Synthesis and Structure of [Zr(R)Cl(η-C$_5$H$_5$)$_2$] [R = Chiral, Highly Hindered Alkyl: ĈHSiMe$_3$C$_5$H$_4$Ṅ-2, ĈHSiMe$_3$C$_6$H$_4$ṖPh$_2$-o, or ĈHSiMe$_3$(C$_{14}$H$_9$-9)];† Influence of the Functional Group on the Nature and Stability of their d^1 Reduction Products

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Reaction of [ZrCl$_2$(η-C$_5$H$_5$)$_2$] with organolithium reagents Li(tmen)(R″) [R″ = a highly hindered alkyl, ĈHSiMe$_3$C$_5$H$_4$Ṅ-2 (R^1), ĈHSiMe$_3$C$_6$H$_4$ṖPh$_2$-o (R^2), ĈHSiMe$_3$(C$_{14}$H$_9$-9) (R^3) (C$_{14}$H$_9$ = anthryl), or ĈHSiMe$_3$(C$_6$H$_4$Me-p) (R^4); tmen = Me$_2$NCH$_2$CH$_2$NMe$_2$] in tetrahydrofuran (thf) yields [Zr(R″)Cl(η-C$_5$H$_5$)$_2$], compounds (2), (4), (6), and (8), respectively. Electrochemical reduction of (6) is reversible (10 < $t_{\frac{1}{2}}$ ≲ 50 s) whereas for (2), (4), and (8) it is irreversible. Reduction of (2) and (4) yields chloride-free persistent d^1 species, respectively [Zr(R^1)(η-C$_5$H$_5$)$_2$], with R^1 chelating or η^3-aza-allyl, and [Zr(ĈHSiMe$_3$C$_6$H$_4$ṖPh$_2$-o)(η-C$_5$H$_5$)$_2$] (^{31}P coupling) either in thf (Na[C$_{10}$H$_8$]) or toluene (Na/Hg). Reduced (2), (4), (6), and (8) react with PMe$_3$ yielding d^1 [Zr(R″)(PMe$_3$)-(η-C$_5$H$_5$)$_2$]. Variable-temperature ^{1}H n.m.r. investigation of (2) in toluene shows an equilibrium between four- and five-co-ordinate complexes; in the solid the latter prevails with a Zr–N distance of 2.34$_1$ Å, and an exceptionally long Zr–Cl distance (2.56$_3$ Å). In (4) the functional group is not bound to the metal centre [Zr–Cl 2.438(1), Zr–C 2.350(4) Å] and in (6) the potentially ambidentate alkyl R^3 is bound through the benzylic carbon [Zr–C 2.349(4), Zr–Cl 2.454(1) Å].

Mononuclear alkyl–metallocene complexes of trivalent zirconium have recently been investigated and there is some ambiguity relating to their structures.[1-5] The only examples of such a class of d^1 compound to have been isolated in the solid are [Zr{CH(SiMe$_3$)$_2$}(η-N$_2$)(η-C$_5$H$_4$R)$_2$] (R = H or Me)[6] and [Zr(CH$_2$ṖPh$_2$)(η-C$_5$H$_5$)$_2$].[3] Reduction of the corresponding Zr^{IV} chloride [Zr(R″)Cl(η-C$_5$H$_5$)$_2$][1-4,6] or photolysis of a dialkylzirconocene(IV) complex (e.g. ref. 5) are the common strategies for their generation.

As part of a broad study of the synthesis and reactivity of organozirconium(III) chemistry we have prepared a series of compounds [Zr(R″)Cl(η-C$_5$H$_5$)$_2$] [R″ = ĈHSiMe$_3$C$_5$H$_4$Ṅ-2 (R^1), ĈHSiMe$_3$C$_6$H$_4$ṖPh$_2$-o (R^2), ĈHSiMe$_3$(C$_{14}$H$_9$-9) (R^3) (C$_{14}$H$_9$ = anthryl), and ĈHSiMe$_3$(C$_6$H$_4$Me-p) (R^4)] and studied their reduction, chemically and using electrochemical techniques. The results are discussed herein together with X-ray structure determinations of [Zr(R″)Cl(η-C$_5$H$_5$)$_2$] for R″ = R^1, R^2, and R^3, and dynamic behaviour in solution of [Zr(R^1)Cl(η-C$_5$H$_5$)$_2$]. The structures are of interest by virtue of the various types of bonding modes possible for each hydrocarbyl group (see below) and that they may give some insight into the nature of the reduced species.

The new ligands R^1—R^4 are related to the benzyl ligand, ĈH$_2$Ph, which has featured significantly in the development of alkyl–transition metal chemistry, being capable of σ-bonding to the benzylic carbon centre, or, more recently defined, η^3-

bonding, e.g. in [Th(η^3-CH$_2$Ph)$_3$(η-C$_5$Me$_5$)].[7] The benzhydryl ligand, ĈHPh$_2$, is related to it but has featured in only a few publications.[8] Like R^1—R^4, benzhydryl is highly hindered, a characteristic that has proved important in the stabilization of unusual bonding configurations and oxidation states, e.g. the above mentioned dinitrogen complex containing ĈH(SiMe$_3$)$_2$.[6]

Noteworthy individual features of chiral R″ are: (i) R^1 can in principle act as a σ-donor ligand (two-electron), bridging or as a novel η^3-aza-allyl ligand, structure (I) (four-electron, established for the bis-silylated analogue[9]), or η^3-aza-allyl coupled with bridging:[9] an alternative chelate ring formation is likely to be stereochemically unfavourable; (ii) R^2 is in contrast to R^1, designed for chelation through the carbon and phosphorus centres, structure (II) (authenticated for the unsilylated analogue[10]), phosphorus favouring stability of a low oxidation state, Zr^{III} in the present study, by its σ/π-acceptor property as well as being a useful e.s.r. probe; and (iii) R^3 has been shown to be an ambident hydrocarbyl group, acting either as a σ donor through the benzylic carbon centre (reported for R^3 and its unsilylated analogue)[11,12] or to the C^{10} ring carbon yielding a species with an exocyclic double bond, e.g. (III; R = SiMe$_3$).[12,13] The ortho-isomeric ligand of R^4, presumably more hindered due to the closer proximity of the aromatic methyl group to the carbanion centre, has featured in organozircono-cene(III) chemistry.[2]

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† Chlorobis(η-cyclopentadienyl)(2-pyridyltrimethylsilylmethyl)-zirconium(IV), chlorobis(η-cyclopentadienyl)[(o-diphenylphosphino)-phenyltrimethylsilylmethyl]zirconium(IV), and (9-anthryltrimethylsilyl-methyl)chlorobis(η-cyclopentadienyl)zirconium(IV) respectively.

(I)   (II)   (III)
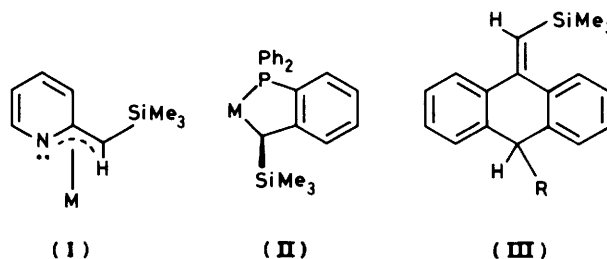
The synthesis of $[Zr(R^3)Cl(\eta-C_5H_5)_2]$ has been published recently as a communication along with a novel carbonylation reaction of it, the product being a metal enolate, exclusively the E isomer, viz. E-$[Zr\{OC(SiMe_3)CH(C_{14}H_9)\}Cl(\eta-C_5H_5)_2]$.[13]

Results and Discussion

Synthesis of d^0 $[Zr(R'')Cl(\eta-C_5H_5)_2]$.—All the d^0 alkyl-zirconocene(IV) compounds, (2), (4), (6), and (8) were prepared by reacting $[ZrCl_2(\eta-C_5H_5)_2]$ with the appropriate organo-lithium reagent of composition $Li(tmen)(R'')$ (tmen = $N,N,-N',N'$-tetramethylethylenediamine), respectively (1),[9] (3),[14] (5),[13] and (7)[15] (Scheme 1). Further alkylation is possible to form $[Zr(R'')_2(\eta-C_5H_5)_2]$ for which *meso* and *rac* diastereo-isomers are possible on account of the presence of two chiral centres within each molecule but this is not pursued in this paper. Dialkylation was part of a previous study for the *ortho*-isomeric ligand of R^4, both *meso* and *rac* isomers having been isolated and interconverted.[2] It is noteworthy, however, that for $R'' = \bar{C}H(SiMe_3)_2$, also highly hindered, attempts to prepare the dialkyl species gave the alkane elimination product $[\{ZrR''(\sigma,\eta-C_5H_4)(\eta-C_5H_5)\}_m]$.[16] Presumably here the steric hindrance is too high to tolerate two bulky alkyl groups around the metal centre.

