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Synthesis, properties and structures of eight-coordinate zirconium(IV) and hafnium(IV) halide complexes with phosphorus and arsenic ligands

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Eight-coordinate $[MX_4(L–L)_2]$ (M = Zr or Hf; X = Cl or Br; L–L = o-$C_6H_4(PMe_2)_2$ or o-$C_6H_4(AsMe_2)_2$) were made by displacement of Me_2S from $[MX_4(Me_2S)_2]$ by three equivalents of L–L in CH_2Cl_2 solution, or from MX_4 and L–L in anhydrous thf solution. The $[MI_4(L–L)_2]$ were made directly from reaction of MI_4 with the ligand in CH_2Cl_2 solution. The very moisture-sensitive complexes were characterised by IR, UV/Vis, and ^1H and ^{31}P NMR spectroscopy and microanalysis. Crystal structures of $[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$, $[ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$, $[ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ and $[HfI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ all show distorted dodecahedral structures. Surprisingly, unlike the corresponding Ti(IV) systems, only the eight-coordinate complex was found in each system. In contrast, the ligand o-$C_6H_4(PPh_2)_2$ forms only six-coordinate complexes $[MX_4\{o\text{-}C_6H_4(PPh_2)_2\}]$ which were fully characterised spectroscopically and analytically. Surprisingly the tripodal triarsine, $MeC(CH_2AsMe_2)_3$, also produces eight-coordinate $[MX_4\{MeC(CH_2AsMe_2)_3\}_2]$ in which the triarsines bind as bidentates in a distorted dodecahedral structure. There is no evidence for seven-coordination as found in some thioether systems.

Introduction

Zirconium(IV) and hafnium(IV) are large, hard, oxophilic metal centres whose coordination chemistry is dominated by neutral N or O donor and anionic ligands.[1] There is also an extensive organometallic chemistry, much of it metallocene based, reflecting the importance of these metals in olefin oligomerisation, polymerisation and hydrozirconation.[2,3] However their coordination chemistry with neutral softer donor ligands is relatively poorly developed, and studies have been hindered both by the extreme moisture sensitivity of the complexes and their often poor solubility in non-donor solvents. We recently reported the synthesis, properties and structural characterisation of a variety of six-, seven- and eight-coordinate complexes of $ZrCl_4$ and $HfCl_4$ with thio- and selenoether ligands, examples including the six-coordinate ligand-bridged dimer $[\{ZrCl_4(MeS(CH_2)_3SMe)\}_2]$, the monomer $[HfCl_4(MeSeCH_2CH_2SMe)]$, and the eight-coordinate $[MCl_4(MeSCH_2CH_2SMe)_2]$ (M = Zr or Hf), whilst rare examples of seven-coordination are the macrocyclic $[MCl_4\{[9]aneS_3\}]$.[4,5] Eight-coordinate $[MCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ were reported many years ago,[6,7] although with very limited characterisation and the assignment of the structure is based on a comparison of the X-ray powder patterns with that of $[TiCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$. There are a number of structurally characterised examples with mono- and di-phosphines, most obtained during attempts to prepare M–M bonded species in lower oxidation states including, $[HfCl_4\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 2, 3),[8] $[Zr_2Cl_8(PMe_3)_4]$ and $[ZrI_4(PMe_3)_n]$ (n = 2, 3),[9,10] although little spectroscopic data are available. There is also an extensive organometallic chemistry of zirconium and hafnium in lower oxidation states based upon an $M(Me_2PCH_2CH_2PMe_2)_2$ core.[11] Dinuclear zirconium complexes of diphosphinophosphide ligands, $[P(CH_2CH_2PR_2)_2]^-$ have been described in which the phosphido groups bridge the zirconium centres.[12] We recently re-examined[13,14] the complexes of TiX_4 (X = Cl, Br or I) with diphosphine and diarsine ligands and found that whilst most ligands gave only six-coordinate $[TiX_4(L–L)]$ (X = Cl or Br), for o-$C_6H_4(EMe_2)_2$ (E = P or As) both six- and eight-coordinate complexes could be obtained. The solution behaviour and interconversions were probed by variable-temperature ^1H and ^{31}P NMR spectroscopy. However, for TiI_4 only six-coordinate $[TiI_4\{o\text{-}C_6H_4(EMe_2)_2\}]$ form, an old report of a yellow eight-coordinate species[7] was shown to be erroneous, the substance being a mixture of lower oxidation state complexes and iodinated ligand.[14]

Here we report systematic studies of MX_4 (M = Zr or Hf; X = Cl, Br or I) with the ligands o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(PPh_2)_2$ and $MeC(CH_2AsMe_2)_3$, with the aims of probing the existence of six-, seven- and eight-coordinate metals in these systems, obtaining detailed structural and spectroscopic data of the isolated complexes, and studying their interconversions.

Results and discussion

Synthesis

The synthesis of complexes of the oxophilic zirconium(IV) and hafnium(IV) halides with phosphine and arsine ligands requires the use of rigorously anhydrous conditions and careful choice of solvent. The direct reaction of the polymeric MX_4 (M = Zr or Hf, X = Cl or Br) with o-$C_6H_4(AsMe_2)_2$ or o-$C_6H_4(PMe_2)_2$ in CH_2Cl_2 or toluene was unsatisfactory even with long reaction times, the products being mixtures of the desired complexes and unchanged MX_4. However, this approach was successful with the corresponding tetraiodides. On stirring a suspension of MI_4 with three molar equivalents of the ligand (L–L) in CH_2Cl_2 the orange (Zr) or yellow (Hf) tetraiodide slowly dissolved, and after some hours the paler $[MI_4(L–L)_2]$ complexes deposited, more complex being produced by concentrating the solutions under vacuum. The $[MX_4(L–L)_2]$ (X = Cl or Br) were made by displacement of Me_2S from $[MX_4(Me_2S)_2]$[15] by three equivalents of L–L in CH_2Cl_2 solution, or directly from MX_4 and L–L in anhydrous thf solution. In the latter route which was most convenient, the anhydrous MX_4 was stirred with anhydrous thf at ambient temperatures until it had completely dissolved, and then three equivalents of L–L added. The reaction times are important, *ca.* 24 h being optimum for M = Zr and *ca.* 36 h for M = Hf. Shorter times appear to give incomplete conversion, whilst the products obtained using much longer times (3–4 d) are contaminated with thf cleavage products, especially in the case of the HfX_4/o-$C_6H_4(PMe_2)_2$ systems. The displacement of the O-donor thf from the oxophilic metal centres in thf solution by the softer Group 15 donor ligands is notable and demonstrates the strong coordinating ability of these o-phenylene bidentates. The poor solubility of the $[MX_4(L–L)_2]$ results in their precipitation from the reaction mixture, which may also help to drive the reaction. Using 1 : 1 MX_4 : L–L ratios led only to mixtures containing $[MX_4(L–L)_2]$ and starting materials. The $[MX_4(L–L)]$ were not obtained in these reactions, which contrasts with the reactions using $MeSCH_2CH_2SMe$ or $MeSeCH_2CH_2SeMe$

(L′–L′), when either [MX_4(L′–L′)] or [MX_4(L′–L′)$_2$] can be isolated depending upon the conditions used.[4,5]

The tripodal triarsine MeC(CH_2AsMe_2)$_3$ reacted easily with the suspended MI_4 in CH_2Cl_2 to form [MI_4(triarsine)$_2$], but reaction of the same ligand with MX_4 (X = Cl or Br) in thf gave mixtures of the triarsine complexes and the thf adducts. Probably the formation of six-membered chelate rings and the more flexible backbone accounts for the failure to completely displace thf in this case. The [MCl_4(triarsine)$_2$] complexes were best obtained from [MCl_4(Me_2S)$_2$][15] and the triarsine in CH_2Cl_2 solution. Attempts to synthesise [MCl_4(triarsine)] complexes using a 1 : 1 molar ratio of reactants were unsuccessful.

