Insertion of Alkynes into an ArS−Pt Bond: Regio- and Stereoselective Thermal Reactions, Facilitation by "*o*-Halogen Effect" and Photoirradiation, Different Alkyne Preferences Depending on the Ancillary Ligand, and Application to a Catalytic Reaction

Hitoshi Kuniyasu,* Kazunobu Takekawa, Fumikazu Yamashita, Kiyoshi Miyafuji, Shigehito Asano, Yasutomo Takai, Atsushi Ohtaka, Aoi Tanaka, Kunihiko Sugoh, Hideo Kurosawa, and Nobuaki Kambe*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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The insertion of alkyne **2** into the S−Pt bond(s) of Pt(SAr)(Cl)$(PPh_3)_2$ (**7**), Pt$(SAr)_2(PPh_3)_2$ (**8**), and Pt(SAr)(Ar′)(dppe) (**9**) has been investigated. Regioselective *cis*-insertion into the S−Pt bond of *trans*-**7** took place with terminal and internal alkynes (RC≡CR′; R′ = H, C(O)OEt, and CH_2OMe) at 70−110 °C to give Pt[(*Z*)-C(R′)=C(SAr)R](Cl)$(PPh_3)_2$ (*Z*-**10**) as stable compounds. The introduction of an electron-donating group in Ar of ArC≡CH and in ArS of **7** slightly facilitated the reactions. It was found that a halogen atom at the *ortho* position in ArS of **7** dramatically promoted the insertion ("*o*-halogen effect"). The insertion of a terminal alkyne (**2**, RC≡CH) into the S−Pt bond of *trans*-Pt$(SAr)_2(PPh_3)_2$ (**8**) also occurred to afford Pt[(*Z*)-C(H)=C(SAr)R](SAr)$(PPh_3)_2$ (*Z*-**16**), which was further converted into Pt$(PPh_3)_2$(RC≡CH) (**18**) and (*Z*,*Z*)-(ArS)(R)C=C(H)-C(H)=C(SAr)(R) (**19**) by C−C bond-forming reductive elimination after the insertion of another **2** into the remaining S−Pt bond of **16**. The "*o*-halogen effect" was also observed for the insertion of **2** into the S−Pt bond of *trans*-**8** to furnish the corresponding *cis*-*Z*-**16** as a kinetic product; the *trans*-isomer of **8** exhibited a higher reactivity than the *cis*-isomer. It was also revealed that photoirradiation (visible light) dramatically promoted the insertion of **2** into the S−Pt bond of *trans*-**8**. Photoinduced insertion was facilitated by introducing an electron-donating group into Ar of ArC≡CH. Contrary to the cases of PPh_3-ligated platinum complexes, the insertion into the S−Pt bond of Pt(SAr)(Ar′)(dppe) (**9**) was realized when the electron-deficient alkyne DMAD (**2t**) was employed as a substrate. Also presented is the insertion of two alkynes into each S−Pt bond of **8** in the Pt-catalyzed stereo- and regioselective dimerization−bisthiolation of alkyne (**2**) by diaryl disulfide ($(ArS)_2$, **30**) to yield functionalized symmetrical 1,3-dienes.

Introduction

Transition metal-catalyzed addition reactions of heteroatom-containing σ-bonds to unsaturated compounds, represented by hydrosilylation of alkenes and alkynes, have been extensively explored for more than three decades and serve as a straightforward strategy to introduce functional groups into unsaturated moieties.[1] In contrast, the utility of transition metal-catalyzed addition reactions with organic sulfur compounds, which have been known to act as a "catalyst poison",[2] has not been well-studied until recently, although Reppe's early study had suggested that reactions with such a combination of catalysts and reagents could be very rewarding.[3] After some scattered works were published during the 1960s and 1980s,[4] a variety of regio- and stereoselective metal-catalyzed addition reactions of the compounds RS-**G** (**G** = H,[5] 9-BBN,[6] CO_2Me,[7] $SiCl_3$,[8] $C(O)NR_2$,[9] Ar′ (from $ArSC(O)Ar'$),[10] $CH_2CH{=}CH_2$,[11] $P(O)(OPh)_2$,[12] and SAr[13]) to terminal alkynes (**2**, RC≡CH) have been conducted since the early 1990s (Scheme 1).[14] These examples clearly demonstrate that the concept of "catalytic poison" does

* Corresponding authors. E-mail: kuni@chem.eng.osaka-u.ac.jp.

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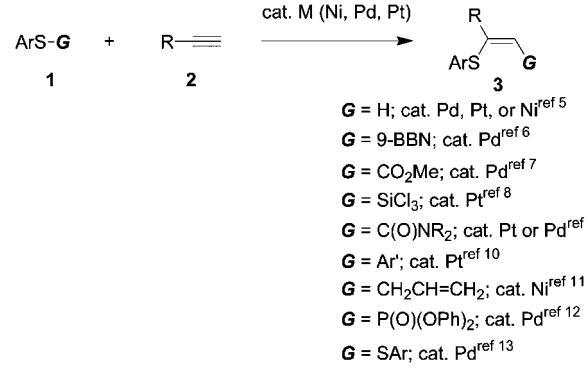
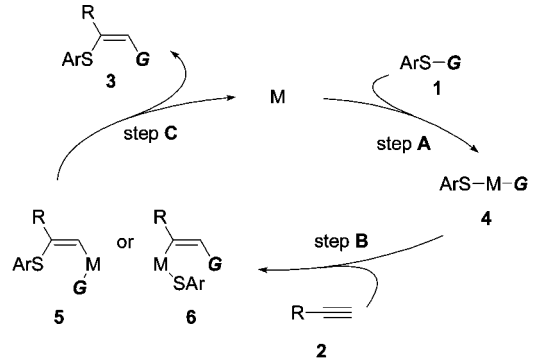
not connote a lack of promise for the transition metal-catalyzed reactions using organic sulfur compounds as reaction substrates. Furthermore, a DFT study indicates that S−M bonds can exhibit moderate reactivity in catalytic transformation (bond energy of CH_3S−Pd is 48.4 kcal/mol).[15] Most reactions shown in Scheme 1 have been conducted using PR_3-ligated Ni triad catalysts to afford vinyl sulfides (**3**) with an ArS group at the internal carbon and **G** at the terminal carbon in a *cis* fashion with one another.

Scheme 1. M-Catalyzed Addition of ArS-G (1) to Alkynes (2)



Scheme 2. Proposed Mechanisms for the M-Catalyzed Addition of 1 to 2



Similar reaction mechanisms have been proposed for these addition reactions (Scheme 2). The oxidative addition of **1** to the M(0) complex can trigger a reaction to provide complex **4** with an ArS-M-**G** fragment (step A).[16] Two pathways are possible for the following insertion of alkyne **2** (step B): One is a *cis*-insertion into the S−M bond of **4** to give M[C(H)═C(SAr)(R)](**G**) (**5**), and the other is a *cis*-insertion into the M−**G** bond of **4** to afford M[C(R)═C(**G**)(H)](SAr) (**6**). Finally, **G**−C or S−C bond-forming reductive elimination produces (*Z*)-(ArS)(R)C═C(**G**)(H) (**3**) with regeneration of M (step C).[17−19] Sufficient evidence has been provided for step A.[5,7,8,10−13,20] However, information about steps B and C is very limited, in part because reductive elimination is faster than insertion.[21,22] For instance, Tanaka et al. reported that the

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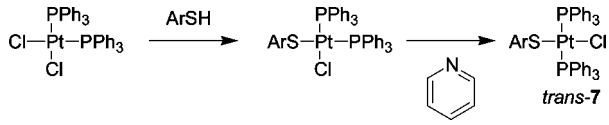
(22) The DFT study on the mechanism of Pd-catalyzed thioboration (**G** = 9-BBN[6]) of **2** proposed that **6** is yielded through bond metathesis between an S−B bond and an alkyne-coordinated C−Pd bond; see ref 15.

Scheme 3. Pyridine-Catalyzed Synthesis of 7[26]



reaction of *trans*-Pd(SPh)(CO_2Me)(PCy_3)$_2$ (**4a**) with 1-octyne produced (*Z*)-(PhS)(*n*-C_6H_{13})C═C(CO_2Me)(H) (**3a**), the product of the Pd-catalyzed addition of PhSC(O)(OMe) to 1-octyne,[7] which indicates that C−C[17] or S−C[18] bond-forming reductive elimination from a vinyl palladium intermediate facilely proceeds after the insertion of 1-octyne into either the S−Pd or the C−Pd bond of **4a**. Accordingly, to clarify step B, the reaction system must be suitably designed to prevent reductive elimination.[23,24]

We predicted that Pt(SAr)(Cl)(PPh_3)$_2$ (**7**) would be an ideal complex for examining the insertion of **2** into the S−M bond, as we expected that the C−Cl bond-forming reductive elimination from the vinyl platinum species produced by insertion was a thermodynamically unfavorable process.[25] Furthermore, we recently developed a general method for the preparation of **7** using pyridine as a catalyst for *cis*-to-*trans* isomerization (Scheme 3).[26] Herein we report the details of the insertion of alkyne into the S−Pt bond of **7**, Pt(SAr)$_2$(PPh_3)$_2$ (**8**), and Pt(SAr)(Ar′)(dppe) (**9**). The application of successive insertions of **2** into each S−Pt bond of **8** in the Pt-catalyzed dimerization−bisthiolation of alkyne (**2**) by disulfide (**30**) is also presented.[27]

Results and Discussion

Insertion of Alkyne (2) into S−Pt Bond(s) of the PPh_3-Ligated Pt(II) Complex. Insertion of 2 into the S−Pt Bond of *trans*-Pt(SAr)(Cl)(PPh_3)$_2$ (7). The reactions of *trans*-Pt(SC_6H_4Cl-*p*)(Cl)(PPh_3)$_2$ (**7a**, 0.01 mmol) with phenylacetylene (**2a**) in toluene-d_8 (0.6 mL) at 110 °C were monitored by ^{1}H and ^{31}P NMR spectroscopies using S═P(C_6H_4Me-*p*)$_3$ as an internal standard (eq 1).[28] The ^{1}H NMR spectra indicated clean formation of the vinyl platinum complex **10a** on the basis of a signal at δ 7.62 (t, $^3J_{P-H}$ = 4.0 Hz) assigned to a vinyl hydrogen atom.[29] The ^{31}P NMR signal of **10a** appeared at δ 23.6 (s, J_{Pt-P} = 3021 Hz). The yield reached 83% after 6 h. Compound **10a** was isolated by recrystallization in 87% yield from a reaction carried out on a preparative scale (0.06 mmol each at 100 °C for 14 h), and its structure was determined by X-ray crystallography. The double bond in **10a** has a *Z*-configuration with the ArS group at the internal position and Pt at the terminal position (Figure 1),[30,31] which provides the definitive evidence for the insertion of a terminal alkyne **2** into the bond between a PR_3-ligated group 10 metal and a sulfur atom.

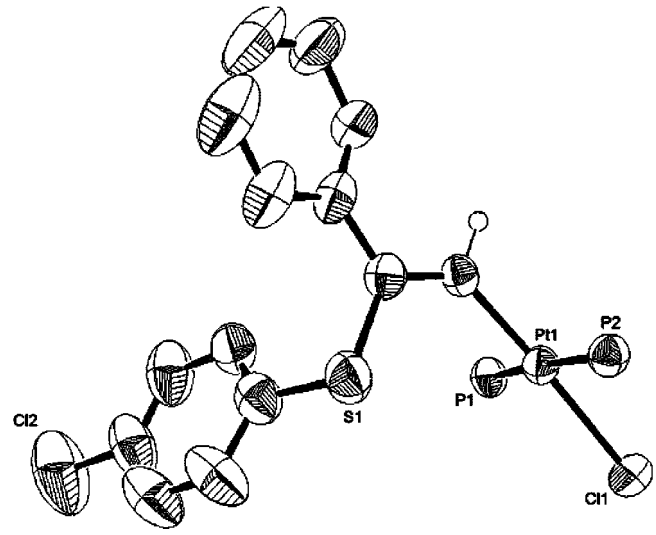
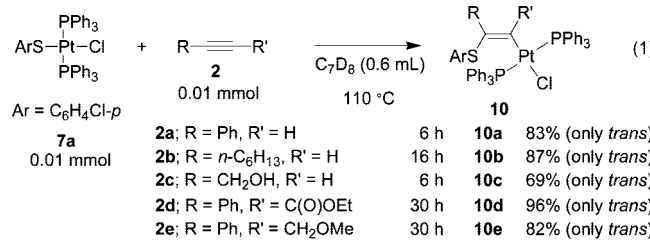


Figure 1. ORTEP diagram of *trans*-Z-**10a** (Ph on PPh_3 omitted).



It should be noted that the configuration and substitution pattern of **10a** are in agreement with the structure of **5** in Scheme 2. Similar insertions were confirmed for the reactions of 1-octyne (**2b**) and propargyl alcohol (**2c**): The corresponding vinyl platinum complexes **10b** (only *trans*) and **10c** (only *trans*) were obtained in 87% and 69% yield after 16 and 6 h, respectively. The observation that no alkyne-exchange reaction took place after the treatment of *trans*-Pt[(*Z*)-C(H)═C(SC_6H_4Cl-*o*)(Ph)](Cl)(PPh_3)$_2$ (*vide infta*) with 1-octyne (**2b**) even after 6 h at 70 °C suggests that the insertion step is an irreversible process. In agreement with the previous findings that internal alkynes are generally inert in addition reactions of ArS-**G** (**1**) to **2** with PR_3-ligated Pd or Pt catalysts, no insertion took place with 4-octyne. However, it was found that ethyl phenylpropiolate (**2d**; R = Ph, R′ = C(O)OEt) exhibits quite high reactivity toward the insertion: The ^{31}P NMR spectroscopy of the reaction mixture of **2d** with **7a** taken after 30 h indicated the formation of vinyl platinum complex **10d** in 96% yield on the basis of a signal at δ 23.3 (s, J_{Pt-P} = 3044 Hz). The reaction of **7a** with 1-phenyl-3-methoxy-1-propyne (**2e**; R = Ph, R′ = CH_2OMe) under the same reaction conditions afforded a similar vinyl platinum, **10e**,

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(28) No interaction between S═P(C_6H_4Me-*p*)$_3$ and other reagents has been confirmed during the course of the present study.

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(30) In the following discussion, *cis* and *trans* refer to the relationship of the two PPh_3 groups at a Pt center; *E* and *Z* refer to the configuration of the double bond of a vinyl substituent.

(31) Crystal data for *trans*-Z-**10a**: space group $P2_1/c$ (#14), a = 12.731(2) Å, b = 10.829(2) Å, c = 33.907(5) Å, β = 92.26(1)°, Z = 4, R = 0.046, R_w = 0.113.

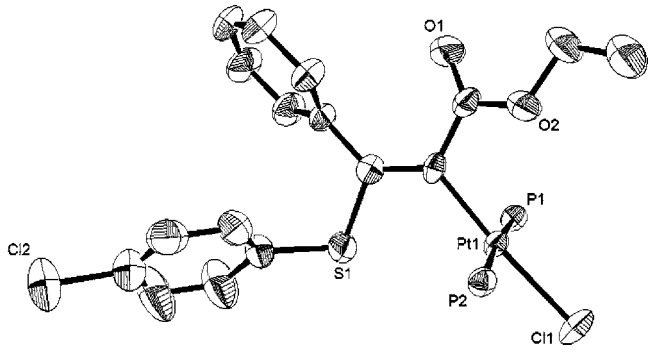


Figure 2. ORTEP diagram of *trans-Z*-**10d** (Ph on PPh_3 omitted).

