DALTON
FULL PAPER

Dipalladium complexes with bridging diorganosilyl ligands. Synthesis, structure, and properties of $[LPd(\mu\text{-}SiH(R)Ph)]_2$ (R = Ph or Me; L = PMe_3, PEt_3 or $PMePh_2$)

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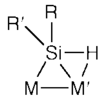
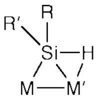
The complexes *trans*-$PdEt_2L_2$ (L = PMe_3, PEt_3 or $PMePh_2$) reacted with equimolar or twofold molar amounts of H_2SiPh_2 to produce various bimetallic palladium(II) complexes with bridging diphenylsilyl ligands, $[(Me_3P)Pd(\mu\text{-}SiHPh_2)]_2$ **1**, $(Me_3P)Pd(\mu\text{-}SiHPh_2)Pd(PMe_3)_2$ **2** and $[LPd(\mu\text{-}SiHPh_2)]_2$ (L = PEt_3 **3** or $PMePh_2$ **4**), in moderate to good yields. Similar reactions using $H_2SiMePh$ afforded the complexes $[LPd(\mu\text{-}SiHMePh)]_2$ (L = PMe_3 **5** or PEt_3 **6**). The isolated complexes were characterized by NMR spectroscopy and elemental analyses. Molecular structures of **3** and **5** have been determined by X-ray crystallography and suggest an agostic interaction between the μ-$SiHPh_2$ or μ-SiHMePh group and the Pd. The NMR study of the complexes revealed the bridging co-ordination of the silyl ligand with the Si–H–Pd three-center, two-electron bond in solution similar to that in the solid state. Complex **2** undergoes exchange of the PMe_3 ligands on the NMR timescale. The reactions of **2** with CO and HSPh afforded **1** and $Pd(SPh)_2(PMe_3)_2$, respectively.

Bridging co-ordination of $SiHR_2$ and SiH_2R groups to two or more transition metal centers is common to many transition metals and, in most cases, exhibits an agostic interaction between the SiH group and the metal center, as schematically depicted in (**A**).[1] The reaction of diorganosilanes with low valent transition metal complexes often gives (**A**) or diorganosilylene co-ordinated dinuclear metal complexes (**B**) that are formed *via* the metal promoted Si–H bond activation of (**A**).


(**A**)


(**B**)

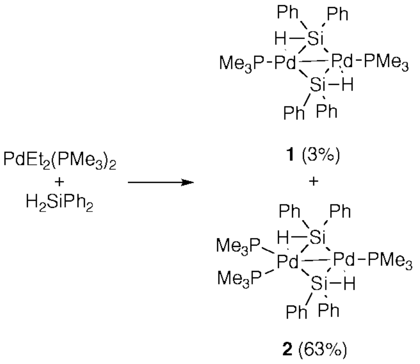
The chemistry of silylpalladium complexes[2] has received particular attention in relation to the mechanism of palladium-catalysed hydrosilylation and bis-silylation of alkenes and alkynes as well as related reactions of organosilanes[3,4] since they probably involve intermediate palladium complexes with organosilyl ligands. Reports on palladium complexes with organosilyl ligands are fewer in number than those on silylplatinum complexes. In particular, there have been few reports on the dinuclear palladium complexes with bridging diorganosilyl ($SiHR_2$) ligands, whereas analogous dinuclear platinum complexes have been reported using many phosphine ligands.[5,6] Studies on the structure and chemical properties of palladium complexes with bridging diorganosilyl ligands are intriguing because the complexes appear to be less stable and more readily reactive than the reported platinum analogues.

In this paper we report the preparation of several dinuclear palladium complexes with bridging diorganosilyl ligands from the reaction of diorganosilane with diethylpalladium complexes as well as results of NMR and X-ray studies of the complexes. Part of this work has been reported preliminarily.[7]

Results and discussion

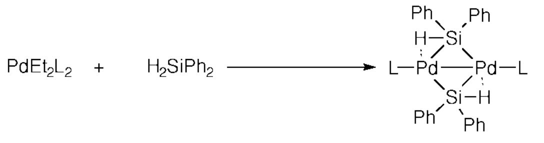
Preparation of diorganosilyl bridged dinuclear palladium complexes

