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Synthesis, Structure, and Reaction of the First Thermally Stable *cis*-(Silyl)(stannyl)palladium(II) Complex

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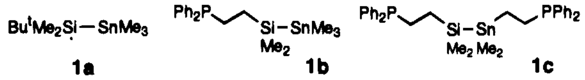
The synthetic utility of the palladium-catalyzed silylstannylation reaction of alkynes has been recognized[1] and recently extended to reactions with various unsaturated organic compounds.[2] Silylstannylation is understood to proceed through an initial oxidative addition of the Si−Sn linkage to palladium(0), forming a (silyl)(stannyl)palladium(II) complex, followed by the insertion of an unsaturated organic compound and reductive elimination to complete the silylstannylation. The mechanism has also been studied theoretically;[3] however, no experimental evidence for the pathway has been reported so far. This paper describes the first synthesis of a thermodynamically stable (silyl)(stannyl)palladium(II) complex[4,5] by oxidative addition of an Si−Sn linkage to palladium(0) and its reaction with an alkyne, thus providing a mechanistic basis for silylstannylation. Our study also lends a general explanation for the occurrence of the *trans* adduct in related palladium-catalyzed addition reactions to C−C triple bonds.

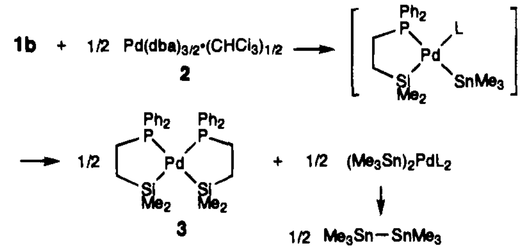
The reactivity of three kinds of silylstannanes, **1a−c**, toward Pd(0) was examined (Chart 1). The tethers leading to a diphenylphosphine group of **1b,c** were introduced in order to bring the silylstannyl group into the proximity of the palladium atom by precoordination, thus facilitating the oxidative addition.

First, the silylstannane **1a** was treated with Pd(dibenzylideneacetone)$_{3/2}$•(CHCl$_3$)$_{1/2}$ (**2**) in C$_6$D$_6$ at room temperature for 20 h, and no reaction took place. Next, the silylstannane **1b**, having a single tether leading to a diphenylphosphine group, was treated with 0.5 equiv of **2**[6] in C$_6$D$_6$ at room temperature. The purple color of **2** disappeared in 15 min. Oxidative addition of the Si−Sn linkage to the palladium was greatly accelerated by the incorporation of the phosphine tether. Monitoring the reaction by ^{1}H NMR revealed, however, that bis(silyl)palladium(II) complex **3** and hexamethylditin were formed via a disproportionation reaction (Scheme 1). No signals that could possibly be assigned to a (silyl)(stannyl)palladium(II) complex were observed. It is likely that oxidative addition of the Si−Sn linkage to palladium(0) is followed by rapid metathesis, although the mechanism of the metathesis is at present unclear. This result suggests the fluxionality of the stannyl ligand on palladium, in accord with previous results of the Pd-catalyzed disproportionation reaction of silylstannanes.[1a,7]

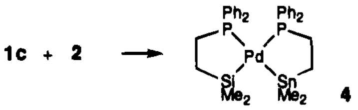
Chart 1



Scheme 1



Scheme 2



Oxidative addition of the Si−Sn bond to palladium(0) also occurred on treatment of the silylstannane **1c** with **2**, leading to quantitative formation of Pd[η^2-(SiMe$_2$CH$_2$CH$_2$PPh$_2$)][η^2-(SnMe$_2$CH$_2$CH$_2$PPh$_2$)] (**4**, Scheme 2).[8] Recrystallization from CH$_2$Cl$_2$/MeOH generated air-stable colorless crystals in 70% isolated yield. The crystal structure depicts the square planar geometry with a *cis* arrangement of the silicon and tin atoms. The Si−Pd−Sn skeleton is disordered between two orientations (70:30), the major of which is shown in Figure 1. Both the silicon and tin atoms are anchored to the palladium atom through the chelating phosphine tethers, preventing the subsequent metathesis. The Pd−Sn distance (2.573(2) Å) of the major component conforms to literature expectations (2.554−2.595 Å).[9]

Next, the reaction of **4** with alkynes was examined. Silylstannylation took place upon treatment of **4** with dimethyl acetylenedicarboxylate[10] at room temperature (Scheme 3). The reaction was complete after 12 h to give (silylstannylated alkene)palladium(0) complex **5** as a mixture of *cis* and *trans* isomers (~10:1 based on ^{31}P NMR).[11] Removal of the solvent and recrystallization of the residue from CH$_2$Cl$_2$/MeOH at −15 °C afforded pale yellow crystals of *cis*-**5**, which was characterized by an X-ray diffraction study (Figure 2).[8] As with the analogous (bis-silylated alkene)palladium(0) complex,[5h,i] the midpoint of the double bond (C43−C44) occupies one coordination site of the trigonal planar geometry.

