

A Blue Digermene (t-Bu₂MeSi)₂Ge=Ge(SiMe_t-Bu₂)₂

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A Blue Digermene (*t*-Bu₂MeSi)₂Ge=Ge(SiMet-Bu₂)₂

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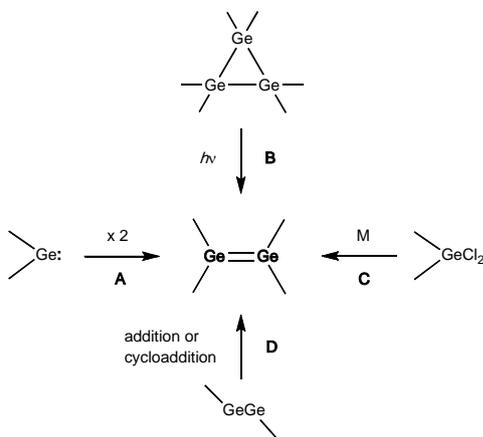
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A novel tetrakis(trialkylsilyl)digermene, featuring rather unusual structural and chemical properties, was synthesized by a straightforward synthetic protocol: reduction of the corresponding dichlorobis(trialkylsilyl)germane precursor with potassium graphite.

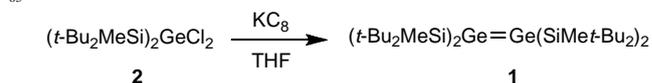
Stable digermenes, that is, heavy alkene analogues featuring Ge=Ge bonds, have been known since the 1976 pioneering report by Lappert's group on the first isolable Dis₂Ge=GeDis₂ [Dis = CH(SiMe₃)₂].¹ Since then and up to date, about forty digermenes (both acyclic and cyclic) have been described as room temperature stable compounds, whose solid-state structures in a majority of cases were determined by X-ray crystallography.² Whereas cyclic digermenes were synthesized by particular methods, their acyclic analogues are available by four general synthetic routes: 1) dimerization of germynes (A), 2) photolysis of cyclotrigermenes (B), 3) reductive dehalogenation of 1,1-dichlorogermenes (C), 4) 1,2-addition or cycloaddition to the heavy analogues of a digermene (D) (Scheme 1).^{2c} Of these methods, route C employing 1,1-dichlorogermenes as readily available starting materials is one of the most widely used. In this contribution, we describe the synthesis of a novel tetrakis(trialkylsilyl)digermene³ prepared by route C, its unusual reactivity and its application for the synthesis of a synthetically very useful 1,1-dilithio-germane derivative.



Scheme 1 Synthetic routes to stable digermenes >Ge=Ge<.

The target tetrakis(di-*tert*-butylmethylsilyl)digermene (*t*-Bu₂MeSi)₂Ge=Ge(SiMet-Bu₂)₂ **1** was readily available by the straightforward reductive dechlorination of the 1,1-

dichlorogermene precursor (*t*-Bu₂MeSi)₂GeCl₂ **2**⁴ with potassium graphite (Scheme 2). Although the crude solid product could be directly used for the following reactions, it can be further purified by glove-box column chromatography (dry silica gel/hexane) followed by recrystallization from hexane to obtain analytically pure **1** as sapphire-blue hexagonal shaped crystals in 91% yield. Reflecting its symmetrical composition, **1** showed one set of signals for the silyl substituents in its ¹H, ¹³C and ²⁹Si NMR spectra. Analytical data are also in agreement with the formulation of **1** as a digermene.



Scheme 2 Synthesis of a digermene **1**.

