Axially Asymmetric Metal Alkyls. Part 5.[1] Synthesis and Reduction to Zr^{III} Species of Group 4 Metallepines $[ML(\eta-C_5H_5)_2]$ [L = $(2-CHRC_6H_4)_2{}^{2-}$, R = H, M = Ti, Zr, or Hf), Isomers of $[ZrL(\eta-C_5H_5)_2]$ (R = $SiMe_3$), and *meso*-$[M\{1,8-(CHSiMe_3)_2C_{10}H_6\}(\eta-C_5H_5)_2]$ (M = Zr or Hf); *X*-Ray Crystal Structures of $[TiL(\eta-C_5H_5)_2]$ (R = H) and λ- and δ-*RS*-$[ZrL(\eta-C_5H_5)_2]$ (R = $SiMe_3$)†

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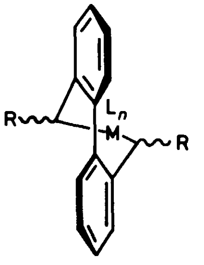
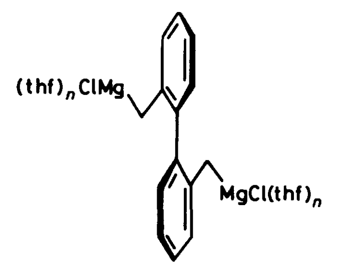
Treating $[MCl_2(\eta-C_5H_4R')_2]$ with a di-Grignard reagent and/or a dilithium reagent based on $(2-CHRC_6H_4)_2{}^{2-}$ (L) yields the metallacycles $[ML(\eta-C_5H_4R')_2]$ (R = R' = H, M = Ti, Zr, or Hf; R = H, R' = $SiMe_3$, M = Zr) (**5**), and a mixture of diastereoisomers of λ-*RS*- and δ-*RS*-$[ZrL(\eta-C_5H_5)_2]$ (R = $SiMe_3$) (**6a**), and λ-*RR*-and δ-*SS*-$[ZrL(\eta-C_5H_5)_2]$ (R = $SiMe_3$) (**6b**). Compound (**6a**) was readily converted to (**6b**) by photolysis in hexane. The 'strained' metallacycles *meso*-$[M\{1,8-(CHSiMe_3)_2C_{10}H_6\}(\eta-C_5H_5)_2]$ (M = Zr or Hf) (**7**) were prepared from an intrinsically unstable dilithium reagent. Reduction of (**5**), (**6a**) and (**6b**), and (**7**) chemically and electrochemically shows that the generated d^1 species are stable at *ca.* 20 °C except for M = Hf, and that for (**5**) [and possibly (**6a**) and (**6b**)] reduction is associated with metal–carbon bond rupture. The structures of (**5**) (M = Ti) and (**6a**) have been established from single-crystal *X*-ray diffraction data [Ti–C^α 2.20_7 Å, C^α–Ti–C^α $87._8$°, dihedral angle between phenyl groups, φ 62.2°; Zr–C^α 2.33_8 Å, C^α–Zr–C^α 98.3(2)°, φ 73.6°].

The hydrocarbyl dianion $(2-CHRC_6H_4)_2{}^{2-}$ (L) can act as a bidentate ligand through the benzylic C-centres, and, by virtue of its flexibility associated with torsion along the biphenyl axis, in so doing it can accommodate a wide variation in metal size without major departure from tetrahedral geometry about the C^α atoms. The resulting axially asymmetric metallacycles (or metallepines) have an unusually high ring size, most emphasis on metallacycles in the literature being on MC_4 or MC_5 ring systems.[2] In the present series we have concentrated on 'metallacycles' (**1**) based on L which show the above feature, and the ability of L to form stable metal complexes over a range of oxidation states. Compounds for R = H include $[SiLPh_2]$,[3] $[SnLPh_2]$,[3] $[ML(\eta-C_5H_5)_2]^{\pm 1,0}$ (M = Nb or Ta),[4,5] and the metallabicyclic complex $[(WL_2O)_2Mg(thf)_4]$ (thf = tetrahydrofuran),[1] and, for R = $SiMe_3$, λ-*SS*- and δ-*RR*-$[SnLPh_2]$.[3] Their synthesis involves at some stage a di-Grignard reagent, (**2**),[3] and/or dilithium reagents, (**3**) (R = H) and (**4**) (R = $SiMe_3$) (tmen = *NNN'N'*-tetramethylethylenediamine), and metal or metalloid halides. Interestingly, in (**3**) in the solid, one lithium centre is part of a metallacycle, the other bridging two methylene carbons, whereas in (**4**) both lithiums are η^3-allyl to the hydrocarbyl group.[6] In addition, the reaction of (**2**) with vanadocene dichloride gives the bimetallic complex $[\{VCl(\eta-C_5H_5)_2\}_2L]$ (R = H)[4] rather than a metallacycle.



(**1**)



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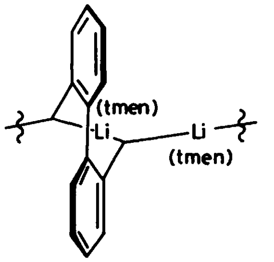

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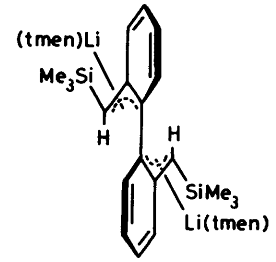

(**4**)

We now report the chemistry of L for the Group 4 transition metals. Notable features are as follows: (*i*) the synthesis of $[ML(\eta-C_5H_5)_2]$ [M = Ti (**5a**), Zr (**5b**), or Hf (**5c**); R = H], $[ZrL(\eta-C_5H_4SiMe_3)_2]$ (**5d**) (R = H), λ-*RS*- and δ-*RS*-$[ZrL(\eta-C_5H_5)_2]$ (**6a**) (R = $SiMe_3$), and λ-*RR*-, and δ-*SS*-$[ZrL(\eta-C_5H_5)_2]$ (**6b**) (R = $SiMe_3$); (*ii*) photolytic conversion of (**6a**) to (**6b**); (*iii*) *X*-ray structure determinations of (**5a**) and (**6a**). The reduction of (**5**) and (**6**) has been studied using e.s.r. spectroscopy and electrochemistry to ascertain the stability of the mononuclear d^1 single-electron transfer reduced species, investigations on d^1 organo-zirconium(III) and -hafnium(III) compounds having recently become prominent, being generated usually from M^{IV} compounds *via* reduction or photolysis.[7] For dialkyl metallocene(IV) compounds, including metallacycles, three categories of Zr^{III} species have been identified, *viz.* $[Zr(alkyl)_2(\eta-C_5H_5)_2]^-$, $[Zr(alkyl)_2(\eta-C_5H_5)(solvent)_n]$, and $[Zr(alkyl)(\eta-C_5H_5)_2(solvent)_n]$.[7–13] Organohafnium(III)

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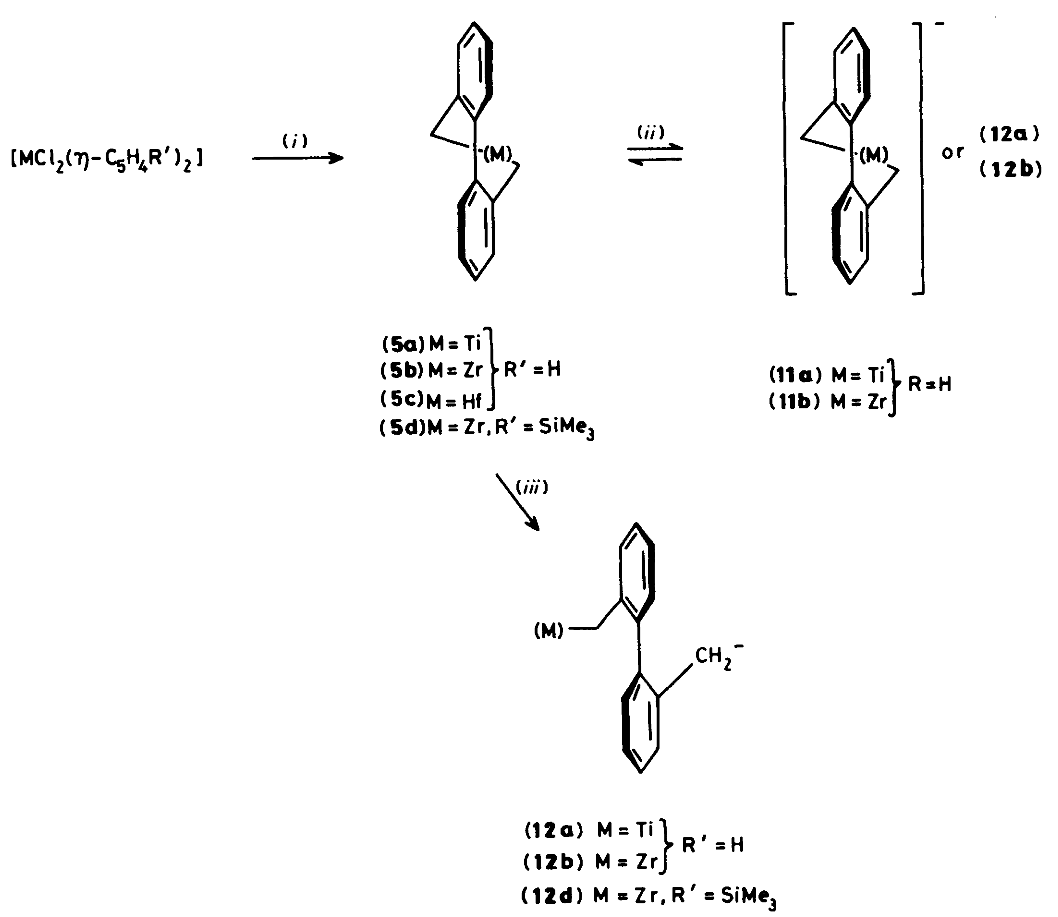
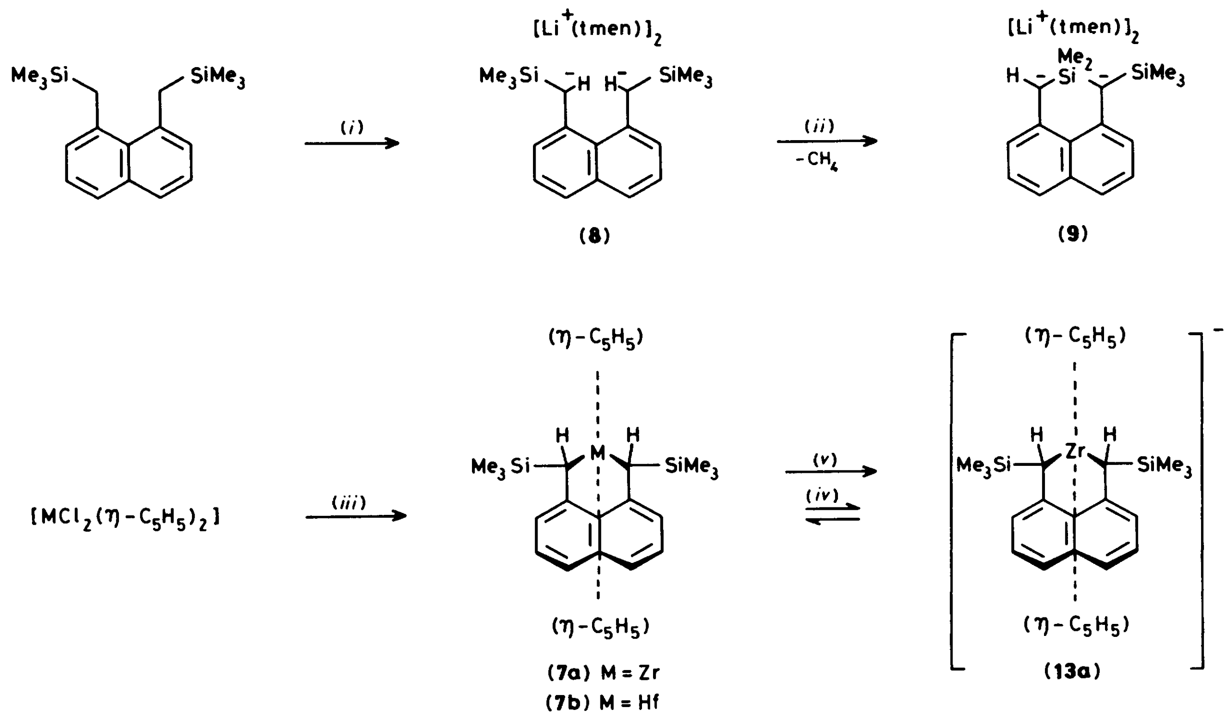
† (Biphenyl-2,2'-ylenedimethylene-C^α,$C^{\alpha'}$)bis(η-cyclopentadienyl)-titanium(IV) and [α,α'-bis(trimethylsilyl)biphenyl-2,2'-ylenedimethyl-ene-C^α,$C^{\alpha'}$]bis(η-cyclopentadienyl)zirconium(IV) respectively.

