A Zirconocene(IV) Chloro-alkyl and Dialkyl Containing Chiral α-Carbon Atoms, $[Zr(\eta\text{-}C_5H_5)_2(R^*)(X)]$ [$R^* = CH(SiMe_3)C_6H_4Me\text{-}o$, X = Cl or R*]: Synthesis, Stereoisomerism, and d^1 Reduction Products

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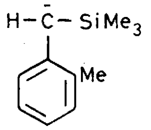
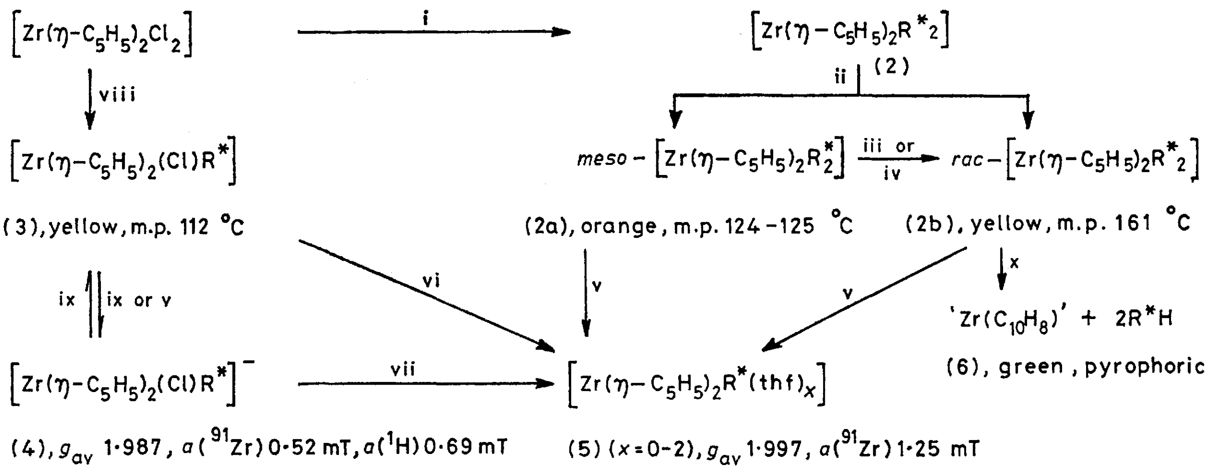
Summary Reactions of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with LiR*(tmeda) [$R^* = CH(SiMe_3)C_6H_4Me\text{-}o$, tmeda = $Me_2NCH_2CH_2NMe_2$] under different conditions yield $[Zr(\eta\text{-}C_5H_5)_2(Cl)R^*]$ (**3**), and the diastereoisomers *meso* - (**2a**) and *rac* - (**2b**) $[Zr(\eta\text{-}C_5H_5)_2R^*_2]$, the latter of which is prepared from (**2a**) by photolysis or thermolysis; $[Zr(\eta\text{-}C_5H_5)_2R^*(thf)_x]$ ($x = 0$—2) is obtained and characterised by e.s.r. spectroscopy in tetrahydrofuran (thf) solution by (a) $Na[C_{10}H_8]$–thf-reduction of complex (**2a**), (**2b**), or (**3**) [*via* the radical anion of (**3**), itself accessible by reversible one-electron reduction of (**3**)], or (b) Na–Hg–thf-reduction of (**3**).



(1) (abbreviated as R^{*-})

We draw attention to a new monodentate alkyl ligand (**1**) which we believe has some potential. The features of interest are (i) the presence of a chiral centre at the ligating carbon atom, (ii) the existence of derived metal alkyls or dialkyls in enantiomeric or diastereoisomeric forms, respectively, and (iii) consequent mechanistic implications for the study of reactions involving metal–carbon bond formation and/or scission. Subsidiary, but important, characteristics of the ligand (**1**) are: (iv) the absence, as for the parent benzyl, of a β-hydrogen atom; (v) the presence of an α-$SiMe_3$ substituent, a useful n.m.r. probe and a factor for solubilising derived metal complexes; and (vi) its close relationship to $\bar{C}H_2Ph$, which already has a significant place in transition metal alkyl chemistry, *e.g.*, see ref. 1. Items (i)—(iii) are illustrated (see Scheme) by (*a*) the isolation (reactions i and ii) of distinct diastereoisomeric forms of the complex $[Zr(\eta\text{-}C_5H_5)_2R^*_2]$, and (*b*) the conversion of *meso*- (**2a**) into *rac*- (**2b**) (reactions iii or iv) by photolysis or controlled thermolysis. As for (*b*), the mechanism involves reversible homolysis [established by e.s.r. identification of Zr^{III}, g_{av} 1·987, $a(^{91}Zr)$ 2·70 mT (in C_6H_6)] or heterolysis of a Zr–R* bond and racemisation of $R^{*}\cdot$ or R^{*-} prior to Zr–R* recombination.