The reaction of *trans*-$PdEt_2(PMe_3)_2$ with equimolar H_2SiPh_2 in THF or hexane at 55 °C proceeds smoothly to give a mixture of dinuclear palladium complexes $[(Me_3P)Pd(\mu\text{-}SiHPh_2)]_2$ **1** and $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)_2$ **2**, eqn. (1). The two products are isolated by fractional crystallization. The reaction in a 1 : 2 molar ratio also led to the formation of complexes. The complexes *trans*-$PdEt_2L_2$ (L = PEt_3 or $PMePh_2$) react with H_2SiPh_2 and with $H_2SiMePh$ in a similar way to give the dinuclear complexes $[LPd(\mu\text{-}SiHPh_2)]_2$ (L = PEt_3 **3** 60%; $PMePh_2$ **4** 52%), eqn. (2), and $[LPd(\mu\text{-}SiHMePh)]_2$ (L = PMe_3 **5** 39%; PEt_3 **6** 30%), eqn. (3), respectively. Products of similar reactions using H_3SiPh and H_2SiEt_2 did not contain these dinuclear palladium complexes due to the decomposition of initially formed palladium complexes during the reaction.



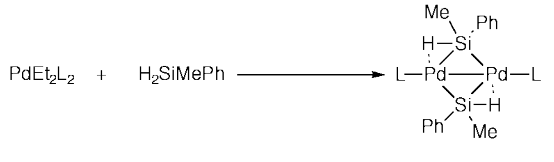
(1)

Complexes **1**–**4** with bridging diphenylsilyl ligands are thermally more stable than the methyl(phenyl)silyl bridged com-



(2)

L = PEt$_3$, **3**
L = PMePh$_2$, **4**

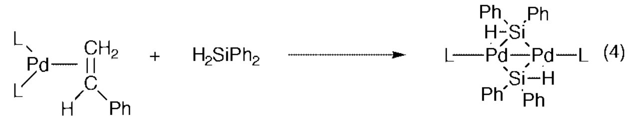


(3)

L = PMe$_3$, **5**
L = PEt$_3$, **6**

plexes **5** and **6** which undergo decomposition gradually at room temperature in solution. Reactions (2) and (3) gave the symmetric dinuclear complexes **3**–**6** as the sole isolated products, whereas the product of the reaction of PdEt$_2$(PMe$_3$)$_2$ with H$_2$SiPh$_2$ contains **2** with three PMe$_3$ ligands as the major product. The yield of the symmetric product **1** with a structure similar to **3**–**6** is much lower. The compact PMe$_3$ ligand tends to form unsymmetric dinuclear palladium(I) complexes by co-ordination of the two phosphine ligands to one Pd, as already noted in the structural study of (Me$_3$P)Pd(μ-CH$_2$CHCH$_2$)(μ-SPh)Pd(PMe$_3$)$_2$.[8] The more bulky PEt$_3$ and PMePh$_2$ ligands do not form the unsymmetric product with a sterically congested palladium center, as shown in reaction (2). The methyl(phenyl)silyl ligand which is more electron donating than the diphenylsilyl ligand does not allow co-ordination of two PMe$_3$ ligands to Pd and gives the symmetric product **5** exclusively.

The above reactions involve activation of Pd–C and Si–H bonds, possibly accompanied by the evolution of ethylene and ethane. Since *trans*-PdEt$_2$(PR$_3$)$_2$ undergoes β-hydrogen elimination and ensuing reductive elimination of ethane to form Pd(CH$_2$=CH$_2$)(PR$_3$)$_2$,[9] one of the plausible paths for the formation of complexes **1**–**6** involves initial formation of the ethylene-co-ordinated palladium(0) complexes and their further reaction with diorganosilane to give Pd(SiHR′$_2$)$_2$(PR$_3$)$_2$ or PdH(SiHR′$_2$)(PR$_3$)$_2$, which then undergoes intermolecular bridging of the metal center through diorganosilyl ligands. To evaluate this possibility, we have examined the reaction of equimolar and twofold molar amounts of H$_2$SiPh$_2$ or H$_2$SiMePh with Pd(CH$_2$=CHPh)L$_2$ (L = PMe$_3$, PEt$_3$ or PMePh$_2$) which has a similar structure to that of Pd(CH$_2$=CH$_2$)(PMe$_3$)$_2$, eqn. (4). The reactions at 55 °C in THF produce



(4)

complexes **1**–**6** in moderate to good yields. In the presence of a twofold molar amount or more of H$_2$SiPh$_2$ the reaction proceeds to completion to give the products in high yields.

