# Three-co-ordinated Transition Metal Compounds. Part I. The Preparation and Characterization of Tris(bistrimethylsilylamido)-derivatives of Scandium, Titanium, Vanadium, Chromium, and Iron

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The compounds $M[N(SiMe_3)_2]_3$, where M = Sc, Ti, V, Cr, and Fe, have been prepared by reactions involving metal chloride complexes and the lithium derivative of hexamethyldisilazane. The compounds have been characterized by analysis, molecular weight determination, i.r., and mass spectra. They are members of a trigonally co-ordinated transition metal series.

THE tris(bistrimethylsilylamido)-derivatives of chromium and iron $M[N(SiMe_3)_2]_3$ (I; M = Cr and Fe) were first reported by Bürger and Wannagat [1,2] as reactive green solids which could be sublimed *in vacuo*, but these interesting new compounds were not adequately characterized and the chromium derivative was obtained in very small yield. Independently we had isolated $Cr(NPr^i{}_2)_3$ and shown it to be monomeric in cyclohexane thus proving that the tervalent chromium was three-co-ordinated.[3,4] An *X*-ray crystal analysis [5] of (I) (M = Cr and Fe) established the configuration of the trigonally co-ordinated bistrimethylsilylamidometal compounds and it was obviously desirable to extend the series to include more of the transition metals in order to explore the ligand field aspects of three-co-ordination. Recently we prepared the titanium and vanadium compounds (I) (M = Ti and V) [6] and the scandium derivative is reported in this paper. Attempts to prepare the manganese, cobalt, and nickel derivatives have so far failed although Bürger and Wannagat [1,2] have isolated the bis-derivatives (II) $M[N(SiMe_3)_2]_2$ (M = Mn, Co, and Ni). Nevertheless, the presently known trigonal compounds (I) constitute a considerable portion of the 3*d* transition metal series with examples of $d^0$, $d^1$, $d^2$, $d^3$, and $d^5$ metal ions.

Here we present a full account of the preparation and characterization of these compounds, and in subsequent papers we shall report on their electronic spectra, magnetism, and e.s.r. spectra.

*Preparation of* $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, V, Cr, and Fe).—Bürger and Wannagat's method of preparation of (I) (M = Cr and Fe) [1,2] involved the reaction of the metal chlorides in tetrahydrofuran (THF) with $NaN(SiMe_3)_2$. We have obtained much higher yields of the chromium derivative using $LiN(SiMe_3)_2$. In contrast to the ready formation of (I; M = Cr and Fe) by this method we were unable to obtain the titanium or vanadium derivatives starting from either the anhydrous trichlorides or the complex chlorides $MCl_3(THF)_3$. The products obtained contained considerable proportions of chloride and suggested that the chloride-bridged octahedral metal complexes were formed which were resistant to further replacement of chlorine. Similar behaviour has been found in reactions of $MCl_3$ (M = Ti and V) with lithium di-isopropylamide.[7] In view of the considerable steric hindrance associated with the bulky bistrimethylsilylamido-ligand which would be at a disadvantage in a nucleophilic reaction at an octahedral metal centre we then tried other metal trichloride complexes $MCl_3L_2$ containing weakly bound neutral ligands (L) in a five-co-ordinated metal complex. Using the trimethylamine adducts $MCl_3(NMe_3)_2$ (M = Ti and V) [8] in reactions with $LiN(SiMe_3)_2$ the new tris-silylamides (I; M = Ti and V) were obtained in reasonable yields (see Experimental section) as coloured crystalline compounds (Table 1) which were highly reactive to oxygen and water. Although the titanium compound could not be sublimed owing to thermal

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[1] H. Bürger and U. Wannagat, *Monatsh.*, 1963, **94**, 1007.

[2] H. Bürger and U. Wannagat, *Monatsh.*, 1964, **95**, 1099.

[3] J. S. Basi and D. C. Bradley, *Proc. Chem. Soc.*, 1963, 305.

