He-I and He-II Photoelectron Studies of Bonding in Metal Silylamido-complexes, $M[N(SiMe_3)_2]_n$ (n = 1, 2, or 3)

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Gas-phase He-I and He-II photoelectron spectra have been obtained for the following bis(trimethylsilyl)amido-metal complexes: $M[N(SiMe_3)_2]$ where M = Li or Na; $M[N(SiMe_3)_2]_2$ where M = Mg or Co; $M[N(SiMe_3)_2]_3$ where M = Al, Cr, Ce, Pr, Nd, Eu, Yb, or U. Nitrogen lone-pair and metal–nitrogen π-bonding ionization energies show a constant trend throughout the series, increasing with the charge and decreasing with the size of the metal ion. A *d* band similar to that of $Cr[N(CHMe_2)_2]_3$ is detected for $Cr[N(SiMe_3)_2]_3$ and a very weak 4*f* band is the first ionization band in the spectrum of $Ce[N(SiMe_3)_2]_3$. The 5*f* band of $U[N(SiMe_3)_2]_3$ has a full width at half maximum of 1 eV, part of which is due to unresolved spin–orbit coupling.

THE bis(trimethylsilyl)amido-ligand forms volatile complexes with a wide variety of metals, so that these complexes readily lend themselves to investigation by gas-phase photoelectron (p.e.) spectroscopy and present an opportunity for a comparative study of metal–ligand bonding.[1] Previous related studies, that were confined to He-I p.e. spectroscopy, obtained information on the complexes of the first-row transition metals Sc, Ti, Cr, and Fe, and the B metals Zn, Hg, Ga, In, Ge, Sn, and Pb.[2,3] We have extended the series to the A metals Li, Na, Mg, and Group 3B Al, the *f*-block transition elements Ce, Pr, Nd, Eu, Yb, and U, and the *d*-block element Co as well as repeating measurements for Cr.

Related work on dialkylamido-compounds of B metals[4] and transition metals[4,5] enables a comparison of the functional group properties of the two types of ligand.

The trivalent, binary silylamides present a curious structural anomaly. The Group 3B (Al, Ga, In, and Tl) and the transition (Ti, V, Cr, and Fe) metal complexes are planar whereas the lanthanide metals (Nd, Eu, and Yb) and scandium have a pyramidal MN_3 unit.[6-8] A π-bonding hypothesis has been presented to account for the planarity of the main group (p_π–p_π) and transition (d_π–p_π) metal compounds. Conversely, the lack of π bonding or/and the predominantly ionic nature of the M–N bonds has been suggested to account for the non-planarity of the *f*-block metal and scandium compounds. This hypothesis has been criticized and the thesis has been put forward that metal–nitrogen bonding in all of the trisilylamides is predominantly ionic.[9] The planarity or lack thereof is attributed to crystal-packing forces. Optical spectroscopic studies, however, have shown that the spectra of $M[N(SiMe_3)_2]_3$, where M = Pr or Nd, are identical in the gas phase, in carbon tetrachloride solution, and in the solid state at 4 K.[10] Thus a satisfactory explanation of the geometry has yet to be given.

EXPERIMENTAL

All compounds were prepared by literature methods: $Li[N(SiMe_3)_2]$,[11] $Na[N(SiMe_3)_2]$,[12] $Mg[N(SiMe_3)_2]_2$,[13] $Co[N(SiMe_3)_2]_2$,[14] $Cr[N(SiMe_3)_2]_3$,[15] $Al[N(SiMe_3)_2]_3$,[16] $M[N(SiMe_3)_2]_3$ where M is Ce, Pr, Eu, and Yb,[17] $Nd[N(SiMe_3)_2]_3$,[8] and $U[N(SiMe_3)_2]_3$.[18] The compounds were crystallized from either pentane or toluene and were sublimed under vacuum at least twice. Their purity was determined by melting-point measurements and i.r. spectroscopy.

