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The first definitive example of oxidative addition of acyclic vinyl selenide to M(0) complex

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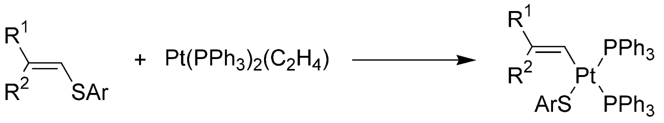
Abstract

The principle of C–S bond activation of acyclic vinlyl sulfide by platinum(0)-complex was applied to the C–Se bond fission of vinyl selenide. The substrate possessing Ph and ArSe ($Ar = C_6H_4Cl$-*p*) substituents at the β-carbon successfully reacted with Pt(0)-complex at 25 °C to produce the vinyl platinum in good yield and its structure was unambiguously determined by X-ray crystallographic analysis. When (*Z*)-(Me_3Si)(ArSe)C═(H)(SeAr) was employed as a reaction substrate, following β-Se elimination took place to liberate Me_3SiCCH with the production of [*trans*-$Pt(SeAr)_2(PPh_3)_2$]. The oxidative addition of C–Se bond of (*E*)-(Ph)(H)C═C(H)(SeAr) to Pt(0) was also confirmed at 25 °C, while no C–S bond-breaking occurred when the corresponding vinyl sulfide was exposed to the same reaction conditions, demonstrating that the cleavage of C–Se bond was more facile than that of C–S bond.

Keywords: Oxidative addition; Vinyl selenide; Platinum; β-Se elimination

1. Introduction

The oxidative addition of C–X bond (X; element or functional group) to low-valent transition-metal-complex (M) to form C–M–X fragment has been exploited as one of the most fundamental reactions in organometallic chemistry [1]. With respect to the C–Se bond fission, however, only sparse information has been provided for both stoichiometric and catalytic reactions. Some stoichiometric C–Se bond dissections of selenophenes by transition-metal-complexes [2] and the oxidative addition of C–Se bond of PhSePh to $[Pt(PEt_3)_3]$ have been reported [3]. As to the catalytic reactions, cross-coupling reactions between vinyl selenides and Grignard reagents, in which oxidative additions of C–Se bond to low-valent transition-metal-complexes were supposedly participated, have also been documented [4]. Independently, we have disclosed that the Pt-catalyzed arylselenation of terminal alkyne was triggered by the oxidative addition of C–Se bond of selenoester to zero-valent platinum complex [5]. On the other hand, regarding to the oxidative addition of acyclic vinyl sulfide, we have recently revealed the concept for the successful C–S bond activation by Pt(0)-complex by introducing two substituents having α-anion stabilization effect such as Ar, ArS, Me_3Si and $MeOCH_2$ groups at β-carbon (Eq. (1)) [6]. Herein, the application of the principle to the cleavage of C–Se bond of vinyl selenide will be reported.



R^1, R^2 = Ar, ArS, Me_3Si, $MeOCH_2$

(1)

2. Results and discussion

First, the reaction of (*Z*)-(Ph)(ArSe)C═C(H)(SeAr) ($Ar = C_6H_4Cl$-*p*, **1a**, 0.50 mmol) [7] with $Pt(PPh_3)_2(C_2H_4)$ (**2**, 0.50 mmol) in C_6H_6 (20 mL) was carried out to afford

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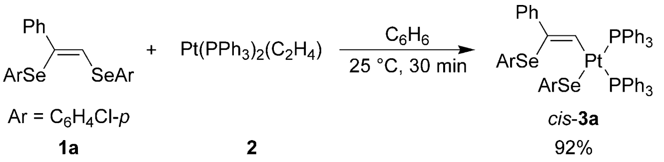
{*cis*-Pt[(*Z*)-C(H)=C(SeAr)(Ph)](SeAr)(PPh_3)$_2$} (*cis*-**3a**) patterned after the oxidative addition of vinyl sulfide with a similar framework [6]. After the solution was stirred at 25 °C for 30 min, *cis*-**3a** was obtained as an yellow solid in 92% yield by simply adding hexane into the solution (Eq. (2)).



