

Selected Papers

Characterization and Phenylacetylene-Assisted Cyclometalation of an Isolable Hydrido–Selenolato Pt^{II} Complex Having Phosphite Ligands, *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$][#]

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A hydrido–selenolato Pt^{II} complex having $P(OPh)_3$ ligands, *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (Trip: 9-triptycyl), was synthesized by the reaction of TripSeH with [Pt{$P(OPh)_3$}$_2$]. The structure was characterized by NMR spectroscopy and X-ray crystallography in comparison with the corresponding PPh_3 complex, *cis*-[PtH(SeTrip)(PPh_3)$_2$], indicating the stronger coordination of $P(OPh)_3$ to the Pt center than that of PPh_3. On heating at 130 °C in xylene for 17 h, *cis*-[PtH(SeTrip)-{$P(OPh)_3$}$_2$] was converted to the corresponding 1,2-selenaplatinacycle (*SP*-4–2)-[Pt(κ*C*^{1},κ*Se*^{9}-TripSe(2−)){$P(OPh)_3$}$_2$] through an intramolecular cyclization (cyclometalation). The reaction with dimethyl acetylenedicarboxylate (DMAD) gave a mixture of hydroselenation products (*E*)- and (*Z*)-(MeO_2C)CH=C(SeTrip)CO_2Me non-stereoselectively together with 1*H*-2-benzoselenin, dimethyl 7*H*-7,11b[1′,2′]-benzenoanthra[9,1-*bc*]selenin-2,3-dicarboxylate. In the reaction with phenylacetylene in toluene at 110 °C, phenylacetylene served as a hydrogen acceptor to form the 1,2-selenaplatinacycle and styrene. Based on the results of controlled experiments using *cis*-[PtD(SeTrip){$P(OPh)_3$}$_2$] and phenylacetylene-*d*, the mechanism of the cyclometalation was proposed as the 1,2- (major) and 2,1- (minor) insertions of phenylacetylene into the Pt–H bond followed by cyclometalation between the Pt center and the triptycyl group. The reaction with phenylacetylene in the presence of excess $P(OPh)_3$ furnished a 1,2,3-oxaphosphaplatinacycle, (*SP*-4–2)-[Pt{κ*C*,κ*P*-(*Z*)-CH=C(Ph)-$OP(OPh)_2$}(SeTrip){$P(OPh)_3$}], as a minor product, together with the 1,2-selenaplatinacycle in a decreased yield.

In recent years, the transition-metal-mediated addition of element–element and element–hydrogen bonds to alkynes has been studied extensively.[1–3] Hydroselenation of alkynes with benzeneselenol (PhSeH) in the presence of [$Pt(PPh_3)_4$][4,5] as the catalyst is one of such reactions to yield synthetically useful vinyl selenides.[6,7] In the stoichiometric reaction of PhSeH with [$Pt(PPh_3)_4$] in benzene-d_6 at room temperature, Ananikov and Beletskaya observed the formation of a hydrido–selenolato Pt^{II} complex, *trans*-[PtH(SePh)(PPh_3)$_2$], by NMR spectroscopy as a minor product together with diselenolato complexes, *cis*- and *trans*-[$Pt(SePh)_2(PPh_3)_2$], as the major products; they proposed the hydrido–selenolato Pt^{II} complex to be the key intermediate in the hydroselenation.[4,5]

Since the first report by Ugo and co-workers on *trans*-[PtH(SePh)(PPh_3)$_2$] in 1971,[8,9] hydrido–selenolato Pt^{II} complexes ([PtH(SeR)L_2]) have been a rare class of compounds probably due to their intrinsic instability. Thus, not only the synthesis but also the reactivity of hydrido–selenolato Pt^{II} complexes have not been explored sufficiently in comparison to the sulfur congener, *trans*-[PtH(SAr)(PPh_3)$_2$].[10–12] Recently, we have succeeded in the isolation and characterization of a series of *cis*-hydrido–selenolato Pt^{II} complexes having phosphine ligands, *cis*-[PtH(SeR)L_2] **1**[13–17] (L = phosphine ligands) by taking advantage of sterically demanding substituents on the selenium (Figure 1). We have also reported the stoichiometric reaction of *cis*-[PtH(SeTrip)(PPh_3)$_2$] (**1a**) (Trip: 9-triptycyl) with an electron-deficient, activated alkyne, dimethyl acetylenedicarboxylate (DMAD) in benzene at 60 °C to produce (*E*)-vinyl selenide **2** stereoselectively together with [Pt(dmad)-(PPh_3)$_2$] (**3**) (Scheme 1), where we showed the necessity of the initial dissociation of a PPh_3 ligand to forward the reaction to the next step.[18]

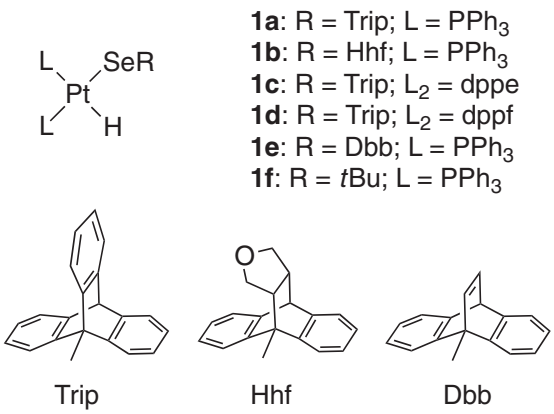

Figure 1. Isolable *cis*-hydrido–selenolato Pt^{II} complexes having phosphine ligands, *cis*-[PtH(SeR)L_2] **1** [dppe: 1,2-bis(diphenylphosphino)ethane; dppf: 1,1′-bis(diphenylphosphino)ferrocene].

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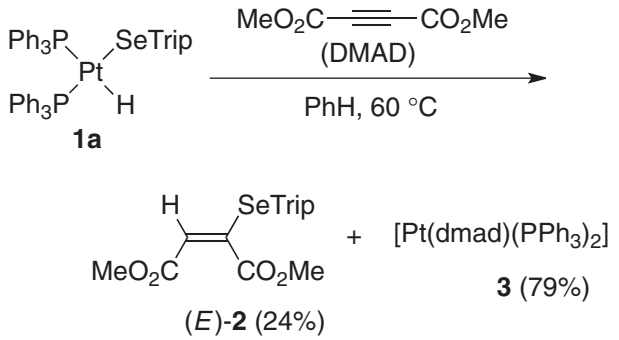


Scheme 1. The stoichiometric reaction of *cis*-[PtH(SeTrip)-$(PPh_3)_2$] (**1a**) with dimethyl acetylenedicarboxylate (DMAD) to yield (*E*)-vinyl selenide **2** and [Pt(dmad)-$(PPh_3)_2$] (**3**).

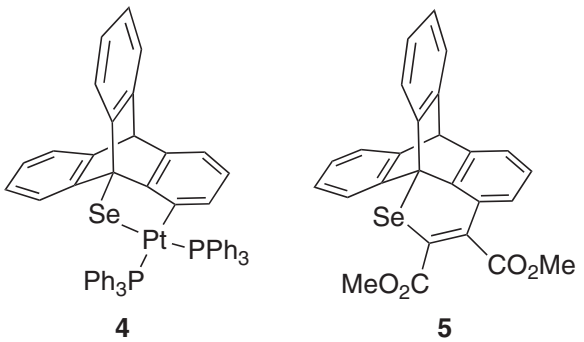
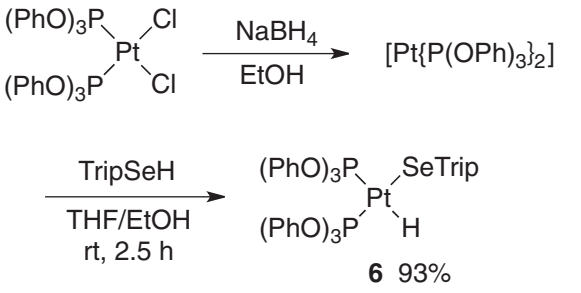


Figure 2. Five-membered 1,2-selenaplatinacycle **4** and 1*H*-2-benzoselenin **5** derived from *cis*-[PtH(SeTrip)$(PPh_3)_2$] (**1a**).

