

# Are Stannylenes Better Ligands than Phosphines?

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Substitution of phosphine ligands by the isolobal cyclic amido-stannylene  $[\text{Sn}(\text{N}^t\text{Bu})_2\text{SiMe}_2]$  (**1**)<sup>[1]</sup> in the well-known Wilkinson catalyst  $[\text{Rh}(\text{PPh}_3)_3(\text{Cl})]$  works straightforward.<sup>[2]</sup> Depending on the stoichiometry, one or three of the phosphines are replaced yielding *cis*- $[\{\text{Sn}(\text{N}^t\text{Bu})_2\text{SiMe}_2\}_2\text{Rh}(\text{PPh}_3)_2(\text{Cl})]$  (**2**), in which two stannylene ligands **1** are inserted into the rhodium-chlorine bond (fig. 1), or  $[\text{Rh}\{\text{Sn}(\text{N}^t\text{Bu})_2\text{SiMe}_2\}_5(\text{Cl})]$  with a trigonal bipyramidal  $\text{RhSn}_5$  core. In hydrosilylation reactions, **2** shows much higher TOF's compared to Wilkinson's catalyst.<sup>[3]</sup>

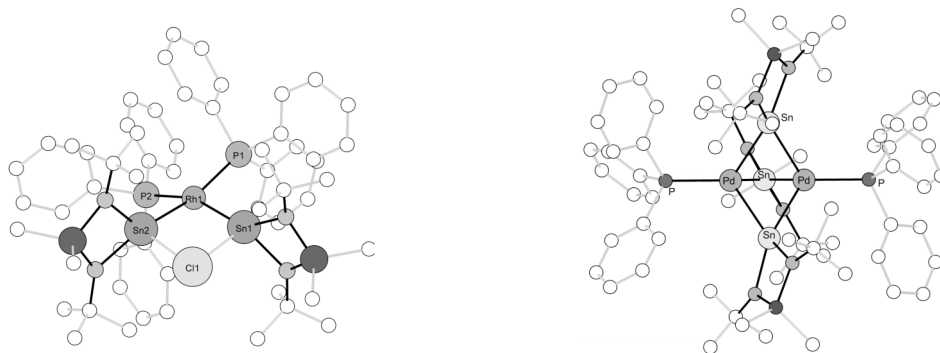


Fig. 1: Molecular Structures of **2** and **3**.

A potential enantioselective catalyst is provided by the reaction of **1** with  $[\text{Pd}(\text{PPh}_3)_4]$ : A chiral dipalladium complex  $[\{(\text{Ph}_3\text{P})\text{Pd}\}_2(\mu\text{-}\{\text{Sn}(\text{N}^t\text{Bu})_2\text{SiMe}_2\}_3)]$  (**3**) is formed.<sup>[4]</sup> The stannylenes exhibit a pronounced tendency to occupy the bridging position, in which they adopt a paddle-wheel like arrangement (fig. 1). The complex can be described as a trigonal bipyramidal cluster with local  $\text{C}_3$  symmetry.

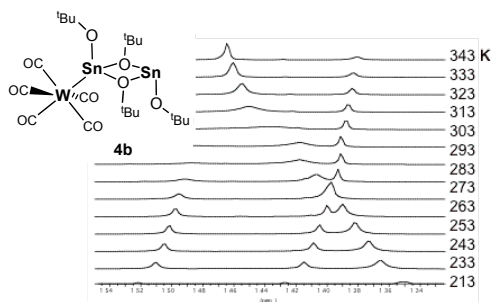


Fig. 2: Temperature dependent  $^1\text{H}$ -NMR of **4b**.

However, due to the high sensitivity of the tin-nitrogen bond, we started to investigate the molecular characteristics of alkoxy-stannylene complexes. The mono-coordinated complexes  $[\{(\text{OC})_5\text{M}\}\{\text{Sn}(\text{O}^t\text{Bu})(\mu\text{-O}^t\text{Bu})_2\}]$  ( $\text{M} = \text{Cr}, \text{W}$ , **4a**, **b**) show a distinct dynamic behaviour: with increasing temperature, first three, and then four  $\text{O}^t\text{Bu}$  substituents exchange rapidly on the NMR time scale (fig. 2).<sup>[5]</sup>

## References

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