DALTON

C-Centred chiral metal alkyls, $[MR^*(Cl)(\eta\text{-}C_5H_5)_2]$, *rac*- and *meso*-$[ZrR^*_2(\eta\text{-}C_5H_5)_2]$† [R* = $CH(SiMe_3)C_6H_4Me$-*o*], and their one-electron reductions; reaction of $Li[CH(SiMe_3)_2]$-$(Me_2NCH_2CH_2NMe_2)$ with $[MCl_2(\eta\text{-}C_5H_5)_2]$ (M = Zr or Hf)‡

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The chloro(alkyl)metallocenes $[MR^*(Cl)(\eta\text{-}C_5H_5)_2]$ [R* = $^-CH(SiMe_3)C_6H_4Me$-*o*; M = Zr **1** or Hf **2**] have been prepared from $[MCl_2(\eta\text{-}C_5H_5)_2]$ and LiR*(tmen) (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine); further alkylation occurred only for M = Zr, affording *rac*-**3a** and *meso*-**3b**, $[ZrR^*_2(\eta\text{-}C_5H_5)_2]$. In contrast, reaction of 2 equivalents of $Li[CH(SiMe_3)_2]$(tmen) with $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ yielded an alkyl elimination product possessing $\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4^{2-}$ ligands. Compound **1** was reversibly reduced ($E^{red}_{1/2} = -1.72$ V *vs.* saturated calomel electrode, SCE) whereas **2**, **3a** or **3b** were irreversibly reduced ($E^{red} = -2.12$, -2.08, -2.00 V respectively *vs.* SCE). Thermolysis of **3b** in toluene gave **3a** (80 °C) or '$Zr(C_{10}H_8)$' (120 °C). Photolysis of **3a** or **3b** at 20 °C in tetrahydrofuran (thf) yielded a 1:1 mixture of **3a** and **3b**; a d^1 intermediate has been unambiguously identified as $[ZrR^*(\eta\text{-}C_5H_5)_2]$. Reduction of **1** (Na–Hg), or **3a** and **3b** ($Na[C_{10}H_8]$), in thf also gave $[ZrR^*(\eta\text{-}C_5H_5)_2]$ but this slowly transformed into $[ZrR^*(\eta\text{-}C_5H_5)_2(thf)]$, and **1** with $Na[C_{10}H_8]$ and PPh_3 gave $[ZrR^*(\eta\text{-}C_5H_5)_2(PPh_3)]$. Reduction of **1**, **3a** or **3b**, or photolysis of **3a** or **3b**, in the presence of PMe_3 gave $[ZrR^*(\eta\text{-}C_5H_5)_2(PMe_3)]$. Crystal structure determinations showed a slightly more crowded metal environment in **2** than in **1**, consistent with the view that dialkylation in **2** is limited on steric grounds; M–σ-C 2.359(4) (**1**), 2.322(8) (**2**), metal–centroid 2.22 (**1**), 2.21 (**2**), M–Cl 2.444(1) (**1**), 2.418(3) (**2**) Å. The structure of **3a** confirms the *rac* assignment, M–σ-C 2.37$_4$ Å, metal–centroid 2.23, 2.24 Å.

In previous papers of the present series dealing with organo-transition Group IV elements the chemistry focused on the d^0 (refs. 1 and 2) and d^1 (Nb)[3] metallocene halides, (chloro)alkyls and dialkyls.[1–4] Herein we develop d^0 and d^1 alkylzirconocene halide chemistry where C_α of the alkyl moiety is chiral. In general compounds of this type are uncommon and are usually associated with the late transition metals, *e.g.* $[Fe\{CH(OMe)Me\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$,[4] $[Pd\{CH(PPhMe_2)(SiMe_3)\}(cod)Cl][PF_6]$[5] (cod = cycloocta-1,5-diene) and $[NiL(\eta\text{-}C_5H_5)]$[6] (L = substituted bicyclo[2.2.1]hepta-2,5-diene) which has been resolved. The study of complexes possessing a metal to chiral carbon linkage may give insight into mechanisms of reactions involving metal–carbon bond formation and/or scission, particularly in dealing with compounds with more than one chiral ligand, since diastereoisomers are possible.

The ligand to which we now draw attention is $^-CH(SiMe_3)C_6H_4Me$-*o* (≡R*). It is related to the benzyl ligand which has a significant place in alkylmetal chemistry, being capable of unusual bonding configurations, *e.g.* η^3-allyl in $[Th(CH_2Ph)_3(\eta\text{-}C_5Me_5)]$;[7] in principle such possibilities are available to R*. Other closely related ligands include $^-CHPh_2$,[8,9] $^-CH(SiMe_3)_2$ (R) (refs. 2, 3, 10 and 11 and refs. therein), and $^-CHSiMe_3(C_{14}H_9\text{-}9)$ ($C_{14}H_9$ = anthryl).[12] These resemble R* in being highly hindered, a feature that has proved important in certain aspects of alkylmetal chemistry, *e.g.* in the synthesis of $[ZrR(\eta^2\text{-}N_2)(\eta\text{-}C_5H_4R')_2]$ (R′ = H or Me).[13]

Results described below include: (*i*) the synthesis of $[MR^*(Cl)(\eta\text{-}C_5H_5)_2]$ (M = Zr **1** or Hf **2**) from LiR*(tmen) **4** (tmen = $Me_2NCH_2CH_2NMe_2$);[14] (*ii*) a further reaction of compound **1**, but not **2**, leading to a mixture of diastereoisomers, *rac*- and *meso*-$[ZrR^*_2(\eta\text{-}C_5H_5)_2]$ **3a** and **3b**; (*iii*) the reaction of $[MCl_2(\eta\text{-}C_5H_5)_2]$ (M = Zr or Hf) with LiR(tmen), a reagent related to **4**, in an attempt to understand the disparity between the alkylation of **1** and **2**; (*iv*) reduction of **1**, **2**, **3a** or **3b** to d^1 species; and (*v*) the crystal structure determinations of **1**, **2** and **3a**. As to item (*iv*), there has been much interest in the characterization of paramagnetic organozirconium(III) compounds[2,13,15–26] but the exact nature of the species studied is only just beginning to emerge with structural authentication for $[NBu^n_4][ZrCl_2\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2]$,[27] $[\{Zr(\mu\text{-}X)[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2\}_2]$ (X = Cl or Br),[28] $[ZrCl\{\eta\text{-}C_5H_3Bu^t_2\text{-}1,3\}_2]$,[29] $[ZrR\{N(SiMe_2CH_2PPr^i_2)_2\}(\eta\text{-}C_5H_5)]$ (R = Ph or CH_2SiMe_3),[30] $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)]$[31] and $[Zr(CH_2SiMe_3)(oep)]$ (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin);[32] organohafnium(III) compounds are less studied and are relatively less stable.[15,24] Of interest in relation to (*v*) is the closeness of the atomic radii of Zr and Hf, and in consequence they have similar chemistry.[25] A slight difference in size (Zr > Hf by *ca.* 0.01–0.02 Å) however may account for the contrast in the alkylation of **1** and **2**. The only authenticated stereochemical difference between organometallic isoleptic complexes of these elements is that of the tetrakis(cyclopentadienyl)metal(IV) species $[Zr(\eta^1\text{-}C_5H_5)(\eta\text{-}C_5H_5)_3]$[33] and $[Hf(\eta^1\text{-}C_5H_5)_2(\eta\text{-}C_5H_5)_2]$.[34]

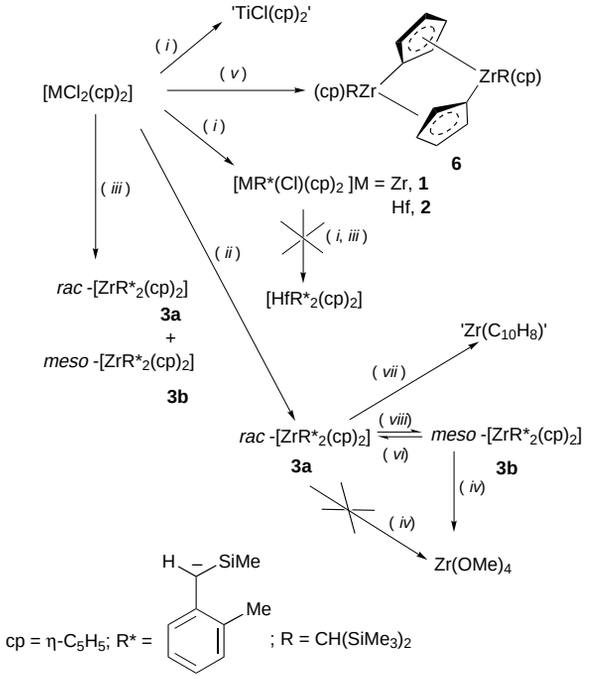
Aspects of items (*i*) and (*ii*) have been previously communicated.[17] Interestingly chiral metallocenes of the transition-metal Group IV elements are well known where the chiral centre is in a cyclopentadienyl substituent,[6] and a different type of chirality in alkylmetal compounds to that in **1**–**3** is axial asymmetry, defined in complexes based on $M\{(o\text{-}CH_2C_6H_4)_2\}$.[35]