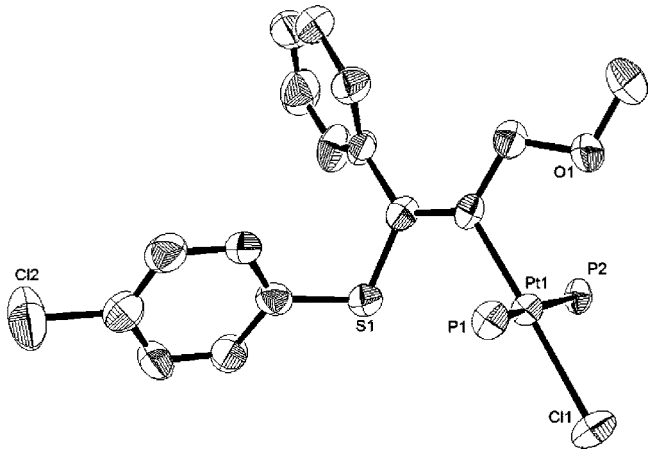


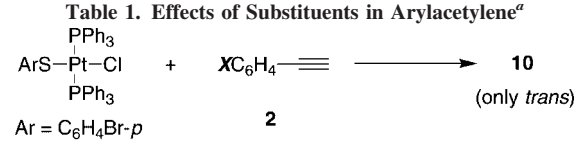
Figure 3. ORTEP diagram of *trans-Z*-**10e** (Ph on PPh_3 omitted).

in 82% yield. The structures of **10d** and **10e** were both unambiguously determined by X-ray crystallographic analyses, proving that the double bonds of the vinyl platinums have a *Z*-configuration with Pt at the α-carbon of either the CO_2Et or the CH_2OMe groups (Figures 2 and 3).[32] It is noteworthy that the Pt−O distances of **10d** (3.0 Å) and **10e** (3.0 Å) are both within the sum of the van der Waals radii (3.2 A) of the two atoms, implying that the interaction between the Pt and O atoms plays a crucial role in achieving regioselective insertion of **2d** and **2e** into the S−Pt bond of **7**. The effects of substituents in $\mathbf{X}C_6H_4C{\equiv}CH$ were then examined under the conditions of 0.01 mmol of *trans*-Pt(SC_6H_4Br-*p*)(Cl)(PPh_3)$_2$ (**7b**) and 0.17 M **2** in C_6D_6 at 70 °C. The consumption rate of *trans*-**7b** obeyed pseudo-first-order kinetics: The half-life ($\tau_{1/2}$) of *trans*-**7b** for each reaction is shown in Table 1. The values range from $\tau_{1/2}$ = 10.2 h for a *p*-CF_3-substituted arylacetylene (**2f**) to $\tau_{1/2}$ = 2.7 h for a *p*-OMe-substituted arylacetylene (**2k**) (entries 1−7).

In comparison with simple σ values, the Hammet plot shows a better linear free-energy relationship with σ^+ values that correlate with the acidity of the equivalently substituted benzoic acids (Figure 4). A small negative slope ($\rho = -0.4$) shows that electron-donating groups (EDGs) slightly facilitate the reaction. The $\tau_{1/2}$ value of 13.1 h observed for **2l** with an *o*-Cl substituent (entry 8) and $\tau_{1/2}$ value of 7.0 h with an *o*-Me group (entry 9) indicate that the steric hindrance caused by the substituent in the *ortho* position of $\mathbf{X}C_6H_4C{\equiv}CH$ retards the insertion.

(32) Crystal data for *trans-Z*-**10d**: space group $P2_1/n$ (#14), a = 12.1258(2) Å, b = 12.6125(3) Å, c = 34.5793(7) Å, β = 100.5756(7)°, Z = 4, ρ = 1.54 g/cm^3, R = 0.040, and R_w = 0.085. Crystal data for *trans-Z*-**10e**: space group $Pna2_1/n$ (#33), a = 39.9145(7) Å, b = 11.9216(3) Å, c = 9.4584(2) Å, β = 101.6122(9)°, Z = 4, ρ = 1.542 g/cm^3, R = 0.040, and R_w = 0.118.

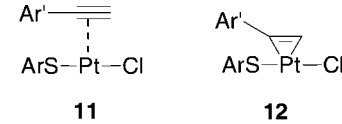
Table 1. Effects of Substituents in Arylacetylene[a]



entry	X	2	$\tau_{1/2}$ (h)
1	*p*-CF_3	**2f**	10.2
2	*p*-Cl	**2g**	7.6
3	*p*-F	**2 h**	6.4
4	H	**2a**	6.3
5	*m*-Me	**2i**	5.4
6	*p*-Me	**2j**	3.8
7	*p*-OMe	**2k**	2.7
8	*o*-Cl	**2l**	13.1
9	*o*-Me	**2m**	7.0

[a] *trans*-**7b** (0.01 mmol) and **2** (0.17 M) in C_6D_6 at 70 °C.

The effects of substituent **X** of Pt($SC_6H_4\mathbf{X}$)(Cl)(PPh_3)$_2$ (**7**) toward insertion of PhC≡CH (**2a**) (0.17 M) at 70 °C were examined next (Table 2). The consumption rate of starting *trans*-**7** obeyed pseudo-first-order kinetics, and the values of the half-lives ($\tau_{1/2}$) range from $\tau_{1/2}$ = 12.2 h for the platinum complex with a *p*-CF_3 group (**7c**) to $\tau_{1/2}$ = 2.8 h with a *p*-OMe substituent (**7f**) for the *para* substituents (entries 1−5). The Hammett plot shows a fairly good linear free-energy relationship with simple σ values (Figure 5). Its negative slope ($\rho = -0.7$) also indicates that EDGs slightly facilitate the insertion reaction. Hartwig et al. have reported that a similar electronic effect was detected for C−S bond-forming reductive elimination from a Pd(II) complex.[18a,b] Considering that the alkyne-coordinated complex **11** has a platinacyclopropene character (**12**), EDGs in the ArS group may similarly promote the migration of an ArS group toward the coordinated alkyne moiety. On the other hand, a slight increase in reaction rate, by introducing EDG in $\mathbf{X}C_6H_4C{\equiv}CH$ (Figure 4), may be attributed to the facilitation of the coordination of an alkyne to a coordinatively unsaturated platinum(II) complex produced after liberation of PPh_3. The reaction was retarded significantly in the presence of additional PPh_3 (3 equiv) ($\tau_{1/2}$ = 16.4 h; Table 2, entry 6). The $\tau_{1/2}$ value of 10.1 h observed for **7g** with an *o*-Me substituent (entry 7) and the $\tau_{1/2}$ value of 13.3 h with an *o*-Pr-*i* group (**7h**, entry 8) suggest that the steric hindrance caused by the substituent in the *ortho* position retards the insertion similarly to the *ortho* substituents in arylacetylene derivatives (entries of 8 and 9 of Table 1). Intriguingly, a $\tau_{1/2}$ value of 0.28 h was observed for *o*-Cl-substituted **7i**: The reaction was approximately 19 times faster than that of the complex with a PhS group (entries 3 and 9). Whereas similar facilitation of the insertion step was observed with an *o*-Br substituent ($\tau_{1/2}$ = 0.26 h; the insertion proceeds approximately 20 times faster than that of the complex with PhS; entry 10) and an *o*-I substituent ($\tau_{1/2}$ = 0.19 h; the insertion proceeds approximately 28 times faster than that of the complex with PhS; entry 11), the insertion was suppressed with an *o*-F substituent ($\tau_{1/2}$ = 7.3 h; 1.4 times slower that of the complex than with PhS; entry 12). Thus, we could conclude that the high-energy lone pairs of electrons at the *ortho* position are required to facilitate the insertion step. On the other hand, no large differences were observed between *p*-OMe ($\tau_{1/2}$ = 2.8 h; entry 5) and *o*-OMe ($\tau_{1/2}$ = 1.5 h; entry 13) substituents: We postulate that steric retardation and a certain degree of electronic facilitation by the *o*-OMe group cancel each other out.



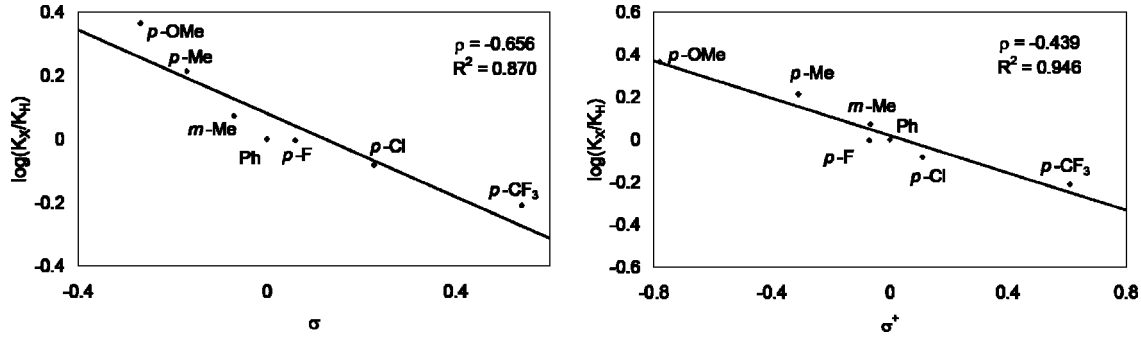
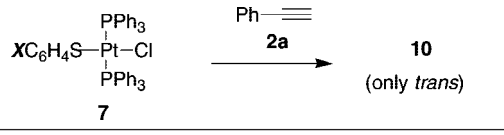


Figure 4. Hammett plot for the reaction rates of insertion of **2a** and **2f**−**2k** into the S−Pt bond of *trans*-**7b**.

Table 2. Effects of Substituents in ArS of 7[a]



entry	X	7	$\tau_{1/2}$ (h)	entry	X	7	$\tau_{1/2}$ (h)
1	*p*-CF_3	**7c**	12.2	8	*o*-Pr-*i*	**7 h**	13.3
2	*p*-Cl	**7a**	6.1	9	*o*-Cl	**7i**	0.28
3	H	**7d**	5.3	10	*o*-Br	**7j**	0.26
4	*p*-Me	**7e**	4.0	11	*o*-I	**7k**	0.19
5	*p*-OMe	**7f**	2.8	12	*o*-F	**7 l**	7.3
6[b]	*p*-Me	**7e**	16.4	13	*o*-OMe	**7m**	1.5
7	*o*-Me	**7g**	10.1				

[a] **7** (0.01 mmol), **2a** (0.17 M) in C_6D_6 at 70 °C. [b] PPh_3 (0.03 mmol) was added.

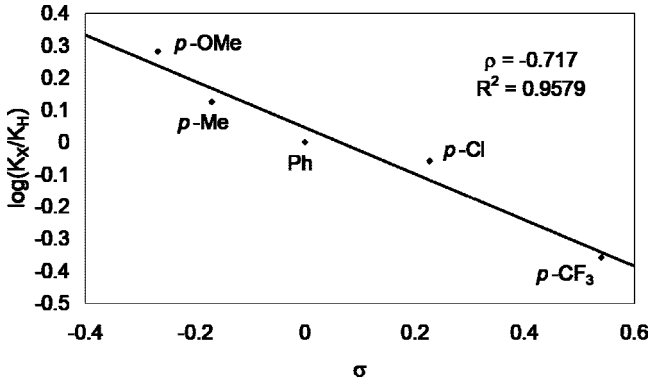
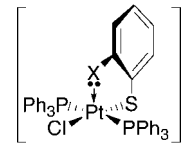


Figure 5. Hammett plot of the rates of IS of **2a** into the S−Pt bond of **7a** and **7c**−**7f**.

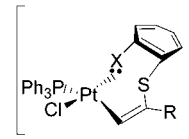
We next sought to elucidate the mechanism underlying the observed "*o*-halogen effect". Intramolecular coordination by *o*-halogen substituents in ligands of the type ArS has previously been documented.[33,34] Thus, we carried out a phosphine-ligand-exchange reaction to determine whether an *o*-halogen substituent accelerates the liberation of PPh_3 (eq 2). The treatment of *trans*-Pt(SC_6H_4Cl-*p*)(Cl)(PPh_3)$_2$ (**7a**) with *trans*-Pt(SC_6H_4Cl-*p*)(Cl)[P(C_6H_4Me-*p*)$_3$]$_2$ (**7a′**) at 25 °C gave *trans*-Pt(SC_6H_4Cl-*p*)(Cl)(PPh_3)[P(C_6H_4Me-*p*)$_3$] (**7a″**) in 23% yield after 1 h. A similar ligand exchange with complexes **7i** and **7i′**, which contain an *o*-Cl substituent, took place at a slightly lower reaction rate (12% yield of **7i″** after 1 h). These results may rule out the possibility that the dissociation of one phosphine ligand triggered by the coordination of *o*-**X** (**X** = Cl, Br, or I) to Pt (**13** in Scheme 4) promotes the insertion of an alkyne into the S−Pt bond. Another possibility is that the *o*-halogen coordinates to the vacant site generated by the migration of ArS to the alkyne (**14** in Scheme 5).[35] It is also possible that one of the electron lone pairs on **X** interacts with the S−Pt σ^* orbital and thus weakens the S−Pt bond (**15** in Scheme 6). In fact, X-ray crystallographic analysis of *trans*-Pt(SC_6H_4Br-*o*)(Cl)(PPh_3)$_2$ (**7j**) showed that the Br−S distance of 3.2 Å is within the sum of the van der Waals radii (3.6 Å) of the two atoms (Figure 6). We have already reported that the efficiency of thiocarbamoylation of terminal alkyne (**2**) by sulfenamide ($ArSNR_2$) and CO was significantly improved by introducing 2,4,5-tri-Cl substituents in Ar (eq 3).[9b] This may be attributed to the present "*o*-halogen effect" under alkyne insertion into the S−Pd bond.

Scheme 4



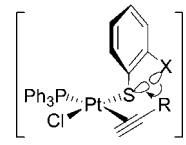
13

Scheme 5



14

Scheme 6



15

Insertion of 2 into the S−Pt Bond of Pt(SAr)$_2$(PPh$_3$)$_2$ (8). Insertion under Thermal Conditions. When the reaction of *trans*-Pt(SC_6H_4Br-*p*)$_2$(PPh_3)$_2$ (**8a**) (0.01 mmol) with 1-octyne

(33) Catala, R. M.; Cruz-Garritz, D.; Hills, A.; Hughes, D. L.; Richards, R. L.; Sosa, P.; Torrens, H. *J. Chem. Soc., Chem. Commun.* **1987**, 261. (b) Davis, J. A.; Davie, C. P.; Sable, D. B.; Armstrong, W. H. *Chem. Commun.* **1998**, 1649. (c) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(34) Intramolecular coordination of a β-*cis*-SAr group of an α,β-unsaturated acyl platinum and palladium complexes facilitated decarbonylation: Kato, T.; Kuniyasu, H.; Kajiura, T.; Minami, Y.; Ohtaka, A.; Kinomoto, M.; Terao, J.; Kurosawa, H.; Kambe, N. *Chem. Commun.* **2006**, 868.