An alternative characteristic reaction of hydrido–selenolato Pt^{II} complexes **1a**–**1e** is an intramolecular cyclization (cyclometalation) under heating conditions to furnish the corresponding 1,2-selenaplatinacycles.[13–16] For example, five-membered 1,2-selenaplatinacycle **4** is formed from **1a**. In addition, the reaction of **4** with DMAD gives the carboselenation product, 1*H*-2-benzoselenin **5** (Figure 2).[18,19]

To gain further insight into the nature of hydrido–selenolato Pt^{II} complexes, we have investigated the electronic and steric effects of phosphorus ligands on the Pt^{II} center in the hydroselenation of alkynes and the cyclometalation. Triphenyl phosphite, $P(OPh)_3$, is recognized as a weaker σ-donor, stronger π-acceptor, and sterically less demanding phosphorus ligand than triphenylphosphine.[20] In the hydroselenation of alkynes utilizing Pt^0 complexes, the oxidative addition step is the reaction of a selenol with a Pt^0 complex giving the hydrido–selenolato Pt^{II} complex, and the reductive elimination corresponds to the final step to produce vinyl selenide. In general, electron-accepting ligands are less advantageous than electron-donating ones in the oxidative addition of transition-metal complexes to an active bond.[21] In the reductive elimination stage, on the other hand, the electronic effect is reverse, and the steric effect is substantially important; sterically small ligands are less advantageous than sterically demanding ligands.[21] In these respects, it seems that $P(OPh)_3$ bears less effective factors than PPh_3 in the both steps. However, $P(OPh)_3$ is expected to exert the electronic and steric features in the insertion step of alkyne to the Pt–X (X = H or Se) bond more advantageously than PPh_3, as observed in the olefin insertion reaction of Rh–H complexes reported by Ziólkowski and co-workers.[22] Here we report the synthesis and structure characterization of *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (**6**) and the reactions with DMAD and phenylacetylene.



Scheme 2. The synthesis of *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (**6**) by the reaction of TripSeH with [Pt{$P(OPh)_3$}$_2$].

Results and Discussion

Synthesis of *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (6). Hydrido–Pt^{II} complex **6** was prepared by the reaction of 9-triptyceneselenol (TripSeH) with [Pt{$P(OPh)_3$}$_2$], generated in situ by reduction of [$PtCl_2${$P(OPh)_3$}$_2$][23] with sodium borohydride in ethanol,[24] in a high yield of 93% as yellow crystals (Scheme 2). Hydrido Pt^{II} complexes with phosphite ligands are fairly rare,[25–28] and to our best knowledge, only *trans*-[PtHCl-{$P(OMe)_3$}$_2$][25] and *trans*-[PtHCl{$P(OPh)_3$}$_2$][26] are known as neutral hydrido complexes. Complex **6** is the first example of the isolable hydrido–selenolato Pt^{II} complex bearing phosphite ligands with *cis*-configuration.

The structure of **6** was determined by NMR spectroscopic analyses and X-ray crystallography. In the ^{1}H NMR spectrum, the hydrido proton appeared at δ −5.23 as doublet of doublets due to the two phosphorus atoms ($^2J_{P(trans)-H} = 311$, $^2J_{P(cis)-H} = 6.4$ Hz) accompanying the satellites due to the ^{195}Pt isotope ($^1J_{Pt-H} = 887$ Hz). The proton is shifted downfield by 0.87 ppm in comparison with that of *cis*-[PtH(SeTrip)$(PPh_3)_2$] (**1a**) (δ −6.10) probably due to the weaker electron-donating ability of $P(OPh)_3$ than PPh_3. The ^{31}P{^{1}H} NMR showed two doublets ($^2J_{P-P} = 34$ Hz) at δ 104.2 and 125.8 with satellites by the ^{195}Pt isotope ($^1J_{Pt-P} = 5184$ and 3094 Hz, respectively). These $^1J_{Pt-P}$ values are substantially larger than those for **1a** [δ 21.3 ($^1J_{Pt-P} = 3281$ Hz) and 30.9 ($^1J_{Pt-P} = 2028$ Hz)].[13] The doublet at δ 104.2 with the larger $^1J_{Pt-P}$ value is assigned to the phosphorus *trans* to the TripSe ligand and the other at δ 125.8 to that *trans* to the hydrido ligand. In the IR spectrum, the absorption due to the Pt–H stretching vibration was observed at 2086 cm^{-1} [cf. **1a**: $\tilde{\nu} = 2093$ cm^{-1}].

The structure of **6** in the crystalline state was characterized by X-ray crystallography (Figure 3). The Pt atom lies in a distorted square-planar geometry; the sum of bond angles around the Pt atom is 359.2°. The P(1)–Pt(1)–P(2) bond angle is 103.08(4)°, and other angles around the Pt atom are less than 90°. The P–Pt–P angle is slightly wider than that of 100.87(4)° in [PtH(SeTrip)$(PPh_3)_2$] (**1a**), suggesting the steric hindrance among two $P(OPh)_3$ and one TripSe ligands being comparable to the corresponding steric hindrance among two PPh_3 and one TripSe in **1a**. The Pt(1)–Se(1) bond length is comparable to that of **1a** [2.4272(5) Å] and slightly shorter than or comparable to

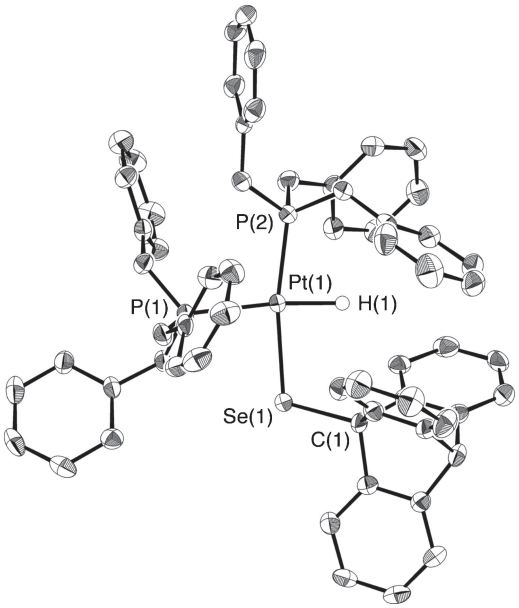


Figure 3. ORTEP drawing of *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (**6**). Thermal ellipsoids are set at 50% probability. Hydrogen atoms except H(1) were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Pt(1)–P(1) 2.2677(11), Pt(1)–P(2) 2.1859(12), Pt(1)–Se(1) 2.4314(5), Pt(1)–H(1) 1.60(5), Se(1)–C(1) 1.974(4), P(1)–Pt(1)–P(2) 103.08(4), P(1)–Pt(1)–Se(1) 87.68(3), P(2)–Pt(1)–Se(1) 168.92(3), P(1)–Pt(1)–H(1) 173.4(19), P(2)–Pt(1)–H(1) 83.3(19), Se(1)–Pt(1)–H(1) 85.8(19).

