Radicals and Anions of Siloles and Germoles

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In memory of Zvi Rappoport

Abstract: The synthesis of persistent sila- and germacyclopentadienyl (silolyl- and germolyl-) radicals by careful stoichiometric reduction of the corresponding halides with potassium is reported. The radicals were characterized by EPR spectroscopy and trapping reactions. The reduction of tris(trimethylsilyl)silyl-substituted halides was successful while smaller substituents (i.e., tert-butyl, Ph) gave the corresponding dimers. The EPR spectroscopic parameter of the synthesized tetrolyl radicals indicate only small spin delocalization to the butadiene unit due to cross-hyperconjugation. Silolyl- and germolyl anions are unavoidable byproducts and are isolated in the form of their potassium salts and characterized by X-ray crystallography. The comparison of the molecular structures of two closely related potassium silolides provided an example for different coordination of the potassium cation to the silolyl anion (η1 vs. η2 coordination) that triggers the switch between delocalized and localized states.

Introduction

Progress in the chemistry of tetroles I, the heavier analogs of cyclopentadiene, is driven by the favorable photophysical properties of these compounds (Figure 1).[1–4] The cross-hyperconjugation between the butadiene part and the tetrylene unit lowers their absorption energy and promotes their application in optoelectronic devices.[5–8] The discovery of the aggregation induced emission effect in perarylated siloles additionally fueled the interest in this class of compounds.[9–12] The second main spring for the development of the chemistry of tetroles was the possible occurrence of aromaticity in the negatively charged ions, II and III, and their applications as ligands in transition metal chemistry.[13–16] During the last years, the group of Saito and the Oldenburg team contributed to this field by demonstrating that tetrolyl dianions III are suitable precursors for a wide variety of novel compounds with the tetrel element in unusual coordination environments.[13,16–18] In view of the vast existing body of knowledge on tetroles’ material chemistry, we asked ourselves if the favorable photophysical properties of tetroles might be combined with magnetic properties resulting from an unpaired spin as for example in tetrolyl radicals IV. An inspiration came from one report by the West group who communicated on the existence and stability of a silolyl-based biradical V with triplet ground state and its surprisingly low reactivity.[20] We report here on the successful preparation of neutral silolyl and germolyl radicals IV (E=Si, Ge) and some of their properties. In addition, we report on a structural study on closely related tetrolyl anions II (E=Si, Ge) and their transformation between delocalized and localized states induced by substituent effects.

Results and Discussion

We attempted the synthesis of germolyl radicals by careful stoichiometric reduction of the corresponding germolyl halides 1 with potassium graphite according to procedures published by the group of Sekiguchi.[21–23] In the case of 1-phenyl and 1-tert-butyl substituted germolyl halides 1a and 1b only the...
corresponding Ge–Ge bonded dimers 2a,b were obtained, indicating insufficient steric shielding of the intermediate germolyl radical. Both compounds were isolated in moderate to good yields and fully characterized by NMR spectroscopy and their molecular structures in the solid state were determined by X-ray diffraction (XRD) analysis. Increasing the size of the substituent R at the germanium atom from the tert-butyl to the tris(trimethylsilyl)silyl group finally allowed the detection of the germolyl radical 3c in high concentrations by EPR spectroscopy after reduction of germolyl chloride 1c (Scheme 1).[24] The trapping reaction with cyclohexadiene gives 1H-germole 4 in high yield. The identity of germole 4 was verified by independent synthesis from germole chloride 1c (Scheme 2).

The results of density functional calculations guided our choice of the substituent R’ of the starting germolyl halides (Table 1).[26] The spatial requirements of the phenyl and the tert-butyl substituent are very similar as shown by their almost identical cone angles Θ.[25] As a result, their influence on the formation of a Ge–Ge linkage is the same. The Ge–Ge atomic distances in bis-germole 2a, b are almost identical and the calculated bond dissociation energies (BDEs) are very similar. In contrast, the steric effect of the tris(trimethylsilyl)silyl group as measured by its cone angle Θ is substantially larger. The results of the computation predicted a significant increase of the Ge–Ge bond length of the dimer 2c and a considerable weakening of the Ge–Ge bond (Table 1). In addition, the tris(trimethylsilyl)silyl substituent stabilizes the germolyl radical compared to the hydrogen substituted germolyl radical (ΔE < 0, see Table 1 and Supporting Information material for details).[24] Both factors favored the formation of the germolyl radical 3c. The comparison with the data calculated for the trimethylsilyl substituent, which also stabilizes the silolyl radical, suggests that the steric factors are however decisive. These results can be transferred to siloles, the tris(trimethylsilyl)silyl substituent allowed the synthesis of the corresponding silolyl radical by reduction of silolyl chloride 5 (Scheme 3).[24]

