Subvalent Group 4B Metal Alkyls and Amides. Part 5.[1] The Synthesis and Physical Properties of Thermally Stable Amides of Germanium(II), Tin(II), and Lead(II) †

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A series of subvalent Group 4B metal amides of general formula $M(NR^1R^2)_2$ [(*i*) $R^1 = SiMe_3$, $R^2 = Bu^t$; M = Ge, Sn, or Pb; (*ii*) $R^1 = R^2 = SiMe_3$; M = Ge, Sn, or Pb; and (*iii*) $R^1 = R^2 = GeMe_3$, $SiEt_3$, or $GePh_3$; M = Ge or Sn] has been prepared from the appropriate lithium amide and metal(II) halide. Under ambient conditions, the amides are pale yellow to red, thermochromic, diamagnetic, low-melting solids or liquids, and are soluble in hydrocarbons (C_6H_6 or C_6H_{12}) in which they are diamagnetic monomers. The lower homologues give parent molecular ions as the highest *m/e* species. Infrared spectra show a band at 380—430 cm^{-1} [$\nu_{asym}(MN_2)$], and ^1H or ^{13}C n.m.r. spectra are consistent with the bent-singlet formulation. In the visible region the compounds exhibit a band (364—495 nm) of moderate intensity (ε = 600—2 050 dm^3 mol^{-1} cm^{-1} in n-C_6H_{14}) indicative of an allowed electronic transition. Photolysis of each diamide in n-hexane in the cavity of an e.s.r. spectrometer affords (*a*) the persistent ($t_{\frac{1}{2}}$ 5 min—3 months at 25° C) metal-centred radical $\dot{M}(NR^1R^2)_3$ [(*i*) $R^1 = SiMe_3$, $R^2 = Bu^t$, M = Ge or Sn; (*ii*) $R^1 = R^2 = SiMe_3$ or $GeMe_3$, M = Ge or Sn; or (*iii*) $R^1 = R^2 = GeEt_3$, M = Sn], (*b*) a lead mirror (for the lead amides), or (*c*) no sign of reaction (for the more bulky diamides). E.s.r. parameters have been derived from the isotropic spectra.

IN a preliminary publication we described the synthesis and some chemical properties of the first Group 4 metal(II) amides $M(NR^1R^2)_2$ ($R^1 = R^2 = SiMe_3$; $R^1 = SiMe_3$, $R^2 = Bu^t$; M = Ge, Sn, or Pb);[2] $Sn[N(SiMe_3)_2]_2$ was found to be a monomer by cryoscopy in benzene or cyclohexane and a parent monomeric molecular ion was the highest peak in the mass spectrum. Almost simultaneously the same compound was reported by Schaeffer and Zuckerman[3] who described it as a dimer by osmometry and mass spectrometry. We now provide details of the earlier[2] work and describe its extension to a wider range of amide ligands $[NR^1R^2]^-$ ($R^1 = R^2 = SiEt_3$, $GeMe_3$, $GeEt_3$, or $GePh_3$; M = Ge or Sn) (see also ref. 4); in addition, we have examined the photochemistry of the metal(II) amides, following previously described experiments[1] on $M[NBu^t(SiMe_3)]_2$ and $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, or Pb), which for Me = Ge or Sn yielded the corresponding persistent metal(III) amide or for M = Pb gave a lead mirror.

Our interest in subvalent Group 4 metal bis(trimethylsilyl)amides derives mainly from work with the isoelectronic bis(trimethylsilyl)methyl derivatives[1,5-8] and

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† No reprints available.

[1] Part 4, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Dalton*, 1976, 2369.

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

[3] C. D. Schaeffer and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1974, **96**, 7160.

[4] M. F. Lappert and P. P. Power, *Adv. Chem. Ser.*, 1976, **157**, 70.

[5] D. H. Harris, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J.C.S. Dalton*, 1976, 945.

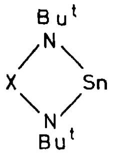
[6] Part 1, P. J. Davidson, D. H. Harris, and M. F. Lappert. *J.C.S. Dalton*, 1976, 2268.

