Stable Germanium Radicals

A Stable and Crystalline Triarylgermyl Radical: Structure and EPR Spectra**

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Dedicated to Professor Michael F. Lappert on the occasion of his 80th birthday

There is much current interest in the chemistry of stable and isolable radicals of the heavier Group 14 elements germanium, tin, and lead.^[1] Since the discovery of persistent heavier Group 14 element radicals almost 30 years ago,^[2] some germanium- or tin-centered radicals with aryl,^[3] alkyl,^[4] or amido ligands^[5] with half lives varying from minutes to years have been detected and studied by EPR spectroscopy. These compounds were generated either by UV irradiation of solutions containing stable low-valent precursors, hydrogen abstraction from metallanes, or reduction of halide derivatives. Despite the fact that these persistent radicals have been successfully detected in solution, they have successfully defied any attempt of isolation in the solid state for a long time.

The first remarkably stable germanium-, tin-, and leadcentered free radicals have been described, including the cyclotrigermenyl radical '[Ge(2,6multinuclear Mes₂C₆H₃)]₃,^[6a] the radical species MAr*GeGeAr* and $M_2Ar^*GeGeAr^*$ (M = Na, K; Ar* = terphenyl),^[6b] and the mononuclear trisilylgermyl/stannyl $M(SiMetBu_2)_3$ (M = Ge, Sn),^[7a,b] and trisilylplumbylradical 'Pb[(Si(SiMe₃)₂Et]₃.^[7c] Whereas the former radicals were synthesized by reduction of the corresponding heteroleptic terphenylgermanium(II) chlorides, the generation of the persilylated germanium and tin radicals was achieved by oxidation of the sodium trisilylmetallates NaM(SiMetBu₂)₃, formed in situ, with [MCl₂(dioxane)]. The latter is both oxidizing agent and substrate for metallate formation in the reaction with NaSiMetBu₂. The silvlated plumbyl radical was synthesized by a similar approach, but using $Pb(2,6-tBu_2C_6H_3O)_2$ as the oxidant for potassium trisilylplumbanide.^[7c] According to Xray crystallography and EPR solution studies, the geometry around the radical centers of $M(SiMetBu_2)_3$ (M = Ge, Sn) is strictly planar, both in the solid state and in solution.^[7a,b] In contrast, EPR studies showed that all other previously

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[**] C.D. gratefully acknowledges Sogem Deutschland GmbH for a donation of germanium tetrachloride and Prof. E. Hey-Hawkins for support. reported germyl and stannyl radicals have a more or less pronounced pyramidal geometry at the metal center.^[1]

Herein we report the isolation, characterization, and an optimized synthesis of the first stable triarylgermyl radical with an almost planar geometry at germanium in solid state. In the course of our studies into mixed-valence compounds of the heavy Group 14 elements,^[8] reaction of Li[3,5-*t*Bu₂-2,6-(EtO)₂C₆H] (LiR) with [GeCl₂(dioxane)] in a 2:1 stoichiometry led to the germyl radical GeR₃ (1) as the only crystalline compound in 9% yield [Equation (1)]. Bright orange crystals of the remarkably thermally stable and thermochromic

$$[GeCl_2(dioxan)] + 2 LiR \xrightarrow{THF} GeR_3$$
(1)

compound **1** were obtained from a *n*-hexane solution. These crystals turned dark red in color upon heating in a sealed capillary under nitrogen to 200 °C, but decomposed rapidly at temperatures above 200 °C, with concurrent decolorization.

The molecular structure of radical **1** is illustrated in Figure 1.^[9] It resembles that of structurally characterized triarylmethyl analogues, with a general propeller-like arrangement of the aryl groups.^[10] In compound **1**, three



Figure 1. Molecular structure of 1 with ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C1 1.943(3), Ge1–C19 1.946(4), Ge1–C37 1.927(4); C1-Ge1-C19 119.36(15), C1-Ge1-C37 119.69(14), C19-Ge1-C37 120.42(13).

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twisted aryl rings radiate from the germanium center, with only a slight deviation from 120° observed in the C_{ipso} -Ge1- C_{ipso} angles. The dihedral angles between the mean plane of each aryl ring and the central $(C_{ipso})_3$ reference plane are $30.23(13)^\circ$ for C1, and 27.19(17)° for C19 and 26.81(18)° for C37. The coordination at germanium is essentially planar (sum of angles = 359.47°), and its deviation from the $(C_{ipso})_3$ reference plane is marginal (0.082(2) Å). The Ge1– C_{ipso} bonds (C1 1.943(3), C19 1.946(4), C37 1.927(4) Å) are somewhat shorter than those reported for hexaphenyldigermane (average 1.96(1) Å).^[11]