(35) Assistance through the intramolecular coordination of an OH group has been reported on the basis of a molecular-orbital study of the insertion of an alkyne into a B−Pt bond: Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355.

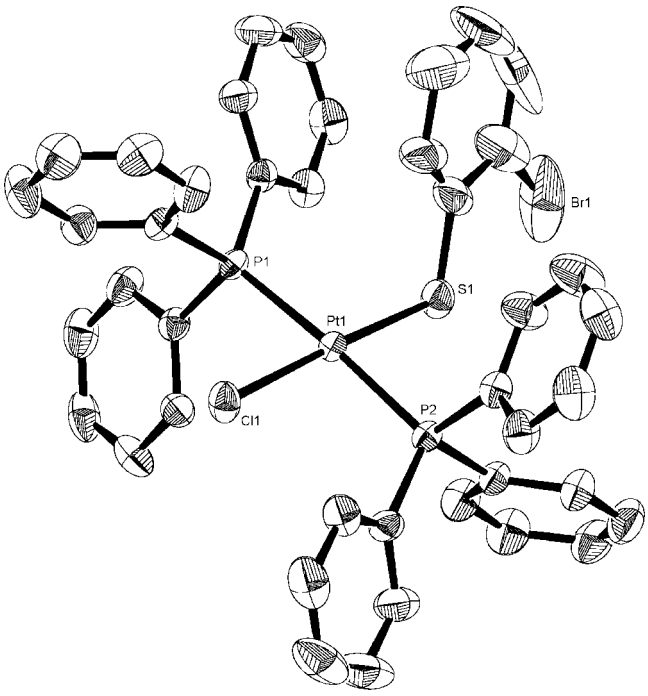
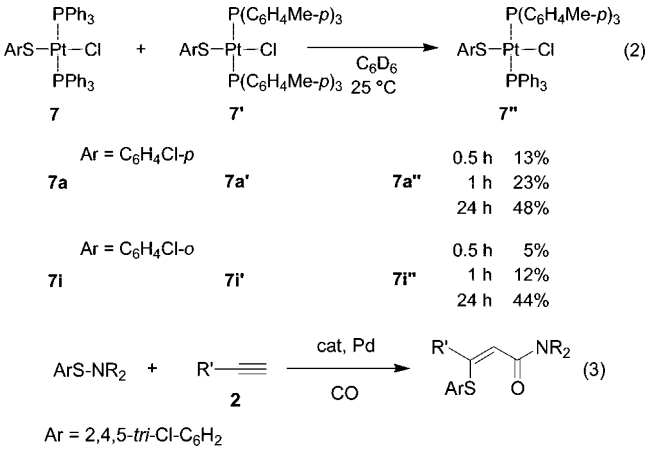
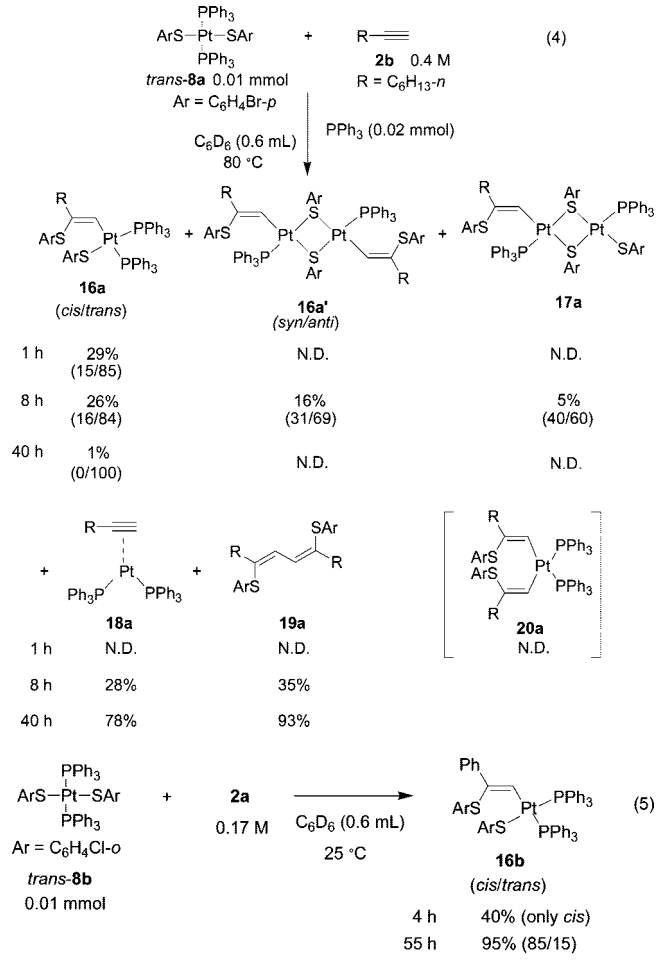


Figure 6. ORTEP diagram of **7j**. Selected bond lengths [Å]: Pt−S 2.319(2), Br−S 3.202 (2).



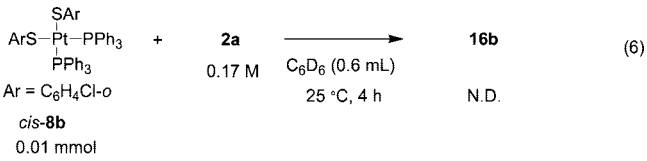
(**2b**) (0.4 M) was conducted at 80 °C in C_6D_6 (0.5 mL) in the presence of additional PPh_3 (0.02 mmol), the formation of vinyl platinum *cis*-Pt[(*Z*)-C(H)═C(SC_6H_4Br-*p*)R](SC_6H_4Br-*p*)(PPh_3)$_2$ (R = C_6H_{13}-*n*, **16a**),[36] a product of insertion of **2b** into the S−Pt bond of **8a**, was confirmed in 29% yield (*cis*/*trans* = 15/85) after 1 h by ^{31}P NMR spectroscopy (eq 4). Signals suspected as S-bridging complexes such as Pt[(*Z*)-C(H)═C(SC_6H_4Br-*p*)-(R)](PPh_3)(μ-SAr)$_2$Pt[(*Z*)-C(H)═C(SC_6H_4Br-*p*)(R)](PPh_3) (**16a′**) and Pt[(*Z*)-C(H)═C(SC_6H_4Br-*p*)(R)](PPh_3)(μ-SAr)$_2$Pt(SC_6H_4-Br-*p*)(PPh_3) (**17a**) were confirmed in 16% (*syn*/*anti* = 31/69) and 5% (40/60) yields, respectively, after 8 h.[37] The signals of Pt(PhC≡CH)(PPh_3)$_2$ (**18a**) and (*Z*,*Z*)-(*p*-BrC_6H_4S)(R)C═C(H)-C(H)═C(SC_6H_4Br-*p*)(R) (**19a**) were also detected in 28% and 35% yields, respectively. It must be noted that (*Z*)-(R)(ArS)C═C(H)(SAr) was not detected at all.[13] While signals of **16a**, **16a′**, and **17a** disappeared after 40 h, the yields of **18a** and **19a** reached 78% and 93%, respectively. This result clearly demonstrates the advantage of the use of *trans*-Pt(SAr)(Cl)(P-Ph_3)$_2$ (*trans*-**7**) for the clear-cut investigation of insertion of an alkyne into a S−Pt bond, because the starting complex Pt(SAr)-(Cl)(PPh_3)$_2$ (**7**) and the product of vinyl platinum Pt[(*Z*)-C(H)═C(SAr)(R)](Cl)(PPh_3)$_2$ (**10**) were both tolerant of the formation of either S- or Cl-bridging complexes. This is presumably attributed to the lower basicities of lone pairs of S and Cl atoms of **7** and **10** compared to those of lone pairs of S atoms of **8** and **16**. The formation of **18a** and **19a** was rationalized by postulating that another **2b** is inserted into the remaining S−Pt bond of **16** to give the bisvinyl platinum complex **20a** (not detected), which undergoes C−C bond-forming reductive elimination to produce **19** and the Pt(0) complex.[38] The "*o*-halogen effect" was next studied with the *trans* and *cis* dithiolate complexes of Pt(SAr)$_2$(PPh_3)$_2$ (Ar = C_6H_4Cl-*o*, **8b**), both of which were selectively prepared.[39] The treatment of *trans*-**8b** with 10 equiv of phenylacetylene (**2a**) at 25 °C furnished the vinyl platinum complex **16b** in 40% yield (only *cis*) after 4 h and 95% yield (*cis*/*trans* = 85/15) after 55 h (eq 5).[36,40] In stark contrast, **16b** was not formed at all when *cis*-**8b** was treated with **2a** for 4 h under the same reaction conditions (eq 6). The higher reactivity of *trans*-**8b** relative to that of *cis*-**8b** toward the insertion of an alkyne may be attributed to the stronger *trans* effect of PPh_3 in *trans*-**8b** than that of SAr in *cis*-**8b** to liberate PPh_3.[41]



Insertion under Photoirradiated Conditions. For the insertion of phenylacetylene (**2a**) into the H−Pt bond of *trans*-

(36) Authentic samples of **16** were synthesized by either oxidative addition of (*Z*)-(ArS)(R)C═C[C(O)SAr](H) to Pt(PPh_3)$_2$(C_2H_4) and the following decarbonylation[34] or the oxidative addition of (*Z*)-(ArS) -(R)C═C(SAr)(H) to Pt(PPh_3)$_2$(C_2H_4): Kuniyasu, H.; Ohtaka, A.; Nakazono, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375.

(37) Treatment of a solution of authentic **16a** at elevated temperature produces **16a′** and an equivalent amount of liberated PPh_3. Complex **17a** was also generated by the stoichiometric reaction of **16a** with *trans*-**8a**.[34].



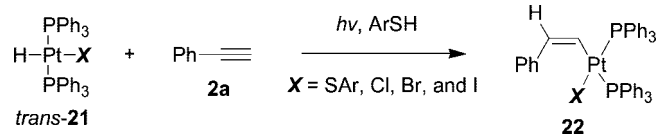
(6)

$Pt(H)(\mathbf{X})(PPh_3)_2$ (**21**, **X** = SAr, Cl, Br, and I), we have reported that unconventional *trans*-insertion proceeds under photo- and thiol-driven reaction conditions to afford *cis*-Pt[(*Z*)-C(H)=C(Ph)(H)]$(PPh_3)_2$ (**22**) in good yields (Scheme 7).[42] Thus, we next examined the effects of photoirradiation under the insertion of **2** into the S−Pt bonds of **7** and **8**.

First, a C_6D_6 (0.5 mL) solution of *trans*-Pt(SPh)(Cl)$(PPh_3)_2$ (**7d**, 0.01 mmol) and PhC≡CH (**2a**, 0.1 mmol) placed in a Pyrex NMR tube, which was soaked in a cooled water bath (25 °C), was irradiated using a 500 W tungsten lamp. The reaction was monitored by ^1H and ^{31}P NMR spectroscopies. After 1 h, the formation of 20% *cis*-**7d** and 4% (*cis*/*trans* = 24/76) $Pt(SAr)_2(PPh_3)_2$ (**8c**) was confirmed, respectively: Isomerization and disproportionation of *trans*-**7b** are induced by photoirradiation. However, no formation of the corresponding vinyl platinum **10** was detected. In marked contrast, regio- and stereoselective *cis*-insertion of alkyne **2** into the S−Pt bond of **8** was remarkably promoted with the aid of photoirradiation: The effect of photoirradiation was scrutinized by the reaction of methyl propargyl ether (**2n**) (0.1 mmol) with $Pt(SAr)_2(PPh_3)_2$ (Ar = *p*-Br; **8a**) (0.01 mmol) in C_6D_6 (0.5 mL) carried out in a Pyrex NMR tube at 25 °C (Table 3). Irradiation of the solution of *trans*-**8a** and **2n** by a 500 W tungsten lamp for 10 min resulted in the selective formation of a *cis*-platinum complex (*cis*-*Z*-**16c**)[36] in 14% yield. After 1 h of photoirradiation, the yield of **16c** reached 91% with *cis*/*trans* = 83/17 (entry 1). Once the isolated *cis*-*Z*-**16c** isomerized into *E*-**16c** under photoirradiation (*trans*-*Z*-**16c** (16%), *cis*-*E*-**16c** (10%), and *trans*-*E*-**16c** (8%) in C_6D_6 after 5 h), *cis*-*Z*-**16c** was also formed as a kinetic product of insertion of **2n** into the S−Pt bond of **8a**: Both stereo- and regiochemistry of **16** were in agreement with the structure of vinyl platinum complex produced under thermal conditions (eq 5). Accordingly, photoirradiation promotes regio- and stereoselective *cis*-insertion of an alkyne into the S−Pt bond as well as *trans*-insertion of an alkyne into the H−Pt bond (Scheme 8).

On the other hand, the samples of **8a** and **2n** left in the dark at 25 °C furnished no **16c**, even after 5 days (entry 2).[43] The insertion was significantly retarded by the addition of PPh_3: *Z*-**16c** was produced in 28%, 19%, and 5% yields in the presence of 0.01, 0.02, and 0.1 mmol of additional PPh_3, respectively (entries 3−5).[44]

Scheme 7. Photo- and Thiol-Driven *trans*-Insertion of Phenylacetylene (2a) into the H−Pt Bond of *trans*-Pt(H)(X)-$(PPh_3)_2$ (21)[42]



Under photoirradiation, complex **8a** existed as a mixture of stereoisomers from the early stage of the reaction of **2n** with **8a** (*cis*/*trans* = 20/80 after 10 min starting from *trans*-**8a**) (entry 1). In order to specify which stereoisomer of **8a** underwent the insertion of **2n**, *trans*-**8a** and *cis*-**8a**[39] were treated with 100 equiv of **2n** under 30 s of photoirradiation (entries 6 and 7). The former reaction produced 2.4% *cis*-*Z*-**16c** (with remaining *cis*-**8a**/*trans*-**8a** = 1/99), while the latter did not produce any detectable amount of insertion product (*cis*-**8a**/*trans*-**8a** = 81/19); these facts demonstrate that *trans*-**8a** is much more reactive than *cis*-**8a** under photoirradiated insertion, which is a scenario that is similar to thermal insertion (eqs 5 and 6). Dimeric complex *anti*-$[Pt(SAr)_2(PPh_3)]_2$ (*anti*-**8a′**), which is thermodynamically more stable than monomeric **8a**,[45] showed no activity for the insertion of **2n** under a photoirradiated reaction (entry 8). Because the reaction of *trans*-**8a** with 1 equiv of **2n** afforded 19% **8a′** together with 25% *Z*-**16c** by 2 h of photoirradiation (entry 9), an excess amount of **2n** relative to *trans*-**8a** was indispensable for attaining the clean formation of **16c** by the reaction of *trans*-**8a** with **2n**.