Selective monoalkylation using (1), (3), (5), and (7) was achieved by addition of a tetrahydrofuran (thf) solution of the organylating agent to a thf solution of $[ZrCl_2(\eta-C_5H_5)_2]$ at $-78\,°C$ [except for (5)] followed by slow warming of the mixture to ambient temperature. Reaction at *ca.* 20 °C yielded either a mixture of products for (7), intractable oils for (1) and (3), or the desired product, after subsequent heating to *ca.* 60 °C, for (5), albeit in low yield. The disparity for (5) possibly relates to greater steric hindrance of the alkyl group, R^3, than in (1), (3), and (7). Is there a simple inequality relating the steric hindrance of bulky alkyl groups? From the above discussion and the facts that *ortho*-substituents are likely to increase the hindrance, and the benzhydryl ligand $\bar{C}HPh_2$ readily yields the zirconocene dialkyl compound,[17] the following sequence appears to hold:
$$\bar{C}HPh_2 \leqslant \bar{C}HSiMe_3C_5H_4\dot{N}\text{-}2 \simeq \bar{C}HSiMe_3(\text{tolyl-}p) < \bar{C}HSi\text{-}Me_3(\text{tolyl-}o) \leqslant \bar{C}HSiMe_3C_6H_4\dot{P}Ph_2\text{-}o < \bar{C}HSiMe_3(C_{14}H_9\text{-}9) \leqslant \bar{C}H(SiMe_3)_2$$

While the steric hindrance of R'' can restrict dialkylation it is also important in stabilizing $[Zr(R'')Cl(\eta-C_5H_5)_2]$ with respect to redistribution to $[Zr(R'')_2(\eta-C_5H_5)_2]$ and $[ZrCl_2(\eta-C_5H_5)_2]$. We find, for example, that for the unsilylated analogue of R^2, a thf solution of $[Zr(R'')Cl(\eta-C_5H_5)_2]$ prepared from $Li(tmen)(CH_2C_6H_4PPh_2\text{-}o)$[14,18] gives isolated products con-
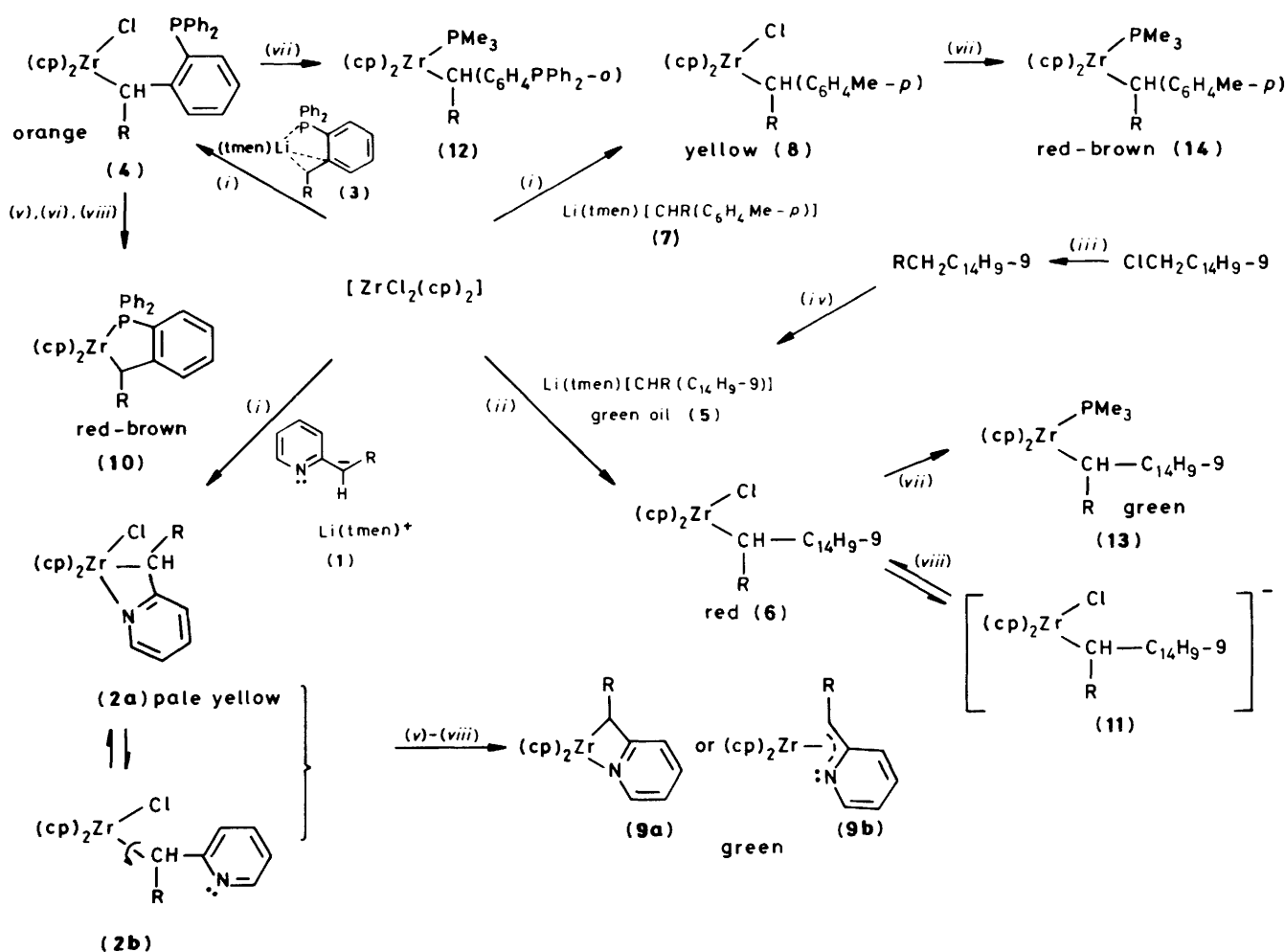
Scheme 1. R = $SiMe_3$, cp = η-C_5H_5, tmen = $Me_2NCH_2CH_2NMe_2$. (*i*) thf, $-78\,°C$; (*ii*) thf, 20 °C; (*iii*) Mg, thf, $SiMe_3Cl$; (*iv*) Li(tmen)Bu^n in hexane; (*v*) $Na[C_{10}H_8]$ (1 mol equiv.), thf, 20 °C or Na/Hg, thf, 20 °C; (*vi*) Na/Hg, toluene, 20 °C; (*vii*) Na/Hg, thf or toluene, PMe$_3$, 20 °C; (*viii*) electrochemistry in 0.2 mol l^{-1} [NBu$^n_4$][BF$_4$] in thf at a Pt electrode
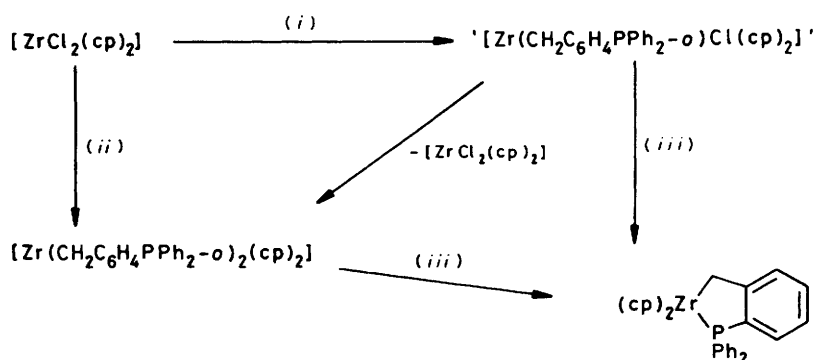
Scheme 2. cp = η-C_5H_5: thf, −78 °C, Li(tmen)($CH_2C_6H_4PPh_2$-o) [1 mol equiv. (i) or 2 mol equiv. (ii)]; (iii) Na[$C_{10}H_8$], thf, 20 °C

sistent with a redistribution reaction (Scheme 2), although there is evidence that the monoalkyl compound is the predominant species initially formed (see below). Similar results have been noted for R^n = $\bar{C}H_2Ph$[19] and $\bar{C}H_2PMe_2$.[20] (The more hindered phosphinomethyl $\bar{C}H_2PPh_2$ yields an isolable monoalkyl complex.)[3]

Syntheses of the organolithium precursors of [Zr(R^n)Cl(η-C_5H_5)$_2$] are, except for Li(tmen)[CHSiMe$_3$($C_{14}H_9$-9)] (5), described elsewhere,[9,14,15] (5) being prepared as a dark green oil (Scheme 1) by the well established route for metallating R'Me and Me$_3$SiCH$_2$R' type compounds (R' = aryl) of treating the organic substrate with Li(tmen)Bu^n in hexane (e.g. ref. 15 and refs. therein). 9-Trimethylsilylmethylanthracene was prepared from 9-chloromethylanthracene via the Grignard in situ trapping method that has proved valuable in preparing a variety of Me$_3$SiCH$_2$R' compounds. (CARE: The rate of addition of organic halide in thf to a suspension of Mg powder in thf and SiMe$_3$Cl is critical. If the addition is too slow an intense green colour results that is associated with a dramatic reduction in yield. The optimum rate corresponds to a reaction temperature close to 40 °C.) This method overcomes difficulties in preparing Grignard reagents of the benzylic type and the need then to treat them with SiMe$_3$Cl; the Grignard reagent of 9-chloromethylanthracene has only recently been prepared, using magnesium(anthracene)(thf)$_3$ as the source of magnesium.[21] Alternative methods for preparing 9-trimethylsilylmethylanthracene, possibly less convenient than the one described herein, include treating a lithium reagent with SiMe$_3$Cl,[12] and a nickel-catalysed cross-coupling reaction of Mg(CH$_2$SiMe$_3$)Cl and 9-bromoanthracene.[22]

Compounds (2), (4), (6), and (8) have been characterized by ^{1}H and ^{13}C n.m.r. spectroscopy, mass spectrometry ([P]$^+$ and [P − R^n]$^+$), microanalyses (C, H, and Cl), and structure determinations [(8) excepted: see structural commentary]. The variable-temperature ^{1}H n.m.r. spectrum of (2) is novel (Figure 1). At ambient temperature there is one cyclopentadienyl resonance while the limiting low-temperature spectrum shows the two distinct peaks that are predicted if a chelate ring is present, the SiMe$_3$ group at C$_α$ being directed out of the chelate ring plane towards one (η-C$_5$H$_5$) and the C$_α$ proton directed towards the other. There is no simple coalescence pattern for increasing temperature which is consistent with a temperature-dependent equilibrium in solution between the nitrogen-bound chelate complex (2a) and the nitrogen-free zirconium species (2b) (Scheme 1). For the latter, any restricted rotation about the Zr–C$_α$ bond, as found in [Zr{CH(SiMe$_3$)$_2$}Cl(η-C$_5$H$_5$)$_2$][17] may be controlled by the Lewis base interacting with the metal centre. Even with free rotation about the Zr–C$_α$ bond the polyhapto ligands are non-equivalent due to C$_α$ being a chiral
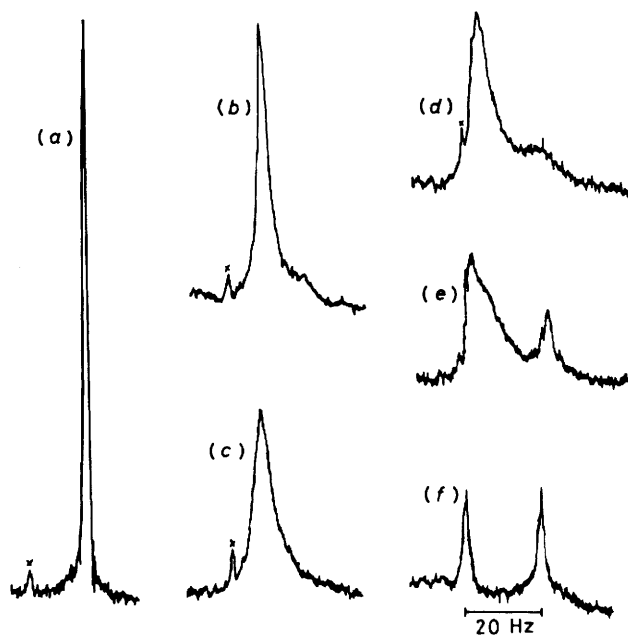
Figure 1. Variable-temperature ^{1}H n.m.r. spectrum (90 MHz, [$^2H_8$]-toluene) of the cyclopentadienyl protons in [Zr(CHSiMe$_3$C$_5$H$_4$N-2)-Cl(η-C$_5$H$_5$)$_2$]: (a) 35, (b) −47, (c) −60, (d) −65, (e) −74, (f) −86 °C (× = impurity)

