The First Alkyl(silyl)palladium Complexes: Formation by Oxidative Addition of Silacyclobutanes to Palladium Complexes, Reductive Elimination, and Other Reactivities Relevant to Catalysis

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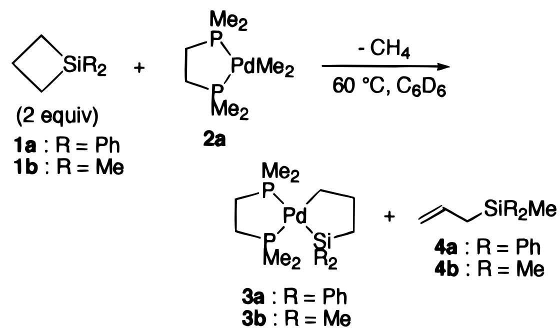
Summary: 1,1-Diphenyl- and 1,1-dimethylsilacyclobutanes reacted with $Me_2Pd(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane) or $Pd(PhCH{=}CH_2)(dmpe)$ to give 2,2-diphenyl- and 2,2-dimethyl-1-pallada-2-silacyclopentane complexes, the diphenyl complex being characterized by X-ray analysis. Treatment of the diphenyl complex with acetylenes or 1,2-disilacyclopentane induced reductive elimination to regenerate the parent 1,1-diphenylsilacyclobutane. A dihydrosilane or a silacyclobutane reacted with the diphenyl complex to afford a 1,3-bis(hydrosilyl)propane or a 1,5-disilacyclooctane, respectively.

Although silicon−carbon bonds usually are unreactive toward transition-metal complexes, those of silacyclobutanes (**1**) are exceptions. They are reactive due to their ring strain.[1] Quite a few reactions of **1** that are catalyzed by transition-metal complexes have been reported, such as ring-opening polymerization,[2] dimerization,[3] cross-dimerization with disilanes,[4] and cycloaddition reactions[5] with acetylenes and allenes. 1-Metalla-2-silacylopentanes are believed to be involved as intermediates in these catalytic reactions. Indeed, 1-ferra-[6] and 1-platina-2-silacyclopentane[3] complexes have been isolated. In a broader view, the chemistry of 1-metalla-2-silacyclopentanes is important in its own right; these complexes provide a rare opportunity to study the reactivities of alkyl(silyl)metal species, a very important class of catalytic intermediates, which are not always sufficiently stable to allow their manipulation. This paper reports the chemistry of 1-pallada-2-silacyclopentane complexes, which are the first alkyl(silyl)palladium species.

In one example $Me_2Pd(dmpe)$ (**2a**, 0.09 mmol; dmpe = 1,2-bis(dimethylphosphino)ethane) and 1,1-diphenylsilacyclobutane (**1a**, 0.27 mmol) were mixed in C_6D_6 (0.3 mL), and the solution was heated in a sealed NMR tube at 60 °C for 7 h. Monitoring of the reaction by ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy revealed the formation of a 1-pallada-2-silacyclopentane complex (**3a**, 90% NMR yield)[7] and allylmethyldiphenylsilane (**4a**, 80% NMR yield) (eq 1). The ^{1}H NMR spectrum displayed a very



(1)

weak signal at δ 0.23, suggesting that methane had been generated. The structure of **4a** was confirmed by GC−MS of the reaction mixture. The mixture was evaporated *in vacuo*, and the residue was recrystallized from toluene-hexane to give **3a** as pale yellow crystals (32.5 mg, 75%). The structure of **3a** was unambiguously confirmed by X-ray diffraction, thus verifying that oxidative addition of the Si−C bond in the ring system had taken place. As the ORTEP[8] drawing (Figure 1) shows,[9] **3a** is a square-planar complex, the deviation from planarity being very small.[10] The Pd-Si bond distance (2.341(2) Å) is within the range of those reported in the literature (2.33−2.43 Å).[11] The Pd−P bond *trans* to the silicon (2.351(2) Å) is significantly longer than the other Pd−P bond *trans* to the carbon (2.291(2) Å). This is due to the strong *trans* influence

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(1) The strain energies of silacyclobutane, silacyclopentane, and silacyclohexane are 102.5, 20.1, and 13.0 kJ mol^{-1}, respectively. See: Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584.

