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Homoleptic hydroxylamides of titanium, zirconium and hafnium†

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The homoleptic *N*,*N*-dimethylhydroxylamides of titanium (**1**), zirconium (**2**) and hafnium (**3**), $M(ONMe_2)_4$, have been prepared in high yield by the reactions of the corresponding metal tetrakis(dimethylamides) and *N*,*N*-dimethylhydroxylamine in diethyl ether. The compounds have been characterised by ^1H and ^{13}C NMR and IR spectroscopy as well as by nominal and high-resolution mass spectrometry and elemental analysis. Compounds **1** and **2** are crystalline solids, which dissolve in ethers and hydrocarbons. They can be sublimed at 90 and 100 °C (0.1 mbar) respectively. These volatility data are discussed in comparison to those of the isoelectronic titanium and zirconium tetra(isopropoxides) and $Ti(ONEt_2)_4$ and in the context of their molecular complexities and structures. Compounds **1** and **2** are monomeric both in benzene solution and in the solid state, as shown by cryoscopy and single-crystal X-ray diffraction, respectively. The Ti and Zr atoms occupy an eight-co-ordinate environment with the $ONMe_2$ ligands co-ordinated in a bidentate fashion. Crystallographic C_2 axes pass through the metal atoms in **1** and **2**. The non-equivalent $ONMe_2$ ligands in one molecule have been found to exhibit markedly different geometries, which are discussed in the context of the molecular geometry of free Me_2NOH.

Volatile metal alkoxides have attracted considerable interest during the last few decades, as they serve as precursors for a wide range of metal oxide materials. This area of research has frequently been reviewed, in particular by Bradley *et al.*,[1] but progress continues to be made, as can be seen in the most recent literature.[2]

Various general methods have been developed for the generation of volatile metal–oxygen compounds. The most generally applicable is based on the prevention of higher aggregation of metal–oxygen cores by steric shielding of these units with bulky organic ligands. The major drawback of this approach is the increase in the number of atoms with the bulkiness of the ligands. As the number of atoms in each molecule of a compound is also an important factor affecting the volatility, a compromise between the effectiveness of the steric shielding and the growing number of atoms has to be found in each individual case. Another problem associated with bulky organic groups is the complex nature of the ligand decomposition pathways during chemical vapour deposition experiments, which might lead to incorporation of elements (*e.g.* carbon) other than those desired into the metal oxide films.

An alternative technique is the introduction of alkoxide ligands bearing additional donor sites in order to saturate the metal co-ordination sphere by intramolecular interactions, thereby isolating individual molecules from one another.[2] The increase in volatility is at least partially compensated by the additional number of atoms of these donor sites and the necessary 'spacer groups'. It should be possible to restrict the latter effect to a minimum if there is no spacer but a direct chemical bond between the oxygen atom and the donor site, *i.e.* if β-donor ligands such as *N*,*N*-dialkylhydroxylamides are used.

N,*N*-Dialkylhydroxylamides(1 –) (and the related oximates) of the early transition elements have been studied to some extent by Mehrotra and co-workers.[3] They showed these compounds to be volatile at elevated temperatures and reduced pressure, but could not distil them without some decomposition occurring. Later, Wieghardt *et al.*[4] prepared the hydroxylamides $Ti(ONEt_2)_4$ and $Zr(ONEt_2)_4$ in pure form and reported the crystal structure for the titanium compound. The titanium atom was found in an eight-co-ordinate environment showing that the concept of intramolecular saturation operated in the solid state. Surprisingly, the interest in this class of compounds was not maintained: in particular, the number of homoleptic metal hydroxylamides is restricted to only a few examples to date.[5,6]

In this paper we compare the physical properties of the homoleptic *N*,*N*-dimethylhydroxylamides of titanium, zirconium and hafnium with those of the corresponding isoelectronic tetraisopropoxy derivatives, based on their molecular structures. As the corresponding members of both series of compound have nearly identical molecular weights, this factor can be neglected in the discussion of their relative volatilities.