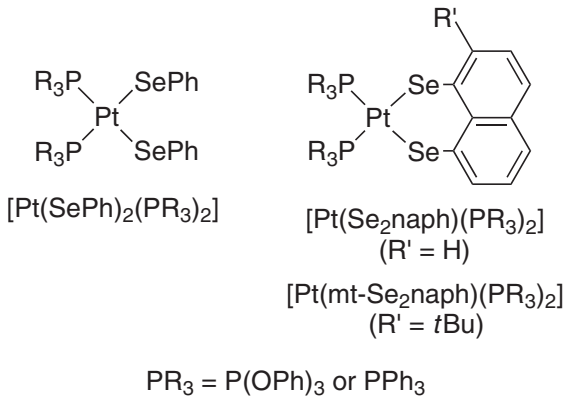
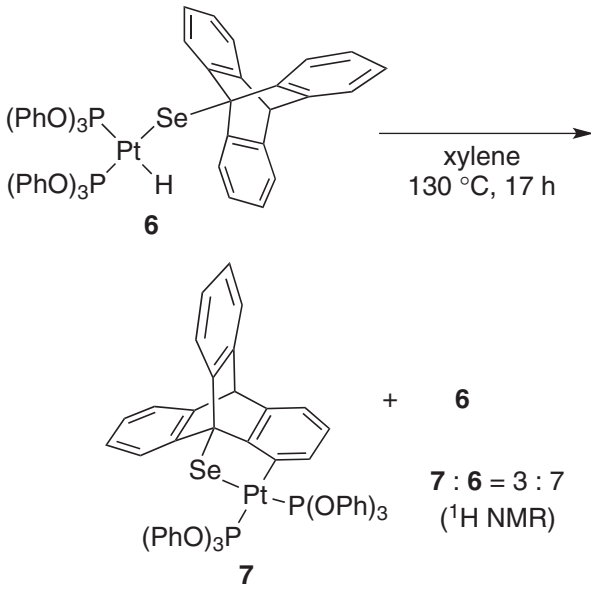


Figure 4. Diselenolato PPh_3– and $P(OPh)_3$–Pt^{II} complexes reported by Woollins and co-workers.[29]

those of reported diselenolato–[$P(OPh)_3$]$_2$–Pt^{II} complexes; *cis*-[Pt(SePh)$_2${$P(OPh)_3$}$_2$] [2.474(2)–2.481(2) Å], [Pt(Se_2naph)-{$P(OPh)_3$}$_2$] [2.4600(7) and 2.4527(7) Å], and [Pt(mt-Se_2naph)-{$P(OPh)_3$}$_2$] [2.4356(5) and 2.4256(5) Å] (Figure 4).[29] The Pt(1)–P(1) bond [2.2677(11) Å] is longer than the Pt(1)–P(2) bond [2.1859(12) Å], showing that the H ligand has larger *trans* influence than that of the TripSe ligand. These Pt–P bond lengths are comparable to those ranging from 2.224(4) to 2.290(2) Å observed in the above diselenolato–[$P(OPh)_3$]$_2$–Pt^{II} complexes, and are shorter than those in (PPh_3)$_2$–Pt^{II} complex **1a** [2.3295(12) and 2.2474(12) Å]. A similar tendency is found between *cis*-[Pt(SePh)$_2${$P(OPh)_3$}$_2$] and *cis*-[Pt(SePh)$_2$-(PPh_3)$_2$][30,31] and between [Pt(Se_2naph){$P(OPh)_3$}$_2$] and [Pt-



Scheme 3. The thermal cyclometalation of **6** in xylene at 130 °C to give 1,2-selenaplatinacycle (**7**).

(Se_2naph)(PPh_3)$_2$].[32] The shorter Pt–P bond lengths in **6** than those in **1a** indicate that the $P(OPh)_3$ ligands coordinate to the Pt^{II} center more strongly than the PPh_3 ligands, which would be explained in terms of the strong π-accepting nature of $P(OPh)_3$ ligands.

Thermal Reaction of *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (6). Heated in refluxing toluene for 17 h, **6** was recovered unreacted, which is in stark contrast to the fact that 50% of (PPh_3)$_2$–Pt^{II} complex **1a** was converted to the corresponding 1,2-selenaplatinacycle **4** on heating in refluxing toluene for 2 h. As a result, higher temperatures were necessary for the cyclometalation of **6**: Heating at 130 °C in xylene for 17 h led to 30% of conversion of **6** to the corresponding 1,2-selenaplatinacycle **7** (Scheme 3).

In the $^{31}P\{^1H\}$ NMR of **7**, two doublets appeared at $\delta = 96.7$ and 116.9 ($^2J_{P-P} = 45$ Hz) accompanied by satellite signals due to the ^{195}Pt isotope ($^1J_{Pt-P} = 5056$ and 2888 Hz, respectively). The doublet at $\delta = 96.7$ having the larger $^1J_{Pt-P}$ value (5056 Hz) is assigned to the phosphorus atom *trans* to the Se atom as similarly as the case for **6**.

In the crystalline state, the Pt atom in **7** adopts a distorted square-planar geometry, and the five-membered ring including platinum and selenium atoms was slightly distorted from planarity (Figure 5). As observed in the comparison between $P(OPh)_3$ complex **6** and PPh_3 complex **1a**, the Pt–Se bond lengths of 1,2-selenaplatinalcycles **7** and **4** are similar [2.4097(4) Å for **4**], and the Pt–P bonds [2.2731(9) and 2.2175(9) Å] in **7** are shorter than those in **4** [2.3318(10) and 2.2975(10) Å]. The Pt(1)–P(1) bond was slightly longer than the Pt(1)–P(2) bond, indicating that the carbon ligand has larger *trans* influence than the selenium ligand does.

Reactions of *cis*-[PtH(SeTrip){$P(OPh)_3$}$_2$] (6) with Alkynes. The stoichiometric reaction of **6** with DMAD was investigated first. Heating of **6** with DMAD in benzene at 80 °C for 3 h gave a mixture of (*E*)- and (*Z*)-vinyl selenides (*E*)-**8** and (*Z*)-**8**, 1*H*-2-benzoselenin **5**, and recovered **6** in the

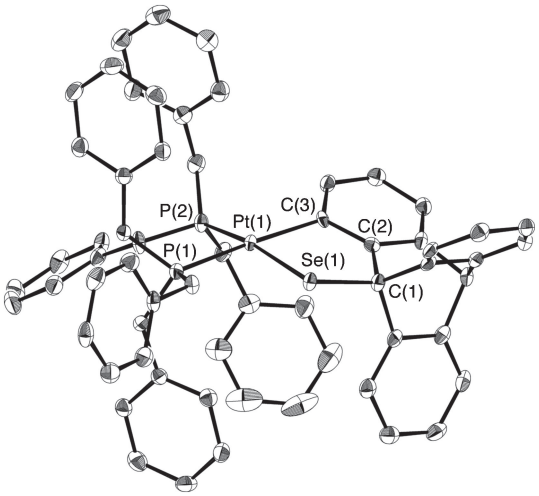
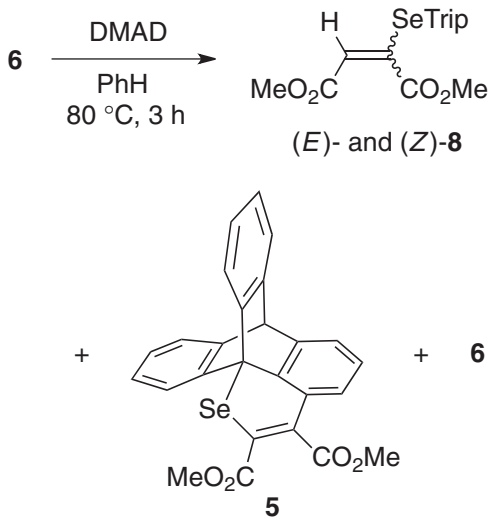
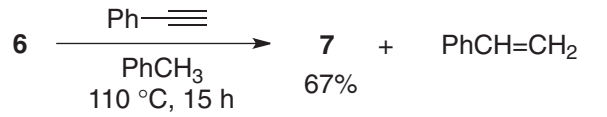


Figure 5. ORTEP drawing of [Pt{κC^1,κSe^9-TripSe(2−)}-{P(OPh)$_3$}$_2$] (**7**). Thermal ellipsoids are set at 50% probability. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Pt(1)–P(1) 2.2731(9), Pt(1)–P(2) 2.2175(9), Pt(1)–Se(1) 2.4139(4), Pt(1)–C(3) 2.087(3), Se(1)–C(1) 1.967(3), P(1)–Pt(1)–P(2) 94.02(3), P(1)–Pt(1)–Se(1) 89.03(2), P(2)–Pt(1)–Se(1) 167.75(3), P(1)–Pt(1)–C(3) 174.88(9), P(2)–Pt(1)–C(3) 91.04(9), Se(1)–Pt(1)–C(3) 85.85(9), Pt(1)–Se(1)–C(1) 97.37(10), Se(1)–C(1)–C(2) 110.0(2), C(1)–C(2)–C(3) 124.6(3), C(2)–C(3)–Pt(1) 117.9(2).

