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Organometallic (Non-transition Metals) Free Radicals

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The available information about the free radicals and radical-ions formed by "true" organometallic compounds of non-transition metals is surveyed and described systematically. The methods of synthesis and the properties of radicals with the free valence located at the metal or in a ligand and the synthesis and structure of organometallic radical-ions are considered.
The bibliography includes 185 references.

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I. INTRODUCTION

The study of organoelemental free radicals and radical-ions constitutes a new branch of physical organic chemistry, which has arisen at the boundary between classical organoelemental chemistry and the physical chemistry of free radicals. For a long time, the intermediate formation of species of this kind was merely postulated in the study of various organometallic reactions and only in recent years they became the object of direct investigation. The first advances in this field led to a flood of hypotheses and postulates, many of which lack experimental justification and are purely speculative. However, progress in outwardly varied fields, such as reaction mechanisms, biochemical electron transport, catalysis, and organic synthesis, depends significantly on the prospects for the development of the chemistry of organoelemental radicals. The aim of the present study was to select and describe systematically the reliable relevant information and to outline the most fruitful pathways to be followed in future research.

The field under consideration can be clearly divided into three main branches: organoelemental radical-ions; element-centred free radicals; organometallic compounds with the unpaired electron localised preferentially in the ligand†.

II. ORGANOMETALLIC RADICAL-IONS

Many organometallic reactions can be usefully regarded as a consequence of electron transfer[1-3]. In this approach one postulates two main types of dissociation of the metal–carbon bond, which are in general unrelated to its homolytic or heterolytic dissociation under the influence of a reactant or the solvent[4]. Electron capture by the organometallic molecule leads to the splitting off of a carbanion with formation of a reduced form of the metal:

$$R{-}m \underset{-e}{\overset{+e}{\rightleftarrows}} [R{-}m]^{\cdot-} \rightarrow R^- + m^{\cdot} \quad .$$

In the one-electron oxidation of the substrate a free radical is produced:

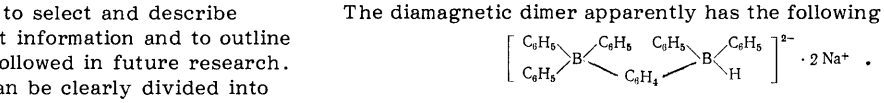
$$R{-}m \underset{+e}{\overset{-e}{\rightleftarrows}} [R{-}m]^{\cdot+} \rightarrow R^{\cdot} + m^+ \quad .$$

The radical-ion states $R{-}m^{\cdot-}$ and $R{-}m^{\cdot+}$ are then formed either as elements of the activated complex or as more or less stable intermediates whose energy corresponds to dips in the energy curve; in the latter case they can be identified directly and investigated. There are as yet few examples of this kind, but it is already evident that the stability of organoelemental radical-ions varies within very wide limits.

Organoboron radical-anions were discovered first. As early as the 1930's, the formation of coloured adducts of alkali metals with triarylboron derivatives was noted[5,6]. Subsequent studies showed that solutions of these compounds contain equilibrium mixtures of the triarylboron radical-anion $Ar_3B^{\cdot-}M^+$ (M is an alkali metal) and the diamagnetic dimeric form[7,8]:

$$2\,Ar_3B^{\cdot-}M^+ \rightleftarrows (Ar_6B_2)^{2-} \cdot 2\,M^+ \quad .$$

The diamagnetic dimer apparently has the following structure[9]:



The ratio of the two forms depends on the nature of the aryl group and the solvent. Thus, whereas the trimesitylboron radical-anion is monomeric in ether, the triphenylboron radical-anion is fully dimerised in this solvent; tri-α-naphthylboron-sodium exists as a dimer in ether but in tetrahydrofuran (THF) it is fully monomeric and paramagnetic[10].

It follows from the EPR spectra of triarylboron radical-anions that the unpaired electron is delocalised over all the aryl groups; in other words, the boron atom does not behave as an isolating bridge. The form of the spectra is determined by the interaction of the unpaired electron with the ^{11}B nucleus ($I = 3/2$), which is responsible for the appearance of the four main lines, each being split owing to the interaction with the protons of the aryl groups[11-13]. The following hyperfine interaction (HFI) constants have been obtained for the triphenylboron radical-anion in dimethoxyethane: $a_B = 7.84$ G, $a_H^{para} = 2.73$ G, $a_H^{ortho} = 1.99$ G, and $a_H^{meta} = 0.67$ G. The assignments were made on the basis of a study of the EPR spectra of deuterated triphenylboron radical-anions[11]. The reduction of alkyl derivatives of boron does not lead to stable radical-anions; only in the case of tribenzylboron is the solution coloured dark-green and the EPR spectrum shows a single line with a width of 30 G.[11]

Being powerful reductants, triarylboron radical-anions are instantly decolorised by iodine and reduce the triphenylmethyl radical to the anion:

$$2\,Ar_3B^{\cdot-} + I_2 \rightarrow 2\,Ar_3B + 2\,I^- \quad ,$$
$$Ar_3B^{\cdot-} + Ph_3C^{\cdot} \rightarrow Ar_3B + Ph_3C^- \quad .$$

†The free radicals of phosphorus compounds, information about which can be found in a recent review by V.V.Pen'kovskii in Uspekhi Khimii, **44**, 969 (1975), have been excluded from consideration.

An interesting reaction of triphenylboron-sodium with methanol leads to the formation of sodium triphenylborohydride[14]:

$$2\,(C_6H_5)_3\,B^{\cdot-}Na^+ + CH_3OH \rightarrow Na\,[(C_6H_5)_3\,BOCH_3] + Na\,[(C_6H_5)_3\,BH]\ .$$

Triarylboron radical-anions are capable of combining with a further electron to form a diamagnetic dianion[7,8,15]:

$$Ar_3B^{\cdot-} \underset{-e}{\overset{+e}{\rightleftarrows}} Ar_3B^{2-}\ .$$

The triarylboron radical-anions are fully stable in solution in dimethoxyethane (DME), but, after prolonged contact with the metal, the EPR spectrum of the radical-anion disappears and is replaced by that of the decomposition products. Depending on the nature of the aryl group, the following processes are observed:

$$Ar_3B^{\cdot-} \xrightarrow{K,DME} ArH^{\cdot-}\ , \qquad (1)$$

$$Ar_3B^{\cdot-} \xrightarrow{K,DME} (Ar{-}Ar)^{\cdot-}\ . \qquad (2)$$

If Ar = 2,4,6-trimethyl-3,5-dinitrophenyl, the decomposition takes place in accordance with Eqn.(1), while in the case of Ar = Ph or MeC_6H_4, it follows Eqn.(2). When Ar = 2,4,6-Me_3.C_6H_2 or 2,4-$Me_2C_6H_3$, the corresponding organoboron radical-anions do not decompose at all. It is important to note that reaction (2) is an intramolecular process, which has been demonstrated by the formation of only symmetrical biphenyls from an equimolar mixture of their radical-anions $(p\text{-}DC_6H_4)_3B^{\cdot-}$ and $(3,5\text{-}D_2C_6H_3)_3B^{\cdot-}$. The elimination of biaryl is accompanied by the formation of the arylboron[11]:

$$n\,Ar_3B^{\cdot-} \xrightarrow{K,DME} n/2\,(Ar{-}Ar)^{\cdot-} + (ArB)_n\ .$$

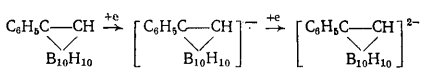
The latter is obtained also in the reduction of phenylboron dichloride by sodium in toluene[16]:

$$n\,C_6H_5BCl_2 \xrightarrow{Na} (C_6H_5B)_n\ .$$

Its hydrolysis leads to phenylboronic acid:

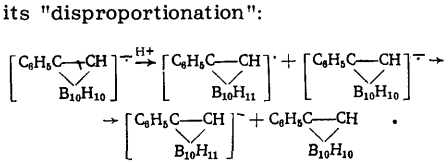
$$(C_6H_5B)_n \xrightarrow{H_2O} n\,C_6H_5B\,(OH)_2 + H_2\ .$$

When phenyl-*o*-carbaborane is acted upon by alkali metals in THF or dimethylformamide (DMF), a coloured paramagnetic solution, whose EPR spectrum shows a single broad signal (11 G) without a hyperfine structure, is readily formed[17,18]. When it is acted upon further by the reductant, a diamagnetic dianion, obtained previously[19–21] in liquid ammonia, is formed:



The absence of a hyperfine structure in the spectrum of the radical-anion indicates a high degree of delocalisation of the unpaired electron over the entire carbaborane system. It is of interest to note that, despite the presence of acidic hydrogen atoms in the phenylcarbaborane molecule, the reaction with alkali metals is not accompanied by the evolution of hydrogen and the formation of a carbanion. On formation of the radical-anion no changes in the skeleton take place, since oxidation of the radical-anion with mercury(II) chloride results in a quantitative regeneration of the initial phenylcarbaborane[18].

