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PAPER

Preparation and structures of coordination complexes of the very hard Lewis acids ZrF_4 and HfF_4†

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$[MF_4(dmso)_2]$ (M = Zr or Hf) and $[MF_4(dmf)_2]$, prepared by dissolving $MF_4{\cdot}nH_2O$ in the appropriate solvent, have been used as synthons for a range of complexes of these otherwise intractable tetrafluorides. These reagents react with OPR_3 (R = Me or Ph) or $OAsPh_3$ (L) in anhydrous CH_2Cl_2 to form six-coordinate $[MF_4L_2]$ which exist as a mixture of *cis* (predominant form) and *trans* isomers in CH_2Cl_2 solution but which crystallise as *trans* ($OPPh_3$, $OAsPh_3$) or *cis* ($OPMe_3$) forms. *Cis*-$[ZrF_4(OAsPh_3)_2]$ crystals were obtained from MeCN. *Cis*-$[MF_4(pyNO)_2]$ and eight-coordinate (distorted dodecahedral) $[MF_4(L–L)_2]$ (L–L = 2,2′-bipy, or 1,10-phen), and $[MF_4(Me_4\text{-cyclam})]$ were also obtained. Attempts to prepare complexes with the N-heterocyclic carbene, 1,3-(2,6-di-isopropylphenyl)imidazol-2-ylidene (IDiPP) or alkyl diphosphines were unsuccessful. Crystal structures are reported for *trans*-$[ZrF_4(OPPh_3)_2]$, *cis*- and *trans*-$[ZrF_4(OAsPh_3)_2]$, *cis*-$[HfF_4(OPMe_3)_2]$, $[ZrF_4(2,2'\text{-bipy})_2]$, *cis*-$[HfF_4(dmf)_2]$, and geometric isomers (both pentagonal bipyramidal) of $[(dmso)_2F_3M(\mu\text{-F})_2MF_3(dmso)_2]$. The failed attempts to make IDiPP adducts led to crystals of $[IDiPPH]_3[M_3F_{15}]$ containing discrete anions based upon a triangle of M atoms with single F bridges. The results are compared with previous work on TiF_4 adducts and with complexes of MCl_4, and demonstrate that the MF_4 are very hard Lewis acids, with a marked preference for O- over N-donors.

Introduction

The coordination chemistry of high valent metal fluorides has been relatively little explored and examples with neutral donor ligands are particularly rare. This is despite the very different electronic properties of fluoride ligands compared to the heavier halides, which can radically modify the Lewis acidity and hardness of the metal centre, and hence produce significantly different coordination chemistry compared to that with heavier halide co-ligands. Recent work addressing this area has included studies of complexes of GeF_4,[1] SnF_4,[1c,2] NbF_5,[3] TiF_4,[4] TaF_5[3,5] VOF_3,[6] VO_2F,[7] MO_2F_2 (M = Mo or W)[8] and WF_6.[9] Following recent studies of TiF_4 adducts, which included the first examples of phosphines[4a] and *N*-heterocyclic carbene complexes,[4b] we report here an investigation of complexes of ZrF_4 and HfF_4 with a variety of neutral O- and N-donor ligands, together with attempts to prepare *N*-heterocyclic carbene and phosphine complexes.

Zirconium and hafnium tetrafluorides are unreactive, polymeric solids which contain eight-coordinate metal centres. Single crystal X-ray studies have confirmed monoclinic (β) forms for both;[10,11] and there is also a tetragonal high temperature (α) form of ZrF_4.[11] A wide range of fluorometallate anions are known, the stoichiometry giving no guide to the structures, hexafluorometallates(IV) $[MF_6]^{2-}$ with six- (octahedral), seven- (both pentagonal bipyramidal and capped octahedral), and eight-coordinate (square antiprismatic) M are established, the structure depending upon the cation present.[12] Very few complexes with neutral ligands have been isolated.[13–20] Structurally authenticated examples include the hydrates $[(H_2O)_3F_3Zr(\mu\text{-F})_2Zr(H_2O)_3F_3]$,[14,15] and $[HfF_4(H_2O)_2]$, which is a chain polymer with $HfO_2F_2F_{4/2}$ coordination,[16] several dmso complexes,[17,18] including $[(dmso)_2F_3Zr(\mu\text{-F})_2ZrF_3(dmso)_2]$, and the *N*,*N*-dimethylformamide complex $[(dmf)_2F_3Zr(\mu\text{-F})_2ZrF_3(dmf)_2]$.[19] Complexes with nitrogen donor ligands are even rarer, but include $[M(NH_3)_4F_4]{\cdot}NH_3$ (M = Zr or Hf)[21] and $[HfF_4(2,2'\text{-bipy})_2]$.[22]

Results and discussion

Synthons

Given the very intractable nature of MF_4 (M = Zr, Hf), development of their coordination chemistry critically depends upon obtaining suitable soluble synthons which can be reacted with the relevant neutral ligands. The anhydrous MF_4 are insoluble in organic solvents,[23] but the hydrates, $MF_4{\cdot}nH_2O$ dissolved‡ on

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† Electronic supplementary information (ESI) available. CCDC 890601–890611. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31501g

‡ Several commercial samples of "anhydrous" MF_4 showed significant water in the IR spectra and dissolved fairly easily in hot dmso or dmf, as did commercial samples of the hydrates. Genuinely anhydrous MF_4 samples were insoluble in the same solvents even after prolonged heating,[23] consistent with literature reports.

heating in dmso or dmf, and crystalline 1 : 2 adducts separated on allowing the solutions to stand. The synthesis of complexes analogous to those used to obtain TiF_4 adducts, $[TiF_4(thf)_2]^{4a}$ or $[TiF_4(MeCN)_2]^{24}$ was explored, but the $MF_4{\cdot}nH_2O$ do not dissolve in MeCN or thf even under reflux, and the $[MF_4(dmso)_2]$ were recovered from attempted recrystallisation from thf or MeCN.

The $[MF_4(dmso)_2]$ and $[MF_4(dmf)_2]$ dissolve easily in the parent solvent on warming, are very poorly soluble in CH_2Cl_2 or methanol and essentially insoluble in MeCN or acetone. The structure of $[ZrF_4(dmso)_2]$ has been determined independently twice[17,18] and shown to have a monoclinic cell, containing $[(dmso)_2F_3Zr(\mu\text{-}F)_2ZrF_3(dmso)_2]$ molecules composed of two pentagonal bipyramidal zirconium centres with axial fluorides. In the present study a few small colourless crystals were obtained serendipitously from a failed attempt to obtain crystals of $[ZrF_4(2,2'\text{-bipy})_2]$ from a 1 : 2 mol. ratio of $[ZrF_4(dmso)_2]$ and 2,2′-bipy in 1 : 1 dmso–CH_2Cl_2 solution. The structure of these revealed them to have a tetragonal cell containing a geometric isomer of the known form (Fig. 1). The key difference is the arrangement of ligands in the pentagonal plane which in the monoclinic form is O–F–O–F–F with an <O–Zr–O of 152.8°, but in the tetragonal form is O–O–F–F–F with <O–Zr–O = 72.6°. The Zr–F, Zr–O and S–O distances are not significantly different in the two isomers.

Colourless crystals of $[\{HfF_4(dmso)_2\}_2]$ (Fig. 2) were found to be isomorphous with the monoclinic form of $[\{ZrF_4(dmso)_2\}_2]$; the Hf–F and Hf–O bond lengths are very slighter shorter (~0.01 Å) than the corresponding bonds in the zirconium complex.

The structure of $[(dmf)_2F_3Zr(\mu\text{-}F)_2ZrF_3(dmf)_2]$ also has pentagonal bipyramidal zirconium centres, axial fluorines, and an O–O–F–F–F sequence of donors in the equatorial plane.[19] In contrast, crystals of $[HfF_4(dmf)_2]$, which separated on standing over several days from a solution of $HfF_4{\cdot}nH_2O$ in dmf, contain *cis*-octahedral monomers (Fig. 3).

