complex **6** reacted with DMAD in refluxing xylene to give **7** in good yield [Equation (8)]. Unexpectedly, the reaction of TripSeH with DMAD in benzene at 60 °C led to the formation of **7** (18%) together with (*E*)-**5** (16%), (*Z*)-**5** (18%), and diselenide **8** (28%) [Equation (9)]. Heating of (*E*)-**5** or (*Z*)-**5** under similar conditions, in the absence or presence of DMAD or TripSeH, did not yield any **7**. These observations suggest that, in the reaction of PtH(SeTrip)(dppe) (**4**) with DMAD [Equation (5)], **4** did not react directly with DMAD, but instead eliminated TripSeH, which reacted with DMAD to yield a mixture of **7**, (*E*)-**5**, and (*Z*)-**5**. Since 2,6-di-*tert*-butyl-4-methylphenol, a radical inhibitor, prevented the formation of **7** in the reaction of TripSeH and DMAD, a radical process may play a role in the formation of **7**. However, the details are not clear at present.



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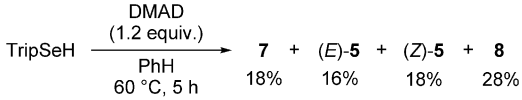

(9)

The structure of **7** was elucidated by its ^1H, ^{13}C, and ^{77}Se NMR spectroscopic data, and finally verified by X-ray crystallography.[12] As depicted in Figure 5, there are two

independent molecules (**7A** and **7B**) in the unit cell, the geometries of which are slightly different in dihedral angles including the Se atom and torsion angles of methoxycarbonyl groups to the respective 1*H*-2-benzoselenin ring. The C3–C8–C9–Se1 dihedral angle in **7A** is 3.4(4)° and the corresponding C29–C34–C35–Se2 dihedral angle in **7B** is –0.4(5)°, indicating that the Se-containing ring in **7A** is slightly more puckered than that in **7B**. The 3- and 4-methoxycarbonyl groups are almost coplanar and perpendicular, respectively, to the 1*H*-2-benzoselenin ring, where the torsion angles are –10.6(6)° (C2–C1–C23–O1) and –87.2(5)° (C1–C2–C25–O3) for **7A** and –1.5(6)° (C28–C27–C51–O7) and 96.3(4)° (C27–C28–C49–O5) for **7B**. Intermolecular short contact distances are also observed in the crystalline state. As shown in Figure 6, the distances Se1···Se1 (3.462 Å) and Se2···Se2 (3.401 Å) are both shorter than the sum of the van der Waals radii (3.80 Å).[16] The benzene ring of the 1*H*-2-benzoselenin moiety adopts a π-stacking arrangement, where the C4···C30 distance is 3.334 Å.

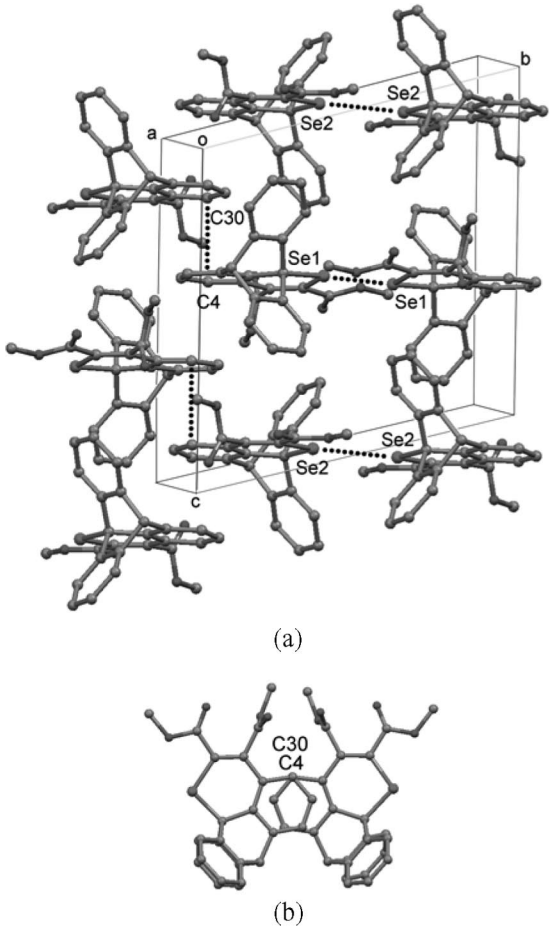

Figure 6. A part of the crystal packing of **7** showing (a) the short contacts between selenium atoms and π-stacking and (b) a top view showing stacking of two benzene rings: Se1···Se1 3.462 Å, Se2···Se2 3.401 Å, C4···C30 3.334 Å.