The photoelectron spectra were obtained using a Perkin-Elmer PS 16/18 spectrometer fitted with a Helectros lamp capable of producing both He-I and He-II radiation. The samples were introduced into the spectrometer under inert-atmosphere conditions and were heated until a spectrum was obtained. Inevitably the initial spectrum was that of the parent amide, $NH(SiMe_3)_2$,[19] resulting presumably from scavenging of water by the gaseous complex, but after a time, 15 min to 1 h, this spectrum died away and, on raising the temperature, a ligand-free spectrum was obtained.

Sample temperatures and maximum counting rates obtained for He-I and He-II spectra are given in Table 1.

TABLE 1

Temperatures (°C) and maximum counting rates (counts s^{-1}) for the spectra of $M[N(SiMe_3)_2]_n$

M	n	Temp.	He-I	He-II
Li	1	147	3 000	200—300
Na	1	160—174	1 000	300
Mg	2	33	1 000	*
Al	3	130	1 000	300
Cr	3	120—130	1 000	200
Co	2	46—74	2 000	200—300
Ce	3	133—140	1 500	300
Pr	3	138—157	3 000	300
Nd	3	133—155	4 000	300
Eu	3	140—155	3 000	300—400
Yb	3	130—136	1 000	*
U	3	136	3 000	300

* Spectrum signal averaged.

RESULTS

Vertical ionization energies obtained for the compounds are recorded in Table 2. Representative spectra are shown in Figures 1—5.

DISCUSSION

The assignments of the spectra presented here are outlined in Table 2. In some instances our assignments are at variance with previous work so we give below their justification in some detail.

The bis- and tris-silylamide metal complexes have been shown to be monomeric in solution and in the gas phase.[20,21] The degree of association of the mono-

TABLE 2

Vertical ionization energies (eV) for the compounds $M[N(SiMe_3)_2]_n$

M	*n*	X	A	B	C	D	E	F	G
Li	1		8.46	9.35	10.25	11.09	13.58	15.7	21.3
Na	1		8.1	8.8	10.1	10.9	13.6	15.5	21.3
Mg	2		8.87	9.77	10.49	11.54	13.22	*	*
Al	3		8.73		10.27	11.36	13.00	15.8	21.3
Cr	3	7.58 7.94	8.81		10.17	11.16	13.30	15.6	18.8, 21.3
Co	2	8.08	8.63	9.60	10.33	11.47	13.22		19.6, 21.2
Ce	3	7.07	8.19	8.99	10.12	11.11	13.42	16.1	21.2
Pr	3		8.19	8.90	10.15	11.02	13.40	15.7	21.3
Nd	3		8.19	8.96	10.11	11.04	13.40	15.6	21.3
Eu	3		8.14	9.08	10.26	11.16	13.53	15.9	21.4
Yb	3		8.1 8.4	9.1	10.2	11.1	13.4	*	*
U	3	5.96	8.04	8.85	9.91	10.92	13.2	15.6	21.1
		f/*d*	N:	M–N	C–Si	N–Si	C–H	Si(3*s*)	C(2*s*)

* Uncalibrated signal-averaged He-II spectrum.

silylamides is more complex. The sodium compound is polymeric in the solid state [22] and dimeric in solution; [23] the lithium compound exists as a trimer in the solid state [24] and a dimer in solution.[23] No evidence has been reported on the degree of molecularity in the gas phase although failure to obtain a mass spectrum of $Li[N(SiMe_3)_2]$, due to its tendency to hydrolyze, is mentioned by Wannagat.[25] As the degree of association of these two compounds is an important consideration in assigning the p.e. spectra we obtained their mass spectra. The mass spectrum of $Na[N(SiMe_3)_2]$ shows a weak mononuclear parent ion ($m/e = 183$, *ca.* 0.14% relative abundance) with characteristic Si satellites and a reasonably strong $M^+ - 15$ ion (*ca.* 0.42% relative abundance) also with Si satellites. Although other weak peaks appear with mass numbers >183, absence of Si satellites for these peaks indicates that the gas-phase species is predominantly monomeric. The mass spectrum of the lithium compound however showed a very weak parent ion corresponding to the dimer ($m/e = 334$) and no sign of the monomer.

