Metallocene Derivatives of Early Transition Elements. Part 3.[1] Synthesis, Characterisation, Conformation, and Rotational Barriers [for the Zr–C(sp^3) Bond] of the Zirconium(IV) Complexes [Zr(η-C₅H₄R)₂{CH(SiMe₃)₂}Cl] and the Crystal and Molecular Structures of the t-Butyl and Trimethylsilyl Complexes (R = CMe₃ or SiMe₃)

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The complexes [Zr(η-C₅H₄R)₂{CH(SiMe₃)₂}Cl] have been prepared from the appropriate metallocene dichloride (R = Me, Et, Pr^i, Bu^t, or SiMe₃) and an equimolar portion of Li[CH(SiMe₃)₂] in diethyl ether. [The same method failed to yield the hafnium analogues (for R = H or SiMe₃).] Except for R = Et, these are white or pale yellow sharp-melting crystalline solids which have been characterised by elemental analysis and i.r., ¹H, and ¹³C n.m.r. spectra. Variable-temperature ¹H n.m.r. spectra show that (i) at low temperature (coalescence temperature, T_c, −4 to 18 °C) the preferred conformation has diastereotopic pairs of SiMe₃ [of CH(SiMe₃)₂] and η-C₅H₄R groups, and (ii) ΔG‡ for rotation about the Zr–C(sp^3) bond is in the range 59.8 to 65.6 kJ mol⁻¹ (R = SiMe₃ > Et > Bu^t > Pr^i ≈ Me > H). The ring cyclopentadienyl ¹³C n.m.r. signals are each split into a doublet at −30 °C but are observed as three distinct sharp singlets at 60 °C. The compounds [Zr(η-C₅H₄R)₂{CH(SiMe₃)₂}Cl] (R = Bu^t or SiMe₃) are isostructural, crystallising in the space group $P2_1/n$, with cell constants, for Z = 4, being a = 10.496(6), b = 15.250(8), c = 18.272(9) Å, β = 100.48(5)° for R = Bu^t, and a = 10.525(5), b = 15.320(7), c = 19.064(8) Å, β = 98.73(4)° for R = SiMe₃. There is considerable strain within the substituted cyclopentadienyl ligands, as exemplified by the distinct spread in the range of Zr–C(π) distances and the significant deviation from the cyclopentadienyl plane of the −XMe₃ moiety. The remainder of the molecule, however, does not seem to be influenced by any steric constraints with the Zr–Cl bonds, of 2.452(2) and 2.447(1) Å (for X = C and Si respectively), and the Zr–C(σ) bonds, of 2.324(8) and 2.327(3) Å, being within previously observed limits. The conformation in the crystal corresponds to that found by low-temperature n.m.r. spectroscopy.

In Part 2[1] we described substituted zirconocene(IV) and hafnocene(IV) complexes of formula [M(η-C₅H₄R)₂Cl₂], [M(η-C₅H₄R)₂ClR'], and [M(η-C₅H₄R)₂R'₂] (M = Zr or Hf; R = Me, Et, Pr^i, Bu^t, or SiMe₃; R' = CH₂CMe₃ or CH₂SiMe₃). The chloro-alkyls and dialkyls were prepared from the dichlorides. The variation of the substituent in the cyclopentadienyl ring was undertaken to discern trends within a closely related series of compounds.

