Subvalent Group 4B Metal Alkyls and Amides. Part 4.[1] An Electron Spin Resonance Study of some Long-lived Photochemically Synthesised Trisubstituted Silyl, Germyl, and Stannyl Radicals

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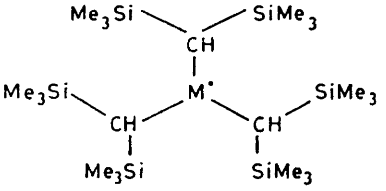
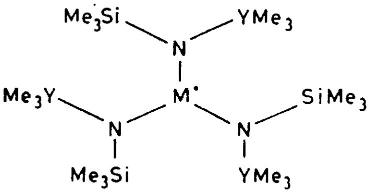
A number of solution-stable species of general formula $MR_3^\bullet$ [$R = CH(SiMe_3)_2$; M = Si, Ge, or Sn], $M(NR'_2)_3^\bullet$, and $M(NR'R'')_3^\bullet$ ($R' = SiMe_3$, $R'' = CMe_3$, M = Ge or Sn) have been prepared and characterised by e.s.r. spectroscopy. Most of the radicals have been generated by photolysis of the bivalent Group 4 species MR_2, $M(NR'_2)_2$, or $M(NR'R'')_2$ when available; others have been obtained by alternative photochemical experiments. The e.s.r. parameters indicate that the radicals have non-planar structures similar to those of analogous transient species such as $MMe_3^\bullet$. The mechanism of formation of the radicals is discussed: their unusual stability (*e.g.* $SnR_3^\bullet$ has a half-life of *ca.* 1 year at 20 °C) is attributed mainly to steric hindrance to dimerisation.

PREVIOUS parts of this series have dealt with the synthesis, structure, and physical properties,[2] chemical behaviour,[3] and Mössbauer spectra [1] of unusual kinetically stable dialkyls of the heavier Group 4B elements which exist in solution as monomeric singlets MR_2 [$R = CH(SiMe_3)_2$; M = Ge, Sn, or Pb]. We now turn to the trivalent derivatives $MR_3^\bullet$ and for these have extended the work to M = Si, although the lead compound has thus far eluded us. The bulky alkyl ligand R^- is isoelectronic with $[N(SiMe_3)_2]^-$ and we therefore also report on the metal-centred amido-radicals $M'(NR'_2)_3^\bullet$ and $M'(NR'R'')_3^\bullet$ ($R' = SiMe_3$, $R'' = CMe_3$, M' = Ge or Sn); the corresponding bivalent metal amides, $M'(NR'_2)_2$ and $M'(NR'R'')_2$, as well as the lead analogues, have been briefly described.[4] These results form parts of wider studies concerned with (*a*) exploring the potential of trimethylsilyl-substituted methyl and amide ligands {such as $[CH_2(SiMe_3)]^-$,[5] $[CH(SiMe_3)_2]^-$,[5] and $[N(SiMe_3)_2]^-$ [6]} in stabilising unusual oxidation states and co-ordination numbers for main-group, transition-metal, and inner-transition metals, and (*b*) organometallic free-radical chemistry.[7]



(1) $MR_3^\bullet$



(2) $M(NR'_2)_3^\bullet$ or $M(NR'R'')_3^\bullet$
Y = C or Si

A large number of e.s.r. studies have been concerned with the structure of carbon-centred free radicals and many ingenious techniques have been devised to facilitate the observation of transient species whose rate of dimerisation or disproportionation is essentially diffusion controlled. However, over the past few years it has become apparent that it is possible to increase the lifetimes of unconjugated free radicals by using bulky substituents. Thus the radical $C(SiMe_3)_3^\bullet$ has a much longer lifetime than $CMe_3^\bullet$.[8] The possibilities of protecting a radical centre in this way, particularly by using t-butyl groups, have been extensively investigated by Ingold and his co-workers.[9] Much less work has been reported on trivalent Si, Ge, Sn, and Pb. Transient silyl [10,11] and germyl [10] radicals were first observed in solution by e.s.r. in 1969 and stannyl radicals in 1972.[12]

This paper describes the generation and e.s.r. parameters of some trialkyl, (1), and triamino, (2; Y = C or Si), radicals of the Group 4B elements which are remarkably persistent in solution at room temperature. The bis(trimethylsilyl)methyl ligand is known to form several stable three-co-ordinate transition-metal derivatives [13] and this metal co-ordination number is also favoured with $[N(SiMe_3)_2]^-$,[6] which although isoelectronic with $[CH(SiMe_3)_2]^-$ differs from the latter in being trigonal planar at N in its metal complexes whereas the alkyls are

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[1] Part 3, J. D. Cotton, P. J. Davidson, J. D. Donaldson, M. F. Lappert, and J. Silver, *J.C.S. Dalton*, 1976, 2286.

[2] Part 1, P. J. Davidson, D. H. Harris, and M. F. Lappert, *J.C.S. Dalton*, 1976, 2268.

[3] Part 2, J. D. Cotton, P. J. Davidson, and M. F. Lappert, *J.C.S. Dalton*, 1976, 2275.

[4] D. H. Harris and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 895.

[5] P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209; *Chem. Rev.*, 1976, **76**, 219.

[6] D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259; D. H. Harris and M. F. Lappert, *J. Organometallic Chem. Library*, 1976, **2**, 13.

[7] M. F. Lappert and P. W. Lednor, *Adv. Organometallic Chem.*, 1976, **14**, 345.

[8] A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Comm.*, 1970, 559.

[9] G. D. Mendenhall, D. Griller, and K. U. Ingold, *Chem. in Britain*, 1974, **10**, 248; D. Griller, J. W. Cooper, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1975, **97**, 4269; D. Griller and K. U. Ingold, *Accounts Chem. Res.*, 1976, **9**, 13.

[10] S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organometallic Chem.*, 1969, **16**, P36.

[11] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3938.

[12] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

[13] G. K. Barker and M. F. Lappert, *J. Organometallic Chem.*, 1974, **76**, C45.

tetrahedral at C; this may be due to N $\longrightarrow$ Si ($p \longrightarrow d$) π bonding.