1 has a very unusual deep-blue color, in sharp contrast to all other isolable digermenes, including cyclic derivatives, which are yellow, orange or red. Accordingly, the longest wavelength absorption maximum in the UV-Vis spectrum of **1** measured in hexane was observed at 618 nm (ϵ : 3200), which did not change upon lowering the measurement temperature to -70 °C (in 3-methylpentane).⁵ We assigned the observed absorption to a π (HOMO)- π^* (LUMO) electronic transition of the Ge=Ge bond because the absorption corresponding to the *n*-*p* transition of bis(silyl)germylenes, such as (*t*-Bu₂MeSi)₂Ge:, is expected to be observed at a much greater wavelength. Although reliable electronic spectra for bis(trialkylsilyl)germylenes have not been reported, one can expect the appearance of their *n*-*p* electronic transitions in a region similar to that calculated for the bis(trialkylsilyl)silylenes, 987 nm for (Me₃Si)₂Si: (lowest energy ¹A₁ → ¹B₁ electronic transition).⁶ Our own computations on the optimized structure of the model singlet bis(silyl)germylene (Me₃Si)₂Ge: gave us a similar value of 1005 nm for its *n*(HOMO)-*p*(LUMO) electronic transition (compared with values of 512 nm calculated for the singlet Me₂Ge: and 517 nm for the singlet Ph₂Ge:).⁷ Moreover, given the well-defined effect of the bond angle R-E-R (E = heavy group 14 element) around the carbene center on the first electronic transition (namely, destabilization of the ¹A₁ ground state and stabilization of the ¹B₁ excited state),⁸ one should expect the lowest *n*-*p* UV absorption for the real (*t*-Bu₂MeSi)₂Ge: germylene to appear in an even more red-shifted region than that calculated for the model (Me₃Si)₂Ge: germylene (1005 nm) because of the larger steric bulk of the

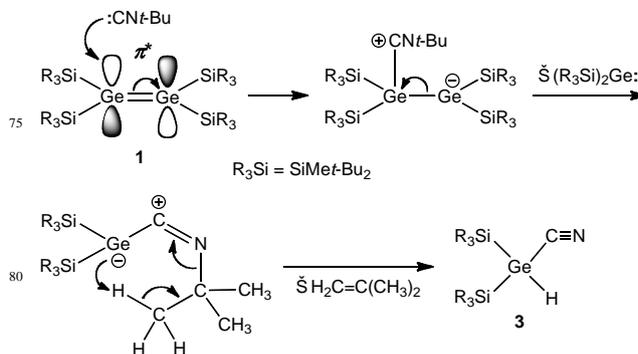
silyl substituents in the former.

Thus, electronic spectral data of **1** indicate that it does not dissociate into germylenes in solution, retaining the integrity of its Ge=Ge bond.⁵ Moreover, the absorption at 618 nm did not show any changes when the UV-Vis spectrum of **1** was measured in THF; this observation further supporting the presence of a Ge=Ge bond rather than germylenes in solution, given the well-known tendency of the UV absorptions of germylenes to undergo remarkable blue shifts upon their complexation with Lewis bases.⁹ The absorption value of 618 nm of **1** is remarkably red-shifted compared with those of other stable digermenes that retain their structural integrity in solution (412–475 nm).² Several reasons may contribute to this unusual bathochromic shift, all originating from the extreme twisting of the Ge=Ge bond in **1**.^{10,11} First of all, such twisting would result in a markedly reduced $4p_{\pi}-4p_{\pi}$ orbital overlap, which destabilizes the HOMO of the molecule. Even more importantly, this partial breaking of the Ge=Ge π -bond that takes place upon its twisting would be expected to result in a progressively increasing contribution of the biradical character to the germanium–germanium bonding in **1**. This, in turn, would lead to an increase in the HOMO and a decrease in the LUMO energy levels, resulting in an overall decrease in the HOMO–LUMO energy gap. On the other hand, such highly distorted structure of **1** featuring some biradical contribution may gain an additional stabilization through the $4p_{\pi}(\text{Ge})-\sigma^*(\text{Ge}-\text{Si})$ orbital mixing, which can be activated upon the twisting of the Ge=Ge bond.

Whereas the extraordinary twisting of the Ge=Ge bond apparently stems from the important steric interaction between the bulky silyl substituents, the other remarkable structural feature of **1**, namely, planarity at the sp^2 -germaniums, may result from an alkene-type interaction mode between the two triplet germylene fragments.^{2c} Indeed, our previous studies on the structurally similar tetrakis(*di-tert*-butylmethylsilyl)distannene ($t\text{-Bu}_2\text{MeSi})_2\text{Sn}=\text{Sn}(\text{SiMe}t\text{-Bu}_2)_2$ showed that its peculiar structural features (planarity at sp^2 -Sn's and highly twisted Sn=Sn bond) can be explained by the interaction of the two triplet stannylene fragments ($t\text{-Bu}_2\text{MeSi})_2\text{Sn}$.¹² The triplet state of these stannylenes can be easily accessed because of their relatively small singlet–triplet energy gap $\Delta E_{S-T} = 8.5$ kcal/mol in favor of the singlet state (B3LYP/SDD level), caused by both the steric and electronic effects of the bulky σ -donating silyl substituents.^{12b} One can expect analogous energetic accessibility of the triplet state for the homologous bis(silyl)germylene ($t\text{-Bu}_2\text{MeSi})_2\text{Ge}$.