Results and Discussion

Metal hydroxylamides are most commonly prepared by the reaction of an OH functional hydroxylamine with a metal alkoxide,[1] whereby the corresponding alcohol is liberated. Complicated equilibria disfavour these slow reactions and often mixtures of products are obtained, which are difficult to separate. Alternative routes include the reaction of metal halides with either $LiONR_2$[7] or Me_3SiONR_2.[8] We found that the reaction (1) of *N*,*N*-dimethylhydroxylamine with the tetrakis(dimethylamides) of titanium, zirconium and hafnium is a convenient way to prepare the compounds $M(ONMe_2)_4$ (M = Ti **1**, Zr **2** or Hf **3**). The major advantages, apart from the ready availability of the starting compounds, are the quantitative reaction and the formation of gaseous NMe_2H and the desired products only. The procedure is also applicable to the ethyl derivatives.

$$M(NMe_2)_4 + 4\,Me_2NOH \longrightarrow M(ONMe_2)_4 + 4\,NMe_2H \quad (1)$$

Compounds **1** and **2** are crystalline solids, whereas **3** is a liquid at ambient temperature crystallising upon cooling to 0 °C; **1** and **2** are easily purified by crystallisation or sublimation, whereas **3** could not be obtained in a completely pure state by either method. The identity of the compounds has been confirmed by ^1H and ^{13}C NMR and IR spectroscopy, mass spectrometry (including high resolution) and elemental analyses (for **1** and **2**). At ambient temperature, $CDCl_3$

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† *Non-SI units employed:* bar = 10^5 Pa, eV ≈ 1.60×10^{-19} J.

solutions of **1**–**3** each show only one sharp resonance in the ^1H and ^{13}C NMR spectra. This indicates either high symmetry in solution or rapid configuration isomerisation as previously shown for $Ti(ONEt_2)_4$.[4]

The molecular weights of compounds **1** and **2** in solution have been determined by cryoscopy in benzene. The results are within 4% of the calculated values, indicating that **1** and **2** are monomeric in solution, so it may be concluded that the bidentate co-ordination of the four ligands is unchanged in solution. This confirms the findings of Mehrotra *et al.*[3] who showed $Ti(ONEt_2)_4$ to be monomeric in solution by ebullioscopy. The aggregation of the homoleptic hydroxylamides is thus independent of the size of the organic groups bound to the N atoms. In contrast, the alkoxides $Ti(OPr^i)_4$ and $Zr(OPr^i)_4$, which are isoelectronic to **1** and **2**, exhibit molecular complexities of 1.4 and 3.0, respectively.[1] This difference is more pronounced for the zirconium compound, as zirconium has a larger covalent radius, allowing for expansion of the co-ordination sphere if not saturated by intramolecular co-ordination.

Compounds **1**–**3** are monomeric in the gas phase as indicated by the absence of mass peaks higher than the calculated molecular weights in their mass spectra. Compounds **1** and **2** can be sublimed at 90 and 100 °C at 0.1 mbar. The sublimation becomes quite rapid on increasing these temperatures by about 10 °C. Comparison of these volatilities with those of the isoelectronic alkoxides is difficult, as sublimation temperatures have to be compared with boiling points. The known boiling points of $Ti(OPr^i)_4$ (49 °C, 0.1 mbar) and $Zr(OPr^i)_4$ (160 °C, 0.1 mbar) show that in the case of the titanium compounds the isopropoxide seems to be the more volatile, whereas in the case of the zirconium compounds the *N*,*N*-dimethylhydroxylamide (**2**) is more volatile. This may be explained by the high degree of molecular complexity for $Zr(OPr^i)_4$ in the neat liquid (which we assume to be similar to 3.0 as determined in solution). Compound **2** is monomeric in the solid state (see below) and therefore more volatile in the sublimation process.

The melting points of compounds **1** (160 °C) and **2** (123 °C) are much higher than those of the analogous ethyl compounds $Ti(ONEt_2)_4$ (69 °C) and $Zr(ONEt_2)_4$ (74 °C) suggesting stronger intermolecular interactions in the crystals of the methyl compounds. This appears to have little effect on the volatilities, as the boiling point of $Ti(ONEt_2)_4$ is quite high (150 °C at 0.7 mbar).

The limits of thermal stability of compounds **1** and **2** were explored by heating samples *in vacuo* to certain temperatures and checking for changes in the melting points afterwards. Approximate decomposition temperatures of 260 (**1**) and 270 °C (**2**) were obtained in this way. These compounds are therefore thermally more resistant than the corresponding ethyl derivatives, $Ti(ONEt_2)_4$ and $Zr(ONEt_2)_4$, which have been stated to undergo decomposition at their boiling points and were obtained in an impure state only when they were first reported.