EXPERIMENTAL AND RESULTS

Generation of Radicals.—This work originated in an attempt to establish whether the interesting compound[2] SnR_2 [R = $CH(SiMe_3)_2$] (formally analogous to a carbene) exists in a singlet or triplet ground state. No evidence was found from e.s.r. spectra of liquid or frozen (−110 °C) solutions for a triplet state, but a weak signal near $g = 2$ was detected. This had quartet structure, which suggested $SnR_3^\bullet$, since the three equivalent β-protons of $Sn[CH(SiMe_3)_2]_3^\bullet$ would give rise to a 1 : 3 : 3 : 1 quartet. Unambiguous assignment, through detection of ^{117}Sn and ^{119}Sn satellites, was not possible due to the low concentration of the species, but later work showed that irradiation of the solution with u.v. or visible light caused a dramatic increase in the signal strength. Neither type of irradiation caused deposition of a tin mirror, and it was also demonstrated that (*i*) heat did not cause any increase in signal strength, and (*ii*) a sample prepared in the dark gave no e.s.r. spectrum. Subsequent irradiation generated the radical. The intensity of the signal obtained on irradiation allowed identification of satellite peaks due to ^{117}Sn and ^{119}Sn, confirming formulation of the radical as $SnR_3^\bullet$. A reproduction of the spectrum is contained in a preliminary account of this work.[14a] The samples, contained in 4-mm quartz tubes, were photolysed in the cavity of a Varian E3 spectrometer using previously described techniques.[14b]

Extension to related alkyls, and the isoelectronic amides, $M(NR'_2)_3^\bullet$ and $M(NR'R'')_3^\bullet$ (R′ = $SiMe_3$, R″ = CMe_3), was carried out by treating other metal(II) chlorides with the appropriate lithium reagent, and irradiating a solution of the product.[15] For the silicon-centred radical, $SiR_3^\bullet$, a different route was required since silicon(II) species are unknown, apart from their existence as short-lived intermediates.[16] The compound Si_2Cl_6 was treated with LiR in the hope of forming R_3SiSiX (X = R_3, Cl_3, R_2Cl, or RCl_2) which would then be expected to fragment readily to $SiR_3^\bullet$. This radical was obtained from Si_2Cl_6 and LiR, followed by irradiation, but the compound isolated from the reaction suggested a different mechanism for radical formation [see (9)—(11)]. Table 1 summarises the generation of the radicals, and some unsuccessful experiments. We comment further on the latter as follows.

(i) PbR_2. *In situ* u.v. irradiation of a solution of PbR_2 at room temperature gave a complex spectrum containing lines attributable to $CH(SiMe_3)_2^\bullet$, and a lead mirror. Assignment was confirmed by generating the same species from the low-temperature (−40 °C) irradiation of $(Bu^tO)_2$ and $CH_2(SiMe_3)_2$ [$CH(SiMe_3)_2^\bullet$, doublet of multiplets, a(α-H) 1.89 mT, a(γ-H) 0.037 mT; other species also present].

(ii) Si_2Cl_6 + $Li(NR'_2)$. Our inability to prepare $Si(NR'_2)_3^\bullet$ may have been due to a lack of reaction between $Li(NR'_2)$ and Si_2Cl_6.

(iii) $Pb(NR'_2)_2$. Irradiation of a solution of $Pb(NR'_2)_2$ with visible or u.v. light at room temperature, or u.v. at −40 °C, gave no signals. Some decomposition of the sample appeared to occur.

(iv) No signals were observed on irradiation of $Sn(C_5H_5)_2$, SnI_2, $SnCl(NR'_2)$, or $Zn(NR'_2)_2$.

E.S.R. Data for $MR_3^\bullet$ *and* $M(NR'_2)_3^\bullet$.—The main feature of the spectra, recorded on a Varian E3 spectrometer, was a multiplet arising from the coupling of the unpaired electron to three equivalent protons (quartet) or three equivalent nitrogen nuclei (septet). For dilute solutions of the amino-radicals, the septets showed further structure; this was believed to be partially resolved proton coupling. Under conditions of higher gain, satellite lines from those isotopes of the central atom which possess non-zero spin were observed. The low abundance of these isotopes makes detection of the satellite lines difficult, but their intensity could be increased by using high microwave power (*e.g.* 50 mW) and high modulation amplitude (*e.g.* 0.5 mT). The spectrum of $SiR_3^\bullet$ is shown in Figure 1. For $SnR_3^\bullet$, the satellite lines were very broad but could be sharpened by an increase in temperature. The width of the lines is attributed to incomplete averaging of the anisotropic contribution to the g and hyperfine tensors, caused by slow tumbling of the radical. Raising the temperature increases the rate of tumbling so that the anisotropy is averaged to zero, and the spectrum becomes isotropic.

TABLE 1

Generation of trivalent Group 4B radicals

Group 4 chloride	Lithium reagent [a]	Bivalent species isolable prior to radical formation	Radiation [b]	Radical
Si_2Cl_6	LiR		U.v.	$SiR_3^\bullet$
$GeCl_2$·dioxan [c]	LiR		None necessary	$GeR_3^\bullet$
$SnCl_2$	LiR	SnR_2	U.v. or visible	$SnR_3^\bullet$
$PbCl_2$	LiR	PbR_2	U.v. or visible	No $PbR_3^\bullet$ detected
Si_2Cl_6	$Li(NR'_2)$		U.v.	None
$GeCl_2$·dioxan	$Li(NR'_2)$	$Ge(NR'_2)_2$	U.v.	$Ge(NR'_2)_3^\bullet$
$SnCl_2$	$Li(NR'_2)$	$Sn(NR'_2)_2$	U.v.	$Sn(NR'_2)_3^\bullet$
$PbCl_2$	$Li(NR'_2)$	$Pb(NR'_2)_2$	U.v. or visible	None
$GeCl_2$·dioxan	$Li(NR'R'')$	$Ge(NR'R'')_2$	U.v.	$Ge(NR'R'')_3^\bullet$
$SnCl_2$	$Li(NR'R'')$	$Sn(NR'R'')_2$	U.v.	$Sn(NR'R'')_3^\bullet$

[a] R = $CH(SiMe_3)_2$, R′ = $SiMe_3$, R″ = CMe_3. [b] Carried out under argon or *in vacuo*. [c] Or GeI_2.

