908 *Organometallics* **1998,** *17,* 908−913

Palladium-Catalyzed Reaction of Diselenide with Isocyanide

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Received October 27, 1997

A Pd-catalyzed reaction providing the first example of insertion of isocyanide into a Pd−Se bond is described. Tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] catalyzes the reaction of a diselenide $(ArSe)_2$ (**1a**) with an isocyanide ArNC (**2**) (Ar = 4-MeC_6H_4) to afford the adducts (ArSe)(C=NAr)$_m$(SeAr) (m = 2, 3). An X-ray crystallographic structure of the palladium intermediate *trans*-$Pd(SeAr)_2(CNAr)(PPh_3)$ (**7a**) is determined. In marked contrast to the Pd-catalyzed reaction using a disulfide, the 1:1-adduct **3a** (m = 1) is not produced. The stoichiometric reaction of **7a** with **1a** also did not provide **3a**. These facts suggest that the reductive elimination of 1:m-adducts takes place only when more than two isocyanides are inserted into Pd−Se bond(s) of **7a** to give Pd[(C=NAr)$_p$(SeAr)][(C=NAr)$_q$(SeAr)]L$_n$ (p, q ≥ 0) (**10a**). In contrast, the reaction of ditelluride $(PhTe)_2$ (**1c**) with **2** is not catalyzed by the Pd complex due in part to the insolubility and instability of the palladium(II) tellurolate intermediates.

Introduction

The insertion of isocyanides into M−Y (M = transition metal) bonds is among the most basic reactions in organometallic chemistry. Most efforts have been focused on insertion into M−C[1] and M−H[2] bonds. Only a few examples of insertion into M−N[3] and M-Cl[4] bonds by stoichiometric reactions and M-Si[5] bonds by catalytic reactions have been reported. We recently reported the palladium-catalyzed reaction of a disulfide with an isocyanide, which included an unprecedented insertion of isocyanide into a Pd−S bond.[6] This paper describes the reaction of a diselenide with an isocyanide under catalytic and stoichiometric conditions, providing the first evidence of insertion of isocyanide into a Pd−Se bond (Scheme 1). The differences in reactivity among chalcogen compounds are also discussed.

Scheme 1. Insertion of Isocyanide into the Pd−Se Bond

Results and Discussion

The reaction of 4-methylphenyl diselenide $(ArSe)_2$ (**1a**) (0.5 mmol) with 4-methylphenyl isocyanide **2** (0.5 mmol) was carried out in the presence of 2 mol % of $Pd(PPh_3)_4$ in benzene (1 mL) at 80 °C for 14 h. The ^1H NMR spectrum of the crude reaction mixture showed the complete consumption of **2** and the formation of a complicated mixture. When the reactant was subjected to preparative TLC, 19% (based on **2**) of the 1:2-adduct **4a**, 18% of the 1:3-adduct **5a**, 80% of **1a** (recovered), and uncharacterized oily products[7] were obtained (Scheme 2). In marked contrast to the result using disulfide **1b**,[6] 1:1-adduct **3a** was not formed. The reaction using 4-methylphenyl ditelluride $(ArTe)_2$ (**1c**) was not catalyzed under similar reaction conditions.

To gain more insight into the difference among dichalcogenides under catalytic conditions, stoichiometric reactions were conducted in an NMR tube. The reaction of **1a** with $Pd(PPh_3)_4$ and subsequently with **2** provided $Pd(SeAr)_2(CNAr)(PPh_3)$ (**7a**) (quantitative yield, *cis*/*trans* = 8/92) via $[Pd(SeAr)_2(PPh_3)]_2$ (**6a**),[8] which is analogous to the reaction using **1b** (Scheme 3).[6] In contrast, the black solid prepared by the reaction of 4-methylphenyl ditelluride $(ArTe)_2$ (**1c**) with $Pd(PPh_3)_4$,

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[1] For example, see: (a) Motz, P. L.; Alexander, J. J.; Ho, D. M. *Organometallics* **1989**, *8*, 2589. (b) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225 and references therein. (c) Ogawa, H.; Joh, T.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1988**, 561. (d) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862. (e) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974**, *13*, 438. (f) Kosugi, M.; Ogata, T.; Tamura, H.; Sano, H.; Migita, T. *Chem. Lett.* **1986**, 1197.

[2] (a) Tanase, T.; Ohizumi, T.; Kobayashi, K.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 707. (b) Christian, D. F.; Clark, H. C. *J. Organomet. Chem.* **1975**, *85*, C9.

[3] (a) Chisholm, M. H.; Hammond, C. E.; Ho, D.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7860. (b) Dormond, A.; Aaliti, A.; Moïse, C. *J. Chem. Soc., Chem. Commun.* **1985**, 1231. (c) Saegusa, T.; Ito, Y.; Kobayashi, S.; Hirota, K.; Yoshioka, H. *Tetrahedron Lett.* **1966**, 6121. (d) Kienzle, F.; Switzerland, B. *Tetrahedron Lett.* **1972**, 1771. (e) Sawai, H.; Takizawa, T. *Tetrahedron Lett.* **1972**, 4263.

[4] Crociani, B.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, 127.

