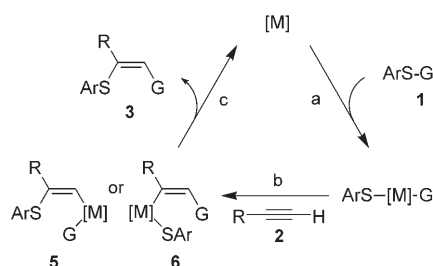


Definitive Evidence for the Insertion of Terminal Alkynes into ArylS–Pt Bonds: “*o*-Halogen Effect” in Stoichiometric and Catalytic Reactions**

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Transition-metal complexes exhibit high catalytic activities for a number of *cis* addition reactions of compounds of the type ArS–G (**1**; G is H or a functional group) to unsaturated C–C bonds.^[1] Among the reported substrates, terminal alkynes **2** have proven to be the most reactive, and a wide range of substituents G are possible, including H,^[2] 9-BBN,^[3] Ar' (from ArSC(O)Ar'),^[4] CO₂Me,^[5] C(O)NR₂,^[6] SiCl₃,^[7] P(O)(OPh)₂,^[8] and SA_r.^[9] In most cases, PR₃-ligated Pd⁰ or Pt⁰ catalysts have been used to produce vinyl sulfides **3** with the ArS group bonded to the internal carbon atom and G at the terminal position.^[10]

Similar pathways have been proposed for these addition reactions (Scheme 1). Sufficient evidence has been provided

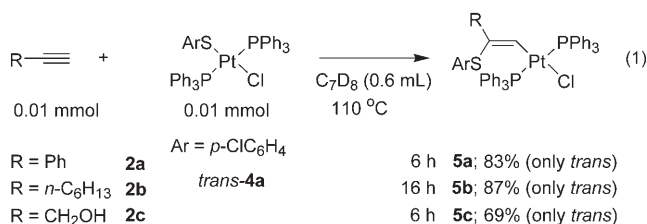


Scheme 1. Possible routes for the addition of **1** to **2** ([M] = PR₃-ligated metal fragment). With Pd cat.: G = H, 9-BBN, CO₂Me, C(O)NR₂, P(O)(OPh)₂, SA_r. With Pt cat.: G = H, SiCl₃, Ar'.

for step a, the oxidative addition of **1** to the low-valent metal center M.^[2,4,5,11] However, information about step b (the insertion of **2** into an S–M or a G–M bond) and step c (reductive elimination to form a C–G or a C–S bond) is very limited, probably because reductive elimination is faster than insertion.^[12] Accordingly, to elucidate step b, the reaction system must be designed suitably to prevent reductive elimination.^[13] We predicted that [Pt(SAr)Cl(PPh₃)₂] (**4**)

would be an ideal complex for examining the insertion of **2** into the S–M bond, as we expected the C–Cl bond-forming reductive elimination from the vinyl platinum species produced by insertion to be a thermodynamically unfavorable process. Furthermore, we developed recently a general method for the preparation of **4** by using pyridine as a catalyst for *cis*-to-*trans* isomerization.^[14] We studied the reactions of **4** with terminal alkynes **2** and report our results herein.

First, we monitored the reactions of *trans*-[Pt(SC₆H₄-*p*-Cl)Cl(PPh₃)₂] (**4a**, 0.01 mmol) with alkynes **2a–c** (0.01 mmol) in [D₈]toluene (0.6 mL) at 110 °C by ¹H NMR spectroscopy by using (*p*-MeC₆H₄)₃P=S as an internal standard [Eq. (1)]. ¹H NMR spectra of the reaction mixture with phenylacety-



lene (**2a**) indicated clean formation of the vinyl platinum complex **5a** on the basis of a signal at $\delta = 7.62$ ppm (t, ³J_{PH} = 4.0 Hz) assigned to a vinyl hydrogen atom.^[15] The yield reached 83% after 6 h. Compound **5a** was isolated by recrystallization in 87% yield from a reaction carried out on a preparative scale, and its structure was determined by X-ray crystallographic analysis. The double bond in **5a** has the *Z* configuration with the ArS group at the internal position and Pt at the terminal position (Figure 1).^[16]

