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Synthesis and characterization of a delocalized germanium-containing dianion: dilithio-2,3,4,5-tetraphenyl germole [1]

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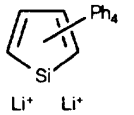
Summary – Sonication of 1,1-dichloro-TPGeCp (TPGeCp = 2,3,4,5-tetraphenyl-1-germacyclopentadiene), with an excess of Li in THF at room temperature gives the germole dianion, $\{[\mathrm{TPGeCp}^{2-}] \bullet 2[\mathrm{Li}^+]\}$, as the major product. Reactions of this salt with RX (methyl iodide, chlorodimethylsilane, chlorotrimethylsilane) give 1,1-R,R-TPGeCp derivatives in high yields. NMR studies (^{1}H and ^{13}C) of $\{[\mathrm{TPGeCp}^{2-}] \bullet 2[\mathrm{Li}^+]\}$ give evidence of a high degree of π-delocalization.

germanium / dianion / π-delocalization / dilithio-2,3,4,5-tetraphenyl germole

Introduction

Group 14-heterole anions are of considerable interest because of their potential aromaticity [2]. However, until our report of the aromaticity in the silacyclopentadienide anion, no convincing evidence for extensive π-delocalization in group 14-heteroles had been documented [3]. Recently, we discovered that the novel 2,3,4,5-tetraphenyl silole dianon $\{[\mathrm{TPSiCp}^{2-}] \bullet [2\mathrm{Li}^+]\}$ **1** and, 1,1′-disila-2,2′,3,3′,4,4′,5,5′-octaphenylfulvalene dianon $\{[\mathrm{TPSiCp}^-]_2 \bullet 2[\mathrm{Li}^+]\}$ **2** (TPSiCp = 2,3,4,5-tetraphenyl-1-silacyclopentadiene) were not only stable for extended periods in solution, but also exhibited spectroscopic properties consistent with aromaticity in the rings [4].



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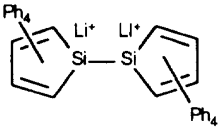

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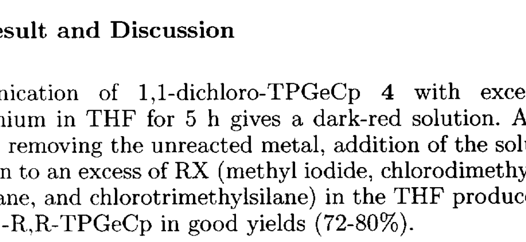
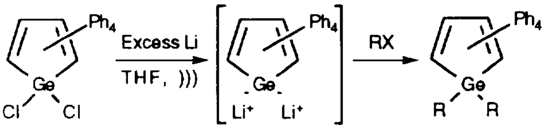
The germole anion is a reasonable candidate for a stable aromatic germanium species [5] but a careful study by Dubac *et al* demonstrated that there is no significant delocalization of the negative charge on germanium into the ring or the phenyl substituent for 1-phenyl-1-lithio-2,3,4,5-tetramethylgermacyclopentadienide **3** [6]. Recently, however, Tilley *et al* provided persuasive NMR and X-ray data that point to extensive π-delocalization in the germole portion of the complex $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Ru}\{\eta^5\text{-C}_4\mathrm{Me}_4\mathrm{GeSi}(\mathrm{SiMe}_3)_3\}]$ [7]. In the paper, we report the preparation and characterization of the novel germole dianion, $\{[\mathrm{TPGeCp}^{2-}] \bullet 2[\mathrm{Li}^+]\}$, in which there is substantial π-delocalization onto the ring.



Result and Discussion

Sonication of 1,1-dichloro-TPGeCp **4** with excess lithium in THF for 5 h gives a dark-red solution. After removing the unreacted metal, addition of the solution to an excess of RX (methyl iodide, chlorodimethylsilane, and chlorotrimethylsilane) in the THF produces 1,1-R,R-TPGeCp in good yields (72-80%).



