Bonding Studies of Compounds of Group 3—5 Elements. Part XVIII.[1] He(I) Photoelectron Spectra of Bivalent Homoleptic Alkyls and Amides, Especially of Group 4 Elements, and of Tin(II) Chloride and Bromide†

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He(I) photoelectron (p.e.) spectra of (*i*) the monomeric, presumed-bent, compounds MR_2, $M(NR'_2)_2$, and $M(NR'R'')_2$ [$M = Ge, Sn$, or Pb; $R = CH(SiMe_3)_2$, $R' = SiMe_3$, and $R'' = CMe_3$], (*ii*) the linear HgR_2 and $M'(NR'_2)_2$ ($M = Zn$ or Hg), and (*iii*) the bent momomeric $SnCl_2$ and $SnBr_2$ have been recorded, as well as the reference compounds RH, R'_2NH, and R'R''NH. For the Group 4 metal(II) alkyls the first vertical ionisation potential (i.p.) is close to that of the free metal; the metal lone-pair orbital is progressively higher in $M(NR'R'')_2$ and $M(NR'_2)_2$, in which compounds it is the second band, being preceded by the antibonding b_2 molecular orbital (m.o.) formed by the nitrogen lone-pair atomic orbitals (a.o.s). Confirmation of this assignment is also provided by comparison of data for the bent and linear metal(II) amides; in the latter, nitrogen lone-pair interactions are negligible. Assignments, on the basis of trends and, for MX_2, of CNDO calculations, are proposed and trends noted. There is evidence of substantial N→Si p_π–d_π interaction in the amides.

We report the He(I) photoelectron (p.e.) spectra and assignments for monomeric bent two-co-ordinate alkyls MR_2 and amides $M(NR'R'')_2$ of the Group 4 elements [$M = Ge$, Sn, or Pb; $R = CH(SiMe_3)_2$, $R' = SiMe_3$, and $R'' = R'$ or CMe_3] and comparative data on the free alkane RH and amines R'R''NH, the halides $SnCl_2$ and $SnBr_2$, and the linear $Zn(NR'_2)_2$, HgR_2, and $Hg(NR'_2)_2$. This study stems from our interest in metal dialkylamides,[2] and in unusual kinetically stable metal alkyls,[3] and the p.e. spectra and molecular-orbital (m.o.) assignments for homoleptic transition-metal dialkylamides $M(NR_2)_n$ [octahedral ($n = 6$),[4] tetrahedral ($n = 4$),[4] and trigonal ($n = 3$)[5]] and the tetrahedral alkyls $M(C\leqslant)_4$.[6]

The use of the sterically demanding $[N(SiMe_3)_2]^-$ was introduced in the early 1960s by Bürger and Wannagat. Their work, and that of Bradley and his co-workers, established the principle that this ligand often stabilises metals in the low and unusual co-ordination number of three.[7] Additionally, some two-co-ordinate monomeric (in solution) homoleptic amides $M[N(SiMe_3)_2]_2$ were prepared (M = Be,[8] Mg,[9] Mn,[10] Co,[11] Ni,[10] Zn,[12] Cd,[12] and Hg[12]). Electron-diffraction analysis for the beryllium compound has established a linear NBeN arrangement with D_{2d} skeletal symmetry for $Si_2NBeNSi_2$,[13] and vibrational-spectroscopic data support a similar arrangement for the compounds of Mg, Zn, Cd, and Hg.[12]

