Metallocene Derivatives of Early Transition Elements. Part 4.[1,‡] Synthesis and Crystal Structures of a Series of Zirconocene(IV) Halides $[Zr(\eta\text{-}C_5H_4SiMe_3)_2X_2]$ (X = Cl or Br) and $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ (X=F, Br, or I)[†]

Antonio Antiñolo, Michael F. Lappert, Anirudh Singh, and Duncan J. W. Winterborn
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ
Lutz M. Engelhardt, Colin L. Raston, and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W. A. 6009, Australia
Arthur J. Carty and Nicholas J. Taylor
Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3GL

A series of zirconocene(IV) halides, $[Zr(\eta\text{-}C_5H_4SiMe_3)_2X_2]$ [X = Cl (**1**) or Br (**2**)] and $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ [X = F (**3**), Br (**4**), I (**5**), or Cl (**6**)], has been prepared, either by (i) substitutive procedures from $ZrCl_4$ [involving the following ligand exchanges: $Cl^-/C_5H_4SiMe_3^-$, $Cl^-/C_5H_3(SiMe_3)_2^-$, Cl^-/Br^-, Cl^-/I^-, or Cl^-/NMe_2^- followed by NMe_2^-/F^-], or (ii), for complexes (**3**), (**5**), or (**6**), by oxidative addition to $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$. The only $\nu_{asym}(ZrX_2)$ vibration to be assigned with confidence is for X = F at 563 cm^{-1}; ^1H and ^{13}C n.m.r. data are unexceptional. *X*-Ray structure determinations of complexes (**1**)—(**5**) have been carried out. Their molecular symmetry is close to *2*, or crystallographically imposed *2* in (**3**), with the stereochemistry about the metal centre best described as distorted tetrahedral. The angle X–Zr–X is 93.70(7), 94.2(1), 100.5(3), 100.25(5), and 100.37(4)° for the halides (**1**)—(**5**), respectively; and the corresponding centroid–Zr–centroid angles are 129.1, 128.2, 131.4, 131.4, and 131.8°. Metal–halogen distances in (**1**) [2.505(2) and 2.476(2) Å] and (**3**) [2.212(6) Å] are significantly longer than in the parent zirconocene(IV) halides $[Zr(\eta\text{-}C_5H_5)_2X_2]$ (*cf.* 2.44 Å for X = Cl and 1.98 Å for X = F) as are [by *ca.* 0.04 Å (average)] the metal–centroid distances in (**3**)—(**5**).

Part 3[1] of the present series dealt with the synthesis, structure, and dynamic behaviour of d^0 zirconocene(IV) complexes of formula $[Zr(\eta\text{-}C_5H_4R)_2ClR']$ [R = alkyl or $SiMe_3$, R′ = $CH(SiMe_3)_2$]. The synthesis of the precursors to such complexes, *viz.* $[Zr(\eta\text{-}C_5H_4R)_2Cl_2]$, was described in Part 2.[2] Herein we further develop zirconocene dihalide chemistry for the case of the cyclopentadienyl ligands possessing one or two of the bulky lipophilic substituents $SiMe_3$, *viz.* $[Zr(\eta\text{-}C_5H_4SiMe_3)_2X_2]$ (X = halide) and $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$.

The ligand $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ is relatively new and has featured in some unusual chemistry, *e.g.*, (i) the deoxygenation of CO_2 upon reduction of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$, the zirconocene product being $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$;[3] (ii) the formation of the first metallocene(III) chlorides of the early lanthanoids, $[\{Ln[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2]$[4] and $[Ln\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]^-$;[5] (iii) novel uranocene(III) halides $[\{U[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}X)\}_n]$ (X = F, Cl, Br, or I; *n* = 2 in the crystal, at least for X = Cl or Br);[6] and (iv) the first tris(η-cyclopentadienyl)metal complex, $[Th\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$.[7] These results presumably relate to the steric hindrance around the metal centres from the large ring substituents coupled with the orientation of the two $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ ligands relative to one another. We have drawn attention to the similarity but also complementarity of this ligand with the much studied $\eta\text{-}C_5Me_5$;[4] however, it appears that $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ is sterically the more demanding as evident, for example, from the existence in the crystal of $[\{U[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2]$,[6] but $[\{U(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)\}_3]$.[8]

In order to study further the effect on the metal environment of incorporating either one or two $SiMe_3$ groups in each of the cyclopentadienyl ligands, we have undertaken *X*-ray structure determinations on several silylated zirconocene dihalides, *viz.* $[Zr(\eta\text{-}C_5H_4SiMe_3)_2X_2]$ [X = Cl (**1**), or Br (**2**)] and $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ [X = F (**3**), Br (**4**), or I (**5**)]. We had hoped to provide such data also for $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ (**6**), which together with (**1**) would have permitted more detailed comparisons to be made with the parent compound $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$. However, crystals of (**6**) were found to be unsatisfactory.

In a subsequent paper we shall present electrochemical data on the one-electron reduction of a series of d^0 complexes of formula $[M(\eta\text{-}C_5H_3R^1R^2)_2X_2]$ [M = Ti, Zr, or Hf; R^1R^2 = H_2, $H(SiMe_3)$, or $(SiMe_3)_2\text{-}1,3$; X = F, Cl, Br, or I], and e.s.r. results on the derived M^{III} d^1 complexes. This will provide a further probe into the stereo-electronic effects associated with progressive $SiMe_3$ substitution in the cyclopentadienyl rings. We are also exploring the role of $\eta\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4$ in this and related areas of chemistry.

Results and Discussion

The syntheses of the zirconocene(IV) halides (**1**)—(**6**) are outlined in Schemes 1 (from Zr^{IV} precursors) and 2 (from a Zr^{II} carbonyl). The general methods, which, in principle, are now well established[9,10] (reference to the first use of each general procedure is given in parentheses), involved (i) $Cl^-/C_5H_4SiMe_3^-$ or $Cl^-/C_5H_3(SiMe_3)_2^-$ exchange (ref. 11), (ii) Cl^-/F^- exchange (*via* the NMe_2^- derivative[12]), (iii) Cl^-/X^- (X = Br or

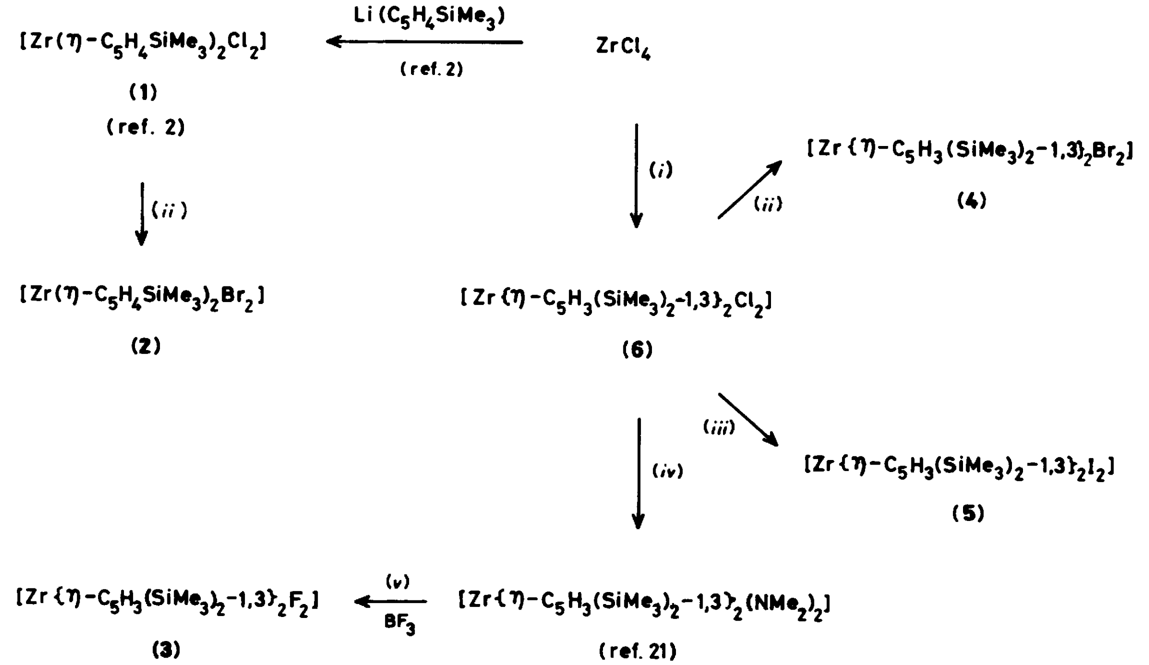
---

[†] Bis(η-trimethylsilylcyclopentadienyl)-dichlorozirconium(IV) and -dibromozirconium(IV); bis[η-1,3-bis(trimethylsilyl)cyclopentadienyl)]-difluorozirconium(IV), -dibromozirconium(IV), and -di-iodozirconium-(IV) respectively.

