Effects of introducing various alkyl chains at the bridgehead position of extended triptycyl groups and their application for highly reactive species

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In the structural chemistry of main group element compounds containing reactive chemical bonds, crystal growth is an essential part for the characterization the bonding nature as well as the crystal structure determination. The solubility and crystallinity of the target compounds are key factors in molecular design. We have designed and synthesized an extended triptycyl group, Trp*, which have been used for kinetic stabilization of highly reactive species. It has superior steric protection and large reaction space around reaction center, however, compounds with bulky substituents, such as Trp*, have low solubility and poor crystallinity in some cases. In fact, the synthetic studies of Trp*-substituted germanium compounds initially yielded only crystals that were too small to be analyzed structurally by X-ray diffraction.

Germylenes (R\(_2\)Ge:), divalent species of germanium, are the germanium analogue of carbene and show high reactivity due to their unique electronic state. The isolation of monomeric germylenes has been achieved by the kinetic stabilization with bulky substituents around the Ge [1]. We have succeeded the isolation of the first dialkygermylene (Trp*\(_2\)Ge:) as a thermally stable compound [2]. However, some derivatives of Trp*\(_2\)Ge: had low solubility and crystallinity, making characterization difficult. To improve these problems of Trp* compounds, we focused on the concept of crystal engineering, in which intermolecular interactions are intentionally controlled to design and synthesize solid-state structures with desired properties. [3, 4]. We report here, the synthesis of R\(\text{Trp}^*\) groups having alkyl chains (R= Pr, Bu, Hex, Oct) at the bridge head position of Trp*. (Fig. 1) and applied them to the synthesis of dialkygermylenes (R\(\text{Trp}^*\)\(_2\)Ge:) in the expectation of improving those crystallinities by intermolecular interactions with the packing forces in the solid states. The isolated R\(\text{Trp}^*\)\(_2\)Ge: showed better solubility and crystallinity than the corresponding Trp*\(_2\)Ge:. Especially, Hex\(\text{Trp}^*\)\(_2\)Ge: showed characteristic change in the packing structure to form suitable single crystals for X-ray analysis (Fig. 2). The details of synthesis and structure of R\(\text{Trp}^*\)\(_2\)Ge:, and packing structures in the solid state will be discussed.

![Figure 1](image1.png)

**Figure 1.** Extended triptycyl group: R\(\text{Trp}^*\)

![Figure 2](image2.png)

**Figure 2.** Packing structure of R\(\text{Trp}^*\)\(_2\)Ge: