The Insertion of Dimethyl Acetylenedicarboxylate into an S-Pd Bond

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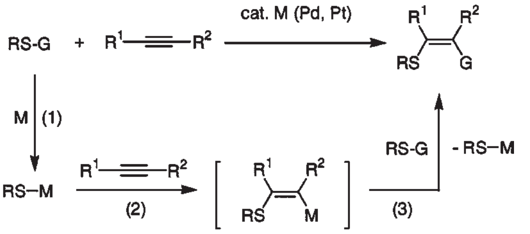
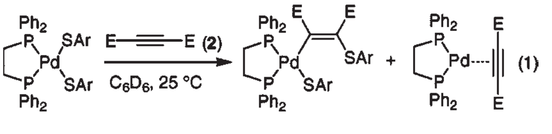
The first definitive evidence of insertion of an alkyne into an S-Pd bond has been presented. The reaction of $Pd(SAr)_2(DPPE)$ with dimethyl acetylenedicarboxylate (DMAD) gave the *cis*-insertion product (*Z*)-Pd-[$C(CO_2Me) = C(SAr)(CO_2Me)$](SAr)(DPPE), whose structure was unambiguously determined by X-ray crystallographic analysis.

With the discovery of the palladium-catalyzed *cis*-addition of disulfides to alkynes as a trailblazing study,[1a)] a significant number of reports on the transition metal-catalyzed additions of RS-G to C-C unsaturated organic compounds have been documented.[1–7] For example, the palladium- or platinum-catalyzed additions to alkynes giving *cis*-adducts have been known when G are SR,[1a)] H,[3a)] BR_2,[4] $P(O)(OAr)_2$,[5] $SiCl_3$[6] and CO_2Me.[7] Although their reaction mechanisms still remain unsettled, all reactions can be explained by a similar reaction pathway: (1) RS-M (M=Pd, Pt) bond formation; (2) *cis*-insertion (IS) of alkynes into S-M bonds; (3) product formation with regeneration of catalysts (Scheme 1).[8] However, to the best of our knowledge, no definitive evidence of IS of alkyne into S-M (M=Pd, Pt) bonds has been provided so far.[9] We wish to report here the first example of IS of alkyne into an S-Pd bond.[10]



Scheme 1.



1a E = CO_2Me ***Z*-3a** **5**

Ar = C_6H_4Me-*p*

First, the reaction of $Pd(SAr)_2(DPPE)$ (Ar=C_6H_4Me-*p*, DPPE = 1,2-bis(diphenylphosphino)ethane) (**1a**) (0.009 mmol) with dimethyl acetylenedicarboxylate (DMAD) (**2**) (0.12 mmol) in C_6D_6 (0.6 mL) at 25 °C was monitored by ^{31}P NMR spectroscopy. The chart taken after 40 min showed that a couple of doublets centered at δ 41.4 and δ 48.4 with $J_{P\text{-}P} = 25$ Hz (**3a**) appeared in 72% yield together with another set of doublets (**4a**; δ 44.8 and δ 45.4 with $J_{P\text{-}P} = 23$ Hz, 13% yield) and a singlet of the complex Pd^0(DMAD)(DPPE) **5**[11] (δ 45.9, 2% yield) (eq 1). From the reaction using 0.7 mmol of **1a**, the compound **3a** was isolated in 46% yield as a yellow solid by recrystallization from benzene/hexane.[12] Although efforts to obtain a high-quality crystal of **3a** were unsuccessful, a single X-ray crystallographic analysis of **3b** obtained by a similar procedure employing $Pd(SAr)_2(DPPE)$ (Ar=C_6H_4Cl-*p*) (**1b**) demonstrated that **3** was (*Z*)-Pd[C(E) = C(E)(SAr)](SAr)(DPPE) (E = CO_2Me) (Figure 1).[13] When the isolated *Z*-**3a** was heated in C_6D_6 at 50 °C, signals assignable to the *E*-isomer, which was different from **4a**, appeared in ^1H and ^{31}P NMR spectra ($E/Z = 71/29$ after 3 days).[14] This result clearly showed that IS of **2** into the S-Pd bond of **1a** kinetically took place in a *cis*-fashion.