centre. This, however, is not evident in the ^{1}H or ^{13}C n.m.r. spectra, in contrast to the spectra of (4), (6), and (8). Their variable-temperature spectra show no unusual features, consistent in the case of (4) with the absence of a Zr–P linkage as is found in the solid. The lack of a Zr–P interaction is most likely a consequence of steric effects since there is a precedent in the literature for Zr^{IV}–P bonding[20] and in principle a five-membered chelate ring for R^2 is stereochemically favourable. The alternative bridging mode for R^2 (or R^1) is unlikely on steric grounds.

d^0 ⟶ d^1 Studies.—Electrochemical and e.s.r. data derived from several reduction experiments of the d^0 compounds [Zr(R^n)Cl(η-C$_5$H$_5$)$_2$] are given in Table 1; $g_{av.}$ values (1.96—2.00), and, with the exception of (2), the reduction potentials [−2.01 to −1.64 V vs. s.c.e. (saturated calomel electrode) measured relative to the ferrocene couple (0.53 V vs. s.c.e.)] are within the range measured for a variety of zirconocene compounds.[17,23] The characteristic sextet for splitting by one

Table 1. E.s.r. and electrochemical data for the reduction of $[Zr(R'')Cl(\eta-C_5H_5)_2]$ in thf

Compound, R''	Reduction in thf			Reduction in thf–PMe₃			$E_{\frac{1}{2}}^{red}/V$ [b]	$t_{\frac{1}{2}}^{red}/s$ [c]
	$g_{av.}$	$a(^{91}Zr)$ [a]	$a(X)$ [a]	$g_{av.}$	$a(^{91}Zr)$ [a]	$a(X)$ [a]		
(2), $\overline{C}HSiMe_3C_5H_4N$-2 [d]	1.992	11.5	—	1.992	11.5	—	−1.17	irr.
(4), $\overline{C}HSiMe_3C_6H_4PPh_2$-o [d]	1.979	9.9	16.3 (d) [$a(^{31}P)$]	1.987	22.5	14.8 (d) [$a(^{31}P)$]	−1.92	irr.
(6), $\overline{C}HSiMe_3(C_{14}H_9$-9)	e	—	—	1.958	23.0	14.8 (d) [$a(^{31}P)$]	−1.64	>10 <50
(8), $\overline{C}HSiMe_3(C_6H_4Me$-p)	1.986	7.2	7.6 (d) [$a(^1H)$]	1.978	25.0	16.0 [$a(^{31}P)$]	−2.01	irr.
$\overline{C}HSiMe_3(C_6H_4Me$-o)	1.997	12.5	—	1.985	25.3	24.5 (d) [$a(^{31}P)$]	−1.72	rev.^f

[a] Measured in Gauss (1G = 10^{-4}T), sextet $a(^{91}Zr)$, d = doublet. [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] Similar e.s.r. data in toluene. [e] Complex spectrum, peaks not assigned. [f] M. F. Lappert and C. L. Raston, ref. 2 and unpublished work.

$^{91}Zr^{III}$ nucleus ($I = \frac{5}{2}$, 11.23% abundance) was invariably associated with hydrogen or phosphorus hyperfine coupling. Combination of the e.s.r. data for Na/Hg- and Na[$C_{10}H_8$]-generated d^1 species with results of the electrochemical studies, and results of the structure determinations of the N- and P-functionalized d^0 compounds, (2) and (4), yields insight into the nature of the d^1 species.

Reduction of (2) and (4) in thf using Na[$C_{10}H_8$] or toluene using Na/Hg at 20 °C gave green and red-brown solutions, respectively, that contained persistent (days) d^1 species. The following results indicate that on reduction heterolytic metal–chlorine bond breakage occurs: (i) the relative ease of irreversible reduction of (2) [$E_{\frac{1}{2}}^{red} = -1.17$ V vs. s.c.e.], compared with (4), (6), and (8) and the ortho-isomeric compound of (8) (Table 1) (this may be related to complexation of the N-Lewis base centre facilitating M–Cl bond rupture); (ii) irreversible reduction of (4), contrasting with reversible one-electron reduction for related compounds devoid of a functional group but with at least one substituent ortho to the benzylic carbon, viz. (6) and [Zr{CHSiMe₃(C₆H₄Me-o)}Cl(η-C₅H₅)₂];[2] (iii) the formation of a colourless precipitate of NaCl in each case; (iv) e.s.r. data for (2) and (4) are independent of solvent (thf or toluene) and reductant, ruling out solvent interaction with the metal centres; and (v) ^{31}P hyperfine coupling for reduced (4). The difference in reduction potentials for (2) and (4) and the relative ease of N- vs. P-complexation in the d^0 compounds suggests that reduction–elimination for (2) is a concerted process and is stepwise for (4).

The question of the type of metal–hydrocarbyl bonding in the d^1 species now arises. In the absence of hydrogen or nitrogen hyperfine coupling in reduced (2), deciding between a chelate complex, (9a), and η³-aza-allyl, (9b) (Scheme 1), or fluxional behaviour that is akin to that of the ubiquitous allyl ligand, would be speculative. It is noteworthy, however, that ^1H coupling is not usually associated with polyhapto ligands, e.g. η-C₅H₅, and this may also be the case for an η³-aza-allyl structure (9b). Moreover, the chelate ring in (9a) could be unfavourable relative to η³-aza-allyl formation due to ring strain within the four membered ring. It is therefore tempting to predict the reduced species to be (9b), an unprecedented transition metal η³-aza-allyl complex. (Only recently has this been established for a main group metal, lithium.)[9] Nevertheless, the related d^2 species [Mo(CHMeC₅H₄N-2)-(η-C₅H₅)₂] has been assigned the chelate ring structure.[24] The structure of reduced (4) is more definitive; all data are consistent with the formation of a stereochemically favoured five-membered chelate ring structure, (10).

Reduction of the d^0 compounds (4), (6), (8), and [Zr-

{CHSiMe₃(C₆H₄Me-o)}Cl(η-C₅H₅)₂][16] in the presence of PMe₃ yield d^1 species formulated as [Zr(R'')(PMe₃)(η-C₅H₅)₂] (Scheme 1). Complexation of PMe₃ on reduction of (6) and (8) is favourable due to its π-acceptor property. On reduction of (4) the preferential complexation of PMe₃ to the intramolecular phosphine most likely arises from PMe₃ being less sterically hindered and/or a stronger base than the internal phosphine residue. No phosphorus complexation was evident on the reduction of (2). This could be a consequence of the reduction product being an η³-aza-allyl, (9b). The alternative chelate structure (9a) has a strained four-membered ring that ought to be less favoured relative to formation of [Zr(R'')(PMe₃)(η-C₅H₅)₂].

Species (13) is relatively unstable ($t_{\frac{1}{2}}$ ca. 2 h, 20 °C) compared to (9), (10), (12), and (14) (days). Attempts to isolate the latter species as analytically pure compounds have been unsuccessful.

Compound (6) is reversibly reduced ($10 < t_{\frac{1}{2}} \lesssim 50$ s) although the separation of peaks, e.g. 70 mV at 100 mV s⁻¹, was higher than theoretical (59 mV) and therefore the experiment cannot be considered rigorously reversible. This 'reversible' behaviour has some precedent for alkylzirconocene chloride in that the related compound [Zr{CHSiMe₃(C₆H₄Me-o)}Cl(η-C₅H₅)₂] is reversibly reduced, having a reduction potential (-1.72 V vs. s.c.e.) similar to (6) (-1.64 V vs. s.c.e.). The fate of the chemically generated zirconate species (11) is unknown; the e.s.r. spectrum of reduced (6) in thf was complex indicating several species to be present. This is consistent with a rather short half life of reduced (11) determined from the electrochemical experiments. The apparently reversible reaction may occur via a pathway analogous to that proposed for [TiCl₂(η-C₅H₅)₂] in which chloride elimination follows the reduction, but a rapid equilibrium permits reco-ordination of the chloride prior to oxidation.[25]

Compound (8) is irreversibly reduced whereas its ortho-isomeric compound[16] and (6) are reversibly reduced. All other alkylzirconocene chloride compounds are irreversibly reduced[1] and the reduction potentials are typically 0.2—0.3 V more negative than the two cases where reversible reduction prevails [e.g., $E_{\frac{1}{2}}^{red}$ for (8) = -2.01 V vs. s.c.e.; cf. -1.64 V vs. s.c.e. for (6)]. The stability of the zirconate d^1 species, (11), and [Zr{CHSiMe₃(C₆H₄Me-o)}Cl(η-C₅H₅)₂]⁻,[16] but instability for that derived from (8) (and others),[1] is difficult to rationalize, although, interestingly, the ligands associated with 'stable' d^1 zirconate species have additional steric hindrance from ortho ring substituents.