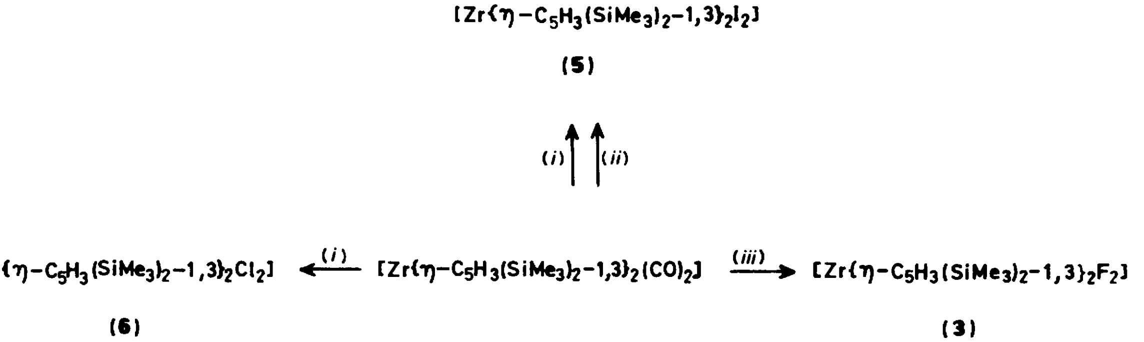
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: Torr ≈ 133 Pa, G = 10^{-4} T.

[‡] No reprints available.



Scheme 1. Substitutive routes to [Zr(η-$C_5H_4SiMe_3)_2Br_2$] and [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2X_2$]. (*i*) Li{$C_5H_3(SiMe_3)_2$-1,3}, thf–C_6H_{14}, 24 h; (*ii*) BBr_3, CH_2Cl_2, 12 h; (*iii*) BI_3, CH_2Cl_2, 6 h; (*iv*) $LiNMe_2$, OEt_2–C_6H_{14}, reflux, 12 h; (*v*) $BF_3(OEt_2)$, C_6H_6, 2.5 h. Each of compounds (3)—(6) was purified [after filtration for (6)] by crystallisation from PhMe–C_6H_{14}; in the case of complex (4), the co-product $BF_2(NMe_2)$ was removed by initial sublimation at 80 °C/0.1 Torr



Scheme 2. Oxidative routes to [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2X_2$] from [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2(CO)_2$]. (*i*) MeI, n-C_6H_{14}, *h*ν, 25 °C, 3 h; (*ii*) I_2, OEt_2, 25 °C, 1 h; (*iii*) Ag[BF_4], thf, −30 °C {*via* a Zr^{III} intermediate, [g_{av} 1.9871, $a(^{31}P)$ 26.7 G]} then 25 °C for 4 h

Table 1. Yields, m.p.s, colours, and analytical data for complexes (2)—(6)

Compound	Yield (%)[a]	M.p. (θ_c/°C)	Colour	Found (Required) (%) C	H
(2) [Zr(η-$C_5H_4SiMe_3)_2Br_2$]	75	143—144	Pale green	36.2 (36.6)	5.2 (5.0)
(3) [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2F_2$]	38[b] (c)	155—157	White	48.0 (48.2)	7.3 (7.7)
(6) [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2Cl_2$]	77 (c)	180—182	White	45.8 (45.5)	7.2 (7.3)
(4) [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2Br_2$]	92	167—169	Pale green	39.4 (39.4)	6.3 (6.3)
(5) [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2I_2$]	94 (91)[d]	180—182	Yellow	34.4 (34.6)	5.4 (5.5)

[a] Yields refer to purified compounds and relate to the methods of Scheme 1 (or Scheme 2, in parentheses). [b] Based on [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2Cl_2$]. [c] Not recorded. [d] From [Zr{η-$C_5H_3(SiMe_3)_2$-1,3}$_2(CO)_2$] + I_2.

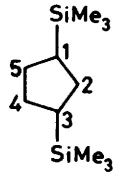
I[12]), or (iv) oxidative addition (*via* Ag[BF_4], $PhCH_2Cl$, MeI, or I_2[3]). The substitution reactions shown in Scheme 1 were perceptibly slower than those for the corresponding C_5H_5 systems,[11,12] no doubt due to the greater steric hindrance associated with the $SiMe_3$-substituted ligands. The Ag[BF_4] experiment was designed to provide a Zr^{III} cationic complex. A Zr^{III} species was detected, but it decayed slowly at ambient temperature; compound (3) was identified among the products, but this is not a viable synthetic route.

In Table 1 we summarise the yields, melting points, microanalyses, and appearance of the compounds. The reported yields represent the cumulative total of two, or sometimes three, successive low-temperature crystallisations from the mother-liquor, made necessary by the high solubility of the compounds in hydrocarbons (a feature associated with the lipophilic $SiMe_3$ groups).

The ^1H, ^{13}C, and, for (3), the ^{19}F n.m.r. data on the zirconocene(IV) halides are presented in Table 2, together with assignments. The ^{19}F chemical shift recorded for (3) appears to be the first for a diamagnetic metallocene(IV) difluoride, *cf.* the f^2 complex $[\{U(\mu\text{-}BF_4)[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}F)\}_2]$.[13]

The i.r. spectra for the complexes (3)—(5) were virtually identical to one another. The majority of the bands are associated with vibrations of the $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ ligand, which appear at slightly higher wavenumber than analogous modes found in $[Zr(\eta\text{-}C_5H_5)_2X_2]$.[12] The only metal–halogen

Table 2. Some n.m.r. chemical shift data (δ/p.p.m.) for complexes (2)—(6)



Compound	^1H N.m.r. (C_6D_6)			^{13}C N.m.r. (C_6D_6)			
	$SiMe_3$	H(2)[a]	H(4), H(5)[a]	$SiMe_3$	C(4), C(5)[a]	C(1), C(3)[a]	C(2)[a]
(2)	0.20 (s)	6.40 (t)[b]	5.87 (t)[b]	0.1	115.4	[125.4, C(1); 12[illegible].1, C(2) and C(3)][c]	
(3)[d]	0.32 (s)	6.62 (t)	6.44 (d)	0.2	123.0	133.9	140.8
(4)	0.20 (s)	7.31 (t)	6.15 (d)	0.1	125.4	130.7	144.6
(5)	0.16 (s)	7.58 (t)	6.09 (d)	0.7	119.6	*e*	143.9
(6)	0.33 (s)	*f*	6.25 (d)	0.2	124.7	132.4	147.7

Data obtained using a Bruker WP80 FT spectrometer. [b] These refer to the A_2B_2 set of ring protons. [c] C(1) refers to the ring carbon bearing the $SiMe_3$ substituent. [d] ^{19}F N.m.r. chemical shift in C_6D_6: 30.6 p.p.m.(s) relative to $BF_3(OEt_2)$. [e] Not observed. [f] Obscured by solvent signal.