In this paper we turn to the compounds [Zr(η-C₅H₄R)₂{CH(SiMe₃)₂}Cl]. The bis(trimethylsilyl)methyl ligand [R″ = CH(SiMe₃)₂] has previously been used by us in a transition-metal context for the following complexes: (i) [MR″₃] (M = Ti, V, or Cr),[2] (ii) [M(η-C₅H₅)₂R″] (M = Ti or V),[3] (iii) [M(η-C₅H₅)₂ClR″] (M = Zr or Hf),[3] (iv) [Zr(η-C₅H₅)₂(Bu^n)R″],[3] (v) [Zr(η-C₅H₄R)₂R″-(η²-N₂)] (R = H or Me),[4] (vi) [Zr(η-C₅H₄R)₂R″] (R = Et, Pr^i, Bu^t, or SiMe₃; identified only in solution),[4] and (vii) [{Zr(η-C₅H₄R)₂R″}₂N₂] (R = H or Me).[4] Additionally, in preliminary communications, we have described the complexes (viii) [Zr(η-C₅H₅)₂R″R‴] (R‴ = Me, Pr^n, CH₂SiMe₃, Ph, Cl, or H)[5] and (ix) [Zr(η-C₅H₅)₂-(η²-CR″=NC₆H₄Me-p)R‴] (R‴ = Me or CH₂SiMe₃);[6] the compounds (ix) were obtained by insertion of p-tolyl isonitrile into the Zr–R″ bond of [Zr(η-C₅H₅)₂-R″R‴]. Two of these prior publications,[4,5] dealing with items (v)—(vii) and (viii), are particularly relevant to the present study.

For items (v)—(vii), it was observed[4] that reduction of [Zr(η-C₅H₄R)₂{CH(SiMe₃)₂}Cl] by sodium amalgam in tetrahydrofuran (thf) under N₂ yielded the dinitrogen complexes (v) when R = H or Me, whereas complexes (vi) were obtained when R was a more bulky group. The interest in the complexes (viii)[5] stemmed in part from variable-temperature n.m.r. studies which showed that the activation free energy for rotation about the Zr–CH(SiMe₃)₂ bond is exceptionally high (see Table 4 for R‴ = Cl) with a preference for a low-temperature conformation in which the two sets of SiMe₃ and η-C₅H₅ groups are diastereotopic, as found also by X-ray diffraction in [Zr(η-C₅H₅)₂{CH(SiMe₃)₂}Ph].

RESULTS AND DISCUSSION

Reaction of one mol equivalent of bis(trimethylsilyl)-methyl-lithium with a substituted zirconocene dichloride[1] in diethyl ether in a similar fashion to that of a published procedure for [Zr(η-C₅H₅)₂{CH(SiMe₃)₂}Cl],[3] gave the appropriate monoalkyl (R = Me, Et, Pr^i, Bu^t, or SiMe₃) equation (1). Recrystallisation from hexane

$$[Zr(η\text{-}C_5H_4R)_2Cl_2] + Li[CH(SiMe_3)_2] \longrightarrow$$
$$[Zr(η\text{-}C_5H_4R)_2\{CH(SiMe_3)_2\}Cl] + LiCl \quad (1)$$
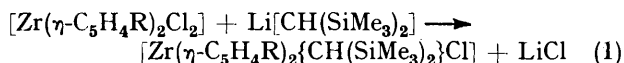
gave the pure complex (Table 1) as white or very pale yellow crystals; [Zr(η-C₅H₄Et)₂{CH(SiMe₃)₂}Cl], however, was a yellow oil which was purified by sublimation onto a cooled probe.

It proved impossible to prepare the complexes [Hf(η-C₅H₄R)₂{CH(SiMe₃)₂}Cl] (R = H or SiMe₃). Repeated attempts using forcing conditions [refluxing diethyl ether or tetrahydrofuran (thf)] were of no avail. The only identifiable product was starting material. Our finding regarding [Hf(η-C₅H₅)₂{CH(SiMe₃)₂}Cl] casts

