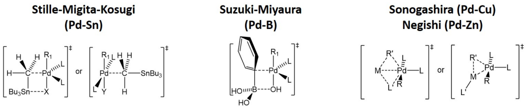
Heterobimetallic d^8-d^{10} complexes as intermediates, transition states, and transition state analogs for the transmetalation step in Sonogashira and Negishi coupling reactions

R. J. Oeschger[1], P. Chen[1]*

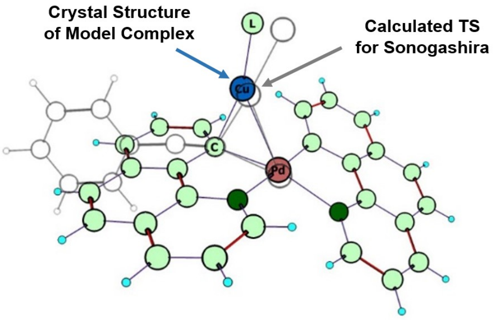
[1]ETH Zürich

Pd-catalyzed cross-coupling reactions have become one of the key processes for carbon-carbon bond formations. Even though their organometallic coupling partners vary, it is understood that they all follow a common general catalytic cycle in which a transmetalation reaction is one of the key steps. The mechanism of transmetalation reactions has been most thoroughly studied for the Stille reaction and for the Suzuki-Miyaura coupling, and it has been proposed that the reaction proceeds via either an open (S_N2 like) or closed transition state. Gas phase and computational studies on the mechanisms of the Sonogashira (Pd/Cu) and Negishi (Pd/Zn) transmetalations suggest that these reactions proceed somewhat different. [1] The main difference is the existence of direct metal-metal (d^8-d^{10}) interactions in calculated structures of transition states and intermediates.



To study the crucial Pd(II)-Cu(I) [2] and Pd(II)-Zn(II) [3] interactions experimentally we have prepared isolable heterobimetallic d^8-d^{10} complexes. The crystal structures resemble computed transition states for the Sonogashira and Negishi transmetalation steps and we have investigated the bonding qualitatively and quantitatively by X-ray, NMR, mass spectrometry (ESI-MS/MS) and calculations (DFT).

Structural and thermochemical work on the isolable model complexes will be used to predict and optimize substrates, ligands, and reaction conditions for cross-coupling reactions, especially the Negishi coupling, so as to suppress undesired side reactions, e.g. homocoupling, by rational design.



[1] Raphael J. Oeschger, David H. Ringger, Peter Chen, *Organometallics*, **2015**, 34, 3888-3892
[2] Raphael J. Oeschger, Peter Chen, *J. Am. Chem. Soc.* **2017**, 139, 1069-1072.
[3] Raphael J. Oeschger, Peter Chen, *Organometallics*, **2017**, 36, 1465–1468