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

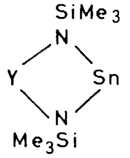
[8] Part 3, J. D. Cotton, P. J. Davidson, J. D. Donaldson, M. F, Lappert, and J. Silver, *J.C.S. Dalton*, 1976, 2286.

on earlier studies on many amides, including $\mathrm{SnMe_3(NMe_2)}$.[9] However, the use of the bulky bis(trimethylsilyl)amido-ligand $[\mathrm{N(SiMe_3)_2}]^-$ is widespread.[10] It was pioneered by Bürger and Wannagat,[11] and was given added impetus especially with regard to the rare three-co-ordinate transition-metal or lanthanoid complexes by the studies of Bradley and Hursthouse. The following advantages derive from the choice of this ligand: (*a*) the parent amine, hexamethyldisilazane, $\mathrm{NH(SiMe_3)_2}$, is readily available and easily converted into its *N*-lithio-derivative; (*b*) its size often stabilises complexes in which the metal has a low co-ordination number; (*c*) the absence of β-hydrogen and the presence of β-silicon makes metal-amide decomposition by a β-elimination path energetically unfavourable; and (*d*) the numerous methyl groups make for good hydrocarbon solubility. Hydrocarbon-soluble subvalent metal bis(trimethylsilyl)-amides are convenient potential precursors for other subvalent metal complexes; the most striking example to date relates to the only published synthesis of $\mathrm{Ge[CH(SiMe_3)_2]_2}$, from $\mathrm{Ge[N(SiMe_3)_2]_2}$–$\mathrm{Li[CH(SiMe_3)_2]}$.[6] The purpose of preparing bis(silyl)amidometal analogues was in part to explore the scope of ' fine-tuning ' of steric effects in this already bulky ligand skeleton, as in $[\mathrm{N(SiEt_3)_2}]^-$ and $[\mathrm{N(GeR^3{}_3)_2}]^-$ ($\mathrm{R^3}$ = Me, Et, or Ph).

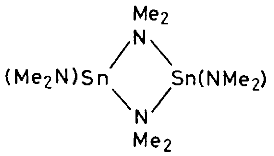
Some related cyclic tin(II) amides, (1a),[12] (1b),[13] and (2),[3] have recently been obtained from the appropriate *NN'*-dilithioamine and tin(II) chloride. The red liquid compound (1a) is monomeric in benzene.[12] On the other hand, the less bulky tin bis(dimethylamide) was dimeric in solution and reasonably formulated as having the bridged structure (3).[14] However, the bulky ligand $[\mathrm{N(SiMe_3)_2}]^-$ has so far only been authenticated as a bridging moiety in three cases, $[\{\mathrm{Li[N(SiMe_3)_2]}\}_3]$ (4),[15] $[\{\mathrm{Cu[N(SiMe_3)_2]}\}_4]$ (5),[16] and $[\mathrm{Al_2Me_5\{N(SiMe_3)_2\}}]$ (6),[17] in each of which a single amide ligand bridges two metal centres, which is to be contrasted with (3) in which two ligands bridge two metal atoms. The latter arrangement is in principle probably unlikely for the bulky $[\mathrm{N(SiMe_3)_2}]^-$ ligand. By analogy with the crystal structure of $[\{\mathrm{Sn[CH(SiMe_3)_2]_2}\}_2]$,[6] we expect the molecular structure of the isoelectronic amide to be as shown in (7), and consider the proposals that two tin atoms are bridged by two to four bis(trimethylsilyl)-amido-ligands, with or without tin–tin bonding,[3] as inherently implausible; all the more so, as the proposals were made[3] for structures in solution where we will show that $\mathrm{Sn[N(SiMe_3)_2]_2}$ is monomeric.



(1a) X = $\mathrm{SiMe_2}$
(1b) X = $\mathrm{SnBu^t{}_2}$



(2a) Y = $(\mathrm{CH_2})_n$ (n = 2–4)
(2b) Y = o-$\mathrm{C_6H_4}$
(2c) Y = 1,8-$\mathrm{C_{10}H_6}$



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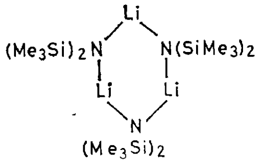

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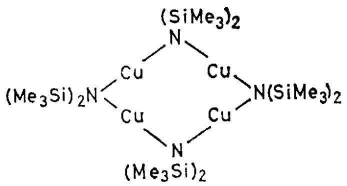

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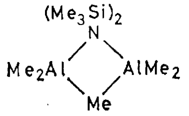
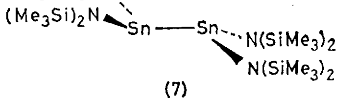


(6)



(7)

RESULTS AND DISCUSSION

The reaction of a metal(II) halide ($\mathrm{GeCl_2 \cdot dioxan}$, $\mathrm{SnCl_2}$, or $\mathrm{PbCl_2}$) with the appropriate lithium amide $\mathrm{Li(NR^1R^2)}$ in diethyl ether afforded the metal(II) amide [equation (1)]. The compounds (8)—(21) (Table 1) are

$$\mathrm{MCl_2} + 2\mathrm{Li(NR^1R^2)} \xrightarrow{\mathrm{OEt_2}} \mathrm{M(NR^1R^2)_2} + 2\mathrm{LiCl} \qquad (1)$$

volatile (except for $\mathrm{R^1 = R^2 = GePh_3}$), yellow or orange, low-melting crystals or oils, and monomeric both in solution (cryoscopy) and the vapour phase (mass spectrometry) (Table 2). They are soluble in hydrocarbons, but the bis[bis(triphenylgermyl)amides] are soluble only in aromatic solvents. The bis[bis(trimethylsilyl)-amides] are much more soluble than corresponding[6] isoelectronic $\mathrm{M[CH(SiMe_3)_2]_2}$. The aliphatic metal(II) amides are monomeric in cyclohexane solution (see also ref. 4), and the lower homologues give the parent molecular ion as the highest peak in the mass spectrum (when trace amounts of adventitious moisture were present, peaks at higher *m*/*e* values were observed) (Table 2).

