Synthesis of a Tridentate Hydrosilane and Its Reaction with Palladium(0) Complexes

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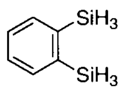
A new tridentate hydrosilane $(2\text{-}SiH_3C_6H_4)_2SiH_2$ reacts with a mixture of $Pd(PEt_3)_4$ and $R_2PCH_2CH_2PR_2$ (R = Me or Et) to give dinuclear (silyl)(μ-silylene)palladium(II) complexes, while the reaction with a mixture of $Pd(PEt_3)_4$ and $Cy_2PCH_2CH_2PCy_2$ (Cy = cyclohexyl) afforded a mononuclear (silyl)(disilanyl)palladium(II) complex, the Si–Si bond of which was formed by the intramolecular dehydrocoupling. The structures of the new complexes were determined by X-ray diffraction.

The chemistry of silyl transition metal complexes is rapidly growing due to its importance for understanding and developing transition metal catalyzed reactions of silicon compounds.[1] Recently we have succeeded in the isolation of mononuclear and dinuclear silyl group 10 metal complexes with high formal oxidation states by using bidentate hydrosilane, 1,2-disilylbenzene (**1**).[2] These results prompted us to investigate the reactivity of a tridentate hydrosilane, bis(2-silylphenyl)silane (**2**), which has analogous structure to **1**. Here we report the synthesis of **2** and its reaction with palladium(0) complexes, resulting in the isolation of dinuclear (silyl)(μ-silylene)palladium(II) complexes as well as a mononuclear (silyl)(disilanyl)palladium(II) complex.



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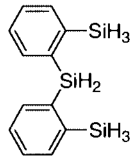
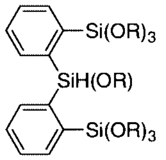
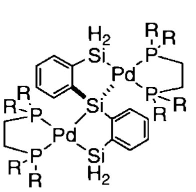


2

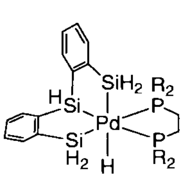


4a: R = *i*-Pr
4b: R = Me

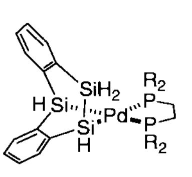
Silane **2** was prepared by the $LiAlH_4$ reduction of the known compound, bis[2-(trichlorosilyl)phenyl]dichlorosilane (**3**),[3] or new alkoxysilane **4a** or **4b**. The compounds **4a** and **4b** were prepared in shorter steps than **3** based on Tamao's method.[3,4] Although **4a** is more stable to moisture than **4b**, purification of **2** after the $LiAlH_4$ reduction was easier for **4b** than for **4a**, because complete removal of byproducts (probably isopropoxyaluminum species) from **2** was difficult in the case of **4a**.[5]



5a: R = Me
5b: R = Et



6a: R = Me
6b: R = Cy



7a: R = Me
7b: R = Cy

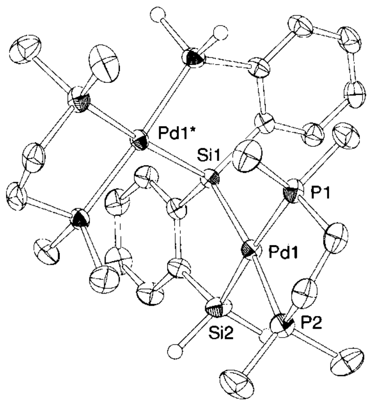
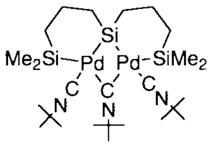


Figure 1. Molecular structure of complex **5a** (50% probability level). Hydrogen atoms attached on carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1-Si1, 2.3818(8); Pd1-Si2, 2.334(1); Pd1-P1, 2.3354(9); Pd1-P2, 2.3375(9); Si1-Pd1-Si2, 80.95(3); Si1-Pd1-P2, 173.47(3); Si2-Pd1-P1, 173.46(4); P1-Pd1-P2, 85.88(3); Pd1-Si1-Pd1*, 101.81(5).

The reaction of **2** with a mixture of $Pd(PEt_3)_4$ and 1,2-bis(dimethylphosphino)ethane (dmpe) (**2** : Pd : dmpe = 1 : 1 : 1)[6] gave a mixture of two complexes consisting of yellow dinuclear complex **5a**[7,8] (21% isolated yield) and a colorless complex. Although the structure of the latter has not been established, ^1H NMR analysis showed that it is neither tris(silyl)(hydrido)palladium(IV) complex **6a** (no Pd–*H* signal was observed), which we expected to be formed, nor (silyl)(disilanyl)palladium(II) complex **7a**, whose analog **7b** was obtained in the reaction of **2** with a mixture of $Pd(PEt_3)_4$ and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) (vide infra). The yield of **5a** increased to 81% when 2 equiv of $Pd(PEt_3)_4$ and dmpe were used. Similar results were obtained for the reaction of **2** with a mixture of $Pd(PEt_3)_4$ and 1,2-bis(diethylphosphino)ethane (depe);[6] dinuclear complex **5b**[7] was isolated in 27% yield for **2** : Pd : depe = 1 : 1 : 1 and in 82% yield for **2** : Pd : depe = 1 : 2 : 2. The structure of **5a** was unambiguously determined by X-ray structure analysis (Figure 1).[9] A dinuclear palladium complex **8** with a tridentate silicon ligand has been reported by Ito.[8a]