Previously, Schubert and Müller[10] reported the reaction of H$_2$SiPh$_2$ with PdMe$_2$(PMePh$_2$)$_2$ in a 2 : 1 molar ratio at room temperature to give *cis*-Pd(SiHPh$_2$)$_2$(PMePh$_2$)$_2$ which is thermally unstable but has been characterized spectroscopically. Similar bis(organosilyl)palladium complexes have been isolated using bulky or chelating diphosphine ligands.[11] These results suggest that mononuclear bis(diorganosilyl)palladium complexes can be formed *via* the reaction of diorganosilane with dialkylpalladium complexes. Scheme 1 depicts possible reaction paths for the formation of dinuclear palladium complexes with bridging diorganosilyl ligands assumed on the basis of the above mentioned results. Coupling of bis(diorganosilyl)palladium(II) complexes with palladium(0) complexes leads to the formation of dinuclear product (i), while an alternative path involving dimerization of hydrido(silyl)palladium(II) complexes also accounts for the product. At present we cannot compare the plausibilities of the reaction paths based on the experimental results.

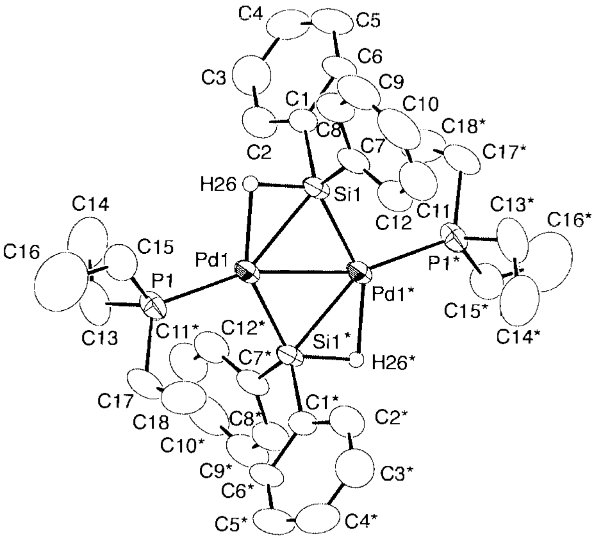
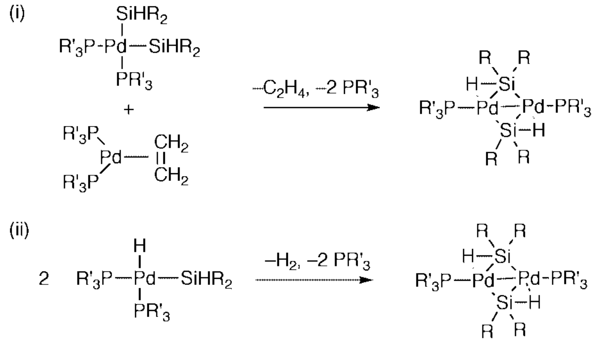


Fig. 1 An ORTEP[12] drawing of [(Et$_3$P)Pd(μ-SiHPh$_2$)]$_2$ **3** showing the atom-labeling scheme and 30% probability thermal ellipsoids. Atoms with asterisks are crystallographically equivalent to those with the same number without asterisks. Selected bond lengths (Å) and angles (°): Pd1–Pd1* 2.699(2), Pd1–Si1 2.332(2), Pd1–Si1* 2.396(2), Pd1–P1 2.301(2), Pd1–H26 2.04 and Si1–H26 1.60; Pd1–Pd1*–P1 159.51(5), Pd1–Si1–Pd1* 69.60(5), Si1–Pd1–Si1* 110.40(5), Pd1–Pd1*–Si1 56.32(6), Pd1*–Pd1–Si1 54.08(4), Pd1–Si1–H26 57, Pd1*–Si1–H26 126, Pd1–Si1–C7 120.6(2), Pd1*–Si1–C7 116.1(2), Pd1–Si1–C1 115.7(2), Pd1*–Si1–C1 121.5(2) and C1–Si1–C7 108.5(2).



Scheme 1

X-Ray crystallography and NMR spectra

Figs. 1 and 2 show the molecular structures of complexes **3** and **5** determined by X-ray crystallography. Molecules of both contain a crystallographic center of symmetry at the midpoint of the Pd–Pd bond. The structural parameters are compared with those of the preliminarily reported **1**[7] and with the platinum analogue [(R′$_3$P)Pt(μ-HSiR$_2$)]$_2$.[5] The Pd–Pd distances are 2.699(2) and 2.707(1) Å, suggesting the presence of a metal–metal bond. The lengths of the two Pd–Si bonds in **3** and **5** differ significantly (2.396(2) and 2.332(2) Å, and 2.387(1) and 2.333(2) Å, respectively) as they do in the structure of **1** (2.328(2) and 2.386(2) Å). The SiH hydrogens are located in the final electron density map and are included in the plane consisting of two Pd and two Si. These structural features suggest the contribution of an Si–H–Pd three-center two-electron bond to the co-ordination of diphenylsilyl or methyl(phenyl)silyl ligands to two Pd, which causes elongation of the Pd–Si bond compared with the Pd–Si single bond. The Pd–H bond of **3** (2.04 Å) and **5** (1.85 Å) suggests an interaction of the Si–H hydrogen