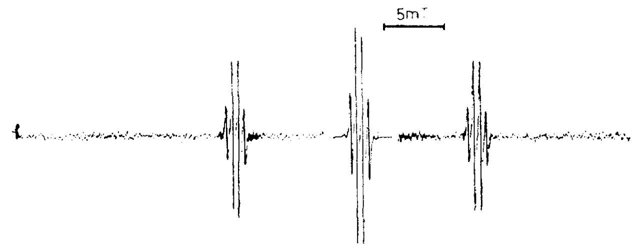

FIGURE 1 E.s.r. spectrum of $Si[CH(SiMe_3)_2]_3^\bullet$ in benzene at 30 °C, together with satellites due to ^{29}Si recorded under increased gain. The spectrum is centred at 322.4 mT

Measurement of the g values [relative to polycrystalline diphenylpicrylhydrazyl (dpph)] and the α-proton [a(H)] or nitrogen [a(N)] couplings was straightforward, but determination of the central-atom hyperfine coupling was not and requires further comment. It is apparent from the

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[14] (*a*) P. J. Davidson, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 829; (*b*) I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

[15] J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1974, 651.

[16] *Cf.*, H. Bürger and R. Eujen, *Fortschr. Chem. Forsch.*, 1974, **50**, 1.

spectra that the satellite lines are not symmetrically placed about the central multiplet; they are shifted downfield, but not by equal amounts. The spectra are therefore far from first order in appearance and the coupling constant is not simply the separation of the high- and low-field satellites. This is particularly true for the tin radicals where the metal coupling is comparable in magnitude to the applied magnetic field. Correct values can only be obtained by application of the Breit–Rabi equation; a second-order treatment is not adequate.

For the Si and Sn central radicals ($I = \frac{1}{2}$), the equation takes the simple form (i) where A_0 is the correct coupling

$$A_0 = \frac{2H_0(H_0 - H_k)}{2H_0 - H_k} \text{ or } \frac{2H_0(H_l - H_0)}{2H_0 - H_l} \qquad \text{(i)}$$

constant, and H_0, H_k, and H_l are the field positions of central line, low-field satellite, and high-field satellite. Since each nucleus (^{29}Si, ^{117}Sn, and ^{119}Sn) gives rise to a pair of lines (at H_k and H_l), two values of the couplings are obtained in each case. This serves as an internal check. Thus for $SnR_3^{\bullet}$ we find the values (mT):

$$^{117}\text{Sn}\begin{cases} H_0 = 324.428 \\ H_k = 208.64 \\ H_l = 391.41 \end{cases}$$

$$^{119}\text{Sn}\begin{cases} H_k = 201.11 \\ H_l = 393.93 \end{cases}$$

$$\left.\begin{array}{l} a(^{117}\text{Sn}) \text{ calculated from } H_k = 170.67 \\ a(^{117}\text{Sn}) \text{ calculated from } H_l = 168.9 \end{array}\right\} \text{average} = 169.78$$

$$\left.\begin{array}{l} a(^{119}\text{Sn}) \text{ calculated from } H_k = 178.7 \\ a(^{119}\text{Sn}) \text{ calculated from } H_l = 176.6 \end{array}\right\} \text{average} = 177.5$$

The ratio of the ^{117}Sn and ^{119}Sn coupling constants (1.046 4) is in excellent agreement with the value calculated from the ratio of the nuclear magnetic moments (1.046 2).

For the germanium-centred radicals, the Breit–Rabi equation was used in a form suggested by Roncin and Debuyst.[17] A computer program was written to calculate the position of the satellite lines using a trial value of the coupling constant and the observed field position of the central multiplet. The value of the coupling was varied until the calculated line positions agreed with the measured ones. Typical results for $Ge(NR'_2)_3^{\bullet}$ are shown in Table 2.

TABLE 2

Line positions (mT) for $Ge(NR'_2)_3^{\bullet}$

Measured	Calculated	Difference
243.974	244.012	0.038
257.411	257.416	0.005
271.702	271.704	0.002
286.849	286.898	0.049
302.968	303.017	0.049
*	320.067	
338.030	338.048	0.018
356.841	356.954	0.113
376.629	376.766	0.137
397.395	397.462	0.67

* Obscured by signal from radical containing Ge nuclei of zero spin.

The extremely large value of the coupling to Sn in $Sn(NR'_2)_3^{\bullet}$ made accurate measurement of line positions difficult; the low-field line due to ^{119}Sn was believed to occur below ' zero-field '. (Due to hysteresis, the magnetic field is not zero even when no current flows through the electromagnet of the spectrometer.) A line at 47.7 mT was assigned to the low-field satellite of ^{117}Sn. The high-field satellites of ^{117}Sn and ^{119}Sn both showed septet structure and overlapped, forming a ten-line pattern with approximately constant splitting (see Figure 2). The relative intensities were also consistent with overlapping of the fourth line of one septet with the first line of the other. A computer simulation of the two binomial septets (splitting *a*, separation 3*a*) was in agreement with the spectrum obtained; septet structure was not found on the low-field ^{117}Sn line. Typical results (mT) obtained were:

$$H_0 = 334.03$$

$$^{117}\text{Sn}\begin{cases} H_k = 47.7 \\ H_l = 443.8 \end{cases}$$

$$^{119}\text{Sn}\begin{cases} H_k \text{ not detected} \\ H_l = 447.3 \end{cases}$$

$$\left.\begin{array}{l} a(^{117}\text{Sn}) \text{ calculated from } H_k = 308.3 \\ a(^{117}\text{Sn}) \text{ calculated from } H_l = 327.0 \end{array}\right\} \text{average} = 317.6$$

$$a(^{119}\text{Sn}) \text{ calculated from } H_l = 342.6$$

The ratio $a(^{119}\text{Sn}) : a(^{117}\text{Sn})$ was 1.079, instead of the 1.046 calculated from the ratio of the nuclear magnetic moments; this is undoubtedly due to inaccuracies in the measurements, arising from the magnitude of the coupling.

