A Zirconocene(IV) Chloro-alkyl and Dialkyl Containing Chiral α-Carbon Atoms, [Zr(η-C₅H₅)₂(R*)(X)] [R* = CH(SiMe₃)C₆H₄Me-o, X = Cl or R*]: Synthesis, Stereoisomerism, and d¹ Reduction Products

By Michael F. Lappert and Colin L. Raston

(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

Summary Reactions of [Zr(η-C₅H₅)₂Cl₂] with LiR*(tmeda) [R* = CH(SiMe₃)C₆H₄Me-*o*, tmeda = Me₂NCH₂CH₂-NMe₂] under different conditions yield [Zr(η-C₅H₅)₂(Cl)R*] (3), and the diastereoisomers *meso* - (2a) and *rac* - (2b) [Zr(η-C₅H₅)₂R*₂], the latter of which is prepared from (2a) by photolysis or thermolysis; [Zr(η-C₅H₅)₂R*(thf)ₓ] (*x* = 0—2) is obtained and characterised by e.s.r. spectroscopy in tetrahydrofuran (thf) solution by (a) Na[C₁₀H₈]–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).
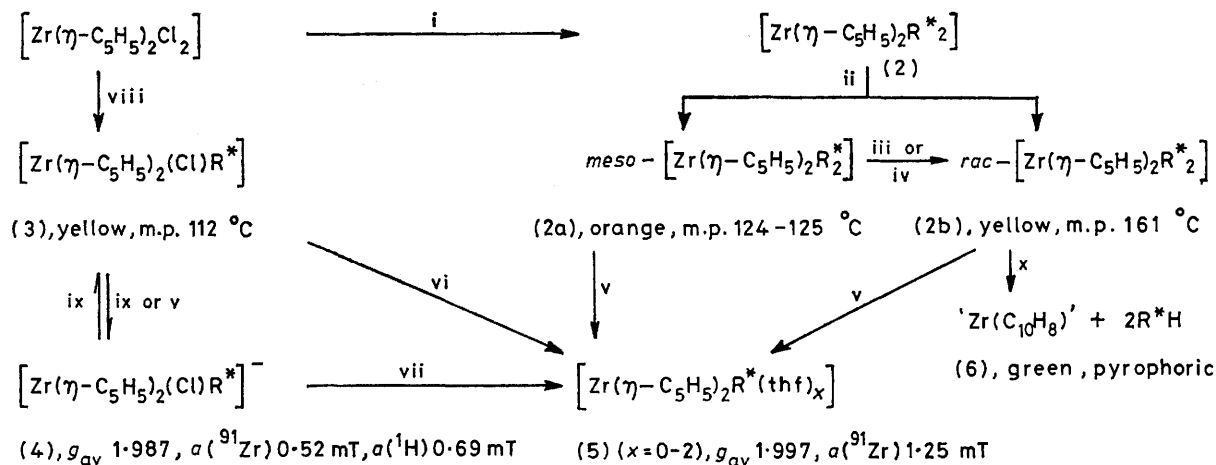
We draw attention to a new monodentate alkyl ligand (1) which we believe has some potential. The features of interest are (i) the presence of a chiral centre at the ligating carbon atom, (ii) the existence of derived metal alkyls or dialkyls in enantiomeric or diastereoisomeric forms, respectively, and (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-SiMe₃ substituent, a useful n.m.r. probe and a factor
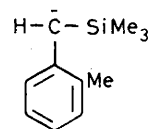
(1) (abbreviated as R*⁻)

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(η-C₅H₅)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 C₆H₆)] or heterolysis of a Zr–R* bond and racemisation of R*· 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

$$\left[Zr(\eta\text{-}C_5H_5)_2Cl_2\right] \xrightarrow{\quad i \quad} \left[Zr(\eta\text{-}C_5H_5)_2R^*_2\right]$$

$$\downarrow viii \qquad\qquad\qquad\qquad\qquad\qquad\qquad ii \downarrow \quad (2)$$

$$\left[Zr(\eta\text{-}C_5H_5)_2(Cl)R^*\right] \qquad\qquad meso-\left[Zr(\eta\text{-}C_5H_5)_2R^*_2\right] \xrightarrow[iv]{iii\ or} rac-\left[Zr(\eta\text{-}C_5H_5)_2R^*_2\right]$$

