Photochemical Synthesis and Electron Spin Resonance Characterisation of Stable Trivalent Metal Alkyls (Si, Ge, Sn) and Amides (Ge and Sn) of Group IV Elements

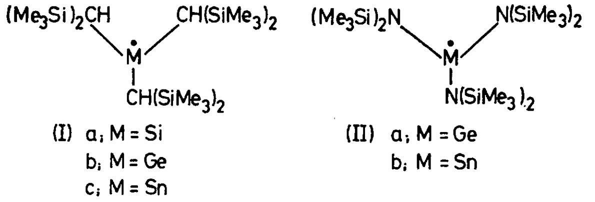
By John D. Cotton, Colin S. Cundy, David H. Harris, Andrew Hudson,* Michael F. Lappert,*
and Peter W. Lednor

(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary The reaction of MCl_2 ($M = Ge$ or Sn) or Si_2Cl_6 with R^1Li or $(R^2{}_2N)Li$ [$R^1 = (Me_3Si)_2CH$, $R^2 = Me_3Si$] and subsequent irradiation affords the stable metal-centred radicals $R^1_3Si\cdot$, $R^1_3M\cdot$, or $(R^2_2N)_3M\cdot$ (*e.g.* $R^1_3Ge\cdot$ has $t_{\frac{1}{2}} > 4$ months in C_6H_6 at 20 °C), the solution e.s.r. spectra of which show well defined hyperfine splittings [*e.g.* for $(R^2_2N)_3Ge\cdot$, a decet of septets, due to coupling with ^{73}Ge ($I = {}^9/_2$) and ^{14}N ($I = 1$)].

We report a general photochemical procedure for the synthesis of group IV metal-centred radicals and their e.s.r. characterisation, illustrated for the isoelectronic trialkylmetal(III) and tris(amido)metal(III) species (I) and (II). This choice of bulky alkyl or amido-groups leads to substantial kinetic stability;[1] compounds (I) and (II) have long half-lives: *e.g.*, *ca.* 10 min for (Ia) in hexane at 30 °C and *ca.* 3 months for (IIb) in hexane at *ca.* 20 °C (see Table).

The trivalent state for the Group IV metals was hitherto unknown [except for transient, metal-centred radicals[2] and our own recent report of (Ic)[3]] and a substantial new chemistry is now to be expected.



Compounds (I) and (II) were obtained by photochemical disproportionation using a metal(II) halide precursor when available ($GeCl_2$,dioxan, GeI_2, or $SnCl_2$) or Si_2Cl_6, as shown in equations (1) and (2). A stable monomeric bivalent intermediate (III) was isolated for R^1_2Sn,[3] $(R^2_2N)_2Ge$,[4] and $(R^2_2N)_2Sn$[4] [$R^1 = (Me_3Si)_2CH$, $R^2 = Me_3Si$]. For reaction (2), we suggest that (IV) may be an intermediate obtained in low concentration because (i) α-eliminations [such as (2a)] to produce silylenes X^1X^2Si: are known,[5] (ii) the *sym*-isomer (V) has been isolated and is not a source of (Ia) under our conditions of photolysis, and (iii) even with an excess of RLi the only polyalkylated disilane identified was (V).

$$MCl_2 \xrightarrow[Et_2O]{2R^1Li \text{ or } 2(R^2_2N)Li} \underset{(III)}{R_2M \text{ or } (R^2_2N)_2M} \xrightarrow[C_6H_6 \text{ or n-}C_6H_{14}]{h\nu} (I) \text{ or } (II) \quad (1)$$

$$Si_2Cl_6 \xrightarrow[(ii)\ h\nu]{(i)\ 6RLi \text{ in } C_6H_6} \underset{(V)}{(RSiCl_2)_2} \quad + \quad \underset{(IV)}{\left[\begin{array}{c} R_2Si\text{–}SiCl_3 \\ | \\ Cl \end{array}\right]} \xrightarrow[(a)]{-SiCl_4} [R_2Si] \rightarrow (Ia) \quad (2)$$