The key IR spectroscopic data is given in the Experimental section. In CD_2Cl_2 at 295 K all four complexes show a broad singlet in the $^{19}F\{^1H\}$ NMR spectra, $\delta \sim +43$ (M = Zr) and ~ -1 (M = Hf) (Table 1), which indicates fluxionality or reversible dissociation. Singlets at similar frequencies are seen in freshly prepared d^6-dmso or d^7-dmf solutions as appropriate (Experimental section). The spectra in d^7-dmf solution are little different at 220 K, but low temperature studies in CD_2Cl_2 were prevented by very poor solubility. There are reports of the low temperature NMR spectra of $[MF_4(dmso)_2]$ in mixed donor solvents,[20,25] which observed several species, but the identities are speculative due to the limited data.

Oxygen donor ligand complexes. The reaction of $[MF_4(dmso)_2]$ and $[ZrF_4(dmf)_2]$ or $[HfF_4(dmf)_2]$ with 2 mol.

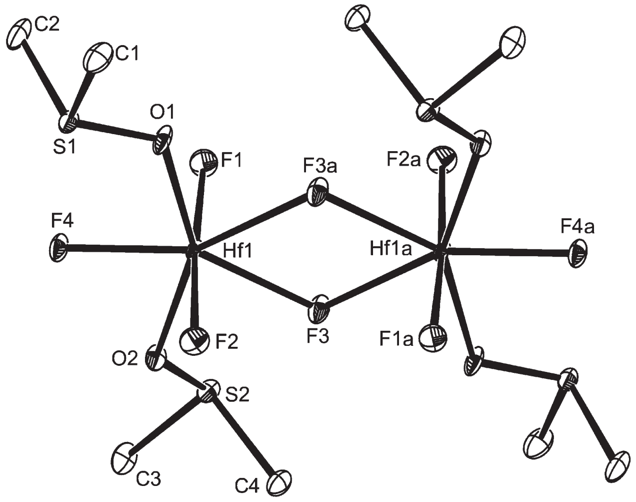

Fig. 2 Crystal structure of $[\{HfF_4(dmso)_2\}_2]$ showing the atom numbering scheme. The dimeric molecule has a centre of symmetry. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = -x, -y, 1 - z$. Selected bond lengths (Å) and angles (°): Hf1–F2 = 1.963(4), Hf1–F1 = 1.979(5), Hf1–F4 = 1.985(4), Hf1–F3a = 2.141(4), Hf1–F3 = 2.144(4), Hf1–O1 = 2.178(5), Hf1–O2 = 2.181(5), F2–Hf1–F1 175.36(18), O1–Hf1–O2 152.53(18).

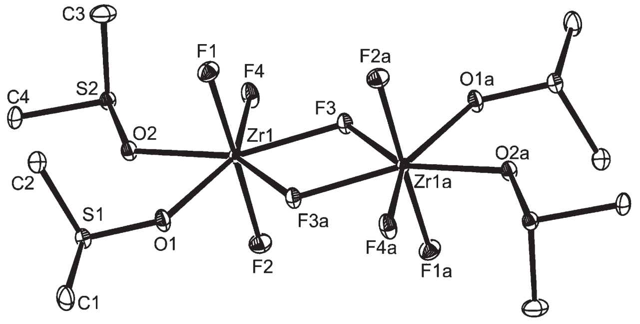

Fig. 1 Crystal structure of $[\{ZrF_4(dmso)_2\}_2]$ (tetragonal form) showing the atom numbering scheme. The dimeric molecule has a centre of symmetry. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = -x, -y, 1 - z$. Selected bond lengths (Å) and angles (°): Zr1–F1 = 1.977(1), Zr1–F2 = 1.977(1), Zr1–F4 = 1.988(1), Zr1–F3 = 2.148(1), Zr1–F3a = 2.155(1), Zr1–O2 = 2.196(2), Zr1–O1 = 2.212(2), F1–Zr1–F2 = 177.23(5), O2–Zr1–O1 = 72.64(5).

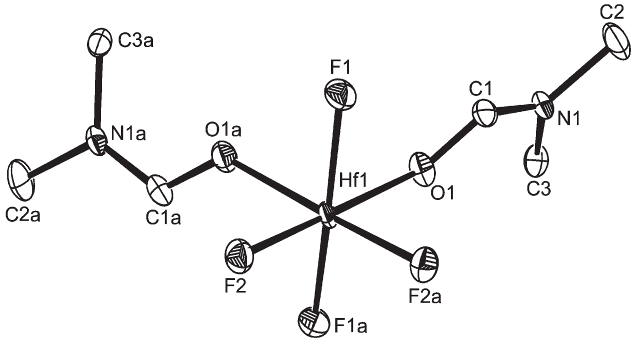

Fig. 3 Crystal structure of *cis*-$[HfF_4(dmf)_2]$ showing the atom numbering scheme. The molecule has a two-fold symmetry axis. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = 1 - x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°): Hf1–F2 = 1.954(4), Hf1–F1 = 1.975(4), Hf1–O1 = 2.159(4). F2–Hf1–F2a = 91.4(2), F2–Hf1–F1 = 94.93(17), F2–Hf1–F1a 92.94(16), F2–Hf1–O1 = 90.38(18), F1–Hf1–O1 = 85.80(17), F1–Hf1–O1a 86.08(17), O1–Hf1–O1a = 87.8(2).

Table 1 $^{19}F\{^1H\}$ NMR data[a]

Complex	δ $^{19}F\{^1H\}$ (295 K)[b]	Complex	δ $^{19}F\{^1H\}$ (295 K)[b]
$[ZrF_4(dmso)_2]$	43.5 (s)	$[HfF_4(dmso)_2]$	−1.5 (s)
$[ZrF_4(dmf)_2]$	43.5 (s)	$[HfF_4(dmf)_2]$	−1.7 (s)
$[ZrF_4(OPPh_3)_2]$	48.1 (s) [2F], 24.2 (s) [2F], 23.8 (sh)[c] (253 K)	$[HfF_4(OPPh_3)_2]$	−2.35 (s) [2F], −17.6 (s) [2F], −18.3 (s)[c] (223 K)
$[ZrF_4(OAsPh_3)_2]$	29.5 (s) [2F], 17.0 (s) [2F], 16.3 (s)[c] (223 K)	$[HfF_4(OAsPh_3)_2]$	−10.7 (s) [2F], −20.7 (s) [2F], −21.9 (s)[c] (243 K)
$[ZrF_4(OPMe_3)_2]$	41.2 (s) [2F], 19.1 (s) [2F], 18.9 (sh)[c] (243 K)	$[HfF_4(OPMe_3)_2]$	−4.1 (s) [2F], −20.2 (s) [2F], −20.7 (s)[c] (243K)
$[ZrF_4(pyNO)_2]$	37.7 (s)	$[HfF_4(pyNO)_2]$	−6.5 (s)
$[ZrF_4(phen)_2]$	21.3 (s)	$[HfF_4(phen)_2]$	−17.8 (s)
$[ZrF_4(bipy)_2]$	24.5 (s)	$[HfF_4(bipy)_2]$	−11.2 (s)
$[ZrF_4(Me_4\text{-cyclam})]$	14.2 (s)	$[HfF_4(Me_4\text{-cyclam})]$	−12.0 (s)
$[ZrF_6]^{2-}$ [d]	−16 (H_2O),[d] −10 (CD_2Cl_2)[e]	$[HfF_6]^{2-}$ [d]	−47 (H_2O),[d] −44 (CD_2Cl_2)[e]

[a] In CH_2Cl_2 solution. [b] Temperature unless indicated otherwise. [c] Resonance of *trans* isomer. [d] M. A. Fedotov and A. V. Belyaev, *J. Struct. Chem.*, 2011, **52**, 69 and references therein. [e] $[NMe_4]^+$ salt this work.