The acid hydrolysis of the phenylcarbaborane radical-anion results in its "disproportionation":



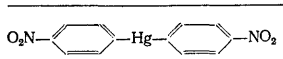
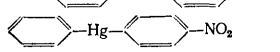
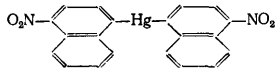
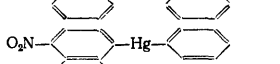
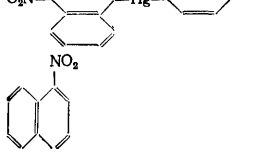
Organoaluminium radical-anions have been generated in the low-temperature γ-radiolysis (^{60}Co) of trialkylaluminium compounds[22]. Analysis of the EPR spectra indicates a pyramidal structure of such radical-anions in which the angle of deviation from the plane is ~21°. This agreed well with the large splitting constants for the ^{27}Al nuclei (324–390 G) due to the appreciable s character of the unpaired electron orbital[28]. The reduction of triphenylaluminium with sodium in ether leads to a dimeric product whose structure is apparently similar to that of its boron analogue[23].

Organogallium radical-anions have not been detected by EPR. It is only known that, when trimethylgallium is reduced with alkali metals in dimethoxyethane, a dimer is formed[24]:

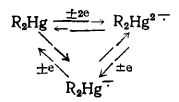
$$2\,K^+\,[(CH_3)_3\,Ga{-}Ga\,(CH_3)_3]^{2-}\ .$$

The existence of organomercury radical-anions of the type $R_2Hg^{\cdot-}$ has been demonstrated in relation to nitroaryl derivatives obtained both in electrochemical reduction[25] and on treatment with sodionaphthalene[26]. Analysis of the HFI constants shows that the mercury atom has hardly any influence on the spin density distribution (cf. the constants for $R_2Hg^{\cdot-}$ and $RH^{\cdot-}$ in Table 1).

Table 1. The nature of the EPR spectra of the radical-anions of certain organomercury compounds R_2Hg and the corresponding hydrocarbons[25,26].

Compound	a_H^{ortho}, G	a_H^{meta}, G	a_H^{para}, G	a_N, G	a_{Hg}, G
	3.25	1.00	—	9.29	42.3
	3.25	1.10	—	9.29	39.2
	3.20	—	4.00	9.50	—
	5.20	—	—	7.35	58.0
	5.08	—	—	7.30	52.3
	5.24	—	5.24	7.43	—

The stepwise nature of the electrochemical reduction of diarylmercury is noteworthy. Thus di-(*p*-nitrophenylmercury) is reduced in DME at a potential of −1.58 V to the radical-anion $R_2Hg^{\cdot-}$, which is also formed on oxidation of the corresponding triplet dianion $R_2Hg^{2\cdot-}$. The latter is a result of the two-electron reduction of di-(*p*-nitrophenyl)mercury at −1.84 V:



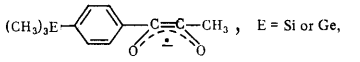
The fact that the ultraviolet spectra of $R_2Hg^{\cdot-}$ and $R_2Hg^{2\cdot-}$ are entirely identical indicates the lack of interaction between the unpaired electrons of the two nitrophenyl groups separated by the mercury atom (i.e. mercury behaves as a non-conducting bridge). The relatively high stability of the radical-anions of the nitrophenyl derivatives of mercury is due to the electron-accepting effect of the nitro-groups,

which prevents the accumulation of excess spin density in the mercury–carbon bond. In the general case radical-anions of the type $R_2Hg^{\cdot-}$ (R = phenyl, benzyl, or phenyl-*o*-carbaboranyl), formed on reduction of substrates with sodionaphthalene or lithium in DME, are unstable and decompose with liberation of metallic mercury and the formation of reactive carbanions, which undergo various transformations[26,27]:

$$R_2Hg + C_{10}H_8^{\cdot-} \rightarrow R_2Hg^{\cdot-} + C_{10}H_8 \rightarrow R^- + {}^1/_2R_2Hg + {}^1/_2Hg \quad .$$

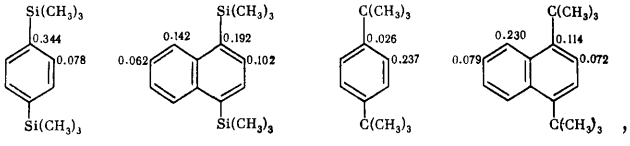
Numerous studies have been devoted to the radical-anions of Group IVA elements. It was of interest to elucidate the possibility of the involvement of the vacant *d* orbitals of these elements in the delocalisation of the unpaired electron. The radical-anions of trimethylsilyl- or trimethylgermyl-substituted benzenes and naphthalenes have EPR spectra with a hyperfine structure due to the methyl protons of the Me_3M groups[28–33]. The splitting of the signal by the methyl protons of the trimethylsilyl and trimethylgermyl groups is observed also in the radical-anions obtained by the reduction of phenylethynyltrimethylsilane and phenylethynyltrimethylgermane by alkali metals THF ($a_H^{SiMe_3} = 0.28$ G, $a_{Si} = 4.4$ G, $a_H^{GeMe_3} = 0.15$ G, and $a_{Ge} = 1.67$ G).[34,35] The chemical and electrochemical reduction of cyclic permethylpolysilane $(Me_2Si)_n$ ($n = 5$, 6, or 7) leads to the corresponding radical-anions, in which the unpaired electron interacts with all the methyl protons[37,38]. The spectrum of the radical-anion of di-(t-butyl)diacetylene is a singlet, while that of the radical-anion of di(trimethylsilyl)diacetylene consists of 19 lines due to the interaction of the unpaired electron with the 18 methyl protons ($a_H^{SiMe_3} = 0.15$ G and $a_{Si} = 5.25$ G).[36]

It is noteworthy that the radical-anions containing the trimethylsilyl and trimethylgermyl groups are more stable than their carbon analogues. With increase of the number of these groups, the stability of the radical-anion increases. Thus the *p*-bis-(t-butyl)benzene radical-anion is stable only at −70 °C, the *p*-bis(trimethylsilyl)benzene radical-anion is stable at 0 °C, and the radical-anion derived from 1,3,5-tris-(trimethylsilyl)benzene does not decompose for a long time at 20 °C.[30,39,40] The Hammett constants of the trimethylsilyl and trimethylgermyl groups in radical-anions of the type