TABLE 1

Zirconocene(IV) chloro-alkyls [a] and their characterisation

Complex	M.p.[b] $(\theta_c/^{\circ}C)$	Yield (%)	Analysis (%) [c] C	H
[Zr(η-C$_5$H$_4$Me)$_2${CH(SiMe$_3$)$_2$}Cl]	104—106	68	50.9 (51.4)	6.9 (7.4)
[Zr(η-C$_5$H$_4$Et)$_2${CH(SiMe$_3$)$_2$}Cl]	d	43	51.2 (54.4)	7.0 (7.9)
[Zr(η-C$_5$H$_4$Pr^i)$_2${CH(SiMe$_3$)$_2$}Cl]	125—128	60	54.5 (55.2)	7.5 (8.2)
[Zr(η-C$_5$H$_4$Bu^t)$_2${CH(SiMe$_3$)$_2$}Cl]	159—162	79	57.2 (56.9)	8.4 (8.5)
[Zr(η-C$_5$H$_4$SiMe$_3$)$_2${CH(SiMe$_3$)$_2$}Cl]	154—156	63	49.2 (49.2)	8.0 (8.0)

[a] All complexes are white or very pale yellow. [b] In vacuo in a sealed capillary. [c] Calculated values are given in parenthesis. [d] Liquid at room temperature.

doubt on a previous claim [3] to its preparation; it is likely, both from the quoted m.p.[3] and our discovery [7] that commercial [Hf(η-C$_5$H$_5$)$_2$Cl$_2$] contains appreciable quantities of the zirconium analogue, that the purported hafnium complex was the isoleptic zirconium compound.

Several unsuccessful attempts were made to prepare a titanium(IV) analogue of the title compounds, viz. [Ti(η-C$_5$H$_4$R)$_2${CH(SiMe$_3$)$_2$}Cl]. These involved (i) reaction of [Ti(η-C$_5$H$_5$)$_2$Cl$_2$] with Mg[CH(SiMe$_3$)$_2$]Cl·OEt$_2$ [8] and (ii) the reaction of [Ti(η-C$_5$H$_4$SiMe$_3$)$_2${CH(SiMe$_3$)$_2$}] with trityl chloride. The rationalisation for procedure (i) was that the Grignard reagent might have been expected to be a milder reducing agent than Li[CH-(SiMe$_3$)$_2$]; [9] use of the latter with titanocene dichloride had yielded successively titanocene(III) chloride and then [Ti(η-C$_5$H$_5$)$_2${CH(SiMe$_3$)$_2$}].[3] In the event, a green titanium(III) product, $g_{av.}$ = 1.978, was obtained from (i) which is probably [{Ti(η-C$_5$H$_5$)$_2$Cl}$_2$]; lit.,[10] $g_{av.}$ = 1.979, cf.[3] 1.96 for [Ti(η-C$_5$H$_5$)$_2${CH(SiMe$_3$)$_2$}]. Reaction (ii) was based on analogy with the [Cr{CH(Si-Me$_3$)$_2$}$_3$]–CPh$_3$Cl system, which afforded ĊPh$_3$ and a chromium(IV) complex believed to be [Cr{CH(SiMe$_3$)$_2$}$_3$-Cl].[2] Although the trityl radical was observed, the titanium product isolated was [Ti(η-C$_5$H$_4$SiMe$_3$)$_2$Cl$_2$].

Spectroscopic Properties.—The ^{1}H n.m.r. spectra (Table 2) at ca. 35 °C of the complexes [Zr(η-C$_5$H$_4$R)$_2$-{CH(SiMe$_3$)$_2$}Cl] show the cyclopentadienyl protons as a series of broad resonances. The trimethylsilyl protons of the bis(trimethylsilyl)methyl ligand are slightly broadened or seen as a barely resolvable doublet in the region τ 9.5—10. The methine proton of the alkyl

group is at τ 6.5—8.0. The alkyl substituents (R) on the cyclopentadienyl rings are at values similar to those found for the corresponding metallocene dichloride,[1] although in some cases broadening of the signals was noted.

