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Notes

Dipalladium Complex with Bridging Silylene Ligands, $[\{Pd(dmpe)\}_2(\mu\text{-}SiPh_2)_2]$, Formed via Dimerization of a Bis(silyl)palladium Complex

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*Summary: Heating a toluene solution of the bis(silyl)palladium complex $[Pd(SiHPh_2)_2(dmpe)]$ (**1**) (dmpe = 1,2-bis(dimethylphosphino)ethane) at 60 °C afforded a dipalladium complex with bridging silylene ligands, $[\{Pd(dmpe)\}_2(\mu\text{-}SiPh_2)_2]$ (**2**), accompanied by H_2SiPh_2 elimination. An X-ray crystallographic study of **2** suggested the presence of a Si···Si interaction in the four-membered Pd_2Si_2 ring.*

Introduction

Silicon−silicon bond formation promoted by late-transition-metal complexes has been of significant interest in organosilicon chemistry, relevant to the dehydrocoupling dimerization or the polymerization of organosilanes catalyzed by Rh,[1] Ni,[2] or Pt[3] complexes. Although early-transition-metal complexes promote metathesis-type dehydrocoupling of organosilanes, this type of reaction is not common for late-transition-metal complexes. Both reductive elimination via a coupling of two silyl ligands[4a,b] and insertion of a silylene (SiR_2) ligand into the M−silyl bond[4c] were proposed as a crucial step in the formation of a new Si−Si bond. A dinuclear rhodium hydride complex catalyzes dehydrogenative coupling of primary and secondary silanes, reactions that have been proposed to involve the oxidative addition of Si−H bonds and the reductive elimination of disilanes at the dinuclear Rh centers.[5] The dimerization of a mononuclear Pt(IV) tris(phenylsilyl)complex was reported to induce another type of Si−Si bond formation, affording a diplatinum complex with a bridging disilene ligand.[6] Diplatinum complexes with two bridging silylene ligands contain a four-membered Pt_2Si_2 ring with short distances between two Si atoms (2.58(2)−2.718(2) Å).[7] They may have a partial contribution of a dinuclear structure with a π,π-bridging disilene ligand, although this is not universally accepted. The diplatinum model complexes, $[\{Pt(PH_3)_2\}_2(\mu\text{-}SiR_2)_2]$, also have a weak Si···Si interaction on the basis of the results of theoretical calculations.[8] Dipalladium complexes with the Pd_2Si_2 rhombi have not been prepared as yet, but a more significant Si···Si interaction than that in the diplatinum model complexes has been suggested to occur by theoretical study.[9] Dipalladium complexes with two bridging N-heterocyclic silylene ligands, namely, $[\{Pd(PPh_3)\}_2\{\mu\text{-}Si({}^tBuNCH{=}CHN{}^tBu)\}_2]$[10] and $[\{Pd(P{}^tBu_3)\}_2\{\mu\text{-}Si({}^tBuNCH_2CH_2N{}^tBu)\}_2]$,[11] were reported to have short Pd−Pd distances (2.6501(2)−2.7070(2) Å) and the separation of two Si atoms in the Pd_2Si_2 ring. In this paper, we report on the preparation of a dinuclear Pd complex with bridging $SiPh_2$ ligands with the structure having a close contact between two Si atoms.

Results and Discussion

Heating a mixture of $[PdMe_2(dmpe)]$ (665 mM) and H_2SiPh_2 (1:3 molar ratio) in toluene at 60 °C produced a bis(silyl)palladium complex, $[Pd(SiHPh_2)_2(dmpe)]$ (**1**), in 91% yield (eq 1). Use of 3 equiv of H_2SiPh_2 led to formation of **1** in high yield and with **1** as the sole product.

Figure 1a shows the molecular structure of **1** (obtained from recrystallization at room temperature): a square-planar Pd(II)

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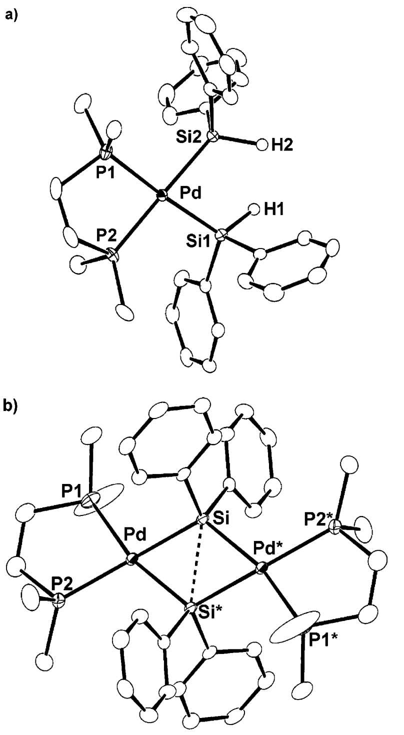
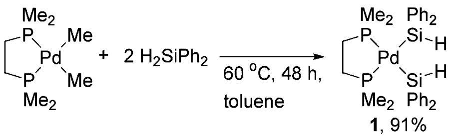


