The Key to Oxidative Addition of Acyclic Vinyl Sulfide to M(0) Complex

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The C−S bond activation by transition-metal complexes has received increasing attention for efficient catalytic and stoichiometric transformations using organic sulfides. For example, great effort has been devoted to the cleavage of the thiophen C−S bond to get insight about hydrodesulfurization that is of great importance in petrochemistry.[1] The oxidative addition (OA) of the C−S bond has also been reported on aryl−S,[2] allyl−S,[3] aroyl−S,[4] imidoyl−S,[5] and strained alkyl−S[6] bonds. However, the fundamental insight on the OA of acyclic vinyl sulfide **1** to low-valent metal (M) (Scheme 1), the simplest sp²-C−S bond cleavage, is much more sparse, though the process has been postulated to be involved in a number of nickel-catalyzed cross coupling reactions using **1** and organometallic reagents.[7] To our knowledge, since an early example of OA of **1** with Fe₂(CO)₁₀ affording a dinuclear complex in 1961,[8] no practical progress has been made to shed light on such a fundamental subject in organometallic chemistry.[9]

We wish to report here the first example of OA of **1** to Pt(0) (M = Pt), in which substituents at *A* and *B* in **1** are proved to play a pivotal role in realizing the reaction. A variety of vinyl

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(10) Crystal data of **4**: space group *P*1̄(No. 2) with *a* = 21.111(9) Å, *b* = 25.113(9) Å, *c* = 11.598(8) Å, α = 90.01(5)°, β = 105.96(5)°, γ = 108.46-(3)°, *Z* = 4, ρ = 1.162 g/cm³, *R* = 0.059, and *R*_w = 0.067.

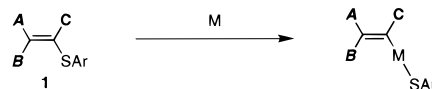**Scheme 1.** Oxidative Addition of Vinyl Sulfide **1** to M

Table 1. OA of **1** to **2** in C₆D₆ (C₆H₆)

run	**1**	condition[a]		time	**3**, yield %
1	**1a**	a	C₆H₆	12 h	**3a**, 78[b]
2	**1a**	b	C₆D₆	20 min	**3a**, 12[c,d]
				24 h	**3a**, 92[c]
3	**1b**	a	C₆H₆	12 h	**3b**, 86[b]
4	**1b**	b	C₆D₆	20 min	**3b**, 9[c,e]
5	**1f**	a	C₆D₆	48 h	**3f**, 54[b]
6	**1g**[f]	b	C₆D₆	24 h	**3g**, 13[c,g]

[a] Conditions: (a) preparative scale (0.17−1.0 mmol); (b) 0.02−0.03 mmol scale in an NMR tube. [b] Isolated yield. [c] NMR yield. [d] No intermediate was confirmed. [e] 13% of Pt[(*E*)-(*p*-tolS)(Ph)C=C(H)(Stol-*p*)](PPh₃)₂ (**5b**) was formed. [f] 10 equiv of **1g** to **2** was used. [g] 15% of Pt[(*Z*)-(*p*-tolS)(CH₃OCH₂)C=C(H)(Stol-*p*)](PPh₃)₂ (**5g**) was formed.
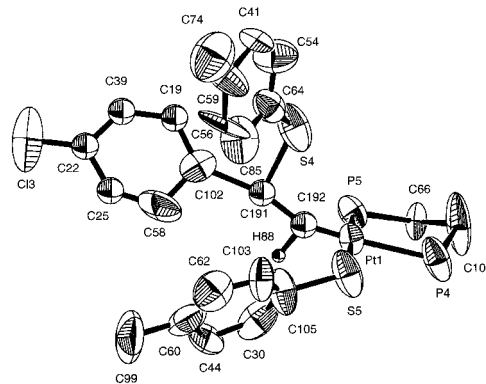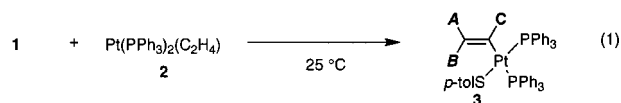

