

## The First Stable Mononuclear Silyl Palladium Hydrides

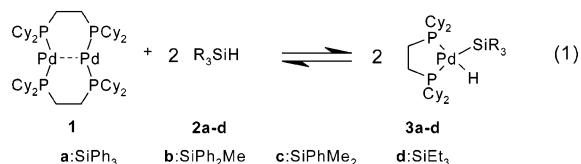
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Palladium-catalyzed reactions of hydrosilanes are involved in a number of important synthetic methodologies.<sup>1</sup> Silyl palladium complexes are certainly key intermediates in these reactions; yet as compared to the better known platinum congeners, the properties of these complexes and their mechanistic roles are much less understood. Stable silyl palladium complexes are rare and are typically stabilized by either very electronegative substituents (i.e., SiCl<sub>3</sub>),<sup>2</sup> inclusion of the silyl substituent in a chelate ring,<sup>3</sup> or via interactions between two or more metal centers.<sup>4</sup> Previously, we have reported a class of simple bis(silyl) palladium complexes, (dcpe)Pd(SiR<sub>3</sub>)<sub>2</sub>, bearing the chelating bisphosphine ligand dcpe,<sup>5</sup> from the reaction of either [(dcpe)Pd( $\mu$ -H)]<sub>2</sub> or [( $\mu$ -dcpe)Pd]<sub>2</sub> with primary or secondary hydrosilanes.<sup>6,7</sup> Presumably, the bis(silyl) palladium complexes are formed by sequential oxidative additions via a silyl palladium hydride intermediate, although these complexes were not detected in our early experiments. We now report the first known examples of mononuclear silyl palladium hydrides, the first solid state structure of such a complex, and highly unusual kinetic isotope effects associated with their dynamic NMR behavior in solution.

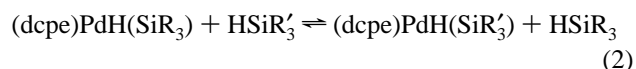
The dinuclear complex [( $\mu$ -dcpe)Pd]<sub>2</sub> (**1**) was reacted with the tertiary hydrosilanes (**2a–2d**) at room temperature in toluene solution (eq 1). Stoichiometric reaction of Ph<sub>3</sub>SiH or Ph<sub>2</sub>MeSiH with **1** results in the instantaneous dissipation of the red color of **1** and the quantitative formation (by <sup>31</sup>P{<sup>1</sup>H} NMR) of the silyl palladium hydrides **3a** and **3b**, respectively. The reaction of **1** with stoichiometric amounts of PhMe<sub>2</sub>SiH, however, is much slower (3 days) and gives only 30% yield of **3c** along with a 25% yield of the palladium hydride, [(dcpe)Pd( $\mu$ -H)]<sub>2</sub> (**4**).<sup>8</sup>



When PhMe<sub>2</sub>SiH is present in 20-fold excess, the reaction proceeds more quickly (1 day), and the yields of **3c** improve considerably (80%), with only 11% of **4** being formed. The reaction of **1** with Et<sub>3</sub>SiH is the most sluggish of the silanes (7 days), giving only 41% yield of **3d** even with a 20-fold excess of silane. The stability of the silyl palladium hydrides in solution is limited due to the reversibility of the reaction of the silanes with **1**. For instance, attempted removal of solvent in vacuo from a solution containing complex **3c** results in reversion to the dipalladium precursor **1** as the volatile silane is also removed. Complexes **3c** and **3d** are only stable in the presence of excess silane, a condition which suppresses dissociation.

These results additionally suggest that the stability of the silyl palladium hydrides is strongly dependent on the degree of phenyl substitution on the silyl substituent. Competition experiments in which an equimolar excess of two different silanes is added to the

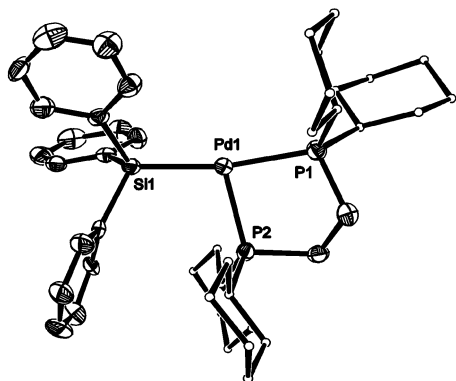
palladium complex **1** result in the fast establishment of an equilibrium represented by eq 2. Measurement of equilibrium constants by <sup>31</sup>P{<sup>1</sup>H} NMR results in a stability order of **3a** > **3b** > **3c** > **3d** with *K*<sub>eq</sub> relative to **3d** (R = Et) of 2400:310:24:1, respectively. A similar dependence of complex stability with increasing substitution by electronegative groups has been observed for the  $\Delta H^\ddagger$  for the reductive elimination of silanes from Cp-(CO)<sub>2</sub>MnHSiR<sub>3</sub> complexes.<sup>9</sup>



