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- [17] 2: ¹HNMR (200 MHz, C_bD_b, 295 K, TMS ext.): $\delta = 0.20 - 4.0$ (br., 8 H, basal and apical BH), 0.17 (br. s, 36 H, SiMe₃); ¹¹B NMR (64.2 MHz, C₆D₆, 295 K, BF₃ · OEt₂ ext.): $\delta = -30.18$ (d, ${}^{-1}J(B, H) = 162.1$ Hz, cage-BH); ¹³C NMR (50.3 MHz, C₆D₆, 295 K, TMS ext.): $\delta = -1.1$ (q, ${}^{1}J(C, H) = 119.5$ Hz, SiMe₃), -33.32 (s. cage-C); IR (C_6H_6) : $\bar{v} = 2581$ (s), 2541 (m) cm⁻¹ (B-H); MS: m/z (%): 435 (M +, 100), 73 (Me₃Si, 60). 3: ¹H NMR (200 MHz, C_6D_6 , 295 K, TMS ext.): $\delta = 0.20-4.0$ (br., 8 H, basal and apical BH), 0.16 (br. s, 36 H, SiMe₃); ^{11}B NMR (64.2 MHz. C_6D_6 , 295 K, $BF_3 \cdot OEt_2$ ext.): $\delta = -5.57 \text{ (d, } {}^{1}J(\text{B},\text{H}) = 146.5 \text{ Hz, cage-BH}); {}^{13}\text{C NMR}$ (50.3 MHz, C_6D_6 , 295 K, TMS ext.): $\delta = -1.4$ (q, $^{1}J(C, H) = 120.3 \text{ Hz}, \text{ SiMe}_{3}), -11.41 \text{ (s, cage C); IR}$ (C_6H_6) ; $\tilde{v} = 2580$ (s), 2539 (m) cm⁻¹ (B-H); MS: m/z (%): 435 (M⁺, 100), 73 (Me₃Si, 58).
- [18] Crystal data for $2(C_{16}H_{44}B_8Si_4, M_r = 435.4)$: monoclinic. $P2_1/n$; a = 9.628(2), b = 7.332(2), c = 19.924(5) Å, $\beta =$ 93.36(2) . V = 1404.0(6) Å³. Z = 2, $\rho_{calcd} = 1.030$ Mg m⁻³. $\mu = 0.214 \text{ mm}^{-1}$; Data were collected on a Siemens R3m/ V diffractometer at -43 C (Mo_{K2}; $2\theta = 3.5-44.0^{\circ}$ and 1841 reflections) and corrected for Lorentz and polarization effects. The structure was solved by direct methods and subsequent difference Fourier synthesis using SHELXTL-Plus (G. M. Sheldrick, Structure Determination Software Program Package, Siemens Analytical X-ray Instruments Inc., Madison, WI (USA) 1990). 2 has a center of symmetry at the geometric center of the cage and was refined on F with all non-H atoms anisotropically and H atoms isotropically. The final refinement converged at R = 0.029, wR = 0.040 and GOF = 1.12 for 1431 observed reflections. Further details of the crystal structure investi-

gation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59274.

- [19] In Figure 1 the interatomic connectivities are drawn such that atoms separated by less than 2.00 Å are connected, while atoms at distances greater than 2.15 Å are considered not to interact and are not connected.
- [20] According to MO calculations, this isomer is an intermediate 40.0 kJ mol⁻¹ higher in energy than 2.
- [21] J. Yang, K.-J. Lu, J. A. Maguire, N. S. Hosmane, unpublished results.

The Dianion of Tetraphenylgermole is Aromatic**

Robert West,* Honglae Sohn, Douglas R. Powell, Thomas Müller, and Yitzhak Apeloig

The anions of siloles and germoles have stimulated a great deal of interest lately.^[1-5] Tetraphenylgermole dianions have been studied in THF by Hong and Boudjouk,^[6] who proposed a delocalized structure on the basis of the ¹³C NMR spectrum. On the other hand, Tilley and co-workers have recently reported the X-ray structure of the germole anion, $[(MeC)_4GeSi-(SiMe_3)_3]^-$, as its lithium salt 1.^[7] The structure is highly localized; the C-C bond lengths within the five-membered ring vary significantly.



Scheme 1. Synthesis of 2 and 3a-c.