Results and Discussion

Synthesis of d^0 compounds

A summary of reactions involving the synthesis of the d^0 compounds is given in Scheme 1: new compounds have been charac-

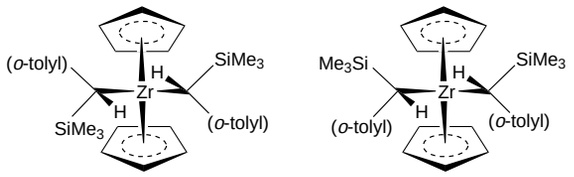
† Chlorobis(η-cyclopentadienyl)[(*o*-tolyl)trimethylsilylmethyl]-zirconium(IV) or -hafnium(IV), *rac*- and *meso*-bis(η-cyclopentadienyl)-bis[(*o*-tolyl)trimethylsilylmethyl]zirconium.
‡ Metallocene derivatives of early transition metals. Part 5.[1]
Non-SI unit employed: G = 10^{-4} T.



Scheme 1 Synthesis of d^0 compounds: (*i*) LiR*(tmen) **4**, tetrahydrofuran (thf), −78 °C; (*ii*) 2 equivalents **4**, thf, −78 °C; (*iii*) 2 equivalents **4**, OEt_2, 20 °C; (*iv*) MeOH; (*v*) LiR(tmen) **5**, OEt_2, −78 °C; (*vi*) C_6H_6 or hexane, 80 °C; (*vii*) toluene, 120 °C; (*viii*) C_6H_6, *hν*

terized using ^1H and ^{13}C NMR, ESR, IR spectroscopy, mass spectrometry and X-ray diffraction techniques. The product of the reaction between a transition-metal Group IV metallocene dichloride and LiR*(tmen) **4** differed for the three elements. For the titanium system we note that reduction to Ti^{III} preceded alkylation for the conditions studied, the reduced species being $[\{TiCl(\eta\text{-}C_5H_5)_2\}_2]$, $g_{av} = 1.978$, with no hyperfine coupling.[36] Subsequent addition of an excess of the alkylating agent **4** gave a brown oil which was insoluble in organic solvents. Such reduction followed by alkylation has been noted in the treatment of titanocene dichloride with $LiCH(SiMe_3)_2$ (≡LiR),[8] R being of similar bulk to R* (see below). The reducing ability of organolithium reagents is well known. It is further highlighted for **4** which with $[PtCl_2(PPh_3)_2]$ gave $[Pt(PPh_3)_3]$ in modest yield (Found: C, 65.5; H, 4.50. Calc. for $C_{54}H_{45}P_3Pt$: C, 66.1; H, 4.60%).

No reduction was evident on treating $[MCl_2(\eta\text{-}C_5H_5)_2]$ (M = Zr or Hf) with compound **4**. The contrast with the reaction of the titanium analogue reflects the relative ease of reduction (Ti ⩾ Zr, Hf) of $M^{IV} \longrightarrow M^{III}$;[15] there is only one case of an organolithium reagent reducing Zr^{IV}.[15] The compounds of formula $[MR^*(Cl)(\eta\text{-}C_5H_5)_2]$ (M = Zr **1** or Hf **2**) have been prepared. Only **1** is susceptible to further alkylation to the dialkyls *rac*-**3a** and *meso*-**3b** $[ZrR^*_2(\eta\text{-}C_5H_5)_2]$. Selective monoalkylation of $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ was achieved by the addition of a thf solution of the lithium alkyl **4** to a thf solution of the dichloride at −78 °C followed by slow warming of the mixture to ambient temperature; a slight excess of **4** ensured that all the zirconocene dichloride was consumed; any dialkyl species generated were extremely soluble in OEt_2, the crystallization solvent of **1**. Similar reaction conditions were found to be necessary in the synthesis of $[Zr(CH_2PPh_2)Cl(\eta\text{-}C_5H_5)_2]$.[18] Other reaction conditions afforded a mixture of unreacted zirconocene dichloride and mono- and di-alkylated species. The reaction of half an equivalent of $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ with **4** at room temperature gave a 1:1 mixture of the diastereoisomers **3a** and **3b**. These were easily identified by ^1H NMR spectroscopy, **3a** showing one and **3b** two cyclopentadienyl signals. At −78 °C, however, the exclusive product was **3a**. Pure **3b** was obtained by fractional crystallization, it being the less soluble of the two isomers. On



I II

heating a benzene or toluene solution of **3b** at *ca.* 80 °C isomerization ($t_{\frac{1}{2}} \approx 1.5$ h) to **3a** occurred. At higher temperatures (*ca.* 120 °C) decomposition to R*H and a green, pyrophoric, insoluble material of composition '$C_{10}H_8Zr$' (Found: C, 55.8; H, 4.40. Calc. for $C_{10}H_8Zr$: C, 54.8; H, 3.70%) was observed. The isomerization presumably involves Zr–R* homolysis or heterolysis followed by radical-pair or ion-pair recombination, respectively; no radical was detected to support the former hypothesis. Photolysis at 20 °C of **3a** or **3b** gave a 1:1 mixture of the two isomers ($t_{\frac{1}{2}} \approx 1$ h for a 250 W mercury lamp). Here a radical intermediate, $[ZrR^*(\eta\text{-}C_5H_5)_2]$, was evident from ESR studies (see below). Interestingly, **3b** but not **3a** reacted with methanol affording $Zr(OMe)_4$ {*cf.* $Zr(OMe)_4$ from $[ZrMe_2(\eta\text{-}C_5H_5)_2]$}.[37] Evidently the kinetic protection of the metal centre by the two hindered alkyl ligands is more efficient in **3a** than **3b**. This difference in reactivity with MeOH has been utilized in the synthesis of pure **3a** (Scheme 1).

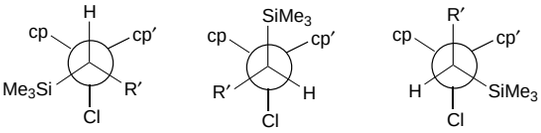
The greater thermodynamic stability of the *rac* isomer **3a** (**I**), compared with the *meso* isomer **3b** (**II**), is attributed to the preference for minimizing non-bonding contacts between the sterically more demanding $SiMe_3$ groups.

The thermal conversion of the *rac* isomer **3a** into '$C_{10}H_8Zr$' may be contrasted with (*i*) the thermolysis of *cis*-$[Pt(CH_2C_6H_4Me\text{-}o)_2(PEt_3)_2]$ in refluxing xylene which proceeded *via* scission of one alkyl group with δ-hydrogen abstraction at the other to generate the metallacycle $[Pt(CH_2C_6H_4CH_2\text{-}o)(PEt_3)_2]$,[38] and (*ii*) the reaction of $[RuCl_2L_4]$ (L = phosphine, *e.g.* $PMePh_2$) which with $MgBr(CH_2C_6H_4Me\text{-}o)$ at −30 °C similarly underwent δ-hydrogen abstraction, yielding $[Ru\{\eta^4\text{-}(CH_2)_2C_6H_4\}L_3]$.[38]

In view of the similar chemistry of zirconium and hafnium it is surprising that hafnocene dichloride was found to be resistant to dialkylation, the exclusive product being $[HfR^*(Cl)(\eta\text{-}C_5H_5)_2]$ **2**, even under the more forcing conditions of refluxing in OEt_2 or thf. This behaviour has however some precedent in the substitution reaction of $[MCl_2(\eta\text{-}C_5H_4Bu^t)_2]$ (M = Zr or Hf) with $LiCH_2SiMe_3$.[2]

A noteworthy difference between dichlorides of zirconocene and hafnocene was that treatment with LiR yielded $[ZrR(Cl)(\eta\text{-}C_5H_5)_2]$ but $[HfCl_2(\eta\text{-}C_5H_5)_2]$ proved to be unreactive[3] which was attributed to steric hindrance of the alkyl and the difference in size of the metal ions. The related dialkylation using $LiCHPh_2$ was observed for both metallocenes.[8] These data indicate that the degree of steric hindrance, at least in metallocene complexes, increases in the sequence $^-CHPh_2 < {}^-CH(SiMe_3)C_6H_4Me\text{-}o$ (= R^{*-}) < $^-CH(SiMe_3)_2$ (= R^-), although the shape of the alkyl group in relation to the orientation of the phenyl planes may allow variability in the steric hindrance of R^{*-} and $^-CHPh_2$.

