

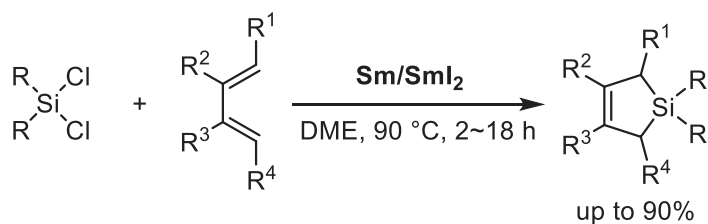
Sm/SmI₂-Induced Reductive Cycloaddition of 1,3-Dienes with Dichlorosilanes

(¹Graduate School of Engineering, Kyoto University, ²Organization for Research Promotion, Osaka Metropolitan University) ○Zhengwei Chen,¹ Tsutomu Mizota,¹ Leo Onishi,¹ Huiying Mu,¹ Koji Miki,¹ Akiya Ogawa,² Kouichi Ohe¹

Keywords: Dichlorosilane; SiR₂ Transfer Reaction; Samarium; Conjugated Diene; [1+4]-cyclization

As one of the most attractive methods, a direct transfer of silylene (SiR₂) moieties to unsaturated organic compounds is desired in construction of silacarbycles. Representative protocols have been established using well-defined precursors as SiR₂ synthons.¹ However, the limited availability of silylene precursors has prompted us to explore the use of easily accessible raw materials as silylene equivalents. Dichlorosilanes are commercially available reagents for reductive silylene transfer reactions, basically achieved by harsh conditions like alkali metals. It was only recently that chemists explored a mild catalytic SiR₂ transfer to unsaturated compounds using dichlorosilanes, which still requires specific ligands synthesized from multistep procedures.²

Samarium reagents find extensive use in organic synthesis, yet their utility in organosilicon chemistry remain underexplored. Although the reductive polymerization of dichlorosilane induced by Sm/SmI₂ has been reported, there have been no reports on Si-C bond formation to date.³ We envisioned that samarium reagents could achieve reductive SiR₂ transfer reactions under mild conditions. Herein, we have developed a facile and efficient SiR₂ transfer reaction to 1,3-dienes using Sm/SmI₂ and readily obtainable dichlorosilanes. This reaction can be applied to a variety of dienes and dichlorosilanes, affording 1,4-dihydrosiloles in good yields with high diastereoselectivity.



1) a) Cirakovic, J.; Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370. b) Ohmura, T.; Masuda, K.; Takase, I.; Sugimoto, M. *J. Am. Chem. Soc.* **2009**, *131*, 16624. 2) Qi, L.; Pan, Q.-Q.; Wei, X.-X.; Pang, X.; Liu, Z.; Shu, X.-Z. *J. Am. Chem. Soc.* **2023**, *145*, 13008. 3) Li, Z.; Iida, K.; Tomisaka, Y.; Yoshimura, A.; Hirao, T.; Nomoto, A.; Ogawa, A. *Organometallics* **2007**, *26*, 1212.