We now report on the structure of the dilithium salt of the tetraphenylgermole dianion (2), which was obtained from 1,1-dichloro-2,3,4,5-tetraphenylgermole (Scheme 1). The dilithium

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COMMUNICATIONS

compound 2 crystallized from dioxane in two structurally distinct forms, depending upon the crystallization temperature. The crystals obtained from dioxane at -20 °C had the composition Li₂[(PhC)₄Ge]·5dioxane (2a) and had a reverse-sandwich structure. The two lithium atoms, each coordinated to two dioxane molecules, lie above and below the C₄Ge ring within bonding distance of all five ring atoms (Fig. 1).^[8] Crystals of 2 obtained at 25 °C had the composition Li₂[(PhC)₄Ge]· 5.5 dioxane (2b). In 2b one lithium atom is η^{5} -coordinated to the ring atoms and the other is η^{1} -coordinated to the germanium atom (Fig. 2).^[9] In both structures the electrons within the ring are highly delocalized, which leads to nearly equal C-C bond lengths. Derivatization of solutions of 2 led to the products 3a-3c (Scheme 1); thus, clearly showing the dianionic character of 2.



Fig. 1. Crystal structure of **2a**. Selected bond lengths [pm] and angles []; Ge1-Li1 273.0(5). Ge1 · Li2 268.1(5). Li1-C1 238.0(6). Li1-C2 227.9(6). Li1-C3 228.8(6). Li1-C4 243.5(6). Li2-C1 240.8(6). Li2-C2 229.7(6). Li2-C3 227.8(6). Li2-C4 234.5(6). Ge1 C1 195.7(3). Ge1-C4 195.6(3). C1-C2 142.9(4). C2-C3 144.9(4). C3 · C4 143.1(4): C1-Ge1-Li1 58.28(14). C1-Ge1-Li2 60.17(14). C4-Ge1-Li1 59.93(14). C4-Ge1-Li2 58.29(14). Ge1-C1-C2 114.5(2). Ge1-C4-C3 114.3(2). C1-C2-C3 113.7(3). C2-C3-C4 114.0(3). C1-Ge1-C4 83.44(12).



Fig. 2. Crystal structure of **2b**. Selected bond lengths [pm] and angles []; Ge1-Li1 261.3(3). Ge1 - Li2 265.4(3), Li2 - C1 235.9(4). Li2 - C2 226.3(3), Li2 - C3 230.8(3), Li2 - C4 242.3(3). Ge1 - C1 193.0(2), Ge1 - C4 193.0(2), C1 - C2 142.3(2), C2 - C3 143.5(2), C3 - C4 142.1(2); C1-Ge1-Li1. 85.62(7), C1-Ge1-Li2. 59.47(8), C4-Ge1-Li1 114.31(9). C4-Ge1-Li2 61.44(8), Li1-Ge1-Li2. 174.48(10), Ge1-C1-C2 112.40(12), Ge1-C4-C3 112.59(12), C1-C2-C3 114.77(14), C2-C3-C4 114.62(14), C1-Ge1-C4 85.62(7).

The structure of **2b** is related to that recently published for $\text{Li}_2[(\text{PhC})_4\text{Si}] \cdot 5\text{THF}$ (**4**), which also contains η^{1-} and η^{5-} coordinated lithium centers.¹⁵¹ A significant difference between the structures is that in **4** the arrangement at the silicon center is nearly planar, whereas in **2b** the η^{1-} coordinated lithium center is shifted to the hemisphere anti to the η^{5-} coordinated lithium center. The angle between the Li–Ge vector and the C-Ge-C plane is 42.9°. Intraring C–C distances for **1**, **2a**. **2b**, and **4** are given in Table 1.

Table 1. Intraring C-C distances for germole and silole anions.

| | C1C2 | C3- C4 | C2 - C3 | Ref. |
|-----|----------|----------|----------|-----------|
| 1 | 136(6) | 135(5) | 146(6) | [7] |
| 2a | 142.9(4) | 143.1(4) | 144.9(4) | this work |
| 2 b | 142.3(2) | 142.1(2) | 143.5(2) | this work |
| 4 | 144.8(4) | 142.6(4) | 143.0(4) | [5] |

Theoretical calculations provide some insight into the sharp differences between 1 and 2. MO calculations reported by Tilley et al. for the anion $(H_4C_4GeSiH_3)^-$ gave a small aromatic stabilization energy (ASE) of 5.3 kcalmol⁻¹, and large differences between C-C intraring bond lengths, leading to a low Julg parameter $A^{(10)}$ of 0.53. Our MO calculations⁽¹¹⁾ for the $(H_4C_4Ge)^{2-}$ ion (Table 2) indicate that the C-C distances within the ring should be nearly identical; the Julg parameter is near 1. An ASE of 13.0 kcalmol⁻¹ is predicted from the isodesmic reaction shown in Equation (a).^[12] The MO calculations reveal



Table 2. Calculated bond lengths [pm] and Julg's parameter .4 for germole anions and dianions.