The difference between the reaction of LiR in OEt_2 with LiR*(tmen) prompted us to synthesize LiR(tmen) **5**[10] and to compare its reactivity with the zirconium and hafnium metallocene dichlorides. In each case 2 mole equivalents of LiCl were produced; the zirconocene product, **6**, was characterized by elemental analysis and ^1H NMR spectral data which indicated the presence of bridging $\eta^1:\eta^5$-cyclopentadienediyl ligands which may also have featured in the above '$C_{10}H_8Zr$' compound. They have been reported for $[\{Zr(\eta\text{-}C_5H_5)(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)\}_2L]$ (L = PMe_2Ph or $PMePh_2$)[39] and $[(\eta\text{-}C_5H_5)_2Zr(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_5)_2Zr\{C_6H_4(CHSiMe_3)_2\text{-}o\}]$.[15] Compound **6** was a pale green, extremely air-sensitive solid which rapidly



III IV V

decomposed in solution to a dark green species, a feature which limited its further characterization. A plausible structure is that of the dimeric molecule shown in Scheme 1. In the analogous reaction for hafnocene dichloride an analytically pure sample was not isolated, but the ^{1}H NMR spectrum of the crude product also indicated the presence of μ-η^1:η^5-C_5H_4 entities, suggestive of a product of similar structure. The $SiMe_3$ and η^5-C_5H_5 resonances of **6** were similar to those found for the corresponding metallocene alkyl chlorides,[18] whereas the C*H*($SiMe_3$) signal was 3.3 ppm to lower frequency, at a value similar to that for the methine protons in *meso*-[Zr{C_6H_4-($CHSiMe_3$)$_2$-*o*}(η-C_5H_5)$_2$].[15]

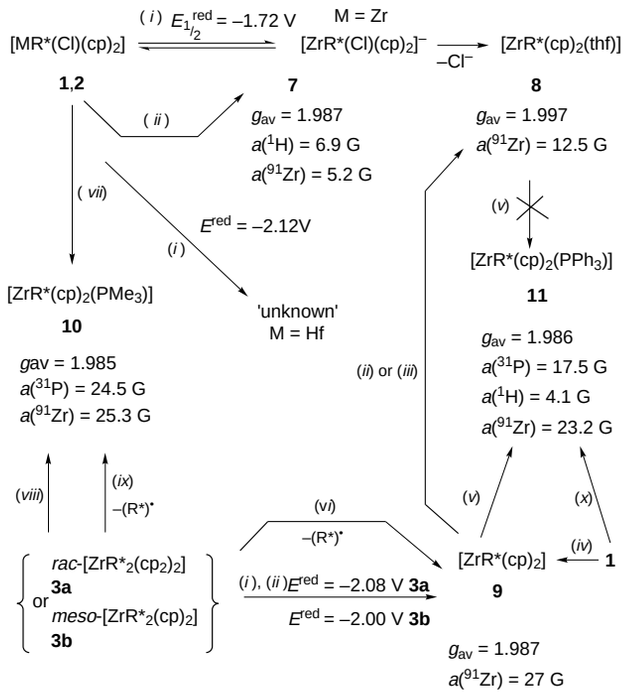
The ability to displace two chloride ligands from zirconocene or hafnocene dichloride using LiR(tmen), but not LiR in OEt_2, may be a consequence of an increase in carbanionic character of the alkyl group by the chelating tmen, a well known activating organolithium reagent.[40] The contrast in reactivity between LiR(tmen) **5** and LiR*(tmen) **4** may reflect the difference in the degree of carbanionic character in each species; complex **4** is likely to be a contact ion pair with charge delocalization, as found in the structures of related compounds, *e.g.* [Li(CH_2Ph)-{N(CH_2CH_2)$_3$N}]$_n$,[41] [{Li(tmen)}$_2${(*o*-$Me_3SiCHC_6H_4$)$_2$}][42] and [{Li(tmen)}$_2${2-$CH_2C_{10}H_6$)$_2$}],[43] while **5** has polarized covalent bonding.

The NMR spectra of [MR*(Cl)(η-C_5H_5)$_2$] (M = Zr **1** or Hf **2**) showed two inequivalent diastereotopic cyclopentadienyl groups, a consequence of the chiral centre at C_α; the $SiMe_3$ and C_5H_5 groups showed signals at values similar to those for related compounds.[3] Over a wide temperature range of −90 to +90 °C, variations in the spectra **1**, **2** or **3** in [$^2H_8$]toluene were minimal, consistent with free rotation about the Zr–C_α linkage and/or the presence of only one conformation over this range. The former postulate is more likely, since for the bulkier alkyl group, R, the coalescence temperature was −4 °C,[8] and a lower value (and activation energy) would be expected for R*. Of the three isomers possible, conformers **III**–**V** (R′ = aryl), the one found in the solid was **III** (see structural discussion).

Generation of zirconocene d^1 species

Scheme 2 summarizes reagents and conditions for generating the d^1 species and their assigned structures, and Fig. 1 shows representative ESR spectra. Each spectrum showed a central signal flanked by a sextet from splitting by one $^{91}Zr^{III}$ nucleus ($I = \frac{5}{2}$, 11.23% abundance). A high degree of certainty as to the nature of the d^1 species was made possible using several alternative d^0 zirconium starting materials, **1**, **3a** and **3b**, and various reduction strategies including chemical, electrochemical (cyclic voltammetry, CV) and photolytic methods coupled with ESR studies. The ESR spectra were unperturbed for chemically derived zirconium(III) species by the addition of [NBu^n_4][BF_4], the electrochemical supporting electrolyte, ruling out the likelihood of anomalous results in the electrochemical experiments.

Reduction of compound **1** using Na–Hg, or **3a** or **3b** using Na[$C_{10}H_8$] in thf, yielded initially [ZrR*(η-C_5H_5)$_2$] **9**, which rapidly formed [ZrR*(η-C_5H_5)$_2$(thf)] **8**, Fig. 1(*b*). Compound **1** with Na[$C_{10}H_8$] afforded [ZrR*(Cl)(η-C_5H_5)$_2$]$^-$ **7**, based mainly on the reversibility of the reduction of **1**. This contrasts with the chloride elimination observed using Na–Hg. Conversion of **7** into **8** was evident [Fig. 1(*a*)] but **9**, a possible intermediate, was not detected, in accordance with the relative $t_{\frac{1}{2}}$ values of *ca.* 1.1 h for **7** ⟶ **8**, and *ca.* 0.5 h for **9** ⟶ **8**. In the presence of PPh_3, **9** (but not **8**) yielded [ZrR*(η-C_5H_5)$_2$(PPh_3)] **11**. Thus **9**



Scheme 2 Generation of d^1 species (at 20 °C): (*i*) CV in 0.2 mol dm^{-3} [NBu^n_4][BF_4] in thf at a platinum electrode measured relative to the saturated calomel electrode (SCE); (*ii*) Na[$C_{10}H_8$] (1 equivalent), thf; (*iii*) Na–Hg, thf; (*iv*) Na–Hg, OEt_2; (*v*), (*ii*) or (*iii*) then PPh_3; (*vi*) *h*ν (250 W medium-pressure mercury lamp), C_6H_6, toluene or thf; (*vii*), (*iii*) + PMe_3; (*viii*), (*ii*) + PMe_3; (*ix*), (*vi*) + PMe_3; (*x*), (*iii*) + PPh_3 (for abbreviations see Scheme 1)