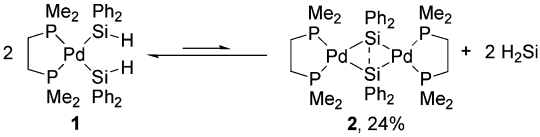
Figure 1. ORTEP drawings of (a) **1** and (b) **2** with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for simplicity. The molecule of **2** has a C_2 symmetric center at the midpoint of two Pd centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Selected distances (Å) and angles (deg) for **1**: Pd−Si1 2.3548(9), Pd−Si2 2.3550(7), Pd−P1 2.3395(9), Pd−P2 2.3356(7), Si1−H1 1.52(4), Si2−H2 1.50(4), P1−Pd−P2 85.17(2), P1−Pd−Si2 96.84(2), P2−Pd−Si1 98.29(3), Si1−Pd−Si2 79.74(3). Selected distances (Å) and angles (deg) for **2**: Pd−P1 2.3346(7), Pd−P2 2.3423(3), Pd−Si 2.3822(4), Pd−Si* 2.3840(6), Si···Si* 2.5227(7), Pd···Pd* 4.0438(2), P1−Pd−P2 85.75(2), P1−Pd−Si 103.53(2), P2−Pd−Si* 108.15(2), Si−Pd−Si* 63.92(2), Pd−Si−Pd* 116.08(2), C1−Si−C7 108.73(9).



(1)

center coordinated by two $\mathrm{SiHPh_2}$ ligands and a chelating dmpe ligand. The Pd−Si bond distances of **1** (2.3548(9) and 2.3550(7) Å) are similar to those in the bis(silyl)palladium complexes (2.3563(9)−2.3818(8) Å).[12]

Heating a dilute toluene solution of **1** (41 mM) at 60 °C produced a dipalladium complex, $[\{\mathrm{Pd(dmpe)}\}_2(\mu\text{-}\mathrm{SiPh_2})_2]$ (**2**), which was isolated in 24% yield from the reaction mixture containing **1**, **2**, and $\mathrm{H_2SiPh_2}$ (eq 2).



(2)

Complex **2** was characterized by X-ray crystallography. A molecule of the dinuclear complex has a crystallographic C_2 symmetry around the midpoint of the two Pd centers (Figure 1b). The palladium atoms of **2** are coordinated by a chelating dmpe ligand and two bridging diphenylsilylene ligands. The distances between the two Si atoms of **2** (2.5227(7) Å) and of analogous diplatinum complexes (Si···Si = 2.58(2)−2.718(2) Å)[7] suggest a weak interaction, although they are longer than a typical covalent Si−Si single bond (2.35 Å). Mononuclear palladium complexes with η^2-disilene ligands, $[\mathrm{Pd}\{\mathrm{Si}(\mathrm{SiMe_2}{}^t\mathrm{Bu})_2\}_2\mathrm{L}_2]$ ($\mathrm{L} = \mathrm{PMe_3}$, $\mathrm{L_2}$ = dmpe) (Si−Si bond: 2.303(1) and 2.318(6) Å), show an elongated Si═Si bond distance of free disilene (2.202(1) Å) due to π-bonding.[13] The Si···Si interaction in the four-membered $\mathrm{Pd_2Si_2}$ ring renders the Si−Pd−Si angle of **2** (63.92(2)°) smaller than that in **1** (79.74(3)°). Chart 1 compares the bond parameters of **1**, **2**, and $[\mathrm{Pd}\{\mathrm{Si}(\mathrm{SiMe_2}{}^t\mathrm{Bu})_2\}_2(\mathrm{dmpe})]$.