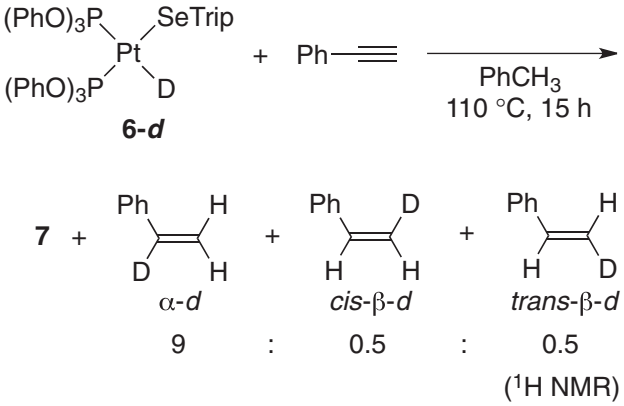


Scheme 4. The stoichiometric reaction of *cis*-[PtH(SeTrip)-{P(OPh)$_3$}$_2$] (**6**) with DMAD in benzene at 80 °C to yield (*E*)-**8**, (*Z*)-**8**, and **5**.

ratio of 37/39/9/15 on the basis the ^{1}H NMR integral ratio (Scheme 4). Previously we have observed a similar non-stereoselective formation of vinyl selenides **8** together with **5** in the stoichiometric reaction of [PtH(SeTrip)(dppe)] [dppe: 1,2-bis(diphenylphosphino)ethane] with DMAD in refluxing benzene. We have also verified that the reaction of TripSeH with DMAD in benzene at 60 °C yielded a mixture of (*E*)-**8**, (*Z*)-**8**, and **5** in the ratio of 16:18:18.[18] Thus, it seems that **6** is in equilibrium with TripSeH and [Pt{P(OPh)$_3$}$_2$] at high temperatures, and TripSeH during the equilibrium reacts with DMAD to yield a mixture of (*E*)- and (*Z*)-**8** and **5**.[18] However, we cannot completely rule out the possibility that **8** and **5** are formed by an identified pathway, because the formation ratio of **5** is lower than that in the controlled experiment.



Scheme 5. The stoichiometric reaction of *cis*-[PtH(SeTrip)-{P(OPh)$_3$}$_2$] (**6**) with phenylacetylene in toluene at 110 °C to give 1,2-selenaplatinacycle **7** and styrene.



Scheme 6. The stoichiometric reaction of **6-*d*** with phenylacetylene in toluene at 110 °C to give α-*d*-styrene and β-*d*-styrene in the ratio of 9:1.

Next, the reaction of **6** with phenylacetylene was examined. While the reaction in refluxing benzene gave unidentifiable materials with the recovery of **6**, that performed at 110 °C in toluene for 15 h produced 1,2-selenaplatinacycle **7** in 67% yield (Scheme 5).[33] Since cyclometalation of **6** to **7** does not occur at 110 °C in toluene as mentioned above, phenylacetylene should play a crucial role for the cyclometalation. Indeed, ^{1}H NMR analysis of the reaction mixture revealed the formation of styrene in an amount comparable to that of **7**, suggesting that the two hydrogen atoms in **6** were transferred to phenylacetylene forming styrene.

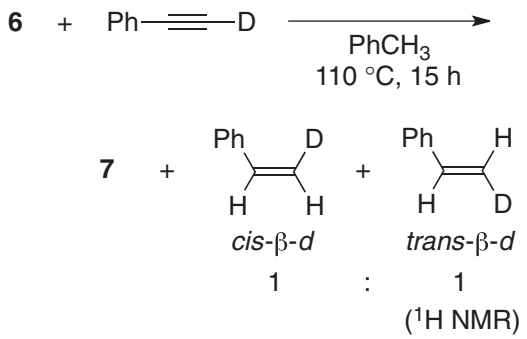
To obtain insight into the mechanism of this unexpected reaction, the following control experiments were carried out employing deuterated **6** (**6-*d***) and phenylacetylene-*d*. When **6-*d*** was heated with phenylacetylene, the deuterium migrated to the α-position of phenylacetylene mainly to yield α-*d*-styrene (PhCD=CH$_2$) together with β-*d*-styrene (*cis*- and *trans*-PhCH=CHD) in the ratio of 9:1 (Scheme 6).[34] This partially regioselective formation of α-*d*-styrene clearly indicates that styrene is not formed by addition of H_2, eliminated from **6**, to phenylacetylene, suggesting that an intermediate is formed by the insertion of phenylacetylene to the Pt–H bond where the 1,2-insertion leading to α-*d*-styrene is dominant. On the other hand, heating of **6** with phenylacetylene-*d* furnished PhCH=CHD as a 1:1 mixture of *cis*- and *trans*-isomers (Scheme 7). It was separately verified that the isomerization of *trans*-β-*d*-styrene to the *cis*-isomer occurred in the presence **6** or **7** in toluene at 110 °C.

A plausible reaction pathway for the reaction of **6** with phenylacetylene is depicted in Scheme 8: 1,2-Insertion of phenylacetylene into the Pt–H bond of **6** occurs as the major path, together with the 2,1-insetion as the minor one, to give (*E*)-vinylplatinum intermediate **9** (only the major 1,2-insertion is shown in Scheme 8). In this stage, the hydrido hydrogen of **6** is transferred to the α-position of phenylacetylene. Then, intramolecular cyclometalation occurs between the platinum atom and the triptycyl group to yield styrene and **7**, where the hydrogen (H″) on the triptycyl group migrates to the *trans*-β position of the styrene. On this mechanism, *trans*-PhCH=CDH should be formed stereoselectively in the control experiment using phenylacetylene-*d* (Scheme 7). The non-stereoselective formation of PhCH=CDH as the result is explained by the ready *cis–trans* isomerization of PhCH=CDH in the presence of platinum complexes **6** or **7** as mentioned above.

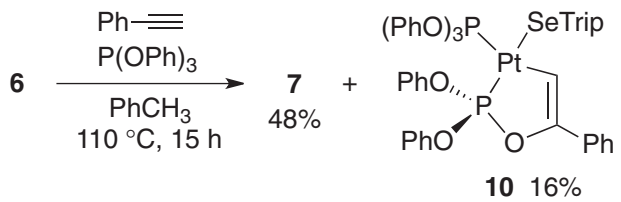
A similar alkyne-assisted cyclometalation, in which an alkyne acts as a two-hydrogen acceptor, has been reported by Chatani and co-workers in the synthesis of isoquinolones by the reaction of *N*-2-pyridylmethyl aromatic amides with internal alkynes in the presence of $[Ni(cod)_2]/PPh_3$.[35] Templeton and co-workers have also reported a related intramolecular cyclization of a three-coordinated Pt^{II} complex, generated via 2,1-insertion of (triphenylsilyl)acetylene to the Pt–H bond of [Pt(Cl-nacnac)H(1-pentene)] [Cl-nacnac: bis(*N*-4-chlorophenyl)-β-diiminato], to produce an alkene-coordinated Pt complex by *ortho*-C–H activation.[36]

