Crystal and Molecular Structures of [MCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$] (M = Zr or Hf) and [TiCl$_{0.5}$Br$_{0.5}$(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$]: * An Unusual π-Interaction with the Metals and Molecular Orbital Calculations on Model Compounds

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The compounds [MCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$] (M = Zr or Hf) and [TiCl$_{0.5}$Br$_{0.5}$(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$], whose structures have been determined by *X*-ray diffraction, all show a π-type of interaction between the phenyl ring and the metal. This is revealed by (*i*) the conformation of the alkenyl ligand, (*ii*) the small value of the angle M–C(1)–C(5), which is 100.3(3)° when M = Zr and 105.7(2)° when M = Ti, and (*iii*) the lengthening of the M–Cl bond, to 2.480(1) Å for M = Zr. A specific electronic effect is demonstrated by charge-iterated extended-Hückel calculations on related model systems.

The geometry of the Group 4 metallocene derivatives [MXX′(η-C$_5$H$_5$)$_2$] (M = Ti, Zr, or Hf) may be described as approximately tetrahedral, regarding the cyclopentadienyl ligands as each occupying a single co-ordination site.[1,2] However, for d^0 metallocenes the angle α (Figure 1) is substantially larger than tetrahedral, ranging from 124.7° [X = X′ = Ru(CO)$_2$(η-C$_5$H$_5$), M = Zr[3]] to 133° (X = X′ = Me, M = Hf[4]), and the angle β correspondingly smaller, lying between 89.9° (X = X′ = CH$_2$SiMe$_3$, M = Zr[5]) and 101.2° [X = Cl, X′ = NC(H)Ph, M = Zr[6]]. Values outside these ranges are found only for compounds where X and X′ form a chelate ring (small β), to metallocenes in other oxidation states, *e.g.* [M(CO)$_2$(η-C$_5$H$_5$)$_2$], or when the metal has a co-ordination number other than four. Thus molecules such as [Zr(η^2-COMe)Me(η-C$_5$H$_5$)$_2$] do not fall into the above pattern, and a larger β value is typical of molecules with interactions involving the vacant 'ninth orbital' of the metal. Such η^2-co-ordination has been reported for acyls[7,8] and related ligands bearing donor atoms, and more interestingly for the benzyl groups in [M(CH$_2$Ph)$_4$] (M = Ti, Zr, or Hf),[9–11] but not previously for σ-bonded sp^2-ligating hydrocarbyls.

We were prompted to investigate such a possible interaction structurally, from the observation that the compound [Hf(CPh=CMe$_2$)$_2$(η-C$_5$H$_5$)$_2$] could not be obtained from either the metallocene dihalides or from the monoalkenyl using either magnesium or lithium reagents under forcing conditions.[12,13] We report here on the results of these studies for the Group 4 metals, and on the results of charge-iterated molecular orbital calculations on titanium and zirconium model species, which reveal energy minima in geometries consistent with the structures found, and enable us to postulate a specific orbital interaction responsible.

Results and Discussion

The structures reported here are those of [ZrCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$], [HfCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$], and [TiCl$_{0.5}$Br$_{0.5}$(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$]. Their preparations have been mentioned[13] and will be published in full elsewhere.[12] The three compounds are isostructural (Table 1) (although the titanium derivative is reported here in the non-standard orientation *P*2$_1$/*n* rather than the standard *P*2$_1$/*c*) but the structure determination of the titanium complex revealed that the crystal used for the determination was composed of approximately equal amounts of the bromo- and the chloro-derivative, arranged in a presumably random distribution throughout the crystal lattice. This deduction is confirmed by an *X*-ray fluorescence study of the crystal used for data collection (see Experimental section). The presence of bromine arises from the use of 1,2-dibromoethane to initiate the preparation of the Grignard reagent.

