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Syntheses and Interconversion of [Bis(silyl)alkene]palladium(0) and Bis(silyl)palladium(II) Complexes: A Mechanistic Model for Palladium-Catalyzed Bis-Silylation

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Summary: Two palladium complexes, [bis(trialkylsilyl)-alkene]palladium(0) and bis(trialkylsilyl)palladium(II), have been synthesized and structurally determined. The interconversion of these palladium complexes supports the postulated mechanism of palladium-catalyzed bis-silylation of C–C triple bonds.

The addition of Si–Si bonds to organic substrates to give bis(organosilyl)alkane (or -alkene), *i.e.*, bis-silylation, is a particularly attractive transformation in that two Si–C bonds are created in one reaction,[1,2] For bis-silylation of C–C triple bonds, palladium is the most often used catalyst. The redox cycle of the palladium in the generally postulated mechanism consists of two major steps (Figure 1): (A) One step is oxidative addition of the Si–Si linkage to palladium(0), forming bis(organosilyl)palladium(II). (B) The other step is the transfer of two organosilyl groups to the C–C triple bond, regenerating palladium(0). The syntheses of the related bis(organosilyl)platinum(II) complexes and the reactivities of those bis(organosilyl)-platinum(II) complexes with unsaturated organic compounds have been reported.[3] However, the chemistry of their palladium counterparts has been far less documented, probably due to the difficulty of preparation.[4] Recently Fink and co-workers reported the synthesis and reaction of the bis(hydrosilyl)palladium complex, which provided a fine corroboration for the pathway from the so-called precatalyst to the bis-silylated olefin.[4c] Our previous synthetic studies on bis-silylation reactions[2] led us to investigate the mechanistic aspect, and our strategy was to stabilize the intermediate palladium complexes involved in the redox cycle by anchoring the silyl groups to phosphine ligands. We herein report the syntheses and structural determinations of two palladium complexes, [bis(trialkylsilyl)alkene]palladium(0) (**4**) and bis(trialkylsilyl)palladium(II) (**2**). We also report the interconversion between these complexes, in particular, regeneration of **2** from **4**.

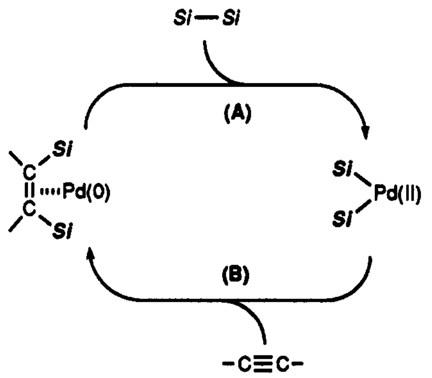

Figure 1. The redox cycle of the palladium in bis-silylation of C–C triple bonds.

Results and Discussion

A disilane flanked by two tethers leading to diphenylphosphine groups (**1**) was designed to bring the disilanyl group into the proximity of the palladium atom by chelation.[5] Treatment of the disilane **1** with Pd_2-(dibenzylideneacetone)$_3$·$CHCl_3$ in THF at room temperature for 30 min resulted in the oxidative addition of the Si–Si bond to the palladium to form the bis(trialkylsilyl)-palladium(II) complex **2** (Figure 2).[6] The color changed from purple to yellow during the reaction. Recrystallization from CH_2Cl_2/MeOH generated colorless crystals of **2** in 82% isolated yield. Although exposure of the solution of **2** to air caused decomposition, the hydrocarbon solution

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(6) Schubert *et al.* reported the reaction of *cis*-$(MePh_2P)_2PdMe_2$ and $Ph_2PCH_2CH_2SiMe_2H$ forming a bis(organosilyl)palladium(II) complex.[4b] However, the reported ^1H and ^{31}P NMR data are not identical with our data for 2, suggesting its trans geometry.