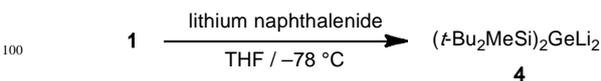
The particular structural motif of the novel digermene **1** featuring a highly twisted Ge=Ge bond markedly altered its reactivity, which does not conform to that of common digermenes.^{2a,b} Thus, as was established by UV studies (vide supra), **1** does not manifest any signs of dissociation into germylenes in solution at room temperature, which was supported by the absence of trapping products with such typical germylene scavengers as triethylsilane and 2,3-dimethylbuta-1,3-diene. On the other hand, **1** behaves as a germylene source while reacting with strongly nucleophilic Lewis bases, such as isonitriles. For example, **1** readily reacts with both *tert*-butyl isonitrile $t\text{-BuNC}$: and 1,1,3,3-

tetramethylbutyl isonitrile ($(\text{H}_3\text{C})_3\text{CCH}_2(\text{CH}_3)_2\text{CNC}$: forming the same formal insertion product **3** along with an equivalent amount of $\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$ (or $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$) (Scheme 3).¹³ Given the highly twisted configuration of the Ge=Ge bond, one can suggest an $n(\text{isonitrile lone pair})-\pi^*(\text{Ge}=\text{Ge bond})$ orbital interaction as the initial step of the reaction, followed by splitting of the Ge–Ge bond and elimination of $\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$ (or $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$) to produce the final formal germylene insertion product **3** (Scheme 3).¹⁴ Thus, **1** represents a unique case of a digermene that does not dissociate into germylenes in solution but behaves as a germylene under appropriate conditions.



Scheme 3 Proposed pathway for the reaction of a digermene **1** with isonitriles RNC : ($\text{R} = t\text{-Bu}$, $(\text{H}_3\text{C})_3\text{CCH}_2(\text{CH}_3)_2\text{C}$), forming formal germylene insertion product **3**; reaction with *tert*-butyl isonitrile is shown as a representative example.

In addition to the specific reactivity of **1** described above, it can be effectively used for the generation of the synthetically very useful 1,1-dilithiogermylene derivative ($t\text{-Bu}_2\text{MeSi})_2\text{GeLi}_2$ **4** (Scheme 4),^{15,16} which was previously prepared by a much more complicated procedure; namely, by the reduction of the hard to prepare germyrene $\text{cyclo}[-(t\text{-Bu}_2\text{MeSi})_2\text{Ge}-\text{C}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)-]$ with metallic lithium. Other examples of novel types of reactivity of digermene **1** are under current investigation.



Scheme 4 Synthetic utility of a digermene **1**.

Notes and References

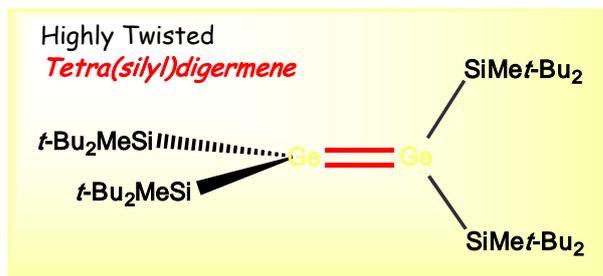
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† Electronic Supplementary Information (ESI) available: Experimental procedures and spectroscopic data for compounds **3** and **4**. See DOI: 10.1039/b000000x/

‡ *Synthesis of digermene 1*: A mixture of dichlorogermylene **2** (2.00 g, 4.36 mmol) and potassium graphite (1.33 g, 9.81 mmol) was placed in a Schlenk tube with a magnetic stirring bar. Dry oxygen-free THF (30 ml) was introduced into this tube by vacuum transfer, and the resulting reaction mixture was stirred for 1 h at -78 °C, then gradually warmed to

