The First Evidence of Insertion of Isocyanide into a Metal−Sulfur Bond: Catalytic and Stoichiometric Behavior of Isocyanide and Thiolate Ligands on Palladium and Platinum

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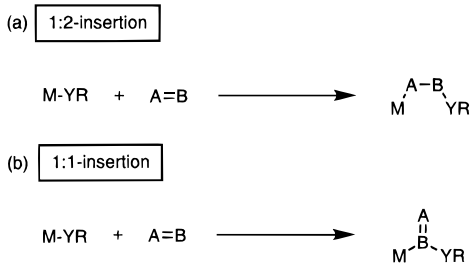
Abstract: The first evidence of insertion of isocyanide into M−S bond has been demonstrated. Tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] catalyzes the reaction of a disulfide $(ArS)_2$ (**1**) with an isocyanide ArNC (**2**) (Ar = 4-MeC_6H_4) to produce the adducts $(ArS)(C{=}NAr)_m(SAr)$. The reactions of 1:*m* adducts with **2** are also catalyzed by the Pd complex to afford 1:*k* adducts ($k \neq m$). The mechanistic study reveals that the complex $Pd(SAr)_2(CNAr)(PPh_3)$ (**8**) is a resting state for giving 1:1 adduct and converted into 1:1 adduct **3** ($m = 1$) *in the presence of another 1 equiv of* ***1***. The stoichiometric reaction of **3** with $Pd(PPh_3)_4$ provides **8**, but the stoichiometric oxidative addition of 1:*m* adducts ($m = 2$, 3, 4) to $Pd(PPh_3)_4$ did not give any definitive Pd(II) species. These facts reveal that both the insertion of isocyanide(s) into Pd−S bond and the reductive elimination of 1:*m* adduct are reversible. The study on reactivities of isocyanide and thiolate ligands on platinum, including the X-ray crystallographic analysis of the imidoyl platinum *trans*-$Pt[(C{=}NAr)_2SAr](SAr)(PPh_3)_2$ (**21**) obtained by the oxidative addition of the C−S bond of 1:2 adduct **4** ($m = 2$) to $Pt(PPh_3)_4$ has also been reported.

Introduction

While the chalcogenates (RY^-; Y = S, Se, Te) have been well-exploited as ligands because of their fairly good affinity to various transition metals, their intrinsic reactivities *on metals* remain open to study. As to the insertion into M−Y bonds, for instance, 1:2 insertion which provides β-chalcogeno metal species (Scheme 1a) has been confirmed in stoichiometric reactions with electron-deficient acetylenes when M is Ru,[1] Rh,[2] Mo,[3] W,[4] Co,[5] and Fe[6] and proposed in some metal-catalyzed reactions when M is Pd, Pt, and Rh.[7−10] Meanwhile, much less general exploration has been made with the 1:1 insertion (Scheme 1b) both stoichiometrically and catalytically. To our knowledge, only the removal of chalcogenide as YCO after the insertion of CO into M−Y bonds and the insertion of CS into Mo−S bond have been the reported examples.[11] We now wish to report a novel palladium-catalyzed reaction of a disulfide with an isocyanide, and its mechanistic study, providing a new entry of 1:1 insertion of isocyanide into the M−S (M = Pd) bond to generate an α-thioimidoyl metal. The similarities and differences of the reactivity of isocyanide and thiolate ligands between palladium and platinum complexes will also be described.

Scheme 1. Insertion of Unsaturated Compound into M−YR (Y = S, Se, Te)



Results and Discussion

Palladium-Catalyzed Reactions and Its Mechanism. We have found that the reaction of 4-methylphenyl disulfide (**1**) with 4-methylphenyl isocyanide (**2**) was catalyzed by palladium complexes to provide a mixture of 1:*m* adducts ($m = 1$, **3**; $m = 2$, **4**; $m = 3$, **5**) (eq 1). Table 1 summarized the effect of catalysts examined. When the reaction of **1** with 1 equiv of **2**

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(1) Koelle, U.; Rietmann, C.; Tjoe, J.; Wagner, T.; Englert, U. *Organometallics* **1995**, *14*, 703.

(2) Wakatsuki, Y.; Yamazaki, H.; Iwasaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 5781.

(3) Halbert, T. R.; Pan, W. H.; Stiefel, E. *J. Am. Chem. Soc*. **1983**, *105*, 5476.

(4) Carlton, L.; Bakar, W. A. W. A.; Davidson, J. L. *J. Organomet. Chem.* **1990**, *394*, 177.

(5) (a) Kajitani, M.; Hisamatsu, N.; Takehera, M.; Mori, Y.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Chem. Lett*. **1994**, 473. (b) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc*., *Dalton Trans.* **1975**, 2283.

(6) (a) Imhof, W.; Hunttner, G. *J. Organomet. Chem.* **1993**, *447*, 31. (b) Petillon, F. Y.; Floch-Perennou, F. L.; Guerchais, J. E. *J. Organomet. Chem.* **1979**, *173*, 89. (c) Fässler, T.; Huttner, G. *J. Organomet. Chem*. **1989**, *376*, 367.

(7) (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902. (b) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Sonoda, N. *Tetrahedron Lett.* **1992**, *33*, 5525. (c) Bäckvall, J. E.; Ericsson, A. *J. Org. Chem.* **1994**, *59*, 5850. (d) Dzhemilev, U. M.; Kunakova, R. V.; Gaisin, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *11*, 2655.

(8) (a) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796. (b) Dzhemilev, U. M.; Kunakova, R. V.; Baibulatova, N. Z.; Mustafina, E. M.; Galkin, E. G.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, *3*, 747. (c) Ogawa, A.; Takeba, M.; Kawakami, J.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1995**, *117*, 7564.

(9) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219.

(10) Han, L.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 7000.

(11) (a) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (b) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609. (c) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935. (d) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *334*, C43. (d) Wang, M. D.; Calet, S.; Alper, H. *J. Org. Chem.* **1989**, *54*, 21. (e) Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (f) Liu, H.; Tan, A. L.; Mok, K. F.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1996**. 4023. (g) Luh, T. Y.; Ni, Z. J. *Synthesis* **1990**, 89. (h) Burgmayer, S. J. N.; Templeton, J. L. *Inorg. Chem.* **1985**, *24*, 3939 and references therein.

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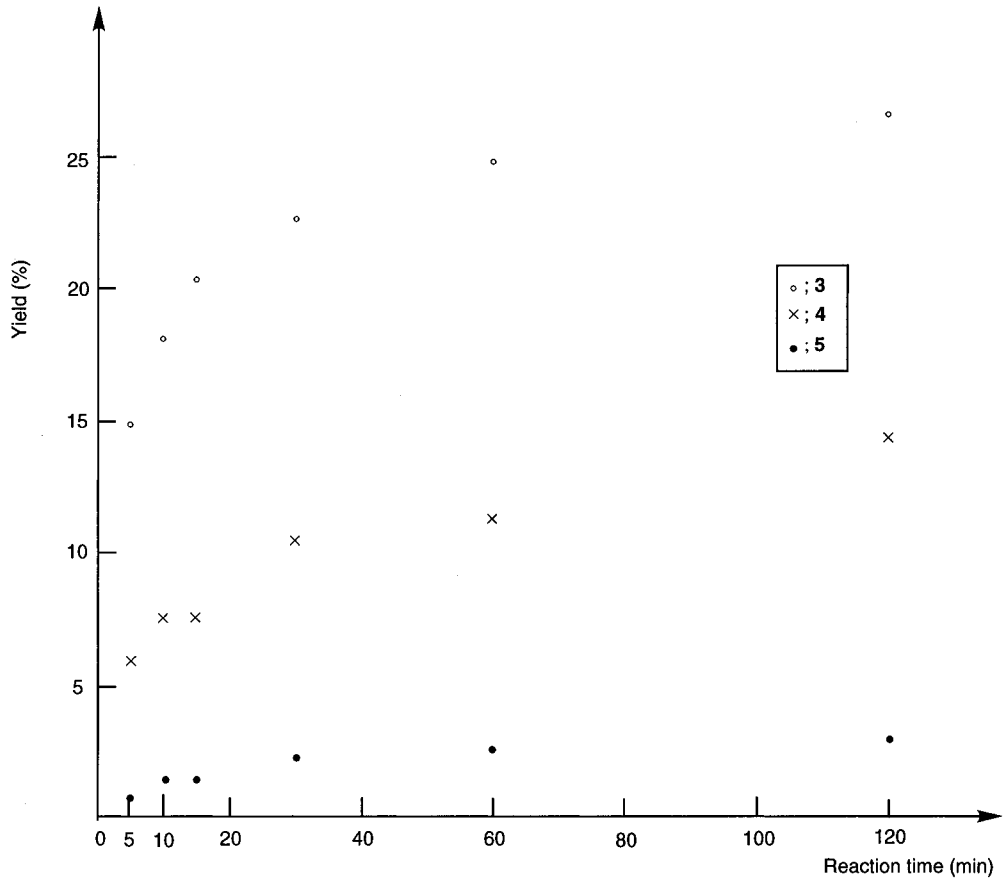
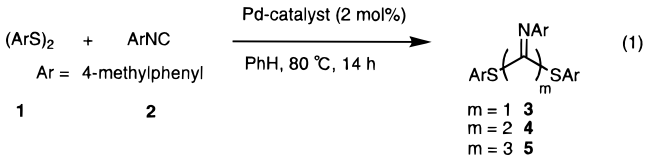


Figure 1. Reactions performed using 1.0 mmol of **1**, 1.0 mmol of **2**, and 2 mol % of $Pd(PPh_3)_4$ in PhH (1 mL) at 80 °C. After the reactions were stopped, the reaction mixtures were directly subjected to PTLC. Isolated yields are based on **1**.



