Electron Spin Resonance of t-Alkyl-, Silyl-, and Germyl-aminyl Radicals and some Observations on the Amides $MBr\{N(SiMe_3)_2\}_3$ (M = Ge, Sn, or Pb)

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Summary The e.s.r. spectra of the π-radicals $:\dot{N}RR'$ ($R = R' = GeMe_3$, $SiEt_3$, or CMe_3, or $R = CMe_3$ and $R' = SiMe_3$, or NR_2 = 2,2,6,6-tetramethylpiperidyl), obtained by photolysis of $M(NRR')_2$ (M = Ge or Sn), are reported; the tetravalent title compounds, prepared by oxidative addition of $BrN(SiMe_3)_2$ to $M'\{N(SiMe_3)_2\}_2$ (M′ = Ge, Sn, or Pb), are not sources of aminyls, but reduction of $GeBr\{N(SiMe_3)_2\}_3$ provides a convenient route to $\dot{G}e\{N(SiMe_3)_2\}_3$.

We report the detection of solution e.s.r. spectra attributed to a series of previously unreported aminyl radicals. The radicals have been prepared by novel routes involving the photolysis of organometallic compounds containing Ge or Sn. The methods employed are summarised in the Table, together with the e.s.r. parameters. The spectra, obtained using Varian E3 and E104A spectrometers,[1] consist of a simple 1 : 1 : 1 triplet; the g-factors and ^{14}N hyperfine splittings are in accord with expectations for aminyl radicals with the unpaired electron in a p_π orbital on nitrogen.[2] The photolysis of Ge^{II} and Sn^{II} compounds with bulky ligands thus provides a new route to aminyls.

Table. E.s.r. parameters of some novel aminyl radicals, $:\dot{N}R_2$ in n-C_6H_{14} at 25 °C

	Radical	$a(^{14}N)$/mT	g	Method of preparation[a]
(**1**)	$:\dot{N}(GeMe_3)_2$	1.21	2.008	i
(**2**)	$:\dot{N}(SiEt_3)_2$	1.27	2.007	ii
(**3**	$:\dot{N}(GeEt_3)_2$	1.20	2.007	iii
(**4**)	$:\dot{N}(CMe_3)(SiMe_3)$	1.44	2.007	i
(**5**)[b]	$:\dot{N}CMe_2[CH_2]_3CMe_2$	1.46	2.004	iii
		(a_H = 0.08, 12 protons)		
(**6**)[c]	$:\dot{N}(CMe_3)_2$	1.50	2.005	ii

[a] i, Photolysis of $Ge(NR_2)_2$; all photolyses were carried out using a high pressure Hg-Xe lamp (see ref. 1). ii, Photolysis of $M(NR_2)_2$ (M = Ge or Sn). iii Photolysis of $Sn(NR_2)_2$. [b] Ref. 3 cites $a(^{14}N)$ 1.43 mT and g 2.0041 at room temperature. [c] D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, 1971, **75**, 3486 cites $a(^{14}N)$ 1.42 mT and g 2.0045 in $HNBu^t_2$ at −70 °C.

The method is not restricted to silyl or germyl substituents; the radicals (**1**)—(**4**) have half-lives of *ca.* 1 s in n-C_6H_{14} at 25 °C. Photolysis of the appropriate Sn^{II} compounds yields the known[3] 2,2,6,6-tetramethylpiperidinyl, (**5**), with a similar half-life. It has also proved possible to prepare the di-t-butylaminyl radical, (**6**), from the di-t-butylamido-tin(II) or -germanium(II) precursors.[4] We estimate that this species has a half-life of 0.5 s in light petroleum (b.p. 30—40 °C) at 25 °C. We have previously shown that certain bulky Ge^{II} or Sn^{II} amides disproportionate upon photolysis to yield the persistent trivalent amide, *e.g.*, $Sn[N(SiMe_3)_2]_2 \rightarrow \dot{S}n\{N(SiMe_3)_2\}_3$.[1] The present results show that photolysis simultaneously induces M–N homolysis, and if the amido-ligand is exceptionally bulky the rate of disproportionation is not competitive with the rate of homolysis. Photolysis of $Me_3Sn^{IV}NEt_2$ has previously been inferred from CIDNP observations.[5]

Bis(alkyl)aminyls typically exhibit ^{14}N coupling constants of *ca.* 1.4 mT, significantly higher than our results for the bis(silyl) and bis(germyl) species (**1**)—(**3**). Precedents for this lowering of $a(^{14}N)$ are found in the e.s.r. spectra of nitroxides[6] and in tetrasilyl-substituted hydrazine radical cations,[6,7] where SiR_3 has a comparable effect to that of Ph. In both cases the e.s.r. results have been taken as evidence for Si–N $d_\pi \rightarrow p_\pi$ back-bonding.

