

Planar Tetranuclear and Dumbbell-Shaped Octanuclear Palladium Complexes with Bridging Silylene Ligands**

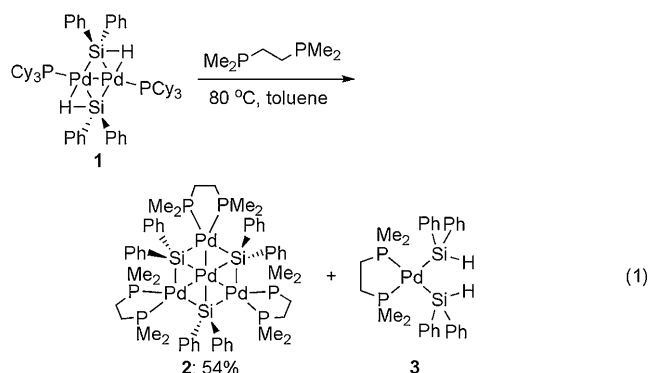
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Late-transition-metal complexes with silylene (SiR_2) ligands have attracted considerable attention since the proposal of platinum–silylene intermediates in the $[\text{PtCl}_2(\text{PEt}_3)_2]$ -catalyzed reactions that convert organodisilanes into oligosilanes and the cyclic adducts into alkynes.^[1] Mononuclear silylene complexes of platinum^[2] and other late transition metals^[3] were not isolated until some years later, probably because of the extremely high reactivity of most $\text{M}=\text{Si}$ double bonds. Dinuclear complexes of late transition metals with bridging silylene ligands are more common.^[4] The dinuclear platinum complex $[\{\text{Pt}(\text{PR}_3)_2(\mu\text{-SiHPh}_2)_2\}]$ ($\text{PR}_3 = \text{PPh}_3$, PCy_3 etc.) has been reported.^[5] However, in spite of the stable coordination of bridging silylene ligands, complexes containing three or more metal atoms with bridging Si ligands have few precedents,^[6] and those known are stabilized by electron-withdrawing CO and CNR ligands.^[7] Braddock-Wilking and co-workers^[8] and our group^[9,10] have reported zero-valent triangular Pt_3 complexes, stabilized by bridging silylene and phosphine ligands. Chen, Shimada, and Tanaka employed 1,2-disilabenzene as a ligand and prepared trinuclear Pd complexes supported by the Si ligands.^[11]

Herein, we report the synthesis and unexpected structure of a planar tetranuclear Pd^0 complex with three bridging SiPh_2 ligands as well as facile exchange of the bridging silylene ligands to yield a dumbbell-shaped octapalladium complex composed of two Pd_4 units bridged by a diphosphine ligand. These complexes, composed of Pd^0 centers and electron-donating Si and phosphine ligands, possess a unique planar $\{\text{Pd}_4\text{Si}_3\}$ core.

Heating a mixture of a dipalladium complex with bridging diphenylsilyl ligands, $[\{\text{Pd}(\text{PCy}_3)_2(\mu\text{-}\eta^2\text{-SiHPh}_2)_2\}]$ (**1**),^[12] and 1,2-bis(dimethylphosphino)ethane (dmpe) in toluene at 80°C produced $[\text{Pd}(\text{Pd}(\text{dmpe}))_3(\mu^3\text{-SiPh}_2)_3]$ (**2**; 54%), which incor-

porates four Pd centers and three bridging SiPh_2 ligands [Eq. (1)]. The accompanying formation of $[\text{Pd}(\text{SiPh}_2\text{H})_2(\text{dmpe})]$ ^[13] (**3**) was also detected. Reaction of $[\text{Pd}(\text{PCy}_3)_2]$ with **3** yields **2** as one of the products.



