Insertion Reactions

DOI: 10.1002/anie.200604986

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

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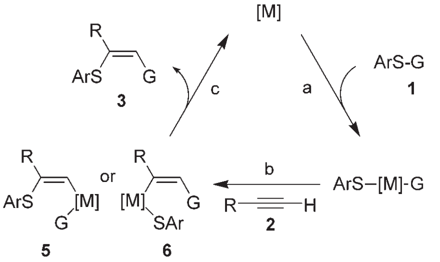
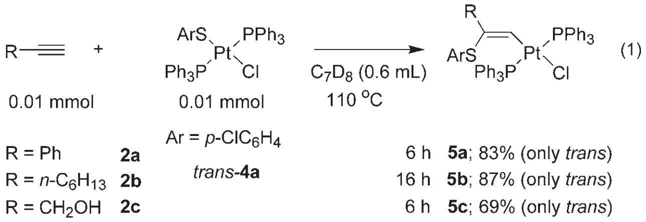
Transition-metal complexes exhibit high catalytic activities for a number of *cis* addition reactions of compounds of the type ArS–G (**1**; G is H or a functional group) to unsaturated C–C bonds.[1] Among the reported substrates, terminal alkynes **2** have proven to be the most reactive, and a wide range of substituents G are possible, including H,[2] 9-BBN,[3] Ar′ (from ArSC(O)Ar′),[4] CO_2Me,[5] $C(O)NR_2$,[6] $SiCl_3$,[7] $P(O)(OPh)_2$,[8] and SAr.[9] In most cases, PR_3-ligated Pd^0 or Pt^0 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 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 $[Pt(SAr)Cl(PPh_3)_2]$ (**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.



Scheme 1. Possible routes for the addition of **1** to **2** ([M] = PR_3-ligated metal fragment). With Pd cat.: G = H, 9-BBN, CO_2Me, $C(O)NR_2$, $P(O)(OPh)_2$, SAr. With Pt cat.: G = H, $SiCl_3$, Ar′.

First, we monitored the reactions of *trans*-$[Pt(SC_6H_4\text{-}p\text{-}Cl)Cl(PPh_3)_2]$ (**4a**, 0.01 mmol) with alkynes **2a–c** (0.01 mmol) in $[D_8]$toluene (0.6 mL) at 110 °C by ^1H NMR spectroscopy by using $(p\text{-}MeC_6H_4)_3P{=}S$ as an internal standard [Eq. (1)]. ^1H NMR spectra of the reaction mixture with phenylacetylene (**2a**) indicated clean formation of the vinyl platinum complex **5a** on the basis of a signal at $\delta = 7.62$ ppm (t, $^3J_{P,H} = 4.0$ 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 PPh_3-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*-$[Pt\{(Z)\text{-}CH{=}C(SC_6H_4\text{-}o\text{-}Cl)Ph\}Cl(PPh_3)_2]$ 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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[**] F.Y. thanks the Center of Excellence (21COE) program "Creation of Integrated EcoChemistry" of Osaka University.

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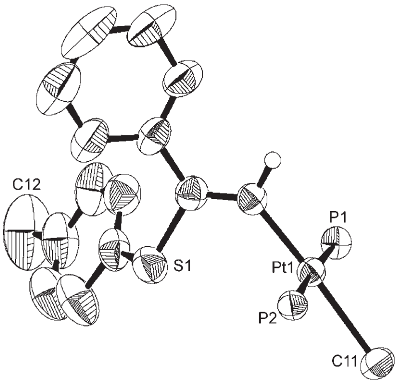


Figure 1. Molecular structure of *trans*-**5a** (thermal ellipsoids set at the 50% probability level). CH_2Cl_2 solvent and Ph groups of PPh_3 are omitted for clarity.