The ^{13}C n.m.r. methine resonances [CH(SiMe$_3$)$_2$] are sharp singlets in the range 46—52 p.p.m. relative to SiMe$_4$ and are at higher field with increased branching at the cyclopentadienyl substituent α carbon. The corresponding methyl resonances, CH[Si(CH_3)$_3$]$_2$, are at 4.0—6.0 p.p.m. and at ca. 35 °C are observed as doublets. The ^{13}C signals attributable to the R substituent in the
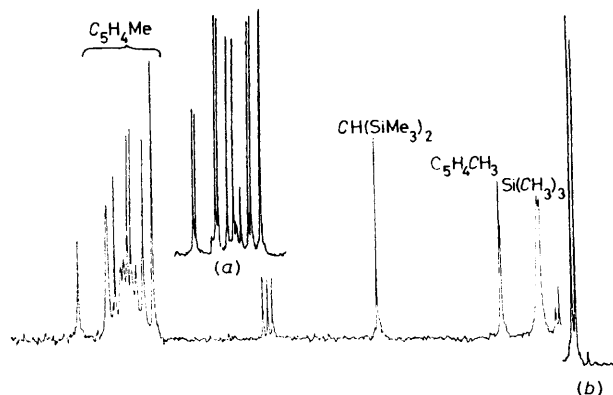

FIGURE 1 Carbon-13 n.m.r. spectrum (25 MHz) of [Zr(η-C$_5$H$_4$-Me)$_2${CH(SiMe$_3$)$_2$}Cl] in CDCl$_3$ at ca. 35 °C; inserts (a) (C$_5$H$_4$Me) and (b) [Si(CH_3)$_3$] show portions of the spectrum at -30 °C

C$_5$H$_4$R$^-$ ligand are at approximately the same values as those in the respective metallocene dichloride; in some cases two resonances were noted. The resonances for the cyclopentadienyl carbons appear as a complex set of signals in the region 100—130 p.p.m. For the parent unsubstituted complex (R = H) two signals were noted for the cyclopentadienyl group, demonstrating the existence of distinct cyclopentadienyl group environments. In general, there was an upfield shift of the cyclopentadienyl resonances on alkylation. A representative ^{13}C n.m.r. spectrum of this type of complex is shown in Figure 1, and ^{13}C n.m.r. parameters are in Table 3.

The i.r. spectra of the complexes [Zr(η-C$_5$H$_4$R)$_2$-{CH(SiMe$_3$)$_2$}Cl] are unexceptional. The broad band at ca. 450 cm^{-1} is assigned to ν(M–C), and the band at ca. 350 cm^{-1} may be due to ν(Zr–Cl).

TABLE 2

Hydrogen-1 n.m.r. (60 MHz) chemical shifts(τ, relative to SiMe$_4$ = 10 τ) at ca. 35 °C in CDCl$_3$ for the zirconocene(IV) chloro-alkyls

Complex	Chemical shift of C$_5$H$_4$	Chemical shift of alkyl substituent	Chemical shift for the group CH(SiMe$_3$)$_2$
[Zr(η-C$_5$H$_5$)$_2${CH(SiMe$_3$)$_2$}Cl]	3.54		6.96 (s) CH; 9.09 (s) CH_3
[Zr(η-C$_5$H$_4$Me)$_2${CH(SiMe$_3$)$_2$}Cl]	3.90 [a]	7.70 (s), CH_3	7.80 (s) CH; 9.70 (s) CH_3
[Zr(η-C$_5$H$_4$Et)$_2${CH(SiMe$_3$)$_2$}Cl]	3.16 [a]	6.59 CH_2;[b] 7.94 (t), J = 7 Hz, CH_2	6.83 (s) CH; 9.00 (s) CH_3
[Zr(η-C$_5$H$_4$Pr^i)$_2${CH(SiMe$_3$)$_2$}Cl]	4.05 [a]	6.9 (spt), J = 7 Hz, CH; 8.65 (d), J = 7 Hz, CH_3	7.74 (s) CH; 9.65 (s) CH_3
[Zr(η-C$_5$H$_4$Bu^t)$_2${CH(SiMe$_3$)$_2$}Cl]	3.88 [a]	8.81 (s), CH_3	7.70 (s) CH; 10.00 (s) CH_3
[Zr(η-C$_5$H$_4$SiMe$_3$)$_2${CH(SiMe$_3$)$_2$}Cl]	3.77 [a]	9.65 (s), Si(CH_3)$_3$	7.70 (s) CH; 9.82 (s) CH_3

[a] The cyclopentadienyl resonances are either broad or complex, except for R = H, and cited values are midpoints. [b] Broad.