The p.e. spectrum of $Na[N(SiMe_3)_2]$ (Figure 1) shows two low-energy bands, A and B (8.1 and 8.8 eV),[*] of approximate relative intensity 1 : 0.8, followed by overlapping bands at 10.1 (C) and 10.9 eV (D) before the broad C–H ionization band, E, centred at 13.6 eV. The complex band C + D is assigned to Si–C and Si–N ionizations as previously; [3] as there are four times as many of the former type of electron as the latter ionizing in this region, it seems likely that the Si–C ionization region spreads over both bands, as has been found for CH_2SiMe_3 complexes,[26,27] whereas the Si–N ionization, which is expected on electronegativity grounds at a higher binding energy, comprises part of D. Assuming a planar structure for the $NaNSi_2$ system, we may classify the lone pairs of the $[N(SiMe_3)_2]^-$ anion as σ and π. On either an ionic or partially covalent model the σ orbital is expected to lie lower in energy than the π orbital and, if differential relaxation effects are small, the π electrons should have a lower ionization energy than the σ electrons. We assign band A to the π ionization and band B to the σ ionization.

The spectrum of $\{Li[N(SiMe_3)_2]\}_2$ (Figure 1) shows bands corresponding to A—E but B is shifted closer to C. As the compound is dimeric in the vapour phase, splitting of nitrogen-based orbital ionizations may well arise from interaction between the two nitrogen atoms. We judge this perturbation to be less than that of the metal ion and assign bands A and B as for the sodium compound. That band A in the spectrum of the lithium derivative is broader than the corresponding band in the spectrum of $Na[N(SiMe_3)_2]$ may well be due to interaction between the two nitrogen π-lone pairs across the bridge. It is noteworthy that the separation of the σ and π ionizations is 0.2 eV greater for $\{Li[N(SiMe_3)_2]\}_2$ than $Na[N(SiMe_3)_2]$.

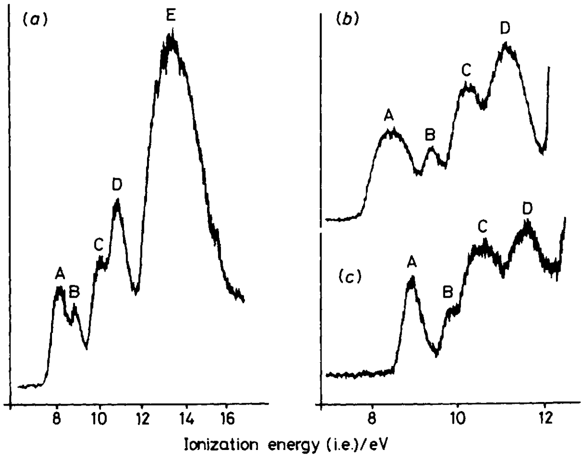

FIGURE 1 He-I photoelectron spectra of NaL (*a*), $(LiL)_2$ (*b*), and MgL_2 (*c*) where $L = N(SiMe_3)_2$

The compounds $M[N(SiMe_3)_2]_3$, where M is an *f*-block element, show practically identical spectra, except for Ce and U which have additional features discussed below. We give He-I and He-II spectra for $Nd[N(SiMe_3)_2]_3$ in Figure 2. The resemblance of these spectra to the spectra of the sodium compound is also striking, the

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

He-I spectra of all compounds showing bands A—E at closely similar ionization energies and of similar relative intensities.