Finally the six-coordinate [MX_4(*o*-C_6H_4(PPh_2)$_2$)] were prepared by stirring 1.5 equivalents of *o*-C_6H_4(PPh_2)$_2$ with the anhydrous metal tetrahalide in a moderately large volume of dry CH_2Cl_2 for 2–3 days. The iodo-complexes form relatively easily, but obtaining complete reaction in the other cases requires rigorously dry glassware, reagents and solvents or the reactions fail to proceed or very impure products result. Using an excess of *o*-C_6H_4(PPh_2)$_2$ (>3 equivalents) does not produce 2 : 1 complexes.

Irrespective of the ligand, all isolated complexes were handled in a dinitrogen filled dry box (<5 ppm water), since all hydrolyse readily, although unlike the titanium analogues,[13] this is not visually evident through colour changes.

Properties

[MX_4{*o*-C_6H_4(EMe_2)$_2$}$_2$]. These complexes all have eight-coordinate metal centres in a distorted dodecahedral geometry as established by the crystal structures of [$ZrCl_4${*o*-C_6H_4($AsMe_2$)$_2$}$_2$], [$ZrBr_4${*o*-C_6H_4(PMe_2)$_2$}$_2$] and [MI_4{*o*-C_6H_4($AsMe_2$)$_2$}$_2$] (M = Zr or Hf) (see below). The chloro- and bromo-complexes are poorly soluble in halocarbon solvents, and are partially or completely decomposed by O or N donor solvents such as thf, $MeNO_2$ or MeCN, and very readily by moisture. The iodo-complexes are moderately soluble in CH_2Cl_2. Diffuse reflectance UV/Vis spectra, recorded from solid samples diluted with dry $BaSO_4$, showed broad absorptions in the near UV region (see Experimental section) which may be assigned as σ(P,As) and π(X) → Zr/Hf charge transfer (CT) bands, consistent with the donor groups present and the white or pale-cream colours†. The iodo-complexes have π(I) → Zr/Hf CT bands which lie in the region 24–30000 cm^{-1} and are responsible for the yellow colours. As with the thioether or selenoether analogues[4] the band energies do not vary significantly with the metal coordination number. The IR spectra of [$ZrCl_4${*o*-C_6H_4(EMe_2)$_2$}$_2$] show *ν*(Zr–Cl) at *ca.* 300 cm^{-1}, and [$ZrBr_4${*o*-C_6H_4(EMe_2)$_2$}$_2$] *ν*(Zr–Br) at *ca.* 220 cm^{-1} with the corresponding values in the hafnium analogues *ca.* 30 cm^{-1} to low frequency in each case. The values in the chloro-complexes correlate well with those reported for eight-coordinate thio- and selenoether complexes.[4] Solution studies were hampered by the poor solubility, however the ^1H NMR spectra of complexes of *o*-C_6H_4($AsMe_2$)$_2$ show single methyl resonances which shift to high frequency with halide Cl < Br < I; the same trend is apparent in the complexes of *o*-C_6H_4(PMe_2)$_2$, although the resonances appear either as broad signals approximating to doublets or multiplets with weaker outer-lines indicating second-order features. The $^{31}P\{^1H\}$ NMR spectra also show systematic high frequency shifts with halide Cl > Br > I, but with very similar values for both metal centres. In the presence of added diphosphine in CH_2Cl_2 solution at 295 K, the resonances of the complexes are unchanged showing exchange is slow on the NMR time scale. The NMR spectra of the [MX_4{*o*-C_6H_4(EMe_2)$_2$}$_2$] in CH_2Cl_2 also show no evidence for significant dissociation into [MX_4{*o*-C_6H_4(EMe_2)$_2$}] and *o*-C_6H_4(EMe_2)$_2$, which contrasts with the behaviour of the corresponding [TiX_4{*o*-C_6H_4(EMe_2)$_2$}$_2$] (X = Cl or Br)[12] where all but the diphosphine chloro-complex are extensively dissociated.‡

[MX_4{*o*-C_6H_4(PPh_2)$_2$}]. The microanalyses are consistent with 1 : 1 stoichiometry and hence six-coordination, similar to that established for the [$HfCl_4${$Ph_2P(CH_2)_nPPh_2$}] complexes.[8] The IR spectra of the six-coordinate complexes show for X = Cl or Br *ν*(M–X) at significantly higher frequencies to those reported for the eight-coordinate compounds, again consistent with results in other systems.[4,12] The poor solubility of the complexes made it difficult to obtain $^{31}P\{^1H\}$ NMR data. However, from saturated CH_2Cl_2 solutions under rigorously anhydrous conditions, there was a single weak resonance in each complex, which shifted to high frequency I < Br < Cl. The resonances in the iodo-complexes were slightly to low frequency of that in *o*-C_6H_4(PPh_2)$_2$. The presence of added *o*-C_6H_4(PPh_2)$_2$ did not produce any evidence for the formation of eight-coordinate complexes. To probe this possibility further, ^{31}P NMR spectra were also recorded from the synthesis solutions, both before isolation of the complexes, and from the residual filtrates after removal of the bulk complex. For the chloride and bromides, only the 1 : 1 complex and free *o*-C_6H_4(PPh_2)$_2$ were significant components, however for the iodo-complex reactions, the spectra showed several extra features. Some of these with *δ*(P) *ca.* 50 were also present in solutions of *o*-C_6H_4(PPh_2)$_2$ + I_2 and are attributable to iodinated diphosphine, but there were also very broad features at lower frequency which are probably due to lower oxidation state (paramagnetic) compounds. These results are reminiscent of the TiI_4/*o*-C_6H_4(PMe_2)$_2$ system reported previously,[13] and with Cotton's isolation of [(Ph_3PI)$_2I_3$]I_3 from reaction of ZrI_4 with PPh_3.[16]