| | C1-C2 | C2-C3 | C1 - Ge | Li- Ge | Li C1 | Li - C2 | A |
|--|----------------------------------|----------------------------------|-------------------------|----------------|----------------|----------------|----------------------------------|
| $\begin{array}{c} H_{4}C_{4}Ge^{2-}\\ Li_{2}(H_{4}C_{4}Ge)\\ Li_{2}(H_{4}C_{4}Ge) \cdot 4 H_{2}O\\ H_{4}C_{4}GeSiH_{3}^{-}[a] \end{array}$ | 139.0 142.5 142.5 136.1 | 143.5 143.6 142.2 148.4 | 199.2 200.5 198.4 | 250.7 273.9 | 217.0 238.6 | 210.4 225.3 | 0.957 0.997 1.000 0.532 |

[a] Data from ref. [7].

that the Li₂(H₄C₄Ge) structure in which both lithium centers are η^5 coordinated is the energy minimum; it is 25 kcalmol⁻¹ (at MP2/LANL2DZ) more stable than the isomer in which one lithium center is η^1 - and the other η^5 -coordinated (see Table 2). Complexation of the dianion by lithium ions further increases the delocalization, as shown by the even larger values of the Julg parameter *A* predicted for the η^5 , η^5 -dilithium derivative of the (H₄C₄Ge)²⁻ ion, and likewise for Li₂(H₄C₄Ge)·4H₂O, in which each lithium center is coordinated by two H₂0 moleules. Thus both the structure for 1 (localized electrons) and that for 2 (delocalized electrons) are consistent with theory.

We note the good agreement between the experimentally determined geometry for **2a** (Fig. 1) and the calculated geometry for the model compound $\text{Li}_2(\text{H}_4\text{C}_4\text{Ge}) \cdot 4\text{H}_2\text{O}$ (Table 2), including the distances between the plane of the germole ring and the Li centers. Comparison with the calculated geometry of $\text{H}_4\text{C}_4\text{GeLi}_2$ reveals the important role of solvation in controlling the Li-germole ring distance. Thus, d(Ge-Li) and

COMMUNICATIONS.

d(C1-Li) distances in Li₂(H₄C₄Ge) increase by 23.2 pm and 21.6 pm, respectively, upon coordination of two water molecules to each of the η^5 -coordinated lithium ions. In contrast, solvation has practically no effect on the intraring distances.

In summary, it appears that anions of Group 14 metalloles $(C_4E \text{ rings})$ may have either localized nonaromatic, or delocalized aromatic structures, depending on the nature of the metal E and the substituents. Further structural studies of metallole anions and dianions of this kind with different substituents will be of value in determining the factors leading to "aromaticity" in these substances.

Experimental Procedure

1,1-Dichloro-2.3,4,5-tetraphenylgermole: Diphenylacetylene (26.7 g, 150 mmol) and lithium (1.38 g, 200 mmol) were stirred in diethyl ether (150 mL) at room temperature for 3.5 h. The reaction gave a brown solution and a yellow precipitate. The solution was frozen with a bath of liquid nitrogen, after removal of lithium metal. GeCl₄ (25.7 mL, 300 mmol) was added by a syringe in one portion. The mixture was kept at -196° C for 5 min before the cooling bath was removed, and the solution was allowed to warm up slowly to room temperature, and stirred for 4 h to give a yellow solution. The reaction product was extracted with diethyl ether and obtained as yellow crystals (30 g, 80%) at -10° C. M.p. 197–199 °C. Selected data; ¹H NMR (300.133 MHz, CDCl₃): $\delta = 6.83 - 6.88$ and 7.04–7.21 (br. m, 20H; Ph); ¹³C {H} NMR (75.403 MHz, CDCl₃ ($\delta = 77.00$)): $\delta = 149.96$, 136.57, 134.66, 132.72, 129.54, 129.50, 128.36, 128.06, 127.48, 127.47; MS(El): *m/z* (%): 500 (23) [M^+], 356 (78) [$M^+ - \text{GeCl}_2$]. High-resolution MS: calcd. for C₂₈H₂₀GeCl₂ 500.0155, found 500.0116.

2: A solution of Ph₄C₄GeCl₂ (10.00 g, 20 mmol) in THF (130 mL) was stirred with 4 equiv Li (0.555 g, 80 mmol) for 12 h at room temperature under an argon atmosphere. The color of the solution rapidly changed to a dark maroon. After removal of solvent, the residue, **2**, was extracted with dioxane and filtered. Orange crystals of **2b** were obtained at room temperature. Cooling of the saturated solution to -20 °C produced instead yellow crystals of **2a**. ¹³C{H} NMR (75.403 MHz, dioxane ($\delta = 66.40$)): $\delta = 165.17, 150.07, 143.83, 131.93, 129.19, 128.04, 125.89, 122.03, 119.45.$