Radical 1 was also investigated by variable-temperature EPR studies. The room-temperature X-band EPR spectrum of 1 in *n*-hexane exhibits a central line, caused by interaction of the unpaired electron with the germanium isotopes having I=0, which is flanked by a nonsymmetrical low-intensity hyperfine structure (hfs) dectet arising from interaction with the ⁷³Ge nucleus (I = 9/2, natural abundance 7.8%). Owing to the low natural abundance of 73Ge, the intensity of an individual ⁷³Ge hfs line amounts only 0.8% of that of the central line. The spectrum was simulated, yielding the values $g_0 = (2.0095 \pm 0.0010)$ and $a_0^{\text{Ge}} = (6.13 \pm 0.10) \text{ mT}$. However, neither hyperfine interactions arising from the ¹³C_{ipso} atoms bonded to the germanium atom nor ¹H hfs couplings with H_{para} atoms of the aryl rings were observed, even for very low radical concentrations (ca. 10^{-5} M); in liquid solution, the minimum linewidth was $\Delta B_{\rm pp} \approx 0.38$ mT. The X-band spectrum of a frozen solution of 1 at 130 K is shown in Figure 2



Figure 2. a) Experimental and b) simulated X-band EPR spectrum of 1 in *n*-hexane at 130 K.

together with its simulation. It is axially symmetric, with $g_{\parallel} = 2.004$, $g_{\perp} = 2.012$ ($g_i = \pm 0.001$), $A_{\parallel}^{\text{Ge}} = 8.07$, and $A_{\perp}^{\text{Ge}} = 4.39 \text{ mT} (A_i = \pm 0.10 \text{ mT})$.

These EPR parameters are in good agreement with those reported for other triarylgermyl radicals that were only observed in solution,^[1,12] and are also indicative of a non-planar structure of **1** in solution. To investigate this structural feature and to obtain information on the spin density distribution in compound **1**, DFT-MO calculations using the

2,6-dimethoxyphenyl group as a model substituent were performed with geometry optimization.

The experimentally obtained and the calculated ⁷³Ge hfs coupling constants for a planar $Ge(C_{aryl})_3$ unit and for a pyramidal structure (the energy minimum from the geometry optimization) are given in Table 1. Moreover, the germanium

Table 1: Experimental^[a] and calculated^{[b]73}Ge hyperfine couplings (in mT) for 1 and spin densities of the germanium s, p, and d orbitals.

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	Experimental	Calculated	
		planar	pyramidal
A	8.07	4.23	8.75
A_{\perp}	4.39	1.06	5.75
2 A _{dip}	2.45	2.11	2.00
$\langle A_{av} \rangle$	5.62	2.12	6.75
<i>a</i> ₀ ^[c]	6.13	-	_
s density	0.068	0.009	0.057
p density	0.718	0.760	0.673
d density	-	0.033	0.044
total density	0.786	0.802	0.774

[a] Measured in *n*-hexane; \pm 0.10 mT. [b] Calculated for the 2,6-dimethoxyphenyl substituent. [c] Obtained from the EPR spectrum obtained in liquid solution.

s and p spin densities calculated from the experimental data using the MORTON/PRESTON formalism^[13] and those gained from the DFT calculations are given. From these data, the following conclusions can be drawn:

- a) The isotropic ⁷³Ge hfs coupling appears to be the key factor in the evaluation of the structure of **1** in solution. Therefore, a satisfactory agreement between the experimentally observed and the calculated values is achieved only for the pyramidal $Ge(C_{arvl})_3$ core structure.
- b) The DFT-optimized C_{ipso}-Ge-C_{ipso} angle for the pyramidal structure is 116.5°; the deviation of the Ge(C_{aryl})₃ unit from planarity and the calculated torsion angle amount to ca. 11° and ca. 34°, respectively (X-ray analysis: 28.1°). The pyramidal structure is favored over the planar structure by 8.5 kJ mol⁻¹.
- c) The calculated dipolar part of the ⁷³Ge hfs tensor $(2A_{dip})$ appears not to be essentially influenced by the geometry of the Ge $(C_{aryl})_3$ unit. Therefore, it cannot be used as a criterium.

The formation of radical **1** in the reaction of Li[3,5-*t*Bu₂-2,6-(EtO)₂C₆H] with [GeCl₂(dioxane)] [Equation (1)] was entirely unforeseen.^[14] In contrast to this reaction, from which no germanium(II) derivative was isolated, the reaction of the Grignard compound BrMg[3,5-*t*Bu₂-2,6-(EtO)₂C₆H] with [GeCl₂(dioxane)] gave the crystalline digermene [Ge{3,5*t*Bu₂-2,6-(EtO)₂C₆H]₂]₂ (**2**) in 85% yield.^[15] Involvement of the lithium germanate LiGe[3,5-*t*Bu₂-2,6-(EtO)₂C₆H]₃ in the formation of **1**, in analogy to the synthesis of 'Ge-(SiMe*t*Bu₂)₃,^[7a] however appears unlikely, as attempts to prepare the lithium germanate from **2** and Li[3,5-*t*Bu₂-2,6-(EtO)₂C₆H] failed, and the solution remained EPR-silent. Instead, radical **1** was isolated in 62% yield after stepwise treatment of digermene **2** with an equimolar amount of