[5] (a) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899. (b) Ito, Y.; Bando, T.; Matsuura, T.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 980. (c) Ito, Y.; Ito, I.; Hirao, T.; Saegusa, T. *Synth. Commun.* **1974**, *4*, 97.

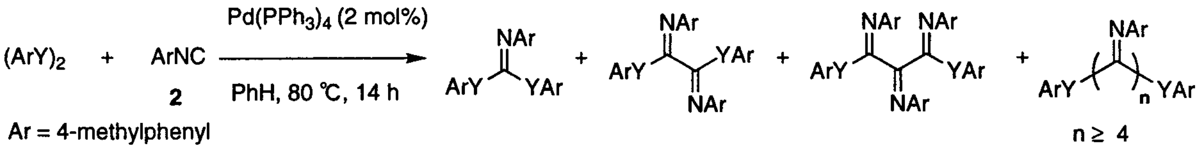
[6] Kuniyasu, H.; Sugoh, K.; Moon, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669.

[7] The retention time of this oil by HPLC indicated many polymeric product inclusions. The polarity of the oil by PTLC was so high that **3a** would not be contained in it.

[8] Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, p 679.

S0276-7333(97)00936-9 CCC: $15.00

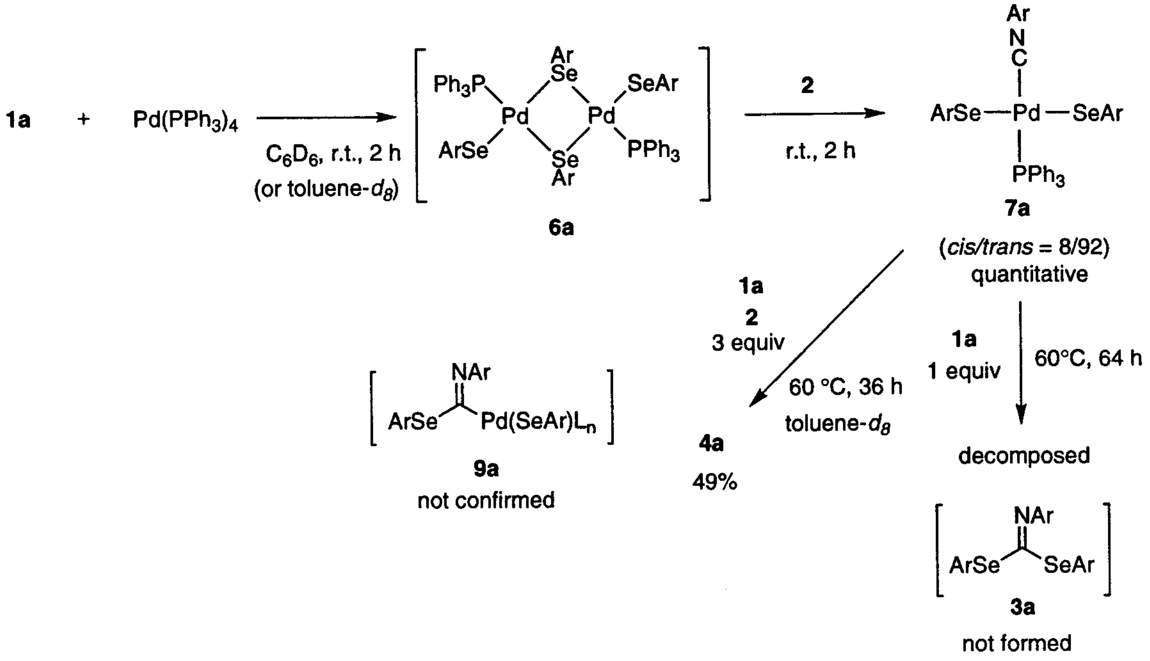
Scheme 2



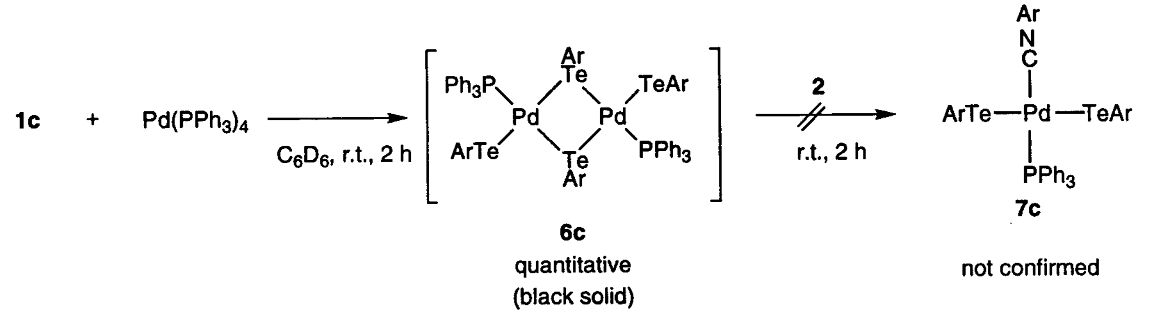
1a: $(ArSe)_2$	**3a** a	**4a** 19%	**5a** 18%	b
1b: $(ArS)_2$[ref 6]	**3b** 41%	**4b** 46%	**5b** 12%	a
1c: $(ArTe)_2$	**3c** a	**4c** a	**5c** a	a

[a] Not obtained. [b] Uncharacterized oily products were obtained.