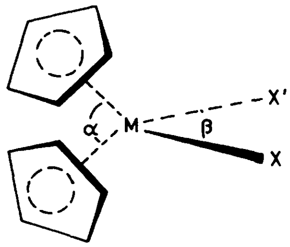

Figure 1. Geometry of [MXX′(η-C$_5$H$_5$)$_2$] metallocenes

Although the presence of the mixed halide for the titanium compound must be borne in mind, this series affords the opportunity for a vertical comparison of molecular parameters, as was the case for the tetrabenzyls [M(CH$_2$Ph)$_4$] [M = Ti, Zr, or Hf (and Sn)].[10]

In all three structures the geometry is only approximately of the 'tetrahedral' type shown in Figure 1, and shows distortions in both ligand and metal geometry (Figure 2 and Table 2). These distortions have their closest parallel in the more extreme distortions found in the η^2-acyl compounds [Zr(η^2-COMe)Me(η-C$_5$H$_5$)$_2$][7] and [TiCl(η^2-COMe)(η-C$_5$H$_5$)$_2$],[8] in which there is close to true five-co-ordination. As in the acyls we find an overall molecular conformation in which there is an approximate mirror plane through the metal, with eclipsed cyclopentadienyl rings (Figure 2). The ligand conformation is such that the phenyl ring plane is approximately orthogonal in each case to the alkenyl plane, and is in turn orthogonal to the plane through the metal and the ring centroids (Figure 3). This places the phenyl ring in the appropriate orientation to interact with the metal 'ninth orbital' [through the *p* orbital on C(5)], resembling the arrangement of the tetrabenzyls and the acyls, but quite unlike the geometry we have previously observed for the same ligand in the homoleptic alkenyl structures [Cr(CPh=CMe$_2$)$_4$] and [Sn(CPh=CMe$_2$)$_4$].[14] In that work we found that the d^2 electron configuration of the chromium atom resulted in

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* Chlorobis(η-cyclopentadienyl)(2-methyl-1-phenylprop-1-enyl)-zirconium(IV) and -hafnium(IV) and hemibromohemichlorobis(η-cyclopentadienyl)(2-methyl-1-phenylprop-1-enyl)titanium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Crystal data and data collection for [MCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$] (M = Zr or Hf) and [TiCl$_{0.5}$Br$_{0.5}$(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$]

	Ti	Zr	Hf
Formula	$C_{20}H_{21}Br_{0.5}Cl_{0.5}Ti$	$C_{20}H_{21}ClZr$	$C_{20}H_{21}ClHf$
M	366.7	387.8	475.3
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	13.992(3)	14.144(2)	14.124
b/Å	8.970(2)	8.935(3)	9.026
c/Å	14.695 0(14)	16.127(2)	15.987
β/°	112.745(13)	121.7(1)	121.4(1)
U/Å^3	1 701	1 734	1 739
D_c/g cm^{-3}	1.436	1.478	1.815
Z	4	4	4
F(000)	756	792	920
μ(Mo-K_α)/cm^{-1}	16.76	6.92	58.66
Crystal size/mm	0.35 × 0.2 × 0.25	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.1
Crystal form	Red rhombs	Pale yellow rhombs	Pale yellow rhombs
Diffractometer	Enraf-Nonius CAD-4	Hilger and Watts Y 290	Hilger and Watts Y 290
Scan mode	θ/2θ	θ/2θ	θ/2θ
θ Range/°	1.5—26	2—27	2—25
Scan width	*A* = 0.80 *B* = 0.35	1.20	1.20
No. reflections measured	3 706	5 373	4 605
Unique observed reflections	2 334	3 381	2 667
Final *R* value	0.0428	0.0325	0.0932
Final *R'* value	0.0627	0.0372	0.1113
Max. in final difference map/e Å^{-3}	0.45	0.44	5.325
Min. in final difference map/e Å^{-3}	−0.31	−0.57	6.44

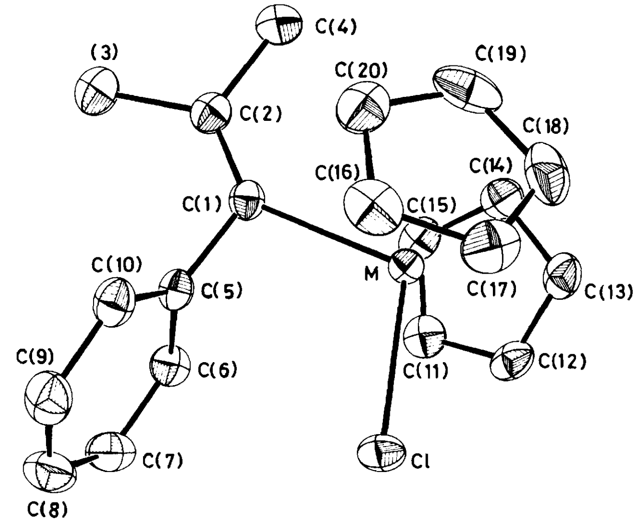

Figure 2. A single molecule of [MCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$] (M = Zr or Hf) showing the atom-numbering scheme

only very small changes in geometry compared with the tin analogue.