(2)

The ^{31}P NMR spectrum of *cis*-**3a** showed a set of doublets centered at δ 17.4 ($J_{P–P} = 16$ Hz, $J_{Pt–P} = 1856$ Hz) and δ 17.8 ($J_{P–P} = 16$ Hz, $J_{Pt–P} = 3280$ Hz). The former was assigned as PPh_3 of *trans* to the vinyl carbon and the latter as PPh_3 of *trans* to the SeAr judging from the $J_{Pt–P}$ values. The *cis*-**3a** gradually isomerized to *trans*-**3a** in solution at 25 °C (*cis*/*trans* = 76/24 after 22 h). A good crystal suitable for X-ray crystallographic analysis of *cis*-**3a** was obtained by recrystallization from benzene/hexane and its ORTEP diagram was shown in Fig. 1. Similarly to the case of the oxidative addition of the corresponding 1-phenyl-1,2-bis(arylthio)alkene to **2**, it was confirmed that the terminal C–Se bond was cleaved by the platinum complex, providing the first definitive example of oxidative addition of acyclic vinyl selenide to transition-metal complex. On the other hand, the attempted isolation of {*cis*-Pt[(*Z*)-C(H)=C(SeAr)($SiMe_3$)]-(SeAr)(PPh_3)$_2$} (*cis*-**3b**) by the reaction of (*Z*)-(Me_3Si)(ArSe)C=C(H)(SeAr) (Ar = C_6H_4Cl-*p*, **1b**) with **2** has failed due to the contamination by impurity. Thus, the reaction of **1b** (0.028 mmol) with **2** (0.020 mmol) in C_6D_6 (0.5 mL) at 25 °C was next monitored by ^{31}P and ^{1}H NMR spectra using S=P(C_6H_4-OMe-*p*)$_3$ as an internal standard (Eq. (3)).

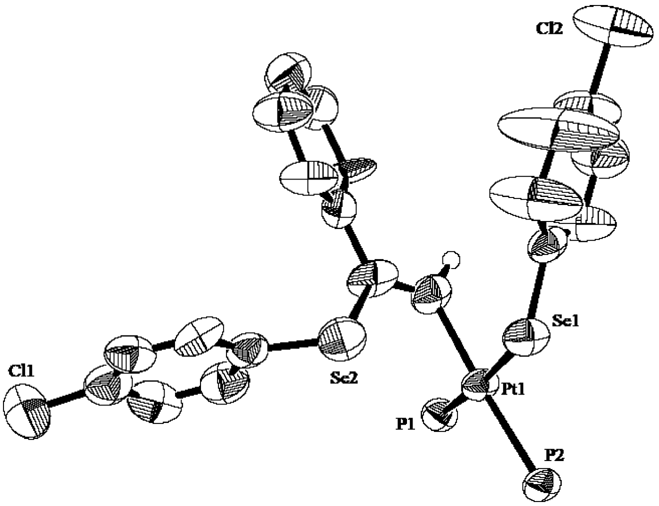
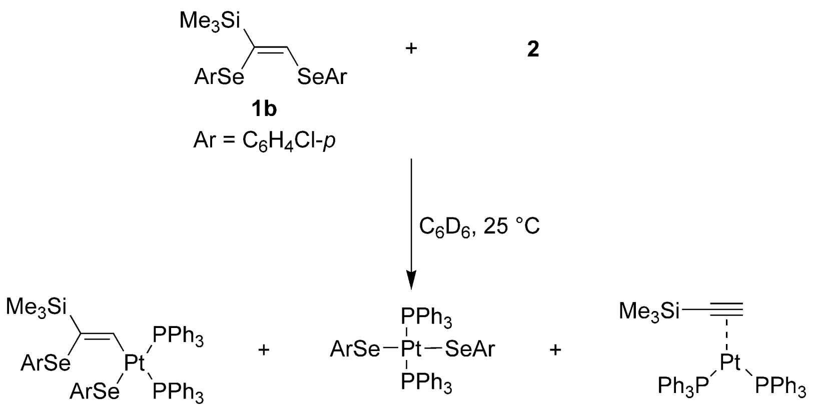


