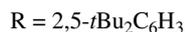
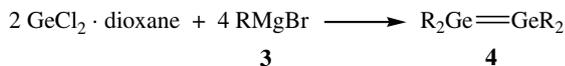


with only one alkyl group in the *ortho*-positions of the aryl groups are accessible and what influence this substituent pattern would have on the structures of the resulting compounds.

We chose 1,4-di-*tert*-butylbenzene as a model compound because it furnishes the Grignard compound **3** after bromination and reaction with magnesium. Reaction of **3** with $\text{GeCl}_2 \cdot \text{dioxane}$ gave orange-coloured crystals of the digermene **4** in acceptable yield. The constitution of **4** was confirmed by X-ray crystallography (Fig. 1).



The Ge=Ge bond length of 236.4 pm is among the longest that has been observed in a digermene to date. Even more unusual are the *trans*-bending angles of 37.2° and 42.6° from the Ge–Ge vector which are larger than the corresponding angles in all as yet synthesised digermenes.

This result is surprising since a similar digermene with 2-*tert*-butyl-4,5,6-trimethylphenyl groups possessing an additional methyl group in the *ortho*-positions exhibits a very short Ge=Ge bond of 225.1 pm and almost planar environments around the two germanium atoms in spite of the increased steric demands [9]. The bonding parameters determined for **4** again clearly show that a correlation with the steric requirements of the substituents is hardly possible [3].

Similarly unanswered is the question of the influence of the spatial demands of the substituents on the behaviour of tetraaryldigermenes in solution. While most digermenes decompose to germynes in solution, tetrakis(2,4,6-triisopropylphenyl)digermene [10] or the 1,2-bis(terphenyl)digermenes [11] retain their structural integrity in solution.

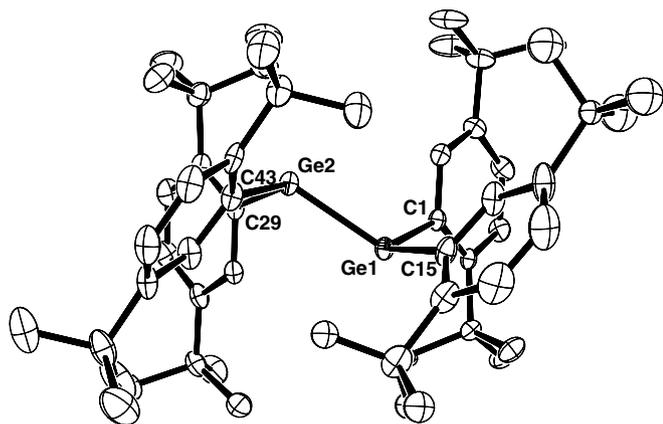
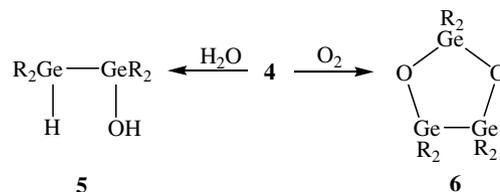


Fig. 1. Molecule of **4** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (pm) and bond angles (°): Ge(1)–Ge(2) 236.43(4), Ge(1)–C(1) 200.2(3), Ge(1)–C(15) 199.4(3), Ge(2)–C(29) 200.2(2), Ge(2)–C(43) 200.1(3) and C(15)–Ge(1)–C(1) 106.2(1), C(43)–Ge(2)–C(29) 107.0(1).

Preliminary experiments on the reactions of **4** with small amounts of oxygen or water seemed to indicate that **4** exists, at least in part, in solution as the digermene. Accordingly, treatment of **4** with water affords the compound **5** which, to the best of our knowledge, represents the first structurally characterised digermanol (Fig. 2).



The Ge–Ge bond length in **5** of 247.6 pm is in the typical range for Ge–Ge single bonds. Further evidence for the proposed constitution was provided by the IR spectrum: absorption bands at 3597 and 2086 cm^{-1} are characteristic for Ge–OH and Ge–H vibrations.