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In contrast, the reaction of **2** with a mixture of $Pd(PEt_3)_4$ and dcpe (**2**:Pd:dcpe = 1:1:1)[6] gave a mononuclear (silyl)(disilanyl)palladium(II) complex **7b** in 86% yield.[7] No dinuclear complex similar to **5a** and **5b** was observed, probably because the steric hindrance of cyclohexyl groups on the phosphorus atoms prevented the formation of the dinuclear structure. The structure of **7b** determined by X-ray structure analysis shows that intramolecular dehydrocoupling reaction has taken place to form a Si–Si bond (Figure 2).[10] Although the mechanism of the formation of **7b** is not clear at the moment, an assumption of the intermediacy of tris(silyl)(hidrido)palladium(IV) **6b** can explain the formation of **7b**.[11] Scheme 1 shows two plausible pathways of the formation of **7b** from **6b**. Reductive elimination on **6b** to form a Si–Si bond provides **9** and successive oxidative addition of Si–H bond and elimination of H_2 from **10** give **7b**. Another possibility is the concerted mechanism; simultaneous elimination of H_2 and Si migration from Pd to another Si via transition state **11** gives **7b**.

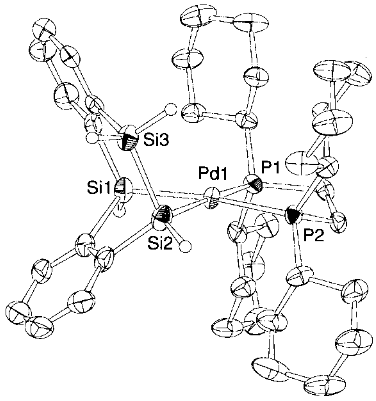
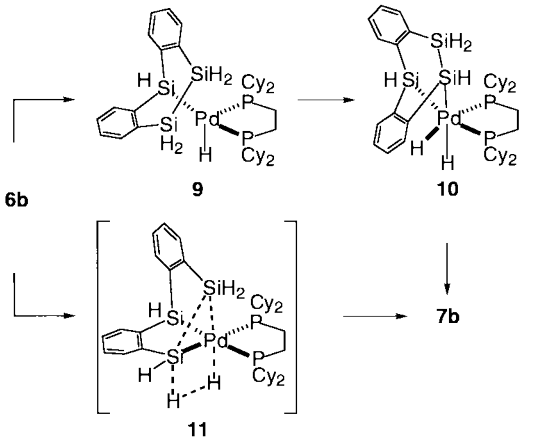


Figure 2. Molecular structure of complex **7b** (50% probability level). Hydrogen atoms attached on carbon atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1-Si1, 2.348(3); Pd1-Si2, 2.356(3); Pd1-P1, 2.333(2); Pd1-P2, 2.315(2); Si2-Si3, 2.333(4); Si1-Pd1-Si2, 75.43(10); Si1-Pd1-P2, 171.56(10); Si2-Pd1-P1, 173.09(10); P1-Pd1-P2, 87.44(8); Pd1-Si2-Si3, 103.3(1).



Scheme 1. A plausible mechanism for the formation of **7b**.

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 For recent reviews, see: M. S. Eisen, in "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig, Wiley, New York (1998), Vol. 2, Part 3, Chap. 35, p 2037; H. Ogino and H. Tobita, *Adv. Organomet. Chem.*, **42**, 223 (1998); J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, **99**, 175 (1999).

2 S. Shimada, M. Tanaka, and K. Honda, *J. Am. Chem. Soc.*, **117**, 8289 (1995); S. Shimada, M. Tanaka, and M. Shiro, *Angew. Chem., Int. Ed. Engl.*, **35**, 1856 (1996); S. Shimada, M. L. N. Rao, and M. Tanaka, *Organometallics*, **18**, 291 (1999); S. Shimada, M. L. N. Rao, T. Hayashi, and M. Tanaka, *Angew. Chem. Int. Ed.*, **40**, 213 (2001).

3 G.-R. Sun, Ph. D. Thesis, Kyoto University, Kyoto, Japan, 1995; private communications from K. Tamao.

4 K. Tamao, H. Yao, Y. Tsutsumi, H. Abe, T. Hayashi, and Y. Ito, *Tetrahedron Lett.*, **31**, 2925 (1990); K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *Organometallics*, **11**, 2099 (1992).

