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Unique Bis-η^5/η^1 Bonding in a Dianionic Germole. Synthesis and Structural Characterization of the Dilithium Salt of the 2,3,4,5-Tetraethyl Germole Dianion

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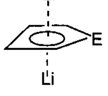
Summary: Reaction of 1,1-dichloro-TEGeCp (TEGeCp = 2,3,4,5-tetraethyl-1-germacyclopentadiene) with excess Li in tetrahydrofuran (THF) at room temperature gave [TEGeCp^{2-}]·2[Li$^+$] quantitatively. X-ray structure determination of this germole dianion shows three lithium cations around one germole ring in η^1, η^5, and η^5 sites to give the composition [η^5-Li·TMEDA][η^5-Li]$_{1/2}$[η^1-Li]$_{1/2}$-[Et_4C_4Ge] (TMEDA = N,N,N′,N′-tetramethylethylenediamine). Nearly equal C−C bond distances in the Et_4C_4Ge ring indicate a delocalized π-system. Reactions of this germole dianion with trimethylchlorosilane provided 1,1-bis(trimethylsilyl)-TEGeCp, in high yields.

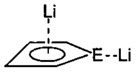
Introduction

The initial report of the synthesis and trapping of the tetraphenylsilole dianion, $Ph_4C_4Si^{2-}$, by Joo and coworkers[1] spurred a number of investigations, experimental and theoretical, of silole dianions and related systems because of their novel structural and electronic properites.[2−6] Hong and Boudjouk provided NMR evidence for significant delocalization in the dilithium salts of $Ph_4C_4E^{2-}$ (E = Si, Ge).[2] Aromaticity in $Ph_4C_4E^{2-}$ (E = Si, Ge) dianions with η^1, η^5 and η^5, η^5 type lithium metal-ring coordination was confirmed by West et al.[3,4] Similarly, Tilley reported the η^5, η^5 coordination pattern with the dipotassium salts of $Me_4C_4E^{2-}$ (E = Si, Ge).[5,6] Recently we discovered that the 1-silaindene system can be converted to a dianionic salt in which the silicon containing ring forms an aromatic silole dianion with lithium ions coordinated η^1, η^5 to the silole portion and the six-membered ring changes from a benzene structure to that of a cyclohexadiene.[7]

Until now, only two types of metal coordination to silole and germole dianions have been characterized by experimental or theoretical methods: η^5, η^5 (**a**) and η^1, η^5 (**b**).[4−8]



a



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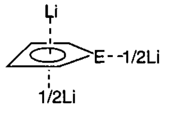
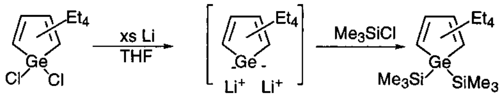


c

Herein we report that the reaction of excess lithium and 1,1-dichloro-2,3,4,5-tetraethylgermole (**1**) produces the novel structure **c** of the dilithium salt of the tetraethylgermole dianion, $Et_4C_4Ge^{2-}$ (**2**) (eq 1). Related to this work, we have reported the novel lithocenophane derivative of a trisgermole dianion, {[Li$^+$]·[(2,3,4,5-tetraethylgermolyl)$_2$](2,3,4,5-tetraethylgermole)}·{[Li$^+$]-(TMEDA)(THF)}, which showed well-resolved lithium ions in the solid state (X-ray) and in solution (NMR).[9]



1 **2** **3** (1)

Result and Discussion

Stirring of **1** with excess Li in THF for 2 h gives a dark red brown solution of **2**. After removing the unreacted metal by filtration, addition of this solution to an excess of trimethylchlorosilane produces 1,1-bis(trimethylsilyl)-TEGeCp (**3**; TEGeCp = 2,3,4,5-tetraethyl-1-germacyclopentadiene) in 95% yield. Compound **2**, which is stable for at least 1 year at room temperature under argon, could be isolated as colorless crystals from a saturated red THF/TMEDA solution.

The X-ray structure of **2** shown in Figure 1, and the selected bond lengths and bond angles are listed in Table 1. Analysis of the X-ray data for **2** shows two η^5−coordinated lithium ions and one η^1−coordinated lithium ion around the C_4Ge ring. Therefore, the composition of this germole dianion is [η^5-Li·TMEDA][η^5−Li]$_{1/2}$[η^1-Li]$_{1/2}$[Et_4C_4Ge].