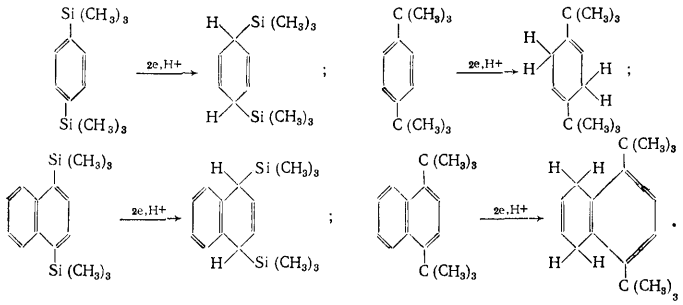
, E = Si or Ge,

are positive, which shows that they have electron-accepting properties[41,42]. This also follows from a comparison of the HFI constants for the radical-anions containing the trimethylsilyl and t-butyl groups and from the calculation of the spin densities by the MacConnell method[39,43]:



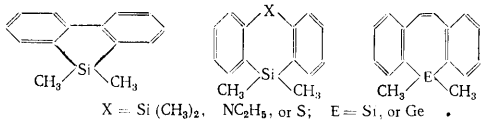
,

The above difference between the silicon and carbon analogues agrees well with the finding that the reduction of these compounds with sodium in liquid ammonia leads to products of different structure[43]:



In the radical-anions of phenylethyl derivatives of silicon and germanium the hyperfine interaction constants for the *meta*-protons of the benzene rings are higher than those for the *ortho*-protons, which confirms yet again the electron-accepting nature of these groups; the opposite relative values of the constants obtain for the t-butyl group[34,35]. The introduction of the trimethylsilyl group into the *N,N*-dimethylaniline molecule increases its electron affinity to such an extent that, despite the influence of the electron-donating dimethylamino-group, it is possible to obtain the radical-anion[44,45]. In the radical-anion of *p*-trimethylsilyl-*N,N*-dimethylaniline[44] the distribution of spin density is analogous to that for the benzene radical-anion, i.e. the influence of the two substituents cancels out.

The radical-anions formed in the reduction of different cyclic silicon and germanium compounds have been detected[46–49]:



X = Si $(CH_3)_2$, NC_2H_5, or S; E = Si, or Ge .

Their stability varies within fairly wide limits, but in this case the heteroatom has a stabilising influence and exhibits the properties of a π-acceptor[48].

The possibility of the delocalisation of the unpaired electron via the silicon in the radical-anions obtained on reduction (with potassium in DME) of dimethyldiphenylsilane, methyltriphenylsilane, and tetraphenylsilane has been studied[46,50,51]. The EPR spectra of the resulting radical-anions were characterised by the main doublet splitting ($a_H^{para} = 8$ G), which initially led to the conclusion that the unpaired electron is localised solely in the benzene ring. The lack of conductivity of the silicon atom was also noted for the radical-anions in which biphenyl groups are separated by a dimethylsilyl bridge[52,53]. Subsequently it was found that the primary radical-anions are extremely unstable even at a low temperature and decompose as a result of the following rapid reactions[54]:

$$(C_6H_5)_4Si \xrightarrow{e} [(C_6H_5)_4Si]^{\cdot-} \xrightarrow{e} (C_6H_5)_3Si^- + C_6H_5^-$$

$$(C_6H_5)_3Si^- \xrightarrow{CH_3OCH_2CH_2OCH_3} (C_6H_5)_3SiCH_3 \xrightarrow{e} [(C_6H_5)_3SiCH_3]^{\cdot-} \rightarrow$$

$$\xrightarrow{e} (C_6H_5)_2SiCH_3^- + C_6H_5^- \xrightarrow{CH_3OCH_2CH_2OCH_3} \ldots . [C_6H_5Si(CH_3)_3]^{\cdot-} \quad .$$

The trimethylphenylsilyl radical-anion is most stable in this series of radical-anions; its spectrum had apparently been detected in all previous instances.

The radical-anions derived from phenylsilanes are more stable in THF and give rise to resolved EPR spectra, which are identical regardless of whether they are produced chemically or electrochemically. The unpaired electron is delocalised over the entire phenyl groups and the form of the spectra is determined by the principal splitting by the *para*-protons

of the benzene rings with additional splitting of each component by the ring protons and the methyl protons of the silyl groups[54–57] (Table 2). For the dimethyldiphenylsilane radical-anion, the dependence of the distribution of spin density on temperature was demonstrated. In THF at temperatures below −70 °C the unpaired electron is localised in only one benzene ring, while on raising the temperature to −40 °C both phenyl groups are involved in the formation of a single conjugated system incorporating the silicon atom[58].

Table 2. EPR spectroscopic parameters for radical-anions of certain silicon-containing compounds (multiplicity in brakets)[54].

Compound	a_H^{ortho}, G	a_H^{ortho}, G	a_H^{meta}, G	$a_H^{CH_3}$, G
$C_6H_5Si(CH_3)_3$	8.06 (2)	2.61 (3)	1.03 (3)	0.26 (10)
$(C_6H_5)_2Si(CH_3)_2$	4.15 (3)	1.44 (5)	0.34 (5)	0.17 (7)
$(C_6H_5)_3SiCH_3$	2.76 (4)	1.01 (7)	0.19 (7)	0.10 (4)
$(C_6H_5)_4Si$	2.12 (5)	0.80 (9)	0.10 (9)	—

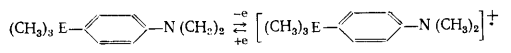
Thus analysis of the EPR data indicates the inclusion of the silicon and germanium atoms in the overall molecular orbital in which the unpaired electron is located. The transfer of spin density apparently takes place via a d_π–p_π interaction, which has been confirmed by the hyperfine structure due to the methyl protons of the trimethylsilyl and trimethylgermyl groups, the π-electron-accepting properties of these groups, and the conductivity of the silicon in the phenylsilane radical-anions.

Organotin and organolead radical-anions are almost unknown. There are data indicating the formation of radical-anions at 77 K by γ-radiolysis (^{60}Co) from tetramethyltin, trimethyltin chloride, and hexaphenyldistannane; the constants for the interaction of the unpaired electron with the $^{117/119}$Sn nuclei and the spin densities in the 5*s* orbitals of these isotopes have been determined. The hexaphenyldistannane radial-anion decomposes in accordance with the equation[59]

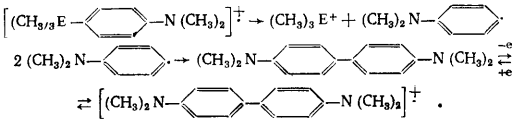
$$[(C_6H_5)_3Sn{-}Sn(C_6H_5)_3]^{\cdot-} \rightarrow (C_6H_5)_3Sn^- + (C_6H_5)_3Sn^{\cdot}\ .$$

Lead-containing radical-anions of the type $R_3PbX^{\cdot-}$ ($R = CH_3$ or C_6H_5; X = Cl or Br),[60,61] characterised by a marked splitting of the EPR signal by the ^{207}Pb nuclei ($a_{Pb} = 2108$–2366 G) and a hyperfine structure due to ^{35}Cl and ^{81}Br, have been generated by the same method.

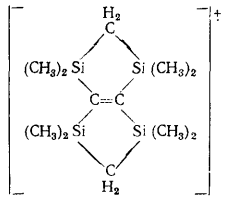
Organoelemental radical-cations were discovered only recently. An unstable radical-cation is formed on electrochemical oxidation of *p*-trimethylsilyl- and *p*-trimethylgermyl-*N*,*N*-dimethylanilines[62,63]:



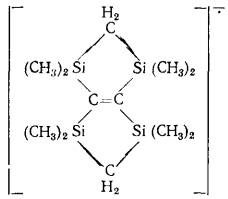
The negligibly small methyl proton hyperfine interaction constants of the organoelemental groups ($a_H < 0.1$ G) indicate only a slight interaction of the silicon and germanium atoms with the π-system of the radical-cation. In the presence of nucleophiles the radical-cations decompose rapidly:



One-electron oxidation of tetrasilylethylenes and tetrasilylhydrazines (by $AlCl_3$, $AgBF_4$, and $SbCl_5$) in CH_2Cl_2 yielded stable silicon-containing radical-cations[64,65]. The splitting constants for the nuclei in the corresponding radical-anions of tetrasilylethylene were much smaller than for the radical-cation[64]:

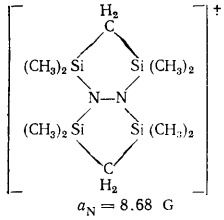


$a_{Si} = 22.716$ G, $a_H^{CH_3} = 0.62$ G, $a_H^{CH_2} = 2.48$ G

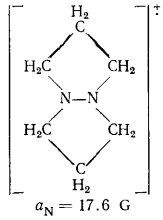


$a_{Si} = 6.72$ G, $a_H^{CH_3} = a_H^{CH_2} = 0.48$ G.

