NUCLEOPHILIC ACTIVATION ENABLED BY Z-TYPE INTERACTIONS: STRONG-BOND ACTIVATION IN ORGANOSILICON CHEMISTRY

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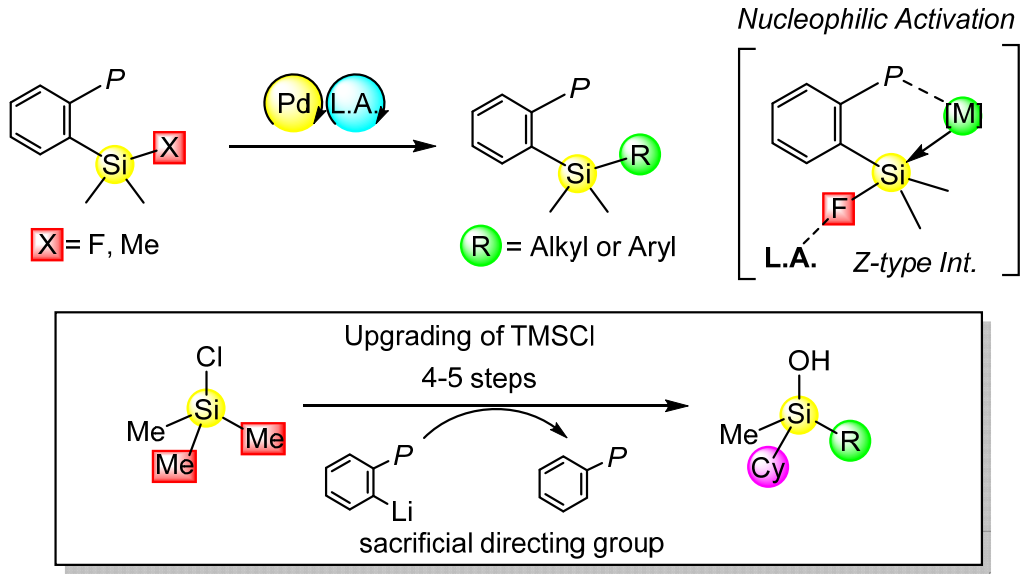
Oxidative addition in transition-metal catalysis is a general entry point to molecular transformations, leading to migratory insertion and reductive elimination. In organosilicon chemistry, however, Si–F, Si–O, and Si–C(sp^3) bonds are exceptionally robust, and examples of their cleavage at a metal center have therefore remained limited. This lecture presents an inversion strategy that reinterprets the interaction between a substrate (or ligand) and a metal center as a Z-type interaction, whereby coordination renders the substrate "nucleophilically" activated.

Using fluorosilanes/fluorogermanes equipped with a phosphine directing group to induce Z-type interactions, Si–F/Ge–F bond cleavage is driven by external Lewis acids (e.g., Mg salts and boranes), enabling—for the first time—catalytic Sila-Negishi and Germa-Suzuki cross-coupling.[1-2] For weakly polarized and otherwise unreactive Si–Me bonds, a cooperative Pd–$GaCl_3$ system is described that combines oxidative addition with post-oxidative-addition alkyl abstraction, allowing selective Si–Me activation and stepwise alkyl exchange.[3] Building on these findings, an upgrading pathway is outlined from industrially important Me_3SiCl feedstocks to silanols bearing three different alkyl groups, highlighting the potential of single-bond editing toward silicon resource circulation.



Figure

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[2] H. Kameo, A. Mushiake, T. Isasa, H. Matsuzaka, D. Bourissou, *Chem. Comm.* **2021**, *57*, 5004-5007.

[3] H. Kameo, K. Oishi, K. Yamanaka, H. Matsuzaka, A. Mushiake, D. Bourissou, *Manuscript under revision*.