The reduction of germolyl chloride 1c and silolyl chloride 5 were performed at low temperature in THF and after changing to a non-polar solvent such as hexane intensive EPR signals of the neutral radicals 3c and 6 were detected. In the absence of air and moisture, the germolyl radical 3c is stable in solution for weeks. In contrast, the silolyl radical is persistent but decomposed over several days. In both cases, we were not able to grow crystals suitable for XRD analysis. The EPR data for both radicals are summarized in Table 2 and the spectrum of silolyl radical 6 is shown in Figure 2 along with its simulation applying the measured parameters. We refer to the Supporting Information for more detailed spectroscopic information. G-value and hyperfine couplings α for both radicals are close to related persistent neutral silyl- or germyl radicals (Figure 3) and the spectroscopic data agree with the suggested molecular structure.[26–31] Particular informative are the hyperfine coupling constants (hfcc) α(E) of the group 14 element with the unpaired electron (deceit with a = 2.7 mT for germolyl radical 3c and duplet of a = 6.1 mT for silolyl radical 6). Their analysis allows a tentative discussion of its coordination environment. Relatively large hyperfine couplings are detected for pyramidal radicals such as 8 and 9, due to the larger contribution of s-type atomic orbitals of the group 14 element to the SOMO

**Table 1.** Cone angles Θ (°) for the substituents R’ along with calculated bond dissociation energies (BDE [kJ mol⁻¹]) and Ge–Ge bond lengths d of bis-germole 2 (pm) and calculated substituent effect of the substituent R’ on the stability of germolyl radicals 3 (ΔE [kJ mol⁻¹]) (at M06-2X/6-311+G(d,p), data for hexamethyl digermane is given in the right column and experimental data in parenthesis).

| R’ | H | Ph | tBu | SiMe₂ | Si(SiMe₃)₂ | Me₃Ge₂ |
|----|---|----|-----|------|----------|-------|
| d  | 247 | 249 | 251 | 247   | 265      | 245   |
| 2a | 246.0 | 248.4 | 247 | 265   | 245 (241.6) |
| BDE | 277 | 280 | 267 | 271   | 96       | 273   |
| ΔE | 0   | +7  | +1  | −11   | −17      | −     |
|    | [a] Ref [25]. [b] This work. [c] Ref. [26] [d] Ref. [27]. |

**Scheme 1.** Synthesis of bis-germole 2 and of germolyl radical 3.

**Scheme 2.** Trapping of germolyl radical 3c and independent synthesis of 1H-germole 4.

**Scheme 3.** Synthesis of silolyl radical 6.
Table 2. Experimental ESR parameters (g-value, hyperfine coupling constant, δ, hexane, r.t.) and calculated hyperfine δ\textsuperscript{calc} for radicals 3c and 6 and for model compounds 7.

| cpd | E | R 1 | R 2 | G | a [mT] | δ [°] |
|-----|----|-----|-----|---|--------|-------|
| 3c  | Ge | Me  | Me  | G | 2.018  | 2.7 | 6.1 [11] |
|     | Si | Ph  | Me  | G | 2.031  | 1.7 | 0.8 [12] |
|     | Si | Ph  | Ph  | G | 2.026  | 0.8 | 1.7 [12] |
|     |    |     | Cl  | G | 1.997  | 3.0 | 1.1 [12] |
| 6   |    |     | Cl  | G | 2.004  | 6.1 | 6.5 [12] |
|     |    |     | Cl  | G | 2.004  | 0.8 | 1.4 [12] |
|     |    |     | Cl  | G | 2.004  | 0.02 | 0.02 [12] |
| 7a  | Ge |     |     | G | 2.018  | 0° | 1.9 [11] |
|     | Ge |     |     | G | 2.018  | 85° | 9.1 [11] |
|     | Ge |     |     | G | 2.018  | 0° | 2.9 [11] |
|     | Ge |     |     | G | 2.018  | 85° | 22.9 [11] |
| 7b  | Si |     |     | G | 2.018  | 0° | 0.8 [12] |
|     | Si |     |     | G | 2.018  | 85° | 13.5 [12] |

[a] At 103 K in frozen hexane. [b] Calculated at PBE0/Def2-TZVPD//M06-
2X/Def2-TZVP. [c] Calculated at M06-2X/6-311+G(d,p). [d] The assignment is based on the high intensity of the satellite signals (3 Si). A signal for the hfc to Si was not detected (see Supporting Information material for further information). [d] Calculated at M06-2X/6-311+G(d,p).