[4] E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *Chem. Comm.*, 1968, 495.

[5] D. C. Bradley, M. B. Hursthouse, and P. F. Rodesiler, *Chem. Comm.*, 1969, 14.

[6] D. C. Bradley and R. G. Copperthwaite, *Chem. Comm.*, 1971, 764.

[7] E. C. Alyea, D. C. Bradley, M. F. Lappert, and A. R. Sanger, *Chem. Comm.*, 1969, 1064.

[8] B. J. Russ and J. S. Wood, *Chem. Comm.*, 1966, 745; M. W. Duckworth, G. W. A. Fowles, and P. T. Greene, *J. Chem. Soc.* (*A*), 1967, 1592.

decomposition it was sufficiently stable to give a mass spectrum whilst the vanadium compound could be sublimed at 95°, 0·005 mmHg and also gave a mass spectrum. *X*-Ray crystallographic studies [9] have shown that all of the compounds (I; M = Ti, V, Cr, and Fe) are monomeric in the crystalline state and thus contain trigonally co-ordinated transition metals. The scandium compound (I; M = Sc) was obtained by addition of the anhydrous trichloride to a tetrahydrofuran solution of $LiN(SiMe_3)_2$. Several methods were tried (see Experimental section) to synthesize $Mn[N(SiMe_3)_2]_3$ and $Co[N(SiMe_3)_2]_3$ but without success.

*Infrared Spectra.*—Excluding hydrogens the $M[N(SiMe_3)_2]_3$ molecules contain 28 atoms and *X*-ray studies [9] have shown that the $M(NSi_2)_3$ units have $D_3$ symmetry. Hence a large number of i.r. and Raman bands would be expected. Unfortunately, attempts to obtain Raman spectra were unsuccessful due to the colour and instability of these compounds and assignment of bands is rather difficult. However, our task was made easier by reference to the work of Bürger *et al.*[10] on the i.r. and Raman spectra of the monomeric three-co-ordinated non-transition metal compounds $M[N(SiMe_3)_2]_3$ (M = Al, Ga, and In). We have included in Table 2 the i.r. spectrum of $Ga[N(SiMe_3)_2]_3$ for comparison with the tervalent transition metal disilylamides in the region below 1300 $cm^{-1}$.

TABLE 1

| | | Analysis | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found | | | | | Calc. | | | | |
| Compound | Colour | M | N | C | H | Si | M | N | C | H | Si |
| $Sc[N(SiMe_3)_2]_3$ | Colourless [a] | | 7·69 | 40·5 | 10·1 | | | 7·99 | 41·1 | 10·3 | |
| $Ti[N(SiMe_3)_2]_3$ | Bright blue | 8·65 | 7·64 | 39·9 | 9·9 | | 9·05 | 7·94 | 40·9 | 10·3 | |
| $V[N(SiMe_3)_2]_3$ | Brown [b] | 9·52 | 7·74 | 40·4 | 10·0 | | 9·57 | 7·90 | 40·6 | 10·2 | 31·6 |
| $Cr[N(SiMe_3)_2]_3$ | Bright green [c] | 9·47 | 7·91 | 39·5 | 10·0 | 31·5 | 9·76 | 7·88 | 40·6 | 10·2 | 31·6 |
| $Fe[N(SiMe_3)_2]_3$ | Dark green [c] | Analytical results unreliable | | | | | | | | | |

[a] M.p. 172—174°. [b] Sublimes 95°, 0·005 mmHg. [c] Sublimes 80°, 0·005 mmHg.