(1)

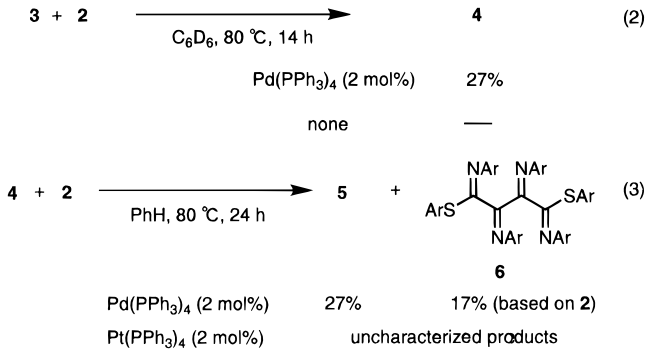
Table 1. Effects of Catalysts on the Reaction of **1** with **2**[a]

			isolated yields (%)[b]		
entry	**2** (equiv)	catalyst	**3**	**4**	**5**
1	1	$Pd(PPh_3)_4$	41	23	4
2	2	none	*c*	*c*	*c*
3	2	$Pd(PPh_3)_4$	28	57	5
4	3	$Pd(PPh_3)_4$	15	70	8
5	4	$Pd(PPh_3)_4$	3	81	10
6[d]	2	$Pd(PPh_3)_4$	30	19	1.7
7	2	$Pd(SPh)_2$	18	49	1.3
8	2	$PdCl_2$	8	25	2
9	2	$Pt(PPh_3)_4$	*e*	*e*	*e*

[a] Reactions were performed using 0.5 mmol of **1**, 1−4 equiv of **2**, and 0.01 mmol of $Pd(PPh_3)_4$ in PhH (1 mL) at 80 °C for 14 h. [b] Based on **1**. [c] Starting 1 and 2 were recovered. [d] 50 °C. [e] Uncharacterized compounds were obtained.

was carried out in the presence of 2 mol % of $Pd(PPh_3)_4$ in benzene solution at 80 °C for 14 h, **3**, **4**, and **5** were obtained in 41%, 23%, and 4% yields (based on **1**), respectively (entry 1).[12] No reaction took place without catalyst (entry 2). The 1:2 adduct **4** was formed up to 81% isolated yield, when an excess amount of **2** for **1** was employed under otherwise identical conditions (entry 5). The reaction at lower temperature (50 °C) provided **3** as a major product (entry 6). Among the complexes examined, $Pd(SPh)_2$ and $PdCl_2$ were also active as catalysts (entries 7 and 8). It should be noted that platinum-catalyzed reactions hardly proceeded, only to give a small amount of an uncharacterized mixture (entry 9). Other transition-metal complexes, such as $Ru_3(CO)_{12}$, $Rh(PPh_3)_3Cl$, and Cu_2O,[13] did not show any catalytic activities.

To obtain insights about the reaction path giving 1:*m* adducts ($m \geq 2$), we examined some reactions as follows. First, the products of the Pd-catalyzed reaction of **1** with **2** (1 equiv) were monitored at 80 °C. The result shown in Figure 1 demonstrates that **3**, **4**, and **5** were formed competitively from the early stage of the reaction. When the reaction of **3** with **2** was carried out at 80 °C in the presence of 2 mol % of $Pd(PPh_3)_4$, **4** was produced in 27% yield after 14 h (eq 2). The palladium catalyst



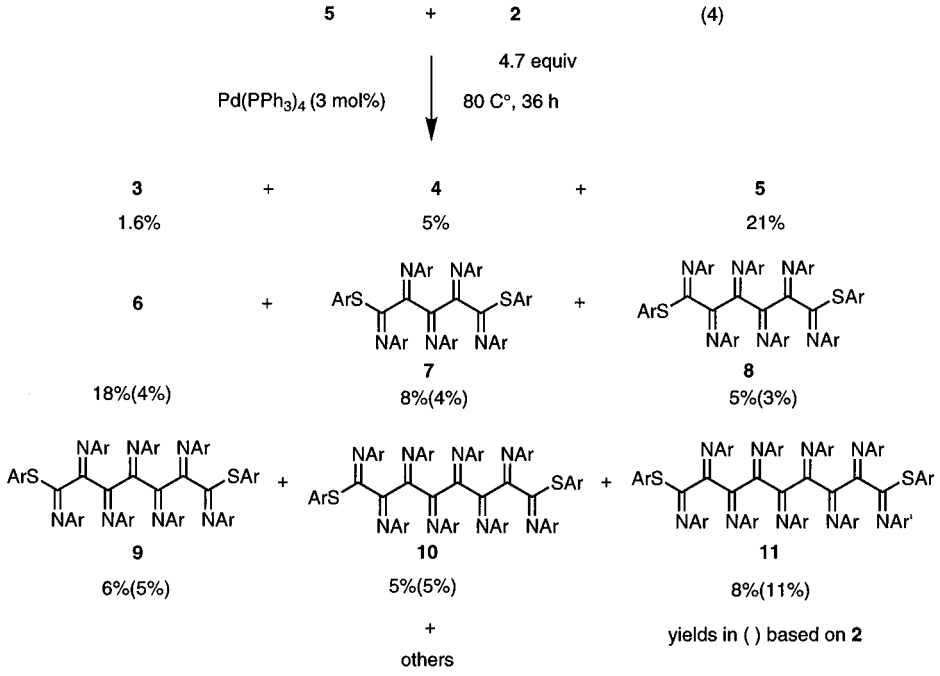
(2)

(3)

was also effective for the reaction of **4** with **2** to give 27% of **5** and 17% (based on **2**) of 1:4 adduct **6** at 80 °C for 24 h (eq 3). Subjection of **5** to **2** (4.7 equiv) in the presence of 3 mol % of $Pd(PPh_3)_4$ at 80 °C for 36 h provided a mixture of adducts

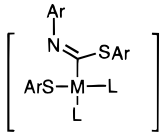
(12) For the utility of 1:*m* adducts in organic synthesis, see: (a) Alcaide, B.; Dominguez, G.; Plumet. J.; Sierra, M. A. *J. Org. Chem.* **1992**, *57*, 447. (b) Reddy, T. I.; Bhawal, B. M.; Rajappa, S. *Tetrahedron Lett.* **1992**, *33*, 2857. (c) Ueno, Y.; Nakai, T.; Okawara, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1933. (d) Milzner, K.; Seckinger, K. *Helv. Chim. Acta* **1974**, *57*, 1614.

(13) Saegusa, T.; Ito, Y. *Synthesis* **1975**, 291.



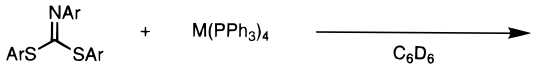
(eq 4). We were able to isolate **6** (18%), 1:5 adduct **7** (8%), 1:6 adduct **8** (5%), 1:7 adduct **9** (6%), 1:8 adduct **10** (5%), 1:9 adduct **11** (8%), and **5** (recovered, 21%) by PTLC and HPLC (no **2** was recovered). Other uncharacterized complex products, which would have incorporated more than 10 molecules of **2** were also obtained. It should be noted that the isocyanide deinserted products **3** (1.6%) and **4** (5%) were also obtained.

To shed light on the mechanism giving 1:1 adduct **3**, we followed the stoichiometric reactions using **1**, **2**, and $M(PPh_3)_4$ (M = Pd) by ^{1}H NMR spectra (Scheme 2). The reaction of $Pd(PPh_3)_4$ (0.02 mmol) with **1** (0.02 mmol) in benzene-d_6 (0.7 mL) gave a mixture of $Pd(SAr)_2(PPh_3)_2$ (**12**) (34%) and $[Pd(SAr)_2(PPh_3)]_2$ (**13**) (44%) at room temperature (rt) within 5 min as determined against an internal standard.[14] This accords with the published report by Graziani *et al.* that the oxidative addition of aromatic disulfides to $Pd(PPh_3)_4$ produced monomeric or dimeric bis(arylthio)palladiums.[15] After 1.5 h, the signals of the monomer **12** disappeared and **13** has started to precipitate as a red solid. This oxidative addition was retarded as the reaction proceeded due to the liberation of free PPh_3 but completed in 12 h to give **13** almost quantitatively as a red solid (no peak of **1**). When 1.0 equiv of **2** was added into the reaction mixture, the solid **13** disappeared gradually, and after 3 h, the solution became homogeneous. The ^{1}H NMR spectrum showed the formation of $Pd(SAr)_2(CNAr)(PPh_3)$ (**14**) in 85% yield (*cis*/*trans* = 10/90).[14] The stereochemistry of **14** was assigned by Me signals on Ar groups on the basis of three equal intensity signals for the *cis*-isomer and two 1:2 intensity signals for the *trans*-isomer, respectively. When the sample was heated at 80 °C, the decomposition of **14** was observed, but the formation of **3** was not confirmed at all. On the other hand, the treatment of **14** (prepared by the same procedure) *with another 1 equiv of 1* afforded **3** in 61% and 73% yields (based on **2**) after 4 and 15 h accompanied with a formation of red precipitation of **13**. The last step would involve unprecedented insertion of isocyanide into the Pd−S bond to provide α-thioimidoyl palladium complex $Pd[(C{=}NAr)(SAr)](SAr)L_2$ (**15**) and subsequent C−S bond-forming reductive elimination.[16] Thus to expect the



M = Pd, **15**
M = Pt, **20**

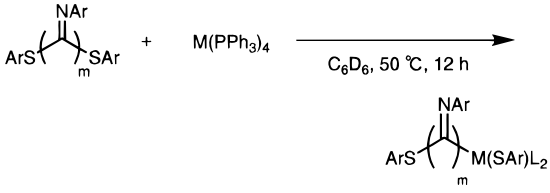
formationof **15** by the reverse pathway, namely, the oxidative addition of C−S bond of **3** to Pd^0L_n, we carried out the stoichiometric reaction of **3** with $Pd(PPh_3)_4$ (eq 5). Interestingly, these reacted gradually at room temperature to give **14** in 70% and 87% yields (*cis*/*trans* = 10/90) after 5 and 20 h, although no intermediates were detected during the course of reaction.