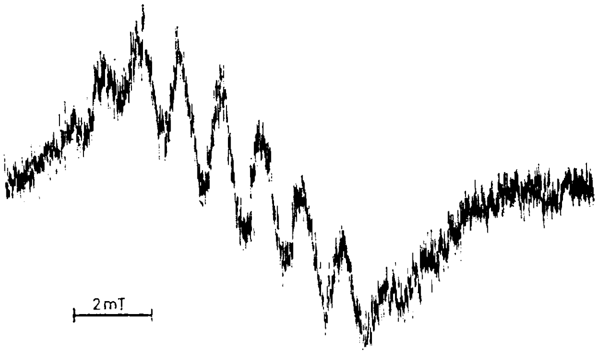

FIGURE 2 High-field ^{117}Sn and ^{119}Sn e.s.r. satellites of $Sn[N(SiMe_3)_2]_3^{\bullet}$ in n-hexane at 30 °C. The two multiplets are centred at 443.8 and 447.3 mT respectively

Stability Measurements on the Radicals $MX_3^{\bullet}$.—These were made using samples in sealed tubes, protected from light and stored at ambient temperature. Spectra were recorded periodically, and stabilities estimated from the decrease in signal strength. The radical $SiR_3^{\bullet}$ decayed in benzene with a half-life of *ca.* 10 min at *ca.* 30 °C. The value of $t_{\frac{1}{2}}$ remained constant over five half-lives, thereby showing that the radical decayed with first-order or pseudo-first-order kinetics. There was some evidence that decay of $SiR_3^{\bullet}$ was reversible in benzene, although not in hexane. Irradiation of the sample in the former solvent caused formation of the radical up to a constant maximum intensity; shutting off the light led to complete decay. This cycle of formation–decay was repeated several times, but does not prove unambiguously that the radical decayed reversibly.

Tabulation of E.S.R. Data.—The e.s.r. data obtained on $MR_3^{\bullet}$, $M(NR'_2)_3^{\bullet}$, and $M(NR'R'')_3^{\bullet}$ are summarised in Table 3. Spectra of $SnR_3^{\bullet}$ and $Ge(NR'_2)_3^{\bullet}$ have been published in preliminary accounts of this work.[14,15] The spectrum of $SiR_3^{\bullet}$ is shown in Figure 1 and the high-field ^{117}Sn and ^{119}Sn satellites of $Sn(NR'_2)_3^{\bullet}$ are illustrated in Figure 2.

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[17] J. Roncin and R. Debuyst, *J. Chem. Phys.*, 1969, **51**, 577.

TABLE 3

E.s.r. parameters for trialkyl and triamido-radicals

Radical [a]	Solvent	g	$a(\alpha\text{-H})$ or $a(\mathrm{N})$ / mT	$a(\mathrm{M})$ [b] / mT	Stability [c]
$\mathrm{SiR_3^{\bullet}}$	Benzene	2.0027	0.48	19.3	$t_{\frac{1}{2}}$ *ca.* 10 min at 30 °C
$\mathrm{GeR_3^{\bullet}}$	Benzene	2.0078	0.38	9.2	unchanged after 4 months
$\mathrm{SnR_3^{\bullet}}$	Benzene	2.0094	0.21	169.8 (^{117}Sn) 177.6 (^{119}Sn)	$t_{\frac{1}{2}}$ *ca.* 1 year
$\mathrm{Ge(NR'_2)_3^{\bullet}}$	Hexane	1.9991	1.06	17.1	$t_{\frac{1}{2}}$ >5 months
$\mathrm{Sn(NR'_2)_3^{\bullet}}$	Hexane	1.9912	1.09	317.6 (^{117}Sn) 342.6 (^{119}Sn)	$t_{\frac{1}{2}}$ *ca.* 3 months
$\mathrm{Ge(NR'R'')_3^{\bullet}}$	Hexane	1.9998	1.29	17.3	$t_{\frac{1}{2}}$ *ca.* 5 min
$\mathrm{Sn(NR'R'')_3^{\bullet}}$	Hexane	1.9928	1.27		$t_{\frac{1}{2}}$ *ca.* 5 min

[a] $\mathrm{R = CH(SiMe_3)_2}$, $\mathrm{R' = SiMe_3}$, $\mathrm{R'' = CMe_3}$. [b] ^{29}Si ($I = \frac{1}{2}$, 4.7%), ^{73}Ge ($I = \frac{9}{2}$, 7.6%), ^{117}Sn ($I = \frac{1}{2}$, 7.7%), ^{119}Sn ($I = \frac{1}{2}$, 8.7%), calculated using the Breit–Rabi equation. [c] Based on the e.s.r. signal strength of a light-protected sealed sample at *ca.* 20°C.

DISCUSSION

Radical Formation.—The initial work was carried out using analytically pure $\mathrm{SnR_2}$, and it is unlikely that $\mathrm{SnR_3^{\bullet}}$ arose from any other compound. Two mechanisms (A or B) are suggested for the formation of $\mathrm{SnR_3^{\bullet}}$.

$$\left.\begin{array}{rl} \mathrm{SnR_2} \xrightarrow{h\nu} & \mathrm{R^{\bullet} + SnR^{\bullet}} \\ \mathrm{R^{\bullet} + SnR_2} \longrightarrow & \mathrm{SnR_3^{\bullet}} \end{array}\right\}\ \mathrm{A} \qquad \begin{array}{c}(1)\\(2)\end{array}$$

$$\left.\begin{array}{rl} \mathrm{SnR_2} \xrightarrow{h\nu} & \mathrm{(SnR_2)^{*}} \\ \mathrm{(SnR_2)^{*} + SnR_2} \longrightarrow & \mathrm{SnR_3^{\bullet} + SnR^{\bullet}} \end{array}\right\}\ \mathrm{B} \qquad \begin{array}{c}(3)\\(4)\end{array}$$