[MX_4{MeC(CH_2AsMe_2)$_3$}$_2$] (X = Cl or I). The triarsine complexes were initially obtained from reactions of [MCl_4(Me_2S)$_2$] with MeC(CH_2AsMe_2)$_3$, which it was hoped might afford examples of seven-coordination. We note that MeC(CH_2AsMe_2)$_3$ gives only six-coordinate 1 : 1 complexes [TiX_4{MeC(CH_2AsMe_2)$_3$}][12] in which the triarsine is bound as a bidentate ligand. However, the crystal structure described below, showed that crystals obtained from the [$ZrCl_4$(Me_2S)$_2$]/MeC(CH_2AsMe_2)$_3$ reaction were [$ZrCl_4${MeC(CH_2AsMe_2)$_3$}$_2$] with the triarsine coordinated as a bidentate on an eight-coordinate zirconium centre. The *ν*(Zr–Cl) modes at 304, 296 cm^{-1} are also consistent with eight-coordination. The complex is poorly soluble in chlorocarbons, but at 300 K the ^1H NMR spectrum shows only three singlets all to high frequency of the resonances in the MeC(CH_2AsMe_2)$_3$, consistent either with symmetrical coordination of the ligand or with fast exchange. The complex precipitates on cooling the solution and no low-temperature NMR studies were possible. The Hf analogue is very similar, but essentially insoluble in chlorocarbons preventing any NMR studies, although its IR spectrum also suggests eight-coordination. An exploratory study of the MBr_4/MeC(CH_2AsMe_2)$_3$ systems also found insoluble products, and these were not pursued, but fortunately the MI_4/MeC(CH_2AsMe_2)$_3$ reactions yielded [MI_4{MeC(CH_2AsMe_2)$_3$}$_2$] complexes which were reasonably soluble in CH_2Cl_2, permitting ^1H and $^{13}C\{^1H\}$ VT NMR studies. The ^1H NMR spectrum of [ZrI_4{MeC(CH_2AsMe_2)$_3$}$_2$] at 300 K contains three singlets assignable to MeC, CH_2 and MeAs groups similar to the chloride case. However, on cooling to 273 K these resonances broaden and then by 223 K the spectrum is that shown in Fig. 1, which is unchanged on further cooling, the changes reversing on warming the solution. The spectrum is readily assigned as due to η^2-coordinated triarsine (see Fig. 1 caption) and hence at ambient temperatures the complex is exchanging the free and coordinated $AsMe_2$ groups. The $^{13}C\{^1H\}$ NMR spectrum is ill-defined at 300 K, but on cooling the resonances sharpen and split and at 220 K the spectrum in Fig. 2 is obtained, again readily assigned to bidentate triarsine. The VT NMR spectra of [HfI_4{MeC(CH_2AsMe_2)$_3$}$_2$] are very similar. Notably there is no evidence in either set of NMR spectra for [MI_4{MeC(CH_2AsMe_2)$_3$}] complexes (either six- or seven-coordinate).

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† The report of pink coloured Hf complexes[6] is in error, and presumably arose from impurities in the Hf halide.

‡ The complexes are very readily hydrolysed which can result in the appearance of uncoordinated diphosphine or diarsine resonances in some samples, but these contain no features attributable to 1 : 1 complexes which would be formed by dissociation.

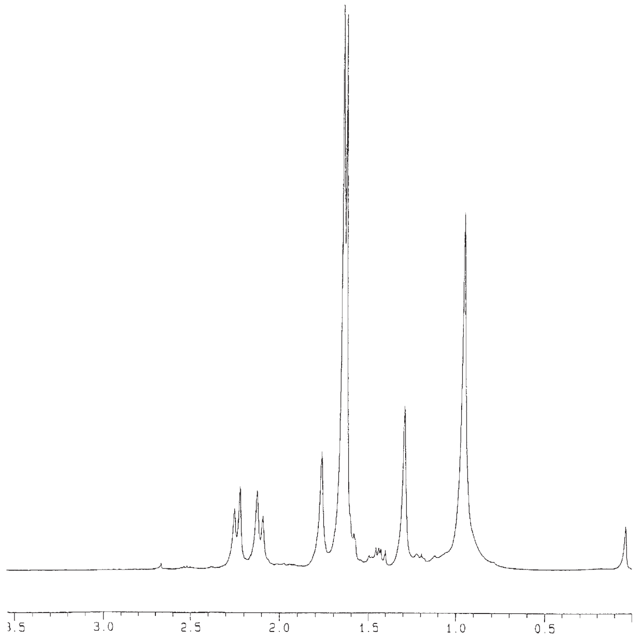

Fig. 1 The ^{1}H NMR spectrum of $[ZrI_4\{MeC(CH_2AsMe_2)_3\}_2]$ in CD_2Cl_2 at 223 K showing the η^2-coordinated triarsine. δ 0.95 (s) (AsMe-free), 1.29 (s) (CMe), 1.62 (s), 1.64 (s) (AsMe-coord), 1.80 (s) (CH_2-free), 2.16 (d), 2.26 (d) (CH_2-coord).

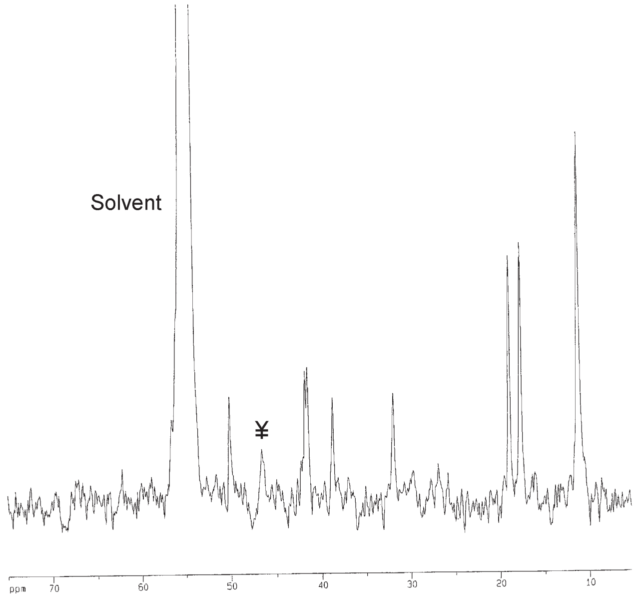

Fig. 2 The $^{13}C\{^1H\}$ NMR spectrum of $[ZrI_4\{MeC(CH_2AsMe_2)_3\}_2]$ in CH_2Cl_2 at 220 K showing the η^2-coordinated triarsine. δ 11.2 (AsMe-free), 17.6, 18.9 (AsMe-coord), 31.8 (CH_2-free), 38.6 (C), 41.4 (CH_2-coord), 50.2 (Me); the resonance marked ¥ is an impurity.

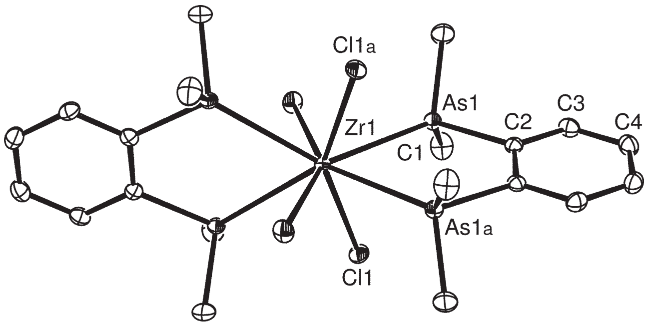

Fig. 3 The structure of $[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ showing the atom labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = $-x, -y, z$.