Next, to determine which wavelength of light facilitates the insertion reaction of **2n** into the S−Pt bond of *trans*-**8a**, photoirradiation was performed using filters to cut a certain range of wavelength of light. The reactions carried out under the irradiation of light with a wavelength of >330 and >430 nm gave 91% (*cis*/*trans* = 83/17) and 83% (only *cis*) *Z*-**16c** after 1 h, respectively (entries 10 and 11). In marked contrast, no reaction took place under the irradiation of >540 nm light (entry 12). These results clearly showed that light in the range of approximately 300 to 500 nm effectively induces the clean conversion of **2n** and *trans*-**8a** into *cis*-*Z*-**16c**.[46,47] Examples of the present photoinduced insertion using other alkynes **2** are shown in eq 7. Insertion with phenylacetylene (**2a**) furnished *cis*-*Z*-**16d** as a kinetic product (15%, only *cis* after 10 min), which gradually isomerized to the *E*-isomer during the course of the reaction (98% *cis*-**10d** with *E*/*Z* = 17/83 after 1 h). Insertion of 1-octyne (**2b**) into the S−Pt bond of *trans*-**8a** also proceeded to furnish the corresponding vinyl platinum *Z*-**16a** in 87% yield (*cis*/*trans* = 97/3) after 1 h. Similar treatment of sterically more hindered 3,3-dimethyl-1-butyne (**2o**) yielded *cis*-*Z*-**16e**, albeit somewhat sluggishly (69% after 1 h). Attempted reactions with internal alkynes such as 4-octyne and dipheny-

(38) For C−C bond-forming reductive elimination from Pt(II) complexes, see:(a) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356. (b) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972, and references therein.

(39) The configurations of *trans*-**8** and *cis*-**8** were independently identified by X-ray crystallographic analysis: Lai, R. D.; Shaver, A. *Inorg. Chem.* **1981**, *20*, 477.

(40) The reaction of **2a** with *trans*-Pt$(SC_6H_4Cl$-*p*$)(Cl)(PPh_3)_2$ (**7i**) under similar reaction conditions did not take place at all.

(41) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Chan, L. T.; Chen, H.-W., Jr.; Masters, A. F.; Pan, W.-H. *Inorg. Chem.* **1982**, *21*, 4291. (c) Tu, T.; Zhou, Y.-G.; Hou, X.-L.; Dai, L.-X.; Dong, X.-C.; Yu, Y.-H.; Sun, J. *Organometallics* **2003**, *22*, 1255.

(42) Ohtaka, A.; Kuniyasu, H.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 14324.

(43) The sample has to be strictly shielded to suppress the insertion because *Z*-**16c** was formed in 40% yield after 48 h with the sample placed under fluorescent light.

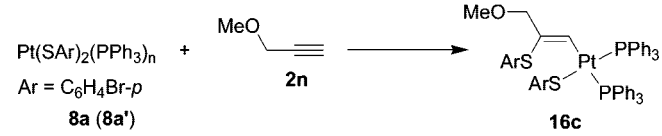
(44) Neither the generation of a new peak nor peak change of **8c** was observed by the addition of PPh_3. This could rule out the possibility that the retardation was caused by forming the five-ligand-coordinated platinum complex.

(45) Kuniyasu, H.; Sugoh, K.; Moon, S; Kurosawa, H. *J. Am. Chem. Soc.* **1997**, *119*, 4669.

(46) Because *cis*-*Z*-**16c** hardly absorbs >430 nm light, the *cis*-to-*trans* isomerization from *cis*-*Z*-**16c** was suppressed under the reaction conditions of entry 11. See the Supporting Information for the UV−vis spectra of *trans*-**8a** and *cis*-*Z*-**16c**.

(47) When a solution of **2n** was treated with *trans*-**8a** under the irradiation of a UV(Hg) lamp (500 W), **8a** was consumed within 10 min to yield 76% **16c** (52% of *cis*-*Z*, 10% *trans*-*Z*, and 14% *cis*-*E*) together with undetermined byproducts.

Table 3. Effect of Photoirradiation on the Reaction of 2n with 8a (8a′)[a]



entry	8	time	yield of *Z*-**16c** (%)[b]	entry	8	time	yield of *Z*-**16c** (%)[b]
1	*trans*-**8a**	10 min[c]	14[d]	7[j]	*cis*-**8a**	30 s	0[l]
		1 h	91[e]				
2[f]	*trans*-**8a**	5 days	0	8[i]	*anti*-**8a′**	2 h	0[m]
3[g]	*trans*-**8a**	1 h	28	9[n]	*trans*-**8a**	2 h	25[eo]
4[h]	*trans*-**8a**	1 h	19	10[p]	*trans*-**8a**	1 h	91[e]
5[i]	*trans*-**8a**	1 h	5	11[q]	*trans*-**8a**	1 h	83[d]
6[j]	*trans*-**8a**	30 s[k]	2.4[d]	12[r]	*trans*-**8a**	1 h	0

[a] Unless otherwise noted, **2n** (0.1 mmol), **8a** (**8a′**) (0.01 mmol of Pt), and C_6D_6 (0.5 mL) in a Pyrex NMR tube were irradiated by a 500 W tungsten lamp at 25 °C. [b] Determined by ^{1}H and ^{31}P NMR. [c] *cis*-**8a**/*trans*-**8a** = 20/80. [d] Only *cis*-*Z*. [e] *cis*/*trans* = 83/17. [f] Under dark. [g] 0.01 mmol of PPh_3 was added. [h] 0.02 mmol of PPh_3 was added. [i] 0.1 mmol of PPh_3 was added. [j] **2a** (0.25 mmol), **8a** (0.0025 mmol). [k] *cis*-**8a**/*trans*-**8a** = 1/99. [l] *cis*-**8a**/*trans*-**8a** = 81/19. [m] *syn*-**8a′**/*anti*-**8a′** = 24/76. [n] **2a** (0.01 mmol). [o] 19% of **8a′** (*syn*/*anti* = 24/76) was formed. [p] >330 nm. [q] >430 nm. [r] >540 nm.

Scheme 8. Photoassisted *trans* vs *cis* Insertion of Alkyne

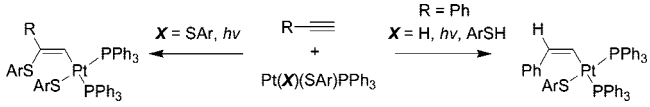
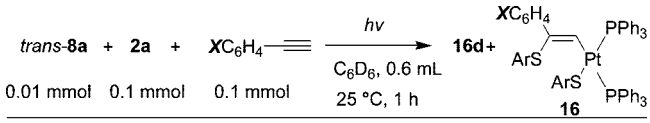


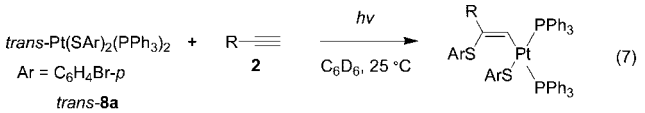
Table 4. Competitive Insertion between 2a and Substituted Arylacetylene[a]



entry	2	X		relative ratio of **16/16d**
1	**2p**	*p*-CO_2Me	**16f**	0.28
2	**2q**	*m*-CO_2Me	**16g**	0.17
3	**2g**	*p*-Cl	**16 h**	0.72
4	**2r**	*m*-OMe	**16i**	1.1
5	**2i**	*m*-Me	**16j**	1.2
6	**2j**	*p*-Me	**16k**	1.6
7	**2k**	*p*-OMe	**16l**	4.6
8	**2s**	*p*-NH_2	**16m**	4.3

[a] *trans*-**8a** (0.01 mmol) and **2** (0.2 M each) in C_6D_6 at 25 °C under 1 h of photoirradation.

lacetylene did not take place, as in the case of thermal insertion into the S−Pt bond of **8**.[48]



2a R = Ph **16d**; 10 min, 15% (only *cis*-*Z*); 1 h, 98% (only *cis*, *E*/*Z* = 17/83)

2b R = *n*-C_6H_{13} **16a**; 10 min, 11% (only *cis*-*Z*); 1 h, 87% (only *Z*, *cis*/*trans* = 97/3)

2o R = *t*-Bu **16e**; 1 h, 69% (only *cis*-*Z*)

To elucidate the electronic effect of **2** for photoirradiated insertion into the S−Pt bond of *trans*-**8a**, the relative reaction rates between **2a** and $XC_6H_4C{\equiv}CH$ having substituents in the *meta* and the *para* position were examined under competitive reaction conditions (Table 4). The Hammett plot (Figure 7) roughly showed a linear free-energy relationship with σ values: Its negative slope ($\rho = -1.3$) suggests that electronically more

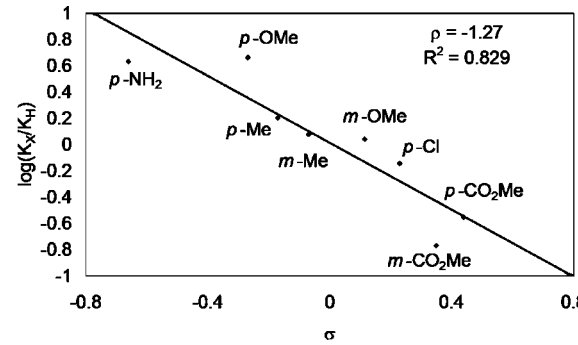
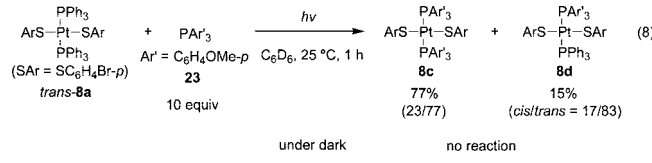


Figure 7. Free-energy relationship for the insertion of arylacetylene into Pt−S bond of *trans*-**8d**.

abundant **2** reacts faster and the effect is greater relative to the thermal insertion of **2** into the S−Pt bond of Pt(SAr)(Cl)$(PPh_3)_2$ (**7b**) ($\rho = -0.7$ in Figure 4). Furthermore, the quantum yield of the present photoinduced reaction of *trans*-**8a** with 10 equiv of **2n** at 313 nm was calculated to be approximately 0.7 by using a merry-go-round apparatus with the disappearance of 2-hexanone as a reference.[49] To clarify the reason photoirradiation facilitates the insertion reaction, a C_6D_6 solution of *trans*-**8a** was treated with PAr'_3 (Ar′ = C_6H_4OMe-*p*, **23**) (10 equiv) (eq 8): The ligand-exchange reaction was dramatically promoted by photoirradiation to yield 77% Pt$(SAr)_2(PAr'_3)_2$ (**8c**) (23/77) and 15% Pt$(SAr)_2(PPh_3)(PAr'_3)$ (**8d**) (*cis*/*trans* = 17/83) under 1 h of photoirradiation, whereas no reaction occurred in the dark under otherwise identical reaction conditions.

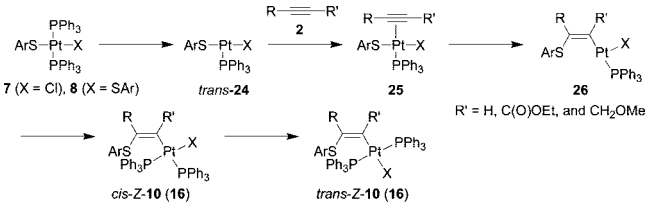


The experiments described above suggest the following reaction pathway leading to the formation of **10** and **16** by the reactions of **7** and **8** with **2** (Scheme 9): Complex **7** (**8**) reacts via complex *trans*-**24**, which is formed by the liberation of PPh_3, with alkyne **2** to afford the alkyne complex **25**. The alkyne with high nucleophlicity preferentially coordinates probably due to the electrophilic character of *trans*-**24**. The migration of the ArS group onto the coordinated alkyne with a Pt bound at either the

(48) (a) The reactivity of DMAD for the insertion into the S−Pt bond of **8a** was not fully revealed because DMAD promptly reacted with PPh_3 of **8a**: Tebby, J. C.; Wilson, I. F.; Griffiths, D. V. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2133. (b) Waite, N. E.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. C* **1969**, 1100.

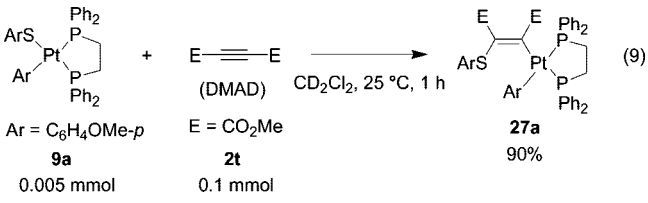
(49) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 207.

Scheme 9. Possible Reaction Pathway for Insertion of 2 into the S−Pt Bond of 7 (8)



sterically less-hindered terminal carbon (R′ = H) or the carbon with RO-group substitution (R = Ph; R′ = C(O)OEt, CH_2OMe) gives **26**. The photoirradiation facilitates the liberation of PPh_3 from **8** to form *trans*-$Pt(SAr)_2(PPh_3)$ (**24**, **X** = SAr), the formation of which can be suppressed by the addition of PPh_3.[50,51] Coordination of PPh_3 at the vacant site results in the formation of *cis*-*Z*-**10** (**16**) as a kinetic product,[52] which isomerizes to the thermodynamically more stable *trans*-*Z*-**10** (**16**).

Insertion of Alkyne (2) into S−Pt Bond of dppe-Ligated Pt(II) Complex. The reactivities of complex Pt(SAr)(Ar′)(dppe) (**9**, dppe; $Ph_2P(CH_2)_2PPh_2$) toward alkynes were next examined. Unlike the cases of reactions with **7** and **8**, unactivated alkynes such as PhC≡CH (**2a**) and 1-octyne (**2b**) reacted with **9** under neither thermal nor photoirradiated reaction conditions. In contrast, DMAD (**2t**), an electronically deficient alkyne, exhibited high reactivity for the insertion. When the reaction of **2t** (0.1 mmol) with $Pt(SC_6H_4OMe\text{-}p)(C_6H_4OMe\text{-}p)$(dppe) (**9a**) (0.005 mmol) in CD_2Cl_2 (0.5 mL) at 25 °C was monitored by ^{31}P NMR spectroscopy, the formation of vinyl platinum complex **27a** was indicated on the basis of a set of doublets centered at δ 40.2 (J_{P-P} = 2.7 Hz, J_{Pt-P} = 2224 Hz) and δ 41.4 (J_{P-P} = 2.7 Hz, J_{Pt-P} = 1695 Hz) in 90% yield after 1 h (eq 9).[53] Compound **27a** was isolated by recrystallization in 33% yield from the reaction carried out on a preparative scale, and its X-ray crystallographic analysis demonstrated that DMAD inserted into the S−Pt bond of **9a** in a *cis*-fashion (Figure 8).[54] Whereas PPh_3-ligated bisvinyl platinum complex **20** underwent C−C bond-forming reductive elimination (eq 4), isolated **27a** was inert for reductive elimination even at 60 °C in C_6D_6.