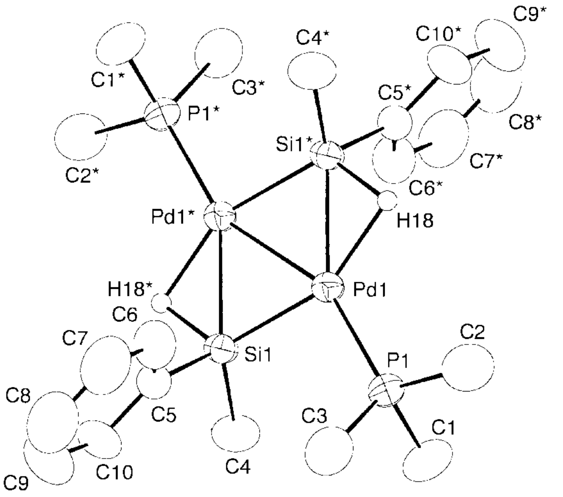


Fig. 2 An ORTEP drawing of $[(Me_3P)Pd(\mu\text{-}SiHMePh)]_2$ **5** showing the atom-labeling scheme and 30% probability thermal ellipsoids. Atoms with asterisks are crystallographically equivalent to those with the same number without asterisks. Selected bond lengths (Å) and angles (°): Pd1–Pd1* 2.707(1), Pd1–Si1 2.387(1), Pd1–Si1* 2.333(2), Pd1–P1 2.297(2), Pd1–H18 1.85 and Si1–H18 1.60; Pd1–Pd1*–P1 155.18(4), Pd1–Si1–Pd1* 69.98(4), Si1–Pd1–Si1* 110.02(4), Pd1–Pd1*–Si1 54.07(4), Pd1*–Pd1–Si1 55.95(4), Pd1–Si1–H18 120.7, Pd1*–Si1–H18 50.7, Pd1–Si1–C4 126.2(2), Pd1*–Si1–C4 118.3(2), Pd1–Si1–C5 112.1(2), Pd1*–Si1–C5 118.5(2) and C4–Si1–C5 107.0(3).

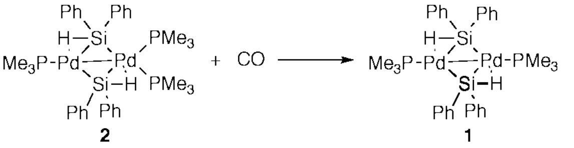
with the Pd, although these bonds are somewhat larger than those in **1** due to insufficient precision in the determination of the position of hydrogen in the crystallography. A platinum analog, $[(R'_3P)Pt(\mu\text{-}HSiR_2)]_2$, has a similar structure to that of **1** but with a larger difference between the Pt–Si bond lengths (2.420(2) and 2.324(2) Å) and a short H–Pt distance (1.78 Å).[5]

Complexes **1** and **3**–**6** exhibit NMR signals from the Si–H hydrogen and phosphorus nuclei at similar positions. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3** at room temperature contains a single resonance at δ 15.3. The presence of ^{29}Si satellite signals with two different coupling constants ($J(^{31}P^{29}Si) = 69$ and 27 Hz) is consistent with the unsymmetrical co-ordination of two Si atoms to Pd. The ^1H NMR spectrum at 25 °C exhibits a signal due to the SiH hydrogen at δ 1.76 flanked with satellite signals ($J(^1H^{29}Si) = 78$ Hz). This coupling constant is smaller than that of $J(^1H^{29}Si)$ in organic molecules and suggests partial activation of the Si–H bond by Pd to form an Si–H–Pd three-center two-electron bond. Complex **3** does not show any significant changes in NMR spectra in the temperature range from 25 to −90 °C and has a structure in solution similar to that found in the crystals.

