Organometallics **1998,** *17,* 4929−4931

Unsymmetrical and Symmetrical Dipalladium Complexes with Bridging Diphenylsilyl Ligands. Structures of $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)_2$ and $[(Me_3P)Pd(\mu\text{-}SiHPh_2)]_2$ in the Solid State and in Solution

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Received July 27, 1998

*Summary: Dinuclear palladium complexes with two bridging diphenylsilyl ligands, $[(Me_3P)Pd(\mu\text{-}SiHPh_2)]_2$ (**1**) and $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)_2$ (**2**), were prepared and characterized by X-ray crystallography and NMR spectroscopy. The molecular structure of these complexes suggests an agostic interaction between H of μ-SiHPh$_2$ and Pd. The symmetrical structure of **1** in solution is similar to that found in the crystals and is maintained in the temperature range +25 to −90 °C. The temperature-dependent ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** show dynamic behavior of the molecule caused by exchange of the phosphine ligands. The structure observed at −90 °C in the solution is similar to the crystallographic structure.*

Silylpalladium complexes have attracted current attention due to their relevance to the mechanism of Pd complex catalyzed reactions such as hydrosilylation of alkenes and dienes,[1] bis-silylation of dienes and alkynes,[2] carbosilylation of alkynes,[3] cross-coupling of organic halides with disilanes,[4] and ring-opening oligomerization and polymerization of cyclic disilanes and polysilanes.[5] Although many mononuclear palladium complexes with organosilyl ligands have been reported,[6] the isolated dinuclear Pd complexes with Pd−Si bonds[7,8] are much less common than the mononuclear silylpalladium complexes and than dinuclear complexes of other transition metals with bridging silylene or silyl ligands. The structure and dynamic behavior of the bridging coordinated $SiHR_2$ group in bimetallic systems are of significant interest in this field.[9]

In this communication we report the preparation of new dinuclear palladium complexes with two bridging diphenylsilyl ligands as well as their structures in the solid state and in solution. $PdEt_2(PR_3)_2$-type complexes which were used as precursors of $Pd^0{-}PR_3$ complexes[10] reacted readily with the Si−H bonds of organosilane to afford new silylpalladium complexes. Previously Schubert reported the reaction of H_2SiPh_2 with $PdMe_2(PMePh_2)_2$ in a 2:1 molar ratio to give the mononuclear silylpalladium complex *cis*-$Pd(SiHPh_2)_2(PMePh_2)_2$ as the sole identified product.[11] The reaction in the present study using PMe_3-coordinated Pd complexes resulted in a different type of product.

H_2SiPh_2 reacted with an equimolar amount of *trans*-$PdEt_2(PMe_3)_2$ in THF or hexane at 55 °C to give a mixture of the dipalladium complexes $[(Me_3P)Pd(\mu\text{-}SiHPh_2)]_2$ (**1**) and $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)_2$ (**2**), which were isolated in 3% and 63% yields, respectively, by fractional recrystallization. The reaction in a 2:1

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Publication on Web 10/10/1998

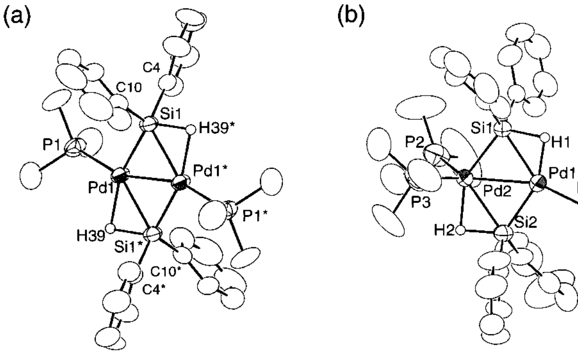
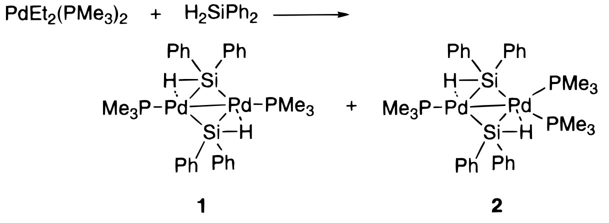