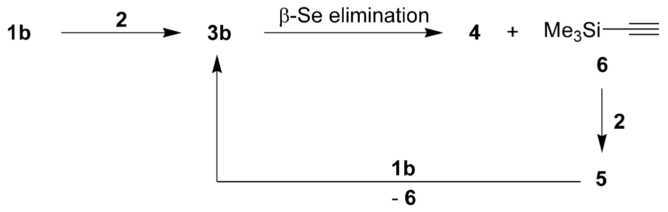
Fig. 1. ORTEP diagram of *cis*-**3a**.

The ^{31}P NMR chart taken after 20 min showed the formation of anticipated *cis*-**3b** by a set of doublets centered at δ 14.4 ($J_{P–P} = 17$ Hz, $J_{Pt–P} = 1781$ Hz) and δ 18.7 ($J_{P–P} = 17$ Hz, $J_{Pt–P} = 3395$ Hz) in 55% yield. However, the spectrum also showed the generation of [*trans*-Pt(SeAr)$_2$-(PPh_3)$_2$] (*trans*-**4**) at δ 20.2 ($J_{Pt–P} = 2766$ Hz) and [Pt(PPh_3)$_2$(Me_3SiCCH)] (**5**) at δ 29.0 ($J_{P–P} = 47$ Hz, $J_{Pt–P} = 3758$ Hz) and δ 32.5 ($J_{P–P} = 47$ Hz, $J_{Pt–P} = 3672$ Hz) in 21% and 11% yields, respectively. After 1 h, the production of *cis*-**3b** (50%), *trans*-**4** (39%) and **5** (9%) were confirmed. Then the yields of *cis*-**3b** and **5** were gradually decreased, while that of *trans*-**4** was increased. After 21 h, the signals of *cis*-**3b** and **5** were disappeared, and 92% of *trans*-**4** was confirmed by ^{31}P NMR spectrum, while its ^{1}H NMR spectrum showed the liberation of Me_3SiCCH (**6**) in 83% yield.



	cis-**3b**	*trans*-**4**	**5**
20 min	55%	21%	11%
1 h	50%	39%	9%
21 h	nd	92%	nd

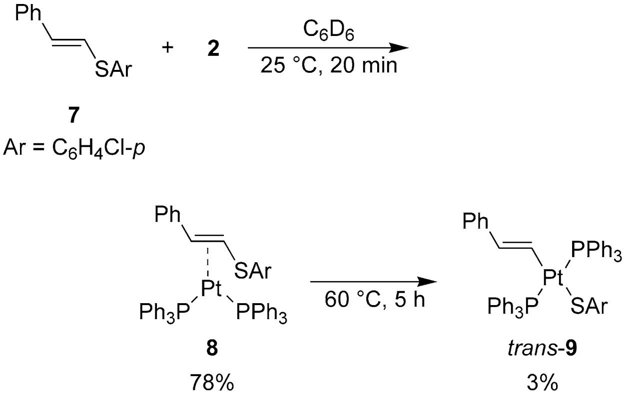
(3)