TABLE 2

| $Ga[N(SiMe_3)_2]_3$ [a] | $Sc[N(SiMe_3)_2]_3$ | $Ti[N(SiMe_3)_2]_3$ | $V[N(SiMe_3)_2]_3$ | $Cr[N(SiMe_3)_2]_3$ | $Fe[N(SiMe_3)_2]_3$ | Assignments [b] |
|---|---|---|---|---|---|---|
| 1260(sh) | 1260(sh) | 1260(sh) | 1260(sh) | 1260(sh) | 1260(sh) | $\delta_sCH_3$ |
| 1252s | 1250vs | 1250vs | 1250vs | 1250vs | 1250vs | $\delta_sCH_3$ |
| 913vs | 950vs | 899vs | 902vs | 902vs | 902vs | $\nu_{as}MNSi_2(A_2,E)$ |
| 874vs | 865vs | 865vs | 865vs | 865vs | 865vs | $\rho_{as}CH_3$ |
| 842vs | 835vs | 840vs | 845vs | 840vs | 840vs | |
| 825(sh) | 820(sh) | 820(sh) | 820(sh) | 820(sh) | 820(sh) | $\nu_sMNSi_2(A_1,E)$ |
| | 780s | 787s | 790s | 790s | 790s | |
| 760m | 759m | 759m | 760m | 758m | 758m | $\rho_sCH_3$ |
| | 675m | 700m | 703m | 708m | 708m | $\nu_{as}SiC_3(A_1)$ |
| 678m | 655m | 669m | 673m | 676m | 676m | $\nu_{as}SiC_3(E)$ |
| 622m | 630m | 618m | 620m | 620m | 620m | $\nu_sSiC_3(E)$ |
| | 420m | 422w | | 420w | 420w | $\nu_sMN_3(A_1)$ |
| 375vs | 382m | 380m | 418w | 376 | 376 | $\nu_{as}MN_3(E)$ |
| | | | | 335 | 335 | |
| 288m | | 275w | | | | $\delta_{as}SiC_3(E)$ |
| 239m | 233w | 235w | | | | $\delta_{as}SiC_3(A_1)$ |

[a] The data for $Ga[N(SiMe_3)_2]_3$ are taken from ref. 10. [b] Provisional assignments based on a comparison with $Ga[N(SiMe_3)_2]_3$.
vs = Very strong, s = strong, m = medium, w = weak, (sh) = shoulder

There is a striking similarity in the spectra of all of these compounds and this is in accordance with their having very similar structures. The $M[N(SiC_3)_2]_3$ skeleton ($D_3$) has vibrational modes with symmetry species $A_1$ (Raman), $A_2$ (i.r.), and $E$ (i.r. and Raman). Bürger *et al.*[10] have carried out a normal co-ordinate analysis on the i.r. and Raman data for (I) (M = Al, Ga, and In) and have made appropriate assignments of bands together with the determination of force constants and interaction constants. We have followed these assignments as far as is possible in interpreting the i.r. data for (I) (M = Sc, Ti, V, Cr, and Fe). A few features call for comment. In the $\nu_{as}(MNSi_2)$ vibration the scandium derivative has a much higher frequency (950 $cm^{-1}$) than the others (*ca.* 900 $cm^{-1}$). Since the potential energy distribution of these vibrations ($A_1$ and $E$) for (I) (M = Al, Ga, and In) showed them to be practically pure fundamentals [10] it would indicate a significant difference in the type of $\pi$-delocalizations in the $M-NSi_2$ system between scandium ($d^0$) and the other transition metals ($d^1$, $d^2$, $d^3$, $d^5$) and gallium ($d^{10}$). Considering the $Si_2N$ unit as a three-centred $\pi$-delocalized system involving silicon $d_\pi$-orbitals and the nitrogen $p_\pi$-orbital it can in principle behave either as a $\pi$-donor using the pair of electrons occupying the bonding $\pi$-orbital or as a $\pi$-acceptor using the vacant $\pi^*$ anti-bonding orbital. If it acts only as a $\pi$-donor (*i.e.* with $Sc^{3+}$) the consequent drain of electrons from the $Si_2N$ $\pi$-framework will lower the bond order and hence lower the force constant and frequency of $\nu_{as}(MNSi_2)$. On the other hand if it acts as a $\pi$-acceptor of *d*-electrons from the transition metal this will also lower the bond order

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[9] C. E. Heath and M. B. Hursthouse, personal communication.

