**Relativistic Effects on C–X Bond Activation by Palladium(0)**

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Palladium is widely used as a metal with catalytic properties. Generally, in substrates S it »activates« bonds S–X to subsequently undergo oxidative addition.

$$PdL_n + S{-}X \rightarrow (PdL_n \bullet S\cdots X) \rightarrow Pd(L_n)(S)(X)$$

Instead of considering the overall reaction system and optimizing it by trial and error through plausible ligand substitutions, we follow a step-by-step approach designated »fragment-oriented design of catalysts«. In this approach, we start with the intrinsic reactivity of the uncoordinated, »naked« Pd atom. In following steps, we will successively add ligands L.

Here, we are interested in the reactivity of uncoordinated Pd towards C–H, C–Cl and C–C bonds. Our model systems are Pd + $CH_4$, Pd + $CH_3Cl$ and Pd + $C_2H_6$.

All calculations are done with the ADF program package on the BP86/TZ(2)P level of theory, with and without consideration of relativistic effects. These are taken into account by (i) a quasi-relativistic approach and (ii) the ZORA method. The interaction energy between Pd and the ligands is split up into several physically meaningful terms that can be associated with familiar terms from MO theory. This serves an in-depth understanding of the bonding situation.

For Pd, as a second-row transition metal, relativistic effects are expected not to be of very high importance. Interestingly, a detailed analysis shows, that relativistic effects have a significant influence on important parts of the Pd–ligand bond. Overall, this results in an notable change in the thermodynamics of the reactions.