The ligands $[N(SiMe_3)_2]^-$ and $[CH(SiMe_3)_2]^-$ are isoelectronic. Exploitation of the latter for the preparation of metal alkyls in low co-ordinate environments was first demonstrated for the case of the tin(II) and lead(II) alkyls which are monomeric in solution (C_6H_6 or C_6H_{12}) and in the gas phase.[14] These remarkable compounds are highly coloured, thermochromic (becoming redder on heating), diamagnetic at room temperature, show no e.s.r. signal in the dark in the absence of oxygen, and give sharp n.m.r. spectra.[14] They are thus believed to be bent molecules in a singlet electronic ground state. Gas-phase structural data are not yet to hand, but *X*-ray diffraction of the stannylene complex $[Cr(CO)_5(SnR_2)]$ shows a trigonal tin environment with $C_2SnCr(CO)_3$ coplanar and $C–Sn–C = 98°$;[15] this proves that the size of $[CH(SiMe_3)_2]^-$ is not such as to prevent a bent arrangement for the SnR_2 fragment. (*X*-Ray data for SnR_2, however, show that in the crystal the molecule is dimeric with a Sn–Sn bond of 2.76 Å.[16]) Yellow GeR_2 has similar properties and is presumed to be isostructural,[16] as are the volatile coloured s^2 ‡ amides $M[N(SiMe_3)_2]_2$ and $M[N(CMe_3)(SiMe_3)]_2$ (M = Ge, Sn, or Pb).[17] {The compound $Sn[N(SiMe_3)_2]_2$ has been obtained independently elsewhere,[18] and formulated as a nitrogen-bridged dimer in both the solution and the gas phase. We believe this to be unlikely because of (*i*) our molecular weight data (cryoscopy in C_6H_6 or C_6H_{12}), (*ii*) the low b.p.s, and (*iii*) the improbability of bridging by the bulky and feebly basic $[N(SiMe_3)_2]^-$ ligand.} The ligand $[N(CMe_3)(SiMe_3)]^-$ has been previously used, but

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† No reprints available.

‡ The formalism (R. S. Nyholm and M. L. Tobe, *Adv. Inorg. Chem. Radiochem.*, 1963, **5**, 1) is not intended to imply that the central-atom valence *s* electrons play no part in bonding.

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only for main-group metal [Li (as the etherate), B, Si^{IV}, Ge^{IV}, Sn^{IV}, and Pb^{IV}] heteroleptic complexes.[19]

Monomeric bent $SnCl_2$ and $SnBr_2$ are high-temperature species and electron-diffraction data establish their C_{2v} structure in the vapour state with $\angle$ X–Sn–X = 95°.[20]

EXPERIMENTAL

Hexamethyldisilazane, R'_2NH, and the tin(II) halides were commercial samples. The following compounds were prepared by published procedures: $(Me_3Si)(Me_3C)NH$ (R′R″NH);[21] $M(NR'_2)_2$ (M = Ge, Sn, or Pb);[17] $M(NR'R'')_2$;[17] $Zn(NR'_2)_2$;[12] $Hg(NR'_2)_2$;[12] $(Me_3Si)_2CH_2$ (RH);[22] GeR_2;[16] SnR_2;[14] and PbR_2.[14] Compounds were purified by distillation (RH, amines, and amides), sublimation (SnX_2), or crystallisation (MR_2), and purity was checked by g.l.c. (RH and amines), ^1H n.m.r., i.r., and analysis.

P.e. spectra were recorded on a Perkin-Elmer PS16 He(I) spectrometer. Some of the more volatile compounds [RH, R'_2NH, R′R″NH, $Zn(NR'_2)_2$, and $Hg(NR'_2)_2$] were bled in remotely, whereas the other samples were vaporised within the spectrometer using the directly heated inlet probe, and a vaporisation temperature below 120 °C, except for $SnCl_2$ (260 °C) and $SnBr_2$ (250 °C). Air-sensitive samples (Group 4 metal derivatives) were prepared for admission to the instrument by sealing in small ampoules under argon and breaking the seals immediately prior to use. Instrumental resolution varied from 20 to 50 meV and the number of counts per second from 150 to 10^4.† Methyl iodide and Ar were used for calibration.