[10] H. Bürger, J. Cichon, U. Goetze, U. Wannagat, and H. J. Wismar, *J. Organometallic Chem.*, 1971, **33**, 1.

(by occupying the $\pi$-antibonding orbital) and hence the frequency. Thus, from the i.r. spectra it seems that scandium is not particularly involved in $\pi$-bonding but the Ti, V, Cr, and Fe derivatives are, although we cannot say in the latter case whether the metal atoms are behaving as $\pi$-acceptors or $\pi$-donors. However, it is noteworthy that in $\nu_s(\mathrm{MNSi_2})$ there is no variation in the band at 820 cm$^{-1}$ ($E$ mode) along the series. The $A_1$ mode is strictly active in the Raman only but it seems likely that the band at *ca.* 790 cm$^{-1}$ in these compounds is an i.r. activated $A_1$ mode. Both $A_1$ and $E$ modes had the same frequency (824 cm$^{-1}$) in (I; M = Ga) and the potential energy analysis showed that considerable coupling with the MN$_3$ vibrations occurred. Although $\nu_s(\mathrm{MN_3})$ ($A_1$) should be inactive in the i.r. we feel that the weak bands at *ca.* 420 cm$^{-1}$ are due to this vibration and that the bands at *ca.* 380 cm$^{-1}$ are due to $\nu_{as}(\mathrm{MN_3})$ ($E$). However (I; M = V) has only one band in this