Variable-temperature Hydrogen-1 N.M.R. Spectra.—As has previously been noted, the ^1H n.m.r. spectrum of the complex $[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$ changes upon cooling: the signals due to the cyclopentadienyl ligand and the trimethylsilyl group protons appear as doublets.[5]

ring upon the $Zr\text{-}C(sp^3)$ rotational parameters; (I) and (II) are Newman projections taken through the $Zr\text{-}C(sp^3)$ bond.

At high temperature, the ^1H n.m.r. spectrum of the complex $[Zr(\eta\text{-}C_5H_4SiMe_3)_2\{CH(SiMe_3)_2\}Cl]$ has two peaks
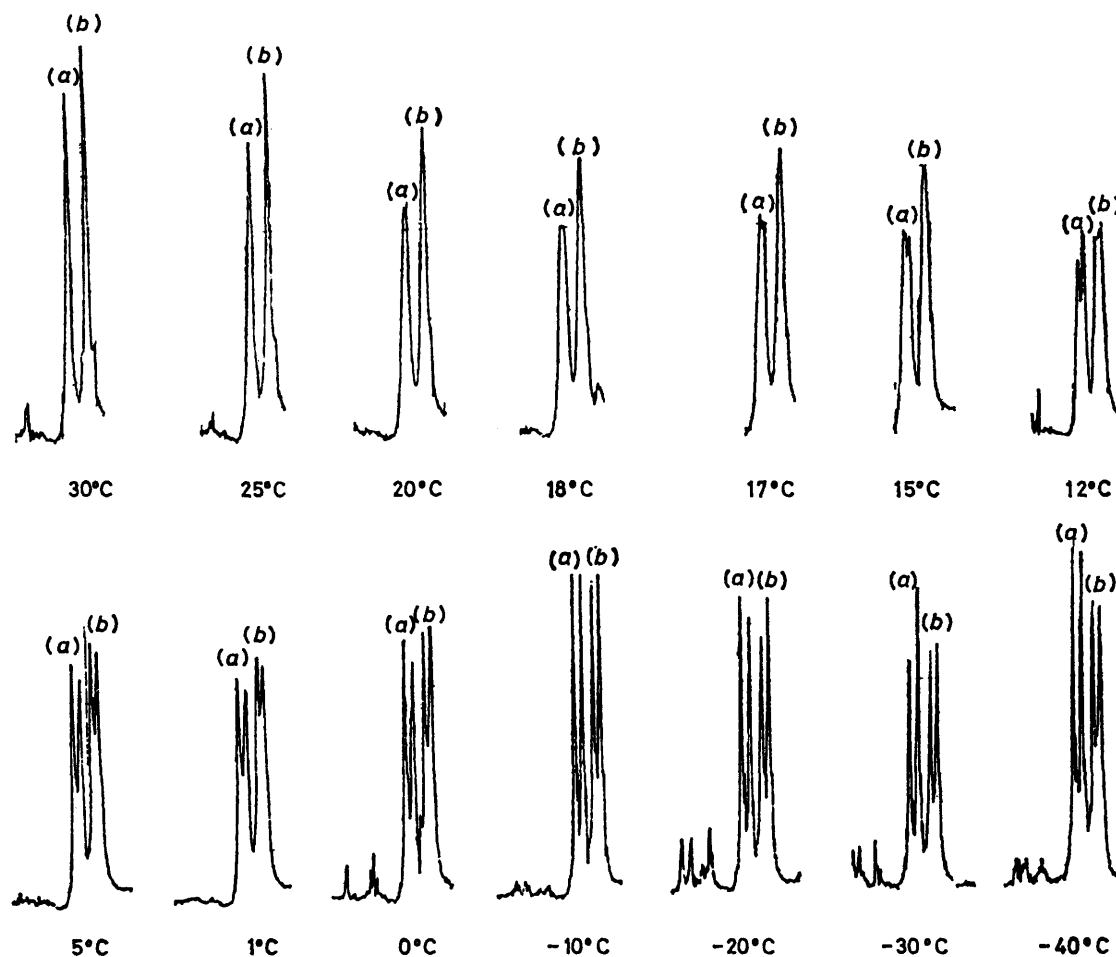