Figure 1. (a) ORTEP drawing of $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)$ (**1**) (30% probability). One of the two crystallographically independent molecules is shown. Atoms with asterisks are crystallographically equivalent to those with the same number without asterisks. Selected bond lengths (Å) and angles (deg): Pd1−Pd1* = 2.691(1), Pd1−Si1 = 2.328(2), Pd1−Si1* = 2.386(2), Pd1−P1 = 2.294(2), Pd1−H39 = 1.91, Si1−H39* = 1.75; Pd1−Si1−Pd1* = 69.61(5), Si1−Pd1−Si1* = 110.39(5), Pd1−Pd1*−Si1 = 54.18(5), Pd1*-Pd1−Si1 = 56.20(5), Pd1−Si1−H39 = 156, Pd1*-Si1−H39 = 46, Pd1−Si1−C4 = 117.5(2), Pd1*-Si1−C4 = 127.6(2), Pd1−Si1−C10 = 114.6(2), Pd1*-Si1−C10 = 115.6(2), C4−Si1−C10 = 107.5(3). (b) ORTEP drawing of $(Me_3P)Pd(\mu\text{-}SiHPh_2)_2Pd(PMe_3)_2$ (**2**) (30% probability). One of the two positions in the disordered phenyl ring is shown. Selected bond lengths (Å) and angles (deg): Pd1−Pd2 = 2.740(1), Pd1−Si1 = 2.351(2), Pd1−Si2 = 2.318(2), Pd2−Si1 = 2.341(2), Pd2−Si2 = 2.411(2), Pd1−P1 = 2.287(2), Pd2−P2 2.336(3), Pd2−P3 2.339(3), Si1−H1 1.68, Si2−H2 1.56, Pd1−H1 1.75, Pd2−H2 = 1.89; Pd1−Si1−Pd2 = 71.47(7), Pd1−Si2−Pd2 = 70.80(7), Si1−Pd1−Si2 = 110.10(8), Si1−Pd2−Si2 = 107.28(8), Pd2−Pd1−Si1 = 54.10(5), Pd2−Pd1−Si2 = 56.18(6), Pd1−Pd2−Si1 = 54.43(6), Pd1−Pd2−Si2 = 53.02(6).

molar ratio and that of H_2SiPh_2 with $PdMe_2(PMe_3)_2$ also led to formation of a mixture of **1** and **2**.



(1)

Figure 1a depicts the structure of one of the two crystallographically independent molecules of **1** which contain a crystallographic center of symmetry at the midpoint of the Pd−Pd bond.[12] The lengths of the two Pd−Si bonds in the molecule are significantly different (2.386(2) and 2.328(2) Å). The SiH hydrogen is included in the plane consisting of two Pd and two Si centers. Close proximity of the SiH hydrogen to Pd (1.91 Å) renders one of the Pd−Si bonds longer than the other.

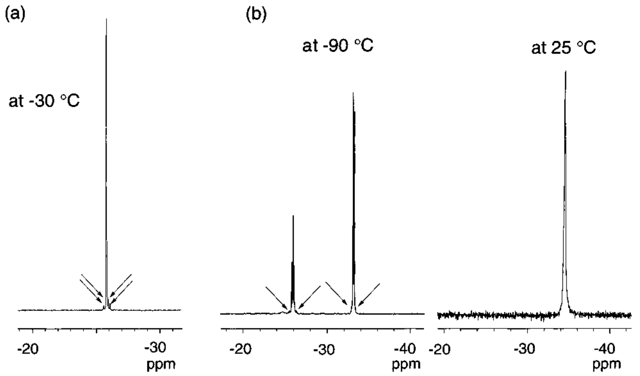


Figure 2. $^{31}P\{^1H\}$ NMR spectra (160 MHz in CD_2Cl_2) of (a) **1** at −90 °C and (b) **2** at −90 and 25 °C. Signals are referenced to external 85% H_3PO_4. The ^{29}Si satellite signal is indicated by an arrow.

These structural features suggest a contribution of a Si−H−Pd three-center−two-electron bond in the coordination of the diphenylsilyl ligand to two Pd centers. A platinum analogue, $[(R'_3P)Pt(\mu\text{-}HSiR_2)]_2$,[8a] has a structure similar to that of **1** but with a larger difference between the Pt−Si bond lengths (2.420(2) and 2.324(2) Å) and shorter H−Pt distance (1.78 Å). The unsymmetrical structure of complex **2** contains two nonequivalent Pd centers which are bonded to one or two PMe_3 ligands, as shown in Figure 1b. Coordination of two PMe_3 ligands to Pd2 seems to weaken the Pd2−Si1 (2.341(2) Å) and Pd2−Si2 (2.411(2) Å) bonds, which are longer than the corresponding Pd1−Si2 (2.318(2) Å) and Pd1−Si1 (2.351 (2) Å) bonds, respectively. Positions of the two SiH hydrogens located by the difference Fourier technique indicate the presence of the three-center−two-electron bonding also. The Pd1−H1 distance (1.75 Å) is somewhat shorter than Pd2−H2 distance (1.89 Å).[13]

The $^{31}P\{^1H\}$ NMR spectrum of **1** at −30 °C contains a single resonance at δ −25.8, as shown in Figure 2. The presence of ^{29}Si satellite signals with two different coupling constants ($J(^{31}P-^{29}Si)$ = 74 and 28 Hz) is consistent with the unsymmetrical coordination of two Si centers to the Pd center. The ^1H NMR spectrum at 25 °C exhibits a signal due to the SiH hydrogen at δ 1.77 flanked by satellite signals ($J(^1H-^{29}Si)$ = 77 Hz). The small coupling constant also suggests partial activation of the Si−H bond by Pd to form an Si−H−Pd three-center−two-electron bond. Complex **1** does not show any significant change in the NMR spectra in the temperature range +25 to −90 °C. Thus, complex **1** in solution has a structure similar to that found in the crystals, and this structure is stable in solution in the above temperature range.

