could indicate that this strong electrophile\textsuperscript{1b} may be immediately trapped by the germole \textsuperscript{2}, with loss of CO, to give 1, i.e. the germacyclopenteny1 moiety π\textsuperscript{-}coordinated to Co(CO)\textsubscript{5}. Precedents of these reactions have been reported in the action of dienes with metal hydrido complexes.\textsuperscript{14}


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\textbf{Supplementary Material Available:} Listings of crystal data and data collection and refinement details, fractional atomic coordinates, bond distances and angles, and anisotropic thermal parameters (7 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

\begin{center}
\textbf{Synthesis and Solid-State Structure of (Me\textsubscript{3}Si\textsubscript{2})\textsubscript{2}GeCH(SiMe\textsubscript{3})\textsubscript{2}, a Monomeric Dialkylgermylene}
\end{center}

P. Jutzi,\textsuperscript{a} A. Becker, H. G. Stammier, and B. Neumann

Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld, Germany

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\textbf{Summary:} The reaction of Me\textsubscript{2}C\textsubscript{2}GeCH(SiMe\textsubscript{3})\textsubscript{2} with LIG-
(SiMe\textsubscript{3})\textsubscript{2} affords (Me\textsubscript{3}Si)\textsubscript{2}GeCH(SiMe\textsubscript{3})\textsubscript{2} (2), the first unsymmetrically substituted dialkylgermylene, which is stable at ambient temperature. In the solid state, the germylene \textsuperscript{2} is monomeric, whereas Lappert's germylene \[(\text{Me}_{3}\text{Si})_{2}\text{CH}]_{2}\text{Ge} (1)\textsuperscript{1} shows a dimeric structure with a Ge=Ge double bond. Steric effects of the additional trimethylsilyl group in \textsuperscript{2} are responsible for these drastic changes in the structure. The germylene \[(\text{Me}_{3}\text{Si})_{2}\text{CH}_{2}\text{Ge}(\text{SiMe}_{3})_{2}\] (3) decomposes at about \(-20 \text{ °C}\).

Germynes—the germanium analogues of carbenes—have been extensively studied during the last 15 years.\textsuperscript{1} Most of these compounds are unstable under normal conditions and thus have been used as reactive intermediates.\textsuperscript{2} A noticeable stabilization is possible by using π-ligands\textsuperscript{3} or bulky ligands such as \(-\text{NR}_{2}\), \(-\text{OR}\), or \(-\text{SR}\);\textsuperscript{4} compounds of this type are stable at ambient temperature, and some of them are monomeric in the solid state and in the gas phase. In the class of dialkylgermylenes, the stable complex \[(\text{Me}_{3}\text{Si})_{2}\text{CH}_{2}\text{Ge} (1)\textsuperscript{1} was described in 1976 by Lappert and co-workers.\textsuperscript{5} This species has interesting structural features: It is a monomer in solution and in the gas phase\textsuperscript{6} and a dimer in the solid state. The

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{X-ray structure of (Me\textsubscript{3}Si\textsubscript{2})CHGeC(SiMe\textsubscript{3})\textsubscript{2} (2). Selected bond distances (Å) and angles (deg): Ge(1)-C(1)-C(2) = 1.871 (6), Ge(1)-C(1)-Si(1) = 115.2 (3), Ge(1)-C(1)-Si(2) = 117.4 (3), Ge(1)-C(1)-Si(3) = 95.2 (2), Ge(1)-C(1)-Si(4) = 109.0 (3), Ge(1)-C(1)-Si(5) = 117.4 (3).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image2.png}
\caption{Unit cell diagram of (Me\textsubscript{3}Si\textsubscript{2})CHGeC(SiMe\textsubscript{3})\textsubscript{2} (2).}
\end{figure}

dimerization is caused by a Ge-Ge interaction that has been interpreted as a new type of double bond.\textsuperscript{7} Up to
now, compound 1 still is the only known dialkygermylene stable at ambient temperature.

Here we wish to report the synthesis and structure of (Me₅Si)₃CGeCH(SiMe₃)₂ (2), a stable dialkygermylene that differs drastically from 1 in its solid-state structure.

According to our experience in germanocene and stannocene chemistry, a possible route to 2 was the nucleophilic substitution of a Me₅C₆ ligand in the π-complex Me₅C₆GeCH(SiMe₃)₂ (4). Thus, reaction of 4 with (Me₅Si)₂Cl·2THF affords, after subsequent workup, red-orange crystals of 2 in 65% yield. The germylene 2 sensibly to air and temperature gave a soluble in aprotic solvents. It can be recrystallized from hexane.

As proved by MS data, 2 is a monomer in the gas phase. Interestingly, the X-ray diffraction study shows that the monomeric structure is preserved also in the solid state (see Figure 1). The two alkyl ligands stabilize a V-shaped molecule with a bonding angle of 111.3° at the Ge atom.

The germanium–carbon distances are 2.012 Å for Ge–CH(SiMe₃)₂ and 2.067 Å for Ga–C(SiMe₃)₂. The shortest distance between the two Ge centers is 5.704 Å, indicating that there is no bonding interaction between these atoms (Figure 2). Furthermore, the orientation of the germylene monomers excludes such an interaction.

We believe that steric reasons are responsible for the monomeric structure of 2. In Lapert’s germylene 1, one of the two bis(trimethylsilyl)methyl ligands at each Ge center has to adopt a conformation in which the C–H bond is oriented in the direction of the Ge–Ge bond, thus minimizing repulsive effects between the two monomer units and allowing a weak bonding interaction (bond energy 20 kJ mol⁻¹). In the germylene 2, a conformation comparable to that in 1 is not possible. The additional trimethylsilyl group in the (Me₅Si)₃C ligand forces the (Me₅Si)₃HC ligand in a position with a trimethylsilyl group being in the direction of a hypothetical Ge–Ge bond. In this orientation a Ge–Ge bonding interaction is prohibited by steric requirements.

In the crystal structure of 2 a disorder is observed, which is caused by a rotation of the (Me₅Si)₃C ligand around the Ge–C bond. This rotation does not have steric consequences, due to the high symmetry of this ligand. On the other side, the (Me₅Si)₃HC ligand remains in a fixed position; this is in accord with the steric constraints in this molecule.

Comparable to the synthesis of 2, we have prepared the germylene Me₅SiCH₂GeCH(SiMe₃)₂ (3) by reaction of 4 with Me₅SiCH₂Li. This compound is stable only up to −20 °C and has been trapped in form of its [2 + 4] cycloaddition product (5) with 2,3-dimethylbutadiene.

In a comparison of the dialkygermylenes 1, 2, and 3, it is evident that the number of trimethylsilyl groups in the alkyl ligands drastically influences the thermal stability and the solid-state structure of this class of compounds.

Supplementary Material Available: Listings of crystal data and structure determination and refinement details, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters for compound 2 (9 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.