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(7) Compounds **3a**,**b** showed satisfactory NMR and/or analytical data (see the Supporting Information). ^{1}H, ^{29}Si, and ^{31}P NMR spectral data (C_6D_6) for **3a** are as follows: ^{1}H NMR δ 0.64 (d, J = 7.3 Hz, 6H, PMe), 0.66−0.95 (m, 4H, PCH_2CH_2P), 0.79 (d, J = 5.9 Hz, 6H, PMe), 1.80 (t, J = 6.6 Hz, 2H, CH_2Si), 2.39−2.53 (m, 2H, CH_2), 2.56−2.68 (m, 2H, CH_2), 7.15−7.33 and 7.92−7.97 (each m, 3H and 2H, C_6H_5); ^{29}Si NMR δ 47.1 (dd, J_{PSi} = 15.9 and 174.6 Hz); ^{31}P NMR δ 10.6 (d, J_{PP} = 9.6 Hz, J_{PSi} = 174.6 Hz), 14.2 (d, J_{PP} = 9.6 Hz).

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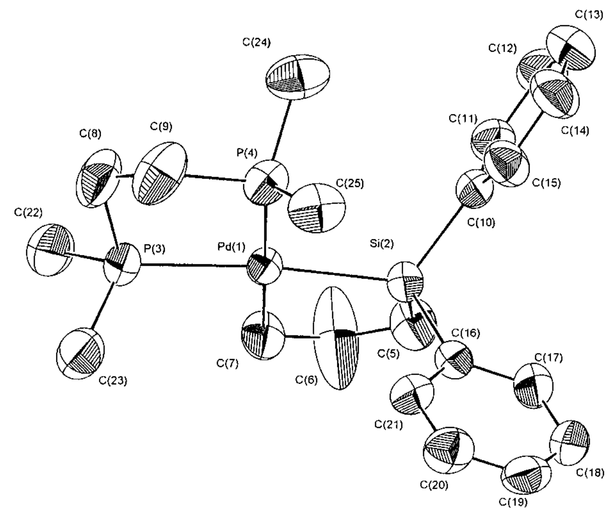


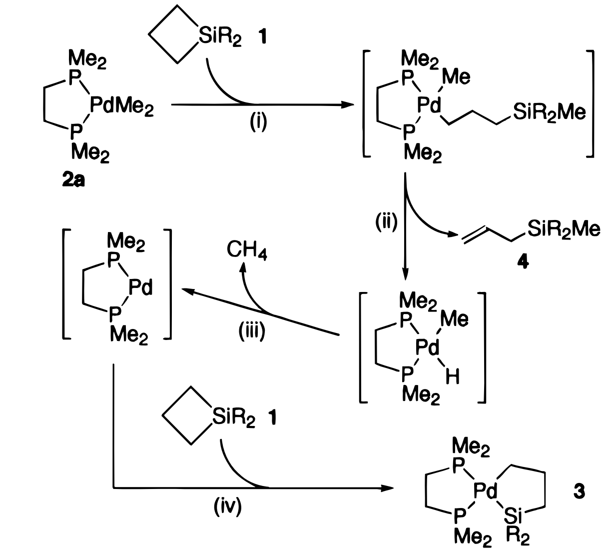
Figure 1. ORTEP drawing of **3a**. C(6) is disordered, resulting in large thermal parameters. Selected bond lengths (Å) and angles (deg): Pd(1)−Si(2), 2.341(2); Pd(1)−P(3), 2.351(2); Pd(1)−P(4), 2.291(2); Pd(1)−C(7), 2.129(7): Si(2)−Pd(1)−P(3), 174.0(1); Si(2)−Pd(1)−P(4), 100.1(1); Si(2)−Pd(1)−C(7), 80.0(2); P(3)−Pd(1)−P(4), 85.0(1); P(3)−Pd(1)−C(7), 95.2(2); P(4)−Pd(1)−C(7), 175.9(2).

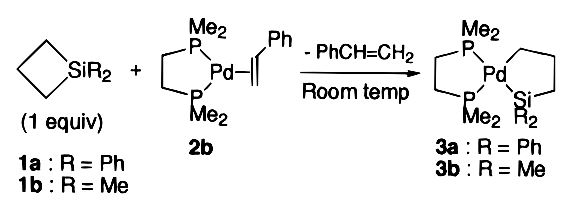
of a silyl ligand as compared with an alkyl ligand. Complex **3a** was unstable to air in solution but only slightly decomposed in air in the crystalline state.

