Preparation, Properties, and Crystal Structures of the Monochlorotris[bis(trimethylsilyl)amido]-compounds of Titanium, Zirconium, and Hafnium

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The monomeric compounds $[MCl\{N(SiMe_3)_2\}_3]$ (M = Ti, Zr, or Hf) have been prepared by the reaction of MCl_4 with excess of $Li[N(SiMe_3)_2]$. Mass and i.r. spectra have been obtained, together with variable-temperature ^1H n.m.r. spectra which shows evidence of fluxional behaviour of the bulky ligands. Molecular structures have been determined by single-crystal *X*-ray diffraction for the whole series. The three compounds are isostructural in space group *R*3*c* with lattice parameters (hexagonal setting) *a* = *b* = 18.076, 18.317, 18.304 and *c* = 17.208, 17.078, and 17.085 Å respectively for Ti, Zr, and Hf. Structure analysis by the heavy-atom method and refinement by full-matrix least-squares has given *R* values of 0.048, 0.029, and 0.053 based on 577, 1 182, and 1 195 unique data for Ti, Zr, and Hf respectively. The structural and spectroscopic results are discussed in terms of steric effects and the nature of the metal–ligand bonding.

BÜRGER and Wannagat[1] isolated $[TiCl_3\{N(SiMe_3)_2\}]$ from the reaction (1). The formation of $Na_2[TiCl_6]$

$$4TiCl_4 + 3Na[N(SiMe_3)_2] \longrightarrow 3[TiCl_3\{N(SiMe_3)_2\}] + Na_2[TiCl_6] + NaCl \quad (1)$$

clearly reduces the yield of titanium trichloride bis(trimethylsilyl)amide. However, using lithium bis(trimethylsilyl)amide we were able to obtain titanium chloride tris[bis(trimethylsilyl)amide].[2] The remaining chloride could not be replaced, even using excess of the lithium silylamide reagent. Further work has shown that zirconium and hafnium form analogous compounds,[3] and together with earlier work on thorium,[4] it has been established that a complete series of compounds $[MCl\{N(SiMe_3)_2\}_3]$ (M = Ti, Zr, Hf, or Th) is available for study. Since the lower aliphatic dialkylamido-compounds $M(NR_2)_4$ (M = Ti, Zr, or Hf; R = Me, Et, Pr, *etc.*) can readily be obtained[5] by a similar route it seems likely that steric hindrance is mainly responsible for the unexpected resistance of all of the $[MCl\{N(SiMe_3)_2\}_3]$ compounds to complete substitution of chlorine. Variable-temperature n.m.r. spectra have revealed interesting differences in fluxional behaviour of the bulky silylamide ligands in this series of compounds and so it was clearly desirable to determine their crystal and molecular structures to provide a quantitative assessment of the steric factors. We now report full details of the preparation and properties of these compounds (M = Ti, Zr, and Hf) including single-crystal *X*-ray analyses. Whilst this manuscript was in preparation Andersen[6] also reported work on some of these compounds.

TABLE 1

Some physical properties and spectroscopic data for the complexes $[MCl\{N(SiMe_3)_2\}_3]$

M	Colour	M.p. (°C)	Volatility (°C, mmHg)	Infrared bands (cm^{-1})[a]		Proton n.m.r. (100 MHz)[b]	
				M–Cl stretch	M–N stretch	Low temp.	High temp.
Ti	Orange	204—205	decomp. 150, 10^{-3}	394	430	0.43, 0.63	0.55[c]
Zr	White	183—188	120, 10^{-3}	349	400, 408[d]	0.29, 0.48	0.38[e]
Hf	White	186—189	100, 10^{-3}	330	395, 397[d]	0.28, 0.47	0.39[f]

[a] Nujol mulls. [b] δ values in p.p.m. (relative to $SiMe_4$) in C_7D_8. [c] Coalescence temperature 34 °C. [d] Unresolved doublet. [e] Coalescence temperature *ca.* 5 °C. [f] Coalescence temperature *ca.* 4 °C.

EXPERIMENTAL

(*a*) *Chemical.*—Although these compounds proved to be less reactive than other dialkylamides,[4] precautions to avoid hydrolysis were taken throughout and reactions were carried out under oxygen-free nitrogen.

Analyses. Metal (as MO_2) and chloride (as AgCl) analyses were carried out gravimetrically (macro-scale) after dissolving samples in nitric acid. Carbon, H, and N analyses were obtained commercially (Butterworth Labs. Ltd.).