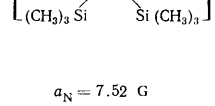
In tetrasilylhydrazine radical-cations the spin density at the >N–N< fragment is reduced compared with the carbon analogues[65,66]:



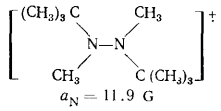
$a_N = 8.68$ G



$a_N = 17.6$ G

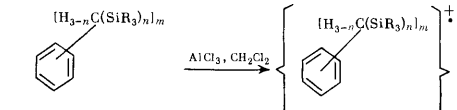


$a_N = 7.52$ G



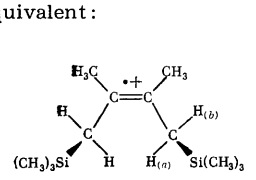
$a_N = 11.9$ G.

In the tetrakis(trimethylsilyl)hydrazine radical-cation the trimethylsilyl group has the same influence as the phenyl group in the tetraphenylhydrazine radical-cation ($a_N = 7.52$ G).[67] All this reflects the electron-donating properties of the trimethylsilyl group, which is capable of delocalising the positive charge in the radical-cation[68]. This conclusion was confirmed in a study of a series of radical-cations obtained from derivatives of poly(trimethylsilylalkyl)-substituted benzenes[69]:

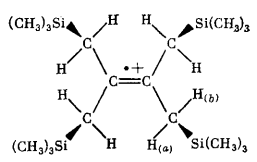


$n = 1,2,$ or 3; $m = 2,4,$ or 6.

Here too a decrease of spin density in the benzene ring was observed with increase of the number of trimethylsilyl substituents. It is noteworthy that the methylene protons in the radical-cations containing trimethylsilylmethyl groups are non-equivalent:



$a_H^a = 1.07$ G, $a_H^b = 0.76$ G



$a_H^a = 0.85$ G, $a_H^b = 0.73$ G.

The difference between the splitting constants ($a_H^a \neq a_H^b$) indicates the absence of free rotation of the $CH_2Si(CH_3)_3$ groups and the conformational stability of these radicals[70,71].

Thus, whereas the trimethylsilyl group in the radical-anions described above behaves as a π-acceptor, in the radical-cations the same group is a powerful electron donor. The transfer of spin density apparently takes place via a mechanism involving hyperconjugation between the silicon–carbon bond and the *p* orbital of the unpaired electron[72].

III. ELEMENT-CENTRED RADICALS

This class of free radicals includes organoelemental radicals in which the unpaired electron is localised preferentially at the atom of the element. The formation of such radicals is frequently an intermediate stage in a whole series of reactions, but there is comparatively little reliable information about them. This is due to the lack of convenient methods for their generation unaccompanied by their rapid subsequent reactions. Being essentially derivatives of elements which do not exhibit their full valence element-centred radicals should behave as active electron donors; in this respect they differ significantly from the majority of "purely" organic free radicals.

The chemistry of organomercury free radicals RHg· has been continuously discussed for more than forty years, but so far it has not been possible to detect them by any of the physical methods. The formation of the free radicals RHg· has been postulated in the classical studies by Razuvaev and coworkers[73–76] on the thermal and photochemical decomposition of organomercury compounds:

$$R_2Hg \rightarrow RHg^{\cdot} + R^{\cdot}; \quad RHgOH \rightarrow RHg^{\cdot} + {}^{\cdot}OH \quad .$$

In halogen-containing media reactions of this kind lead to organomercury halides (formally, this entails the abstraction of the halogen atom):

$$RHg^{\cdot} + R'Cl \rightarrow RHgCl + R'^{\cdot} \quad .$$

However, it is perhaps more correct to treat the last reaction as a one-electron transfer process:

$$RHg^{\cdot} + R'Cl \rightarrow RHg^{+} + R'^{\cdot} + Cl^{-} \quad .$$

The radicals RHg· are clearly incapable of abstracting a hydrogen atom and in solvents without a halogen they decompose, according to Razuvaev, in one of two ways:

$$RHg^{\cdot} \rightarrow R^{\cdot} + Hg, \quad 2\,RHg^{\cdot} \rightarrow R_2Hg + Hg \quad .$$

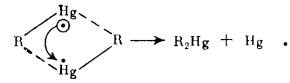
Radicals of the type RHg· are undoubtedly formed in the electrochemical reduction of organomercury solvents[77–79]:

$$RHg^{+} + e \rightleftarrows RHg \quad .$$

However, the electrode reaction, which is in principle reversible, in the present instance becomes in fact irreversible owing to the rapid subsequent reactions of the radical RHg·. The final products are dialkylmercury and mercury[79,80]; the majority of investigators are at present inclined to the idea that an "organic calomel" RHgHgR is formed as an intermediate, but not a single compound of this type has so far been isolated[77–79]. The electrochemical symmetrisation of the stereoisomeric β-chlorovinylmercury chlorides takes place with complete retention of the configuration of the organic group[81], which means that the β-chlorovinyl free radicals are not involved in such symmetrisation and the reaction

$$ClCH{=}CHHg^{\cdot} \rightarrow ClCH{=}CH^{\cdot} + Hg$$

can occur only as a side process (liberation of the radical from the "cage"). The intermediate formation of "organic calomel" is at present only a hypothesis; the available data can be accounted for no less successfully by the disproportionation of two RHg· radicals occurring as a one-electron transfer process in the transition complex:

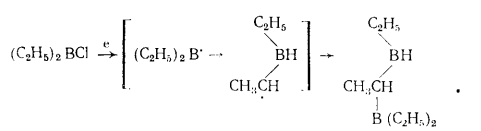


Substances readily conducting electric current and decomposing on heating with formation of dialkylmercury and mercury have been isolated in the electrolysis of solutions of alkylmercury chlorides in liquid ammonia at the cathode[82–84]. However, EPR study of these substances showed that they are diamagnetic[85]. Evidently the compounds obtained have a metallic lattice formed by ions and all the conduction electrons belong to it as a single whole. The view that the homolysis of fully substituted organomercury compounds takes place, like their electrochemical reduction, with the simultaneous abstraction of both organic groups, has been established recently. However, one should bear in mind the meaning attributed to the concept of simultaneity. In their discussion of the mechanism of one-electron transport, Basolo and Pearson correctly note that the "concept of simultaneity is unsatisfactory"[86]. True simultaneity is kinetically indistinguishable from a sequence of two reactions the first of which is rate-limiting:

$$R_2Hg \xrightarrow{\text{slow}} RHg^{\cdot} + R^{\cdot}; \quad RHg^{\cdot} \xrightarrow{\text{fast}} R^{\cdot} + Hg \quad .$$

There is at present no reason to abandon Razuvaev's initial treatment and the reduction of organic halides in the course of photolysis of dialkylmercury can be regarded as important evidence in support of the actual existence of RHg· radicals. The possibility, in principle, of the stepwise electrochemical reduction of diarylmercury also clearly follows from the study of Dessy et al.[25] already quoted.