The molecular structure of **2** was determined by single-crystal X-ray diffraction (Figure 1).^[14] Complex **2** has a hexagonal $\{\text{Pd}_4\text{Si}_3\}$ core incorporating one central Pd atom,

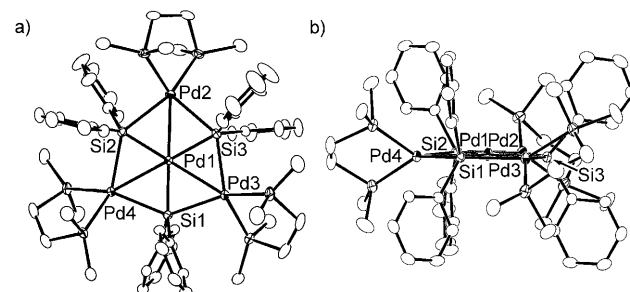


Figure 1. ORTEP representation of **2** viewed from (a) above and (b) in the plane of the $\{\text{Pd}_4\text{Si}_3\}$ core. Thermal ellipsoids are set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.7122(3), Pd1–Pd3 2.7358(2), Pd1–Pd4 2.7326(2), Pd1–Si1 2.2521(8), Pd1–Si2 2.2649(8), Pd1–Si3 2.2674(8), Pd2–Si2 2.5351(8), Pd2–Si3 2.5052(8), Pd3–Si1 2.5210(6), Pd3–Si3 2.5398(8), Pd4–Si1 2.5456(7), Pd4–Si2 2.5116(8); Si1–Pd1–Si2 119.96(2), Si1–Pd1–Si3 119.88(2), Si2–Pd1–Si3 120.03(3).

Pd_{cent} , three outer Pd atoms, Pd_{out} , and three bridging Si atoms arranged within the same plane; the six $\text{Pd}_{\text{out}}\text{--Pd}_{\text{cent}}\text{--Si}$ bond angles add up to a total of $359.98(2)^\circ$. The $\text{Pd}_{\text{cent}}\text{--Si}$ bond lengths, 2.2521(8)–2.2674(8) Å, are comparable to those of $\text{Pd}=\text{Si}$ bonds in a mononuclear Pd complex with two non-

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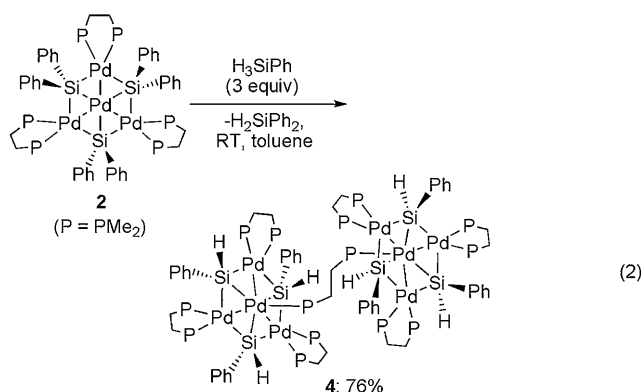
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bridging silylene ligands, $[\text{Pd}\{\text{SiC}(\text{SiMe}_3)_2\text{CH}_2\text{CH}_2\text{C}(\text{SiMe}_3)_2\}_2]$, (2.263(1) and 2.260(2) Å),^[15] and are shorter than the Pd–Si single bonds of **3** (2.3548(9) and 2.3550(7) Å).^[13] The Pd_{cent}–Pd_{out} bond lengths in **2** (2.7122(3)–2.7358(2) Å) are within the range of Pd–Pd bond lengths in neutral tripalladium clusters (2.6207(4)–3.000(5) Å).^[16] The two Pd_{cent}–Si–C_{ipso} angles (122.39(8)–127.5(1)°) and the C_{ipso}–Si–C_{ipso} angle (109.1(1)–110.1(1)°) around each Si atom add up to approximately 360°. These bond parameters suggest that three SiPh₂ ligands are bonded to the central palladium atom giving rise to Si centers with distorted trigonal-bipyramidal geometries.^[17] A similar μ^3 -coordination mode has recently been reported for germylene (GeR₂) and stannylene (SnR₂) ligands to three Ru atoms [Ru₃(CO)₈(μ -SPh)₂(μ^3 -EPh₂)(EPh₃)₂] (E = Ge, Sn).^[18] The {Pd₄Si₃} core is stabilized by bonds between Pd_{out} and Si atoms that are weaker than Pd_{cent}–Si bonds, in addition to a d¹⁰–d¹⁰ interaction between the Pd_{cent} and Pd_{out} atoms.^[19] The ³¹P{¹H} NMR spectrum of **2** displayed a single signal (δ = –2.41 ppm) flanked by satellite signals of ²⁹Si nuclei (J (P,Si) = 22 Hz). The ²⁹Si{¹H} NMR signal of **2** was detected as a multiplet at δ = 195 ppm. The downfield Si NMR spectroscopic shifts in the range of δ = 200–370 ppm were attributed to the paramagnetic shielding effect of the bridging silylene coordination with metal–metal bonds.^[4a] Shimada and co-workers have recently described a multinuclear complex containing a {Pd₄Si₅} framework composed of a planar Pd₄Si₃ core, similar to **2**, and two additional Si ligands at the central Pd atom.^[20] The Pd_{cent}–Si bond lengths of the {Pd₄Si₃} plane (2.3265(13) and 2.2944(9) Å) are significantly longer than the corresponding bonds in **2**.