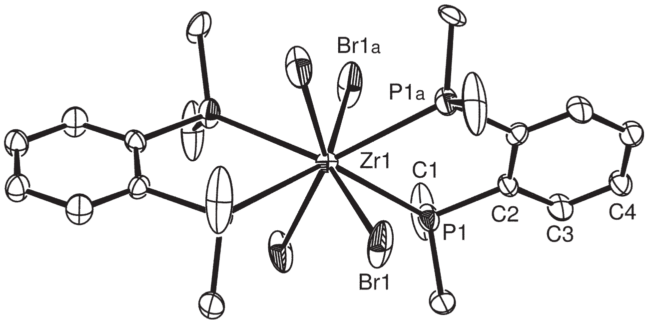

Fig. 4 The structure of $[ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$ showing the atom labelling scheme. Refinement in space group $I\bar{4}2m$. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = $-x, -y, z$.

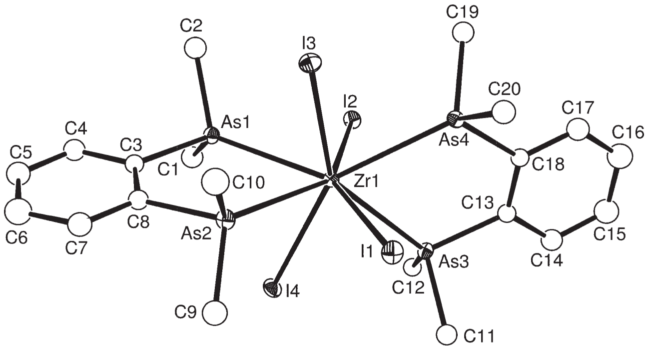

Fig. 5 The structure of $[ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ showing the atom labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Note that the structure of $[HfI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ is the same.

Crystal structures

X-Ray quality crystals were difficult to obtain from these systems, and except for the iodo-complexes, which were grown from solutions of pre-isolated samples, could only be obtained from the mother-liquors from the bulk syntheses. The structures of $[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$, $[ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$ and $[MI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ (M = Zr or Hf) all reveal eight-coordinate metal centres with a dodecahedral geometry (Figs. 3–5, Tables 1–4), similar to those reported previously for the Ti(IV) chloro- and bromo-complexes of these two ligands,[13] although these are the first Zr and Hf examples to be structurally authenticated. As before, the halogens occupy the "B" sites of the flattened tetrahedron.[17] The chloro- and bromo-complexes have $\bar{4}2m$ (D_{2d}) crystallographic symmetry whereas the iodides have no crystallographic symmetry but the geometry is in good accord with the D_{2d} model. There are few directly analogous structures of phosphine or arsine complexes of these two metals from which to draw comparisons. The bond lengths in $[ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$ Zr–Br = 2.649(1), Zr–P = 2.800(3) Å may be compared with the corresponding values in $[TiBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$ Ti–Br = 2.578(1), Ti–P = 2.672(2) Å. Notably, the increase in M–Br between Ti and Zr is *ca.* 0.07 Å whilst that in M–P is 0.13 Å suggesting rather weaker interaction of the hard oxophilic Zr with the soft phosphine compared to the halide. The result of the long Zr–P distance is an acute (70°) P–Zr–P chelate angle. In $[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ the As–Zr–As angle within the chelate ring is also *ca.* 70°, whilst Zr–Cl = 2.515(1), Zr–As = 2.846(1) Å. The data on $[TiCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$[17] are old and not of high precision, but the reported values of Ti–As = 2.71(2) Å and Ti–Cl = 2.46(2) Å show similar trends between Ti and Zr analogues.

The two iodo-complexes are very similar with slightly smaller corresponding bond lengths in the hafnium complex, reflecting the slightly smaller covalent radius of hafnium.[10] Again, the As–M–As angles within the chelate rings are *ca.* 70°, although in $[ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ the Zr–As distances are *ca.* 0.05 Å longer than in the chloro-analogue. This may be due to either the greater steric requirement of the larger iodide co-ligands, or to the weaker Lewis acidity of the ZrI_4. We also note that the Zr–I bond lengths in this complex (2.8835(6)–2.9332(6) Å), compared to those in the

Table 1 Selected bond lengths (Å) and angles (°) for $[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

Zr1–Cl1	2.5145(11)	Zr1–As1	2.8460(6)
As1–C1	1.939(3)	As1–C2	1.953(5)
As1–Zr1–As1^a	70.45(2)	Cl1–Zr1–Cl1^a	146.29(5)
As1–Zr1–As1^b	131.86(1)	Cl1–Zr1–Cl1^b	94.82(2)
Zr1–As1–C	117.0(1), 116.2(2)	C–As1–C	101.0(2), 101.4(2)

Symmetry operations: $^a = -x, -y, z$. $^b = -x, y, -z$.

Table 2 Selected bond lengths (Å) and angles (°) for $[ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]^c$

Zr1–Br1	2.6488(13)	Zr1–P1	2.800(3)
P1–C1	1.825(10)	P1–C2	1.822(10)
P1–Zr1–P1^a	70.25(12)	Br1–Zr1–Br1^a	146.00(6)
P1–Zr1–P1^b	131.99(8)	Br1–Zr1–Br1^b	94.90(2)
Zr1–P1–C	115.3(4), 116.4(4)	C–P1–C	101.7(4), 103.0(9)

Symmetry operations: $^a = -x, -y, z$. $^b = -x, y, -z$. ^{c}Refinement in space group $I\bar{4}2m$.

seven-coordinate $[ZrI_4\{PMe_3)_3\}]$ (2.829(2)–2.904(2) Å),[10] and the six-coordinate $[ZrI_4(PMe_2Ph)_2]$ (2.7787(6), 2.7902(7) Å),[9] show the expected (small) increase with increasing coordination number. The Hf–I bonds in $[HfI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ (2.8722(5)–2.9096(5) Å) are significantly shorter than those in the eight-coordinate Hf(II) carbonyl $[HfI_2(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ (2.986(1), 3.028(1) Å).[11]

Eight-coordination also occurs for the complex $[ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2]$ which involves two bidentate triarsine ligands, (Fig. 6, Table 5), with the remaining free $AsMe_2$ groups directed away from and not interacting with the zirconium centre. The complex has crystallographic two-fold symmetry, with the Zr on the two-fold axis. It is also possible to compare the key structural features of $[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ and $[ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2]$, which show that whilst the Zr–Cl are little different, the Zr–As distance in the triarsine complex is *ca.* 0.05 Å longer and the As–Zr–As angle some 4° wider, both attributable to the larger six-membered chelate ring present.