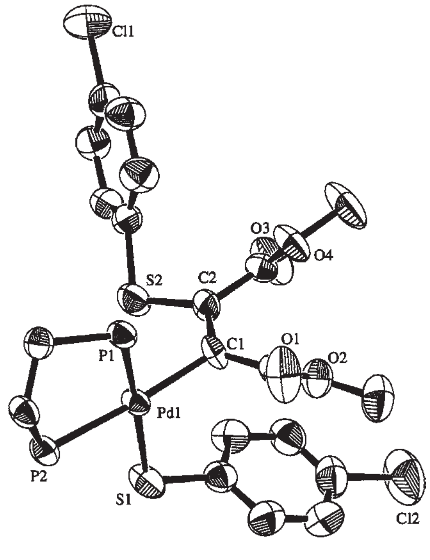


Figure 1. ORTEP diagram of *Z*-**3b** (hydrogens and Ph group on DPPE omitted).

After 5.5 h of the reaction of **1a** with **2**, the yield of **4a** (44%) and **5** (13%) increased, and a new pair of doublets (**6a**; δ 44.8 and δ 45.4 with $J_{P\text{-}P} = 23$ Hz, 16% yield) appeared. After 44 h, all such doublet signals disappeared and the yield of **5** reached 80%. Moreover, the compounds (ArS)(EC = CE)$_n$(SAr) **7** (n = 1), **8** (n = 2) were isolated by preparative TLC in 14% and 23% yield, respectively[15] and the mass spectra of other fractions showed fragment peaks of 549 and 691 corresponding to (ArS)(EC = CE)$_n$ (n = 3, 4). The foregoing results suggested that the complex **3a** underwent the successive IS of **2** into C-Pd bond of **3a**,[16] and that organic moieties were reductively eliminated from Pd(II) complexes.

When the reactions of **1b** with excess amount of **2** in CD_2Cl_2 at 25 °C were monitored by ^{31}P NMR spectroscopy, the disappearance rate of **1b** obeyed first-order kinetics with respect to the concentrations of **1b** and **2**.[17] The pseudo-first-order rate constants of disappearance of **1a–c** (Ar=Ph in **1c**) measured using 0.016 M of **1** and 0.19 M of **2** showed that the electron-donating group on Ar groups facilitated the IS of **2** (Table 1). This fact

Table 1. Pseudo-first-order rate constants for the IS of **2** into the S-Pd bond of **1**[a]

1	k_{obs}/s^{-1}
1a; Ar=C_6H_4Me-*p*	1.37×10^{-3}
1c; Ar=Ph	6.52×10^{-4}
1b; Ar=C_6H_4Cl-*p*	2.04×10^{-4}

[a] Kinetic measurements were conducted in CD_2Cl_2 at 25 °C. Initial concentrations are [**1**] = 0.016 M and [**2**] = 0.19 M.

indicated that nucleophilic character of SAr group stabilized the transition state of the IS of **2** into an S-Pd bond.

In summary, the first example of IS of alkyne into an S-Pd bond has been reported. The secret of success to observe the vinyl thiolato palladium would be attributable to the utilization of DMAD as an alkyne. Further studies on the details of IS into S-M bonds (M=Pd, Pt) using various ligands and alkynes are now under investigation.

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8 An alternative pathway: (1) G-M bond formation; (2) *cis*-IS of alkynes into M-G bonds; and (3) ^{vinyl}C-S bond-forming reductive elimination with regeneration of catalysts is also possible for all reactions.

9 The ISs of alkynes into S-M have been reported with other metals. For Ru, see: a) U. Koelle, C. Rietmann, J. Tjoe, T. Wagner, and U. Englert, *Organometallics*, **14**, 703 (1995). For Rh, see: b) Y. Wakatsuki, H. Yamazaki, and H. Iwasaki, *J. Am. Chem. Soc.*, **95**, 5781 (1973). For Mo, see: c) T. R. Halbert, W. H. Pan, and E. I. Stiefel, *J. Am. Chem. Soc.*, **105**, 5476 (1983). For W, see: d) L. Carlton, W. A. W. A. Bakar, and J. L. Davidson, *J. Organomet. Chem.*, **394**, 177 (1990). For Co, see: e) J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, **1975**, 2283. For Fe, see: f) W. Imhof and G. Huttner, *J. Organomet. Chem.*, **447**, 31 (1993). g) F. Y. Petillon, F. L. Floch-Perennou, and J. E. Guerchais, *J. Organomet. Chem.*, **173**, 89 (1979).