Scheme 3



Scheme 4



which was deduced to be $[Pd(TeAr)_2PPh_3]_2$ (**6c**) according to the literature,[9] did not react with **2** (Scheme 4).[10]

An authentic sample of *trans*-**7a** was characterized crystallographically and found to exhibit approximately a square-planar coordination geometry with the bond distances of Se(1)−Pd = 2.438(3) Å, Se(2)−Pd = 2.467(3) Å, C−Pd = 1.97(2) Å, P−Pd = 2.307(5) Å, and N−C = 1.15(2) Å (Figure 1).[11]

Contrary to the reaction of $Pd(SAr)_2(CNAr)(PPh_3)$ (**7b**) with **1b**, which produced the 1:1-adduct **3b** and $[Pd(SAr)_2(PPh_3)]_2$ (**6b**),[6] *3a was not obtained by the reaction of 7a with 1 equiv of 1a* (Scheme 3). When 3 equiv of **2** was added into the solution of **7a** (prepared in toluene-d_8 by the above procedure), broad peaks were observed at room temperature. The ^1H NMR spectrum taken at −35 °C showed the sharp peaks of **7a** and $Pd(SeAr)_2(CNAr)_2$ (**8a**)[12] in a ratio of 4:1, indicating fast ligand exchange of coordinated PPh_3 in **7a** with free **2** at room

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[9] Chia, L. Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1978**, *148*, 165.

[10] The corresponding platinum complex $Pt(TeAr)_2(CNAr)(PPh_3)$ (**7c′**) synthesized by the reaction of **1c** with $Pt(PPh_3)_4$ and **2** was not stable even at room temperature. So the palladium complex **7c** would not tolerate benzene reflux conditions even if formed.

[11] Crystal data of *trans*-**7**: space group $P2_1/a$ (No. 14) with a = 13.410(3) Å, b = 18.032(4) Å, c = 15.005(3) Å, β = 94.64(2)°, Z = 4, ρ = 1.517 g/cm^3, R = 0.091, and R_w = 0.069.

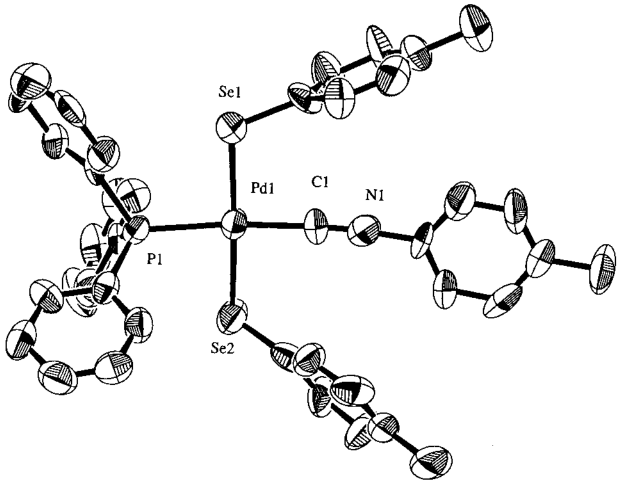
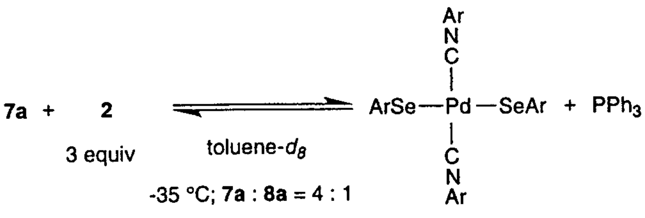


Figure 1. ORTEP diagram of *trans*-**7a**. Selected bond lengths (Å): Se(1)−Pd(1) 2.438(3), Se(2)−Pd(1) 2.467(3), C(1)−Pd(1), 1.97(2), P(1)−Pd(1) 2.307(5), and N(1)−C(1) 1.15(2).

Scheme 5



8a
(one isomer)

temperature (Scheme 5). After another equivalent of **1a** was added to the solution at 60 °C, the 1:2-adduct **4a** formed (49% based on added **1a**) after 36 h, although formation of Pd[(C=NAr)(SeAr)](SeAr)L_n (**9a**) was not observed during the course of reaction, which was monitored by ^{31}P NMR spectroscopy (Scheme 3).

The foregoing results and our previous observation[6] allow us to predict the relative free energies of reaction stages starting with 2 equiv of **1** (Y = Se (**1a**), S (**1b**)), 1 equiv of **2**, and 1 equiv of Pd(PPh$_3$)$_4$ (Scheme 6, system A). Both the oxidative addition of **1** to Pd(PPh$_3$)$_4$ to give **6** and the coordination of **2** to **6** to provide **7** lower the total energy (A > B (**1**, **2**, and **6**) > C (**1** and **7**)).