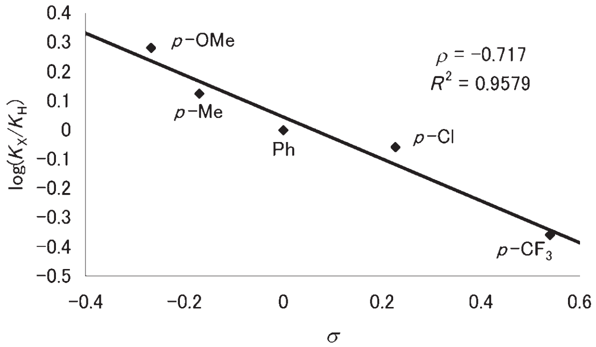
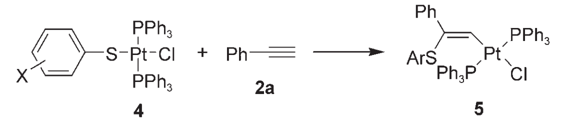


Figure 2. Hammett plot of the rates of insertion of **2a** into the S–Pt bond of **4a–e**.

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 with a *p*-OMe-substituted aromatic ring to $\tau_{1/2} = 12.2$ h with a *p*-CF_3 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 ($\rho = -0.7$) 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 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.

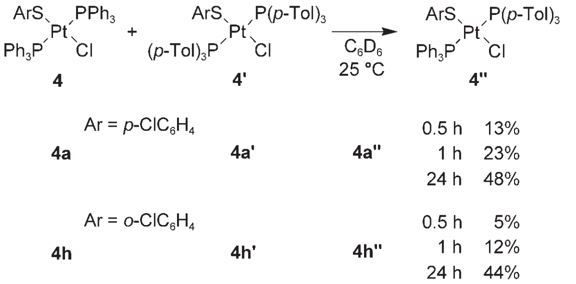
Table 1: The effect of substituents in the ArS moiety.[a]



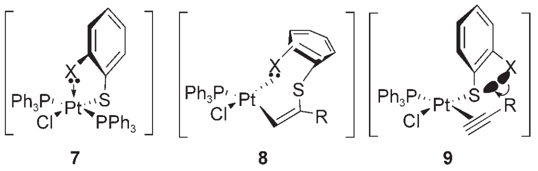
Entry	4	X	$\tau_{1/2}$ [h]	Entry	4	X	$\tau_{1/2}$ [h]
1	**4b**	*p*-CF_3	12.2	7	**4f**	*o*-Me	10.1
2	**4a**	*p*-Cl	6.1	8	**4g**	*o*-*i*Pr	13.3
3	**4c**	H	5.3	9	**4h**	*o*-Cl	0.28
4	**4d**	*p*-Me	4.0	10	**4i**	*o*-Br	0.26
5	**4e**	*p*-OMe	2.8	11	**4j**	*o*-I	0.19
6[b]	**4d**	*p*-Me	16.4	12	**4k**	*o*-F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

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(SC_6H_4-*p*-Cl)Cl(PPh_3)$_2$] (**4a**) with *trans*-[Pt(SC_6H_4-*p*-Cl)Cl{P(*p*-Tol)$_3$}$_2$] (**4a′**) at 25 °C gave *trans*-[Pt(SC_6H_4-*p*-Cl)Cl(PPh_3){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)



(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(SC$_6$H$_4$-*o*-Br)Cl(PPh$_3$)$_2$] (**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).