1,1-Dimethylsilacyclobutane (**1b**) reacted similarly with **2a** at 60 °C over 100 h to generate another five-membered alkyl(silyl)palladium complex (**3b**)[7] in 60% yield along with allyltrimethylsilane (**4b**, 60%). However, before total consumption of **1b**, slight decomposition of **3b** started to form Pd(dmpe)$_2$[12] to a small extent, indicating that **3b** is thermally less stable than **3a**. Complex **3b** could not be isolated in a pure form. The thermal instability of **3b** presumably is associated with reductive elimination to re-form **1b**.[13]

As illustrated in Scheme 1, the foregoing reactions forming compounds **3** can be best explained by a sequence comprising (i) metathesis of Me$_2$Pd(dmpe) with the Si−C bond of **1** to generate methyl[3-(methyldiorganylsilyl)propyl]palladium species, (ii) β-hydride elimination to result in the formation of **4**, (iii) extrusion of a methane molecule to generate Pd(0) species, and (iv) reaction of the resulting Pd(0) species with a second molecule of **1** to give **3**. Accordingly, a Pd(0) complex having a more labile ligand, such as an olefin complex, is expected to react more readily with **1** to form the five-membered-ring complex. Indeed, as monitored by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, Pd(η^2-PhCH=CH$_2$)(dmpe) (**2b**, 0.025 mmol) reacted with **1a** or **1b** (1 equiv) in C$_6$D$_6$ (0.25 mL) even at room temperature to give, within 10 min, **3a** or **3b** in quantitative yield (eq 2). Even though the formation of **3b** in the solution was quantitative, its isolation was not successful.[14]

Scheme 1





(2)

Palladium complexes are able to catalyze the reactions of silacyclobutanes with acetylenes to give silacyclohexenes and/or vinyl(allyl)silanes, and the catalysis is envisioned to proceed *via* 1-pallada-2-silacyclopentane intermediates.[5] However, when **3a** (0.06 mmol) was allowed to react with diphenylacetylene (**5a**, 1.5 equiv) in C$_6$D$_6$ (0.3 mL) at room temperature for 30 min in a sealed NMR tube, neither the corresponding silacyclohexene nor vinyl(allyl)silane was formed. NMR spectroscopic analysis of the resulting mixture revealed that **1a** was formed in ~12% yield along with a (diphenylacetylene)palladium dmpe complex (~13%).[15] Contin-

(9) Crystal data for **3a**: colorless transparent prism, 0.40 × 0.25 × 0.15 mm^3; C$_{21}$H$_{32}$P$_2$PdSi; FW = 479.0; monoclinic, space group $P2_1/a$, a = 15.939(3) Å, b = 10.083(3) Å, c = 14.834(3) Å, β = 105.08(2)°, V = 2302.0(9) Å^3, Z = 4; D_{calcd} = 1.38 g cm^{-3}; μ(Mo Kα) = 9.85 cm^{-1}; Mac Science MXC18 diffractometer; ambient temperature, Mo Kα radiation (λ = 0.710 73 Å); 3.0° < 2θ < 55.0°, $\omega-2\theta$ scan; 258 parameters; 4700 observed reflections ($F > 3.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to yield the final residuals of R = 0.044 and R_w = 0.075. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated at idealized calculated positions. All hydrogen atoms were then included in the calculations but not refined. All calculations were performed using the Crystan GM crystallographic software package.

(10) The high thermal parameters for C(6) suggest that C(6) is disordered.

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(13) Me$_2$Pd(PPh$_2$Me)$_2$ also reacted with **1a** (2 equiv) in C$_6$D$_6$. at 60 °C for 1 h to give **4a** (80% based on Pd), Pd(PPh$_2$Me)$_4$, and a black precipitate (presumably metallic palladium). However, the corresponding cyclic complex was not found by NMR in the reaction mixture, suggesting its thermal instability. Me$_2$Pd(PMe$_3$)$_2$ behaved very similarly to give **4a** (90% based on Pd) when treated with **1a** at 60 °C for 30 min.