We have attempted to prepare [Zr(CH₂C₆H₄PPh₂-o)Cl(η-C₅H₅)₂] using Li(tmen)(CH₂C₆H₄PPh₂-o)[18] for a comparative reduction study of the C_α-silylated analogue, (4). Although it is the predominant species generated in thf (see below) it proved

Table 2. Non-hydrogen atom co-ordinates for (2)

	Molecule 1			Molecule 2		
Atom*	x	y	z	x	y	z
Zr	0.159 28(4)	0.240 99(3)	0.229 34(5)	−0.154 21(5)	0.014 99(3)	0.211 44(5)
Cl	0.149 7(1)	0.132 1(1)	0.127 1(2)	−0.147 9(1)	0.119 7(1)	0.323 5(1)
C(0A)	0.201 1(−)	0.204 5(−)	0.395 9(−)	−0.206 3(−)	0.058 9(−)	0.050 3(−)
C(1A)	0.182 4(6)	0.150 6(4)	0.367 5(6)	−0.191 5(7)	0.110 8(3)	0.083 3(6)
C(2A)	0.265 9(5)	0.180 5(4)	0.374 0(5)	−0.269 4(6)	0.077 4(5)	0.078 5(6)
C(3A)	0.259 0(6)	0.243 6(4)	0.412 7(6)	−0.260 5(9)	0.017 9(5)	0.033 7(7)
C(4A)	0.173 0(7)	0.253 3(4)	0.425 4(6)	−0.176 0(10)	0.013 0(5)	0.013 3(6)
C(5A)	0.125 1(5)	0.194 7(5)	0.399 8(6)	−0.133 8(6)	0.071 9(5)	0.043 8(7)
C(0B)	0.027 4(−)	0.284 4(−)	0.152 8(−)	−0.019 0(−)	−0.027 1(−)	0.273 9(−)
C(1B)	0.016 1(9)	0.244 4(8)	0.092 6(11)	−0.045 8(6)	−0.077 5(5)	0.278 1(13)
C(2B)	0.053 9(8)	0.300 6(11)	0.083 1(12)	−0.036 1(8)	−0.034 3(8)	0.353 6(8)
C(3B)	0.057 8(10)	0.336 1(6)	0.169 8(22)	−0.000 0 7(8)	0.019 1(7)	0.322 1(16)
C(4B)	0.016 6(10)	0.298 8(12)	0.234 5(10)	0.008 4(8)	0.010 1(11)	0.220 6(16)
C(5B)	−0.007 2(6)	0.242 3(8)	0.183 8(16)	−0.020 6(10)	−0.052 9(10)	0.194 9(10)
Pyridine ligand						
N(1)	0.241 9(4)	0.338 3(3)	0.242 4(4)	−0.229 8(4)	−0.086 2(3)	0.189 6(4)
C(1)	0.242 3(5)	0.399 7(4)	0.285 5(2)	−0.226 2(5)	−0.144 8(4)	0.139 2(5)
C(2)	0.265 8(6)	0.453 6(4)	0.236 1(6)	−0.241 8(6)	−0.202 6(4)	0.184 5(7)
C(3)	0.289 2(6)	0.446 4(4)	0.139 3(6)	−0.259 4(6)	−0.202 5(4)	0.283 5(7)
C(4)	0.291 8(5)	0.385 7(4)	0.096 4(5)	−0.261 5(5)	−0.144 4(4)	0.336 6(6)
C(5)	0.270 2(4)	0.330 2(3)	0.151 7(5)	−0.248 8(4)	−0.084 4(3)	0.286 2(5)
C(6)	0.268 4(4)	0.259 6(3)	0.125 4(5)	−0.251 7(5)	−0.016 8(3)	0.323 1(5)
Si	0.382 9(1)	0.223 8(1)	0.154 2(2)	−0.367 5(2)	0.013 2(1)	0.310 3(2)
C(7)	0.448 7(5)	0.253 5(4)	0.282 5(6)	−0.414 0(7)	−0.022 5(6)	0.422 4(8)
C(8)	0.382 1(6)	0.131 7(4)	0.149 6(8)	−0.375 7(6)	0.105 9(5)	0.321 0(10)
C(9)	0.445 9(6)	0.251 4(5)	0.053 0(7)	−0.440 2(5)	−0.016 9(4)	0.186 5(8)

* C(0A) and C(0B) are the cyclopentadienyl centroids.

Table 3. Non-hydrogen atom co-ordinates for (4)

Atom*	x	y	z	Atom*	x	y	z
Zr	0.250 06(3)	0.283 10(3)	0.278 58(2)	C(5A)	0.293 6(4)	0.356 7(4)	0.195 8(2)
Cl	0.201 45(8)	0.126 65(8)	0.299 13(6)	C(0B)	0.169 2(−)	0.389 3(−)	0.304 9(−)
C(0A)	0.285 5(−)	0.272 9(−)	0.195 5(−)	C(1B)	0.176 9(4)	0.437 8(4)	0.267 0(2)
C(1A)	0.351 6(3)	0.289 5(4)	0.217 3(2)	C(2B)	0.121 5(3)	0.367 9(4)	0.265 8(3)
C(2A)	0.317 6(3)	0.199 4(3)	0.208 9(2)	C(3B)	0.131 0(4)	0.329 2(4)	0.318 4(3)
C(3A)	0.239 3(3)	0.210 9(4)	0.181 6(2)	C(4B)	0.193 3(5)	0.371 5(5)	0.353 1(3)
C(4A)	0.225 3(4)	0.307 9(4)	0.173 9(2)	C(5B)	0.223 2(3)	0.440 0(4)	0.320 3(3)
Silane ligand							
C(0)	0.362 3(2)	0.280 9(3)	0.350 6(2)	C(11B)	0.407 8(3)	0.204 5(3)	0.500 6(2)
Si	0.430 07(9)	0.385 46(10)	0.369 72(6)	C(12B)	0.386 7(3)	0.271 8(3)	0.537 1(2)
C(1)	0.399 1(4)	0.454 6(4)	0.427 7(2)	C(13B)	0.442 5(4)	0.314 5(4)	0.578 2(2)
C(2)	0.532 6(4)	0.346 8(5)	0.396 5(3)	C(14B)	0.519 8(4)	0.291 9(4)	0.582 7(2)
C(3)	0.436 3(4)	0.471 0(4)	0.311 7(2)	C(15B)	0.541 6(3)	0.226 1(4)	0.547 1(2)
P	0.329 14(6)	0.151 67(8)	0.447 59(5)	C(16B)	0.486 8(3)	0.183 1(3)	0.506 5(2)
C(11A)	0.386 3(2)	0.116 1(3)	0.394 5(2)	C(11C)	0.312 4(2)	0.038 5(3)	0.481 2(2)
C(12A)	0.400 4(2)	0.183 7(3)	0.354 5(2)	C(12C)	0.247 8(3)	−0.015 3(4)	0.456 3(2)
C(13A)	0.453 8(3)	0.157 7(4)	0.321 4(2)	C(13C)	0.230 6(3)	−0.099 9(4)	0.479 9(3)
C(14A)	0.488 2(3)	0.067 8(4)	0.324 2(2)	C(14C)	0.274 1(3)	−0.129 8(4)	0.530 3(2)
C(15A)	0.469 9(3)	0.000 9(3)	0.360 6(2)	C(15C)	0.336 9(3)	−0.077 9(4)	0.555 2(2)
C(16A)	0.419 8(3)	0.024 9(3)	0.395 8(2)	C(16C)	0.356 0(3)	0.005 4(3)	0.530 9(2)

* C(0A) and C(0B) are the cyclopentadienyl centroids.

difficult to isolate owing to redistribution to the dialkyl zirconocene and [ZrCl₂(η-C₅H₅)₂]. Reduction of the thf solution yielded a persistent d^1 species showing hyperfine coupling to two equivalent protons and one phosphorus [e.s.r. data: $g_{av.}$ 1.981, $a(^{91}Zr)$ 6.6 G, $a(^{31}P)$ 20.7 G (doublet), $a(^{1}H)$ 6.3 G (triplet)]. The same species was generated on reduction of [Zr(CH₂C₆H₄PPh₂-o)₂(η-C₅H₅)₂] (not isolated; see Scheme 2) in thf. Thus the d^1 species is most likely to be

[Zr(CH₂C₆H₄PPh₂-o)(η-C₅H₅)₂]. The presence of the dialkyl species in a thf solution of the monoalkyl can be ruled out since no reduced [ZrCl₂(η-C₅H₅)₂], the other redistribution product, was evident. E.s.r. data are similar to those recently reported for Zr^{III} intermediates [ZrR(L)(η-C₅H₅)₂] (R = primary alkyl, L = phosphine or phosphite)[5,26] and [Zr(CH₂PPh₂)(η-C₅H₅)₂].[3] The latter is prepared from the monoalkyl chloride,

Table 4. Non-hydrogen atom co-ordinates for (6)

Atom *	x	y	z	Atom *	x	y	z
Zr	0.810 95(2)	0.500 18(5)	0.347 00(2)	C(5A)	0.951 0(3)	0.392 2(6)	0.312 1(3)
Cl	0.841 29(8)	0.396 21(13)	0.479 62(6)	C(0B)	0.694 5(−)	0.395 6(−)	0.300 9(−)
C(0A)	0.934 2(−)	0.509 3(−)	0.287 8(−)	C(1B)	0.667 6(3)	0.509 3(7)	0.282 3(4)
C(1A)	0.909 7(3)	0.424 2(7)	0.239 3(4)	C(2B)	0.656 7(3)	0.442 0(7)	0.355 2(4)
C(2A)	0.901 4(3)	0.574 4(7)	0.234 6(3)	C(3B)	0.698 3(4)	0.309 1(7)	0.352 3(4)
C(3A)	0.939 3(3)	0.633 4(7)	0.302 5(3)	C(4B)	0.734 9(3)	0.296 5(6)	0.279 6(3)
C(4A)	0.969 6(3)	0.522 1(6)	0.350 1(3)	C(5B)	0.715 2(4)	0.421 2(7)	0.235 2(4)

Silane ligand

	x	y	z		x	y	z
C(0)	0.768 7(2)	0.727 2(4)	0.394 2(2)	C(6)	0.618 7(4)	1.025 8(5)	0.185 3(3)
Si	0.839 35(8)	0.862 91(13)	0.446 44(7)	C(7)	0.616 2(3)	0.952 2(5)	0.260 5(2)
C(1S)	0.886 6(4)	1.003 6(7)	0.381 1(4)	C(8)	0.545 0(3)	0.948 5(6)	0.304 5(3)
C(2S)	0.777 1(5)	0.967 2(7)	0.519 6(4)	C(9)	0.541 4(3)	0.875 0(5)	0.377 2(3)
C(3S)	0.924 8(4)	0.773 3(8)	0.507 0(4)	C(10)	0.467 3(3)	0.870 2(7)	0.420 4(4)
C(1)	0.690 3(2)	0.802 5(4)	0.364 4(2)	C(11)	0.463 9(4)	0.803 3(8)	0.491 2(4)
C(2)	0.689 2(3)	0.876 9(4)	0.289 7(2)	C(12)	0.534 8(4)	0.733 8(6)	0.523 7(3)
C(3)	0.759 8(3)	0.877 0(5)	0.239 7(3)	C(13)	0.607 9(3)	0.734 0(5)	0.484 7(3)
C(4)	0.758 8(4)	0.946 8(6)	0.167 4(3)	C(14)	0.615 2(2)	0.803 2(4)	0.408 0(2)
C(5)	0.687 1(4)	1.022 5(5)	0.141 3(3)				

* C(0A) and C(0B) are the cyclopentadienyl ring centroids.