The monomeric nature of the compounds **1** and **2** in the solid state was established by determination of their crystal structures. Solvent-free crystals were grown by slowly cooling diethyl ether solutions to -30 °C. Crystals of **1** and **2** are isomorphous and belong to the orthorhombic system, space group $P2_12_12$. A graphical representation of the molecular structure of **1** is shown in Fig. 1, while Fig. 2 shows a space-filling plot of **2** in the same orientation. Selected bond angles and distances are given in Table 1.

The high similarity of the molecular geometries is obvious from the geometrical parameters. The overall symmetry of compounds **1** and **2** is lower than that of $Ti(ONEt_2)_4$, which is S_4 in the solid state.[4] In **1** and **2** crystallographic two-fold axes pass through the metal atoms and relate two pairs of geometrically different hydroxylamide ligands. The MO_4 cores in **1** and **2** adopt very irregular geometries as indicated by the angles O–M–O (90.17, 101.23, 2 × 102.79, 2 × 132.42° for **1**, with similar values for **2**). The geometries are best described as tetrahedra with two angles extremely wide and one markedly narrowed. A similar situation arises for the MN_4 units, which are also extremely distorted tetrahedra (N–M–N angles for **1**: 2 × 90.84, 104.74, 118.29, 2 × 127.71°). For both compounds, there is also a marked difference from the TiO_4 and TiN_4 geometry in $Ti(ONEt_2)_4$, which has an almost planar TiO_4 unit and a TiN_4 skeleton which is a more moderately distorted tetrahedron (see Table 1). The overall eight-co-ordination in **1** and **2** can thus be described as two interpenetrating strongly distorted O_4 and N_4 tetrahedra with the metal atom in their centres, whereas $Ti(ONEt_2)_4$ can be seen as a TiO_4 plane intersecting an N_4 tetrahedron.

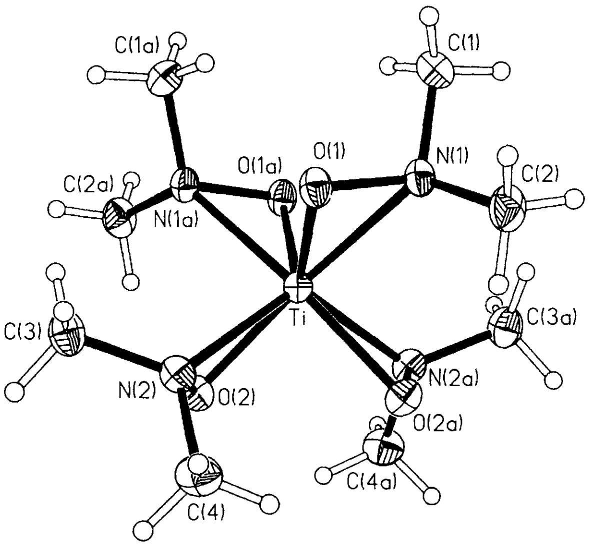

Fig. 1 Molecular structure of compound **1** showing the eight-co-ordination of the titanium atom

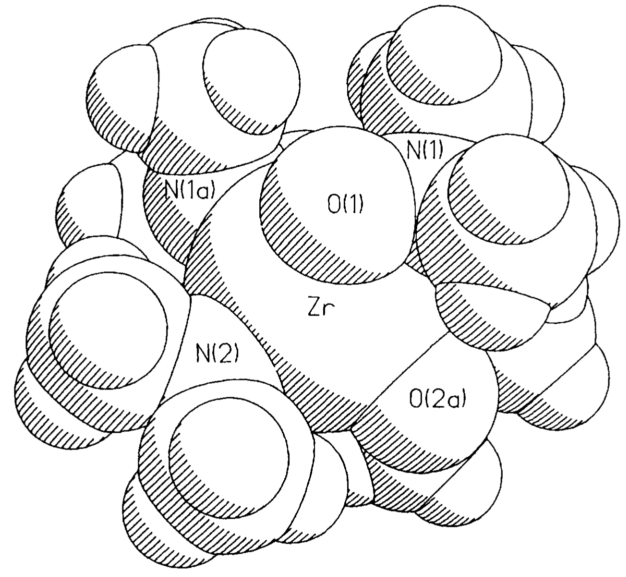

Fig. 2 Space-filling plot of the molecular structure of compound **2** showing the extent of steric shielding and accessibility of the zirconium and oxygen atoms