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

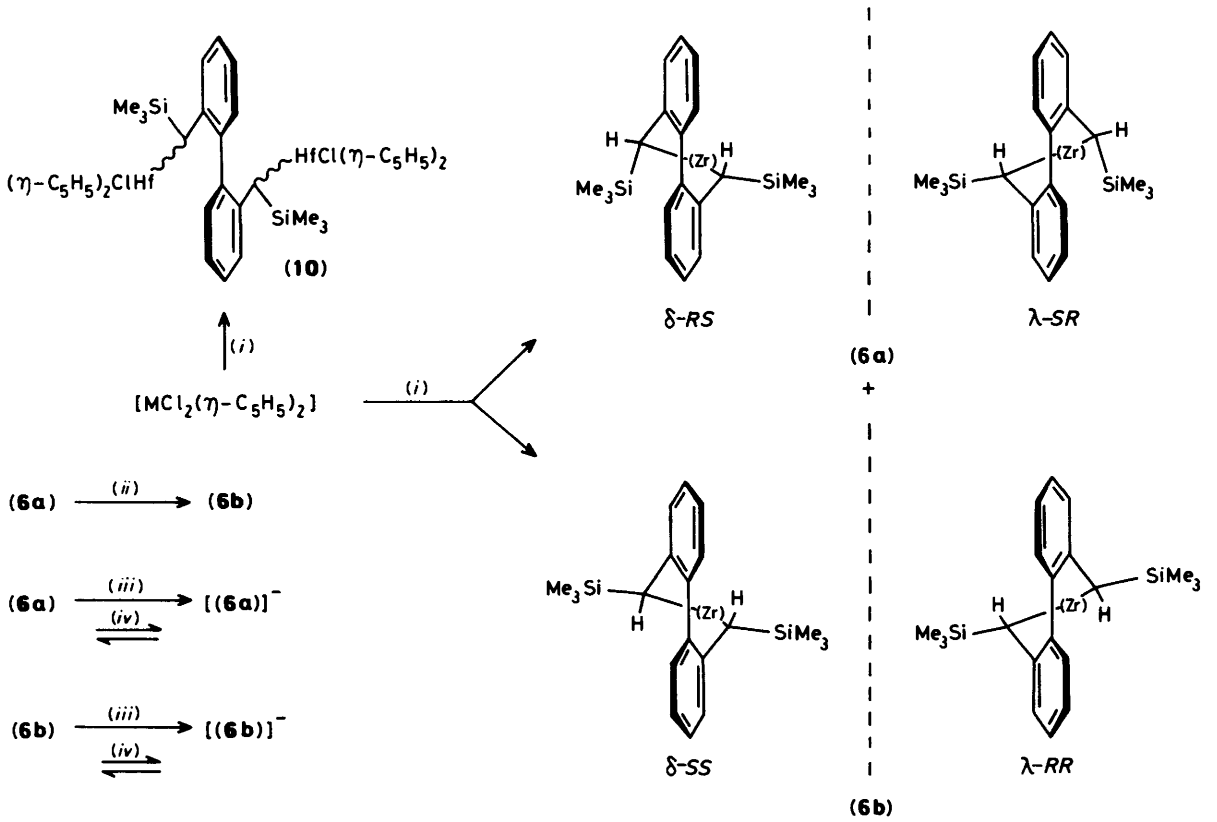
Non-S.I. unit employed: mmHg ≈ 133 Pa.



Scheme 1. (M) = M(η-C$_5$H$_4$R′)$_2$. (*i*) (3), Et$_2$O, 25 °C or (2), thf, −78 °C; (*ii*) electrochemistry in 0.2 mol dm^{-3} [NBu$^n_4$]BF$_4$ in thf at a Pt electrode; (*iii*) Na[C$_{10}$H$_8$] (1 mol equiv.), thf, 20 °C or −78 °C for (5c)



Scheme 2. (*i*) LiBu^n(tmen), hexane, 20 °C (ref. 19); (*ii*) hexane, 20 °C, *ca.* 6 d (ref. 19); (*iii*) (8), Et$_2$O, 35 °C; (*iv*) electrochemistry in 0.2 mol dm^{-3} [NBu$^n_4$]BF$_4$ in thf at a Pt electrode; (*v*) Na[C$_{10}$H$_8$] (1 mol equiv.), thf, 20 °C or −78 °C for (13a)



Scheme 3. (Zr) = $Zr(\eta\text{-}C_5H_5)_2$. (*i*) (4), Et_2O, −78 °C to *ca.* 20 °C over *ca.* 12 h; (*ii*) $h\nu$ (1 000-W Hg–Xe lamp), quartz vessel, hexane, *ca.* 20 °C, 5 h; (*iii*) electrochemistry in 0.2 mol dm^{-3} $[NBu^n{}_4]BF_4$ in thf at a Pt electrode; (*iv*) $Na[C_{10}H_8]$ (1 mol equiv.), thf, 20 °C

species in general remain rather ill defined mainly because of the absence of hyperfine coupling in their e.s.r. spectra and their relatively short half-lives.[7] In contrast organotitanium(III) species are well characterized.[14] Synthesis of (**5a**)—(**5c**)[15] and e.s.r. data on reduced (**5b**)[5] have been briefly reported elsewhere.

The presence of two chiral centres coupled with axial asymmetry in (**1**) is noteworthy. Three diastereoisomers are possible and for (**6**) two of these have been isolated, one being converted to the other with associated mechanistic implications. We also report the synthesis and reduction of the novel strained six-membered ring metallacycles $[M\{1,8\text{-}(CHSiMe_3)_2C_{10}H_6\}(\eta\text{-}C_5H_5)_2]$ [M = Zr (**7a**) or Hf (**7b**)], which are related to (**6**) in that two chiral carbon centres are present. The *meso* isomer would dictate the metal centre to reside well out of the planar naphthalene group close to its π-cloud whereas the '*rac* isomer' would necessitate a twisted ring system of the type well known for 1,8-substituted naphthalenes,[16] giving it axial asymmetry. The syntheses of compounds (**7**) have previously been communicated.[17]

Results and Discussion

Syntheses of the Zr^{IV} *Compounds.*—The syntheses are summarized in Schemes 1—3. The compounds were characterized using ^1H and ^{13}C n.m.r. spectroscopy, microanalysis and mass spectrometry, and by *X*-ray structure determinations for (**5a**) and (**6a**). Compounds (**5a**)—(**5d**) were prepared from the di-Grignard reagent (**2**) in thf at *ca.* −78 °C (Scheme 1), the di-Grignard reagent being prepared by the classical method involving elemental magnesium.[3] In Part 4[1] the use of (**2**) prepared from $(2\text{-}ClCH_2C_6H_4)_2$ and $[Mg(anth)(thf)_3]$ (anth = anthracene)[18] rather than using the classical method gave higher yields of a tungsten(V) complex (*ca.* 45% *vs.* <10%).