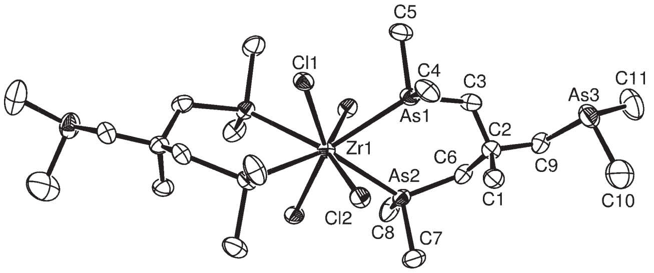

Fig. 6 The structure of $[ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2]$ showing the atom labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Conclusions

The detailed studies of the $Zr(Hf)X_4/o\text{-}C_6H_4(EMe_2)_2$ (X = Cl or Br, E = P or As) systems show that only eight-coordinate $[MX_4(L\text{–}L)_2]$ form. This is in marked contrast to the corresponding titanium systems where both 1 : 1 and 2 : 1 L–L : Ti species can be isolated under appropriate conditions. For these two larger metal ions, the MI_4 also form 2 : 1 complexes only, whereas with titanium(IV) iodide the six-coordinate $[TiI_4(L\text{–}L)]$ are obtained, probably due to steric factors at the smaller titanium centre. The preference for eight-coordination is also demonstrated by the triarsine ligand, where there is no evidence for 1 : 1 complexes with either six- or seven-coordinate metal centres. These results suggest a significant electronic driving force for eight-coordination in these compounds, since with low ligand : metal ratios the reactions still proceed to form the eight-coordinate complexes (leaving unreacted MX_4), but no six-coordinate species. However, weakening the donor power and increasing the steric bulk of the diphosphine, as in $o\text{-}C_6H_4(PPh_2)_2$, leads to six-coordination only.

The coordination chemistry of zirconium and hafnium tetraiodides has been very little studied, and the much improved solubilities of their complexes in non-coordinating solvents was unexpected. Usefully, this permitted much better quality solution spectroscopic data being obtained. We suggest that MI_4 should be considered as the reagent of choice in other studies where good solubility is required.

Experimental

Physical measurements were made as described previously.[4,13] All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and dry-box techniques. Zirconium and hafnium halides were obtained from Aldrich. The ligands were made by literature methods: $o\text{-}C_6H_4(AsMe_2)_2$,[18] $o\text{-}C_6H_4(PMe_2)_2$,[19] $MeC(CH_2AsMe_2)_3$,[18] and $o\text{-}C_6H_4(PPh_2)_2$.[20] Toluene, tetrahydrofuran (thf) and *n*-hexane were dried by distillation from sodium/benzophenone ketyl, dichloromethane from CaH_2.

$[ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

Method 1. The diarsine (0.24 g, 0.84 mmol) in dry CH_2Cl_2 (10 cm^3) was added to a solution of $[ZrCl_4(Me_2S)_2]$ (0.10 g, 0.28 mmol) in CH_2Cl_2 (50 cm^3), and the reaction stirred for 1 h. The mixture was concentrated *in vacuo* to *ca.* 20 cm^3, and the white solid isolated by filtration, washed with dry n-hexane (5 cm^3) and dried *in vacuo*. Yield 0.17 g (77%). Required for $[C_{20}H_{32}As_4Cl_4Zr]$: C, 29.8; H, 4.0. Found: C, 30.1; H, 4.0%. IR (Nujol mull)/cm^{-1} ν(Zr–Cl): 300, 295. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 32200, 35700 (sh), 38500. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.62 (s, [3H]), 7.6, 7.7 (m, [H]).

Method 2. $ZrCl_4$ (0.07 g, 0.3 mmol) was dissolved in the minimum amount of dry thf (*ca.* 10 cm^3) and a solution of the diarsine (0.25 g, 0.86 mmol) in thf (10 cm^3) added and the reaction mixture stirred for 24 h. The solution was concentrated *in vacuo* to *ca.* 5 cm^3, and the white solid filtered off, rinsed with thf and dried *in vacuo*. Yield 0.15 g (62%).

$[ZrBr_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

The diarsine (0.26 g, 0.91 mmol) in dry CH_2Cl_2 (10 cm^3) was added to a solution of $ZrBr_4$ (0.15 g, 0.37 mmol) in dry thf (50 cm^3), and the reaction stirred for 24 h. The mixture was concentrated *in vacuo* to *ca.* 10 cm^3, and the white solid isolated by filtration, washed with dry *n*-hexane (5 cm^3) and dried *in vacuo*. Yield 0.26 g (41%). Required for $[C_{20}H_{32}As_4Br_4Zr]$: C, 24.4; H, 3.3. Found: C, 24.3; H, 3.1%. IR (Nujol mull)/cm^{-1} ν(Zr–Br): 225, 222. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 29000 (sh), 32500. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.74 (s, [3H]), 7.6, 7.7 (m, [H]).

$[ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

ZrI_4 (0.15 g, 0.25 mmol) was suspended in dry CH_2Cl_2 (20 cm^3) and a solution of the diarsine (0.21 g, 0.75 mmol) in dry CH_2Cl_2 (5 cm^3) added. The reaction was stirred for 24 h, the solution reduced *in vacuo* to *ca.* 5 cm^3, and the yellow precipitate filtered off and dried *in vacuo*. Yield 0.21 g (71%). Required for $[C_{20}H_{32}As_4I_4Zr]\cdot CH_2Cl_2$: C, 20.0; H, 2.7. Found: C, 19.4; H, 2.6%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 24000 (sh), 27000, 33000. ^{1}H NMR (300 K, CD_2Cl_2): δ 2.1 (s, [3H]), 7.65, 7.85 (m, [H]).

Table 3 Selected bond lengths (Å) and angles (°) for $[ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

Zr1–I1	2.8982(6)	Zr1–As1	2.9073(7)
Zr1–I2	2.9086(6)	Zr1–As2	2.8844(7)
Zr1–I3	2.8835(6)	Zr1–As3	2.8842(7)
Zr1–I4	2.9332(6)	Zr1–As4	2.8977(7)
As–C	1.939(6)–1.957(5)		
As1–Zr1–As2	70.25(2)	I1–Zr1–I2	145.47(2)
As3–Zr1–As4	69.94(2)	I3–Zr1–I4	145.50(2)
As1–Zr1–As3	130.35(2)	I1–Zr1–I3	93.78(2)
As1–Zr1–As4	132.64(2)	I1–Zr1–I4	94.24(2)
As2–Zr1–As3	130.17(2)	I2–Zr1–I3	96.68(2)
As2–Zr1–As4	135.02(2)	I2–Zr1–I4	95.46(2)
Zr1–As–C(Ph)	114.4(2)–115.3(2)	Zr1–As–C(H$_3$)	118.6(2)–120.1(2)
C–As–C	98.2(3)–102.1(2)		

Table 4 Selected bond lengths (Å) and angles (°) for $[HfI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

Hf1–I1	2.8843(5)	Hf1–As1	2.8781(8)
Hf1–I2	2.9096(5)	Hf1–As2	2.8966(7)
Hf1–I3	2.8796(6)	Hf1–As3	2.8665(7)
Hf1–I4	2.8722(5)	Hf1–As4	2.8847(7)
As–C	1.919(8)–1.969(7)		
As1–Hf1–As2	70.20(2)	I1–Hf–I3	145.65(2)
As3–Hf1–As4	70.18(2)	I2–Hf–I4	145.10(2)
As1–Hf1–As3	130.18(2)	I1–Hf–I2	94.36(2)
As1–Hf1–As4	134.69(2)	I1–Hf–I4	93.53(2)
As2–Hf1–As3	130.55(2)	I2–Hf–I3	95.71(2)
As2–Hf1–As4	132.57(2)	I3–Hf–I4	96.67(2)
Hf1–As–C(Ph)	114.4(2)–115.6(2)	Hf1–As–C(H$_3$)	118.6(3)–120.1(2)
C–As–C	97.4(3)–102.1(3)		