Table 5. The zirconium environments *

Compound (2)

	r(Zr–L)	C(6)	N	C(0A)	C(0B)
Cl	2.564(2), 2.563(2)	79.5(2), 80.6(3)	137.7(2), 139.0(2)	100.9, 99.4	98.9, 100.5
C(6)	2.38(1), 2.37(1)		58.2(2), 58.5(2)	119.7, 121.3	111.2, 109.2
N	2.334(5), 2.347(6)	58.2(2), 58.5(2)		99.2, 98.9	97.5, 96.5
C(0A)	2.25_2, 2.26_7	119.7, 121.3	99.2, 98.9		127.7, 127.9
C(1A)	2.54(1), 2.55(1)	119.9(3), 121.2(2)	124.1(2), 123.1(2)	27.4, 26.6	125.5, 126.7
C(2A)	2.55(1), 2.55(1)	94.1(2), 96.3(3)	95.3(2), 95.2(3)	27.9, 27.1	154.7, 154.4
C(3A)	2.56(1), 2.54(1)	99.4(3), 100.9(3)	72.4(2), 72.4(3)	27.4, 27.2	136.2, 135.8
C(4A)	2.52(1), 2.53(1)	128.8(3), 130.1(4)	84.7(2), 84.3(3)	27.7, 28.0	107.1, 106.7
C(5A)	2.55(1), 2.53(1)	146.9(2), 148.0(3)	116.8(2), 115.8(3)	28.0, 27.3	101.8, 102.7
C(0B)	2.25_1, 2.24_1	111.2, 109.2	97.5, 96.5	127.7, 127.9	
C(1B)	2.54(1), 2.54(1)	102.2(4), 92.5(4)	114.4(4), 70.9(3)	136.1, 133.7	26.0, 25.8
C(2B)	2.54(2), 2.53(1)	85.3(4), 84.1(3)	85.0(4), 90.6(4)	152.9, 154.3	25.9, 26.5
C(3B)	2.50(1), 2.51(1)	99.5(6), 107.1(5)	70.7(4), 119.0(4)	126.6, 129.6	27.3, 26.8
C(4B)	2.50(2), 2.48(1)	131.3(5), 135.5(5)	93.8(5), 116.2(5)	102.4, 103.2	27.2, 27.8
C(5B)	2.51(1), 2.52(2)	131.6(5), 121.9(4)	121.5(4), 84.6(4)	108.3, 106.4	26.5, 27.1

Compound (4)

	r(Zr–L)	C(0)	C(0A)	C(0B)
Cl	2.438(1)	96.1(1)	107.2	106.4
C(0)	2.350(4)		109.7	105.9
C(0A)	2.222	109.7		127.2
C(1A)	2.519(6)	82.2(2)	28.2	134.3
C(2A)	2.526(6)	93.7(2)	28.0	154.7
C(3A)	2.532(5)	125.8(2)	27.9	126.7
C(4A)	2.513(5)	134.9(2)	28.0	101.7
C(5A)	2.501(6)	105.3(2)	28.3	105.1
C(0B)	2.225	105.9	127.2	
C(1B)	2.503(6)	115.1(2)	100.3	27.9
C(2B)	2.495(6)	133.7(2)	108.5	28.0
C(3B)	2.530(8)	110.0(2)	138.8	27.2
C(4B)	2.542(8)	81.9(2)	152.8	27.9
C(5B)	2.504(6)	84.5(2)	121.9	28.1

Compound (6)

	r(Zr–L)	C(0)	C(0A)	C(0B)
Cl	2.454(1)	95.5(1)	105.3	106.5
C(0)	2.349(4)		112.4	105.1
C(0A)	2.234	112.4		127.2
C(1A)	2.530(6)	132.8(2)	27.9	99.6
C(2A)	2.503(6)	100.8(2)	28.2	110.8
C(3A)	2.525(6)	84.7(2)	27.8	142.4
C(4A)	2.544(5)	102.7(2)	27.6	150.3
C(5A)	2.535(5)	134.0(2)	27.9	119.1
C(0B)	2.215	105.1	127.2	
C(1B)	2.507(6)	81.2(2)	127.9	27.9
C(2B)	2.532(5)	83.2(2)	154.9	27.9
C(3B)	2.526(3)	113.6(2)	132.9	27.7
C(4B)	2.493(6)	133.3(2)	104.6	28.3
C(5B)	2.490(6)	109.8(2)	102.0	28.3

* Selected geometries: the values in the first column are the zirconium–ligand atom distances (Å). Other entries are the angles subtended at the zirconium atom by the relevant atoms at the head of the row and column. C(0A) and C(0B) are the cyclopentadienyl centroids. The two values in each entry for (2) are for molecules 1,2 respectively.

the dialkyl analogue undergoing loss of $C_5H_5^-$ on reduction[4] in contrast to the Zr–C_α cleavage for [Zr(CH$_2$C$_6$H$_4$PPh$_2$-o)$_2$(η-C$_5$H$_5$)$_2$] which is usually associated with reduction of dialkyl zirconocene compounds.[16,27]

E.s.r. spectra of reduced solutions of (2), (4), (6), and (8) under a dinitrogen atmosphere were the same as under argon. Thus no dinitrogen complexation occurred, in contrast to formation of [Zr{CH(SiMe$_3$)$_2$}(η-N$_2$)(η-C$_5$H$_4$R)$_2$] (showing coupling to
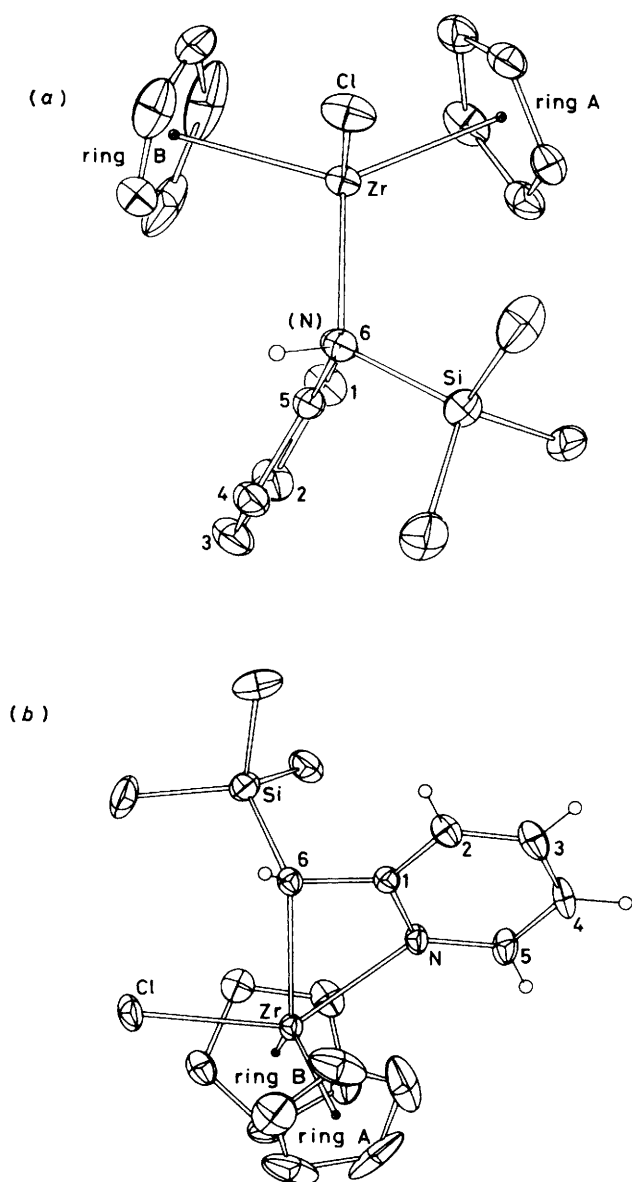
(a)

(b)

Figure 2. Molecular projections of [Zr(CHSiMe₃C₅H₄N-2)Cl(η-C₅H₅)₂] (2) (molecule 1) onto (a) C(0A),C(0B),N plane, and (b) approximately the ZrNCl plane, showing 20% thermal ellipsoids for non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å

two equivalent N centres) on the reduction of [Zr{CH(Si-Me₃)₂}Cl(η-C₅H₄R)₂] (R = H or Me).[6] While R² and R³ are like ČH(SiMe₃)₂ in being highly hindered alkyls, factors other than steric must be important for dinitrogen uptake.

Structural Commentary.—X-Ray structure determinations of (2), (4), and (6) show that they comprise discrete molecules, the asymmetric unit being two molecules of the same connectivities and geometries, (2), or a single molecule, (4) and (6). Results are given in Tables 2—5 and Figures 2—4.

