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Dynamic Processes in Silyl Palladium Complexes: Evidence for Intermediate Si−H and Si−Si σ-Complexes

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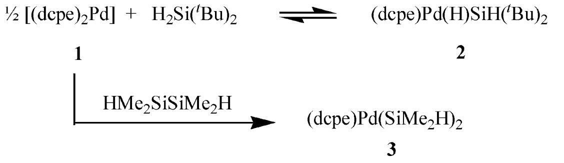
The activation of Si−H and Si−Si bonds by transition metals is a key step in catalytic hydrosilation[1] and bis-silation[2] reactions. Knowledge of the detailed mechanism of these bond activations is important for controlling these catalytic reactions as well as for providing useful comparisons to C−H and C−C bond activations. In the case of silicon, multicentered Si−H and Si−Si σ-complexes likely play an important role.[3,4] One characteristic of these complexes is their ability to undergo rapid fluxional processes involving either rotations perpendicular to the Si−H or Si−Si bond axis or exchange of hydrides between the metal and the silicon. We now report evidence for both processes, including evidence for a transitory Si−Si σ-complex.

We have previously reported that the reactions of tertiary silanes with the low-valent palladium complex, $[(\mu\text{-dcpe})Pd]_2$ (**1**, dcpe = 1,2-bis(dicyclohexylphosphino)ethane), give silyl palladium hydrides which exhibit fluxionality due to intramolecular Si−H coordination interchange about the palladium center.[5] The temperature-dependent isotope effects associated with this process were interpreted as evidence for intermediate Si−H σ-complexes. We now report the first reactions of **1** with secondary silanes to give silyl palladium hydrides as well as bis(silyl) palladium complexes. Both types of complexes display fluxional behavior that we attribute to the intermediacy of a σ-complex.

The reaction between **1** and excess $H_2Si^tBu_2$ yields the silyl palladium hydride, $(dcpe)Pd(H)SiH^tBu_2$ (**2**), which is in equilibrium with the starting materials. The complex could not be isolated since attempted removal of solvent in vacuo results in the reversion of **2** to the dinuclear palladium complex **1** and the volatile $H_2Si^tBu_2$. The complex **2**, however, does form stable solutions in the presence of excess silane.[6]



As previously reported for mononuclear silyl palladium hydrides, **2** displays NMR spectra that vary with temperature.[5] In toluene-d_8 at −80 °C, the NMR spectrum of **2** is consistent with a square planar Pd(II) coordination environment. Two distinct resonances (δ = 60 and 63) are observed in the $^{31}P\{^1H\}$ NMR spectrum. Removal of broadband ^1H decoupling causes the upfield ^{31}P resonance to become a doublet ($^2J_{PH} = 156$ Hz) due to coupling to the trans Pd−H. In the ^1H NMR spectrum, both the palladium hydride resonance and the silicon hydride resonance appear as a doublet of doublet of doublets. The palladium hydride resonance appears at $\delta = -1.86$ ($^2J_{PH} = 156$ Hz, $^2J_{PH} = 6$ Hz, $^3J_{HH} = 6$ Hz), while the silicon hydride signal is centered at $\delta = 4.80$ ($^3J_{PH} = 30$ Hz, $^3J_{PH} = 20$ Hz, $^3J_{HH} = 6$ Hz).

As the solution is warmed to room temperature, the resonances in the ^{31}P NMR spectrum broaden and eventually coalesce to give a single resonance at $\delta = 53.8$. Unexpectedly, the *coupled* room-temperature ^{31}P NMR spectrum of **2** gives a broadened triplet ($J_{P-H} = 50$ Hz), *not* the expected doublet that has been previously observed for tertiary silyl palladium hydrides. This implies that, at room temperature, the phosphorus nuclei are strongly coupled to two equivalent protons, which indicates the presence of a second dynamic process not observed for tertiary silyl palladium hydrides.