Mass spectra. A special sampling device[7] for direct insertion of reactive compounds was used with an A.E.I. MS902 machine operating at 70 eV and *ca.* 10^{-8} mmHg pressure.† Sample temperatures for the compounds of Ti, Zr, and Hf were 121, 77, and 91 °C respectively. Parent ions were rather weak but some fragment ions, *e.g.* (P − Me). $[P - HN(SiMe_3)_2]$, $[P - Me - HN(SiMe_3)_2]$, were very strong.

Infrared spectra. A Perkin-Elmer 225 machine was used with KBr or CsI cell windows. Nujol-mull spectra were obtained as described previously.[8] Some metal–ligand band frequencies are listed in Table 1.

N.m.r. spectra. A Varian HA 100 machine was used with variable-temperature probe unit. Solutions were *ca.* 0.05 mol dm^{-3} in perdeuteriotoluene with internal $SiMe_4$ as calibrant. Chemical-shift data are given in Table 1.

Preparations. (1) $[TiCl\{N(SiMe_3)_2\}_3]$. Titanium tetra-

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

chloride (4.8 cm^3, 0.043 mol) in pentane (20 cm^3) was added slowly with stirring to a solution of Li[N(SiMe$_3$)$_2$] (0.17 mol), obtained by allowing the amine NH(SiMe$_3$)$_2$ (38 cm^3) to react with n-butyl-lithium (109 cm^3 of a 10% w/v solution in hexane) followed by addition of tetrahydrofuran (38 cm^3). The reaction was moderated by cooling during addition of the reactants followed by refluxing for 3 h and then leaving to cool overnight. After evaporation of solvents *in vacuo* the residue was extracted with pentane and filtered to remove LiCl. Concentration of the filtrate gave orange crystals (4.7 g, 19.6%). The compound was recrystallized from pentane to constant melting point (204—205 °C) (Found: C, 38.5; H, 8.45; Cl, 6.30; N, 7.45; Ti, 8.60. $C_{18}H_{54}ClN_3Si_6Ti$ requires C, 38.3; H, 9.15; Cl, 6.30; N, 7.45; Ti, 8.50%). Accurate mass measurement on [P − Me]$^+$ gave *M* 546.188 144; $^{12}C_{17}{}^{1}H_{51}{}^{35}Cl^{14}N_3{}^{28}Si_6{}^{46}Ti$ requires 546.191 342. The chief bands in the i.r. spectrum (200—1 300 cm^{-1} region) were 1 265(sh), 1 250vs, 1 095w, 1 055w, 905br (sh), 850vs, br, 780vs, br, 700vs, 680vs, br, 623vs, 430vs, 393vs, 370m, 325w, 299w, 270w, and 244w cm^{-1}.

TABLE 2

Crystal data and details of intensity measurement and structure refinement for [MCl{N(SiMe$_3$)$_2$}$_3$] (M = Ti, Zr, or Hf) [a]

Crystal data	Ti	Zr	Hf
M	564.5	607.8	695.1
a/Å } Hexagonal axes	18.076(9)	18.317(3)	18.304(3)
c/Å } Hexagonal axes	17.208(11)	17.078(4)	17.085(13)
U/Å^3	4 869.8	4 962.2	4 957.2
D_c/g cm^{-3}	1.15	1.23	1.40
F(000)	1 836	1 944	2 136
μ(Mo-K_α)/cm^{-1}	5.8	5.7	33.0
Data collection			
Crystal size/mm	0.38 × 0.23 × 0.20	0.22 × 0.09 × 0.06	0.64 × 0.25 × 0.12
Crystal faces			{001}, {1 − 10}, {110}
$\theta_{min.}$,$\theta_{max.}$/°	2.0, 21.0	1.5, 30	1.5, 30
Scan parameters, *A*,*B* (width, $\omega = A + B\tan\theta$)		0.8, 0.2	0.75, 25
Horizontal aperture parameters, *A* and *B* (aperture = $A + B\tan\theta$)		3.0, 0.5	4.0, 0.0
Total data recorded	612	1 838	1 835
Unique observed data $F_o > 3\sigma(F_o)$	577	1 182	1 195
Refinement			
No. of parameters	87	160	87
Weighting scheme coefficient *g* in $w = 1/[\sigma^2(F_o) + g\|F_o\|^2]$	*b*	0.0003	0.0006
Final $R = \Sigma\Delta F/\Sigma\|F_o\|$	0.048	0.0289	0.0532
$R' = \Sigma w\Delta^2/\Sigma(wF_o)^2$	0.048	0.0283	0.0454

Space group = *R*3*c*, *Z* = 6

[a] The estimated standard deviations are given in parentheses, in this and other tables throughout this paper. [b] For this compound, a Hughes-type weighting scheme, $w^{\frac{1}{2}} = F_o/F^*$ for $F_o < F^*$ and $w^{\frac{1}{2}} = F^*/F_o$ for $F_o > F^*$ was used with F^* 70.0 on an absolute scale giving reasonable agreement analyses.