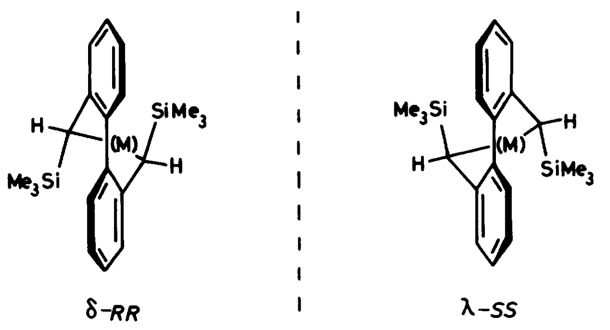
The lithium reagent (**3**) was also used in the synthesis of (**5a**)—(**5c**); yields were typically 10—20% higher than for the di-Grignard reagent. The reactions were carried out in Et_2O at *ca.* 20 °C mainly to minimize competing reactions that have been identified for other systems at lower temperatures. For example, treating zirconocene dichloride with $[\{Li(tmen)\}_2\{(CHSiMe_3)_2C_6H_4\text{-}o\}]$ in thf at −78 °C gives a pyrophoric dark green solid, thought to be a Zr^{III} compound, and at the same temperature in Et_2O a binuclear complex, *viz.* $[(\eta\text{-}C_5H_5)_2Zr(\mu\text{-}\sigma{:}\eta\text{-}C_5H_4)_2Zr\{(CHSiMe_3)_2C_6H_4\text{-}o\}]$, the metallacycle *meso*-$[Zr\{(CHSiMe_3)_2C_6H_4\text{-}o\}(\eta\text{-}C_5H_5)_2]$ being prepared in Et_2O at *ca.* 35 °C.[13] The latter conditions were found necessary for the synthesis of compounds (**7**) from a related dilithium reagent, (**8**) (Scheme 2), which is intrinsically unstable with respect to elimination of methane to form a silicon heterocycle containing dianion complex, (**9**).[19] Accordingly fresh solutions of (**8**) were used. (A similar rearrangement/elimination occurs for the corresponding germanium compound, $[\{Li(tmen)\}_2\{1,8\text{-}(CHGeMe_3)_2C_{10}H_6\}]$.[20]) The titanium analogue of (**7**) could not be prepared, presumably because of the ease of reduction of Ti^{IV} to Ti^{III}. In general Zr^{IV} and Hf^{IV} compounds are more difficult to reduce than Ti^{IV} compounds by *ca.* 1.0 V.[7]

Treatment of zirconocene dichloride with (**4**) gave a 7:3 mixture of metallacycles (**6a**) and (**6b**) which could not be separated [but see below for the formation of pure (**6b**)]. In contrast only one isomer is formed on treating $[SnCl_2Ph_2]$ with (**4**).[3] Conditions for obtaining any (**6a**) and (**6b**) were critical. These included the choice of Et_2O solvent and a reaction temperature of *ca.* −78 °C with a subsequent low-temperature gradient to room temperature. An insoluble dark green material, possibly a Zr^{III} compound (see above), was also obtained; reactions at room temperature and in other solvents gave intractable brown oils. Reacting $[HfCl_2(\eta\text{-}C_5H_5)_2]$ with (**4**) under a variety of conditions, including those optimized for (**6a**) and (**6b**), gave a yellow solid which was only sparingly soluble in thf and hexane. The same product, also obtained under more forcing conditions and using half a mol equiv. of (**4**), proved difficult to purify but its low solubility compared to that of (**6a**) and (**6b**), i.r. data (bands at 250 and 285 cm^{-1} assigned to ν_{Hf-Cl}), and *m/e* data [344 and 668 with isotope patterns for hafnium and chlorine corresponding to $HfCl(\eta\text{-}C_5H_5)_2^+$ and $HfCl(\eta\text{-}C_5H_5)_2L^+$] suggest it to be a binuclear complex, (**10**) (Scheme 3), similar to that obtained from vanadocene dichloride and (**2**).[4] 'Dialkylation' for zirconium but not for hafnium is unusual given the similarity of their chemistry.[7] The result could, however, be due to steric effects since L ($R = SiMe_3$) is a highly hindered alkyl and Hf^{4+} is slightly smaller than Zr^{4+} (ref. 7). This finding is similar to that found in the reaction of the metallocene dichlorides of zirconium and hafnium with $[\{Li(tmen)\}R'']$ ($R'' = \text{-}CHSiMe_3C_6H_4Me\text{-}o$) where mono- or di-alkylation occurs for zirconium but only mono-alkylation for hafnium,[10] and also for the reaction of $[MCl_2(\eta\text{-}C_5H_4Bu^t)_2]$ (M = Zr or Hf) with $LiCH_2Bu^t$ (ref. 9). R″ is a hindered alkyl which is related to L ($R = SiMe_3$). Evidently two R″ ligands are equivalent in steric hindrance to L ($R = SiMe_3$) in (**6a**) and (**6b**). Mention should be made of the differences in structure of the tetrakis(cyclopentadienyl) compounds of the two elements[21] which is related to the difference in size of M^{4+} for zirconium and hafnium.

Compounds (**5a**)—(**5c**) were crystallized from Et_2O. Complex (**5d**) is very soluble in Et_2O and thus was crystallized from hexane in which (**5a**)—(**5c**) are only sparingly soluble. The enhanced solubility of (**5d**) is a consequence of the well known solubilizing effect of lipophilic $SiMe_3$ groups attached to poly-hapto ligands, *e.g.* Group 4 metallocenes.[9] The same groups incorporated in metallacycles (**6a**), (**6b**), and (**7**) had a similar effect, these being also crystallizable from hexane.

All the metallacycles are air and moisture sensitive and thermally robust; (**5**) and (**7**) can be sublimed *in vacuo* at 160 °C and 0.1 mmHg, and (**6a**) and (**6b**) at 130 °C and 10^{-3} mmHg. The stability of (**5a**) contrasts with that of the related open-chain analogue, $[Ti(CH_2Ph)_2(\eta\text{-}C_5H_5)_2]$, which decomposes in benzene at *ca.* 80 °C.[22] The ratio of (**6a**) to (**6b**) is unchanged at 130 °C *in vacuo* and also after *ca.* 80 °C in benzene for several hours, *i.e.* no isomerization was evident. This contrasts with the conversion of *meso*-$[ZrR''_2(\eta\text{-}C_5H_5)_2]$ to *rac*-$[ZrR''_2(\eta\text{-}C_5H_5)_2]$ under similar conditions,[10,23] the mechanism of which presumably involves hetero- or homolytic bond breaking–bond forming accompanied by inversion at C^α. In (**6a**) and (**6b**) bond breaking–bond forming may be too rapid to allow inversion since the released C^α involved remains in proximity to the primary co-ordination sphere of zirconium. One isomerization process which cannot be ruled out is that arising from inversion along the biphenyl axis, *viz.* torsion mobility, although this could be blocked by steric congestion. Such a process for (**6a**) is equivalent to interconversion of its two optical isomers. For compound (**6b**) formation of the δ-*RR*- and λ-*SS*-diastereoisomer, (**6c**), would result. This isomer has never been detected and molecular model considerations suggest it to be stereochemically unfavourable; both bulky trimethylsilyl groups would have unfavourable non-bonding interactions with the cyclopentadienyl groups. Moreover, δ-*SS*- and λ-*RR*-$[SnLPh_2]$ ($R = SiMe_3$) is stable with respect to torsional isomerization up to 100 °C.[3]

Photolysis of a mixture of (**6a**) and (**6b**) in hexane gave pure (**6b**). This contrasts with photolysis of *meso*- or *rac*-$[ZrR''(\eta\text{-}C_5H_5)_2]$ where a 1:1 mixture of the two isomers is obtained. This proceeds *via* Zr–C^α homolysis with some inversion at C^α prior to recombination, $[ZrR''(\eta\text{-}C_5H_5)_2]$ being detected using e.s.r. spectroscopy.[10,23] Presumably the Zr–C^α homolysis mechanism prevails in the present system even though no Zr^{III} species, or organic centred radicals, were detected down to −80 °C. Such species may be too short lived to be detected since they are restricted to be in close proximity to one another. Conversion of (**6a**) to (**6b**) possibly involves breaking of one bond followed by inversion before reforming. A less likely mechanism is inversion at C^α and torsion inversion along the biphenyl axis.



(**6c**) (M) = $Zr(\eta\text{-}C_5H_5)_2$

The methylene protons in (**5**) are non-equivalent exhibiting a characteristic AB pattern with J_{AB} constant at 10.9 Hz but then with a decrease in $\delta(H_A - H_B)$ in the order Ti > Hf > Zr paralleling the size of the metal centres [δ 3.35 (**5a**), 1.32 (**5b**), 1.72 (**5c**), and 1.49 (**5d**)]. This presumably arises from different degrees of torsion along the biphenyl axis affecting the orientation of the methylene protons with respect to shielding by the cyclopentadienyl groups. Metallacycles (**5**) have C_2 symmetry with the symmetry axis passing through the midpoint of the aryl–aryl linkage (see structural commentary).

Assignment of the *meso* isomer for (**7**) was based on ^1H and ^{13}C n.m.r. data; the cyclopentadienyl groups are magnetically distinct whereas the $SiMe_3$ groups and H^α protons are equivalent, consistent with the latter being directed towards one cyclopentadienyl ligand and the aromatic fragment folded towards the other. The *rac* isomer is expected to have unfavourable non-bonding interactions between the $SiMe_3$ and cyclopentadienyl groups and/or a severely twisted naphthalene ring system. The *meso* isomer is the expected kinetically controlled product if the reaction proceeds *via* facial attack of a planar or pseudo-planar dicarbanion. A 5—10% zirconium impurity was evident in the ^1H n.m.r. spectrum of the hafnium metallacycle, (**7b**), the zirconium resonances being slightly upfield.

Isomers (**6a**) and (**6b**) were also assigned using n.m.r. data; the $SiMe_3$ groups and cyclopentadienyls are equivalent in (**6b**) whereas in (**6a**) both of the $SiMe_3$ groups and cyclopentadienyls are magnetically distinct. There was no evidence for torsion mobility of these metallacycles, or of (**5**), over the temperature range −90 to +90 °C.

