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

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A Blue Digermene (t-Bu₂MeSi)₂Ge=Ge(SiMe₅-Bu₂)₂

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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. 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. Whereas cyclic digermenes were synthesized by particular methods, their acyclic analogues are available by four general synthetic routes: 1) dimerization of reductive dehalogenation of 1,1-dichlorogermanes (C), 2) photolysis of cyclotrigermanes (A), 3) reductive dehalogenation of 1,1-dichlorogermanes (C), 4) 1,2-addition or cycloaddition to the heavy analogues of a digermene (D) (Scheme 1). Of these methods, route C employing 1,1-dichlorogermanes as readily available starting materials is one of the most widely used. In this contribution, we describe the synthesis of a novel tetrakis(trialkylsilyl)digermene prepared by route C, its unusual reactivity and its application for the synthesis of a synthetically very useful 1,1-dilithiogermylene derivative.

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

The target tetrakis(di-tert-butyldimethylsilyl)digermene (t-Bu₂MeSi)₂Ge=Ge(SiMe₇-Bu₂)₂ 1 was readily available by the straightforward reductive dechlorination of the 1,1-dichlorogermylene (t-Bu₂MeSi)₂GeCl₂ 2 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). 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). 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:). 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), 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. 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 supports 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. 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). Several reasons may contribute to this unusual bathochromic shift, all originating from the extreme twisting of the Ge–Ge bond in 1. First of all, such twisting would result in a markedly reduced π–π 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 4pπ(Ge)–σ*(Ge–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 sp²-germaniums, may result from an alkene-type interaction mode between the two triplet germylene fragments. Indeed, our previous studies on the structurally similar tetrakis(di-tert-butylmethylsilyl)dianosilane (t-Bu₂MeSi)₄SnSn=(SiMet-Bu₂)₂ showed that its peculiar structural features (planarity at sp²-Sn’s and highly twisted Sn=Sn bond) can be explained by the interaction of the two triplet stannylene fragments (t-Bu₂MeSi)₄Sn. The triplet state of these stannylene can be easily accessed because of their relatively small singlet–triplet energy gap ΔEₛ–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.

One can expect analogous energetic accessibility of the triplet state for the homologous bis(silyl)germylene (t-Bu₂MeSi)₂Ge:. 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. 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 triethyilsilane 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-BuNC: and 1,1,3,3-tetramethylbutyl isonitrile (H₃C)₃CCH₂(CH₃)₂CNC: forming the same formal insertion product 3 along with an equivalent amount of H₂C=C(CH₃)₂ (or H₂C=C(CH₃)CH₂C(CH₃)₃) (Scheme 3). Given the highly twisted configuration of the Ge–Ge bond, one can suggest an n(isonitrile lone pair)–π*(Ge–Ge bond) orbital interaction as the initial step of the reaction, followed by splitting of the Ge–Ge bond and elimination of H₂C=C(CH₃)₂ (or H₂C=C(CH₃)CH₂C(CH₃)₃) to produce the final formal germylene insertion product 3 (Scheme 3). 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.

In addition to the specific reactivity of 1 described above, it can be effectively used for the generation of the synthetically very useful (t-Bu₂MeSi)₄GeLi: which was previously prepared by a much more complicated procedure; namely, by the reduction of the hard to prepare germirene cyclo[–(t-Bu₂MeSi)₄Ge–C(SiMe₃)–C(SiMe₃)–] with metallic lithium. Other examples of novel types of reactivity of digermene 1 are under current investigation.

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 dichlorogerma 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

Scheme 3 Proposed pathway for the reaction of a digermene 1 with isonitriles RNC: (R = t-Bu, (H₃C)₃CCH₂(CH₃)₂C), forming formal germylene insertion product 3; reaction with tert-butyl isonitrile is shown as a representative example.

Scheme 4 Synthetic utility of a digermene 1.
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 (elucent) as a mixture of blue air-and moisture-sensitive crystals 

$^1$H NMR (C$_6$D$_6$): δ 70.72 (s, 12 H, CH$_3$), 1.27 (s, 72 H, C(CH$_3$)$_3$). $^{13}$C NMR (C$_6$D$_6$): δ 1.61 (CH$_3$), 25.35 (CH$_3$)$_2$, 31.61 (CH$_3$Cu). $^{29}$Si NMR (C$_6$D$_6$): δ 30.56. UV–Vis (hexane) $\lambda_{max}$/nm (e) 283 (10000), 369 (5700), 618 (3200). Anal. calc. for $\text{C}_{10}\text{H}_{25}\text{Ge}_{2}\text{Si}_{x}\text{Si}_{y}$, C: 55.82; H: 10.93. Found: C: 55.50; H: 10.75.


3. Persilylsubstituted 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.


5. Similarly to Lappert’s $\text{DisGe} = \text{GeDis}$, some other digermenes are reported to be in equilibrium with the corresponding germynes 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-Mes$_2$-C$_6$H$_3$) and Tbt (2,4,6-{(Me$_3$Si)CH}$_2$-C$_6$H$_3$) substituents retains its Ge=Ge bond in solution only at low temperatures ($\pi$-$\pi^*$: 439 nm at 190 K), while it undergoes dissociation into blue germynes Tbt(Mes)Ge at room temperature ($\pi$-$\pi^*$: 575 nm at 295 K): N. Tokitoh, K. Kishikawa, R. Okazaki, T. Sasamori, N. Nakata and N. Takeda, Polyhedron, 2002, 21, 563.


7. UV TD-DFT computations of the model compounds were performed at the UB3LYP/6-31G(d) level with the GAUSSIAN 03 set of programs.


9. UV absorption of the free MesGe (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).

10. Preliminary X-ray data of digermene 1 revealed rather long Ge=Ge bond distance of 2.346(2) Å, nearly planar geometry at the sp$^2$-Ge centers (sum of the bond angles 359.2° and 358.8°), and extreme twisting of the Ge=Ge bond in previous ly reported tetrakis(trialkylsilyl)digermenes i is noteworthy in view of the absolutely untwisted configuration of the Ge=Ge bonds in previously reported tetrakis(trialkylsilyldigermenes (i-(Pr$_3$Me)$_2$Si)Ge=Ge(SiMe$_3$-Pr$_2$) and (i-(Pr$_3$Si)$_2$Ge=Ge(SiMe$_3$-Pr$_2$) (see ref. 3). Such pronounced structural differences between 1 and the above-mentioned tetrakis(silyldigermenes are most likely due to the substantially greater steric hindrances in 1 caused by the very bulky t-Bu$_2$MeSi-substituents. This trend is quite parallel to that of the homologous tetrakis(silyldigermenes (i-(Pr$_3$Me)$_2$Si)Si=Si(SiMe$_3$-Pr$_2$), (i-(Pr$_3$Si)$_2$Si=Si(SiMe$_3$-Pr$_2$) and (t-Bu$_2$MeSi)$_2$Si=Si(SiMe$_3$-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-Bu$_2$Me$_2$Si)(i-Si(SiMe$_3$-Bu$_2$) is extraordinarily twisted by 54.5° [A. Sekiguchi, S. Inoue, M. Ichinohe, Y. Arai, J. Am. Chem. Soc., 2004, 126, 9626].


13. 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 i 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.


Graphical Abstract:
The synthesis, unusual structural and chemical properties of a novel tetrakis(trialkylsilyl)digermene \((t\text{-}Bu_2\text{MeSi})_2\text{Ge} = \text{Ge(SiMe_3\text{-}t-Bu)_2}\) are presented in this communication.