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Synthesis of tetrakis(2,6-diisopropylphenyl)digermene and its reductive cleavage to the corresponding digermenyllithium-(DME) complex

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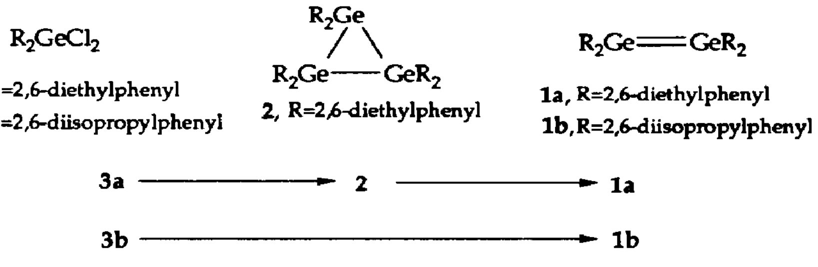
Abstract

Tetrakis(2,6-diisopropylphenyl)digermene is synthesized directly from bis(2,6-diisopropylphenyl)dichlorogermane by reductive coupling with lithium naphthalenide in dimethoxyethane (DME). Its structural integrity (double bond) is retained in solution and addition of methanol leads to 1-methoxy-1,1,2,2-tetrakis(2,6-diisopropylphenyl)digermane. Treatment of the digermene with further equivalents of lithium naphthalenide in DME provided a novel digermenyllithium species.

Introduction

Several digermene (Ge=Ge) derivatives have yielded to synthesis in recent years to show that the digermene system is intrinsically reactive toward a variety of reactions, e.g. addition of protic species, cycloaddition, oxidation, and reduction. For this reason, the final step of the digermene synthesis is almost invariably carried out in the absence of reactive species [1,2]. For instance, tetrakis(2,6-diethylphenyl)digermene (**1a**) is prepared by photolysis of hexakis(2,6-diethylphenyl)cyclotrigermane (**2**), the major product that forms in the reductive coupling of the



Scheme 1. Syntesis of digermenes from dichloro(mono)germanes

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corresponding dichlorogermane (**3a**, Scheme 1) [1c]. We have found, however, that the reaction of bis(2,6-diisopropylphenyl)dichlorogermane (**3b**) with lithium naphthalenide directly produces the corresponding digermene (**1b**) which exhibits unique chemical reactivities compared with known digermene derivatives, e.g. **1a** [1c]. Of particular interest is further treatment of **1b** with the same reductant which leads to Ge,C bond cleavage to provide the isolable digermenyllithium **4** (germanium analog of a vinyllithium), a species hitherto unknown in group 14 dimetallene chemistry.

Results and discussion

Successive treatment of $GeCl_4$ with 2,6-diisopropylphenylmagnesium bromide (2.1 equiv.) and then $LiAlH_4$ (2 mol equiv.) provided in 72% yield the corresponding diarylgermane which was chlorinated with CCl_4 and benzoyl peroxide (0.1 mol equiv.) to produce in 82% yield the corresponding diaryldichlorogermane (**3b**). Compound **3b** in DME was added to a solution of lithium naphthalenide (2 equiv.) in the same solvent. After stirring for 2 h at −78 °C and warming to 20 °C for 4 h the solvent and naphthalene were removed in vacuo. The usual workup of the residue provided in 25% yield yellow crystalline **1b** *. The yield of **1b** before purification was estimated to be about 65% by ^1H NMR spectroscopy. Although in low yield (10%), **1b** was also obtained through a different route: The reaction of GeI_2 with 2,6-diisopropylphenyllithium (2 equiv.) in DME apparently generated the corresponding diarylgermanium(II) species which underwent dimerization to form **1b**.