Although the limited solubility of **2** in any organic solvent prevented $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR measurement in solution, the solid-state $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR spectrum of **2** exhibited a single resonance at δ −51.0 (Figure 2). The diplatinum complexes, having a close Si···Si contact, also exhibit $^{29}\mathrm{Si}$ NMR chemical shifts in the negative region, $[\{\mathrm{Pt(PPr_3)_2}\}_2(\mu\text{-}\mathrm{SiH(Hex)})_2]$ (δ −94)[7c] and $[\{\mathrm{Pt(dmpe)}\}_2(\mu\text{-}\mathrm{SiHAr})_2]$ (Ar = 2-isopropyl-6-methylphenyl) (δ −134.2).[7d] The $^{29}\mathrm{Si}$ resonance of the dipalladium complex bridged by N-heterocyclic silylene ligands, $[\{\mathrm{Pd(PPh_3)}\}_2\{\mu\text{-}\mathrm{Si}({}^t\mathrm{BuNCH{=}CHN}{}^t\mathrm{Bu})\}_2]$,[10] was observed at highly positive position (δ 109.5), which was partly due to the N-donors on the Si atom.

cis-Bis(silyl)palladium complexes with monophosphine ligands have a tendency to decompose in solution due to the rapid reductive elimination of disilane,[14] whereas **1**, with the chelating ligand, is stable in solution, as is the palladium bis(silyl)complex reported by Fink, $[\mathrm{Pd(SiHMe_2)_2(dcpe)}]$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[12a] The ^{1}H NMR signal of the Si−H hydrogens of **1** appears at δ 5.69, accompanied by the coupling of two phosphorus nuclei ($J_{\mathrm{P-H}}$ = 9.9 Hz). The chemical shift of **1** is similar to that of the Si−H hydrogens of an analogous platinum complex, $[\mathrm{Pt(SiHPh_2)_2(dmpe)}]$ (δ 5.81 in $\mathrm{C_6D_6}$).[15] The $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR spectrum of **1** shows a doublet of doublets at δ −4.5 ($J_{\mathrm{P-Si}}$ = 13.6 and 160 Hz), consistent with the crystal structure of **1**. Heating a solution of **1** in toluene-d_8 at 60 °C induced the partial conversion of **1** to palladium dimer **2** and $\mathrm{H_2SiPh_2}$, as shown in eq 2. Figure 3 plots the amounts of **1**, **2**, and $\mathrm{H_2SiPh_2}$ present during the course of the thermal reaction, as obtained on the basis of intensity of $\mathrm{C_6H_5}$ ortho signals. After 5 h, the concentration of **1** was reduced from its original value (40 mM), whereas that of **2** and $\mathrm{H_2SiPh_2}$ increased gradually to attain an equilibrium mixture of [**1**] = 24 mM, [**2**] = 7.2 mM, and $[\mathrm{H_2SiPh_2}]$ = 11 mM. The quantitative conversion of the isolated **2** to **1** was confirmed by the addition of an excess of $\mathrm{H_2SiPh_2}$ at room temperature and leaving the mixture standing for 24 h, indicating the reversible reaction of eq 2. Almost exclusive formation of **1** in reaction 1

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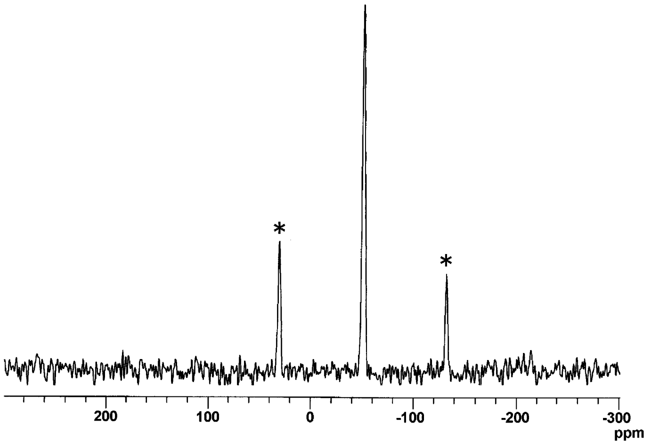
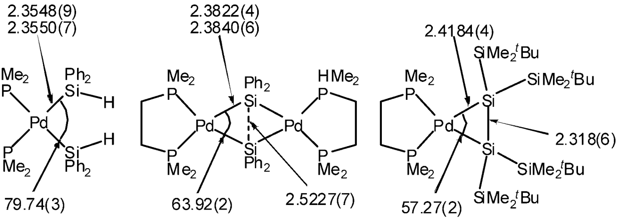


Figure 2. CPMAS $^{29}Si\{^1H\}$ NMR spectrum of **2**. Signals with asterisks are attributed to the spinning sideband that resulted from the spinning speed of 6.478 kHz.