(2) [ZrCl{N(SiMe$_3$)$_2$}$_3$]. Zirconium tetrachloride (6 g, 0.025 mol) was added in portions to a vigorously stirred, ice-cold solution of Li[N(SiMe$_3$)$_2$] (17 g, 0.10 mol) in tetrahydrofuran (100 cm^3). The mixture was kept at room temperature for 2 d, then evaporated to dryness *in vacuo* and the residue extracted with pentane and filtered. The solid obtained by evaporating the filtrate to dryness was sublimed at 120 °C (10^{-3} mmHg) and the sublimate recrystallized from pentane as white needles (3 g, 19.2%; m.p. 183—188 °C) (Found: C, 35.75; H, 9.35; Cl, 5.75; N, 7.00; Zr, 15.1. $C_{18}H_{54}ClN_3Si_6Zr$ requires C, 35.55; H, 8.90; Cl, 5.85; N, 6.90; Zr, 15.0%). Accurate mass measurement on the parent ion gave *M* 605.167 629; $^{12}C_{18}{}^{1}H_{54}{}^{35}Cl^{14}N^{28}Si_6{}^{90}Zr$ requires 605.166 880. Infrared spectrum (200—1 300 cm^{-1} region): 1 265vs, (sh), 1 250vs, 1 180w, 1 075w, (sh), 905vs, 855vs, br, 782vs, 765(sh), 696vs, 667vs, 640vs, 621vs, 408vs, 400vs, 387s, (sh), 348vs, 290m, 267w, 245m, and 233w cm^{-1}.

(3) [HfCl{N(SiMe$_3$)$_2$}$_3$]. Hafnium tetrachloride (5 g, 0.015 6 mol) was added portion-wise with vigorous stirring to an ice-cold solution of Li[N(SiMe$_3$)$_2$] (7.81 g, 0.046 8 mol) in tetrahydrofuran (40 cm^3). After standing for 2 d at room temperature the mixture was refluxed for 4 h, cooled, and the solvent evaporated *in vacuo*. The residue was extracted with pentane, filtered, evaporated to dryness, and the solid sublimed at 100 °C (10^{-3} mmHg). The sublimate was recrystallized from pentane as white needles (0.7 g, 6.5%; m.p. 186—189 °C) (Found: Cl, 4.90; Hf, 25.5. $C_{18}H_{54}ClHfN_3Si_6$ requires Cl, 5.10; Hf, 25.7%). Accurate mass measurement on the parent ion gave *M* 695.209 738. $^{12}C_{18}{}^{1}H_{54}{}^{35}Cl^{180}Hf^{14}N_3{}^{28}Si_6$ requires 695.209 184. Infrared spectrum (200—1 300 cm^{-1} region): 1 260(sh), 1 243vs, 965m, (sh), 903vs, 870—845 (unresolved doublet, vs), 780vs, 760(sh), 698vs, 665vs, 635vs, 615vs, 397—395 (unresolved doublet, vs), 330s, 325(sh), 285w, 260w, and 240w cm^{-1}.

(*b*) X-*Ray Crystallography*.—Crystals of all three compounds were mounted under nitrogen in Lindemann capillaries. Unit-cell parameters and the space group were determined from oscillation and Weissenberg photographs. The crystal system was found to be trigonal, with Laue group $\bar{3}m$, and limiting reflection conditions (hkl : $\bar{h} + k + l = 3n$, $h\bar{h}l = 2n$) indicated space group *R*3*c* or $R\bar{3}c$. Accurate cell dimensions and intensity data were obtained diffractometrically as described in previous publications from this laboratory (Ti as in ref. 9; Zr, Hf as in ref. 10).

The crystal data and details of the intensity-data collection are summarized in Table 2. Trial calculations showed that, with the crystals used, absorption corrections could reasonably be neglected for the compounds of Ti and Zr, but were applied to the hafnium derivative.

The structure was solved for the titanium compound by using the Patterson method (Ti, Cl, and Si atoms) and developed and refined by successive difference electron-density syntheses and full-matrix least squares. The structures of the compounds of Zr and Hf were refined starting from the atomic parameters of the titanium structure and successful refinements were based on *R*3*c* as the common space group. Details of the structure refinements are also given in Table 2. Hydrogen atoms were not included in the titanium structure but all were located experimentally and refined isotropically for Zr. The resulting co-ordinates were used to calculate positions for the hydrogens in the hafnium structure which were included in the calculation of F_c but not refined.

