Synthesis and characterization of a germanium bismethanediide complex[†]

Cechao Foo,^a Kai-Chung Lau,^b Yi-Fan Yang^a and Cheuk-Wai So^{*a}

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The reaction of $[(PPh_2=S)_2CH_2]$ (1) with MeLi followed by a salt elimination reaction with GeCl₄ in toluene afforded a novel germanium bismethanediide complex, 2. The structure of compound 2 has been determined by X-ray crystallography. The topological analysis of the electron densities of compound 2 was performed.

Compounds containing a double bond between carbon and heavier group 14 elements (>M=C<; M = Si, Ge, Sn) have attracted much attention in the past 20 years, and have been the focus of several reviews.¹ It was found that the thermal stability of the M=C bond is intrinsically low, and it can undergo oligomerization readily. Nevertheless, stable silenes (>Si=C<),² germenes $(>Ge=C<)^3$ and stannenes $(>Sn=C<)^4$ can be synthesized by incorporating sterically hindered substituents at both carbon and heavier group 14 elements. In contrast, heavier allene analogues with >M=C=C< or >C=M=C< skeletons are rare.⁵ Until now, only two examples of 1-germaallenes have been synthesized by the reaction of t-BuLi with a fluorogermylalkyne or by the dechlorination of dichlorogermapropene with t-BuLi.⁶ On the other hand, 2-germaallene (>C=Ge=C<) is still unknown. Theoretical studies of heavier group 14 allene analogues showed that 2-germaallene is highly unstable due to the presence of two reactive Ge=C double bonds.⁷

In this communication, we report the synthesis and characterization of a novel germanium bismethanediide complex, 2, which is regarded as a spirocyclic derivative of 2-germaallene.

The reaction of **1** with two equivalents of MeLi in toluene followed by addition of 0.5 equivalents of GeCl₄ afforded compound **2** (Scheme 1).⁸ Other examples consisting of the >C=M=C < skeleton derived from a bis(phosphinoyl)methanediide ligand are [(PMe₂=NSiMe₃)₂C=Zr=C(PMe₂= NSiMe₃)₂]⁹ and Li(THF)₄[(PPh₂=S)₂C=Sm=C(PPh₂=S)₂].¹⁰

Compound **2** was isolated as a colorless crystalline solid which is soluble in CH_2Cl_2 and THF only. It has been characterized by NMR spectroscopy and elemental analysis.¹¹ The ¹H and ¹³C NMR spectra display resonances for the phenyl protons. It is noteworthy that there is no ¹³C NMR



Scheme 1 Synthesis of 2.

signal for the carbenic carbon. Similarly, there is no ¹³C NMR signal for the carbenic carbon in $[(PPh_2=S)_2C=Pd(PPh_3)]$.¹² The ³¹P NMR spectrum at room temperature or at -60 °C shows one signal (δ 33.7 ppm) which is inconsistent with the solid-state structure. It is suggested that two thiophosphinoyl substituents of each ligand could be coordinated with the germanium center in the solution and the structure should be similar to that of $[(PPh_2=S)_2C=Tm=C(PPh_2=S)_2]^{-13}$ The solid-state ³¹P CP/MAS NMR spectrum displays two signals (δ 4.72, 6.05 ppm) due to two non-equivalent phosphorus nuclei.

The molecular structure of compound **2** is shown in Fig. 1.¹⁴ It consists of two bidentate bis(thiophosphinoyl)methanediide ligands bound to the germanium center in a spirocyclic fashion. One of the thiophosphinoyl groups of the ligand remains uncoordinated. The C(1)–Ge(1) bond distance (1.882(2) Å) is significantly longer than the theoretical calculations for



Fig. 1 Molecular structure of 2. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)–Ge(1) 1.882(2), C(1)–P(1) 1.747(2), C(1)–P(2) 1.723(2), P(1)–S(1) 1.964(6), P(2)–S(2) 2.060(6), Ge(1)–S(2) 2.325(4); C(1)–Ge(1)–C(1A) 142.6(1), S(2)–Ge(1)–S(2A) 114.1(3), C(1)–Ge(1)–S(2) 85.3(5), C(1A)–Ge(1)–S(2) 115.5(5), Ge(1)–C(1)–P(2) 99.0(8), Ge(1)–C(1)–P(1) 131.3(9), P(2)–C(1)–P(1) 128.0(9).