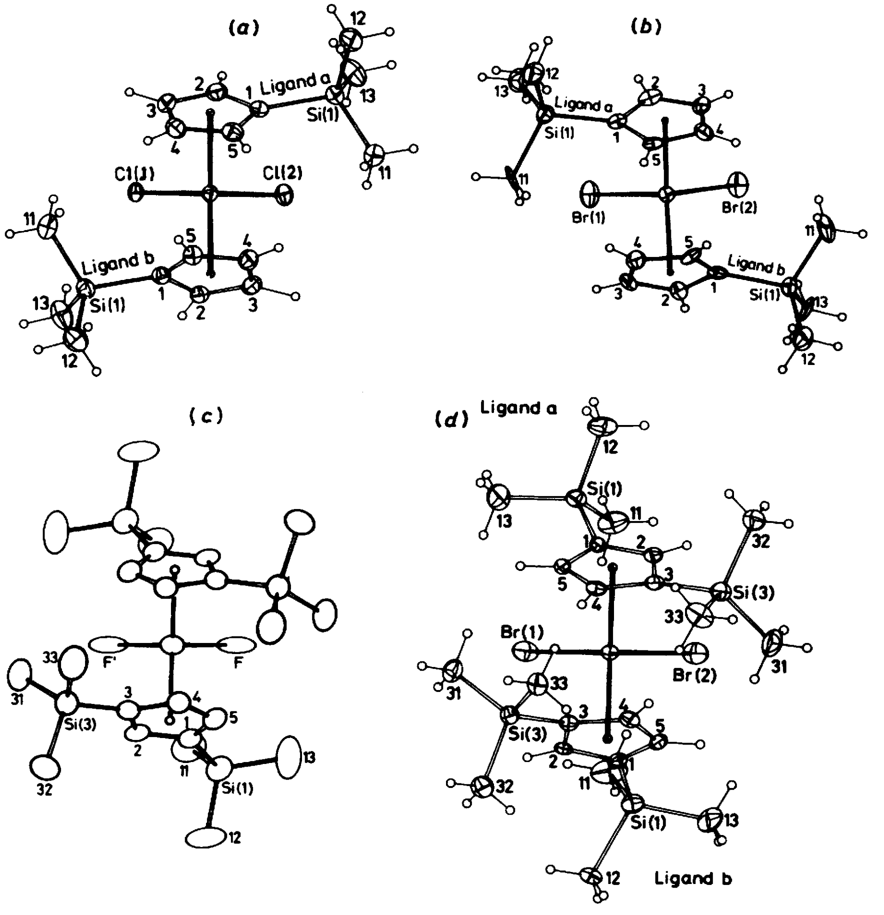


Figure 1. Molecular projections down the X-Zr-X bisector for (*a*) (1), (*b*) (2), (*c*) (3), and (*d*) (4): 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å [except (3)]. Complex (5) is isostructural with (4) and therefore has the same orientation of ligands

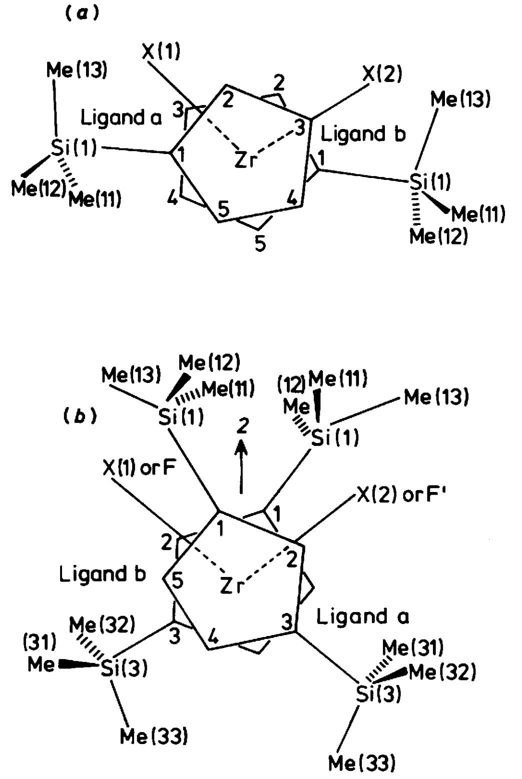
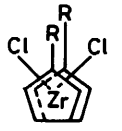


Figure 2. Diagrammatic representation of the structures of (*a*) (**1**) and (**2**), (*b*) (**3**)–(**5**), in projection down the line through the C_5 ring centroids. In (**3**), ligands a and b, and X(1) and X(2), are related by a crystallographic *2* symmetry axis



(**I**) R = CH_2Ph

stretching mode to be definitively identified was $\nu_{asym}(ZrF_2)$ at 563 cm^{-1} (Nujol mull) in (**3**), *cf.* 528 cm^{-1} in [Zr(η-$C_5H_5)_2F_2$].[14]

Single-crystal *X*-ray structure determinations of complexes (**1**)—(**5**) showed that in each case the unit-cell contents comprised discrete molecules of the expected stoicheiometry [Zr(η-$C_5H_3R^1R^2)_2X_2$] [X = F, Cl, Br, or I; R^1R^2 = H($SiMe_3$) or $(SiMe_3)_2$-1,3], Figure 1. The asymmetric unit was a single molecule, except for (**3**) in which it was half a molecule, the other half being generated by a two-fold rotor. The stereochemistry about the zirconium atom was invariably that found in previously studied bent sandwich complexes of the type [ML_2X_2] (M = Zr or Hf, L = η-cyclopentadienyl or an analogue),[10] conveniently described as a distorted tetrahedron by considering the ligand L^- as a sterically demanding unidentate moiety. For (**2**), (**4**), and (**5**), the space group of the structure was found to be chiral. The parent compounds [Zr(η-$C_5H_5)_2X_2$] may have either an 'eclipsed' or a 'staggered' conformation (as assessed by projection of the pair of ring systems down the line through their centroids); thus, the highest molecular point symmetry is either *mm* or *m*. The introduction of a single substituent in each cyclopentadienyl ring usually has the effect of removing the mirror planes, limiting the maximum point symmetry of the substituted molecule to *2*; consequently, in the absence of a suitable scrambling mechanism, a molecule [Zr(η-$C_5H_4R)_2X_2$] could be optically active. Given the

Table 3. Non-hydrogen atom co-ordinates for [Zr(η-$C_5H_4SiMe_3)_2X_2$] [X = Cl (**1**) or Br (**2**)]

	(**1**)			(**2**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Zr	0.263 34(4)	0.251 38(4)	0.141 99(8)	0.153 2(2)	0.0000*	0.252 4(2)
X(1)	0.094 0(1)	0.169 1(1)	0.249 2(2)	−0.094 7(3)	−0.115 9(2)	0.139 9(2)
X(2)	0.395 4(1)	0.331 1(1)	0.506 5(2)	−0.107 8(3)	0.095 9(2)	0.365 5(2)
Ligand a						
C(1)	0.140 0(5)	0.342 6(5)	−0.063 4(9)	0.310(3)	−0.161(1)	0.317(2)
Si(1)	−0.018 1(2)	0.284 5(2)	−0.204 6(3)	0.335 0(9)	−0.278 5(4)	0.228 9(6)
C(11)	−0.065 3(7)	0.138 4(6)	−0.340 1(12)	0.369(3)	−0.253(2)	0.067(2)
C(12)	−0.045 9(8)	0.364 3(8)	−0.404 7(14)	0.553(4)	−0.345(2)	0.290(2)
C(13)	−0.094 5(7)	0.303 5(8)	−0.019 3(13)	0.131(4)	−0.359(2)	0.250(2)
C(2)	0.199 1(6)	0.415 4(5)	0.138 9(10)	0.167(3)	−0.140(2)	0.404(2)
C(3)	0.317 8(6)	0.455 6(5)	0.167 0(12)	0.219(4)	−0.053(2)	0.462(2)
C(4)	0.332 9(6)	0.408 6(5)	−0.013 0(11)	0.392(3)	−0.018(2)	0.421(2)
C(5)	0.225 0(5)	0.341 7(5)	−0.155 1(9)	0.444(3)	−0.081(1)	0.330(2)
Ligand b						
C(1)	0.404 0(5)	0.156 5(5)	0.120 0(9)	0.248(3)	0.170(2)	0.185(2)
Si(1)	0.563 2(2)	0.213 8(2)	0.267 6(3)	0.234 4(9)	0.2950(5)	0.259 9(6)
C(11)	0.624 0(7)	0.359 9(7)	0.264 2(15)	−0.306(3)	0.281(2)	0.418(2)
C(12)	0.629 9(7)	0.134 9(7)	0.125 0(16)	0.411(4)	0.378(2)	0.189(2)
C(13)	0.593 6(8)	0.195 0(9)	0.537 4(14)	−0.015(4)	0.348(1)	0.240(2)
C(2)	0.317 3(6)	0.082 9(5)	0.165 6(11)	0.128(3)	0.134(2)	0.096(2)
C(3)	0.216 4(6)	0.049 8(5)	−0.005 3(14)	0.209(4)	0.047(2)	0.042(2)
C(4)	0.236 9(6)	0.104 3(6)	−0.158 7(11)	0.381(3)	0.032(2)	0.095(2)
C(5)	0.352 3(6)	0.167 6(5)	−0.084 2(10)	0.412(3)	0.111(2)	0.180(2)

* Defines origin.