A list of the final non-hydrogen atom co-ordinates is given in Table 3. Anisotropic thermal parameters for these atoms and the co-ordinates and isotropic thermal parameters for the hydrogen atoms are given, along with lists of $|F_o|$ and F_c, in Supplementary Publication No. SUP 22805 (21 pp.).[*]

Neutral-atom scattering factors were taken from refs. 11 (H) and 12 (other atoms), with those for the heavier atoms corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 13. All calculations were performed using the program SHELX [14] and diagrams drawn using ORTEP [15] and PLUTO.[16]

RESULTS AND DISCUSSION

Some physicochemical data are given in Table 1. The compounds were all noticeably less reactive than metal dialkylamides containing less bulky ligands.[5] The titanium compound was the least stable as indicated by difficulties in subliming it *in vacuo* and obtaining a mass spectrum. A solution of the titanium compound in C_7D_8 sealed under nitrogen showed n.m.r. signals due to decomposition products after a few days when exposed to light but a similar sample of the zirconium compound kept over 2 years shows no sign of decomposition. The colour of the light-sensitive titanium compound (d^0) is presumably due to a charge-transfer transition tailing into the visible region. A ligand-to-metal transition should occur at lower energy for Ti than for Zr or Hf because titanium is more readily reduced to the III state. This would explain why the titanium compound is coloured, while the zirconium and hafnium derivatives are white. The higher melting point of the titanium compound can be correlated with its smaller molar volume (Table 2) and more compact crystal structure.

All three compounds gave similar i.r. spectra characteristic of the $N(SiMe_3)_2$ ligand [17] with additional bands corresponding to M–Cl and MN_3 stretching vibrations (Table 1). The metal(III) tris(silylamides), $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, V, Cr, or Fe), give bands at *ca.* 390 cm^{-1} which were assigned to the antisymmetric MN_3 stretching vibration,[8,17] and it would be expected that $[TiCl\{N(SiMe_3)_2\}_3]$ would have MN_3 bands at a higher frequency, hence the assignment of the band at **430** cm^{-1} to this mode and that at **394** cm^{-1} to the Ti–Cl stretch. The corresponding vibrations in the compounds of Zr and Hf occur as expected at lower frequencies. In fact, using the simple relationship between force constant, frequency, and reduced mass for a 'diatomic' vibration, the force constants are practically the same for Ti, Zr, and Hf, both for M–Cl and M–N vibrations, with the M–Cl values greater than for M–N. It is also noteworthy that the compounds of Zr and Hf showed splitting of the MN_3 band in accordance with the requirement of two M–N vibrations for $ClMN_3$ with local C_{3v} symmetry. Nevertheless, it must be remembered that the bands discussed here are probably subject to extensive coupling.[17] Our results were substantially confirmed by those of Andersen [6] on the compounds of Zr and Hf, although our melting points are slightly higher, perhaps due to additional recrystallizations of our products. Of particular interest was Andersen's success in preparing the methyl metal compounds $[MMe\{N(SiMe_3)_2\}_3]$ (M = Zr or Hf) by reaction of $[MCl\{N(SiMe_3)_2\}_3]$ with methyllithium.

TABLE 3

Fractional co-ordinates * (× 10^4) of the non-hydrogen atoms

Atom	M	*x*	*y*	*z*
M	Ti	0	0	0
	Zr	0	0	0
	Hf	0	0	0
Cl	Ti	0	0	1 313(3)
	Zr	0	0	1 402(1)
	Hf	0	0	1 426(3)
N	Ti	280(5)	1 153(3)	−274(5)
	Zr	300(2)	1 214(2)	−299(2)
	Hf	285(6)	1 202(6)	−261(6)
Si(1)	Ti	1 005(2)	1 817(2)	−1 010(3)
	Zr	1 013(1)	1 857(1)	−1 031(1)
	Hf	1 018(3)	1 859(3)	−998(3)
Si(2)	Ti	−145(2)	1 630(2)	335(3)
	Zr	−118(1)	1 694(1)	312(1)
	Hf	−121(2)	1 690(2)	351(2)
C(11)	Ti	1 870(9)	2 829(9)	−546(9)
	Zr	1 894(4)	2 854(4)	−613(5)
	Hf	1 890(10)	2 856(10)	−570(11)
C(12)	Ti	1 512(9)	1 306(9)	−1 559(8)
	Zr	1 489(5)	1 307(4)	−1 557(4)
	Hf	1 491(12)	1 308(12)	−1 505(11)
C(13)	Ti	503(8)	2 152(9)	−1 801(8)
	Zr	531(4)	2 179(4)	−1 826(4)
	Hf	530(10)	2 185(10)	−1 785(10)
C(21)	Ti	598(9)	2 181(10)	1 201(8)
	Zr	582(5)	2 239(6)	1 161(4)
	Hf	582(12)	2 222(12)	1 199(8)
C(22)	Ti	−278(9)	2 486(10)	−172(9)
	Zr	−275(5)	2 506(5)	−196(4)
	Hf	−269(12)	2 511(12)	−166(9)
C(23)	Ti	−1 230(8)	867(9)	706(9)
	Zr	−1 181(4)	898(4)	679(5)
	Hf	−1 148(12)	887(9)	698(10)