To get insight on the mechanism of the insertion, the effects of substituents in the ArS and Ar′ moieties of Pt(SAr)(Ar′)(dppe) (**9**) were then examined in the presence of an excess amount of **2t** (0.17 M). The consumption rates of **9** obeyed pseudo-first-order kinetics, and half-lives ($\tau_{1/2}$) are shown in Tables 5 and 6, respectively. The values range from $\tau_{1/2}$ = 11.3 h for the platinum complex with a *p*-CF_3-substituted aromatic ring of ArS to $\tau_{1/2}$ = 0.34 h with a *p*-OMe-substituted aromatic ring (entries 1−5, Table 5). The Hammet plot shows a good linear free-energy relationship with simple σ values (Figure 9). Its negative slope (ρ = −2.0) indicates that EDGs facilitate the insertion. The $\tau_{1/2}$ = 7.4 h for the *o*-Br-substituted platinum complex **9g** demonstrates that the "*o*-halogen effect" is not observed for a dppe-ligated reaction system (entry 6). The Hammet plot about substituents in the Ar′ of **9** (Table 6, Figure 10) also shows a good linear free-energy relationship with simple σ values. The negative slope (σ = −0.5) indicates that EDGs also promote insertion, but the effect is more subtle relative to the electronic effect in ArS. The possible reaction mechanisms for the insertion of **2t** into the S−Pt bond of **9** is depicted in Scheme 10. Complex **9** can react with **2t** to give either cationic platinum complex **28** or the five-ligand-coordinated platinum complex

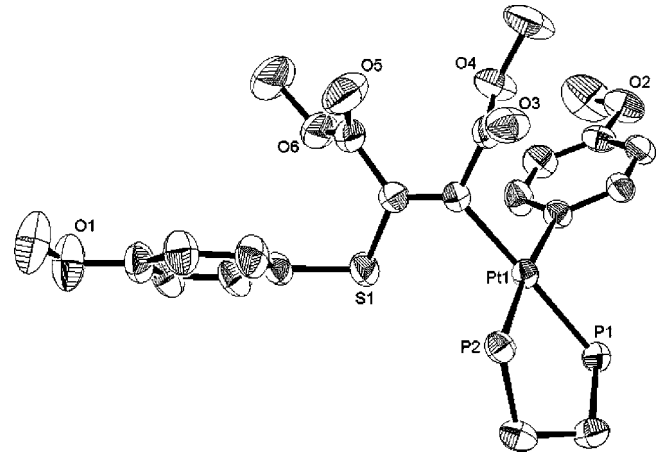
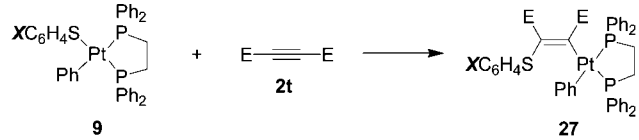


Figure 8. ORTEP diagram of **23a** (Ph on DPPE omitted).

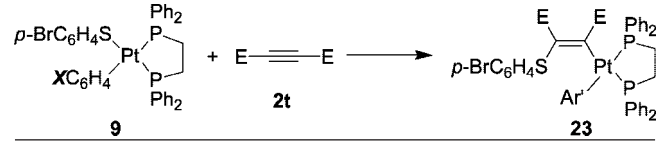
Table 5. Effect of Substituent in Ar of Pt(SAr)Ph(DPPE) (9)[a]



entry	9	27	Ar	$\tau_{1/2}$ (h)
1	**9b**	**27b**	*p*-CF_3	11.3
2	**9c**	**27c**	*p*-Br	3.5
3	**9d**	**27d**	Ph	1.6
4	**9e**	**27e**	*p*-Me	0.35
5	**9f**	**27f**	*p*-OMe	0.34
6	**9g**	**27g**	*o*-Br	7.4

[a] **9** (0.01 mmol) and **2t** (0.17 M) in C_6D_6 at 25 °C.

Table 6. Effect of Substituent in Ar′ of $Pt(SC_6H_4Br\text{-}p)$(Ar′)(DPPE) (9)[a]



entry	9	23	Ar	$\tau_{1/2}$ (h)
1	**9h**	**23h**	*p*-CO_2Et	5.8
2	**9i**	**23i**	*p*-Cl	4.4
3	**9e**	**23e**	Ph	3.5
4	**9j**	**23j**	*p*-Me	3.0
5	**9k**	**23k**	*p*-OMe	2.5

[a] **9** (0.01 mmol) and **2t** (0.17 M) in C_6D_6 at 25 °C.

(50) (a) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401. (b) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (c) Sakakura, T.; Sodeyama, T.; Sakaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221.

(51) For photoirradiated ligand dissociation, see:(a) Wada, M.; Kumazoe, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1204. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 4838. (c) Ruiz, J.; Garland, M.; Roman, E.; Astruc, D. *J. Organomet. Chem.* **1989**, *377*, 309.

(52) The *cis* vinyl platinum complex was also detected as a kinetic product in the early stages of the reaction of **7j** with **2a**.

(53) Complex **9** was hardly soluble in C_6D_6.

(54) Crystal data for **27a**: space group $P\bar{1}$(#2), a = 12.631(1) Å, b = 17.188(2) Å, c = 11.455(1) Å, α = 90.219(4)°, β = 114.082(5)°, γ = 107.153(3)°, Z = 2, ρ = 1.518 g/cm^3, R = 0.028, R_w = 0.038.

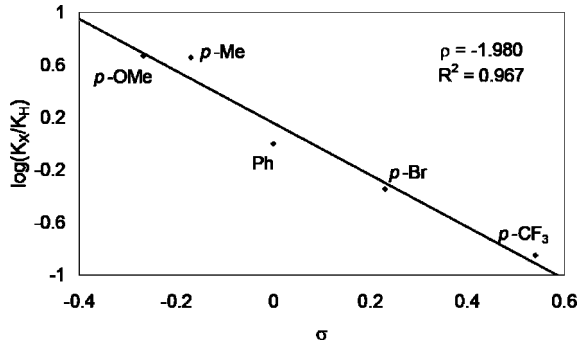


Figure 9. Hammet plot of the rates of insertion of **2t** into the S−Pt bond of **9b−f**.

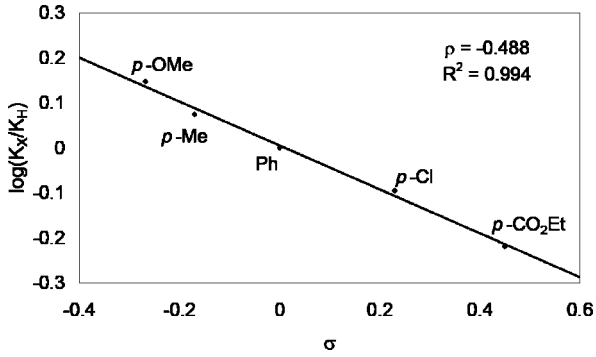
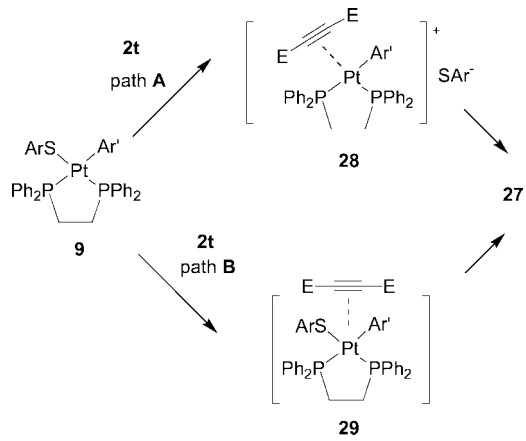


Figure 10. Hammet plot of the rates of insertion of **2t** into the S−Pt bond of **9e** and **9h−k**.

Scheme 10. Plausible Reaction Pathways for the Insertion of 2t into the S−Pt Bond of 9



29. Given the fact that *cis*-insertion took place, the formation of **29** and *cis*-migration of SAr is more likely.[55] The EDG in ArS would facilitate the formation of **29** due to the nucleophilic character of complex **9** for the formation of **29** or the nucleophilic migration of an ArS group onto the coordinated alkyne moiety in **29**.

Pt-Catalyzed Dimerization−Bisthiolaton of Alkyne (2) by Diaryl Disulfide (ArS)$_2$ (30). The result of the reaction of *trans*-**8a** with **2b** (eq 4) suggests that the reaction of **2** with (ArS)$_2$ (**30**) giving (*Z*,*Z*)-(ArS)(R)C═C(H)-C(H)═C(SAr)(R) (**19**) is catalyzed by a PPh$_3$-ligated Pt(0) complex on the basis of the reaction mechanism shown in Scheme 11: (1) oxidative addition of **30** to Pt(PPh$_3$)$_n$ to afford **8**;[45] (2) insertion of **2** into

(55) It has been proposed that the insertion of CF_2═CF_2 into the O−Pt bond of Pt(OMe)(CH$_3$)(dppe) proceeds via a similar five-ligand-coordinated complex; see:Bryndza, H. *Organometallics* **1985**, *4*, 406.

Scheme 11. Plausible Reaction Pathway for the Pt-Catalyzed Reaction of Alkyne (2) with Diaryl Disulfide (30) (PPh$_3$ on Pt omitted)

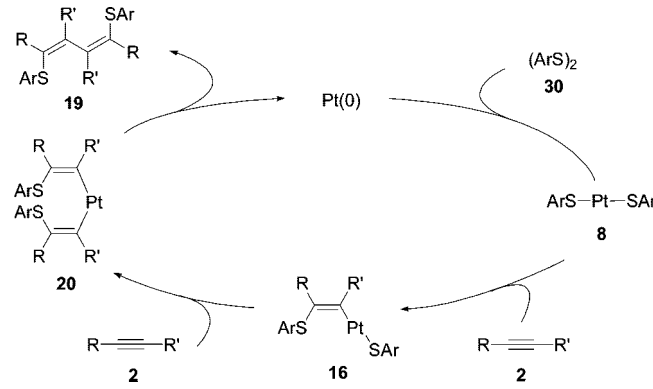
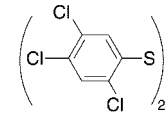
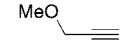
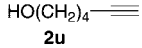
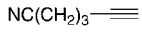
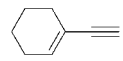
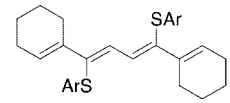
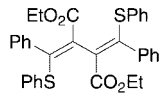


Table 7. Pt-Catalyzed Dimerization−Bisthiolation of 2 with 30

2 + **30** ⟶ **19**

entry	**2**	**30**			Isolated yield (%)
1	**2b**	$(PhS)_2$	**30a**	**19b**	86
2	**2b**	$(p\text{-}MeC_6H_4S)_2$	**30b**	**19c**	82
3	**2b**	$(p\text{-}BrC_6H_4S)_2$	**30c**	**19a**	81
4	**2b**	$(o\text{-}BrC_6H_4S)_2$	**30d**	**19d**	74
5	**2b**		**30e**	**19e**	73
6[b]	 **2n**	**30c**		**19f**	46[c]
7	**2a**	**30a**		**19g**	62
8	 **2u**	**30a**		**19h**	62
9	 **2v**	**30a**		**19i**	64
10	 **2w**	**30a**		 **19j**	80
11[d]	 **2d**	**30a**		 **19k**	38

[a] **30** (1.0 mmol), **2** (2.4 mmol), and Pt(PPh$_3$)$_4$ (0.05 mmol) in toluene (1 mL) at 110 °C for 20 h. [b] 120 °C for 41 h. [c] 14% of 1,3-adducts were obtained. [d] In xylene at 140 °C for 48 h

the S−Pt bond of **8** to generate vinyl platinum **16**; (3) insertion of another **2** into the remaining S−Pt bond of **16** to yield bisvinyl platinum **20**; and (4) C−C bond-forming reductive elimination of **19** with regeneration of Pt(0).[38] The results of the Pt(PPh$_3$)$_4$-catalyzed reaction of some alkynes (**2**) with diaryl disulfide (**30**) are summarized in Table 7. The treatment of 1-octyne (**2b**, 2.4 mmol) with (PhS)$_2$ (**30a**, 1.0 mmol) in the presence of Pt(PPh$_3$)$_4$ (0.05 mmol) under toluene (1 mL) reflux for 20 h resulted in the production of the anticipated **19b** in 86% yield (entry 1). Functional groups such as *p*-Me (**30b**), *p*-Br (**30c**), *o*-Br (**30d**), and 2,4,5-tri-Cl (**30e**) on aromatic rings in **30** barely interfered with the reactions to furnish the corresponding symmetrical 1:3-dienes (1:2 adducts) in good yields (entries 2−5). When propargyl alcohol (**2n**) was em-

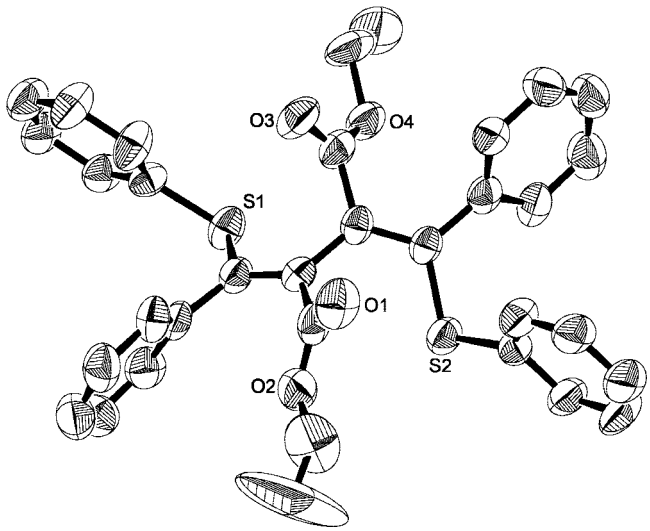
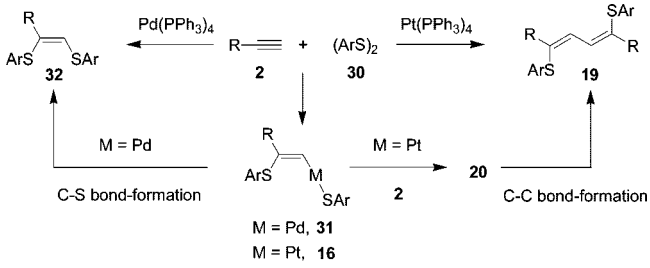


Figure 11. ORTEP diagram of **19k**.

Scheme 12. Pd-Catalyzed vs Pt-Catalyzed Reaction of 2 with 30



ployed as an alkyne, the 1:2 adduct (**19f**; 46%), as well as 1:3 adducts, the formation of which was suggested by mass spectroscopy, was produced in 14% yield. This result demonstrates that the multiple insertion of **2** into the S−Pt bond of **8** takes place when **2n** was employed as an alkyne. The reactions with phenylacetylene (**2a**) and alkynes having OH (**2u**) and CN (**2v**) groups also occurred to afford **19g**, **19h**, and **19i** in moderate yields (entries 7−9). When eneyne **2w** was employed, conjugated tetraene **19j** was obtained in 80% yield as a single isomer (entry 10). Ethyl phenylpropiolate (**2d**) also reacted with **30a** under xylene reflux (48 h) to afford 38% of the dimerization−bisthiolation product **19k**, the structure of which was unambiguously determined by X-ray crystallographic analysis; EtOC(O) groups are located at the 2,3-position of the 1,3-diene moiety (Figure 11).[56] The regio- and stereoselectivity are consistent with those anticipated from the structure of vinyl platinum **10d**, as shown in Figure 2. It should be noted that the pattern of the reaction of **2** with **30** can be facilely converted from the simple 1:1 addition producing **32** into a 1:2 addition and affording **19** by just changing the catalysts from $Pd(PPh_3)_4$ to $Pt(PPh_3)_4$ (Scheme 12).[13] These contrastive reactivities are attributable to the differing tendencies for C−S bond-forming reductive elimination of vinyl palladium **31** and vinyl platinum **16**; the former underwent C−S bond-forming reductive elimination, whereas the latter is thermodynamically stable and C−C bond-formation took place via bisvinyl platinum complex **20**.[10a]

(56) Crystal data for *Z,Z*-**19k**: space group $P2_1$ (#4), $a = 8.1456(4)$ Å, $b = 16.984(1)$ Å, $c = 11.5882(6)$ Å, $\beta = 111.984(2)°$, $Z = 2$, $\rho = 1.271$ g/cm^3, $R = 0.047$, $R_w = 0.117$.

