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Photo-and-Thiol-Driven Trans Insertion of Phenylacetylene into H−Pt Bonds

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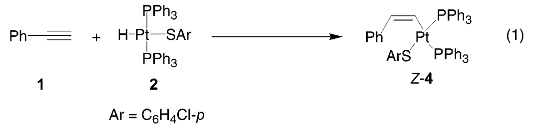
Insertion (IS) of unsaturated molecules into the H−M bonds is among the most basic topics in organometallic chemistry.[1] As to the mechanism, cis IS has been widely established, although a limited number of trans ISs, mostly exploiting activated alkynes such as DMAD, have been reported.[2,3] In connection with the mechanisms of some Pt-catalyzed reactions including thiols and alkynes as substrates[4] and our study on the reactions of unsaturated molecule with thiolato palladium and platinum complexes,[5,6] we were initially interested in the reactivity of alkynes toward the complexes having H−Pt−SAr fragment. Herein we wish to report on our findings that trans IS of phenylacetylene (**1**) into the H−Pt bonds took place with the assistance of unexpected factors.

First, the reaction of **1** (0.05 mmol) with *trans*-Pt(H)(SAr)$(PPh_3)_2$ (**2**, Ar = C_6H_4Cl-*p*) (0.01 mmol), which was prepared in situ by the reaction of $Pt(PPh_3)_2(C_2H_4)$ (0.01 mmol) with ArSH (**3**, Ar = C_6H_4Cl-*p*) (0.06 mmol),[7] was carried out in C_6D_6 (0.5 mL) using O═P(tol-*p*)$_3$ as an internal standard under N_2 atmosphere at 25 °C under room light (just without covering the NMR tube). The ^{31}P NMR spectra indicated the formation of a platinum complex *Z*-**4** in 36% (*cis*/*trans* = 64/36)[8] and 81% (*cis*/*trans* = 64/36) yields after 2 and 5 h, respectively (eq 1, run 1 of Table 1). In stark contrast, no reaction took place in the reaction of **1** with isolated **2** under otherwise identical conditions even after 48 h (run 2). After many trials, it was found that both of the presence of **3** and photoirradiation were essential for the successful formation of *Z*-**4**.



(1)

Table 1. Reaction of **1** with **2**[a]

run	condition	ArSH (**3**) (mmol)	*T* (°C)	time	*Z*-**4**, yield %[b]	(*cis*/*trans*)[c]
1	room light	0.05[d]	25	2 h	36	(64/36)
				5 h	81	(64/36)
2	room light	0	25	48 h	0	
3	500-W tungsten lamp	0.05	10	10 min	77	(73/27)
4[e]	500-W tungsten lamp	0.05	10	10 min	85	(85/15)
5[f]	500-W tungsten lamp	0.5	10	1 h	65[g]	(78/22)
6	under dark	0.05	25	20 h	8	(42/58)
7	500-W tungsten lamp	0	10	10 min	0	
8[h]	under dark	0.05	60	1 h	76	(only *trans*)
9[h]	under dark	0	60	3 h	3	(only *trans*)

[a] Unless otherwise noted, 0.05 mmol of **1**, 0.01 mmol of **2** in C_6D_6 (0.5 mL) in a Pyrex NMR glass tube. [b] NMR yield. [c] Stereochemistry of two PPh_3 on Pt. [d] **2** was prepared in situ by the reaction of $Pt(PPh_3)_2(C_2H_4)$ (0.01 mmol) with **3** (0.06 mmol). [e] In acetone-d_6 (0.5 mL). [f] Preparative scale (0.1 mmol of **2**). [g] Isolated yield. [h] 0.01 mmol of AIBN.

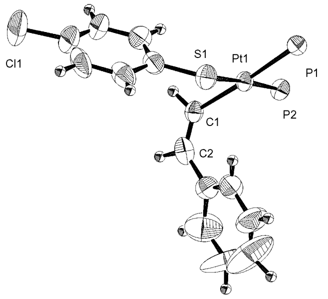


Figure 1. ORTEP diagram of *cis*-*Z*-**4** (Ph on PPh_3 omitted).