In the step of alkyne insertion into hydrido–selenolato Pt^{II} complexes, there are two possible pathways, Pt–H insertion and Pt–Se insertion, which correspond to Chalk–Harrod mechanism and modified Chalk–Harrod mechanism, respectively, in hydrosilylation of alkynes with transition-metal catalysts.[37] Ananikov and Beletskaya have described the insertion of alkyne to the Pt–Se bond for their hydroselenation on the basis of the formation of Markovnikov-type vinyl selenides.[4,5] We have also proposed the Pt–Se insertion mechanism in the reaction shown in Scheme 1.[18] The Pt–H insertion in Scheme 8 presents an alternative pathway in the reaction of alkynes with Pt^{II} complexes. Incidentally, the reaction of hydrido–thiolato Pt^{II} complex *trans*-$[PtH(SC_6H_4\text{-}4\text{-}Cl)(PPh_3)_2]$, with phenylacetylene in the presence of $4\text{-}ClC_6H_4SH$ has been reported to furnish the Pt–H insertion product, *cis*-[Pt{(*Z*)-CH=CHPh}-$(SC_6H_4\text{-}4\text{-}Cl)(PPh_3)_2$], under photoirradiation or in the presence of AIBN.[11] In the reaction, a pivotal role of thiyl radical was proposed in the insertion with the *anti*-addition manner. In addition, the insertion of 1-dodecyne to the Rh–H bond of *trans*-$[RhCl(H)(SPh)(PPh_3)_2]$ was observed to give the (*E*)-vinylrhodium intermediate ($[RhCl\{(E)\text{-}CH{=}CH\text{-}n\text{-}C_{10}H_{21}\}(SPh)(PPh_3)_n]$).[38] Reportedly, no solo reductive eliminations of the vinylplatinum complex and the vinylrhodium complex to yield vinyl sulfides occurred.[11,38,39]

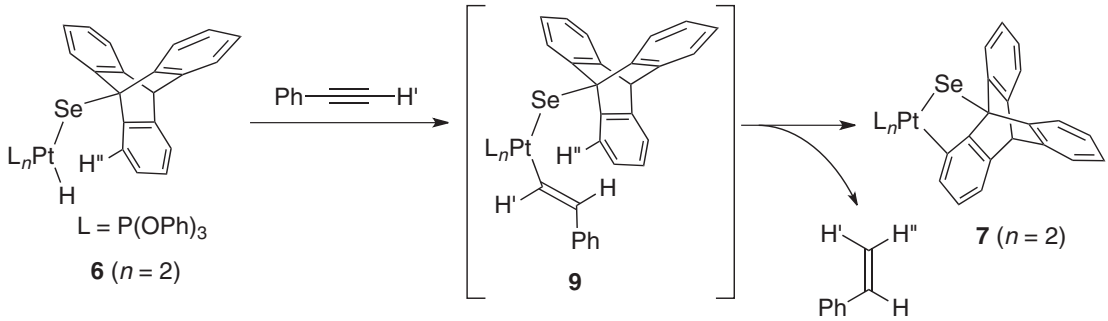
In the stoichiometric hydroselenation of DMAD with *cis*-$[PtH(SeTrip)(PPh_3)_2]$ (**1a**), we have shown the necessity of the initial dissociation of a PPh_3 ligand from **1a** to promote the following reactions on the basis of the result that the addition of excess PPh_3 depressed the hydroselenation completely.[18] To ascertain whether this is true or not for the reaction of **6** with phenylacetylene, a mixture of **6**, phenylacetylene, and excess $P(OPh)_3$ was heated in toluene at 110 °C. As a result, the yield of 1,2-selenaplatinacycle **7** was somewhat decreased from 67% to 48%, and unexpectedly, complex **10** was isolated albeit in a low yield of 16% (Scheme 9). The formation of **7** in a considerable yield even in the presence of excess $P(OPh)_3$, the formation of **10** aside, suggests that hydrido–Pt^{II} complex **6**



Scheme 7. The stoichiometric reaction of **6** with phenylacetylene-*d* in toluene at 110 °C to give *cis*- and *trans*-β-*d*-styrenes.



Scheme 9. The stoichiometric reaction of **6** with phenylacetylene in the presence of excess $P(OPh)_3$ in toluene at 110 °C to give **7** and 1,2,3-oxaphosphaplatinacycle **10**.



Scheme 8. A possible reaction pathway for the formation of selenaplatinacycle **7** and styrene in the reaction of *cis*-$[PtH(SeTrip)\{P(OPh)_3\}_2]$ (**6**) with phenylacetylene.

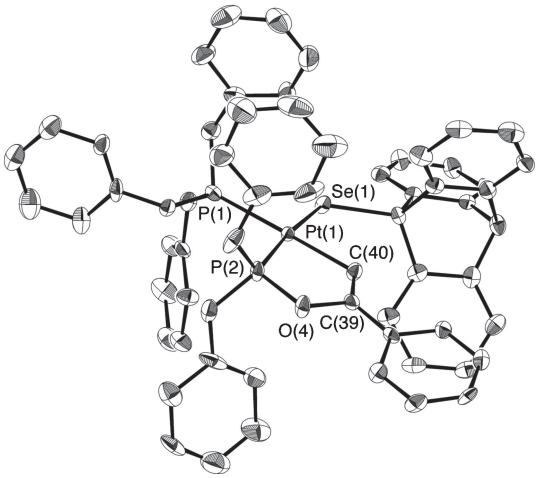


Figure 6. ORTEP drawing of (*SP*-4–2)-[Pt{κ*C*,κ*P*-(*Z*)-CH=C(Ph)OP(OPh)$_2$}(SeTrip){P(OPh)$_3$}] (**10**). Thermal ellipsoids are set at 50% probability, and hydrogen atoms were omitted for clarity. One of two independent molecules is shown and geometric parameters of the other molecule are given in brackets: Selected bond lengths [Å] and bond angles [°]: Pt(1)–P(1) 2.256(2) [2.253(2)], Pt(1)–P(2) 2.188(2) [2.189(2)], Pt(1)–Se(1) 2.4413(7) [2.4422(9)], Pt(1)–C(40) 2.074(9) [2.057(7)], C(39)–C(40) 1.31(1) [1.33(1)], P(2)–O(4) 1.600(6) [1.599(6)], P(1)–Pt(1)–P(2) 96.95(8) [97.66(8)], P(1)–Pt(1)–Se(1) 86.24(6) [85.17(6)], P(2)–Pt(1)–Se(1) 171.92(6) [174.53(6)], P(1)–Pt(1)–C(40) 176.3(3) [177.1(2)], P(2)–Pt(1)–C(40) 79.6(3) [79.5(2)], Se(1)–Pt(1)–C(40) 97.3(2) [97.7(2)], C(39)–C(40)–Pt(1) 119.8(7) [120.6(6)], C(40)–C(39)–O(4) 118.7(8) [118.6(7)], C(39)–O(4)–P(2) 113.7(5) [113.2(5)], O(4)–P(2)–Pt(1) 108.0(2) [108.3(2)].

undergoes the attack of phenylacetylene at the four-coordinated state and phenylacetylene inserts predominantly into the Pt–H bond being sterically less hindered than the Pt–Se bond.

The formation of **10** formally requires the cleavage of a strong Ph–O bond of P(OPh)$_3$ in addition to the Pt–H bond with formation of O–C$_{vinyl}$ and Pt–C$_{vinyl}$ bonds. Since we have not determined the fate of the phenyl and the hydrogen, the formation mechanism of **10** is not clear at present. Complex **10** has a novel ring system, five-membered 1,2,3-oxaphosphaplatinacycle.[40] In the ^{1}H NMR spectrum of **10**, the vinyl proton resonated at $\delta = 5.49$–5.51 as a doublet of doublets by two ^{31}P nuclei ($^2J_{P(trans)–H} = 6.5$, $^2J_{P(cis)–H} = 4$ Hz) accompanying satellite signals due to the ^{195}Pt isotope. In the ^{31}P{^{1}H} NMR, two doublets were observed at $\delta = 113.0$ ($^2J_{P–P} = 33$, $^1J_{Pt–P} = 4606$ Hz) and 116.7 ($^2J_{P–P} = 33$, $^1J_{Pt–P} = 3393$ Hz). The structure of **10** was finally identified by X-ray crystallography as depicted in Figure 6. The Pt atom adopts a distorted planar geometry and the five-membered ring involving Pt, P, and O atoms is almost planar.