A detailed comparison of molecular parameters with those of the acyls [Zr(η^2-COMe)Me(η-C$_5$H$_5$)$_2$][7] and [TiCl(η^2-COMe)(η-C$_5$H$_5$)$_2$][8] shows that in each case the sense of the deviations is the same, and most pronounced for the zirconium derivative. Thus we find M–C(1)–C(5) to be 100.3(3)° for the Zr, 105.7(2)° for the Ti, and 103.7(1.5)° for the Hf derivatives, whereas in the acyls the M–C–O angle is 79.7(6)° for Ti, and 78.6(4)° for Zr. The X–M–C(1) angle is 103.5(1)° for Ti, 108.9(1)° for Zr, and 104.7(6)° for Hf, but is opened even further to 112.2(3) and 110.3(2)° for the titanium [8] and zirconium [7] acyls respectively. As expected, the metal–halogen distances are lengthened in our structures; to 2.480(1) Å when M = Zr, which is longer than that in any other [ZrCl(R)(η-C$_5$H$_5$)$_2$] structure apart from that of 2.545(1) Å found when R is the extremely bulky group -CH(SiMe$_3$)(C$_{14}$H$_9$) (C$_{14}$H$_9$ = anthracen-9-yl).[15] For this bond, a direct comparison with the acyl structures cannot be made,* since the Zr acyl structure is that of the methyl derivative, and our titanium structure is that of a mixed halide containing Br and Cl in approximately equal amounts (as shown by the refined values of the site occupation factor) and therefore giving only an average bond length of 2.477(1) Å. Data on Hf–Cl distances are sparse;[17] the value here of 2.422(1) Å being comparable to that of 2.418(3) Å found for [HfCl{CH(SiMe$_3$)(C$_6$H$_4$Me-*o*)}(η-C$_5$H$_5$)$_2$],[18] a molecule containing a very sterically demanding ligand. In summary, the degree of metal–ligand interaction is lower than that of the η^2-acyls, as would be expected both from the electron configuration of O (compared with C) and the oxophilic character of

Table 2. Selected bond distances (Å) and angles (°) for [MCl(CPh=CMe$_2$)(η-C$_5$H$_5$)$_2$] (M = Zr or Hf) and [TiCl$_{0.5}$Br$_{0.5}$(CPh=CMe$_2$)-(η-C$_5$H$_5$)$_2$][a]

	Ti	Zr	Hf
M–C(1)	2.239(4)	2.296(3)	2.332(19)
M–Cl	2.477 4(7)[b]	2.479 7(9)	2.422 4(7)
C(1)–C(5)	1.494(5)	1.497(5)	1.55(4)
C(1)–C(2)	1.332(5)	1.329(5)	1.30(3)
M–Cen(1)	2.074(—)	2.213(—)	2.175(—)
M–Cen(2)	2.073(—)	2.209(—)	2.181(—)
Cl–M–C(1)	103.50(9)	108.87(9)	104.7(6)
M–C(1)–C(5)	105.7(2)	100.3(3)	103.7(1.5)
M–C(1)–C(2)	132.6(3)	137.4(3)	132.4(1.9)
C(2)–C(1)–C(5)	121.6(3)	122.2(3)	123.9(2.1)
Cen(1)–M–Cen(2)	133.2(—)	130.3(—)	130.3(—)

[a] Cen refers to the calculated centroids of the cyclopentadienyl rings.
[b] Average of the Ti–Cl and Ti–Br bond lengths.