3 + $M(PPh_3)_4$ → (C_6D_6) → **14** (**19**) (5)

M = Pd; r.t., 5 h	70% (*cis*/*trans* = 10/90)
20 h	87%
M = Pt; r.t., 5 h	no reaction
50 °C, 42 h	60% (*cis*/*trans* = 83/17)

As the reactions in eqs 3 and 4 are thought to be initiated by the oxidative addition of 1:*m* adducts to $Pd(PPh_3)_4$, stoichiometric reactions of **4** or **5** with $Pd(PPh_3)_4$ were carried out (eq 6). However, the reactions gave only small amounts of complicated products, but the formation of imidoyl palladium $Pd[(C{=}NAr)_m(SAr)](SAr)L_2$ (**16**) was not confirmed in both cases.



4 (m = 2), **5**, (m = 3) + $M(PPh_3)_4$ → (C_6D_6, 50 °C, 12 h) → (6)

4 (m = 2), **5**, (m = 3)	M = Pd	**16** not confirmed
4 (m = 2)	M = Pt	**21**, L = PPh_3 64% (*cis*/*trans* = 9/91)

(14) The complex **12** was confirmed only *in situ* because of fast dimerization to **13**. The authentic **13**, **14**, **18**, and **19** were synthesized and fully characterized. See the Experimental Section.

(15) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736.
(16) Barañano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

Scheme 2

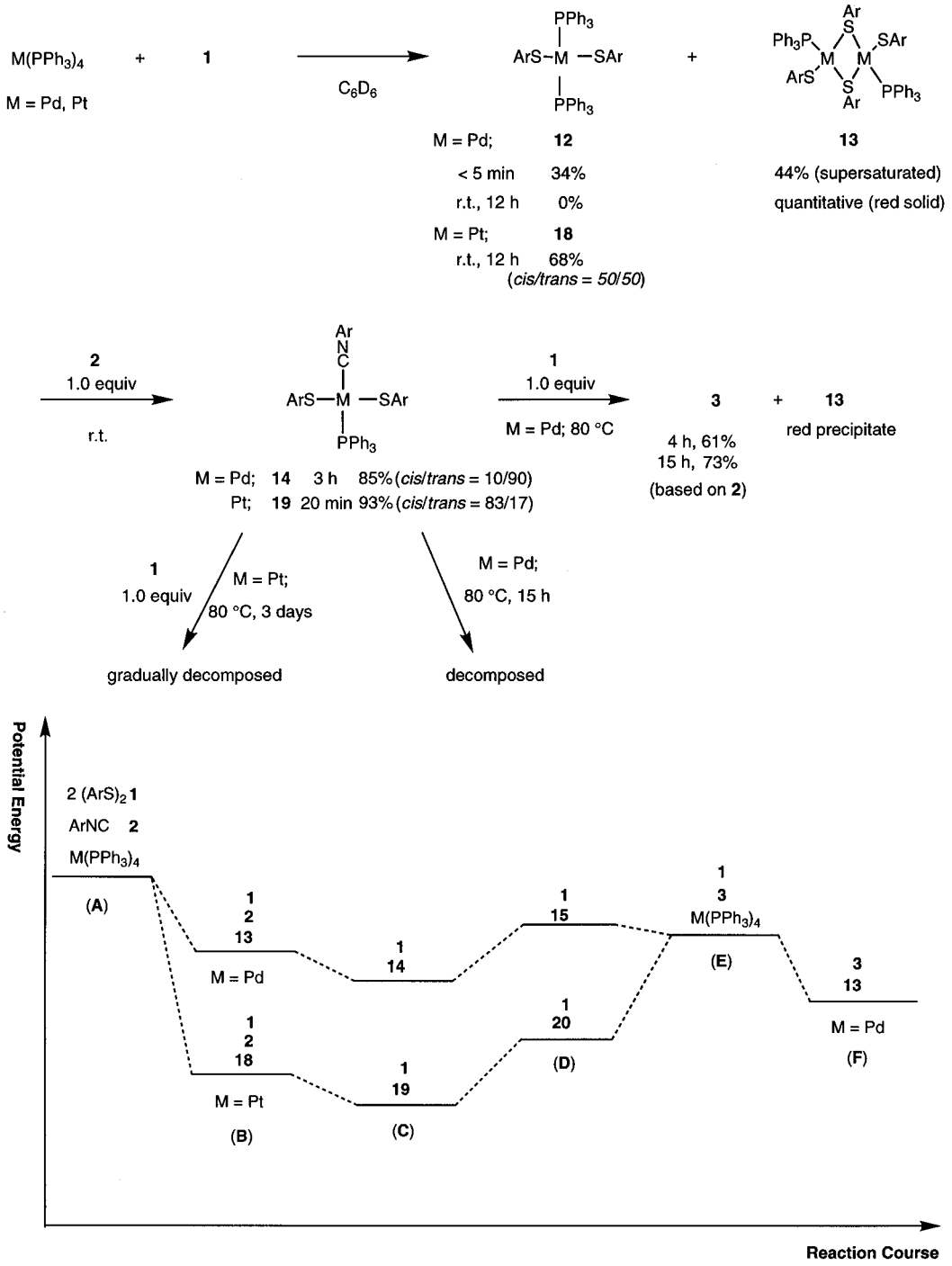


Figure 2. Predicted qualitative reaction coordinate diagrams (free PPh_3's omitted).

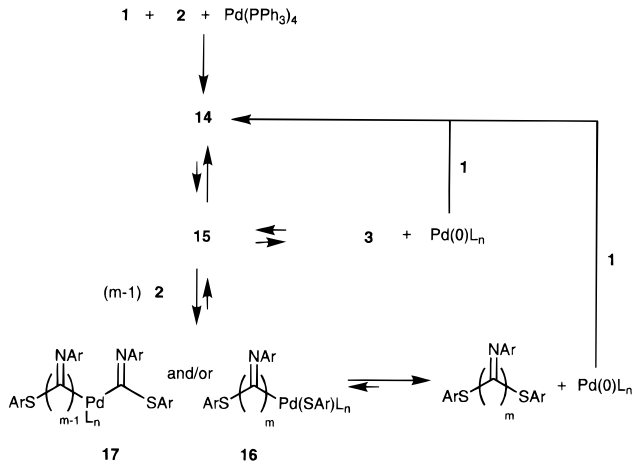
The foregoing experiments demonstrate the following. The results shown in Scheme 2 and eq 5 allow us to predict the relative free energies starting from a reaction system consisting of 2 equiv of **1**, 1 equiv of **2**, and 1 equiv of $Pd(PPh_3)_4$ (system **A**, M = Pd, Figure 2). Both the oxidative addition of **1** to $Pd(PPh_3)_4$ to give **13** and the coordination of **2** to **13** to provide **14** lower the total energy (**A** > **B** (**1**, **2**, and **13**) > **C** (**1** and **14**)).

The system **E**, *i.e.*, the combination of **1** and **3** with $Pd(PPh_3)_4$, should be lower than system **A** because Pd complexes do catalyze the reaction of **1** with **2** to afford **3**. As **14** is also produced by the reaction of **3** with $Pd(PPh_3)_4$ without detecting **15** at room temperature, systems **E** and **D** (**1** and **15**) must be higher than **C**. The relative position between **D** and **E** remains ambiguous, but **D** is at least not so high as to suppress the conversion from **E** to **C** at room temperature. Furthermore, now that the reaction of **14** with **1** gave **3**/**13**, system **F** (**3**/**13**) should be lower than **C**. The existence of route **E** to **C** and route **C** to **F** indicates that both the insertion of isocyanide into Pd−S bond (**C** to **D**) and the reductive elimination of **3** from **15** (**D** to **E**) are reversible. And the equilibrium between **C** and **D** would lean to the former side, *i.e.*, deinsertion direction with low reaction barrier. Therefore the α-thioimidoyl palladium **15** is kinetically unstable and not detected as an intermediate.[17]

Under the actual Pd-catalyzed reaction (eq 1, Table 1), the formation of **14** would be the initiation of the catalytic reaction (Scheme 3).[18] From the complex **15**, reductive elimination of **3** and the further insertion of isocyanide(s) giving Pd-

(17) The attempted reaction of **3** with $Pd_2(dba)_3$/dppe to confirm the α-thioimidoyl palladium also provided isocyanide deinserted $Pd(SAr)_2$(dppe).

Scheme 3. Mechanism of Pd-Catalyzed Reaction of **1** with **2**



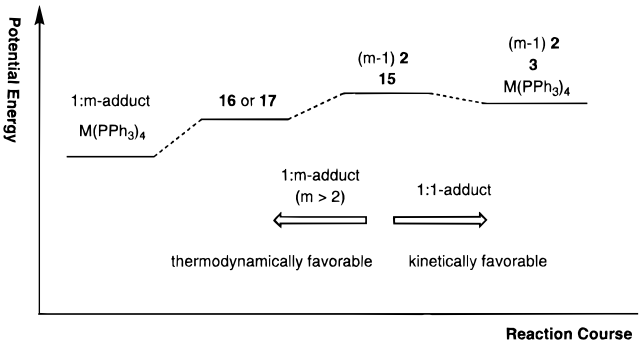


Figure 3. Reaction fate of **15**.