RESULTS AND DISCUSSION

The p.e. spectra are shown in Figures 1—5 and the low-energy vertical ionisation potentials (i.p.s) are listed (except SnX_2) in Table 1; the i.p.s. are accurate to ± 0.05 eV. The first i.p. for the Group 4 metal(II) alkyl, assigned to ionisation from the metal lone-pair orbital, is compared with data on the gaseous metal in Table 2. In Table 3, the experimental i.p.s for the tin(II) halides are compared with orbital energies obtained from CNDO calculations. Numerous unsuccessful attempts were made to record the p.e. spectra of tin(II) fluoride and iodide, but the problem of disproportionation into the tin(IV) species was not overcome.

We consider first the p.e. spectra of the alkyls (Figure 2) and the parent alkane, $(Me_3Si)_2CH_2$ (Figure 1). The latter showed no bands at lower i.p. than 9 eV; hence, we assume that any band in this region in the alkyls comes from an m.o. involving the central metal atom. The dialkylmercury, $Hg[CH(SiMe_3)_2]_2$, had a band at 8.12 eV, and by analogy with dimethylmercury (*ca.* 9.3 eV),[23] this is assigned to the antisymmetric C–Hg–C m.o. in the linear complex. No bands, corresponding to ionisation of Hg inner *s* or *d* electrons, were observed.

TABLE 1

Experimental vertical i.p.s (eV) for bivalent metal alkyls, $M[CH(SiMe_3)_2]_2$, amides, $M[N(SiMe_3)_2]_2$ and $M[N(CMe_3)(SiMe_3)]_2$, and reference alkane, $(Me_3Si)_2CH_2$, and amines, $(Me_3Si)_2NH$ and $(Me_3Si)(Me_3C)NH$ (<10 eV)

Reference compounds	Orbital M–C (σ_{asym}) †		Alkyls	a_1 $\ddot{M}$	Orbital * b_2 (M–C σ_{asym})		
HgR_2	8.12		GeR_2	7.75	8.87		
	$\ddot{N}$		SnR_2	7.42	8.33		
R′R″NH	8.41		PbR_2	7.25	7.98		
R'_2NH	8.79		Amides	b_2 ($\ddot{N}$)	a_1 ($\ddot{M}$)	a_1 ($\ddot{N}$)	b_2(M–N σ_{asym})
	$\ddot{N}$	(M–N σ_{asym})	$Ge(NR'_2)_2$	7.71	8.68	8.99	
$Zn(NR'_2)_2$	8.50	9.55	$Sn(NR'_2)_2$	7.75	8.38	8.85	9.50
$Hg(NR'_2)_2$	8.33	9.38	$Pb(NR'_2)_2$	7.92	8.16	8.81	9.39
			$Ge(NR'R'')_2$	7.24	8.27	8.61	
			$Sn(NR'R'')_2$	7.26	7.90	8.47	9.33
			$Pb(NR'R'')_2$	7.26	7.69	8.49	9.00

* Symmetry symbols refer to C_{2v} local symmetry of MC_2 and MN_2 frameworks. † Antisymmetric.

Turning to the Group 4 alkyls, $M[CH(SiMe_3)_2]_2$, we note that there are now two bands in the region below 9 eV, both of which decrease in i.p. from Ge through to Pb. On the basis of a C_{2v} singlet electronic-ground-state model, three m.o.s with central-atom character are expected to be accessible to He(I) ionisation. These are the a_1 lone-pair orbital, the b_2 antisymmetric C–M–C m.o., and the a_1 symmetric C–M–C m.o. The metal lone-pair i.p.s are expected to lie close to the respective weighted atomic i.p.s (and the trends in i.p.s are accordingly likely to reflect group trends in the weighted i.p. of the *np* level) of the elements (see Table 2);[24] we thus assign the first i.p. to the a_1 lone-pair orbital. While comparisons of the weighted atomic i.p. and the molecular i.p. are a useful aid to assignment, it should be noted that the ' lone-pair ' orbital in the molecule mixes with both the metal *ns* orbital and the carbon 2*p* orbitals.