Metallacycles (**5**) and (**6a**) and (**6b**) failed to react with carbon monoxide at ambient temperature and pressure. This is unusual for metallocene alkyls of the Group 4 elements, and possibly relates to the rather large bite of the ligand blocking the primary carbonylation process, *viz.* complexation. No insertion occurred also on photolysis using a 1-kW Hg–Xe lamp. In contrast compound (**7a**) rapidly reacted with CO without photolysis but yielded an intractable mixture of compounds. The chelating alkyl in (**7**) is unusual in having a small bite and is thus less effective in blocking complexation of CO. Interestingly, the geometrical requirement of a large metal atom incorporated in a six-membered ring dictates that the metal resides well out of the

Table 1. E.s.r. and electrochemical data for the reduction of metallocene(IV) compounds in thf

Compound	g_{av}	$a(^{47}Ti, ^{49}Ti,$ or $^{91}Zr)^a$	$a(^1H)^a$	$E_{\frac{1}{2}}^{red}/V^b$	$t_{\frac{1}{2}}^{red}/s^c$
(5a)	1.935	7.6	6.6(t)	−1.59	$>10^3$
(5b)	1.983	9.1	8.5(t)	−2.09	$>10^2$
(5c)	1.958				
(5d)	1.985	8.3	8.0(t)		
(6a)[d]	1.977	24.8	4.0(d)	−2.21	>10
(6b)	1.981	25.6		−2.21	>10
(7a)	1.985	28.0	18.0(t)	1.99	Rev.
(7b)	1.909[e]				

[a] Measured in Gauss (1 G = 10^{-4}T); s = singlet, d = doublet, t = triplet. [b] $E_{\frac{1}{2}}^{red}$ = half-wave potential for reduction; cathodic peak potential is given for irreversible (irr.) processes. [c] $t_{\frac{1}{2}}^{red}$ = half-life of reduced species. [d] E.s.r. data derived by subtracting peaks corresponding to compound **(6b)**. [e] Recorded at −80 °C.

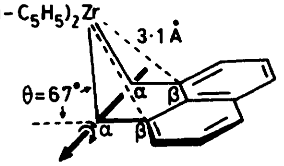


Figure 1. Calculated fold angle, θ, Zr–C^β distance in the zirconocene metallacycle based on 1,8-$(CHSiMe_3)_2C_{10}H_6^{2-}$; the Zr–$C^\alpha$ and $C^\alpha \cdots C^\alpha$ distances, and Zr–C^α–C^β angle were estimated as respectively 2.3 and 2.4 Å, and 109°

naphthalene plane. The extent of this becomes apparent in calculating a fold angle for **(7a)**, defined as the angle between the aromatic plane and the Zr$(C^\alpha)_2$ plane, by fixing the ligand bite at 2.4 Å, the M–C^α–C^β angle at 109°, and a metal–C^α distance at *ca.* 2.3 Å, typical of zirconocene complexes. The fold angle is rather large at 67° and the associated Zr–C^β distances are 3.1 Å (Figure 1), less than the van der Waals limits, so that the formally electron-deficient metal centre would reside close to the π cloud of the naphthalene ring system. Such an interaction may be reflected in some of the properties of **(7)**, *e.g.* thermal stability and reduction characteristics (below), and be related to the authenticated Zr–C^β interactions in the solid *meso*-$[Zr\{(CHSiMe_3)_2C_6H_4\text{-}o\}(\eta\text{-}C_5H_5)_2]$.[13]

$d^0 \longrightarrow d^1$ *Reduction Studies.*—d^1 M^{III} species were generated by treating the alkyl metal(IV) compounds with $Na[C_{10}H_8]$ in thf at ambient temperature and −80 °C and the e.s.r. spectra recorded immediately. E.s.r. data for the d^1 species together with electrochemical data of the metal(IV) compounds are presented in Table 1; g_{av} values, hyperfine coupling constants and reduction potentials [measured relative to the ferrocene couple, 0.53 V *vs.* saturated calomel electrode (s.c.e.)] are within the limits established in other studies. Peak separations in the cyclic voltammograms for reversibly reduced compounds were *ca.* 70 mV (*cf.* theoretical 59 mV). Only the d^1 hafnium species rapidly decompose at room temperature, although they are stable indefinitely at −80 °C; loss of the broad singlet for hafnium species derived from reduction of **(5c)** and **(7b)** at room temperature yielded spectra identical to reduced **(5b)** and **(7a)** respectively, a consequence of zirconium impurities (< 10%) in commercially available hafnium compounds. As is normal for hafnium d^1 species,[9,10,13] e.s.r. spectra of reduced **(5c)** and **(7b)** lacked metal hyperfine coupling. Reduction potentials for **(5c)** and **(7b)** could not be determined, presumably due to the closeness of the potential for the decomposition of thf solvent. This and the results in Table 1 adhere to the established reduction potential inequalities Ti ≫ Zr ≫ Hf.[9,13] A combination of e.s.r. and electrochemical data derived for the metallacycles **(5a)**, **(5b)**, **(6a)**, **(6b)**, and **(7a)** gives insight into the nature of the reduced species (Schemes 1—3). All solutions containing reduced d^1 species were red-brown, with the exception of that derived from **(6a)** and **(6b)** which was green. Attempts to isolate complexes from such solutions were unsuccessful.

Compounds **(5a)**, **(5b)**, and **(5d)** give e.s.r. spectra consisting of a central triplet with triplet satellites for the metal hyperfine coupling, the d^1 species being stable for several days at room temperature. The triplets most likely arise from hyperfine coupling to two hydrogen atoms. If the chelate ring is maintained on reduction, *e.g.* **(11)** (Scheme 1), a triplet of triplets is expected due to coupling to two sets of non-equivalent hydrogens attached to the C^α atoms. If there is heterolytic loss of $-CH_2^-$ yielding **(12a)**, **(12b)**, and **(12d)** (Scheme 1), coupling to two hydrogens could result. However, the hydrogens attached to the metal bound carbon should still be non-equivalent because of the chiral nature of the alkyl, and in order to yield a symmetrical triplet, coupling to the two protons must be similar *or* the protons must be equivalent on the e.s.r. time-scale due to rapid inversion *via* rotation along the biphenyl axis. Cleavage of M–C^α bonds has precedents in the reduction of the related metallacycles $[M\{(CH_2)_2C_6H_4\text{-}o\}(\eta\text{-}C_5H_4R)_2]$ (R = H or $SiMe_3$, M = Ti or Zr), which yield coupling constants similar to those of the present study.[11]

Electrochemical reduction of **(5a)** and **(5b)** was reversible and this would normally imply the formation of the metalate species **(11)** (Scheme 1). If heterolytic cleavage of M–C^α occurs, the close proximity of released $-CH_2^-$ to the primary co-ordination sphere of the metal could still be consistent with reversible reduction providing there is no complexation of thf solvent to the d^1 metal centre blocking M–C bond formation. Given our inability to generate d^1 species from **(5)** in the absence of thf, such complexation could not be investigated. However, reduction of **(5b)** in the presence of PMe_3, which is a better ligand than thf or Zr^{III},[24] gives the same e.s.r. spectra as in the absence of the phosphine which suggests that reduced **(5)** is devoid of metal–solvent interaction.

The e.s.r. spectrum of reduced **(7a)** consisted of a central triplet superimposed on the characteristic sextet from ^{91}Zr coupling; the triplet presumably arises from hyperfine coupling to the two equivalent protons on the C^α atoms. This and the reversible reduction of compound **(7a)** are consistent with the reduced species being the metallacyclic metalate, **(13a)** (Scheme 2), and *not* the metalate with one of the C^α atoms dissociated from the metal centre which is likely for the species derived from **(5a)**, **(5b)**, and **(5d)** (above) and **(6a)** and **(6b)** (below). No complexation of phosphine is evident when the reduction is carried out in the presence of excess PMe_3, in support of the formation of co-ordinatively saturated **(13a)**.

The e.s.r. spectrum derived from the reduction of pure **(6b)** comprises a central singlet flanked by the six lines corresponding to ^{91}Zr hyperfine coupling. Compound **(6a)** could not be obtained free of **(6b)** and a complex e.s.r. signal is obtained on a 7:3 mixture of the two components (Figure 2). It is possible, however, to deconvolute by computer simulation that part of the spectrum which corresponds to reduced **(6b)** and show that spectrum of **(6a)** consists of a central doublet and the characteristic lines for coupling to ^{91}Zr. The doublet most likely arises from coupling to one proton suggesting cleavage of one metal–C^α bond on reduction of **(6a)**, *cf.* reduction of **(5b)** (Scheme 1). Complex **(6b)** is reversibly reduced. Electrochemistry on a mixture of **(6a)** and **(6b)** clearly showed that both are reversibly reduced at the same potential, or the potential of **(6a)** is outside the potential for decomposition of thf. The latter is highly unlikely given that all zirconocene

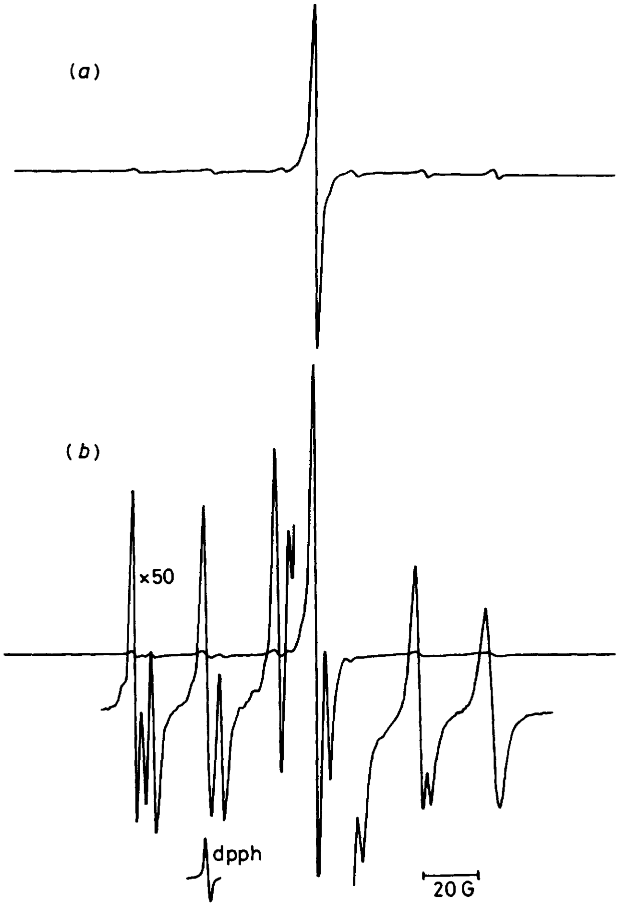


Figure 2. E.s.r. spectra of thf solutions prepared at 20 °C by treating pure δ-*SS*- and λ-*RR*-[Zr{(2-CHSiMe$_3$C$_6$H$_4$)$_2$}(η-C$_5$H$_5$)$_2$] (**6b**), (*a*), and a mixture of (**6b**) with the δ-*RS*- and λ-*RS*-isomers (**6a**), (*b*), with Na[C$_{10}$H$_8$]; dpph = diphenylpicrylhydrazyl

compounds studied to date have accessible reduction potentials in thf. The lack of ^{1}H hyperfine coupling for reduced (**6b**) is difficult to explain except to note that coupling to a proton attached to a carbon bearing trimethylsilyl and aryl groups is not always observed.[9,15] Like the reduction of (**5**) (above) there is no ^{31}P coupling for reduction of (**6a**) and (**6b**) in the presence of PMe$_3$, which is not surprising given the steric hindrance of the alkyl ligand. Reduced (**6a**) is less stable than reduced (**6b**), their respective stabilities being several days and weeks.