The NMR spectra of unsymmetric complex **2** indicate fluxional behavior arising from exchange of the PMe_3 ligands. The $^{31}P\text{-}\{^1H\}$ NMR spectrum at −90 °C contains a doublet (δ −33.0, $J(^{31}P^{31}P) = 23$ Hz, $J(^{31}P^{29}Si) = 42$ Hz) and a triplet (δ −25.9, $J(^{31}P^{31}P) = 23$ Hz, $J(^{31}P^{29}Si) = 129$ Hz) in a 2:1 peak area ratio. The ^1H NMR spectrum at −90 °C exhibits a doublet (δ 1.24 , $^3J(^{31}P^1H) = 8$, $J(^{29}Si^1H) = 84$ Hz) and a triplet (δ −2.34, $^3J(^{31}P^1H) = 11$, $J(^{29}Si^1H) = 86$ Hz) of equal intensity, indicating that the two SiH hydrogens are magnetically inequivalent at that temperature. These ^1H and ^{31}P NMR spectra show coalescence of these signals when the temperature is raised and exhibit a single resonance for the phosporous nuclei of the PMe_3 ligands and for the SiH hydrogens at 25 °C. The changes in the NMR spectra are brought about by intra- or intermolecular exchange of the co-ordinated PMe_3.

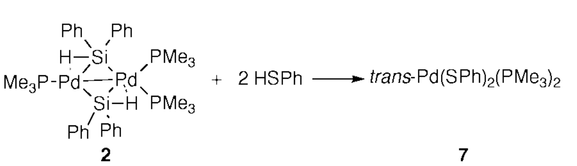
Chemical properties of the complexes

In connection with gaining insight into the chemical properties of the complexes and their relationship to several synthetic organic reactions catalysed by palladium complexes, we have examined reactions of phenylacetylene and diphenylacetylene with **2**. The reactions of **2** with an equimolar or twofold molar amount of these acetylenes did not occur and resulted in stoichiometric recovery of the starting complex. The reaction of **2** with CO (1 atm) liberates PMe_3 ligand and affords **1** in 79% isolated yield, eqn. (5), but does not give any other products



(5)

from further carbonylation of the complex. Many organopalladium complexes with tertiary phosphine ligands were reported to react with CO to give multinuclear carbonyl palladium compounds, $Pd(CO)_m(PR_3)_n$, *via* elimination of the organic ligands. The inertness of the palladium complex toward carbonylation suggests the stable co-ordination of the bridging diphenylsilyl ligands to two Pd. Treatment of **2** with a twofold molar amount of HSPh in diethyl ether at room temperature results in *trans*-$Pd(SPh)_2(PMe_3)_2$ **7**, eqn. (6), which was identified by comparison of the NMR data with those of authentic complexes. Poor yields of the complex are partly due to insufficient amount of PMe_3 ligands to complete the above reaction.



(6)

In summary, this study has provided dinuclear palladium(I) complexes with bridging diorganosilyl ligands which have no precedent in organopalladium chemistry. The complexes are stabilized by two symmetrically bridging diorganosilyl ligands which form a σ bond with one Pd and are bonded to another Pd in a three-center two-electron manner. This dinuclear framework is stable once it is formed and does not react with carbon monoxide. The inert co-ordination of the diorganosilyl ligands contrasts with the bridging co-ordination of the diorganosilyl ligands in other late transition metal complexes which undergo facile and reversible Si–H bond activation by the metal center and exhibit fluxional NMR spectra at around room temperature.

Experimental

General, materials, and measurements

All manipulations of the air-sensitive compounds were performed under a N_2 or argon atmosphere with use of a standard Schlenk technique. Solvents were distilled from sodium–benzophenone and stored under a nitrogen atmosphere. The complexes *trans*-$PdEt_2L_2$ and *trans*-$PdMe_2L_2$ ($L = PMe_3$, PEt_3 or $PMePh_2$) were prepared according to the literature methods.[9] H_2SiPh_2 and $H_2SiMePh$ were obtained from Aldrich Co. and used without further purification.

Elemental analyses were carried out by analytical laboratories at the Basic Science Institute and at SangJi university in Korea. IR spectra were recorded on a Hitachi 270-30 spectrophotometer, NMR (^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$) spectra on Bruker 400 MHz and JEOL Lambda 300 MHz spectrometers. Chemical shifts were referenced to internal Me_4Si or to external 85% H_3PO_4.