TABLE 2

Comparison of vertical first i.p.s (eV) of $M[CH(SiMe_3)_2]_2$ with those of M

M	Atomic first i.p.*	Metal lone-pair i.p. in MR_2
Ge	7.5	7.75
Sn	7.0	7.42
Pb	6.8	7.25

* Calculated from weighted average of the p^2 terms of the atom and of the p^1 terms of the ion using data from ref. 24.

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† 1 eV ≈ 1.60 × 10^{-19} J.

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These relatively small and opposing effects seem to balance out as seen from the data of Table 2; the deviation from weighted atomic i.p. is invariably less than 3%. The second i.p. corresponds to ionisation from the b_2 C–M–C antisymmetric bonding m.o., because this must lie at a lower i.p. than the symmetric a_1 bonding C–M–C m.o. The latter is probably obscured by the broad unresolved band due to ionisations from the ligand orbitals. Trends in the i.p.s of the b_2 m.o.s parallel those for the t_2 m.o.s in the corresponding metal(IV) alkyls $M(CH_2CMe_3)_4$ and $M(CH_2SiMe_3)_4$ and the i.p.s are similar in magnitude.[6] The p.e. spectra of the alkyls $\dot{M}R_2$ are thus readily interpreted in terms of a bent MC_2 framework, with a ' lone-pair ' orbital essentially localised at the metal. This is consistent with their observed Lewis-base character;[15] the Lewis-acid behaviour is attributed to an energetically low-lying vacant b_1 metal orbital.

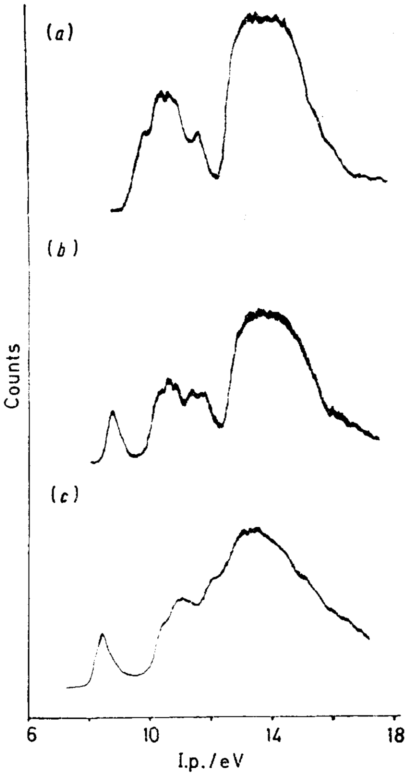

FIGURE 1 P.e. spectra of (*a*) $(Me_3Si)_2CH_2$, (*b*) $(Me_3Si)_2NH$, and (*c*) $(Me_3Si)(Me_3C)NH$

Three factors facilitate analysis of the p.e. spectra of the Group 4 metal amides $M[N(SiMe_3)_2]_2$ and $M[N(CMe_3)(SiMe_3)]_2$. First, we have recorded the spectra of the parent amines. These provide a guide to the energies of the ligand m.o.s. Secondly, the spectra of the linear bis(dialkyl)amides of Zn and Hg were recorded, because in these compounds there is no low-i.p. central-atom lone-pair orbital. Finally, comparisons of the p.e. spectra of the Group 4 metal(II) amides with those of the corresponding alkyls are of assistance, especially in the higher-energy region.

The spectrum of $(Me_3Si)_2NH$ has been reported previously[25] and we agree with the assignments;[5] the first i.p. (8.42 eV) of the unsymmetrical amine, $(Me_3Si)(Me_3C)NH$, clearly corresponds to the lone-pair orbital on the nitrogen atom; since both amines are bulky, and are likely to have a similar geometry, the nitrogen lone-pair i.p. provides a measure of the relative sigma and pi effects of the substituents at nitrogen. Since $SiMe_3$ is less electronegative than CMe_3, the lower i.p. of R′R″NH reflects a stabilisation of the nitrogen lone pair by the $SiMe_3$ groups through $(p\rightarrow d)$ π bonding (*cf.* ref. 26). Thus, we suggest that there is good evidence for the participation of vacant Si 3*d* orbitals. Both the linear amides $[Zn(NR'_2)_2$ and $Hg(NR'_2)_2]$ showed a single band below 9.3 eV. The m.o.s derived from the nitrogen lone pairs are therefore degenerate in these compounds. If the nitrogen lone pairs are rigid and orthogonal, as with the beryllium amide,[13] this is understandable. Alternatively, free rotation may occur about the M–N bond, a