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* However Zr–Cl distances in five-co-ordinate molecules are available: 2.550(2) Å in [ZrCl{OC(NMe$_2$)S}(η-C$_5$H$_5$)$_2$], and 2.556(2) Å in [ZrCl{SC(NMe$_2$)S}(η-C$_5$H$_5$)$_2$].[16]

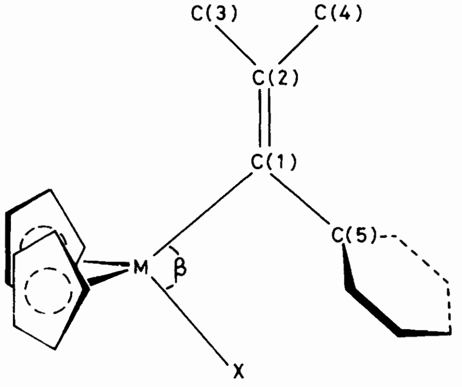

Figure 3. Schematic illustration of the relationship between the orthogonal phenyl and alkenyl planes in the compounds. Atoms M, X, C(1), C(2), C(3), C(4), and C(5) are essentially coplanar [root mean square deviations 0.04 (M = Zr), 0.04 (M = Ti), and 0.03 Å (M = Hf)] and the angles between the phenyl and alkenyl planes are 86.9 (M = Zr), 88.6 (M = Ti), and 87.1° (M = Hf) {*cf.* the interaction of the phenyl groups of the benzyl ligands in [M(CH$_2$Ph)$_4$] with the metal[9,10]}

zirconium(IV). There is one further point to be made. The Zr–O$_{\text{acyl}}$ distance is 2.290(4) Å[7] compared with a typical Zr–O distance of 1.9—2.0 Å,[19,*] whereas our Zr–C(5) distance is 2.956(3) Å compared with our measured Zr–C(1) distance of 2.296(3) Å. However, in the case of the acyls, the assumed interaction is with an sp^2 lone pair on the oxygen, lying at 120° to the C–O vector, whereas in the CPh=CMe$_2$ ligand (and the benzyl ligand) the interaction is with a *p* orbital at 90° to the C(1)–C(5) vector. The carbon orbital is therefore better placed for overlap.

Although not metallocenes, the tetrabenzyls[9,10] parallel the present work and reveal common features. Thus the mean value for the M–C–C angle increases in the order Zr < Hf < Ti < Sn. We find the angle M–C(1)–C(5) to increase in the order Zr < Hf < Ti {<Sn in [Sn(CPh=CMe$_2$)$_4$]} similarly, and may reflect the spatial extent of the *d*-orbital combination on the metal (4*d* > 5*d* > 3*d*), although energetic considerations will also be significant.

Other features of the molecular geometry are normal. The M–C bond lengths are typical of moderate steric crowding [*e.g.* 2.294(8) Å is reported for Zr–C(sp^3) in bis(neopentyl)-zirconocene[20] compared with our value of 2.296(3) Å]. The centroid–M–centroid angles and distances are entirely typical.

The ligand geometries prompted us to carry out charge-iterated extended-Hückel molecular orbital calculations to establish whether the angle contractions observed for the alkenyls, and earlier for the benzyls, were consistent with a specific, identifiable, electronic effect. To reduce the calculations to a manageable size, model structures were employed; replacing the interacting phenyl ligands with the CH=CH$_2$ fragment, and the metal ligands not directly involved by hydrogen atoms. Thus calculations were performed on [MH$_3$(CH$_2$CH=CH$_2$)] and [MH$_3${C(CH=CH$_2$)=CH$_2$}] to model compounds with sp^3 and sp^2 ligands respectively. The total electronic energies were calculated as a function of the M–C(1)–C(5) angle, with bond distances taken either from the present work, or, in the case of M–H, from standard sources. In each case the energies passed through a minimum at values of this angle, paralleling those found experimentally. Results for the system [TiH$_3${C(CH=CH$_2$)=CH$_2$}] are shown graphically in Figure 4. Also shown are the results of similar calculations on the organic system H–C(CH=CH$_2$)=CH$_2$ showing a minimum at a substantially higher value, and revealing the importance of the metal atom. For the case of [TiH$_3$(CH$_2$CH=CH$_2$)] consideration of individual eigenvectors revealed a pair of appropriate energy located (*i*) substantially on C(5), essentially a C *p*(π) orbital, doubly occupied; and (*ii*) predominantly on the metal, composed of two 3*d* orbitals, unoccupied; and with the correct symmetry and orientation for overlap.† Similar results have also been obtained for the zirconium species, and are currently being extended to include the phenyl and cyclopentadienyl groups.