The trigermanol-1,3-dioxolane **6** (Fig. 3), accessible by the action of air on **4**, possesses an almost planar five-membered ring (sum of angles: 539.5°) just like other rings of this type [12]. Starting from tetramesityldigermene, Baines et al. [12b] showed that the formation of this ring system can be rationalised by addition of O_2 to the digermene to

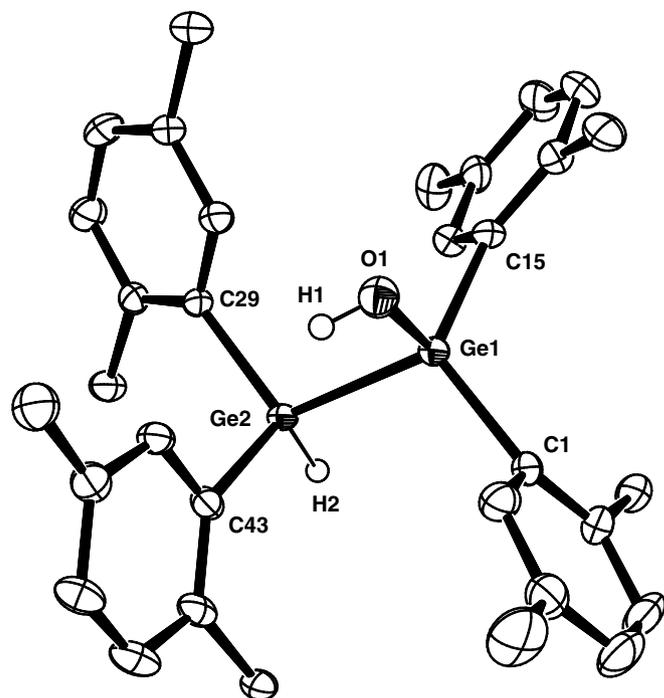


Fig. 2. Molecule of **5** in the crystal (C–H hydrogen atoms and methyl groups omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (pm) and bond angles (°): Ge(1)–Ge(2) 247.6(1), Ge(1)–C(1) 201.6(2), Ge(1)–C(15) 199.8(2), Ge(2)–C(29) 202.3(1), Ge(2)–C(43) 200.4(2), Ge(1)–O(1) 182.0(3) and C(15)–Ge(1)–C(1) 121.3(1), C(43)–Ge(2)–C(29) 109.5(1).