TABLE 3

| | Sc | | Ti | | V | | Cr | | Fe | |
|---|---|---|---|---|---|---|---|---|---|---|
| Possible species | *m/e* | *I* | *m/e* | *I* | *m/e* | *I* | *m/e* | *I* | *m/e* | *I* |
| $P^+$ | 525 | 1·0 | 528 | 1·0 | 531 | 1·0 | 532 | 1·0 | 536 | 1·0 |
| $(P - \mathrm{H})^+$ | | | | | | | 531 | 0·5 | | |
| $(P - \mathrm{Me})^+$ | 510 | 1·5 | 513 | 0·1 | 516 | 0·2 | 517 | 3·0 | 521 | 0·5 |
| $(P - \mathrm{CH_4})^+$ | | | 512 | 0·1 | | | | | | |
| $(P - \mathrm{2Me})^+$ | | | | | | | | | 506 | 0·6 |
| $[P - \mathrm{Si(CH_2)_2}]^+$ | | | | | | | 476 | 0·8 | | |
| $[P - \mathrm{Si(CH_2)_2Me}]^+$ | | | | | | | 461 | 0·9 | | |
| $(P - \mathrm{SiHMe_2})^+$ | | | 454 | 0·1 | | | | | | |
| $(P - \mathrm{CH_2SiMe_3})^+$ or $(P - \mathrm{NSiMe_3})^+$ | 438 | 0·1 | | | 444 | 0·1 | | | | |
| $(P - \mathrm{SiMe_4})^+$ or $(P - \mathrm{HNSiMe_3})^+$ | | | 440 | 0·2 | | | | | | |
| $(P - \mathrm{SiMe_4} - \mathrm{Me})^+$ or $(P - \mathrm{HNSiMe_3} - \mathrm{Me})^+$ | | | | | | | 429 | 0·7 | | |
| $(P - \mathrm{SiMe_4} - \mathrm{Me} - \mathrm{CH_4})^+$ | 406 | 0·1 | | | | | | | | |
| $(P - \mathrm{NSiMe_3} - \mathrm{5CH_4})^+$ | | | | | | | 389 | 2·2 | | |
| | | | | | 386 | 0·1 | | | | |
| $(P - \mathrm{L})^+$ | 365 | 7·0 | | | | | | | | |
| $(P - \mathrm{HL})^+$ | 364 | 17·0 | 367 | 0·8 | 370 | 0·2 | 371 | 39·0 | 375 | 9·0 |
| $(P - \mathrm{NSiMe_3} - \mathrm{5CH_4})^+$ | 358 | 0·3 | | | | | | | | |
| $(P - \mathrm{L} - \mathrm{Me})^+$ | | | | | | | | | 361 | 0·5 |
| $(P - \mathrm{HL} - \mathrm{Me})^+$ | 349 | 1·1 | | | | | | | | |
| $(P - \mathrm{HL} - \mathrm{CH_4})^+$ | | | 351 | 0·5 | | | 355 | 24·0 | | |
| $(P - \mathrm{HL} - \mathrm{CH_4} - \mathrm{H})^+$ | | | | | 353 | 0·1 | | | | |
| $(P - \mathrm{L} - \mathrm{2Me})^+$ | | | | | | | | | 346 | 1·0 |
| $(P - \mathrm{9Me} - \mathrm{3CH_4})^+$ | 342 | 1·8 | | | | | | | | |
| $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{CH_4})^+$ | 333 | 3·5 | | | 339 | 0·9 | 340 | 9·4 | | |
| $(P - \mathrm{HL} - \mathrm{2CH_4})^+$ | | | 335 | 0·2 | | | | | | |
| $(P - \mathrm{HL} - \mathrm{2Me} - \mathrm{CH_4})^+$ | | | | | | | 325 | 2·2 | | |
| $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{2CH_4})^+$ | 317 | 0·8 | | | | | | | | |
| $(P - \mathrm{HL} - \mathrm{3CH_4})^+$ | | | | | | | 309 | 3·0 | | |
| $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{3CH_4})^+$ | 301 | 2·1 | | | 307 | 0·1 | | | | |
| $(P - \mathrm{HL} - \mathrm{4CH_4})^+$ | | | 303 | 0·2 | | | | | | |
| | 291 | 0·1 | | | | | | | | |
| $(P - \mathrm{HL} - \mathrm{4Me} - \mathrm{CH_4})^+$ | | | | | | | 295 | 23·6 | | |
| $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{4CH_4})^+$ | 285 | 0·8 | | | | | | | | |
| $(P - \mathrm{L} - \mathrm{CH_2SiMe_3})^+$ or $(P - \mathrm{L} - \mathrm{NSiMe_3})^+$ | | | | | | | | | 289 | 7·0 |
| $(P - \mathrm{2Me})^{2+}$ | 247·5 | 0·8 | | | | | | | | |
| $(P - \mathrm{2Me} - \mathrm{CH_4})^{2+}$ | 239·5 | 0·1 | | | | | | | | |
| $(P - \mathrm{2HL} - \mathrm{Me})^+$ | 188 | 2·0 | | | | | | | | |
| $(P - \mathrm{2HL} - \mathrm{Me} - \mathrm{CH_4})^+$ | 172 | 1·0 | | | | | | | | |
| $(P - \mathrm{9Me} - \mathrm{3CH_4})^{2+}$ | 171 | 1·1 | | | | | | | | |
| $\mathrm{HL}^+$ | 161 | 3·5 | 161 | 3·5 | 161 | 0·8 | 161 | 380 | 161 | 100 |
| $(\mathrm{HL} - \mathrm{Me})^+$ | 146 | 28 | 146 | 32 | 146 | 10·5 | 146 | >500 | 146 | >500 |
| Probe temperature (°C) | 75 | | 70 | | 105 | | 75 | | 75 | |

$P = \mathrm{M[N(SiMe_3)_2]_3}$; $\mathrm{L} = \mathrm{N(SiMe_3)_2}$; *m/e* values correspond to species containing the most abundant metal isotope and $^{12}$C, $^{1}$H, $^{14}$N, $^{28}$Si; *I* values for each compound are relative to the parent ion $P^+ = 1{\cdot}0$, and are based on the intensity of the line due to the most abundant metal isotope.