* As referred to the hexagonal axes.

The monochlorides gave some interesting ^1H n.m.r. spectra over a range of temperature. The limiting high-temperature spectrum for each compound was a single sharp peak (Table 1) due to the equivalence of all protons. The titanium compound had a greater downfield chemical shift than the zirconium and hafnium derivatives, but it would be unwise to attempt to relate this

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

difference to any difference in bonding in these molecules because of the proximity of the chlorine to the Si–Me groups. Our chemical-shift data for the Zr and Hf derivatives are significantly different from those of Andersen [6] but different solvents were used. On lowering the temperature, line-broadening occurred, eventually leading to splitting into two equal peaks (Table 1). The simplest interpretation is that rotation of each $N(SiMe_3)_2$ ligand about the M–N axis is restricted, giving at low temperature a frozen conformation of three equivalent silylamide ligands with each ligand having magnetically non-equivalent trimethylsilyl groups (proximal and distal to the chlorine). Such a configuration is enantiomorphic but the enantiomers are indistinguishable by n.m.r. This is in agreement with the molecular structure determined by *X*-ray crystallography which it is reasonable to suppose could represent the low-energy conformation in solution. The titanium compound exhibited a much higher coalescence temperature (34 °C) than those of Zr and Hf (4—5 °C); this is understandable on steric grounds. Thus the smaller Ti atom is more crowded than Zr and Hf, and its silylamide ligands experience a higher barrier to rotation. Interestingly, Andersen [6] reported that the methylhafnium tris(silylamide) gave a coalescence temperature of *ca.* −25 °C and this suggests greater freedom of rotation in this compound than in the monochloride. However, the difference in chemical shifts between proximal and distal $SiMe_3$ groups was much less in the methyl (0.10 p.p.m.) than in the chloro-derivative (0.19 p.p.m.) and this would lead to a lower coalescence temperature, all other things being equal. On steric grounds the much larger thorium atom should provide more freedom of rotation for the silylamide groups in $[ThCl\{N(SiMe_3)_2\}_3]$, and the ^1H n.m.r. spectrum gave a single peak ($\delta = 0.40$ p.p.m. in C_6H_6 relative to $SiMe_4$).[3] Not surprisingly, we have found that this compound shows no splitting down to −100 °C. Similarly the methyl and tetrahydridoborato-derivatives $[ThMe\{N(SiMe_3)_2\}_3]$ and $[Th(BH_4)\{N(SiMe_3)_2\}_3]$ gave single $SiMe_3$ peaks down to −65 and −80 °C respectively.[18] It seems, therefore, that the interesting variation in fluxional behaviour of the series of compounds $[MCl\{N(SiMe_3)_2\}_3]$ (M = Ti, Zr, Hf, or Th) can be understood in terms of decreasing intramolecular congestion as the size of the central atom is increased. However, it should also be borne in mind that rotation about the M–N bonds would also be restricted by ligand-to-metal π bonding and this would be expected to change in descending the series.

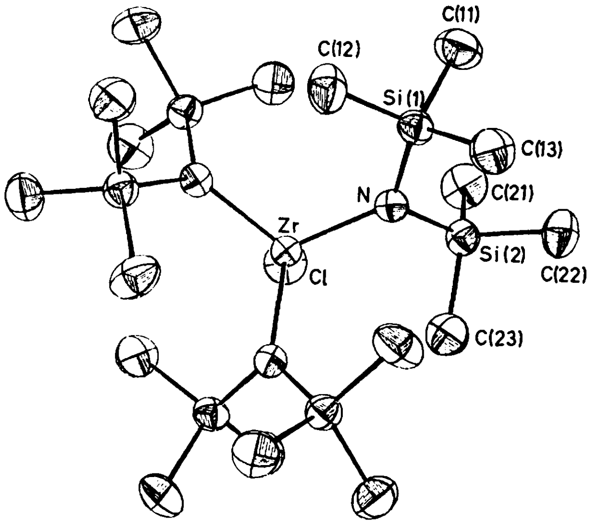

FIGURE 1 ORTEP drawing of the $[ZrCl\{N(SiMe_3)_2\}_3]$ molecule. Vibrational ellipsoids are drawn at the 50% probability level