The reaction of H₂SiPh₂ with **2** (5 equivalents) at room temperature afforded a mixture of **2** and **3** in 3:1 ratio. This result indicates that the silylene ligands in **2** can be converted into SiHPh₂ ligands with degradation of the tetranuclear {Pd₄Si₃} framework. Treatment of **2** with a threefold molar excess of H₃SiPh produced an octanuclear Pd complex, [(Pd(Pd(dmpe))₃{ μ^3 -SiHPh₂})₂(μ -dmpe)] (**4**; 76%), accompanied by the elimination of H₂SiPh₂ [Eq. (2)].



The reaction appears to involve exchange of the bridging SiPh₂ ligands with the SiHPh₂ group derived from H₃SiPh^[21] and subsequent bridging coordination of a dmpe ligand to the central Pd atom of the resultant [Pd{Pd(dmpe)}₃(μ^3 -SiHPh₂)] intermediate. Complex **4** has a crystallographic inversion

center at the midpoint of the two carbon atoms of the bridging dmpe ligand (Figure 2).^[14] The phenyl substituents are oriented away from the {Pd₄Si₃} unit to avoid steric conges-

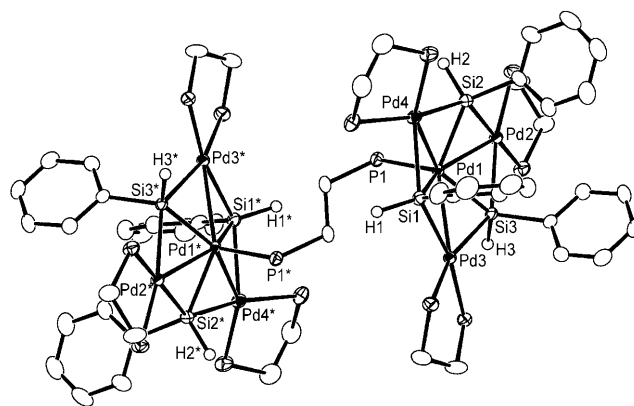


Figure 2. ORTEP representation of **4** with thermal ellipsoids set at 50% probability. The complex has an inversion center at the midpoint between two carbon atoms of the bridging dmpe ligand. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. Hydrogen atoms, except for SiH hydrogen atoms, and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.7659(2), Pd1–Pd3 2.7988(3), Pd1–Pd4 2.7785(3), Pd1–Si1 2.3152(9), Pd1–Si2 2.3292(9), Pd1–Si3 2.3075(9), Pd2–Si2 2.5706(9), Pd2–Si3 2.5114(9), Pd3–Si1 2.448(1), Pd3–Si3 2.5134(9), Pd4–Si1 2.495(1), Pd4–Si2 2.5078(9), Pd1–P1 2.3399(8), Si1–Pd1–Si2 109.62(3), Si1–Pd1–Si3 109.64(3), Si2–Pd1–Si3 108.20(3).