Table 4. Non-hydrogen atom co-ordinates for $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2F_2]$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr	0.0000*	0.207 7(1)	0.250 0(—)	C(5)	−0.095 7(5)	0.328 6(9)	0.172 5(5)
F	0.086 5(4)	0.048 6(7)	0.217 3(3)	C(11)	−0.075 8(8)	−0.145 8(13)	0.120 5(7)
Si(1)	−0.128 3(2)	0.031 6(3)	0.106 8(2)	C(12)	−0.146 0(8)	0.049 8(15)	0.006 2(6)
Si(3)	0.112 4(1)	0.463 1(3)	0.117 9(1)	C(13)	−0.216 3(7)	0.034 2(17)	0.156 4(10)
C(1)	−0.095 7(5)	0.197 0(10)	0.133 7(4)	C(31)	0.190 5(6)	0.332 4(16)	0.131 9(7)
C(2)	0.001 5(5)	0.224 2(9)	0.114 0(4)	C(32)	0.107 6(6)	0.516 3(15)	0.020 7(6)
C(3)	0.025 3(4)	0.370 3(10)	0.139 8(4)	C(33)	0.123 7(6)	0.635 0(13)	0.175 1(7)
C(4)	−0.038 6(5)	0.433 0(10)	0.175 7(4)				

* Defines origin.

Table 5. Non-hydrogen atom co-ordinates for $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ [X = Br (**4**) or I (**5**)]

	(**4**)			(**5**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Zr	0.986 61(4)	0.492 53(4)	0.396 77(7)	0.014 85(6)	0.502 00(6)	0.594 71(9)
X(1)	1.097 22(5)	0.590 28(7)	0.354 76(10)	−0.101 79(5)	0.390 71(5)	0.639 23(8)
X(2)	1.024 92(6)	0.367 09(6)	0.260 11(10)	−0.030 82(5)	0.635 50(5)	0.743 20(8)
Ligand a						
C(1)	1.066 4(4)	0.448 1(4)	0.583 1(8)	−0.067 8(6)	0.547 0(6)	0.409 7(10)
Si(1)	1.170 7(1)	0.438 8(2)	0.595 9(3)	−0.170 4(2)	0.557 4(2)	0.396 5(4)
C(11)	1.208 6(6)	0.391 1(8)	0.452 3(10)	−0.217 4(8)	0.593 0(10)	0.531 6(15)
C(12)	1.187 1(5)	0.367 7(7)	0.728 8(10)	−0.181 9(6)	0.630 0(8)	0.263 4(15)
C(13)	1.211 8(6)	0.539 1(7)	0.631 7(15)	−0.210 0(7)	0.458 5(8)	0.348 5(16)
C(2)	1.017 7(5)	0.383 7(5)	0.558 2(8)	−0.018 9(7)	0.610 7(6)	0.433 6(8)
C(3)	0.942 5(4)	0.407 6(5)	0.577 7(7)	0.056 1(7)	0.589 7(6)	0.415 4(9)
Si(3)	0.861 8(1)	0.333 7(2)	0.583 4(3)	0.136 5(2)	0.661 5(2)	0.406 2(3)
C(31)	0.840 0(7)	0.289 5(7)	0.428 4(11)	0.161 6(7)	0.704 6(8)	0.554 6(13)
C(32)	0.888 6(6)	0.251 4(6)	0.695 3(11)	0.106 4(7)	0.745 4(7)	0.300 6(11)
C(33)	0.777 4(5)	0.389 3(7)	0.647 0(11)	0.217 0(6)	0.608 1(8)	0.339 5(12)
C(4)	0.946 5(4)	0.490 7(5)	0.619 2(7)	0.054 4(7)	0.505 8(7)	0.372 8(9)
C(5)	1.020 5(5)	0.515 0(5)	0.620 1(7)	−0.021 2(7)	0.481 2(6)	0.371 5(9)
Ligand b						
C(1)	0.922 5(4)	0.540 3(5)	0.196 5(7)	0.078 7(6)	0.455 5(6)	0.795 8(9)
Si(1)	0.957 3(2)	0.532 7(2)	0.030 9(2)	0.048 7(2)	0.458 0(2)	0.958 0(3)
C(11)	1.058 2(6)	0.533 1(9)	0.015 3(10)	−0.054 2(7)	0.458 1(9)	0.986 6(11)
C(12)	0.915 9(5)	0.629 9(5)	−0.056 9(7)	0.086 1(8)	0.365 9(8)	1.031 0(11)
C(13)	0.917 7(7)	0.439 5(7)	−0.041 7(9)	0.090 5(9)	0.546 9(8)	1.039 5(11)
C(2)	0.926 1(4)	0.610 0(5)	0.277 4(7)	0.078 3(6)	0.388 1(6)	0.712 6(10)
C(3)	0.883 8(4)	0.598 8(5)	0.386 2(8)	0.121 6(5)	0.401 7(6)	0.603 8(9)
Si(3)	0.858 7(1)	0.682 8(1)	0.496 8(2)	0.146 4(2)	0.319 0(2)	0.490 6(3)
C(31)	0.943 4(5)	0.727 9(6)	0.565 2(9)	0.062 5(6)	0.270 9(7)	0.423 7(11)
C(32)	0.808 5(6)	0.761 5(6)	0.405 3(10)	0.202 4(7)	0.243 1(8)	0.575 1(12)
C(33)	0.793 2(5)	0.642 0(5)	0.623 4(9)	0.208 4(7)	0.359 1(6)	0.363 7(12)
C(4)	0.851 6(4)	0.518 7(5)	0.371 1(8)	0.151 8(6)	0.482 1(6)	0.615 4(9)
C(5)	0.875 1(4)	0.484 4(5)	0.257 3(8)	0.126 4(6)	0.512 1(7)	0.733 1(11)

observed space groups of (**2**) ($P2_1$), (**4**) ($P2_12_12_1$), and (**5**) ($P2_12_12_1$), the growth of substantial crystals could therefore provide a possible starting point for stereospecific synthesis, using the solid state as a suitable orientating medium.

The ligand substituents are opposite each other in the η-$C_5H_4SiMe_3$ complexes (**1**) and (**2**), Figure 2(*a*), in contrast with their being eclipsed in $[Zr\{(\eta\text{-}C_5H_4CH_2)_2CH_2\}Cl_2]$,[15] where the pentahapto ligands are linked, and in $[Zr(\eta\text{-}C_5H_4CH_2Ph)_2Cl_2]$ (**I**).[16] Although complexes (**1**) and (**2**), like (**I**), are monosubstituted zirconocene(IV) dihalides, their different conformation [*cf.* (**I**) and Figure 2(*a*)] is ascribed to the larger steric requirements of the $SiMe_3$ substituents. Thus for (**1**) or (**2**), unfavourable non-bonding interactions would result if the $SiMe_3$ substituents were eclipsed and astride the two halides. In the η-$C_5H_3(SiMe_3)_2$-1,3 complexes (**3**)—(**5**), a set of substituents lies close to those (R) found in (**I**), but with the rings staggered, Figure 2(*b*).