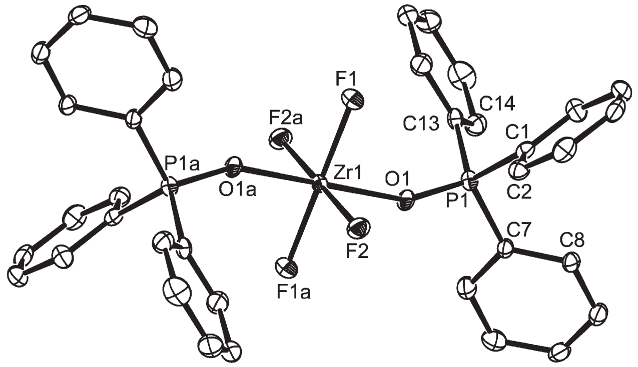

Fig. 4 Crystal structure of *trans*-$[ZrF_4(OPPh_3)_2]\cdot 2CH_2Cl_2$ showing the atom numbering scheme. The molecule has a centre of symmetry. The carbon atoms are numbered cyclically starting at the *ipso* C. Ellipsoids are drawn at the 50% probability level and H atoms and the solvate molecule are omitted for clarity. Symmetry operation: $a = 1 - x, 1 - y, -z$. Selected bond lengths (Å) and angles (°): Zr1–F2 = 1.9742(19), Zr1–F1 = 1.987(2), Zr1–O1 = 2.116(2), P1–O1 = 1.516(2). F2–Zr1–F1a = 88.96(8), F2–Zr1–F1 = 91.04(8), F2–Zr1–O1a = 91.03(8), F2–Zr1–O1 = 88.97(8), F1–Zr1–O1 = 91.24(9), F1–Zr1–O1a = 88.76(9), O1–Zr1–O1a = 180.00(11).

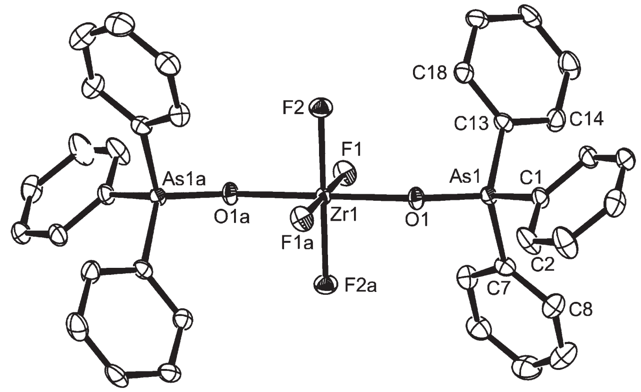

Fig. 5 Crystal structure of *trans*-$[ZrF_4(OAsPh_3)_2]\cdot 2CH_2Cl_2$ showing the atom numbering scheme. The molecule has a centre of symmetry. Ellipsoids are drawn at the 50% probability level and H atoms and the solvate molecules are omitted for clarity. Symmetry operation: $a = 1 - x, 1 - y, -z$. Selected bond lengths (Å) and angles (°): Zr1–F1 = 1.993(3), Zr1–F2 = 1.994(3), Zr1–O1 = 2.093(3), As1–O1 = 1.668(3). F1–Zr1–F2a = 89.08(13), F1–Zr1–F2 = 90.92(14), F1–Zr1–O1a = 88.88(13), F1–Zr1–O1 = 91.12(13), F2–Zr1–O1 = 88.97(14), F2–Zr1–O1a = 91.03(14), O1–Zr1–O1a = 180.00(18).

equivalents of $OEPh_3$ (E = P or As) in CH_2Cl_2 led to high yields of $[ZrF_4(OEPh_3)_2]$ or $[HfF_4(OAsPh_3)_2]$. The $[MF_4(OEPh_3)_2]$ were also obtained using a two-fold excess of $OEPh_3$, and *in situ* ^{31}P and ^{19}F NMR studies showed no evidence of species with a higher $OEPh_3$: M ratio. Unusually for the fluoride complexes of these two metals, the pnictogen oxide complexes are easily soluble in chlorocarbon solvents. They also dissolve in dmso or dmf, but NMR studies suggest partial displacement of the OER_3 occurs. The filtrates from the bulk preparations deposited colourless crystals $[ZrF_4(OEPh_3)_2]\cdot 2CH_2Cl_2$, which are isomorphous and contain *trans*-octahedral molecules (Fig. 4 and 5). The Zr–F and Zr–O distances are very similar in the two complexes, with the Zr–O(As) very slightly shorter than Zr–O(P); the corresponding effect is much more pronounced in the *cis*-$[TiF_4(OEPh_3)_2]$ complexes.[4a]

Unexpectedly, a few crystals of *cis*-$[ZrF_4(OAsPh_3)_2]\cdot 2CH_2Cl_2$ were deposited from a solution of $[ZrF_4(2,2'\text{-bipy})_2]$ and $OAsPh_3$ in MeCN–CH_2Cl_2 (Fig. 6). Comparison of the bond lengths in the two structures reveal that whilst Zr–F_{transF} are effectively identical, Zr–F_{transO} in the *cis*-isomer is shorter by

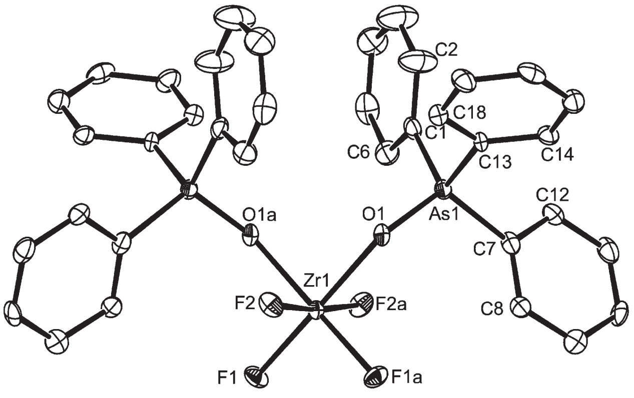

Fig. 6 Crystal structure of *cis*-$[ZrF_4(OAsPh_3)_2]\cdot 2CH_2Cl_2$ showing the atom numbering scheme. Symmetry operation: $a = 1 - x, y, 1/2 - z$. Ellipsoids are drawn at the 50% probability level. The solvate molecules and the H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–F1 = 1.973(3), Zr1–F2 = 1.995(3), Zr1–O1 = 2.125(4), As1–O1 = 1.680(4), F1–Zr1–F1a = 93.1(2), F1–Zr1–F2 = 95.21(14), F1–Zr1–F2a = 88.99(15), F1–Zr1–O1a = 89.54(15), F2–Zr1–O1a = 86.28(15), F2–Zr1–O1 = 89.34(15), O1–Zr1–O1a = 88.2(2).

~0.02 Å and Zr–O_{transF} longer than Zr–O_{transO} by ~0.03 Å, showing the dominant Zr–F bonding.[4]

The IR spectra of the bulk solid [$MF_4(OPPh_3)_2$] show single sharp strong bands at ~1080 and ~514 (Zr) or ~493 (Hf) cm^{-1} assigned as ν(PO) and ν(MF) respectively, as expected for *trans* isomers (D_{4h}). In the [$MF_4(OAsPh_3)_2$] the ν(AsO) at ~875 cm^{-1} are only slightly shifted from the value in $OAsPh_3$ (881 cm^{-1}) as is often the case in arsine oxide complexes,[26] but are relatively more intense and much broader. In solution in CD_2Cl_2 at 295 K very broad resonances are present in the $^{19}F\{^1H\}$ NMR spectra of all four complexes, consistent with exchanging systems, but on cooling the solutions two broad singlets of approximately equal intensity appear which sharpen on further cooling, but no FF couplings were resolved. This indicates that the predominant forms in solution are *cis* isomers. Careful integration of the resonances measured at 243 K show typically 1 : ≤1.2, with the lower frequency resonance the more intense, and under high resolution, a small peak or a shoulder is evident on the lower frequency resonance which are attributable to a small amount of the *trans* isomer. The $^{31}P\{^1H\}$ NMR spectra of the phosphine oxide complexes show a singlet with a modest high frequency coordination shift assigned to the *cis* isomers; again under high resolution at low temperatures a second weak feature with a very similar chemical shift is observed in each, due to the *trans* isomer. The fact that [$MF_4(OEPh_3)_2$] are *trans* in the solid state presumably reflects crystallisation of the least soluble isomer from the solution containing reversibly dissociating ligands. In contrast, the IR spectra of the [$MF_4(OPMe_3)_2$] indicate they are *cis* isomers in the solid state and this was confirmed by the X-ray structure of the Hf complex (Fig. 7); the data were collected from a twinned crystal of modest quality and detailed comparison of bond lengths are not appropriate.

The reaction of [$MF_4(dmso)_2$] with pyridine-*N*-oxide in CH_2Cl_2 solution formed [$MF_4(pyNO)_2$], the IR spectra suggesting *cis* isomers in the solid state (Experimental section), but the complexes were too poorly soluble for low temperature NMR studies. The complexes dissolve easily in d^7-dmf, but the ^1H and ^{19}F NMR spectra show the pyNO is largely displaced by dmf.