The configuration and substitution pattern of **5a** are in agreement with structure **5** in Scheme 1 and provide the first solid evidence for the insertion of a terminal alkyne into the bond between a PPh₃-ligated Group 10 metal and a sulfur atom.^[17,18] Similar insertions were confirmed for the reactions of 1-octyne (**2b**) and propargyl alcohol (**2c**): The corresponding vinyl platinum complexes **5b** (only *trans*) and **5c** (only *trans*) were obtained in 87 and 69% yield after 16 and 6 h, respectively. The observation that no alkyne-exchange reaction took place upon the treatment of *trans*-[Pt{(Z)-CH=C-(SC₆H₄-*o*-Cl)Ph}Cl(PPh₃)₂] with 1-octyne (**2b**) even after 6 h at 70 °C suggested that the insertion step is an irreversible process. In agreement with previous findings that internal alkynes are generally inert in addition reactions of ArS–G (**1**)

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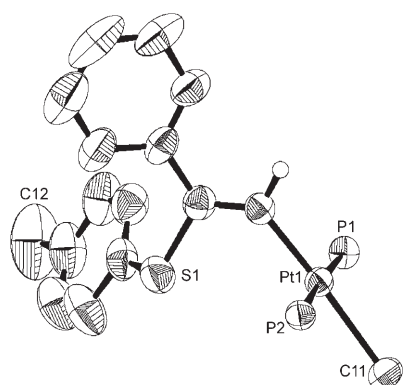


Figure 1. Molecular structure of *trans*-**5a** (thermal ellipsoids set at the 50% probability level). CH_2Cl_2 solvent and Ph groups of PPh_3 are omitted for clarity.

to **2** with PR_3 -ligated Pd or Pt catalysts, no insertion took place with 4-octyne.

The effects of substituents in the ArS moiety of the platinum complex **4** were then examined in the presence of an excess amount of **2a** (0.17 M). The consumption rate of the starting complex **4** at 70 °C obeyed pseudo-first-order kinetics. The half-life ($\tau_{1/2}$) of **4** for each reaction is shown in Table 1. The values range from $\tau_{1/2}$ = 2.8 h for the platinum complex

Table 1: The effect of substituents in the ArS moiety.^[a]

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

[a] Reaction conditions: **4** (0.01 mmol), **2a** (0.17 M), C_6D_6 , 70 °C. [b] PPh_3 (0.03 mmol) was added.

with a *p*-OMe-substituted aromatic ring to $\tau_{1/2}$ = 12.2 h with a *p*-CF₃ substituent (Table 1, entries 1–5). The Hammett plot shows a good linear free-energy relationship with simple σ values that correlate with the acidity of the equivalently substituted benzoic acids (Figure 2). Its negative slope (ρ = –0.7) indicates that electron-donating groups (EDG) slightly facilitate the insertion.^[19] In the presence of additional PPh_3 (3 equiv), the reaction was retarded significantly ($\tau_{1/2}$ = 16.4 h; Table 1, entry 6). The rate of insertion was influenced even more drastically by *ortho* substituents. The $\tau_{1/2}$ value of 10.1 h observed for **4** with an *o*-Me substituent (Table 1, entry 7) and the $\tau_{1/2}$ value of 13.3 h with an *o*-*i*Pr group (entry 8) suggest that the steric hindrance caused by the substituent in the *ortho* position retards the insertion. Intriguingly, a $\tau_{1/2}$ value of 0.28 h was observed for *o*-Cl-substituted **4h**: The reaction was

