Telluradigermiranes. A Novel Three-membered Ring System Containing Tellurium

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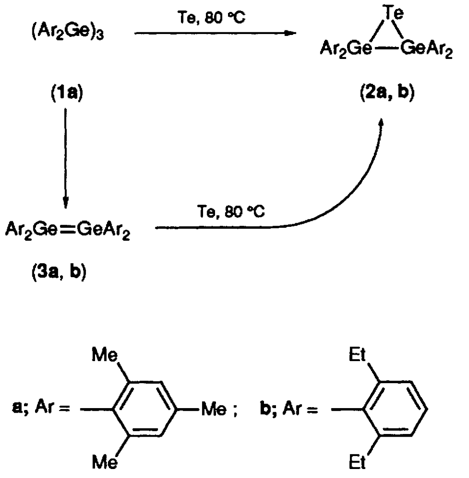
Reactions of hexamesitylcyclotrigermane (**1a**) and tetrakis(2,6-diethylphenyl)digermene (**3b**) with tellurium at 80 °C produce telluradigermiranes (**2a**) and (**2b**) respectively; the structure of (**2b**) has been confirmed by a single-crystal *X*-ray diffraction study, showing the existence of a Ge_2Te ring.

In recent years the chemistry of metal–group 14 three-membered heterocycles has progressed rapidly owing to the synthesis of a variety of small-ring systems involving group 14 elements.[1] However, to our knowledge the chemistry of three-membered rings containing tellurium remains rather limited.[2] Recently, we and another group prepared thia- and selena-digermiranes by the reactions of digermene with sulphur and selenium.[3] In this communication we report a novel synthesis of telluradigermiranes by the reaction of cyclotrigermanes and digermenes with tellurium.

When a benzene solution of hexamesitylcyclotrigermane (**1a**) (1.0 mmol)[4] and tellurium (3.0 mmol)† was heated to reflux for 14 h, a yellow crystalline product identified as 2,2,3,3-tetramesityltelluradigermirane (**2a**)‡ was obtained in 45% yield (Scheme 1). An intermediate digermene (**3a**) would be expected to react with tellurium to afford (**2a**) as in the reactions with sulphur and selenium.[3] Indeed, the isolable digermene tetrakis(2,6-diethylphenyl)digermene (**3b**)[4b] reacted with tellurium at 80 °C to yield the telluradigermirane (**2b**)‡ in 80% yield. Telluradigermiranes (**2a,b**) thus obtained are stable towards atmospheric oxygen and moisture;§ they exhibit thermochromism, being colourless at −196 °C, pale yellow at room temperature, and orange at *ca.* 140 °C. In the ^1H NMR spectra of (**2a**) and (**2b**), single sets of mesityl and 2,6-diethylphenyl protons were observed, which indicates that they have twofold symmetry. Their mass spectra also support



Scheme 1

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† Tellurium was purchased from Nacalai Tesque Inc., and was used as received.

‡ Satisfactory elemental analyses were obtained for the compounds described.

Spectral and physical data for (**2a**): m.p. 158—159 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 12H), 2.32 (s, 24H), 6.74 (s, 8H); MS (EI) *m/z* 740—755 (M^+). For (**2b**): m.p. 171—173 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* 7.5 Hz, 24H), 2.76 (dq, *J* 7.5 and 15.0 Hz, 8H), 3.60 (br dq, *J* 7.5 and 15.0 Hz, 8H), 6.79 (d, *J* 7.6 Hz, 8H), 7.20 (t, *J* 7.6 Hz, 4H); MS (EI) *m/z* 796—811 (M^+).

§ After prolonged standing in air, the yellow crystals of (**2a**) decomposed very slowly accompanied by the formation of a grey precipitate, probably metallic tellurium. (**2b**) is more stable than (**2a**).