Notably, upon allowing a solution of the isolated *cis*-**5** in C$_6$D$_6$ to stand at room temperature, gradual isomerization to *trans*-**5** proceeded according to the first-order rate law ($k \approx$ 1.1

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[1] (a) Chenard, B. L.; Zyl, C. M. V. *J. Org. Chem.* **1986**, *51*, 3561. (b) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868. (c) Murakami, M.; Morita, Y.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 428. (d) Murakami, M.; Amii, H.; Takizawa, N.; Ito, Y. *Organometallics* **1993**, *12*, 4223.

[2] (a) Ito, Y.; Bando, T.; Matsuura, T. Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 980. (b) Tsuji, Y.; Obora, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9368. (c) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem.* **1991**, *407*, 319. (d) Obora, Y.; Tsuji, Y.; Asayama, M.; Kawamura, T. *Organometallics* **1993**, *12*, 4697.

[3] Hada, M.; Tanaka, Y.; Ito, M.; Murakami, M.; Amii, H.; Ito, Y.; Nakatsuji, H. *J. Am. Chem. Soc.* **1994**, *116*, 8754.

[4] For syntheses of bis(stannyl)palladium and -platinum complexes, see: (a) Weichmann, H. *J. Organomet. Chem.* **1982**, *238*, C49. (b) Müller, C.; Schubert, U. *Chem. Ber.* **1991**, *124*, 2181. (c) Yamakawa, T.; Fujita, T.; Shinoda, S. *Chem. Lett.* **1992**, 905.

[5] For syntheses of bis(silyl)palladium and -platinum complexes, see: (a) Holmes-Smith, R. D.; Stobart, S. R.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Chem. Commun.* **1981**, 937. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (c) Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165. (d) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447. (e) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. (f) Michalczyk, M. J.; Recatto, C. A.; Calabrese, J. C.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7955. (g) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495. (h) Murakami, M.; Yoshida, T.; Ito, Y. *Organometallics* **1994**, *13*, 2900. (i) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237 and references cited therein.

[6] The use of 1 equiv of **2** gave a complex mixture.

[7] Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993**, *58*, 3607.

[8] The supplementary material contains synthetic details, spectroscopic data, and X-ray crystallographic analysis.

[9] (a) Mason, R.; Whimp, P. O. *J. Chem. Soc. (A)* **1969**, 2709. (b) Musco, A.; Pontellini, R.; Grassi, M.; Sironi, A.; Meille, S. V.; Rüegger, H.; Ammann, C.; Pregosin, P. S. *Organometallics* **1988**, *7*, 2130. (c) Grassi, M.; Meille, S. V.; Musco, A.; Pontellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1989**, 615. (d) Braunstein, P.; Knorr, M.; Piana, H.; Schubert, U. *Organometallics* **1991**, *10*, 828.

[10] Ordinary internal or terminal alkynes failed to react with **4**.

[11] Formation of a mixture of *cis* and *trans* adducts in a catalytic silylstannylation reaction has been reported in refs 1a and b.

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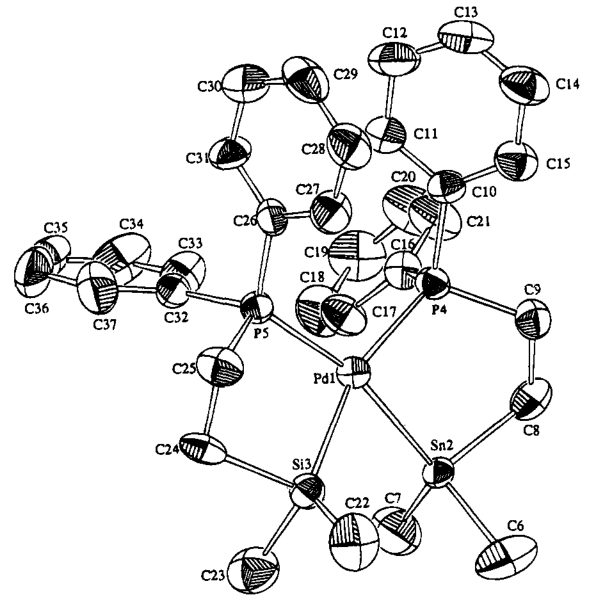
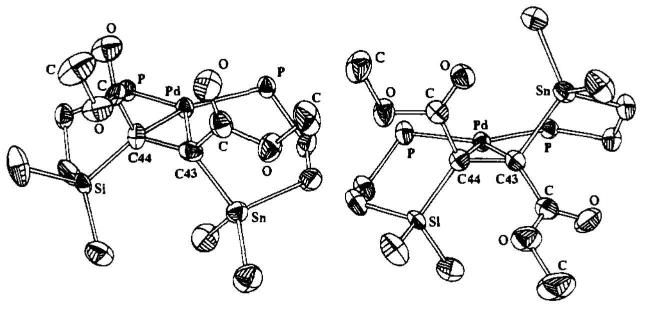


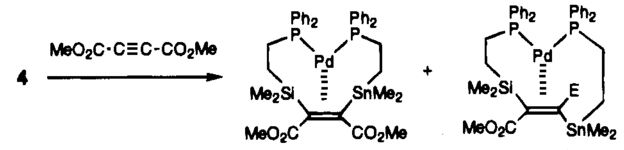
Figure 1. Molecular structure of **4** with the hydrogen atoms omitted for clarity (40% probability thermal ellipsoids).