FIGURE 2 The high-field region of the variable-temperature hydrogen-1 n.m.r. (60 MHz) spectrum of $[Zr(\eta\text{-}C_5H_4SiMe_3)_2\{CH(Si\text{-}Me_3)_2\}Cl]$ in $CDCl_3$ $[(a) = \eta\text{-}C_5H_4Si(CH_3)_3, (b) = CH\{Si(CH_3)_3\}_2]$

This was interpreted as evidence that the two diastereotopic trimethylsilyl groups exist in different environments and, due to the reciprocal nature of the effect, so do the cyclopentadienyl groups; and hence that (I),

(I) (II)
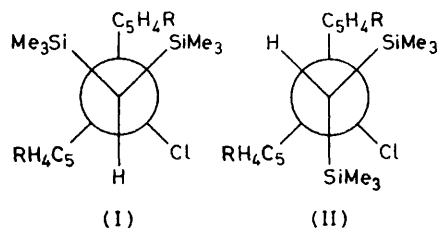
rather than (II) (R = H), is the preferred low-temperature conformation. Not surprisingly the complexes reported here show the same behaviour and indeed the purpose of these variable-temperature n.m.r. studies was to evaluate the substituent effect in the cyclopentadienyl

attributed to trimethylsilyl groups: one due to the ring substituent and the other to the alkyl group. As the temperature is lowered both resonances are split into doublets; some variable-temperature n.m.r. spectra of the high-field region are shown in Figure 2.

For some of the other complexes, the signals of the ring substituent were further complicated by proton coupling and in all cases rather broad complex resonances resulted; thus, the variable-temperature behaviour of the ring substituent was only investigated for R = $SiMe_3$. The variable-temperature n.m.r. spectra of the cyclopentadienyl ligand were, however, examined. At room temperature the cyclopentadienyl signals were broad humps, but as the temperature was lowered, four complex multiplets were observed, Figure 3. At low temperatures, the cyclopentadienyl groups are inequivalent and eight such multiplets are expected but only four are noted (probably due to the coincidence of their chemical shift).

TABLE 3

Carbon-13 n.m.r. (25 MHz) chemical shifts (p.p.m. relative to $SiMe_4 = 0$) at *ca.* 35 °C in $CDCl_3$ for the zirconocene(IV) chloro-alkyls

Complex	Chemical shift of C_5H_4 carbon atoms			Chemical shift of alkyl group $CH(SiMe_3)_2$	Chemical shift of $CH(SiMe_3)_2$	Chemical shift of alkyl substituents
$[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$				51.3	5.4	
$[Zr(\eta\text{-}C_5H_4Me)_2\{CH(SiMe_3)_2\}Cl]$	118.9	112.6	126.5	48.0	5.4, 4.9	15.2, 15.5 CH_3
	116.9	109.3				
	113.4	106.8				
$[Zr(\eta\text{-}C_5H_4Et)_2\{CH(SiMe_3)_2\}Cl]$	117.7	112.0	136.8	48.1	5.9, 5.0	23.2 CH_2; 14.5, 15.3 CH_3 *
	113.7	111.6	133.7			
	113.2	111.2				
$[Zr(\eta\text{-}C_5H_4Pr^i)_2\{CH(SiMe_3)_2\}Cl]$	116.5	106.2		47.5	4.7, 4.7	28.3 CH; 23.2, 23.8 CH_3 *
	114.6					
	112.0					
$[Zr(\eta\text{-}C_5H_4Bu^t)_2\{CH(SiMe_3)_2\}Cl]$	149.9	114.2	106.3	46.2	6.0, 5.2	31.4, 33.4 CH_3; 149.9 CMe_3
	117.0	107.8	105.3			
	115.1	107.2				
$[Zr(\eta\text{-}C_5H_4SiMe_3)_2\{CH(SiMe_3)_2\}Cl]$	126.6	119.2		48.8	6.0, 5.3	
	125.9	117.1				
	124.9	109.8				