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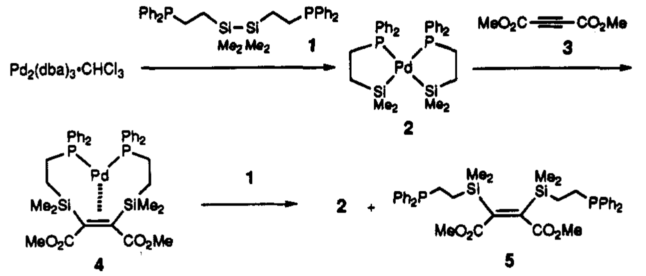

Figure 2.

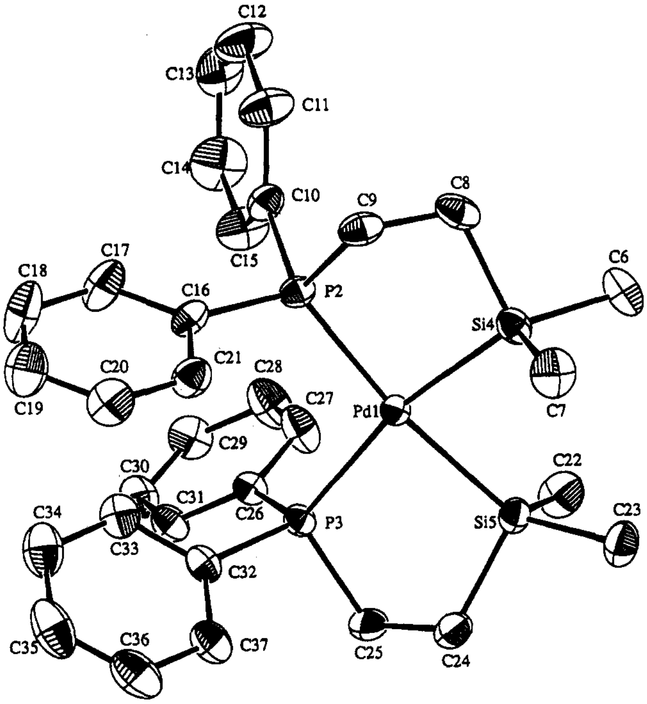

Figure 3. Molecular structure of the bis(organosilyl)palladium(II) complex 2 (30% probability thermal ellipsoids). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and bond angles (deg) are as follows: Pd1–P2 = 2.373(1), Pd1–P3 = 2.372(1), Pd1–Si4 = 2.368(1), Pd1–Si5 = 2.367(1); P2–Pd1–P3 = 106.69(4), P2–Pd1–Si4 = 84.82(4), P3–Pd1–Si5 = 83.77(4), Si4–Pd1–Si5 = 84.63(4).

under nitrogen atmosphere was fairly stable at temperatures of up to 80 °C. Furthermore, crystalline 2 was so stable in air that X-ray data could be collected without any special care to prevent decomposition. The crystal structure of 2 is shown in Figure 3. It adopts a square planar geometry with a cis arrangement of two silicon atoms. The Si–Pd bond lengths (2.368(1) and 2.367(1) Å) are similar to the Si–Pd and Si–Pt bond lengths of the analogous complexes (2.34–2.41 Å).[3,4] The long distance between Si4 and Si5 (3.19 Å) suggests the absence of considerable Si–Si interaction.