- room temperature and stirred for an additional 2 h. The reaction mixture was filtered from the graphite and the solvent was removed under vacuum. The deep blue solid residue was dissolved in hexane, and the target compound **1** was isolated by glove-box column chromatography on silica gel (eluent: hexane) as sapphire-blue air- and moisture-sensitive crystals (1.54 g, 91% yield). Mp. 201–202 °C (dec). ¹H NMR (C₆D₆): δ 0.72 (s, 12 H, CH₃), 1.27 (s, 72 H, C(CH₃)₃). ¹³C NMR (C₆D₆): δ 1.61 (CH₃), 25.35 (C(CH₃)₃), 31.61 (C(CH₃)₃). ²⁹Si NMR (C₆D₆): δ 30.56. UV–Vis (hexane) λ_{max}/nm (ε) 283 (10900), 369 (5700), 618 (3200). Anal. calc. for C₃₆H₈₄Ge₂Si₄: C, 55.82; H, 10.93. Found: C, 55.50; H, 10.75.
- (a) D. E. Goldberg, D. H. Harris, M. F. Lappert and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1976, 261. (b) P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
 - Recent reviews on stable digermenes: (a) K. W. Klinkhammer, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, ed. Z. Rappoport, John Wiley & Sons, Ltd, Chichester, 2002, vol. 2, part 1, ch. 4, p. 283. (b) N. Tokitoh and R. Okazaki, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, ed. Z. Rappoport, John Wiley & Sons, Ltd, Chichester, 2002, vol. 2, part 1, ch. 13, p. 843. (c) V. Ya. Lee and A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn, Pb: From Phantom Species to Stable Compounds*, John Wiley & Sons, Ltd, Chichester, 2010, chapter 5.
 - Persilysubstituted digermenes are rare and only three of them have been previously reported: M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto and H. Sakurai, *Organometallics*, 1996, **15**, 3767.
 - V. Ya. Lee, M. Ichinohe and A. Sekiguchi, *J. Organomet. Chem.*, 2003, **685**, 168.
 - Similarly to Lappert's Dis₂Ge=GeDis₂, some other digermenes are reported to be in equilibrium with the corresponding germlylenes in solution, as was confirmed by studies of their UV–Vis spectra and germylene trapping reactions (see ref. 2c). For example, orange digermene (*E*)-Tbt(Mes)Ge=Ge(Tbt)Mes with very bulky Mes (2,4,6-Me₃-C₆H₂) and Tbt (2,4,6-[(Me₃Si)₂CH]₃-C₆H₂) substituents retains its Ge=Ge bond in solution only at low temperatures (π–π*: 439 nm at 190 K), while it undergoes dissociation into blue germlylenes Tbt(Mes)Ge: at room temperature (n–p: 575 nm at 295 K): N. Tokitoh, K. Kishikawa, R. Okazaki, T. Sasamori, N. Nakata and N. Takeda, *Polyhedron*, 2002, **21**, 563.
 - Y. Apeloig, M. Karni, R. West and K. Welsch, *J. Am. Chem. Soc.* 1994, **116**, 9719.
 - UV TD-DFT computations of the model compounds were performed at the UB3LYP/6-31G(d) level with the GAUSSIAN 03 set of programs.
 - Y. Apeloig and M. Karni, *J. Chem. Soc., Chem. Commun.* 1985, 1048.
 - UV absorption of the free Mes₂Ge: (550 nm) in 3-methylpentane at 77 K was remarkably blue-shifted (360 nm) upon its complexation with *n*-donor ligands, such as 2-Me-THF: (a) W. Ando, H. Itoh, T. Tsumuraya and H. Yoshida, *Organometallics*, 1988, **7**, 1880. (b) W. Ando, H. Itoh and T. Tsumuraya, *Organometallics*, 1989, **8**, 2759. (c) See also ref. 2c (chapter 4).