(3), yellow, m.p. 112 °C   (2a), orange, m.p. 124 –125 °C   (2b), yellow, m.p. 161 °C

$$ix \updownarrow\ ix\ or\ v \qquad\qquad vi \qquad\qquad\qquad v \downarrow \qquad\qquad v \qquad\qquad \downarrow x$$

$$\left[Zr(\eta\text{-}C_5H_5)_2(Cl)R^*\right]^- \xrightarrow{\quad vii \quad} \left[Zr(\eta\text{-}C_5H_5)_2R^*(thf)_x\right] \qquad 'Zr(C_{10}H_8)' + 2R^*H$$

(6), green, pyrophoric

(4), g_{av} 1·987, $a(^{91}Zr)$ 0·52 mT, $a(^1H)$ 0·69 mT   (5) $(x=0\text{-}2)$, g_{av} 1·997, $a(^{91}Zr)$ 1·25 mT

SCHEME. *Reagents and conditions:* i, $2Li\{CH(SiMe_3)C_6H_4Me\text{-}o\}(NMe_2CH_2CH_2NMe_2)$ [abbreviated as $2LiR^*(tmeda)$], OEt_2, 20 °C; ii, fractional crystn. ($n\text{-}C_6H_{14}$), (2b) being less soluble; iii, $h\nu$ (250 W Hg medium pressure lamp), quartz vessel, C_6H_6, 25 °C, 5 h; iv, C_6H_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 ¹H and ¹³C 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 $[Pt(CH_2C_6H_4Me\text{-}o)_2(PEt_3)_2]$ which proceeds *via* scission of one alkyl group with δ-hydrogen abstraction at the other to generate the metallocycle $[\overline{Pt(CH_2C_6H_4CH_2\text{-}o)}(PEt_3)_2]$.[3]

TABLE. Hydrogen-1 n.m.r. chemical shifts (τ) in C_6D_6 at 60 MHz and 34 °C.

Complex	$C_5H_5^a$	$Si(CH_3)_3^a$	$o\text{-}CH_3^a$	ArH^b	$CHSiMe_3^a$
(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), $[Zr(\eta\text{-}C_5H_5)_2R^*_2]$, is based on ¹H n.m.r. data (see Table) which show non-equivalence of the $\eta\text{-}C_5H_5^-$ ligands but equivalent $\alpha\text{-}SiMe_3$ 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 $[Zr(\eta\text{-}C_5H_5)_2(CHPh_2)_2]$.[4] It
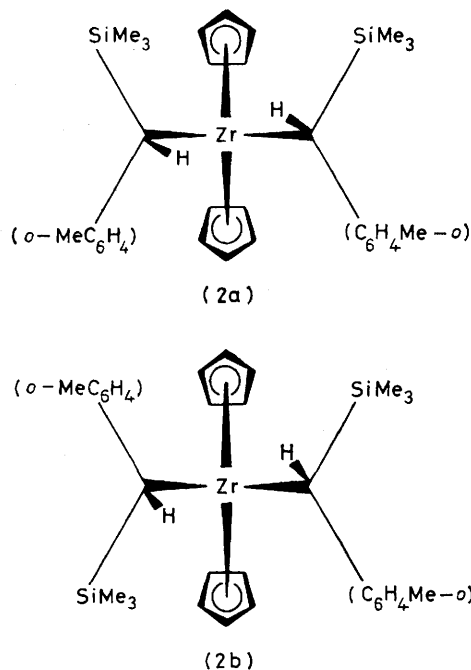

(2a)

(2b)

FIGURE. Perspective view of the *meso*- (2a) and *rac*- (2b) diastereoisomers of $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)C_6H_4Me\text{-}o\}_2]$.

is interesting that for $[Zr\{CH(SiMe_3)C_6H_4\overline{CH(SiMe_3)\text{-}o}\}(\eta\text{-}C_5H_5)_2]$ only the *meso*-diastereoisomer is formed.[5]

Zirconocene(iv) chloro-alkyls were formerly shown to be reduced irreversibly;[2] the reversible one-electron reduction

(reaction ix in the Scheme) of $[Zr(\eta-C_5H_5)_2(Cl)R^*]$ (3) is therefore noteworthy.

We thank the S.R.C. for support and Dr. C. J. Pickett

for advice and provision of facilities for the electrochemical experiments.

[1] P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.,* 1976, **76**, 219.
[2] *Cf.* M. F. Lappert, C. J. Pickett, P. I. Riley, and P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.,* 1981, 805.
[3] S. D. Chappell and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.,* 1980, 238.
[4] J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Am. Chem. Soc.,* 1977, **99**, 6645.
[5] M. F. Lappert and C. L. Raston, *J. Chem. Soc., Chem. Commun.,* 1980, 1284.