Assuming the polyhapto groups occupy one co-ordination site, the complex molecules are five-co-ordinate, (2), or four-co-ordinate, (4) and (6); the functional group in (4), unlike in (2), is not bound to the metal centre. In each structure, the angle subtended at the metal by the 'staggered' cyclopentadienyl groups is enlarged relative to those within the other section of

the co-ordination sphere, a consequence of the large steric requirements of η-C₅H₅. These angles lie within the range established for d^0 [ZrX₂(η-C₅H₄R)₂] (R = H or alkyl, X = unidentate) compounds of 126—133°.[23] It is an angle that has proved relatively insensitive to variation in steric hindrance of the alkyl ligand, e.g. 129.2 and 128.1° for [Zr{CH(SiMe₃)₂}Cl-(η-C₅H₄R)₂] (R = Bu' or SiMe₃),[17] 127.4° for [Zr{CHSi-Me₃(C₆H₄Me-o)}Cl(η-C₅H₅)₂],[16] 127.7 and 127.9° for (2), 127.2° for (4), and 127.2° for (6). Comparable with these centroid–Zr–centroid angles is that of the parent compound [ZrCl₂(η-C₅H₅)₂] (126°).[28]

Five-co-ordinate 18-electron zirconocene complexes that have been structurally authenticated are relatively few in number compared with four-co-ordinate 16-electron compounds. The former include [Zr(OSO₂CF₃)₂(thf)(η-C₅H₅)₂] and [Zr(OH₂)₃(η-C₅H₅)₂][O₃SCF₃]₂,[29] and some with a bidentate ligand, viz. [(η-C₅H₅)₂ClZr(PR₂CHCO)ZrCl(η-C₅-H₅)₂] (R = Me[20] or Ph[30]), [{Zr(μ-OCH₂CH₂CHMe)(η-C₅H₅)₂}₂] (15),[31] [Zr(S₂CNEt₂)Cl(η-C₅H₅)₂] (16), and [Zr(OCSNMe₂)Cl(η-C₅H₅)₂] (17).[32] The arrangement of ligands around the metal centre in (2) approximates to a bidentate ligand residing above a triangle of unidentate ligands with the unique unidentate ligand, Cl, lying in the plane of the bidentate [Figure 2(a)]. The absence of a Zr–P linkage in (4) is most likely due to steric effects (see above).

In five-co-ordinate (2) [and four-co-ordinate (4) and (6)] the Zr–η-C distances lie within the range for four-co-ordinate zirconocene species.[23] Other metal–ligand distances in (2) are 1—2% longer than is usual in four-co-ordinate species. (This has previously been noted for five-co-ordinate complexes, having been ascribed to steric crowding around the metal centre.[31]) The Zr–σ-C distances in (2) (2.38₁ Å) and (15) [2.38(1) Å][31] are, for example, longer than those in (4) [2.350(4) Å] and (6) [2.349(4) Å] which are within the limit established for four-co-ordinate alkylzirconocene complexes;[23] only in highly hindered dialkyl compounds are the Zr–σ-C distances closer to that in (2), e.g. in [Zr(CHPh₂)₂(η-C₅H₅)₂] (2.388 Å)[8] and meso-[Zr{(CHSiMe₃)₂C₆H₄-o}(η-C₅H₅)₂] (2.37₄ Å).[33]

The Zr–Cl distance in (2) is also long, 2.56₃ Å, hitherto the longest for a metallocene complex; it is, however, only marginally longer than in five-co-ordinate (16) [2.556(2) Å] and (17) [2.550(2) Å][32] but significantly longer than in (4) [2.438(1) Å] and (6) [2.454(1) Å], which are typical Zr–Cl distances (range in the literature 2.42—2.52 Å).[23] Surprisingly the Zr–N distance is short (2.34₁ Å) compared with that in [Zr(NC₅H₅)(η²-COCH₂)(η-C₅Me₅)₂] [2.403(1) Å];[34] it is, of course, longer than for an anionic N-centred ligand as in [Zr{N(CH₂)₄}₂(η-C₅H₅)₂] [Zr–N 2.198(6) Å].[35]

In (2), at least in the solid state, the hindered anionic centre, C_{α}, is in the least sterically encumbered position cis to the chlorine atom. An interesting feature of the 'alkyl' ligand is the 'folding' of the bidentate ligand along the C_{α}–N vector, the dihedral angles between the pyridine plane and the ZrClNC(0) plane being 28.4 and 28.2° for molecules 1 and 2 respectively. The origin of this appears to be otherwise unfavourable non-bonding contacts between SiMe₃ and its adjacent η-C₅H₅ moiety [close contacts H(7b)···H(2A),H(3A) 2.33, 2.36, H(8a)···H(1A) 2.44 Å, molecule 1; H(7b)···H(5A) 2.44, H(9a)···H(4A) 2.46 Å, molecule 2]. The Zr–C₈[C(5)] distances in (2), 2.81(1) and 2.77(1) Å, are short compared with the corresponding distances in (4) [3.206(4) Å] and (6) [3.414(4) Å]. The origin of this may be an interaction of the π bond with the metal centre and/or steric effects (see above). The bonding of the ligand appears to be intermediate between a chelate structure as in (2a) and an η³-aza-allyl structure that is possible for reduced (2), being reminiscent of the intermediate σ,η⁴-bonding for o-xylenediyl ligands (ref. 33 and refs. therein). Some

(a)

(b)
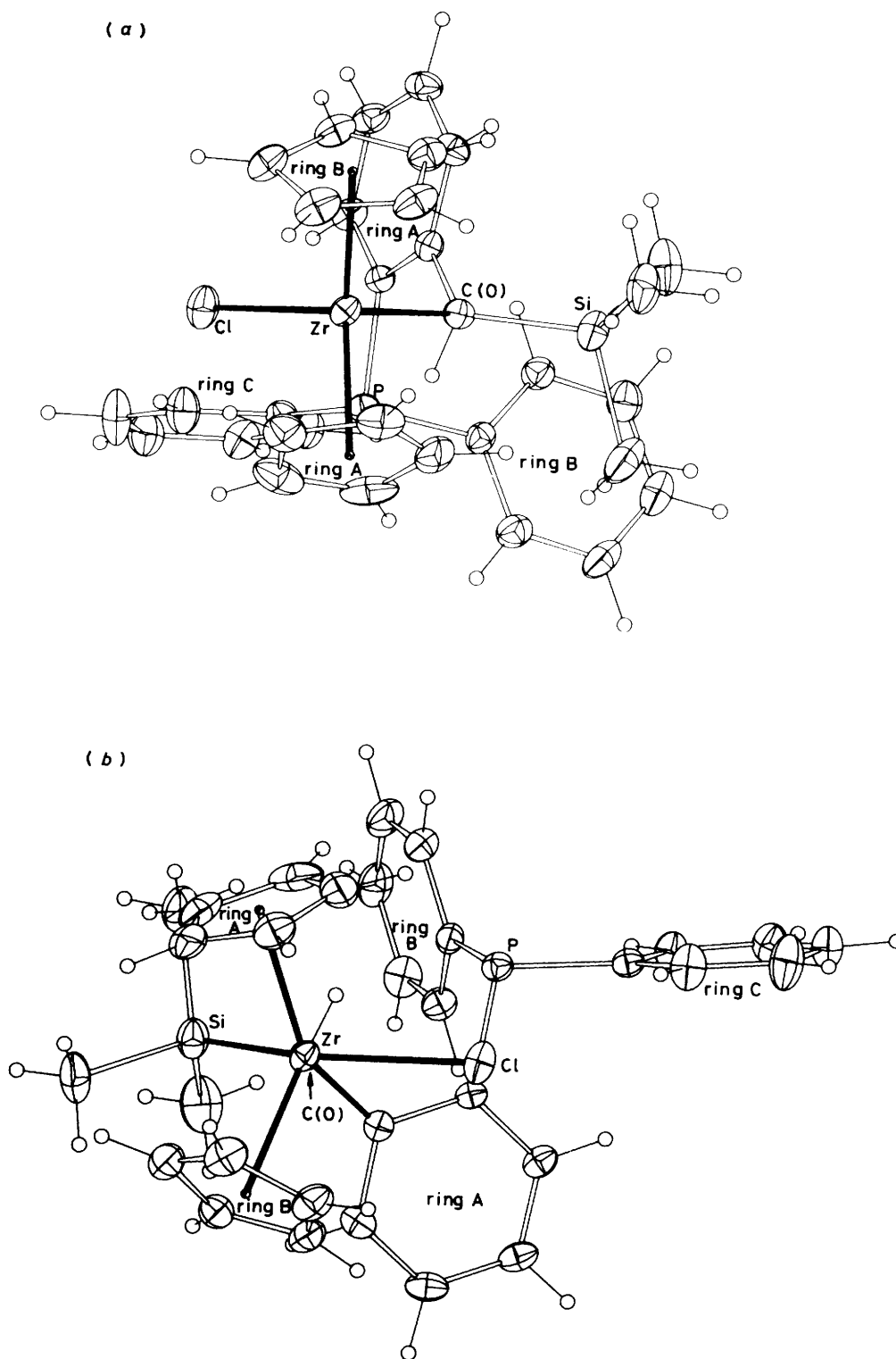
Figure 3. Molecular projections of [Zr(CHSiMe$_3$C$_6$H$_4$PPh$_2$-o)Cl(η-C$_5$H$_5$)$_2$] (4) down (a) bisector of C(0A)–Zr–C(0B) angle and (b) Zr–C(0) bond; other details as in Figure 2