Both the mass spectrum and the room temperature electronic absorption spectrum recorded for **1b** are consistent with the formulation of this compound as a digermene derivative. The effects of excessive steric congestion in **1b** manifest themselves clearly in the ^1H NMR spectrum (see Experimental): The spectrum of **1b** clearly demonstrates two types of isopropyl groups and is temperature independent in toluene-d_8 from −80 to +100 °C. The hindered rotation of the aryl groups along the Ge–C axes are certainly responsible for the non-equivalence of the isopropyl groups. In contrast, the toluene-d_8 spectrum of **1a** at room temperature has only one type of ethyl group, but can be induced to show two types of ethyl groups upon cooling to below −80 °C. The Ge,Ge double bond in **1b** is effectively protected from attack by external reagents. For instance, addition of methanol to **1a** in methylcyclohexane containing 100 equiv. of MeOH is complete in 30 min at room temperature [1c], but the same reaction with **1b** proceeds only to 33% completion in 7 days (see Experimental **). This distinctly diminished reactivity is characteristic of **1b** in many other reactions including oxygenation with O_2, DMSO, N_2O and *N*-methylmorpholine-*N*-oxide [3] and other cycloadditions as documented elsewhere [4].

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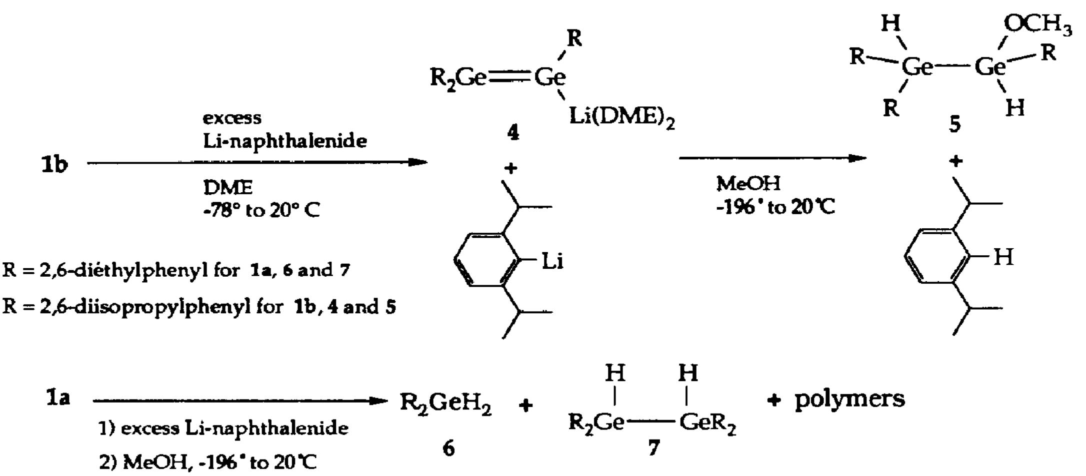
* Similarly, tetrakis(2,4,6-triisopropylphenyl)digermene has also been prepared: ^1H NMR (300 MHz, C_6D_6, 20 °C) δ 0.73 (d, 24H, J 6.6 Hz), 1.14 (d, 12 H, J 6.6 Hz), 1.16 (d, 12H, J 6.6 Hz), 1.37 (d, 12H, J 6.6 Hz), 1.42 (d, 12H, J 6.6 Hz), 2.72 (sept, 4H, J 6.6 Hz), 3.60 (sept, 4H, J 6.6 Hz), 4.27 (sept, 4H, J 6.6 Hz), 6.99 (s, 4H, 7.10 (s, 4H); UV (methylcyclohexane) λ_{max} (log ϵ) 279 (4.1), 305 (4.1), 418 nm (4.5).

** The X-ray diffraction analysis of this compound has been performed by William M. Davis of this department and will be published elsewhere.



Scheme 2. Reduction of digermenes with lithium naphthalenide

While these reactions follow analogous paths to those observed for **1a**, reduction of **1b** with lithium naphthalenide has disclosed a totally unexpected reaction pathway (Scheme 2): After addition of a DME solution of **1b** to excess lithium naphthalenide (in DME) at $-78\,^\circ C$, the resulting mixture was warmed to $20\,^\circ C$ and maintained at that temperature for 1 h. The solvent and volatile materials after filtration through Celite were removed in vacuo and the deep red residue was washed twice with degassed hexane to afford, in 50–60% yield, analytically pure, extremely air-sensitive, red microcrystals. The appearance of three different signals for the isopropyl groups in the ^1H NMR spectrum, combined with the fact that one aryl group has been removed from **1b** in the course of the reduction as has been shown in a separate experiment *, leads to the proposal that the structure of the reduction product is best represented by **4**. Furthermore, the incorporation of two DME molecules (through chelation to the lithium cation) as indicated by ^1H NMR and the bathochromic shift of the visible absorption maximum observed for **4** compared to that for **1b** represent supportive evidence for the existence of a digermenyl-lithium linkage in **4**. Methanol reacts with **4** at $-78\,^\circ C$ to provide **5** **. Assuming the proposed structure of **4** is correct, a straightforward interpretation of this reaction is available: Initial protonolysis of the Ge,Li linkage is followed by addition of methanol to the resulting trisubstituted digermene.