When the reaction of **1** (0.05 mmol) with **2** (0.01 mmol) in the presence of **3** (0.05 mmol) was performed under the irradiation of 500-W tungsten lamp at 10 °C, the reaction finished within 10 min to afford *Z*-**4** in 77% (*cis*/*trans* = 73/27) and 85% (*cis*/*trans* = 85/15) yields in C_6D_6 and acetone-d_6, respectively (runs 3 and 4).[9] The complex *Z*-**4** was isolated from a preparative-scale reaction (0.1 mmol of **2**) in 65% (*cis*/*trans* = 78/22) yield (run 5), and the X-ray single-crystal structure analysis of its *cis*-isomer proved the structure to be *cis*-Pt[(*Z*)-C(H)═C(H)(Ph)](SAr)$(PPh_3)_2$ (*cis*-*Z*-**4**) (Figure 1), implying that **1** inserted into the H−Pt bond of **2** with Pt bound at terminal position in a *trans-fashion*.[10] Because the isolated *Z*-**4** isomerized to the "cis IS" product Pt[(*E*)-C(H)═CH(Ph)](SAr)$(PPh_3)_2$ (*E*-**4**) under photoirradiation for 30 min (*E*/*Z* = 32/68), the possibility of kinetic formation of *E*-**4** and subsequent isomerization to *Z*-**4** can be ruled out.[11]

In the case of lapping the tube in aluminum foil, the reaction was significantly retarded even in the presence of **3**; only 8% of *Z*-**4** was formed even after 20 h (run 6). No reaction took place without the addition of **3** even when the tube was irradiated with 500-W tungsten lamp (run 7). The reaction of **1** (0.05 mmol) with **2** (0.01 mmol) carried out in the presence of AIBN (0.01 mmol) and **3** (0.05 mmol) at 60 °C also furnished *Z*-**4** in 76% (only trans) yield (run 8), while the reaction in the presence of AIBN without **3** produced only 3% of *Z*-**4** even after 3 h (run 9), showing that the role of photoirradiation was replaceable by AIBN, but the presence of **3** was crucial to obtain *Z*-**4** effectively.

Prompted by these intriguing results, the generality of the trans IS has been next tested. It became evident that the present protocol was also applicable to the complexes *trans*-Pt(H)(X)$(PPh_3)_2$ (**6**: X = Cl, **7**: X = Br, **8**: X = I). When the reaction of **1** with **6** was carried out in the presence of 5 equiv of **3** under the irradiation of 500-W tungsten lamp at 10 °C for 30 min, the selective formation of the trans IS product Pt[(*Z*)-C(H)═C(H)(Ph)](Cl)$(PPh_3)_2$ (*Z*-**9**)[12] was confirmed in 79% (*cis*/*trans* = 79/21) yield after 30 min (eq 2, run 1 of Table 2). Similarly to the case of reaction of **1** with **2**, photoirradiation can be replaced by AIBN to furnish *Z*-**9** in 74% (only trans) yield after 1 h at 70 °C (run 2) and

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3 was again indispensable (runs 3 and 4). The reaction of **1** with **7** in the presence of **3** under photoirradiation afforded the trans IS product *Z*-**10**[13] in 83% (*cis*/*trans* = 16/84) yield after 30 min (run 5). Although accompanied by the *Z*-to-*E* isomerization, vinylplatinum **11** was also obtained from **8** in 42% yield after 30 min (run 6).[14]

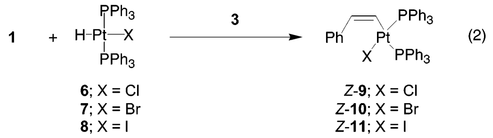
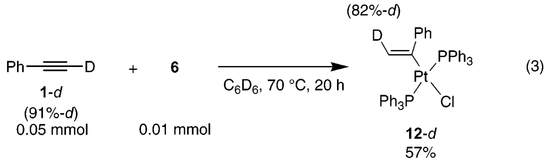


Table 2. Reaction of **1** with H−Pt Bonds of $Pt(X)(H)(PPh_3)_2$ (X = Cl, Br, and I)[a]

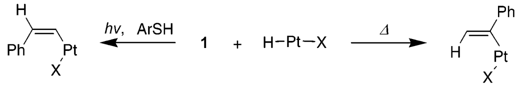
run	X	condition	*T* (°C)	time	yield %[b]	(*cis*/*trans*)
1	Cl	500-W tungsten lamp	10	30 min	79	(79/21)
2[c]		under dark	70	1 h	74	(only *trans*)
3[d]		500-W tungsten lamp	10	30 min	0	
4[c,d]		under dark	70	1 h	0	
5	Br	500-W tungsten lamp	10	30 min	83	(16/84)
6	I	500-W tungsten lamp	10	10 min	11	(only *trans*)
				30 min	42[e]	(only *trans*)

[a] Unless otherwise noted, 0.05 mmol of **1**, 0.01 mmol of Pt complex, 0.05 mmol of **3** in C_6D_6 (0.5 mL). [b] NMR yield. [c] 0.01 mmol of AIBN. [d] Without **3**. [e] 12% of *E*-**11** was included.