Next, the reaction of the bis(trialkylsilyl)palladium(II) complex 2 with alkynes was examined. Ordinary internal or terminal alkynes failed to react with 2. However, bis-silylation took place upon treatment of 2 with dimethyl acetylenedicarboxylate (3) in benzene to give the [bis(trialkylsilyl)alkene]palladium(0) complex 4. The reaction was complete after 20 h at room temperature. Removal of the solvent followed by addition of acetone brought about the precipitation of white solids. Recrystallization from CH_2Cl_2/acetone afforded colorless crystals in 57% isolated yield, which were characterized by X-ray diffraction and NMR studies (Figure 4). The midpoint of the double bond (C43–C44) occupies one coordination site of the trigonal planar geometry, and the double bond lies in this plane. As a consequence of π-coordination, the substituents of the double bond are bent back away from the palladium; the angle between the planes Si4–C43–C42 and Si5–C44–C45 is 28.7°. In ^{13}C NMR, the vinylic carbons resonate at 91.6 ppm higher field than those of an analogous free maleate [dimethyl 3,4-bis(trimethylsilyl)maleate]. The two Pd–P distances are significantly different although the reason is unclear. Complex 4 was even more stable than 2 and could be isolated by open column chromatography of silica gel. In normal transition metal-catalyzed reactions, the produced compound dissociates from the metal, allowing the metal to react with a new molecule of the substrate. In the present case, incorporation of two chelating phosphine tethers in the organic substrate led to a significant stabilization of the product–metal complex. This made its isolation and characterization possible.

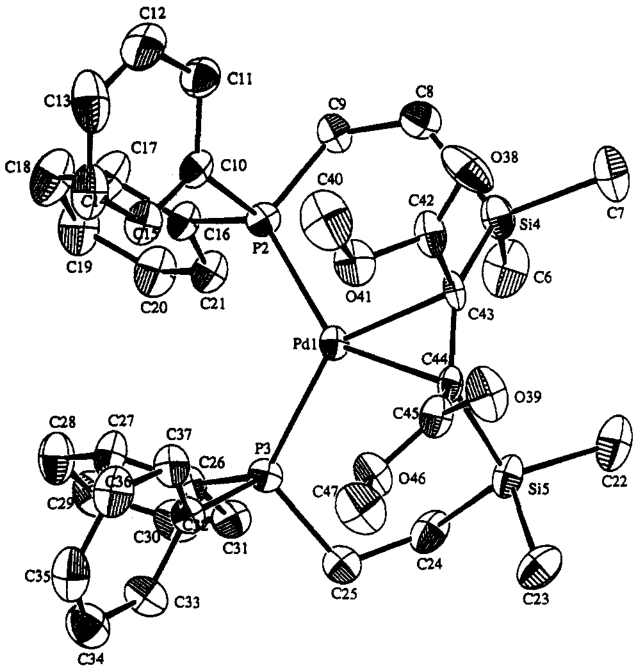

Figure 4. Molecular structure of the [bis(trialkylsilyl)alkene]palladium(0) complex 4 (30% probability thermal ellipsoids). Hydrogen atoms and acetone were omitted. Selected bond lengths (Å) and bond angles (deg) are as follows: Pd1–P2 = 2.316(3), Pd1–P3 = 2.294(4), Pd1–C43 = 2.17(1), Pd1–C44 = 2.14(1), Si4–C43 = 1.86(1), Si5–C44 = 1.89(1), C43–C44 = 1.42(1); P2–Pd1–P3 = 115.1(1), P2–Pd1–C43 = 103.6(3), P3–Pd1–C44 = 102.7(3), C43–Pd1–C44 = 38.6(4).

Of note was that the reaction of the complex 4 with disilane 1 resulted in oxidative addition of 1 to reproduce bis(organosilyl)palladium(II) complex 2 together with liberation of the bis-silylated olefin 5. When 4 was treated with 1 equiv of 1 in C_6D_6 at room temperature for 48 h, 10% of 4 and 1 were converted into 5 and 2. The liberated 1,2-bis(trialkylsilyl)alkene 5 was isolated and characterized. The reaction proceeded much faster at 60 °C, and after 48 h, bis(organosilyl)palladium(II) complex 2 was formed in 84% NMR yield (^{31}P). However, the liberated 5 decomposed at 60 °C and its isolation failed with this case.