The tetrel element. In agreement, the results of DFT calculations heterolyl radicals suggest hyperfine coupling constants close to the experimental values are calculated (Table 2). The shape of the calculated surface diagrams of the SOMO indicate predominant localization of the unpaired electron at the tetrel atom with delocalization tails at the carbon atoms C2 and C3 (see Figure 2c, for an example). This suggests interaction between the π* orbital of the butadiene part and the singly occupied orbital at the tetrel element, which is reminiscent to the π*-π* cross hyperconjugation in the closed shell heteroles. The here derived localized electronic structure of heterolyl radicals 3c and 6 agrees with the calculated structural parameters which indicate a localized heterocyclopentadiene structure for both radicals comparable to that of the precursor chlorides 1c and 5 or the bisgermoles 2 (Table 3).

In several runs, we isolated from hexane solutions of the reduction of germole chloride 1c crystals of the potassium germolide K[13]. K[13] was independently synthesized by reduction of chloride 1c with two equivalents of KC in THF in

Figure 2. a) EPR spectrum of 1-tris(trimethylsilyl)silyl)radical 6 in hexane solution at room temperature; 9403.0 MHz; Mod-Ampl. = 0.075 mT; MW-Att. = 3.0 dB. b) Simulated EPR spectrum of radical 6 (blue experimental, orange simulated). c) Calculated spin density of radical 6 at isovalue = 0.004 (PBE0/Def2-TZVPD//M06-2X/Def2-TZVP, hydrogen atoms are omitted for clarity.)

Figure 3. EPR parameters of stable neutral germyl and silyl radicals.
49% isolated yield (Scheme 4). It was characterized by NMR spectroscopy and by XRD analysis of suitable crystals of K[13] and of its THF solvate. The isolation of the potassium germodile K[13] suggested to us that radical 3c might be formed by a comproportionation reaction between germodyl chloride 1c and the germodile [13]⁺, after over-reduction of the chloride by KC₈. Similarly, the potassium silodile K[14] was isolated in small quantities from the reaction mixtures of the reduction of silodyl chloride 5 with KC₈ and its solid state structure was solved.

The dominating structural motif in the solid state structures of potassium germodile K[13] and of its THF solvate are dimers in which two germodile anions are connected via two η¹-η¹-coordinated potassium cations (Figure 4). The potassium silodile K[14] forms a one-dimensional coordination polymer, in which the individual silodile anions are connected via potassium cations that are η¹-coordinated to the tricoordinated silicon atom and to the phenyl substituents in 3,4 position (Figure 5a). Like previous examples of 1-tris(trimethylsilyl)silyl-substituted germodile and silodile anions reported by the Tilley group, η¹-coordinated anions [13]⁺ and [14]⁺ show a trigonal pyramidal coordination around the tetrel atom and a localized ring structure with strongly alternating C–C double and C–C single bonds as shown by the bond length difference Δ (Table 3). These structural features are strong and conclusive arguments for the non-aromaticity of silodile and germodile anions.

There is however clear evidence that coordination of metal cations to the heteroanion do influence the structure of the five-membered ring and that a switch between delocalized aromatic and localized non-aromatic structures can be triggered by the counter cation. The Tilley group reported germolylyl- and silolylyl complexes of transition metal ions such as Hf(IV), Fe(II) and Ru(II) with η¹-coordinated heteroanions and Ru(II) with η¹-coordinated heteroanions. Kovacs and coworkers recently reported the structure of a contact ion pair between lithium cation and a silodile anion with a delocalized

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**Table 3.** Structural parameters of heteroaryl radicals and anions (from XRD analysis, calculated parameters for radicals and for free anions are given in italics).

| cpd | E | C–C/P | C–C¹ | Δ | E–C | Σ(Δ) |
|-----|---|--------|--------|---|------|-------|
| 1c  | Ge | 135.8  | 150.9  | 15.1 | 195.8 | 323.1 |
| 5a  | Si | 136.4  | 151.4  | 15.0 | 187.1 | 324.4 |
| 2a  | Ge | 135.5  | 150.3  | 14.8 | 195.7 | 313.1 |
| 2b  | Ge | 135.7  | 150.0  | 14.3 | 196.6 | 308.3 |
| 3c  | Ge | 135.8  | 149.4  | 13.6 | 195.2 | 340.4 |
| 6a  | Si | 137.1  | 148.2  | 11.1 | 184.3 | 334.8 |
| K[13]| Ge  | 137.8 | 147.1 | 9.3 | 200.4 | 292.6 |
| K[13]| Ge  | 137.1 | 145.5 | 8.4 | 200.7 | 289.7 |

[a] Δ: difference between C–C and the mean value of C–C¹ and C–C². (b) From ref. [24] (c) Calculated at M06-2X/6-311+G(d,p). (d) Sum of the bond angles around the tetrel element E. [e] Measured as sum of the bond angles involving carbon and silicon atoms and the tetrel element E.

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**Figure 4.** Structure of the coordination dimer of K[13] in the crystal. (representation as thermal ellipsoid at 50% probability, hydrogen atoms are omitted, the alkyl groups at all silicon atoms are not shown, color code: black C, pink Si, turquoise Ge, violet K, red O). Selected structural parameters (pm): K[13]· Ge 327, K[13]· Ge 350, K[13]· C = 319, K[13]· C = 321, K[13]· C = 32. For additional relevant structural parameters, see Table 3.