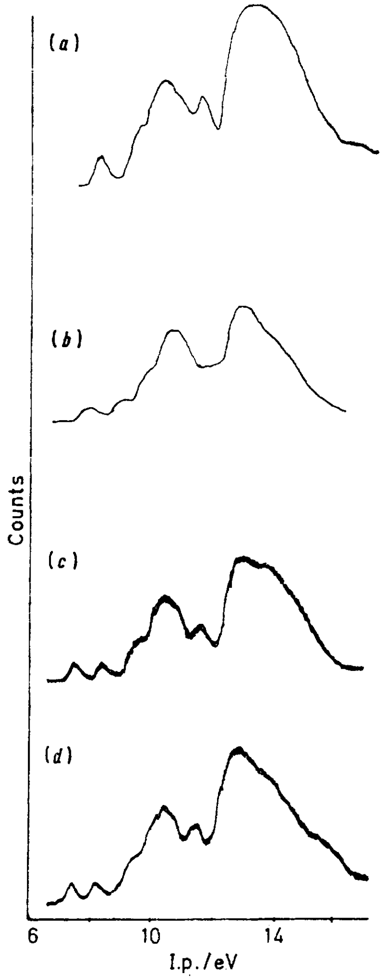

FIGURE 2 P.e. spectra of (*a*) HgR_2, (*b*) GeR_2, (*c*) SnR_2, and (*d*) PbR_2 [$R = CH(SiMe_3)_2$]

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[25] K. A. O. Starzewski, H. T. Dieck, and H. Bock, *J. Organometallic Chem.*, 1974, **65**, 311.

[26] D. C. Frost, F. G. Herring, A. Katrib, R. A. McLean, J. E. Drake, and N. P. C. Westwood, *Chem. Phys. Letters*, 1971, **10**, 347; *Canad. J. Chem.*, 1971, **49**, 4033; P. Baybutt, M. F. Guest, and I. H. Hillier, *Proc. Roy. Soc.*, 1973, **A333**, 225; and refs. therein.

feature we have observed before in amido-complexes of main-group elements.[4] The second band in the mercury(II) amide at 9.38 eV corresponds to the antisymmetric N–Hg–N m.o. (*cf.*, for HgR_2, where the second band is assigned to the corresponding C–Hg–C m.o.). This m.o. is also observed in the p.e. spectrum of the zinc amide, as the high-energy shoulder of the ligand i.p.s. The higher value for zinc reflects the higher atomic i.p. of zinc. The energies of these MN_2 m.o.s provide a guide as to the energies of the corresponding m.o.s for the Group 4B amides. Within the bent C_{2v} MN_2 framework, the angle between the NSi_2 units and the MN_2 plane is not known for the Group 4B amides. We infer from molecular models, however, that the steric strains are minimised when this angle is 90°, and accordingly the nitrogen lone-pair m.o.s have the symmetry shown in Figure 6.