$[(C{=}NAr)_{m-1}(SAr)][(C{=}NAr)(SAr)]L_n$ **17** and/or **16** ($m \geq 2$) take place competitively (Figure 1). Both paths are reversible (note the formation of **3** and **4** in eq 4), but the former is kinetically favorable and the latter is thermodynamically favorable (Figure 3) (compare entry 3 with entry 6 of Table 1). As the concentration of **2** is increased, more isocyanides are incorporated into the products (Table 1, entries 1, 3, 4, and 5). The 1:*m* adducts could reenter into the catalytic cycle (eqs 2−4), but the equilibrium between the imidoyl palladiums **16** and 1:*m* adduct/Pd^0L_n predominantly leans to the latter side when $m \geq 2$ (eq 6). This is why the 1:2 adduct **4** becomes a major product by the reaction of **1** even with an excess amount of **2** under 14 h of reaction time (Table 1, entry 5). The reaction path of the formation of 1:*k* adducts from 1:*m* adducts ($m \geq 2$, $k \neq m$) is only important under the very low concentration of **1** or in the absence of **1** (eqs 2−4). As far as **1** is used as a reactant, Pd^0L_n would react predominantly with **1** to afford **14** as the resting state of the reaction (Scheme 3).[19] Because $Pd(SPh)_2$ and $PdCl_2$ had considerable catalytic activity (Table 1, entries 7 and 8), phosphine-free bis(arylthio)palladium complexes like $Pd(SAr)_2(CNAr)_2$ would be also active as catalysts.[20]

Comparison with Platinum Complex. The stoichiometric reactions using a platinum complex, which did not catalyze the reaction of **1** with **2** (Table 1, entry 9) were examined to elucidate the contrastive outcome by the metals. As also shown in Scheme 2, the oxidative addition of **1** to $Pt(PPh_3)_4$ gave

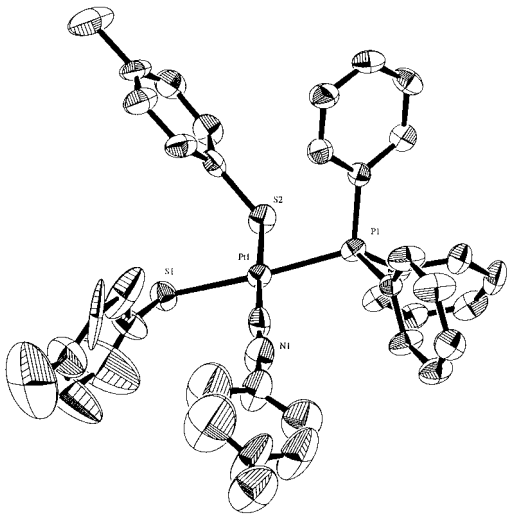


Figure 4. ORTEP diagram of *cis*-**19**.

monomeric complex $Pt(SAr)_2(PPh_3)_2$ **18** in 68% yield (50/50).[14,15,21,22] The coordination of **2** to **18** took place to afford $Pt(SAr)_2(CNAr)(PPh_3)$ (**19**) for 20 min in 93% yield (*cis*/*trans* = 83/17).[14] Compound *cis*-**19** was characterized crystallographically and found to exhibit approximately square planar coordination geometry with the bond distances of S(1)−Pt (2.333(4) Å) and S(2)−Pt (2.330(3) Å), reflecting similar *trans*-influence of ArNC and PPh_3 (Figure 4). The other bond distances of P−Pt, C−Pt, and N−C were 2.274(4), 1.84(2), and 1.17(2) Å, respectively. Unlike the corresponding palladium analogue **14**, however, **19** did not provide **3** at all even in the presence of **1** at 80 °C for 3 days (gradually decomposed),[23] while $Pt(PPh_3)_4$ also reacted with **3** to provide **19** in 60% yield at 50 °C for 42 h (*cis*/*trans* = 83/17) without detecting the α-thioimidoyl platinum complex **20** (eq 2).

Contrary to the case of palladium complex, the Pt-catalyzed reaction of **4** with **2** hardly proceeded and gave a small amount of uncharacterized mixture (eq 3). On the other hand, the stoichiometric reaction of **4** with $Pt(PPh_3)_4$ successfully afforded an imidoyl platinum complex $Pt[(C{=}NAr)_2SAr](SAr)(PPh_3)_2$ (**21**) provided by the oxidative addition of C−S bond to Pt(0)-L_n in 64% yield (*cis*/*trans* = 9/91) (eq 6). An intense singlet at δ −131.46 ($P(OMe)_3$ as a reference; J_{Pt-P} = 3175 Hz) of ^{31}P NMR helped us to assign the major isomer as *trans*. The structure of *trans*-**21** in solid state was unambiguously confirmed by X-ray crystallographic analysis (Figure 5). The crystal data were monoclinic, space group $P2_1/n$ (no. 14), with a = 10.576(2) Å, b = 21.664(2) Å, c = 26.694(2) Å, β = 100.29(1)°, Z = 4, and R = 0.059. The bond distances of S_2−Pt, P_1−Pt, P_2−Pt, and C−Pt were 2.399(3), 2.300(3), 2.309(3), and 2.02(1) Å, respectively.

Then the stoichiometric reaction of *trans*-**21** with **1** was carried out to ascertain the possibility of the generation of **4** and Pt^0L_n, which would be trapped by **1** to afford **18** (eq 7). Leaving the sample at room temperature for 4 h, only ended up with the isomerization (*cis*/*trans* = 6/94). And upon heating

(18) The oxidative addition of **1** to $Pd(PPh_3)_4$ in the presence of 3 equiv of **2** provided **14** without forming **12** and **13**, implying the precedence of coordination of **2** to Pd(0) over the oxidative addition or fast coordination of **2** to **12** in the actual catalytic condition.

(19) The competitive oxidative addition of **1** with **3** to $Pd(PPh_3)_4$ showed that Pd(0) exclusively reacted with **1** over **3**.

(20) It has been reported that the formation of $Pd(SAr)_2(CNR)_2$ by the reaction of $Pd(SAr)_2$ with RNC, see: Rauchfuss, T. B.; Shu, J. S.; Roundhill, D. M. *Inorg. Chem.* **1976**, *15*, 2096.

(21) The dimer $[Pt(SAr)_2(PPh_3)]_2$ was also produced under more severe reaction conditions, demonstrating that the dimer was also thermodynamically more stable than monomer **18**. See the Experimental Section.

(22) The stereochemistry of **18** was not able to be assigned by the coupling constant J_{Pt-P} because of similar *trans*-influence of PPh_3 and ArS (J_{Pt-P} = 2898 Hz vs 2917 Hz), see: (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1299.

(23) In solution, the pure *cis*-**19** isomerized to a stereomixture of *cis*/*trans* = 83/17 within 5 min in the presence of PPh_3, so the different reactivities of the metal complexes would not rely on the different geometry of the complexes.

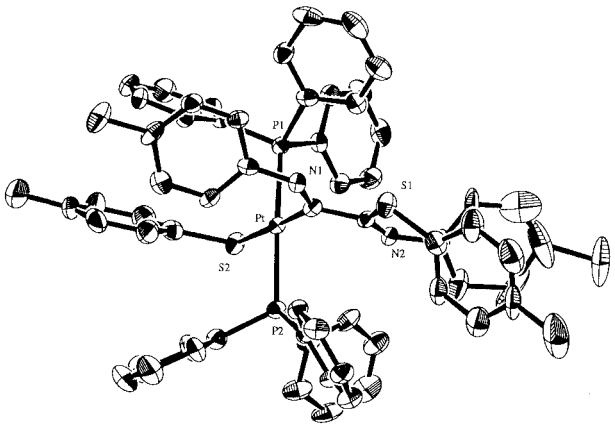
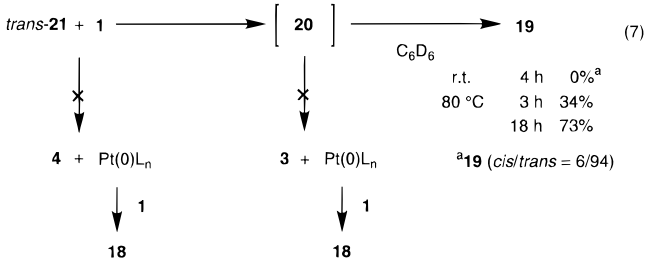


Figure 5. ORTEP diagram of *trans*-**21**.



(7)

at 80 °C, **19** was formed by the successive deinsertion of isocyanides in 34% and 73% yield after 3 and 18 h, respectively, with complex byproducts; however, no formations of **4**, **3**, **18**, **20** and even free **2** were confirmed.

The different reactivities of the metal complexes described above can be explained as follows. As the oxidative addition of **1** to the metals involves the formal charge change from M(0) to M(II), the platinum species would lie much lower than the corresponding palladium species in **B** and **D** (inevitably also in **C**) in Figure 2. Therefore, in marked contrast to the palladium complexes, *there would not be equilibrium between **C** and **E***.[24] It is not clear whether there is an equilibrium between **C** and **D**, but the imidoyl platinum complex **20**, if generated, does not reductively eliminate **3** (eq 7). The results of metal-catalyzed reaction of **4** with **2** (eq 3) and the trend of the oxidative addition **4** to $M(PPh_3)_4$ (eq 6) also can be understood on the basis of the same concept.

Structure of Adducts. The NMR spectra of the adducts $(ArS)(C{=}NAr)_m(SAr)$ showed temperature dependence due to the fluxional movement of the molecules. In the ^1H NMR spectrum of **3**, Ar group on S appeared as broad peaks by the inversion of N lone pair on the imino group (Scheme 4).[25] In the case of **4**, three isomers, *anti*−*anti*, *anti*−*syn*, and *syn*−*syn*, are possible as shown in Scheme 5. In benzene solution, the ^1H NMR spectrum of **4** at 25 °C appeared as a mixture of two isomers with broad signals in a ratio of ca. 95/5 (stereochemistry undetermined). On the other hand, in the solid state, **4** had *syn*−*syn* structure with twisted configuration between C═N bonds (Figure 6). As for the 1:*m* adducts ($m \geq 3$), ^1H NMR spectra were not simple because of the presence of several isomers. The X-ray diffraction of 1:4 adduct **6** (Figure 7), however, showed that there was an inversion center, central C═N bonds lay in the same plane with *anti*-configuration, and terminal ArN and ArS groups took *syn*-configuration twisting to the center C═N bonds similar to 1:2 adducts **4**.