The non-symmetry-equivalent Me_2NO ligands in both compounds **1** and **2** have significant different geometries. The M–O(1) bonds in **1** and **2** are 0.058 and 0.048 Å shorter than the M–O(2) bonds in the same molecule, but the M–N(1) distances are 0.135 and 0.094 Å longer than the corresponding M–N(2) lengths. These differences are also reflected in the N(1)–O(1)–M angles, which are 8.0 (**1**) and 5.5° (**2**) wider than the N(2)–O(2)–M angles and cause the O(1)–N(1)–M angles to be

Table 1 Selected geometrical parameters (lengths in Å, angles in °) for the solid-state structures of compounds **1**, **2** and $Ti(ONEt_2)_4$

	$Ti(ONMe_2)_4$	$Zr(ONMe_2)_4$	$Ti(ONEt_2)_4$ (ref. 4)	
M–O(1)	1.918(1)	2.054(2)	Ti–O	1.980(3)
M–O(2)	1.976(1)	2.102(1)		
M–N(1)	2.230(1)	2.336(2)	Ti–N	2.108(5)
M–N(2)	2.095(1)	2.242(1)		
O(1)–N(1)	1.432(1)	1.451(2)	O–N	1.402(7)
N(1)–C(1)	1.465(2)	1.460(3)	N–C(1)	1.474(7)
N(1)–C(2)	1.468(2)	1.465(2)	N–C(2)	1.493(7)
O(2)–N(2)	1.424(1)	1.436(2)		
N(2)–C(4)	1.461(2)	1.459(3)		
N(2)–C(3)	1.469(2)	1.460(2)		
N(1)–O(1)–M	82.1(1)	81.6(1)	N–O–Ti	75.0(2)
N(2)–O(2)–M	74.1(1)	76.1(1)		
O(1)–N(1)–M	58.4(1)	60.5(1)	O–N–Ti	65.1(2)
O(2)–N(2)–M	65.1(1)	65.5(1)		
O(1)–M–N(1)	39.5(1)	37.9(1)	O–Ti–N	40.0(2)
O(2)–M–N(2)	40.8(1)	38.4(1)		
O(1)–M–N(1a)	89.8(1)	91.1(1)	O(c)–Ti–N(a)	90.7(2)
O(1)–M–N(2)	92.5(1)	93.8(1)		
O(1)–M–N(2a)	127.4(1)	125.4(1)	O–Ti–N(a)	143.8(2)
O(2)–M–N(2a)	91.9(1)	93.6(1)		
O(2)–M–N(1)	167.0(1)	165.0(1)	O(b)–Ti–N(a)	87.0(2)
O(2)–M–N(1a)	83.6(1)	83.9(1)		
O(1a)–M–O(1)	101.2(1)	101.9(1)	O–Ti–O(a)	176.3(3)
O(2a)–M–O(2)	90.2(1)	90.5(1)	O–Ti–O(b)	90.1(1)
O(1a)–M–O(2)	102.8(1)	102.9(1)		
O(1)–M–O(2)	132.4(1)	131.5(1)		
N(1a)–M–N(1)	104.8(1)	104.8(1)	N–Ti–N(a)	103.9(3)
N(2)–M–N(2a)	118.3(1)	118.4(1)	N(a)–Ti–N(b)	112.3(1)
N(2)–M–N(1)	127.7(1)	127.8(1)		
N(2)–M–N(1a)	90.8(1)	90.7(1)		
O(1)–N(1)–C(1)	110.5(1)	110.0(2)	O–N–C(1)	110.6(4)
O(1)–N(1)–C(2)	107.7(1)	107.4(2)	O–N–C(2)	108.9(4)
C(1)–N(1)–C(2)	110.9(1)	110.7(2)		
O(2)–N(2)–C(4)	111.8(1)	109.7(1)		
O(2)–N(2)–C(3)	110.7(1)	110.6(1)		
C(3)–N(2)–C(4)	110.8(1)	111.2(2)		