4 **5** **6**(RX = MeI)
7(RX = $\mathrm{Me_2HSiCl}$)
8(RX = $\mathrm{Me_3SiCl}$)

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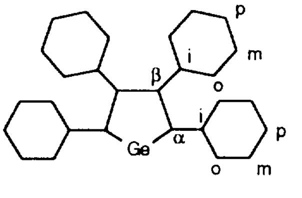
* Correspondence and reprints

Table. ^{13}C NMR δ and $\Delta\delta$ values for the neutral (**4**)^a and germole dianion (**5**)^b.

	4		5			5-4	
C_α	132.76		129.92		ΔC_α	−2.84	
C_β	149.99		165.57		ΔC_β	15.58	
	α Ph	β Ph	α Ph	βPh		αPh	β Ph
C_i	134.69	136.59	146.30	152.17	ΔC_i	11.61	15.58
C_o	129.51	129.59	129.92	133.49	ΔC_o	0.41	3.90
C_m	128.37	128.08	126.38	126.38	ΔC_m	−1.99	−1.70
C_p	127.47	127.71	119.29	121.91	ΔC_p	−8.18	−5.80
C_i-C_p	7.22	8.88	27.01	30.26			
ΔC_{i-p}^{c}	8.05		28.64				

^{a}In CDCl$_3$, reference; CDCl$_3$ = 77.00 ppm. ^{b}In THF-d_8, reference; THF-d_8 = 25.30 ppm. ^{c}The average chemical shift differences of C_i-C_p.

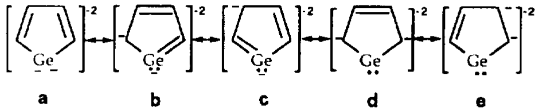
Sonication of **4** with excess Li in THF-d_8 in an NMR tube gives the corresponding germole dianion $\{[TPGeCp^{2-}] \bullet 2[Li^+]\}$ **5** exclusively, showing only ten peaks in the ^{13}C NMR, consistent with a C_2 axis of symmetry (fig). Typically, in ^{13}C NMR, upfield shifts of C_α and C_β are generally observed for five-membered ring compounds having aromatic contributors such as cyclopentadienyl anions [8] and silole anions [3, 4] relative to those of the corresponding neutrals. In those anions, the negative charge is delocalized onto the ring carbons to increase the electron density at their positions resulting in upfield chemical shifts. In contrast, downfield shifts are observed for the ring carbons [$\Delta\delta(C_\alpha)$ = 10.5 ppm and $\Delta\delta(C_\beta)$ = 2.6 ppm] in 1-phenyl-1-lithio-2,3,4,5-tetramethyl-1-germacyclopentadienide **3**, in which the negative charge is localized on the germanium atom. These shifts are rationalized in terms of a fields effect induced by that negative charge [6].

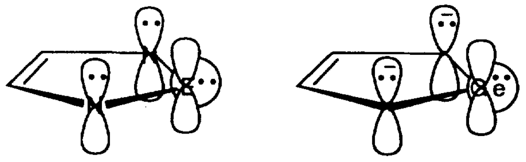


Upon metalation of **4** to form **5**, the C_α of the ring shifts upfield [$\Delta\delta(C_\alpha)$ = −2.84 ppm] and the C_β shifts downfield [$\Delta\delta(C_\beta$ = 15.58 ppm] (table).

One possible explanation of these observations is that the α-carbon atoms bear significant additional electron density compared with **4** but that the β carbon atoms participate in a more conventional π-bonding arrangement. In valence bond formalism this amounts to resonance form **d** making an important contribution to the ground state of **5**. This rationale differs only slightly from that used to explain the NMR data of the silole analog, *ie* that the upfield shifts of the C_β carbons in the silole dianion suggest that resonance forms **b**, **c** and **e** are also important contributors in addition to **d** [4a].

There is also a reasonable orbital picture model of the electronic structure of **5**. The germole dianion is isoelectronic with the known 6 π electron ring system of carbene analogs, CH=CH(t-Bu)NEN(t-Bu) (E = C [9], Si [10], and Ge [11]), which calls for a singlet ground state in which stabilization of the divalent atom E is attributed to synergistic σ-withdrawal and π-donation of the two neighboring nitrogen atoms.