One lithium ion (Li1) is η^5-coordinated to the C_4Ge ring and to TMEDA while the other (Li2) is η^5 -coordinated to the C_4Ge ring fragment and also η^1-coordinated

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[1] Joo, W.-C.; Hong, J.-H.; Choi, S.-B.; Son, H.-E. *J. Organomet. Chem.* **1990**, *391*, 27.

[2] (a) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387. (b) Hong, J.-H.; Boudjouk, P. *Bull. Chem. Soc. Fr.* **1995**, *132*, 495.

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[9] Hong, J.-H.; Pan, Y.; Boudjouk, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 186. The trisgermole dianion was generated from the same reaction in the presence of TMEDA (TMEDA = tetramethylethylenediamine) as a mixed solvent.

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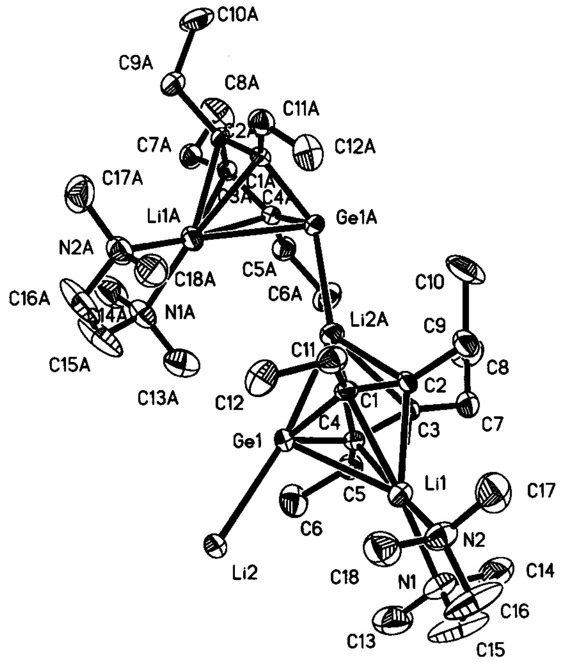

Figure 1. Structure of **2** in the solid state. All hydrogens are omitted for clarity. Symmetry transformations used to generate equivalent atoms: *x*, $-y + {}^3/_2$, $z + {}^1/_2$.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 2

Ge(1)−C(1)	1.959(4)	Ge(1)−C(4)	1.967(4)
Ge(1)−Li(2)A	2.583(7)	Ge(1)−Li(1)	2.675(6)
Ge(1)−Li(2)	2.684(6)	Li(1)−C(3)	2.291(7)
Li(1)−C(2)	2.304(7)	Li(1)−C(4)	2.392(7)
Li(1)−C(1)	2.412(7)	C(1)−C(2)	1.417(5)
C(1)−Li(2)A	2.319(7)	C(2)−C(3)	1.444(5)
C(2)−Li(2)A	2.256(8)	C(3)−C(4)	1.416(5)
C(3)−Li(2)A	2.256(8)	C(4)−Li(2)A	2.316(7)
C(1)−Ge(1)−C(4)	84.09(16)	Li(2)A−Ge(1)−Li(1)	94.6(2)
Li(2)A−Ge(1)−Li(2)	171.49(8)	Li(1)−Ge(1)−Li(2)	93.8(2)
C(2)−C(1)−Ge(1)	113.4(3)	C(1)−C(2)−C(3)	114.7(3)
C(4)−C(3)−C(2)	114.8(3)	C(3)−C(4)−Ge(1)	113.1(3)

to a germanium atom of another C_4Ge ring. This combination of linkages results in a polymeric network (Figure 2).

The three Li−Ge bond distances are almost equal (Li(1)−Ge(1) = 2.675, Li(2)−Ge(1) = 2.684, and Li(2A)−Ge(1) = 2.583 Å, respectively). The angle between the Li(2)−Ge(1) vector and the plane of the C_4Ge ring is 38.6°. The nearly equal carbon−carbon bond lengths in the GeC_4 ring (bond distances of the C_1−C_2, C_2−C_3, and C_3−C_4 are 1.417, 1.444, and 1.416 Å, respectively), and its planar geometry (bond angle summation of the GeC_4 ring; 540.0°) is consistent with a high degree of aromaticity.