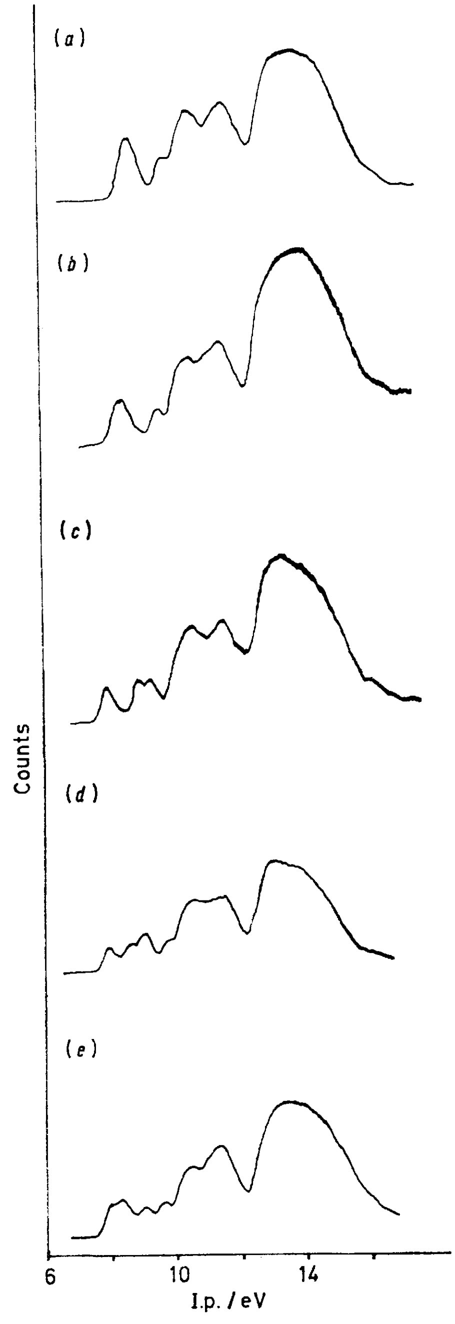

FIGURE 3 P.e. spectra of (a) $Zn(NR'_2)_2$, (b) $Hg(NR'_2)_2$, (c) $Ge(NR'_2)_2$, (d) $Sn(NR'_2)_2$, and (e) $Pb(NR'_2)_2$ ($R' = SiMe_3$)

The germanium(II) amides showed three bands in the low-i.p. region, while the tin and lead compounds showed four bands. The fourth band in the latter occurred

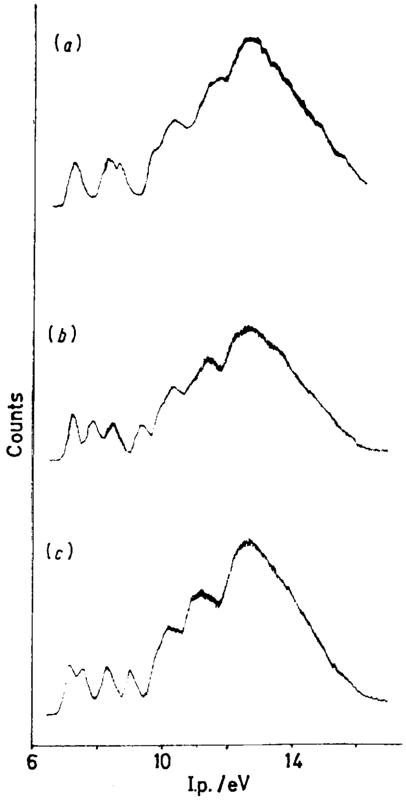

FIGURE 4 P.e. spectra of (a) $Ge(NR'R'')_2$, (b) $Sn(NR'R'')_2$, and (c) $Pb(NR'R'')_2$ ($R' = SiMe_3$, $R'' = CMe_3$)