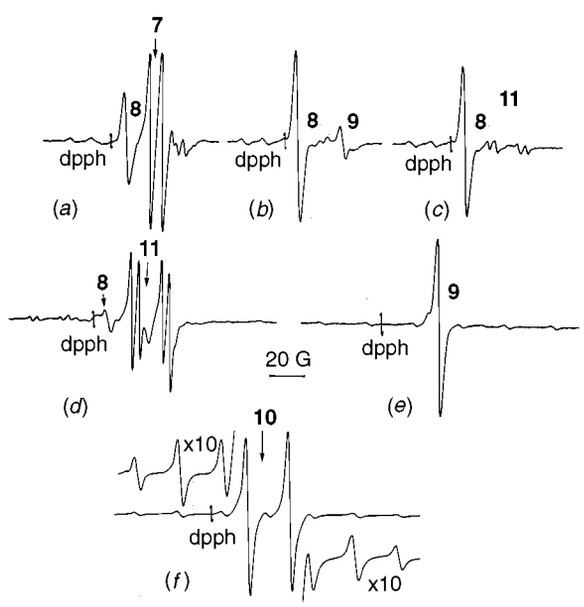


Fig. 1 The ESR spectra of solutions prepared at 20 °C by: (*a*) treating compound **1** with Na[$C_{10}H_8$] in thf (after *ca.* 10 min); (*b*) treating **3b** with Na[$C_{10}H_8$] in thf; (*c*) reaction as for (*b*) then PPh_3 added; (*d*) reaction as for (*b*) but with PPh_3 present [similar spectra from **3a** were obtained for (*b*)–(*d*)]; (*e*) photolysis of **3a** or **3b** in thf; and (*f*) photolysis of **3a** or **3b** in thf–PMe_3, treating **3a** or **3b** with Na[$C_{10}H_8$] in thf–PMe_3, or treating **1** with Na–Hg in thf–PMe_3. Assigned structures corresponding to the signals are indicated (see Scheme 2 for definitions); dpph = diphenylpicrylhydrazyl

was intercepted by the addition of PPh_3; Fig. 1(*c*) shows a spectrum obtained on adding PPh_3 after reduction of **1**, and before complete conversion of **9** ⟶ **8**, while Fig. 1(*d*) illustrates the reduction in the presence of PPh_3. (Note that a trace of **8** remained and this was unaffected by time.)

Photolysis of the *rac*-**3a** and *meso*-**3b** isomeric compounds in thf (or benzene) also gave **9**, presumably with (R*)$^\bullet$ as a radical

cage. However, an ESR signal assignable to $(R^*)^{\bullet}$ was not observed. The signal for **9** rapidly decayed in the dark ($t_{\frac{1}{2}} \approx 8$ min) due to recombination yielding **3a** or **3b**. Thus reaction (1)

$$\mathbf{3a} + \mathbf{3b} \overset{h\nu}{\rightleftharpoons} (R^*)^{\bullet}, [ZrR^*(\eta\text{-}C_5H_5)_2] \qquad (1)$$

was evidently faster than **9** ⟶ **8** for which $t_{\frac{1}{2}} \approx 0.5$ h was established in the above chemical reductions; hence a detectable quantity of **8** in the photolytic experiment is ruled out. Radical cages rather than solvent-separated radicals may also disfavour formation of **8**. Reduction of **1** (Na–Hg or $Na[C_{10}H_8]$) or photolysis of **3a** and/or **3b** in toluene or thf and an excess of PMe_3 rapidly yielded solutions containing only the d^1 species $[ZrR^*(\eta\text{-}C_5H_5)_2(PMe_3)]$ **10** [Fig. 1(*f*)]. In all the reductions yielding solutions of **7**–**11** the primary reduction processes are believed to be: (*i*) electron transfer **1** ⟶ **7**; (*ii*) electron transfer coupled with M–Cl or M–C bond rupture (**1** ⟶ **9** or **3** ⟶ **9**); and (*iii*) M–C bond fission ($\mathbf{3} \overset{h\nu}{\longrightarrow} \mathbf{9}$).

Treatment of $[HfR^*(Cl)(\eta\text{-}C_5H_5)_2]$ **2** with either Na–Hg or $Na[C_{10}H_8]$ afforded no hafnium(III) ESR-active species, even for reactions performed at −78 °C with the spectra recorded immediately. However, zirconium(III) species with the same spectral features as those for the reduction of an authentic sample of **1** were obtained. This originates from the presence of up to 10% zirconium in commercially available hafnium compounds. Compound **2** was irreversibly reduced ($E^{red} = -2.12$ V *vs.* SCE, measured relative to the ferrocene–ferrocenium couple) whereas the zirconium analogue, **1**, underwent a reversible one-electron reduction process ($E^{red}_{1/2} = -1.72$ V *vs.* SCE). [The experiment cannot be considered rigorously reversible, however, since the separation of peaks was higher than theory (59 mV), with a magnitude dependent upon the scan rate.] The failure to detect a d^1 hafnium(III) species from **2** contrasts with the formation of a d^1 species from *meso*-$[M\{[CH(SiMe_3)C_6H_4\text{-}o]_2\}(\eta\text{-}C_5H_5)_2]$ **12** (M = Hf), although like the d^1 species in the present study this was less persistent than the zirconium analogue.[15] The difference in reduction potentials (reversible) of **12** (M = Zr or Hf) (Hf < Zr) of 0.3 V is similar to that between **1** (reversible) and **2** (irreversible).

Compound **1** and $[Zr\{CHSiMe_3(C_{14}H_9\text{-}9)\}Cl(\eta\text{-}C_5H_5)_2]$[44] are the only alkylzirconocene chlorides that undergo reversible reduction, having similar $E^{red}_{1/2}$ values (−1.72 and −1.64 V *vs.* SCE, respectively), outside the range for the irreversibly reduced alkylzirconocene chlorides (−1.90 to 1.97 V *vs.* SCE).[2] Compound **1** and the above 'anthryl' compound showed $E^{red}_{1/2}$ values within the range established for reversibly reduced zirconocene chlorides.[2,45] The dialkyl compounds **3a** and **3b** were irreversibly reduced ($E^{red} = -2.08$ and −2.00 V *vs.* SCE), a characteristic feature of such compounds (range −2.06 to −2.09 V *vs.* SCE).[2] Only **12** (M = Zr) is a reversibly reducible dialkyl, but is unusual in being intermediate between a bis(cyclopentadienyl)metal η^4-bonded species and a metallacycle.[15] The authenticated metallacycles $[Zr\{(CH_2)_2C_6H_4\text{-}o\}(\eta\text{-}C_5H_5)_2]$[46] and $[Zr\{(o\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$[16] underwent Zr–C cleavage upon reduction, yielding $[Zr(CH_2C_6H_4\bar{C}H_2\text{-}o)(\eta\text{-}C_5H_5)_2]$ and $[Zr(o\text{-}CH_2C_6H_4C_6H_4\bar{C}H_2\text{-}o)(\eta\text{-}C_5H_5)_2]$, and this resembled the reduction of **3**. No peak corresponding to the oxidation of free $C_5H_5^-$ was found in the reverse-scan cyclic voltammogram for **3a** or **3b** (to **1** and **2**) in support of the proposal of loss of $(R^*)^-$ on reduction. Interestingly, loss of $C_5H_5^-$ occurred on reducing $[Zr(CH_2PPh_2)_2(\eta\text{-}C_5H_5)_2]$ (no electrochemical data available).[19]

There have been several studies on the photolysis of dialkylzirconocene compounds, but for alkyl groups considerably less hindered than R*. A feature of these has been the detection of unidentified zirconium(III) hydrides formed after loss of $R^{\bullet}$ (refs. 20, 47 and 48) or $C_5H_5^-$ (refs. 20 and 48) (see ref. 49 for a general survey of the photochemistry of organo-transition-metal complexes). In our study no hydrides were detected. The lability of $[ZrR^*(\eta\text{-}C_5H_5)_2]$ **9** appears to be solely due to its recombination with $(R^*)^{\bullet}$. Presumably the stability of **9** towards hydride formation relates to the steric hindrance of $(R^*)^{\bullet}$ suggesting that α-hydrogen elimination[20] is not the route to hydride species for less-hindered alkyls.