The *X*-ray diffraction studies show the three compounds (M = Ti, Zr, or Hf) to be isostructural with a crystallographically imposed C_3 symmetry and distorted tetrahedral geometry. A single molecule is shown in Figure 1 along with the atom-numbering scheme used. A list of bond lengths and angles is given in Table 4. The overall molecular geometry reflects strongly the bulky nature of the silylamide ligands. Not only are the tetrahedral Cl–M–N angles less than 109°, but the compression in the lower half of the $M[N(SiMe_3)_2]_3$ grouping results in an unsymmetrical alignment of the ligand with respect to the M–N bonds, with M–N–Si angles of *ca.* 116° (upper, *i.e.* proximal to Cl) and *ca.* 127° (lower, *i.e.* distal to Cl). Some idea of the closeness of the ligand packing in the molecule is given by the interligand contacts listed in Table 5. The geometry found for the silylamide ligand (*i.e.* fairly long Si–N distances and decreased Si–N–Si angles, <120°) could likewise be a result of steric crowding but it could also partly arise from electronic effects such as π bonding. The effects of the packing forces on molecular geometry seem to be negligible, considering the loose nature of the molecular packing (Figure 2) in which the shortest intermolecular Me • • • Me contact is 3.88 Å.

Bearing in mind that these molecules involve the d^0 metals in abnormally low co-ordination, there must be a tendency for the metal to gain a greater share of electrons by ligand-to-metal π bonding. In the limit, an 18-electron configuration could be attained by π bonding with the aid of two pairs of electrons from chlorine and one pair from each nitrogen, although this does not seem very likely. However, comparison of M–Cl with M–N distances for each molecule shows an interesting trend with Δ(MCl — MN) = 0.319, 0.324, and 0.387 Å for Ti, Zr, and Hf. This suggests that *either* the M–Cl bond gets relatively weaker *or* the M–N bond gets relatively stronger (or both) in the sequence Ti, Zr, Hf. In fact all of these values of Δ(MCl — MN) are greater than the value of *ca.* 0.29 Å expected for the difference between covalent Cl and sp^2-hybridized N. This could be explained if N→M π bonding is more effective than Cl→M π bonding in the order Hf > Zr > Ti. Alternatively the data can be compared in another way. Thus the covalent radius of Ti is *ca.* 0.13 Å less than that of Zr and the differences Δ(ZrCl — TiCl) and Δ(ZrN — TiN) are 0.135 and 0.130 Å respectively, which seems normal. For Zr and Hf the covalent radii differ by only 0.01 Å

(Zr > Hf), but we find for Δ(ZrCl — HfCl) and Δ(ZrN — HfN) values of —0.042 and +0.03 Å respectively. From this it appears that the Hf–Cl distance is 0.05 Å too long and the Hf–N distance is 0.02 Å short. One explanation of this is that N→Hf π bonding is greater than N→Zr π bonding and this is consistent with other evidence suggesting that *5d* transition metals are better at π bonding with nitrogen than the *4d* metals. Thus tantalum readily forms $M(=NR)(NR_2)_3$ compounds in contrast to niobium,[19] tungsten gives $M(=NR)_2(NR_2)_2$,[20] and osmium forms $Os(=NR)O_3$,[21] $Os(=NR)_2O_2$,[22] and $Os(=NR)_3O$.[22] If there is greater N→M π bonding in the hafnium compound compared with Zr then it should be reflected in the Si–N distances because N→M π bonding will be at the expense of N→Si π bonding. Unfortunately the data on the hafnium compound are not as accurate as those for Zr and whilst N–Si(1) is significantly longer in the former compound than in the latter, N–Si(2) appears to be shorter. In connection with this it is interesting to note that the very intense i.r. bands due to the antisymmetric NSi_2 stretching vibration show only a small variation in frequency from Ti (905) to Zr (905) and Hf (903 cm^{-1}); this suggests very little change in the degree of N→Si π bonding. However, the crystal structures show very clearly the distortion enforced on the silylamide ligands in these crowded molecules, with Cl–M–N angles of *ca.* 104, M–N–Si(1) *ca.* 127, and M–N–Si(2) *ca.* 116°.