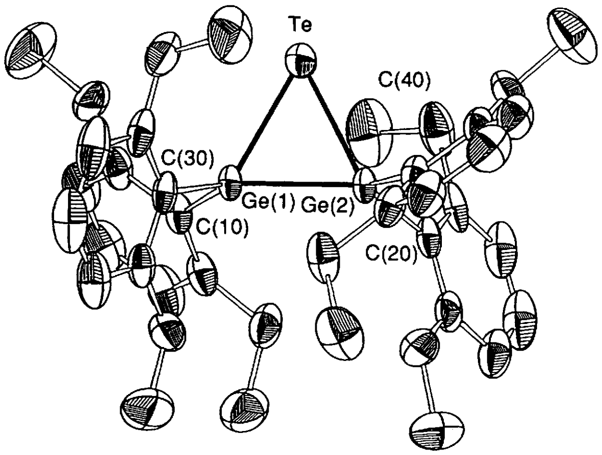

Figure 1. Perspective ORTEP drawing of (**2b**) showing 50% thermal ellipsoids for non-hydrogen atoms. The molecule contains an approximate C_2 axis which bisects the Ge_2Te ring. The approximately equivalent bond lengths (Å) and angles (°) are paired below: Te–Ge(1) and Te–Ge(2) 2.597(2); Ge(1)–Ge(2), 2.435(2); Ge(1)–C(10) and Ge(2)–C(40), 2.00(1); Ge(1)–C(30) and Ge(2)–C(20), 1.993(9)–2.00(1); Ge(1)–Te–Ge(2), 55.9(4); Te–Ge(1)–Ge(2) and Te–Ge(2)–Ge(1), 62.04(4)–62.05(4); Ge(2)–Ge(1)–C(10) and Ge(1)–Ge(2)–C(40), 121.0(4)–121.2(4); Ge(2)–Ge(1)–C(30) and Ge(1)–Ge(2)–C(20), 122.5(3).

the proposed molecular formulae, having the expected isotope pattern for Ge_2Te.

Finally the structure of (**2b**) has been determined crystallographically, as shown in Figure 1.¶ Owing to the slightly disordered arrangement of the four aryl groups about each germanium atom, the crystal structure of (**2b**) possesses approximate (not strict) two-fold symmetry. The Ge_2Te core has the most acute angle and the largest triangle recorded for Ge_2X ring systems (X = S[3b], C, N[5b]): the Ge–Te–Ge bond angle and length are 55.9° and 2.597 Å respectively. The Ge–Ge bond length (2.435 Å) is almost normal (2.44 Å), which contrasts with the lengths in other Ge_2X ring systems (X = S, C, N) which range between 2.376 and 2.397 Å. However, the bonded aryl carbon atoms and the germanium atoms are almost coplanar, as in other Ge_2X ring systems; the sums of the bond angles, Ge(2)–Ge(1)–C(10), Ge(2)–Ge(1)–C(30), C(10)–Ge(1)–C(30) and Ge(1)–Ge(2)–C(20), Ge(1)–Ge(2)–C(40), C(20)–Ge(2)–C(40) are 355.4 and 355.5° respectively. Although the short Ge–Ge bond distance and planarity around germanium are diagnostic features for the π-complex model,[6] our finding that the Ge–Ge bond distance falls within the normal Ge–Ge bond length is interesting.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan (No. 63106003).

Received, 18th April 1990; Com. 0/01716G

References

1 *E.g.*: T. J. Barton, in 'Comprehensive Organometallic Chemistry,' Pergamon, Oxford, 1983, Ch. 9.2, p. 205; R. West, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1201; W. Ando and T. Tsumuraya, *Organometallics*, 1989, **8**, 1467, and references cited therein.

2 C. N. Smit and F. Bickelhaupt, *Organometallics*, 1987, **6**, 1156; W.-W. du Mont, T. Severengiz, and M. Meyer, *Angew. Chem.*, 1988, **95**, 1025.

3 W. Ando and T. Tsumuraya, *Tetrahedron Lett.*, 1986, **27**, 3251; (b) T. Tsumuraya, S. Sato, and W. Ando, *Organometallics*, 1988, **7**, 2015; (c) S. A. Batcheller and S. Masamune, *Tetrahedron Lett.*, 1988, **29**, 3383.

4 (a) S. Masamune, Y. Hanzawa, and D. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 6136; (b) J. T. Snow, S. Murakami, S. Masamune, and D. J. Williams, *Tetrahedron Lett.*, 1984, **25**, 4191; (c) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, 1987, 1514.

5 (a) W. Ando and T. Tsumuraya, *Organometallics*, 1988, **7**, 1882; (b) T. Tsumuraya, S. Sato, and W. Ando, *ibid.*, 1989, **8**, in the press.

6 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **18**, C71; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; D. Kremer and E. Kraka, *J. Am. Chem. Soc.*, 1985, **107**, 3800; R. S. Grev and H. F. Schaefer, *ibid.*, 1987, **109**, 6577.

¶ *Crystal data:* Compound (**2b**): $C_{40}H_{52}Ge_2Te$, M_r = 805.64, triclinic, a = 9.556(1), b = 12.650(1), c = 17.209(2) Å, α = 90.54(1), β = 106.12(1), γ = 112.19(1)°, V = 1835.1 Å^3, Z = 2, space group $P\bar{1}$, D_c = 1.46 g/cm^3. 5085 Independent observed reflections ($2\theta \leqslant 50°$; $|F_o^2|>3\sigma|F_o^2|$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation and an ω–2θ scan. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically to R = 0.061 and R_w = 0.089. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.