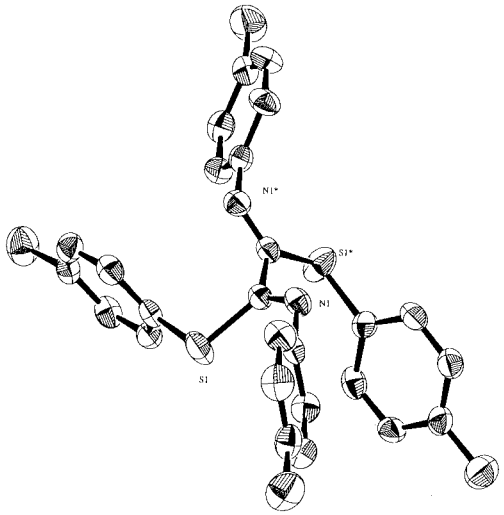


Figure 6. ORTEP diagram of **4**.

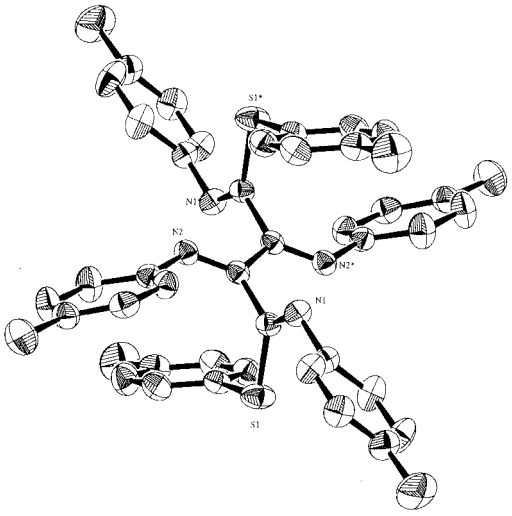
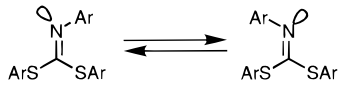


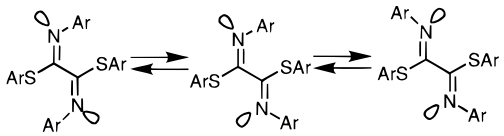
Figure 7. ORTEP diagram of **6**.

Scheme 4



3

Scheme 5



4

Conclusion

While the insertion of isocyanides into M−C,[26] M−H,[27] and non-carbon analogue M−Si[28] bonds have been well-docu-

(24) Goddard *et al.* have demonstrated the differences of C−C or C−H reductive elimination between palladium(II) and platinum(II) complexes by *ab initio* calculation, see: Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc*. **1984**, *106*, 6928.

(25) (a) Clericuzio, M.; Alagona, G.; Ghio, C.; Salvadori, P. *J. Am. Chem. Soc*. **1997**, *119*, 1059. (b) Christian, D. F; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem*. **1976**, *112*, 209. (c) Saegusa, T.; Bobayashi, S.; Hirota, K.; Okumura, Y.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1638.

(26) For example: (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.

mented, other examples of insertion into M−E (E = heteroatom) bonds have been extremely rare.[29,30] This study described a novel palladium-catalyzed reaction and its mechanistic study, demonstrating the reversibility of the insertion of isocyanide into Pd−S bond. The different reactivities of isocyanide and thiolate ligands between palladium and platinum complexes were rationalized uniformly on the basis of the relative stability of the oxidation state of the metal complexes.

Experimental Section

^{1}H, ^{13}C, and ^{31}P NMR spectra in benzene-d_6, $CDCl_3$, and CD_2Cl_2 solution were recorded with JEOL JNM-GSX-270 (270 MHz) and JEOL JSX-400 (400 MHz) spectrometers. Chemical shifts in the ^{1}H spectra were recorded relative to Me_4Si or C_6H_6 (δ 7.16). Chemical shifts in the ^{13}C spectra were recorded relative to Me_4Si, C_6D_6 (δ 128.0), or $CDCl_3$ (δ 77.0). Chemical shifts in the ^{31}P spectra were recorded relative to $P(OMe)_3$ 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 **1** was prepared according to the literature.[31] Disulfides and dppe were obtained commercially. 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 prepared according to the literature.[32,33] $Pd(SPh)_2$ was prepared by the reaction of $Pd(OAc)_2$ with 2 equiv of PhSH in THF at room temperature. Other transition-metal complexes were obtained commercially. Preparative TLC was carried out using Wakogel B-5F silica gel. Purification of 1:*m* adducts ($m \geq 3$) 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 *cis*-**19**, *trans*-**21**, **4**, and **6** are summarized in the Supporting Information. All ORTEP drawings in Figures 4−7 are shown in 30% probability ellipsoids.

Palladium-Catalyzed Reaction of 1 with 2 (Eq 1, Table 1): General Procedure (Entry 1). Preparation of 3, 4 and 5. Into a dry two-necked flask equipped with a reflux condenser and a magnetic stirring bar were placed $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), **1** (123 mg, 0.5 mmol), **2** (59 mg, 0.5 mmol), and benzene (1.0 mL) under an argon atmosphere. After the solution was refluxed with stirring for 14 h, ca. 15 mL of hexane was added into the solution. Then, the colorless precipitation **4** was separated by filtration and washed by hexane (10 mL × 3). And the filtrate combined was evaporated *in vacuo* and separated by PTLC (a mixture of hexane and Et_2O (9:1) as an eluent). The combined products and yields were 75 mg of **3** (41%), 55 mg of **4** (23% based on **1**), and 15 mg of **5** (4% based on **1**). The 1:2 adduct **4** was recrystallized from THF and hexane. All reactions listed in Table 1 were conducted and analyzed similarly. The catalysts, reaction conditions, and the yields of the products are listed in Table 1. Reaction times were unoptimized. The $Pt(PPh_3)_4$-catalyzed reaction provided 26 mg of brown uncharacterized mixture (more than 10 fractions by PTLC).

3: mp 129 °C (a colorless solid); ^{1}H NMR (270 MHz, $CDCl_3$ at rt) δ 2.29 (s, 3 H), 2.34 (s, 6 H), 6.76 (d, J = 8.3 Hz, 2 H), 7.08 (d, J = 8.3 Hz, 2 H), 7.16 (d, J = 7.3 Hz, 4 H), 7.44 (br s, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$ at rt) δ 20.89, 21.35, 120.07, 129.34, 129.77, 133.38, 135.0−137.0 (br), 147.28, 161.30; IR (KBr) 3024, 2918, 1572, 1502, 1492, 953, 941, 921, 807, 506, 492 cm^{-1}; mass spectrum (EI) 363 (M^+, 5). Anal. Calcd for $C_{22}H_{21}NS_2$: C, 72.69; H, 5.82; N, 3.85; S, 17.64. Found: C, 72.98; H, 5.78; N, 3.81; S, 17.35.

4: mp 194 °C (an off-white solid); ^{1}H NMR (270 MHz, $CDCl_3$ at rt) of a major isomer δ 2.30 (s, 6 H), 2.42 (s, 6 H), 6.31 (d, J = 8.1 Hz, 4 H), 7.05 (d, J = 8.1 Hz, 4 H), 7.21 (d, J = 7.8 Hz, 4 H), 7.54 (d, J = 7.8 Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$ at rt) δ 20.94, 21.25, 119.56, 125.46, 129.36, 129.65, 134.44, 136.58, 140.00, 145.52, 159.25; IR (KBr) 3020, 2920, 1626, 1603, 1502, 1490, 888, 811, 494 cm^{-1}; mass spectrum (EI) *m*/*e* 480 (M^+, 2). Anal. Calcd for $C_{30}H_{28}N_2S_2$: C, 74.96; H, 5.87; N, 5.83; S, 13.34. Found: C, 74.86; H, 5.96; N, 5.78; S, 13.10.

5: mp 61−62 °C (an orange solid); ^{1}H NMR (270 MHz, $CDCl_3$ at rt) of a major isomer δ 2.81 (s, 3 H), 2.32 (s, 3 H), 2.34 (s, 6 H), 2.36 (s, 3 H), 6.60−6.90 (m, 8 H), 7.01−7.28 (m, 12 H); ^{13}C NMR (68 MHz, $CDCl_3$ at rt) δ 21.00, 21.11, 21.29, 119.58, 119.82, 121.63, 124.71, 127.83, 128.65, 128.96, 129.01, 129.36, 129.62, 133.35, 134.33, 134.52, 135.59, 135.66, 137.42, 139.80, 144.50, 145.78, 146.65, 156.46, 160.61, 162.71; IR (KBr) 3023, 2920, 1606, 1501, 1449, 1197, 1107, 1018, 865, 807, 590 cm^{-1}; mass spectrum (EI) *m*/*e* 597 (M^+, 18). Anal. Calcd for $C_{38}H_{35}N_3S_2$: C, 76.35; H, 5.90; N, 7.03. Found: C, 76.61; H, 5.93; N, 7.25.

Monitoring the Pd-Catalyzed Reaction of 1 with 2 (Figure 1). Into six dry 5 mL two-necked flasks equipped with a reflux condenser and a magnetic stirring bar were placed $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), **1** (246 mg, 1.0 mmol), **2** (117 mg, 1.0 mmol), and benzene (1.0 mL) under an argon atmosphere. Then each flask was put into a hot oil bath (>80 °C). After the heating was continued for certain periods, the oil bathes were removed and replaced with ice bathes quickly. Then the reaction mixture was analyzed by a procedure similar to that as listed in Table 1. The reaction time, yield of **3**, yield of **4**, yield of **5** were as follows: 5 min, 15%, 6.3%, 1.3%; 10 min, 18%, 8.0%; 1.8%; 15 min, 21%, 8.0%, 1.8%; 30 min, 23%, 11%, 2.4%; 60 min, 25%, 12%, 2.7%; 120 min, 27%, 14%, 2.9%. (The reaction was not able to be followed by ^{1}H NMR and GLC because the products did not show good separation by ^{1}H NMR and the compound **5** was not detected by GLC.)