TABLE 4

Bond lengths (Å) and angles (°)

	Ti	Zr	Hf
(*a*) Bond lengths			
M–Cl	2.259(6)	2.394(2)	2.436(5)
M–N	1.940(10)	2.070(3)	2.040(10)
N–Si(1)	1.787(9)	1.766(3)	1.793(11)
N–Si(2)	1.759(12)	1.766(4)	1.762(12)
Si(1)–C(11)	1.89(1)	1.871(6)	1.87(2)
Si(1)–C(12)	1.85(2)	1.858(6)	1.84(2)
Si(1)–C(13)	1.90(2)	1.869(6)	1.87(2)
Si(2)–C(21)	1.92(1)	1.861(7)	1.86(2)
Si(2)–C(22)	1.89(2)	1.865(6)	1.88(2)
Si(2)–C(23)	1.86(1)	1.863(6)	1.81(2)
(*b*) Angles			
Cl–M–N	104.1(3)	104.3(1)	102.6(3)
N–M–N	114.3(3)	114.1(1)	115.4(2)
Si–N–Si	116.5(6)	116.6(2)	116.1(6)
M–N–Si(1)	127.2(6)	126.9(2)	125.6(6)
M–N–Si(2)	116.0(5)	116.2(2)	118.1(5)
N–Si(1)–C(11)	109.0(6)	111.7(3)	111.6(8)
N–Si(1)–C(12)	113.9(6)	111.9(2)	111.3(6)
N–Si(1)–C(13)	114.6(6)	114.5(2)	113.8(6)
C(11)–Si(1)–C(12)	108.8(7)	107.7(3)	108.2(9)
C(11)–Si(1)–C(13)	106.9(7)	106.4(3)	106.2(8)
C(12)–Si(1)–C(13)	103.3(7)	104.1(3)	105.5(9)
N–Si(2)–C(21)	110.7(7)	111.9(3)	111.8(7)
N–Si(2)–C(22)	113.1(6)	113.6(3)	113.1(6)
N–Si(2)–C(23)	113.5(6)	110.6(2)	108.2(6)
C(21)–Si(2)–C(22)	106.0(7)	106.0(4)	106.7(8)
C(21)–Si(2)–C(23)	108.8(7)	109.1(4)	109.6(9)
C(22)–Si(2)–C(23)	104.3(7)	105.2(3)	107.3(9)

TABLE 5

Intramolecular interligand contacts (Å)

Contact *	Ti	Zr	Hf
Cl · · · N	3.32	3.53	3.50
Cl · · · C(21)	3.53	3.71	3.67
Cl · · · C(23)	3.46	3.53	3.46
C(12) · · · C(13′)	3.42	3.55	3.56
C(11) · · · C(23′)	3.79	3.93	>4.00

* Primed atoms generated by *y* — *x*, — *x*, *z*.

With regard to $[TiCl\{N(SiMe_3)_2\}_3]$, the structural data in Table 4 may be compared with data for three other related compounds. One is the linear polymer $[\{(Me_3SiN)TiCl_2(NSiMe_3)\}_\infty]$ which has five-co-ordinated titanium with bridging chloride and $NSiMe_3$ groups.[23] The terminal Ti–Cl distance is 2.21 Å and the Ti–N distance is 1.89 Å; both are significantly shorter than the corresponding bonds in $[TiCl\{N(SiMe_3)_2\}_3]$. In fact the metal–ligand distances in five-co-ordinated titanium would be expected to be slightly longer than in a comparable four-co-ordinated molecule. Nevertheless, it must be remembered that the ligand environment of titanium with two bridging $NSiMe_3$ ligands, two bridging chlorines, and one terminal chlorine is rather different from the titanium in $[TiCl\{N(SiMe_3)_2\}_3]$ and electrostatic considerations could be more important than steric factors in affecting these bond distances. Another comparable compound is $[Ti(\eta\text{-}C_5H_5)Cl_2\{N(SiMe_3)_2\}]$ [24] which has Ti–Cl 2.268, 2.286, Ti–N 1.882, and Si–N 1.80, 1.77 Å. In this case the Ti–Cl distances are slightly longer and the Ti–N distance rather shorter than in $[TiCl\{N(SiMe_3)_2\}_3]$. However, the presence of the π-cyclopentadienyl group prevents a strict comparison,