Although the relative position between C and D (**1** and **9**) remains ambiguous, D is at least not so high as to suppress the conversion of **7** into Pd[(C=NAr)$_p$(YAr)][(C=NAr)$_q$(YAr)]L_n (p, $q \geq 0$) **10** (Scheme 7), because 1:m-adducts ($m \geq 2$) were actually afforded under catalytic conditions in the reactions of Scheme 2.[13] System E must be lower than system A in the case of Y = S, because the Pd complex does catalyze the reaction of **1b** with **2** to afford **3b**. In the case of Y = Se, however, the position of E relative to A is not clear but we can at least say that the activation barrier from D to E is high enough to prevent the reductive elimination of **3a** from **9a**. Only when more than two isocyanides are incorporated into the palladium complexes as in **10a** does the formation of 1:m-adducts become possible (Scheme 7).

Moreover, while the 1:2-adduct **4b** once formed under palladium-catalyzed reaction of **1b** with **2** hardly became a precursor of the 1:m-adducts ($m \geq 3$),[6] **4a** would easily reenter the catalytic cycle, because the reaction of **4a** with Pd(PPh$_3$)$_4$ gave *trans*-Pd[(C=NAr)$_2$(SeAr)](SeAr)(PPh$_3$)$_2$ (**11a**) even at room temperature (5 min, 10%) (Scheme 8).[14] That would explain the low yield of **4a** and the formation of an uncharacterized oily product under the catalytic conditions (Schemes 2 and 7).

Although it is not yet clear why the palladium complex did not catalyze the reaction of **1c** with **2**, the low solubility and instability[10] of Pd(II) tellurolate intermediates might contribute to the lack of the catalytic activity.

Conclusion

This paper describes a synthetic and mechanistic study of the palladium-catalyzed reaction of a diselenide with an isocyanide to provide the first example of insertion of isocyanide into a Pd−Se bond. Marked differences between disulfide and diselenide under Pd-catalyzed conditions are rationalized on the basis of the relative propensity toward the reductive elimination of the 1:1-adduct and 1:m-adducts ($m \geq 2$) from the palladium intermediates **9** and **10**.

Experimental Section

^{1}H, ^{13}C, and ^{31}P NMR spectra in benzene-d_6 or CDCl$_3$ solution were recorded with a JEOL JNM-GSX-270 (270 MHz) or a JEOL JSX-400 (400 MHz) spectrometer. Chemical shifts in the ^{1}H NMR spectra were recorded relative to Me$_4$Si or C$_6$H$_6$ (δ 7.16). Chemical shifts in the ^{13}C NMR spectra were recorded relative to Me$_4$Si, C$_6$D$_6$ (δ 128.0), or CDCl$_3$ (δ 77.0). Chemical shifts in the ^{31}P NMR spectra were recorded using 85% H$_3$PO$_4$ as an external standard. IR spectra were recorded with a Perkin-Elmer model 1600 spectrometer. GC-mass spectra were recorded with a Shimazu QP-5000 spectrometer. Combustion analyses and mass spectra were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Isocyanide **2** was prepared according to the literature.[15] Diselenide and ditelluride were also prepared according to the literature.[16] Benzene and benzene-d_6 were purified by distillation from CaH$_2$ before use. Pd(PPh$_3$)$_4$, Pt(PPh$_3$)$_4$, and Pd$_2$(dba)$_3$ were also synthesized.[17,18] Preparative TLC was carried out using Wakogel B-5F silica gel. Purification of 1:3-adduct **5a** was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., model LC-908 equipped with JAIGEL-1H and -2H columns (GPC)) using CHCl$_3$ as an eluent. X-ray crystal data were collected by Rigaku AFC5R diffraction. Crystal and data collection parameters for *trans*-**7a** are summarized in the Supporting

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[12] Authentic **8a** was synthesized and characterized by the reaction of Pd$_2$(dba)$_3$ with **2** and **1a**. See Experimental Section. Rauchfuss, T. B.; Shu, J. S.; Roundhill, D. M. *Inorg. Chem.* **1976**, *15*, 2096.

[13] Because the reaction of **3b** with Pd(PPh$_3$)$_4$ gave **7b** without detection of **9b** at room temperature, **D** would be higher than **C** and not so high relative to **E** in the case of Y = S. See ref 6.

[14] The low conversion would depend on the suppression effect by free PPh$_3$ generated as the oxidative addition proceeded. Complex **9a** was confirmed only in situ due to the facile decomposition at room temperature. See Experimental Section.