^a Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371. E-mail: CWSo@ntu.edu.sg;

Fax: +65 6791 1961; Tel: +65 6513 2730

^b Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

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Å),^{7a} $[{(Me_3Si)_2N}_2]$ $[H_2C = Ge = CH_2]$ (1.745 - 1.795)Ge=C(Bt-Bu)₂C(SiMe₃)₂] (1.827(4) Å)^{3a} and [Mes₂Ge=CR₂] (Mes = 2,4,6-trimethylphenyl, CR_2 = fluorenylidene) (1.803 Å),^{3b} but it is shorter than that of bisgermavinylidene $[(PPh_2 = NSiMe_3)_2C = Ge:]_2$ (1.908(7), 1.905(8) Å) due to the higher oxidation state of the germanium atom in 2^{15} This demonstrates some double bond character in the C(1)-Ge-C(1A) skeleton. The differences in the P-S and C-P bond distances in 2 suggest the delocalization of π -electrons resulted from the conjugation of P=S and C=Ge double bonds, which lengthens the C=Ge double bond distance. The C(1)-Ge(1)-C(1A) angle (142.6(1)°) is smaller than the theoretical studies of $[H_2C = Ge = CH_2]$ (153–173°) as two thiophosphinovl substituents coordinate to Ge(1) at a distance of 2.325(4) Å.⁷ The sum of the angles at C(1) in $\mathbf{2}$ is 358.3° which is in good agreement with that of $[H_2C = Ge = CH_2]$ (355.4–360°). The C(1)–P(1) (1.747(2) Å) and C(1)-P(2) (1.723(2) Å) bonds in 2 are longer than those in $[(PPh_2=S)_2C=ZrCp_2]$ (1.670(2), 1.666(2) Å),¹⁶ $[(PPh_2=S)_2C=Tm(THF)_2(\mu-I)]_2$ (1.661(5), 1.653(5) Å)¹³ and $[(PPh_2=S)_2C=Pd(PPh_3)]$ (1.689(2), 1.690(2) Å)¹² which result from the negative hyperconjugation from carbon to phosphorus σ^* orbitals.

Compound 2 was investigated by means of quantum chemical calculations. The molecule was first fully optimized with the DFT-variant B3LYP¹⁷ as implemented in the Gaussian 03 program¹⁸ using the 6-31+G(d) basis set.¹⁹ The calculated structural parameters (Ge(1)-S(2): 2.379 Å, Ge(1)–C(1): 1.888 Å, Ge(1)–P(2): 2.789 Å, P(2)–S(2): 2.095 Å, C(1)-P(1): 1.749 Å; C(1)-Ge(1)-C(1A): 142.0°) are in good agreement with the crystallographic data. The naturalbond-orbital (NBO) analysis²⁰ (Table S1, see ESI[†]) shows that the Ge(1)-C(1) bond is formed by $sp^{1.85}$ hybrids on the germanium atom and sp^{2.22} hybrids on the carbon atom, with the carbon atom contributing 71.8% of the electron density. For simplification, 2A (Fig. 2) is applied as a model for the theoretical calculations of compound 2. The calculated structural parameters of optimized 2A (Ge-S: 2.371 Å, Ge-C: 1.877 Å, Ge-P: 2.760 Å, P-S: 2.094 Å, C-P: 1.727 Å; C-Ge-C: 133.6°) are also comparable with the crystallographic data of 2. When the C-Ge-C angle is 180.0° and the P, C, S and Ge atoms are constrained on the same plane, the resulting structure is more unstable by 43.1 kJ/mol than 2A. When both sulfur donors are not coordinated with the germanium atom, the optimized structure 2B (Ge-C: 1.789 Å, P-S: 1.959 Å, C-P: 1.825 Å; C-Ge-C: 153.9°) is higher in energy than 2A by 218.8 kJ/mol. It is noteworthy that the Ge-C bond (1.789 Å) in 2B is similar to that in $[H_2C = Ge = CH_2]$ (1.745–1.795 Å). The coordination of the sulfur donors with the germanium atom in 2A leads to the delocalization of π -electrons, which lengthens the Ge=C double bond distance (1.877 Å).