Complex **2** shows a temperature-dependent change in the NMR spectra. The $^{31}P\{^1H\}$ 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

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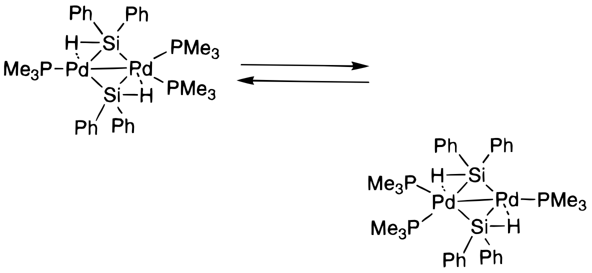
[12] Crystal data for **1** (298 K): $C_{30}H_{39}Si_2P_2Pd_2$, triclinic, $P\bar{1}$ (No. 2), $a = 11.317(5)$ Å, $b = 15.119(5)$ Å, $c = 10.625(4)$ Å, $\alpha = 98.43(3)°$, $\beta = 105.90(3)°$, $\gamma = 71.58(3)°$, $V = 1655(1)$ Å^3, $Z = 2$, $D_{calcd} = 1.466$ g cm^{-3}, $F(000) = 738$, μ(Mo Kα) = 12.73 cm^{-1} for monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). R (R_w) = 0.038 (0.045) for 3482 reflections with $I > 3\sigma(I)$ among 5821 unique reflections ($R_{int} = 0.027$); GOF = 1.00. Crystal data for **2** (298 K): $C_{33}H_{47}Si_2P_3Pd_2$, monoclinic, $P2_1/c$, $a = 13.219(6)$ Å, $b = 15.702(3)$ Å, $c = 19.399(4)$ Å, $\beta = 107.50(2)°$, $V = 3840(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.393$ g cm^{-3}, $F(000) = 1640$, μ(Mo Kα) = 11.44 cm^{-1} for monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). R (R_w) = 0.042 (0.044) for 4095 reflections with $I > 3\sigma(I)$ among 9153 unique reflections ($R_{int} = 0.036$); GOF = 0.95.

[13] The final results of the structural calculation contains the SiH hydrogens, whose positions were located by a difference map and included in the calculation without refinement of the parameters. Further calculations to examine isotropic refinement of positions of the SiH hydrogens converged to give the same R (R_w) value as above. The Pd2−H2 bond (2.05 Å) was elongated by the additional structural calculation more significantly than the Pd1−H1 distance (1.83 Å). The Pd2−H2 bond is considered to be intrinsically longer than the Pd1−H1 bond.

(Figure 2). The ^{1}H NMR spectrum at −90 °C exhibits a doublet (δ 1.24, $^3J(^{31}P-^1H) = 8$ Hz, $J(^{29}Si-^1H) = 84$ Hz) and a triplet (δ −2.34, $^3J(^{31}P-^1H) = 11$ Hz, $J(^{29}Si-^1H) = 86$ Hz) of equal intensity for the two Si−H hydrogens. The latter signal could be assigned to H1 in Figure 1b on the basis of the coupling pattern.[14] The position of the signal in the hydrido region is consistent with the crystallographic results showing that the Pd1−H1 bond is shorter than the Pd2−H2 bond. These ^{1}H and ^{31}P NMR spectra show coalescence of these signals on raising the temperature and exhibited a single resonance for the P nuclei of the PMe$_3$ ligands and for the SiH hydrogens at 25 °C. The change in the NMR spectra is brought about by intra- or intermolecular exchange of the coordinated PMe$_3$ ligands, shown in eq 2, on the NMR time scale.



(2)

The present study has revealed the first preparation and full characterization of dinuclear palladium complexes with bridging HSiR$_2$-type ligands. Complex **1** retains its symmetrical structure both in the solid state and in solution. Coordination of two PMe$_3$ ligands to a Pd center in complex **2** renders the Pd centers nonequivalent in the solid state and at low temperature in solution. Although the two HSiPh$_2$ groups are coordinated to the Pd center with three-center−two-electron bonds, the crystallographic bond parameters and position of the ^{1}H NMR signals of the SiH hydrogens at −90 °C suggests that H1 has partial hydride character more significantly than does H2. The rapid and reversible exchange of the phosphine ligands between the two Pd centers averages the coordination of the two SiHPh$_2$ ligands to two Pd centers.

Acknowledgment. This work was supported by the Basic Science Research Institute Program (No. BSRI-97-3440), Korean Ministry of Education. Y.-J.K. is indebted also to a bilateral exchange program between the JSPS (Japan Society for the Promotion of Science) and KOSEF (Korea Science and Engineering Foundation).

Supporting Information Available: Text giving full experimental details and tables giving crystallographic data for **1** and **2** (18 pages). Ordering information is given on any current masthead page.

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(14) $^2J(^{31}P-^1H)$ through a bond between the Pd center and the η^2-coordinated Si−H group is probably much smaller, taking the large Pd−H distances (ca. 1.8 Å) into account.