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[GeCl₂(dioxane)] followed by two equivalents of Li[3,5- tBu_2 -2,6-(EtO)₂C₆H] (see Experimental Section). However, the constitution of the intermediate from the reaction of digermene **2** with [GeCl₂(dioxane)], and thus the formation of **1**, remains an open question; trapping reactions have so far been unsuccessful, and further experiments are in progress.

In summary, we have synthesized the first crystalline triarylgermyl radical **1**. The compound was characterized by X-ray analysis and variable-temperature EPR spectroscopy. The results obtained support an almost planar structure for **1** in the solid state and a pyramidal geometry in solution. Furthermore, DFT calculations show that a pyramidal structure is energetically slightly favored.

Experimental Section

All manipulations were carried out under vacuum or nitrogen by using standard Schlenk techniques.

Optimized synthesis for 1: [GeCl₂(dioxane)] (0.07 g, 0.30 mmol) was added in small portions to a solution of 2 (0.190 g, 0.15 mmol) in THF (20 mL) at 0 °C. The pale yellow reaction mixture was stirred for approximately 2 min at 0°C. A solution of Li[3,5-tBu2-2,6- $(EtO)_2C_6H]$ (0.176 g, 0.62 mmol) was then added (this compound was prepared from 1-Br-3,5-tBu₂-2,6-(EtO)₂C₆H and nBuLi (2.5 M in *n*-hexane) at -20 °C in Et₂O; all volatile compounds were subsequently removed, and after washing with hexane, THF (10 mL) was added). The mixture was stirred for 10 h. All volatile compounds were removed in vacuo, and the residual solid was extracted into n-hexane. After filtration and concentration, the solution was set aside for 12 h at ambient temperature and a further 12 h at -30 °C to give 1 as bright orange crystals (0.17 g, 62 %). M.p. (nitrogen, sealed capillary): 201 °C (decomp.); elemental analysis (%) calcd for C₅₄H₈₇O₆Ge: C 71.70, H 9.70, O 10.60; found: C 72.2, H 9.8, O 11.3. EI-MS: m/z (%): 905 $(53) [M]^+, 876 (100) [M-Et]^+, 627 (100) [M-R]^+. UV/Vis (n-hexane)$ λ_{\max} (ε): 274 (24430), 353 (43200), 464 nm (9500).

2: A solution of [GeCl₂(dioxane)] (0.70 g, 3.02 mmol) in THF (5 mL) was added dropwise to a cooled $(-78 \, {}^{\circ}\text{C})$ solution of the Grignard compound BrMg[3,5-tBu₂-2,6-(EtO)₂C₆H] (prepared from 1-Br-3,5-tBu₂-2,6-(EtO)₂C₆H (2.2 g, 6.16 mmol) and magnesium shavings (0.5 g, 20.75 mmol) in 40 mL of THF). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. All volatile compounds were removed under vacuum and the residue was extracted into hot n-hexane and subsequently filtered. Concentration of the filtrate until the onset of crystallization and storage at ambient temperature gave yellow 2 (1.61 g, 85%). M.p. (nitrogen, sealed capillary): 171 °C; elemental analysis (%) calcd for C₃₆H₅₈O₄Ge: C 68.91, H 9.32, O 10.20; found: C 68.78, H 9.13, O 10.33; NMR $(C_6D_6, \text{ tetramethylsilane, } 300 \text{ K}): {}^{1}\text{H} (400 \text{ MHz}): \delta = 1.31 \text{ (t, } J =$ 7.2 Hz, 6H, OCH₂Me), 1.41 (s, 18H, tBu), 4.14 (q, J=7.2 Hz, 4H, OCH₂Me), 7.23 ppm (s, 1H, aryl); ${}^{13}C{}^{1}H{}$ (100.6 MHz): $\delta = 15.03$ (CH2Me), 31.0 (CMe3), 34.6 (CMe3), 71.9 (CH2Me3), 125.7, 134.2, 143.8, 160.0 ppm (aryl); EI-MS: m/z (%): 628 (100) $[M]^+$, 613 $[M - Me]^+$.

EPR spectra of **1** were recorded in *n*-hexane solutions (concentration $< 10^{-3}$ M) at T=295 and 130 K with a BRUKER ESP 300 E spectrometer. The spectra were simulated using the program package XSophe.^[16]

DFT calculations were carried out using the Gaussian03 program package^[17] with B3LYP functionals^[18,19] and the standard 6-31g(d) basis set.^[20]

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