Conclusion

We have succeeded in the synthesis of an isolable hydrido–selenolato Pt^{II} complex *cis*-[PtH(SeTrip){P(OPh)$_3$}$_2$] (**6**) that has two P(OPh)$_3$ ligands with *cis*-configuration and in the full characterization of the structure in comparison with the PPh$_3$ analogue *cis*-[PtH(SeTrip)(PPh$_3$)$_2$] (**1a**). The P(OPh)$_3$ ligands in **6** coordinate to the Pt^{II} center more strongly than the PPh$_3$ ligands in **1a**, probably due to the stronger π-accepting ability of P(OPh)$_3$ ligands,[20] leading to the dissociation of a P(OPh)$_3$ ligand from **6** making the coordination-unsaturated state less facile than that of a PPh$_3$ ligand from **1a**. This would result in the non-stereoselective hydroselenation of DMAD with **6** unlike the case of the *syn*-selective hydroselenation of DMAD with **1a**. In addition, it is well known that P(OPh)$_3$ is a weak σ-donor,[20] and consequently the platinum center in **6** would be electron-deficient compared with the platinum center in **1a**. As our previous studies on the cyclometalation of the hydrido Pt^{II} center to the triptycyl group in **1c**[15] or the dibenzobarrelenyl group in **1e**[16] indicated that the dissociation of a phosphorus ligand was not always important, the kinetics of the present cyclometalation seems to be dependent on the electronic nature of the Pt center. Thus, while we cannot deduce the mechanistic aspect of the cyclometalation[41] from the present results, the result that **6** is less reactive than **1a** to cyclometalation would imply an important role of the nucleophilicity of the Pt centers rather than electrophilicity. On the other hand, the cyclometalation of **6** was assisted by phenylacetylene to produce selenaplatinacycle **7** together with styrene. A controlled experiment evidenced that the hydrogen atom on the Pt^{II} center in **6** was transferred mainly to the α-position of phenylacetylene, indicating that 1,2-insertion of phenylacetylene into the Pt–H bond occurred there. The electron-deficient nature of the Pt center in **6**, in addition to the steric reason, would make the hydroplatination of an alkyne favorable.[22] Thus, we found that the strongly coordinated P(OPh)$_3$ ligands lead to a change of the reaction pathway from the Pt–Se insertions for [PtH(SeR)(PPh$_3$)$_2$] to the Pt–H insertion for **6**. We also reported the formation of Pt^{II} complex **10** in the thermal reaction of **6** and phenylacetylene in the presence of excess P(OPh)$_3$. **10** has a novel five-membered 1,2,3-oxaphosphaplatinacycle ring system.

Experimental

General Procedure. Melting points were determined on a Melt-Temp capillary tube apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AVANCE-300 (300 MHz for ^{1}H), AVANCE-400 (400, 101, and 162 MHz, respectively), and AVANCE-500 (500, 126, and 202 MHz, respectively) spectrometers at room temperature, unless otherwise noted. IR spectra were recorded with a Perkin-Elmer System 2000 FTIR spectrometer. Elemental Analyses were performed at Comprehensive Analysis Center for Science, Saitama University. Solvents were dried by standard methods and freshly distilled prior to use. Anhydrous diethyl ether and THF were purchased from Kanto Chemical Co., Inc. and used without further purification. Column chromatography was performed with silica gel (70–230 mesh) and eluent is shown in parentheses. TripSeH was prepared according to a reported procedure.[42] Styrene-*trans*-β-*d* was prepared as a mixture with styrene-α-*d* (the ratio of *trans*-β-*d*/α-*d* 84:16) by reduction of phenylacetylene with DIBAH in the presence of [NiCl$_2$(PPh$_3$)$_2$] followed by quenching with D$_2$O.[43]

Synthesis of *cis*-[PtH(SeTrip){P(OPh)$_3$}$_2$] (6). [PtCl$_2${P(OPh)$_3$}$_2$] was prepared by a reported procedure:[26] A solution of K$_2$[PtCl$_4$] (1.414 g, 3.41 mmol) and P(OPh)$_3$ (1.8 mL, 6.85 mmol) in H$_2$O (30 mL) and CH$_2$Cl$_2$ (30 mL) was stirred at room

temperature for 4 days to give $[PtCl_2\{P(OPh)_3\}_2]$ (2.25 g, 74%) as a white powder: $^{31}P\{^1H\}$ NMR $\delta = 60.2$ ($^1J_{Pt-P} = 5696$ Hz). To a mixture of $[PtCl_2\{P(OPh)_3\}_2]$ (227.2 mg, 0.256 mol) and $NaBH_4$ (44.0 mg, 1.165 mmol) was added ethanol (4 mL), and the mixture was stirred at room temperature for 10 min.[24] To the solution of $[Pt\{P(OPh)_3\}_2]$ was added a solution of TripSeH (77.8 mg, 0.233 mmol) in THF (3 mL), and the reaction mixture was stirred at room temperature for 2.5 h. After removal of the solvent under reduced pressure, to the residue was added dichloromethane (ca. 5 mL) and the solution was filtered through a pad of Celite®. After removal of the solvent of the filtrate under reduced pressure, the residue was purified by column chromatography (hexane/$CH_2Cl_2 = 1/1$) to give *cis*-[PtH(SeTrip){$P(OPh)_3\}_2$] (**6**) (251.8 mg, 93%): Pale yellow crystals, mp 184–186 °C decomp. ^1H NMR (500 MHz, $CDCl_3$): δ −5.23 (dd, $^2J_{P(trans)-H} = 311$, $^2J_{P(cis)-H} = 6.4$, $^1J_{Pt-H} = 887$ Hz, 1H), 5.24 (s, 1H), 6.61 [br s, 3H; Trip; at 328 K: $\delta = 6.64$ (br t, $J = 7$ Hz)], 6.72 (d, $J = 6.5$ Hz, 6H; *o*-H of $P(OPh)_3$), 6.84 (t, $J = 7.3$ Hz, 3H; *p*-H of $P(OPh_3)$), 6.99–7.07 (m, 9H; 3H for *p*-H of $P(OPh)_3$ and 6H of Trip), 7.19–7.24 (m, 6H), 7.36 (t, $J = 7.0$ Hz, 6H; *m*-H of $P(OPh)_3$), 7.45 (d, $J = 7.5$ Hz, 6H; *o*-H of $P(OPh)_3$), 7.73 (br s, 3H; Trip; at 328 K: $\delta = 7.73$ (d, $J = 7.5$ Hz)); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 54.6 (CH), 58.1 (dd, $^3J_{P-C} = 15$, 6 Hz, C), 120.9 [d, $J = 4$ Hz, CH; *o*-CH of $P(OPh)_3$], 121.2 [d, $J = 6$ Hz, CH; *o*-CH of $P(OPh)_3$], 122.0 (CH; Trip), 123.8 (CH; Trip), 124.1 (CH; Trip), 124.8 [CH; *p*-CH of $P(OPh)_3$], 125.0 [CH; *p*-CH of $P(OPh)_3$], 126.9 (br s, CH; Trip), 129.3 [CH; *m*-CH of $P(OPh)_3$], 129.7 [CH; *m*-CH of $P(OPh)_3$], 146.0 (br s, C; Trip), 148.5 (C; Trip), 150.4 [d, $J =$ 7 Hz, C; *ipso*-C of $P(OPh)_3$], 151.2 [d, $J = 5$ Hz, C; *ipso*-C of $P(OPh)_3$]; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 104.2 (d, $^2J_{P-P} = 34$, $^1J_{Pt-P} = 5184$ Hz), 125.8 (d, $^2J_{P-P} = 34$, $^1J_{Pt-P} =$ 3094 Hz); IR (KBr): $\tilde{\nu}$ 2086 cm^{-1} (Pt–H). Anal. Calcd for $C_{56}H_{44}O_6P_2PtSe$: C, 58.54; H, 3.86%. Found: C, 58.08; H, 3.89%.

Thermal Reaction of *cis*-[PtH(SeTrip){$P(OPh)_3\}_2$] (6). A solution of **6** (13.6 mg, 0.011 mmol) in xylene (2 mL) was heated at 130 °C for 17 h. The solvent was removed under reduced pressure to give a mixture of (*SP*-4–2)-[Pt{κ*C*^{1},κ*Se*^{9}-TripSe(2−)}{$P(OPh)_3\}_2$] (**7**) and **6** in the ratio of 3:7 on the basis of the integral ratio in the ^1H NMR spectrum.