Under any situation of three-fold symmetry, the two sets of nitrogen lone pairs (σ and π) both transform as *a* + *e*, thus there is the possibility in the tris compounds of four ionization bands. Lappert *et al.*,[3] who reported a similar He-I spectrum for $Cr[N(SiMe_3)_2]_3$, found two low-energy bands in the p.e. spectra of the tris-silylamides of Sc, Ti, Cr, and Fe, and assigned the bands to the *a* and *e* combinations of the nitrogen π-lone pairs, which may, in the latter three cases, be overlapping with *d* ionizations. By analogy with the sodium case, we propose that for the *f*-block elements band A is due to all N π-lone pair ionizations and band B is due to ionization of M–N σ-bonding electrons. Lappert *et al.* placed the σ ionizations under band C.

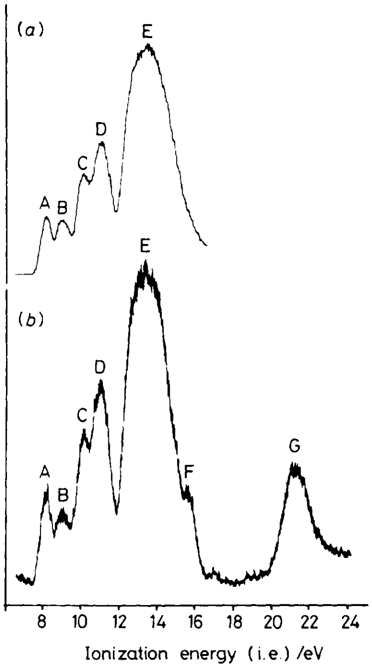

FIGURE 2 He-I (*a*) and He-II (*b*) photoelectron spectra of NdL_3 where L = $N(SiMe_3)_2$

That *ca.* 9 eV is a reasonable ionization energy for the M–N σ-bonding electrons in these compounds may be demonstrated by comparison with M–N ionization energies in dialkylamide complexes, after taking into account the relative inductive effects of Me and $SiMe_3$. However, few direct comparisons exist. Comparison of the spectra of the compounds $Sn(NMe_2)_4$ and $Sn[N(SiMe_3)_2]_2$ reveals that the binding energies of the M–N σ-bonding electrons are *ca.* 1.3 eV higher in the former compound,[2-5] and, whereas the Group 4B elements in the series $M(NMe_2)_4$ show M–N σ-binding energies in the range 10.8—11.2 eV, the Group 4A elements Ti, Zr, and Hf have values from 10.3 to 10.6 eV.[4] A similar difference is found between Group 4B alkyl M–C σ-ionization energies and the analogous ionizations in Group 4A alkyls.[27] Extrapolation of these trends to the Group 4A silylamido-compounds places their M–N σ ionizations in the region of 9 eV.

Although we conclude that the most reasonable assignment of band B is to an M–N σ-bonding ionization, it is not possible to distinguish whether it is due to the M–N *e* ionization alone or to both the *e* and *a* ionizations. The relative energies of the *e* and *a* N π ionizations and their dependence on molecular geometry has been discussed by both Lappert *et al.*[3] and Cowley and coworkers;[5] as we observed no splitting of the N π-ionization band there is no need to reiterate the arguments here.

The p.e. spectrum of $Mg[N(SiMe_3)_2]_2$ given in Figure 1 shows clearly distinguishable bands A, C, D, and E, but B is now a shoulder on the leading edge of C. In addition the bands all lie at higher energy than those of $Na[N(SiMe_3)_2]$, the shifts in the bands, Δ, being Δ_B (0.95 eV) > Δ_A (0.76 eV) > Δ_D (0.65 eV) > Δ_C (0.4 eV). The effect of these shifts is to place B much closer to C.