An X-ray structure determination was performed on a crystal of **3a** grown in hexane solution.<sup>10</sup> The two independent molecules of **3a** in the unit cell are essentially identical; one of the molecules is shown in Figure 1. Although the position of the metal bound hydrogen could not be determined,<sup>11</sup> the effects of its coordination are apparent in the structure. The coordination geometry about the palladium is reasonably described as distorted square planar with the sum of the bond angles involving the non-hydrogen atoms being 357° (ideal planar, 360°).

The silyl palladium hydrides **3a–3d** show highly temperature-dependent NMR spectra. In *d*<sub>8</sub>-toluene solution at room temperature, each complex shows a single resonance in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum ( $\delta$  = 55–58 ppm), which upon cooling to –80 °C broadens and recombines to two distinct resonances. One of the <sup>31</sup>P resonances (trans to hydride) is shown to couple strongly with one proton. In the <sup>1</sup>H NMR spectrum at room temperature, a 1:2:1 triplet is observed for the metal hydride resonance ( $\delta$  = –1 to –2 ppm), which at –80 °C evolves into a partially resolved doublet of doublets from coupling to two unique phosphorus atoms. Both the low temperature <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra (–80 °C) are fully consistent with the classical square planar structure that is found for **3a** in the solid state. The temperature dependence of these spectra is explainable by rapid *intramolecular* interchange of coordination environments between the silyl and hydride substituents.<sup>12</sup> Activation parameters for this process were obtained for several complexes and their metal deuteride analogues as shown in Table 1.<sup>13</sup>

Stereochemical nonrigidity has been previously observed for related Pd(II) and Pt(II) systems which include P<sub>2</sub>PdSn<sub>2</sub>,<sup>14</sup> P<sub>2</sub>PtSi<sub>2</sub>,<sup>14</sup> P<sub>2</sub>PtH<sub>2</sub>,<sup>15</sup> and P<sub>2</sub>PtHSi<sup>16</sup> (P = phosphine) complexes. In the case of P<sub>2</sub>PdSn<sub>2</sub> and P<sub>2</sub>PtSi<sub>2</sub> complexes, a twist-rotational mechanism via a pseudo-tetrahedral transition state has been proposed for the interconversion of phosphine sites. An alternative mechanism involving the intermediacy of  $\sigma$ -complexes has been proposed for interchange of phosphorus environments in certain P<sub>2</sub>PtH<sub>2</sub> and P<sub>2</sub>-PtHSi systems. The two mechanisms are potentially distinguishable on the basis of kinetic isotope effects involving isotopic substitution at the metal hydride. In the case of the silyl palladium hydrides **3a–c**, there exists a remarkably strong temperature-dependent deuterium kinetic isotope effect (KIE) when the metal hydride is replaced by a deuterium. The metal deuterides, (**3a–c**)-d<sub>1</sub>, have



**Figure 1.** ORTEP drawing of one of the two independent molecules of (dcpe)Pd(H)SiPh<sub>3</sub> (**3a**) in the unit cell. Thermal ellipsoids are at the 50% probability level; cyclohexyl carbons are represented by spheres of arbitrary radius. Important bond lengths (Å) and angles (deg) for molecule 1 followed by equivalent values for molecule 2: Pd1–Si1, 2.335(2), 2.330(2); Pd1–P1, 2.350(2), 2.350(2); Pd1–P2, 2.323(2), 2.323(2); Si1–Pd1–P1, 166.09(8), 166.58(8); Si1–Pd1–P2, 104.28(8), 104.99(8); P1–Pd1–P2, 86.27(8), 87.12(8).