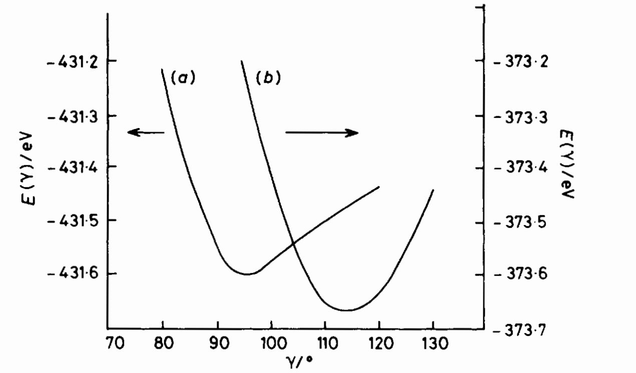

Figure 4. Total calculated electronic energie (eV ≈ 1.60 × 10^{-19} J), *E*(γ), as a function of the angle γ for (*a*) H$_3$*Ti*–*C*(=CH$_2$)–*C*H=CH$_2$ and (*b*) *H*–*C*(=CH$_2$)–*C*H=CH$_2$, where γ is defined as the angle *Ti*–*C*–*C* and *H*–*C*–*C* respectively. Note the different absolute vertical scales for (*a*) and (*b*). For other systems the minimum values of *E*(γ) were found at γ = 90° for H$_3$*Ti*–*C*H$_2$–*C*H=CH$_2$, 109° for *H*–*C*H$_2$–*C*H=CH$_2$ and 82° for H$_3$*Zr*–*C*(=CH$_2$)–*C*H=CH$_2$

Experimental

Crystals used in this study were all air-sensitive, the zirconium and hafnium derivatives particularly, and were mounted in sealed Lindemann capillaries under argon after recrystallisation from dichloromethane. Crystals of the titanium compound were prepared by Mr. G. Lawless. Crystals were studied photographically, and the space groups assigned from zero- and first-level Weissenberg photographs.

Data Collection.—Data were collected by a four-circle diffractometer at ambient temperature, using graphite-monochromatised Mo-K_α radiation. None of the crystals decomposed significantly during data collection (three standard reflections monitored every 100 reflections showed no significant change) although the hafnium crystal showed signs of surface decomposition before the start of data collection. For the titanium compound the scan width was determined by the formula (A + Btanθ)°; for the other two compounds a fixed scan width was used. A unique quadrant of data was measured for all three compounds. The data were reduced by applying Lorentz and polarisation corrections, but were not corrected for absorption. The relatively high *R* value for the Hf compound is probably due to neglect of absorption, and these results are therefore of limited accuracy. The titanium structure was solved by the direct method. An anomalously low thermal parameter for the chlorine atom at the end of the isotropic refinement together with a long Ti–Cl bond length and difference map peaks adjacent to this atom position suggested the presence of a bromine atom at this site. An *X*-ray fluorescence spectrum of the crystal used for data collection revealed peaks due to both bromine and chlorine in approximately equal amounts. The

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[*] For many other values see also ref. 17.

[†] Details of these and other calculations will be published elsewhere.

Table 3. Fractional atomic co-ordinates for $[TiCl_{0.5}Br_{0.5}(CPh{=}CMe_2)(\eta\text{-}C_5H_5)_2]$