Carboselenation of other alkynes with selenaplatinacycle **6** did not progress as expected. Heating of **6** with methyl propiolate (5.6 equiv.) either in refluxing benzene or in chlorobenzene at 50 °C resulted in decomposition of **6**, whereas the reaction of **6** with diphenylacetylene, 4-octyne, or methyl 2-butynoate did not occur, and the starting material was recovered almost quantitatively. As selenaplatinacycle **6** itself is stable under the reaction conditions (no decomposition took place when heated in toluene at 80 °C overnight), the above observations suggest an interaction between **6** and methyl propiolate leads to the decomposition of **6**.

Conclusions

We have shown for the first time that the reactions of isolable (hydrido)(selenolato)platinum(II) complex **3** with activated alkynes (DMAD and methyl propiolate) proceed through *syn* addition. The initial dissociation of one of the PPh_3 ligands from **3** is necessary for the hydroselenation. These results provide a necessary condition for the hydroselenation of alkynes with selenols catalyzed by Pt^0 complexes and offer an insight into the reaction mechanism. Carboselenation of DMAD with selenaplatinacycle **6** yielded 1*H*-2-benzoselenin derivative **7**, which was also formed by the reaction of TripSeH with DMAD.

Experimental Section

General: Melting points were determined with a Mel-Temp capillary-tube apparatus. ^1H (400 MHz), ^{13}C (100.7 MHz), and ^{77}Se (76.3 MHz) NMR spectra were obtained with Bruker DRX400 or DPX400 spectrometers. IR spectra were recorded with a Perkin–Elmer System 2000 FTIR spectrometer. Mass spectra were determined with a JEOL JMS-700AM spectrometer operating at 70 eV in the EI mode. X-ray crystallography was performed with a Bruker AXS SMART diffractometer. The intensity data were collected at 103 K by employing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), and the structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[17] Gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-908. Elemental analyses were performed at the Molecular Analysis and Life Science Center of Saitama University.

Reaction of [PtH(SeTrip)(PPh_3)$_2$] (3) with DMAD: A mixture of **3** (32.0 mg, 0.0304 mmol) and DMAD (4.4 mg, 0.0309 mmol) in benzene (2.5 mL) was heated at 60 °C under argon for 2 h. The residue was subjected to column chromatography (acidic silica gel; dichloromethane) to give diselenide **8** (1.2 mg, 12%), a mixture of selenaplatinacycle **6** and **3** (6.5 mg; **6**: 7%; **3**: 13%), and a mixture of (*E*)-**5** and 1*H*-2-benzoselenin **7** [3.8 mg; (*E*)-**5**: 24%; **7**: 2%] in this order. The yields of **6**, **3**, (*E*)-**5**, and **7** were calculated on the basis of the integral ratios in the ^1H NMR spectra of the respective mixtures. The yield of [Pt(dmad)(PPh_3)$_2$][18] (79%) was estimated from the integral ratio in the ^1H NMR spectrum (δ = 3.31 ppm for CO_2Me) of the reaction mixture.

Reaction of [PtH(SeTrip)(PPh_3)$_2$] (3) with Methyl Propiolate: To a solution of **3** (81.8 mg, 0.0777 mol) in benzene (7 mL), was added a solution of methyl propiolate in benzene (0.378 M, 0.420 mL, 0.159 mmol) under argon. The mixture was heated at 60 °C for 3 h, then the solvent was removed in vacuo. The residue was subjected to column chromatography (acidic silica gel; dichloromethane) to give a mixture of selenaplatinacycle **6** and diselenide **8** (28.5 mg; **6**:

24%; **8**: 35%, based on the integral ratio) and (*E*)-**9** (11.6 mg, 36%). A signal assignable to the CH_3 group of $[Pt(mp)(PPh_3)_2]$[19] was detected at δ = 3.32 ppm in the ^1H NMR spectrum of the reaction mixture; the ratio of (*E*)-**9**/$[Pt(mp)(PPh_3)_2]$ was 9:16 based on the integral ratio. An analytical sample of (*E*)-**9** was obtained by purification with GPC.