Conclusion

The significance of the present paper is summarized as follows: (1) solid evidence for the insertion of **2** between the sulfur and the group 10 metal bond of the PR_3-ligated complexes has been provided; (2) the "*o*-halogen effect" was discovered under insertion reactions with *trans*-Pt(SAr)(Cl)$(PPh_3)_2$ (**7**) and *trans*-Pt$(SAr)_2(PPh_3)_2$ (**8**); (3) the photofacilitated insertion of alkyne **2** into the S−Pt bond of *trans*-Pt$(SAr)_2(PPh_3)_2$ (**8**) was revealed; (4) the preference of alkynes for the insertion into S−Pt bonds, which differs according to the species of phosphine ligand, was presented; and (5) the insertion of **2** into the S−Pt bonds of **8** was successfully applied to the Pt-catalyzed dimerization−bisthiolation of alkyne (**2**) by disulfide (**30**). We do believe these findings make a great contribution toward a deeper understanding of the mechanisms of M-catalyzed addition reactions, such as RS-**G** (**1**) to alkynes (Scheme 1).

Experimental Section

General Comments. ^{1}H, ^{13}C, and ^{31}P NMR spectra in benzene-d_6, $CDCl_3$, and CD_2Cl_2 solution were recorded using JEOL JNM-GSX-270 (270 MHz) and JEOL JNM-Alice 400 (400 MHz) spectrometers. The chemical shifts in the ^{1}H and ^{13}C NMR were recorded relative to Me_4Si as an internal standard. The chemical shifts in the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 as an external standard. In order to calculate NMR yield, S=P(C_6H_4Me-*p*)$_3$ or O=P(C_6H_4Me)$_3$ was used as an internal standard after relative intensities with products were measured. IR spectra were recorded with a Perkin-Elmer model 1600 spectrometer. Combustion analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. GC-mass spectra were recorded with a Shimazu QP-5000 spectrometer. Preparative TLC was carried out using Wakogel B-5F silica gel. All reactions were carried out under a N_2 atmosphere. All solvents were distilled before use. Complex *trans*-**7** was prepared according to the method we have developed.[26] Complex *trans*-Pt$(SAr)_2(PPh_3)_2$ (Ar = C_6H_4Br-*p*) (*trans*-**8**) and *anti*-[Pt$(SAr)_2(PPh_3)]_2$ (**8′**) were synthesized by the oxidative addition of $(ArS)_2$ to $Pt(PPh_3)_4$.[45] The complex *cis*-Pt$(SAr)_2(PPh_3)_2$ (*cis*-**8**) was also prepared according to the literature.[39] Complex Pt(SAr)(Ar′)(dppe) (**9**) was prepared from the reaction of *trans*-Pt(I)(Ph)$(PPh_3)_2$ with ArSNa in the presence of dppe. The *m*- and *p*-substituted phenylacetylenes were synthesized according to the literature.[57] Other acetylenes and $(ArS)_2$ (**30**) were commercially available. Photoirradiation was performed using a Toshiba 500 W tungsten lamp. Toshiba UV-33, Y-43, and O-54 were used to filter the light. The X-ray crystal data of *trans*-*Z*-**10a**, *trans*-Z-**10d**, *trans*-*Z*-**10e**, **7j**, **27a**, and **19k** were collected by Rigaku AFC5R diffraction, ORTEP diagrams of them are shown with 50% probability ellipsoids, and the crystal and data collection parameters of them can be accessed either in the Supporting Information of this article or in the Supporting Information of literature shown in ref 27.

Reaction of Pt$(SC_6H_4Cl$-*p*$)(Cl)(PPh_3)_2$ (7a) with Phenylacetylene (2a) (eq 1). *trans*-**7a** (9.0 mg, 0.01 mmol), S=P(C_6H_4Me-*p*)$_3$ (1.7 mg, 0.0051 mmol as an internal standard), and toluene-d_8 (0.6 mL) were added to a Pyrex NMR tube under a N_2 atmosphere. After the initial ratio of signals of *trans*-**7a** and S=P(C_6H_4-*p*-Me)$_3$ was checked by ^{1}H and ^{31}P NMR spectra, **2a** (1.0 mg, 0.01 mmol) was added in the NMR tube under a N_2 atmosphere. The reaction at 110 °C was then monitored by ^{1}H and ^{31}P NMR spectra. The formation of *trans*-**10a** was confirmed in 83% yield after 6 h. The reactions using other alkynes shown in eq 1 were similarly carried out and monitored by ^{1}H and ^{31}P NMR spectroscopies.

Reaction of Pt$(SC_6H_4Br$-*p*$)(Cl)(PPh_3)_2$ (7b) with an Excess Amount of *p*-CF_3-Substituted Arylacetylene (2f) (Table 1, entry 1). *trans*-**7b** (9.8 mg, 0.010 mmol), S=P(C_6H_4-*p*-Me)$_3$ (1.7 mg, 0.0051 mmol as an internal standard), and C_6D_6 (0.6 mL) were

added in a Pyrex NMR tube under a N_2 atmosphere. After the ratio of signals of *trans*-**7a** and S=P(C_6H_4Me-*p*)$_3$ was checked by ^{1}H and ^{31}P NMR spectroscopies, **2f** (17.0 mg, 0.1 mmol) was added to the NMR tube under a N_2 atmosphere. The reaction at 70 °C was then monitored by ^{1}H and ^{31}P NMR spectroscopies. The consumption rate of the starting *trans*-**7b** obeyed pseudo-first-order kinetics. The half-life of *trans*-**7b** was calculated to be 10.2 h. The reactions with other arylacetylenes **2** shown in Table 1 were similarly carried out and monitored by NMR spectroscopy. The half-lives of *trans*-**7b** are summarized in Table 1. Figure 4 shows the correlation between the values of log($k_{obs}/k_{obs(H)}$) and Hammett's substituent constants σ and σ^+ of **X** in **X**C_6H_4C≡CH.

Reaction of *trans*-7a with an Excess Amount of 2a (Table 2, entry 2). *trans*-**7a** (9.0 mg, 0.010 mmol), S=P(C_6H_4Me-*p*)$_3$ (1.7 mg, 0.0051 mmol as an internal standard), and C_6D_6 (0.6 mL) were added to a Pyrex NMR tube under a N_2 atmosphere. After the ratio of signals of *trans*-**4a** and S=P(C_6H_4Me-*p*)$_3$ was checked by ^{1}H and ^{31}P NMR spectroscopies, **2a** (10.2 mg, 0.1 mmol) was added to the NMR tube under a N_2 atmosphere. The reaction at 70 °C was then monitored by ^{1}H and ^{31}P NMR spectroscopies. The consumption rate of the starting *trans*-**7a** obeyed pseudo-first-order kinetics. The half-life of *trans*-**7a** was calculated to be 6.1 h.

The reactions using other platinum complexes *trans*-**7** shown in Table 2 were similarly carried out and monitored by NMR spectroscopy. The half-lives of *trans*-**7** are summarized in Table 2. Figure 5 shows the correlation between the values of log($k_{obs}/k_{obs(H)}$) and the Hammett's substituent constants σ of **X** in *trans*-Pt(SC_6H_4**X**-*p*)(Cl)(PPh_3)$_2$.

Ligand-Exchange Reaction between 7a and *trans*-Pt(SC_6H_4Cl-*p*)(Cl)[P(C_6H_4Me-p)$_3$]$_2$ (7a′) (eq 2). *trans*-**7a** (4.5 mg, 0.005 mmol), *trans*-**7a′** (4.9 mg, 0.005 mmol), S=P(C_6H_4Me-*p*)$_3$ (1.7 mg, 0.0051 mmol as an internal standard), and C_6D_6 (0.6 mL) were added to a Pyrex NMR tube. The reaction was then monitored by ^{1}H and ^{31}P NMR spectra at 25 °C. The formation of *trans*-Pt(SC_6H_4Cl-*p*)(Cl)(PPh_3)[P(C_6H_4Me-*p*)$_3$] (**7a″**) was confirmed. The reaction time and yield of **7a″** were as follows: 0.5 h, 13%; 1 h, 23%; 24 h, 48%.

7a″: ^{31}P NMR (160 MHz, C_6D_6) δ 23.7 (s, J_{Pt-P} = 2692 Hz), 23.3 (s, J_{Pt-P} = 2715 Hz).

The reaction of **7i** with **7i′** was similarly carried out and monitored by NMR spectroscopy. The reaction time and yield of *trans*-Pt(SC_6H_4Cl-*o*)(Cl)(PPh_3)[P(C_6H_4Cl-*p*)$_3$] (**7i″**) were as follows: 0.5 h, 5%; 1 h, 12%; 24 h, 44%.

7i″: ^{31}P NMR (160 MHz, C_6D_6) δ 22.5 (s, J_{Pt-P} = 2710 Hz), 21.9 (s, J_{Pt-P} = 2688 Hz).

Reaction of Pt(SAr)$_2$(PPh_3)$_2$ (8a, Ar = C_6H_4Br-*p*) with 2b (eq 4). Into a Pyrex NMR tube were added **8a** (10 mg, 0.01 mmol), PPh_3 (5.2 mg, 0.02 mmol), O=P(C_6H_4Me-*p*)$_3$ (3.0 mg, 0.01 mmol as an internal standard), **2b** (26.4 mg, 0.24 mmol), and C_6D_6 (0.6 mL) under a N_2 atmosphere. When the sample was heated at 80 °C for 1 h, the formation of Pt[(*Z*)-C(H)=C(SAr)(*n*-C_6H_{13})](SAr)(PPh_3)$_2$ (**16a**) was confirmed by ^{31}P NMR spectroscopy in 29% yield. While the yield of **16a** was decreased to 26% after 8 h, formation of S-bridged complexes **16a′** and **17a** was confirmed at 16% (*syn*/*anti* = 31/69) and 5% (40/60) yields, respectively. The formation of Pt(0) complex **18a** and 1,3-diene **19a** was also confirmed at 28% and 35% yields, respectively. The yields of **18a** and **19a** reached 78% and 93%, respectively, after 40 h, whereas the complexes *trans*-**8a**, **16a**, **16a′**, and **17a** disappeared.

Preparation of Authentic 16a.[36] Into a two-necked 5 mL reaction vessel equipped with a stirring bar were added (*Z*)-(ArS)(*n*-C_6H_{13})C=C[C(O)SAr](H) (Ar = C_6H_4Br-*p*) (102 mg, 0.20 mmol), Pt(PPh_3)$_2$(C_2H_4) (143 mg, 0.20 mmol), and C_6H_6 (4 mL) under a N_2 atmosphere. After the solution was stirred at 25 °C for 3 h, the solvent was removed *in vacuo* to give *trans*-Pt[(Z)-C(H)=C(SAr)(*n*-C_6H_{13})](SAr)(PPh_3)$_2$ (*trans*-**16a**) as a yellow solid (182 mg, 0.15 mmol, 75% yield).

16a: yellow solid; mp 123 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.83 (t, *J* = 7.2 Hz, 3 H), 0.85−0.93 (m, 4 H), 1.00−1.07 (m, 2 H), 1.09−1.17 (m, 2 H), 1.66−1.74 (m, 2 H), 6.39 (d, *J* = 8.6 Hz, 2 H), 6.73 (d, *J* = 8.4 Hz, 2 H), 6.97−7.05 (m, 20 H), 7.07 (d, *J* = 8.6 Hz, 2 H), 7.29 (t, *J* = 3.4 Hz, 1 H), 7.80−7.82 (m, 12 H); ^{31}P NMR (160 MHz, C_6D_6) δ 20.3 (s, J_{Pt-P} = 3065 Hz); IR (KBr) 3054, 2922, 1480, 1463, 1434, 1085, 1006, 808, 742, 692, 522, 512 cm^{-1}. Anal. Calcd for $C_{56}H_{52}Br_2P_2S_2Pt$: C, 55.77; H, 4.35. Found: C, 56.00; H, 4.43.

Reaction of *trans*-8b with 2a (eq 5). *trans*-**8b** (10 mg, 0.01 mmol), S=P(C_6H_4OMe-*p*)$_3$ (2.3 mg, 0.0060 mmol as an internal standard), C_6D_6 (0.6 mL), and phenylacetylene (**2a**, 10 mg, 0.1 mmol) were added to a Pyrex NMR tube under a N_2 atmosphere. The reaction was then monitored by ^{1}H and ^{31}P NMR spectroscopies at 25 °C. The formation of *cis*-Pt[(*Z*)-C(H)=C(SAr)-(Ph)](SAr)(PPh_3)$_2$ (Ar = C_6H_4Cl-*o*) (*cis*-*Z*-**16b**) was confirmed in 40% yield after 4 h. After 55 h, complex *Z*-**16b** was formed in 95% yield as a mixture of stereoisomers (*cis*/*trans* = 85/15). On the other hand, the reaction of *cis*-**8b** with **2a** did not produce **16b** at all after 4 h at 25 °C (eq 6). The authentic **16b** was prepared by the reaction of (*Z*)-(ArS) (Ph)C=C(SAr)(H) (0.01 mmol) with Pt(PPh_3)$_2$(C_2H_4) (0.01 mmol) in C_6D_6 at 25 °C to give **16b** (85% yield with *cis*/*trans* = 95/5 after 22 h).[36]

***cis*-Pt[(*Z*)-C(H)=C(SAr)(Ph)](SAr)(PPh_3)$_2$ (Ar = C_6H_4Cl-*o*) (*cis*-16b):** ^{31}P NMR (160 MHz, C_6D_6) δ 19.1 (d, J_{P-P} = 18 Hz, J_{Pt-P} = 3327 Hz), 17.5 (d, J_{P-P} = 18 Hz, J_{Pt-P} = 1855 Hz).

***trans*-Pt[(*Z*)-C(H)=C(SAr)(Ph)](SAr)(PPh_3)$_2$ (Ar = C_6H_4-Cl-*o*) (*trans*-16b):** ^{31}P NMR (160 MHz, C_6D_6) δ 18.3 (s, J_{Pt-P} = 2982 Hz).

