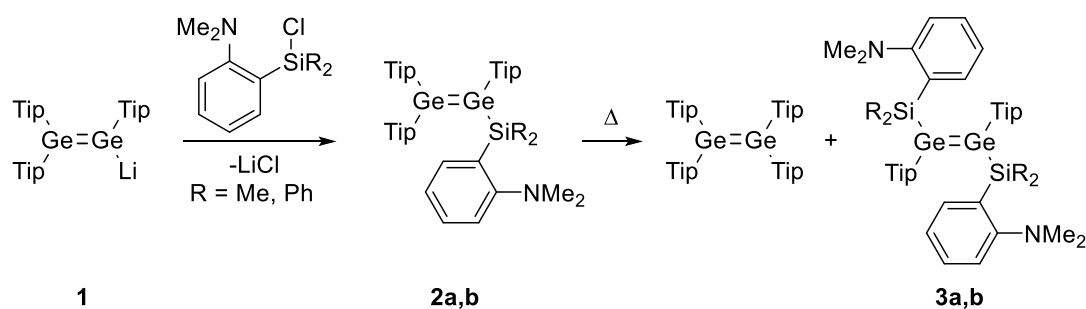


Metathesis of Digermenes

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Since its first report,^[1] olefin metathesis sparked the interest of countless chemists, leading to new possibilities in the synthesis of organic molecules and polymers.^[2] Metathesis of heavier multiply bonded species is limited to a couple of spectroscopic studies on diphosphenes, which require irradiation or the presence of transition metal catalysts.^[3] In contrast, digermenes are known to be readily cleaved into the constituting germylene fragments.^[4] As our recently reported digermenide **1** grants synthetic access to asymmetric Ge-Ge double bonds,^[5] we anticipated that digermenes **2a,b** might be suitable for metathesis reactions. Thermal treatment of **2a,b** (in turn prepared from the nucleophilic digermenide) indeed leads to the selective formation of $\text{Tip}_2\text{Ge}=\text{GeTip}_2$ and the bis-functionalized digermenes **3a** and **3b**, respectively, through intermittent dissociation into the corresponding germylene fragments. As the first example for selective metathesis of heavier multiply bonded species, the reaction proceeds at moderate temperatures and without a transition metal catalyst, paving the way for possible unsaturated hybrid polymers.



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