In mechanism A a tin–carbon bond is cleaved homolytically and the resulting alkyl radical is trapped by another molecule of $\mathrm{SnR_2}$, acting as a spin trap. Four attemdts were made to add other radicals to $\mathrm{SnR_2}$, the first two using radical precursors, and the second two using stable radicals. The radical precursors were $\mathrm{(Bu^tON)_2}$ ($t_{\frac{1}{2}}$ 29 min at 65 °C) [18] and azobisisobutyronitrile (aibn) ($t_{\frac{1}{2}}$ 20 h at 60 °C),[19] but both reacted with $\mathrm{SnR_2}$ at ambient temperature. The red colour due to $\mathrm{SnR_2}$ disappeared, and the solution contained no paramagnetic species. Galvinoxyl and $\mathrm{CPh_3^{\bullet}}$ were also added to $\mathrm{SnR_2}$. The former reacted to give non-radical products whereas there was no reaction with the latter (the red colour of $\mathrm{SnR_2}$ and the e.s.r. spectrum of $\mathrm{CPh_3^{\bullet}}$ were both unchanged in the mixture of the two).

In mechanism B $\mathrm{SnR_3^{\bullet}}$ is formed from a bimolecular reaction between an excited state of $\mathrm{SnR_2}$ (possibly triplet) and a ground-state $\mathrm{SnR_2}$. Both mechanisms require formation of a tin(I) species; since no tin mirror develops on photolysis (even under u.v.), and no solid is deposited, it is assumed that $\mathrm{SnR^{\bullet}}$ reacts with solvent or forms a soluble oligomer. Exotic species such as hexa-alkylhexastannabenzene or octa-alkyloctastannacubane may be postulated, but a preliminary experiment in which $\mathrm{SnR_2}$ was photolysed on a preparative scale indicated a mixture of products of which none was isolated.

No estimate was made of the yield of $\mathrm{SnR_3^{\bullet}}$ from $\mathrm{SnR_2}$. The radical could easily be formed in the concentration range 10^{-2}—10^{-3} mol dm^{-3}, but it was not possible to prepare $\mathrm{SnR_2}$ at similar dilutions, due to its extreme air sensitivity in solution. It is tempting to assume that all the other radicals obtained also arose from the action of light on the appropriate bivalent species. However, this seems unlikely for $\mathrm{GeR_3^{\bullet}}$ as prepared below, and may also be incorrect for $\mathrm{SiR_3^{\bullet}}$.

The green product obtained from the reaction of $\mathrm{GeI_2}$ with LiR was not characterised, but a solution contained large amounts of the radical $\mathrm{GeR_3^{\bullet}}$ without prior photolysis. (The preparation and recording of the e.s.r. spectrum were carried out with the exclusion of as much light as possible.) Furthermore, visible or u.v. irradiation had no effect on the signal strength. This strongly suggests that formation of the radical is not photolytic. Two other possible mechanisms are (*i*) a thermal disproportionation [equation (5)] and (*ii*) alkylation by $\mathrm{R^-}$

$$\mathrm{2GeI_2} \xrightarrow{\mathrm{4LiR}} \mathrm{2GeR_2} \xrightarrow{\mathrm{Heat}} \mathrm{GeR_3^{\bullet} + GeR^{\bullet}} \qquad (5)$$

competing with reduction by $\mathrm{R^-}$ [equations (6)—(8)].

$$\mathrm{GeI_2 + 2R^-} \xrightarrow{\text{alkylation}} \mathrm{GeR_2} \qquad (6)$$

$$\mathrm{GeI_2 + R^-} \xrightarrow{\text{reduction by } \mathrm{R^-}} \mathrm{GeI^{\bullet} + R^{\bullet} + I^-} \qquad (7)$$

$$\mathrm{GeR_2 + R^{\bullet}} \longrightarrow \mathrm{GeR_3^{\bullet}} \qquad (8)$$

While the formation of $\mathrm{GeR_3^{\bullet}}$ in these reactions remains an open question, it is clear that there is a marked difference in behaviour compared to $\mathrm{SnR_3^{\bullet}}$ formation. [Since this work was completed, the bright yellow $\mathrm{GeR_2}$ has been prepared and characterised; [2,20] photolysis in benzene slowly produced $\mathrm{GeR_3^{\bullet}}$, but *no green colouration* and the signal decayed on continued irradiation. To test whether the formation of $\mathrm{GeR_3^{\bullet}}$, in the *in situ* reactions described above, involves LiR, a hexane solution of $\mathrm{GeR_2}$ was shown by e.s.r. to contain no $\mathrm{GeR_3^{\bullet}}$, but addition of one or two drops of LiR in diethyl ether caused the immediate formation of a strong e.s.r. signal due to $\mathrm{GeR_3^{\bullet}}$, which lost intensity on irradiation. Mixing $\mathrm{GeR_2}$ and LiR in equimolar quantities gave $\mathrm{GeR_3^{\bullet}}$ in high concentration, which slowly decayed on irradiation. It thus appears that $\mathrm{GeR_3^{\bullet}}$ photodecays, perhaps by Ge–R cleavage. There therefore appear to be at least two alternative routes to $\mathrm{GeR_3^{\bullet}}$ from $\mathrm{GeR_2}$: a rapid reaction with LiR, or a slower photolysis. Interestingly, addition of $\mathrm{Li(NR'_2)}$ to $\mathrm{GeR_2}$ failed to produce a radical. The $\mathrm{GeR_2}$–LiR reaction may proceed *via* $\mathrm{GeR_3^-}$.]