Figure 1. ORTEP diagram of **4** (Ph on DPPE omitted).

sulfides **1** shown in Scheme 2 were prepared and the feasibility of OA to Pt(PPh₃)₂(C₂H₄) (**2**) was investigated (eq 1 and Table 1). After many attempts, we have ultimately found that the


reaction of (*Z*)-1,2-bis(*p*-tolylthio)styrene (**1a**) with **2** under very mild conditions (25 °C) in benzene indeed provided the desired OA product *cis*-Pt[(*Z*)-C(H)=C(Stol-*p*)(Ph)](Stol-*p*)(PPh₃)₂ (**3a**) in 78% isolated yield as a single product by simple filtration of the crude reaction mixture (eq 1). The ³¹P NMR spectrum of **3a** showed a couple of doublets centered at δ 18.9 (*J*_{P−P} = 17 Hz, *J*_{Pt−P} = 1847 Hz) and δ 20.1 (*J*_{P−P} = 17 Hz, *J*_{Pt−P} = 3240 Hz), meaning two PPh₃s positioned cis. No intermediates or byproducts were observed, when a small-scale reaction was monitored by ¹H and ³¹P NMR spectra (run 2). Because the complex **3a** isomerized to trans-isomer in C₆D₆ at 50 °C in the presence of PPh₃ (cis/trans = 20/80 after 22 h), the *cis*-**3a** was definitely the kinetic product of the OA of **1a** to **2**. Although efforts to obtain a high-quality crystal of **3a** were unsuccessful, a single X-ray crystallographic analysis of Pt[(*Z*)-C(H)=C(Stol-*p*)(C₆H₄Cl-*p*)]-(Stol-*p*)(DPPE) (**4**; DPPE; bis(diphenylphosphino)ethane) produced by the OA of **1c** to **2** followed by the clean PPh₃-for-DPPE substitution demonstrated that OA took place at the terminal vinyl-C−S bond with the stereochemistry of the vinyl moiety retained (Figure 1).[10]

The OA of the *E*-isomer **1b** to **2** provided 86% of *cis*-Pt[(*E*)-C(H)=C(Stol-*p*)(Ph)](Stol-*p*)(PPh₃)₂ (**3b**) by a similar preparative

Scheme 2
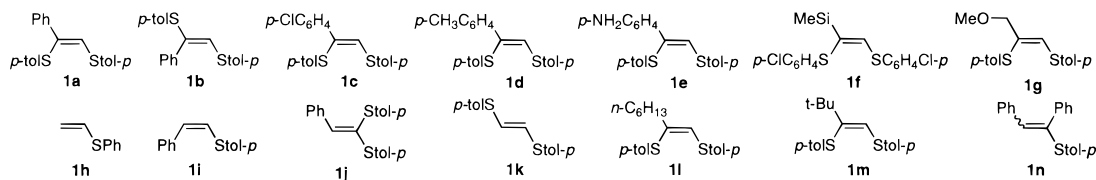
Scheme 3. A Proposed Route of OA of **1** to **2**
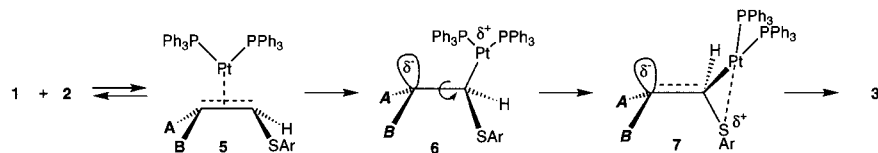
procedure (run 3). Contrary to the reaction using **1a**, the formation of olefin-coordinated complex[11] Pt[(*E*)-(*p*-tolS)(Ph)C=C(H)(Stol-*p*)](PPh$_3$)$_2$ (**5b**) was confirmed by ^{1}H and ^{31}P NMR spectra at the early stage of the reaction (run 4). To understand the electronic effect of substrates on the present OA of **1** to **2** in more detail, competitive reactions were performed by using vinyl sulfides (**1a** and **1c**−**e**) possessing different substituents in *p*-XC$_6$H$_4$ at *A* (eq 2). The results clearly indicated that the electron-withdrawing group facilitated the OA; **1c** (X = Cl) reacted about 2.0 times faster than **1a** (X = H), and **1a** about 2.2 times faster than **1d** (*X* = Me) and 14 times faster than **1e** (X = NH$_2$).
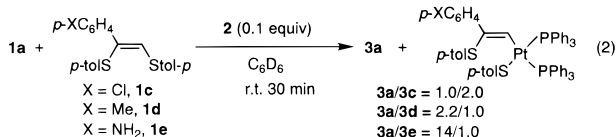
The OA of vinyl sulfide **1f** having Me$_3$Si or **1g** (10 equiv) having MeOCH$_2$ in place of Ar at *A* also took place to furnish the corresponding vinyl platinum complexes **3f** and **3g** in 54% (48 h) and 13% (24 h) yield, respectively (runs 5 and 6). Both Ar (or R$_3$Si or MeOCH$_2$) and ArS groups at *A* and *B* (*not C*) in **1** were indispensable to achieve the OA; attempted reactions using