* Signal as a doublet due to restricted rotation.

At high temperature only broad featureless signals were observed.

The low temperature (−30 °C) [13]C n.m.r. spectrum of the complex $[Zr(\eta\text{-}C_5H_4Me)_2\{CH(SiMe_3)_2\}Cl]$ shows, in addition to the doublets of the trimethylsilyl group and the methyl group, five doublets for the carbon atoms of the cyclopentadienyl ligand.

From the coalescence temperature (T_c) and the separation $(\Delta\nu)$ of the two coalescing peaks in the limiting spectrum in the absence of any exchange, the free energy for rotation about the $Zr\text{-}C(sp^3)$ bond was calculated, according to equation (2).[11] The values for

$$\Delta G_{T_c}{}^\ddagger = -RT_c\ln(\pi\Delta\nu h/\sqrt{2}kT_c) \qquad (2)$$

the coalescence temperature, T_c, and for $\Delta G_{T_c}{}^\ddagger$ are in Table 4.

The magnitude of $\Delta G_{T_c}{}^\ddagger$ is exceptionally high for a metal–carbon σ bond. This is due to steric crowding; the transition state for rotation involves eclipse of the bulky trimethylsilyl group and a cyclopentadienyl ring.

The introduction of a substituent into the ring increases the value of $\Delta G_{T_c}{}^\ddagger$. The results were not as decisive as had been anticipated. It is clear that the largest ring substituent, the trimethylsilyl group, gives rise to the largest $\Delta G_{T_c}{}^\ddagger$, but the values of $\Delta G_{T_c}{}^\ddagger$ do not show the expected monotonic increase. However, the general trend is that as the size of the substituent increases so does the value of $\Delta G_{T_c}{}^\ddagger$, with the exception of R = Et (this anomaly is as yet unexplained).
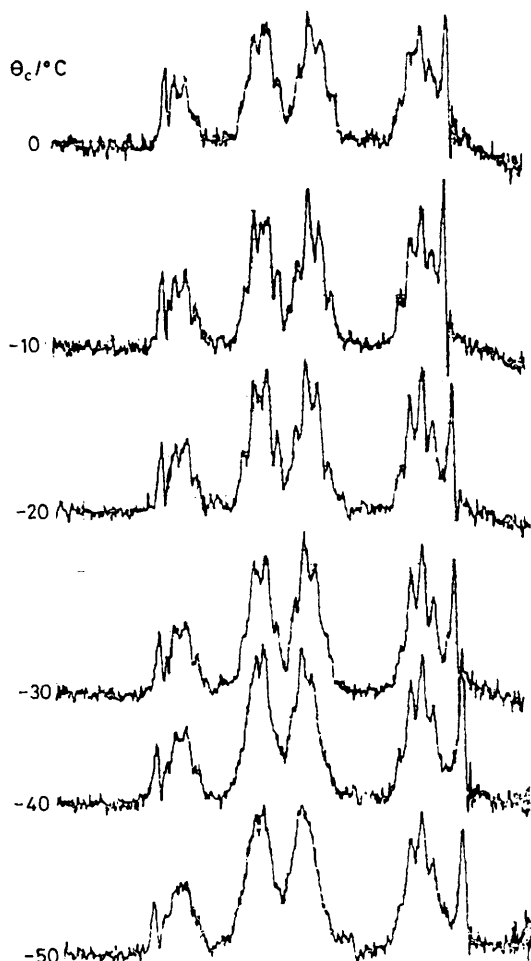