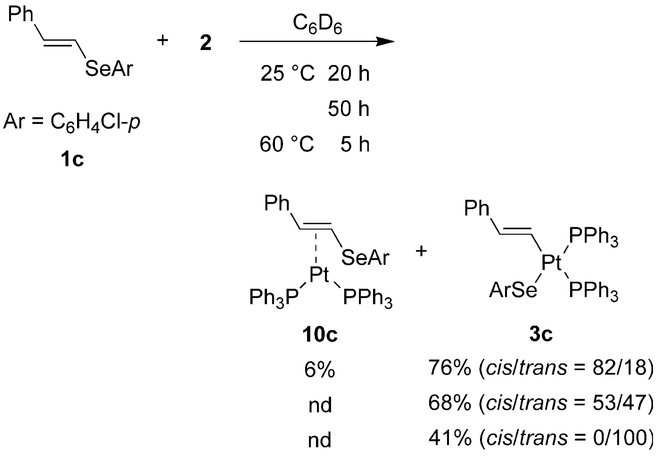
Scheme 1. Proposed reaction pathway of reaction of **1b** with **2**.

The foregoing results clearly showed that after the oxidative addition of terminal C–Se bond of **1b** to **2** took place, β-SeAr elimination, a reverse process of insertion of **6** into Se–Pt bond, took place to afford *trans*-**4** and **6**, the latter of which was partially trapped by the Pt(0)-complex to furnish **5** at the beginning stage of the reaction (Scheme 1) [8]. The facts that the complex **5** was eventually all consumed and **6** was liberated in good yield indicated that **5** also reacted with **1b** to yield *cis*-**3b** and **6**.

To compare the reactivity of vinyl selenide with that of vinyl sulfide, the reactions of (E)-(Ph)(H)C=C(H)(YAr) (YAr = SC_6H_4Cl-p, **7**; YAr = SeC_6H_4Cl-p, **1c**) with **2** were conducted. In the case of reaction using **7**, the formation of π-complex **8** [9] was confirmed in 78% yield with the unreacted **2** (22%) at 25 °C after 20 min; however, the signal of {*trans*-Pt[(E)-C(H)=C(H)(Ph)](SAr)$(PPh_3)_2$} (**9**) [10] was detected only in 3% yield even after 5 h at 60 °C (Eq. (4)). In stark contrast, the ^{31}P NMR spectrum of the reaction of **1c** with **2** taken after 20 h at 25 °C suggested the formation of 6% of π-complex {Pt[(E)-(Ph)(H)C=C(H)(SeAr)]$(PPh_3)_2$} (**10c**) and 76% (*cis*/*trans* = 82/18) of {Pt[(E)-C(H)=C(H)(Ph)](SeAr)$(PPh_3)_2$} (**3c**) (Eq. (5)), proving higher reactivity of the vinyl selenide than the vinyl sulfide toward the oxidative addition reaction [4]. After 50 h, all **10c** was disappeared and 68% of **3c** (*cis*/*trans* = 53/47) was confirmed together with the unassigned by-products, indicating that the equilibrium between **10c** and *cis*-**3c** strongly leaned to the latter side. Further heating the solution resulted in the complete isomerization to thermodynamically more stable *trans*-**3c** (41%).

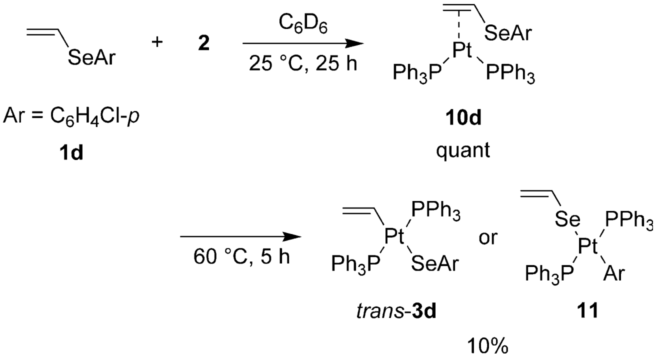


(4)