tion. Pd_{cent} deviates from the {Pd₄Si₃} plane by 0.62 Å. The Pd_{cent}–Pd_{out} (2.7659(2)–2.7988(3) Å) and Pd_{cent}–Si bond lengths (2.3075(9)–2.3292(9) Å) of **4** are elongated compared with the corresponding bonds of **2**. The ¹³C{¹H} NMR spectrum of **4** at –60 °C indicated the presence of PCH₂ and P(CH₃)₂ groups of bridging dmpe ligands (δ = 31.3 and 22.8 ppm) and the P(CH₃)₂ groups of the chelating dmpe ligands at the inside and outside of the dumbbell-shaped structure (δ = 15.3 and 14.2 ppm). The ¹H NMR signal corresponding to the SiH hydrogen atom is detected at δ = 8.13 ppm, which is shifted downfield compared with the SiH hydrogen of organosilanes, in a similar fashion to the mononuclear silylene complexes, [Cp*(CO)(H)Ru=Si(H){C(SiMe₃)₃}] (δ = 9.14 ppm; Cp* = C₅Me₅)^[22] and [Cp*(*i*Pr₃P)(H)Os=Si(H){C₆H₂iPr₃-2,4,6}] (δ = 12.1 ppm).^[23] The downfield shift of the SiH hydrogen signals is characteristic of sp² hybridization of the Si atom.^[24]

The ³¹P{¹H} NMR spectrum of **4**, at –60 °C in [D₈]THF (Figure 3a), is consistent with the crystal structure of **4**. Two ³¹P{¹H} NMR signals at δ = 7.34 and –15.2 ppm are detected with an intensity ratio of approximately 6:1, and are assignable to the phosphine nuclei of chelating (P^A) and bridging (P^B) dmpe ligands, respectively. The addition of an equimolar amount of dmpe to the solution of **4** gave rise to new signals at δ = 7.81 (P^C), –15.6 (P^D), and –49.7 ppm (P^E), accompanied by free dmpe (δ = –47.5 ppm, Figure 3b). Two doublets at δ = –15.6 and –49.7 ppm, with the same coupling constant (J (P,P) = 23 Hz), were assigned to the coordinated (P^D) and

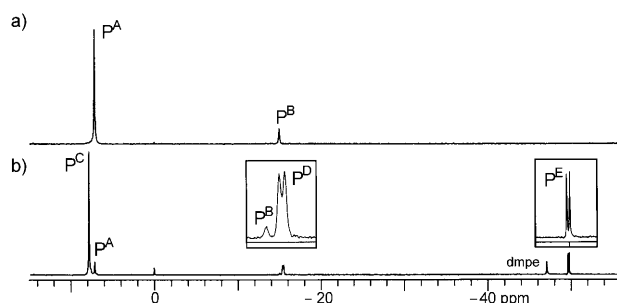
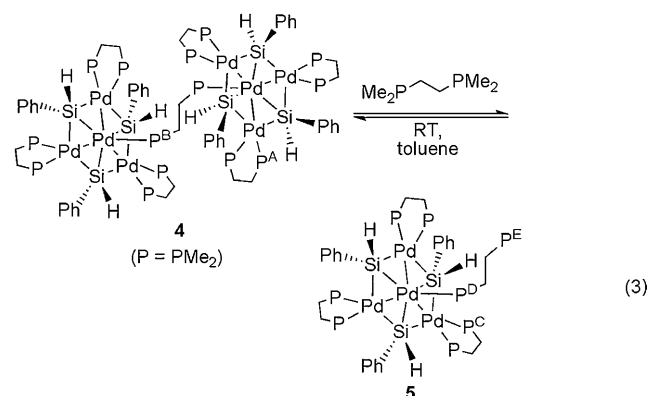