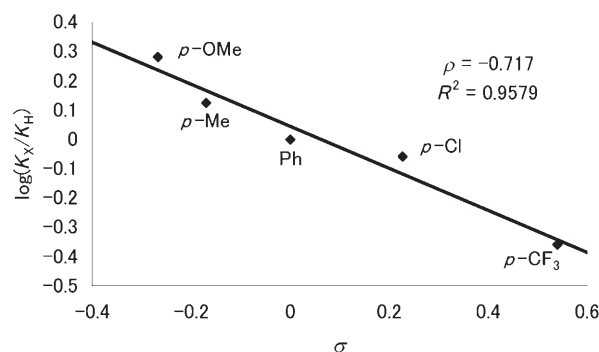
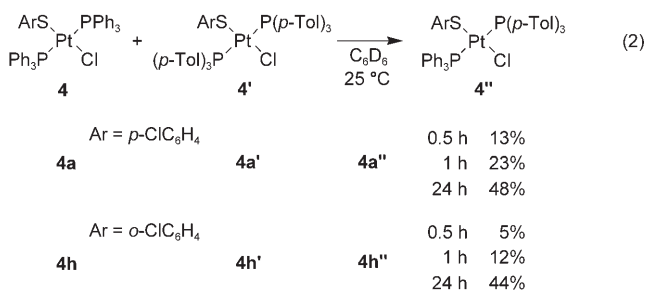


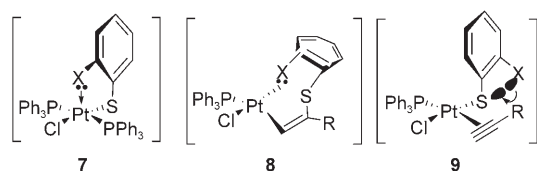
Figure 2. Hammett plot of the rates of insertion of **2a** into the S–Pt bond of **4a–e**.

approximately 19 times faster than that of the complex with a PhS group (Table 1, entries 3 and 9). Whereas similar facilitation of the insertion step was also observed with an *o*-Br substituent ($\tau_{1/2}$ = 0.26 h; the insertion proceeds approximately 20 times faster than with PhS; Table 1, entry 10) and an *o*-I substituent ($\tau_{1/2}$ = 0.19 h; the insertion proceeds approximately 28 times faster than with PhS; entry 11), the insertion was suppressed significantly with an *o*-F substituent ($\tau_{1/2}$ = 7.3 h; 1.4 times slower than with PhS; entry 12). Thus, we could conclude that the low-energy lone pairs of electrons on F do not facilitate the insertion step. On the other hand, no large difference was observed between the substituents *p*-OMe ($\tau_{1/2}$ = 2.8 h; Table 1, entry 5) and *o*-OMe ($\tau_{1/2}$ = 1.5 h; entry 13): We postulate that steric retardation and a certain degree of electronic facilitation by the *o*-OMe group cancel each other out.

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 been documented previously.^[20,21] Thus, we carried out a phosphine-ligand-exchange reaction to determine whether the *o*-halogen substituent accelerates the liberation of PPh_3 [Eq. (2); Tol = tolyl]. The treatment of *trans*-[Pt(SC₆H₄-*p*-Cl)Cl(PPh₃)₂] (**4a**) with *trans*-[Pt(SC₆H₄-*p*-Cl)Cl{P(*p*-Tol)₃}]₂ (**4a'**) at 25 °C gave *trans*-[Pt(SC₆H₄-*p*-Cl)Cl(PPh₃){P(*p*-Tol)₃}]



(**4a''**) in 23% yield after 1 h. A similar ligand exchange with complexes **4h** and **4h'**, which contain an *o*-Cl substituent, took place at a slightly lower reaction rate (12% yield of **4h''** 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 (**7** in Scheme 2)



Scheme 2. “*o*-Halogen effect”: Possible roles of the *ortho* substituent (X = Cl, Br, I).

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 (**8** in Scheme 2).^[22] 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 (**9** in Scheme 2). In fact, X-ray crystallographic analysis of *trans*-[Pt(SC₆H₄-*o*-Br)Cl(PPh₃)₂] (**4i**) 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 3).

