Coordination Modes

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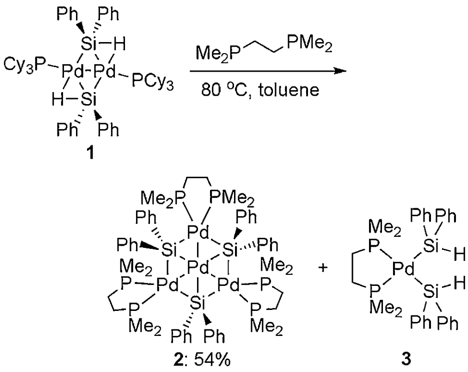
Planar Tetranuclear and Dumbbell-Shaped Octanuclear Palladium Complexes with Bridging Silylene Ligands**

Tetsuyuki Yamada, Akane Mawatari, Makoto Tanabe, Kohtaro Osakada, and Tomoaki Tanase*

Late-transition-metal complexes with silylene (SiR_2) ligands have attracted considerable attention since the proposal of platinum–silylene intermediates in the $[PtCl_2(PEt_3)_2]$-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 M=Si double bonds. Dinuclear complexes of late transition metals with bridging silylene ligands are more common.[4] The dinuclear platinum complex $[\{Pt(PR_3)\}_2(\mu\text{-}SiHPh_2)_2]$ ($PR_3 = PPh_3$, 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 coworkers[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 $\{Pd_4Si_3\}$ core.

Heating a mixture of a dipalladium complex with bridging diphenylsilyl ligands, $[\{Pd(PCy_3)\}_2(\mu\text{-}\eta^2\text{-}SiHPh_2)_2]$ (**1**),[12] and 1,2-bis(dimethylphosphino)ethane (dmpe) in toluene at 80 °C produced $[Pd\{Pd(dmpe)\}_3(\mu^3\text{-}SiPh_2)_3]$ (**2**; 54 %), which incorporates four Pd centers and three bridging $SiPh_2$ ligands [Eq. (1)]. The accompanying formation of $[Pd(SiPh_2H)_2(dmpe)]$[13] (**3**) was also detected. Reaction of $[Pd(PCy_3)_2]$ with **3** yields **2** as one of the products.



(1)

The molecular structure of **2** was determined by single-crystal X-ray diffraction (Figure 1).[14] Complex **2** has a hexagonal $\{Pd_4Si_3\}$ core incorporating one central Pd atom, Pd_{cent}, three outer Pd atoms, Pd_{out}, and three bridging Si atoms arranged within the same plane; the six Pd_{out}-Pd_{cent}-Si bond angles add up to a total of 359.98(2)°. The Pd_{cent}–Si bond lengths, 2.2521(8)–2.2674(8) Å, are comparable to those of Pd=Si bonds in a mononuclear Pd complex with two non-

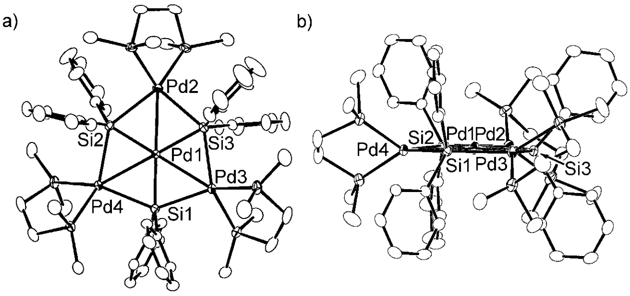


Figure 1. ORTEP representation of **2** viewed from (a) above and (b) in the plane of the $\{Pd_4Si_3\}$ core. Thermal ellipsoids are set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.7122(3), Pd1–Pd3 2.7358(2), Pd1–Pd4 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).

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[*] T. Yamada, A. Mawatari, Dr. M. Tanabe, Prof. K. Osakada
Chemical Resources Laboratory, Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama, 226-8503 (Japan)
Fax: (+81) 45-924-5224
E-mail: kosakada@res.titech.ac.jp

Prof. T. Tanase
Department of Chemistry, Faculty of Science
Nara Women's University
Kitauoya-higashi-machi, Nara 630-8506 (Japan)