Reaction of *cis*-[PtH(SeTrip){$P(OPh)_3\}_2$] (6) with DMAD. A solution of DMAD in benzene (0.8 M, 0.32 mL, 0.261 mmol) was added to a solution of **6** (99.1 mg, 0.0863 mmol) in benzene (4 mL) at room temperature under argon atmosphere. The mixture was heated at 80 °C for 3 h. The solvent was removed under reduced pressure to give a mixture of **6** (14.9 mg, 15%), (*E*)-**8**[7] (15.3 mg, 37%), (*Z*)-**8**[7] (15.9 mg, 39%), and 1*H*-2-benzoselenin **5**[7] (3.7 mg, 9%). The yields of **6**, (*E*)-**8**, (*Z*)-**8**, and **5** were calculated on the basis of the integral ratio in the ^1H NMR spectrum of the reaction mixture.

Thermal Reaction of *cis*-[PtH(SeTrip){$P(OPh)_3\}_2$] (6) in the Presence of Phenylacetylene. Isolation of (*SP*-4–2)-[Pt{κ*C*^{1},κ*Se*^{9}-TripSe(2−)}{$P(OPh)_3\}_2$] (7): A solution of phenylacetylene in toluene (0.9 M, 0.04 mL, 0.038 mmol) was added to a solution of **6** (29.0 mg, 0.025 mmol) in toluene (2 mL) at room temperature under argon atmosphere. The mixture was heated at 110 °C for 15 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexane/$CH_2Cl_2 = 1/1$) to give 1,2-selenaplatinacycle **7** (19.5 mg, 67%): Pale yellow crystals, mp 193–194 °C decomp. ^1H NMR (400 MHz, $CDCl_3$): δ 5.23 (s, 1H), 6.60 (dt, $J = 7.5$, 2.5 Hz, 1H), 6.88–6.94 (m, 20H), 7.12 (t, $J = 7$ Hz, 3H), 7.20–7.28 (m, 14H), 7.77–7.83 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 55.7 (CH), 64.6 (C), 119.2 (CH; CH of Trip), 120.8 [CH; *o*-CH of $P(OPh)_3$], 120.9 [CH; *o*-CH of $P(OPh)_3$], 122.1 (CH; 2CH of Trip), 124.2 (CH; 2CH of Trip), 124.5 (CH; 2CH of Trip), 124.6 (CH; 2CH of Trip), 124.7 [CH; 2(*p*-CH) of $P(OPh)_3$], 129.4 [CH; *m*-CH of $P(OPh)_3$], 129.6 [CH; *m*-CH of $P(OPh)_3$], 137.6 (dd, $J_{P-C} = 12$, 6.7 Hz, CH; CH of Trip), 144.0 (d, $J_{P-C} = 5$ Hz, C; C of Trip), 145.9 (C; 2C of Trip), 146.6 (d, $J_{P-C} = 126$ Hz, C; C of Trip), 149.3 (C; 2C of Trip), 150.6 [d, $J_{P-C} = 7$ Hz, C; *ipso*-C of $P(OPh)_3$], 151.2 [d, $J_{P-C} = 7$ Hz, C; *ipso*-C of $P(OPh)_3$], 165.6 (d, $J_{P-C} = 5$ Hz, C; C of trip) (one of CH carbons of Trip, which correlates to the proton observed at δ 6.60 (dt), was not assigned due to overlapping with signals appearing between δ 124.2 to 124.7); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 96.7 (d, $^2J_{P-P} = 45$, $^1J_{Pt-P} = 5056$ Hz), 116.9 (d, $^2J_{P-P} = 45$, $^1J_{Pt-P} =$ 2888 Hz). Anal. Calcd for $C_{56}H_{42}O_6P_2PtSe$: C, 58.64; H, 3.69%. Found: C, 58.41; H, 3.65%.

Detection of Styrene: **6** (27.7 mg, 0.0241 mmol) and phenylacetylene (4.0 μL, 3.7 mg, 0.036 mmol) were placed in a valved NMR tube, and the NMR tube was connected to a vacuum line. The NMR tube was cooled with liquid nitrogen and evacuated, and into it was condensed ca. 0.5 mL of toluene-d_8. The valve of the NMR tube was closed and the tube was disconnected from the vacuum line and warmed naturally. The NMR tube was heated by being immersed in an oil bath at 110 °C for 6 h. The ^1H NMR spectrum (300 MHz) displayed the signals of styrene at δ 5.08 (dd, $J = 11$, 0.9 Hz) for the *trans*-β-proton, at δ 5.60 (dd, $J = 18$, 0.9 Hz) for the *cis*-β-proton, and at δ 6.56 (dd, $J = 18$, 11 Hz) for the α-proton together with signals for 1,2-selenaplatinacycle **7** and unreacted **6**. The integral ratio of **7**/styrene/**6** was 34/39/27.

Thermal Reaction of *cis*-[PtD(SeTrip){$P(OPh)_3\}_2$] (6-*d*) in the Presence of Phenylacetylene. Synthesis of [PtD(SeTrip)-{$P(OPh)_3\}_2$] (6-*d*): D_2O (0.4 mL) was added to a solution of **6** (70 mg, 0.061 mmol) in toluene (2 mL) under argon atmosphere, and the mixture was heated under reflux for 1.5 h. Removal of the solvent in vacuo left $[PtD(SeTrip)\{P(OPh)_3\}_2]$ (**6-*d***). The ^1H NMR spectrum showed the complete disappearance of the Pt–H signal. **6-*d***: $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 103.6 (d, $^2J_{P-P} = 34$, $^1J_{Pt-P} = 5184$ Hz), 124.6 (td, $^2J_{D-P} =$ 78, $^2J_{P-P} = 36$, $^1J_{Pt-P} = 3094$ Hz).

Thermal Reaction of *cis*-[PtD(SeTrip){$P(OPh)_3\}_2$] (6-*d*) with Phenylacetylene: **6-*d*** (13.9 mg, 0.0121 mmol) and phenylacetylene (2.0 μL, 1.9 mg, 0.0182 mmol) were placed in a valved NMR tube, and the NMR tube was connected to a vacuum line. The NMR tube was cooled with liquid nitrogen and evacuated, and into it was condensed ca. 0.5 mL of toluene-d_8. The valve of the NMR tube was closed and the tube was disconnected from the vacuum line and warmed naturally. The NMR tube was heated by being immersed in an oil bath at 110 °C for 15 h. The ^1H NMR spectrum (300 MHz) displayed signals of α-*d*-styrene ($PhCD{=}CH_2$), *cis*- and *trans*-β-*d*-styrenes (PhCH=CDH) and styrene ($PhCH{=}CH_2$) at δ 5.07 (d, $J = 11$ Hz, *trans*-β-H of *cis*-PhCH=CDH), 5.08 (dd, $J =$

11, 1 Hz, *trans*-β-H of PhCH=CH_2), 5.08 (pseudo q, $J_{D-H} = J_{H-H} = 1.4$ Hz, *trans*-β-H of PhCD=CH_2), 5.57 (dt, $J_{D-H} = 2.6$ Hz, $J_{H-H} = 1.0$ Hz, *trans*-β-H of PhCD=CH_2), 5.58 (d, $J = 18$ Hz, *cis*-β-H of *trans*-PhCH=CDH), 5.59 (dd, $J = 18$, 1 Hz, *cis*-β-H of PhCH=CH_2), 6.53–6.61 (m, α-Hs of *cis*- and *trans*-PhCH=CDH and PhCH=CH_2) together with 1,2-selenaplatinacycle **7**, recovered **6-*d*** and a small amount of **6**. The ratio of PhCD=CH_2/*cis*-PhCH=CDH/*trans*-PhCH=CDH/PhCH=CH_2 was 63/3.5/3.5/30.