The reaction of $\mathrm{Si_2Cl_6}$ with LiR gave a precipitate,

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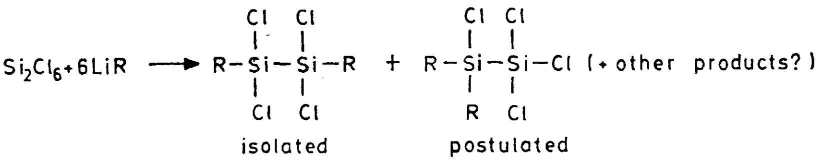
[18] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.

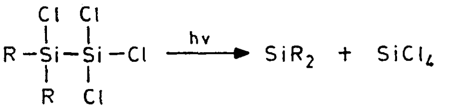
[19] C. Walling and E. S. Huyser, *Org. Reactions*, 1963, **13**, 91.

[20] D. H. Harris and M. F. Lappert, unpublished work, 1975.

presumed to be LiCl. Irradiation of the supernatant liquid led to formation of $SiR_3^{\bullet}$, but the product isolated from the reaction, $(SiRCl_2)_2$, was not a source of $SiR_3^{\bullet}$. It is possible, however, that the radical arose from the unsymmetrically disubstituted disilane, $ClR_2SiSiCl_3$, according to equations (9)—(11). Supporting evidence for equation (10) is provided by the photolysis of dodecamethylcyclohexasilane, which eliminates $SiMe_2$.[21] The formation of $SiMe_2$ was inferred from the isolation of $(SiMe_2)_n$ ($n = 4$ or 5) in this reaction, or of $SiMeEt_2(SiMe_2)_nH$ ($n = 1$ or 2) when the photolysis was carried out in presence of $SiMeEt_2H$; these are evidently very fast reactions. However, Si_2Me_6 was not observed, and this might have been expected if the silylene itself was very rapidly photolysed to trimethylsilyl radicals.

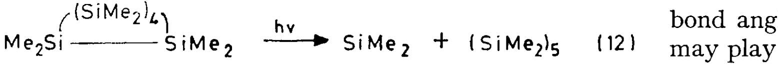


$$Si_2Cl_6 + 6LiR \longrightarrow \underset{\text{isolated}}{R-\overset{Cl}{\underset{Cl}{Si}}-\overset{Cl}{\underset{Cl}{Si}}-R} + \underset{\text{postulated}}{R-\overset{Cl}{\underset{R}{Si}}-\overset{Cl}{\underset{Cl}{Si}}-Cl} \text{ (+ other products?)} \qquad (9)$$



$$R-\overset{Cl}{\underset{R}{Si}}-\overset{Cl}{\underset{Cl}{Si}}-Cl \xrightarrow{h\nu} SiR_2 + SiCl_4 \qquad (10)$$

$$2SiR_2 \xrightarrow{h\nu} SiR_3^{\bullet} + SiR^{\bullet} \qquad (11)$$



$$Me_2Si\overset{(SiMe_2)_4}{\text{————}}SiMe_2 \xrightarrow{h\nu} SiMe_2 + (SiMe_2)_5 \qquad (12)$$

$$SiMe_2 \xrightarrow{h\nu} SiMe_3^{\bullet} \longrightarrow Si_2Me_6 \qquad (13)$$

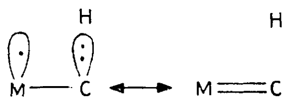
In our work, *in situ* irradiation of $(SiMe_2)_6$ (toluene, -60 °C) did not lead to e.s.r. detection of $SiMe_3^{\bullet}$. However, for SiR_2 the bulky R groups probably stabilise the silylene sufficiently for photolysis to $SiR_3^{\bullet}$ to be favoured over alternative reactions,[3] such as those available to $SiMe_2$. Certainly, there is no tendency for monomeric SnR_2 to oligomerise in solution, although it exists as the dimer in the crystal.[2,20]

Thus there is some doubt as to the mechanism of formation of $GeR_3^{\bullet}$ (from $GeX_2 + 2LiR$) and $SiR_3^{\bullet}$; in the other cases, photolysis of the bivalent compound generates the radical. In these latter systems the overall process is represented by (14).

$$2M^{II} \overset{h\nu}{\rightleftharpoons} M^{I} + M^{III} \qquad (14)$$

g Factors.—It is evident from Table 3 that the deviation of the *g* factors from free spin increases on going down the Group. This is not unexpected since spin–orbit coupling is increasingly important for heavy elements; the *g* shifts arise from a mixing of excited states into the doublet ground state by spin–orbit coupling. The effect of promotion to empty orbitals is to decrease *g*, whereas excitation from filled orbitals increases *g*. The trend for $MR_3^{\bullet}$ is similar to that found for $MH_3^{\bullet}$ and $MMe_3^{\bullet}$. It is interesting, therefore, that $g[Ge(NR'_2)_3^{\bullet}] > g[Sn(NR'_2)_3^{\bullet}]$. Lloyd and Rogers[22] found a similar result for $MCl_3^{\bullet}$ with $g[GeCl_3^{\bullet}] > g[SnCl_3^{\bullet}]$. A lowering of the *g* value is an indication of low-lying empty orbitals and has often been taken as evidence for *d*-orbital participation. However, it is difficult to rationalise these results without a full determination of the *g* tensor. A lowering of *g* is generally associated with a pyramidal structure for an $AX_3^{\bullet}$ radical. The lower *g* values for the triamino-radicals compared with the trialkyl radicals are thus consistent with the former having more pyramidal structures (see below); effects due to differences of bond angle at C and N referred to in the introduction may play a role.

a(H) *and* a(N).—The β-H splittings for the radicals $M[CH(SiMe_3)_2]_3^{\bullet}$ are close to those for $M(CH_3)_3^{\bullet}$. The most notable feature of the β-H couplings of the Group 4 alkyl radicals is the large difference between $CMe_3^{\bullet}$ [*a*(H) 2.25 mT] and the analogous silicon, germanium, and tin species [*a*(H) 0.634, 0.5, and 0.275 mT, respectively]. This difference is attributed to (*i*) the more pyramidal geometry of the radicals of Si, Ge, Sn, and Pb; (*ii*) the reluctance of the heavier elements to form multiple bonds; and (*iii*) the greater size of the heavier elements compared to C. All three factors reduce hyperconjugative coupling, which is believed to be the main cause of β-H splittings in simple alkyl radicals. In this process there is a contribution to the bonding from a structure in which the unpaired electron couples with one of the electrons in a C–H bonding orbital. This will be maximised when (*a*) the geometry around M is planar; (*b*) partial double-bond character between M and C can occur, and (*c*) the size of M is such that good overlap between the two orbitals is feasible. These conditions are met more fully for M = C than M = Si, Ge, Sn, or Pb.