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**Figure 5.** a) Part of the polymeric structure of K[14]((C₆H₅)Si) in the crystal. b) Structure of the ion pair of K[16]·2THF. c) Molecular structure of silodile anion [14]⁻ in the crystal. d) Molecular structure of silodile anion [16]⁻ in the crystal (representation as thermal ellipsoid at 50% probability, hydrogen atoms are omitted, in c and d also the alkyl groups at all silicon atoms are not shown, color code: black C, pink Si, violet K, red O). For relevant structural parameters, see Table 3.
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the delocalized aromatic structure. Lee and colleagues gave evidence for similar phenomena in the case of disilagermolyl anion and trisilagermolyl anions. Finally, we showed that potassium salts from germolyl anions switch from delocalized aromatic to localized non-aromatic states triggered by the complexation of the potassium ion. Before this background, we tested computationally several structures of the ion pair K[14] and found that η1 coordination of the potassium cation is preferred by 38 kJ mol⁻¹ over the corresponding η1*-structure (Figure 6). In the η1*-structure the coordination environment of the silicon atom is almost ideal trigonal planar, and the CC atomic distances are almost equal (Δ = −1.3 pm, Table 3). These structural details hint to electron delocalization in the five-membered ring. Nucleus independent chemical shift (NICS) calculations support the higher degree of aromaticity for the η1*-structure of K[14] (Figure 6). Nevertheless, in the polymeric structure of K[14](C₅H₆) the η1 coordination of the potassium cation by the silicon atom is favored (Figure 5a,c). Since we were not successful to crystallize the delocalized η1*-coordinated variant of K[14], we tested small variations of the silyl groups in 1,4 position of the silolyl anion. Reduction of triethylylsilyl-substituted silole chloride 15 with potassium graphite in THF gave K[16] as THF solvate (Scheme 5). Its molecular structure in the crystal is shown in Figure 5b,d and pertinent structural parameters are given in Table 3. The potassium cation is η1-coordinated and the silolyl ring adopts a delocalized structure as shown by almost equalized inner cyclic CC bonds (Δ = −2.1 pm), short Si–C bonds and an almost trigonal planar coordination environment for the silicon atom (see Table 3). The pair of potassium silolides K[14] and K[16] are an additional example, which shows that subtle changes in the constitution (different remote substituents SiEt₃ vs. SiMe₃) and/or solvent (THF solvate vs. benzene solvate) forces different coordination between heterolyl anion and counter cation in the solid state that are accompanied by a significant change of the degree of delocalization in the heterole ring.

Conclusion

Neutral silolyl and germolyl radicals were prepared by reduction of the corresponding chlorides and were characterized by ESR spectroscopy supported by the results of quantum mechanical calculations. Substituents at the radical centers as large as the tris(trimethylsilyl)silyl group are needed to prevent dimerization to the corresponding ditetrelanes. The obtained radicals 3c and 6 are persistent but reach by far not the stability reported for the bis-silolyl radical V by the West group. The analysis of the hyperfine coupling constant of the unpaired electron with the tetrel element indicates a pyramidalized structure of the heterol radical with only little delocalization into the heterole ring. Our computational analysis suggests that the discernable spin delocalization in tetrolyl radicals 3c and 6 is the result of cross hyperconjugation between the butadiene group and the tetrylenyl R=E unit. Tris(trimethylsilyl)silyl-substituted heterol anions [13]− and [14]−, which were isolated in the form of their potassium salts, are unavoidable byproducts of these reductions. Both anions show in the solid state the expected localized heterole structures with a trigonal pyramidal coordination environment of the germanium or silicon atom. Interestingly, the solid state structure of the closely related potassium silolide K[16] reveals a η1*-coordinated potassium ion, an almost trigonal planar coordination of the silole silicon atom and structural parameters of the silole ring that are typical for delocalized silolyl anions. Therefore, the pair K[14] and K[16] represent another example where the degree of delocalization in heterocyclopentadienyl anions is triggered by the coordination of the countercation.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure 6. Relative energies E° of computed gas phase structures of the ion pair K[14] with different coordination environments and the calculated NICS(1)° parameter (Banquo atom 100 pm below the plane of the five-membered ring, only the tensor component orthogonal to the ring plane is given). The data for cyclopentadienide is shown for comparison (M06-2X/6-311 + G(d,p)). Selected structural parameters (pm): η1*: η-Si 317.8, η1*: η-Si 317.7. For additional relevant structural parameters, see Table 3.

Scheme 5. Synthesis of potassium silolide THF solvate K[16] • 2THF.

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See the Supporting Information for details on the computations.