The Reaction of 3 with 2 (Eq 2). In a dry Pyrex NMR tube were added **3** (72 mg, 0.2 mmol), **2** (26 mg, 0.22 mmol), $Pd(PPh_3)_4$ (4.6 mg, 0.004 mmol), and benzene-d_6 (0.7 mL). After the sample was sealed under reduced pressure, the sample was heated at 80 °C for 14 h. The formation of **4** was confirmed in 27% yield by ^{1}H NMR. On the other hand, the reaction of **3** and **2** in the absence of catalyst did not take place under the same reaction conditions.

$Pd(PPh_3)_4$-Catalyzed Reaction of 4 with 2 (Eq 3). Into a dry two-necked flask equipped with a reflux condenser and a magnetic stirring bar were placed $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), **4** (240 mg, 0.5 mmol), **2** (71 mg, 0.6 mmol), and benzene (1.0 mL) under an argon atmosphere. After the solution was refluxed with stirring for 24 h, ca. 30 mL of hexane was added into the solution. The light yellow solid (140 mg, **4** (58%)) was separated by filtration and the filtrate was combined and evaporated *in vacuo*. Then the reaction mixture was purified by PTLC (a mixture of hexane and Et_2O (9:1) as an eluent) to give 36 mg of **5** (27% based on **4**) and 80 mg of 1:4 adduct **6** (17% based on **2**). The compound **6** was recrystallized from benzene.

6: mp 193−195 °C (an yellow crystal); ^{1}H NMR (270 MHz, $CDCl_3$ at rt) of a major isomer δ 2.15 (s, 3 H), 2.23 (s, 3 H), 2.29 (s, 3 H), 2.32 (s, 6 H), 2.43 (s, 3 H), 6.33 (d, J = 8.1 Hz, 2 H), 6.71 (d, J = 8.1 Hz, 2 H), 6.75 (d, J = 8.1 Hz, 2 H), 6.91 (d, J = 8.1 Hz, 2 H), 6.98−7.15 (m, 12 H), 7.23 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (270 MHz, $CDCl_3$ at rt) δ 21.00−21.80 (br), 119.18, 119.43, 122.49, 124.17, 127.48, 128.85, 129.04, 129.50, 129.92, 130.78, 133.84, 134.03, 134.24, 134.70, 134.88, 135.96, 137.39, 139.84, 145.00, 145.35, 145.75, 145.96, 146.76, 159.37, 159.80, 160.17, 161.45; IR (KBr) 3023, 2919, 1625, 1501, 1448, 1216, 869, 822, 485 cm^{-1}; mass spectrum (EI) *m*/*e* 714 (M^+, 5). Anal. Calcd for $C_{46}H_{42}N_4S_2$: C, 77.28; H, 5.92; N, 7.84.; S, 8.97. Found: C, 77.36; H, 5.92; N,7.85; S, 8.79.

Oligomerization of Isocyanide by the Reaction of 5 with 2 (Eq 4). Into a dry two-necked flask equipped with a reflux condenser and a magnetic stirring bar were placed $Pd(PPh_3)_4$ (6.3 mg, 0.0055 mmol),

(27) (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.

(28) (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.

(29) (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.

(30) Crociani, B.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, 127.

(31) (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.

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

(33) Ukai, T.; Kawazura, H.; Isii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

5 (120 mg, 0.2 mmol), **2** (109 mg, 0.93 mmol), and benzene (1.0 mL) under an argon atmosphere. After the solution was refluxed with stirring for 36 h, the reaction mixture was separated by PTLC and then HPLC. From 1:1 to 1:9 adducts were isolated and assigned by ^{1}H NMR and mass spectra; however, the products which have larger mass number were not able to be assigned. The products and their yields (based on **5** and **2**) were as follows: 1:1 adduct **3**, 1.2 mg (1.6%); 1:2 adduct **4**, 5 mg, (5%); 1:3 adduct **5** recovered, 25 mg (21%); 1:4 adduct **6**, 25 mg (18% (4%)); 1:5 adduct **7**, 8 mg (8% (4%)); 1:6 adduct **8**, 9 mg (5% (3%)); 1:7 adduct **9**, 12 mg (6% (5%)); 1:8 adduct **10**, 11 mg (5% (5%)); 1:9 adduct **11**, 22 mg (8% (11%)), and undetermined compounds, 61 mg combined. The mass spectra of these undetermined products showed 1404, 1527, and 1644 as fragments which correspond to $(C{=}NAr)_{12}$, $(ArS)(C{=}NAr)_{12}$, and $(ArS)(C{=}NAr)_{13}$ fragments, indicating more than 10 isocyanides were incorporated into the molecules.

7: mp 73−74 °C (an yellow solid); ^{1}H NMR (270 MHz, C_6D_6 at rt) of a major isomer δ 1.78 (s, 6 H), 1.99 (s, 3 H), 2.05−2.13 (9 H), 2.18 (s, 3 H), 6.56 (d, J = 7.8 Hz, 4 H), 6.67 (d, J = 8.3 Hz, 2 H), 6.81−7.28 (m, 16 H), 7.37−7.41 (6 H); IR (KBr) 3023, 2921, 1630, 1611, 1501, 1212, 1198, 1018, 880, 862, 806 cm^{-1}; mass spectrum (EI) *m*/*e* 831 (M^+, 5).

8: mp 222−223 °C (an yellow solid); ^{1}H NMR (270 MHz, C_6D_6 at rt) of a major isomer δ 1.71 (s, 3 H), 1.94 (s, 3 H), 2.05 (s, 3 H), 2.09 (s, 3 H), 2.14 (s, 3 H), 2.14 (s, 3 H), 2.15 (s, 3 H), 2.18 (s, 3 H), 6.52 (d, J = 8.3 Hz, 4 H), 6.65 (d, J = 8.3 Hz, 2 H), 6.95−7.18 (m, 20 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.46 (d, J = 8.3 Hz, 4 H); mass spectrum (EI) *m*/*e* 948 (M^+, 3).

9: mp 215−216 °C (an yellow solid); ^{1}H NMR (270 MHz, C_6D_6 at rt) of a major isomer δ 1.70 (s, 3 H), 1.85 (s, 3 H), 1.86 (s, 3 H), 2.03 (s, 3 H), 2.10 (s, 3 H), 2.15 (s, 3 H), 2.19 (s, 3 H), 2.02 (s, 3 H), 2.23 (s, 3 H), 6.26 (d, J = 8.3 Hz, 2 H), 6.48−6.55 (m, 4 H), 6.65−6.75 (m, 6 H), 6.82−7.38 (m, 18 H), 7.43−7.54 (m, 6 H); IR (KBr) 3024, 2920, 1634, 1593, 1558, 1500, 1446, 1212, 1198, 1018, 878, 807, 706, 518 cm^{-1}; mass spectrum (EI) *m*/*e* 1065 (M^+, 4). Anal. Calcd for $C_{70}H_{63}N_7S_2$: C, 78.84 H, 5.95; N, 9.19; S, 6.01. Found: C, 78.09; H, 6.09; N, 8.85; S, 5.81.

10: mp 232−233 °C (an yellow needle); ^{1}H NMR (270 MHz, C_6D_6 at 60 °C) of a mixture of isomers δ 1.60, 1.79, 1.86, 1.89, 1.94, 2.02, 2.04, 2.08, 2.14, 2.19, 2.23, 2.25, 6.21 (d, J = 8.1 Hz), 6.28 (d, J = 8.1 Hz), 6.50−7.50 (m); ^{13}C NMR (68 MHz, $CDCl_3$ at 45 °C) δ 20.67−21.11 (m), 118.11−121.16; 127.22−129.45 (m); IR (KBr) 3023, 2920, 1631, 1620, 1609, 1597, 1501, 1199, 1037, 1018, 889, 802 cm^{-1}; mass spectrum (EI) *m*/*e* 1182 (M^+, 4). Anal. Calcd for $C_{78}H_{70}N_8S_2$: C, 79.15; H, 5.96; N, 9.47. Found: C, 78.96; H, 5.94; N, 9.34.

11: mp 105−106 °C (an orange solid); ^{1}H NMR (270 MHz, C_6D_6 at rt) of a major isomer δ 1.73 (s, 3 H), 1.83 (s, 6 H), 1.95 (s, 6 H), 2.01 (s, 3 H), 2.18 (br, 15 H), 6.60−7.44 (br, 44 H); IR (KBr) 3023, 2921, 1636, 1606, 1449, 1211, 1197, 862, 807 cm^{-1}; mass spectrum (EI) *m*/*e* 1299 (M^+, 2).

Stoichiometric Reactions of $Pd(PPh_3)_4$ with 1 and Then 2 in NMR Tubes (Scheme 2). In two dry Pyrex NMR tubes were added $Pd(PPh_3)_4$ (21.9 mg, 0.019 mmol), **1** (4.7 mg, 0.019 mmol), and benzene-d_6 (0.7 mL), respectively. The samples were degassed under reduced pressure and purged with Ar several times. After 1,4-dioxane (2.9 mg, 0.033 mmol) was added as an internal standard, the ^{1}H NMR and ^{31}P NMR spectra were taken (<5 min). The formation of $Pd(SAr)_2(PPh_3)_2$ (**12**) (stereochemisty unassigned) and $[Pd(SAr)_2(PPh_3)]_2$ (**13**) (stereochemisty unassigned) was confirmed in 34% and 44% yields, respectively. After 1.5 h the peaks of **12** disappeared and a red solid started to precipitate. After 12 h, the signal of **1** disappeared and only the signals of free PPh_3 and **13** were confirmed by the measurement of ^{1}H NMR. Then, **2** (2.2 mg, 0.019 mmol) was added into the NMR tubes. After 3 h at room temperature, the red solid **13** disappeared and the formation of $Pd(SAr)_2(CNAr)(PPh_3)$ **14** was confirmed in 85% yield (*cis*/*trans* = 10/90). Then a sample was heated at 80 °C and monitored by ^{1}H NMR. Gradual decomposition into complex products was confirmed, but **3** was not detected at all. On the other hand, when another 1 equiv of **1** (4.7 mg, 0.019 mmol) was added into the other sample and the mixture was heated at 80 °C, a gradual formation of **3** was confirmed in 61% and 73% yields (based on **2**) accompanied with a formation of red precipitate **13** after 4 and 15 h, respectively.