Zr π contribution to bonding has been noted in complexes with unidentate ligands, e.g. Zr–C$_\beta$ in [Zr(CH$_2$Ph)$_4$] is 2.96 Å [36] and in [Zr{C(Ph)CMe$_2$}Cl(η-C$_5$H$_5$)$_2$], 2.953 Å.[23] The Cl–Zr–σ-C angle in the latter is anomalously high at 108.9°, further evidence for a π interaction that is absent in (4) and (6) in which

the angles in question are 96.1(1) and 95.5(1)°, respectively, lying within the range for complexes with less hindered unidentate ligands, 90—96°.[23] Only in highly congested systems and the one described above with close metal–C$_\beta$ contacts is this angle significantly enlarged, e.g. [Zr{CH(SiMe$_3$)$_2$}Cl(η-C$_5$-
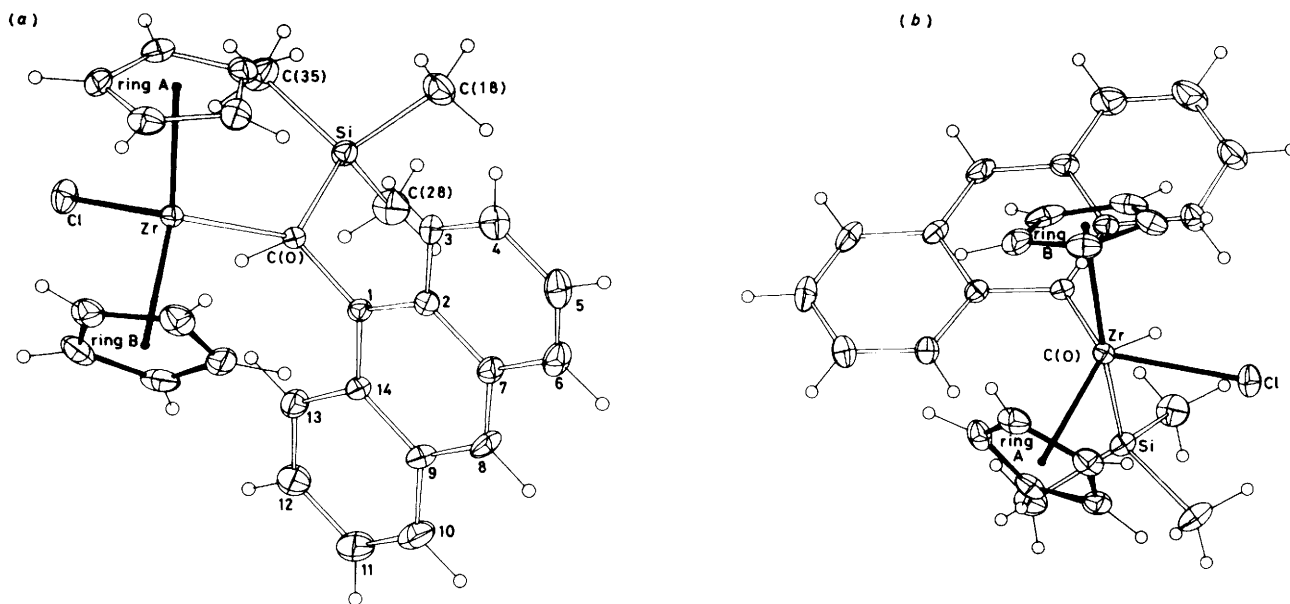
Figure 4. Molecular projections of $[Zr\{CHSiMe_3(C_{14}H_9\text{-}9)\}Cl(\eta\text{-}C_5H_5)_2]$ (**6**); definitions of (*a*) and (*b*) and other details as in Figure 3

$H_4R)_2]$ [R = Bu^t (98.2) or SiMe$_3$ (99.9°)][17] and [Zr{CH-(SiMe$_3$)$_2$}Ph(η-C$_5$H$_5$)$_2$], 100.4°.[37]

The conformation of (**4**) and (**6**) along the Zr–chiral C_α bond is shown in Figures 3(*b*) and 4(*b*). In (**4**) the SiMe$_3$ moiety lies astride the cyclopentadienyl ligands as for one SiMe$_3$ group in $[Zr\{CH(SiMe_3)_2\}Cl(\eta\text{-}C_5H_4R)_2]$ (R = Bu^t or SiMe$_3$)[17] and in $[Zr\{CH(SiMe_3)_2\}Ph(\eta\text{-}C_5H_5)_2]$.[37] The similarity in conformation and the relationship between steric hindrance and conformation further highlights the similarity in steric hindrance of $\overline{R^2}$ and $\overline{CH(SiMe_3)_2}$, discussed above. A new conformation, in between staggered and eclipsed, is found in (**6**) which possibly results from greater steric hindrance associated with the aryl group bearing two *ortho* substituents. In this context the $Zr\text{-}C_\alpha\text{-}C_\beta$ angle is high, 123.2(3)° *cf.* 110.3(4)° in (**4**) and 90.4(8) and 89.2(8)° in (**2**); other angles about C_α are similar to those in (**4**) [and (**2**)] *viz.* Si$\text{-}C_\alpha\text{-}C_\beta$ 116.4(3)° in (**4**), 109.0(3)° in (**6**), 110.8(4) and 111.8(5)° in (**2**); Si$\text{-}C_\alpha\text{-}Zr$ 124.1(2)° in (**4**), 125.2(2)° in (**6**), twice 124.5(3)° in (**2**). The similarity in Zr, Si$\text{-}C_\alpha\text{-}C_\beta$ angles in (**6**) is further evidence for the large steric hindrance of the aryl group R^3. Interestingly the C_α substituents, SiMe$_3$ and ZrCl(η-C$_5$H$_5$)$_2$, are approximately equally disposed on either side of the aromatic plane with the C_α proton residing in the plane [see Figure 4(*a*)].

Experimental

General Procedures.—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 LiAlH$_4$ (thf), CaH$_2$ (hexane), and Na (toluene, OEt$_2$, and tmen).

Materials.—The organolithium reagents (**1**) and (**3**) (Scheme 1) were prepared as highly crystalline solids by metallation of the appropriate silylated pyridine and phosphine respectively using Li(tmen)Bu^n in hexane.[14] Li(tmen)[CHSiMe$_3$(C$_6$H$_4$-Me-*p*)] (**7**) was prepared according to the literature procedure.[15]

Physical and Analytical Measurements.—The $g_{av.}$ values from e.s.r. data were measured at 20 °C relative to polycrystalline 2,2-diphenylpicrylhydrazyl (dpph) using a Brüker ER100 spectro-

meter. Proton and ^{13}C n.m.r. were recorded on Hitachi–Perkin-Elmer R-24B (60 MHz) or Brüker WP-80 (80 MHz) spectro-meters; J values are in Hz. I.r. spectra were recorded on a Perkin-Elmer 283 spectrometer. Elemental (C, H, Cl) analyses of the compounds were performed by the Canadian Micro-analytical Service Ltd., Vancouver. The electrochemical experiments were carried out using a P.A.R. 173 potentiostat, P.A.R. 175 programmer, and Bryans 26000 X–Y chart recorder. Details of the cell, fitted with a Ag/Ag$^+$ reference electrode have been described elsewhere.[38] All solutions were prepared to be 0.2 mol l^{-1} in [NBu$^n_4$][BF$_4$] and 1.0 × 10^{-3} mol l^{-1} in the active species. Potentials were internally referenced by adding ferrocene or bis(biphenyl)chromium(I) tetraphenylborate and are reported against the s.c.e. Half lives of unstable species were determined from cyclic voltammetry using the method of Nicholson and Shain.[39] The uncertainties in these values, due to difficulty in obtaining reproducible measurements, give error bounds such that the true value can be considered to be between half the value quoted and twice the value quoted.

Synthesis of $\overline{[Zr(CHSiMe_3C_5H_4N\text{-}2)Cl(\eta\text{-}C_5H_5)_2]}$ (**2**).—A solution of Li(tmen)(CHSiMe$_3$C$_5$H$_4$N-2) (**1**) (1.56 g, 5.5 mmol) in thf (10 cm^3) was added slowly to a solution of [ZrCl$_2$(η-C$_5$H$_5$)$_2$] (1.9 g, 6.5 mmol) in thf (20 cm^3). On warming to room temperature the solvent was removed *in vacuo* from the resulting yellow solution. The residue was then extracted with a refluxing hexane–diethyl ether mixture (4:1, 25 cm^3) and the extract filtered and concentrated to *ca.* 5 cm^3. On standing overnight pale yellow crystals of the *title compound* formed. These were collected, washed with hexane (2 × 2 cm^3) and dried *in vacuo* (1.75 g, 76%), m.p. 108—110 °C (decomp.) (Found: C, 53.8; H, 5.55; N, 3.50. Calc. for C$_{19}$H$_{24}$ClNSiZr: C, 54.2; H, 5.75; N, 3.35%). ^{1}H N.m.r. (60 MHz, C$_6$D$_6$), δ −0.20 (s, 9 H, MeSi), 1.75 (s, 1 H, CHSi), 5.2 (s, 10 H, C$_5$H$_5$), 5.65—6.70 (m, 3 H, pyridyl), 7.65 (d, 1 H, NCH); ^{13}C n.m.r. (^{1}H decoupled, C$_6$D$_6$), δ 2.7 (Me$_3$Si), 38.8 (CHSi), 114.7 (C$_5$H$_5$), 112.4, 116.6, 131.4, 139.1, 148.5 (C$_5$H$_4$N); mass spectrum (*m/e*), 421 [*P*]$^+$, 256 [C$_{10}$H$_{10}$ClZr]$^+$.

Synthesis of [Zr(CHSiMe$_3$C$_6$H$_4$PPh$_2$-*o*)Cl(η-C$_5$H$_5$)$_2$] (**4**).—A solution of Li(tmen)(CHSiMe$_3$C$_6$H$_4$PPh$_2$-*o*) (**3**) (2.0 g, 4.3

mmol) in thf (20 cm^3) was added slowly to a solution of [ZrCl$_2$(η-C$_5$H$_5$)$_2$] (1.24 g, 4.3 mmol) in thf (40 cm^3) at -78 °C. On warming to room temperature the solvent was removed *in vacuo* from the resulting orange-red solution. The residue was then extracted with toluene (50 cm^3), and the extract filtered and concentrated to *ca.* 10 cm^3. Cooling of this solution overnight at -30 °C afforded orange-red crystals of the *title compound* which were collected, washed with toluene–hexane (1:1, 3 $\times$ 5 cm^3) and dried *in vacuo* (2.0 g, 78%), m.p. 182—183 °C (Found: C, 63.4; H, 5.50; Cl, 5.25. Calc. for C$_{32}$H$_{34}$ClPSiZr: C, 63.6; H, 5.60; Cl, 5.90%). ^{1}H N.m.r. (60 MHz, C$_6$D$_6$), δ 0.17 (s, 9 H, SiMe$_3$), 4.39 (d, 1 H, HCSi, J_p 21 Hz), 5.90, 6.10 (s, 10 H, 2C$_5$H$_5$), 6.99—7.67 (m, 14 H, C$_6$H$_4$ + 2Ph); ^{13}C n.m.r. (^{1}H decoupled, C$_6$D$_6$), δ 3.5 (Me$_3$Si), 66.0 (CHSi), 114.0 (C$_5$H$_5$), 114.6 (C$_5$H$_5'$), 115.0, 115.4, 116.2, 122.5, 125.7, 126.1, 129.4, 130.6, 132.3, 134.2, 135.2, 135.7 (C$_6$H$_4$ + 2 Ph); ^{31}P n.m.r. (C$_6$D$_6$,H$_3$PO$_4$), δ -16.0; mass spectrum (*m/e*), 604 [*P*]$^+$, 256 [C$_{10}$H$_{10}$ClZr]$^+$.