Table 3 provides a comparison of the numerical data for $\mathrm{Sn[N(SiMe_3)_2]_2}$ as obtained in this work[2] and by

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[9] *Cf.*, K. Jones and M. F. Lappert, in ' Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1971, vol. 2, ch. 7.

[10] *Cf.*, D. H. Harris and M. F. Lappert, *J. Organometallic Chem., Library*, 1976, **2**, 13.

[11] *Cf.*, U. Wannagat, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 225; D. C. Bradley, *Chem. in Britain*, 1975, **11**, 393; D. C. Bradley and M. H. Chisholm, *Accounts Chem. Res.*, 1976, **9**, 273.

[12] M. Veith, *Angew. Chem. Internat. Edn.*, 1975, **14**, 263.

[13] D. Hänssgen, J. Kuna, and B. Ross, *Chem. Ber.*, 1976, **109**, 1797.

[14] P. Foley and M. Zeldin, *Inorg. Chem.*, 1975, **14**, 2264.

[15] D. Mootz, A. Zinnius, and B. Böttcher, *Angew. Chem. Internat. Edn.*, 1969, **8**, 378.

[16] M. B. Hursthouse, personal communication.

[17] N. Wiberg and W. Baumeister, *J. Organometallic Chem.*, 1972, **36**, 277.

TABLE 1

Physical properties, analytical data, and yields for the metal(II) amides

Compound	Yield (%)	M.p. (θ_c/°C)	B.p. (θ_c/°C) [a]	Colour	Analysis (%) [b] C	H	N
$Ge[N(SiMe_3)_2]_2$ (8)	67	32—33	60	Pale yellow	36.6 (36.4)	9.2 (9.1)	7.0 (7.1)
$Sn[N(SiMe_3)_2]_2$ (9)	79	37—38	84	Orange	32.6 (32.8)	8.1 (8.3)	6.2 (6.4)
$Pb[N(SiMe_3)_2]_2$ (10)	69	37—38	60	Deep yellow	27.3 (27.3)	6.7 (6.9)	5.3 (5.3)
$Ge[NBu^t(SiMe_3)]_2$ (11)	76	21—22	50	Orange-yellow	46.5 (46.5)	9.9 (10.0)	7.8 (7.8)
$Sn[NBu^t(SiMe_3)]_2$ (12)	80	18—19	50	Red	41.1 (41.3)	8.9 (8.9)	7.1 (6.9)
$Pb[NBu^t(SiMe_3)]_2$ (13)	70	21—22	50	Red	34.1 (33.9)	7.2 (7.3)	5.6 (5.6)
$Ge[N(GeMe_3)_2]_2$ (14)	71	28—29	70	Pale yellow	25.0 (25.2)	6.1 (6.3)	4.9 (4.9)
$Sn[N(GeMe_3)_2]_2$ (15)	82	35—37	70	Orange	23.3 (23.3)	5.75 (5.9)	4.6 (4.5)
$Ge[N(SiEt_3)_2]_2$ (16)	55		150	Yellow	52.8 (52.4)	11.4 (11.2)	4.6 (4.9)
$Sn[N(SiEt_3)_2]_2$ (17)	63		150	Orange	47.5 (47.4)	10.1 (10.0)	4.8 (4.9)
$Ge[N(GeEt_3)_2]_2$ (18)	58		150	Yellow	38.7 (38.9)	8.4 (8.2)	3.9 (3.8)
$Sn[N(GeEt_3)_2]_2$ (19)	69		150	Orange	37.1 (36.7)	7.8 (7.7)	3.6 (3.55)
$Ge[N(GePh_3)_2]_2$ (20)	70			Yellow	65.6 (65.7)	4.7 (4.6)	2.0 (2.1)
$Sn[N(GePh_3)_2]_2$ (21)	73			Orange	63.3 (63.5)	4.6 (4.4)	1.95 (2.05)

[a] At 0.04 mmHg. [b] Calculated values are given in parentheses.