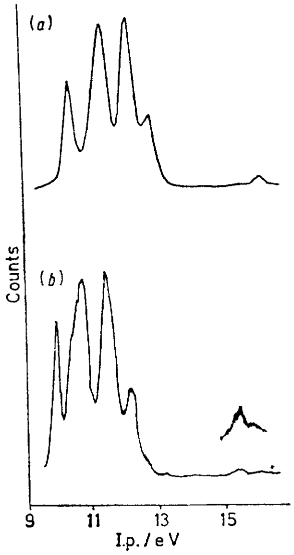

FIGURE 5 P.e. spectra of (a) $SnCl_2$ and (b) $SnBr_2$

above 9 eV and, by analogy with the linear amides and with the M–N bonding region in the compounds $M(NMe_2)_4$,[4] is assigned to the b_2 N–M–N m.o. The i.p. of this m.o. decreases with the increasing mass of the central atom, and this suggests that for the germanium amides the b_2 orbital is concealed by the ligand orbitals. The remaining three bands in the low-i.p. region derive from the nitrogen lone-pair orbitals and the lone pair on the central metal atom. The nitrogen lone-pair m.o.s are split in these compounds by through-space interaction as shown in Figure 6. The ' bonding ' (a_1) combination must lie at higher i.p. than the ' antibonding ' (b_2) m.o. The clue to the final assignment of the three high-energy orbitals is provided by comparing the atomic i.p.s [24] and the central-atom lone-pair i.p.s in MR_2. The trend in these i.p.s is closely matched by that of the second bands in the series of amides (see Table 1), a decrease of *ca.* 0.35 eV from Ge to Sn and a further decrease of *ca.* 0.2 eV from Sn to Pb. Hence this band is assigned to the a_1 lone-pair orbital on the metal. This is further substantiated by examination of the first and third bands in the amides. In these bent molecules there is a ' through-space ' interaction between the nitrogen lone pairs causing a splitting of 0.9—1.2 eV as between the b_2 (higher-energy) and a_1 (lower-energy) m.o.s. This interaction, if it is purely ' through space ', is expected to decrease with increasing M–N bond length if the N–M–N bond angle remains unaltered. Accordingly, we note that the i.p. of the first band increases slightly, and that of the third band decreases slightly, on passing from Ge through to Pb, *i.e.* as the separation of the nitrogen atoms increases.

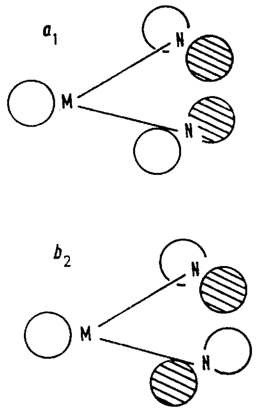

FIGURE 6 Through-space interaction of the nitrogen lone-pair orbitals in the preferred geometry

Although the $[CMe_3]^-$ ($[R'']^-$) group is less inductively electron donating than $[SiMe_3]^-$($[R']^-$), the i.p.s of the central-atom lone pairs are *ca.* 0.4—0.5 eV higher for $M(NR'_2)_2$ than for $M(NR'R'')_2$. This is explained (as for the corresponding effect in the free amines) by assuming significant p_π–d_π mesomeric interactions between the nitrogen lone pairs and the vacant Si 3*d* orbitals, thus reducing the electron density at M. Such delocalisation is reduced in $M(NR'R'')_2$, where there are no vacant low-energy orbitals on $[CMe_3]^-$. The same interpretation accounts for the difference in nitrogen lone-pair i.p.s between the two sets of compounds. The assigned metal lone-pair orbital i.p.s are *ca.* 0.5 [for $M(NR'R'')_2$] or 1 eV [for $M(NR'_2)_2$] higher than for the corresponding metal alkyls. It is therefore not unexpected that there is decreasing central-atom basicity in the order $MR_2 > M(NR'R'')_2 > M(NR'_2)_2$, as indicated by preliminary experiments.[1,17]

Finally, we turn to the p.e. spectra of $SnCl_2$ and $SnBr_2$ (Figure 5). The observed vertical i.p.s are compared with the calculated CNDO m.o. energies in Table 3.