Conclusion

We have prepared the new [bis(trialkylsilyl)alkene]palladium(0) complex 4 and bis(trialkylsilyl)palladium-

(II) complex **2**, which are found to interconvert by addition of substrate molecules; disilane **1** caused conversion of **4** into **2**, and the acetylenic compound **3** caused conversion of **2** back to **4**. Determination of the structures and elucidation of the reactivities of the palladium complexes described herein provide a mechanistic model for the postulated catalytic cycle of bis-silylation of C–C triple bonds and, thus, serve to support the mechanism.

Experimental Section

General Procedures. Column chromatography was performed with silica gel (Wakogel C-200). ^{1}H, ^{31}P, and ^{13}C NMR spectra (200, 80, and 50 MHz, respectively) were acquired in chloroform-*d*, unless otherwise noted. Chemical shifts of ^{31}P NMR are relative to external H_3PO_4. All reactions were performed under a dry nitrogen atmosphere. Melting points are uncorrected.

3,3,4,4-Tetramethyl-3,4-disilahexa-1,5-diene was prepared by the reaction of 1,2-dichloro-1,1,2,2-tetramethyldisilane with vinyl Grignard reagent. THF was distilled from sodium diphenylketyl and toluene from $LiAlH_4$.

Preparation of 1,6-Bis(diphenylphosphino)-3,3,4,4-tetramethyl-3,4-disilahexane (1). A mixture of 3,3,4,4-tetramethyl-3,4-disilahexa-1,5-diene (570 mg, 3.35 mmol) and diphenylphosphine (1.10 g, 6.69 mmol) in a quartz tube was irradiated by a high-pressure mercury lamp for 3.5 h. Purification by silica gel column chromatography and the following recrystallization from CH_2Cl_2/hexane afforded **1** (1.29 g, 70%): mp 72–73 °C; ^{1}H NMR δ 0.01 (s, 12 H), 0.57–0.72 (m, 4 H), 1.90–2.02 (m, 4 H), 7.26–7.43 (m, 20 H); ^{31}P{^{1}H} NMR δ −8.80; ^{13}C{^{1}H} NMR δ −4.0, 10.6 (d, J = 10.3 Hz), 22.3 (d, J = 14.3 Hz), 128.4 (d, J = 2.1 Hz), 132.7 (d, J = 17.6 Hz), 138.7 (d, J = 14.1 Hz). Anal. Calcd for $C_{32}H_{40}P_2Si_2$: C, 70.81; H, 7.43. Found: C, 70.51; H, 7.48.

Preparation of Pd(SiMe$_2$CH$_2$CH$_2$PPh$_2$)$_2$ (2). To a solution of Pd_2(dibenzylideneacetone)$_3$·$CHCl_3$ (244 mg, 0.236 mmol) in THF (3 mL) at room temperature was added **1** (258 mg, 0.475 mmol). After the mixture was stirred for 30 min, the solvent was removed under vacuum. MeOH (5 mL) was added to the residue, and the resulting white solid was washed with MeOH twice to remove free dibenzylideneacetone. Recrystallization from CH_2Cl_2/MeOH at −15 °C afforded **2** (253 mg, 82%) as colorless crystals: mp 128–130 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 0.31 (d, J = 1.6 Hz, 12 H), 0.60–0.85 (m, 4 H), 2.20 (dt, J = 6.4, 8.2 Hz, 4 H), 7.06–7.26 (m, 20 H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 43.22 (s); ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ 4.33 (t, J = 2.5 Hz), 20.85 (t, J = 22.5 Hz), 28.04 (dd, J = 15.2, 18.2 Hz), 128.33 (t, J = 4.3 Hz), 129.22, 133.02 (t, J = 6.7 Hz), 136.73 (the second-order complex coupling).