Table 1 Metal atom environment (distances in Å, angles in °) in compounds **1** and **2**

	1	**2***
Zr–Cl	2.444(1)	2.418(3)
Zr–C(11)	2.359(4)	2.322(8)
Zr–C(1A,B)	2.531(5), 2.507(7)	2.530(9), 2.517(11)
Zr–C(2A,B)	2.535(7), 2.516(6)	2.541(12), 2.520(11)
Zr–C(3A,B)	2.496(7), 2.512(5)	2.481(13), 2.512(9)
Zr–C(4A,B)	2.490(5), 2.498(5)	2.468(11), 2.481(9)
Zr–C(5A,B)	2.506(5), 2.502(7)	2.501(11), 2.490(12)
Zr–C(0A,0B)	2.217(–), 2.221(–)	2.210(–), 2.214(–)
Cl–Zr–C(1A,B)	90.6(1), 83.4(2)	90.6(2), 83.0(3)
Cl–Zr–C(2A,B)	78.7(1), 86.2(1)	78.8(3), 85.8(2)
Cl–Zr–C(3A,B)	100.7(2), 116.7(2)	101.3(3), 116.1(3)
Cl–Zr–C(4A,B)	131.0(1), 134.6(2)	131.5(3), 134.7(3)
Cl–Zr–C(5A,B)	122.8(1), 110.6(2)	122.5(2), 110.9(3)
Cl–Zr–C(0A,B)	105.6(–), 107.3(–)	105.8(–), 107.1(–)
C(11)–Zr–C(1A,B)	86.7(2), 124.8(2)	87.0(3), 125.5(3)
C(11)–Zr–C(2A,B)	117.8(2), 92.9(2)	117.4(3), 93.8(3)
C(11)–Zr–C(3A,B)	134.0(2), 78.9(2)	134.3(3), 78.9(3)
C(11)–Zr–C(4A,B)	108.5(2), 100.0(2)	108.5(4), 100.6(4)
C(11)–Zr–C(5A,B)	81.3(2), 129.8(2)	81.0(3), 130.8(3)
C(11)–Zr–C(0A,B)	106.6(–), 106.3(–)	106.6(–), 107.0(–)
C(0)–Zr–C(0)	127.4(–)	127.6(–)
Cl–Zr–C(11)	100.5(1)	99.3(2)

* Read Hf instead of Zr.

The organozirconium(III) phosphines **10** and **11** were easily identified by the ^{31}P hyperfine coupling; their ESR spectral parameters were similar to those found for (*i*) $[ZrR''(PPh_3)(\eta\text{-}C_5H_5)_2]$ {formed by photolysis of $[ZrR''_2(\eta\text{-}C_5H_5)_2]$ in the presence of PPh_3} [R″ = CH_2Ph, $g_{av} = 1.984$, $a(^{31}P) = 20.7$, $a(^1H) = 4$ G, $a(^{91}Zr) = 16.5$ G; R″ = CH_2SiMe_3, $g_{av} = 1.988$, $a(^{31}P) = 19.2$, $a(^1H) = 4.6$, $a(^{91}Zr) = 19.9$ G],[20] (*ii*) $[Zr\{CHSiMe_3(C_{14}H_9\text{-}9)\}(\eta\text{-}C_5H_5)_2(PMe_3)]$ [$g_{av} = 1.958$, $a(^{31}P) = 14.0$, $a(^{91}Zr) = 23.0$ G], (*iii*) and $[Zr(CHSiMe_3C_6H_4PPh_2\text{-}o)(\eta\text{-}C_5H_5)_2]$ [$g_{av} = 1.979$, $a(^{31}P) = 16.3$, $a(^{91}Zr) = 9.9$ G], (*iv*) $[Zr\{CH(SiMe_3)C_6H_4PPh_2\text{-}o\}(\eta\text{-}C_5H_5)_2(PMe_3)]$ [$g_{av} = 1.987$, $a(^{31}P) = 14.8$, $a(^{91}Zr) = 22.5$ G],[44] and (*v*) other zirconium(III) intermediates reported.[21,22,27]

Reduction of compound **1** under a dinitrogen atmosphere with stirring for several hours gave **9** rather than an η^2-dinitrogen complex as had been identified for such a reduction of $[ZrR(Cl)(\eta\text{-}C_5H_4R''')_2]$ (R‴ = H or Me).[13] Interestingly for more-hindered cyclopentadienyl substituents (R‴ = Pr^i, Bu^t or $SiMe_3$) there was no dinitrogen complexation; the derived zirconium(III) species was possibly related to **9** or **8**. Attempts to isolate **7**–**11** were unsuccessful.

Molecular structures of compounds 1, 2 and 3a

Crystal structure determination of compounds **1**, **2** and **3a** show that they are comprised of discrete monomeric species, Figs. 2 and 3, with the asymmetric unit being one molecule. Compounds **1** and **2** are isostructural. Selected bond lengths and angles are given in Tables 1–3.

As expected, each molecule possesses a pseudo-tetrahedral arrangement of ligands about the metal atom, assuming the polyhapto groups to occupy one co-ordination site, and by virtue of their size the angle subtended at the metal by the two cyclopentadienyl centroids is enlarged relative to the C_α–M–Cl or C_α–M–C_α angle. For zirconocene complexes of the type $[ZrL_2(\eta\text{-}C_5H_4R''')]$ (R‴ = H or alkyl) the centroid–zirconium–centroid angle is relatively insensitive to variation in the uniden-

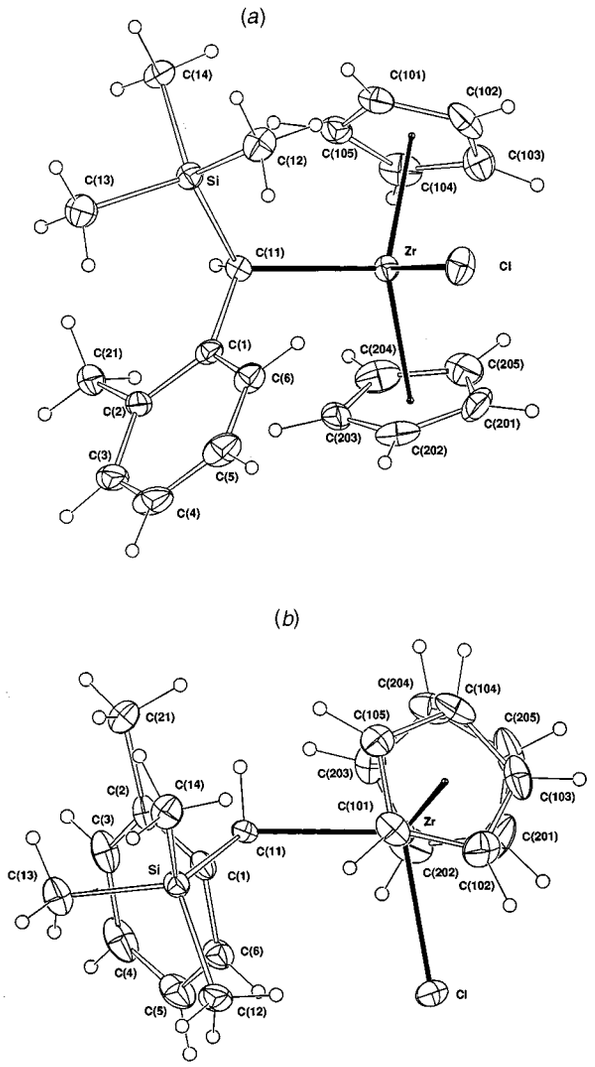


Fig. 2 A single molecule of [ZrR*(Cl)(η-C_5H_5)$_2$] **1**, projected (*a*) approximately down the bisector of the angle subtended at the zirconium by the two cyclopentadienyl centroids and (*b*) onto the ZrClC(σ) plane

tate ligands, even for bulky alkyl ligands such as R and R*. For example, the centroid–zirconium–centroid angles for zirconocene structures with highly hindered alkyls (Table 3) are within the range established for d^0 [ZrX_2(η-C_5H_4R''')$_2$] (R''' = H or alkyl), 126–133°.[25] {In considering angles associated with the η^5 centroid, more often than not the centroid does not correspond to the vector normal to the η^5-C_5 plane, particularly for substituted cyclopentadienyl ligands, *e.g.* in [$ZrCl_2$(C_5H_4-CH_2Ph)$_2$].[51]} The distances from the metal to ligand planes are 2.21 and 2.22$_1$ Å in **1**, 2.20$_8$ and 2.21$_3$ Å in **2**, and 2.23$_0$ and 2.23$_8$ Å in **3a**, while the metal–centroid distances are 2.21 and 2.21$_0$ Å, 2.22$_1$ and 2.21$_4$ and 2.23 and 2.24 Å respectively.