Synthesis of 9-Trimethylsilylmethylanthracene.—To a stirred suspension of magnesium powder (May and Baker; 0.2 g, 8.3 mmol) in SiMe$_3$Cl (1 g, 8.6 mmol) and thf (10 cm^3) was added a thf solution of 9-chloromethylanthracene (1.0 g, 4.4 mmol) over *ca.* 1 h. The resulting green solution was then stirred for a further 0.5 h whereupon the solvent was removed *in vacuo* and HCl (5 cm^3, 2 mol l^{-1}) added. The organic residue was extracted with hexane (50 cm^3), the extract separated and dried (MgSO$_4$), and the solvent removed *in vacuo* yielding a yellow solid. Recrystallization from methanol (10 cm^3) at -30 °C afforded crystals of the *title compound* (1.05 g, 90%), m.p. 62—63 °C (Found: C, 81.4; H, 7.80. Calc. for C$_{18}$H$_{20}$Si: C, 81.8; H, 7.60%). ^{1}H N.m.r. (60 MHz, CDCl$_3$), δ -0.10 (s, 9 H, SiMe$_3$), 3.02 (s, 2 H, CH$_2$Si), 7.21 (m, 4 H, aromatic), 7.83 (m, 5 H, aromatic); ^{13}C n.m.r. (^{1}H decoupled, CDCl$_3$), δ 0.1 (Me$_3$Si), 19.2 (CH$_2$), 124.0, 124.8, 125.1, 125.8, 129.5, 132.1, 134.6 (aromatic); mass spectrum (*m/e*), 264 [*P*]$^+$, 249, 233, 191, 189.

Synthesis of [Zr{CHSiMe$_3$(C$_{14}$H$_9$-9)}Cl(η-C$_5$H$_5$)$_2$] (6).— To a hexane solution of 9-trimethylsilylmethylanthracene (1.0 g, 3.78 mmol) in hexane (5 cm^3) at 0 °C was added LiBu^n (2.45 cm^3, 1.7 mol l^{-1} in hexane, 4.2 mmol) then tmen (0.62 cm^3, 4.4 mmol), yielding a dark green oil. The solvent was removed *in vacuo* and the residue washed with hexane (2 $\times$ 5 cm^3) and dried *in vacuo*. The green oil was then taken up in thf (20 cm^3) and added to a solution of zirconocene dichloride (1.12 g, 3.8 mmol) in thf (50 cm^3). The mixture was heated to *ca.* 60 °C for 0.5 h then the solvent removed *in vacuo* and the residue extracted with hot hexane (50 cm^3). After cooling to 0 °C the extract was filtered and kept at -30 °C overnight whereupon red prisms of the *title compound* deposited (0.64 g, 33%), m.p. 149—150 °C (decomp.) (Found: C, 64.7; H, 5.55; Cl, 6.65. Calc. for C$_{28}$H$_{29}$ClSiZr: C, 64.6; H, 5.60; Cl, 6.80%). ^{1}H N.m.r. (60 MHz, C$_6$D$_6$), δ 0.20 (s, 9 H, SiMe$_3$), 2.65 (s, 1 H, CHSi), 5.77 (s, 10 H, C$_5$H$_5$), 7.37 (m, 4 H, anthryl), 7.92 (m, 3 H, anthryl), 8.35 (m, 2 H, anthryl); ^{13}C n.m.r. (^{1}H decoupled, C$_6$D$_6$), δ 3.7 (SiMe$_3$), 63.8 (CHSi), 114.1 (C$_5$H$_5$), 114.2 (C$_5$H$_5'$), 121.7, 123.3, 124.7, 125.3, 125.6, 129.2, 130.4, 132.3, 132.7, 153.4 (C$_{14}$H$_9$); mass spectrum (*m/e*), 520 [*P*]$^+$, 256 [C$_{10}$H$_{10}$ZrCl]$^+$.

Synthesis of [Zr{CHSiMe$_3$(C$_6$H$_4$Me-*p*)}Cl(η-C$_5$H$_5$)$_2$] (8).— To a solution of [ZrCl$_2$(η-C$_5$H$_5$)$_2$] (2.20 g, 7.55 mmol) in thf (200 cm^3) at -78 °C was added dropwise a solution of Li(tmen)[CHSiMe$_3$(C$_6$H$_4$Me-*p*)] (7) (2.28 g, 7.55 mmol) in thf (100 cm^3). The resulting orange solution was warmed to room temperature, stirred for 2 h, then the solvent was removed *in vacuo* and the product extracted with diethyl ether (*ca.* 100 cm^3). Concentration of the filtrate to *ca.* 100 cm^3 and cooling for 18 h at *ca.* -30 °C afforded orange crystals of the *title compound*

(2.06 g, 63%), m.p. 152 °C (Found: 58.1; H, 6.30. Calc. for C$_{21}$H$_{27}$ClSiZr: C, 58.1; H, 6.30%). ^{1}H N.m.r. (60 MHz, C$_6$D$_6$), δ 0.35 (s, 9 H, SiMe$_3$), 2.35 (s, 1 H, HCSi), 2.37 (s, 3 H, C$_6$H$_4$*Me*), 5.85 (s, 5 H, C$_5$H$_5$), 6.08 (s, 5 H, C$_5$H$_5$), 7.00 (m, 4 H, C$_6$H$_4$); ^{13}C n.m.r. (^{1}H decoupled, C$_6$D$_6$), δ 2.4 (Me$_3$Si), 20.8 (CH$_3$), 66.5 (CH), 113.4 (C$_5$H$_5$), 114.1 (C$_5$H$_5'$), 126.8, 129.0, 130.3, 148.5 (C$_6$H$_4$); mass spectrum (*m/e*), 433 [*P*]$^+$, 398 [*P* $-$ Cl]$^+$, 256 [C$_{10}$H$_{10}$ClZr]$^+$.

Reduction of [Zr(R^n)Cl(η-C$_5$H$_5$)$_2$], *Complexes* (2), (4), (6), *and* (8).—Dropwise addition of a thf solution of sodium dihydronaphthylide (<1 mol equiv.) to a thf solution of (2), (4), and (6) (1 mol equiv.) generated a green [(2) and (6)] or red-brown solution. The e.s.r. spectra were then recorded immediately; in each case the e.s.r. spectrum was identical to that derived from reduction using Na/Hg ($\leqslant 1$ mol equiv. of Na) in thf, or toluene for (2) and (4). Compounds (6) and (8) were reduced to Zr^{III} species using Na/Hg, as for (2) and (4), in thf. The derived e.s.r. data, and those for the reduction of (2), (4), (6), and (8) using the same methods but with PMe$_3$ ($\geqslant 1$ mol equiv.) present, are given in Table 1.

Crystallography.—Unique data sets were measured at 295 K on crystals mounted in capillaries to a $2\theta_{max.}$ limit determined by the scope of the data using a Syntex $P2_1$ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source ($\lambda = 0.710\,6_9$ Å), in conventional $2\theta/\theta$ scan mode. N Independent reflections were obtained, N_o with $I > 2\sigma(I)$ for (2) and $I > 3\sigma(I)$ for (4) and (6) being considered 'observed' and used in the (basically) 9×9 block-diagonal least-squares refinement in each case, after absorption correction [(4) excepted], and solution of the structures by the heavy-atom method. At convergence (residuals R and R', 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 $(f',f'').^{[40]}$ Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms were constrained in the refinement with idealized (x,y,z,U). Computation used the X-RAY 76 program system implemented on a Perkin-Elmer 3240 computer by S. R. Hall.$^{[41]}$ Atom numbering is shown in Figures 2—4.

Crystal data for (2). C$_{19}$H$_{24}$ClNSiZr, $M = 421.2$, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14), $a = 15.37(1)$, $b = 20.27(1)$, $c = 12.97(1)$ Å, $\beta = 101.39(2)°$, $U = 3\,960(3)$ Å^3, $Z = 8$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1\,728$. Specimen: polyhedron, approximated as a sphere, 0.21 mm radius for absorption correction; $\mu_{Mo} = 7.4$ cm^{-1}, $2\theta_{max.} = 45°$, $N = 5\,094$, $N_o = 3\,532$, $R = 0.047$, $R' = 0.050$.

Crystal data for (4). C$_{32}$H$_{34}$ClPSiZr, $M = 604.3$, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 17.367(6)$, $b = 14.035(4)$, $c = 24.238(9)$ Å, $\beta = 101.23(3)°$, $U = 5\,795(3)$ Å^3, $Z = 8$, $D_c = 1.39$ g cm^{-3}, $F(000) = 2\,496$. Specimen: compact fragment, *ca.* 0.25 mm diameter (capillary), no absorption correction; $\mu_{Mo} = 5.8$ cm^{-1}, $2\theta_{max.} = 50°$, $N = 5\,120$, $N_o = 3\,186$, $R = 0.037$, $R' = 0.045$.

Crystal data for (6). C$_{28}$H$_{29}$ClSiZr, $M = 520.2$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 15.984(7)$, $b = 9.245(3)$, $c = 16.738(6)$ Å, $\beta = 91.74(3)°$, $U = 2\,473$ Å^3, $Z = 4$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\,072$. Specimen: spheroid, 0.25 mm diameter enclosed in capillary (spherical absorption correction); $\mu_{Mo} = 6.1$ cm^{-1}, $2\theta_{max.} = 50°$, $N = 4\,508$, $N_o = 2\,686$, $R = 0.031$, $R' = 0.037$.

Abnormal features. Strong suggestions of pseudo-symmetry are observed in the co-ordinates for the two molecules of the asymmetric unit of (2); no evidence for the occurrence of a space group of higher symmetry has been found, however.

Acknowledgements

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