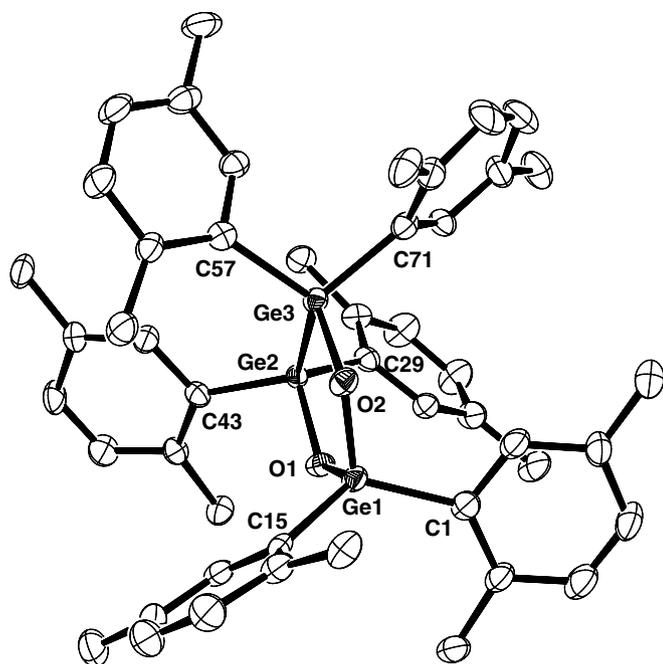


Fig. 3. Molecule of **6** in the crystal (hydrogen atoms and methyl group omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (pm) and bond angles ($^{\circ}$): Ge(1)–O(1) 178.5(3), Ge(1)–O(2) 178.6(3), Ge(2)–O(1) 180.3(3), Ge(2)–Ge(3) 251.3(1), Ge(3)–O(2) 178.8(3) and O(1)–Ge(1)–O(2) 101.9(1), Ge(1)–O(1)–Ge(2) 125.3(1), O(1)–Ge(2)–Ge(3) 93.1(1), O(2)–Ge(3)–Ge(2) 95.2(1), Ge(1)–O(2)–Ge(3) 124.0(2).

form a digerma-1,2-dioxetane with subsequent insertion of a germylene into the O–O single bond.

Although digermenes and simple germenes have been known for many years, the synthesis and structural characterisation of acetylene-bridged bis(germaethenes) were realised only recently [6,7]. The conjugation between the multiple bonds of these molecules is reflected principally in the electronic spectra which show bands shifted bathochromically by more than 100 nm in comparison to those of the simple germenes. These compounds are prepared by the addition of a germylene to 1,4-diphenyl- and 1,4-di-*n*-butylbuta-1,3-diyne. Earlier attempts to achieve the addition of a germylene to hexa-2,4-diyne as the as yet simplest diacetylene gave rise to red solutions that could be characterised by NMR spectroscopy but from which no compound could be isolated [13]. On repetition of this reaction, we obtained red crystals of the compound **7** which was unambiguously characterised by, among others, an X-ray crystal structure analysis (Fig. 4).

Apart from a somewhat increased sensitivity towards air and moisture, compound **7** hardly differs from the 1,4-di-*n*-butyl compound **1**. The electronic spectrum of the dark red solution of **7** in toluene shows the band at longest wavelength at 500 nm ($\epsilon = 8000$), which barely differs from that of **1** ($\lambda = 518$ nm). In contrast, the blue-violet diphenyl derivative **2** shows the corresponding absorption at 595 nm, indicating that the two phenyl groups participate in the conjugation.

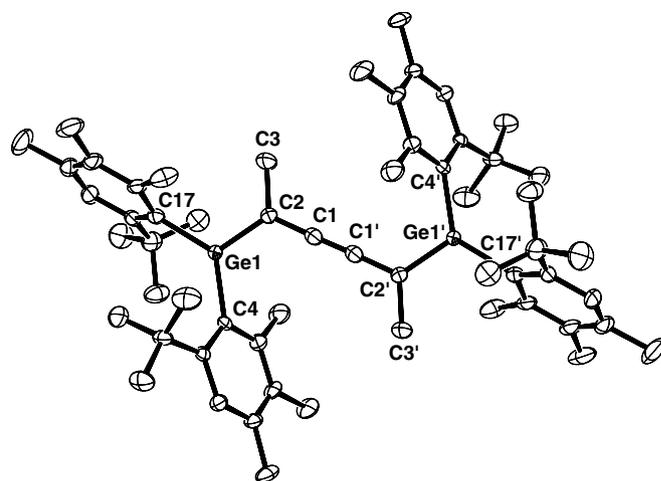
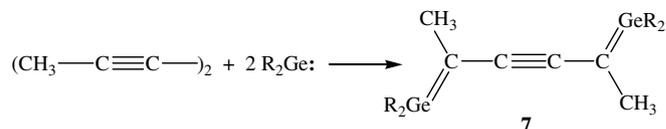
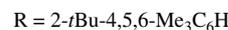
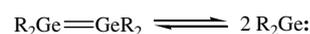


Fig. 4. Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (pm) and bond angles ($^{\circ}$): C(1)–C(1') 122.8(13), C(1)–C(2) 138.9(9), C(2)–C(3) 152.9(8), Ge(1)–C(2) 181.9(6), Ge(1)–C(4) 199.7(5), Ge(1)–C(17) 197.6(6) and Ge(1)–C(2)–C(1) 120.7(4), Ge(1)–C(2)–C(3) 121.4(5), C(1)–C(2)–C(3) 117.9(5).