5 based on diazagermolylidene model

The *ipso* carbon atoms, C_i, of **5** show large downfield shifts [$\Delta\delta(C_i)$ = 11.61 and 15.58 ppm] and the *ortho* carbon atoms, C_o, show small downfield shifts [$\Delta\delta C_o$ = 0.41 and 3.90 ppm]. In contrast, the *meta* carbons, C_m, show small upfield shifts [$\Delta\delta(C_m)$ = −1.99 and −1.70 ppm] and the *para* carbons, C_p, show large upfield shifts [$\Delta\delta(C_p)$ = −8.18 and −5.80 ppm] (table). As expected, there is no π-resonance between the ring carbons (C_α and C_β) and the four phenyl groups because of the perpendicular orientation of the phenyl groups with respect to the germole ring [12].

We observed a pattern worthy of note: the average chemical shift differences in the *ipso* and *para* carbons, ΔC_{i-p}, are similar for dianions regardless of the heteroatom and that dianions are significantly more polarized than monoanions. For the silole monoanions $\{[TPSiCp^-] \bullet [Li^+]\}$, $\{[TPSiCp^-] \bullet [Na^+]\}$, the dianions **1** and **2**, and the germole dianion **5**, the ΔC_{i-p} values (in ppm) are 24.65, 24.16, 28.10, 25.82, and 28.64, respectively [3, 4]. This suggests that π-polarization in silole and germole species is similar. Proton NMR data for **5** show only phenyl protons and over a broader region than the dichloro precursor **4** (from 6.8-7.2 to 6.5-7.1 ppm). Similar observations were made for the silole analogs.

Conclusion

1,1-Dichloro-2,3,4,5-tetraphenyl-1-germacyclopentadiene **4** is a precursor to the novel species, 2,3,4,5-tetraphenyl germole dianion, $\{[TPGeCp^{-2} \bullet 2[Li^+]\}$ **5**. ^{13}C NMR spectra are consistent with a high degree of π-delocalization. Dianion **5** can be derivatized to give high yields of 1,1-disubstituted-1-germacyclopentadienes.

Experimental section

General procedures

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air-sensitive reagents were transferred in a nitrogen-filled glovebox. Ether or THF was distilled from sodium benzophenone ketyl under nitrogen. Pentane or toluene was stirred over concentrated H_2SO_4 and distilled from CaH_2. A common cleaning bath was used to sonicate the reaction mixtures. NMR spectra were recorded on JEOL GSX270 and GSX400 spectrometers. Elemental analyses were done by Desert Analytics (Tucson, Arizona).

1,1-Dichloro-TPGeCp 1

Diphenylacetylene (17.8 g, 100 mmol) and finely cut lithium (1.50 g, mmol) were stirred at room temperature for 3.5 h in 170 mL of dry ether producing a brown solution and a yellow precipitate. The reaction mixture was cooled to −78°C and tetrachlorogermane (12.84 mL, 100 mmol) was added by syringe. The cooling bath was removed and the reaction mixture, as it stirred, was allowed to warm to room temperature. Stirring it for 5 h gave a yellow solution with a lot of yellow precipitate. Filtration using a glass filter separated a yellow solution from a yellow solid mixed with unreacted lithium metal. The yellow solid was dissolved in 150 mL of hot toluene and filtered followed by washing of the solid with 50 mL of hot toluene. Cooling of the combined toluene solutions and a separate flask containing the ether filtrate in the freezer led to the isolation of yellow crystals.

Yield, 19.74 g (79%), mp 198-199°C (Lit [5] 197-199°C).

^1H NMR ($CDCl_3$, ref; ext TMS = 0.00 ppm), 6.80-6.86 and 7.00-7.20 (brd m, 20H, Ph).