In contrast with the observed reduction of **1b** to **4**, treatment of **1a** with lithium naphthalenide under the same conditions led to products which were converted upon methanolysis to diarylgermane (**6**) (7%), tetraaryldigermane (**7**) (14%) and unidentifiable polymers (40%). 1,3-Diethylbenzene was apparently not formed; and, therefore, cleavage of a Ge,C bond is not a favorable process in this case.

The Kipping reaction of bis(2,6-dialkylphenyl)dihalometallanes (metal = group 14) has attracted intense interest in recent years [1a]. The data now available

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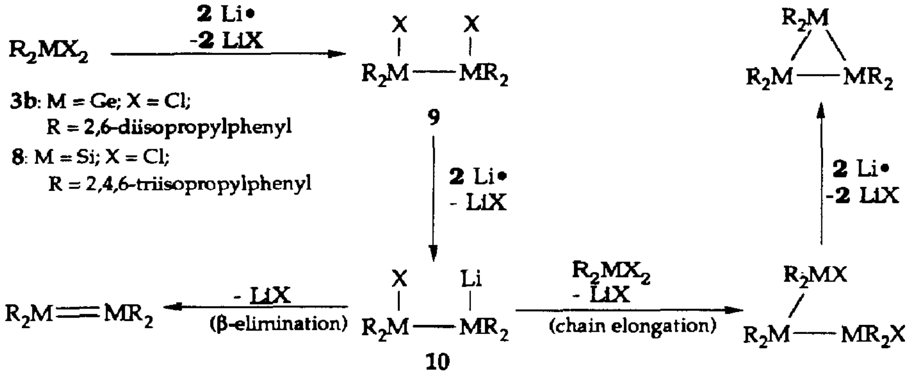
* Reduction of **1b** with lithium naphthalenide followed by quenching with methanol provided approximately 1 equiv. of 1,3-diisopropylbenzene and 1 equiv. of **5**.

** The structure assignment for **5** is based on the ^1H NMR signals for the Ge–H protons (two doublets at 5.99 and 6.69 ppm), which do not show signs of collapsing to a singlet upon heating as would be expected for the other possible structure, a geminal germanium dihydride.



Scheme 3. Reductive coupling of dihalometallanes

suggests that there are distinct parallels in the silicon and germanium series. Thus, upon treatment with lithium naphthalenide, bis(2,6-dimethylphenyl)- and bis(2,6-diethylphenyl)dichlorosilanes [5a,b] and the corresponding dichlorogermanes [1b,c] provide cyclotrimetallanes, whereas the dimetallenes are the major products obtained from bis(2,4,6-triisopropylphenyl)dichlorosilane **8** [5c] and bis(2,6-diisopropylphenyl)dichlorogermane (**3b**) under similar reaction conditions. Providing the linear chain elongation mechanism is operant in these reactions, this trend is readily understandable in terms of the steric bulk of the ligands attached to the silicon and germanium atoms. In other words, the likely intermediate **10** resulting from further reduction of a 1,2-dichlorodimetallane (**9**) may choose between two pathways (Scheme 3): either β-elimination or chain elongation with another molecule of dichloro(mono)metallane. The former process is preferred in the reductive couplings of **8** and **3b**. With even bulkier ligands such as the 2,4,6-tri-t-butylphenyl groups, the (monomeric) dihalometallanes may not be coupled into their corresponding (dimeric) dihalodimetallanes. Instead it appears that the monomer undergoes reductive α-elimination to produce the corresponding metallylenes [6].