Schaeffer and Zuckerman.[3] There can be little doubt that the two compounds are identical. The discrepancy between the two sets of data relates to the molecular weight in solution and in the vapour. We prefer the assignment of a monomer for the following reasons: (*a*) the boiling point is similar to tin compounds of molecular weight *ca.* 450, *e.g.* whereas $Sn[N(SiMe_3)_2]_2$ monomer has M 440, $Sn(NEt_2)_4$ has b.p. 90 °C (0.05 mmHg) [*] and M 406; (*b*) cryoscopic molecular weights are now available for a range of related compounds, all of which appear to be monomeric [see Table 2 and (1)]; (*c*) the cryoscopic constant for cyclohexane is very high, so that the freezing-point depressions relating to Table 2 are between 0.5 and 1.0 °C and consequently there is a small possibility of significant error; and (*d*) the cryoscopic determinations have been carried out independently by a number of us, and on various samples some of which had been stored in the dark for several weeks at 20 °C. We conclude that the compounds are thermally stable and show no observed tendency to polymerise (see also the electron-diffraction data below); this stability is attributed to kinetic effects.

TABLE 2

Molecular weights of some metal(II) amides

Compound	Calculated	Found [a]	m/e [b]
(8)	393.4	*ca.* 430 (A, B)	394
(9)	439.5	*ca.* 440 (A, B)	440
(10)	528	*ca.* 500 (A)	528
(11)	361.2		362
(12)	407.3		408
(13)	495.9		496
(14)	561.3	*ca.* 590 (A)	
(15)	617.4	*ca.* 630 (A)	
(16)	561.5	*ca.* 530 (A)	
(17)	607.6	*ca.* 650 (A)	
(18)	739.7	*ca.* 780 (A)	
(19)	785.8	*ca.* 750 (A)	

[a] Cryoscopy in cyclohexane (A) or benzene (B). [b] For parent ions.

TABLE 3

Comparison of data for $Sn[N(SiMe_3)_2]_2$ obtained in this work and in ref. 3

Property	This work	Data from ref. 3
$\lambda_{max.}$/nm	389 (ε 3 100 dm^3 mol^{-1} cm^{-1}) [a]	387
B.p. (θ_c/°C, P/mmHg)	84, 0.04	109—110, 0.75
^{1}H n.m.r. (δ)	0.40 [b]	0.23 [b]
$^2J(^{29}Si-C-^1H)$/Hz	6.5 [c]	6.5 [d]
$^1J(^{13}C-^1H)$/Hz	117.6 [c]	116.0 [d]
$^1J(^{29}Si-^{13}C)$/Hz	54.9 [c]	55.3 [d]
$^3J(^{119}Sn-N-Si-^{13}C)$/Hz	23.2 [c]	24.9 [d]
M (solution)	*ca.* 440 [e]	*ca.* 880 [f]
Highest m/e	P^+ (440)	2 P^+ (880)
Mössbauer isomer shift/mm s^{-1}	2.78	2.88
Mössbauer quadrupole splitting/mm s^{-1}	3.11	3.52

[a] In C_6H_{14}. [b] In C_6H_6. [c] In C_6D_6. [d] Neat liquid. [e] Cryoscopy in C_6H_{12} or C_6H_6. [f] Osmometry in C_6H_6.

TABLE 4

Spectroscopic data for the metal(II) amides

Compound	^{1}H n.m.r. [a] τ(Me)	τ(Et)	τ(Ph)	I.r. (cm^{-1}) [b] $\nu_{asym}(MN_2)$	1st i.p. [c]/eV
(8)	9.56			428	8.68
(9)	9.60			400	8.38
(10)	9.65			395	8.16
(11)	9.51 : 8.41 [d]			422	8.27
(12)	9.55 : 8.45 [d]			405	7.90
(13)	9.60 : 8.46 [d]			386	7.69
(14)	9.59			418	
(15)	9.61			408	
(16)		8.86 [e]		422	
(17)		8.84 [e]		411	
(18)		8.74 [e]		410	
(19)		8 70 [e]		412	
(20)			2.85 [f] 2.69 [g]	388	
(21)			2.69 [g]	380	

[a] All the spectra were recorded in benzene solution, except those for (20) and (21) (CH_2Cl_2 solvent). The signals are singlets unless otherwise stated. [b] All except compounds (20) and (21) (Nujol mulls) were recorded as neat liquids. [c] See ref. 5, vertical i.p. of metal lone-pair orbital. The vapour-phase p.e. spectrum for $Sn[N(SiMe_3)_2]_2$ gave the following observed binding energies (eV): Sn ($3d_{5/2}$), 491.93 ± 0.05; N (1*s*), 402.01 ± 0.07; Si ($2p_{3/2}$), 105.97 ± 0.07; and Cl (1*s*), 289.36 ± 0.07.[18] [d] In 1 : 1 ratio $SiMe_3 : Bu^t$. [e] Complex multiplet. [f] *meta*. [g] *ortho, para*.