Methyl (*E*)-3-(9-Triptycylseleno)propenoate [(*E*)-9]: Colorless crystals; m.p. 178–180 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.68 (s, 3 H, OCH_3), 5.43 (s, 1 H, Trip-10-H), 6.27 (d, J = 16 Hz, 1 H, vinyl-H), 7.00–7.09 (m, 6 H, Ar-H), 7.41–7.47 (m, 6 H, Ar-H), 8.18 (d, J = 16 Hz, 1 H, vinyl-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 51.61 (CH_3), 54.10 (CH), 61.52 (C), 122.30 (CH), 123.60 (CH), 123.83 (CH), 125.28 (C), 126.01 (CH), 141.12 (CH), 143.72 (C), 145.27 (C), 164.94 (C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$, 25 °C): δ = 250.3 ppm. IR: $\tilde{\nu}$ = 1715 (C=O) cm^{-1}. $C_{24}H_{18}O_2Se$ (417.37): calcd. C 69.07, H 4.35; found C 68.90, H 4.44. Crystallographic data: $C_{24}H_{18}O_2Se{\cdot}0.5C_6H_{14}$; MW = 460.43; triclinic; space group $P\bar{1}$; a = 8.1389(5), b = 11.4869(8), c = 12.1267(8) Å, α = 88.351(2), β = 72.4300(10), γ = 84.0920(10)°; V = 1075.10(12) $Å^3$; Z = 2; $D_{calcd.}$ = 1.422 $g\,cm^{-3}$; R_1 [$I > 2\sigma(I)$] = 0.0341, wR_2 = 0.0873 (all data) for 4201 reflections, 273 parameters, GOF = 1.073.

Reaction of [PtH(SeTrip)(dppe)] (4) with DMAD: A mixture of **4** (30.2 mg, 0.0326 mmol) and DMAD (34.7 mg, 0.244 mmol) in benzene (3 mL) was heated under reflux for 38 h. The solvent was removed in vacuo, and the residue was subjected to preparative TLC (silica gel, dichloromethane) to give diselenide **8** (3.4 mg, 31%), a mixture of **4** and **6** (2.3 mg), (*Z*)-**5** (3.2 mg, 21%), and a mixture of (*E*)-**5** and **7** (2.1 mg; 11% and 3%, respectively). An analytical sample of (*Z*)-**5** containing 0.5 equiv. of H_2O in 1 equiv of (*Z*)-**5** (detected by ^1H NMR) was obtained by recrystallization from a solvent mixture (dichloromethane/hexane). A pure sample of (*E*)-**5** was obtained by purification with GPC.

Dimethyl 2-(9-Triptycylseleno)maleate [(*E*)-5]: Colorless crystals; m.p. 210–212 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.57 (s, 3 H, OCH_3), 4.02 (s, 3 H, OCH_3), 5.29 (s, 1 H, vinyl-H), 5.43 (s, 1 H, Trip-10-H), 7.01–7.08 (m, 6 H, Ar-H), 7.41–7.43 (m, 3 H, Ar-H), 7.51–7.53 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 51.80 (CH_3), 53.42 (CH_3), 54.04 (CH), 63.11 (C), 123.61 (CH), 123.64 (CH), 124.00 (CH), 125.30 (CH), 126.24 (CH), 141.42 (C), 142.24 (C), 144.95 (C), 163.85 (C), 167.01 (C) ppm. $C_{26}H_{20}O_4Se$ (475.40): calcd. C 65.68, H 4.24; found C 65.50, H 4.32. Crystallographic data: $C_{26}H_{20}O_4Se$; MW = 475.40; triclinic; space group $P\bar{1}$; a = 9.4998(9), b = 9.6335(9), c = 13.1369(12) Å, α = 74.787(2), β = 69.956(2), γ = 71.244(2)°; V = 1053.67(17) $Å^3$; Z = 2; $D_{calcd.}$ = 1.498 $g\,cm^{-3}$; R_1 [$I > 2\sigma(I)$] = 0.0457, wR_2 = 0.1145 (all data) for 3912 reflections, 282 parameters, GOF = 1.043.

