Monomeric, Volatile Bivalent Amides of Group IVB Elements, $M(NR^1{}_2)_2$ and $M(NR^1R^2)_2$ ($M{=}Ge$, Sn, or Pb; $R^1{=}Me_3Si$, $R^2{=}Me_3C$)

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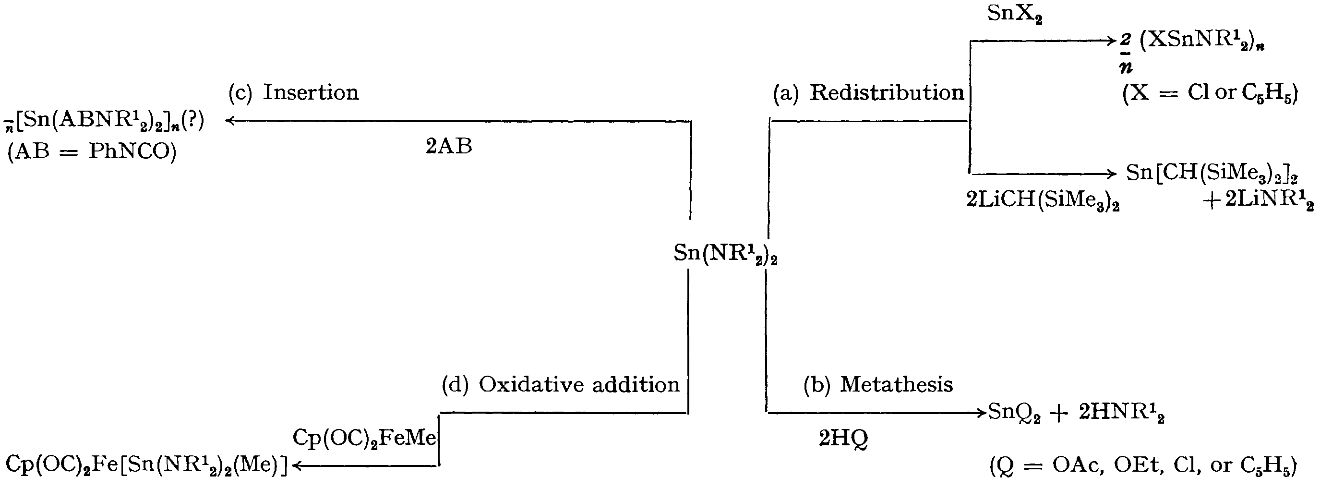
Summary The reactions of $SnCl_2$, $PbCl_2$, or $GeCl_2$,dioxan with $LiNR^1{}_2,OEt_2$ or $LiNR^1R^2,OEt_2$ in Et_2O at 0° yield the stable, monomeric, diamagnetic, coloured, volatile, hydrocarbon-soluble title compounds which are highly reactive.

We report the preparation and characterisation of unusual stable, monomeric, diamagnetic, coloured, volatile, hydrocarbon-soluble, dialkylamides (I) and (II) (M = Ge, Sn, or Pb) of the Group IVB elements (see Table).

$M[N(SiMe_3)_2]_2$ (I) $M[N(SiMe_3)(CMe_3)]_2$ (II)

These compounds represent rare examples of bivalent two-co-ordinate Group IVB complexes MX_2 which are monomeric and long-lived under ambient conditions. For germanium, the only other case is that of the cyclopentadienide ($X = C_5H_5$) which, however, readily (hours) polymerises.[1] The corresponding polymerisable Sn and Pb species $M'(C_5H_5)_2$ are known as well as the dialkyls[2] $M'[CH(SiMe_3)_2]_2$ isoelectronic with the Sn and Pb amides (I). More complicated examples refer to a (presumed monomeric) tin(II) carbamate[3] and a tin(II) 1,2-diazole derivative which readily (hours) polymerises.[4] The use of $Me_3Si(Me_3C)N^-$ as a ligand has not hitherto been described but $(Me_3Si)_2N^-$ has been employed, especially in transition-metal chemistry.[5]