Table 4 contains i.r. and ^{1}H n.m.r. data with assignments for the various metal(II) amides. Attempts to study the Raman spectra of certain of these compounds were thwarted owing to their high background fluorescence. Although i.r. assignments have been made for

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[*] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

$\nu_{asym}(MN_2)$, these are not necessarily pure normal modes, especially for derivatives of the more bulky ligands, *e.g.* $[N(GePh_3)_2]^-$, where vibrational coupling is likely between the $\nu(M^{IV}N)$ and $\nu(M^{II}N_2)$ modes. Nevertheless, the bands are diagnostically useful.

The ^1H n.m.r. spectra of compounds (8)—(10), (14), and (15) are extremely simple, with only a sharp singlet for the methyl protons. The spectra of compounds (11)—(13) each show two singlets of equal intensity ($Bu^t : SiMe_3$). Cooling a sample of $Sn[N(SiMe_3)_2]_2$ in dimethyl ether to −110 °C caused no broadening of the methyl resonance, indicating that {assuming an angular [Figure 1(*a*)] rather than a linear [Figure 1(*b*)] structure} there is free rotation about the metal–nitrogen bond on the n.m.r. time scale. The ^{13}C n.m.r. spectra of $Sn[N(SiMe_3)_2]_2$ and $Sn[NBu^t(SiMe_3)]_2$ are consistent with free rotation. Both ^1H decoupled and undecoupled spectra were examined (Figure 2). The decoupled spectrum of $Sn[N(SiMe_3)_2]_2$ shows a sharp singlet, while that for $Sn[NBu^t(SiMe_3)]_2$ has three singlets. Various ^{13}C couplings for the former compound are listed in Table 3. The undecoupled spectra appear as central quartets due to coupling of ^{13}C with the three methyl protons, and appropriate ^{29}Si, ^{117}Sn, and ^{119}Sn satellites.

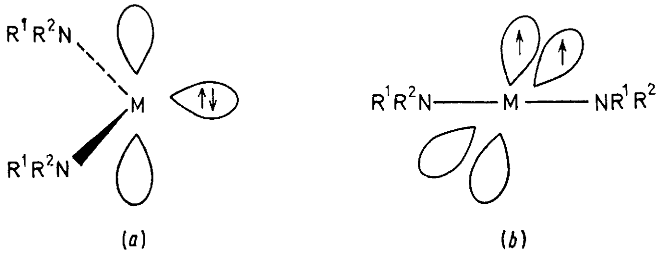

FIGURE 1 Expected structures for monomeric $M(NR^1R^2)_2$: (*a*) singlet and (*b*) triplet ground state

For completeness, included in Table 4 are some He(I) [5] and *X*-ray [18] vapour-phase photoelectron (p.e.) spectroscopic data. Interpretations were based on a structure similar to that of Figure 1(*a*).

The metal(II) amides (8)—(21) are heavy-metal analogues of carbenes. Hence, in principle, bent singlet [Figure 1(*a*)] or linear triplet [Figure 1(*b*)] structures should be considered. We prefer the former for the following reasons: (*a*) the sharp ^1H and ^{13}C spectra; (*b*) the diamagnetism observed for $Sn[N(SiMe_3)_2]_2$ (8) at ambient temperature; (*c*) the absence of an e.s.r. signal under anaerobic and dark conditions; (*d*) the satisfactory interpretation of He(I) [5] or *X*-ray [18] p.e. data; and (*e*) preliminary electron-diffraction results [19] for (8), which show that at *ca.* 120 °C (10 mmHg) the vapour is entirely that of the monomer, with angle NSnN *ca.* 96°.

TABLE 5

U.v.–visible spectroscopic data ($\lambda_{max.}$/nm and ε/dm^3 mol^{-1} cm^{-1} in parentheses) for the metal(II) amides in n-hexane

$Ge[N(SiMe_3)_2]_2$	$Ge[NBu^t(SiMe_3)]_2$	$Ge[CH(SiMe_3)_2]_2$	$Sn[N(SiMe_3)_2]_2$	$Sn[NBu^t(SiMe_3)]_2$	$Sn[CH(SiMe_3)_2]_2$
364 (2 050)	392 (1 300)	414 (970)	389 (3 100)	433 (1 200)	495 (610)
ca. 300 (sh)	325 (620)	302 (1 450)	287 (4 600)	*ca.* 330 (sh)	332 (910)
228 (6 300)	230 (60 900)	227 (19 600)	230 (23 000)	305 (2 800)	239 (32 750)
				236 (15 000)	