3a: An excess of trimethylchlorosilane was added slowly to a solution of 2 (20 mmol) in THF (130 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 2 h. Then the volatiles were removed under reduced pressure. The residue was extracted with pentane (100 mL) and filtered. Yellow crystals of 3a (quantitative yield) were obtained after the solution was concentrated and cooled to -10° C. M.p. 114 °C. Selected data for 3a; ¹H NMR (300.133 MHz, CDCl₃): $\delta = 6.76 \cdot 6.89$ and 6.94 - 7.10 (br. m, 20H, Ph), 0.16 (s, 18H, SiCH₃); ¹³C{H} NMR (75.403 MHz, CDCl₃ ($\delta = 77.00$)): $\delta = 151.55$, 149.34, 142.40, 140.34, 130.61, 129.53, 127.55, 127.19, 125.54, 124.90, 0.26 (SiMe₃); MS(El): *m/z* (%): 576 (74) [*M*⁺], 503 (22) [*M*⁺ - SiMe₃]. High-resolution MS: calcd. for C₃₄H₃₈GeSi₂ 576.1742, found 576.1720.

3b: Yellow crystals, quantitative yield, M.p. 78-80 °C; ¹H NMR (300.133 MHz, CDCl₃): $\delta = 6.75 - 7.10$ (br. m, 20H, Ph), 1.45 - 1.52 (br. m, 4H, CH₂), 1.30 (t, 4H, Ge-CH₂), 0.95 (t, 6H, -CH₃); ¹³C{H} NMR (75.403 MHz, CDCl₃): $\delta = 152.28$, 143.30, 140.98, 139.65, 130.14, 128.91, 127.80, 127.35, 125.90, 125.31, 18.80, 17.58, 17.37; MS(El): m/z (%): 516 (100) [M^{+1}], 473 (10) [M^{+-} nPr], 429 (69) [M^{+-} -2nPr]. High-resolution MS : calcd. for C₃₄H₃₄Ge 516.1882, found 516.1883.

3c: Yellow crystals, quantitative yield, M.p. 148–150 C; ¹H NMR (300.133 MHz. CDCl₃): $\delta = 6.78-7.23$ (br. m, 20H, Ph), 1.15–1.39 (br. m, 4H, -CH₂-), 1.00–1.15 (br. m, 4H, -CH₂-), 0.88 and 0.80 (t, 6H, -CH₃), 0.64 (t, 4H, Ge-CH₂); ¹³C{H} NMR (75.403 MHz, CDCl₃): $\delta = 151.84$, 145.40, 140.74, 139.50, 130.38, 129.46, 127.80, 127.39, 126.01, 125.54, 28.04, 25.01, 15.94, 13.44; MS(El): m/z (%): 544 (59) [M^{+} – 2nBu]. High-resolution MS: calcd. for C₃₆H₃₉Ge 544.2197, found 544.2188.

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- [8] X-ray structure analysis of 2a: $C_{28}H_{20}GeLi_2 \cdot 5C_4H_8O_2$, $M_r = 795.33$, triclinic, *P*1, a = 9.9864(13), b = 13.573(2), c = 15.881(2) Å, $\alpha = 98.190(9)$, $\beta = 15.881(2)$ Å, $\alpha = 98.190(9)$, $\beta = 13.573(2)$, $\beta = 15.881(2)$ Å, $\alpha = 98.190(9)$, $\beta = 15.881(2)$ Å, $\alpha = 98.190(9)$, $\beta = 15.881(2)$ Å, $\beta = 15.881(2)$ 95.827(10), $\gamma = 109.280(9)^\circ$, $V = 1985.6(4) \text{ Å}^3$, Z = 2, $\rho_{\text{caled}} = 1.330 \text{ M gm}^{-3}$, F(000) = 836, $\lambda = 0.71073$ Å, $\theta = 113(2)$ K. A yellow single crystal (dimensions $0.40 \times 0.40 \times 0.10$ mm) was mounted under a coating of Paratone-N. Data were collected by the ω scan method in the range of $1.50^{\circ} \le \theta \le 22.50^{\circ}$ on a Siemens P4 diffractometer. Of a total of 5533 reflections, 5177 ($R_{int} = 0.0310$) were independent. The structure was solved by direct methods with the SHELXS-86 program and refined by the full-matrix least-squares method on using the SHELXL-93 program. R(F) = 0.0370, $R_w(F^2-all) = 0.0887$. There is one lithium cation on each face of the five-membered Ge ring. Each Li is coordinated to two dioxane molecules, both of which are in chair conformations. One of the dioxane molecules that is coordinated to one lithium ion is also coordinated through its other oxygen atom to the lithium ion in another molecule. Thus these groups form infinite chains in the a direction of the crystal. There is also one dioxane molecule in a chair conformation that is not coordinated to any other group. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-16 and CCDC-179-17. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033; e-mail: teched(a chemcrys. cam.ac.uk).
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