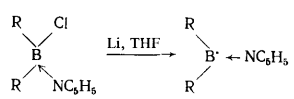
Attempts have been made in a number of investigations to obtain organic derivatives of Group IIIA elements not in their maximum valence state. The reduction of dialkylboron chlorides by alkali metals did not lead to organoboron radicals which could be detected by EPR, owing to their rapid dimerisation[87,88]:



On treatment with potassium in benzene, diphenylboron chloride gives rise to a dimeric product, which is reduced in DME to a radical-anion; the EPR spectrum consists of 7 lines due to the interaction of the unpaired electron with two boron atoms ($a_B = 2.9$ G):[11]

$$(C_6D_5)_2BCl \xrightarrow{\text{K, benzene}} (C_6D_5)_2B{-}B(C_6D_5)_2 \xrightarrow{\text{K, DME}} [(C_6D_5)_2B{-}B(C_6D_5)_2]^{-} \quad .$$

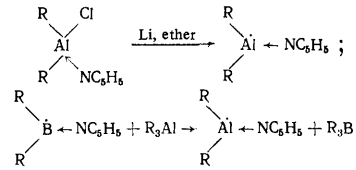
Data apparently indicating the formation of the dimesitylboron radical on reduction of dimesitylboron fluoride proved to be erroneous[89]. The spectrum of the radical obtained proved to be identical with the spectrum of the trimesitylboron radical-anion[11]. However, dialkylboron radicals stabilised by bases (pyridine, quinoline) are fairly stable[87,88]:



(R = C_2H_5 or C_6H_5).

Depending on the base, boron-centred radicals are associated

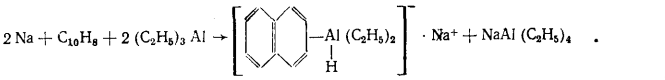
to different extents in solution. Thus the diethylboron radical stabilised with 4-methylquinoline is monomeric. In the case of 4-methylpyridine the analogous radical exists as the trimer; the EPR spectrum exhibits 10 lines due to the splitting of the unpaired electron signal by three boron nuclei ($a_B = 3.83$ G). Aluminium-centred radicals have been obtained similarly[87]:



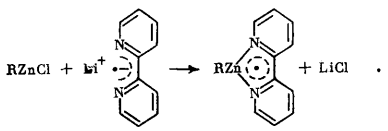
They are also formed on electrochemical reduction or on treatment of trialkylaluminium compounds with sodionaphthalene[90,91]. It is believed that the dialkylaluminium cation, obtained by the reaction[92]

$$[(C_2H_5)_3\,Al]_2 \rightleftarrows (C_2H_5)_2\,Al^+ + (C_2H_5)_4\,Al^-$$

is then reduced. The radicals formed in the reduction process are stabilised in the presence of bases. The following adduct has been obtained with sodionaphthalene[91]:



One must note that the true structure of the boron- and aluminium-centred radicals involves an appreciable transfer of spin density to the stabilised ligand. In the organozinc radicals having a similar structure the unpaired electron is fully localised in the ligand:

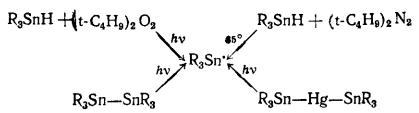


This is indicated by the absence of a hyperfine coupling with ^{67}Zn and the protons of the alkyl substituents[93]. These radicals have in fact the structure of an ion pair.

The greatest successes in the field of element-centred free radicals have been achieved for derivatives of Group IVA elements. A convenient method for the generation of radicals of the type $R_3E^\cdot$ involves the interaction of the hydrides of these elements with t-butyl peroxide under irradiation[94,99]:

$$R_3EH + t\text{-}C_4H_9O^\cdot \rightarrow R_3E^\cdot + t\text{-}C_4H_9OH\ .$$

The tris-(2-phenyl-2-methylpropyl)stannyl radical has been obtained by several methods[100]:



Unusually stable radicals of this type are formed when the dihalides ECl_2 (E = Sn or Ge) interact with bis(trimethylsilyl)methyl-lithium and this is followed by ultraviolet irradiation[101–103]:

$$ECl_2 + RLi \rightarrow R_3E \xrightarrow{h\nu} R_3E^\cdot$$

$$Si_2Cl_6 + RLi \rightarrow (RSiCl_2)_2 + [R_2SiCl{-}SiCl_3] \xrightarrow{-SiCl_4} [R_2Si] \xrightarrow{h\nu} R_2Si\ .$$

The corresponding bivalent derivatives R_2E have been isolated for tin and germanium[104]; therefore the photochemically initiated decomposition actually leads to the formation of stable element-centred radicals. The same radicals can be obtained on ultraviolet irradiation of the trialkyl derivatives of the halides of the elements in the presence of electron-donating olefins[105]:

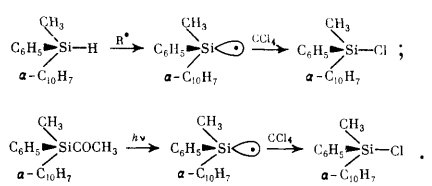
$$2\,R_3ECl + (Me_2N)_2C{=}C(NMe_2)_2 \xrightarrow{h\nu} [R_3ECl]^{\mp} \rightarrow R_3E^\cdot + [(Me_2N)_2C{=}C(NMe_2)_2]^{2+} \cdot 2\,Cl^-\ .$$

The multiplet EPR spectra of element-centred radicals with satellite lines due to the magnetic isotopes ^{29}Si, ^{73}Ge, and $^{117/119}$Sn have been recorded (Table 3).

Table 3. EPR spectroscopic parameters for certain element-centred radicals[100–105].

Radical	a_H, G	a_E, G	g-Factor
$(CH_3)_3Si^\cdot$	6.28	181	2.0032
$(CH_3)_3Ge^\cdot$	5.28	84.7	2.0101
$(CH_3)_3Sn^\cdot$	2.76	1899 and 1986	2.0154
$[(Me_3Si)_2CH]_3Si^\cdot$	4.8	198	2.0027
$[(Me_3Si)_2CH]_3Ge^\cdot$	3.8	92	2.0078
$[(Me_3Si)_2CH]_3Sn^\cdot$	2.1	1698 and 1776	2.0094

The high values of the splitting constants for the nuclei of the central elements indicate significant s character of the unpaired electron orbital, as a result of which 80% of the spin density corresponds to the heteroatom[106–109]. This also indicates a pyramidal structure of the radicals, in which the metal–carbon bonds deviate from the plane by 12–14°. This structure has been confirmed by a chemical study of the radicals derived from asymmetric silicon compounds, which react with retention of configuration[110,111]:



The latter factor shows that the large series of old studies on the mechanism of substitution at the silicon atom, where the reaction mechanism was inferred from the retention of optical activity, are evidently incorrect[112].

Element-centred radicals are very reactive and their lifetime is therefore extremely short. However, there exists a group of radicals which are unusually stable: the half-lives of $R_3E^\cdot$ [E = Si, Ge, or Sn; R = bis(trimethylsilyl)methyl] at 30 °C are respectively 10 min, 4 months, and 1 year[102]. This is caused by the steric hindrance due to the bulky alkyl groups, as a result of which the central metal atom cannot assume the tetrahedral configuration and hence the recombination or abstraction of a hydrogen atom from the solvent becomes impossible.

Measurements of the magnetic susceptibilities of solutions of compounds of the type $R_3E{-}ER_3$ ($R = C_6H_5$; E = Ge, Sn, or Pb) showed that they are incapable of dissociating into free radicals[113–115]. Small amounts of trimesityl-lead radicals, detected by EPR, are formed only in highly dilute solutions of hexamesityldiplumbane[116].

Thus the stability of organoelemental radicals R_3E is determined mainly by the size of the organic groups linked to the central metal atom. The radicals are most stable in the presence of bulky substituents.

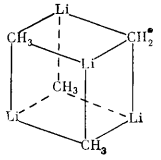
Information about the principal reactions of element-centred radicals can be found in recent monographs[117,118].

IV. ORGANOELEMENTAL COMPOUNDS WITH PARAMAGNETIC LIGANDS

This group of compounds is most varied among those considered. Naturally the classification adopted in the present study is conventional and there are no absolutely clear-cut boundaries between the three groups of paramagnetic species which we have distinguished. Thus in many compounds of the last group a definite proportion of spin density corresponds also to the metal.

