

Si...H...Si VIBRATIONS IN ORGANOMETALLIC COMPLEXES

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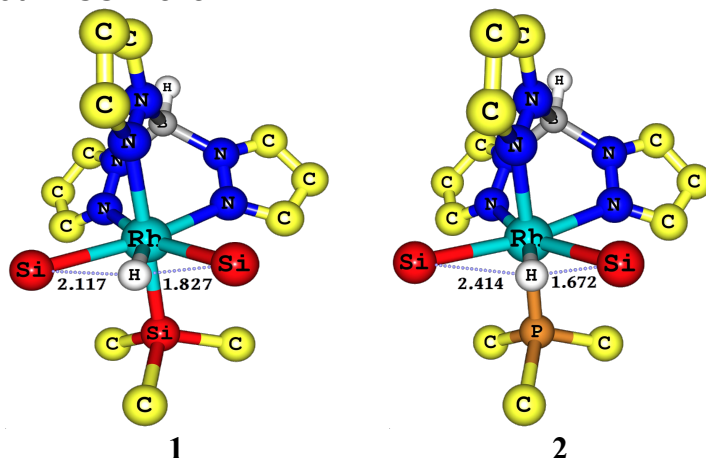
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Transition metal silane σ -complexes $L_nM(H-SiR_3)$ result from silane coordination to a metal center and play an important role as intermediates in transition metal catalyzed hydrosilylation reactions. The silane ligand is linked to the metal by a ligand-to-metal ($\sigma(Si-H) \rightarrow M$) donation and metal-to-ligand ($M \rightarrow \sigma^*(Si-H)$) back-donation.

A metal complex $L_nM(H)(SiR_3)_2$ that formally contains two silyl and one hydride ligand can exhibit silyl-silane or bis-silyl-hydride behavior. If the metal complex is a silyl-silane complex, there are two types of interligand interactions. In the first case, the hydrogen is connected either to one silicon or to the other, and these forms are in dynamic equilibrium (hydrogen fluxionality). The potential energy surface (PES) has two minima separated by a moderate barrier. In the second type of complexes, the hydrogen interacts with both silicon atoms simultaneously. Essentially, the entire $R_3Si \cdots H \cdots SiR'_3$ fragment behaves as a single ligand.

Various density functionals (PBEPBE, B3LYP, M06L, M062X, BP86, TPSSH) and MP2 methods deliver very different geometries. Therefore, we performed CCSD calculations on hydride-silyl complexes of niobium and rhodium, which indicate that the TPSSH functional delivers more reliable results than any other functional or MP2.

Two different shapes of the PES were found for the complexes **1** and **2**. Complex **1** has a barrier of $0.03 \text{ kcal}\cdot\text{mol}^{-1}$, and complex **2** has a barrier $1.14 \text{ kcal}\cdot\text{mol}^{-1}$ at TPSSH level.



The dynamic behavior of the hydrogen in these complexes was studied by solving the vibrational Schrödinger equation. For the complex **1** the ground-state vibrational wavefunction has a single maximum located at the transition state. Complex **2** has the vibrational wavefunction with two maxima located near the PES minima.