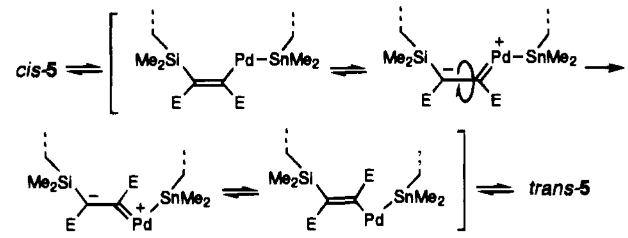
cis-**5** *trans*-**5**

Figure 2. Molecular structures of *cis*-**5** and *trans*-**5** with the phenyl groups and the hydrogen atoms omitted for clarity (40% probability thermal ellipsoids).

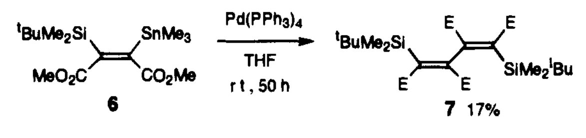
Scheme 3



Scheme 4



Scheme 5

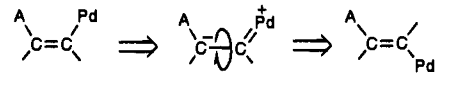


$\times 10^{-2}$ h^{-1}). Pale yellow crystals were obtained from CH_2Cl_2/hexane, and the *trans* geometry was established by X-ray crystallography (Figure 2).[8] In spite of the change in geometry, the C−C double bond lies in the trigonal plane. The isolated *trans*-**5** failed to undergo isomerization even when heated, suggesting a substantial thermodynamic preference. An appealing mechanistic possibility for this *cis*−*trans* isomerization is based on the zwitterionic palladium carbene intermediate (Scheme 4).[12] The fixation of the produced alkene on the palladium causes reversible oxidative addition of the C_{sp2}−Sn linkage.[4b,13] The resulting vinylpalladium intermediate undergoes isomerization via the zwitterionic palladium carbene complex, the anionic charge of which is significantly stabilized by the ester and silyl groups. Finally, reductive elimination furnishes the *trans* isomer. No *cis*−*trans* isomerization has been observed with the analogous (bis-silylated alkene)palladium complex,[5h] which can be ascribed to the lower reactivity of the C_{sp2}−Si bond to undergo oxidative addition.

Treatment of a silylstannylated alkene **6** with $Pd(PPh_3)_4$ at room temperature afforded the homocoupling product **7** in 17% yield (Scheme 5).[14] The formation of **7** is accounted for by postulating oxidative addition of the C_{sp2}−Sn bond to palladium(0), metathesis, and reductive elimination. Thus, oxidative addition of the C_{sp2}−Sn linkage to palladium(0) is likely to occur with *cis*-**5**, leading to isomerizaion.

Two points should be noted in the present study. (i) The first thermodynamically stable (silyl)(stannyl)palladium(II) complex was synthesized and its reaction with an alkyne studied, providing an experimental basis for the postulated mechanism of the silylstannylation. (ii) The observed *cis*−*trans* isomerization of the C−C double bond coordinating to the palladium was explained on the basis of a zwitterionic palladium carbene intermediate. The catalytic cycle of related palladium-catalyzed additions to C−C triple bonds, like hydrogenation and bis-silylation, also involves vinylpalladium(II). Although the occurrence of anomalous *trans* adducts in those reactions[15,16] has been a controversial issue, a plausible explanation can be given by postulating a similar zwitterionic palladium carbene intermediate (Scheme 6). A study in progress in our laboratory is aimed at obtaining experimental evidence for involvement of a zwitterionic palladium carbene complex.

Scheme 6



Supplementary Material Available: Experimental details, spectroscopic data, crystal structure determination data, and tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[12] Involvement of a zwitterionic rhodium carbene complex has been proposed in the rhodium-catalyzed hydrosilation: (a) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

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[14] Although the mechanism is equivocal, the palladium-catalyzed homocoupling of alkenylstannanes has been well documented; see: (a) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813. (b) Kanemoto, S.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *Chem. Lett.* **1987**, 5. (c) Tolstikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel'der, Y. L.; Spirikhin, L. V. *Synthesis* **1989**, 633. (d) Friesen, R. W.; Sturino, C. F. *J. Org. Chem.* **1990**, *55*, 2572. (e) Dubois, E.; Beau, J.-M. *Tetrahedron Lett.* **1990**, *31*, 5165. (f) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434.

[15] (a) Burwell, R. L., Jr. *Chem. Rev.* **1957**, *57*, 895. (b) Siegel, S.; Hawkins, J. A. *J. Org. Chem.* **1986**, *51*, 1638 and references cited therein.

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