Organoelemental free radicals in which the unpaired electron is localised mainly in the ligand include, in particular, α-substituted alkyl radicals of the type $^{\cdot}CR_2ER'_n$, where ER'_n is an organometallic group.

The reaction of methyl-lithium with photochemically generated t-butoxy-radicals in ether yielded a radical containing the CH_2Li fragment[119]. The well-resolved EPR spectrum of this radical consists of a triplet of decets due to the interaction of the unpaired electron with two equivalent protons ($a_H = 18.23$ G) and three equivalent ^7Li nuclei ($a_{Li} = 1.67$ G), which corresponds to the following structure of the radical:



Consequently the structure of tetrameric methyl-lithium[120,121] is not significantly distorted following the abstraction of a hydrogen atom and the system comprising three lithium atoms is non-conducting.

The interaction of t-butoxy-radicals with organomagnesium compounds proceeds in two ways[122]:

$$RCH_2MgX + t\text{-}C_4H_9O^{\cdot} \begin{cases} \longrightarrow R_2\dot{C}H_2 + t\text{-}C_4H_9OMgX \\ \longrightarrow R\dot{C}HMgX + t\text{-}C_4H_9OH \end{cases}$$

The hyperfine interaction constants for the α-protons are almost independent of R for magnesium-containing radicals and are in all cases 18.5 G. The absence of hyperfine structure due to the ^{35}Cl and ^{19}F nuclei in the radicals $^{\cdot}CH_2MgCl$ and $^{\cdot}CH_2MgF$ and the methyl protons in $^{\cdot}CH_2MgCH_3$ shows that the magnesium atom is non-conducting in radicals of this type. Low-temperature γ-radiolysis of trialkylaluminium compounds[123] and methylmercury chloride[124] leads to the corresponding alkyl radicals containing the organometallic group in the α-position. The negative sign of the hyperfine interaction constants for ^{27}Al is evidence for the transfer of spin density via a spin polarisation mechanism.

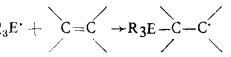
Analogous radicals of Group IVA elements have been obtained via the same general mechanism[125,126]:

$$R_3ECH_3 + t\text{-}C_4H_9O^{\cdot} \rightarrow R_3E\dot{C}H_2 + t\text{-}C_4H_9OH$$

In view of the independence of $a_H^{CH_2}$ and the *g*-factor of the type of element, it was concluded that there is no direct delocalisation of the unpaired electron over the vacant *d* orbitals of these elements[127,128].

Thus the nature of the substituent in the radicals of the type $^{\cdot}CR_2ER'_n$ has little influence on the spin density distribution (the $a_H^{CH_2}$ constant changes only slightly) and the observed splittings by the nuclei of the elements are caused by spin polarisation.

The addition of element-centred radicals to carbon–carbon double bonds leads to radicals in which the organoelemental group is in a β-position with respect to the radical centre[126, 129–132]:



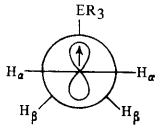
E = Si, Ge, or Sn.

The EPR spectra of these radicals are characterised by an anomalously small splitting by β-protons (Table 4).

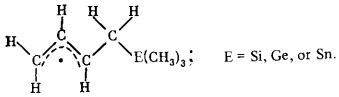
Table 4. EPR spectroscopic parameters for β-substituted ethyl radicals $^{\cdot}CH_2–CH_2–E(CH_3)_3$.[126,129–132]

E	a_H^{α}, G	a_H^{β}, G	$a_H^{CH_3}$, G	a_E, G	*g*-Factor
C	22.06	24.71	0.1	—	2.00268
Si	21.05	17.68	0.10	37.4	2.00265
Ge	20.70	16.57	0.14	488.9	2.00255
Sn	19.69	15.84	0.15	467	2.00255

The temperature dependence of the constant a_H^{β} indicates the presence of a barrier to rotation about the $C_\alpha–C_\beta$ bond. In the most stable configuration the organoelemental group is eclipsed by the *p* orbital, in which the unpaired electron is located:

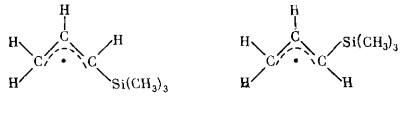


Allyl radicals also exhibit conformational stability[133,134]:



E = Si, Ge, or Sn.

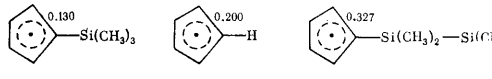
This is confirmed by the non-equivalence of the methylene protons attached to the carbon atom linked to the organoelemental group; here too the organoelemental group is eclipsed by the *p* orbital of the unpaired electron. It is of interest to note the significant difference between the hyperfine interaction constants of the methyl protons in *cis*- and *trans*-trimethylsilylallyl radicals[136]:



$a_H^{CH_3} < 0.05$ G $\qquad$ $a_H^{CH_3} = 0.27$ G

These radicals proved incapable of isomeric interconversion.

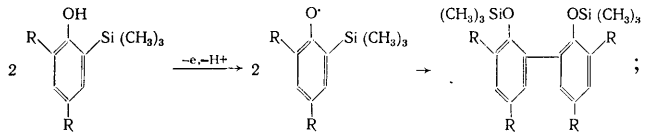
In trimethylsilyl-substituted cyclopentadienyl radicals the trimethylsilyl group in the α-position with respect to the radical centre behaves as an electron acceptor, while the same group in the β-position with respect to the π-system exhibits electron-donating properties. This follows from a comparison of the spin densities in the following radicals[136]:



Thus the conformational stability of β-substituted ethyl radicals $\cdot CH_2CH_2ER_3$ is due to the interaction of the unpaired electron with the organoelemental group, which exhibits the properties of an electron-donating substituent. This interaction apparently takes place via the hyperconjugation of the metal–carbon bond with the *p* orbital of the unpaired electron[137–139].

The radicals obtained by the oxidation of organoelemental derivatives of sterically hindered phenols are convenient objects for the study of the structure and properties of radicals in which the metal atom is involved in conjugation with a paramagnetic fragment. The phenoxy-radicals known hitherto, containing the substituents R_nE (E = Si, Ge, Sn, P, or As), differ sharply in their stability and reactions from their carbon analogues.

When 4,6-di-t-butyl-2-trimethylsilylphenol is oxidised by PbO_2 or an alkaline solution of $K_3Fe(CN)_6$, the phenoxy-radical formed dimerises rapidly with simultaneous migration of the *o*-trimethylsilyl group to the oxygen atom[140,141]:

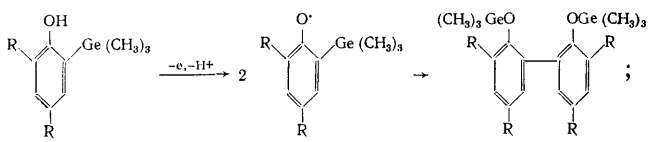


R = C $(CH_3)_3$.