6.7 (**1**) and 5.0° (**2**) more acute than the O(2)–N(2)–M angles. Comparison of the structure of **1** with that of $Ti(ONEt_2)_4$, which has four symmetry-equivalent Et_2NO groups, shows the $Me_2N(2)O(2)$ groups in **1** and the Et_2NO groups in $Ti(ONEt_2)_4$ to have very similar geometries, whereas large deviations occur for the $Me_2N(1)O(1)$ groups in **1** (see Table 1). Even the O(2)–Ti–O(2a) angle in **1** is almost exactly the same as in $Ti(ONEt_2)_4$ [90.2(1) and 90.1(1)°, respectively], but the orientation of the N–O vectors in the ligand is different.

We cannot offer a simple explanation for the fact that $Ti(ONEt_2)_4$ molecules, with conformationally much more flexible Et_2NO ligands, prefer to crystallise in the highly symmetric point group S_4 (space group $P\bar{4}2_1c$), whereas the more rigid Me_2NO ligands lead to less symmetric crystalline phases and marked distortions of the MO_4N_4 skeletons, which are very similar for M = Ti and Zr.

As shown above, the two crystallographically independent Me_2NO ligands in compounds **1** and **2** are bound to the metal atoms with different geometries. Within the ligands the N(1)–O(1) and N(2)–O(2) distances are also significantly different, with the differences being quite small for **1** (0.008 Å), but more significant for **2** (0.015 Å) and all N–C distances (for **1** and **2**) fall within a range of 0.01 Å. All the O–N–C and C–N–C angles are also found within a narrow range.

As we have recently studied the structure of Me_2NOH in the crystal, in the gas phase and by *ab initio* methods,[9] a discussion of the structural differences between it and the metal-co-ordinated Me_2NO fragment is now possible. We focus here on comparisons with the crystal structure of Me_2NOH, because there are only solid-state data for compounds **1** and **2**. The average N–O bond length in Me_2NOH is 1.452 Å [1.452(2) and 1.451(2) Å for two independent molecules], which is slightly longer than those in **1** and the N(2)–O(2) distance in **2**, but very close to the N(1)–O(1) distance in **2**. The O–N–C angles in the metal hydroxylamides **1** and **2** are markedly wider [107.4(1)–110.7(1)°] than those in crystalline Me_2NOH [104.1(2)–106.5(2)°], where the nitrogen atom is involved in hydrogen bonding and therefore also four-co-ordinate. The N–O–C angle in free Me_2NO is 105.4° according to 6-311G**/MP2 calculations. This widening in the metal compounds **1** and **2** can be explained by the bonding of the nitrogen lone pair to the metal atom. The C–N–C angles in **1** and **2** [110.7(2)–111.2(2)°] are close to those in crystalline Me_2NOH [110.6(2) and 110.5(2)°] and those of free Me_2NO (calculated to be 110.3°).

The space-filling model of compound **2** (Fig. 2) shows that the zirconium atom is not completely shielded by its ligand sphere, but enough to prevent further co-ordination (a similar situation is observed for **1**). The oxygen atoms are relatively freely accessible, whereas the nitrogen atoms are encapsulated by the methyl groups and oxygen atoms. The closest intermolecular M···O contacts in **1** and **2** are 5.782(1) and 5.795(1) Å respectively, indicating the absence of any bonding interaction.

Conclusion

We have shown that homoleptic *N*,*N*-dialkylhydroxylamides are a class of compounds which is easily accessible *via* the reaction of metal amides with free hydroxylamines ('metal amide route'). The low molecular complexities in solution and the monomeric nature in the solid state suggest that complete intramolecular saturation of the co-ordination sphere can be achieved with a minimum amount of steric shielding and 'spacer groups' by using β-donor ligands. This might be an advantage for the preparation of other volatile transition-metal compounds which contain metal–oxygen cores and have reasonable thermal stability, but which include weak N–O bonds as predetermined breaking points between the metal–oxygen core and the remaining parts of the ligands.