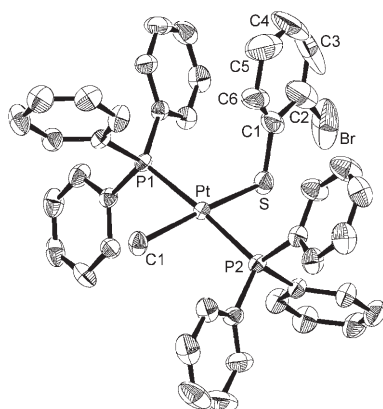
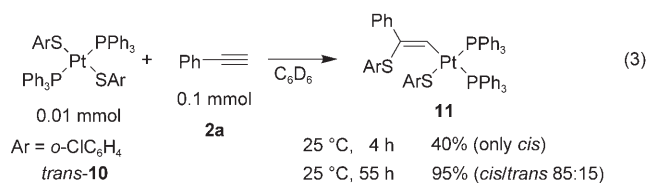
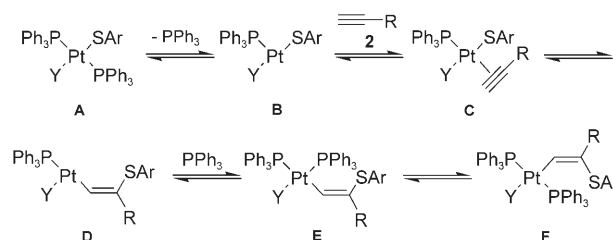


Figure 3. Molecular structure of **4i** (thermal ellipsoids set at the 50% probability level). Selected bond lengths [Å]: Pt–S 2.299(2), Pt–Cl 2.342(2), Pt–P1 2.332(2), Pt–S 2.319(2), S–Cl 1.73(1), Br–C2 1.82(2), Br–S 3.202(2).

The “*o*-halogen effect” was next studied with the *trans* and *cis* dithiolate complexes [Pt(SC₆H₄-*o*-Cl)₂(PPh₃)₂] (**10**).^[23] The treatment of *trans*-**10** with 10 equivalents of phenylacetylene (**2a**) at 25 °C furnished the vinyl platinum complex **11** in 40% yield (only *cis*) after 4 h and 95% yield (*cis/trans* 85:15) after 55 h [Eq. (3)].^[24,25] In stark contrast, **11** was not formed at all when *cis*-**10** was treated for 4 h under the same reaction conditions. The higher reactivity of *trans*-**10** relative to that of *cis*-**10** toward the insertion of an alkyne may be attributed to the stronger *trans* effect of PPh₃ relative to that of SAR.^[26]



The experiments described above suggest the following reaction pathway (Scheme 3): Complex **A** (Y = Cl, SAR) reacts via complex **B**, which is formed by the liberation of



Scheme 3. A plausible reaction route for the insertion of an alkyne into the S–Pt bond of *trans*-[Pt(SAR)Y(PPh₃)₂] (Y = Cl, SAR).

PPh₃, with alkyne **2** to afford the alkyne complex **C**. The migration of ArS to the coordinated alkyne then gives complex **D**. Coordination of PPh₃ at the vacant site results in the formation of **E** as the kinetic product,^[27] which isomerizes to the thermodynamically more stable *trans* isomer **F**.

Finally, the effect of an *ortho* substituent was examined in the Pd-catalyzed dithiolation of 1-octyne (**2b**) with a disulfide **12** of the type (ArS)₂ (G = SAR in Scheme 1).^[9a] The treatment of **2b** with **12a** or **12b** at 60 °C for 5 h produced the adducts **13a** and **13b**, respectively (Table 2, entries 1 and 2). Significantly lower conversions were observed for the reactions with **12c**, **12d**, and **12e** (Table 2, entries 3–5).

Table 2: Pd-catalyzed addition of (ArS)₂ (**12**) to 1-octyne (**2b**).^[a]

(ArS) ₂ + <i>n</i> -C ₈ H ₁₃ ≡		cat. [Pd(dba) ₂], PPh ₃		<i>n</i> -C ₈ H ₁₃ → ArS–CH=CH–SAr	
12	2b			13	
Entry	12	Ar	13	Yield [%] ^[b]	
1	12a	<i>o</i> -ClC ₆ H ₄	13a	68 (60) ^[c]	
2	12b	<i>o</i> -BrC ₆ H ₄	13b	80 (75) ^[c]	
3	12c	<i>p</i> -ClC ₆ H ₄	13c	2	
4	12d	<i>p</i> -BrC ₆ H ₄	13d	13	
5	12e	<i>o</i> -MeC ₆ H ₄	13e	18	

[a] Reaction conditions: **12** (0.5 mmol), **2b** (0.6 mmol), [Pd(dba)₂] (0.015 mmol), PPh₃ (0.033 mmol), C₆H₆ (0.5 mL), 60 °C, 5 h. [b] The yield was determined by ¹H NMR spectroscopy. [c] The yield of the isolated product is given in parentheses. dba = dibenzylideneacetone.