TABLE 4

| | Process | Metastable ion, *m/e* | |
|---|---|---|---|
| Metal (M) | $\{P = \mathrm{M[N(SiMe_3)_2]_3};\ \mathrm{L} = \mathrm{N(SiMe_3)_2}\}$ | Obs. | Calc. |
| Sc | $P^+$ (525) $\longrightarrow$ $(P - \mathrm{CH_2SiMe_3})^+$ (438) | 365 | 365·4 |
| Sc | $(P - \mathrm{HL})^+$ (364) $\longrightarrow$ $(P - \mathrm{HL} - \mathrm{Me})^+$ (349) | 335 | 334·6 |
| Sc | $(P - \mathrm{HL} - \mathrm{Me})^+$ (349) $\longrightarrow$ $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{CH_4})^+$ (333) | 318 | 317·7 |
| Sc | $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{CH_4})^+$ (333) $\longrightarrow$ $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{2CH_4})^+$ (317) | 302 | 301·8 |
| Sc | $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{2CH_4})^+$ (317) $\longrightarrow$ $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{3CH_4})^+$ (301) | 286 | 285·8 |
| Sc | $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{3CH_4})^+$ (301) $\longrightarrow$ $(P - \mathrm{HL} - \mathrm{Me} - \mathrm{4CH_4})^+$ (285) | 270 | 269·8 |
| Sc | $(P - \mathrm{Me})^+$ (510) $\longrightarrow$ $(P - \mathrm{HL} - \mathrm{Me})^+$ (349) | 239 | 238·8 |
| V | $P^+$ (531) $\longrightarrow$ $(P - \mathrm{Me})^+$ (516) | 501 | 501·4 |
| | $\mathrm{HL}^+$ (161) $\longrightarrow$ $(\mathrm{HL} - \mathrm{Me})^+$ (146) | 132·3 | 132·4 |
| | $(\mathrm{HL} - \mathrm{Me})^+$ (146) $\longrightarrow$ $(\mathrm{L} - \mathrm{2Me})^+$ (130) | 115·6 | 115·75 |

region and we assign it to the $E$ mode. Both $\nu_s(MN_3)$ and $\nu_{as}(MN_3)$ vibrations are very strongly coupled to other vibrations in the framework and it would be unwise to infer anything about the nature of the metal–nitrogen bond from them.[11]

*Mass Spectra.*—Parent molecular ions were obtained for all the compounds (I; M = Sc, Ti, V, Cr, and Fe) together with several metal-containing fragment ions (Table 3) and some metastable peaks (Table 4). For titanium and vanadium the most abundant metal-containing ion was the parent ion $M[N(SiMe_3)_2]_3^+$ (= $P^+$) but for the other metals it was $(P - HL)^+$ where L = $N(SiMe_3)_2$. The base peak in all cases was the ligand fragment ion $(HL - Me)^+$ but the species $HL^+$ was also very abundant. Although the constitution of the species in Table 3 are not sufficiently established to justify a fragmentation pattern the data do show some common features. Thus all compounds gave $(P - Me)^+$ and $(P - HL)^+$ fragment ions. In the case of scandium the subsequent breakdown of $(P - HL)^+$ by loss of methyl radicals or methane was established by metastable peaks (Table 4) and it appears that the other compounds also favour fragments formed by the loss of several molecules of methane from $(P - HL)^+$. Bearing in mind the uncertainties involved in comparing intensities of different mass spectra it is possible to deduce an order of relative stabilities of the parent ions. Thus it is clear that loss of HL from $P^+$ and $(P - Me)^+$ constitutes a major source of free ligand base which generates the species $(HL)^+$, $(HL - Me)^+$ and other characteristic fragment ions which are also found in the mass spectrum of HL. We suggest that the higher the stability of $P^+$ the lower will be the ratio of $(HL)^+ : P^+$ or of $(HL - Me)^+ : P^+$ or the ratio of the sum of all metal-containing fragment ions to the parent ion. Independent of which ratio is chosen the vanadium species appears most stable and the chromium species least stable whilst the order of stabilities of the others is not uniquely determined. However, the majority of the data favour the stability order $V > Ti \sim Sc > Fe > Cr$. All except the titanium derivative could be sublimed *in vacuo* but the iron compound was notably thermally unstable.