Atom	*x*	*y*	*z*
Ti	−0.016 71(5)	0.385 26(7)	0.248 61(4)
Br	0.075 98(5)	0.332 51(7)	0.426 84(4)
Cl	0.075 98(5)	0.332 51(7)	0.426 84(4)
C(1)	−0.040 4(3)	0.159 0(4)	0.179 1(3)
C(2)	−0.088 9(3)	0.112 7(5)	0.086 4(3)
C(3)	−0.104 0(4)	−0.054 8(5)	0.058 9(4)
C(4)	−0.137 2(3)	0.211 8(5)	−0.002 5(3)
C(5)	0.005 7(3)	0.051 5(4)	0.262 25(25)
C(6)	0.109 6(3)	0.009 7(4)	0.294 4(3)
C(7)	0.153 1(3)	−0.085 0(5)	0.374 3(3)
C(8)	0.095 5(4)	−0.139 1(5)	0.423 4(3)
C(9)	−0.009 6(4)	−0.100 3(5)	0.391 4(3)
C(10)	−0.053 4(3)	−0.007 0(4)	0.312 0(3)
C(11)	0.153 7(3)	0.385 1(5)	0.244 7(3)
C(12)	0.144 7(3)	0.520 6(5)	0.287 6(3)
C(13)	0.064 6(4)	0.603 3(5)	0.218 6(3)
C(14)	0.023 4(3)	0.519 9(5)	0.130 0(3)
C(15)	0.080 7(3)	0.383 7(5)	0.145 7(3)
C(16)	−0.164 6(3)	0.354 0(5)	0.290 5(4)
C(17)	−0.129 7(4)	0.500 3(6)	0.315 3(4)
C(18)	−0.142 5(4)	0.575 1(6)	0.228 6(4)
C(19)	−0.184 9(4)	0.474 0(7)	0.150 6(4)
C(20)	−0.199 3(3)	0.338 8(6)	0.188 4(4)

Table 4. Fractional atomic co-ordinates for $[ZrCl(CPh{=}CMe_2)(\eta\text{-}C_5H_5)_2]$

Atom	*x*	*y*	*z*
Zr	0.234 62(2)	0.123 99(4)	0.245 06(2)
Cl	0.148 66(7)	0.168 99(11)	0.068 18(6)
C(1)	0.283 06(25)	0.350 0(4)	0.324 76(24)
C(2)	0.326 5(3)	0.399 2(4)	0.415 5(3)
C(3)	0.337 3(4)	0.564 5(5)	0.443 2(3)
C(4)	0.366 2(3)	0.295 8(5)	0.502 0(3)
C(5)	0.244 9(3)	0.454 1(4)	0.240 28(25)
C(6)	0.312 4(3)	0.491 0(4)	0.204 9(3)
C(7)	0.273 5(4)	0.578 4(5)	0.122 6(3)
C(8)	0.165 6(4)	0.632 1(5)	0.073 5(3)
C(9)	0.097 6(3)	0.596 9(5)	0.108 2(3)
C(10)	0.135 5(3)	0.509 8(4)	0.190 2(3)
C(11)	0.420 0(3)	0.114 8(5)	0.256 8(3)
C(12)	0.365 8(3)	−0.019 9(5)	0.212 0(3)
C(13)	0.353 9(3)	−0.102 9(4)	0.278 8(3)
C(14)	0.401 2(3)	−0.019 6(5)	0.366 6(3)
C(15)	0.442 9(3)	0.114 1(5)	0.352 7(3)
C(16)	0.039 8(3)	0.146 1(5)	0.209 3(3)
C(17)	0.050 3(4)	0.001 4(6)	0.181 2(4)
C(18)	0.125 1(4)	−0.076 4(5)	0.264 3(4)
C(19)	0.160 1(4)	0.019 5(6)	0.343 6(3)
C(20)	0.107 0(4)	0.156 8(5)	0.309 7(3)

structure was therefore refined as the mixed halide with the chlorine and bromine atoms fixed to the same positional parameters and the site occupancies tied to sum to unity, when refinement converged well, to give final occupation factors of 0.44 for Br and 0.56 for Cl.

The zirconium and hafnium structures were solved by Patterson methods, and for the former, refined straightforwardly. For the hafnium structure, the population parameter ($P_{Hf} + P_{Zr} = 1$) was refined to 0.9155 for Hf (and 0.0845 for Zr) by refining to convergence with a damping factor of 1 000 from a starting value of 0.9, and then completing the refinement by fixing the population parameters and using common positional and thermal parameters for the Hf and Zr atoms. The programs SHELX 76,[21] XANADU,[22] and ORTEP[23] were used for all calculations.