 - Preliminary X-ray data of digermene **1** revealed rather long Ge=Ge bond distance of 2.346(2) Å, nearly planar geometry at the sp²-Ge centers (sum of the bond angles 359.2° and 358.8°), and extreme twisting of the Ge=Ge bond (52.8°). However, we do not discuss the structural characteristics of **1** in detail because of insufficiently good refinement of its X-ray measurement.
 - The remarkable twisting of the Ge=Ge bond in **1** is particularly noteworthy in view of the absolutely untwisted configuration of the Ge=Ge bonds in previously reported tetrakis(trialkylsilyl)digermenes (*i*-Pr₃MeSi)₂Ge=Ge(SiMei-Pr₂)₂ and (*i*-Pr₃Si)₂Ge=Ge(Si-Pr₃)₂ (see ref. 3). Such pronounced structural differences between **1** and the above-mentioned tetra(silyl)digermenes are most likely due to the substantially greater steric hindrances in **1** caused by the very bulky *t*-Bu₂MeSi-substituents. This trend is quite parallel to that of the homologous tetra(silyl)disilenes: (*i*-Pr₂MeSi)₂Si=Si(SiMei-Pr₂)₂, (*i*-Pr₃Si)₂Si=Si(Si-Pr₃)₂ and (*t*-BuMe₂Si)₂Si=Si(SiMe₂*t*-Bu)₂ are almost undistorted (twist angles = 0–8.9°) [M. Kira, T. Maruyama, C. Kabuto, K. Ebata and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1489], whereas their bulkier substituted analogue (*t*-Bu₂MeSi)₂Si=Si(SiMe*t*-Bu)₂ is extraordinarily twisted by 54.5° [A. Sekiguchi, S. Inoue, M. Ichinohe, Y. Arai, *J. Am. Chem. Soc.*, 2004, **126**, 9626].
 - (a) T. Fukawa, V. Ya. Lee, M. Nakamoto and A. Sekiguchi, *J. Am. Chem. Soc.*, 2004, **126**, 11758. (b) V. Ya. Lee, T. Fukawa, M. Nakamoto, A. Sekiguchi, B. L. Tumanskii, M. Karni and Y. Apeloig, *J. Am. Chem. Soc.*, 2006, **128**, 11643.
 - An analogous pathway was observed in the reaction of a very sterically congested disilene Tbt(Mes)Si=Si(Mes)Tbt with *tert*-butyl isonitrile, although in contrast to the case of digermene **1** this thermal reaction (70 °C) proceeded via the initial dissociation of the Si=Si bond and formation of a silylene Tbt(Mes)Si: N. Takeda, T. Kajiwara, H. Suzuki, R. Okazaki and N. Tokitoh, *Chem. Eur. J.*, 2003, **9**, 3530.
 - The possibility of a similar mechanism in the reaction of an anionic gallium *N*-heterocyclic carbene with tetramesityldigermene was recently discussed: P. A. Rupar, M. C. Jennings and K. M. Baines, *Can. J. Chem.*, 2007, **85**, 141.
 - A. Sekiguchi, R. Izumi, S. Ihara, M. Ichinohe and V. Ya. Lee, *Angew. Chem. Int. Ed.*, 2002, **41**, 1598.
 - Synthetic application of 1,1-dilithiogermene derivative (*t*-Bu₂MeSi)₂GeLi₂ **4**: (a) N. Nakata, R. Izumi, V. Ya. Lee, M. Ichinohe and A. Sekiguchi, *Chem. Lett.*, 2005, **34**, 582. (b) V. Ya. Lee, H. Yasuda, M. Ichinohe and A. Sekiguchi, *Angew. Chem. Int. Ed.*, 2005, **44**, 6378. (c) V. Ya. Lee, H. Yasuda, M. Ichinohe and A. Sekiguchi, *J. Organomet. Chem.*, 2007, **692**, 10. (d) N. Nakata, R. Izumi, V. Ya. Lee, M. Ichinohe and A. Sekiguchi, *Chem. Lett.*, 2008, **37**, 1146. (e) V. Ya. Lee, M. Kawai, A. Sekiguchi, H. Ranaivonjatovo and J. Escudié, *Organometallics*, 2009, **28**, 4262.

Graphical Abstract:



The synthesis, unusual structural and chemical properties of a novel tetrakis(trialkylsilyl)digermene ($t\text{-Bu}_2\text{MeSi}$)₂Ge=Ge(SiMe₂t-Bu₂)₂ are presented in this communication.