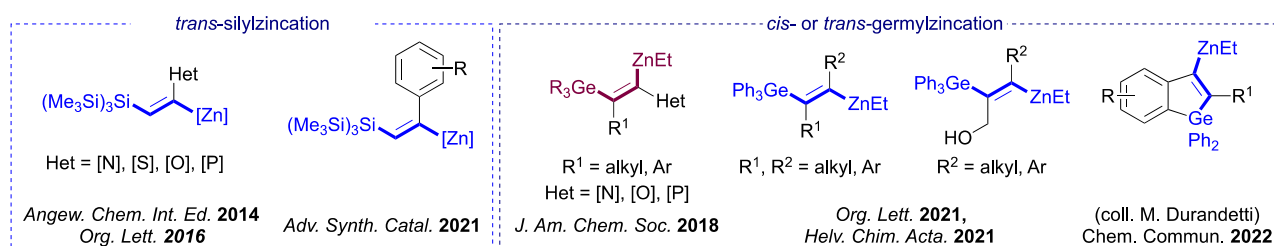
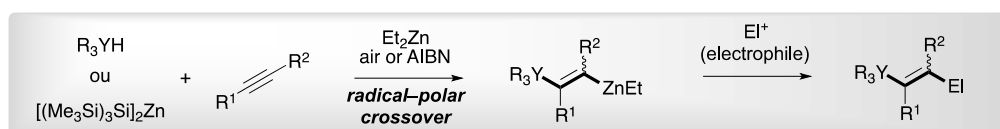


Radical-based Silyl- and Germlyzincation of Alkynes

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Addition reactions of silicon–metal and germanium–metal bonds across carbon–carbon triple bonds attract considerable interest as they give access in a single synthetic operation to alkenes having two vicinal reactive sites (α -metalated vinylsilanes or vinylgermanes). We have developed a new entry into this family of reactions relying on mixed radical–polar processes using the radical chemistry of diorganozinc reagents. This original approach offers reactivity trends distinct and complementary to those available with established metal-catalyzed or anionic strategies. Specifically, on reaction with $(\text{Me}_3\text{Si})_3\text{SiH}$ in the presence Et_2Zn or with $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Zn}$, terminal alkynes undergo *trans*-selective silylzincation,^{1–3} which was previously unknown. Similarly, the reaction with triorganogermanes (R_3GeH) in the presence of Et_2Zn allows for the regio- and stereoselective germlyzincation of terminal and internal alkynes,^{4–6} including intramolecular addition processes.⁷ The protocols developed for silyl- and germlyzincation can be combined, in the same pot, with the electrophilic substitution of the $\text{C}(\text{sp}^2)\text{–Zn}$ formed during the addition step, with retention of the double-bond geometry. Hence, from a synthetic methodology standpoint, the methods developed offer an efficient access to original organosilanes and organogermanes through a modular strategy that does not require transition-metal catalysts.



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