Nitrogen donor ligands. The reaction of 2,2′-bipyridyl or 1,10-phenanthroline with [$MF_4(dmso)_2$] or [$MF_4(dmf)_2$] in a >2 : 1 mol. ratio in CH_2Cl_2 results in precipitation of the [$MF_4(L–L)_2$] (L–L = 2,2′-bipy, 1,10-phen) as white powders. The [$ZrF_4(2,2'\text{-bipy})_2$] has been obtained previously by melting together ZrF_4 and 2,2′-bipy.[27] [$HfF_4(2,2'\text{-bipy})_2$] has an eight-coordinate geometry in crystals which separated from a HfF_4/dmso/2,2′-bipy solution in which the complex was a minor constituent (NMR evidence).[14] Crystals of [$ZrF_4(2,2'\text{-bipy})_2$] obtained in this study by slow evaporation of a dilute solution of the complex in MeCN, were isomorphous with the Hf analogue and show a flattened dodecahedron with very similar geometry (Fig. 8).

The complexes are very slightly soluble in CD_2Cl_2 and $^{19}F\{^1H\}$ NMR spectra show a single sharp resonance in each, with chemical shifts to low frequency of those in O-donor ligand complexes (Table 1). The diimine complexes dissolve more easily in dmso or dmf, but the ^1H and $^{19}F\{^1H\}$ NMR spectra show partial displacement of the diimine occurs. Repeated attempts to isolate pyridine adducts from reaction of [$MF_4(dmf)_2$] with excess pyridine in anhydrous CH_2Cl_2 or from neat pyridine failed, the products always retained significant amounts of the dmf complex, whilst if the reactions were exposed to moisture, the IR and $^{19}F\{^1H\}$ showed pyridinium fluorometallates formed.

The addition of a solution of [$MF_4(dmf)_2$] in the minimum amount of warm dmf to a solution of Me_4-cyclam in CH_2Cl_2 under strictly anhydrous conditions, gave clear solutions, which over ~2 d deposited white precipitates of [$MF_4(Me_4\text{-cyclam})$].

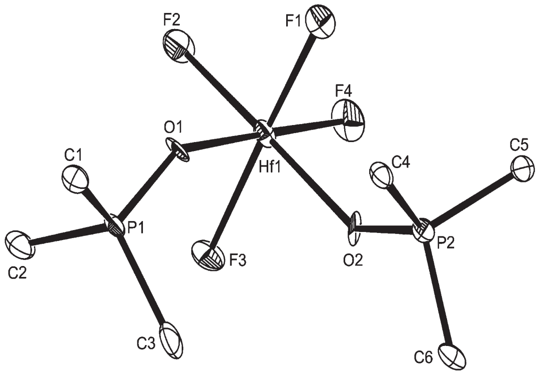

Fig. 7 Crystal structure of *cis*-[$HfF_4(OPMe_3)_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hf1–F4 = 1.973(9), Hf1–F1 = 1.983(7), Hf1–F2 = 1.983(8), Hf1–F3 = 1.990(7), Hf1–O2 = 2.116(9), Hf1–O1 = 2.121(9), P1–O1 = 1.518(8), P2–O2 = 1.532(8), F4–Hf1–F1 = 92.4(3), F4–Hf1–F2 = 89.8(4), F1–Hf1–F2 = 92.9(3), F4–Hf1–F3 = 93.7(4), F2–Hf1–F3 = 92.5(3), F4–Hf1–O2 = 91.0(4), F1–Hf1–O2 = 87.6(3), F3–Hf1–O2 = 86.9(3), F1–Hf1–O1 = 87.3(3), F2–Hf1–O1 = 91.5(4), F3–Hf1–O1 = 86.4(3), O2–Hf1–O1 = 87.8(4).

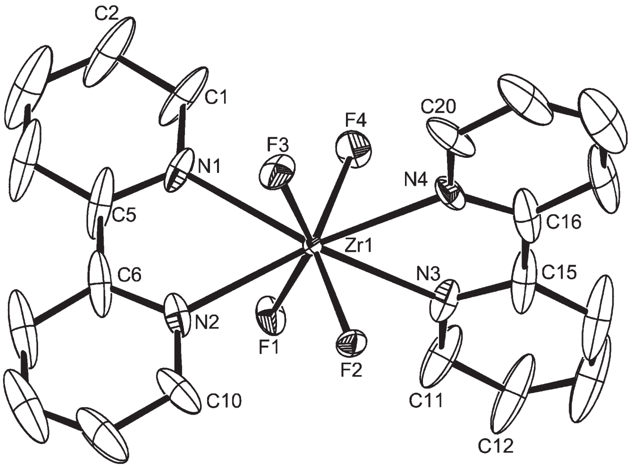

Fig. 8 Crystal structure of [$ZrF_4(2,2'\text{-bipy})_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–F1 = 1.980(3), Zr1–F4 = 1.987(4), Zr1–F2 = 1.989(3), Zr1–F3 = 1.991(4), Zr1–N3 = 2.465(5), Zr1–N2 = 2.467(5), Zr1–N1 = 2.473(5), Zr1–N4 = 2.482(5), F1–Zr1–F4 = 93.72(17), F1–Zr1–F2 = 96.96(16), F4–Zr1–F3 = 96.62(19), F2–Zr1–F3 = 94.04(16), N2–Zr1–N1 = 65.1(2), N3–Zr1–N4 = 66.05(19).

The complexes are poorly soluble in CD_2Cl_2, but show simple ^1H NMR spectra with a single δ(Me) resonance and three rather broad $\delta(CH_2)$ resonances with ill-defined couplings, indicating a symmetrical coordination of the ligand with all four Me groups on the same side of the N_4 plane.[28] Together with a singlet ^{19}F NMR resonance, this suggests an eight-coordinate environment, possibly a square antiprism. Low temperature NMR studies were not possible due to the very poor solubility. The solutions are readily hydrolysed to form $[MF_6]^{2-}$ salts and these are a major impurity in the products if the Me_4-cyclam is not thoroughly dried before use.

Attempted synthesis of soft donor complexes. $Me_2PCH_2CH_2PMe_2$ did not displace dmso from $[ZrF_4(dmso)_2]$ in CH_2Cl_2, which is not particularly surprising given the difficulties experienced with the harder N-donor ligands. Stirring a CH_2Cl_2 solution of $[ZrI_4(\text{diphosphine})_2]$ (diphosphine = $Me_2PCH_2CH_2PMe_2$ or $o\text{-}C_6H_4(PMe_2)_2$)[29,30] with 4.5 mol. equivalents of powdered Me_3SnF caused the initially orange-yellow solutions to become colourless after ~12 h and after 48 h fine white precipitates had formed. These were identified as ZrF_4 (and some residual Me_3SnF) by IR spectroscopy. The filtrates examined by ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy showed Me_3SnI,[31] free diphosphine, and traces of phosphine oxides, presumably from some air oxidation. Thus, I/F exchange is accompanied by dissociation of the phosphine from the "ZrF_4" which then polymerises and precipitates. Similar loss of phosphine and precipitation of TiF_4 was observed in dilute CH_2Cl_2 solutions of $[TiF_4(\text{diphosphine})]$,[4a] and with the even harder zirconium(IV) centre, the diphosphine coordination cannot compete with the formation of fluorine bridges and precipitation of ZrF_4. Attempts to react $[ZrF_4(dmf)_2]$ or $ZrF_4{\cdot}3H_2O$ with neat SMe_2 failed, no reaction being apparent after 48 h. This contrasts with the Group V pentafluorides, MF_5 (M = Nb or Ta), and with ZrX_4 (X = Cl or Br) which react easily with SMe_2 to form $[MF_5(SMe_2)]$[3a,5] and $[ZrX_4(SMe_2)_2]$[32] respectively.