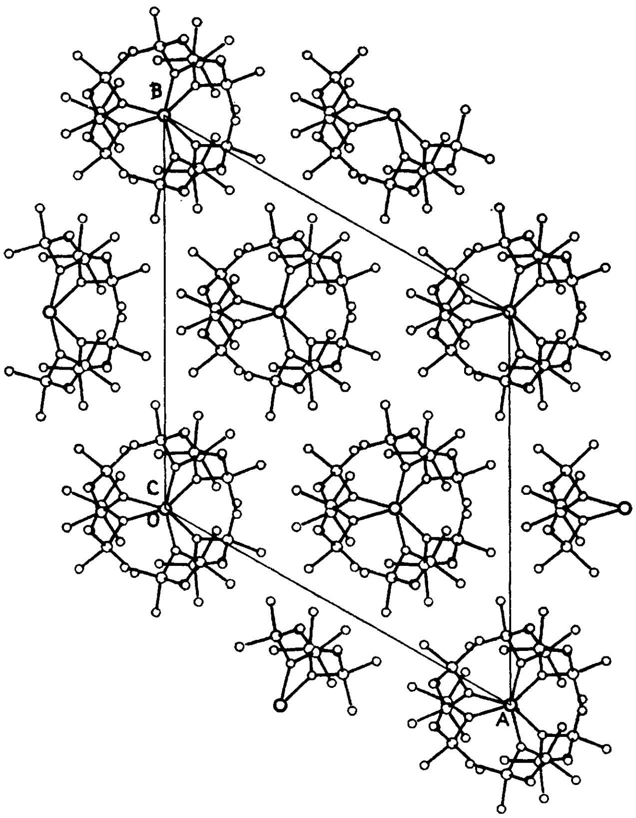

FIGURE 2 The unit-cell contents viewed along *c*

although the shorter Ti–N bond is associated with slightly longer Si–N bonds (1.80 and 1.77 Å), consistent with enhanced N→Ti π bonding in $[Ti(\eta\text{-}C_5H_5)Cl_2\{N(SiMe_3)_2\}]$. Finally, it is interesting to compare bond distances in $[TiCl\{N(SiMe_3)_2\}_3]$ with those in the trigonal three-co-ordinated titanium(III) compound $[Ti\{N(SiMe_3)_2\}_3]$ [8] (Ti–N 1.929 and Si–N 1.750 Å).[25] With less steric hindrance and the lower co-ordination number, the latter would be expected to have a shorter Ti–N distance, but these factors are opposed by the lower oxidation state, which causes a lengthening of the bond. Actually the Ti–N bond is slightly shorter in the titanium(III) compound, but its shorter Si–N distance suggests less N→Ti π bonding than in $[TiCl\{N(SiMe_3)_2\}_3]$, and this would be expected.

In summary, the crystallographic results give a quantitative measure of the steric compression in these isostructural molecules and it is clear why the introduction of a fourth bulky ligand is prohibited.

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REFERENCES

[1] H. Bürger and U. Wannagat, *Monatsch.*, 1963, **94**, 761.

[2] C. Airoldi and D. C. Bradley, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 155.

[3] C. Airoldi, D. C. Bradley, and H. Chudzynska, *Proc.* 18*th Internat. Conf. Co-ordination Chem., Sao Paulo*, 1977, 207.

[4] D. C. Bradley, J. S. Ghotra, and F. A. Hart, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 209.

[5] D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857.

[6] R. A. Andersen, *Inorg. Chem.*, 1979, **18**, 1724.

[7] R. G. Copperthwaite and P. Cook, *Chem. and Ind.*, 1973, 906.

[8] E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J.C.S. Dalton*, 1972, 1580.

[9] J. Drew, M. B. Hursthouse, and P. Thornton, *J.C.S. Dalton*, 1972, 1658.

[10] M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1979, **101**, 4128.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[13] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[14] G. M. Sheldrick, SHELX Crystal Structure Analysis Program, University of Cambridge, 1976.

[15] C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

[16] W. D. S. Motherwell, PLUTO, University of Cambridge.

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

[18] H. W. Turner, R. A. Anderson, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1979, **18**, 1221.

[19] D. C. Bradley and I. M. Thomas, *Canad. J. Chem.*, 1962, **40**, 449; see also W. A. Nugent and R. L. Harlow, *J.C.S. Chem. Comm.*, 1978, 579.

[20] D. C. Bradley, M. H. Chisholm, and W. Extine, *Inorg. Chem.*, 1977, **16**, 1791.

[21] A. F. Clifford and C. S. Kobayashi, *Inorg. Synth.*, 1960, **6**, 207.

[22] A. O. Chong, K. Oshima, and K. B. Sharpless, *J. Amer. Chem. Soc.*, 1977, **99**, 3420.

[23] N. W. Alcock, M. Pierce-Butler, and G. R. Willey, *J.C.S. Chem. Comm.*, 1974, 627.

[24] D. C. Bradley, C. Bennett, M. B. Hursthouse, and P. R. Raithby, unpublished work.

[25] P. G. Eller, D. C. Bradley, M. B. Hursthouse, and D. W. Meek, *Co-ordination Chem. Rev.*, 1977, **24**, 1.