These trends are readily understood when the more polarizing or covalent effect of magnesium(II) compared with sodium(I) is considered. The electrons that are most stabilized are the nitrogen σ-bonding lone pairs of the ligand, which point directly at the metal; the next is the nitrogen π-lone pair followed by the N–Si bonding electrons. The Si–C bonding electrons furthest from the metal centre are least perturbed. Again, implicit in this interpretation, band B is assumed to be associated with the M–N σ-bonding ionization rather than a N π-lone pair ionization. In the case of this bis-silylamide, if two N π-lone pairs were observed their intensities would be expected to be comparable, yet the relative heights of A and B are very similar to those found for the mono-silylamide of sodium and the tris-silylamides of the *f*-block elements. In the spectrum of $Al[N(SiMe_3)_2]_3$, band B can no longer be distinguished and is assumed to lie on the edge of band C.

These considerations for $Mg[N(SiMe_3)_2]_2$ and $Al[N(SiMe_3)_2]_3$ enable us to put forward an assignment of the spectra of $Co[N(SiMe_3)_2]_2$ and $Cr[N(SiMe_3)_2]_3$ shown in Figure 3. For both these spectra the band pattern is more complex, so only bands C and D may be clearly identified. In the case of the chromium compound we have an additional handle on the assignment in that the p.e. spectra of $Cr[N(CHMe_2)_2]_3$ have been reported.[5] This shows a structured *d* band [6.3 (sh), 6.53 eV] followed by N π-lone pair ionizations (7.38, 7.9 eV) with an M–N σ-bonding ionization at 9.9 eV. The tris-dialkylamide of chromium has been shown to have the same ground-state configuration as $Cr[N(SiMe_3)_2]_3$ and the first band in the p.e. spectrum of the latter has a similar structure to the first band of the former, albeit at significantly higher ionization energy [7.6 (sh), 7.9 eV]. The ionization energy of band D (11.16 eV) lies between the values found for $Na[N(SiMe_3)_2]$ and $Mg[N(SiMe_3)_2]_2$ so by simple interpolation we would expect band A for the chromium compound to lie between 8.1 and 8.9 eV. The best candidate for band A is, therefore, the ionization at 8.8

eV, and we assume that B has merged with band C; there is a trace of a shoulder on the leading edge of this band.

In the He-II spectra we would expect an intensity increase of the *d*-ionization bands relative to the ligand bands. In fact under these conditions band A can no longer be distinguished as it has been swamped by an intensity increase in the region corresponding to band X.

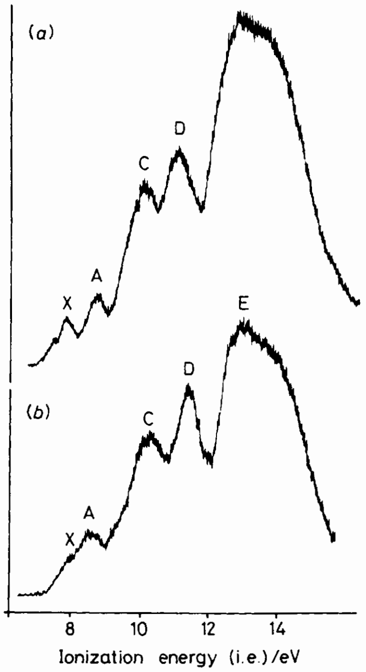

FIGURE 3 He-I photoelectron spectra of CrL_3 (*a*) and CoL_2 (*b*) where L = $N(SiMe_3)_2$

Thus the general pattern of the evidence suggests that band X is a *d* band and following Cowley and co-workers[5] we assign the shoulder at 7.58 eV to the $^3A_2$ ion state and the main vertical ionization energy (i.e.) at 7.94 eV to the ^3E ion state. Band A is a nitrogen π-lone pair band, C comprises the M–N σ-bonding orbital ionization as well as C–Si ionizations, and D is assigned as previously. This assignment differs from that of Lappert *et al.*[3] who, by analogy with their assignment of the p.e. spectrum of $Sc[N(SiMe_3)_2]_3$, suggest that both X and A were due to N lone-pair ionizations.

