

Synthesis, Structure and Bonding in Triorganogermyl-alanes and Triphenylgermyl-aluminates

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Triphenylgermyl-lithium in diethyl ether/THF did not react with Al_2Me_6 to form $[(\text{Ph}_3\text{Ge})\text{AlMe}_3]\text{-Li}(\text{THF})_n$. Addition of TMEDA to this solution yielded crystalline $\text{Ph}_3\text{GeLi}(\text{THF})\text{TMEDA}$. The reaction of Ph_3GeLi in diethyl ether/hexane solution with $\text{H}_3\text{Al-NMe}_3$ in diethyl ether/THF generated $[\text{Ph}_3\text{GeAlH}_3]\text{Li}(\text{THF})_4$ while the reaction with Me_2AlCl led to $\text{Ph}_3\text{GeAlMe}_2(\text{OEt}_2)$ and the trigermyl-aluminate $[(\text{Ph}_3\text{Ge})_3\text{AlMe}]\text{Li}$. The analogous aluminate $[(\text{Ph}_3\text{Ge})_3\text{AlH}]\text{Li}(\text{THF})_3$ was obtained by reacting LiGePh_3 with $\text{AlH}_2\text{Cl}(\text{OEt}_2)$ in the presence of THF. It was expected that the bulky bis(tetramethylpiperidino)chloroalane would react with Ph_3GeLi to give the germyl-alane $\text{tmp}_2\text{AlGePh}_3$ which was observed when only diethyl ether was used as a solvent, but in an Et_2O /toluene mixture only Ph_8Ge_3 could be isolated. Increasing the steric requirement of the germyl-lithium compound by using the bulky $(t\text{Bu}_3\text{Si})\text{Me}_2\text{Ge}$ group instead of the Ph_3Ge group led to a straightforward reaction generating the first structurally characterized germyl-alane $(t\text{Bu}_3\text{Si})\text{Me}_2\text{Ge-Al}(\text{tmp})_2$ with a planar tri-coordinated Al center. The X-ray structure determinations showed that the germyl-aluminates have shorter Ge–Al bonds than the germyl-alane in spite of the lower coordination number.

Key words: Triphenylgermyl-aluminates, Triorganogermyl-alanes, X-Ray Structures