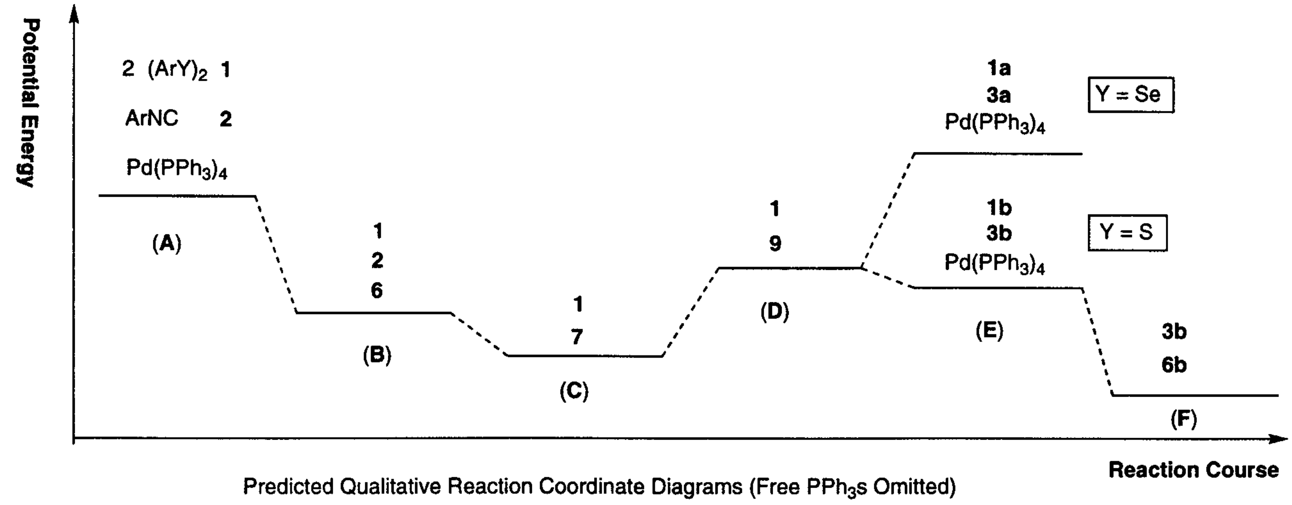
[15] (a) Obrecht, R.; Herrmann, R.; Ugi, I. *Synthesis* **1985**, 400. (b) Ugi, I.; Merv, R.; Lipinski, M.; Bodesheim, F.; Rosendahl, F. In *Organic Syntheses*; Wiley: New York, 1973; Vol. V, p 300.

[16] (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (b) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

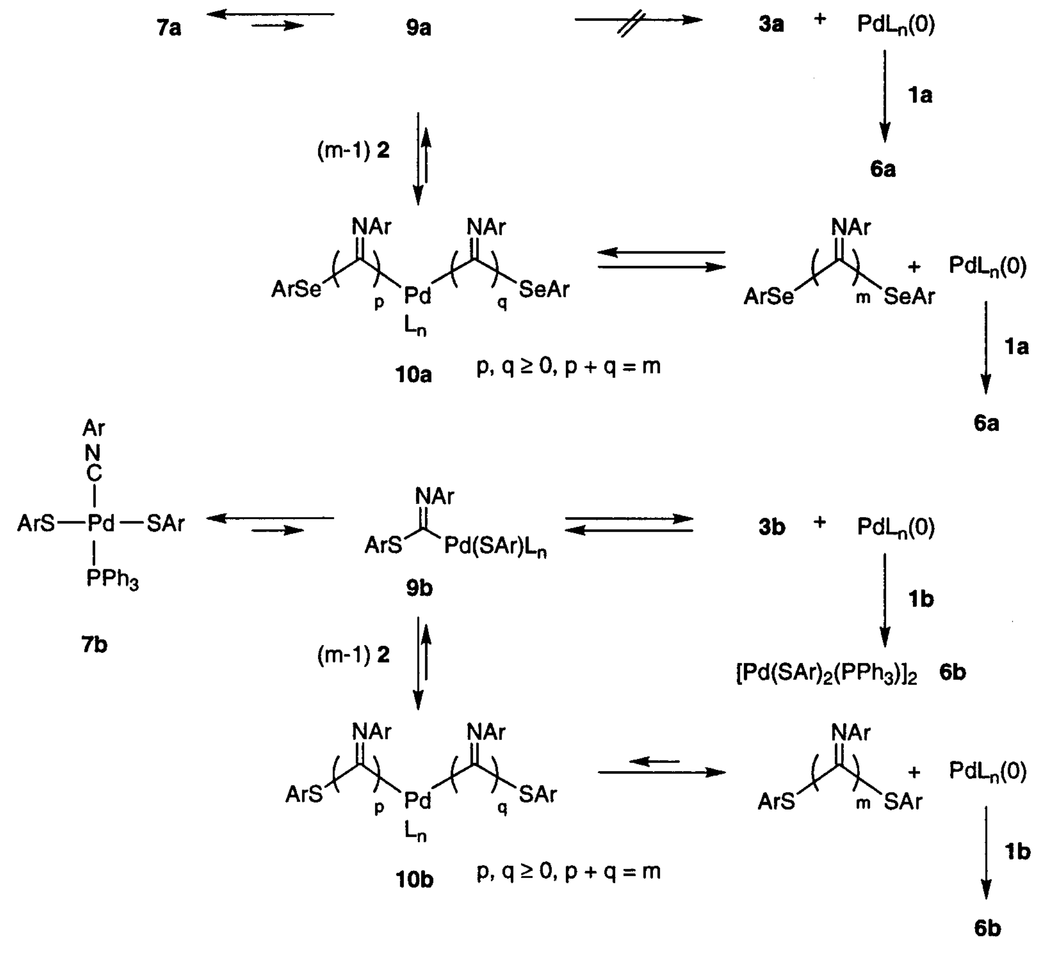
[17] (a) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121. (b) Ugo, R.; Cariati, F.; Monica, G. L. *Inorg. Synth.* **1968**, *11*, 105.

[18] Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

Scheme 6. Predicted Qualitative Reaction Coordinate Diagrams (Free PPh$_3$s Omitted)



Scheme 7. Comparison of the Reaction Mechanisms between 1a and 1b under Pd-Catalyzed Reactions with 2

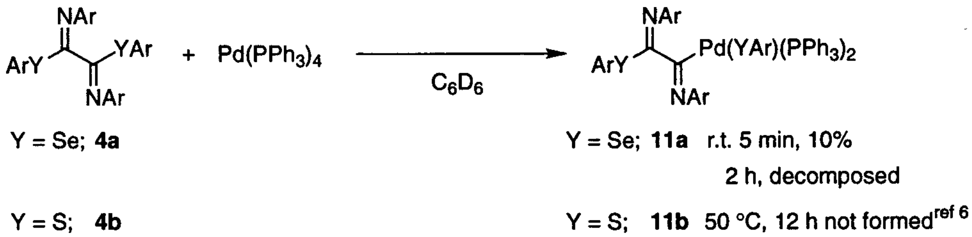


Information. The ORTEP drawing in Figure 1 has been shown with 50% probability ellipsoids.

Palladium-Catalyzed Reaction of 1a with 2 (Scheme 2). Preparation of 4a and 5a. Into a dry two-necked flask equipped with a reflux condenser and a magnetic stirring bar were placed Pd(PPh$_3$)$_4$ (12 mg, 0.010 mmol), **1a** (170 mg, 0.511 mmol), **2** (59 mg, 0.50 mmol), and benzene (0.5 mL) under an argon atmosphere. After the solution was refluxed with stirring for 14 h, the resulting catalyst was removed by filtration through Celite and the filtrate was evaporated under reduced pressure. The ^{1}H NMR spectrum showed a complicated result with complete consumption of **2**. Then the reaction mixture was separated by PTLC (a mixture of hexane and Et$_2$O (9:1) as an eluent). The products obtained were 27 mg of **4a** (19% based **2**), 21 mg of **5a** (18% based on **2**), 136 mg of **1a** (80%, recovered), and a total of 38 mg of an uncharacterized complex oily mixture.

4a: mp 202–204 °C (off-white solid); ^{1}H NMR (270 MHz, CDCl$_3$, room temperature) δ 2.30 (s, 6 H), 2.42 (s, 6 H), 6.20 (d, J = 7.8 Hz, 4 H), 7.04 (d, J = 7.8 Hz, 4 H), 7.19 (d, J = 7.8 Hz, 4 H), 7.66 (d, J = 7.8 Hz, 4 H); ^{13}C NMR (68 MHz, CDCl$_3$, room temperature) δ 20.96, 21.27, 119.18, 123.26, 129.42,

Scheme 8



129.87, 134.85, 138.10, 138.35, 139.58, 146.48; IR (KBr) 1630, 1611, 1504, 1436 cm^{-1}; MS (EI) 576 *m/e* (M$^+$, 2). Anal. Calcd for $C_{30}H_{28}N_2Se_2$: C, 62.72; H, 4.91; N, 4.88. Found: C, 62.79; H, 4.87; N, 4.89.

5a: yellow oil; ^{1}H NMR (270 MHz, CDCl$_3$, room temperature) δ 2.20 (s, 3 H), 2.26 (s, 3 H), 2.34 (s, 3 H), 2.38 (s, 3 H), 2.39 (s, 3 H), 6.66 (d, J = 8.3 Hz, 2 H), 6.74 (d, J = 7.8 Hz, 2 H), 6.81 (d, J = 7.8 Hz, 2 H), 6.91 (d, J = 8.3 Hz, 4 H), 7.01−7.20 (m, 8 H), 7.28 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz, CDCl$_3$, room temperature) δ 20.90, 21.02, 21.02, 21.18, 21.38, 119.02, 122.23, 124.73, 128.70, 128.97, 129.72, 134.25, 134.76, 135.48, 135.91, 137.18, 139.48, 144.12, 145.74, 147.65, 157.84, 159.30, 162.16; IR (NaCl) 3023, 2922, 1622, 1503, 1455, 1196, 909, 855, 821, 803 cm^{-1}; MS (EI) *m/e* 693 (M$^+$, 2); exact mass (M$^+$) calcd for $C_{38}H_{35}N_3Se_2$ 693.1161, found 693.1179.

The reaction using **1c** in lieu of **1a** was carried out under similar reaction conditions. However, no reaction took place.