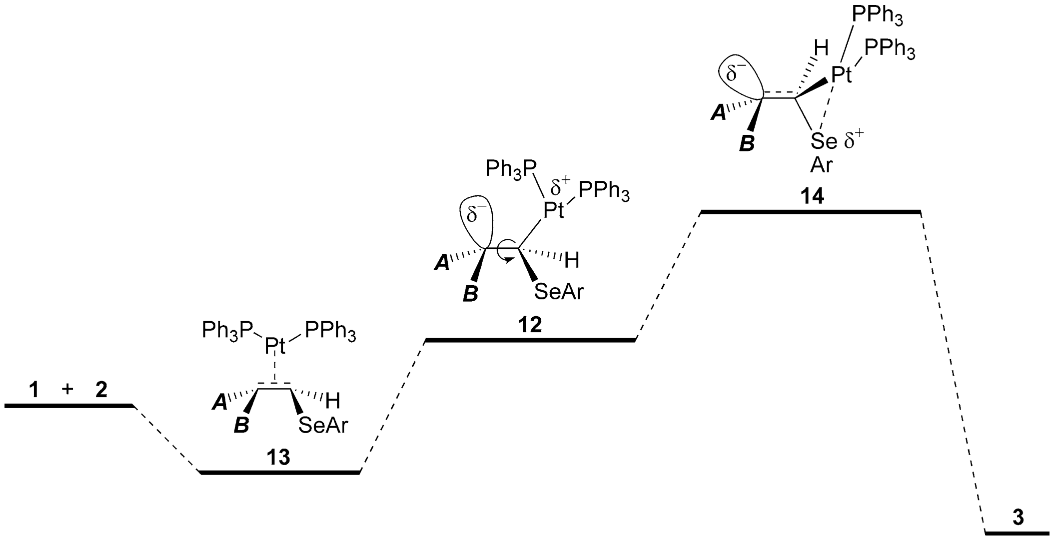
(5)

On the other hand, ^{31}P NMR spectrum taken after 20 min at 25 °C of the reaction of $H_2C=C(H)(SeAr)$ (Ar = C_6H_4Cl-p, **1d**) with **2** resulted in quantitative formation of π-complex {Pt[$H_2C=C(H)(SeAr)$]$(PPh_3)_2$} (**10d**), which was stable for 25 h (Eq. (6)). Even when the solution was heated at 60 °C for 5 h, the suspected signal of either *trans*-**3d** or **11** was detected only in 10% yield.



(6)

In conclusion, the first definitive evidence of oxidative addition of vinyl selenides to low-valent transition-metal-complex to furnish vinyl platinum was demonstrated. Foregoing experimental data were rationalized by assuming that the oxidative addition of vinyl selenide **1** to **2** took place through the zwitterionic intermediate (or the transition state) **12**, which could be generated by the nucleophilic attack of the $Pt(PPh_3)_2$ fragment of π-complex **13** onto the α-carbon (Scheme 2). Unlike the case of oxidative addition of vinyl sulfide to **2**, only one substituent with the α-anion stabilization effect [11] was requisite at the β-carbon (***A*** or ***B***) to realize this transformation at room temperature. Finally, the C–Se bond was weakened by pushing anionic charge at the β-carbon into the C–Se σ^* orbital after a minimum rotation about the C–C bond to form the transition state (or the intermediate) **14**, and then SeAr group was migrated into coordination sphere of the platinum. During the process, Y-shape structure constructed by two PPh_3 and the Pt would be retained to afford *cis*-**3** as a kinetic product.



Scheme 2. A proposed route of oxidative addition of **1** to **2**.