Experimental

The *N*,*N*-dialkylhydroxylamides and dialkylamides of Group 4 elements are sensitive to hydrolysis. They were handled using standard Schlenk-line techniques with purified nitrogen (BTS-catalyst, 4 Å molecular sieve) as inert gas. Diethyl ether and tetrahydrofuran were dried over K/Na alloy and distilled prior to use, $CDCl_3$ was dried over P_2O_5, distilled and stored over 4 Å molecular sieve. Melting points were measured in capillaries under nitrogen and are uncorrected. The NMR spectra were recorded as $CDCl_3$ solutions using a Bruker AC250 spectrometer (^1H, 250.13 MHz; ^{13}C, 62.90 MHz), IR spectra with a Perkin-Elmer FT-IR 577 spectrometer (range 4000–450 cm^{-1}). The cryoscopic measurements were carried out in duplicate experiments using *ca.* 0.01 mol dm^{-3} solutions in C_6H_6 (dried over CaH_2 and distilled using a 30 cm Vigreux column) and a Beckmann thermometer. The dimethylamides of titanium, zirconium and hafnium were prepared by literature methods.[10]

Preparations

$Ti(ONMe_2)_4$ 1. The compound $Ti(NMe_2)_4$ (2.5 cm^3, 10.6 mmol) was dissolved in diethyl ether (40 cm^3). *N*,*N*-Dimethylhydroxylamine (3.4 cm^3, 5% excess) was added dropwise at −78 °C. The mixture was allowed to warm to ambient temperature. After addition of diethyl ether (40 cm^3), small amounts of tetrahydrofuran were slowly added until a clear solution resulted. This was cooled very slowly to −20 °C, with precipitation of well shaped cubes. The liquid was removed with a cannula at this temperature. Yield 2.96 g (97%), m.p. 160 °C (Found: C, 33.35; H, 8.65; N, 19.40. Calc. for $C_8H_{24}N_4O_4Ti$: C, 33.35; H, 8.40; N, 19.45%). NMR: ^1H, δ 2.81 (s); ^{13}C, δ 49.7 [qq, $^1J(CH) = 142$, $^3J(CNCH) = 4$ Hz]. IR (KBr): 3039w, 3025m, 3005w, 2964m, 2863m, 2812m, 2764w, 1468m, 1457m, 1436m, 1414w, 1390m, 1234w, 1218m, 1203vw, 1170vw, 1090vw, 1002m, 979m, 964s [ν(NO)], 817s, 808m, 628vs [ν(TiO)] and 546s cm^{-1}. Mass spectrum (electron impact, EI, 70 eV): m/z = 228, 219, 206, 193, 181, 169, 149, 142, 131, 124, 111 and 100. High-resolution mass spectrum (EI, 70 eV): m/z = 288.12616 (Calc. for $C_8H_{24}N_4O_4Ti$: 288.12770).

$Zr(ONMe_2)_4$ 2. The procedure was the same as described for compound **1** but using $Zr(NMe_2)_4$ (3.0 g, 11.0 mmol) and *N*,*N*-dimethylhydroxylamine (3.4 cm^3). Yield 3.41 g (94%), m.p. 123 °C (Found: C, 28.35; H, 7.30; N, 16.60. Calc. for $C_8H_{24}N_4O_4Zr$: C, 29.00; H, 7.30; N, 16.90%). NMR: ^1H, δ 2.75 (s); ^{13}C, δ 50.4 [qq, $^1J(CH) = 137$, $^3J(CNCH) = 5$ Hz]. IR (KBr): 2964m, 2900m, 2872m, 2817m, 2768w, 1464m, 1457m, 1451m, 1439m, 1415w, 1394w, 1232w, 1216w, 1202w, 1168vw, 1092vw, 1002m, 961s [ν(NO)], 804vs, 797s and 474vs cm^{-1} [ν(ZrO)]. Mass spectrum (EI, 70 eV): m/z = 330, 289, 272, 255, 227, 211, 200, 191, 185, 166, 150, 141 and 125. High-resolution mass spectrum (EI, 70 eV): m/z = 330.08591 (Calc. for $C_8H_{24}N_4O_4Zr$: 330.08446).