Stoichiometric Reactions of 1a with Pd(PPh$_3$)$_4$ and 2 in NMR Tubes (Scheme 3). Into a dry Pyrex NMR tube were added Pd(PPh$_3$)$_4$ (34.5 mg, 0.0299 mmol), **1a** (10.2 mg, 0.0306 mmol), and benzene-d_6 (0.7 mL). After the samples were degassed under reduced pressure and purged with Ar several times, 1,4-dioxane (2.7 mg, 0.029 mmol) was added as an internal standard. After 2 h at room temperature, **2** (3.5 mg, 0.030 mmol) was added. Then the sample was left for 2 h, and ^{1}H and ^{31}P NMR spectra were taken. The formation of Pd(SeAr)$_2$(CNAr)(PPh$_3$) (**7a**) was confirmed almost quantitatively (*cis*/*trans* = 8/92). Then another equivalent of **1a** (10.8 mg, 0.0320 mmol) was added into the sample, and the reaction was monitored at 60 °C; however, only the gradual decomposition of **7a** was observed. Although the complete decomposition of **7a** was confirmed after 64 h, no formation of **3a** was detected at all.

Preparation of Authentic 7a. Into a two-necked dry 30 mL flask equipped with a stirring bar were added Pd(PPh$_3$)$_4$ (57.8 mg, 0.0500 mmol), **1a** (15.6 mg, 0.0468 mmol), and benzene (5 mL). After the mixture was stirred at room temperature for 2 h, **2** (5.7 mg, 0.049 mmol) was added and the mixture was stirred for 30 min. Then 10 mL of hexane was added into the mixture. The precipitate was separated by filtration and washed by hexane to give 16.2 mg of Pd(SeAr)$_2$(CNAr)(PPh$_3$) (**7a**; 41%). The solid was recrystallized from THF and hexane to give a pure *trans*-**7a**.

7a: mp 139 °C (an yellow solid); ^{1}H NMR (400 MHz, C$_6$D$_6$) trans isomer δ 1.71 (s, 3 H), 1.94 (s, 6 H), 6.00 (d, J = 8.4 Hz, 2 H), 6.37 (d, J = 8.1 Hz, 2 H), 6.65 (d, J = 8.4 Hz, 4 H), 7.04 (m, 9 H), 7.39 (m, 6 H), 7.96 (d, J = 7.8 Hz, 4 H); ^{31}P NMR (160 MHz, C$_6$D$_6$) trans isomer δ 28.51; ^{31}P NMR cis isomer (collected from a stereomixture) δ 24.87; IR (KBr) 3054, 2359, 2187, 1483, 1434, 1096 cm^{-1}. Anal. Calcd for $C_{40}H_{36}NPPdSe_2$: C, 58.16; H, 4.39; N, 1.70. Found: C, 57.84; H, 4.40; N, 1.39.

Stoichiometric Reactions of 1c with Pd(PPh$_3$)$_4$ and 2 in NMR Tube (Scheme 4). Into a dry Pyrex NMR tube were added Pd(PPh$_3$)$_4$ (34.5 mg, 0.0299 mmol), **1c** (13.1 mg, 0.0299 mmol), and benzene-d_6 (0.7 mL). After the sample was degassed under reduced pressure and purged with Ar several times, 1,4-dioxane (2.7 mg, 0.029 mmol) was added as an internal standard. A black solid was precipitated gradually. After 2 h at room temperature, only the peaks of PPh$_3$ were observed by ^{1}H NMR. Then **2** (3.5 mg, 0.030 mmol) was added into the mixture. However, the ^{1}H NMR spectrum showed only the peaks of **2** and PPh$_3$, and the solid did not dissolve at all after 2 h.

Reaction of 7a with 2 (Scheme 5). Into a toluene-d_8 solution of **7a** prepared in situ (0.017 mmol from **1a**, Pd(PPh$_3$)$_4$, and **2**) was added **2** (6.0 mg, 0.051 mmol). The ^{1}H NMR spectrum at room temperature showed the broad peaks of **7a** and **2**. As the temperature was lowered, peak separation was gradually observed. ^{1}H NMR spectrum at −35 °C clearly showed the presence of **7a** and Pd(SeAr)$_2$(CNAr)$_2$ **8a** in a ratio of 4:1. Then another one equivalent of **1a** was added into the mixture, and the sample was heated at 60 °C. After 36 h, the formation of 49% of **4a** (based on added **1a**) was confirmed; however, no formation of **9a** was observed during the course of reaction.

Preparation of Authentic 8a. Into a two-necked dry 30 mL flask equipped with a stirring bar were added Pd$_2$(dba)$_3$·CHCl$_3$ (15.5 mg, 0.0150 mmol), **2** (7.0 mg, 0.060 mmol), and benzene (3 mL). After the mixture was stirred at room temperature for 1 h, **1a** (10.2 mg, 0.0306 mmol) was added and the mixture was stirred for 2 h. Then 10 mL of hexane was added into the mixture. The precipitate was separated by filtration and washed with hexane to give 9.0 mg of **8a** (38%).

8a: mp 124−130 °C (yellow solid); ^{1}H NMR (270 MHz, C$_6$D$_6$) (one isomer, stereochemistry undetermined) δ 1.71 (s, 6 H), 1.96 (s, 6 H), 6.20 (d, J = 8.3 Hz, 4 H), 6.36 (d, J = 7.8 Hz, 4 H), 6.69 (d, J = 7.8 Hz, 4 H), 8.11 (d, J = 7.8 Hz, 4 H); IR (KBr) 2180, 1503, 1483, 1015 cm^{-1}. Anal. Calcd for $C_{30}H_{28}N_2Se_2Pd$: C, 52.92; H, 4.14; N, 4.11. Found: C, 53.05; H, 4.16; N, 3.87.