Comment on the values of *a*(N) requires data on analogous radicals, centred on other Group 4 elements or with other amido-ligands, but these are not at present

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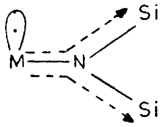
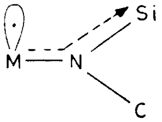
[21] M. Ishikawa and M. Kumada, *Chem. Comm.*, **1970**, 612.

[22] R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, **95**, 2459.

known. Radicals of the type $>\dot{\mathrm{C}}-\mathrm{N}<$ (where the substituents are H or alkyl groups) have been studied; a(N) ranges from 0.3 to 0.7 mT.[23]

The similarity in g values between the radicals $\mathrm{M[N(SiMe_3)_2]_3^{\bullet}}$ and $\mathrm{M[N(CMe_3)(SiMe_3)]_3^{\bullet}}$ suggests very little change in bond angle; this is supported by the closely related values of $a(^{73}\mathrm{Ge})$ for the two germanium-centred radicals. Thus some factor other than change in structure is responsible for the greater values of a(N) in the mixed amino-radicals [containing $\mathrm{N(CMe_3)(SiMe_3)}$]. One possibility is that some of the unpaired electron density is distributed between the two sets of Si d orbitals and the single N p orbital; replacement of Si by C would thus reduce the delocalisation into Si d orbitals, and hence increase a(N). Structure (4) has a greater amount of unpaired electron density on N than (3). A similar effect is found on comparing silyl nitroxides[24] with their alkyl analogues, a(N) 0.59 mT for $\mathrm{(Me_3Si)_2\dot{N}O}$ and 1.52 mT for $\mathrm{Bu^t_2\dot{N}O}$.


(3)


(4)

a(M).—Whereas the methyl radical is planar, there is considerable evidence that other Group 4B-centred radicals exhibit varying degrees of deviation from planarity. The main evidence comes from hyperfine coupling to those isotopes of the central atom which possess non-zero spin (^{13}C, ^{29}Si, ^{73}Ge, ^{117}Sn, ^{119}Sn, and ^{207}Pb). The metal splitting changes rapidly with bending as the s character of the odd-electron orbital changes from zero to 25% on going from sp^2 to sp^3 hybridisation. The values of a(M) for $\mathrm{MR_3^{\bullet}}$ are very close to literature values for $\mathrm{MH_3^{\bullet}}$ and $\mathrm{MMe_3^{\bullet}}$. The increased values for $\mathrm{M(NR'_2)_3^{\bullet}}$ indicate that these species are more pyramidal. However, $\mathrm{Ge(NR'_2)_3^{\bullet}}$ is less pyramidal than $\mathrm{GeCl_3^{\bullet}}$ which has $a(^{73}\mathrm{Ge})$ 22.9 mT.

Trends in radical structure can be expressed by the following scheme:

$$\mathrm{CH_3^{\bullet}}\quad \underbrace{\underbrace{\left(\begin{array}{ccc} \mathrm{SiH_3^{\bullet}} & \mathrm{SiMe_3^{\bullet}} & \mathrm{SiR_3^{\bullet}} \\ \mathrm{GeH_3^{\bullet}} & \mathrm{GeMe_3^{\bullet}} & \mathrm{GeR_3^{\bullet}} \\ \mathrm{SnH_3^{\bullet}} & \mathrm{SnMe_3^{\bullet}} & \mathrm{SnR_3^{\bullet}} \\ & \mathrm{PbMe_3^{\bullet}} & \end{array}\right)}_{\text{similar geometries}} \begin{array}{ccc} & \mathrm{CCl_3^{\bullet}} & \mathrm{CF_3^{\bullet}} \\ & \mathrm{SiCl_3^{\bullet}} & \mathrm{SiF_3^{\bullet}} \\ \mathrm{Ge(NR'_2)_3^{\bullet}} & \mathrm{GeCl_3^{\bullet}} & \\ \mathrm{Sn(NR'_2)_3^{\bullet}} & \mathrm{SnCl_3^{\bullet}} & \end{array}}_{\text{all show marked deviations from planarity}}$$

Approximately planar — Increasingly pyramidal — Approximately tetrahedral

The tendency for radicals of the type $\mathrm{MX_3^{\bullet}}$ to become pyramidal has usually been related to the electronegativity difference between the central atom and its substituents. The following predictions have been made: (*i*) If $\chi(\mathrm{X}) < \chi(\mathrm{M})$ the radical will be planar; (*ii*) If $\chi(\mathrm{X}) > \chi(\mathrm{M})$ the radical will be pyramidal. These predictions are consistent with the observed couplings. However, recent results on the t-butyl radical[25] have suggested it possesses a pyramidal structure with a low barrier to inversion, and it has been proposed[26] that conjugative destabilisation rather than electronegativity is the primary electronic factor which gives rise to non-planar radical structures.

For the radicals prepared in this work electronegativity and/or conjugative delocalisation acts in opposition to a steric effect. Sterically demanding ligands will favour planarity, since this geometry increases the bond angles around the central atom (120° if planar, 109° if pyramidal), and reduces non-bonded interactions between the $\mathrm{SiMe_3}$ groups. In view of the size of $\mathrm{CH(SiMe_3)_2}$ and $\mathrm{N(SiMe_3)_2}$, it is perhaps surprising that the electronic effects are dominant.