The *X*-ray parameters are summarised as follows: non-hydrogen atom co-ordinates in Tables 3 [(**1**) and (**2**)], 4 [(**3**)], and 5 [(**4**) and (**5**)]; selected metal atom geometries in Table 6; and ligand planes in Table 7. Some of the key molecular parameters now reported for complexes (**1**)—(**5**) are placed in the context of relevant literature data in Table 8.

The binding of the rings in each of the structures of complexes (**1**)—(**5**) is slightly unsymmetrical; the substituted carbon atoms and nearest ring neighbours are the furthest from the metal centre, by up to 0.08 Å relative to the others. Interestingly, in (**I**) this effect is somewhat more pronounced (maximum difference 0.13 Å),[16] while in $[ZrCl_2(C_{13}H_9)_2]$ it is so great that the bonding of one fluorenyl group ($C_{13}H_9$) is best described as

Table 6. Metal atom geometries (selected) for the zirconocene(IV) complexes (**1**)—(**5**). The first column is the metal–ligand atom distance (Å); other entries are the angles (°) subtended by the relevant atoms at the head of the row and column

Complex (**1**)	r_{Zr-X}	Cl(1)	Cl(2)	C(a0)	C(b0)
Cl(1)	2.505(2)		93.70(7)	107.9(–)	106.8(–)
Cl(2)	2.476(2)	93.70(7)		105.8(–)	108.0(–)
C(a1)	2.516(7)	84.0(2)	125.0(1)	29.1(–)	125.3(–)
C(a2)	2.523(8)	84.3(2)	92.2(1)	28.4(–)	155.9(–)
C(a3)	2.513(7)	114.3(2)	77.6(2)	28.5(–)	138.1(–)
C(a4)	2.485(8)	136.8(2)	99.0(1)	29.0(–)	108.1(–)
C(a5)	2.495(7)	114.6(2)	130.0(1)	28.4(–)	102.2(–)
C(a0)	2.199(–)	107.9(–)	105.8(–)		129.1(–)
C(b1)	2.528(7)	122.9(2)	82.7(1)	128.1(–)	28.6(–)
C(b2)	2.514(8)	91.0(2)	86.4(2)	156.5(–)	28.1(–)
C(b3)	2.509(7)	79.8(2)	117.2(2)	135.9(–)	27.9(–)
C(b4)	2.490(8)	102.8(2)	136.7(2)	106.6(–)	29.0(–)
C(b5)	2.502(8)	132.0(1)	111.7(1)	103.4(–)	27.8(–)
C(b0)	2.209(–)	106.8(–)	108.0(–)	129.1(–)	

Centroid co-ordinates: C(a0) (0.2430, 0.3928, 0.0149); C(b0) (0.3054, 0.1122, 0.0075)

Complex (**2**)	r_{Zr-X}	Br(1)	Br(2)	C(a0)	C(b0)
Br(1)	2.626(4)		94.2(1)	107.8(–)	106.8(–)
Br(2)	2.592(4)	94.2(1)		105.6(–)	109.1(–)
C(a1)	2.52(2)	84.4(5)	126.0(5)	29.3(–)	123.0(–)
C(a2)	2.54(2)	84.2(5)	92.9(5)	28.0(–)	154.1(–)
C(a3)	2.50(2)	113.0(6)	77.7(6)	28.0(–)	139.0(–)
C(a4)	2.50(2)	136.5(5)	97.6(5)	28.8(–)	108.4(–)
C(a5)	2.44(2)	115.9(5)	129.2(5)	28.8(–)	100.4(–)
C(a0)	2.20(–)	107.8(–)	105.6(–)		128.2(–)
C(b1)	2.50(2)	124.7(5)	83.6(5)	126.1(–)	29.5(–)
C(b2)	2.52(2)	93.0(5)	87.5(5)	154.2(–)	27.1(–)
C(b3)	2.50(2)	78.8(6)	118.1(6)	135.4(–)	28.7(–)
C(b4)	2.45(2)	100.6(5)	138.2(5)	106.6(–)	29.2(–)
C(b5)	2.49(2)	131.7(5)	112.8(5)	102.6(–)	27.8(–)
C(b0)	2.19(–)	106.8(–)	109.1(–)	128.2(–)	

Centroid co-ordinates: C(a0) (0.3064, −0.0906, 0.3866); C(b0) (0.2755, 0.0989, 0.1195)

Complex (**3**)	r_{Zr-X}	F	F′	C(0)	C(0)′
F	2.212(6)		100.5(3)	103.9(–)	106.7(–)
C(1)	2.545(8)	96.8(2)	80.5(2)	29.1(–)	154.7(–)
C(2)	2.536(7)	75.8(2)	108.6(3)	28.3(–)	146.4(–)
C(3)	2.552(8)	90.6(2)	135.6(2)	29.4(–)	113.9(–)
C(4)	2.535(9)	123.7(2)	117.0(3)	28.6(–)	103.2(–)
C(5)	2.515(8)	128.1(2)	86.0(3)	28.6(–)	121.8(–)
C(0)	2.223(–)				131.4(–)

Centroid co-ordinates: C(0) (−0.0360, 0.3106, 0.1471). Primed atoms at equivalent position $-x, y, \frac{1}{2} - z$

Complex (**4**)	r_{Zr-X}	Br(1)	Br(2)	C(a0)	C(b0)
Br(1)	2.590(1)		100.25(5)	106.5(–)	104.5(–)
Br(2)	2.602(1)	100.25(5)		104.7(–)	105.5(–)
C(a1)	2.564(8)	82.8(2)	93.9(2)	28.5(–)	157.4(–)
C(a2)	2.534(8)	112.1(2)	77.2(2)	27.5(–)	142.3(–)
C(a3)	2.507(8)	135.7(2)	95.0(2)	29.3(–)	110.9(–)
C(a4)	2.488(8)	113.4(2)	127.3(2)	28.8(–)	103.8(–)
C(a5)	2.494(8)	83.5(2)	126.0(2)	28.3(–)	125.8(–)
C(a0)	2.213(–)	106.5(–)	104.7(–)		131.4(–)
C(b1)	2.556(8)	91.0(2)	83.5(2)	158.7(–)	28.7(–)
C(b2)	2.543(8)	77.5(2)	114.8(2)	139.1(–)	27.3(–)
C(b3)	2.537(8)	98.0(2)	134.6(2)	109.4(–)	29.2(–)
C(b4)	2.488(8)	129.1(2)	109.4(2)	104.8(–)	28.5(–)
C(b5)	2.509(8)	123.1(2)	80.6(2)	128.6(–)	28.5(–)
C(b0)	2.222(–)	104.5(–)	105.5(–)	131.4(–)	

Centroid co-ordinates: C(a0) (0.9987, 0.4490, 0.5917); C(b0) (0.8918, 0.5505, 0.2977)

Complex (**5**)	r_{Zr-X}	I(1)	I(2)	C(a0)	C(b0)
I(1)	2.824(1)		100.37(4)	106.5(5)	104.4(–)
I(2)	2.832(1)	100.37(4)		104.4(–)	105.3(–)
C(a1)	2.61(1)	83.4(2)	93.1(2)	28.3(–)	158.1(–)
C(a2)	2.56(1)	112.6(3)	77.6(2)	26.8(–)	141.8(–)
C(a3)	2.53(1)	135.7(3)	95.0(2)	29.2(–)	111.1(–)

Table 6 (*continued*)

Complex (**5**)	r_{Zr-X}	I(1)	I(2)	C(a0)	C(b0)
C(a4)	2.51(1)	113.1(3)	127.5(2)	29.0(–)	104.0(–)
C(a5)	2.53(1)	83.4(3)	124.9(3)	27.9(–)	127.2(–)
C(a0)	2.244(–)	106.5(–)	104.4(–)		131.8(–)
C(b1)	2.58(1)	90.0(2)	82.9(2)	160.1(–)	29.6(–)
C(b2)	2.53(1)	77.3(2)	114.2(2)	140.1(–)	27.4(–)
C(b3)	2.53(1)	98.4(2)	134.2(2)	109.6(–)	29.1(–)
C(b4)	2.51(1)	129.7(2)	109.7(2)	103.9(–)	29.6(–)
C(b5)	2.52(1)	122.5(3)	81.0(3)	129.1(–)	27.7(–)
C(b0)	2.222(–)	104.4(–)	105.3(–)	131.8(–)	