Oxidative Addition of 4a to Pd(PPh$_3$)$_4$ (Scheme 8). Into a dry Pyrex NMR tube were added Pd(PPh$_3$)$_4$ (17.5 mg, 0.0152 mmol), **4a** (9.0 mg, 0.0157 mmol), and benzene-d_6 (0.7 mL). The ^{1}H NMR spectrum after 5 min showed the formation of 10% of *trans*-Pd[(C=NAr)$_2$(SeAr)](SeAr)(PPh$_3$)$_2$ (**11a**), whose structure was assigned by comparison of the chemical shift of *trans*-Pt[(C=NAr)$_2$(SAr)](SAr)(PPh$_3$)$_2$ (**11b**) and *cis*-Pt[(C=NAr)$_2$(SeAr)](SeAr)(PPh$_3$)$_2$ (**11a′**). Compound **11a** decomposed within 2 h at room temperature. For the spectrum data of **11b**, see ref 6.

***trans*-11a:** ^{1}H NMR (270 MHz, C$_6$D$_6$) δ 1.90 (s, 3 H), 2.31 (s, 3 H), 6.27 (d, J = 8.4 Hz, 2 H), 6.33 (d, J = 7.8 Hz, 2 H) (the other peaks overlapped with the peaks of Pd(PPh$_3$)$_4$ and **4a**).

Synthesis of 11a′. Into a dry Pyrex NMR tube were added Pt(PPh$_2$)(CH$_2$=CH$_2$) (37.2 mg, 0.0498 mmol), **4a** (24.8 mg, 0.0432 mmol), and benzene-d_6 (0.5 mL). The sample was degassed under reduced pressure and purged with Ar several times. After 7 h, dry hexane was added into the solution and the precipitated solid was collected to give 17 mg (30%) of **11a′**.

11a′: mp 132−135 °C (yellow solid); ^{1}H NMR (400 MHz, C$_6$D$_6$) cis isomer δ 2.04 (s, 3 H), 2.09 (s, 3 H), 2.15 (s, 3 H), 2.42 (s, 3 H), 6.53 (d, J = 7.8 Hz, 2 H), 6.74−7.24 (m, 26 H), 7.32 (d, J = 7.8 Hz, 2 H), 7.32−7.90 (m, 12 H), 7.98 (d, J = 7.8 Hz, 2 H), 8.17 (d, J = 7.8 Hz, 2 H); ^{31}P NMR (160 MHz, C$_6$D$_6$)

cis isomer δ 15.98 (d, $J = 19.4$ Hz, $J_{\mathrm{Pt-P}} = 3398$ Hz), 17.45 (d, $J = 19.4$ Hz, $J_{\mathrm{Pt-P}} = 1835$ Hz); IR (KBr) 3049, 1633, 1600, 1500, 1435, 1198, 1096 cm^{-1}. Anal. Calcd for $C_{66}H_{58}N_2Se_2Pt$: C, 61.25; H, 4.52; N, 2.16. Found: C, 60.90; H, 4.81; N, 2.09.

Preparation of Pt(TeAr)$_2$(CNAr)(PPh$_3$) (7c′).[10] Into a dry Pyrex NMR tube were added Pt(PPh$_3$)$_4$ (37.3 mg, 0.0300 mmol), **1c** (13.5 mg, 0.0309 mmol), and benzene-d_6 (0.7 mL). After the samples were degassed under reduced pressure and purged with Ar several times, 1,4-dioxane (2.5 mg, 0.028 mmol) was added as an internal standard. After 2 h at room temperature, **2** (3.5 mg, 0.030 mmol) was added. Then the sample was left for 2 h, and a ^{1}H NMR spectrum was taken. The formation of Pt(TeAr)$_2$(CNAr)(PPh$_3$) **7c′** was confirmed in 94% yield (cis/trans = 10/90). The complex **7c′** was not able to be isolated due to facile decomposition at room temperature.

7c′: ^{1}H NMR (400 MHz, C_6D_6) trans isomer δ 1.74 (s, 3 H), 1.88 (s, 6 H), 5.88 (d, $J = 8.4$ Hz, 2 H), 6.36 (d, $J = 7.8$ Hz, 2 H), 6.53 (d, $J = 7.8$ Hz, 4 H), 7.04 (m, 9 H), 7.39 (m, 6 H), 8.06 (d, $J = 7.8$ Hz, 4 H); cis isomer δ 2.07 (s, 3 H), 5.78 (d, $J = 8.4$ H, 2 H), 6.82 (d, $J = 7.8$ Hz, 2 H) (the other peaks overlapped with the trans isomer).

Acknowledgment. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining the mass spectra with a JEOL JMS-DX303 instrument. Financial support of this work through a Grant-in-Aid for Scientific Research, the Ministry of Education, and Nagase Research Foundation is also acknowledged.

Supporting Information Available: Tables of crystal data and data collection parameters, atomic coordinates, isotropic thermal parameters, anisotropic displacement parameters, and bond lengths and angles (25 pages). Ordering information is given on any current masthead page.

OM970936P