1,1-Dimethyl-TPGeCp 6

Sonication of **4** (1.00 g, 2.00 mol) with an excess of Li (0.11 g, 15.71 mmol) and 50 mL of THF for 5 h gives a dark-red solution. After removing the unreacted metal, the THF solution was added to an excess of methyl iodide with stirring at room temperature producing a yellow solution. Removing volatile reagents under reduced pressure, yellow residue was extracted with pentane. Crystallization in pentane gave yellow crystals of **6**, which was identified by comparision with an authentic sample. For dimethylchlorosilane and trimethylchlorosilane, the same procedures were followed. All yields were calculated by proton NMR.

Yield, 80%, mp 179-180°C (Lit [13] 179-181°C, Lit [14] 183-184°C).

^1H NMR ($CDCl_3$, ref; ext TMS = 0.00 ppm), 0.68 (s, 6H, $GeMe_2$), 6.80-7.15 (brd m, 20H, Ph).

^{13}C NMR ($CDCl_3$, ref; $CDCl_3$ = 77.00 ppm), −2.57 ($GeMe_2$), 151.20 (C_β), 143.88 (C_i of C_β), 140.32 (C_α), 139,39 (C_i of C_α), 130.12, 128.85, 127.87, 127.39 (C_m, C_o), 125.49 (C_p).

1,1-Bis(dimethylsilyl)-TPGeCp 7

Yield, 72%, mp 118-123°C.

^1H NMR ($CDCl_3$, ref; ext TMS = 0.00 ppm), 0.19 (d, 12H, $SiMe_2$, J = 4.40 Hz), 4.38 (sept, 2H, SiH, J = 4.40 Hz), 6.7-7.1 (brd m, 20H, Ph).

^{13}C NMR ($CDCl_3$, ref; $CDCl_3$ = 77.00 ppm), −4.81 ($SiMe_2$), 151.73(C_β), 147.93 (C_i of C_β), 141.64 (C_i of C_α), 140.13 (C_α), 130.49, 129,43, 127.71, 127.37 (C_m, C_o), 125.78, 125.23 (C_p).

^{29}Si NMR ($CDCl_3$, ref; ext TMS = 0.00 ppm), −28.14,

Anal calc for $C_{32}H_{34}Si_2Ge$: C, 70.12; H, 6.39, Found : C, 70.03; H, 6.28.

1,1-Bis(trimethylsilyl)-TPGeCp 8

Yield, 80%, mp 114-115°C (Lit[15] 114°C).

^1H NMR $CDCl_3$, ref ext TMS = 0.00 ppm), 0.18 (s, 12H, $SiMe_3$), 6.8-7.1 (brd m, 20H, Ph).

^{13}C NMR ($CDCL_3$, ref; $CDCl_3$ = 77.00 ppm), 0.26 ($SiMe_3$), 142.38 (C_β), 151.52 (C_i of C_β), 149.33 (C_i of C_α), 140.32 (C_α), 130.59, 127.18 (C_m, 129.53, 127.55 (C_o), 125.52, 124.88 (C_p.

^{29}Si NMR ($CDCl_3$, ref; ext TMS = 0.00 ppm), −4.27.

NMR study of 2,3,4,5-tetraphenyl germole dianion $\{[TPGeCp^{2-}] \bullet 2[Li^+]\}$ 5

Sonication of **4** (0.10 g, 0.20 mol) with an excess of Li (0.027 g, 1.10 mmol) and 1.5 mL of THF-d_8 in 5 mm NMR tube for 5 h gives a dark red solution. NMR spectra (^1H and ^{13}C) show that only **5** is formed.

^1H NMR (THF-d_8, ref; THF-d_8 = 1.73 ppm), 7.02 (d, H_o, 4H, J = 7.3 Hz), 6.84 (d, H_o, 4H, J = 7.3 Hz), 6.83 (t, H_m, 4H, J = 7.3 Hz), 6.68 (t, H_m, 4H, J = 7.3 Hz), 6.65 (d, H_p, 2H, J = 7.3 Hz), 6.47 (d, H_p, 2H, J = 7.3 Hz).

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