Centroid co-ordinates: C(a0) (0.0005, 0.5469, 0.4006); C(b0) (0.1114, 0.4479, 0.6922)

Table 7. Least-squares planes, defined by the C_5 ring of each cyclopentadienyl ligand, given in the form $pX + qY + rZ = s$, where the right hand orthogonal Å frame (X, Y, Z) has X parallel to a and Z in the ac plane. Atom deviations, δ, are in Å

Compound	(1)		(2)		(3)	(4)		(5)	
Ligand	a	b	a	b		a	b	a	b
10^4p	−2 502	−6 058	5 004	4 319	3 041	869	7 890	730	8 011
10^4q	7 749	7 624	−5 427	5 901	−4 133	−3 026	−4 058	−3 095	−3 880
10^4r	−5 805	2 275	6 746	−6 821	8 583	9 506	4 614	9 481	4 558
s	3.898	−1.169	4.613	0.676	1.010	5.055	10.53	1.358	2.197
δC(1)	−0.007	−0.003	0.006	−0.032	0.002	0.002	−0.004	−0.003	−0.008
δC(2)	0.002	−0.006	0.005	0.020	0.003	0.004	0.005	0.009	0.001
δC(3)	0.004	0.012	−0.014	−0.001	−0.006	−0.009	−0.003	−0.010	0.005
δC(4)	−0.009	−0.014	0.018	−0.019	0.008	0.010	0.001	0.007	−0.011
δC(5)	0.010	0.010	0.015	0.031	−0.006	−0.008	0.002	−0.004	0.014
δZr	−2.199	−2.209	−2.195	−2.193	−2.223	−2.212	−2.220	−2.241	−2.221
δSi(1)	0.279	0.238	0.293	0.331	0.135	0.307	0.268	0.322	0.328
δC(11)	−0.876	−0.868	−0.984	−0.803	−1.029	−0.872	−1.088	−0.826	−0.913
δC(12)	2.004	2.006	1.987	2.079	1.908	2.030	1.931	2.071	2.036
δC(13)	0.138	−0.032	0.324	0.157	−0.157	0.229	0.577	0.388	0.344
δSi(3)					0.199	0.312	0.361	0.342	0.343
δC(31)					−0.941	−1.074	−0.885	−0.999	−0.980
δC(32)					1.975	1.889	2.046	1.891	1.828
δC(33)					−0.198	0.581	0.399	0.652	0.788

approaching an η^3 interaction (Table 8).[17] The departure from symmetrical binding in complexes (**1**)—(**5**), and also in (**I**) and in $[Zr\{CH(SiMe_3)_2\}(\eta\text{-}C_5H_4R)_2Cl]$ (R = Bu^t or SiMe$_3$),[1] relates to the substituents being forced to reside out of the ligand planes, away from the metal centre, as a consequence of steric effects.[1] The central atom of the ring substituents lies close to 0.3 Å out of the C_5 ring plane (Table 7) except in the fluoride (**3**) where it is less, possibly due to lower crowding around the metal by the smaller halides.

In each of the structures of complexes (**1**)—(**5**), one of the $SiMe_3$ methyl groups is disposed pseudo-coplanar with the ligand C_5 plane [*C*(*mn*3)], one lies out-of-plane on the side of the zirconium by rather less than 1 Å [*C*(*mn*1)], while the third [*C*(*mn*2)] is located out-of-plane on the side opposite the zirconium by *ca.* 2 Å (Table 7). The overall substituent disposition is, in fact, a good approximation in (**1**), (**2**), (**4**), and (**5**) to the ideal *2* symmetry postulated above, with a suitably snug disposition of close substituent–ligand contacts within each molecule. There is no systematic asymmetry in the exocyclic angles at the points of attachment of the silicon atoms.

While the centroid–Zr–centroid angle in each of the $\eta\text{-}C_5H_4SiMe_3$ complexes (**1**) and (**2**) differs substantially from that of the appropriate parent compound $[Zr(\eta\text{-}C_5H_5)_2X_2]$ (X = F,[18] Cl,[19] or I[18]), the more reliable X–Zr–X angle differs only marginally (Table 8) in a direction consistent with mutual repulsion of the ring $SiMe_3$ substituents and the halide ligands, see Figure 2(*a*). For (**I**), the X–Zr–X angle is similar to that found in (**1**) and (**2**), but in (**I**) such repulsion would operate in the opposite direction and would be minimal because of the smaller size of the benzyl substituents in the C_5 rings and of the chloride ligands.

The effect of changing the halide for the system $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ is small, as was also found[18,19] for the parent compounds $[Zr(\eta\text{-}C_5H_5)_2X_2]$. For each of the complexes (**3**)—(**5**), both the centroid–Zr–centroid and X–Zr–X angles are remarkably similar; the X–Zr–X angle is larger by *ca.* 3° than in $[Zr(\eta\text{-}C_5H_5)_2X_2]$, the converse trend from that observed for the $\eta\text{-}C_5H_4SiMe_3$ complexes (**1**) or (**2**). It is noteworthy that two of the $SiMe_3$ substituents project within the X–Zr–X angle, but are not eclipsed as in (**I**); the $SiMe_3$–halide repulsions associated with these particular $SiMe_3$ groups would tend to favour an increase in the X–Zr–X angle at the expense of repulsions between the other $SiMe_3$ groups and X^-. The centroid–Zr–centroid angle is uniformly larger in complexes (**3**)—(**5**) than in (**1**) or (**2**) (consistent with the disilylated ligand being more sterically demanding), as is the increase in average metal–carbon distance, Table 8. Interestingly, the neodymate ion $[Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]^-$ has structural angular parameters (see above) defining the distorted tetrahedral co-ordination sphere of the metal,[5] which are similar to those of the isoleptic complexes (**3**)—(**5**).

The Zr–Cl distances in (**1**), 2.505(2) and 2.476(2) Å, are longer than those of the parent compound $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$,[19] and are the longest Zr–Cl distances yet recorded for a zirconocene chloride.[10] [Unfortunately data on (**6**), the $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ analogue of (**1**), are not available, but it is likely that complex (**6**) would have even longer Zr–Cl bonds.] For the di-iodide (**5**), however, no change in the Zr–X distance relative to the parent

Table 8. Selected structural data for zirconocene dihalides

Complex	⟨Zr–centroid⟩/Å[a]	⟨Zr–C⟩/Å	⟨Zr–X⟩/Å	⟨X–Zr–X⟩/°	Centroid–Zr–Centroid/°	Ring conformation[b]	Ref.
$[Zr(\eta\text{-}C_5H_5)_2F_2]$	2.21	2.50	1.98	96	127.8	e	18, *c*
$[Zr(\eta\text{-}C_5H_5)_2Cl_2]$	2.20	2.49	2.44	97	134	s	19, *c*
$[Zr(\eta\text{-}C_5H_5)_2I_2]$	2.19	2.48	2.83	96	126.3	e	18, *c*
$[Zr\{(\eta\text{-}C_5H_4CH_2)_2CH_2\}Cl_2]$	2.19	2.49	2.44	97	130	e	15, *c*
$[Zr(\eta\text{-}C_5H_4CH_2Ph)_2Cl_2]$	2.16	2.49	2.46	94	126	e	16
$[ZrCl_2(\eta^3\text{-}C_{13}H_9)(\eta^5\text{-}C_{13}H_9)]$[d]	2.33[e]	2.40—2.81 (η^3) 2.40—2.65 (η^5)	2.42	94	125[f]	s	17
$[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cl_2]$	2.21, 2.22	2.50, 2.53	2.442	97.78	130	s	*g*
$[Zr\{(\eta\text{-}C_5Me_4CH_2)_2\}Cl_2]$	2.21	2.52	2.441	98.4	127.7	e	*h*
$[Zr\{(\eta\text{-}C_5H_4)_2SiMe_2\}Cl_2]$	2.20	2.50	2.435	97.98	125.4	e	*i*
(**1**) $[Zr(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$	2.21	2.51	2.49	94	129.1	s	*j*
(**2**) $[Zr(\eta\text{-}C_5H_4SiMe_3)_2Br_2]$	2.19	2.50	2.61	94	128.2	s	*j*
(**3**) $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2F_2]$	2.22	2.54	2.212	100.5	131.4	s	*j*
(**4**) $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Br_2]$	2.22	2.52	2.60	100	131.4	s	*j*
(**5**) $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2I_2]$	2.23	2.54	2.83	100	131.8	s	*j*
$[Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]^-$[k]		2.78	2.67	99	126	f	5

