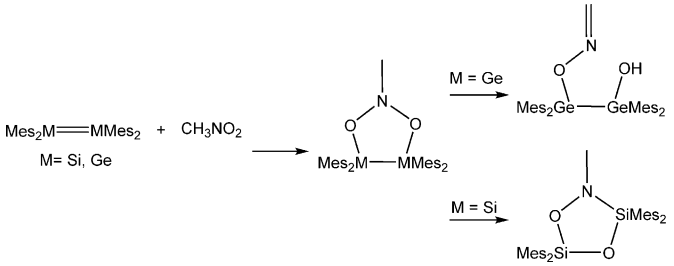
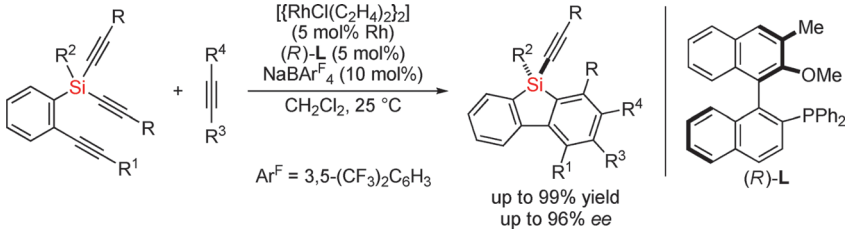
[3+2] Cycloaddition Reactions



Nitromethane addition to tetramesityldisilene and tetramesityldigermene leads to the formation of 1,3,2,4,5-dioxazadisil- and digermolidine ring systems, respectively. The 1,3,2,4,5-dioxazadisilolidine isomerizes to the 1,4,2,3,5-dioxazadisilolidine ring system, whereas the 1,3,2,4,5-dioxazadigermolidine undergoes ring opening to the isomeric oxime.

Asymmetric Catalysis



Silicon cycles: An axially chiral monophosphine ligand is employed in the Rh-catalyzed reaction between silicon-containing prochiral triynes and internal alkynes to form silicon-stereogenic dibenzosiloles with high yields and enantioselectivities. A germanium-stereogenic dibenzogermole is also prepared by this method.

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Flashback: 50 Years Ago . . .

Giulio Natta, who shared the 1963 Nobel Prize in Chemistry with Karl Ziegler, contributed a Review on the analogies between the stereochemical properties of macromolecules and those of classic organic cyclic compounds. In another Review, Dieter Seebach discussed the properties of three- and four-membered polycyclic systems, in particular tetrahedrane, Dewar benzene, prismane, and cubane. Seebach published a Minireview on geminal disubstitution in the 50th Jubilee Issue of *Angewandte Chemie International Edition* (see *Angew. Chem. Int. Ed.* **2014,** *50*, 96).

Hubert Schmidbaur (former Chairman of the Editorial Board of *Angewandte Chemie*) contributed three Communications on gallium-containing compounds. The first was on the synthesis of dichlorogallane $HGaCl_2$, which was formed by the reaction of trimethylsilane with gallium trichloride. The second report was on organoheterosilanes $Me_3SiOXMe_2$ and Me_3COXMe_2 (X = Al, Ga, or In), which occur as dimers that have a four-membered ring structure, and the third on the synthesis of trimethylaluminum trimethylphosphorus oxide and trimethylarsenic trimethylgallium oxide. Schmidbaur's Review on argentophilic interactions is currently in press (see *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201405936).

Hermann Stetter, after whom the Stetter reaction was named, described a new synthesis of the adamantane derivatives substituted in the 3-position, which were constructed by the cyclization of 3-methylenebicyclo[3.3.1]nonan-7-one or 3,7-dimethylenebicyclo[3.3.1]nonane in the presence of acids. This method could also be used to synthesize adamantane-containing polymers.

Read more in Issue 5/1965.