In spite of many attempts, we have been unable to obtain a reproducible e.s.r. spectrum for bis(trimethylsilyl)-aminyl (**7**). Photolysis of solutions of $Ge(NR_2)_3Cl$ or the corresponding bromide, in the presence of an electron-rich olefin[8] in toluene at *ca.* 300 K gave only $\dot{G}e(NR_2)_3$.[1] No spectra were detected during the photolysis of $Li(NR_2)$ (in the absence or presence of the electron-rich olefin or CuI) or Me_3SnNR_2 in toluene at *ca.* 300 K. In their studies of (**7**) Roberts *et al.*[9,10] have reported that this species is extremely reactive and readily abstracts hydrogen from hydrocarbons, even from cyclopropane at 140 K. No e.s.r. spectrum attributable to (**7**) was observed, although the spectra of secondary radicals were readily detectable. The behaviour of bis(trimethylsilyl)aminyl is more typical of a σ-radical than the π-radicals we have observed in our experiments. This raises the interesting possibility that (**7**) either has a σ-ground state or a low-lying σ-excited state. Evidence has been presented[11] to suggest that two different electronic states are involved in the free-radical chemistry of succinimidyl. There are obvious analogies with the situation in (**7**). The two states can be thought of as arising from raising the degeneracy of the $^2\pi$ ground state of linear NR_2 by bending. Silyl-substituted aminyls are likely to be less strongly bent than dialkylaminyls (bond angle *ca.* 110—115°) since ∠SiNSi is normally greater than ∠CNC. This would tend to decrease the energy separation between the two states in support of our suggestion.

During the course of this study some new bis(trimethylsilyl)amides of Ge^{IV}, Sn^{IV}, and Pb^{IV} of formula $M\{N(SiMe_3)_2\}_3X$ were synthesised, as potential sources of $\dot{N}(SiMe_3)_2$ [and fully characterised by elemental analyses and i.r. and n.m.r. spectroscopy: (i) M = Ge, X = Cl, m.p. 262—263 °C, (ii) M = Ge, X = Br, m.p. 208—210 °C, (iii) M = Sn, X = Br, m.p. 228—229 °C, and (iv) M = Pb, X = Br, b.p. 120 °C/0.5 mmHg]. Although that part of the work was unsuccessful, *vide supra*, a number of features of interest emerged, namely (a) the discovery of a new oxidative addition reaction (M = Ge, Sn, or Pb) $M\{N(SiMe_3)_2\}_2 + BrN(SiMe_3)_2 \rightarrow MBr\{N(SiMe_3)_2\}_3$; (b) an alternative pathway to $GeCl\{N(SiMe_3)_2\}_3$ from $GeCl_4 + 3Li\{N(SiMe_3)_2\}$ [curiously $SnCl_4 + 3Li(amide) \rightarrow SnCl_2(amide)_2$]; (c) the demonstration of a new route to the persistent $\dot{\mathrm{Ge}}\{\mathrm{N(SiMe_3)_2}\}_3$ (the $\mathrm{Pb^{IV}}$ bromotrisamide yielded lead as the only identified product on photolysis, and the $\mathrm{Sn^{IV}}$ analogue was insufficiently soluble), (d) the $\mathrm{Pb^{IV}}$ compound is the first amide of $\mathrm{Pb^{IV}}$ so far reported which is other than of type $\mathrm{PbR_3(NR'R'')}$,[12] and (e) *X*-ray data on $\mathrm{SnBr\{N(SiMe_3)_2\}_3}$ show this to be a discrete monomer in the crystal: Sn–Br 2·52, Sn–N 2·08, and N–Si 1·77 Å, ∠BrSnN 102, ∠NSnN 116, and ∠NSiN 120·2°.[13]

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