Experimental

General procedures

All experiments were performed under argon or nitrogen in a standard high vacuum system unless otherwise noted. DME and THF were distilled from sodium benzophenone ketyl. Melting points were determined on a Thomas-Hoover melting point aparatus and are uncorrected. Electronic spectra were recorded on a Hewlett-Packard 8450A Diode Array spectrometer. Proton (^{1}H) NMR spectra were recorded on either a Bruker WM-250 (FT, 250 MHz) or a Varian-300 (FT, 300 MHz) spectrometer. Mass spectra were obtained on a Finnigan MAT 8200 spectrometer. Digermene **1a** was prepared by literature procedures [1h].

Preparation of bis(2,6-diisopropylphenyl)germane

To a solution of $GeCl_4$ (42 mmol) in ether (20 ml) at −78 °C was added (2,6-diisopropylphenyl)magnesium bromide (90 mmol) in THF (65 ml). The resulting yellow suspension was warmed to 20 °C and stirred for 24 h. A suspension of $LiAlH_4$ (84 mmol) in ether (30 ml) was added to the reaction mixture at 0 °C.

After 5 h at 20 °C unreacted $LiAlH_4$ was destroyed by slow addition of saturated NH_4Cl solution (30 ml) at 0 °C. The resulting suspension was poured into a separatory funnel filled with water (50 ml) and ether (100 ml). The aqueous layer was extracted with ether (100 ml × 2), and the extract was combined with the original organic layer. The organic solution was washed with brine (100 ml) and concentrated on a rotary evaporator. Purification of the residue by flash chromatography using hexane afforded bis(2,6-diisopropylphenyl)germane (12 g, 72%) as a colorless oil: ^1H NMR (250 MHz, C_6D_6) δ 1.12 (d, 24 H, J 6.8 Hz, $CHMe_2$), 3.45 (sept, 4 H, J 6.8 Hz, $CHMe_2$), 5.55 (s, 2 H, Ge–H), 7.08 (d, 4 H, J 7.8 Hz), 7.23 (t, 2 H, J 7.8 Hz); mass spectrum (EI, 70 eV) m/z 393–400 (M^+ cluster).

Preparation of bis(2,6-diisopropylphenyl)dichlorogermane (3b)

A solution of bis(2,6-diisopropylphenyl)germane (13.07 mmol) and benzoylperoxide (1.29 mmol) in CCl_4 (40 ml) was heated to reflux for 3 h. After concentration on a rotary evaporator Kugelrohr distillation (110–125 °C/0.05 torr) provided **2** (4.96 g, 82%) as a white solid: m.p. 68–70 °C; ^1H NMR (250 MHz, C_6D_6) δ 1.08 (d, 24H, J 6.7 Hz, $CHMe_2$), 3.88 (sept, 4H, J 6.7 Hz, $CHMe_2$), 6.99 (d, 4H, J 7.5 Hz), 7.13 (t, 2H, J 7.8 Hz); mass spectrum (EI, 70 eV) m/z 462–470 (M^+ cluster).

Synthesis of tetrakis(2,6-diisopropylphenyl)digermene (1b)

A dark green suspension of lithium naphthalenide was prepared by stirring a mixture of lithium powder (3.26 mmol) and freshly sublimed naphthalene (3.26 mmol) in DME (5 ml) at 20 °C for 1 h. A solution of **3b** (1.583 mmol) in DME (5 ml) was added through a cannula into the suspension of lithium naphthalenide at −78 °C. After stirring for 2 h at −78 °C and warming to 20 °C for 4 h the solvent and naphthalene were removed in vacuo. The resulting residue was dissolved in toluene (5 ml), filtered through Celite, concentrated and recrystallized from 1/1 toluene/isopropanol (2 ml) to produce yellow crystalline **1b** (158 mg, 25%): m.p. > 280 °C; UV (methylcyclohexane) λ_{max} (log ϵ) 273 nm (4.1), 418 nm (4.6); ^1H NMR (250 MHz, C_6D_6, 20 °C) δ 0.68 (d, 12H, J 6.6 Hz), 0.70 (d, 12H, J 6.6 Hz), 1.31 (d, 12H, J 6.6 Hz), 1.36 (d, 12H, J 6.6 Hz), 3.54 (sept, 4H, J 6.6 Hz), 4.26 (sept, 4H, J 6.6 Hz), 6.99 (d, 2H, J 7.3 Hz), 7.00 (d, 2H, J 7.3 Hz), 7.09 (d, 2H, J 7.3 Hz), 7.10 (d, 2H, J 7.3 Hz), 7.18 (2 overlapping t, 4H, J 7.3 Hz); mass spectrum (EI, 70 eV) m/z 785–796 (M^+ cluster).