Confirmation of 12. To retard the dimerization of **12** to **13**, the reaction of **1** with $Pd(PPh_3)_4$ was carried out in the presence of an excess amount of PPh_3. After **1** (2.5 mg, 0.01 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), PPh_3 (26.2 mg, 0.1 mmol), and benzene-d_6 (0.6 mL) were added into a dry NMR tube, ^{1}H and ^{31}P NMR spectra were taken. The peaks of **12** close to the corresponding platinum complex **18** were confirmed in 18% yield (one isomer; stereochemistry undetermined).

12: ^{1}H NMR (400 MHz, C_6D_6) δ 2.08 (s, 6 H), 6.58 (d, J = 8.1 Hz, 4 H), 6.88 (d, J = 8.1 Hz, 4 H), 7.80−7.84 (m, 12 H) (the other peaks were not assigned because of overlapping with the peaks of PPh_3); ^{31}P NMR (149 MHz, C_6D_6) δ −118.05.

Preparation of Authentic 13. In a two-necked dry 50 mL flask equipped with stirring bar were added $Pd(PPh_3)_4$ (1.3 g, 1.1 mmol), **1** (740 mg, 3.0 mmol), and benzene (25 mL). After the mixture was stirred at room temperature for 21 h, the red solid was emptied by filtration. Then the solid was recrystallized from CH_2Cl_2 and hexane to give a dark red needle-shaped crystal.

13: mp 166−167 °C (a dark red solid); ^{1}H NMR (270 MHz, CD_2Cl_2) of a major isomer δ 2.11 (s, 6 H), 2.20 (s, 6 H), 6.52 (d, J = 7.8 Hz, 4 H), 6.61 (d, J = 7.8 Hz, 4 H), 7.07 (d, J = 7.8 Hz, 4 H), 7.09 (d, J = 7.8 Hz, 4 H), 7.24−7.29 (m, 12 H), 7.36−7.43 (m, 18 H); ^{31}P NMR (160 MHz, CD_2Cl_2) of major-isomer δ −113.66 and minor-isomer δ −114.82; IR (KBr) 3056, 3006, 1482, 1433, 1096, 801, 748, 692, 526 cm^{-1}. Anal. Calcd for $C_{64}H_{58}P_2Pd_2S_4$: C, 62.49; H, 4.75. Found: C, 61.95; H, 5.08.

Preparation of Authentic 14. Into a Pyrex NMR tube were added **13** (11.5 mg, 0.0093 mmol), **1** (2.2 mg, 0.019 mmol) and benzene-d_6 (0.7 mL). After the formation of **14** was confirmed at room temperature for 1 h, the reaction mixture was concentrated *in vacuo* and 0.1 mL of CH_2Cl_2 was added. When 0.5 mL of hexane was added into the reaction mixture, a brown solid precipitated. The solution was removed by syringe, and the solid was washed by 0.5 mL × 2 of hexane to give 8.0 mg of **14** (58%).

14: mp 115−117 °C (a brown solid);^{1}H NMR (270 MHz, C_6D_6) of *trans*-isomer δ 1.69 (s, 3 H), 1.99 (s, 6 H), 6.07 (d, J = 7.8 Hz, 2 H), 6.35 (d, J = 7.8 Hz, 2 H), 6.72 (d, J = 7.8 Hz, 4 H). 7.00−7.10 (m, 9 H), 7.87 (d, J = 7.8 Hz, 4 H), 7.90−8.05 (m, 6 H) and *cis*-isomer δ 1.72 (s, 3 H), 1.95 (s, 3 H), 2.07 (s, 3 H), 5.91 (d, J = 7.8 Hz, 2 H), 6.48 (d, J = 7.8 Hz, 2 H) (the other peaks overlapped with the peaks of *trans*-isomer); ^{31}P NMR (160 MHz, C_6D_6) of *trans*-isomer δ −112.09 and *cis*-isomer δ −113.51; IR (KBr) (a mixture of stereoisomers) 3056, 2915, 2196, 1504, 1484, 1434, 1096, 1086, 809, 743, 705, 692, 528, 504 cm^{-1}. Anal. Calcd for $C_{40}H_{36}NPPdS_2$: C, 65.60; H, 4.95; N, 1.91; S, 8.76. Found: C, 65.82; H, 5.27; N, 1.79; S, 8.91.

The Reaction of 3 with $Pd(PPh_3)_4$ (Eq 5). Into a dry Pyrex NMR tube were added **3** (6.8 mg, 0.019 mmol), $Pd(PPh_3)_4$ (21.6 mg, 0.019 mmol), and benzene-d_6 (0.7 mL). Then the tube was purged with Ar and sealed under reduced pressure. By leaving the sample at room temperature, **14** was formed in 70% yield (*cis*/*trans* = 10/90) after 5 h and in 87% yield (**3**, trace) after 20 h.

The Reaction of 4 or 5 with $Pd(PPh_3)_4$ (Eq 6). In a dry Pyrex NMR tube were added **4** (24.4 mg, 0.05 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and benzene-d_6 (0.7 mL). Then the tube was purged with Ar, sealed under reduced pressure, and heated at 50 °C. However, most of the starting **4** remained unreacted, although partial decomposition of **4** was observed after 12 h. The reaction of **5** with $Pd(PPh_3)_4$ also gave only a small amount of undetermined complex products.

The Reaction of 3 with $Pd_2(dba)_3$/dppe (Ref 17). Into a dry Pyrex NMR tube were added **3** (7.3 mg, 0.02 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (10.4 mg, 0.01 mmol), dppe (8.0 mg, 0.02 mmol), and benzene-d_6 (0.7 mL). Then the tube was purged with Ar and sealed under reduced pressure. By leaving the sample at room temperature for 5 h, the formation of $Pd(SAr)_2$(dppe) was confirmed in 45% yield.

$Pd(SAr)_2$(dppe): ^{1}H NMR (270 MHz, C_6D_6) δ 1.83 (d, J_{P-H} = 20.5 Hz, 4 H), 2.01 (s, 6 H), 6.63 (d, J = 8.4 Hz, 4 H), 7.04−7.09 (m, 4 H), 7.25−7.31 (m, 8 H), 7.63 (d, J = 8.4 Hz, 4 H), 7.68−7.76 (m, 8 H).

Oxidative Addition of 1 to $Pd(PPh_3)_4$ in the Presence of 2 (Ref 18). In a dry Pyrex NMR tube were added $Pd(PPh_3)_4$ (23.1 mg, 0.020 mmol), **2** (7.6 mg, 0.065 mmol), and benzene-d_6 (0.7 mL). After the sample was left at room temperature for 10 min, **1** (4.9 mg, 0.020 mmol) was added. The ^{1}H NMR spectrum after 2 h at room temperature showed the formation of **14** in 73% yield. The signals of **14** and **2**

appeared as broad peaks, indicating the exchange of free isocyanide for coordinating isocyanide. No formation of **12** and **13** were confirmed during the course of reaction.

Competitive Oxidative Addition of 1 and 3 to Pd(PPh$_3$)$_4$ (Ref 19). In a dry Pyrex NMR tube were added Pd(PPh$_3$)$_4$ (9.9 mg, 0.0086 mmol), **1** (5.0 mg, 0.020 mmol), **3** (7.3 mg, 0.020 mmol), and benzene-d_6 (0.7 mL). The ^{1}H NMR spectrum after 1.5 h showed the exclusive consumption of **1** accompanied with a formation of red solid **13**.

Stoichiometric Reaction of Pt(PPh$_3$)$_4$ with 1 and Then 2 in a NMR Tube (Scheme 2). In a dry Pyrex NMR tube were added Pt(PPh$_3$)$_4$ (25.0 mg, 0.020 mmol), **1** (4.9 mg, 0.020 mmol), and benzene-d_6 (0.7 mL). By the measurement of ^{1}H and ^{31}P NMR after 12 h at room temperature, the formation of Pt(SAr)$_2$(PPh$_3$)$_2$ **18** was confirmed in 68% yield as a 50/50 stereoisomer. Then **2** (2.3 mg, 0.020 mmol) was added into the NMR tube. After 20 min at room temperature, the formation of Pt(SAr)$_2$(CNAr)(PPh$_3$) (**19**) was confirmed in 93% yields (*cis*/*trans* = 83/17). To the reaction mixture was added **1** (5.1 mg, 0.021 mmol), and the reaction was monitored at 80 °C for 3 days. The gradual decomposition of **19** was observed; however, the formation of **3** was not confirmed at all.

Preparation of Authentic 18. In a two-necked 50 mL flask equipped with a stirring bar were added Pt(PPh$_3$)$_4$ (1.85 g, 1.5 mmol), **1** (738 mg, 3.0 mmol), and benzene (25 mL). After the mixture was stirred at room temperature for 21 h, the yellow solid was separated by filtration. Then the solid was washed by ca. 50 mL of Et$_2$O/hexane (1/1) and dried under reduced pressure to give 475 mg of **18** (33%).