(14) The deterioration of the complex during the evaporation (0.1 Torr/room temperature) of the solvent appeared to be induced by removal of **1b** extruded by spontaneous reductive elimination, suggesting the reversibility of the oxidative-addition−reductive-elimination processes under the conditions. In the resulting mixture were found Pd(dmpe)$_2$ by ^{1}H NMR and a black precipitate (presumably metallic palladium).

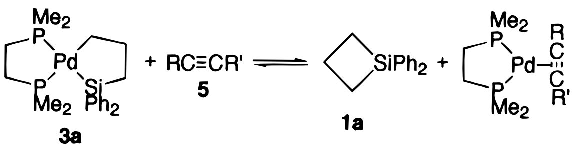
(15) ^{1}H NMR: δ 0.95−1.17 (m, 16H, PMe and PCH$_2$CH$_2$P), 6.92−8.04 (m, 10H, C$_6$H$_5$). ^{31}P NMR: δ −7.7. These NMR data are consistent with those of an authentic sample of (PhC≡CPh)Pd(dmpe) generated by the reaction of Pd(η^3-CH$_2$=CHCH$_2$)(η^5-C$_5$H$_5$), diphenylacetylene, and dmpe in C$_6$D$_6$. See: Krause, J.; Bonrath, W.; Pörschke, K. R. *Organometallics* **1992**, *11*, 1158. Since the ^{1}H NMR signals for PMe and PCH$_2$CH$_2$P of (PhC≡CPh)Pd(dmpe) were distinctly separated from those for PCH$_2$CH$_2$P of **3a** (0.66−0.95 ppm), the yield of (PhC≡CPh)Pd(dmpe) was readily evaluated by integration.

Table 1. Reactions of 1-Pallada-1-silacyclopentane Complex 3a with Acetylenes 5[a]

RC≡CR′ (**5**)	temp (°C)/time (h)[b]	yield of **1a** (%)[c]
PhC≡CPh (**5a**)	60/0.5	66 (12)
PhC≡CH (**5b**)	60/3	30 (4)
PhC≡CMe (**5c**)	60/3	16 (0)
^{n}PrC≡C^{n}Pr (**5d**)	80/12	10 (0)
	100/12	30
CH≡CCOOEt (**5e**)	room temp/5.5	73 (20)
MeOOCC≡CCOOMe (**5f**)	room temp/5.5	80 (54)

[a] Complex **3a** (0.06 mmol) was treated in a sealed NMR tube with **5** (0.09 mmol) in C_6D_6 (0.3 mL), first at room temperature for 0.5 h, and then under the conditions given in the table. [b] Reaction conditions after the beginning 0.5 h. [c] ^{1}H NMR yield. Figure in parentheses indicate yields after the beginning 0.5 h at room temperature.

ued reaction at 60 °C for 30 min increased the yields of **1a** and the complex to 66 and 67% respectively, but the yields remained unchanged thereafter (eq 3). The reac-

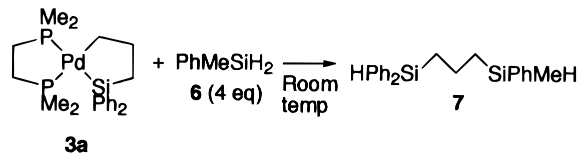


(3)

tion was very clean; the starting **3a** was still found (34%) in the reaction mixture, and no other byproducts were formed in substantial amounts. The results strongly suggest that the incomplete conversion to **1a**, *i.e.*, 66% yield of **1a** at the 30 min reaction time and thereafter, is due to attainment of an equilibrium under the conditions.