The absence of ^{31}P coupling for the d^1 species derived from reduction of the metallacycles in the presence of PMe$_3$ is consistent with maintaining both of the polyhapto ligands on each metal centre; removal of a cyclopentadienyl group would render the d^1 species co-ordinatively unsaturated and susceptible to phosphine complexation. In some metallocene dialkyls, *e.g.* [Zr(CH$_2$Ph)$_2$(η-C$_5$H$_5$)$_2$], an open-chain analogue of (**5b**), loss of C$_5$H$_5^-$ prevails on reduction,[9] and in complexes with more hindered alkyls, *e.g. meso*- and *rac*-[Zr(CHSiMe$_3$C$_6$H$_4$-Me-*o*)$_2$(η-C$_5$H$_5$)$_2$], open-chain analogues of (**6a**) and (**6b**), M–C$^\alpha$ bond rupture takes place.[10]

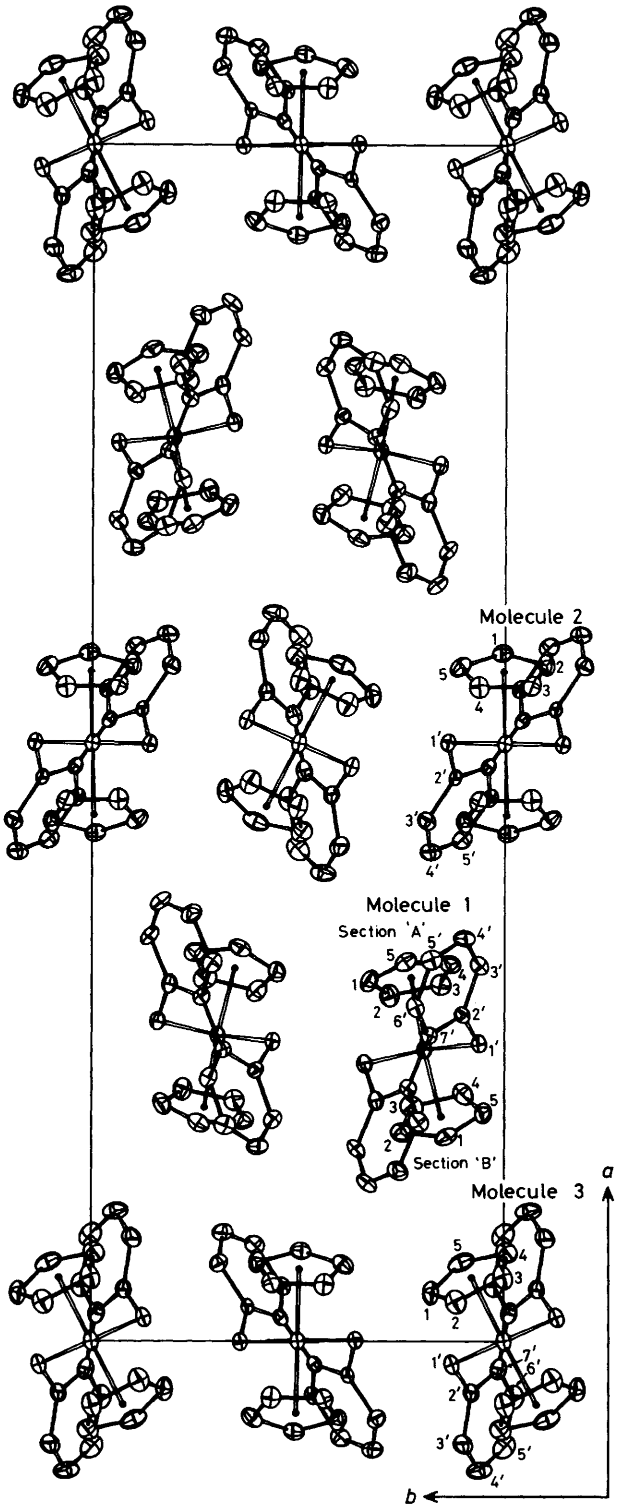


Figure 3. Unit-cell contents of [Ti{(2-CH$_2$C$_6$H$_4$)$_2$}(η-C$_5$H$_5$)$_2$] (**5a**) down *c* showing 20% thermal ellipsoids for the non-hydrogen atoms

The compatibility of the reduction data of the metallacycles (**5**), (**6a**), and (**6b**) towards M–C$^\alpha$ cleavage, whereas those of (**7a**) support a metallacyclic metalate, is noteworthy. The 'bite' of the bidentate alkyl in the former (see structural commentary) is much larger than that in (**7a**). Molecular orbital calculations on metallocene complexes possessing two bidentate ligands (= L) predict a decrease in the L–M–L angle at zirconium from *ca.* 94—97° for d^0 species to *ca.* 85—88° on the addition of an electron.[25] Reduction of the C–M–C angle in (**5**), (**6a**), and (**6b**) would have the effect of straining the metallacycle closer to the transition state for racemization *via* torsion along the biphenyl axis and thereby favouring M–C cleavage. In the case of (**7a**) the angle at the metal subtended by the two carbons is already less than that predicted for a d^1 species (63° for the structure in Figure 1). Therefore, reduction without the introduction of ring

Table 2. Non-hydrogen atom co-ordinates for $[Ti\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**5a**)[a]

	Molecule *m* = 1					
	Section *n* = A			Section *n* = B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cyclopentadienyl						
C(1*n*1)	0.301 4(2)	0.329 6(6)	-0.037 6(9)	0.171 2(2)	0.142 0(7)	0.013 1(9)
C(1*n*2)	0.289 2(2)	0.280 6(7)	-0.156 5(8)	0.174 6(2)	0.250 8(7)	-0.058 4(8)
C(1*n*3)	0.298 5(2)	0.155 3(7)	-0.149 0(7)	0.196 3(2)	0.225 9(8)	-0.170 7(7)
C(1*n*4)	0.315 4(2)	0.132 6(7)	-0.028 2(8)	0.207 0(2)	0.100 9(7)	-0.170 2(8)
C(1*n*5)	0.317 3(2)	0.240 9(8)	0.040 5(7)	0.191 0(2)	0.052 0(6)	-0.054 9(10)
C(1*n*0)[b]	0.3044	0.2278	-0.0662	0.1880	0.1543	-0.0882
Ligand						
C(1*n*1′)	0.249 2(2)	0.061 9(5)	0.162 4(6)	0.232 2(2)	0.340 6(5)	0.147 0(6)
C(1*n*2′)	0.273 1(2)	0.103 1(5)	0.277 3(6)	0.201 2(2)	0.312 2(5)	0.251 2(6)
C(1*n*3′)	0.314 4(2)	0.061 5(6)	0.300 4(6)	0.161 0(2)	0.359 9(6)	0.248 5(7)
C(1*n*4′)	0.337 1(2)	0.098 3(7)	0.408 1(7)	0.132 2(2)	0.334 3(7)	0.344 0(9)
C(1*n*5′)	0.319 1(2)	0.177 7(6)	0.497 7(7)	0.142 7(2)	0.259 2(7)	0.44 38(8)
C(1*n*6′)	0.279 3(2)	0.217 2(6)	0.476 4(6)	0.183 7(2)	0.209 0(6)	0.449 8(7)
C(1*n*7′)	0.255 9(2)	0.183 5(6)	0.368 7(6)	0.212 2(2)	0.234 2(5)	0.354 5(6)
Metal						
Ti(1)	0.244 23(3)	0.195 31(9)	0			
	Molecule *m* = 2			Molecule *m* = 3		
Ti(*m*)	½	0	0.182 2(2)	0	0	0.124 5(2)
Cyclopentadienyl						
C(*m*1)	0.575 4(2)	0.007 4(7)	0.157 1(6)	0.040 1(3)	0.178 0(6)	0.177 8(9)
C(*m*2)	0.565 9(2)	-0.098 6(6)	0.227 8(7)	0.032 6(3)	0.116 7(7)	0.290 9(7)
C(*m*3)	0.548 3(2)	-0.064 1(6)	0.345 0(7)	0.053 4(3)	0.001 9(7)	0.287 0(7)
C(*m*4)	0.547 1(2)	0.063 7(7)	0.349 0(7)	0.074 1(2)	-0.007 0(7)	0.168 2(8)
C(*m*5)	0.564 0(2)	0.109 7(7)	0.233 9(7)	0.065 7(2)	0.104 0(9)	0.102 8(8)
C(*m*0)[b]	0.5602	0.0036	0.2626	0.0532	0.0787	0.2053
Ligand						
C(*m*1′)	0.500 7(2)	0.139 2(5)	0.031 2(5)	-0.019 55(2)	0.126 8(5)	-0.028 5(6)
C(*m*2′)	0.471 5(2)	0.121 2(5)	-0.078 5(6)	-0.043 3(2)	0.078 8(5)	-0.137 5(7)
C(*m*3′)	0.435 0(2)	0.191 2(6)	-0.090 0(6)	-0.086 3(2)	0.098 2(6)	-0.148 8(8)
C(*m*4′)	0.409 1(2)	0.181 8(7)	-0.196 3(7)	-0.108 6(2)	0.058 7(9)	-0.252 2(10)
C(*m*5′)	0.419 5(2)	0.104 5(6)	-0.296 9(7)	-0.088 8(3)	-0.002 1(8)	-0.351 6(8)
C(*m*6′)	0.454 4(2)	0.036 5(5)	-0.285 9(6)	-0.046 7(3)	-0.025 2(6)	-0.342 8(6)
C(*m*7′)	0.480 7(2)	0.041 1(5)	-0.178 8(5)	-0.023 2(2)	0.012 7(6)	-0.237 4(6)

[a] The co-ordinate setting follows that employed for the niobium analogue.[4] [b] Cyclopentadienyl ring centroids.

strain is possible. Five-membered metallacycles of titanocene and zirconocene,[11–13] which also have rather small ligand 'bites', undergo reduction in the same way as (**7a**).