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Scheme 4. A Proposed Route of RE of the C−S Bond[18]
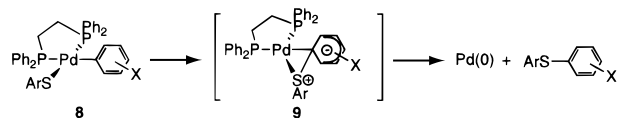
vinyl sulfides **1h** (*A* = *B* = *C* = H), **1i** (*A* = *C* = H, *B* = Ph), **1j** (*A* = Ph, *B* = H, *C* = Stol-*p*), **1k** (*A* = Stol-*p*, *B* = *C* = H), **1l** (*A* = *n*-C$_6$H$_{13}$, *B* = Stol-*p*, *C* = H), **1m** (*A* = *t*-Bu, *B* = Stol-*p*, *C* = H), and **1n** (*A* = *C* = Ph, *B* = H) did not give any desired OA products and ended in no reaction (**1l**, **1m**, and **1n**) or formation of olefin-coordinated complex (**1h**, **1i**, **1j**, and **1k**) even under more forcing conditions (50 °C).[12]

On the basis of the above observations, we propose the reaction mechanism of the OA of **1** to **2** as follows. The olefin-coordinated complex **5** generated by the ligand exchange of ethylene for **1** would be an intermediate, where all four substituents are bent down (Scheme 3).[13] Then Pt(0) would move toward sterically less hindered terminal vinyl carbon to form a zwitterionic species **6** possessing anionic charge at β-carbon. The complex **6** can be stabilized to a great extent by both Ar[14] (or Me$_3$Si[15] or MeOCH$_2$) and ArS[16] groups at *A* and *B* through delocalization of the negative charge, and presumably that is why the electron-withdrawing group in Ar at *A* accelerates the reaction. Finally, after a minimum rotation about the C−C bond to direct the anion lobe coplanar with the C−S antibonding orbital to afford **7**,[17] the SAr$^-$ group would be pushed out and migrate onto the Pt atom, resulting in the formation of **3**. During the process, the two PPh$_3$s on Pt remain cis coordinated and the stereochemistry of substituents on vinyl is retained. Recently, Hartwig and co-workers have reported the mechanism of C−S bond-forming reductive elimination (RE) from Pd(II), in which they found that the electron-withdrawing group in C$_6$H$_4$X in **8** promoted RE and proposed intriguing transition state **9** (Scheme 4).[18] Considering the microscopic reversibility between RE and OA, similar electronic effects to stabilize the transition state of OA of the C−S bond to M(0) could be equally rationalized.[19]

In summary, we substantiated here the first experimental evidence of OA of vinyl sulfide to a platinum complex, in which the modulation of the electronic factor of substituents as well as their position on vinyl was the secret to attain the reaction. The generality of the present methodology for the cleavage of other vinylic compounds is currently under investigation.

Supporting Information Available: Experimental details, X-ray data, and tables of atomic coordinates and B_{iso}/B_{eq},anisotropic displacement parameters, bond lengths, and bond angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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