

The first experimental detection, by OD ESR spectroscopy, of radical anions of siloles and germoles bearing hydrogen and chlorine substituents attached to the heteroatom

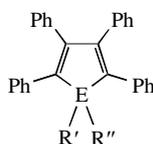
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Short-lived radical anions of 2,3,4,5-tetraphenylsiloles and 2,3,4,5-tetraphenylgermoles have been detected for the first time by OD ESR spectroscopy.

1-Heterocyclopenta-2,4-dienes (metaloles), siloles and germoles, have become the subject of great interest from both synthetic and fundamental points of view.¹ Special attention has been paid to the mono- and dianions of metaloles. Dianions of siloles and germoles were found to be aromatic heterocyclic systems.² Information about the other negatively charged derivatives of metaloles, the radical anions, is still scarce. Dessy and Pohl³ have detected by ESR spectroscopy the formation of relatively stable paramagnetic intermediates upon partial reduction of 1,1,2,3,4,5-hexaphenylsilole and -germole. The unresolved ESR signals observed were tentatively assigned to the corresponding radical anions of metaloles. However, electrochemical reduction of these metaloles occurred *via* a two-electron irreversible process.³ The reduction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene with potassium in 1,2-dimethoxyethane produced a stable blue solution which gave a well resolved ESR spectrum (approximately 60 lines).⁴ The authors assigned this spectrum to the silole radical anion without an analysis of the hyperfine structure of the ESR spectra of the paramagnetic species detected.



- 1 E = C, R' = R'' = H
 2 E = Si, R' = R'' = H
 3 E = Ge, R' = R'' = H
 4 E = Ge, R' = R'' = Cl
 5 E = Ge, R' = Me, R'' = Cl

Recently⁵ the electrochemical behaviour of different substituted 2,3,4,5-tetraphenylmetaloles (siloles, germoles and stannoles) was studied in MeCN solutions. All metaloles were found to reduce in a single one-electron irreversible step, indicating a very short lifetime (on the time scale of cyclic voltammetry) of the corresponding radical anions. However, using the method of quantum beats we were able to detect extremely short-lived ($\tau \sim 10\text{--}100$ ns) radical anions of 1,2,3,4-tetraphenylcyclopenta-1,3-diene and 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene

Table 1 HFS constants and linewidth in the ESR spectra of radical anions of compounds 1–5.

| Compound | X in EX ₂ fragment | $a(X)/G$ (OD ESR) | $a(X)/G$ (quantum beats) ^a | H_{pp}/G |
|----------|-------------------------------|-------------------|---------------------------------------|------------|
| 1 | H, H | 24.6 | 25.0 | 7.4 |
| 2 | H, H | 17.0 | 15.6 | 7.8 |
| 3 | H, H | 15.4 | 15.0 | 5.5 |
| 4 | Cl, Cl | 7.0 ^b | 7.0 | 5.5 |
| 5 | Cl | 12.4 ^b | 11.4 | 7.0 |

^aFrom ref. 11. ^bCorresponds to ³⁵Cl. Upon simulation the ratio of hfs constants for isotopes ³⁵Cl and ³⁷Cl was suggested to be equal to the ratio of their magnetic moments.

in decane solutions.⁶ Here we report on the detection of radical anions of 1,2,3,4-tetraphenylcyclopenta-1,3-diene **1** and its heteroanalogues, 2,3,4,5-tetraphenylsilole **2** and 2,3,4,5-tetraphenylgermoles **3–5**, by the optically detected (OD) ESR technique.

OD ESR spectra of spin-correlated radical ion pairs generated by X-ray irradiation were recorded with an X-band ER-200D Bruker spectrometer under stationary conditions described earlier.⁷ Data were accumulated in a lock-in amplifier SR-800 and processed on a computer. The microwave power applied to the cavity was 700 mW. Samples were degassed by a repeat freeze-pump-thaw procedure before the experiments. A chromatographically pure solvent squalane (99%, Fluka) was additionally purified on a column with an activated silica gel. Metaloles **2–5** were obtained according to known procedures.^{8–10}

OD ESR spectra of paramagnetic species produced from the compounds **1–5** in squalane (10^{-3} M) at room temperature are