In contrast the unidentate ligand–metal–unidentate ligand angle is sensitive to the nature of the unidentate ligands and, to a lesser extent, the nature of substituents on the cyclopentadienyl ligands. For sterically hindered alkyls this angle is usually close to 100°. In the present structures the respective values are 100.5 and 99.3°, which compare favourably with those in [ZrR(Cl)(η-$C_5H_4XMe_3$)$_2$],[14] (X = C, 98.2; or Si, 99.9°) or [ZrR(Ph)(η-C_5H_5)$_2$], 100.4°.[52] The corresponding angle in [Zr{C(Ph)=CMe_2}Cl(η-C_5H_5)$_2$] (Table 3) is anomalously high, 108.9°, attributed to an interaction of the alkenyl π cloud with the metal centre, there being a short Zr–C_β distance of 2.953 Å.[53] This type of interaction, which has been postulated in [$Zr(CH_2Ph)_4$],[50] is not evident in **1**, **2** or **3a** [Zr–C_β 3.28$_2$; Hf–C_β 3.28$_2$; Zr–C_β 3.369(8) and 3.347(9) Å]. For less bulky groups the

Table 2 Zirconium environment (selected geometry) in compound **3a**. The first column is the metal–ligand distance (Å); other entries are the angles (°) subtended at the metal by the relevant atoms at the head of the row and column. Silane ligand atoms are italicized; C(0A)–Zr–C(0B) is 125.6°

	r_{M-C}	*C(11A)*	*C(11B)*
C(11A)	2.372(9)	—	99.5(3)
C(11B)	2.376(8)	99.5(3)	—
C(1A)	2.51(1)	132.5(3)	97.5(4)
C(2A)	2.50(1)	106.9(4)	82.4(4)
C(3A)	2.49(1)	80.9(3)	102.4(4)
C(4A)	2.50(1)	86.0(4)	131.9(4)
C(5A)	2.51(1)	114.8(4)	127.4(4)
C(1B)	2.49(1)	106.6(3)	131.4(3)
C(2B)	2.47(1)	135.5(3)	103.8(3)
C(3B)	2.53(1)	122.3(3)	79.6(3)
C(4B)	2.58(1)	91.5(3)	89.0(3)
C(5B)	2.55(1)	83.1(3)	119.4(3)
C(0A)	2.23(–)	105.1(–)	109.5(–)
C(0B)	2.24(–)	108.7(–)	105.4(–)

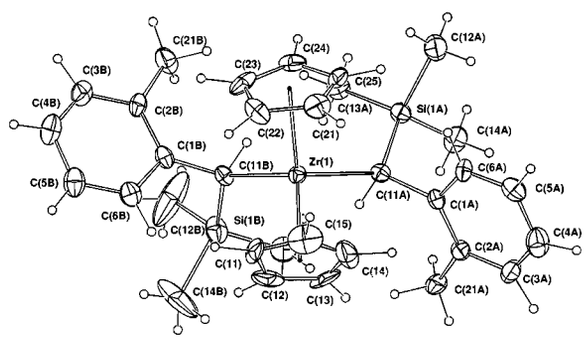


Fig. 3 A single molecule of *rac*-[ZrR*$_2$(η-C_5H_5)$_2$] **3a** projected down the bisector of the angle subtended at the zirconium by the two cyclopentadienyl centroids

angle is typically within the range 90–96°, as for example in [$Zr(CH_2PPh_2)Cl$(η-C_5H_5)$_2$], 90.4°.[18]

The M–Cl distance for compound **1** is unexceptional (Table 3). Comparative data on hafnium compounds are limited to a few structures. The Hf–Cl distance for **2** [2.418(3) Å] is similar to those in [$HfCl_2${(η-$C_5H_4CH_2$)$_2$$CH_2$}], 2.417(3) and 2.429(2) Å.[54]

Of the structurally characterized alkylzirconocene chlorides, those with bulky groups [R*, $^-$CH($SiMe_3$)$_2$,[2,53] $^-$$CHSiMe_3$-($C_{14}H_9$-9), $^-$CH($SiMe_3$)$C_6H_4PPh_2$-*o*[44] and $^-$$CHPh_2$[8] (Table 3)] have significantly longer Zr–C_α distances than for less-hindered hydrocarbyl groups.[25] This also includes other metallocene types such as in [$ZrMe_2$(η^5-C_9H_7)$_2$] in which the Zr–C_α distance is 2.251(6) Å;[46] *cf.* 2.359(4) Å in **1** and 2.37$_4$ Å in **3a**. The only compound with a zirconium–secondary carbon linkage not listed in Table 3 is [ZrR(Ph)(η-C_5H_5)$_2$] [full details not available,[53] also with a relatively long Zr–C_α (sp^3) distance, 2.964(4) Å].

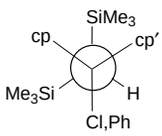
For hafnium compounds the Hf–σ-C distance appears to be little affected by the bulk of the alkyl group. In **2** the relevant distance is 2.322(8) Å, compared with 2.33(1) Å in [$HfMe_2$-(η^5-C_9H_7)$_2$][55] and 2.36(4) Å in [$Hf(CHPh_2)_2$(η-C_5H_5)$_2$].[8]

Each complex in Table 3 possessing the ligand R, as well as [ZrR(Ph)(η-C_5H_5)$_2$],[53] has a conformation with respect to the Zr–σ-C bond of type **VI**, similar to that found in the bis(benzhydryl) complex,[8] and differ from the conformation **III** found in **1**, **2** and **3a**. In **VI** a $SiMe_3$ group lies astride the bulky cyclopentadienyl groups whereas in **1**, **2** and **3a** the proton attached to C_α occupies this position. For ligand R the expected Si–C–Si angle is *ca.* 114°, while for R* the corresponding angle is significantly smaller, 104.7(3) in **1**, 103.5(5) in **2**, 108.1(6) and 107.4(6)° in **3a**. (This is further evidence that R is more sterically demanding than R*.) The difference in conformation for R- and R*-

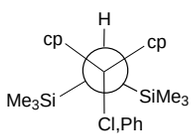
Table 3 Selected X-ray crystallographic data (distances in Å and angles in °) for zirconium and hafnium metallocenes $[MR''_nCl_{2-n}(\eta\text{-}C_5H_4R''')_2]$ (n = 1 or 2; R''' = H, $SiMe_3$ or Bu^t)

Complex	Mean M–σ-C	M–Cp (centroid)	Cp–M–Cp	M–σ-C	M–Cl	σ-C–M–Cl	Ref.
$[ZrR(Cl)(\eta\text{-}C_5H_4Bu^t)_2]$	2.56	2.26	129.1	2.324(8)	2.452(2)	98.2	2
$[ZrR(Cl)(\eta\text{-}C_5H_4SiMe_3)_2]$	2.54	2.24	128.1	2.327(3)	2.447(1)	99.9	2
$[Zr\{C(Ph)=CMe_2\}Cl(\eta\text{-}C_5H_5)_2]$	2.51	2.21	130.5	2.297(3)	2.476(1)	108.9	50
$[Zr\{CHSiMe_3(C_{14}H_9\text{-}9)\}Cl(\eta\text{-}C_5H_5)_2]$	—	2.22	127.2	2.349(4)	2.454(1)	95.5	44
$[Zr\{CH(SiMe_3)C_6H_4PPh_2\text{-}o\}Cl(\eta\text{-}C_5H_5)_2]$	—	2.22	127.2	2.350(4)	2.438(1)	96.1	44
1 $[ZrR^*(Cl)(\eta\text{-}C_5H_5)_2]$	2.51	2.22	127.4	2.359(4)	2.444(1)	100.5	*a*
2 $[HfR^*(Cl)(\eta\text{-}C_5H_5)_2]$	2.51	2.21	127.8	2.322(8)	2.418(3)	99.3	*a*
3a *rac*-$[ZrR^*_2(\eta\text{-}C_5H_5)_2]$	2.51	2.24	125.9	2.37_4	—	99.5	*a*
$[Zr(CHPh_2)_2(\eta\text{-}C_5H_5)_2]$	2.51	2.22	128.2	2.38_6	—	95.5	8
$[Hf(CHPh_2)_2(\eta\text{-}C_5H_5)_2]$	2.46	2.16	128.2	2.35_5	—	95.5	8

[a] This work.



IV



VII

containing complexes may be a consequence of this difference. The larger angle for R may cause unfavourable $\eta\text{-}C_5H_5\cdots SiMe_3$ interactions for a conformation of type **VII**. In R* the angle in question is below the tetrahedral value and the aryl and $SiMe_3$ groups straddle the chloride, the least bulky ligand. Interestingly, in $[Zr\{CH(SiMe_3)C_6H_4PPh_2\text{-}o\}Cl(\eta\text{-}C_5H_5)_2]$ conformation **III**, with $SiMe_3$ and Ar interchanged, is found in the solid,[44] while in $[Zr\{CHSiMe_3(C_{14}H_9\text{-}9)\}Cl(\eta\text{-}C_5H_5)_2]$ the conformation is intermediate between **III** and eclipsed. The R′–C_α–Si (R′ = aryl) angle of 110.7(8)° for the latter is greater than the corresponding angle in **1** and **2**. This, and the conformation anomaly, is most likely due to the presence of two *ortho* substituents on the aryl group imparting greater steric hindrance than R* or R.