One of the most striking features associated with the Group 4B metal(II) amides is their colour. They are thermochromic, becoming reversibly redder on heating and very pale yellow at −196 °C. Compared with the alkyls $M[CH(SiMe_3)_2]_2$,[6] they are less red, but similar in their thermochromism. Hence the u.v.–visible spectra of several of the compounds were recorded and are available (Table 5) for comparison with that of $M[CH(SiMe_3)_2]_2$ (M = Ge or Sn). The moderate absorption coefficients (600—3 000 dm^3 mol^{-1} cm^{-1}) found for the visible absorption bands do not suggest a forbidden electronic transition or a charge-transfer mechanism

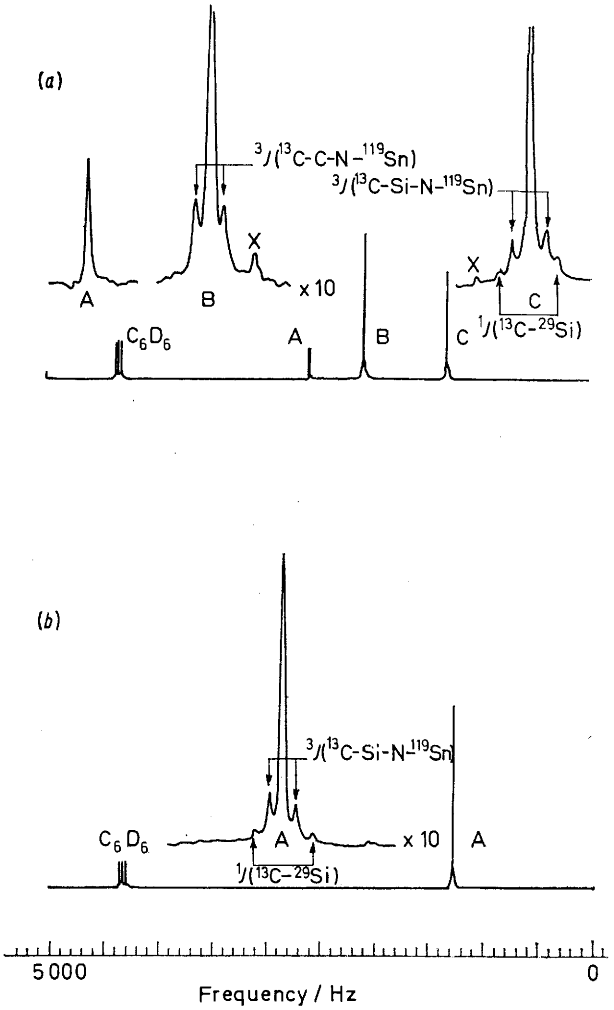

FIGURE 2 Carbon-13 ^1H-decoupled n.m.r. spectra of (*a*) $Sn[NBu^t(SiMe_3)]_2$ and (*b*) $Sn[N(SiMe_3)_2]_2$ in C_6D_6 at 30 °C

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[18] W. L. Jolly and S. Avanzine, personal communication.

[19] K. Hedberg and L. Hedberg, personal communication, 1977.

(*e.g.* metal lone pair ⟶ Si 3*d* orbital). Nevertheless, such a transition, as far as energy is concerned, is compatible with the observed[5] metal lone-pair orbital energy. To account also for thermochromism, a transition involving a thermally accessible singlet state is possible.

We had earlier shown[1] that irradiation of $\mathrm{M[N(SiMe_3)_2]_2}$ or $\mathrm{M[NBu^t(SiMe_3)]_2}$ (M = Ge, Sn, or Pb), (8)—(13), in the cavity of an e.s.r. spectrometer resulted for the germanium or tin compounds in the generation of a persistent signal attributable to the corresponding metal(III) amide.[1] We have now extended the experiment to the other amides of $\mathrm{Ge^{II}}$ and $\mathrm{Sn^{II}}$, (14)—(21). In this way three new metal-centred radicals, from $\mathrm{Ge[N(GeMe_3)_2]_2}$ and $\mathrm{Sn[N(GeR_3)_2]_2}$ (R = Me or Et), have been generated, and e.s.r. data for these are shown in Table 6 for comparison with those of the four known[1] radicals. As before,[1] we assume that these reactions are photochemical disproportionations (Scheme), with a diamagnetic oligomer of a metal(I) amide as co-product. We take this view because, unlike the case of the lead(II) amides, irradiation of a hydrocarbon solution of the germanium(II) or tin(II) amide does not produce a metal mirror and the solution remains homogeneous.