The low-energy region of the spectrum of $Co[N(SiMe_3)_2]_2$ is difficult to interpret. The ionization bands are less distinct than in any other spectrum of this series, presumably due to the greater number of *d* electrons on the metal. Intensity comparisons between He-I and He-II spectra suggest that bands at 8.08 and 8.63 eV both contain *d* ionizations. Ionization-energy comparisons suggest that the shoulder at 9.60 eV may well be band B. The nitrogen π ionizations cannot be independently located, but presumably comprise part of band A.

f-*Bands*.—The spectrum of $U[N(SiMe_3)_2]_3$ (Figure 4) shows, in addition to bands A—E discussed above, a broad band at low ionization energy (5.96 eV), that shows a substantial increase in relative intensity on increasing the photon energy. It may, therefore, be unambiguously assigned to ionization of the $5f^3$ configuration.

A striking feature of this band is its width [full width at half maximum (f.w.h.m.) = 1 eV]. This is due to a combination of two factors. Although the *f* electrons can be considered to be technically non-bonding in a molecular-orbital sense, the removal of one of them creates a considerable perturbation of molecular geometry. The ground-state molecule is U^{III} while the ion formed is U^{IV} so a bond-length difference of *ca.* 0.1 Å may be anticipated. As the Franck–Condon principle applies to photoionization the ion will be formed in a highly excited vibrational state and the p.e. band shows a broad unresolved vibrational envelope. Also, the ground state for a uranium(III) ion is $^4I_{9/2}$. Calculation predicts[28] that on ionization the probabilities of ionization to the various triplet states are as follows: $^3H_4$, 2.1; $^3H_5$, 0.19; $^3F_2$, 0.61. The $^3H_5$ state is presumably too low in intensity to be readily observed but the $^3F_2$ state, which should lie *ca.* 0.5 eV above the $^3H_4$ state,[29] should be detectable. It is likely that the *f* band is due to both the $^3H_4$ and $^3F_2$ states, the combination of unresolved spin–orbit splitting and unresolved vibrational structure accounting for its width. The *f* band in the p.e. spectrum of $[U(\eta\text{-}C_5H_5)_3(C_4H_8O)]$ shows similar breadth.[30]

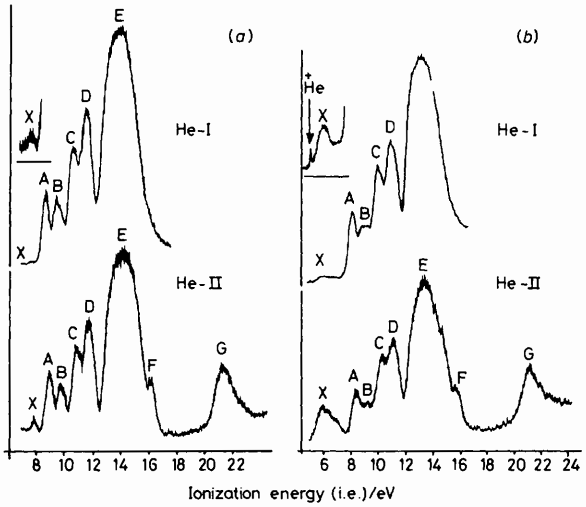

FIGURE 4 He-I and He-II photoelectron spectra of CeL_3 (*a*) and UL_3 (*b*) where L = $N(SiMe_3)_2$

At He-I and He-II ionizing energies, 4*f* bands are expected to be very low in intensity but, like 5*f* ionization bands, are expected to increase in intensity on passing from He-I radiation to He-II. All the spectra show structure at higher kinetic energy than band A due to ionization by He-Iβ and He-IIβ lines from the discharge lamp. Thus each of the main spectra has a shadow displaced to the left. In the case of the He-I spectrum it is displaced by 1.87 eV and is *ca.* 1% of the intensity of the main spectrum; for He-II it is displaced by 7.56 eV and is about 5% of the He-II spectrum. These satellite ionizations complicate the identification of weak *f* bands but in the case of Ce[N(SiMe$_3$)$_2$]$_3$ an extra band is detectable at 7.07 eV in both the He-I and He-II spectra (Figure 4). This band shows a seven-fold intensity change (relative to the ligand bands) and is assigned to a 4*f* ionization of the ^2F ground state to the ^1S ion state. The band is broad having a f.w.h.m. of 0.7 eV due, presumably, to unresolved vibrational fine structure as discussed above.