It is noteworthy that the ^{7}Li NMR spectrum of solutions of X-ray quality crystals of **2** shows a broad signal at $\delta = -5.63$ ppm consistent with π-complexation.[9,10] Compound **1** shows only six peaks in the ^{13}C NMR, consistent with a C_2 axis of symmetry. Upon lithiation of **1** to form **2**, the ring carbons shift downfield [$\Delta\delta(C_{\alpha/\beta}) = 6.02$ ppm]. The trend in chemical shifts of the ring carbons in **2** is the same as in the aromatic 2,3,4,5-tetraphenyl substituted germole dianion {[TPGeCp^{2-}]·2[Li$^+$] (TPGeCp = 2,3,4,5-tetraphenyl-1-germacyclopentadiene), $\Delta\delta(C_{\alpha/\beta}) = 12.74$ ppm}.[2]

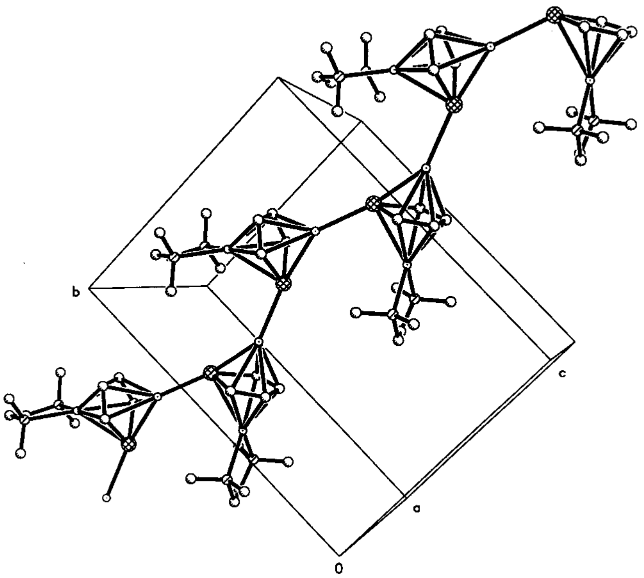

Figure 2. Stereoview of crystal structure of **2** in the solid state. All hydrogens and ethyl groups are omitted for clarity.

In summary, our results strongly suggest that the processes involving η^1, η^5 exchanges proceed through structure **c** without breaking aromaticity in the C_4E ring. This supports the mechanism proposed earlier by West[4] and could account for the rapidity of the exchanges resulting in the observation of only one lithium peak in solution for **2**.

Experimental Section

General Procedures. All reactions were performed under an inert argon atmosphere using standard Schlenck techniques. Air-sensitive reagents were transferred in an argon-filled glovebox. THF was freshly distilled under nitrogen from sodium/benzophenone ketyl immediately prior to use. Hexane was stirred over sulfuric acid, distilled from calcium hydride, and stored over 4 Å molecular sieves. Literature methods were used to prepare 1,1-dichloro-2,3,4,5-tetraethylgermole (**1**).[9] MS data were obtained on a Hewlett-Packard 5988A GC-MS system equipped with a methyl silicon capillary column. NMR spectra were recorded on a JEOL GSX400 spectrometer at 400 (^{1}H), 155 (^{7}Li), and 100 MHz (^{13}C).