$Hf(ONMe_2)_4$ 3. The compound $Hf(NMe_2)_4$ (0.568 g, 1.6 mmol) was dissolved in diethyl ether (10 cm^3) and cooled to −10 °C. *N*,*N*-Dimethylhydroxylamine (0.66 cm^3, 6.4 mmol) was added dropwise. The solution was stirred for 2 h. After removing the solvent under reduced pressure a slightly yellow liquid remained: this solidified at *ca.* 2 °C. NMR: ^1H, δ 2.43 (s); ^{13}C, δ 49.9 [qq, $^1J(CH) = 135$, $^3J(CNCH) = 5$ Hz]. Mass spectrum (EI, 70 eV): m/z = 420, 401, 379, 358, 341, 317, 292, 274, 256, 237, 227, 212, 192, 184, 167 and 155. IR (KBr): 2957s, 2925s, 2856s, 1470s, 1435m, 1417w, 1379w, 1261w, 1203w, 1170w, 1000w, 956m, 810s, 800s, 749w and 738w cm^{-1}. High resolution mass spectrum (EI, 70 eV): m/z = 420.12681 (Calc. for $C_8H_{24}HfN_4O_4$: 420.12631).

X-Ray crystallography

Crystals were transferred and examined under inert perfluoropolyether oil (RS3000) and mounted on glass fibres. Data were collected on a Stoe Stadi-4 four-circle diffractometer fitted with an Oxford Cryosystems low-temperature device[11] and graphite-monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). The structures were solved for all non-H atoms by direct methods,[12,13] and refined against F^2 with full-matrix least-squares analysis.[14] The non-H atoms were refined with anisotropic thermal displacement parameters. The hydrogen atoms on the methyl groups were located in a difference synthesis and freely refined with isotropic thermal displacement parameters.

$Ti(ONMe_2)_4$ 1. $C_8H_{24}N_4O_4Ti$, $M = 288.21$, orthorhombic, space group $P2_12_12$, $a = 9.4828(13)$, $b = 9.618(1)$, $c = 7.849(2)$ Å, $U = 715.9(2)$ Å^3, $Z = 2$, $D_c = 1.337$ g cm^{-3}, $F(000) = 308$. Colourless cuboid, 0.93 × 0.52 × 0.36 mm. $T = 150(2)$ K, 2076 reflections collected (ω–2θ scans, $-13 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 13, -6 \leqslant l \leqslant 11$), 1225 independent ($R_{int} = 0.0362$). Semiempirical absorption correction by ψ scans (maximum, minimum transmission factors = 0.730, 0.612). The refinement converged with a conventional R value of 0.0184 [based on F and 1188 data with $I \geqslant 2\sigma(I)$] and a $wR2$ value of 0.0532 (based on F^2 and all 1225 data for 127 refined parameters). In the final difference synthesis the maximum and minimum residual electron densities were 0.22 and −0.24 e Å^{-3}, respectively. Weighting scheme employed: $w = [\sigma^2(F_o^2) + 0.0234P^2 + 0.0802P]^{-1}$, where $P = 0.333\,33(F_o^2 + 2F_c^2)$.

$Zr(ONMe_2)_4$ 2. $C_8H_{24}N_4O_4Zr$, $M = 331.53$, orthorhombic, space group $P2_12_12$, $a = 9.7297(14)$, $b = 9.7456(14)$, $c = 7.8968(11)$ Å, $U = 748.8(2)$ Å^3, $Z = 2$, $D_c = 1.470$ g cm^{-3}, $F(000) = 344$. Colourless cube, 0.7 × 0.7 × 0.7 mm. $T = 150(2)$ K, 3370 reflections collected (ω–2θ scans, $-1 \leqslant h \leqslant 14$, $-1 \leqslant k \leqslant 14$, $-1 \leqslant l \leqslant 11$), 1916 independent ($R_{int} = 0.0146$). Semiempirical absorption correction by ψ scans (maximum, minimum transmission factors = 0.455, 0.394). The refinement converged with a conventional R value of 0.0191 [based on F and 1817 data with $I \geqslant 2\sigma(I)$] and a $wR2$ value of 0.1174 (based on F^2 and all 1916 data for 127 refined parameters). In the final difference synthesis the maximum and minimum residual electron densities were 0.47 and −0.88 e Å^{-3}, respectively. Weighting scheme employed: $w = [\sigma^2(F_o^2) + 0.0255P^2 + 0.1645P]^{-1}$, where $P = 0.333\,33(F_o^2 + 2F_c^2)$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/37.

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