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Bulky Alkyls and a Hydridoalkyl of Zirconium(IV): Influence of Steric Constraints Upon (i) Conformation and the Zr–C Rotational Barrier and (ii) the Zr–C Bond Length. *X*-Ray Crystal and Molecular Structure of $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Ph]$†

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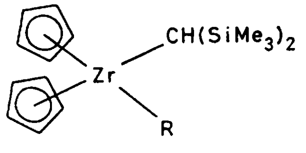
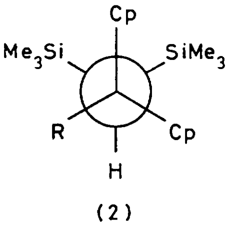
Summary Variable temperature ^1H n.m.r. spectra of $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}R]$ (R = Me, Pr^n, CH_2SiMe_3, Ph, Cl, or H) in $[^2H_8]$toluene show that the activation free energy for rotation about the $Zr\text{–}CH(SiMe_3)_2$ bond is exceptionally high [11·6—15·3 kcal mol^{-1}: R = H (a dimer in vapour or in C_6H_6) $>$ Cl $>$ alkyl $>$ Ph] with a preference to a low temperature conformation in which the two sets of $SiMe_3$ and $\eta\text{-}C_5H_5$ groups are diastereotopic; this is established for the crystalline state (*X*-ray) in the case of R = Ph [Zr–Ph, 2·324(7) Å], in which the Zr–C(sp^3) bond is very long [2·329(6) Å], *cf.* $[Zr(\eta\text{-}C_5H_5)_2(CH_2MMe_3)_2]$ [M = C, 2·29(1); or Si; 2·279(4) Å, respectively].

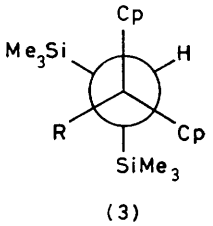
WE present data on the synthesis and characterisation of (i) thermally stable bulky mixed hydrocarbyls of Zr^{IV} of formula (**1**) (R = Me, Pr^n, CH_2SiMe_3, or Ph), and (ii) a dimeric Zr^{IV} hydride (**1**) (R = H). Variable temperature ^1H n.m.r. spectra show that all the compounds (**1**) adopt conformation (**2**) rather than (**3**) at low temperature and from these studies a remarkably high barrier to Zr–C rotation has been revealed. This is substantiated for the crystalline state by *X*-ray analysis of compound (**1**) (R = Ph). Crystallographic data on l[Zr-C(sp^3)] in $[Zr(\eta\text{-}C_5H_5)_2(CH_2MMe_3)_2]$ (M = C or Si[1]) are also reported.



(1)



(2)



(3)

$Cp = \eta\text{-}C_5H_5$

Compounds (**1**) illustrate that the $\bar{C}H(SiMe_3)_2$ ligand may provide a stabilising environment for unexpected co-ligands (*cf.* refs. 2 and 3). Particularly noteworthy is the hydridoalkyl $[\{Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}H\}_2]$, which gives a (dimer − 1)$^+$ ion in the mass spectrum, whether the source

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† No reprints available.

is at 50 or 200 °C. Its structure (*X*-ray analysis awaited) is believed to involve a μ-H_2-bridge, as has been proposed recently[4] for less hindered analogues such as $[\{Zr(\eta\text{-}C_5H_5)_2(CH_2Ph)(H)\}_2]$ (described as indefinitely stable below −30 °C), and as established for $[\{Th(\eta\text{-}C_5Me_5)_2(\mu\text{-}H)H\}_2]$.[5] It is a dimer in C_6H_6, as shown by cryoscopy.

TABLE 1. Variable temperature ^1H n.m.r. data for complexes (**1**) in $C_6D_5CD_3$

R in $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}R]$	m.p./°C	$T_{c,1}$[a]/K	$\Delta G^{\ddagger}(T_{c,1})$[b] /kcal mol^{-1}	$T_{c,2}$[c]/K	$\Delta G^{\ddagger}(T_{c,2})$[b] /kcal mol^{-1}
Me[d]	(190—193)	272	13·6	249	13·1
Pr^n [d]	(88—90)	258	12·9	241	12·6
CH_2SiMe_3[d]	(53—55)	264	13·1	205	10·6
Ph[d]	(116—118)	238	11·6	237	11·5
Cl[e]		278	13·9	283	14·0
H[f]	(85—90, decomp.)	303	15·3	293	14·9

[a] Refers to the coalescence temperature of the η-C_5H_5 signals (1:1 doublet at $< T_{c,1}$). [b] Calculated according to D. Kost, R. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656. [c] Refers to the coalescence temperature of the $SiMe_3$ signal (1:1 doublet at $< T_{c,2}$). [d] In 55—65% yield from $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$ and LiR in C_5H_{12}–OEt_2 at −20 °C; ν(ZrC): 2 bands 435—490 cm^{-1}. [e] Prepared and characterised as reported in ref. 2. [f] From $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$ and $Li[AlH_4]$, or $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and successively $Li[AlH(OBu^t)_3]$ and $Li\{CH(SiMe_3)_2\}$. Shows (dimer − 1)$^+$ in mass spectrum, and is dimeric in C_6H_6 (cryoscopy); ν(Zr–H) is broad at 1590 cm^{-1} (Nujol or C_5H_{12}).