3. Experimental

All reactions described in this paper were performed under a N_2 atmosphere. The ^{31}P and ^{1}H NMR spectra were recorded with a JEOL JMN Alice-400 (160 and 400 MHz, respectively) spectrometer in C_6D_6 solution. The chemical shifts of the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 (aq) as an external standard, and $S{=}P(C_6H_4OMe\text{-}p)_3$ was used as an internal standard to calculate the yields of products. The chemical shifts in the ^{1}H NMR spectra were recorded relative to C_6D_6 (δ 7.15). IR spectra were recorded with a Perkin Elmer FT-IR (Model 1600) spectrometer. The X-ray crystal data of *cis*-**3a** were collected by Rigaku RAXIS-RAPID Imaging Plate diffractometer and the ORTEP drawing in Fig. 1 has been shown with 50% probability ellipsoids. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Vinyl selenides (**1a**–**d**) were synthesized according to the literature (J. Am. Chem. Soc. 113 (1991) 9796/Synth. Commun. 26 (1996) 671/Tetrahedron 56 (2000) 1445). Vinyl sulfide **7** was also prepared according to the literature (J. Am. Chem. Soc. 121 (1999) 5108). The platinum complex $Pt(PPh_3)_2(C_2H_4)$ (**2**) was synthesized according to the literature (Inorg. Synth. 18 (1978) 120). C_6H_6 and C_6D_6 were purified by distillation from sodium benzophenon ketyl before use.

3.1. The reaction of **1a** with **2** (Eq. (2))

Into a dry two-necked reaction vessel equipped with a stirring bar were added **2** (373.9 mg, 0.50 mmol), **1a** (241.6 mg, 0.50 mmol) and C_6H_6 (20 mL) under a N_2 atmosphere. After the reaction mixture was stirred at 25 °C for 30 min, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. Then the solid was washed by hexane (10 mL × 3) and dried to give *cis*-**3a** (553.3 mg, 92%). The good crystal of *cis*-**3a** for X-ray crystallographic analysis was prepared by recrystallization from benzene/hexane.

cis-**3a:** m.p. 148 °C (an yellow solid); ^{1}H NMR (400 MHz, C_6D_6) δ 6.80–6.86 (m, 27 H), 7.25 (d, $J = 8.0$ Hz, 2 H), 7.55–7.63 (m, 8 H), 7.70–7.74 (m, 5 H), 7.79 (d, $J = 8.0$ Hz, 2 H); ^{31}P NMR (160 MHz, C_6D_6) δ 17.4 (*trans* to C) (d, $J_{P-P} = 16$ Hz, $J_{Pt-P} = 1856$ Hz), 17.8 (*trans* to Se) (d, $J_{P-P} = 16$ Hz, $J_{Pt-P} = 3280$ Hz); IR (KBr) 3051, 1472, 1435, 1088, 1010, 811, 744, 692, 538, 523, 487 cm^{-1}; Anal. Calc. for $C_{56}H_{44}Cl_2P_2PtSe_2$: C, 55.92; H, 3.69. Found: C, 55.65; H, 3.74%.

3.2. Monitoring the solution of *cis*-**3a**

Into a dry Pyrex NMR tube were added *cis*-**3a** (25.0 mg, 0.021 mmol), $S{=}P(C_6H_4OMe\text{-}p)_3$ (0.9 mg, 0.0024 mmol) and C_6D_6 (0.5 mL) under a N_2 atmosphere. The ^{31}P NMR spectrum taken after 22 h at 25 °C showed the signals of 61% of *cis*-**3a** and 19% of *trans*-**3a** with some unassignable peaks. Its ^{1}H NMR spectrum did not show the liberation of phenyl acetylene, indicating that no β-SeAr elimination took place from **3a**.

***trans*-3a:** ^{31}P NMR (160 MHz, C_6D_6)δ 19.3 (s, $J_{Pt-P} = 3004$ Hz).

3.3. The reaction of **1b** with **2** (Eq. (3))

Into a dry Pyrex NMR tube were added **2** (15.0 mg, 0.020 mmol), **1b** (13.4 mg, 0.028 mmol), $S{=}P(C_6H_4OMe\text{-}p)_3$ (1.6 mg, 0.0042 mmol) and C_6D_6 (0.5 mL) under a N_2 atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. The ^{31}P NMR spectrum showed the formation of *cis*-**3b**, *trans*-**4** and **5**. On the other hand, ^{1}H NMR spectrum showed the formation of **6**. The reaction times and the yields of *cis*-**3b**, *trans*-**4**, **5** and **6** at the time were 20 min, 55%, 21%, 11%, 25%; 1 h, 50%, 39%, 9%, 39%; 21 h, 0%, 92%, 0%, 83%.