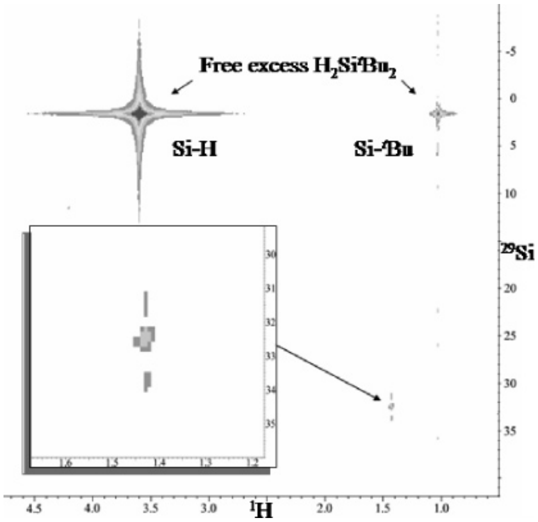


Figure 1. Room-temperature $^{29}Si-^1H$ HMQC spectrum of **2**. Inset: Cross-peaks due to exchanging hydrogens.

The ^1H NMR spectrum at room temperature shows no discernible resonances due to Si−H or Pd−H. Since the expected average of these two chemical shifts is $\delta = 1.47$, it is likely that the averaged resonance would be obscured by the *tert*-butyl resonance or the broad signal of the dcpe ligand. The resonance of the exchanging protons, however, can be resolved in the two-dimensional $^1H-^{29}Si$ HMBC and HMQC spectra (Figure 1). A cross-peak is found which correlates the ^{29}Si triplet ($\delta = 33$, $^2J_{SiP} = 66$ Hz) with a proton resonance at $\delta = 1.4$, roughly the average of the low-temperature Si−H and Pd−H resonances. All of these observations are consistent with a dynamic process by which the palladium hydride and the silicon hydride rapidly exchange at room temperature.

Exchange of hydrogen (or H/D exchange) between a metal and an α-carbon atom is a classic test for determining the presence of a C−H σ-complex.[7] The exchange is usually slow, requiring observation of H/D exchange in isotopically labeled complexes. Exchange rapid enough to be observed on the NMR time scale is very rare, and to our knowledge has been reported only for the metal−alkane complex, $(C_5Me_5)Os(dmpm)(CH_3)H^+$.[8] Recently, the related fast interchange of coordinated and pendant Si−H groups in the silane complex, $Mo(CO)_5(\eta^2\text{-}H_2SiPh_2)$, has been reported on the basis of NMR line broadening.[9]

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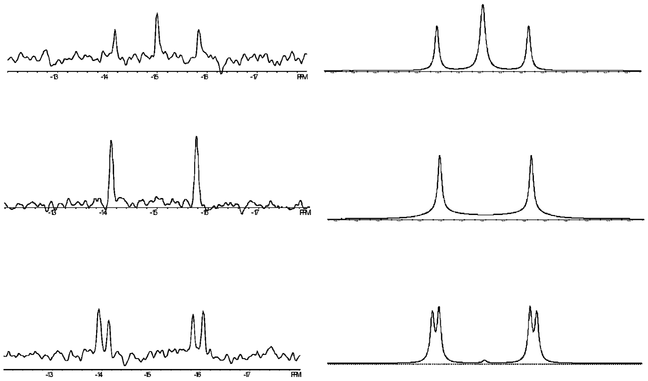
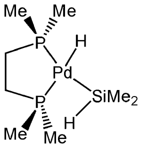
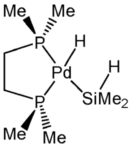


Figure 2. Variable-temperature $^{29}Si\{^{1}H\}$ NMR of (dcpe)Pd(SiHMe$_2$)$_2$. Top, 80 °C; middle, 20 °C; bottom, −70 °C; experimental on left, simulation on right.