The reaction of the NHC, 1,3-(2,6-di-isopropylphenyl)imidazol-2-ylidene (IDiPP) with $[ZrF_4(dmf)_2]$ in CH_2Cl_2 produced [IDiPPH]Cl, indicating protonation of the carbene rather than adduct formation. From anhydrous thf solutions isomorphous brown crystals were obtained which proved to be $[IDiPPH]_3[M_3F_{15}]{\cdot}4thf$ (M = Zr or Hf) from crystal structure determinations. The hafnium system formed poor quality crystals, but the zirconium data set was satisfactorily refined. Discrete trinuclear anions were clear in both structures (Fig. 9), and have not been identified previously. There are literature examples of LnM_3F_{15} (Ln = lanthanide),[12] but these contain infinite polymers rather than discrete anions. The latter, which are composed of octahedral MF_6 units sharing two *cis*-vertices, are reminiscent of units present in TiF_4 or $[Ti_4F_{18}]^{2-}$.[4a,33,34]

In solution the $^{19}F\{^1H\}$ NMR spectra (at 295 and 243 K) show only singlets at $\delta = -11.5$ (Zr) or -44.5 (Hf), indicating breakdown to $[MF_6]^{2-}$ anions or possibly dynamic exchange. Cl/F exchange using $[ZrCl_4(IDiPP)_2]$[35] and Me_3SnF gave crystals of $[IDiPPH][SnMe_3Cl_2]$ (ESI†), showing halide exchange had occurred, but there was no spectroscopic evidence for formation of a carbene adduct.

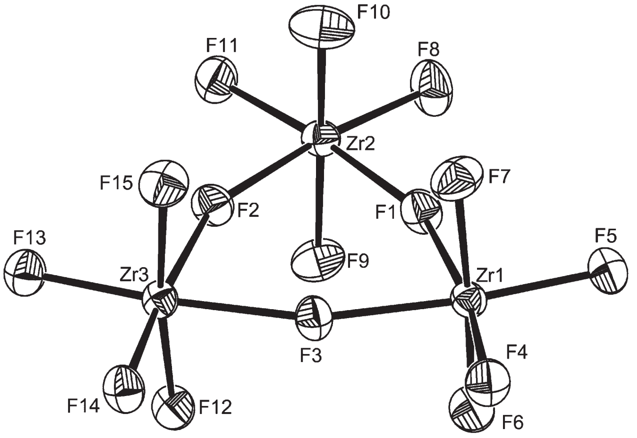

Fig. 9 Crystal structure of the anion in $[IDiPPH]_3[Zr_3F_{15}]{\cdot}4thf{\cdot}nCH_2Cl_2$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): $Zr\text{–}F_{terminal}$ = 1.942(4)–1.988(4), $Zr\text{–}F_{bridging}$ = 2.124(4)–2.139(4), Zr–F–Zr 155.6(2)–159.6(2).

Conclusions

A series of O- and N-donor complexes of the tetrafluorides with a range of coordination numbers (6, 7 or 8) and geometries have been characterised both structurally and spectroscopically. Most complexes show systematic changes on replacing Zr by Hf, for example in the ^{19}F NMR chemical shifts (Table 1), which are good indicators of the speciation, although some unexpected differences remain such as the dimer *vs.* monomer structures of the dmf adducts $[(dmf)_2F_3Zr(\mu\text{-}F)_2ZrF_3(dmf)_2]$ and $[HfF_4(dmf)_2]$. The large metal centres clearly accommodate eight-coordination without any steric problems, and hence the failure of the OPR_3 and $OAsPh_3$ ligands to achieve a coordination number higher than six must be electronic in origin. In contrast, TiF_4 adducts are six-coordinate, apart from some seven coordinate cations with crown ethers.[34,36] The chemistry of the MF_4 acceptor units are dominated by two factors, the ability to form very strong F-bridges, which means that reformation of the polymeric parent tetrafluoride can compete with coordination to a neutral ligand in many cases, and also their extreme oxophilicity. The difficulty of displacing O-donor dmso or dmf from the synthons, and the (at least partial) displacement of usually strong chelating ligands such as 2,2′-bipyridyl or 1,10-phenanthroline by O-donor solvents, clearly demonstrates the latter point. The failure to obtain complexes with the soft, but usually very strong, σ-donor alkyl diphosphines, could simply be a mismatch of orbital size and energy, but given that the Cl/F exchange route resulted in precipitation of ZrF_4 and liberation of the diphosphine, it seems to be a clear example of the zirconium centre preferring fluorine bridges to the soft donor. This is a more extreme case of the chemistry observed previously with TiF_4.[4a] The failure to form adducts with SMe_2 is less surprising and ascribed to the same cause, although it should be noted that NbF_5 and TaF_5 both form $[MF_5(SMe_2)]$ and $[MF_4(SMe_2)_4][MF_6]$ adducts by direct reaction with the $[MF_5]_4$.[3a,5] Similarly, thio- and seleno-ethers and diphosphines and diarsines form stable (although very readily hydrolysed) complexes with the heavier ZrX_4 and HfX_4 salts.[29,30,32] We note that $[MX_4(L\text{–}L)_2]$ (M = Zr of Hf; X = Cl or Br; L–L =

o-$C_6H_4(PMe_2)_2$ or *o*-$C_6H_4(AsMe_2)_2$) can be made by reaction of the diphosphine or diarsine ligand with MX_4 in thf solution,[29] *i.e.* in the presence of a large excess of the O-donor solvent, which contrasts with their inability to displace O-donor ligands from ZrF_4 adducts in a non-coordinating solvent in the present work. The case of the NHC's is slightly more complicated in that whilst metal tetrafluoride adducts were not obtained, protonation of the carbene to the imidazolium salt was observed. Extrapolation from the properties of the known TiF_4/NHC adducts[4b] would suggest that Zr(Hf)F_4 adducts may well be less stable, but does not allow us to conclude that they do not exist. The isolation of examples of the new trimeric anions $[M_3F_{15}]^{3-}$ (M = Zr or Hf) can be added to our previous structural authentication of protonated thioethers (in NbF_5 chemistry)[3b] or diprotonated *o*-phenylene-diphosphines (from TiF_4 systems)[4a] as unexpected spin-offs arising from the very different reaction conditions in high valent metal fluoride coordination chemistry. The isolation of the geometric isomers of $[(dmso)_2F_3Zr(\mu\text{-}F)_2ZrF_3(dmso)_2]$, albeit from different solvents, was unexpected in that the complex appears to be exchanging ligands in solution and the isomers identified structurally both contain pentagonal bipyramidal geometry, but differ in the sequence of donors in the pentagonal plane, so one would expect their interconversion to be facile.[37]

Experimental

Anhydrous and hydrated ZrF_4 and HfF_4 was obtained from Apollo or Aldrich and used as received. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, MeCN, dmf), Na-benzophenone-ketyl (thf, Et_2O) or over molecular sieves (dmso). Ligands (Aldrich or Strem) were dried by heating *in vacuo* (0.1 torr) (2,2′-bipyridyl, 1,10-phenanthroline, $OPPh_3$, $OAsPh_3$, $OPMe_3$, pyNO, Me_4-cyclam) or distilled from BaO (py) and stored in a glove box. The ligand *o*-$C_6H_4(PMe_2)_2$ was made by the literature method,[38] $Me_2P(CH_2)_2PMe_2$ was obtained from Strem and used as received. 1,3-(2,6-Di-isopropylphenyl)-imidazolium chloride was made as described,[39] deprotonated using potassium hexamethyldisilazide in toluene, and the free NHC ligand (IDiPP) was stored in a glove box.

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded from d^7-dmf, d^6-dmso or CD_2Cl_2 solutions using a Bruker DPX400 spectrometer and are referenced to the residual protiosolvent resonance. $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external $CFCl_3$ and external 85% H_3PO_4 respectively. Microanalyses on new complexes were undertaken by Medac Ltd. All preparations were carried out under a dry dinitrogen atmosphere using Schlenk and glove-box techniques. Generally pure and dry samples of the O- and N-donor complexes can be handled in air, although most take up water on prolonged exposure.

$[ZrF_4(dmso)_2]$

Finely powdered ZrF_4 hydrate (0.50 g, ~3 mmol) was suspended in dmso (10 mL) and the mixture stirred and heated to 80 °C when the solid dissolved. The colourless solution was cooled and allowed to stand at ambient temperatures for 2 d. A mixture of white powder and colourless crystals separated, which were filtered off, rinsed with diethyl ether (5 mL) and dried *in vacuo*. Yield: 0.85 g, 87%. Anal. Calc. for $C_4H_{12}F_4O_2S_2Zr$ (323.5): C, 14.8; H, 3.7. Found: C, 14.3; H, 3.9%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.56$ (s); (d^7-dmf, 295 K): 2.68 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 43.5 (s); (d^6-dmso, 295 K): 43.5 (s); (d^7-dmf, 295 K): 43.1 (s); (220 K): 41.7 (s). IR (Nujol/cm^{-1}): ν = 1012vbr (S=O), 537s, 489s, 449s (Zr–F), 353 (Zr–F–Zr).