X-ray Structure Determination of $C_{18}H_{36}GeLi_2N_2$ (2). X-ray quality crystals of **2** were grown from a concentrated THF/TMEDA solution at room temperature. A single crystal of **2** was mounted in a thin-walled glass capillary tube and sealed under argon. The space group is $P2_1/c$, monoclinic, with unit cell dimensions $a = 17.4334(9)$ Å, $b = 12.3698(6)$ Å, $c = 10.0941(5)$ Å, $\alpha = 90°$, $\beta = 105.5250(10)°$, $\gamma = 90°$, volume = 2097.35(18) Å^3, $Z = 4$, fw = 366.96, $d_{calc} = 1.162$ mg/m^3, $F(000) = 784$, and abs coeff = 1.460 mm^{-1}. Intensity data were collected at 298(2) K on a Siemens CCD SMART diffractometer with Mo Kα radiation and a graphite monochromator. A total of 12251 unique reflections were measured, and 4899 [R(int) = 0.0895] having $I > 2\sigma(I)$ were independent. The structure was solved by direct methods and refined by the full-matrix least-squares techniques on F^2 using the SHELXTL program (1953 data and 208 parameters). Final $R = 0.0642$, $R_w = 0.1454$ (for all reflections, $R = 0.0779$, $R_w = 0.1529$), and goodness-of-fit on $F^2 = 1.173$. Full details can be found in the Supporting Information.

NMR Study of 2. The NMR samples were prepared by dissolving the X-ray quality crystals of **2** in THF-d_8. The selected data for **2**: ^{1}H NMR (THF-d_8, ref; THF-d_8 = 1.73

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ppm): δ 1.08 (t, 6H), 1.28 (t, 6H), 2.14 (s, 12H), 2.27 (s, 4H), 2.58 (q, 4H), 2.69 (q, 4H). ^{13}C NMR (THF-d_8, ref; THF-d_8 = 25.48 ppm): δ 167.35, 126.44, 58.93, 46.41, 28.65, 22.65, 22.60, 19.12. ^{7}Li NMR (THF-d_8, ref; ext. LiBr (0.1 mol in D_2O) = 0.00): δ −5.63 (br s).

Preparation of 3.[6] Stirring or sonication[11] in a cleaning bath of **1** (1.72 g, 5.88 mmol) and lithium (0.191 g, 27.52 mmol) in THF for 2 h gives a dark red solution. Filtration and addition to an excess of trimethylchlorosilane (2.50 mL, 19.74 mmol) with stirring at room temperature produces a pale brown solution immediately. Additional stirring for 3 h gives a colorless solution with salt. All volatiles are removed under reduced pressure; the residue is extracted with hexane. Evaporation of hexane yields **3** as a colorless oil; yield, 95% by ^{1}H NMR integration. ^{1}H NMR (CDCl$_3$, ref; ext. TMS = 0.00 ppm): δ 0.20 (s, SiMe$_3$, 18H), 2.41 (q, 6H, Me, J = 7.33 Hz), 2.30 (q, 6H, Me, J = 7.33 Hz), 0.97 (t, 4H, CH$_2$, J = 7.33 Hz), 1.06 (t, 4H,CH$_2$, J = 7.33 Hz). ^{13}C NMR (CDCl$_3$, ref; CDCl$_3$ = 77.00 ppm): δ 0.63 (SiMe), 150.59 (C_{sp^2}), 143.99 (C_{sp^2}), 24.60 (CH$_2$), 21.43 (CH$_2$), 17.25 (CH$_3$), 15.35 (CH$_3$). ^{29}Si NMR (CDCl$_3$, ext. TMS): δ −7.89 (SiMe$_3$). MS (M$^+$, relative abundance): 384 (M$^+$; 6), 369 (M$^+$ − Me; 10), 311 (M$^+$ − SiMe$_3$; 16), 73 (100). Anal. Calcd for $C_{18}H_{38}GeSi_2$: C, 56.41; H, 9.99. Found: C, 56.68; H, 9.64.

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Supporting Information Available: Tables of bond distances and angles, hydrogen atom coordinates, and anisotopic thermal parameters for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Sonication can activate lithium metal by keeping the lithium surface clean. A common ultrasonic cleaner (Branson, 50/60 Hz) was used for sonication of synthetic scale reactions. The sample was placed in a location in the bath that produced maximum cavitation in the reaction flask. For reviews of the effects of ultrasonic waves on heterogeneous reactions see: (a) Boudjouk, P. In *High Energy Processes in Oganometallic Chemistry;* Suslick, K. S., Ed.; ACS Symposium Series 333; American Chemical Society: Washington, DC, 1987; Chapter 13. (b) Boudjouk, P. In *Ultrasound: Chemical, Physical and Biological Effects;* Suslick, K. S., Ed.; Verlag Chemie: Deerfield Beach, FL, 1988; Chapter 5.