**Table 1.** Activation Parameters for Intramolecular Si–H Interchange in Selected Silyl Palladium Hydrides and Deuterides

complex	E <sub>a</sub> (kcal mol <sup>-1</sup> )	ΔH <sup>‡</sup> (kcal mol <sup>-1</sup> )	ΔS <sup>‡</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )
(dcpe)Pd(H)SiPh <sub>3</sub>	12.9(4)	12.4(4)	8.3(8)
(dcpe)Pd(D)SiPh <sub>3</sub>	8.0(6)	6.5(3)	–15.6(6)
(dcpe)Pd(H)SiPh <sub>2</sub> Me	10.7(6)	10.2(6)	–1(1)
(dcpe)Pd(D)SiPh <sub>2</sub> Me	6.8(7)	6.4(7)	–18.3(2)
(dcpe)Pd(H)SiMe <sub>2</sub> Ph	10.7(6)	10.3(6)	–1(1)
(dcpe)Pd(H)SiEt <sub>3</sub>	9.6(6)	9.2(6)	–3(1)
(dippe)Pd(H)SiPh <sub>3</sub>	11.8(4)	11.6(5)	6.8(1)
(dippe)Pd(D)SiPh <sub>3</sub>	8.7(4)	7.6(4)	–10.0(3)

activation enthalpies 4–6 kcal mol<sup>-1</sup> less than their corresponding hydrides, whereas the activation entropies are almost 17–25 cal mol<sup>-1</sup> K<sup>-1</sup> more negative. The resultant effect is a crossover in the KIE ( $k_H/k_D$ ) over the measured temperature range. The KIE is inverse at low temperatures (**3a**: –60 °C;  $k_H/k_D = 0.13$ ) but normal at higher temperatures (**3a**: –10 °C;  $k_H/k_D = 2.0$ ).<sup>17</sup> Temperature-dependent changes in KIE are typically indicative of a change of the rate-limiting step, implying that there exist two or more consecutive steps (and one or more intermediates) in the fluxional process. A reasonable intermediate would be a discrete well-defined Si–H  $\sigma$ -complex.<sup>18</sup>

The fluxionality in silyl palladium hydrides may parallel the steps involved in C–H reductive elimination. Both normal and inverse isotope effects have been observed for the reductive elimination of C–H bonds in alkylmetal hydrides, a process proposed to proceed via intermediate C–H  $\sigma$ -complexes.<sup>19</sup> The differences in the observed isotope effects (normal vs inverse) for C–H reductive elimination have been attributed to differences in the rate-determining steps for the formation (via reductive coupling) and dissociation of the alkane  $\sigma$ -complexes.<sup>20</sup> The fluxionality of the silyl palladium hydrides may reflect a similar situation, whereupon the relative free energies of the transition states associated with the formation of the Si–H  $\sigma$ -complex (via reductive coupling) and its isomerization (via rotational interchange) are highly temperature dependent, resulting in both inverse and normal KIEs for the *same* complex. We are currently pursuing computational and mechanistic studies to help elucidate the details of the hydride exchange and to determine the origin of this remarkable isotope effect.

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**Supporting Information Available:** Crystallographic data for **3a** (CIF), experimental preparations for **3a–d**, and kinetic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Complete characterization (room temperature) for **3a**, <sup>1</sup>H NMR ( $\delta$ , ppm): –1.81 (1H, triplet;  $J_{P-H} = 77$ ), 0.8–2 (48H, broad), 7.1 (3H, multi), 7.2 (6H, multi), 8.4 (6H, multi). <sup>13</sup>C{<sup>1</sup>H}NMR ( $\delta$ , ppm): 26.3, 26.9, 27.0, 27.2, 27.3, 29.1, 30.1, 30.2, 34.6 (d of d: <sup>1</sup> $J_{PC} = 13.0$ , <sup>2</sup> $J_{PC} = 2.3$ ), 126.9, 127.2, 128.2, 136.1, 137.4, 148.6 (t:  $J_{PC} = 5.4$ ). <sup>31</sup>P{<sup>1</sup>H}NMR ( $\delta$ , ppm): 58.23 (singlet). <sup>29</sup>Si NMR:  $\delta$  –5.08. <sup>2</sup>J(SiH) = 29 Hz. IR (KBr, cm<sup>-1</sup>): 1895 (PdH), 1427 (SiPh). Anal. Calcd for C<sub>44</sub>H<sub>64</sub>SiP<sub>2</sub>Pd: C, 66.98; H, 8.18. Found: C, 66.10; H, 8.44.
- (11) The presence of a palladium hydride in the solid is clearly evident from the stretching frequency  $\nu$ (Pd–H, KBr) = 1895 cm<sup>-1</sup> in the IR spectrum.
- (12) The intramolecular nature of the interchange is evidenced by the retention of P–H (hydride) and P–Si coupling at both low- and high-temperature exchange limits as well as by the insensitivity of the exchange rate to the concentration of the complex and to extraneous silane.
- (13) Rate constants were obtained at various temperatures employing full line shape analysis with the gNMR 4.1 software package (Budzelaar, P. H. M. Chermwell Scientific Limited, 1999). Eyring plots of the rate constants over the measured temperature range afforded the experimental activation parameters.
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