The spectrum of the scandium compound is noteworthy in having strong doubly charged ions $(P - 2Me)^{2+}$ and $(P - 2Me - CH_4)^{2+}$ without the corresponding singly charged species. Also the doubly charged ion $(P - 9Me - 3CH_4)^{2+}$ has about half the intensity of the singly charged species. The spectrum of HL also shows a doubly charged fragment ion $(HL - 2Me)^{2+}$ which is much more intense than the singly charged species. The vanadium compound gave a metastable peak for loss of a methyl group from the parent ion. Some spectra of the vanadium compound also showed significant amounts (not recorded in Table 3) of the parent ion and fragment ions of the dioxygen adduct $V(O_2)L_3$ although stringent precautions were taken to exclude air. None of the other metal silylamides gave any peaks corresponding to oxygenated species although they are all sensitive to air and we infer that $[V(O_2)L_3]^+$ has enhanced stability. The compound $Cr(NPr^i_2)_3$ forms an unstable oxygenated derivative $Cr(O_2)(NPr^i_2)_3$ which gives a mass spectrum containing oxygenated fragment ions.[12]

## EXPERIMENTAL

Special precautions were taken to exclude air and moisture from chemicals and apparatus, and all experiments were carried out under nitrogen.

*Analyses.*—Titanium was determined gravimetrically as $TiO_2$ after removal of silicon by treatment with HF–$H_2SO_4$. Other metals were determined by atomic absorption spectrophotometry (Perkin-Elmer model 303). Carbon, hydrogen, nitrogen, and silicon analyses were obtained commercially (A. Bernhardt, Mülheim). Satisfactory elemental analyses could not be obtained for $Fe[N(SiMe_3)_2]_3$ due to its instability but the compound was adequately characterized by its i.r. and mass spectrum, and molecular weight. The analytical data are given in Table 1.

*Molecular Weights.*—An all-glass cryoscopic apparatus was used with thermistor-bridge temperature measurements. Determinations were carried out in benzene or cyclohexane using fluorene as calibrant.

*Infrared Spectra.*—Perkin-Elmer models 337 and 225 instruments were used covering the range 4000—200 $cm^{-1}$. Samples were examined as Nujol mulls using special cells with KBr, polythene, or CsI windows. The instability and high reactivity of the metal silylamides necessitated the use of a special mulling procedure in which the sample was dissolved in a solution of pentane containing Nujol. Evaporation of the pentane *in vacuo* left the sample suitably dispersed in Nujol. After obtaining a spectrum the sample was exposed to the air and the spectrum was taken again to identify bands due to the products of oxidation and hydrolysis.

*Mass Spectra.*—An AEI MS 902 instrument operating at 70 eV and *ca.* $10^{-7}$ mmHg pressure was used with a special sampling device for direct insertion of the reactive compound designed by P. Cook. The elemental composition of each peak was checked by comparing the isotopic distribution for the species with that calculated using a computer programme developed by Dr. K. D. Sales. The results with intensities uncorrected for isotopic abundance are presented in Tables 3 and 4.

*N.m.r. Spectra.*—A Varian A-60 instrument was used to obtain the n.m.r. spectra of 10% solutions of $Sc[N(SiMe_3)_2]_3$ in benzene and in carbon tetrachloride with TMS internal standard.