In conclusion, the present study demonstrates that the platinum complexes **4** (M = Pt, G = Cl) and **10** (M = Pt, G = SAR) are useful for examining the insertion of **2** into the S–M bond of PPh₃-ligated complexes (M: Group 10 metal). Details of the mechanism of the insertion of alkynes into the S–Pt bond and the application of the observed “*o*-halogen effect” to other catalytic reaction systems are currently under extensive investigation.^[6b]

Experimental Section

Typical procedure: The complex *trans*-**4a** (9.0 mg, 0.0010 mmol), S=P(*p*-Tol)₃ (1.7 mg, 0.0051 mmol (as an internal standard), and C₆D₆

(0.6 mL) were placed in a pyrex NMR tube under a nitrogen atmosphere. After the relative sensitivity of the signals of *trans*-**4a** and *S*=P(*p*-Tol)₃ had been checked by recording ¹H and ³¹P NMR spectra of this mixture, phenylacetylene (**2a**; 10.2 mg, 0.1 mmol) was added to the NMR tube under a nitrogen atmosphere. The reaction was then monitored by ¹H and ³¹P NMR spectroscopy at 70 °C. The NMR spectra showed clean formation of the platinum complex **5a**, and the consumption rate of the starting complex *trans*-**4a** obeyed pseudo-first-order kinetics. The half-life of *trans*-**4a** was found to be 6.1 h.

5a: The complex *trans*-**4a** (54 mg, 0.06 mmol), toluene (3 mL), and **2a** (61 mg, 0.06 mmol) were placed in a dry three-necked flask, and the reaction mixture was stirred for 14 h at 100 °C. Hexane (ca. 50 mL) was then added to the mixture, and the resulting precipitate was collected by filtration. The complex **5a** (54 mg, 87%) was obtained by recrystallization from CH₂Cl₂/hexane as a pale-yellow solid. M.p.: 228 °C; ¹H NMR (400 MHz, C₆D₆): δ = 7.93–7.87 (m, 12 H), 7.62 (t, *J*_{PH} = 4.0 Hz, 1 H), 7.01–6.98 (m, 18 H), 6.91–6.83 (m, 5 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 6.22 ppm (d, *J* = 8.4 Hz, 2 H); ³¹P NMR (160 MHz, C₆D₆): δ = 23.5 ppm (s, *J*_{PLP} = 3023 Hz); IR (KBr): $\tilde{\nu}$ = 3450, 3054, 1891, 1591, 1572, 1522, 1482, 1474, 1435, 1389, 1311, 1221, 1186, 1159, 1029, 1010, 999, 894, 810, 767, 743, 707, 693, 618, 576, 542, 522, 455, 430 cm⁻¹; C,H analysis: calcd (%) for C₅₁H₄₂Cl₄P₂TS: C 56.42, H 3.90; found: C 56.28, H 3.87.

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- [25] The insertion of **2a** into a *trans*-dithiolate complex without an *o*-halogen substituent required harsher reaction conditions: The formation of the Pt⁰ complex probably occurred via the divinyl platinum complex. See the discussion about the possible course of reactions of platinum dithiolates with alkynes in reference [4b].
- [26] a) T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335; b) L. T. Chan, H.-W. Chen, J. P. Fackler, Jr., A. F. Masters, W.-H. Pan, *Inorg. Chem.* **1982**, *21*, 4291; c) T. Tu, Y.-G. Zhou, X.-L. Hou, L.-X. Dai, X.-C. Dong, Y.-H. Yu, J. Sun, *Organometallics* **2003**, *22*, 1255.
- [27] The *cis* vinyl platinum complex was also detected as a kinetic product in the early stages of the reaction of **4i** with **2a**.
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