The X-ray crystal structure analysis of **7** also exhibits major similarities with that of **1**. The bond lengths of 138.9 pm for the C1–C2 single bond and of 122.8 pm for the formal C1–C1' triple bond can be considered as further evidence for the conjugation in this molecule.

3. Experimental

3.1. General procedure

All reactions were carried out under an atmosphere of dry argon. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM 300 or a Bruker ARX 500 spectrometer using C_6D_6 as solvent. The IR spectra were recorded on a Bruker Vector 22 spectrometer. The UV/Vis spectra were obtained on a ComSpec spectrometer with fibre optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

3.2. Tetrakis(2,5-di-*tert*-butylphenyl)digermene (**4**)

To a stirred solution of ≈ 27 mmol of 2,5-di-*tert*-butylphenylmagnesium bromide (**3**) {prepared from 1-bromo-2,5-di-*tert*-butylbenzene [14] (7.35 g, 27.3 mmol) and a large excess of magnesium turnings (2.5 g, 0.1 mol) in 40 ml of THF} at -40 $^{\circ}\text{C}$, a solution of germanium(II)

chloride · dioxane (3.16 g, 13.6 mmol) in a mixture of THF (40 ml) and 1,4-dioxane (10 ml) was added dropwise. The mixture was then allowed to warm to room temperature and the solvents were removed by vacuum distillation. The residue was extracted with 200 ml of *n*-hexane. The resulting dark red solution was concentrated to a volume of 100 ml and cooled to $-30\text{ }^{\circ}\text{C}$ to furnish 3.41 g (56% yield) of a red solid of **4**; m.p. $135\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (500 MHz): δ 1.31 [s, 9H, C(CH₃)₃], 1.38 [s, 9H, C(CH₃)₃], 7.20 (dd, 1H, $^3J = 8.32\text{ Hz}$, $^4J = 2.19\text{ Hz}$), 7.34 (d, 1H, $^3J = 8.34\text{ Hz}$), 8.30 (d, 1H, $^4J = 2.06\text{ Hz}$) ppm. ^{13}C NMR (75 MHz): δ 31.57 (CH₃), 33.69 (CH₃), 34.32 [C(CH₃)₃], 36.97 [C(CH₃)₃], 125.24, 125.83, 126.93, 146.59, 146.79, 152.86 ppm. UV/Vis: λ_{max} (ϵ) 425 (4000) nm. Anal. Calc. for C₅₆H₈₄Ge₂ (902.55): C, 74.52; H, 9.38. Found: C, 73.94; H, 9.19%. Single crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at $-4\text{ }^{\circ}\text{C}$.

3.3. 2,5-Bis[bis(2-*tert*-butyl-4,5,6-trimethylphenyl)germylene]hex-3-yne (**7**)

To a solution of bis(2-*tert*-butyl-4,5,6-trimethylphenyl)germylene (0.71 g, 1.68 mmol) in toluene (60 ml) was added hexa-2,4-diyne (0.20 g, 2.56 mmol). The colour of the solution changed from orange to dark red. The mixture was stirred for 3 days at room temperature. After this time the solvent was removed by vacuum distillation and the residue redissolved in *n*-hexane to furnish 0.56 g (72% yield) of a red solid of **7**. m.p. $80\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz): δ 1.37 [s, 9H, C(CH₃)₃], 1.41 [s, 9H, C(CH₃)₃], 1.55 (s, 3H, CH₃), 2.01 (s, 3H, Ar-CH₃), 2.04 (s, 3H, Ar-CH₃), 2.08 (s, 3H, Ar-CH₃), 2.14 (s, 3H, Ar-CH₃), 2.18