Compounds of formula (**1**) show singlet η-C_5H_5 and $Si(CH_3)_3$ ^1H n.m.r. signals in $C_6D_5CD_3$ at ambient temperature. However, the limiting low temperature spectrum indicates equally populated but distinct diastereotopic cyclopentadienyl and trimethylsilyl environments, *cf.* (**2**). Variable temperature data lead to activation free energies to rotation about the metal–C(sp^3) bond which (see Table 1) are far higher than any previously recorded; *e.g.*, most recently 1·17 kcal mol^{-1} about the B–C bond in $BEtF_2$.[6] The highest value is found for the hydridoalkyl, consistent with its dimeric formulation. *X*-Ray results for the crystalline $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Ph]$ are illustrated in the Figure; *n.b.*, conformation (**2**), unlike (**3**), requires that the C(8)–Si(1) and C(8)–Si(2) lengths are different, and are determined to be 3·855 and 5·385 Å, respectively.

Thermochemical data have shown that the mean M–C bond energy term in $[M'(CH_2MMe_3)_4]$ (M′ = Ti, Zr, or Hf) is greater for M = Si than M = C.[7] *X*-Ray data, however, indicate that the Zr–C(sp^3) bond lengths in $[Zr(\eta\text{-}C_5H_5)_2(CH_2MMe_3)_2]$ are not significantly different, although other results reveal that l[Zr–C(sp^3)] [2·251(6)—2·388(12) Å] may be influenced by steric effects (see Table 2).

TABLE 2. Some Zr–C(sp^3) bond lengths.

Compound	l[Zr–C(sp^3)]/Å	Ref.
$[Zr(\eta\text{-}C_9H_7)_2Me_2]$	2·251(6)	8
$[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$	2·279(4)	a
$[Zr(\eta\text{-}C_5H_5)_2(CH_2CMe_3)_2]$	2·288(10)	b
$[Zr(\eta\text{-}C_5H_5)_2(CHPh_2)_2]$	2·388(12)	2
$[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Ph]$	2·329(6)	c

[a] Synthesis in ref. 1; *X*-ray: 2688 reflections considered, $R_1 = 2\cdot84$, $R_2 = 3\cdot07$. [b] ^1H N.m.r. (C_6D_6) τ 4·00 (C_5H_5), 8·88 (Me), and 9·28 (CH_2); *X*-ray: 487 reflections considered, R_1 *ca.* 3·3. [c] See text and Figure.

Crystal data: $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Ph]$, *M* = 457·9, monoclinic, *a* = 10·208(5), *b* = 11·992(6), *c* = 18·966(8) Å, β = 99·09(4)°, *U* = 2292·6 Å^3, *Z* = 4, D_c = 1·33 g cm^{-3}, μ(Mo-K_α) = 5·79 cm^{-1}, space group $P2_1/c$. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan technique. All reflections in one independent quadrant out to 2θ = 50° were measured; 2712 reflections were considered observed [$I \geqslant 3\sigma(I)$]. The structure was solved by Patterson and difference Fourier techniques, and refined with anisotropic thermal for all non-hydrogen atoms to a conventional *R* value of 0·048. The molecular structure is shown in the Figure.‡

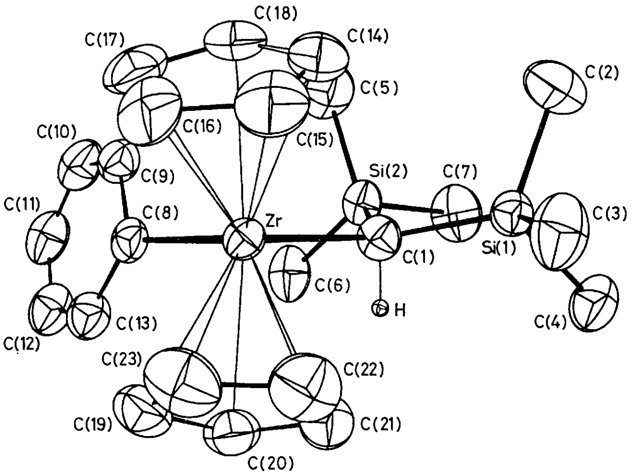

FIGURE. Molecular structure of $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Ph]$. Other important bond lengths are Zr–C(η^5) for ring 1 = 2·541(18) Å and Zr–C(η^5) for ring 2 = 2·543(5) Å. Angles include: cent. 1-Zr-cent. 2 = 126·9°, cent. 1–Zr–C(1) = 111·0°, cent. 1–Zr–C(8) = 104·4°, cent. 2–Zr–C(1) = 105·7° and cent. 2–Zr–C(8) = 105·2°.

Several features of the structure point to the large steric requirements of the combination of the phenyl and bis(trimethylsilyl)methyl ligands: (i) the high (see Table 2) Zr–C(sp^3) distance, (ii) the Zr–C(sp^2) length, 2·324(7) Å, is

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

long, especially when the contraction of the *C*(sp^2) *vs.* the *C*(sp^3) orbital is considered, (iii) the C(1)–Zr–C(8) bond angle, 100·4(2)°, is the largest found for a crystallographic determination of an $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{L_2}]$ complex,[2] and (iv) the Zr–C(η^5) average length, 2·542 Å, is the longest yet reported with the exception of that found in $[\mathrm{Zr(C_5H_5)_4}]$.[9]

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