Synthesis and Characterization of Novel Titanium, Germanium, and Tin Silazane Complexes Bearing a Cyclohexasilazanetriido Ligand

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Novel heterometallic silazane complexes were synthesized by reactions starting from 1,1,3,3,5,5-hexamethylcyclotrisilazane (H₃(HMCTS)) and MCl₄ (M=Ti, Ge, Sn) under various reaction conditions [1].

\[
\begin{align*}
\text{HN} & \quad \text{Me₂Si} \\
\text{Si} & \quad \text{HN} \\
\text{Me₂Si} & \quad \text{Me₂}
\end{align*}
\]

+ MCl₄ → -3 HCl

\[
\begin{align*}
\text{HN} & \quad \text{Si} & \quad \text{N} & \quad \text{Me₂} \\
\text{Si} & \quad \text{HN} & \quad \text{N} & \quad \text{Me₂} \\
\text{Me₂Si} & \quad \text{Si} & \quad \text{HN} & \quad \text{Me₂Si}
\end{align*}
\]

M= Ti, Ge, Sn

The products \([\text{H₃(DMCHS)TiCl}], [\text{H₃(DMCHS)GeCl}], \text{and} [\text{H₃(DMCHS)SnCl}] \) \{H₃(DMCHS)=2,2,4,4,6,6,8,8,10,10,12,12-dodecamethylcyclohexasilizane-1,5,9-triido\} were obtained as colorless crystalline solids in good yield. Characterization was performed by \(^1\text{H}, ^{13}\text{C}, ^{14}\text{N}, \text{and} ^{29}\text{Si}\) NMR spectroscopy, elemental analyses and single-crystal X-ray structure analyses. Obviously, dimerization of the cyclotrisilazane and elimination of three equivalents of HCl occurs resulting in a dodecamethylcyclohexasilazane system with the Ti, Ge, or Sn atom in the center. These metal atoms are coordinated by one chlorine atom and three nitrogen atoms. They are part of three six-membered hetero-silazane rings.

The formation of the novel cyclohexasilazane framework emphasizes the striking reactivity patterns of \text{H₃(HMCTS)} in reactions with metal chlorides. It marks a new reaction pathway in addition to well-known ring-contraction reactions and substitution reactions of the cyclotrisilazane system [2,3,4]. The titanium and germanium complexes are potentially good candidates to act as single-source precursors for ceramic materials of the quaternary SiCNTi and SiCNGe systems. Furthermore, all three compounds represent valuable starting materials for the syntheses of further cyclohexasilazane derivatives because of their reactive M–Cl bonds.