Reaction of GeI_2 with 2,6-diisopropylphenyllithium

A solution of 2,6-diisopropylphenyllithium (0.27 M, 0.60 mmol) in DME (3 ml) was added to a flask containing GeI_2 (0.30 mmol) at −78 °C. After 1 h at 20 °C solvent was removed in vacuo and the residue was extracted with hexane (1 ml × 2). The hexane solution was filtered through Celite. After removal of solvent the residue was analyzed by ^1H NMR to show the characteristic resonances for **1b** (ca. 10% yield estimated by integrating the region of methyl groups)

Reaction of 1b with methanol

Digermene **1b** (0.241 mmol) was dissolved in a 1/1 mixture of methanol and toluene (10 ml). After 7 days at 20 °C the reaction mixture was concentrated on a rotary evaporator and the residue was purified by flash chromatography using hexane to afford 1-methoxy-1,1,2,2-tetrakis(2,6-diisopropylphenyl)digemane (55 mg, 28%): m.p. (dec) 203°C; ^{1}H NMR (250 MHz, C_6D_6, 20°C) δ 0.32 (d, 3H, J 6.6 Hz), 0.33 (d, 3H, J 6.6 Hz), 0.41 (d, 3H, J 6.6 Hz), 0.44 (d, 3H, J 6.6 Hz), 0.77 (2 overlapping d, 6H, J 6.6 Hz), 0.80 (d, 3H, J 6.6 Hz), 0.93 (d, 3H, J 6.6 Hz), 1.24 (2 overlapping d, 6H, J 6.6 Hz), 1.26 (2 overlapping d, 6H, J 6.6 Hz), 131 (d, 3H, J 6.6 Hz), 1.33 (d, 3H, J 6.6 Hz), 1.36 (d, 3H, J 6.6 Hz), 1.38 (d, 3H, J 6.6 Hz), 1.48 (d, 3H, J 6.6 Hz), 2.92 (sept, 1H, J 6.6 Hz), 3.15 (sept, 1H, J 6.6 Hz), 3.21 (sept, 1H, J 6.6 Hz), 3.24 (sept, 1H, J 6.6 Hz), 3.40 (sept, 1H, J 6.6 Hz), 3.53 (sept, 1H, J 6.6 Hz), 3.77 (s, 3H, OCH_3), 4.06 (sept, 1H, J 6.6 Hz), 4.09 (sept, 1H, J 6.6 Hz), 5.99 (s, 1H, Ge–H), 6.90–7.30 (m, 12H); mass spectrum (EI, 70 eV) m/z 824 (M^+).

Reductive cleavage of ***1b*** *to* ***4***

After addition of a solution of **1b** (0.092 mmol) in DME (2 ml) to a suspension of lithium naphthalenide (1 mmol) at −78°C, the resulting mixture was warmed to 20°C and maintained at that temperature for 1 h. The solvent and volatile materials after filtration through Celite were removed in vacuo and the deep red residue was washed with degassed haxane (2 × 0.5 ml) to afford **4** as red microcrystals (41 mg, 54%): m.p. 141°C (dec); Vis (THF) λ_{max} (log ϵ) 378 nm (3.9), 458 nm (4.0); ^{1}H NMR (300 MHz, toluene-d_8, 80°C) δ 1.02 (d, 12H, J 6.9 Hz, $CHMe_2$), 1.22 (d, 12H, J 6.9 Hz, $CHMe_2$), 1.28 (d, 12H, J 6.9 Hz, $CHMe_2$), 2.92 (s, 8H, DME CH_2OCH_3), 2.94 (s, 12H, DME CH_2OCH_3), 4.06 (sept, 2H, J 6.9 Hz, $CHMe_2$), 4.47 (sept, 2H, J 6.9 Hz, $CHMe_2$), 4.48 (sept, 2H, J 6.9 Hz, $CHMe_2$), 7.07–7.23 (m, 9H, Ar–H).