The EPR spectrum of this radical contains four lines due to the interaction of the unpaired electron with the two non-equivalent *meta*-protons ($a_H = 1.7$ G, $a_H = 2.2$ G).[142,143] The migration of the *o*-trimethylsilyl group and the formation of a dimer are also possible on oxidation of 4-t-butyl-2,6-bis-(trimethylsilyl)phenol. The spectrum of the intermediate phenoxy-radical consists of a triplet ($a_H = 1.8$ G) with additional splitting of each component by the protons of the trimethylsilyl group ($a_H^{SiMe_3} = 0.4$ G).[142]

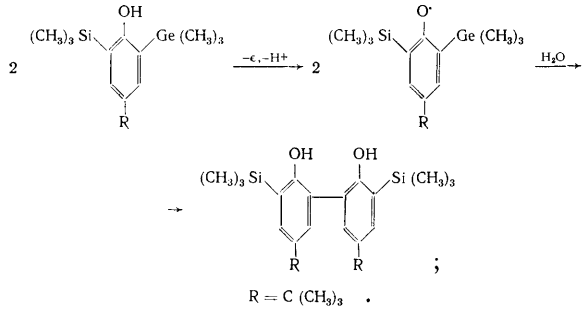
o-Phenyldimethylsilyl and *o*-triphenylsilyl groups are also able to migrate to the oxygen atom of the aryloxy-radical[144,145]. The introduction of the *o*-triphenylsilyl group reduces the capacity of the *o*-trimethylsilyl group for migration, increasing at the same time the stability of the corresponding phenoxy-radical. In the radical formed on oxidation of 4-cyclohexyl-2-trimethylsilyl-6-triphenylsilylphenol the "inhibiting" effect of the triphenylsilyl group makes the trimethylsilyl group altogether incapable of migration, while the 4-t-butyl-2-trimethylsilyl-6-triphenylsilylphenoxy-radical is the most stable silicon-containing phenoxy-radical; its EPR spectrum consists of a triplet (1:2:1) with additional splitting of each component by the protons of the $(CH_3)_3Si$ and $(C_6H_5)_3Si$ groups ($a_H^{meta} = 1.8$ G, $a_H^{Si(CH_3)_3} = 1.5$ G).[145] The hyperfine interaction constants for the protons of the t-butyl groups in the *ortho*-positions in the 2,4,6-tri-t-butylphenoxy-radical ($a_H = 0.072$ G)[146] and the trimethylsilyl groups in the 4-t-butyl-2,6-bis(trimethylsilyl)phenoxy-radical ($a_H = 0.4$ G) differ by a factor of approximately 6. This shows that the spin conductivity of silicon is much higher than that of carbon[147].

The trimethylgermyl group is also capable of migrating to the oxygen atom of the aryloxy-radical[148–150]:



R = C $(CH_3)_3$.

In order to compare the migratory capacities of R_3Si and R_3Ge, mixed silicon-germanium-containing phenoxy-radicals have been synthesised. The oxidation of 4-t-butyl-6-trimethylgermyl-2-trimethylsilylphenol leads to 5,5′-di-t-butyl-2,2′-dihydroxy-3,3′-bis(trimethylsilyl)biphenyl[149,150]:



R = C $(CH_3)_3$.

This indicates a greater capacity of the trimethylgermyl group for migration. The replacement of the trimethylsilyl group by the triphenylsilyl group increases the stability of the radical[149]. Thus the capacity for migration of the group in the *ortho*-position diminishes in the sequence $(CH_3)_3Ge > (CH_3)_3Si > (C_6H_5)_3Si$.

2,6-Di-t-butylphenoxy-radicals containing an organometallic group in the *para*-position are more common. The EPR spectra contain, apart from the main signal due to the interaction of the unpaired electron with the *meta*-protons, additional lines due to coupling with the magnetic nuclei of the substituents (Table 5).

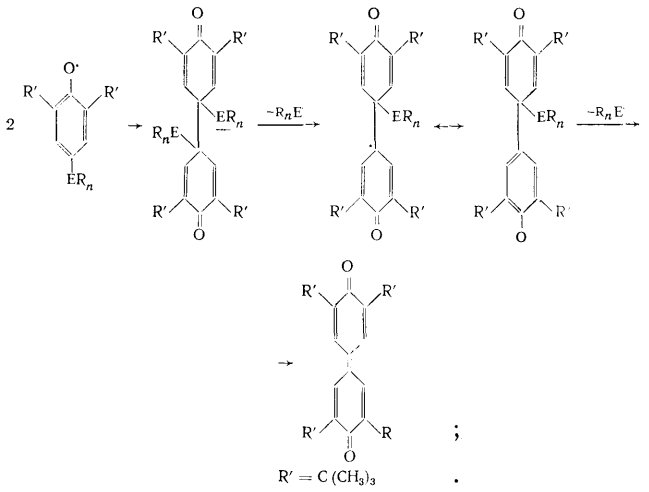
Table 5. EPR spectroscopic parameters for 2,6-di-t-butylphenoxy-radicals containing an organoelemental group R in the *para*-position.

R	a_H^{meta}, G	a_E, G	References
$(CH_3)_3Si$—	1.8	12.4	148
$(CH_3)_3Ge$—	1.7	2.9	148
$(C_6H_5)_3Sn$—	1.82	58.13 и 61.0	151
$(C_6H_5)_2P$—	1.6	6.8	152—154
$(C_6H_5)_2P$ (O)—	2.0	14.7	152—154
$(C_6H_5)_2P$ (S)—	2.0	15.4	152—154
$(C_6H_5)_2As$—	1.83	24.7	153—155
$(C_6H_5)_2As$ (O)—	2.0	14.1	153—155
$(C_6H_5)_2As$ (S)—	2.0	14.5	153—155

It follows from a comparison of a_H^{meta} for the 2,4,6-tri-t-butylphenoxy-radical ($a_H = 1.80$ G)[157] and the data in Table 5 that the organometallic group has only a weak influence on the spin density distribution in the radical. The splitting constants for Ge and Si in the *para*-position are greater than those for Ge and Si in the *ortho*-position, which shows that, as regards the distribution of spin density, such radicals are analogous to the 2,4,6-tri-t-butylphenoxy-radical[158].

In contrast to the *ortho*-analogues, in *para*-substituted organoelemental phenoxy-radicals the organometallic group proved to be incapable of migrating to the oxygen atom of

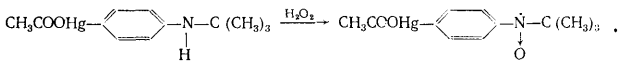
the aryloxy-radical. The most common property is elimination of the organometallic group with formation of 3,3',5,5'-tetra-t-butyldiphenoquinone as the final product[152,153]:



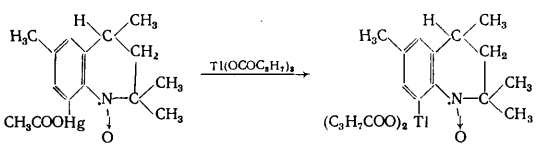
A qualitatively new spin density distribution has been observed for phenoxy-radicals containing electron-accepting carbaboranyl substituents[159]. Analysis of the hyperfine structure of the EPR spectra showed that the unpaired electron hardly interacts with the protons located in the *meta*-positions in the ring. The observed spectra can be interpreted as a result of the splitting of the signal by six boron nuclei ($a_B = 0.9$ G) closest to the carbon–carbon bond in the carbaborane ring. These radicals are distinguished by high stability in solution; in particular, they persist for several hours in acetic acid and hardly interact with atmospheric oxygen. It has been observed[160] that the 2,6-di-t-butyl-4-(2-carbaboranyl)phenoxy-radical readily rearranges to the *ortho*-isomer.

Thus the presence of the unpaired electron in the *m*-carbaborane ring significantly distorts the system of many-centre orbitals linking the boron–carbon skeleton, as a result of which the *meta–ortho* rearrangement, noted previously for the diamagnetic *m*-carbaborane dianions[161,162], is considerably facilitated.