Table 5 Selected bond lengths (Å) and angles (°) for $[ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2]$

Zr1–Cl1	2.5314(14)	Zr1–As1	2.8976(7)
Zr1–Cl2	2.4943(14)	Zr1–As2	2.9064(7)
As–C	1.929(6)–1.974(6)		
As1–Zr1–As2	74.64(2)	Cl1–Zr1–Cl2^a	143.12(5)
As1–Zr1–As1^a	122.65(3)	Cl1–Zr1–Cl2	93.87(5)
As1–Zr1–As2^a	130.53(2)	Cl1–Zr1–Cl1^a	99.41(7)
As2–Zr1–As2^a	132.70(4)	Cl2–Zr1–Cl2^a	95.77(8)
Zr1–As–C(H$_2$)	127.8(2), 126.0(2)	Zr1–As–C(H$_3$)	111.6(2)–116.1(2)

Symmetry operation: $^a = y, x, 1 - z$.

$[ZrCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$

$ZrCl_4$ (0.06 g, 0.26 mmol) was dissolved in the minimum amount of dry thf (10 cm^3) and a solution of $o\text{-}C_6H_4(PMe_2)_2$ (0.15 g, 0.75 mmol) in thf (10 cm^3) added and the reaction mixture stirred for 24 h. The resulting solution was concentrated *in vacuo* to *ca.* 5 cm^3, and the white solid filtered off, rinsed with thf and dried *in vacuo*. Yield 0.062 g (38%). Required for $[C_{20}H_{32}Cl_4P_4Zr]$: C, 38.2; H, 5.1. Found: C, 37.8; H, 4.9%. IR (Nujol mull)/cm^{-1} ν(Zr–Cl): 303, 285. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 32800, 37000. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.74 (d, [3H], $J = 6$ Hz), 7.6, 7.8 (m, [H]). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ +2.2.

$[ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$

This was made similarly to the above from $ZrBr_4$ (0.15 g, 0.37 mmol) and $o\text{-}C_6H_4(PMe_2)_2$ (0.18 g, 0.90 mmol). Yield 0.17 g (56%). Required for $[C_{20}H_{32}Br_4P_4Zr]$: C, 29.8; H, 4.0. Found: C, 30.4; H, 4.5%. IR (Nujol mull)/cm^{-1} ν(Zr–Br): 221, 218. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 29000 (sh), 33000. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.89 (d, [3H], $J = 6$ Hz), 7.62, 7.66 (m, [H]). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ −3.1.

$[ZrI_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$

This was made similarly to $[ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ from ZrI_4 (0.15 g, 0.25 mmol) and the diphosphine (0.15 g, 0.75 mmol) in CH_2Cl_2. After 24 h the yellow solution was concentrated to *ca.* 5 cm^3 and the pale yellow solid filtered off and dried *in vacuo*. Yield 0.17 g (68%). Required for $[C_{20}H_{32}I_4P_4Zr]$: C, 24.1; H, 3.2. Found: C, 23.7; H, 3.1%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 25000 (sh), 26800, 33200. ^{1}H NMR (300 K, CD_2Cl_2): δ 2.29 (d, [3H], $J = 7$ Hz) 7.66, 7.86 (m, [3H]). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ −14.5.

$[HfCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

$HfCl_4$ (0.16 g, 0.5 mmol) was dissolved in dry thf (30 cm^3) and a solution of the diarsine (0.44 g, 1.5 mmol) in thf (10 cm^3) added and the reaction mixture stirred for 36 h. The solution was concentrated *in vacuo* to *ca.* 5 cm^3, and the white solid filtered off, rinsed with thf and dried *in vacuo*. Yield 0.35 g (40%). Required for $[C_{20}H_{32}As_4Cl_4Hf]$: C, 26.9; H, 3.6. Found: C, 26.5; H, 3.6%. IR (Nujol mull)/cm^{-1} ν(Hf–Cl): 272 vbr. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 32300 (sh), 36300, 40000. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.60 (s, [3H]), 7.55, 7.66 (m, [H]).

$[HfBr_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

This was made similarly from $HfBr_4$ (0.25 g, 0.5 mmol) and the diarsine (0.42 g, 1.5 mmol) in thf. White solid. Yield 0.19 g (40%). Required for $[C_{20}H_{32}As_4Br_4Hf]$: C, 22.4; H, 3.1. Found: C, 22.4; H, 3.1%. IR (Nujol mull)/cm^{-1} ν(Hf–Br): 200, 190. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 29070 (sh), 32250, 36000 (vbr). ^{1}H NMR (300 K, CD_2Cl_2): δ 1.77 (s, [3H]), 7.61, 7.73 (m, [H]).

$[HfI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$

This was made from HfI_4 (0.23 g, 0.33 mmol) and the ligand (0.29 g, 1.0 mmol) in CH_2Cl_2 (50 cm^3) in a similar manner to the zirconium analogue above, except that the reaction mixture was stirred for 36 h before work up. Cream solid. Yield 0.30 g (72%). Required for $[C_{20}H_{32}As_4HfI_4]$: C, 19.1; H, 2.6. Found: C, 18.8; H, 2.6%. UV/Vis

(Diffuse reflectance in $BaSO_4$)/cm^{-1}: 25000 (sh), 29400, 32250. ^{1}H NMR (300 K, CD_2Cl_2): δ 2.08 (s, [3H]), 7.65, 7.81 (m, [H]).

[$HfCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$]

$HfCl_4$ (0.16 g, 0.50 mmol) was dissolved in the minimum amount of dry thf (*ca.* 15 cm^3) and a solution of *o*-$C_6H_4(PMe_2)_2$ (0.30 g, 1.5 mmol) in thf (10 cm^3) added and the reaction mixture stirred for 36 h. The resulting solution was concentrated *in vacuo* to *ca.* 5 cm^3, and the white solid filtered off, rinsed with thf and dried *in vacuo.* Yield 0.062 g (42%). Required for [$C_{20}H_{32}Cl_4HfP_4$]: C, 33.5; H, 4.5. Found: C, 32.6; H, 4.7%. IR (Nujol mull)/cm^{-1} ν(Hf–Cl): 267 (vbr). UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 33900 (sh), 36400, 40000. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.79 (br s, [3H]), 7.62, 7.87 (m, [H]). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ +1.0.

[$HfBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$]

This was made similarly from $HfBr_4$ (0.25 g, 0.5 mmol) and the ligand (0.30 g, 1.5 mmol) in thf. Cream solid. Yield 0.23 g (51%). Required for [$C_{20}H_{32}Br_4HfP_4$]: C, 26.9; H, 3.6. Found: C, 26.4; H, 4.1%. IR (Nujol mull)/cm^{-1} ν(Hf–Br): 192, 183. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 34500 (br), 42500. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.99 (br s [3H]), 7.62, 7.83 (m, [H]). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ −3.8.