Structural Commentary.—*X*-Ray structure determinations of (**5a**) and (**6a**) show that they comprise discrete molecules of the expected stoicheiometry, the asymmetric unit in (**5a**) being one half of two independent molecules each located with the metal atom on a crystallographic two-fold axis, and a single molecule devoid of crystallographic symmetry, all with the same connectivity, while in (**6a**) it is a single molecule. (**5a**) is isostructural with the d^1 niobium analogue described in Part 3.[4] Results are given in Tables 2—5, and Figures 3—5 which define the atom-numbering schemes used. Differences in bond distances and angles defining the metal environment in the two compounds reflect the 0.07-Å smaller radius of Ti^{4+} compared to Zr^{4+} (ref. 26).

Assuming the cyclopentadienyl ligands occupy one co-ordination site the molecules are four-co-ordinate; the angle subtended at the metal by the polyhapto groups, 133.3° (mean), (**5a**), and 126.8°, (**6a**), is enlarged relative to those within the remainder of the co-ordination sphere in consequence of the large steric requirements of $\eta\text{-}C_5H_5$, and lies within the range established for d^0 titanocenes and zirconocenes possessing two unidentate ligands.[7,14] The metal is reasonably symmetrically bound to the cyclopentadienyl ligands in both structures as is usual for such compounds; the actual M–C(η) distances, 2.357(8)—2.429(7) Å, (**5a**), 2.501(5)—2.554(7) Å, (**6a**), are unexceptional. It appears, therefore, that the alkyl ligand which possesses highly hindered $SiMe_3$ substituents in (**6a**) imposes little, if any, distortion on the metallocene sections of the molecules. In (**5a**) the cyclopentadienyl ligands are eclipsed whereas in (**6b**) they are staggered.

The mean Ti–C^{α} distance of 2.20_7 Å in (**5a**) may be compared to 2.21(2) Å in $[TiMe_2(\eta^5\text{-}C_9H_7)_2]$[27] and 2.203(6) Å in the metallacycle $[Ti\{(CH_2)_2C_6H_4\text{-}o\}(\eta\text{-}C_5H_5)_2]$.[11] In the metallacycle $[Ti(C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ bearing sp^2 rather than sp^3 C^{α} atoms this distance is, as expected, smaller [2.16(2) Å].[28] The

Table 3. Non-hydrogen atom co-ordinates for $[Zr\{(2\text{-}CHSiMe_3C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ **(6a)**

	Section *n* = A			Section *n* = B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Zr	−0.020 67(5)	0.536 50(3)	0.242 94(3)			
Cyclopentadienyl						
C(*n*1)	−0.076 9(5)	0.524 6(3)	0.387 5(3)	0.118 3(6)	0.534 7(4)	0.128 8(4)
C(*n*2)	−0.177 8(5)	0.488 9(3)	0.334 1(3)	0.127 0(5)	0.459 6(4)	0.166 1(4)
C(*n*3)	−0.129 2(5)	0.421 7(3)	0.300 2(3)	0.005 6(6)	0.424 8(3)	0.146 0(4)
C(*n*4)	0.002 5(5)	0.416 2(2)	0.332 7(4)	−0.077 0(6)	0.476 0(4)	0.102 4(3)
C(*n*5)	0.035 2(5)	0.479 0(2)	0.386 6(3)	−0.010 2(6)	0.542 6(4)	0.090 9(3)
C(*n*0)	−0.0860	0.4661	0.3482	0.0327	0.4875	0.1268
Ligand						
C(*n*1′)	−0.192 5(4)	0.624 1(2)	0.201 5(2)	0.139 9(5)	0.629 4(3)	0.292 7(3)
C(*n*2′)	−0.187 6(4)	0.678 2(3)	0.274 5(3)	0.114 0(5)	0.700 0(3)	0.235 9(3)
C(*n*3′)	−0.279 6(5)	0.673 4(3)	0.327 5(3)	0.199 9(5)	0.720 7(3)	0.182 9(4)
C(*n*4′)	−0.277 2(5)	0.724 1(3)	0.394 2(3)	0.181 8(5)	0.786 2(3)	0.131 3(3)
C(*n*5′)	−0.183 2(5)	0.781 3(3)	0.408 5(3)	0.076 4(6)	0.832 7(3)	0.132 5(3)
C(*n*6′)	−0.092 8(5)	0.788 3(3)	0.357 4(3)	−0.008 0(5)	0.816 3(3)	0.184 4(3)
C(*n*7′)	−0.091 4(4)	0.737 3(2)	0.291 1(3)	0.007 3(4)	0.750 8(2)	0.237 0(3)
Si(*n*′)	−0.357 0(2)	0.607 59(8)	0.140 51(8)	0.245 6(2)	0.646 18(9)	0.390 40(9)
C(*n*11′)	−0.458 0(5)	0.698 4(3)	0.143 2(3)	0.378 7(6)	0.739 8(3)	0.386 9(4)
C(*n*12′)	−0.451 2(6)	0.522 7(3)	0.173 6(4)	0.162 0(7)	0.656 8(4)	0.482 8(3)
C*n*(13′)	−0.349 0(6)	0.591 9(4)	0.028 7(3)	0.365 6(6)	0.566 3(4)	0.411 5(5)

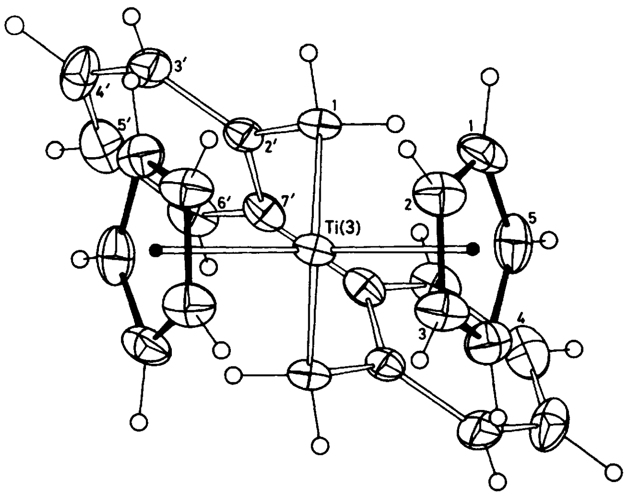


Figure 4. Projection of molecule 3 of $[Ti\{(2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ **(5a)** down its *2* axis showing 20% thermal ellipsoids and numbering scheme; the hydrogen atoms have arbitrary radii

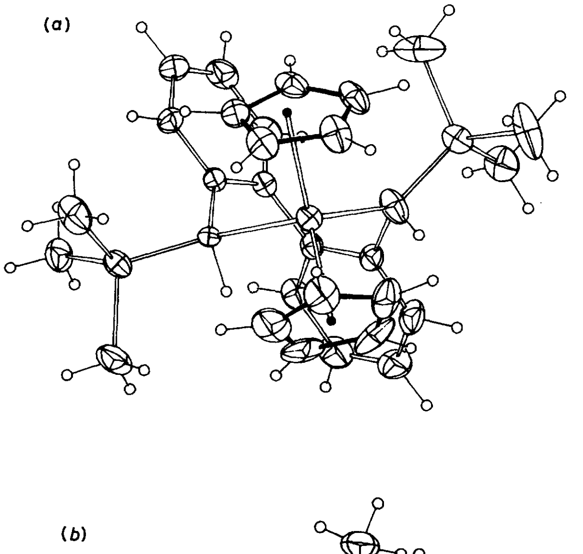


Figure 5. Projections of δ-*RS*-$[Zr\{(2\text{-}CHSiMe_3C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ **(6a)** showing 20% thermal ellipsoids and numbering scheme; the hydrogen atoms have arbitrary radii; projection (*a*) is down the bisector of the ring centroid—Zr bonds

$Ti\text{-}C^{\alpha}\text{-}C^{\beta}$ angle of 117_4° (mean) and $Ti\text{-}C^{\beta}$ distance of 3.172(7) Å show that a π interaction between the metal and the alkyl ligand of the type in $[Ti(CH_2Ph)_4]$ ($Ti\text{-}C^{\alpha}\text{-}C^{\beta}$ 88—89°, $Ti\cdots C^{\beta}$ 2.6—2.8 Å)[29] is not present and that bonding is exclusively of the σ type. Nor is there evidence for an agostic $CH_2\cdots Ti$ interaction recently identified in $[Ti(CH_2Ph)_3(\eta\text{-}C_5Me_5)]$,[30] where one of the benzyl ligands has an exceptionally large $Ti\text{-}C^{\alpha}\text{-}C^{\beta}$ angle of 139.0(7)°.