Preparation of 4. To a solution of **2** (45 mg, 69 μmol) in benzene (1 mL) at room temperature was added dimethyl acetylenedicarboxylate (15 mg, 0.11 mmol). After the mixture was stirred for 20 h, the solvent was removed under vacuum. The residue was recrystallized from CH_2Cl_2/acetone to afford **4** (39 mg, 57%) as colorless crystals. The crystal contains one molecule of **4** and one molecule of acetone in an asymmetric unit. **4**·Me_2CO: mp 196–199 °C; ^{1}H NMR (C_6D_6) δ 0.40 (s, 6 H), 0.53 (s, 6 H), 0.67–1.04 (m, 2 H), 1.06–1.40 (m, 2 H), 1.56 (s, 6 H, acetone), 2.24–2.57 (m, 4 H), 3.21 (s, 6 H), 6.72–6.93 (m, 6 H), 6.96–7.22 (m, 10 H), 7.65–7.80 (m, 4 H); ^{31}P{^{1}H} NMR (C_6D_6) δ 22.81 (s); ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) δ 1.38 (t, J = 2.0 Hz), 2.43, 15.93–16.12 (m), 24.51–24.77 (m), 30.04 (s, acetone), 50.56, 63.06 (dd, J = 19.4, 4.8 Hz), 128.19, 128.33, 128.43, 129.39, 131.92 (d, J = 13.5 Hz), 133.85 (d, J = 15.3 Hz), 137.35 (d, J = 28.7 Hz), 139.00 (d, J = 25.6 Hz), 174.81 (t, J = 2.8 Hz). Anal. Calcd for $C_{41}H_{52}O_5P_2Si_2Pd$ (**4**·Me_2CO): C, 57.98; H, 6.17. Found: C, 57.66; H, 5.98.

Table 1. Crystallographic Data for Diffraction Studies

	2	**4**·Me_2CO
empirical formula	$C_{32}H_{40}P_2Si_2Pd$	$C_{41}H_{52}O_5P_2Si_2Pd$
fw	649.2	849.4
cryst syst	monoclinic	monoclinic
a, Å	12.629(2)	10.551(9)
b, Å	10.425(1)	16.02(1)
c, Å	24.552(1)	25.078(8)
β, deg	102.214(6)	98.62(4)
V, Å^3	3159.3(5)	4190(4)
space group	$P2_1/c$	$P2_1/n$
Z value	4	4
D_{calc}, g/cm^3	1.365	1.346
2θ range, deg	3–60	3–55
μ, cm^{-1}	7.84	6.17
temp, °C	23	23
no. of unique data	6259 [$I > 3\sigma(I)$]	4371 [$I > 4\sigma(I)$]
no. of variables	491	460
R, R_w	0.050, 0.058	0.069, 0.059
GOF	2.45	3.96

Reaction of 4 with 1. To a solution of **4** (76 mg, 90 μmol) in benzene (1 mL) at room temperature was added **1** (53 mg, 98 μmol). After the mixture was stirred for 48 h, the solvent was removed under vacuum. The residue was subjected to column chromatography to afford **5** (6.0 mg, 10%): ^{1}H NMR (C_6D_6, 200 MHz) δ 0.12 (s, 12 H), 0.86–1.00 (m, 4 H), 2.07–2.16 (m, 4 H), 3.35 (s, 6 H), 7.05–7.17 (m, 8 H), 7.46–7.55 (m, 12 H); ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz) δ −8.89 (s); MS *m*/*z* 684 (M$^+$).

Crystallographic Analysis. Measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). A crystal of **4** was coated with an adhesive material to avoid the loss of the crystallization solvent. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. The data were collected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scans of several reflections was applied. The structures were solved by direct methods using the SHELX86 program and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. For **2**, all hydrogen atoms except H11 were refined isotropically and H11 was included in a fixed position. For **4**, all hydrogen atoms were included in the refinement at the calculated positions (0.95 Å) with isotropic thermal parameters calculated from those of the bonded atoms. Crystal data are reported in Table 1.

Supplementary Material Available: Tables of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for complexes 2 and 4 (30 pages). Ordering information is given on any current masthead page.

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