[a] 'Centroid' is the centre of gravity of each C_5-ring ligand. [b] Symbols e = eclipsed, s = staggered, f = intermediate (e–s). [c] J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Am. Chem. Soc.*, 1977, **99**, 6645. [d] $C_{13}H_9$ = fluorenyl. [e] Zr–plane normal distance; Zr–C distances are quoted under ⟨Zr–C⟩. [f] Angle between plane normals intersecting at Zr. [g] R. D. Rogers, M. M. Benning, L. K. Kurihara, K. J. Moriarty, and M. D. Rausch, *J. Organomet. Chem.*, 1985, **293**, 51. [h] F. Wochner, L. Zsolnai, G. Huttner, and H. Brintzinger, *J. Organomet. Chem.*, 1985, **288**, 69. [i] C. S. Bajgur, W. R. Tikkanen, and J. L. Petersen, *Inorg. Chem.*, 1985, **24**, 2539. [j] This work. [k] Nd replaces Zr in the headings.

compound[18] was evident (Table 8); this is likely therefore also to be the case for the as yet unknown intermediate compound $[Zr(\eta\text{-}C_5H_4SiMe_3)_2I_2]$. In the two bromides (**2**) and (**4**), the Zr–Br distances are similar. A surprising result is the exceptionally long Zr–F distance in (**3**), 2.212(6) Å, compared to that[18] in $[Zr(\eta\text{-}C_5H_5)_2F_2]$, 1.98(1) Å. Thus, for zirconocene fluorides, and to a lesser extent chlorides, there is an increase in metal–halide distance with increase in trimethylsilyl substitution of the rings. In the case of (**6**) this is reflected in its chemistry by the greater ease of displacement of the chloride ligands than in $\eta\text{-}C_5H_4SiMe_3$ or $\eta\text{-}C_5H_5$ analogues, *e.g.*, in the reductive carbonylation to yield $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$.[3]

Experimental

General procedures have been described in Parts 1[20] and 2.[2]

Synthesis of $[Zr(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$ (**1**).—Compound (**1**) was prepared using a modification of the literature method.[2] Trimethylsilylcyclopentadiene (20.0 g, 145 mmol) was added to a mixture of sodium sand (3.0 g, 130 mmol) and tetrahydrofuran (thf, 100 cm^3). A white precipitate formed over several days; when no sodium remained (*ca.* 5 d), the stirred suspension was cooled (0 °C) and freshly sublimed zirconium(IV) chloride (15.2 g, 65 mmol) was added slowly over 0.5 h. The mixture was then stirred at 20 °C for 2 h. Removal of thf *in vacuo*, followed by extraction with boiling hexane (200 cm^3), filtration, concentration of the filtrate (to *ca.* 100 cm^3), and cooling to −30 °C gave colourless needles of complex (**1**) (14.0 g, 50%), m.p. 130—131 °C (lit.[2] 130—133 °C).

Synthesis of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2F_2]$ (**3**).—(*a*) Boron trifluoride–diethyl ether (0.33 g, 2.3 mmol) was added at 0 °C to a solution of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(NMe_2)_2]$[21] (1.31 g, 2.3 mmol) in benzene (20 cm^3). After stirring for 30 min, the colour of the supernatant liquor had changed from orange-yellow to colourless and a white precipitate had formed. Stirring was continued for *ca.* 2 h, whereafter volatiles were removed *in vacuo*. Sublimation of the solid residue yielded dimethylamidoboron difluoride (sublimes at 80 °C/10^{-2} Torr). The involatile residual solid was extracted into toluene (25 cm^3); the extract was filtered and the filtrate concentrated. Cooling the latter overnight to −30 °C produced colourless crystals of the *complex* (**3**) (1.02 g, 81%), which were washed with cold pentane and dried *in vacuo*.

(*b*) Silver tetrafluoroborate (0.4 g, 2.27 mmol) was added to a solution of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$ (1.5 g, 2.27 mmol) in thf (40 cm^3) at −30 °C. A copious precipitate was instantly formed. The mixture became brown and was slowly brought to 25 °C. The e.s.r. spectrum showed that a Zr^{III} species had formed (see Scheme 2). This paramagnetic material slowly decayed during *ca.* 4 h. From the filtrate, (**3**) was obtained and characterised by comparison with the material obtained from (*a*).

Synthesis of $[Zr(\eta\text{-}C_5H_4SiMe_3)_2Br_2]$ (**2**).—Boron tribromide (1 cm^3, 10 mmol) in dichloromethane (15 cm^3) was added to a stirred solution of (**1**) (1.0 g, 2 mmol) in CH_2Cl_2 (15 cm^3). Stirring was continued for 1 h, and volatiles were removed *in vacuo*. The residue was extracted into toluene (25 cm^3). The filtrate, upon concentration and cooling to −30 °C, gave pale green crystals of *complex* (**2**) (0.9 g, 75%), which were washed with pentane and dried *in vacuo*.

Synthesis of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ (**6**).—(*a*) This compound was prepared using a modification of the literature method.[22] n-Butyl-lithium (23 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 36 mmol) was added to a stirred solution of bis(trimethylsilyl)cyclopentadiene (7.5 g, 30 mmol) in thf (100 cm^3). After stirring overnight, the solution was cooled to 0 °C and freshly sublimed zirconium(IV) chloride (4.15 g, 18 mmol) was added in portions over 1 h. The reaction mixture was again stirred overnight, whereafter it had become golden yellow. Solvent was removed *in vacuo* and the resulting yellow solid was dissolved in hot toluene (100 cm^3), activated charcoal was added, and the hot mixture was filtered. The yellow filtrate was concentrated and cooled to −30 °C to give white crystals of complex (**6**) (8.0 g, 77%), m.p. 180—182 °C (lit.,[22] 180—181 °C).

(*b*) This experiment was not carried out in a quantitative manner. Excess of benzyl chloride was added to $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$ (*ca.* 1 g) in n-hexane (25 cm^3). The solution was irradiated for 3 h at 25 °C using a medium-pressure mercury lamp, whereafter (**6**) was isolated as a precipitate by concentration and cooling (−30 °C).

Synthesis of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Br_2]$ (**4**).—Boron tribromide (2.9 g, 11 mmol) in dichloromethane (10 cm^3) was added to a stirred solution of (**6**) (6.2 g, 11 mmol) in the same solvent (20 cm^3). Stirring was continued for 1 h, whereafter volatiles were removed *in vacuo*. The residue was extracted into pentane (20 cm^3) and, after filtration and concentration, the filtrate upon cooling to −30 °C gave pale green crystals of the *complex* (**4**) (6.0 g, 92%), which were washed with cold pentane and dried *in vacuo*.

Synthesis of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2I_2]$ (**5**).—(*a*) Boron tri-iodide (3.50 g, 8.95 mmol) in CH_2Cl_2 (35 cm^3) was added to a stirred solution of $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ (**6**) (5.18 g, 8.92 mmol) in dichloromethane (30 cm^3) during *ca.* 10 min at 20 °C. The initially colourless solution became deep pink and after stirring for *ca.* 1 h had developed a deep orange colour. Stirring was continued for *ca.* 5 h, whereafter volatiles were removed *in vacuo*. The solid residue was extracted into hexane (40 cm^3). The extract was filtered and the filtrate concentrated and cooled to *ca.* −30 °C to yield a yellow powder, which was recrystallised twice in the same manner to afford bright yellow crystals of the *complex* (**5**) (6.40 g, 94%), which were dried *in vacuo*.