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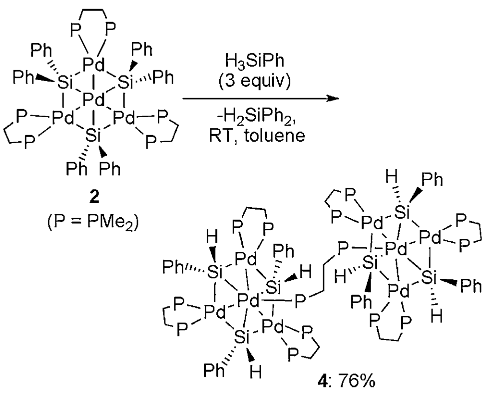
bridging silylene ligands, $[\mathrm{Pd}\{\overline{\mathrm{SiC(SiMe_3)_2CH_2CH_2C}}(\mathrm{SiMe_3})_2\}_2]$, (2.263(1) and 2.260(2) Å),[15] and are shorter than the Pd−Si single bonds of **3** (2.3548(9) and 2.3550(7) Å).[13] The $\mathrm{Pd_{cent}}$−$\mathrm{Pd_{out}}$ bond lengths in **2** (2.7122(3)–2.7358(2) Å) are within the range of Pd−Pd bond lengths in neutral tripalladium clusters (2.6207(4)–3.000(5) Å).[16] The two $\mathrm{Pd_{cent}}$-Si-$\mathrm{C_{ipso}}$ angles (122.39(8)–127.5(1)°) and the $\mathrm{C_{ipso}}$-Si-$\mathrm{C_{ipso}}$ angle (109.1(1)–110.1(1)°) around each Si atom add up to approximately 360°. These bond parameters suggest that three $\mathrm{SiPh_2}$ 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 ($\mathrm{GeR_2}$) and stannylene ($\mathrm{SnR_2}$) ligands to three Ru atoms $[\mathrm{Ru_3(CO)_8(\mu\text{-}SPh)_2(\mu^3\text{-}EPh_2)(EPh_3)_2}]$ (E = Ge, Sn).[18] The $\{\mathrm{Pd_4Si_3}\}$ core is stabilized by bonds between $\mathrm{Pd_{out}}$ and Si atoms that are weaker than $\mathrm{Pd_{cent}}$−Si bonds, in addition to a d^{10}–d^{10} interaction between the $\mathrm{Pd_{cent}}$ and $\mathrm{Pd_{out}}$ atoms.[19] The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **2** displayed a single signal ($\delta = -2.41$ ppm) flanked by satellite signals of $^{29}\mathrm{Si}$ nuclei (*J*(P,Si) = 22 Hz). The $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR signal of **2** was detected as a multiplet at $\delta = 195$ ppm. The downfield Si NMR spectroscopic shifts in the range of $\delta = 200$–370 ppm were attributed to the paramagnetic shielding effect of the bridging silylene coordination with metal–metal bonds.[4a] Shimada and coworkers have recently described a multinuclear complex containing a $\{\mathrm{Pd_4Si_5}\}$ framework composed of a planar $\mathrm{Pd_4Si_3}$ core, similar to **2**, and two additional Si ligands at the central Pd atom.[20] The $\mathrm{Pd_{cent}}$−Si bond lengths of the $\{\mathrm{Pd_4Si_3}\}$ plane (2.3265(13) and 2.2944(9) Å) are significantly longer than the corresponding bonds in **2**.

The reaction of $\mathrm{H_2SiPh_2}$ 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 $\mathrm{SiHPh_2}$ ligands with degradation of the tetranuclear $\{\mathrm{Pd_4Si_3}\}$ framework. Treatment of **2** with a threefold molar excess of $\mathrm{H_3SiPh}$ produced an octanuclear Pd complex, $[(\mathrm{Pd}\{\mathrm{Pd(dmpe)}\}_3\{\mu^3\text{-}\mathrm{SiHPh}\}_3)_2(\mu\text{-dmpe})]$ (**4**: 76%), accompanied by the elimination of $\mathrm{H_2SiPh_2}$ [Eq. (2)].



(2)

The reaction appears to involve exchange of the bridging $\mathrm{SiPh_2}$ ligands with the SiHPh group derived from $\mathrm{H_3SiPh}$[21] and subsequent bridging coordination of a dmpe ligand to the central Pd atom of the resultant $[\mathrm{Pd}\{\mathrm{Pd(dmpe)}\}_3(\mu^3\text{-}\mathrm{SiHPh})_3]$ 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 $\{\mathrm{Pd_4Si_3}\}$ unit to avoid steric congestion. $\mathrm{Pd_{cent}}$ deviates from the $\{\mathrm{Pd_4Si_3}\}$ plane by 0.62 Å. The $\mathrm{Pd_{cent}}$−$\mathrm{Pd_{out}}$ (2.7659(2)–2.7988(3) Å) and $\mathrm{Pd_{cent}}$−Si bond lengths (2.3075(9)–2.3292(9) Å) of **4** are elongated compared with the corresponding bonds of **2**. The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum of **4** at −60 °C indicated the presence of $\mathrm{PCH_2}$ and $\mathrm{P(CH_3)_2}$ groups of bridging dmpe ligands ($\delta = 31.3$ and 22.8 ppm) and the $\mathrm{P(CH_3)_2}$ groups of the chelating dmpe ligands at the inside and outside of the dumbbell-shaped structure ($\delta = 15.3$ and 14.2 ppm). The ^{1}H NMR signal corresponding to the SiH hydrogen atom is detected at $\delta = 8.13$ ppm, which is shifted downfield compared with the SiH hydrogen of organosilanes, in a similar fashion to the mononuclear silylene complexes, $[\mathrm{Cp^*(CO)(H)Ru{=}Si(H)\{C(SiMe_3)_3\}}]$ ($\delta = 9.14$ ppm; $\mathrm{Cp^* = C_5Me_5}$)[22] and $[\mathrm{Cp^*(\mathit{i}Pr_3P)(H)Os{=}Si(H)\{C_6H_2\mathit{i}Pr_3\text{-}2,4,6\}}]$ ($\delta = 12.1$ ppm).[23] The downfield shift of the SiH hydrogen signals is characteristic of sp^2 hybridization of the Si atom.[24]