*Preparations.*—(i) $Sc[N(SiMe_3)_2]_3$. Lithium bistrimethylsilylamide [0·094 mol; from 60·0 ml of 1·56 N n-butyl-lithium and $(Me_3Si)_2NH$ (20 ml, 0·1 mol)] in tetrahydrofuran (80 ml) was cooled (0°) and treated in portions with $ScCl_3$ (0·030 mol, 4·6 g). The system was allowed to attain room temperature and was stirred for 24 h before all solvent was removed *in vacuo*. From the pentane extract of the residue were obtained thin colourless needles of

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[11] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 980.

[12] D. C. Bradley, C. W. Newing, J. C. W. Chien, and W. Kruse, *Chem. Comm.*, 1970, 1178; D. C. Bradley, M. B. Hursthouse, and C. W. Newing, *Chem. Comm.*, 1971, 411; D. C. Bradley and C. W. Newing, unpublished results (mass spectra).

$Sc[N(SiMe_3)_2]_3$ (analyses in Table 1). The n.m.r. spectra gave single sharp peaks in benzene ($\tau$ 9·667) and carbon tetrachloride ($\tau$ 9·773).

(ii) $Ti[N(SiMe_3)_2]_3$. $TiCl_3$ (0·032 mol, 5·0 g) was treated with trimethylamine (125 ml) to form $TiCl_3(Me_3N)_2$. Lithium bistrimethylsilylamide (0·096 mol, 16·03 g) was next added in portions and the mixture refluxed for 72 h. After evaporating off all solvent *in vacuo* the residue was extracted with pentane and gave bright blue crystals (10·2 g, 60·4%; analysis in Table 1). Attempts to sublime the compound *in vacuo* were unsuccessful due to decomposition.

(iii) $V[N(SiMe_3)_2]_3$. The complex $VCl_3(Me_3N)_2$ (0·026 mol, 7·16 g) was added to a cooled benzene solution of lithium bistrimethylsilylamide (0·077 mol, 12·86 g) and then stirred at room temperature for 48 h. After filtration to remove lithium chloride the filtrate was concentrated and kept at 0°. Small brown crystals (4·90 g, 35·5%) of $V[N(SiMe_3)_2]_3$ (analyses in Table 1) were deposited. The compound sublimed at 95°, 0·005 mmHg.

(iv) $Cr[N(SiMe_3)_2]_3$. Lithium bistrimethylsilylamide [0·0234 mol; from 1·56 N n-butyl (15 ml) and $(Me_3Si)_2NH$ (5·2 ml, 0·0248 mol)] in tetrahydrofuran (25 ml) was treated with $CrCl_3$ (0·076 mol, 1·2 g) and then refluxed for 2 h. After filtration to remove lithium chloride the filtrate was evaporated *in vacuo* leaving a green solid which sublimed at 80°, 0·005 mmHg (1·3 g, 32%). Molecular weight measurements in cyclohexane (Found: 519 ± 17, 491 ± 30, 550 ± 30; Calc.: 533) proved that $Cr[N(SiMe_3)_2]_3$ was monomeric.

(v) $Fe[N(SiMe_3)_2]_3$. This was prepared in the same manner as for $Cr[N(SiMe_3)_2]_3$. The dark green product sublimed at 80°, 0·005 mmHg with decomposition and a purer material was obtained by crystallization from pentane. Molecular weight determination in cyclohexane showed (Found: 502 ± 24; Calc.: 537) $Fe[N(SiMe_3)_2]_3$ was monomeric.

(vi) *Attempts to Prepare* $M[N(SiMe_3)_2]_3$ (M = Mn or Co). The following reactions were tried: (*a*) addition of $LiN(SiMe_3)_2$ to $MnCl_2$ and CuI in THF; or to $MnCl_3(THF)_4$ or $MnCl_3(Et_3N)_3$ or $K_2MnCl_5$; (*b*) electrolytic oxidation of $Mn[N(SiMe_3)_2]_2$ in THF; (*c*) addition of $LiN(SiMe_3)_2$ to $CoCl_2$ and CuCl; (*d*) addition of $(Me_3Si)_3N$ to $CoF_3$. In no case was any tris-silylamido-metal compound isolated.

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