TABLE 6

Isotropic e.s.r. parameters for the metal(III) amides[a]

Radical	g	a(N)[b]	a(M)[b,c]	Stability ($t_{\frac{1}{2}}$)
$\mathrm{\dot{S}n[N(SiMe_3)_2]_3}$	1.991 2	1.09	313.95 (^{119}Sn) 331.75 (^{117}Sn)	*ca.* 3 months
$\mathrm{\dot{G}e[N(SiMe_3)_2]_3}$	1.999 1	1.06	17.1	>5 months
$\mathrm{\dot{S}n[NBu^t(SiMe_3)]_3}$	1.992 8	1.27		5 min
$\mathrm{\dot{G}e[NBu^t(SiMe_3)]_3}$	1.999 8	1.29	17.3	*ca.* 5 min
$\mathrm{\dot{S}n[N(GeMe_3)_2]_3}$	1.992 4	1.07		*ca.* 10 h
$\mathrm{\dot{G}e[N(GeMe_3)_2]_3}$	1.999 4	1.10	14.5	*ca.* 22 h
$\mathrm{\dot{S}n[N(GeEt_3)_2]_3}$	1.993 9	1.19		*ca.* 20 h

[a] Solutions in n-hexane at room temperature. [b] In mT. [c] The naturally abundant (percentage in parentheses) spin-active nuclei are: ^{73}Ge (7.8%), $I = \frac{9}{2}$; ^{117}Sn (7.9%), $I = \frac{1}{2}$; and ^{119}Sn (8.6%), $I = \frac{1}{2}$.

$$\mathrm{2M[N(M'R_3)_2]_2} \xrightarrow[\text{n-hexane, 20 °C}]{h\nu} \mathrm{\dot{M}[N(M'R_3)_2]_3} + \frac{1}{n}\,[\{\mathrm{M[N(M'R_3)_2]}\}_n]$$

Those which disproportionate on photolysis are (8), (9), (11), (12), (14), (15), and (19). Those which do not disproportionate on photolysis are (16)—(18), (20), and (21). Compounds (10) and (13) decompose to give a lead mirror when irradiated

SCHEME Photochemical behaviour of the metal(II) amides

It is interesting that the exceptionally bulky metal(II) amides $\mathrm{M[N(SiEt_3)_2]_2}$ (M = Ge or Sn), $\mathrm{Ge[N(GeEt_3)_2]_2}$, or $\mathrm{M[N(GePh_3)_2]_2}$ (M = Ge or Sn) failed to disproportionate in a similar fashion. Clearly, therefore, steric effects are sensitive both to the nature of the central metal (Ge > Sn) and the ligands at nitrogen (*e.g.* $\mathrm{SiEt_3 > GeEt_3}$). It is noteworthy, however, that in these cases the photolysis does generate an aminyl radical $\mathrm{\dot{N}(MEt_3)_2}$ (M = Si or Ge), the e.s.r. spectra of which are poorly resolved, but gives clear 1 : 1 : 1 triplets with $g = 2.004$ and $a(\mathrm{N}) = 1.44$ mT. Previously,[1] two alternative mechanisms for photochemical generation of a Group 4 metal-centred radical from a metal(II) precursor were proposed: either initial $\mathrm{M{-}N{<}}$ homolysis and subsequent capture of the aminyl radical by the metal(II) species, or a bimolecular disproportionation. The former mechanism receives some support from these data using particularly-hindered metal(II) amides.

The main feature of the e.s.r. spectra of the $\mathrm{\dot{M}(NR^1R^2)_3}$ species (*cf.* ref. 1) is a septet arising from three equivalent ^{14}N nuclei ($I = 1$), while under increased gain satellite spectra are observed (Table 6). Although the nitrogen hyperfine coupling, a(N), was measured directly, the large central-atom hyperfine coupling, a(M), had to be calculated (using the Breit–Rabi equation) because the satellite signals were displaced downfield due to second-order effects (see Figure 3). The size of the central-metal interactions indicate quite clearly the non-planarity of these tris(amide) metal-centred radicals which is rather surprising from steric considerations, since a planar structure would be less congested. Previously we reported[1] that only the low-field satellite of ^{117}Sn was observed for $\mathrm{\dot{S}n[N(SiMe_3)_2]_3}$. Now using a more sensitive instrument, the Varian 104A, we find both the ^{119}Sn and ^{117}Sn low-field satellites as well as the overlapping high-field satellites [a ten-line pattern with approximately constant splitting, the relative intensities being consistent with the overlapping of the fourth line of one septet with the first line of the other (Figure 3)]; this allowed us to determine more accurate values for the tin-satellite coupling constants shown in Table 6 than those previously noted.[1]