[$HfI_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$]

This was made from HfI_4 (0.23 g, 0.33 mmol) and the ligand (0.20 g, 1.0 mmol) in CH_2Cl_2 (50 cm^3) in a similar manner to the zirconium analogue above, except that the reaction mixture was stirred for 36 h, before work up. Cream solid. Yield 0.30 g (83%). Required for [$C_{20}H_{32}HfI_4P_4$]: C, 22.2; H, 3.0. Found: C, 22.4; H, 3.2%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 24400 (sh), 28800, 33780. ^{1}H NMR (300 K, CD_2Cl_2): δ 2.33 (d, [3H] J = 8 Hz), 7.71, 7.90 (m, [H]). $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ −15.2.

[$ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2$]

The triarsine (0.28 g, 0.70 mmol) in dry CH_2Cl_2 (10 cm^3) was added to a solution of [$ZrCl_4(Me_2S)_2$] (0.10 g, 0.28 mmol) in CH_2Cl_2 (50 cm^3), and the reaction stirred for 1 h. The mixture was slowly concentrated *in vacuo* over *ca.* 3 h to 10 cm^3, and the white solid isolated by filtration, washed with dry *n*-hexane (5 cm^3) and dried *in vacuo.* Yield 0.19 g (70%). Required for [$C_{22}H_{54}As_6Cl_4Zr$]: C, 26.4; H, 5.5. Found: C, 26.0; H, 5.0%. IR (Nujol mull)/cm^{-1} ν(Zr–Cl): 304, 296. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 31100, 39200. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.04 (s), 1.31 (s), 1.79 (s); (248 K) insoluble.

[$ZrI_4\{MeC(CH_2AsMe_2)_3\}_2$]

Zirconium tetraiodide (0.20 g, 0.33 mmol) was suspended in dry CH_2Cl_2 (25 cm^3), and the triarsine (0.32 g, 0.83 mmol) added. On stirring the orange tetraiodide slowly dissolved forming a deep yellow solution, which slowly deposited some yellow solid. After 24 h the solution was concentrated *in vacuo* to *ca.* 5 cm^3 and the yellow powder filtered off, rinsed with dry *n*-hexane, and dried *in vacuo.* Yield 0.20 g (45%). Required for [$C_{22}H_{54}As_6I_4Zr$]: C, 19.3; H, 4.0. Found: C, 19.6; H, 4.3%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 25000 (br sh), 27000, 32500. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.30 (s), 1.35 (s), 2.01 (s); (223 K) 0.95 (s) [6H] (AsMe-free), 1.29 (s) [3H] (CMe), 1.62 (s), 1.64 (s) [6H, 6H] (AsMe-coord), 1.80 (s) [2H] (CH_2-free), 2.16 (d), 2.26 (d) [2H, 2H] (CH_2-coord). $^{13}C\{^1H\}$ NMR (220 K, CD_2Cl_2): δ 11.2 (AsMe-free), 17.6, 18.9 (AsMe-coord), 31.8 (CH_2-free), 38.6 (C), 41.4 (CH_2-coord), 50.2 (Me).

[$HfCl_4\{MeC(CH_2AsMe_2)_3\}_2$]

This was made by reacting $HfCl_4$ (0.16 g, 0.50 mmol), Me_2S (0.12 g, 1.9 mmol) in CH_2Cl_2 (50 cm^3). After 24 h the solution was filtered and the filtrate taken to dryness *in vacuo.* Dry CH_2Cl_2 (30 cm^3) was added followed by the triarsine (0.45 g, 1.2 mmol). After 24 h the solution was concentrated to *ca.* 10 cm^3, and the white solid separated by filtration, rinsed with hexane and dried *in vacuo.* Yield 0.40 g (73%). IR (Nujol mull)/cm^{-1} ν(Hf–Cl): 284, 275 (sh). UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 33900, 41300. ^{1}H NMR (300 K, CD_2Cl_2): insoluble.

[$HfI_4\{MeC(CH_2AsMe_2)_3\}_2$]

This was made similarly to the zirconium complex from HfI_4 (0.23 g, 0.33 mmol) and the triarsine (0.32 g, 0.83 mmol). Pale yellow solid. Yield 75%. Required for [$C_{22}H_{54}As_6HfI_4$]: C, 18.2; H, 3.7. Found: C, 17.7; H, 4.5%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 25500 (br sh), 30300, 35000. ^{1}H NMR (300 K, CD_2Cl_2): δ 1.02 (s), 1.07 (sh), 1.17 (br), 1.80 (br); (223 K) 0.94 (s) [6H] (AsMe-free), 1.22 (s) [3H] (CMe), 1.60 (s), 1.61 (s) [6H, 6H] (AsMe-coord), 1.80 (s) [2H] (CH_2-free), 2.14 (d), 2.20 (d) [2H, 2H] (CH_2-coord). $^{13}C\{^1H\}$ NMR (220 K, CD_2Cl_2): δ 11.1 (AsMe-free), 17.0, 18.2 (AsMe-coord), 31.9 (CH_2-free), 38.6 (C), 41.4 (CH_2-coord), 50.2 (Me).

[$ZrCl_4\{o\text{-}C_6H_4(PPh_2)_2\}$]

$ZrCl_4$ (0.20 g, 0.86 mmol) was suspended in dry CH_2Cl_2 (60 cm^3) and powdered *o*-$C_6H_4(PPh_2)_2$ (0.57 g, 1.3 mmol) added. The mixture was stirred for 48 h during which time the zirconium halide dissolved to give a clear solution, which slowly re-precipitated a white powder. The latter was filtered off and dried *in vacuo.* Yield 0.40 g (59%). Required for [$C_{30}H_{24}Cl_4P_2Zr$]·CH_2Cl_2: C, 48.7; H, 3.5. Found: C, 49.5; H, 3.8%. IR (Nujol mull)/cm^{-1} ν(Zr–Cl): 350 (br). UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 31250, 36000. $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ +13.5.

[$ZrBr_4\{o\text{-}C_6H_4(PPh_2)_2\}$]

This was made similarly in 72% yield. Required for [$C_{30}H_{24}Br_4P_2Zr$]·CH_2Cl_2: C, 39.5; H, 2.8. Found: C, 39.1; H, 2.8%. IR (Nujol mull)/cm^{-1} ν(Zr–Br): 261 (br). UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 29850, 33000. $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ +11.5.

[$ZrI_4\{o\text{-}C_6H_4(PPh_2)_2\}$]

This was made similarly, the ZrI_4 dissolved very slowly in the CH_2Cl_2 in the presence of the diphosphine, but the resulting complex was more soluble and the solution was concentrated to *ca.* 20 cm^3 before removal of the yellow complex by filtration. Yield 60%. Required for [$C_{30}H_{24}I_4P_2Zr$]: C, 34.4; H, 2.3. Found: C, 34.5; H, 2.1%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 24000, 30300 (sh), 32000. $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ −15.7.