$[HfF_4(dmso)_2]$

Was made similarly to the zirconium complex, although crystallisation took ~1 week, to produce colourless crystals. Yield: 90%. Anal. Calc. for $C_4H_{12}F_4HfO_2S_2$ (410.7): C, 11.7; H, 2.9. Found: C, 11.5; H, 2.6%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.55$ (s); (d^7-dmf, 295 K): 2.82 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): −1.5 (s); (d^6-dmso, 295 K): −1.5 (s); (d^7-dmf, 295 K): −1.2 (s); (220 K): −1.0 (s). IR (Nujol/cm^{-1}): ν = 1003vbr (S=O), 508s, 492s, 453s (Hf–F), 347vbr (Hf–F–Hf).

$[ZrF_4(dmf)_2]$

Was made similarly to $[ZrF_4(dmso)_2]$ as colourless crystals. Yield: 76%. Anal. Calc. for $C_6H_{14}F_4N_2O_2Zr$ (313.4): C, 23.0; H, 4.5; N, 8.9. Found: C, 22.8; H, 5.2; N, 8.8%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.89$ (s) [3H], 2.91 (s) [3H], 8.00 (s) [H]. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 43.5 (s); (d^7-dmf, 295 K): 43.9 (s); (220 K): 44.2 (s). IR (Nujol/cm^{-1}): ν = 1651s,br (C=O), 554s, 524s (Zr–F), 375m (Zr–F–Zr).

$[HfF_4(dmf)_2]$

Was made similarly to the Zr complex, as colourless crystals which separated from the synthesis solution over ~3 d. Yield: 74%. Anal. Calc. for $C_6H_{14}F_4HfN_2O_2$ (400.7): C, 18.0; H, 3.5; N, 7.0. Found: C, 17.8; H, 2.9; N, 6.5%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.82$ (s) [3H], 2.92 (s) [3H], 7.99 (s) [H]. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): −1.7 (br s); (d^7-dmf, 295 K): −1.26 (s); (220 K): −1.44 (s). IR (Nujol/cm^{-1}): ν = 1671s, 1656s (C=O), 584s, 531br, 520sh (Hf–F).

$[ZrF_4(OPPh_3)_2]$

$[ZrF_4(dmso)_2]$ (0.32 g, 21.0 mmol) was dissolved in hot dmso (5 mL), the solution cooled, and a solution of $OPPh_3$ (0.56 g, 2.0 mmol) in CH_2Cl_2 (25 mL) added. The colourless solution was stirred for 5 h, and then concentrated to ~10 mL *in vacuo*. On standing at room temperature for 3 d a mixture of white powder and some colourless crystals separated. These were filtered off and dried *in vacuo*. Yield: 0.75 g, 76%. Anal. Calc. for $C_{36}H_{30}F_4O_2P_2Zr\cdot 3CH_2Cl_2$ (978.6): C, 47.9; H, 3.7. Found: C, 48.1; H, 3.3%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 7.42$ (s) [2H], 7.63 (m) [3H]. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 49.0 (vbr) [2F], 26.0 (vbr) [2F]; (253K): 48.1 (s) [2F], 24.2 (s) [2F], 23.8 (sh). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): 40.6 (s); (243 K): 40.9, 40.7

(sh); (180 K): 41.2 (s). IR (Nujol/cm^{-1}): ν = 1076 *vs* (P=O), 514 *vs* (Zr–F).

The following complexes were made by the same general method as used for [$ZrF_4(OPPh_3)_2$].

[$ZrF_4(OAsPh_3)_2$]

White powder. Yield: 86%. Anal. Calc. for $C_{36}H_{30}As_2F_4O_2Zr{\cdot}2CH_2Cl_2$ (981.6): C, 46.5; H, 3.8. Found: C, 46.5; H, 4.3%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 7.41 (s) [2H], 7.63 (m) [H], 7.74 (m) [2H]. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): ~18 (vbr); (223 K): 29.5 (s) [2F], 17.0 (s) [2F], 16.3 (s). IR (Nujol/cm^{-1}): ν = 875s (As=O), 515 vs (Zr–F). Colourless crystals used for the X-ray data collection were grown from a solution of the complex in CH_2Cl_2 in a freezer (−18 °C) for several days.

[$HfF_4(OAsPh_3)_2$]

White powder. Yield: 83%. Anal. Calc. for $C_{36}H_{30}As_2F_4HfO_2{\cdot}1/2CH_2Cl_2$ (941.4): C, 46.6; H, 3.3. Found: C, 47.2; H, 3.9%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 7.50 (m) [2H], 7.64 (m) [H], 7.73 (m) [2H]. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): −9.1 (br), −20.6 (br); (243 K): −10.7 (s) [2F], −20.7 (s) [2F], −21.9 (s). IR (Nujol/cm^{-1}): ν = 875s (As=O), 490 vs (Hf–F).

[$HfF_4(OPPh_3)_2$]

White powder prepared similarly using [$HfF_4(dmf)_2$] in dmf/CH_2Cl_2 in place of [$HfF_4(dmso)_2$], since use of the latter resulted in isolation of a mixture containing substantial amounts of [$HfF_4(dmso)_2$]. Yield: 55%. Anal. Calc. for $C_{36}H_{30}F_4HfO_2P_2$ (811.1): C, 53.3; H, 3.7. Found: C, 52.8; H, 3.4%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 7.42 (m) [2H], 7.61 (m) [3H]. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): 4.1 (s) [2F], −16.6 (s) [2F]; (243 K): 2.35 (s) [2F], −17.6 (s) [2F], −18.3 (sh). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): 41.9 (s); (273 K): 42.2 (s); (243 K): 42.4, 42.3 (sh). IR (Nujol/cm^{-1}): ν = 1090s (P=O), 493 vs br (Hf–F).

[$ZrF_4(OPMe_3)_2$]

[$ZrF_4(dmf)_2$] (0.31 g, 1.0 mmol) was dissolved in warm dmf (5 mL), the solution cooled to ambient, and a solution of $OPMe_3$ (0.28 g, 3.0 mmol) in CH_2Cl_2 (25 mL) added. The colourless solution was stirred for 5 h, and then all the solvents removed by warming *in vacuo*, to leave a colourless oil. The oil was redissolved in CH_2Cl_2 (10 mL), filtered to remove a small amount of insoluble material, and diethyl ether (5 mL) added. On standing for ~24 h, a mixture of colourless crystals and a white powder separated. These were filtered off and dried *in vacuo*. Yield: 0.29 g, 65%. Anal. Calc. for $C_6H_{18}F_4O_2P_2{\cdot}CH_2Cl_2$ (436.3): C, 19.3; H, 4.6. Found: C, 19.5; H, 4.6%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.74 (d) $^2J_{PH}$ = 13.5 Hz. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): 31.1 (br); (243 K): 41.2 (s) [2F], 19.1 (s) [2F], 18.9 (sh). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): 62 (s); (243 K): 61.9 (s). IR (Nujol/cm^{-1}): ν = 1092br (P=O), 527br, 480 vs br, 469sh (Zr–F).

[$HfF_4(OPMe_3)_2$]

Was made similarly from [$HfF_4(dmf)_2$]. Yield: 48%. Anal. Calc. for $C_6H_{18}F_4HfO_2P_2$ (438.6): C, 16.4; H, 4.1. Found: C, 16.9; H, 4.1%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.73 (d) $^2J_{PH}$ = 13.5 Hz. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): −12 (br); (243 K): −4.1 (s) [2F], −20.2 (s) [2F], −20.7 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): 63.6 (br); (243 K): 64.8 (s). IR (Nujol/cm^{-1}): ν = 1076vbr (P=O), 559m, 515sh, 486 vs (Hf–F).