***cis*-3b:** ^{31}P NMR (160 MHz, C_6D_6) δ 14.4 (*trans* to C) (d, $J_{P\text{–}P} = 17$ Hz, $J_{Pt\text{–}P} = 1781$ Hz), 18.7 (*trans* to Se) (d, $J_{P\text{–}P} = 17$ Hz, $J_{Pt\text{–}P} = 3395$ Hz).

6: ^{1}H NMR (400 MHz, C_6D_6) δ 0.10 (s, 9 H), 2.06 (s, 1 H).

3.4. The preparation of 4

Into a dry two-necked reaction vessel equipped with a stirring bar were added **2** (379.3 mg, 0.51 mmol), (p-$ClC_6H_4Se)_2$ (202.2 mg, 0.53 mmol) and C_6H_6 (5 mL) under a N_2 atmosphere. After the reaction mixture was stirred at 25 °C for 20 min, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The resultant solid was washed by hexane (10 mL × 3) and then dried to give **4** (516.1 mg, 92%, *cis*/*trans* = 85/15). The stereochemistry of two PPh_3 on Pt was determined according to the ^{31}P NMR data (chemical shifts and the values of $J_{Pt\text{–}P}$) for $[Pt(SePh)_2(PPh_3)_2]$ documented in Organometallics 22 (2003) 1414. **4** (the following data were collected from a mixture of stereoisomers): m.p. 208 °C (an orange solid); ^{1}H NMR (160 MHz, C_6D_6) (*cis* isomer): δ 7.54–7.59 (m, 12 H), 7.65 (d, $J = 8.4$ Hz, 4 H); (*trans* isomer): δ 6.64 (d, $J = 8.4$ Hz, 4 H), 7.74–7.76 (m, 12 H). Other peaks overlapped in the region of δ 6.76–6.95 were not able to be read distinctively.; ^{31}P NMR (160 Hz, C_6D_6) (*cis* isomer): δ 19.0 (s, $J_{Pt\text{–}P} = 2935$ Hz); (*trans* isomer): δ 20.2 (s, $J_{Pt\text{–}P} = 2766$ Hz); IR (KBr) 3078, 1465, 1433, 1090, 1009, 806, 743, 701, 539, 503 cm^{-1}; Anal. Calc. for $C_{48}H_{38}Cl_2P_2PtSe_2$: C, 52.38; H, 3.48. Found: C, 52.71; H, 3.65%.

3.5. The confirmation of 5

Into a dry Pyrex NMR tube were added **2** (15.4 mg, 0.021 mmol), **6** (7.2 mg, 0.0733 mmol), S=P(C_6H_4O-Me-$p)_3$ (0.5 mg, 0.0013 mmol) and C_6D_6 (0.5 mL) under a N_2 atmosphere. The ^{31}P NMR spectrum taken after 20 min at 25 °C showed the formation of **5** in 97% yield with 3% of **2**.

5: ^{1}P NMR (160 MHz, C_6D_6) δ 29.0 (d, $J_{P\text{–}P} = 47$ Hz, $J_{Pt\text{–}P} = 3758$ Hz), 32.5 (d, $J_{P\text{–}P} = 47$ Hz, $J_{Pt\text{–}P} = 3672$ Hz).

3.6. The reaction of 7 with 2 (Eq. (4))

Into a dry Pyrex NMR tube were added **2** (14.5 mg, 0.019 mmol), **7** (5.8 mg, 0.024 mmol), S=P(C_6H_4OMe-$p)_3$ (0.7 mg, 0.0019 mmol) and C_6D_6 (0.5 mL) under a N_2 atmosphere. Then the reaction was monitored by the ^{31}P and ^{1}H NMR spectra at 25 °C. The ^{31}P NMR spectrum after 20 min showed the formation of **8** in 78% yield with the recovery of 22% of **2**. When the sample was additionally heated at 60 °C for 5 h, the signal of oxidative addition product *trans*-**9**, whose structure has been assigned by comparing the spectrum data with those of authentic sample (The spectral data was described in the supporting information of the paper cited in Ref. [9]), was detected (3%) together with **2** (16%) and **8** (60%).