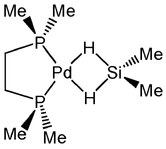
Density functional theory calculations on the model complex (dmpe)PdH(SiMe$_2$H) show three local minima, **A**−**C**.[10] The minima



A



B



C

A and **B** each correspond to rotational isomers possessing the silyl palladium hydride structure. The trans H−H isomer, **A**, is the global minimum. It is 1.1 kcal/mol more stable than its cis H−H counterpart, **B**. Another intermediate, **C**, has a doubly hydrogen-bridged structure with the hydrogen atoms bisecting the P$_2$PdSi coordination plane. The doubly bridged structure is 6.9 kcal/mol higher in energy relative to **A**. This symmetric intermediate is likely responsible for *both* the interchange about the palladium coordination environment and the observed Si−H/Pd−H scrambling process. The activation energy for the rearrangement **A** → **C** is calculated to be 8.1 kcal/mol. Reductive elimination to give (dmpe)Pd + Me$_2$SiH$_2$, in contrast, is a much more unfavorable process ($\Delta E = 27.5$ kcal/mol; $\Delta G(298\ \mathrm{K}) = 16.0$ kcal/mol).

Bis(silyl) palladium complexes also show dynamic processes similar to those observed for silyl palladium hydrides. The reaction of **1** with (SiMe$_2$H)$_2$ gives the square planar palladium bis(silyl) complex, (dcpe)Pd(SiHMe$_2$)$_2$ (**3**).[11] The $^{29}Si\{^{1}H\}$ NMR of **3** at low temperature (−70 °C) shows a doublet of doublets centered at $\delta = -15$, consistent with the previously reported X-ray crystal structure (Figure 2).[11a] As the temperature is raised, the multiplet evolves to a triplet, indicating rapidly exchanging silicon nuclei.

Similar fluxional behavior has also been noted for some bis(silyl) and bis(stannyl) platinum compounds as well as bis(stannyl) palladium complexes.[12] In these cases, the fluxionality was attributed to a "twist-rotation" mechanism in which the group 14 elements are rotated with respect to the palladium-phosphorus plane. In part, this reasoning derives from the known twisted ground state of these molecules. In the case of **3**, the molecule not only is essentially square planar[11a] but also shows significant deuterium isotope effects for the interchange of the two silyl groups. NMR line shape analysis derived from the ^{31}P NMR spectrum gives the following activation parameters: $E_a = 14.1(7)$ kcal/mol, $\Delta H^{\ddagger} = 13.6(7)$ kcal/mol, and $\Delta S^{\ddagger} = -0.7(5)$ cal. The corresponding deuterated analogue, (dcpe)Pd(SiDMe$_2$)$_2$, gives activation parameters of $E_a = 17.7(8)$ kcal/mol, $\Delta H^{\ddagger} = 17.1(8)$ kcal/mol, and $\Delta S^{\ddagger} = 11(2)$ cal. The activation energies are only slightly higher than those previously obtained for tertiary silyl palladium hydrides (9−13 kcal/mol).[5]

Silyl palladium hydrides with tertiary silyl groups show extraordinary primary kinetic isotope effects which increase with temperature. The bis(silyl) complex **3**, however, shows a much less pronounced isotope effect which decreases with temperature (at −20 °C, $k^{\mathrm{H}}/k^{\mathrm{D}} = 1.37$; at 20 °C, $k^{\mathrm{H}}/k^{\mathrm{D}} = 0.85$). Although large for a typical secondary isotope effect, it is much smaller than the primary isotope effect that is observed for tertiary silyl palladium hydrides. The deuterium kinetic isotope effect for this process, however, does indicate that the silyl groups are not merely spectators in the rotational process but these groups undergo significant electronic changes affecting the Si−H bond. The likely cause is the formation of an intermediate Si−Si σ-complex. Disilane σ-complexes have recently been described in an unusual trinuclear palladium complex in which one of the palladium atoms participates in two agostic Si−Si interactions.[13] The rigid geometry of the complex supports these Si−Si interactions. In contrast, the fluxional behavior of **3** provides the first example of an intermediate with an unsupported Si−Si interaction.

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Supporting Information Available: Experimental details for synthesis of new compounds, kinetic analysis, and spectra, as well as computational details and Cartesian coordinates for optimized molecules are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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