5 Preparation of **2** via **4b**: A pentane solution of ^{t}BuLi (1.54 M, 137 mL, 0.21 mol) was added to $PhSi(NMe_2)_2$-$(NMeCH_2CH_2NMe_2)$[3] (**12**) (47.7 g, 0.162 mol) in 200 mL of hexane at 0 °C, and the mixture was stirred overnight at room temperature. To the resulting solution cooled to –40 °C was added $SiHCl_3$ (13.0 g, 0.096 mol), and the solution was allowed to warm to room temperature. Successive addition of dry MeOH (100 mL) and $SiCl_4$ (30 mL, as a source of HCl) at 0 °C, filtration of the resulting white precipitates, and removal of volatiles under vacuum gave crude **4b** as a pale-yellow waxy solid (^{29}Si NMR (C_6D_6, δ) –13.52 (d, ^1J(H,Si) = 219, *Si*–H)). $LiAlH_4$ (21 g, 0.55 mol) was added to an ether solution (500 mL) of crude **4b** at 0 °C, and the mixture was refluxed overnight. Filtration of insoluble materials, evaporation of the solvent, and bulb-to-bulb distillation afforded **2** as a colorless liquid (4.3 g, 22.0% based on **12**). ^{1}H NMR (C_6D_6, δ) 4.32 (s, 6H, SiH_3), 5.31 (s, 2H, SiH_2), 7.04 (m, 4H), 7.47 (m, 4H); ^{29}Si (C_6D_6, δ) –61.1(qd, ^1J(H,Si) = 201, ^2J(H,Si) = 5.9, *Si*H_3), –38.4 (tt, ^1J(H,Si) = 200, ^2J(H,Si) = 5.0, *Si*H_2); Anal. Calcd for $C_{12}H_{16}Si_3$: C, 58.95; H, 6.60%. Found: C, 58.79; H, 6.57%.

6 To a toluene solution of $Pd(PEt_3)_4$ and dmpe, depe, or dcpe was added **2** at 0 °C. Then, the mixture was stirred at room temperature for 20 min. The products were isolated by recrystallization from toluene (for **5a** and **7b**) or Al_2O_3 column chromatography (for **5b**).

7 **5a**: ^{29}Si{^{1}H} NMR: (C_4D_8O, δ) –23.8 (tt, *J*(Si,P) = 11, 79), 79.8 (tt, *J*(Si,P) = 11, 128). **5b**: ^{29}Si{^{1}H} NMR: (C_7D_8, δ) –22.8 (tt, *J*(Si,P) = 10, 76), 82.4 (tt, *J*(Si,P) = 11, 125). **7b**: ^{29}Si NMR (C_6D_6, δ) 23.8 (dd, ^2J(P–Si) = 13, 143 Hz, C*Si*HC), –31.4 (dd, ^2J(P–Si) = 13, 142 Hz, Pd*Si*HSiH_2), –61.8 (s, *Si*H_2SiH).

8 Examples of μ-silylene-bridged dinuclear palladium complexes, see: a) M. Suginome, Y. Kato, N. Takeda, H. Oike, and Y. Ito, *Organometallics*, **17**, 495 (1998). b) Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, and T. Yamamoto, *Organometallics*, **17**, 4329 (1998). c) Y.-J. Kim, S.-C. Lee, J.-I. Park, K. Osakada, J.-C. Choi, and T. Yamamoto, *J. Chem. Soc., Dalton Trans.*, **2000**, 417.

9 Crystal Data for **5a**·toluene: $C_{31}H_{52}P_4Pd_2Si_3$, fw = 845.70, a = 18.759(1), b = 15.071(2), c = 14.609(1) Å, β = 113.008(5)°, V = 3801.7(5) Å^3, monoclinic, space group *C*2/*c*, Z = 4, D_{calc} = 1.477 g·cm^{-3}, R_1 = 0.040 (for 3894 reflections with $I > 2\sigma(I)$), wR_2 = 0.140 (for all data (4366 reflections)).

10 Crystal Data for **7b**: $C_{38}H_{60}P_2PdSi_3$, fw = 769.50, a = 20.080(2), b = 9.696(3), c = 20.275(2) Å, V = 3947(1) Å^3, orthorhombic, space group $Pna2_1$, Z = 4, D_{calc} = 1.295 g·cm^{-3}, R_1 = 0.047 (for 3164 reflections with $I > 2\sigma(I)$), wR_2 = 0.135 (for all data (4650 reflections)).

11 Tilley has reported that a tris(silyl)(hidorido)platinum(IV) complex can be an intermediate for the dehydrocoupling reaction of phenylsilane: R. H. Heyn and T. D. Tilley, *J. Am. Chem. Soc.*, **114**, 1917 (1992).