Stable organomercury radicals have been obtained by the oxidation of mercurated phenylamines by hydrogen peroxide in dioxan in the presence of sodium tungstate[163]:



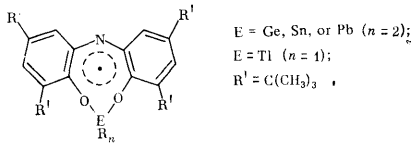
The EPR spectra of these radicals show the main triplet splitting by the ^{14}N nucleus and the additional groups of lines, due to splitting by the magnetic mercury isotopes, reproduce exactly the structure of the "nitrogen" component. A common feature of mercury-containing nitroxy-radicals is increased splitting by nitrogen and the phenyl protons compared with the unsubstituted radicals. An interesting fact was observed in the study of the reaction of 8-acetoxymercuri-2,2,4,6-tetramethyl-1,2,3,4-tetrahydroquinoline nitroxy-radical with thallium tri-isobutyrate[164]:



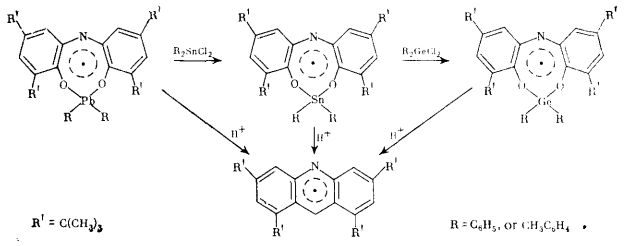
The exchange of mercury for thallium gives rise to a new thallium-containing radical. The hyperfine structure of its EPR spectrum indicates the interaction of the unpaired electron with two thallium isotopes—^{203}Tl ($I = 1/2$) and ^{205}Tl ($I = 1/2$) ($a_{Tl} \approx 240$ G).

The reduced nitrogen splitting constant ($a_N = 6.5$ G) for the bis(trimethylsilyl)nitroxy-radical $(Me_3Si)_2NO^{\cdot}$ indicates an intense d_π–p_π interaction between the silicon and nitrogen atoms. The trimethylgermyl group is a weaker acceptor; thus the hyperfine interaction constant for nitrogen in $(Me_3Ge)_2NO^{\cdot}$ is 8.8 G.[165]

The interaction of the 2-amino-4,6-t-butylphenoxy-radical with the diaryl derivatives of the halides of Group IVA elements[166–168] and thallium[169] leads to radicals having the following structure:

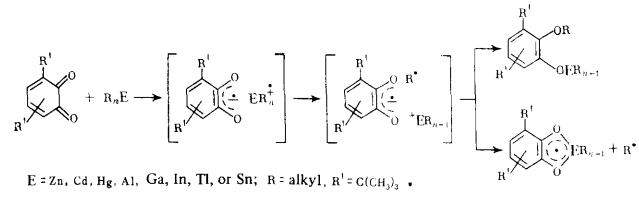


They are stable with respect to the action of atmospheric oxygen and can be isolated in a solid state. Their EPR spectra exhibit lines due to the interaction of the unpaired electron with the nuclei of the elements ^{73}Ge ($a = 3.02$ G), ^{119}Sn ($a = 46.5$ G), ^{117}Sn ($a = 44.5$ G), and ^{207}Pb ($a = 41.68$ G). The hyperfine interaction constants for the protons and the nitrogen atom are virtually the same for all the radicals and are independent of the nature of the substituent R attached to the element. In the series Pb, Sn, Ge each succeeding element can substitute the preceding element in the radical via the mechanism

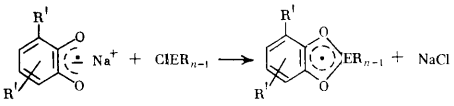


On treatment with acid, the 2,4,6,8-tetra-t-butylphenoxazinyl radical is formed[170].

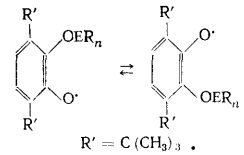
o-Quinones are effective oxidants for metals capable of one-electron oxidation[171–173]; the reactions of organometallic compounds with substituted *o*-quinones also involve a one-electron transfer stage and lead to the formation of relatively stable intermediates[174–178]:



Paramagnetic semiquinolates containing the organoelemental groups ER_{n-1} have been detected by EPR. The same radicals can be obtained by an exchange reaction:

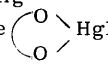


The nature of the metal–carbon bond has a strong influence on the spin density distribution in *o*-semiquinolates and on the hyperfine interaction with the paramagnetic nuclei of the central atom. In the *o*-semiquinolates obtained from 3,6-di-t-butyl-*o*-quinone and organometallic compounds of zinc, cadmium, or tin an intramolecular migration of the organometallic residue between the oxygen atoms at a rate measurable by EPR was observed[175,176]:

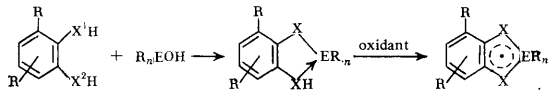


$R' = C(CH_3)_3$.

Thus, owing to the temperature variation of the frequency of the intramolecular migration of the chlorodimethylstannyl group, the EPR spectrum of the radical is transformed from a doublet of doublets with splitting by the ring protons ($a_H = 5.2$ G and $a_H = 2.6$ G) at a low temperature into a triplet ($a_H = 3.6$ G) at a high temperature. The splitting constants for tin change little under these conditions ($a_{^{117}Sn} = 21.5$ G, $a_{^{119}Sn} = 22.5$ G).[176] In paramagnetic chelates formed with central atoms of other elements this effect was not observed, which can be explained either by the rapid migration of the organometallic group or by its localisation on the C_2 symmetry axis or in the symmetry plane of the benzene ring.

A sharp decrease of the *g*-factor has been noted for mercury derivatives compared with other derivatives as well as a dependence of a_{Hg} on the nature of the substituent at the mercury atom[175,177]. With increase of the bulk of the alkyl substituent, a_{Hg} increases from 5.3 G for the methyl group to 10.4 G for the t-butyl group. The nature of the influence of the group at the mercury atom on a_{Hg} has been explained by a change in the configuration of the  fragment as the bulk of the substituent is altered. It is believed that in the complex the mercury atom has a pyramidal structure, but, with increase of the substituent bulk, the fragment is flattened, which leads to an increase of the amount of *s* character of the bonding orbitals of the Hg–O bond. For the most bulky substituent, pure sp^2-hybridisation occurs at the mercury atom, which corresponds to the maximum value of a_{Hg} and this is due to the spin polarisation of the σ-bonds by the unpaired electron in the *p* orbital of the oxygen atom[175]. The increase of splitting by the Al, Ga, Tl, and In nuclei in the alkyl derivatives of the corresponding elements relative to their halides[179,180] has also been attributed to a change in the geometry of the chelate on passing to the more bulky alkyl substituents[174].

Paramagnetic nitrogen-containing thallium and tin chelates have been obtained via the mechanism[181–184]



R = phenyl; E = Sn or Tl; $X^1 = O$, $X^2 = NH$ or $X^1 = X^2 = NH$.

An increase in the splitting constants for the nuclei or the elements on passing to nitrogen-containing chelates has been noted. Whereas $a_{Tl} = 10$ G for the *o*-semiquinolates of diphenylthallium, the constants for the chelates formed by *o*-aminophenol and *o*-phenylenediamine are 40 and 90 G respectively. The dependence of a_{Tl} on the solvating capacity of the solvent increases in the same sequence, which has been explained by the increasing covalence of the metal–ligand bonds for complexes of the latter type[182,183].

The influence of the solvent on the splitting constants due to the interaction with the nuclei of the central elements is apparently associated with a change in the geometry of the chelate under the influence of the solvating solvent, as a result of which the contributions of the *s* and *p* orbitals of the elements to the atomic orbital responsible for the hyperfine structure is changed and the direct appearance of the spin density is caused by the polarisation of these orbitals[185].

Thus there are good prospects for the further development of the chemistry of paramagnetic organic derivatives of non-transition elements established at the present time. The relatively stable radical-ions of the type $R-m^-$ and $R-m^+$ are convenient models for the determination of the detailed features of the mechanism of the dissociation of the element–carbon bonds. The study of the properties and reactions of element-centred radicals creates the necessary basis for the development of fundamentally new synthetic methods in the field of organoelemental chemistry. Both these fields make it possible in many instances to solve problems of the electronic structure of organoelemental compounds, in particular the problem of the resonance conductivity of the heteroatom. The extensive field of the chemistry of stable radicals will be undoubtedly enriched by data for organoelemental species of this class.

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