(s, 3H, Ar-CH₃), 3.30 (s, 3H, Ar-CH₃), 7.19 (s, 2H, ArH). ^{13}C NMR (75 MHz): δ 16.59 (Ar-CH₃), 16.74 (Ar-CH₃), 21.17 (Ar-CH₃), 21.28 (Ar-CH₃), 24.29 (Ar-CH₃), 24.70 (Ar-CH₃), 32.65 [C(CH₃)₃], 32.86 [C(CH₃)₃], 33.68 (C-CH₃), 36.67 [C(CH₃)₃], 36.85 [C(CH₃)₃], 111.15 (C≡C), 116.92 (Ge=C), 126.48 (Ar-CH), 126.81 (Ar-CH), 133.20, 133.52, 136.78, 137.11, 138.60, 139.19, 142.32, 143.29, 151.71, 152.17 ppm. UV/Vis: λ_{max} (ϵ) 500 (8000) nm. C₅₈H₈₂Ge₂ (924.55) Anal. Calc.: C, 75.35; H, 8.94. Found: C, 74.89; H, 8.97%. Single crystals suitable for X-ray diffraction analysis were obtained from *n*-pentane at $4\text{ }^{\circ}\text{C}$.

3.4. Crystallographic analyses

Crystal and numerical data of structure determinations are given in Table 1. In each case the crystal was mounted in an inert oil. Data collection were performed with a Stoe IPDS area detector at 153 K using graphite-monochromated Mo K α radiation (71.073 pm). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system [15]. Hydrogen atoms were placed in the calculated positions, and the other atoms were refined anisotropically. Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 602 042 (**7**), CCDC 602 043 (**6**) CCDC 602 044 (**5**), and CCDC 602 045 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Table 1
Crystallographic data for compounds **4–7**

Compound	4	5 ^a	6 ^b	7
Empirical formula	C ₅₆ H ₈₄ Ge ₂	C ₁₁₅ H ₁₁₇ Ge ₄ O	C ₉₃ H ₁₄₇ Ge ₃ O ₂	C ₆₃ H ₉₄ Ge ₂
Formula weight	902.41	1865.93	1514.88	996.56
Crystal dimensions (mm)	0.35 × 0.25 × 0.13	0.35 × 0.24 × 0.20	0.40 × 0.18 × 0.08	0.20 × 0.09 × 0.08
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbcn</i>	<i>P</i> $\bar{1}$
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
<i>a</i> (pm)	2142.29(7)	1565.11(6)	4430.20(12)	1027.55(7)
<i>b</i> (pm)	1103.76(3)	1694.58(8)	1959.77(4)	1070.47(10)
<i>c</i> (pm)	2302.86(5)	2161.18(7)	2041.84(4)	1332.37(11)
α (°)		99.229(5)		89.800(11)
β (°)	103.724(3)	105.723(4)		89.826(9)
γ (°)		91.150(5)		85.892(10)
Volume (×10 ⁶ pm ³)	5289.8(3)	5433.8(4)	17727.6(7)	1461.8(2)
<i>Z</i>	4	2	8	1
μ (mm ⁻¹)	1.169	1.140	1.054	1.063
$2\theta_{\text{max}}$	52	52	48	52
Total number of reflections	45495	68128	118033	18001
Observed reflections	6554	13901	10210	3714
<i>R</i> ($I > 2\sigma(I)$)	0.0354	0.0442	0.0521	0.0756
<i>wR</i> ₂ (all data)	0.0760	0.1078	0.1341	0.2045
GOF (F^2)	0.850	0.923	1.008	1.034

^a The digermanol co-crystallised with **4** and $\frac{1}{2}\text{C}_6\text{H}_{14}$.

^b Compound **6** crystallises with 1.5 C₆H₁₄.

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