Radical Stability.—The extreme longevity of the radicals obtained in this work must be due in the main part to steric hindrance to dimerisation. While many compounds with M–M bonds are known (M = Si, Ge, or Sn), the bulkiness of the ligands $\mathrm{CH(SiMe_3)_2}$ and $\mathrm{N(SiMe_3)_2}$ is believed to prevent combination of two radicals. The low values of the M–H bond strengths [D(M–H): C, 104; Si, 81; Ge, 73; Sn, 70 kcal mol^{-1}] [27,*] do not favour hydrogen abstraction from the C–H bonds of the solvent. The shorter lifetimes of the $\mathrm{Sn(NR'_2)_3^{\bullet}}$ and $\mathrm{Ge(NR'_2)_3^{\bullet}}$ radicals in hexane compared to $\mathrm{SnR_3^{\bullet}}$ and $\mathrm{GeR_3^{\bullet}}$ in benzene may reflect the ease of H abstraction from the two solvents, but the differences of bond angle at N and C may again play a part. A third factor for the trialkyl radicals is the non-availability of disproportionation paths. These occur readily for carbon-centred radicals but for Si, Ge, and Sn no stable species containing a double bond from these elements to C has been isolated, although they may occur as transient intermediates. The absence of β-hydrogen atoms on the ligands may also be significant, because β-hydride elimination is a common decomposition path, especially for metal alkyls.[5] Some or all of these factors must contribute to the stability of the radicals $\mathrm{C(SiMe_3)_3^{\bullet}}$,[2] $\mathrm{CHBu^t_2{}^{\bullet}}$,[9] *etc.*, but their effect is much more dramatic for $\mathrm{M[CH(SiMe_3)_2]_3^{\bullet}}$ and $\mathrm{M[N(SiMe_3)_2]_3^{\bullet}}$.

The decay of the radical $\mathrm{SiR_3^{\bullet}}$ in benzene was found to be first order; this implies reaction with solvent or an intramolecular rearrangement. One possibility for the latter is internal hydrogen-atom abstraction to give a short-lived intermediate present in insufficient steady-state concentration for detection by e.s.r. It is interesting that there was some evidence that decay of $\mathrm{SiR_3^{\bullet}}$ in benzene was reversible. However, since this was not proved unambiguously, and since the solution almost certainly contained a mixture of compounds, any explanation would be highly speculative.

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[*] Throughout this paper: 1 cal = 4.184 J.

[23] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **53**, 3932.

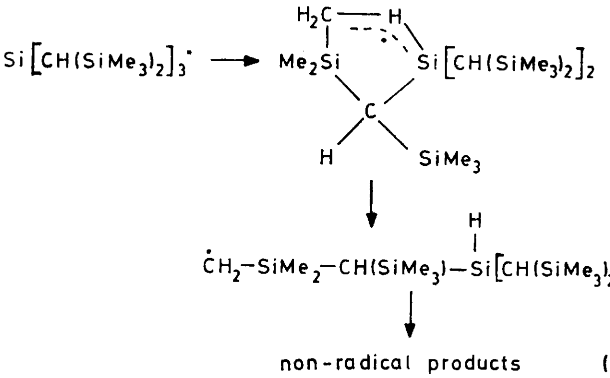
[24] R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, 1971, **93**, 5901.

[25] J. B. Lisle, L. F. Williams, and D. E. Wood, *J. Amer. Chem. Soc.*, 1976, **98**, 227; P. J. Krusic and P. Meakin, *ibid.*, p. 228.

[26] P. J. Krusic and R. C. Bingham, *J. Amer. Chem. Soc.*, 1976, **98**, 230.

[27] R. A. Jackson, *Chem. Soc. Spec. Publ.*, No. 24, 1970, 295.

The cause of the greater stability of the $N(SiMe_3)_2$ species compared to the mixed amino-radicals is uncertain. However, generation of the latter was not as clean as the former. For both the germanium and tin mixed radicals some experiments led to detection of a three-line spectrum [relative intensities 1 : 1 : 1, *a* 1.44 mT, possibly $N(CMe_3)(SiMe_3)^{\bullet}$] in addition to the signal for $M[N(CMe_3)(SiMe_3)]_3^{\bullet}$. Furthermore, the central septet of the latter species was superimposed on other signals; for M = Ge there appeared to be two sets of ^{73}Ge satellite lines, one set being much weaker than that assigned to $Ge[N(CMe_3)(SiMe_3)]_3^{\bullet}$. Thus the presence of these other paramagnetic species, or products derived from them, may reduce the stability of the triamino-radicals.



(15)

The most significant conclusion to be drawn from this work is that stable trivalent compounds of Group 4B can be prepared. The oxidation state III was previously unknown for this Group, apart from transient or matrix-isolated species. While yields of the radicals are probably low (apart from $GeR_3^{\bullet}$), and must not be confused with the very high intensity of the e.s.r. signals, it should still prove feasible to examine aspects of the chemistry of these species without their prior isolation as pure compounds. For example, there exists the possibility of forming the nitrosyls $MR_3(NO)$ by addition of the paramagnetic NO to a solution of $MR_3^{\bullet}$. [The

$$NO^{\bullet} + MR_3^{\bullet} \longrightarrow MR_3(NO) \qquad (16)$$

related compounds $MPh_3(NO)$ (M = Si, Ge, Sn, and Pb) have been characterised in solution, and were found to be thermally unstable.[28]]

The generation of other radicals, stabilised by steric factors, should prove of considerable interest. Within Group 4B, the photolysis of other MX_2 compounds (X = a bulky group bonded to M by atoms other than C or N, *e.g.* PR_2 or $SCPh_3$) would test the generality of the photolytic disproportionation. The method of radical generation described in this paper, photolytic disproportionation, may not be so readily applicable to radicals centred on C or elements outside Group 4.

We thank Drs. J. D. Cotton, C. S. Cundy, P. J. Davidson, and D. H. Harris for providing most of the compounds used in this work, and the S.R.C. for the award of a studentship (to P. W. L.).

[6/538 *Received*, 22*nd March*, 1976]

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[28] J. Jappy and P. N. Preston, *J. Organometallic Chem.*, 1969, **19**, 196.