Fig. 2 Simple derivative of **2**.

Table 1 Theoretical topological features at the BCP of 2, $[H_2C=Ge=CH_2]$ and $[H_3C-GeH_2-CH_3]^a$

Bond	ρ	$\nabla^2 \rho$	Н	G	V
2					
Ge(1)-C(1)	0.9	3.10	-0.52	0.74	1.26
C(1) - P(2)	1.21	-0.77	-1.22	1.16	2.38
P(2)-S(2)	0.93	-5.25	-0.60	0.24	0.84
Ge(1) - S(1)	0.51	1.28	-0.20	0.29	0.49
C(1) - P(1)	1.14	-0.04	-1.11	1.11	2.21
[H ₂ C=Ge=C	$[H_2]$				
Ge-C	1.10	5.24	-0.70	1.06	1.76
[H ₃ C-GeH ₂ -C	CH ₃				
Ge–C	0.84	2.85	-0.47	0.67	1.14
^{<i>a</i>} Units: ρ : e Å	Λ^{-3} ; $\nabla^2 \rho$: e	Å ⁻⁵ ; <i>H</i> , <i>G</i> ,	V : hartree	$\mathbf{\dot{A}}^{-3}$.	

The topological analysis of the electron densities of compound **2**, $[H_2C==Ge==CH_2]$ and $[H_3C-GeH_2-CH_3]$ according to Bader's quantum theory of atoms in molecules (QTAIM) was performed.²¹ The Laplacian of electron density $\nabla^2 \rho$ and the total energy density *H* at the (3,-1) bond critical



Fig. 3 $\nabla^2 \rho$ in the GeCH planes in (a) CH₃–GeH₂–CH₃ and (b) CH₂==Ge==CH₂; (c) $\nabla^2 \rho$ in the GeCS plane of compound 2. Green lines indicate negative values in $\nabla^2 \rho$, black lines stand for positive values.

point (BCP) show that the Ge–C bonds in compound 2, $[H_2C=Ge=CH_2]$ and $[H_3C-GeH_2-CH_3]$ are polar and covalent (Table 1). The bond nature of the Ge–C bonds in compound 2 is in-between that of Ge=C in $[H_2C=Ge=CH_2]$ and that of Ge–C in $[H_3C-GeH_2-CH_3]$. As there may be substantive π -electron delocalization along the Ge–C bonds in compound 2, it is unsurprising to find that the Ge–C bonds in compound 2 may have little double bond character compared with the Ge=C bond in $[H_2C=Ge=CH_2]$. Fig. 3(a)–(c) depict the Laplacian distributions in the GeCH planes of $[CH_3-GeH_2-CH_3]$ and $[CH_2=Ge=CH_2]$ and in the GeCS plane of compound 2, respectively. It reveals that the bonding nature of the Ge=C bond in $[CH_2=Ge=CH_2]$ and in compound 2 are similar.

In conclusion, the first example of a germanium bismethanediide compound, **2**, has been synthesized successfully by the reaction of **1** with two equivalents of MeLi in toluene, followed by reaction with 0.5 equivalents of GeCl₄. X-Ray crystallography shows that the Ge–C bonds in compound **2** have double bond character. DFT calculations show that the coordination of the sulfur donors with the germanium atom in **2** leads to the delocalization of π -electrons, which lengthens the Ge=C double bond distance. Topological analysis of the electron densities shows that the Ge–C bonds in **2** are polar and covalent and their bond nature is between a single and double bond.

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