Table 5. Fractional atomic co-ordinates for $[HfCl(CPh{=}CMe_2)(\eta\text{-}C_5H_5)_2]$

Atom	*x*	*y*	*z*
Hf	0.234 7(1)	0.118 6(1)	0.246 2(1)
Cl	0.150 9(5)	0.169 0(7)	0.072 8(5)
C(1)	0.282 0(20)	0.351 2(23)	0.320 5(16)
C(2)	0.322 9(20)	0.393 7(26)	0.410 6(18)
C(3)	0.333 4(29)	0.559 1(29)	0.438 4(21)
C(4)	0.360 7(24)	0.296 1(30)	0.492 4(21)
C(5)	0.259 6(24)	0.456 8(33)	0.236 0(21)
C(6)	0.312 9(20)	0.495 7(28)	0.205 8(20)
C(7)	0.268 9(25)	0.586 2(31)	0.117 3(23)
C(8)	0.170 3(28)	0.640 7(32)	0.069 5(21)
C(9)	0.095 8(21)	0.602 2(31)	0.102 4(23)
C(10)	0.139 4(19)	0.511 3(28)	0.192 2(21)
C(11)	0.415 2(24)	0.109 7(34)	0.253 8(24)
C(12)	0.362 8(25)	−0.022 7(31)	0.214 3(22)
C(13)	0.350 6(20)	−0.101 9(29)	0.276 6(18)
C(14)	0.399 0(24)	−0.023 7(31)	0.368 4(26)
C(15)	0.441 0(20)	0.111 3(32)	0.352 6(23)
C(16)	0.039 6(25)	0.142 1(34)	0.210 9(27)
C(17)	0.054 3(30)	−0.004 5(38)	0.184 4(30)
C(18)	0.129 0(28)	−0.080 5(32)	0.262 6(27)
C(19)	0.162 2(29)	0.014 6(44)	0.345 0(30)
C(20)	0.105 6(25)	0.150 1(33)	0.307 8(28)

The crystal and data collection parameters for each structure are reported in Table 1 and atomic co-ordinates for the three structures in Tables 3—5.

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References

1 K. Prout, T. J. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290.

2 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

3 C. P. Casey, R. F. Jordan, and A. L. Rheingold, *Organometallics*, 1984, **3**, 504.

4 W. E. Hunter, D. C. Hrncir, R. V. Bynum, R. E. Pentilla, and J. L. Atwood, *Organometallics*, 1984, **3**, 750.

5 M. F. Lappert, P. I. Riley, P. I. W. Yarrow, J. L. Atwood, W. E. Hunter, and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 1981, 814.

6 G. Erker, V. Frömberg, J. L. Atwood, and W. E. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 68.

7 G. Fachinetti, C. Floriani, F. Marchetti, and S. Merlino, *J. Chem. Soc., Chem. Commun.*, 1976, 522.

8 G. Fachinetti, C. Floriani, and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1977, 2297.

9 G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *Chem. Commun.*, 1971, 677.

10 G. R. Davies, J. A. J. Jarvis, and B. T. Kilbourn, *Chem. Commun.*, 1971, 1511.

11 I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Am. Chem. Soc.*, 1971, **93**, 3787.

12 C. J. Cardin, D. J. Cardin, J. M. Kelly, and A. Roy, unpublished work.

13 C. J. Cardin, D. J. Cardin, J. M. Kelly, R. J. Norton, and A. Roy, *J. Organomet. Chem.*, 1977, **132**, C23.

14 C. J. Cardin, D. J. Cardin, J. M. Kelly, R. J. Norton, A. Roy, B. J. Hathaway, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1983, 671.
15 C. L. Raston and A. H. White, unpublished work cited in ref. 16.
16 M. E. Silver, O. Eisenstein, and R. C. Fay, *Organometallics*, 1983, **2**, 44.
17 D. J. Cardin, M. F. Lappert, and C. L. Raston, 'Chemistry of Organo-Zirconium and -Hafnium Compounds,' Horwood, Chichester, 1986.
18 M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, unpublished work cited in ref. 16.
19 B. Stutte, V. Bätzel, R. Bose, and G. Schmid, *Chem. Ber.*, 1978, **111**, 1603.
20 J. Jeffrey, M. F. Lappert, N. T. Luong-Thi, M. Webb, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1981, 1593.
21 G. M. Sheldrick, SHELX 76, program for crystal structure solution, University of Cambridge, 1976.
22 S. Motherwell, XANADU, University of Cambridge, 1975.
23 C. K. Johnson, ORTEP, report ORNL-3794, Oak Ridge National Laboratory, Tennessee.

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