The main feature of the e.s.r. spectra is a multiplet arising from three equivalent protons (quartet) or three equivalent ^{14}N nuclei (septet). Under increased gain satellite spectra are readily observed (see Table). Thus (IIa) (Figure) gives a decet of septets from the 7·61% of ^{73}Ge ($I = {}^9/_2$) present in natural abundance. The large metal hyperfine coupling constants were obtained from an exact solution of the Breit–Rabi equation. The ^{119}Sn splitting in (IIb) is larger than the spectrometer operating frequency and only the high field satellite was detectable; a peak attributed to the low field ^{117}Sn satellite was found near zero field.

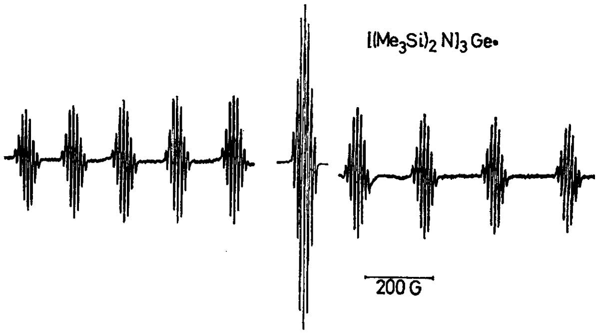
TABLE

Hyperfine splittings (mT), *g* values, and stabilities

Radical[a]	*g*	*a*(H) for (I) *a*(N) for (II)	*a*(M)	Stability
(Ia)	2·0027	0·48	19·3 (^{29}Si)	$t_{½}$ ca. 10 min at 30 °C[c]
(Ib)	2·0078	0·38	9·2 (^{73}Ge)	Unchanged after 4 months
(Ic)	2·0094	0·21	169·8 (^{117}Sn) 177·6 (^{119}Sn)	$t_{½}$ *ca.* 1 year
(IIa)	1·9991	1·06	17·1 (^{73}Ge)	$t_{½}$ > 5 months
(IIb)	1·9912	1·09	317·6 (^{117}Sn) 342·6 (^{119}Sn)	$t_{½}$ *ca.* 3 months

[a] Alkyls (I) in C_6H_6; amides (II) in n-C_6H_{14}. [b] Based on e.s.r. signal strength of a light-protected, sealed sample. [c] Decays by apparent first-order kinetics.

Trends for (Ia)—(Ic) follow a similar pattern to those reported for $Me_3M\cdot$ (M = Si, Ge, or Sn)(VI),[2] with *a*(H) decreasing and *g* increasing as a function of atomic number of M. The similarity of *a*(M) for (I) and (VI) suggests that these radicals all have pyramidal structures with not greatly different geometries.[2b] The increased *a*(M) found for (II) suggests that these species are more pyramidal in accord with the greater electronegativity of nitrogen; (IIa) is less pyramidal than $Cl_3Ge\cdot$ which has $a(^{73}Ge) = 22$ mT.[6]



FIGURE

It is interesting that the stability, unlike the geometry, of main group IV metal-centred radicals $X_3M\cdot$ is particularly sensitive to steric effects. These are thus of paramount importance for a four-co-ordinate metal environment, as in $X_3M{-}MX_3$ or X_3MH.

We thank the S.R.C. for their support.

(*Received, 3rd June* 1974; *Com.* 630.)

---

[1] *Cf.* P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209, for a discussion of kinetically stable metal alkyls.

[2] (a) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. P. J. Root, *J. Chem. Soc.* (*A*), 1970, 348; (b) R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, **95**, 2459; (c) J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

[3] P. J. Davidson, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 829.

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

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

[6] J. Roncin and R. De Guyst, *J. Chem. Phys.*, 1969, **51**, 577.