8: ^{31}P NMR (160 MHz, C_6D_6) δ 28.4 (d, $J_{P\text{–}P} = 42$ Hz, $J_{Pt\text{–}P} = 3603$ Hz), 29.5 (d, $J_{P\text{–}P} = 42$ Hz, $J_{Pt\text{–}P} = 3717$ Hz).

trans-**9**: ^{31}P NMR (160 MHz, C_6D_6) δ 23.7 (s, $J_{Pt\text{–}P} = 2988$ Hz).

3.7. The reaction of 1c with 2 (Eq. (5))

Into a dry Pyrex NMR tube were added **2** (15.4 mg, 0.021 mmol), **1c** (6.5 mg, 0.022 mmol), S=P(C_6H_4OMe-$p)_3$ (1.1 mg, 0.0028 mmol) and C_6D_6 (0.5 mL) under a N_2 atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. The ^{31}P NMR spectrum indicated the formation of **10c** and **3c**, whose structure was tentatively characterized by comparing the ^{31}P NMR data with those of **9**. The reaction times and the yields of **10c** and **3c** at the time were 20 h, 6%, 76% (*cis*/*trans* = 82/18); 50 h, 0%, 68% (*cis*/*trans* = 53/47). When the sample was additionally heated at 60 °C for 5 h, the complete isomerization of *cis*-**3c** to *trans*-**3c** (41%) was confirmed.

10c: ^{31}P NMR (160 MHz, C_6D_6) δ 28.4 (d, $J_{P\text{–}P} = 42$ Hz, $J_{Pt\text{–}P} = 3619$ Hz), 29.8 (d, $J_{P\text{–}P} = 42$ Hz, $J_{Pt\text{–}P} = 3695$ Hz).

***cis*-3c:** ^{31}P NMR (160 MHz, C_6D_6) δ 18.0 (*trans* to Se) (d, $J_{P\text{–}P} = 16$ Hz, $J_{Pt\text{–}P} = 3194$ Hz), 22.6 (*trans* to C) (d, $J_{P\text{–}P} = 16$ Hz, $J_{Pt\text{–}P} = 1815$ Hz).

***trans*-3c:** ^{31}P NMR (160 MHz, C_6D_6) δ 23.6 (s, $J_{Pt\text{–}P} = 2985$ Hz).

3.8. The reaction of 1d with 2 (Eq. (6))

Into a dry Pyrex NMR tube were added **2** (15.0 mg, 0.020 mmol), **1d** (7.5 mg, 0.035 mmol), S=P(C_6H_4OMe-$p)_3$ (0.8 mg, 0.0022 mmol) and C_6D_6 (0.5 mL) under a N_2 atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. The ^{31}P NMR spectrum taken after 20 min showed the formation of **10d** quantitatively. No signal change was observed after 25 h. When the sample was additionally heated at 60 °C for 5 h, signals of 10% of suspected *trans*-**3d** (or **11**) and 56% of **10d** were detected.

10d: ^{31}P NMR (160 MHz, C_6D_6) δ 31.6 (d, $J_{P\text{–}P} = 43$ Hz, $J_{Pt\text{–}P} = 3626$ Hz), 31.9 (d, $J_{P\text{–}P} = 43$ Hz, $J_{Pt\text{–}P} = 3612$ Hz).

***trans*-3d (or 11):** ^{31}P NMR (160 MHz, C_6D_6) δ 23.9 (s, $J_{Pt\text{–}P} = 3025$ Hz).

4. Supplementary material

CCDC 287189 contains the supplementary crystallographic data for this paper (*cis*-**3a**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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