

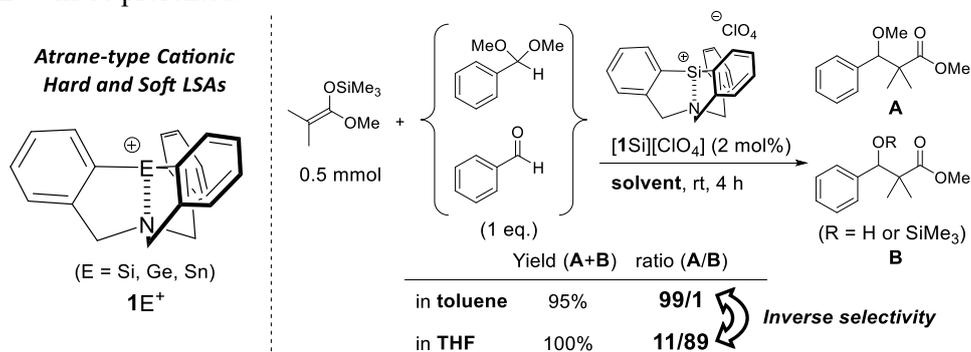
## Synthesis and Catalytic Activity of Atrane-type Group 14 Cations with Hard and Soft Lewis Superacidity

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Lewis acid is one of the most vital reagents utilized for many chemical transformations. Recently, hard and soft Lewis superacids (LSAs) with a neutral heavier group 14 element center have attracted attention in terms of their broad range of affinity for various substrates from hard to soft Lewis basic substrates.<sup>1,2</sup> Heavier group 14 cations ( $R_3E^+$ : E = Si, Ge, Sn) also have the potential to work as hard and soft LSAs because they have a high electron affinity and Lewis acidity enough to cleave various bonds such as a C–F and Si–H bond. However, the application of these species as a catalyst remains a challenging issue mainly due to the high affinity of substrates. The introductions of various substituents stabilize the cationic center but inhibit the employment as catalysts. For silyl cation species, there are some reports that describe the utilizations of them to catalytic reactions. In the case of germyl and stannyl cation species, only a few stoichiometric reactions have been reported and their reactivities remain unclear.

The synthesis and isolation of atrane-type molecules  $1E^+$  (E = Si, Ge, and Sn) having a cationic group 14 metal center will be reported.<sup>3</sup> The cations  $1E^+$  act as hard and soft LSAs, which readily interact with various hard and soft Lewis basic substrates. The rigid atrane-framework stabilizes the localized positive charge on the metal center and assists the formation of the well-defined highly coordinated states of  $1E^+$ . The cations were applicable to the hydrodefluorination, Friedel-Crafts reaction, alkyne cyclization, and carbonyl reduction as Lewis acid catalysts. Most notably,  $[1Si][ClO_4]$  exhibited an unique chemoselectivity that depends on a solvent in the competitive reaction of silyl enol ether with a mixture of benzaldehyde dimethyl acetal and benzaldehyde. The structures, Lewis acidity, and reactivity of  $1E^+$  will be presented.



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