Preparations

Complexes 1 and 2. To a Schlenk flask containing *trans*-$PdEt_2(PMe_3)_2$ (1.470 g, 4.64 mmol) at 0 °C were added H_2SiPh_2

(0.856 g, 4.64 mmol) and THF (7 cm^3) in that order. The mixture was heated at 55 °C for 30 min to give a deep red solution. After the solution was stirred at room temperature for 1 h, the solvent was evaporated under reduced pressure to give an orange residue. The addition of hexane and ensuing storage of the residue for several hours at −30 °C produced an orange solid which was collected by filtration, washed with hexane, and recrystallized with THF–hexane to give complex **2** as red crystals (1.18 g, 63%). The filtrate was evaporated under reduced pressure to give a yellow solid from which **1** was obtained as pale yellow crystals after recrystallization from ether (0.053 g, 3%). Data for **1**: mp 105 °C (decomp.) (Found: C, 49.08; H, 5.77. $C_{15}H_{20}PPdSi$ requires C, 49.25; H, 5.51%); δ_H (400 MHz, CD_2Cl_2 at 25 °C) 7.63 (8 H, m, C_6H_5), 7.31 (12 H, m, C_6H_5), 1.77 (2 H, s, SiH, $J(^{29}Si^1H)$ = 77 Hz) and 1.19 (18 H, br, CH_3); (at 0 °C) 7.61 (8 H, m, C_6H_5), 7.33 (4 H, m, C_6H_5), 7.31 (8 H, m, C_6H_5), 1.76 (2 H, d, SiH, $J(^{31}P^1H)$ = 7, $J(^{29}Si^1H)$ = 80 Hz) and 1.17 (18 H, br, CH_3); (at −30 °C) 7.60 (8 H, m, C_6H_5), 7.31 (12 H, m, C_6H_5), 1.72 (2 H, d, SiH, $J(^{31}P^1H)$ = 7, $J(^{29}Si^1H)$ = 77 Hz) and 1.14 (18 H, br, CH_3); (at −70 °C) 7.56 (8 H, m, C_6H_5), 7.29 (12 H, m, C_6H_5), 1.66 (2 H, br, SiH, $J(^{29}Si^1H)$ = 82 Hz) and 1.10 (18 H, br, CH_3); (at −90 °C) 7.53 (8 H, m, C_6H_5), 7.30 (12 H, m, C_6H_5), 1.62 (2 H, br, SiH, $J(^{29}Si^1H)$ = 80 Hz) and 1.08 (18 H, br, CH_3); δ_P (160 MHz in CD_2Cl_2) (at 25 °C) −34.4 (br, $\nu_{1/2}$ = 43 Hz); (at 0 °C) −26.5 (s, $J(^{29}Si^{31}P)$ = 74 Hz); (at −30 °C) −25.8 (s, $J(^{29}Si^{31}P)$ = 74 and 28 Hz); (at −70 °C) −25.1 (s, $J(^{29}Si^{31}P)$ = 74 Hz); (at −90 °C) −24.7 (s, $J(^{29}Si^{31}P)$ = 74 Hz). Data for **2**: mp 109 °C (decomp.) (Found: C, 48.75, H, 6.27. $C_{33}H_{49}P_3Pd_2Si_2$ requires C, 49.08; H, 6.11%); δ_H (400 MHz, CD_2Cl_2) (at 25 °C) 7.63 (8 H, m, C_6H_5), 7.29 (12 H, m, C_6H_5), 1.00 (27 H, d, CH_3, J(PH) = 7) and 0.59 (2 H, br, SiH, $J(^{29}Si^1H)$ = 79 Hz); (at 0 °C) 7.63 (8 H, m, C_6H_5), 7.28 (12 H, m, C_6H_5), 0.93 (27 H, s, CH_3) and 0.15 (2 H, br, SiH, $J(^{29}Si^1H)$ = 76 Hz); (at −30 °C) 7.59 (8 H, m, C_6H_5), 7.29 (12 H, m, C_6H_5), 0.87 (27 H, s, CH_3) and −0.17 (2 H, br, SiH, $\nu_{1/2}$ = 53 Hz); (at −70 °C) 7.55 (8 H, br, C_6H_5), 0.99 (10 H, br, CH_3 and SiH), 0.68 (18 H, br, CH_3) and −2.33 (1 H, br, SiH, $\nu_{1/2}$ = 84 Hz); (at −90 °C) 7.53 (8 H, m, C_6H_5), 7.27 (12 H, m, C_6H_5), 1.24 (1 H, d, SiH, $J(^{31}P^1H)$ = 8 Hz, $J(^{29}Si^1H)$ = 84 Hz), 1.03 (9 H, s, CH_3), 0.63 (18 H, s, CH_3), −2.34 (1 H, t, SiH, $J(^{31}P^1H)$ = 11, $J(^{29}Si^1H)$ = 86 Hz); (160 MHz in CD_2Cl_2) (at 25 °C) −34.4 (br, $\nu_{1/2}$ = 43 Hz); (at 0 °C) −33.3 (br, $\nu_{1/2}$ = 43 Hz); (at −30 °C) −32.2 (br, $\nu_{1/2}$ = 102 Hz); (at −70 °C) −26.4 (br, $\nu_{1/2}$ = 98) and −33.6 (br, $\nu_{1/2}$ = 81 Hz); (at −90 °C) −25.9 (t, $J(^{31}P^{31}P)$ = 23, $J(^{29}Si^{31}P)$ = 129) and −33.0 (t, $J(^{31}P^{31}P)$ = 23, $J(^{29}Si^{31}P)$ = 42 Hz).