General Comments.—The assignments presented above result in a general trend in ionization energies. In Figure 5 we plot the ionization energy of band B *versus* the ionization energy of band A. Included in the plot are values for Zn[N(SiMe$_3$)$_2$]$_2$, Hg[N(SiMe$_3$)$_2$]$_2$,[2] and In[N(SiMe$_3$)$_2$]$_3$[3] where analogous bands may be distinguished. This figure demonstrates that A and B change uniformly, B being more sensitive to the metal than A: C and D show a similar trend but it is much less marked than for A or B. As mentioned above these trends might be anticipated on either an ionic or covalent bonding model. Band B, due to M–N σ-bonding ionizations, is expected to be more sensitive to metal variations than the nitrogen lone pair; also the i.e. increases with the valency of the metal and decreases with its size. It is interesting in this context that U^{III} gives values in the same region as Na^{I}.

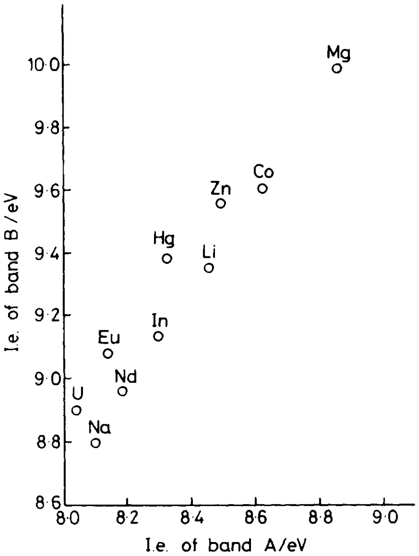

FIGURE 5 Plot of the ionization energy of band A *versus* the ionization energy of band B

Although the data we have obtained do not solve the dilemma posed by the structural information discussed above they do illuminate it to some extent. Our analysis shows no energy separation of the *e* and *a* N π ionizations for the compounds studied. This suggests little lone-pair interaction through the metal and minimal M–N π bonding. Thus any explanation of the geometry round the metal based on differential interactions would seem to be unlikely.

Of particular interest is the comparison of i.e. (eV) between Cr[N(SiMe$_3$)$_2$]$_3$ and Cr[N(CHMe$_2$)$_2$]$_3$.

d				
^3A	^3E	N	M–N	
6.3	6.53	7.38, 7.9	9.9	Cr[N(CHMe$_2$)$_2$]$_3$
7.58	7.94	8.81	10	Cr[N(SiMe$_3$)$_2$]$_3$

Whereas the M–N σ-bonding i.e. occurs in a similar region for the two compounds {assuming B lies on the edge of C for Cr[N(SiMe$_3$)$_2$]$_3$}, the X and A bands are much lower in energy for the alkylamido-compound. Similar differences have been observed for germanium and tin alkyl- and silyl-amides [1,31,32] and were attributed to the differing π-bonding systems of the two ligands. In the bis(trimethylsilyl)amido-ligand the nitrogen lone pair can delocalize onto the silicon atoms with the result that this ligand is not a π donor to the metal. In the alkylamido-ligand there is no such comparable delocalization, with the consequence that the N lone pairs have a lower ionization energy, and that π donation to the metal occurs, which in turn results in an observable splitting of the N lone-pair ionization band and lower metal *d* ionization energies.

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