The reaction of MCl_2 (M = Sn or Pb) or $GeCl_2$,dioxan with $LiN(SiMe_3)_2,OEt_2$ or $LiN(SiMe_3)(CMe_3),OEt_2$ in Et_2O at 0° gives yellow crystalline $M(NR^1{}_2)_2$ (M = Ge, Sn, or Pb; R^1 = Me_3Si) or orange to red liquids $M(NR^1R^2)_2$ (R^2 = Me_3C) in high yield (Table). All complexes are analytically pure, show monomeric molecular ions in the mass spectra (20 and 70 eV), sharp singlets (Me_3C or Me_3Si) in the ^1H n.m.r. spectrum (C_6H_6), and no e.s.r. signal in hexane, consistent with a singlet metal(II) formulation.



Scheme. Cp = cyclopentadienyl.

A probable intermediate in the synthesis of these amides is $[ClMNR^1{}_2]_n$ or $[ClM(NR^1R^2)]_m$; white crystalline $[ClSnN(SiMe_3)_2]_n$ was obtained from an equimolar reaction between (i) $SnCl_2$ and $LiNR^1{}_2,OEt_2$ or (ii) $SnCl_2$ and $Sn(NR^1{}_2)_2$. Another redistribution reaction of type (ii) yielded (C_5H_5)-

$SnNR^1_2$, from $Sn(NR^1_2)_2$ and $(C_5H_5)_2Sn$, still containing a delocalised cyclopentadienyl $[^2J(^{119}Sn–^1H) = 12{\cdot}0$ Hz]. The metal(II) diamides are highly reactive. We currently recognise the four classes of reactions illustrated as (a)—(d) in the Scheme for $Sn(NR^1_2)_2$, as well as (e) photochemical disproportionation $[\xrightarrow{h\nu} {\cdot}Sn(NR^1_2)_3]$.[6] To date we have not succeeded in showing that the amides (I) possess Lewis base properties (associated with the metal);[7] for example, whereas $Sn[CH(SiMe_3)_2]_2$ with $Mo(CO)_6$ yields $[(Me_3Si)_2CH]_2SnMo(CO)_5$,[2] $Sn(NR^1_2)_2$ does not react with (norbornadiene)$Mo(CO)_4$. Consistent with this, He^I photoelectron (PE) data (see Table) show that the metal s^2 lone pair of electrons is more tightly bound in (I) than in (II), or in the Sn or Pb alkyls isoelectronic with (I).[2]

TABLE

Compound	Colour	M.p.[d] °C	Yield (%)	He^I PE [First I.P. (eV)]
$Ge[N(SiMe_3)_2]_2$[a] ..	Yellow[e]	32—33	67	7·72
$Sn[N(SiMe_3)_2]_2$[b,c] ..	Yellow[e]	37—38	79	7·75
$Pb[N(SiMe_3)_2]_2$ ..	Yellow[e]	37—38	69	7·92
$Ge[N(SiMe_3)(CMe_3)]_2$ ..	Orange[e]	21—22	76	7·26
$Sn[N(SiMe_3)(CMe_3)]_2$ ..	Red	18—19	80	7·25
$Pb[N(SiMe_3)(CMe_3)]_2$ ..	Red	15—16	70	7·18
$ClSn[N(SiMe_3)_2]$	White	*ca.* 150 (decomp.)	51	—

[a] *M*, 429 (cryoscopy in C_6H_6) (required, 393). [b] *M*, 443 (cryoscopy in C_6H_6) (required, 439). [c] λ_{max} (n-C_6H_{14}) 487 (ϵ *ca.* 40), 389 (ϵ *ca.* 3100), 287 (ϵ *ca.* 4600), 230 (ϵ *ca.* 23,000) nm. [d] All volatile at *ca.* 60° and 10^{-3} mmHg. [e] Compounds are thermochromic, becoming redder on heating; redness increases in the series Ge < Sn < Pb.

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