Complexes 3–6. To a Schlenk flask containing *trans*-$PdEt_2(PEt_3)_2$ (0.171 g, 0.43 mmol) at 0 °C were added H_2SiPh_2 (0.079 g, 0.43 mmol) and THF (3 cm^3) in that order. The mixture was heated at 55 °C for 30 min to give a deep orange solution which was stirred for an additional 1 h at room temperature. The solvent was evaporated under reduced pressure to give an orange residue. The addition of hexane and ensuing storage of the product for several hours at −30 °C produced an orange solid which was collected by filtration, washed with hexane, and recrystallized from ether–hexane to give complex **3** as pale yellow crystals (0.105 g, 60%) (Found: C, 52.70; H, 6.74. $C_{18}H_{26}PPdSi$ requires C, 53.01; H, 6.43%); δ_H (300 MHz, in CD_2Cl_2) 0.85 (18 H, br quintet due to virtual coupling, $PCH_2C\mathit{H}_3$), 1.50 (12 H, m, $PC\mathit{H}_2CH_3$), 1.76 (2 H, br d, Si–H, $J(^1H^{29}Si)$ = 78), J(HP) = 4.8 Hz), 7.32, 7.67 (20 H, m, Ph); δ_P(^{31}P-{^{1}H} from external 85% H_3PO_4 at 120 MHz in CD_2Cl_2) 15.3 (s, $J(^{31}P^{29}Si)$ = 69, 27 Hz).

Complexes **4**–**6** were prepared analogously: **4** (52%) (Found: C, 61.61; H, 5.02. $C_{25}H_{24}PPdSi$ requires C, 61.29; H, 4.94); δ_H (300 MHz, in CD_2Cl_2) 1.67 (6 H, s, $PC\mathit{H}_3Ph_2$), 2.15 (2 H, br s, SiH) and 7.17–7.49 (40 H, m, Ph); δ_P(^{31}P{-^{1}H} from external 85% H_3PO_4 at 120 MHz in CD_2Cl_2) 7.89 (s); ($J(^{31}P^{29}Si)$ not obtained due to broading of signal; **5** (39%) (Found: C, 39.27; H, 5.66. $C_{10}H_{18}PPdSi$ requires C, 39.54; H, 5.97%); δ_H (300 MHz, in CD_2Cl_2) 0.92 (6 H, br s, $SiHC\mathit{H}_3Ph$), 1.07 (2 H, br t, SiH, J(HP) = 2.0 Hz), 7.20, 7.44 (10 H, m, Ph); δ_P(external 85% H_3PO_4 standard at 120 MHz in CD_2Cl_2) −24.3 (s); **6** (30%) (Found: C, 45.37; H, 6.79. $C_{13}H_{24}PPdSi$ requires C, 45.15; H, 7.00%); δ_H (300 MHz, in CD_2Cl_2) 0.80 (18 H, br quintet due to virtual coupling, $PCH_2C\mathit{H}_3$), 0.93 (6 H, br s, $SiHC\mathit{H}_3Ph$), 0.99 (2 H, br s, SiH), 1.42 (12 H, m, $PC\mathit{H}_2CH_3$), 7.13, 7.40 (10 H, m, Ph); δ_P(^{31}P-{^{1}H} from external 85% H_3PO_4 at 120 MHz in CD_2Cl_2) 16.7 (s, $J(^{31}P^{29}Si)$ = 72, 27 Hz).

Reaction of $Pd(CH_2{=}CHPh)L_2$ with H_2SiPh_2 or $H_2SiMePh$

To a Schlenk flask containing *trans*-$PdEt_2(PMe_3)_2$ (0.244 g, 0.77 mmol) at 0 °C were added styrene (0.322 g, 3.09 mmol) and THF (3 cm^3) in that order. The mixture was heated at 55 °C for 3 h to give a pale yellow solution. The solution was cooled to room temperature and H_2SiPh_2 (0.142 g, 0.77 mmol) added. The initial red solution instantly turned dark red. After stirring for 3 h the solvent was removed under reduced pressure to give a dark red residue. The addition of hexane and ensuing storage of the product for several hours at −30 °C produced an orange solid which was collected by filtration and washed with hexane to give complex **2** (0.257 g, 82%).