In the analysis of structural differences between compounds **1** and **2** (Table 3) the minor variations are attributed to the slightly smaller atomic radius of hafnium compared to zirconium (1.44 and 1.45 Å, respectively), causing a slightly greater steric crowding in **2**, the hafnium complex. The resistance of **2** to diorganylation using LiR*(tmen) is consistent with this view. Other structural details for **1** and **2** are very similar.

Experimental

General procedures

Owing to the air-sensitivity of the lithium alkyl complexes and their transition-metal derivatives, all manipulations were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from Na (toluene or benzene), Na–Ph_2CO (diethyl ether or thf), CaH_2 (hexane), or $LiAlH_4$ (pentane) under a dinitrogen atmosphere, prior to use.

Physical and analytical measurements

Elemental analyses were performed by the microanalytical laboratory at the University of Sussex. Hydrogen-1 and carbon-13 NMR (at 298 K in C_6D_6) and mass spectra (P^+ parent molecular ion) were recorded on Varian T60 or Perkin-Elmer R32, JEOL PFT 100, and HP-5986 instruments respectively. Cyclic voltammetry was carried out in thf with the electrolyte $[NBu^n_4][BF_4]$ (0.2 mol dm^{-3}) and at a platinum working electrode under an atmosphere of dinitrogen in accordance with the procedure described in ref. 56; measurements were made using a Hi-Tek Instruments Limited type DT 2101 potentiostat, a Chemical Electronics (Birtley) type 01 waveform generator and recorded on a Philips type 2400 A4 *X*-*Y* recorder. The g_{av} values from electron spin resonance spectra were measured relative to polycrystalline diphenylpicrylhydrazyl using a Varian E3 or Bruker ER100 spectrometer.

Materials

The compounds $[MCl_2(\eta\text{-}C_5H_5)_2]$ (M = Ti or Zr) were from Ventron and Aldrich respectively; $[HfCl_2(\eta\text{-}C_5H_5)_2]$,[2] Li[$CH(SiMe_3)_2$](tmen) **5**[10] and Li[$CH(SiMe_3)C_6H_4Me\text{-}o$](tmen) **4**[14] were prepared by the literature procedures.

Syntheses

$[Zr\{CH(SiMe_3)C_6H_4Me\text{-}o\}Cl(\eta\text{-}C_5H_5)_2]$ 1. To a solution of $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ (3.4 g, 11.6 mmol) in thf (75 cm^3) at −78 °C was slowly added with stirring a solution of Li[$CH(SiMe_3)$-$C_6H_4Me\text{-}o$](tmen) **4** (3.58 g, 11.9 mmol) in thf (30 cm^3). The solution became red; stirring was continued for 0.5 h at −78 °C. On warming to ambient temperature the solvents were removed *in vacuo* to afford an orange solid to which diethyl ether (100 cm^3) was added. Filtration yielded an orange filtrate which was concentrated *in vacuo* to *ca.* 10 cm^3; yellow prisms of compound **1** (3.69 g, 73%) were obtained (Found: C, 57.8; H, 6.05. $C_{21}H_{27}ClSiZr$ requires C, 58.1; H, 6.25%), m.p. 112 °C (decomp.). NMR (C_6D_6): ^{1}H, δ 0.41 (s, 9 H, $SiCH_3$), 2.37 (s, 3 H, CCH_3), 2.46 (s, 1 H, C*H*$SiMe_3$), 6.09, 6.05 (s, 2 × 5 H, C_5H_5) and 7.20 (m, 4 H, C_6H_4); ^{13}C-{^{1}H}, δ 3.3 ($SiCH_3$), 22.18 ($C_6H_4CH_3$), 62.04 (C_6H_4CHSi) 114.05, 114.15 (C_5H_5), 122.34, 126.23, 130.05, 131.33 (C_6H_4) and 132.27, 152.56 (C_oMe, CSi). Mass spectrum: *m/z* 432 (P^+), 417 ([P − Me]$^+$), 397 ([P − Cl]$^+$) and 255 ([P − R*]$^+$).

$[Hf\{CH(SiMe_3)C_6H_4Me\text{-}o\}Cl(\eta\text{-}C_5H_5)_2]$ 2. The compounds $[HfCl_2(\eta\text{-}C_5H_5)_2]$ (4.0 g, 10.5 mmol) and **4** (3.85 g, 11.9 mmol) yielded pale yellow prisms of **2** (3.52 g, 64%) using the procedure and quantities of solvent described for **1**. (The reaction mixture at −78 °C was green and became yellow on warming to room temperature.) (Found: C, 48.1; H, 5.20. $C_{21}H_{27}ClHfSi$ requires C, 48.4; H, 5.20%), m.p. 112–114 °C (decomp.). NMR (C_6D_6): ^{1}H, δ 0.46 (s, 9 H, $SiCH_3$), 2.37 (s, 3 H, CCH_3), 1.62 (s, 1 H, C*H*$SiMe_3$), 5.78, 5.87 (s, 2 × 5 H, C_5H_5) and 7.20 (m, 4 H, C_6H_4); ^{13}C-{^{1}H}, δ 3.55 ($SiCH_3$), 22.12 ($C_6H_4CH_3$), 22.12 ($C_6H_4CH_3$), 61.19 (C_6H_4CHSi), 112.04, 113.03 (C_5H_5), 122.46, 126.11, 130.11, 131.20 (C_6H_4) and 133.02, 152.68 (C_oMe, CSi). Mass spectrum: *m/z* 522 (P^+), 507 ([P − Me]$^+$), 487 ([P − Cl]$^+$) and 344 ([P − R*]$^+$).

***rac*-$[Zr\{CH(SiMe_3)C_6H_4Me\text{-}o\}_2(\eta\text{-}C_5H_5)_2]$ 3a.** *Method* 1. Diethyl ether (50 cm^3) was added to a mixture of compound **4** (3.2 g, 10.6 mmol) and $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ (1.45 g, 5.0 mmol), warmed to *ca.* 30 °C and stirred for 15 min. The mixture was filtered and the solvent removed from the filtrate *in vacuo*. The residue was then extracted into hexane and MeOH (5 cm^3)

added. The white precipitate was collected, washed with hexane (20 cm^3), dried *in vacuo* and identified as $Zr(OMe)_4$ (0.3 g, 28.1%) (Found: C, 22.4; H, 5.55. Calc. for $C_4H_{12}O_4Zr$: C, 22.3; H, 5.60%). The filtrate was concentrated *in vacuo* to *ca.* 5 cm^3 affording on cooling to −30 °C for 12 h yellow needles of **3a** which were collected, washed with ice-cooled hexane (2 × 2 cm^3) and dried *in vacuo* (1.2 g, 43%) (Found: C, 66.5; H, 7.75. $C_{32}H_{44}Si_2Zr$ requires C, 66.7; H, 7.70%), m.p. 124–125 °C. NMR (C_6D_6): ^{1}H, δ 0.29 (s, 9 H, $SiCH_3$), 1.58 (s, 2 H, C*H*$SiMe_3$), 2.48 (s, 6 H, CCH_3), 5.87 (s, 10 H, C_5H_5), 7.04 (m, 6 H, C_6H_4) and 6.49 (m, 2 H, C_6H_4); ^{13}C-{^{1}H}, δ 2.8 ($SiCH_3$), 22.2 ($C_6H_4CH_3$), 59.6 (C_6H_4CHSi), 112.2 (C_5H_5) 121.9, 125.9, 125.3, 129.9, 131.9 (C_6H_4) and 133.5, 149.8 (C_oMe, CSi). Mass spectrum: *m/z* 398 ([*P* − R*]$^+$), 254 and 220.

Method 2. A thf solution of compound **4** (4.0 g, 13.3 mmol in 40 cm^3) was added slowly to a stirred solution of [$ZrCl_2$-(η-C_5H_5)$_2$] (1.8 g, 6.2 mmol) in thf (80 cm^3) at −78 °C. After warming to room temperature over *ca.* 1 h the solvent was removed *in vacuo* and the residue extracted into hexane (150 cm^3). The extract was then filtered, concentrated to *ca.* 20 cm^3 and stored at −30 °C for 12 h yielding yellow crystals of **3a** (2.0 g, 56%) which were isolated as described in method 1.