Dimethyl 2-(9-Triptycylseleno)fumarate [(*Z*)-5]: Colorless crystals; m.p. 209 °C (dichloromethane/hexane). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.50 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 5.37 (s, 1 H, Trip-10-H), 6.99–7.02 (m, 7 H, Ar-H and vinyl-H), 7.35–7.38 (m, 3 H, Ar-H), 7.59–7.61 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 51.43 (CH_3), 52.24 (CH_3), 54.09 (CH), 62.81 (C), 123.08 (CH), 123.70 (CH), 124.39 (CH), 124.63 (CH), 125.51 (CH), 144.76 (C), 145.09 (C), 146.33 (C), 165.65 (C), 166.69 (C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$, 25 °C): δ = 346.7 ppm. $C_{26}H_{20}O_4Se{\cdot}0.5H_2O$ (484.41): calcd. C 64.47, H 4.37; found C 64.31, H 4.09.

Reaction of TripSeH with DMAD in the Presence of [PtH(SeTrip)(PPh$_3$)$_2$] (3) (0.1 Equiv.): A mixture of TripSeH (99.7 mg, 0.299 mmol), DMAD (64 mg, 0.45 mmol), and **3** (30.2 mg, 0.0287 mmol) in benzene (2 mL) was heated at 50 °C under argon for 5 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (silica gel; hexane/dichloromethane, 1:2 and then dichloromethane) to give diselenide **8** (24.4 mg, 25%), (*Z*)-**5** (43 mg, 30%), and (*E*)-**5** (27.9 mg, 20%) in this order.

Reaction of TripSeH with Methyl Propiolate in the Presence of [PtH(SeTrip)(PPh$_3$)$_2$] (3) (0.1 Equiv.): To a solution of TripSeH (98.5 mg, 0.295 mmol) and **3** (31.1 mg, 0.0295 mg) in benzene (3 mL) under argon, was added a solution of methyl propiolate in benzene (1.2 M, 2.00 mL, 2.36 mmol). The mixture was heated at 60 °C for 5 h, then the solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel; hexane/dichloromethane, 1:2 and then diethyl ether) to give a mixture of TripSeH and diselenide **8** (18.7 mg), (*Z*)-**9** (47.2 mg, 38%), and (*E*)-**9** (26.2 mg, 21%) in this order. An analytical sample of (*Z*)-**9** was obtained by purification with GPC.

Methyl (*Z*)-3-(9-Triptycylseleno)propenoate [(*Z*)-9]: Colorless crystals; m.p. 170–172 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.92 (s, 3 H, OCH_3), 5.43 (s, 1 H, Trip-10-H), 6.53 (d, J = 9.6 Hz, 1 H, vinyl-H), 6.99–7.08 (m, 6 H, Ar-H), 7.41–7.57 (m, 6 H, Ar-H), 7.72 (d, J = 9.6 Hz, 1 H, vinyl-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 51.8 (CH_3), 54.2 (CH), 60.3 (C), 117.2 (CH), 123.6 (CH), 123.9 (CH), 125.1 (CH), 125.8 (CH), 144.4 (CH), 145.6 (C), 145.8 (C), 168.1 (C) ppm. IR (KBr): $\tilde{\nu}$ = 1714 (C=O) cm^{-1}. $C_{24}H_{18}O_2Se$ (417.37): calcd. C 69.07, H 4.35; found C 68.67, H 4.30.

Reaction of TripSeH with Methyl Propiolate: To a solution of TripSeH (35.6 mg, 0.107 mmol) in benzene (2 mL) under argon, was added a solution of methyl propiolate in benzene (1.2 M, 0.105 mL, 0.128 mmol). The mixture was heated at 60 °C for 5 h, then the solvent was removed under reduced pressure. The ^1H NMR spectrum, which was measured with bibenzyl (2.1 mg, 0.012 mmol) as the internal standard, showed the formation of (*Z*)-**9** (4%) and (*E*)-**9** (1%), together with TripSeH (89%).