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at -60°C in $[\text{D}_8]\text{THF}$ of a) **4** and b) the reaction mixture after the addition of bis(dimethylphosphino)ethane (dmpe, 1 equivalent) to the solution of **4**.

terminal (P^{E}) atoms, respectively of the dmpe ligand bonded to the central Pd atom. The product was identified as a tetranuclear palladium complex with a dangling dmpe ligand, $[\text{Pd}(\text{dmpe})(\text{Pd}(\text{dmpe})_3)(\mu^3\text{-SiHPh})_3]$ (**5**) [Eq. (3)], based on the multinuclear NMR spectra. The product mixture contained **4** and **5** in a 6:94 ratio. However, purification of **5** by recrystallization was not feasible. The above NMR spectroscopic data indicate that the octanuclear structure of complex **4** does not change in solution, although the addition of dmpe converts it into the tetranuclear complex **5**. A similar reaction



of dmpe with an equimolar dinickel complex, having a dmpe ligand that bridges two metal centers, was reported to produce the mononuclear complex with pendant dmpe at the apical position of the metal centers.^[25]

In summary, we obtained the tetra- and octanuclear Pd^0 complexes with novel and unique structures using simple and common ligands, namely, SiPh_2 , SiHPh , and dmpe. The former complex had a stable structure in solution, but the addition of PhSiH_3 induced rapid exchange of the Si ligands and production of an octanuclear complex. Four Pd^0 centers having three bridging silylene ligands are expected to show unique chemical properties, which are of continuing interest in this study.

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- Crystallographic data for (**2**)· C_6H_{14} : $\text{C}_{60}\text{H}_{92}\text{P}_6\text{Pd}_4\text{Si}_3$; $M_r = 1509.09$; crystal size $0.18 \times 0.33 \times 0.65 \text{ mm}^3$; monoclinic; $P2_1/c$; $a = 13.614(2)$, $b = 27.398(4)$, $c = 18.687(3) \text{ \AA}$; $\beta = 99.218(2)^\circ$; $V = 6880(2) \text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.457 \text{ g cm}^{-3}$; $\mu = 1.2552 \text{ mm}^{-1}$; $F(000) = 3072$, $T = 133 \text{ K}$; Rigaku Saturn CCD area detector equipped with monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$); variables = 750; 50104 reflections measured ($2\theta_{\text{max}} = 55.0^\circ$); 15569 independent reflections ($R_{\text{int}} = 0.034$); $R1 = 0.0295$; $wR2 = 0.0730$; $\text{GOF} = 1.021$. Crystallographic data for (**4**)· $2\text{C}_6\text{H}_{14}$: $\text{C}_{90}\text{H}_{176}\text{P}_{14}\text{Pd}_8\text{Si}_6$; $M_r = 2711.73$; crystal size $0.43 \times 0.68 \times 0.75 \text{ mm}^3$; monoclinic; $P2_1/c$; $a = 14.231(2)$, $b = 18.514(2)$, $c = 22.498(3) \text{ \AA}$; $\beta = 98.047(2)^\circ$; $V = 5869(2) \text{ \AA}^3$; $Z = 2$; $\rho_{\text{calcd}} =$

- 1.534 g cm⁻³; μ = 1.4874 mm⁻¹; $F(000)$ = 2756; T = 133 K; Rigaku Saturn CCD area detector equipped with monochromated MoK α radiation (λ = 0.71070 Å); variables = 629; 39847 reflections measured ($2\theta_{\text{max}}$ = 55.0°); 13084 independent reflections (R_{int} = 0.024); $R1$ = 0.0413; $wR2$ = 0.1177; GOF = 0.980. CCDC 702935 (2) and 702937 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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