(*b*) The procedure was identical to that described for the $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$–$PhCH_2Cl$ system, except that MeI was used in place of $PhCH_2Cl$, giving yellow crystals of (**5**).

(*c*) A solution of di-iodine (0.45 g, 1.77 mmol) in diethyl ether (10 cm^3) was added slowly to $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(CO)_2]$ (1.0 g, 1.77 mmol) in the same solvent (10 cm^3) at 25 °C. Gas evolution was observed, and the solution became yellow. Cooling to −30 °C afforded yellow crystals of complex (**5**) (1.23 g, 91%), m.p. 185 °C.

X-*Ray Data Collection, Structure Solution, and Refinement for* (**1**)—(**5**).—*Crystal data for* (**1**). $C_{16}H_{26}Cl_2Si_2Zr$, M = 436.7, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 13.051(7), b = 13.054(6), c = 6.859(4) Å, α = 97.72(4), β = 106.17(4), γ = 107.43(4)°, U = 1 040.0(9) Å^3, D_c = 1.39 g cm^{-3} (Z = 2), $F(000)$ = 448, μ_{Mo} = 8.8 cm^{-1}. Specimen: irregular wedge, *ca.* 0.5 mm (capillary), $2\theta_{max.}$ = 50°, N = 3 660, N_o = 3 080, R = 0.049, R' = 0.085.

Crystal data for (**2**). $C_{16}H_{26}Br_2Si_2Zr$, M = 525.5, monoclinic, space group $P2_1$ (C_2^2, no. 4), a = 6.958(7), b = 13.436(13), c = 11.298(11) Å, β = 91.56(8)°, U = 1 056(2) Å^3, D_c = 1.65 g cm^{-3} (Z = 2), $F(000)$ = 520, μ_{Mo} = 46.2 cm^{-1}. Specimen: 0.4 × 0.1 × 0.05 mm (capillary), $2\theta_{max.}$ = 45°, N = 1 472, N_o = 907, R = 0.044, R' = 0.047 (preferred chirality).

Crystal data for (**3**). $C_{22}H_{42}F_2Si_4Zr$, M = 548.1, orthorhombic, space group *Pbcn* (D_{2h}^{14}, no. 60), a = 18.356(8), b = 8.888(4), c = 18.620(7) Å, U = 3 038(2) Å^3, D_c = 1.198 g cm^{-3} (Z = 4), $F(000)$ = 1 152, μ_{Mo} = 4.84 cm^{-1}. Specimen: 0.2 × 0.2 × 0.3 mm (capillary), $2\theta_{max.}$ = 50°, N = 2 701, N_o = 1 368, R = 0.060, R' = 0.073.

Crystal data for (**4**). $C_{22}H_{42}Br_2Si_4Zr$, M = 669.9, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), a = 18.041(5), b = 16.244(4), c = 10.703(3) Å, U = 3 137(1) Å^3, D_c = 1.42 g cm^{-3} (Z = 4), $F(000)$ = 1 360, μ_{Mo} = 32.0 cm^{-1}. Specimen: 0.2 × 0.2 × 0.4 mm (capillary), $2\theta_{max.}$ = 45°, N = 2 262, N_o = 1 824, R = 0.031, R' = 0.038 (preferred chirality).

Crystal data for (**5**). $C_{22}H_{42}I_2Si_4Zr$, M = 763.9, orthorhombic, space group $P2_12_12_1$, a = 18.075(4), b = 16.319(3), c = 10.844(2) Å, U = 3 199(1) Å, D_c = 1.59 g cm^{-3} (Z = 4), $F(000)$ = 1 504, μ_{Mo} = 24.4 cm^{-1}. Specimen: 0.28 × 0.18 × 0.45 mm, $2\theta_{max.}$ = 50°, N = 2 400, N_o = 2 075, R = 0.032, R' = 0.020 [preferred chirality the reverse of (**4**); co-ordinate setting ($1 - x$, $1 - y$, $1 - z$)].

Structure determination. Unique data sets were measured within the specified $2\theta_{max.}$ limits using a Syntex $P2_1$ four-circle diffractometer in a conventional $2\theta/\theta$ scan mode; T was 295 K and a monochromatic Mo-K_α radiation source was used (λ = 0.710 6_9 Å). N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block diagonal [except (**3**): full matrix] least-squares refinement after analytical absorption correction [except (**1**) and (**3**)] and solution of each structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso})H [except (**3**)] constrained to reasonable values and U_{iso} values taken as equal to those of the atoms to which each H is attached. The quality of the *X*-ray data for (**3**) did not justify inclusion of the hydrogen atom positions; the most significant electron residuals were located in the vicinity of the fluorine atom (0.75 e Å^{-3}) compared with 0.45 e Å^{-3} for cyclopentadienyl hydrogens. Reflection weights were $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$, or for (**3**) $[3.24 - 0.0128|F_o| + 0.000\,39|F_o|^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[23] Computation used the *X*-RAY 76 program system[24] implemented on a Perkin-Elmer 3240 computer by S. R. Hall [except (**3**), for which computer programs are described elsewhere[25]].

Acknowledgements

We gratefully acknowledge support from the S.E.R.C. (CASE studentship for D. J. W. W., and fellowship for A. S.), I.C.I. Plastics Division (for D. J. W. W.), the Australian Research Grant Scheme, and the National Science and Engineering Research Council of Canada, and Drs. J. McMeeking and J. A. Segal for their interest.

References

1 Part 3, 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.
2 Part 2, M. F. Lappert, C. J. Pickett, P. I. Riley, and P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1981, 805.
3 A. Antiñolo, M. F. Lappert, and D. J. W. Winterborn, *J. Organomet. Chem.*, 1984, **272**, C37.
4 M. F. Lappert, A. Singh, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1981, 1190.
5 M. F. Lappert, A. Singh, J. L. Atwood, W. E. Hunter, and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1983, 69.
6 P. C. Blake, M. F. Lappert, R. G. Taylor, J. L. Atwood, W. E. Hunter, and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1986, 1394.
7 P. C. Blake, M. F. Lappert, J. L. Atwood, and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1986, 1148.
8 P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, S. H. Vollmer, and V. W. Day, *Organometallics*, 1982, **1**, 170.
9 D. J. Cardin, M. F. Lappert, C. L. Raston, and P. I. Riley, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch. 23, p. 568.
10 D. J. Cardin, M. F. Lappert, and C. L. Raston, 'Chemistry of Organo-Zirconium and -Hafnium Compounds,' Ellis Horwood, Chichester, 1986.
11 G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, 1954, **76**, 4281.
12 P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc. A*, 1969, 2106.

13 P. B. Hitchcock, M. F. Lappert, and R. G. Taylor, *J. Chem. Soc., Chem. Commun.*, 1984, 1082.

14 P. M. Druce, B. M. Kingston, M. F. Lappert, R. C. Srivastava, M. J. Frazer, and W. E. Newton, *J. Chem. Soc. A*, 1969, 2814.

15 C. H. Saldarriaga-Molina, A. Clearfield, and I. Bernal, *J. Organomet. Chem.*, 1974, **80**, 79.

16 Y. Dusausoy, J. Protas, P. Renaut, B. Gautheron, and G. Tainturier, *J. Organomet. Chem.*, 1978, **157**, 167.

17 C. Kowala and J. A. Wunderlich, *Acta Crystallogr., Sect. B*, 1976, **32**, 820.

18 M. A. Bush and G. A. Sim, *J. Chem. Soc. A*, 1971, 2225.

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

20 Part 1, P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180.

21 D. J. W. Winterborn, D. Phil. Thesis, University of Sussex, 1986.

22 G. A. Tolstikov, M. S. Miftakhov, and Yu. B. Monakov, *Zh. Obschch. Khim.*, 1976, **46**, 1778.

23 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

24 J. M. Stewart 'The *X*-RAY System,' Technical Report TR-192, Computer Science Center, University of Maryland, U.S.A., June, 1972.

25 A. J. Carty, G. N. Mott, N. J. Taylor, and J. E. Yule, *J. Am. Chem. Soc.*, 1978, **100**, 3051.

Received 7th July 1986; *Paper* 6/1355