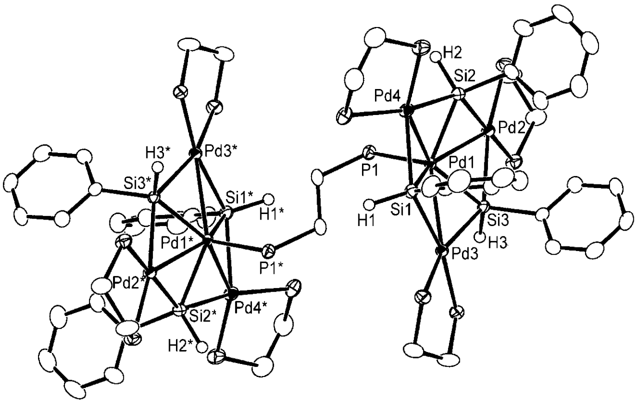


Figure 2. ORTEP representation of **4** with thermal ellipsoids set at 50% probability. The complex has an inversion center at the midpoint between two carbon atoms of the bridging dmpe ligand. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. 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).

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **4**, at −60 °C in [D$_8$]THF (Figure 3a), is consistent with the crystal structure of **4**. Two $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR signals at $\delta = 7.34$ and −15.2 ppm are detected with an intensity ratio of approximately 6:1, and are assignable to the phosphine nuclei of chelating ($\mathrm{P^A}$) and bridging ($\mathrm{P^B}$) dmpe ligands, respectively. The addition of an equimolar amount of dmpe to the solution of **4** gave rise to new signals at $\delta = 7.81$ ($\mathrm{P^C}$), −15.6 ($\mathrm{P^D}$), and −49.7 ppm ($\mathrm{P^E}$), accompanied by free dmpe ($\delta = -47.5$ ppm, Figure 3b). Two doublets at $\delta = -15.6$ and −49.7 ppm, with the same coupling constant (*J*(P,P) = 23 Hz), were assigned to the coordinated ($\mathrm{P^D}$) and

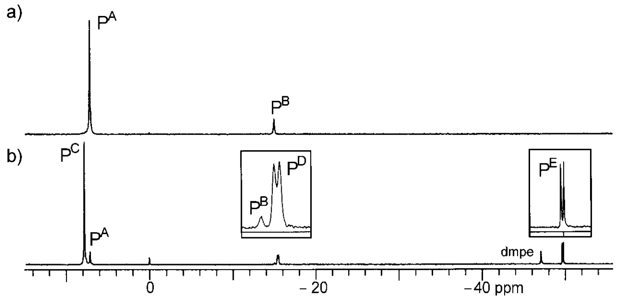
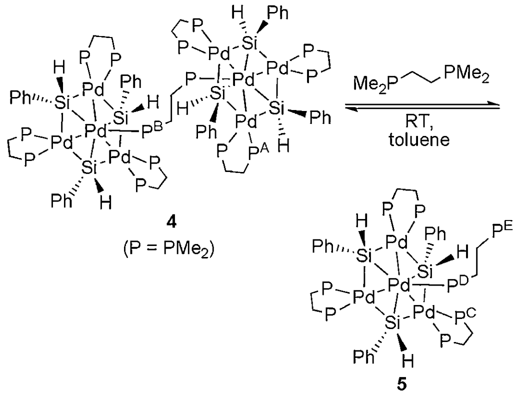


Figure 3. $^{31}P\{^1H\}$ NMR spectra at −60 °C in [D$_8$]THF of a) **4** and b) the reaction mixture after the addition of bis(dimethylphosphino)ethane (dmpe, 1 equivalent) to the solution of **4**.

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, [Pd(dmpe){Pd(dmpe)}$_3$(μ^3-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]



(3)

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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Keywords: bridging ligands · coordination modes · P ligands · palladium · Si ligands

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

1.534 g cm^{-3}; $\mu = 1.4874$ mm^{-1}; $F(000) = 2756$; $T = 133$ K; Rigaku Saturn CCD area detector equipped with monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å); variables = 629; 39847 reflections measured ($2\theta_{max} = 55.0°$); 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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