Reaction of Selenaplatinacycle 6 with DMAD: A mixture of **6** (91.9 mg, 0.0874 mmol) and DMAD (92.6 mg, 0.652 mmol) in xylene (16 mL) was heated under reflux under argon for 5 h, and then the solvent was removed in vacuo. The residue was subjected to column chromatography (acidic silica gel; dichloromethane) to give 1*H*-2-benzoselenin **7** (27.4 mg, 66%). $[Pt(dmad)(PPh_3)_2]$ was detected in the ^1H NMR spectrum of the reaction mixture, and the yield was estimated to be 12% on the basis of the integral ratio to **7**. An analytical sample of **7** was obtained by recrystallization from a solvent mixture (diethyl ether/dichloromethane/hexane). The ^1H NMR spectrum showed that the sample contained 1 equiv. of H_2O in 1 equiv. of **7**.

2,3-Bis(methoxycarbonyl)-1-selena-7*H*-7,11b[1′,2′]-benzeno-1*H*-benzo[*de*]anthracene (1*H*-2-Benzoselenine 7): Colorless crystals; m.p. 234 °C (Et_2O/dichloromethane/hexane). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.92 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 5.40 (s, 1 H, 7-H), 6.81 (d, J = 8 Hz, 1 H, 4-H or 6-H), 7.01 (t, J = 8 Hz, 1 H, 5-H), 7.05 [t, J = 8 Hz, 2 H, 9(4′)-H or 10(5′)-H], 7.12 [dt, J = 8, 1 Hz, 2 H, 10(5′)-H or 9(4′)-H], 7.41 [d, J = 8 Hz, 2 H, 8(3′)-H or 11(6′)-H], 7.45 (d, J = 8 Hz, 1 H, 6-H or 4-H), 7.83 [d, J = 8 Hz, 2 H, 11(6′)-H or 8(3′)-H] ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 52.8 (CH_3), 53.4 (CH_3), 54.0 (CH), 54.9 (C), 118.5 (C), 123.6 (CH), 124.9 (CH), 125.42 (CH), 125.44 (CH), 125.7 (CH), 126.46 (C), 126.53 (CH), 126.6 (CH), 135.5 (CH), 136.8 (CH), 144.0 (C), 145.9 (C), 146.0 (C), 164.3 (C), 169.1 (C) ppm. ^{77}Se NMR (76.3 MHz, $CDCl_3$, 25 °C): δ = 136.8 ppm. IR (KBr): $\tilde{\nu}$ = 1718, 1736 cm^{-1}. $C_{26}H_{18}O_4Se{\cdot}H_2O$ (491.40): calcd. C 63.55, H 4.10; found C 63.35, H 3.81. Crystallographic data:

$C_{26}H_{18}O_4Se$; MW = 473.36; triclinic; space group $P\bar{1}$; a = 12.6203(7), b = 12.8827(7), c = 13.7795(8) Å, α = 103.7120(10), β = 103.4520(10), γ = 103.0010(10)°; V = 2021.6(2) Å^3; Z = 4; $D_{calcd.}$ = 1.555 g cm^{-3}; R_1 [$I > 2\sigma(I)$] = 0.0399, wR_2 (all data) = 0.0973 for 7490 reflections, 563 parameters, GOF = 1.015.

Reaction of TripSeH with DMAD: A mixture of TripSeH (36.7 mg, 0.110 mmol) and DMAD (0.8 M in benzene, 0.160 mL, 0.132 mmol) in benzene (2 mL) was heated at 60 °C under argon for 6 h. The solvent was removed in vacuo, and the residue was subjected to column chromatography (acidic silica gel; hexane/dichloromethane, 1:2) to give **2** (10.6 mg, 28%), (*Z*)-**5** (9.4 mg, 18%), 1*H*-2-benzoselenin **7** (3.8 mg, 7%), and a mixture of **7** and (*E*)-**5** (14.4 mg; 11% and 16%, respectively) in this order.

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