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12 **3a**: yellow solid (two molecules of benzene per molecule of **3a** were incorporated in the crystal); mp 124 °C; ^{1}H NMR (270 MHz, CD_2Cl_2) δ 1.62–1.80 (br, m, 1 H), 2.10 (s, 3 H), 2.11–2.43 (br, m, 2 H), 2.24 (s, 3 H), 2.46–2.60 (br, m, 1 H), 3.30 (s, 3 H), 3.31 (s, 3 H), 6.46 (d, $J = 8.2$ Hz, 2 H), 6.66 (d, $J = 8.2$ Hz, 2 H), 6.90 (d, $J = 8.1$ Hz, 2 H), 6.99 (d, $J = 8.1$ Hz, 2 H), 7.18–7.60 (m, 26 H), 7.63–7.70 (m, 2 H), 7.76–7.83 (m, 2 H), 8.00–8.07 (m, 2 H); ^{31}P NMR (109 MHz, CD_2Cl_2) δ 44.1 (d, $J_{P\text{-}P} = 23$ Hz), 49.4 (d, $J_{P\text{-}P} = 23$ Hz); IR (KBr) 3457, 3051, 2941, 1723, 1708, 1686, 1543, 1484, 1433, 1222, 1103, 1016, 874, 809, 746, 692, 680, 528, 492 cm^{-1}; Anal. Calcd for $C_{58}H_{56}O_4P_2PdS_2$: C, 66.37; H, 5.38; S, 6.11%. Found: C, 66.08; H, 5.41; S, 6.07%.

13 Crystal data for **3b**: $C_{56}H_{50}Cl_2O_4P_2PdS_2$ (two molecules of benzene per molecule of **3b** were incorporated in the crystal), $M_w = 1090.38$, monoclinic, $P2_1/n(\#14)$, $a = 10.2(1)$ Å, $b = 20.92(8)$ Å, $c = 24.27(7)$ Å, $\beta = 98.6(5)°$, $V = 5098(65)$ Å^3, $Z = 4$, $D_{calcd} = 1.421$ g/cm^3, T = 296 K, Mo Kα, A total of 13093 reflections were measured in which 12420 were independent ($R_{int} = 0.043$). $R = 0.078$, and $R_w = 0.084$ for 6566 reflections with $I > 3\sigma(I)$.

14 *E*-**3a**: ^{1}H NMR (270 MHz, C_6D_6) δ 2.04 (s, 3 H), 2.15 (s, 3 H), 3.17 (s, 3 H), 3.44 (s, 3 H), 8.28–8.39 (m, 2 H) (the other peaks were not assigned because of overlapping with the peaks of *Z*-isomer); ^{31}P NMR (109 MHz, C_6D_6) δ 42.5 (d, $J_{P\text{-}P} = 26$ Hz), 51.5 (d, $J_{P\text{-}P} = 26$ Hz).

15 **7**: ^{1}H NMR (270 MHz, C_6D_6) δ 1.92 (s, 6 H), 3.16 (s, 6 H), 6.75 (d, $J = 8.1$ Hz, 4 H), 7.38 (d, $J = 8.1$ Hz, 4 H); mass spectrum (EI) m/e 388 (M^+, 13). HRMS Calcd for $C_{20}H_{20}O_4S_2$ 388.0803. Found 388.0802. **8**: ^{1}H NMR (270 MHz, C_6D_6) δ 1.89 (s, 6 H), 3.26 (s, 6 H), 3.40 (s, 6 H), 6.73 (d, $J = 8.4$ Hz, 4 H), 7.54 (d, $J = 8.4$ Hz, 4 H); mass spectrum (EI) m/e 407 ($(M\text{-}SAr)^+$, 100).

16 The complexes **4a** and **6a** can be tentatively assigned to be $Pd[(EC = CE)_n(SAr)](SAr)(DPPE)$ (n = 2 and 3), respectively. For multiple insertion of DMAD into C-Pd bond, see: T. Yagyu, K. Osakada, and M. Brookhart, *Organometallics*, **19**, 2125 (2000).

17 The kinetic measurement was performed using 0.016 M of **1b**. The initial concentrations of **2** and pseudo-first-order rate constants of **1b** were as follows; 0.19 M, 2.04×10^{-4} s^{-1} (shown in Table 1); 0.45 M, 4.72×10^{-4} s^{-1}; 0.82 M, 8.86×10^{-4} s^{-1}; 1.10 M, 1.16×10^{-3} s^{-1}.