Thermal Reaction of *cis*-[PtH(SeTrip){P(OPh)$_3$}$_2$] (6) with Phenylacetylene-*d*. Phenylacetylene-*d*: Phenylacetylene (1.0 mL, 9.11 mmol) in ether (10 mL) was treated with BuLi (1.59 M, 6.9 mL, 10.9 mmol) at 0 °C. After stirring for 1 h at 0 °C, D_2O (4 mL) was added. The mixture was extracted with ether, and the extract was dried over anhydrous sodium sulfate and evaporated to dryness to give phenylacetylene-*d* (0.82 g, 87%, 97%-D).

Thermal Reaction of 6 with Phenylacetylene-*d*: Complex **6** (14.3 mg, 0.0124 mmol) and phenylacetylene-*d* (2.0 μL, 1.9 mg, 0.018 mmol) were placed in a valved NMR tube, and the NMR tube was connected to a vacuum line. The NMR tube was cooled with liquid nitrogen and evacuated, and into it was condensed ca. 0.5 mL of toluene-d_8. The valve of the NMR tube was closed and the tube was disconnected from the vacuum line and warmed naturally. The NMR tube was heated by being immersed in an oil bath at 110 °C for 15 h. The ^{1}H NMR spectrum (300 MHz) displayed signals at δ 5.07 (d, $J = 11$ Hz, *trans*-β-H of *cis*-PhCH=CDH), 5.08 (dd, $J =$ 11, 1 Hz, *trans*-β-H of PhCH=CH_2), 5.58 (d, $J = 18$ Hz, *cis*-β-H of *trans*-PhCH=CDH), 5.59 (dd, $J = 18$, 1 Hz, *cis*-β-H of PhCH=CH_2), and 6.53–6.59 (m, α-Hs of *cis*- and *trans*-PhCH=CDH and PhCH=CH_2) together with 1,2-selenaplatinacycle **7** and unreacted **6**. The ratio of *cis*-PhCH=CDH/*trans*-PhCH=CDH/PhCH=CH_2 was 45.7/45.7/8.6.

Thermal Isomerization of *trans*-β-*d*-Styrene in the Presence of 6 or 7. A toluene-d_8 (0.5 mL) solution of *trans*-PhCH=CDH (the ratio of *trans*-PhCH=CDH/PhCD=CH_2 = 84:16) (5 μL, 0.043 mmol) and **6** (24.8 mg, 0.0216 mmol) in an NMR tube under argon atmosphere was heated at 110 °C for 6 h. The ratio of *cis*-PhCH=CDH/*trans*-PhCH=CDH determined by ^{1}H NMR spectroscopy was 0.9:1.0. In a similar manner, a toluene-d_8 solution (0.5 mL) of *trans*-PhCH=CDH (4 μL, 0.0345 mmol) and **7** (19.1 mg, 0.0167 mmol) was heated at 110 °C for 6 h. The ratio of *cis*-PhCH=CDH and *trans*-PhCH=CDH determined by ^{1}H NMR spectroscopy was 0.8:1.0.

Reaction of *cis*-[PtH(SeTrip){P(OPh)$_3$}$_2$] (6) with Phenylacetylene in the Presence of P(OPh)$_3$. A solution of phenylacetylene in toluene (0.9 M, 0.04 mL, 0.038 mmol) was added to a mixture of **6** (29.0 mg, 0.025 mmol) and P(OPh)$_3$ (10 μL, 0.038 mmol) in toluene (2 mL) at room temperature under argon atmosphere. The mixture was heated at 110 °C for 15 h, and then the solvent was removed under reduced pressure. The residue was subjected to column chromatography (hexane/CH_2Cl_2 = 1/1) to give 1,2,3-oxaphosphaplatinacycle **10** (4.6 mg, 16%) and 1,2-selenaplatinacycle **7** (14.0 mg, 48%) in this order.

(*SP*-4-2)-[Pt{κ*C*,κ*P*-(*Z*)-CH=C(Ph)OP(OPh)$_2$}(SeTrip){P(OPh)$_3$}] (10): Yellow white crystals, mp 205–206 °C decomp. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.38 (s, 1H), 5.50 (dd, $J = 6.5$, 4 Hz, $^2J_{Pt-H} = 33$ Hz, 1H), 6.24 (d, $J = 7.8$ Hz, 2H), 6.75 (dt, $J = 7.5$, 0.8 Hz, 3H), 6.84 (t, $J = 7.8$ Hz, 2H), 6.88 (dt, $J = 7$, 1 Hz, 3H), 6.94 (t, $J = 7.5$ Hz, 1H), 7.13 (t $J = 7$ Hz, 3H), 7.16 (d, $J = 8.5$ Hz, 4H), 7.21–7.26 (m, 8H), 7.29–7.33 (m, 13H), 7.75 (d, $J = 7.5$ Hz, 3H); ^{13}C{H} NMR (101 MHz, $CDCl_3$): δ 54.6 (CH), 54.9 (dd, $^3J_{P-C} = 12$, 4 Hz, C), 120.4 (d, $J = 6$ Hz, CH), 121.4 (d, $J = 6$ Hz, CH), 122.0 (CH), 122.8 (dd, $^2J_{P-C} = 153$, 8 Hz, CH), 124.0 (CH), 124.6 (CH), 124.8 (CH), 125.1 (CH), 125.2 (CH), 126.9 (CH), 126.9 (CH), 127.7 (CH), 129.6 (CH), 129.7 (CH), 145.1 (C), 147.9 (C), 150.8 (d, $J =$ 7 Hz, C), 151.0 (d, $J = 7$ Hz, C), 153.9 (d, $J = 6$ Hz, C), 154.2 (d, $J = 6$ Hz, C); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 113.0 (d, $^2J_{P-P} = 33$, $^1J_{Pt-P} = 4606$ Hz), 116.7 (d, $^2J_{P-P} = 33$, $^1J_{Pt-P} =$ 3393 Hz). Anal. Calcd for $C_{58}H_{44}O_6P_2PtSe$: C, 59.39; H, 3.78%. Found: C, 59.86; H, 3.92%.

X-ray Crystallographic Analyses of 6, 7, and 10. Pale-yellow single crystals of **6**, **7**, and **10** were grown by slow evaporation of their saturated toluene solutions at −18 °C. The intensity data were collected at 103 K on a Bruker AXS SMART diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[44] Hydrogen atoms except the PtH hydrogen of **6** were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-965691, -965692, and -965693 for compounds **6**, **7**, and **10**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal Data for 6: $C_{56}H_{44}O_6P_2PtSe$, MW: 1148.90, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 13.0955(6)$, $b = 13.7065(6)$, $c = 15.4994(8)$ Å, $\alpha = 97.141(1)$, $\beta = 103.705(1)$, $\gamma = 116.683(1)°$, $V = 2328.14(19)$ Å^3, $D_{calcd} = 1.639$ g cm^{-3}, R_1 [$I > 2\sigma(I)$] = 0.0350, wR_2 (all data) = 0.0878 for 8643 reflections, 599 parameters, GOF = 1.019.

Crystal Data for 7: $C_{56}H_{42}O_6P_2PtSe$, MW: 1146.89, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 11.7925(12)$, $b = 12.9308(13)$, $c = 17.7593(17)$ Å, $\alpha = 95.307(2)$, $\beta = 104.917(2)$, $\gamma = 116.598(2)°$, $V = 2271.2(4)$ Å^3, $D_{calcd} = 1.677$ g cm^{-3}, R_1 [$I > 2\sigma(I)$] = 0.0282, wR_2 (all data) = 0.0716 for 8398 reflections, 595 parameters, GOF = 0.950.

Crystal Data for 10: $C_{58}H_{44}O_6P_2PtSe$, MW: 1172.92, orthorhombic, space group $Pca2_1$, $Z = 8$, $a = 17.2952(7)$, $b = 16.7925(7)$, $c = 33.0774(13)$ Å, $V = 9606.7(7)$ Å^3, $D_{calcd} = 1.622$ g cm^{-3}, R_1 [$I > 2\sigma(I)$] = 0.0503, wR_2 (all data) = 0.0690 for 21275 reflections, 1225 parameters, and 1 restraint, GOF = 1.021.

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