[$HfCl_4\{o\text{-}C_6H_4(PPh_2)_2\}$]

This was made similarly to the zirconium chloride complex but with stirring for 72 h. Yield 70%. Required for [$C_{30}H_{24}Cl_4HfP_2$]: C, 47.0; H, 3.2. Found: C, 46.8; H, 3.5%. IR (Nujol mull)/cm^{-1} ν(Hf–Cl): 325, 302. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 30300, 35000. $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ +18.0.

[$HfBr_4\{o\text{-}C_6H_4(PPh_2)_2\}$]

This was made as above in 45% yield. Required for [$C_{30}H_{24}Br_4HfP_2$]: C, 38.2; H, 2.6. Found: C, 38.2; H, 2.7%. IR (Nujol mull)/cm^{-1} ν(Hf–Br): 219 (br), 206 (sh). UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 30000 (sh), 33000. $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ +13.5.

[$HfI_4\{o\text{-}C_6H_4(PPh_2)_2\}$]

This was made similarly in 65% yield. Required for [$C_{30}H_{24}HfI_4P_2$]: C, 31.8; H, 2.2. Found: C, 31.4; H, 2.4%. UV/Vis (Diffuse reflectance in $BaSO_4$)/cm^{-1}: 24100 (sh), 30300, 33000. $^{31}P\{^1H\}$ NMR (300 K, CH_2Cl_2): δ −17.0.

X-Ray crystallography

Brief details of the crystal data and refinement are given in Table 6. Data collections were carried out using a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and with the crystals held at 120 K in a gas stream. Crystals of [$ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$], [$ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$] and [$ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2$], were obtained with difficulty by allowing the filtrate from the preparations to evaporate slowly in the glove box. Crystals of [$MI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$] (M = Zr or Hf) were obtained by allowing dichloromethane solutions of the pre-formed complexes to evaporate slowly in the glove box. Structure solution and refinement were routine[21–24] (except as described below) with H atoms introduced in calculated positions. [$ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$] was initially solved in the space group $I\bar{4}$ (no. 82) by comparison with previous related structures,[13] but it became clear that the space group $I\bar{4}2m$ (no. 121) in the higher symmetry Laue group 4/*mmm* gave an equally satisfactory structure solution and this was adopted.§ The Flack parameter[25] established the absolute structure. The tetragonal [$ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2$] belongs to one of a pair of enantiomorphous space groups and correct choice for the crystal selected ($P4_32_12$) was also established from the Flack parameter. [$ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$] presented a difficulty in that the crystal system, unit cell and lattice type produced by the diffractometer software and the intensity data collected yielded a satisfactory structure. However, this orthorhombic *A* lattice can be transformed more easily to a smaller tetragonal *I* lattice. Following the transformation the rejected reflections were on average much lower in intensity and among these there were no very intense reflections. The tetragonal structure in the $I\bar{4}2m$ space group found for related compounds has a marginally better fit to the data and has lower residual peaks in the difference electron-density map. Both sets of crystallographic data are included in Table 6 and Table 2 presents the bond lengths and angles in the tetragonal model. Attempts to grow other crystals of this complex have not been successful so the question of whether the structure really is orthorhombic with a sub-cell which is very close to tetragonal is unresolved (although in chemical terms the two answers are identical). The two tetraiodides have a cell metrically close to tetragonal but the absences do not correspond to a tetragonal space group and a satisfactory solution in an orthorhombic space group emerged. Racemic twinning was observed and the DELU command[22] was used in the Hf compound to control non-positive definite anisotropic thermal parameters which probably arose from an inadequate absorption correction.

CCDC reference numbers 241865–241869.

See http://www.rsc.org/suppdata/dt/b4/b409051a/ for crystallographic data in CIF or other electronic format.

Table 6 Crystal data and structure refinement details[a]

Compound	[$ZrCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$]	[$ZrCl_4\{MeC(CH_2AsMe_2)_3\}_2$]	[$ZrBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$][c]	[$ZrI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$]	[$HfI_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$]
Formula	$C_{20}H_{32}As_4Cl_4Zr$	$C_{22}H_{54}As_6Cl_4Zr$	$C_{20}H_{32}Br_4P_4Zr$	$C_{20}H_{32}As_4I_4Zr$	$C_{20}H_{32}As_4HfI_4$
M	805.16	1001.19	807.20	1170.96	1258.23
Crystal system	Tetragonal	Tetragonal	Orthorhombic (tetragonal)	Orthorhombic	Orthorhombic
Space group	$I\bar{4}2m$ (no. 121)	$P4_32_12$ (no. 96)	*Aba*2 (no. 41) ($I\bar{4}2m$ (no. 121))	$Pca2_1$ (no. 29)	$Pca2_1$ (no. 29)
a/Å	9.2424(10)	10.6325(10)	13.017(3) (9.203(2))	17.0213(15)	16.9964(15)
b/Å	9.2424(10)	10.6325(10)	13.013(3) (9.203(2))	10.6761(5)	10.6538(10)
c/Å	16.670(4)	33.084(4)	16.725(3) (16.725(3))	16.9776(15)	16.9467(15)
U/Å^3	1424.0(4)	3740.2(7)	2833.0(10) (1416.5(5))	3085.2(4)	3068.6(5)
Z	2	4	4 (2)	4	4
μ/mm^{-1}	5.381	5.859	6.263	8.624	11.712
F(000)	784	1968	1568 (784)	2144	2272
Total no. of obsns. (R_{int})	3083 (0.048)	12646 (0.070)	6691 (0.052) (3046 (0.056))	23664 (0.030)	26896 (0.055)
Unique obsns.	787	3266	2939 (683)	6737	6916
Min., max. transmission	0.653, 0.812	0.688, 0.894	0.456, 0.618	0.358, 1.000	0.080, 1.000
No. of parameters, restraints	44, 0	151, 0	133, 1 (44, 0)	264, 1	164, 16
Goodness-of-fit on F^2	1.08	1.04	1.14 (1.11)	1.05	1.05
Resid. electron density /e Å^{-3}	−0.54 to +0.58	−0.81 to +0.85	−2.21 to +3.90 (−1.75 to +1.05)	−0.97 to +0.74	−2.29 to +2.32
$R1$, $wR2$ ($I > 2\sigma(I)$)[b]	0.025, 0.058	0.035, 0.081	0.064, 0.155 (0.050, 0.112)	0.024, 0.049	0.030, 0.069
$R1$, $wR2$ (all data)	0.026, 0.058	0.042, 0.085	0.070, 0.159 (0.053, 0.114)	0.026, 0.050	0.032, 0.070

[a] Common items: temperature = 120 K; λ(Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. [c] The details in parentheses refer to the refinement in the tetragonal space group $I\bar{4}2m$ (see text).

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§ The crystal structures of the three compounds [$TiCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$], [$TiBr_4\{o\text{-}C_6H_4(PMe_2)_2\}_2$] and [$TiBr_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2$] were originally reported in the space group $I\bar{4}$ (no. 82).[13] It became clear during this work that the space group $I\bar{4}2m$ was probable and re-refinement of the original data confirmed this. The CCDC has allocated reference numbers 235199 (TIHRUX), 235200 (TIHSAE), 235201 (TIHSEI) to the new database entries (refcode entries in parentheses).

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