Reaction of Pt(SAr)$_2$(PPh_3)$_2$ (Ar = C_6H_4Br-*p*, 8a) with Methyl Propargyl Ether (2n). Photoirradiated Insertion (Table 3). Into a Pyrex NMR tube were added *trans*-**8a** (11.0 mg, 0.01 mmol), **2n** (7.0 mg, 0.1 mmol), and 0.5 mL of C_6D_6 under a N_2 atmosphere. The tube immersed into a water bath (25 °C) was irradiated with a 500 W tungsten lamp placed at 5 cm from the tube, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopies (entry 1). The spectrum taken after 10 min of photoirradiation showed the formation of 14% *cis*-*Z*-**16c** accompanied with the isomerization of *trans*-**8a** to *cis*-**8a** (*cis*/*trans* = 80/20). After 1 h, *Z*-**16c** was formed in 91% yield (*cis*/*trans* = 83/17). The *cis*-*Z*-**16c** was isolated by a similar 0.18 mmol scale reaction carried out in 10 NMR tubes (0.018 mmol scale each) followed by recrystallization from benzene/hexane to provide 102 mg of pure *cis*-*Z*-**16c** (48% yield).

cis-*Z*-**16c**: colorless solid; mp 151 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 2.73 (s, 3 H), 3.44 (s, 2 H), 6.82−6.89 (m, 18 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.46 (dd, J_{H-P} = 5.4 Hz, J_{H-P} = 7.3 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 22 H), 7.62−7.68 (m, 14 H); ^{31}P NMR (109 MHz, C_6D_6) δ 19.3 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 1810 Hz), 21.7 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 3306 Hz); IR (KBr) 3094, 1559, 1464, 1435, 1180, 1002, 693, 523 cm^{-1}. Anal. Calcd for $C_{52}H_{44}Br_2OP_2PtS_2$: C, 53.57; H, 3.80. Found: C, 53.45; H, 3.75.

The reaction of *trans*-**8a** (0.01 mmol) with **2n** (0.1 mmol) in darkness was monitored by ^{31}P NMR spectrum, with no insertion confirmed after 5 days (entry 2). When the photoirradiated reactions were conducted in the presence of additional PPh_3 (0.01 mmol, 0.02 and 0.1 mmol), the formation of **16c** was significantly suppressed (28%, 19%, and 5% of *Z*-**16c**, respectively) (entries 3−5). The photoirradiated reaction of *trans*-**8a** (0.0025 mmol) with **2n** (0.25 mmol) and the reaction of *cis*-**8a** (0.0025 mmol) with **2n** (0.25 mmol) were performed for 30 s (entries 6 and 7): The former provided 2.4% *cis*-*Z*-**16c** (with the remaining *cis*-**8a**/*trans*-**8a** = 1/99); however, the latter did not produce any detectable amount of insertion product (*cis*-**8a**/*trans*-**8a** = 81/19). The treatment of *anti*-[Pt($SAr)_2$(PPh_3)]$_2$ (*anti*-**8a′**) (0.005 mmol) with **2n** (0.1 mmol) in the presence of PPh_3 (2.6 mg, 0.01 mmol) produced no insertion

product even after 2 h of photoirradiation; only the isomerization of **8a′** was observed (*syn*-**8a′** (δ 19.5)/*anti*-**8a′** (δ 18.9) = 24/76) (entry 8). When the reaction of *trans*-**8a** with 1 equiv of **2n** (0.01 mmol each) was carried out under photoirradiation for 2 h, the formation of 25% *Z*-**16c** (*cis*/*trans* = 83/17) and 19% **8a′** (*syn*/*anti* = 24/76) was confirmed (entry 9). Irradiation of the solutions of *trans*-**8a** (0.01 mmol) and **2n** (0.1 mmol) with >330 and >430 nm light using UY33 and Y43 as filters for 1 h resulted in the formation of **16c** in 91% (only *Z*, *cis*/*trans* = 83/17) and 83% yield (only *cis*-*Z*), respectively (entries 10 and 11). On the other hand, no insertion took place from irradiation of light at <1770 nm using O54 as the filter (entry 12). When the reaction of **2n** (0.1 mmol) with *trans*-**8a** (0.01 mmol) was performed under the irradiation of a UV(Hg) lamp (500 W), the complete disappearance of **8a** and the formation of 76% **16c** (52% *cis*-*Z*, 10% *trans*-*Z*, and 14% *cis*-*E*) with a small amount of undetermined products were confirmed by ^{31}P NMR spectroscopy after 10 min.

Photoinduced Isomerization of *cis*-*Z*-16c. The isolated complex *cis*-*Z*-**16c** (0.01 mmol) and C_6D_6 (0.5 mL) were placed in a NMR tube, and the solution was irradiated using a tungsten lamp for 5 h. The formation of *trans*-*Z*-**16c** (16%) (δ 19.8, s, J_{Pt-P} = 3093 Hz), *cis*-*E*-**16c** (10%) (δ 19.2, J_{P-P}= 17.2 H, δ 20.9, J_{P-P} = 17.2 Hz, J_{Pt-P} unreadable), and *trans*-*E*-**16c** (8%) (δ 19.52, s, the value of J_{Pt-P} was unreadable) was confirmed by ^{31}P NMR spectrum.

Insertion of Other Alkynes into the S−Pt Bond of 8a (eq 7). The reactions of 0.1 mmol of phenylacetylene (**2a**), 1-octyne (**2b**), and 1,1-dimethyl-3-butyne (**2o**) with 0.01 mmol of *trans*-**8a** were carried out in C_6D_6 under photoirradiation and were monitored by ^{31}P NMR spectroscopies in a manner similar to the case of reactions with **2n**. Each reaction provided the corresponding insertion product Pt[(*Z*)-C(H)═C(SAr)(R)](SAr)$(PPh_3)_2$ (*Z*-**16**). The reaction times and the yields were as follows: **16d** (R = Ph), (*cis*-*Z*, 10 min, 15%), (*cis*, *E*/*Z* = 17/83, 1 h, 98%); **16a** (R = *n*-C_6H_{13}), (*cis*-*Z*, 10 min, 11%), (*Z*, *cis*/*trans* = 97/3, 1 h, 87%); **16e** (R = *t*-Bu), (*cis*-*Z*, 1 h, 69%). *Z*-**16d**: ^{31}P NMR (109 MHz, C_6D_6) *cis*-isomer: δ 18.4 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 1803 Hz), 21.0 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 3336 Hz); *trans*-isomer: δ 20.3 (s, J_{Pt-P} 3065 Hz). *cis*-*Z*-**16a**: ^{31}P NMR (109 MHz, C_6D_6) δ 18.3 (d, J_{P-P} = 18.4 Hz, J_{Pt-P} = 1755 Hz), 22.0 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 3336 Hz). *cis*-*E*-**16e**: ^{31}P NMR (160 MHz, C_6D_6) (data collected from a mixture of stereoisomers) δ 18.8 (d, J_{Pt-P} = 18.3 Hz, J_{Pt-P} = 1756 Hz), 21.8 (d, J_{P-P} = 18.3 Hz, J_{Pt-P} = 3273 Hz). The spectral data of **16d** and **16e** were confirmed by comparison with those of authentic samples produced by the oxidative addition of corresponding vinylsulfides to $Pt(PPh_3)_2(C_2H_4)$.[36] The attempted reactions of *trans*-**8a** with 4-octyne, diphenylacetylene, and 2-octynoic acid produced only **8a′** (*syn*/*anti* = 13/87) after 2 h of photoirradiation.

Competitive Insertion between 2a and Substituted Arylacetylene (Table 4). The C_6D_6 solutions of mixtures of **2a** (0.1 mmol), **2** (0.1 mmol), and *trans*-**8a** (0.01 mmol) were photoirradiated for 1 h, and the ratios of *cis*-**16** (*E*/*Z* combined)/*cis*-**16d** (*E*/*Z* combined) were calculated by taking ^{31}P NMR spectra: **16g/16d** = 0.17/1; **16f/16d** = 0.28/1; **16h/16d** = 0.72/1; **16i/16d** = 1.1/1; **16j/16d** = 1.2/1; **16k/16d** = 1.6/1; **16l/16d** = 4.6/1; **16m/16d** = 4.3/1. The ^{31}P NMR chemical shifts of **16** were confirmed independently by either the photoirradiated reactions of **2** with *trans*-**8a** or the oxidative addition of the corresponding vinyl sulfide to $Pt(PPh_3)_2(C_2H_4)$.[36]

cis-*Z*-**16f**: ^{31}P NMR (160 MHz, C_6D_6) δ 19.3 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 1803 Hz), 21.9 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 3336 Hz). *cis*-**16g**: ^{31}P NMR (160 MHz, C_6D_6) *Z*-isomer: δ 19.3 (d, J_{P-P} = 18.4 Hz, J_{Pt-P} = 1869 Hz), 20.9 (d, J_{P-P} = 18.4 Hz, J_{Pt-P} = 3275 Hz); *E*-isomer: δ 18.6 (d, J_{P-P} = 18.3 Hz, J_{Pt-P} = 3231 Hz), 21.7 (d, J_{P-P} = 18.3 Hz, J_{Pt-P} = 3231 Hz). *cis*-*Z*-**16h**: ^{31}P NMR (160 MHz, C_6D_6) δ 19.4 (d, J_{P-P} = 18.3 Hz, J_{Pt-P} = 1865 Hz), 20.9 (d, J_{P-P} = 18.3 Hz, J_{Pt-P} = 3286 Hz). *cis*-*Z*-**16i**: ^{31}P NMR (160 MHz, C_6D_6) δ 19.5 (d, J_{P-P} = 17.8 Hz, J_{Pt-P} = 1853 Hz), 20.7 (d, J_{P-P} = 17.8 Hz, J_{Pt-P} = 3304 Hz). *cis*-*Z*-**16j**: ^{31}P NMR (160 MHz, C_6D_6) δ 19.5 (d, J_{P-P} = 17.8 Hz, J_{Pt-P} = 1849 Hz), 20.75 (d, J_{P-P} = 17.8 Hz, J_{Pt-P} = 3312 Hz). *cis*-**16k**: ^{31}P NMR (160 MHz, C_6D_6) *Z*-isomer: δ 19.5 (d, J_{P-P} = 17.7 Hz, J_{Pt-P} = 1849 Hz), 20.7 (d, J_{P-P} = 17.7 Hz, J_{Pt-P} = 3310 Hz); *E*-isomer: δ 20.9 (d, J_{P-P} = 18.4 Hz), 22.4 (d, J_{P-P} = 18.4 Hz). *cis*-**16l**: ^{31}P NMR (160 MHz, C_6D_6) *Z*-isomer: δ 19.5 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 1848 Hz), 21.7 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 3315 Hz); *E*-isomer: δ 18.8 (d, J_{P-P} = 18.4 Hz, J_{Pt-P} = 1741 Hz), 22.2 (d, J_{P-P} = 18.4 Hz, J_{Pt-P} = 3270 Hz). *cis*-**16m**: ^{31}P NMR (160 MHz, C_6D_6) *Z*-isomer: δ 19.6 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 1841 Hz), 20.5 (d, J_{P-P} = 17.2 Hz, J_{Pt-P} = 3337 Hz); *E*-isomer: δ 18.9 (d, J_{P-P} = 17.2 Hz), 22.4 (d, J_{P-P} = 17.2 Hz).

Measurement of Quantum Yield for the Formation of *cis*-Z-16c from the Reaction of *trans*-8a with 2n. The quantum yield for the formation of *cis*-*Z*-**16c** was determined with 313 nm light using a 2-hexanone actinometer. Into four NMR tubes were placed *trans*-**8a** (0.01 mmol), **2n** (0.1mmol), and C_6D_6 (0.6 mL), respectively. Then into four other NMR tubes was placed 2-hexanone (58 mM) in C_6D_6, which was set to match the absorbance of *cis*-*Z*-**16c**. The samples were irradiated by 313 nm light using K_2CrO_4−Na_2CO_3 aqueous solution as a cutoff filter at 25 °C for 4 h on a merry-go-round apparatus (300 W). The quantum yield of **8a** was estimated to be ca. 0.7 by assuming the quantum yield of the disappearance of 2-hexanone to be 0.327 (Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 207).

Photoinduced Ligand Exchange of 8a with PAr′$_3$ (Ar′ = C$_6$H$_4$OMe-*p*; 23) (eq 8). Into both of two NMR tubes were added *trans*-**8a** (0.01 mmol), **23** (2.0 mg, 0.1 mmol), and C_6D_6 (0.5 mL). The ^{31}P NMR spectrum taken after 1 h of photoirradiation showed the formation of 77% $Pt(SAr)_2(PAr'_3)_2$ (**8c**) (77/23) and 15% $Pt(SAr)_2(PPh_3)(PAr'_3)$ (**8d**) (*cis*/*trans* = 17/83). On the other hand, no reaction was confirmed by the ^{31}P NMR spectra of the other sample in darkness for 1 h. The authentic complex **8c** was prepared from the reaction of $Pt(Cl)_2(PAr'_3)_2$ (0.15 mmol) with *p*-BrC_6H_4SH (0.45 mmol) in CH_2Cl_2 (10 mL) in the presence of Et_3N at 25 °C for 3 h (58% yield). **8c**: a major isomer; ^{1}H NMR (270 MHz, C_6D_6) δ 3.17 (s, 18 H), 6.59 (d, *J* = 8.8 Hz, 12 H), 6.90 (d, *J* = 8.8 Hz, 4 H), 7.10 (d, *J* = 8.8 Hz, 4 H), 7.66 (dd, *J* = 8.8 Hz, J_{P-H} = 5.4 Hz, 12 H); ^{31}P NMR (109 MHz, C_6D_6) δ 21.16 (s, J_{Pt-P} = 2972 Hz). Anal. Calcd for $C_{54}H_{50}Br_2O_6P_2PtS_2$: C, 50.59; H, 4.40. Found: C, 50.79; H, 4.00. **8c**: a minor isomer (data collected from a mixture of stereoisomers) ^{1}H NMR (270 MHz, C_6D_6) δ 3.20 (s, 18 H), 6.63 (d, *J* = 8.8 Hz, 12 H), 6.89 (d, *J* = 8.8 Hz, 4 H), 7.20 (d, *J* = 8.8 Hz, 4 H), 7.80 (dd, *J* = 8.8 Hz, J_{H-P} = 5.1 Hz, 12 H); ^{31}P NMR (109 MHz, C_6D_6) δ 21.5 (s, J_{Pt-P} = 2745 Hz). **8d**: ^{31}P NMR (109 MHz, C_6D_6) *cis*-isomer: δ 20.4 (d, J_{P-P} = 18.4 Hz), 25.3 (d, J_{P-P} = 18.4 Hz); *trans*-isomer: δ 19.3 (d, J_{P-P} = 505 Hz, J_{Pt-P} = 2750 Hz), 24.8 (d, J_{P-P} = 505 Hz, J_{Pt-P} = 2812).

Reaction of Pt(SAr)(Ar)(dppe) (Ar = C$_6$H$_4$OMe-p, 9a) with DMAD (2t) (eq 9). Into a Pyrex NMR tube were added **9a** (8.4 mg, 0.005 mmol), **2t** (14.9 mg, 0.10 mmol), and CD_2Cl_2 (0.6 mL) under a N_2 atmosphere. The reaction at 25 °C was monitored by ^{31}P NMR spectroscopies. The chart taken after 1 h showed the formation of **27a** in 90% yield.

Preparation of 27a. In a dry two-necked flask equipped with a magnetic stirring bar were placed **9a** (84 mg, 0.1 mmol), CH_2Cl_2 (6 mL), and DMAD (284 mg, 2.0 mmol). Then the solution was stirred at 25 °C for 5 h. The resultant mixture was filtered, dried under vacuum, and purified by recrystallization from CH_2Cl_2/hexane to give **27a** as a white solid (324 mg, 33%).