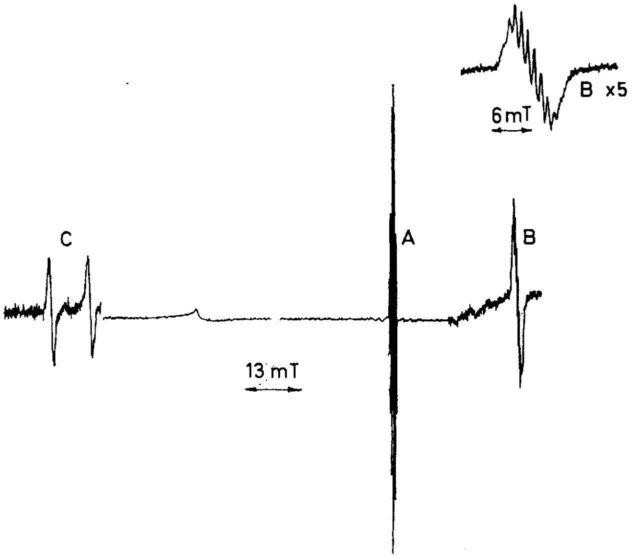

FIGURE 3 E.s.r. spectrum of $\mathrm{\dot{S}n[N(SiMe_3)_2]_3}$ in $\mathrm{C_6H_6}$ at 20 °C [showing central resonance A (septet) and the upper (B) and lower (C) ^{117}Sn and ^{119}Sn satellite lines]

For the tin(III) amides $\mathrm{\dot{S}n(NR^1R^2)_3}$ there is a progressive decrease in g values in the sequence $\mathrm{R^1 = R^2 = GeEt_3 > GeMe_3 > SiMe_3}$, which also reflects the inverse order of steric crowding at tin. Shifts in g values within a related series (*i.e.* having comparable ligand electronegativities) of Group 4 metal-centred radicals have been correlated with their geometry, which in extreme situations are planar or pyramidal, and the lower the *g* value the more pyramidal is the radical.[1] Accordingly, the above sequence shows that a distinct steric effect is being observed.

EXPERIMENTAL

All the compounds are exceedingly air- and moisture-sensitive; Schlenk-tube and vacuum-line manipulative techniques were used. Compounds were thus handled *in vacuo* or under dry and anaerobic conditions at ambient pressures of nitrogen or argon. Hydrogen-1 n.m.r. spectra were recorded on Varian T60, Varian A60, and Perkin-Elmer HA100 spectrometers, ^{13}C n.m.r. spectra on a Jeol PFT spectrometer. Ultraviolet spectra were obtained on a Unicam SP 800 spectrophotometer, using vacuum-line techniques for introducing the sample into the cell, and i.r. spectra (250—4 000 cm^{-1}) as Nujol mulls on a Perkin-Elmer 457 spectrometer. Mass spectra were measured on an A.E.I. MS9 spectrometer. Cryoscopic molecular weights were determined in a closed system by the Beckmann procedure. The compounds $NH(GeR_3)_2$ (R = Me, Et, or Ph) and $NH(SiEt_3)_2$ were prepared as in ref. 20, and $NH(SiMe_3)_2$ was obtained from Dow Corning Ltd.; $NH(SiEt_3)_2$ (ref. 21) was prepared from $SiEt_3Cl$ and sodium in liquid ammonia which yields (59%) $SiEt_3(NH_2)$,[21] and the latter with successively $LiBu^n$ in OEt_2 at 0 °C and $SiEt_3Cl$ gave $NH(SiEt_3)_2$ (84%).

Preparation of Metal(II) *Amides*.—A representative example of the preparative technique is given below; further details are in Tables 1—5.

Lithium bis(trimethylsilyl)amide–diethyl ether (prepared by the reaction of the parent amine and n-butyl-lithium in diethyl ether) was added slowly to a stirred suspension of tin(II) chloride in the same solvent in a 2 : 1 molar ratio. An immediate reaction was observed with precipitation of lithium chloride and the formation of an orange-yellow solution. After stirring at room temperature for *ca.* 2 h the solvent was removed *in vacuo*. The metal amide was extracted with n-hexane or benzene and filtered to give an orange solution. Removal of volatiles *in vacuo* gave the *metal*(II) *amide* (Table 1) which was purified by distillation or [for $N(GePh_3)_2$ derivatives] by recrystallisation.

Photolysis Experiments.—A solution of the metal(II) amide in n-hexane (or benzene) (*ca.* 1 mol dm^{-3}) was irradiated at 25 °C in a quartz e.s.r. tube in the cavity of a Varian E3 (or later 104A) e.s.r. spectrometer, using an Osram ME/D 250-W high-pressure mercury lamp. The u.v. light was focused on to the cavity by a quartz-lens system; *g* values were measured relative to polycrystalline diphenylpicrylhydrazyl(dpph) in conjunction with a frequency meter.

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[20] *Cf.*, M. Lesbre, P. Mazerolles, and J. Satgé, 'The Organic Compounds of Germanium,' Wiley–Interscience, New York, 1971; M. Rivière-Baudet, Thèse, Toulouse University, 1972.

[21] *Cf.*, V. Bažant, V. Chvalovský, and J. Rathouský, 'Organosilicon Compounds,' Academic Press, New York, 1965.