Reactions of $Pd(CH_2{=}CHPh)L_2$ (L = PMe_3, PEt_3 or $PMePh_2$) with equimolar or twofold molar amounts of H_2SiPh_2 or $H_2SiMePh$ were analogously carried out to give the corresponding complexes.

Reactions of complex 2

With alkyne. To an ether (5 cm^3) solution of complex **2** (0.106 g, 0.13 mmol) was added diphenylacetylene (0.024 g, 0.13 mmol) at room temperature. The initial red solution slowly turned dark red. After stirring for 4 h the solvent was removed under reduced pressure to give a dark red residue. The addition of hexane and ensuing storage of the product for several hours at −30 °C enabled the recovery of **2** (0.93 g, 87%). Reaction of **2** with a twofold molar amount of phenylacetylene proceeded analogously to give the starting material (92%).

With CO. Complex **2** (0.145 g, 0.18 mmol) was dissolved in toluene (3 cm^3) at room temperature. After evacuation of the system, CO (1 atm) was introduced and the initial red solution turned dark red. After stirring for 1 h the solvent was evaporated under reduced pressure to give an oily residue. The addition of hexane (2 cm^3) and ensuing storage of the residue for several hours at −30 °C produced an orange solid which was collected by filtration and washed with hexane (1 cm^3 × 3) to give **1** (0.104 g, 79%).

With HSPh. To an ether (6 cm^3) solution of complex **2** (0.125 g, 0.15 mmol) was added benzenethiol (0.034 g, 0.30 mmol) at room temperature. The initial red solution slowly turned orange accompanied by gradual formation of the solid product. After stirring for 1 h the reaction mixture was stored at −30 °C for several hours to cause complete precipitation of a yellow solid which was collected by filtration, washed with hexane (2 cm^3 × 2) and dried *in vacuo* to give **7** (0.032 g, 43%). δ_H (300 MHz, in CD_2Cl_2) 1.31 (18 H, s, $P(C\mathit{H}_3)_3$, J(PH) = 3.4 Hz), 6.80 (1 H, t, Ph), 7.19 (2 H, t, Ph) and 7.68 (2 H, d, Ph). δ_P(^{31}P-{^{1}H} from external 85% H_3PO_4 at 120 MHz in CD_2Cl_2) −13.1 (s). Complex **7** was also obtained from the reaction of *trans*-$PdMe_2(PMe_3)_2$ with an excess of benzenethiol and identified using the spectroscopic data.

Crystallography

Crystals of complexes **3** and **5** suitable for X-ray diffraction study were obtained by recrystallization from ether–hexane and mounted in glass capillary tubes under argon. Intensities were collected for Lorentz-polarization effects on a Rigaku AFC-5R automated four-circle diffractometer by using Mo-Kα radiation ($\lambda = 0.71069$ Å) and the ω–2θ scan method, and an empirical absorption correction (ψ scan) was applied. Calculations were carried out by using the program package TEXSAN[13] on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from ref. 14. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Positions of the SiH hydrogens were determined by the Fourier-difference technique, while the other hydrogens were located by assuming the ideal geometry. The hydrogens were included in the structure calculation without further refinement of the parameters.

Crystal data. $C_{36}H_{52}P_2Pd_2Si_2$ **3**, $M = 815.77$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.242(9)$, $b = 11.447(6)$, $c = 9.725(8)$ Å, $\alpha = 112.13(5)°$, $\beta = 115.65(6)°$, $\gamma = 78.56(6)°$, $U = 951(1)$ Å^3, $T = 298$ K, $Z = 1$, μ(Mo-Kα) = 1.116 mm^{-1}, 3544 reflections measured, 3340 unique ($R_{int} = 0.012$), from which 2835 with $I > 3.00\sigma(I)$ were used in refinement. Final $R1$ and $wR2$ 0.038 and 0.045.

$C_{20}H_{36}P_2Pd_2Si_2$ **5**, $M = 607.46$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.419(4)$, $b = 16.222(4)$, $c = 10.240(4)$ Å, $\beta = 108.58(3)°$, $U = 1325.7(9)$ Å^3, $T = 298$ K, $Z = 2$, μ(Mo-Kα) = 1.572 mm^{-1}, 3319 reflections measured, 3152 unique ($R_{int} = 0.042$), from which 2114 with $I > 3.00\sigma(I)$ were used in refinement. Final $R1$ and $wR2$ 0.033 and 0.036.

CCDC reference number 186/1754.

See http://www.rsc.org/suppdata/dt/a9/a907745f/ for crystallographic files in cif. format.

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