27a: colorless solid; mp 161−163 °C; ^{1}H NMR (270 MHz, CD_2Cl_2) δ 2.03 (m, 2 H), 2.43 (m, 2 H), 3.64 (s, 3 H), 3.72 (s, 3

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H), 6.40 (t, $J = 7.6$ Hz, 2 H), 6.65 (dd, $J = 9.6$ Hz, $J = 22.0$ Hz, 4 H), 6.69−7.87 (m, 22 H); ^{31}P NMR (109 MHz, CD_2Cl_2) δ 40.2 (d, $J_{P-P} = 2.5$ Hz, $J_{Pt-P} = 2247$ Hz), 41.9 (d, $J_{P-P} = 2.5$ Hz, $J_{Pt-P} = 1744$ Hz); IR (KBr) 3446, 2944, 1709, 1690, 1492, 1435, 1230, 1103, 1028, 826, 747, 694, 532 cm^{-1}. Anal. Calcd for $C_{46}H_{44}O_6P_2PtS$: C, 56.27; H, 4.52. Found: C, 56.20; H, 4.38.

The following data were collected by the reactions of **9** with **2t**.

27b: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.2 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2358$ Hz), 42.6 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1583$ Hz). **27c**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.3 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2275$ Hz), 42.2 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1660$ Hz). **27d**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.3 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2230$ Hz), 41.9 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1697$ Hz). **27e**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.4 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2228$ Hz), 41.6 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1697$ Hz). **27f**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.2 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2224$ Hz), 41.9 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1697$ Hz). **27g**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.6 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2424$ Hz), 43.4 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1502$ Hz).. **27h**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 41.1 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2213$ Hz), 42.2 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1728$ Hz). **27i**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 41.0 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2206$ Hz), 42.4 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1753$ Hz); **27j**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 39.8 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2397$ Hz), 42.5 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1542$ Hz). **27k**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 40.0 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 2387$ Hz), 42.6 (d, $J_{P-P} = 2.7$ Hz, $J_{Pt-P} = 1566$ Hz).

Reaction of 9f with an Excess Amount of 2t (entry 5, Table 5). 9f (8.1 mg, 0.010 mmol), S=P(C_6H_4-*p*-OMe)$_3$ (1.9 mg, 0.0049 mmol as an internal standard), and CD_2Cl_2 (0.6 mL) were added to a Pyrex NMR tube under a N_2 atmosphere. After the ratio of signals of **9f** and S=P(C_6H_4-*p*-OMe)$_3$ was checked by ^{1}H and ^{31}P NMR spectra, **2t** (10.2 mg, 0.1 mmol) was added to the NMR tube under a N_2 atmosphere. The reaction was then monitored by ^{1}H and ^{31}P NMR spectroscopies at room temperature. The consumption rate of the starting **9f** obeyed pseudo-first-order kinetics. The half-life of **9f** was calculated to be 0.34 h. The reactions using other platinum complexes **9**, shown in Tables 5 and 6, were similarly carried out and monitored by NMR spectroscopy. The half-lives for each reaction are shown in Tables 5 and 6.

General Procedure of the Pt-Catalyzed Reaction of 2 with 30 (Table 7). Into a 3 mL reaction flask equipped with reflux condenser and stirring bar were placed **30** (1 mmol), $Pt(PPh_3)_4$ (62 mg, 0.05 mmol), toluene (0.5 mL), and **2** (2.4 mmol) under a N_2 atmosphere. After the solution was vigorously refluxed for 20 h, the resultant mixture was separated by PTLC to afford the desired 1:2 adduct **19**. When the reaction of $(PhS)_2$ (**30**) with $MeOCH_2C{\equiv}CH$ (**2n**) was performed in a 5 mL reaction flask equipped with a Teflon cock at 120 °C for 41 h, **19f** was isolated by recrystallization from Et_2O/MeOH (235 mg, 46%). Separation of the residue by HPLC afforded a mixture of suspected 1:3 adducts (84 mg, 14% yield), whose formula was tentatively determined by mass spectroscopy. The reaction of **30a** with $PhC{\equiv}CC(O)(OEt)$ (**2d**) was performed using xylene as a solvent at 140 °C for 48 h.

19b (entry 1): pale yellow oil; 377 mg, 86%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (t, $J = 7.1$ Hz, 6 H), 1.10−1.34 (m, 12 H), 1.39−1.52 (m, 4 H), 2.21 (t, $J = 7.3$ Hz, 4 H), 7.01 (s, 2 H), 7.16−7.34 (m, 10 H). NOE experiment: Irradiation of a vinyl singlet at δ 7.01 resulted in a 20% enhancement of the signal of an allyl proton at δ 2.21; ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.16, 22.53, 28.55, 28.63, 31.53, 37.71, 126.32, 128.86, 130.07, 130.68, 135.00, 137.58; IR (NaCl) 2956, 2929, 2856, 1583, 1562, 1477, 1465, 1440, 1024, 740, 691 cm^{-1}; mass spectrum (EI) *m/e* 438 (M^+, 27). Anal. Calcd for $C_{28}H_{38}S_2$: C, 76.65; H, 8.73; S, 14.62. Found: C, 76.25; H, 8.63; S, 14.45.

19c (entry 2): pale yellow oil; 370 mg, 82%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (t, $J = 6.8$ Hz, 6 H), 1.11−1.34 (m, 12 H), 1.38−1.53 (m, 4 H), 2.18 (t, $J = 7.6$ Hz, 4 H), 2.33 (s, 6 H), 6.96 (s, 2 H), 7.09 (d, $J = 8.1$ Hz, 4 H), 7.22 (d, $J = 8.1$ Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.06, 21.06, 22.52, 28.56, 28.67, 31.56, 37.47, 129.62, 129.64, 130.79, 131.10, 136.50, 137.89; IR (NaCl) 3019, 2987, 2927, 2855, 1561, 1491, 1462, 1456, 1399, 1378, 1302, 1274, 1210, 1180, 1117, 1104, 1089, 1018, 807, 725 cm^{-1}; mass spectrum (EI) *m/e* 466 (M^+, 3). Anal. Calcd for $C_{30}H_{42}S_2$: C, 77.19; H, 9.07; S, 13.74. Found: C, 76.76; H, 9.03; S, 13.39.

19a (entry 3): pale yellow oil; 485 mg, 81%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.84 (t, $J = 6.7$ Hz, 6 H), 1.12−1.34 (m, 12 H), 1.38−1.52 (m, 4 H), 2.20 (t, $J = 7.5$ Hz, 4 H), 6.98 (s, 2 H), 7.15 (d, $J = 8.5$ Hz, 4 H), 7.40 (d, $J = 8.5$ Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.05, 22.51, 28.51, 28.60, 31.51, 37.72, 120.28, 131.00, 131.46, 131.95, 134.23, 137.49; IR (NaCl) 2954, 2928, 2855, 1566, 1471, 1387, 1087, 1068, 1009, 813, 728 cm^{-1}; mass spectrum (EI) *m/e* 594 (M^+, 38). Anal. Calcd for $C_{28}H_{36}Br_2S_2$: C, 56.38; H, 6.08. Found: C, 56.51; H, 6.12.

19d (entry 4): pale yellow oil; 440 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, $J = 6.8$ Hz, 6 H), 1.19−1.26 (m, 12 H), 1.47−1.54 (m, 4 H), 2.23 (t, $J = 7.3$ Hz, 4 H), 7.02−7.07 (m, 2 H), 7.08 (s, 2 H), 7.15−7.17 (m, 2 H), 7.20−7.24 (m, 2 H), 7.54−7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.04, 22.51, 28.56, 28.67, 31.51, 38.16, 123.81, 127.15, 127.60, 130.13, 132.56, 133.08, 136.60, 137.37; IR (NaCl) 2927, 2855, 1574, 1446, 1427, 1251, 1106, 1020, 889, 747 cm^{-1}; mass spectrum (EI) *m/e* 594 (M^+, 14); HRMS calcd for $C_{28}H_{36}Br_2S_2$ 594.0625, found 594.0623.

19e (entry 5): colorless solid; 472 mg, 73%; mp 82 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, $J = 6.7$ Hz, 6 H), 1.14−1.35 (m, 12 H), 1.44−1.55 (m, 4 H), 2.25 (t, $J = 7.5$ Hz, 4 H), 7.06 (s, 2 H), 7.20 (s, 2 H), 7.45 (s, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.03, 22.50, 28.48, 28.62, 31.48, 38.12, 130.42, 130.51, 130.87, 131.55, 132.25, 133.15, 134.75, 136.83; IR (KBr) 2930, 2836, 1570, 1461, 1433, 1322, 1252, 1112, 1059, 874, 752, 727, 643, 434 cm^{-1}; mass spectrum (EI) *m/e* 644 (M^+, 24). Anal. Calcd for $C_{28}H_{32}Cl_6S_2$: C, 52.11; 5.00. Found: C, 52.56; H, 4.94.

19f (entry 6): 46%; colorless solid; mp 135 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.27 (s, 6 H), 3.93 (s, 4 H), 7.21 (d, $J = 8.6$ Hz, 4 H), 7.30 (s, 2 H), 7.42 (d, $J = 8.6$ Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 58.16, 74.61, 120.93, 130.46, 131.85, 131.97, 132.92, 135.07; IR (KBr) 2922, 2851, 2821, 1470, 1386, 1377, 1261, 1194, 1116, 1085, 1006, 891, 807, 783, 476 cm^{-1}; mass spectrum (EI) *m/e* 514 (M^+, 14). Anal. Calcd for $C_{20}H_{20}Br_2O_2S_2$: C, 46.53; H, 3.90. Found: C, 46.77; H, 3.80.

Suspected 1:3 adduct: yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.30 (s, 6 H), 3.31 (s, 3 H), 3.92 (d, $J = 1.3$ Hz, 2 H), 3.93 (s, 2 H), 4.17 (s, 2 H) (the other peaks were unreadable because the vinyl protons and aromatic protons overlapped with each other); mass spectrum (EI) *m/e* 584 (M^+, 32); HRMS calcd for $C_{24}H_{26}Br_2O_3S_2$ 583.9690, found 583.9668.

19g (entry 7): yellow solid; 262 mg, 62%; mp 195−197 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.01−7.29 (m, 16 H), 7.64 (d, $J = 7.8$ Hz, 4 H), 7.75 (s, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 125.82, 127.86, 128.30, 128.68, 128.79, 133.41, 135.58, 138.13, 139.60 (two signals overlapped); IR (KBr) 3050, 1580, 1478, 1438, 1076, 1025, 895, 892, 765, 737, 700, 689, 600, 473 cm^{-1}; mass spectrum (EI) *m/e* 422 (M^+, 44). Anal. Calcd for $C_{28}H_{22}S_2$: C, 79.58; H, 5.25; S, 15.17. Found: C, 79.29; H, 5.35; S, 15.04.

19h (entry 8): colorless solid; 255 mg, 62%; mp 84−85 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.14 (br, 2 H), 1.36−1.56 (m, 10 H), 2.19 (t, $J = 7.0$ Hz, 4 H), 3.31−3.43 (m, 4 H), 6.95 (s, 2 H), 7.14−7.39 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.11, 32.21, 37.65, 62.89, 126.55, 128.97, 130.26, 130.26, 130.77, 134.75, 137.42; IR (KBr) 3285, 2934, 2862, 1582, 1576, 1555, 1476, 1438, 1066, 1056, 1024, 749, 739, 692 cm^{-1}; mass spectrum (EI) *m/e* 414 (M^+, 29). Anal. Calcd for $C_{24}H_{30}O_2S_2$: C, 69.52; H, 7.29; S, 15.46. Found: C, 69.21; H, 7.17; S, 15.03.

19i (entry 9): colorless solid; 260 mg, 64%; mp 88−90 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.84 (quint, $J = 7.2$ Hz, 4 H), 2.23 (t,

$J = 7.2$ Hz, 4 H), 2.38 (t, $J = 7.2$ Hz, 4 H), 7.03 (s, 2 H), 7.18−7.35 (m, 10 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.12, 24.22, 36.07, 119.27, 127.17, 129.21, 130.65, 131.12, 133.53, 136.40; IR (KBr) 2241, 1587, 1562, 1477, 1460, 1440, 1423, 1294, 1070, 1024, 900, 892, 840, 737, 699, 688, 603, 466, 436, 418 cm^{-1}; mass spectrum (EI) *m/e* 404 (M^+, 16). Anal. Calcd for $C_{24}H_{24}N_2S_2$: C, 71.25; H, 5.98; N, 6.92. Found: C, 70.72; H, 5.98; N, 6.85.

19j (entry 10): yellow solid; 345 mg, 80%; mp 120−121 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.41−1.65 (m, 8 H), 2.00−2.13 (m, 4 H), 2.16−2.27 (m, 4 H), 6.43−6.50 (m, 2 H), 7.05−7.30 (m, 10 H), 7.47 (s, 2 H); ^{13}C NMR (68 MHz, CDCl3) δ 22.04, 22.79, 26.23, 27.01, 125.06, 127.37, 128.67, 130.74, 131.23, 135.81, 137.56, 137.69; IR (KBr) 2944, 2922, 2855, 2819, 1613, 1580, 1477, 1438, 1261, 1108, 1100, 1024, 842, 798, 736, 687 cm^{-1}; mass spectrum (EI) *m/e* 430 (M^+, 32); HRMS calcd for $C_{28}H_{30}S_2$ 430.1789, found 430.1782.

19k (entry 11): yellow solid; 106 mg, 38%; mp 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, $J = 7.3$ Hz, 6 H), 3.94 (q, $J = 7.1$ Hz, 4 H), 7.02−7.14 (m, 12 H), 7.23−7.26 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.63, 60.54, 127.34, 127.70, 127.80, 127.98, 128.39, 129.21, 131.75, 133.94, 137.52, 154.54, 165.99; IR (KBr) 3057, 2986, 1710, 1581, 1482, 1440, 1363, 1259, 1208, 1040, 746, 698, 532 cm^{-1}. Anal. Calcd for $C_{34}H_{30}O_4S_2$: C, 72.06; H, 5.34. Found: C, 71.79; H, 5.27. The structure of **19k** was unambiguously determined by X-ray crystallographic analysis.

Confirmation of Regiochemistry of 19 (Ni-catalyzed reaction of 19b with PhMgBr). Into a 10 mL flask equipped with an addition funnel and a reflux condenser were placed **19b** (213 mg, 0.49 mmol), $NiCl_2(PPh_3)_2$ (9.9 mg, 0.015 mmol), and THF (6 mL) under a N_2 atmosphere. PhMgBr (1.0 mL of a 0.8 M solution in THF, 0.8 mmol) was added from the addition funnel at 0 °C over a period of 5 min. After the mixture was refluxed for 19 h, 6 mL of HCl (1 N) was added. The reaction mixture was extracted with Et_2O/H_2O and dried over $MgSO_4$. The sample was subjected to PTLC to give 10% (n-C_6H_{13})(PhS)C═CH-CH═C(Ph)(n-C_6H_{13}) with vinyl protons ($J = 12.2$ Hz), indicating that two vinyl protons of **19b** were located at the vicinal positions.

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Supporting Information Available: X-ray crystal data for **19k** and **27a** (CIF) and UV−vis spectra of *trans*-**8a** and *cis*-*Z*-**16c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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