TABLE 3

Comparison of experimental vertical i.p.s and CNDO orbital energies (eV) for $SnCl_2$ and $SnBr_2$

	Experimental i.p.	Calculated orbital energy [a]	
$SnCl_2$	10.37	10.72	$4a_1$
	11.0 [b]	11.01	$3b_2$
	11.33	11.50	$1a_2$
	12.12 [c]	11.82	$1b_1$
		11.84	$2b_2$
	12.77	11.93	$3a_1$
	15.90	14.01	$2a_1$
$SnBr_2$	9.87	10.39	$4a_1$
	10.2 [b]	10.54	$3b_2$
	10.65	11.06	$1a_2$
	11.35 [c]	11.40	$1b_1$
		11.41	$2b_2$
	12.05	11.55	$3a_1$
	15.24	14.25	$2a_1$

[a] Numbering begins with valence orbitals. [b] Shoulder. [c] Unresolved band.

Although the absolute m.o. energies calculated at this level of sophistication are unreliable, the overall pattern gives a useful qualitative view of the m.o. scheme. The spectra are clearly very similar (with the usual shift to higher i.p. on replacing bromine by chlorine) and a 1 : 1 correspondence exists between the bands for the two compounds. Five bands were observed in both spectra, although in each a slight shoulder on the low-i.p. side of the second band could be discerned. The compounds each possess 14 electrons accessible to He(I) radiation (tin 5*s* and 5*p*, halogen *np* electrons), so that ionisation from seven occupied m.o.s should be observed. This is supported by the calculation, so that at least one band is unresolved. The values obtained for the first i.p.s compare well with those obtained by electron-impact (e.i.) experiments [$SnCl_2$, 10.37 (p.e.) and 10.1 ± 0.4 eV (e.i.);[27] $SnBr_2$, 9.87 (p.e.) and 10.0 ± 0.4 eV (e.i.)[28]]. It is likely that the first band corresponds to ionisation from the tin lone-pair orbital ($4a_1$) (which, however, has some *s* character), and that the highest observed band corresponds to ionisation from an orbital with predominantly metal *s* character ($2a_1$). (A similar band occurs in the p.e. spectra of monomeric Group 3 metal halides.[29]) The remaining three bands in the spectra correspond to ionisation from orbitals predominantly localised on the halogen atoms. We have previously

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found[30] that in-plane (σ-type) lone-pair halogen orbitals give rise to bands of lower intensity than perpendicular (π-type) lone-pair orbitals. Thus it is reasonable to assign each of the two intense bands to halogen π-type lone-pair orbitals ($1a_2$ and $1b_1$ in order of increasing i.p.). Because of the fairly small bond angle (95°)[20] in these dihalides, the σ-type lone pairs must interact strongly, the $3a_1$ being a strongly halogen–halogen bonding m.o. while the $2b_2$ is halogen–halogen antibonding. For this reason we assign the first intense band to ionisation from the $1a_2 + 2b_2$ lone-pair orbitals, the second intense band to the $1b_1$ π-lone-pair orbitals and the $1b_2$ metal–halogen bonding m.o., and the next (weak) band to the $3a_1$ σ-lone-pair orbital. This orbital assignment is supported by the calculation (see Table 3), although the calculation implies that there must be some doubt remaining about the ordering of the $3a_1$ and $2b_2$ orbitals. It is noteworthy that the orbital assignment is substantially the same as that proposed for SiF_2.[31] The p.e. spectra of a number of simple halides, including MCl_2 and MBr_2 (M = Sn or Pb), have recently been reported,[32] but the proposed assignments differ notably for the first band (suggested to be the $3b_2$ in-plane lone-pair m.o., using our choice of axes).

The rather low first i.p.s are consistent with the recently observed Lewis-base character of these compounds, in forming complexes with certain transition-metal carbonyls, *e.g.* $[Mo(CO)_5(SnCl_2)]$.[33] The energy of the central-atom lone-pair orbital has been shown to be directly related to the degree of Lewis basicity for a series of phosphines.[34] The fact that tin(II) halides have higher first i.p.s, but form donor complexes more readily than $Sn(NR'_2)_2$, indicates that such a correlation should be treated with care. Other factors, including latent heats of vaporisation, solvation energies, and steric strains, play a role.

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