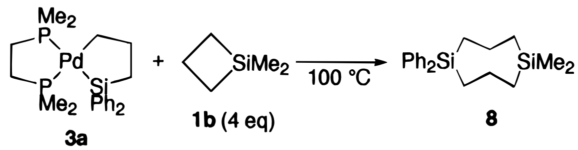
Other acetylenes reacted similarly with **3a** to give **1a** (Table 1). Very interestingly, however, the reaction rate and the yield very much depended on the structure of the acetylenes. For instance, 4-octyne (**5d**) was very reluctant to induce reductive elimination; **1a** was not found by ^{1}H NMR at all below 60 °C, and heating at 80 °C for 12 h resulted in only a 10% yield of **1a**. The yield remained as low as 30% even after heating to 100 °C over 12 h. On the other hand, treatment of **3a** with dimethyl acetylenedicarboxylate (**5f**) at room temperature for 30 min already gave **1a** in 54% yield. The yield increased over 6 h to 80% and remained unchanged for an additional 42 h. These results, inclusive of those with other acetylenes shown in Table 1, clearly indicate that electron-withdrawing groups bound to the acetylenic carbon increase the reactivity in the reductive elimination both kinetically and thermodynamically. Similar observations have been reported for a *cis*-alkyl(silyl)-bis(phosphine)platinum complex.[16] A mechanism that involves dissociation of a phosphine ligand *trans* to the silyl group and coordination of an acetylene to the coordination site prior to the extrusion of an alkylated silane has been proposed as a major pathway. The similarity between the platinum and our palladium cases tempts us to consider essentially the same mechanism. However, taking into account the difficulty of dissociation of one of the phosphorus atoms of the dmpe ligand, it may be premature to extend further discussion along these lines.[17] Five-coordinate species proposed in a similar π−acid-induced reductive elimination from a dialkyl(bipyridyl)nickel[18] complex also has to be considered.

Besides the reaction with acetylenes, 1-metalla-2-silacyclopentane complexes are envisioned to be involved in several catalytic reactions of **1** (*vide supra*).[2−5] In this context, the reactivities of complex **3a** with those substrates relevant to the catalyses were briefly examined. Methylphenylsilane (**6**, 0.24 mmol) reacted with **3a** (0.06 mmol) in C_6D_6 (0.3 mL) in a sealed NMR tube even at room temperature, and the 1,3-bis(hydrosilyl)-propane compound **7** was formed in 70% yield after 24 h (eq 4). This result is in good agreement with the ring-opening reaction of silacyclobutanes with hydrosilanes.[2a]



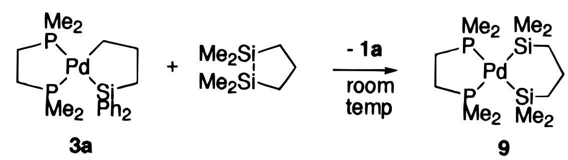
(4)

The reaction of **3a** (0.06 mmol) with **1b** (0.24 mmol) in C_6D_6 (0.3 mL) in a sealed NMR tube also proceeded at 100 °C to afford a 1,5-disilacyclooctane (**8**, 44%) in 30 h (eq 5). This also provides a good model for the dimerization of silacyclobutanes.[3]



(5)

We have reported palladium-catalyzed selective Si-C/Si-Si cross-metathesis between a silacyclobutane and a 1,2-disilacyclopentane to form a cross-dimer.[4] When 1,1,2,2-tetramethyl-1,2-disilacyclopentane (0.066 mmol) was added to **3a** (0.06 mmol) in C_6D_6 (0.3 mL) in a sealed NMR tube, nearly quantitative formation of a bis-(silyl)complex (**9**) was observed after 24 h at room temperature, together with **1a** (97%) arising from reductive elimination. Thus, the reaction was unable to provide a good model for the catalysis.



(6)

Acknowledgment. We are grateful to the Japan Science and Technology Corporation (JST) for partial financial support through the CREST program. Y.T. thanks Prof. Wataru Ando for helpful discussions.

Supporting Information Available: Text giving procedures to generate authentic samples of Pd(dmpe)$_2$ and (PhC≡CPh)Pd(dmpe) and characterization data for **3a**, **3b**, **4a**, **4b**, **7**, **8**, and **9** and tables giving full details of the crystal structure analysis for **3a** (8 pages). Ordering information is given on any current masthead page.

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(17) On the basis of our observation,[11] reductive elimination from a T-shaped intermediate generated *via* dissociation of one of the phosphorus atoms of the dmpe ligand is also plausible. Such a mechanism is more generally accepted for the reductive elimination from *cis*-dialkylpalladium species. See: Yamamoto, A. *Organotransition Metal Chemistry: Fundamental Concepts and Applications*; Wiley-Interscience: New York, 1986; p 240. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley-Interscience: New York, 1988; p 151.

(18) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.