Chart 1



1 **2** $[Pd\{Si(SiMe_2{}^tBu)_2\}_2(dmpe)]$[13a]

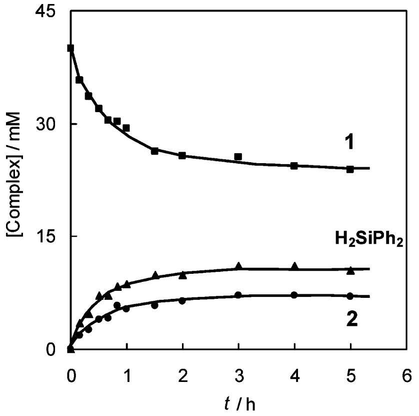


Figure 3. Change in amounts of **1**, **2**, and H_2SiPh_2 during the thermal reaction of **1** at 60 °C. [**1**] = 40 mM in toluene-d_8. Dibenzyl was used as an internal standard (48 mM).

is ascribed to a shift of the equilibrium to the left at much higher Pd concentration (665 mM).

This study revealed that dipalladium complex **2**, with two bridging diphenylsilylene ligands, possesses a strong Si⋯Si interaction in its four-membered Pd_2Si_2 framework, as suggested by the previous theoretical study reported by Sakaki and co-workers.[9] Transformation from **1** to **2** and H_2SiPh_2 occurs reversibly in solution, but details of the reversible reaction are not clear at present.

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere or in a nitrogen-filled glovebox (Miwa MFG). Hexane and toluene were purified by passing through a solvent purification system (Glass Contour). THF was distilled from sodium benzophenone ketyl and stored in a nitrogen atmosphere. ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 or JEOL EX-400 spectrometer. The peak positions of the $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 and external $SiMe_4$ in C_6D_6, respectively. Solid-state CPMAS $^{29}Si\{^1H\}$ NMR measurements were carried out at 79.3 MHz on a JEOL ECA-400 spectrometer using a spinning speed of 6480 Hz. ^{29}Si chemical shifts were referenced to poly(dimethylsilane)s (δ −34.0). $[PdMe_2(dmpe)]$ was prepared according to a previous report.[16] Ph_2SiH_2 is a commercially available product from Aldrich. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analysis was carried out with a LECO CHNS-932 CHNS or Yanaco MT-5 CHN autocorder.

Table 1. Crystallographic Data and Details of Refinement for 1 and 2

	1	2
formula	$C_{30}H_{38}P_2PdSi_2$	$C_{36}H_{52}P_4Pd_2Si_2$
fw	623.16	877.68
cryst color	colorless	yellow
cryst syst	monoclinic	triclinic
cryst size/mm	0.70 × 0.20 × 0.10	1.00 × 0.65 × 0.60
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	11.862(2)	9.386(2)
b/Å	19.652(3)	10.946(2)
c/Å	13.331(2)	11.355(2)
α/deg		102.354(1)
β/deg	104.291(2)	113.113(1)
γ/deg		104.349(2)
V/Å^3	3011.3(8)	974.0(3)
Z	4	1
D_{calcd}/g cm^{-3}	1.368	1.496
F(000)	1276	448
μ/mm^{-1}	0.8195	1.1737
no. of rflns measd	21 677	6110
no. of unique rflns	6663 (R_{int} = 0.028)	3775 (R_{int} = 0.011)
no. of obsd rflns ($I > 2.00\sigma(I)$)	5824	3614
no. of variables	360	225
R1 ($I > 2.00\sigma(I)$)	0.0383	0.0252
wR2 ($I > 2.00\sigma(I)$)	0.1386	0.0805
GOF	0.973	1.003