There has been much recent interest in the characterisation of organozirconium(III) compounds and controversy relating to their structures, none of which can yet be regarded as definitive.[2] We now show (see Scheme) that a



SCHEME. *Reagents and conditions:* i, 2Li{CH(SiMe$_3$)C$_6$H$_4$Me-*o*}(NMe$_2$CH$_2$CH$_2$NMe$_2$) [abbreviated as 2LiR*(tmeda)], OEt$_2$, 20 °C; ii, fractional crystn. (n-C$_6$H$_{14}$), (**2b**) being less soluble; iii, *hν* (250 W Hg medium pressure lamp), quartz vessel, C$_6$H$_6$, 25 °C, 5 h; iv, C$_6$H$_6$, 80 °C, 8 h; v, Na[C$_{10}$H$_8$]-tetrahydrofuran (thf), 20 °C; vi, Na–Hg–thf, 20 °C; vii, thf, 20 °C, 2 h; viii, LiR*(tmeda), thf, −78 °C; ix, cyclic voltammetry in 0·2 M [NBu$^n_4$][BF$_4$] in thf at a Pt electrode at scan rates down to 10 mV s^{-1}; x, PhMe, 120 °C, 4 h.

Characterisation of new compounds: compounds (**2a**), (**2b**), and (**3**) were isolated as crystals and yielded satisfactory microanalytical, i.r., and ^{1}H and ^{13}C n.m.r. spectroscopic data.

greater degree of certainty than hitherto is made possible when various alternative Zr starting materials [(**2a**), (**2b**), (**3**), or (**4**)] and reduction methods (v—vii) are employed to yield a single Zr^{III} product (**5**). In this study, the combination of chemical and electrochemical methods with e.s.r. spectroscopy has been fruitful.

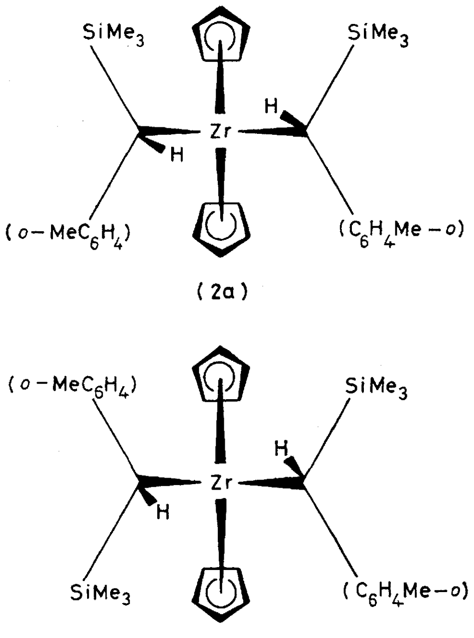
The thermal decomposition of the dialkyl (**2a**) → (**2b**) → (**6**) (reactions iv and x) may be contrasted with that of [Pt(CH$_2$C$_6$H$_4$Me-*o*)$_2$(PEt$_3$)$_2$] which proceeds *via* scission of one alkyl group with δ-hydrogen abstraction at the other to generate the metallocycle [$\overline{\text{Pt(CH}_2\text{C}_6\text{H}_4\text{CH}_2}$-*o*)(PEt$_3$)$_2$].[3]

TABLE. Hydrogen-1 n.m.r. chemical shifts (τ) in C$_6$D$_6$ at 60 MHz and 34 °C.

Complex	C$_5H_5$^{a}	Si(CH_3)$_3$^{a}	*o*-CH_3^{a}	Ar*H*^{b}	C*H*SiMe$_3$^{a}
(**2a**)	3·78, 4·34	9·84	7·81	3·0	8·38
(**2b**)	4·13	9·71	7·52	2·96 (3 H) 3·51 (1 H)	8·42
(**3a**)	3·91, 3·95	9·59	7·63	2·80	7·54

[a] Singlet. [b] Multiplet.

Assignment of *meso*- and *rac*-configurations (see Figure) for complexes (**2a**) and (**2b**), [Zr(η-C$_5$H$_5$)$_2$R*$_2$], is based on ^{1}H n.m.r. data (see Table) which show non-equivalence of the η-C$_5$H$_5$$^-$ ligands but equivalent α-SiMe$_3$ and -H groups. The greater thermodynamic stability of the *rac*- compared with the *meso*-isomer is attributed to the preference for minimising non-bonding contacts between the sterically more demanding SiMe$_3$ groups. The relative disposition of the α-C substituents in (**2a**) and (**2b**) is assumed (see Figure) on the basis of the *X*-ray-authenticated structure of the closely related compound [Zr(η-C$_5$H$_5$)$_2$(CHPh$_2$)$_2$].[4] It is interesting that for [$\overline{\text{Zr\{CH(SiMe}_3\text{)C}_6\text{H}_4\text{CH(SiMe}_3}$)-*o*}(η-C$_5H_5$)$_2$] only the *meso*-diastereoisomer is formed.[5]



(2a)

(2b)

FIGURE. Perspective view of the *meso*- (**2a**) and *rac*- (**2b**) diastereoisomers of [Zr(η-C$_5$H$_5$)$_2${CH(SiMe$_3$)C$_6$H$_4$Me-*o* }$_2$].

Zirconocene(IV) chloro-alkyls were formerly shown to be reduced irreversibly;[2] the reversible one-electron reduction (reaction ix in the Scheme) of [Zr(η-C_5H_5)$_2$(Cl)R*] (**3**) is therefore noteworthy.

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