[$ZrF_4(pyNO)_2$]

Finely powdered [$ZrF_4(dmso)_2$] (0.32 g, 1.0 mmol) was suspended in rapidly stirred CH_2Cl_2 (40 mL) and a solution of pyNO (0.19 g, 2.0 mmol) in CH_2Cl_2 (10 mL) added. After some hours, a colourless solution was formed, which was concentrated to ~15 mL and stirred for a further 48 h. A fine white powder precipitated. This was filtered off and dried *in vacuo*. Yield: 0.25 g, 70%. Anal. Calc. for $C_{10}H_{10}F_4N_2O_2Zr$ (357.4): C, 33.6; H, 2.6, N 7.8. Found: C, 33.4; H, 3.2; N, 7.9%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 7.36 (s) [3H], 8.17 (m) [2H]. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): 37.7 (br); (253 K): insoluble. IR (Nujol/cm^{-1}): ν = 1232 vs, 1225s (N=O), 518s, 505s (Zr–F).

[$HfF_4(pyNO)_2$]

Finely powdered [$HfF_4(dmf)_2$] (0.42 g, 1.0 mmol) was suspended in rapidly stirred CH_2Cl_2 (40 mL) and a solution of pyNO (0.19 g, 2.0 mmol) in CH_2Cl_2 (10 mL) added. After some hours a colourless solution was formed, which was concentrated to ~15 mL and stirred for a further 48 h. A fine white powder precipitated over this time. This was filtered off and dried *in vacuo*. Yield: 0.29 g, 66%. Anal. Calc. for $C_{10}H_{10}F_4HfN_2O_2{\cdot}2CH_2Cl_2$ (614.6): C, 23.5; H, 2.3, N, 4.6. Found: C, 23.2; H, 2.0; N, 5.4%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 7.27 (m) (s) [3H], 8.16 (m) [2H]. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): −6.5 (s); (253 K): insoluble. IR (Nujol/cm^{-1}): ν = 1231s, 1221s (N=O), 504m, 490s, 480s (Hf–F).

[$ZrF_4(1,10\text{-}phen)_2$]

Finely powdered [$ZrF_4(dmso)_2$] (0.32 g, 1.0 mmol) was dissolved in warm dmso (5 mL) and vigorously stirred whilst adding a solution of 1,10-phen (0.32 g, 2.05 mmol) in dry CH_2Cl_2 (80 mL). After *ca.* 1 h a clear solution was formed which was stirred at room temperature for 48 h, during which time a large amount of fine white precipitate formed. This was filtered off, rinsed with CH_2Cl_2 (5 mL) and dried *in vacuo*. Yield: 0.42 g, 80%. Anal. Calc. for $C_{24}H_{16}F_4N_4Zr$ (527.6): C, 54.6; H, 3.1; N, 10.6. Found: C, 54.5; H, 3.1; N, 10.4%. ^{1}H NMR (CD_2Cl_2, 295 K): very poorly soluble, 7.87 (m) [2H], 8.10 (s) [2H], 8.58 (m) [2H], 9.79 (m) [2H]. ^{19}F{^{1}H} NMR (CD_2Cl_2, 295 K): 21.3 (s). IR (Nujol/cm^{-1}): ν = 505s, 478s, Zr–F.

[$HfF_4(1,10\text{-}phen)_2$]

Was made similarly to the zirconium complex as a fine white powder. Yield: 83%. Anal. Calc. for $C_{24}H_{16}F_4HfN_4{\cdot}1/2CH_2Cl_2$

(657.4): C, 44.8; H, 2.6; N, 8.5. Found: C, 44.7; H, 3.0; N, 8.2%. ^{1}H NMR (CD_2Cl_2, 295 K): very poorly soluble, 7.89 (m) [2H], 8.07 (s) [2H], 8.55 (m) [2H], 9.79 (m) [2H]. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): −17.8 (s). IR (Nujol/cm^{-1}): ν = 502s, vbr, 480sh (Hf–F).

[ZrF_4(2,2′-bipy)$_2$]

[$ZrF_4(dmf)_2$] (0.32 g, 1.0 mmol) was dissolved in warm dmf (5 mL) and a solution of 2,2′-bipy (0.40 g, 2.5 mmol) in dry CH_2Cl_2 (80 mL) added. Initially a clear colourless solution formed, which over the course of *ca.* 1 h stirring at room temperature precipitated a white powder. The mixture was allowed to stand for 48 h and then the precipitate was filtered off, rinsed with CH_2Cl_2 (5 mL) and dried *in vacuo.* Yield: 0.44 g, 68%. Anal. Calc. for $C_{20}H_{16}F_4N_4Zr\cdot 2CH_2Cl_2$ (649.4): C, 40.1; H, 3.1; N, 8.6. Found: C, 39.1; H, 2.5; N, 9.2%. ^{1}H NMR (CD_2Cl_2, 295 K): very poorly soluble, 7.34 (m) [2H], 7.87 (m) [2H], 8.43 (m) [2H], 8.66 (s) [2H]. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): 24.5 (s). IR (Nujol/cm^{-1}): ν = 525 vs, br (Zr–F).

[HfF_4(2,2′-bipy)$_2$]

Was made similarly using either [$HfF_4(dmf)_2$] in dmf/CH_2Cl_2 or [$HfF_4(dmso)_2$] in dmso/CH_2Cl_2, the product being obtained as a very pale pink powder. Yield: 78%. Anal. Calc. for $C_{20}H_{16}F_4HfN_4$ (566.9): C, 42.4; H, 2.9; N, 9.9. Found: C, 42.2; H, 3.1; N, 9.9%. ^{1}H NMR (CD_2Cl_2, 295 K): very poorly soluble, 7.23 (m) [2H], 7.80 (m) [2H], 8.30 (m) [2H], 8.50 (s) [2H]. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): −11.2 (s). IR (Nujol/cm^{-1}): ν = 505vbr, 490sh (Hf–F).

[ZrF_4(Me_4-cyclam)]

[$ZrF_4(dmf)_2$] (0.32 g, 1.0 mmol) was dissolved in warm dmf (5 mL) and a solution of Me_4-cyclam (0.25 g, 1.0 mmol) in dry CH_2Cl_2 (30 mL) added. Initially a clear colourless solution formed, which over the course of *ca.* 1 h stirring at room temperature deposited a white precipitate. The mixture was stirred for 48 h, and then the precipitate was filtered off, rinsed with CH_2Cl_2 (5 mL) and dried *in vacuo.* Yield: 0.22 g, 52%. Anal. Calc. for $C_{14}H_{32}F_4N_4Zr\cdot CH_2Cl_2$ (508.6): C, 35.4; H, 6.8; N, 11.0. Found: C, 35.7; H, 7.2; N, 11.0%. ^{1}H NMR (CD_2Cl_2, 295 K): 1.88 (br,s) [4H], 2.45 (s) [12H], 2.78 (m) [8H], 2.92 (m) [8H]. $^{19}F\{^{1}H\}$ (CD_2Cl_2, 295 K): 14.2 (s). IR (Nujol/cm^{-1}): ν = 540s, 502s, 477m (Zr–F).

[HfF_4(Me_4-cyclam)]

Was made similarly from [$HfF_4(dmf)_2$] as a white powder in 68% yield. Anal. Calc. for $C_{14}H_{32}F_4HfN_4\cdot CH_2Cl_2$ (595.9): C, 30.3; H, 5.8; N, 9.4. Found: C, 30.8; H, 6.6; N, 10.0%. ^{1}H NMR (CD_2Cl_2, 295 K): 1.90 (m) [4H], 2.42 (s) [12H], 2.72 (m) [8H], 2.82 (m) [8H]. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): −12.0 (s), very poorly soluble. IR (Nujol/cm^{-1}): ν = 552s, 493s, 460m (Hf–F).

Attempted preparation of $[ZrF_4\{o\text{-}C_6H_4(PMe_2)_2\}_n]$ (n = 1 or 2)

$[ZrI_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$[29] (0.2 g, 0.2 mmol) was added to dry CH_2Cl_2 (80 mL) and finely powdered dry Me_3SnF (0.165 g, 0.9 mmol) added. The mixture was vigorously stirred when the orange-yellow colour discharged slowly and a fine white precipitate formed. After stirring for 48 h, the precipitate was filtered off, rinsed with CH_2Cl_2 (2 × 25 mL) and dried *in vacuo*. The solid was identified as ZrF_4 with some residual Me_3SnF by its IR spectrum. The filtrate and washings were examined by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy which showed $o\text{-}C_6H_4(PMe_2)_2$ δ(P) = −55.0 and Me_3SnI δ(H) = +0.9, $^{2}J(^{1}H{-}^{119}Sn)$ = 56 Hz,[31,38] and did not exhibit any ^{19}F resonances. The reaction of $[ZrI_4(Me_2PCH_2CH_2PMe_2)_2]$[30] with Me_3SnF similarly gave ZrF_4 and Me_3SnI and $Me_2PCH_2CH_2PMe_2$. The iodides were used in preference to the chlorides due to much higher solubility in CH_2Cl_2.