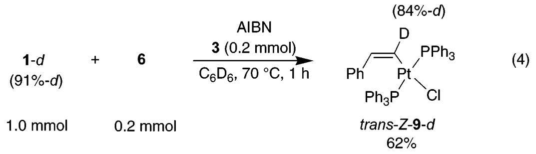
As to the reaction of **1** with **6**, the IS of **1** into the H−Pt bond has been already reported to yield *trans*-$Pt[C(Ph){=}CH_2](Cl)(PPh_3)_2$ (**12**).[15] Actually, when the reaction of deuterated phenylacetylene (**1**-*d*) with **6** was conducted at 70 °C under dark, the cis IS product **12**-*d* was formed in 57% (only *trans*) yield after 20 h (eq 3). That is, both the stereo- and regiochemistry of IS of **1** into the H−Pt bonds could be controlled by simply switching the reaction conditions; the conventional thermal reaction produced cis IS product with Pt bound at the internal carbon, while the present photo-and-thiol-driven reaction produced trans IS product with Pt bound at the terminal carbon (Scheme 1).



Scheme 1. Photo-and-Thiol-Driven Trans IS vs Conventional Thermal Cis IS of **1** into H−Pt Bonds



Finally, to get the information on the reaction course of trans IS, deuterium-labeling experiments were conducted as follows. The reaction of **1**-*d* with **6** in the presence of AIBN and **3** to produce *trans-Z* isomer (Table 2, run 2) was performed at 70 °C under dark for 1 h, and the resultant complex was analyzed by ^1H NMR spectrum. Although a small portion of D−H exchange was suggested (91%-*d* to 84%-*d*), D was selectively incorporated into the α-carbon, denying the involvement of vinylidene intermediate (eq 4). Unfortunately, the attempt to specify the origin of β-hydrogen failed due to the faster D−H scrambling between *trans*-$Pt(H)(X)(PPh_3)_2$ (**2**: X = SAr, **6**: X = Cl) and ArSD (**3**-*d*, Ar = C_6H_4Cl-*p*) than IS,[16] and the reaction mechanism still remains elusive; however thiyl radical, which could be generated from **3** under photoirradiation or in the presence of AIBN[17] would play a pivotal role for the present trans IS methodology.



In summary, this study demonstrated that both modes of cis and trans IS of alkynes into H−M bonds could be achieved by employing different reaction conditions. The work to elucidate the scope and limitations of the present trans IS into H−M bonds as well as the participation of trans IS in Pt-catalyzed reactions[4] is now in progress.

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Supporting Information Available: Listing of experimental procedures and analysis data for the compounds in this communication (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) "*cis*/*trans*" and "*E*/*Z*" refer to the stereochemistry of two PPh_3 on Pt and the geometry of vinyl moiety, respectively.

(9) It must be noted that the radical addition of **3** to **1** to give (Ph)(H)C=C(H)(SAr) (**5**) was significantly suppressed by the presence of **2**; the formation of **5** was confirmed in 12% (only *Z* isomer) yield by ^1H NMR spectrum in run 3, while the reaction conducted without **2** produced **5** in 76% (*E*/*Z* = 23/77) yield. Similar suppression of radical addition by $Fe(CO)_5$ has been reported, See: Kandror, I. I.; Petrova, R. G.; Petrovski, P. V.; Freidlina, R. Kh. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, *7*, 1621.

(10) Crystal data of *cis*-*Z*-**4**: space group P-1 (no. 2) with $a = 16.721(2)$ Å, $b = 19.129(3)$ Å, $c = 15.646(2)$ Å, $\alpha = 110.955(4)°$, $\beta = 99.908(6)°$, $\gamma = 106.192(5)°$, $Z = 4$, $\rho = 1.50$ g/cm³, $R = 0.047$, and $R_w = 0.089$.

(11) Considering the steric hindrance, the isomerization of the possible three-coordinate intermediate Pt[(*E*)-C(H)=C(H)(Ph)](SAr)(PPh_3) to Pt[(*Z*)-C(H)=C(H)(Ph)](SAr)(PPh_3) prior to the formation of *Z*-**4** is also unlikely. Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

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(16) The reaction of **2** (0.01 mmol) or **6** (0.01 mmol) with **3**-*d* (94%-*d*, 0.05 mmol) in C_6D_6 afforded *trans*-$Pt(D)(X)(PPh_3)_2$ (X = SAr; 0.035 mmol, X = Cl; 0.0054 mmol) after 5 min.

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