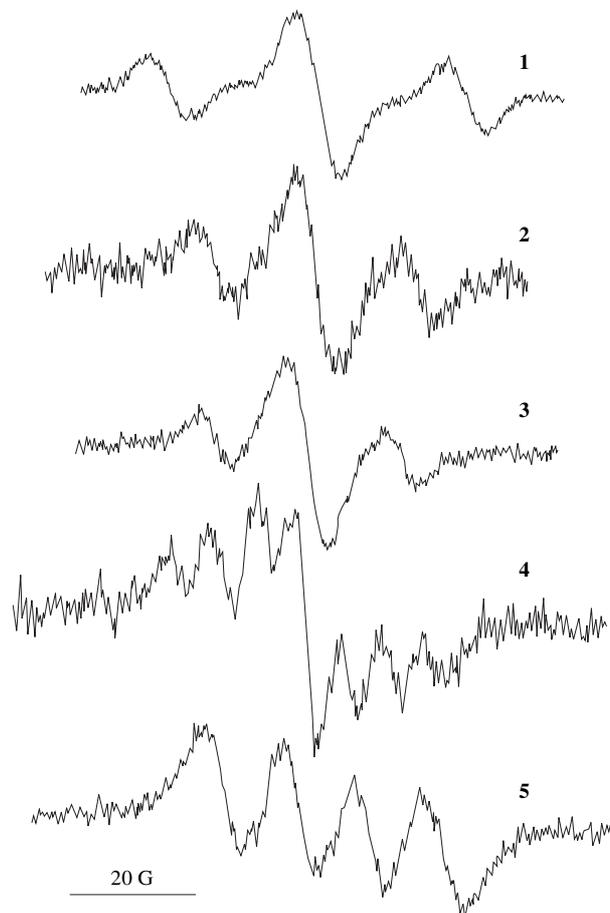


Figure 1 OD ESR spectra of radical ion pairs generated by the X-ray irradiation of 10^{-3} M solutions of **1–5** in squalane at room temperature.

given in Figure 1. Simulation revealed the presence (when separated from the level of noise) of unresolved signals of *ca.* 20 G width along with the observed components of hyperfine structure. In the case of paramagnetic species from compounds **3** and **4** these unresolved signals are rather intense and have a width of *ca.* 10 G. This results in an increase in the intensity of the central component of the multiplets.

We assigned the resolved components of the ESR spectra (Figure 1) to the radical anions of compounds **1–5**. Indeed, the hyperfine splittings in these spectra correspond to the interaction of an unpaired electron with two equivalent hydrogen atoms (**1–3**; EH_2 moieties; E = C, Si, Ge), two equivalent chlorine atoms (**4**; GeCl_2 moiety), and one chlorine atom (**5**; GeClMe moiety) in the radical anions of **1–5**. The corresponding hyperfine splitting (hfs) constants and line widths obtained by computer simulation are shown in Table 1. The counter ion of $(\mathbf{1-5})^-$ in the radical ion pairs can be either radical cations $(\mathbf{1-5})^+$ or squalane holes which exhibit a wide unresolved spectrum.

The following facts also confirm the correctness of our assignment of ESR spectra (Figure 1) to radical anions $(\mathbf{1-5})^-$. The value of the hfs constant $a(\text{H})$ for paramagnetic species generated from **1** is close to that reported¹² for the radical anion $(\mathbf{1})^-$ (25.3 G). Moreover, the hfs constants found in this work are close to those recently obtained by the analysis of the shape of quantum beats¹¹ (see Table 1). It has been demonstrated¹¹ that the quantum beats are caused by hyperfine interaction in the radical anions $(\mathbf{1-5})^-$ rather than in the radical cations $(\mathbf{1-5})^+$. In the case of radical cations $(\mathbf{1-5})^+$ one could expect much smaller hfs constants. For example, $a(\text{H})$ constant corresponding to the interaction of an unpaired electron with a CH_2 moiety in the cyclopentadiene radical cation is less than 2 G.¹³ The small value of $a(\text{CH}_2)$ in the cyclopentadiene radical cation can be explained within the framework of the Hückel approximation. The system of π -electrons in cyclopentadiene is similar to that in butadiene. In the butadiene radical ions an unpaired electron occupies the molecular orbital with contributions from the atomic orbitals of edged atoms of the same sign in the radical anion and of the opposite sign in the radical cation. This means that in the cyclopentadiene radical cation the protons of the CH_2 moiety are situated in the nodal plane which results in a weak hyperfine interaction with these atoms.

A decrease in temperature (to $-25\text{ }^\circ\text{C}$) does not change the pattern of the spectra, but instead causes line broadening up to 2–3 G and an increase in the signal to noise ratio. In the case of radical anion $(\mathbf{4})^-$, the hyperfine structure disappears almost completely at $-25\text{ }^\circ\text{C}$.

Radical anions $(\mathbf{4})^-$ and $(\mathbf{5})^-$ are the first radical anions of group 14 organoelement halides to be detected in solution. The formation of radical anions of R_3EHal (E = Si, Ge) during the electrochemical reduction of R_3EHal was suggested,¹⁴ but the most accepted point of view is that the electrochemical reduction occurs *via* dissociative attachment of an electron.¹⁵ However, it was shown recently by electron-transmission and dissociative attachment spectroscopies that the replacement of the central carbon atom in compounds Me_3EX (E = C, Si, Ge, Sn; X = Cl, Br) with a heavier group element led to a dramatic reduction of the halogen anion yield indicating the stabilization of the corresponding radical anions.¹⁶ In fact, radical anions of halo-silanes¹⁷ and halogermanes¹⁸ were detected by ESR spectroscopy only in low temperature matrices.

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