Attempted preparation of NHC complexes

Method 1. A CH_2Cl_2 solution of IDiPP (0.26 g, 0.67 mmol) was added to a solution of [$ZrF_4(dmf)_2$] (0.104 g, 0.33 mmol). The solution was stirred for 16 h, then concentrated to *ca.* 5 mL and crystallised through the slow diffusion of Et_2O into the CH_2Cl_2 solution. Large, pale brown crystals grew, which were identified by their crystal structure as the imidazolium salt [IDiPPH]-$Cl\cdot 2CH_2Cl_2$. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy supported this result and no fluorine signal was observed in the $^{19}F\{^{1}H\}$ NMR spectrum. Repeating the reaction using [$HfF_4(dmf)_2$] resulted in the same product crystallising.

If thf is used as the solvent instead of CH_2Cl_2, then the suspension of [$ZrF_4(dmf)_2$] mostly dissolves after addition of a thf solution of IDiPP and stirring for one week. After this time the reaction mixture was filtered, the supernatant concentrated to *ca.* 5 mL and the product crystallised through the slow diffusion of hexane into the thf solution. Pale brown crystals of $[IDiPPH]_3[Zr_3F_{15}]\cdot 4thf\cdot xCH_2Cl_2$ formed, with disorder in some of the thf moieties. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): −11.5. Repeating the reaction using [$HfF_4(dmf)_2$] in thf afforded the hafnium analogue with an $[Hf_3F_{15}]^{3-}$ anion. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 295 K): −44.5. The crystals are isomorphous with the zirconium compound, but the dataset was of poor quality and is not presented.

Method 2. The compound [$ZrCl_4(IDiPP)_2$] made by the method of Niehaus *et al.*[35] (0.15 g, 0.27 mmol) was dissolved in thf (10 mL), Me_3SnF (0.23 g, 1.23 mmol) added, and the reaction stirred for one week. After this time, the reaction mixture was filtered and the supernatant concentrated to *ca.* 5 mL, then crystallised through the slow diffusion of hexane into the thf solution. Crystals produced were identified by a structure determination and ^{1}H NMR spectroscopy as [IDiPPH][$SnMe_3Cl_2$] (ESI†).

X-Ray crystallography

Crystals were obtained as described above. Details of the crystallographic data collection and refinement are in Table 2. Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724* + detector mounted at the window of an *FR-E* + *SuperBright* molybdenum rotating anode generator

Table 2 Crystal data and structure refinement details[a]

Compound	$[Zr_2F_8(Me_2SO)_4]$	$[Hf_2F_8(Me_2SO)_4]$	$[HfF_4(Me_2NCHO)_2]$	$[ZrF_4(OPPh_3)_2]\cdot 2CH_2Cl_2$	$[ZrF_4(OAsPh_3)_2]\cdot 2CH_2Cl_2$
Formula	$C_8H_{24}F_8O_4S_4Zr_2$	$C_8H_{24}F_8Hf_2O_4S_4$	$C_6H_{14}F_4HfN_2O_2$	$C_{38}H_{34}Cl_4F_4O_2P_2Zr$	$C_{38}H_{34}As_2Cl_4F_4O_2Zr$
M	646.95	821.49	400.68	893.61	981.51
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group (no.)	$P4_2/n$ (no. 86)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	16.473(5)	8.675(4)	13.591(3)	8.900(3)	8.898(3)
b/Å	16.473(5)	11.750(4)	7.2522(12)	14.700(5)	14.688(4)
c/Å	7.699(3)	10.667(4)	11.6584(19)	14.547(5)	14.688(4)
α/°	90	90	90	90	90
β/°	90	108.269(7)	100.919(7)	95.77(2)	94.348(7)
γ/°	90	90	90	90	90
U/Å^3	2089.2(11)	1032.4(7)	1128.3(4)	1893.5(11)	1933.8(10)
Z	4	2	4	2	2
μ(Mo-Kα)/mm^{-1}	1.478	10.534	9.284	0.711	2.312
F(000)	1280	768	752	711	976
Total no. reflections	5120	5749	3801	9830	9807
Unique reflections	2388	2359	1283	4270	4383
R_{int}	0.0161	0.1632	0.0601	0.1296	0.0391
Min., max. transmission	0.892, 1.0	0.690, 1.0	0.613, 1.0	0.517, 1.0	0.608, 1.0
No. of parameters, restraints	122, 0	118, 0	71, 0	230, 0	237, 0
Goodness-of-fit on F^2	1.045	1.027	1.061	0.548	1.107
Resid. electron density/e Å^{-3}	0.601	4.035	2.539	0.650	0.748
R_1[b] $[I_o > 2\sigma(I_o)]$	0.0224	0.0489	0.0351	0.0432	0.0570
R_1 (all data)	0.0253	0.0518	0.0367	0.1201	0.0746
wR_2[b] $[I_o > 2\sigma(I_o)]$	0.0526	0.1159	0.0824	0.0548	0.1172
wR_2 (all data)	0.0538	0.1172	0.0838	0.0548	0.1172

Compound	$[ZrF_4(OAsPh_3)_2]\cdot 2CH_2Cl_2$	$[HfF_4(OPMe_3)_2]$	$[ZrF_4(2,2'\text{-bipy})_2]$	$[C_{27}H_{37}N_2\ ]_3[Zr_3F_{15}]\cdot 4thf\cdot 0.55(CH_2Cl_2)$
Formula	$C_{38}H_{34}As_2Cl_4F_4O_2Zr$	$C_6H_{18}F_4HfO_2P_2$	$C_{20}H_{16}F_4N_4Zr$	$C_{97.55}H_{144.10}Cl_{1.10}F_{15}\ N_6O_4Zr_3$
M	981.51	438.63	479.59	2062.54
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group (no.)	$Pbcn$ (no. 60)	$C2/c$ (no. 15)	Cc (no 9)	$P\bar{1}$ (no. 2)
a/Å	15.175(5)	438.63	12.991(4)	15.935(4)
b/Å	16.254(6)	12.701(5)	13.134(4)	17.240(4)
c/Å	16.340(6)	14.612(5)	11.714(4)	21.679(7)
α/°	90	90	90	81.698(16)
β/°	90	128.905(11)	100.919(7)	85.337(17)
γ/°	90	90	90	66.454(13)
U/Å^3	4030(2)	2734.2(17)	1962.3(10)	5401(3)
Z	4	8	4	2
μ(Mo-Kα)/mm^{-1}	2.218	7.892	0.610	0.382
F(000)	1952	1664	960	2154
Total no. reflections	15 254	4797	4178	46 126
Unique reflections	3811	4797	2920	19 032
R_{int}	0.0739	0.0	0.0217	0.0707
Min., max. transmission	0.628, 1.0	0.70, 1.0	0.906, 1.0	0.9737, 0.9924
No. of parameters, restraints	231, 0	143, 3	262, 144	1062, 2
Goodness-of-fit on F^2	1.304	1.108	1.065	1.153
Resid. electron density/e Å^{-3}	1.471	2.211	1.434	1.480
R_1[b] $[I_o > 2\sigma(I_o)]$	0.0787	0.0748	0.0384	0.1010
R_1 (all data)	0.0887	0.0758	0.0420	0.1229
wR_2[b] $[I_o > 2\sigma(I_o)]$	0.1168	0.1992	0.0951	0.2098
wR_2 (all data)	0.1203	0.2000	0.0983	0.2231

[a] Common items temperature = 120 K; wavelength (Mo-Kα) = 0.71073 Å. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

with HF or VHF *Varimax* optics (100 µm or 70 µm focus). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrystalClear-SM Expert 2.0 r7 (Rigaku, 2011). Structure solution and refinement were routine[40,41] except as noted below.

$[HfF_4(OPMe_3)_2]$

The data was indexed and integrated using the Twinsolve tool.[42] The initial structure was solved by using HKLF 4 format data from one twin component. Further refinement was completed by replacing the HKLF4 data with HKLF5 data combining the data from both components.

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