Preparation of $[Pd(SiHPh_2)_2(dmpe)]$ (1). To a toluene solution (20 mL) of $[PdMe_2(dmpe)]$ (3.81 g, 13.3 mmol) in an evacuated Schlenk flask was added a 3-fold molar amount of Ph_2SiH_2 (7.88 mL, 39.9 mmol). The reaction mixture was stirred at 60 °C for 46 h in an inert-gas atmosphere. The solution changed from colorless to orange. The solvent was removed under reduced pressure. The residue material was washed four times with 5 mL of hexane and dried *in vacuo* to give **1** as a pale yellow solid (7.51 g, 91%). Crystals of **1** suitable for X-ray crystallography were obtained from recrystallization from toluene/hexane (1:10) at room temperature. Anal. Calcd for $C_{30}H_{38}P_2PdSi_2$: C, 57.82; H, 6.15. Found: C, 57.49; H, 6.34. ^1H NMR (300 MHz, C_6D_6, room temperature): δ 7.83 (d, 8H, C_6H_5 ortho, $^3J_{H-H}$ = 7.5 Hz), 7.21 (m, 12H, C_6H_5 meta and para), 5.69 (apparent triplet, 2H, SiH, $^3J_{P-H}$ = 9.9 Hz), 0.75 (d, 4H, PCH_2, $^2J_{P-H}$ = 16 Hz), 0.54 (d, 12H, PCH_3, $^2J_{P-H}$ = 6.9 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, −50 °C): δ 144.4 (C_6H_5 ipso), 136.6 (C_6H_5 ortho), 127.4 (C_6H_5 meta), 28.2 (m, PCH_2), 11.6 (m, PCH_3). The para-carbon signals of the C_6H_5 group were overlapped with the solvent signals. $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6, room temperature): δ 12.6 ($^2J_{Si-Pcis}$ = 13 Hz, $^2J_{Si-Ptrans}$ = 160 Hz). $^{29}Si\{^1H\}$ NMR (79 MHz, toluene-d_8, −50 °C): δ −4.5 (dd, $^2J_{Pcis-Si}$ = 13 Hz, $^2J_{Ptrans-Si}$ = 160 Hz). IR (KBr): 2040 (ν_{SiH}) cm^{-1}.

Preparation of $[\{Pd(dmpe)\}_2(\mu\text{-}SiPh_2)_2]$ (2). This experiment should be performed in the strict absence of oxygen and moisture. In a glovebox, a toluene solution (20 mL) of **1** (511 mg, 0.82 mmol) was heated at 60 °C for 20 h. The reaction solution gradually

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changed from a yellow liquid to an orange suspension. The solvent was removed under reduced pressure. To remove the starting material and H_2SiPh_2, the resulting residue was washed three times with 5 mL of hexane and five times with 5 mL of toluene and dried *in vacuo* to yield **2** as a yellow powder (85.7 mg, 24%). Orange crystals suitable for X-ray crystallography were obtained by recrystallization from THF/hexane (1:10). Anal. Calcd for $C_{36}H_{52}P_4Pd_2Si_2$: C, 49.26; H, 5.97. Found: C, 48.96; H, 6.11. ^1H NMR (300 MHz, C_6D_6, room temperature): δ 8.19 (d, 8H, C_6H_5 ortho, $J_{H-H} = 7.5$ Hz), 7.26 (t, 8H, C_6H_5 meta, $J_{H-H} = 7.5$ Hz), 0.88 (d, 8H, PCH_2, $J_{P-H} = 14$ Hz), 0.76 (br, 24H, PCH_3). The para-hydrogen signals of the C_6H_5 group were overlapped with the solvent signals. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, room temperature): δ 136.8 (C_6H_5 ortho), 126.8 (C_6H_5 meta), 125.5 (C_6H_5 para), 30.2 (m, PCH_2), 14.4 (m, PCH_3), The ipso-carbon signals of the C_6H_5 group were not observed due to their small intensity. $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6, room temperature): δ 2.97. Solid-state CPMAS $^{29}Si\{^1H\}$ NMR (79 MHz, room temperature): δ −51.0.

Thermal Reaction of 1. 1 (14.9 mg, 0.024 mmol) and dibenzyl (5.2 mg, 0.029 mmol) as an internal standard in toluene-d_8 (0.6 mL) were heated at 60 °C in an NMR sample tube, and the reaction mixture was monitored for 5 h. The concentrations of **1** (δ 7.69), **2** (δ 8.02), and H_2SiPh_2 (δ 7.46) were estimated from the intensity of the C_6H_5 ortho signals in the ^1H NMR spectra. An almost equilibrium mixture of **1**, **2**, and H_2SiPh_2 (24 mM, 7.2 mM, and 11 mM) was obtained within 5 h of heating of the sample solution.

Reaction of 2 with an Excess of H_2SiPh_2. In a glovebox, an excess of H_2SiPh_2 (50 μL, 0.253 mmol) was added to a C_6D_6 solution (1 mL) of **2** (20.5 mg, 0.023 mmol) in an NMR sample tube. After 24 h at room temperature, the quantitative reversible conversion into **1** was confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

X-ray Crystallography. Crystals of **1** and **2** suitable for X-ray diffraction study were mounted on a glass capillary. Data for **1** and **2** were collected at −160 °C on a Rigaku Saturn CCD diffractometer equipped with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Calculations were carried out using the program package Crystal Structure, version 3.7, for Windows. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms, except for the SiH hydrogens of **1**, were located by assuming the ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 1.

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Supporting Information Available: Crystallographic data for **1** and **2** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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