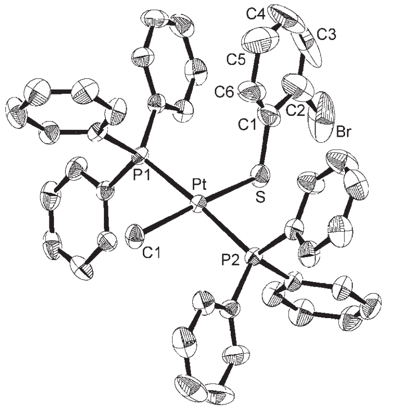
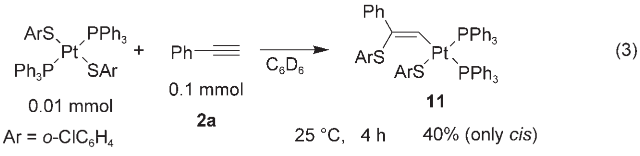
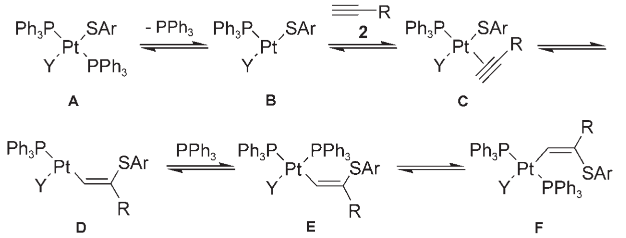


Figure 3. Molecular structure of **4i** (thermal ellipsoids set at the 50% probability level). Selected bond lengths [Å]: Pt–S 2.299(2), Pt–Cl 2.342(2), Pt–P1 2.332(2), Pt–S 2.319(2), S–C1 1.73(1), Br–C2 1.82(2), Br–S 3.202(2).

The "*o*-halogen effect" was next studied with the *trans* and *cis* dithiolate complexes [Pt(SC$_6$H$_4$-*o*-Cl)$_2$(PPh$_3$)$_2$] (**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 PPh$_3$ relative to that of SAr.[26]



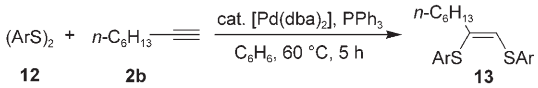
The experiments described above suggest the following reaction pathway (Scheme 3): Complex **A** (Y = Cl, SAr) reacts via complex **B**, which is formed by the liberation of PPh$_3$, with alkyne **2** to afford the alkyne complex **C**. The migration of ArS to the coordinated alkyne then gives complex **D**. Coordination of PPh$_3$ 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**.



Scheme 3. A plausible reaction route for the insertion of an alkyne into the S–Pt bond of *trans*-[Pt(SAr)Y(PPh$_3$)$_2$] (Y = Cl, SAr).

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]



Entry	12	Ar	13	Yield [%][b]
1	**12a**	*o*-ClC$_6$H$_4$	**13a**	68 (60)[c]
2	**12b**	*o*-BrC$_6$H$_4$	**13b**	80 (75)[c]
3	**12c**	*p*-ClC$_6$H$_4$	**13c**	2
4	**12d**	*p*-BrC$_6$H$_4$	**13d**	13
5	**12e**	*o*-MeC$_6$H$_4$	**13e**	18

[a] Reaction conditions: **12** (0.5 mmol), **2b** (0.6 mmol), [Pd(dba)$_2$] (0.015 mmol), PPh$_3$ (0.033 mmol), C$_6$H$_6$ (0.5 mL), 60 °C, 5 h. [b] The yield was determined by ^{1}H 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 PPh$_3$-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 C$_6$D$_6$

(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 ^{1}H and ^{31}P 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 ^{1}H and ^{31}P 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 CH$_2$Cl$_2$/hexane as a pale-yellow solid. M.p.: 228 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 7.93$–7.87 (m, 12 H), 7.62 (t, $J_{\mathrm{P,H}} = 4.0$ 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); ^{31}P NMR (160 MHz, C$_6$D$_6$): $\delta = 23.5$ ppm (s, $J_{\mathrm{Pt,P}} = 3023$ 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 C$_{51}$H$_{42}$Cl$_4$P$_2$PtS: C 56.42, H 3.90; found: C 56.28, H 3.87.

Received: December 9, 2006
Revised: April 17, 2007

Keywords: alkynes · insertion · neighboring-group effects · platinum · S ligands

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