***meso*-[Zr{CH(SiMe$_3$)C$_6$H$_4$Me-*o*}$_2$(η-C$_5$H$_5$)$_2$] 3b.** Reagents (and quantities) were the same as for method 1 for the synthesis of compound **3a** up to and including the removal of solvent *in vacuo*. The residue was then extracted into hexane (50 cm^3), the extract filtered and cooled to −30 °C for 12 h to afford massive cuboids of **3b** (0.50 g, 14%) (Found: C, 66.6; H, 7.70. $C_{32}H_{44}Si_2Zr$ requires C, 66.7; H, 7.70%), using the same isolation procedure as for **3a**. The mother-liquor was heated to 60–80 °C for *ca.* 8 h then cooled to *ca.* 20 °C and concentrated *in vacuo* to *ca.* 10 cm^3 yielding at −30 °C **3a** (1.51 g, 52%), m.p. 161–162 °C. NMR (C_6D_6): ^{1}H, δ 0.16 (s, 9 H, $SiCH_3$), 1.62 (s, 2 H, C*H*$SiMe_3$), 2.19 (s, 6 H, CCH_3), 5.66, 6.22 (s, 2 × 5 H, C_5H_5) and 7.00 (m, 8 H, C_6H_4); ^{13}C-{^{1}H}, δ 3.2 ($SiCH_3$), 22.1 ($C_6H_4CH_3$), 61.9 (C_6H_4CHSi), 111.1, 113.1 (C_5H_5), 121.8, 125.5, 129.9, 131.1 (C_6H_4) and 132.9, 152.1 (C_oMe, CSi). Mass spectrum: *m/z* 569 (P^+), 398 ([*P* − R*]$^+$), 333, 317 and 301.

Reaction of [TiCl$_2$(η-C$_5$H$_5$)$_2$] with compound 4. A solution of compound **4** (3.0 g, 10.0 mmol) in thf (30 cm^3) was slowly added with stirring to a solution of [$TiCl_2$(η-C_5H_5)$_2$] (2.5 g, 10.1 mmol) in thf (100 cm^3) at −78 °C. The solution became green and, after addition was complete, stirring was continued for 0.5 h at −78 °C then warmed to ambient temperature. Removal of the solvent *in vacuo* yielded a yellow-green crystalline solid (g_{av} for a thf solution = 1.975), which was dissolved in thf (50 cm^3), cooled to −78 °C, to which a solution of **4** (3.0 g, 10.0 mmol) in thf (30 cm^3) was slowly added with stirring. The resulting brown solution was warmed to room temperature. Removal of solvent *in vacuo* gave an intractable brown oil.

[{Zr[CH(SiMe$_3$)$_2$](η-C$_5$H$_5$)(μ-η^1:η^5-C$_5$H$_4$)}$_n$] 6. To a solution of LiBu^n in hexane (15.7 cm^3, 1.6 mol dm^{-3}, 25 mmol) at 0 °C was added tmen (3.75 cm^3, 25 mmol) then $CH_2(SiMe_3)_2$ (4.0 g, 25 mmol). The solution was maintained at ambient temperature for 12 h, the solvent was removed *in vacuo* and pentane (20 cm^3) was added. Cooling to −78 °C afforded colourless crystals of Li[$CH(SiMe_3)_2$](tmen) **5** which were washed with pentane (4 × 5 cm^3) and dried *in vacuo* (5.5 g, 78%) (Found: C, 55.0; H, 12.4; N, 9.40. Calc. for $C_{13}H_{35}LiN_2Si_2$: C, 55.3; H, 12.5; N, 9.9%). To a mixture of **5** (1.76 g, 6.2 mmol) and [$ZrCl_2$-(η-C_5H_5)$_2$] (0.88 g, 3.0 mmol) at −78 °C was added with stirring cooled (−78 °C) Et_2O (100 cm^3). After warming to room temperature the solvent was removed *in vacuo* and pentane (50 cm^3) added. The mixture was filtered and on cooling the filtrate to −30 °C pale green crystals of compound **6** (0.49 g, 44%) (Found: C, 53.8; H, 7.35. $C_{17}H_{28}Si_2Zr$ requires C, 53.8; H, 7.45%), decomposed >315 °C, were deposited. NMR (C_6D_6): ^{1}H, δ 0.00 (s, 18 H, $SiCH_3$), −0.30 (s, 1 H, CHSi) 4.53, 5.24, 5.34, 6.77 (m, 4 H, μ-η^1:η^5-C_5H_4) and 5.67 (s, 5 H, η^5-C_5H_5).

Reaction of [HfCl$_2$(η-C$_5$H$_5$)$_2$] and compound 5. Using the quantities and procedure described for the previous reaction afforded an impure white solid and 2 mole equivalents of LiCl. The ^{1}H NMR spectrum showed similar features to those for the zirconium analogue: δ 0.00 (s, 18 H, $SiCH_3$), −0.28 (s, 1 H, CHSi), 4.50, 5.26 (2 H), 5.67 (s, 5 H, η^5-C_5H_5) and 6.14 (m, 4 H, μ-η^1:η^5-C_5H_4).

Reduction of compounds 1, 2, 3a and 3b (data summarised in Scheme 2). *Method* 1. Dropwise addition of a thf solution of sodium dihydronaphthylide (≤1 mol equivalent) to a thf solution of compound **1**, **3a** or **3b** yielded a brown paramagnetic d^1 species (ESR spectra were then recorded immediately); **2** yielded an orange ESR-silent solution. Similar reduction of **1**, **3a** or **3b** in the presence of PMe_3 and with PPh_3 added after reduction gave the data in Scheme 2.

Method 2. Compound **1** (0.5, 1.1 mmol) was added to thf or OEt_2 (20 cm^3), with or without PMe_3, and sodium amalgam (0.03 Na, 1.3 mmol, in 10 g Hg). After several minutes in an ultrasonic bath ESR spectra were recorded.

Crystallography

Crystal data. *Compound* **1**. $C_{21}H_{27}ClSiZr$, *M* = 434.2, monoclinic, space group $P2_1/n$ [C_{2h}^5, no. 14 (variant)], *a* = 13.847(3), *b* = 17.856(5), *c* = 8.334(5) Å, β = 97.95(2)°, *U* = 2041(1) Å^3, D_c (*Z* = 4) = 1.41 g cm^{-3}, *F*(000) = 896, μ_{Mo} = 7.3 cm^{-1}. Specimen: 0.30 × 0.40 × 0.26 mm (capillary). $2\theta_{max}$ = 60°, *N* = 5985, N_o = 3552, *R* = 0.047, *R′* = 0.057.

Compound **2**. $C_{21}H_{27}ClHfSi$, *M* = 521.5, monoclinic, space group $P2_1/n$, *a* = 13.869(6), *b* = 17.871(9), *c* = 8.322(4) Å, β = 97.97(3)°, *U* = 2045(2) Å^3, D_c (*Z* = 4) = 1.69 g cm^{-3}, *F*(000) = 1024, μ_{Mo} = 50.8 cm^{-1}. Specimen: 0.20 × 0.27 × 0.24 mm (capillary). $2\theta_{max}$ = 50°, *N* = 3608, N_o = 2477, *R* = 0.038, *R′* = 0.042.

Compound **3a**. $C_{32}H_{44}Si_2Zr$, *M* = 576.1, tetragonal, space group $P4/_2/n$ (C_{4h}^4, no. 86), *a* = 26.760(8), *c* = 8.575(3) Å, *U* = 6141(4) Å^3, D_c (*Z* = 8) = 1.24 g cm^{-3}, *F*(000) = 2432, μ_{Mo} = 4.0 cm^{-1}. Specimen: 0.30 × 0.35 × 0.45 mm (capillary). $2\theta_{max}$ = 40°, *N* = 2904, N_o = 1799, *R* = 0.047, *R′* = 0.058.

Structure determinations. Unique data sets were measured within the given $2\theta_{max}$ limits using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ–θ scan mode at 295 K; a monochromatic Mo-Kα radiation source was fitted (λ = 0.7106$_9$ Å). *N* Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the (basically) 9 × 9 block-diagonal least-squares refinement after analytical absorption correction and solution of the structures by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms (*x*, *y*, *z*, U_{iso}) were constrained at estimated values. Residuals at convergence *R*,*R′* are quoted; reflection weights were $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion.[57] (In accordance with the expected 10% zirconium impurity in the hafnium, a composite scattering factor was employed.) Computation used the X-RAY 76 program system,[58] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/564.

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