Reaction of ***4*** *with methanol*

Methanol (ca. 0.5 ml) was added by vacuum-transfer at −78°C to a dark red suspension of **3** in DME (9 ml), which was prepared from **1b** (0.921 mmol) and lithium naphthalenide (5.4 mmol) via procedures described above. After warming to 20°C the solvent and naphtalene were removed in vacuo. Crystallization of the residue from hexane afforded **5** (163 mg, 54%): m.p. 158–159°C; ^{1}H NMR (250 MHz, C_6D_6) δ 0.89 (d, 6H, J 6.9 Hz, $CHMe_2$), 1.02 (d, 6H, J 6.9 Hz, $CHMe_2$), 1.10 (d, 6H, J 6.9 Hz, $CHMe_2$), 1.12 (d, 12H, J 6.9 Hz, $CHMe_2$), 1.22 (d, 6H, J 6.9 Hz, $CHMe_2$), 3.38 (sept, 4H, J 6.5 Hz, $CHMe_2$), 3.50 (sept, 2H, J 6.6 Hz, $CHMe_2$), 3.60 (s, 3H, Ge–OMe), 5.99 (d, 1H, J 7.6 Hz, Ge–H), 6.69 (d, 1H, J 7.6 Hz, Ge–H), 7.00–7.30 (m, 9H); mass spectrum (FAB, nitrophenyl octyl ether matrix) m/z 656–665 (M^+ cluster).

Reaction of ***1a*** *with lithium naphthalenide followed by addition of methanol*

A solution of **1a** (0.071 mmol) in DME (2 ml) was added to a suspension of lithium naphthalenide (0.30 mmol) in DME (1 ml) at −78°C. After 1 h at 20°C methanol (ca. 0.2 ml) was added by vacuum-transfer at −78°C. After warming up to 20°C the reaction mixture was concentrated on a rotary evaporator. The residue was analyzed by ^{1}H NMR (250 MHz, C_6D_6): two singlets of approximately equal intensities at δ 5.83 and 6.00 ppm were recorded for **6** and **7**, respectively. The residue was purified by flash column chromatography using mixtures of hexane/ether (100/1 and 10/1) to afford **7** (6.4 mg, 14%) and polymers (19 mg, ca. 40%).

Acknowledgements

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References

1 (a) For a review see: S. Masamune, in E.R. Corey, J.Y. Corey and P.P. Gaspar, (Eds.), Silicon Chemistry, Ellis Horwood, Ltd., New York, 1988 Chap. 25; (b) S. Masamune, Y. Hanzawa and D.J. Williams, J. Am. Chem. Soc., 104 (1982) 6136; (c) J.T. Snow, S. Murakami, S. Masamune and D.J. Williams, Tetrahedron Lett., 25 (1984) 4191; (d) S. Collins, S. Murakami, J.T. Snow and S. Masamune, ibid., 26 (1985) 1281; (e) W. Ando and T. Tsumuraya, ibid., 27 (1986) 3251.

2 For an exception see P.B. Hitchcock, M.F. Lappert, S.J. Miles, and A.J. Thorne, J. Chem. Soc., Chem. Commun., (1984) 480.

3 S. Masamune, S.A. Batcheller, J. Park, W.M. Davis, O. Yamashita, Y. Ohta and Y. Kabe, J. Am. Chem. Soc., in press.

4 S.A. Batcheller and S. Masamune, Tetrahedron Lett., 29 (1988) 3383.

5 (a) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and J.F. Blount, J. Am. Chem. Soc., (1982) 1150; (b) S. Masamune, S. Murakami, J.T. Snow, H. Tobita and D.J. Williams, Organometallics, 3 (1984) 333; (c) H. Watanabe, K. Takeuchi, N. Fukawa, M. Kato, M. Goto and Y. Nagai, Chem. Lett., (1987) 1341.

6 L. Lange, B. Meyer and W.-W. du Mont, J. Organomet. Chem., 329 (1987) C17.