18: one isomer obtained after the purification by PTLC (Et$_2$O/hexane = 1/1 as an eluent; the stereochemistry was undetermined; mp 196 °C (an yellow solid); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.08 (s, 6 H), 6.58 (d, J = 7.8 Hz, 4 H), 6.98 (m, 22 H), 7.86 (m, 12 H); ^{31}P NMR (161 MHz, C$_6$D$_6$) δ −120.32 (J_{Pt-P} = 2898 Hz); IR (KBr) 3055, 1484, 1435, 693, 535 cm^{-1}. Anal. Calcd for $C_{50}H_{44}P_2PtS_2$: C, 62.17; H, 4.59; S, 6.64. Found: C, 62.16; H, 4.88; S, 6.84.

18: the other isomer (the following spectral data were collected from a crude reaction mixture) ^{1}H NMR (270 MHz, C$_6$D$_6$) δ 2.11 (s, 6 H), 6.78 (d, J = 7.8 Hz, 4 H) (the other peaks overlapped with the peaks of the other isomer and PPh$_3$); ^{31}P NMR (161 MHz, C$_6$D$_6$) δ −119.85 (J_{Pt-P} = 2917 Hz).

The Reaction of 3 with Pt(PPh$_3$)$_4$ (Eq 5). In a dry Pyrex NMR tube were added **3** (18.2 mg, 0.05 mmol), Pt(PPh$_3$)$_4$ (62 mg, 0.05 mmol), and benzene-d_6 (0.7 mL). No reaction took place at rt for 5 h. After 42 h at 50 °C, the formation of **19** was confirmed in 60% yield (*cis*/*trans* = 83/17). No intermediates were observed during the course of reaction.

Stoichiometric Reaction of Pt(PPh$_3$)$_4$ with (PhS)$_2$ (Ref 21). In a dry 50 mL flask were added Pt(PPh$_3$)$_4$ (1.25 g, 1.0 mmol), (PhS)$_2$ (438 mg, 2.02 mmol), and toluene (20 mL). After the reaction mixture was refluxed for 16 h, the yellow solid precipitated. Then the solid was separated by filtration and washed by toluene and dried to give 567 mg (84%) of [Pt(SPh)$_2$(PPh$_3$)]$_2$.

[Pt(SPh)$_2$(PPh$_3$)]$_2$: mp 242 °C (a yellow solid); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.81 (m, 4 H), 6.88 (m, 26 H), 7.64 (br, 12 H), 7.78 (d, J = 7.8 Hz, 4 H), 7.88 (d, J = 7.8 Hz, 4 H); ^{31}P NMR (160 MHz, C$_6$D$_6$) δ −124.57 (J_{Pt-P} = 3389 Hz). IR (KBr) 3057, 1576, 1470, 1435, 1098, 1023, 736, 689, 536, 512 cm^{-1}. Anal. Calcd for $C_{60}H_{50}P_2Pt_2S_4$: C, 53.33; H, 3.73; S, 9.46. Found: C, 53.55; H, 3.79; S, 9.23.

The yellow solid obtained by treatment of Pt(PPh$_3$)$_4$ (1.0 mmol) with **1** (2.28 mmol) under a similar reaction condition (benzene (20 mL), reflux 53 h) was not able to be fully characterized because of the insolubility in organic solvents (639 mg, 98%).

[Pt(SAr)$_2$(PPh$_3$)]$_2$: mp 245−246 °C (a yellow solid); IR (KBr) 3564, 2358, 1479, 1433, 1097, 800, 748, 692 cm^{-1}.

Preparation of Authentic 19. Into a 30 mL two-necked flask, Pt(PPh$_3$)$_4$ (629 mg, 0.50 mmol), **1** (126 mg, 0.50 mmol), **2** (70 mg, 0.50 mmol), and benzene (15 mL) were added. After being stirred for 16 h at room temperature, the reaction mixture was subjected to short column (aluminum oxide, neutral, benzene as an eluent). The yellow solution collected was concentrated *in vacuo* to give 330 mg of **19** (80%). The yellow solid was recrystallized from benzene and hexane to provide 65 mg of pure *cis*-**19**.

***cis*-19:** mp 161 °C (a yellow crystal); ^{1}H NMR (400 MHz, C$_6$D$_6$) of *cis*-isomer δ 1.73 (s, 3 H), 1.96 (s, 3 H), 2.09 (s, 3 H), 5.87 (d, J = 8.3 Hz, 2 H), 6.39 (d, J = 8.3 Hz, 2 H), 6.69 (d, J = 7.8 Hz, 2 H), 6.92 (d, J = 8.3 Hz, 2 H), 6.95−6.99 (m, 10 H), 7.78−7.84 (m, 5 H), 7.92 (d, J = 7.8 Hz, 2 H), 7.95 (d, J = 7.8 Hz, 2 H). ^{31}P NMR (160 MHz, C$_6$D$_6$) of *cis*-isomer δ −126.6 (J_{Pt-P} = 2626 Hz); IR (KBr) 3058, 3009, 2916, 2177, 1503, 1484, 1435, 1097, 1085, 811, 694, 535, 516, 498 cm^{-1}. Anal. Calcd for $C_{40}H_{36}NPPtS_2$: C, 58.52; H, 4.42; N, 1.71; S, 7.81. Found: C, 58.32; H, 4.66; N, 1.78; S, 7.93.

***trans*-19:** (the following data were collected from a mixture of stereoisomers) ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 1.67 (s, 3 H), 2.02 (s, 6 H), 6.04 (d, J = 7.8 Hz, 2 H), 6.38 (d, J = 7.8 Hz, 2 H), 6.85 (d, J = 8.3 Hz, 4 H) (the other peaks overlapped with the peaks of the *cis*-isomer); ^{31}P NMR (160 MHz, C$_6$D$_6$) of *trans*-isomer δ −121.22 (J_{Pt-P} = 3639 Hz).

Isomerization of *cis*-19 (Ref 23). In a dry Pyrex NMR tube were added *cis*-**19** (8.1 mg, 0.01 mmol), PPh$_3$ (5.2 mg, 0.02 mmol), and benzene-d_6 (0.7 mL). The isomerization completed within 5 min to give *cis*/*trans* = 83/17 mixture of **19**. This isomerization also took place in the absence of PPh$_3$ more slowly (<1 h) at room temperature.

Pt(PPh$_3$)$_4$-Catalyzed Reaction of 4 with 2 (Eq 3). Into a dry two-necked flask equipped with a reflux condenser and a magnetic stirring bar were placed Pt(PPh$_3$)$_4$ (12 mg, 0.01 mmol), **4** (240 mg, 0.5 mmol), **2** (59 mg, 0.5 mmol), and benzene (1.0 mL) under an argon atmosphere. After the solution was refluxed with stirring for 24 h, ca. 30 mL of hexane was added into the solution. Then, the solid **4** was removed by filtration and the filtrate was purified by PTLC (a mixture of hexane and Et$_2$O (9:1) as an eluent). More than 10 uncharacterized products (total 62 mg) were obtained.

The Reaction of 4 with Pt(PPh$_3$)$_4$ (Eq 6). In a dry Pyrex NMR tube were added **4** (9.5 mg, 0.02 mmol), Pt(PPh$_3$)$_4$ (24.6 mg, 0.02 mmol), and benzene-d_6 (0.7 mL). Then the tube was purged with Ar and sealed under reduced pressure. After the sample was heated for 12 h at 50 °C, the formation of Pt[(C═NAr)$_2$SAr](SAr)(PPh$_3$)$_2$ (**21**) was confirmed in 64% yield by ^{1}H NMR (*cis*/*trans* = 9/91 by ^{31}P NMR). The compound **21** was recrystallized from benzene and hexane.

***trans*-21:** mp 119−120 °C (an orange crystal); ^{1}H NMR (270 MHz, C$_6$D$_6$) δ 1.94 (s, 3 H), 2.02 (s, 3 H), 2.10 (s, 3 H), 2.34 (s, 3 H), 6.24 (d, J = 8.3 Hz, 2 H), 6.34 (d, J = 7.8 Hz, 2 H), 6.42 (d, J = 7.8 Hz, 2 H), 6.58 (d, J = 7.8 Hz, 2 H), 6.60 (d, J = 8.3 Hz, 2 H), 6.72 (d, J = 8.3 Hz, 2 H), 6.96−7.08 (m, 18 H), 7.21 (d, J = 8.3 Hz, 2 H), 7.79−7.90 (m, 14 H); IR (KBr) 3052, 2919, 1595, 1500, 1483, 1435, 1196, 1096, 847, 806, 743, 692, 522, 512, 500 cm^{-1}; ^{31}P NMR (149 MHz, C$_6$D$_6$) δ −131.46 (J_{Pt-P} = 3175 Hz). Anal. Calcd for $C_{66}H_{58}N_2P_2PtS_2$ C, 66.04; H, 4.87; N, 2.33; S, 5.34. Found: C, 65.31; H, 4.82; N, 2.33; S, 5.39.

***cis*-21:** (the following data were collected from a mixture of stereoisomers) ^{31}P NMR (149 MHz, C$_6$D$_6$) δ −125.92 (d, J = 18.2 Hz), −125.14 (d, J = 18.2 Hz). These peaks were too small to allow us to read the coupling constant J_{Pt-P}.

The Stoichiometric Reaction of 21 with 1 (Eq 7). In a dry Pyrex NMR tube were added *trans*-**21** (11.8 mg, 0.01 mmol), **1** (2.5 mg, 0.01 mmol), and benzene-d_6 (0.7 mL). Then the tube was purged with Ar and sealed under reduced pressure. After 4 h at room temperature, only the isomerization to a stereomixture *cis*/*trans* = 6/94 was observed. Then the sample was heated at 80 °C. The formation of **19** was confirmed in 34% after 3 h, 73% after 18 h with a formation of complicated products; however, **4**, **3**, **18**, **20**, and **2** were not produced at all.

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Supporting Information Available: Listing of complete crystal and data collection parameters, atomic coordinates, isotropic thermal parameters, anisotropic displacement parameters, and interatomic distances and bond angles of **4**, **6**, *cis*-**19**, and *trans*-**21** (112 pages). See any current masthead page for ordering and Internet access instructions.

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