The mean $Zr\text{-}C^{\alpha}$ distance of 2.33_8 Å is within the range established for zirconocene dialkyls of 2.28—2.39 Å[7] and thus there is no apparent elongation originating from steric effects (above). $Zr\text{-}C^{\alpha}$ distances in related structurally authenticated compounds are 2.38_8 and 2.37_4 Å in $[Zr(CHPh_2)_2(\eta\text{-}C_5H_5)_2]$[31] and *rac*-$[Zr(CHSiMe_3C_6H_4Me\text{-}o)_2(\eta\text{-}C_5H_5)_2]$[27] respectively, and 2.301(6) and 2.305(4) Å in the metallacycles $[Zr\{(CH_2)_2C_6H_4\text{-}o\}(\eta\text{-}C_5H_5)_2]$[11] and *meso*-$[Zr\{(CHSiMe_3)_2$-

Table 4. Titanium environment in (**5a**); distances in Å, angles in °

Molecule	1	2	3
Ti–C(A0)	2.069	2.095	2.079
Ti–C(B0)	2.063		
Ti–C(A1′)	2.229(6)	2.179(6)	2.193(6)
Ti–C(B1′)	2.230(6)		
C(A0)–Ti–C(A0)	134.2	133.1	132.5
C(A0)–Ti–C(A1′)	107.2	105.2	105.2
C(A0)–Ti–C(B1′)	105.4		
C(B0)–Ti–C(A1′)	104.7	107.9	108.6
C(B0)–Ti–C(B1′)	107.8		
C(A1′)–Ti–C(A1′)	87.7(2)	88.2(2)	87.5(2)

Individual Ti–C_5H_5(1,2,3,4,5) distances (Å):

Molecule 1, C_5H_5 A	2.373(8), 2.357(8), 2.360(8), 2.391(7), 2.421(7)
C_5H_5 B	2.406(7), 2.382(7), 2.363(8), 2.364(8), 2.377(8)
Molecule 2	2.424(7), 2.409(7), 2.390(7), 2.394(7), 2.429(7)
Molecule 3	2.389(7), 2.382(8), 2.395(8), 2.412(7), 2.395(8)

Table 5. Zirconium environment (**6a**); distances in Å, angles in °

Zr–C(A0)	2.295	Zr–C(A1′)	2.335(4)
Zr–C(B0)	2.234	Zr–C(B1′)	2.341(5)
C(A0)–Zr–C(B0)	126.82	C(B0)–Zr–C(A1′)	105.87
C(A0)–Zr–C(A1′)	103.88	C(B0)–Zr–C(B1′)	106.39
C(A0)–Zr–C(B1′)	111.65	C(A1′)–Zr–C(B1′)	98.3(2)

Individual Zr–C_5H_5(1,2,3,4,5) distances (Å):
Ring A: 2.548(5), 2.528(6), 2.507(5), 2.501(5), 2.531(5)
Ring B: 2.554(7), 2.510(6), 2.516(6), 2.505(6), 2.522(6)

C_6H_4-*o*}(η-$C_5H_5)_2$][13] although the latter has rather short Zr···C^β distances of 2.71(1) Å, similar to compounds that can be considered as ziroconocene π complexes to *cis*-butadienes.[12,32] There is no evidence for π interactions in (**6a**) like that in [Zr($CH_2Ph)_4$][29] (Zr···C^β 2.74 Å) and perhaps in [Zr(CPhCMe_2)Cl(η-$C_5H_5)_2$][33] [Zr···C^β 2.953(3) Å], the Zr···C^β distances being 3.054(5) and 3.110(5) Å and Zr–C^α–C^β angles 103.3(2) and 105.7(3)° respectively. The Zr–C^α distances contrast with shorter distances, 2.25$_7$ Å, in the metallacycle [Zr($C_4Ph_4)_2$(η-$C_5H_5)_2$] bearing *sp*^{2} C^α atoms.[28]

The C^α–Ti–C^α angle in (**5a**), 87.$_8$°, reflects the rather large 'bite' of the dialkyl when attached to titanium, in contrast with 76.7(2)° in [Ti{($CH_2)_2C_6H_4$-*o*}(η-$C_5H_5)_2$][11] and 80.3° in [Ti(C_4Ph_4)(η-$C_5H_5)_2$],[28] and more akin to those of non-chelating complexes, *e.g.* 92.9(8)° in [TiMe_2(η^5-$C_9H_7)_2$].[27] The large bite is also reflected in the torsion angle about the bonds between the two phenyl rings [62.2° (mean)] (*i.e.* the bigger the metal atom the greater the torsion angle unless electronic effects circumvene). The angle in the isovalent niobium cation [Nb{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2]^+$ is 78.4°; in the d^1 and d^2 niobium analogues the angles are much lower at 62.4 and 59.0° respectively, as are the C^α–Nb–C^α angles at 83.0 and 80°,[4] the metal environment changing in the sequence $d^0 \longrightarrow d^1 \longrightarrow d^2$ in accord with molecular orbital predictions.[25]

Similarly, the C^α–Zr–C^α angle in (**6a**), 98.3(2)°, is more typical of a metallocene dialkyl complex, *e.g.* 99.5° in *rac*-[Zr(CHSi$Me_3C_6H_4$Me-*o*$)_2$(η-$C_5H_5)_2$].[23] In [Zr{($CH_2)_2C_6H_4$-*o*}(η-$C_5H_5)_2$][11] this angle is 77.3(2)°, and the 'predicted' angle for (**7a**) is 63° (Figure 1). The torsion angle for (**6a**), 73.6°, fits in with the scheme of variation in torsion with C^α–M–C^α angle and metal-atom size discussed above.

Molecules of (**6a**) lack symmetry with respect to the vector from the metal to the bisector of the bond joining the two phenyl groups [Figure 5(*a*)]; one of the trimethylsilyl groups resides approximately between the two cyclopentadienyl ligands, the other being directed towards one of them. The isomeric compound, (**6b**), would have both SiMe_3 groups in positions of the former type, which is presumably the less congested. In this context the photolytic conversion of (**6a**) to (**6b**) is not surprising. Moreover in λ-*SS*- and δ-*RR*-[SnLPh_2] (R = SiMe_3)[8] the SiMe_3 groups lie approximately astride the phenyl ligands (Figure 3 of ref. 3).

Experimental

General procedures, and physical and analytical measurements were detailed in Parts 1,[6] 2,[3] and 3.[4]

Materials.—The Grignard reagent (**2**)[3] was prepared by the classical method, and the dilithium reagents (**3**), (**4**), and (**9**) were prepared by lithiation of the appropriate hydrocarbon using LiBu^n(tmen) as detailed in the literature.[6,19] [ZrCl_2(η-C_5H_4Si$Me_3)_2$] was prepared according to the literature[9] whereas [MCl_2(η-$C_5H_5)_2$] were purchased from Fluka (M = Ti), Aldrich (M = Zr), and Alfa (M = Hf).

Synthesis of [Ti{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$] (**5a**).—*Method* 1. To a solution of [TiCl_2(η-$C_5H_5)_2$] (1.62 g, 6.5 mmol) in thf (20 cm^3) at −78 °C was added the di-Grignard reagent (**2**) (100 cm^3, 0.065 mol dm^{-3}, 6.5 mmol). The purple solution was warmed to room temperature and stirred for 2 h. The solvent was then removed *in vacuo* and the product extracted with diethyl ether (*ca.* 200 cm^3). Concentration of the filtrate to *ca.* 100 cm^3 and cooling for 18 h at *ca.* −30 °C afforded purple crystals of (**5a**). These were washed with hexane (3 × 5 cm^3), and then dried *in vacuo* (1.42 g, 61%), m.p. 168 °C. The compound can be sublimed under vacuum (0.1 mmHg) at *ca.* 160 °C (Found: C, 80.3; H, 6.35. Calc. for $C_{24}H_{22}Ti$: C, 80.4; H, 6.20%); ^1H n.m.r. (60 MHz, C_6D_6), δ −0.15 (d, 2 H), 3.20 (d, 2 H) (J_{AB} 10.9 Hz), 5.40 (s, 10 H), 8.00 (m, 8 H); ^{13}C n.m.r. (^1H decoupled, C_6D_6), δ 70.21 (CH_2), 114.28 (C_5H_5), 122.5, 126.8, 127.3, 129.2, 138.5, 151.8 (C_6H_4); mass spectrum (*m/e*): 360 $[P]^+$, 180 $[C_{10}H_{10}Ti]^+$.

Method 2. To a mixture of [TiCl_2(η-$C_5H_5)_2$] (1.5 g, 4.62 mmol) and (**3**) (1.97 g, 4.62 mmol) at room temperature was added diethyl ether (200 cm^3). The resulting solution was stirred for 2 h and then filtered. Concentration of the filtrate (*ca.* 100 cm^3) followed by cooling to *ca.* −30 °C afforded purple crystals of (**5a**) (1.12 g, 68%).

Synthesis of [Zr{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$] (**5b**).—*Method* 1. The procedure was as described for the titanium analogue. [ZrCl_2(η-$C_5H_5)_2$] (1.60 g, 5.47 mmol) and the di-Grignard reagent (**2**) (100 cm^3, 0.055 mol dm^{-3}) yielded (**5b**) (1.54 g, 70%) as orange crystals, m.p. 172 °C (Found: C, 70.8; H, 5.80. Calc. for $C_{24}H_{22}Zr$: C, 71.75; H, 5.50%); ^1H n.m.r. (60 MHz, C_6D_6), δ 1.20 (d, 2 H), 2.52 (d, 2 H) (J_{AB} 10.9 Hz), 5.30 (s, 10 H), 7.00 (m, 8 H); ^{13}C n.m.r. (^1H decoupled, C_6D_6), δ 53.1 (CH_2), 111.3 (C_5H_5), 121.8, 128.2, 129.9, 130.6, 140.6, 148.4 (C_6H_4); mass spectrum (*m/e*): 402 $[P]^+$, 337 $[P - C_5H_5]^+$, 222 $[C_{10}H_{10}Zr]^+$, 182 $[C_{14}H_{12}]^+$.

Method 2. The reaction between [ZrCl_2(η-$C_5H_5)_2$] (2.0 g, 6.85 mmol) and dilithium reagent (**3**) (2.98 g, 7.0 mmol) was carried out as described for the titanium analogue (2.10 g, 75%).

Synthesis of [Hf{(2-$CH_2C_6H_4)_2$}(η-$C_5H_5)_2$] (**5c**).—*Method* 1. The reaction between [HfCl_2(η-$C_5H_5)_2$] (2.47 g, 6.5 mmol) and di-Grignard reagent (**2**) (100 cm^3, 0.065 mol dm^{-3}, 6.5 mmol) was performed in a similar fashion to that described for the titanium analogue. Compound (**5c**) was isolated as a yellow crystalline solid (1.74 g, 55%), m.p. 192 °C (Found: C, 58.4; H, 4.50. Calc. for $C_{24}H_{22}Hf$: C, 58.95; H, 4.55%); ^{1}H n.m.r. (60 MHz, C_6D_6), δ 0.63 (d, 2 H), 2.35 (d, 2 H) (J_{AB} 10.9 Hz), 5.33 (s, 10 H), 7.10 (m, 8 H); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ 69.6 (CH_2), 110.8 (C_5H_5), 126.4, 127.1, 127.4, 128.5, 129.3, 130.2 (C_6H_4); mass spectrum (*m/e*): 488 $[P]^+$, 308 $[C_{10}H_{10}Hf]^+$, 180 $[C_{14}H_{12}]^+$.

Method 2. The procedure was as described for the titanium analogue, using $[HfCl_2(\eta\text{-}C_5H_5)_2]$ (1.56 g, 4.1 mmol) and dilithium reagent (**3**) (1.75 g, 4.1 mmol) (1.70 g, 85%).

Synthesis of $[Zr\{2\text{-}CH_2C_6H_4)_2\}(\eta\text{-}C_5H_4SiMe_3)_2]$ (**5d**).—The procedure was as described for (**5a**) except that hexane was used to extract the product. The reaction between the di-Grignard (**3**) (100 cm^3, 0.065 mol dm^{-3}, 6.5 mmol) and $[ZrCl_2(\eta\text{-}C_5H_4SiMe_3)_2]$ (2.8 g, 6.4 mmol) yielded (**5d**) as orange crystals (1.80 g, 52%), m.p. 118 °C; ^{1}H n.m.r. (60 MHz, C_6D_6), δ 0.03 (s, 18 H), 1.18 (d, 2 H), 2.67 (d, 2 H) (J_{AB} 10.9 Hz), 5.61 (m, 4 H), 6.14 (m, 4 H), 7.34 (m, 8 H); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), δ −0.1 (Me_3Si), 54.0 (CH_2), 113.7, 115.4, 118.1, 119.1, 119.4 (C_5H_4), 121.5, 126.9, 127.7, 129.5, 140.2, 148.2 (C_6H_4); mass spectrum (*m/e*): 546 $[P]^+$, 366 $[(C_5H_4SiMe_3)_2Zr]^+$.

Synthesis of δ-*RS*- *and* λ-*RS*-$[Zr\{(2\text{-}CHSiMe_3C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**6a**) *and* λ-*RR*-$[Zr\{(2\text{-}CHSiMe_3C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**6b**).—To a stirred solution of $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ (0.68 g, 2.3 mmol) in thf (30 cm^3) at −78 °C was added the dilithium reagent (**4**) (1.48, 2.6 mmol) in Et_2O (20 cm^3). After addition was complete the mixture was brought to room temperature with stirring over 18 h whereupon the solvent was removed *in vacuo* and the residue extracted with hexane (50 cm^3). Concentration of the filtrate to *ca.* 5 cm^3 and cooling for 48 h at *ca.* −30 °C afforded orange crystals of a 7:3 mixture of (**6a**) and (**6b**) which were subsequently washed with pentane (3 × 5 cm^3) and then dried *in vacuo* (0.56 g, 45%), m.p. 191—194 °C (Found: C, 65.90; H, 6.95. Calc. for $C_{30}H_{38}Si_2Zr$: C, 66.00; H, 7.00%); ^{1}H n.m.r. (300 MHz, C_6D_6): (**6a**) δ −0.07 (s, 9 H), 0.04 (s, 9 H), 1.52 (s, 1 H), 2.20 (s, 1 H), 5.68 (s, 5 H), 5.69 (s, 5 H), 6.78—7.34 (m, 8 H); (**6b**), δ 0.07 (s, 18 H), 2.48 (s, 2 H), 5.68 (s, 10 H), 6.78—7.34 (m, 8 H); ^{13}C n.m.r. (300 MHz, ^{1}H decoupled, C_6D_6): (**6a**), δ 3.31, 3.51 (2 × $SiMe_3$), 51.08, 67.47 (2 × CH), 109.9, 110.5 (2 × C_5H_5), 120.0, 122.3, 127.4, 127.6, 129.2, 130.3, 130.9, 133.6 (8 × aryl CH), 140.9, 143.9, 144.1, 151.5 (4 × aryl C); (**6b**), δ 3.61 ($SiMe_3$), 65.69 (CH), 110.6 (2 × C_5H_5), 121.1, 126.9, 128.4, 128.6 (4 × aryl CH), 141.6, 149.4 (2 × 2 aryl C); mass spectrum (*m/e*) 545 $[P]^+$, 479 $[P - C_5H_5]^+$, 222 $[C_{10}H_{10}Zr]^+$.

Synthesis of δ-*SS*- *and* λ-*RR*-$[Zr\{(2\text{-}CHSiMe_3C_6H_4)_2\}(\eta\text{-}C_5H_5)_2]$ (**6b**).—A solution of (**6a**) and (**6b**) (0.60 g, 1.10 mmol) in benzene (20 cm^3) was photolyzed for 20 min. The solvent was then removed *in vacuo* and the residue extracted with hexane (10 cm^3). Concentration to *ca.* 1 cm^3 and cooling at *ca.* −30 °C for 72 h, afforded orange crystals of (**6b**) (0.57 g, 95%).

Synthesis of meso-$[Zr\{1,8\text{-}(CHSiMe_3)_2C_{10}H_6\}(\eta\text{-}C_5H_5)_2]$, (**7a**).—To a solution of $LiBu^n$ (5.2 cm^3, 8.6 mmol) and tmen (1.41 cm^3, 8.6 mmol), $(1,8\text{-}CH_2SiMe_3)_2C_{10}H_6$ (1.48 g, 8.4 mmol) was added dropwise yielding a deep red solution. After stirring for *ca.* 1 h at room temperature the solvent was removed *in vacuo*, $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ (1.3 g, 4.5 mmol) in diethyl ether (20 cm^3) at 30 °C was then added and the solution stirred for *ca.* 30 min after which the solvent was removed *in vacuo* and the resulting red oil extracted into hexane (40 cm^3). The solution was filtered and concentrated to *ca.* 10 cm^3. Cooling of this solution overnight at −30 °C afforded dark red needles of (**7a**), which were washed with pentane (3 × 5 cm^3) and then dried *in vacuo* (1.42 g, 61%), m.p. 162—164 °C (Found: C, 64.85; H, 7.25. Calc. for $C_{28}H_{36}Si_2Zr$: C, 64.70; H, 7.00%); ^{1}H n.m.r. (60 MHz, C_6D_6), δ −0.1 (s, 18 H, $SiMe_3$), 2.9 (s, 2 H, HCSi), 5.5 (s, 5 H, C_5H_5), 5.9 (s, 5 H, C_5H_5), 7.1 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), 4.6 ($SiMe_3$), 72.6 (CHSi), 112.4, 113.1 (C_5H_5), 124.0 (C^4), 128.5 (C^2, C^7), 129.7 (C^3, C^6), 135.9 (C^{10}), 138.9 (C^9), 150.4 (C^1, C^8).

Synthesis of meso-$[Hf\{1,8\text{-}(CHSiMe_3)_2C_{10}H_6\}(\eta\text{-}C_5H_5)_2]$, (**7b**).—The preparative procedure was identical to the zirconium analogue. Addition of $[HfCl_2(\eta\text{-}C_5H_5)_2]$ (2.16 g, 45 mmol) yielded orange-red needles of (**7b**) (1.53 g, 56%), m.p. 162—166 °C; ^{1}H n.m.r. (60 MHz, C_6D_6), δ 0.2 (s, 18 H, $SiMe_3$), 2.5 (s, 2 H, HCSi), 5.3 (s, 5 H, C_5H_5), 5.7 (s, 5 H, C_5H_5), 7.0 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (^{1}H decoupled, C_6D_6), 4.8 ($SiMe_3$), 72.3 (CHSi), 111.6, 112.1 (C_5H_5), 124.2 (C^4), 127.8 (C^2, C^7), 129.0 (C^3, C^6), 135.8 (C^{10}), 138.6 (C^9), 149.9 (C^1, C^8).

Reduction of Complexes (**5**), (**6**), *and* (**7**).—The electrochemical experiments were carried out according to ref. 24. Chemical reductions were performed as follows. Dropwise addition of a thf solution of sodium dihydronaphthylide (< 1 mol equiv.) to a thf solution of the above compounds (1 mol equiv.) generated red-brown or green solutions. The e.s.r. spectra were recorded immediately. These were performed at room temperature, except for (**5c**) and (**7b**) which were reduced at −78 °C. Reductions were also carried out in the presence of PMe_3. The e.s.r. and electrochemical data are given in Table 1.

Crystallography.—Unique data sets were measured to the specified $2\theta_{max.}$ limit using Syntex $P2_1$ and $P\bar{1}$ four-circle diffractometers, fitted with monochromatic Mo-K_α radiation sources, and operating in conventional 2θ–θ scan mode. *N* Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement with statistical weights, after solution of the structure by the heavy-atom method. Anisotropic thermal parmeters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included at idealized values, although in some cases it was possible meaningfully to refine $(x, y, z)_H$ (see below). Residuals *R* and *R′* on $|F|$ at convergence are quoted. Neutral complex scattering factors were used;[34] computation used the XTAL-83 program system[35] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Crystal data. (**5a**).* $C_{24}H_{22}Ti$, $M = 358.3$, orthorhombic, space group $Pnn2$ (C_{2v}^{10}, no. 34), $a = 31.93(1)$, $b = 10.898(4)$, $c = 10.359(5)$ Å, $U = 3\,605(3)$ Å^3, D_c ($Z = 8$) = 1.32 g cm^{-3}, $F(000) = 1\,504$, $\mu_{Mo} = 5.0$ cm^{-1}. Specimen (capillary): cuboid, *ca.* 0.3 mm (no absorption correction); $2\theta_{max.} = 50°$, $N = 3\,377$, $N_o = 2\,463$, $R = 0.045$, $R' = 0.050$, $T \sim 295$ K.

(**6a**).* $C_{30}H_{38}Si_2Zr$, $M = 546.0$, monoclinic, space group $P2_1/n$ (C_{2h}^{5}, no. 14), $a = 10.415(10)$, $b = 16.905(5)$, $c = 16.442(6)$ Å, $\beta = 99.50(6)°$, D_c ($Z = 4$) = 1.27 g cm^{-3}, $F(000) = 1\,144$, $\mu_{Mo} = 4.8$ cm^{-1}. Specimen (capillary): cuboid *ca.* 0.3 mm (no absorption correction); $2\theta_{max.} = 50°$, $N = 3\,617$, $N_o = 2\,658$, $R = 0.048$, $R' = 0.033$, $T \sim 295$ K.

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* Crystals of the zirconium and hafnium analogues of (**5a**) were also subject to examination with a view to structure determination; the latter was frustrated by wide linewidths, apparently imperfect orthorhombic symmetry and decomposition/phase transition in the *X*-ray beam, although in each case a basically similar unit cell suggests no doubt as to the identity of the compound or its basic structure. Similarly frustration occurred in attempting the structure determination of (**6b**), an imperfect transition to a related $C2/c$ cell yielding an unsatisfactory solution with disorder and suggestive of contamination by cocrystallized (**6a**).

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