FIGURE 3 The cyclopentadienyl region of the variable-temperature hydrogen-1 n.m.r. (60 MHz) spectrum of $[Zr(\eta\text{-}C_5H_4\text{-}SiMe_3)_2\{CH(SiMe_3)_2\}Cl]$ in $CDCl_3$

TABLE 4

Variable-temperature [1]H n.m.r. (60 MHz) data for the zirconocene(IV) chloro-alkyls [a]

Complex	T_c [b] $(\theta_c/°C)$	$\Delta G_{T_c}{}^\ddagger$ /kJ mol^{-1}
$[Zr(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Cl]$	−4	60.2
	−4 [c]	59.8 [d]
$[Zr(\eta\text{-}C_5H_4Me)_2\{CH(SiMe_3)_2\}Cl]$	−4	62.3
$[Zr(\eta\text{-}C_5H_4Et)_2\{CH(SiMe_3)_2\}Cl]$	5	64.5
$[Zr(\eta\text{-}C_5H_4Pr^i)_2\{CH(SiMe_3)_2\}Cl]$	2	62.3
$[Zr(\eta\text{-}C_5H_4Bu^t)_2\{CH(SiMe_3)_2\}Cl]$	6	63.5
$[Zr(\eta\text{-}C_5H_4SiMe_3)_2\{CH(SiMe_3)_2\}Cl]$	15	65.6
	18 [e]	65.6 [f]

[a] Solvent $CDCl_3$. [b] Coalescence temperature of the alkyl group trimethylsilyl signal. [c] Coalescence temperature of the cyclopentadienyl ring signal. [d] $\Delta G_{T_c}{}^\ddagger$ based on [c]. Coalescence temperature of the trimethylsilyl substituent on the cyclopentadienyl ring. [f] $\Delta G_{T_c}{}^\ddagger$ based on [e].

Molecular Structures of Crystalline [Zr(η-C$_5$H$_4$R)$_2$-{CH(SiMe$_3$)$_2$}Cl] (R = CMe$_3$ *or* SiMe$_3$).—The two title

TABLE 5

Interatomic bond lengths (Å) and angles (°) for
[Zr(η-C$_5$H$_4$R)$_2${CH(SiMe$_3$)$_2$}Cl] (R = XMe$_3$)

(a) Bond lengths

	X = C	X = Si
Zr–Cl	2.452(2)	2.447(1)
Zr–C(8)	2.573(8)	2.544(4)
Zr–C(9)	2.506(8)	2.542(4)
Zr–C(10)	2.500(9)	2.517(4)
Zr–C(11)	2.550(9)	2.532(4)
Zr–C(12)	2.633(8)	2.558(4)
C(1)–Si(1)	1.887(8)	1.895(3)
C(1)–H(11)	1.09	1.00
Si(1)–C(2)	1.912(11)	1.870(5)
Si(1)–C(3)	1.884(10)	1.839(5)
Si(1)–C(4)	1.908(10)	1.862(5)
C(8)–C(9)	1.367(14)	1.395(6)
C(8)–C(12)	1.410(12)	1.419(5)
C(9)–C(10)	1.429(14)	1.400(6)
C(10)–C(11)	1.398(14)	1.402(6)
C(11)–C(12)	1.411(14)	1.420(5)
X(1)–C(12)	1.494(13)	1.868(4)
X(1)–C(13)	1.544(15)	1.838(6)
X(1)–C(14)	1.593(18)	1.849(6)
X(1)–C(15)	1.574(17)	1.865(5)
Zr–C(1)	2.324(8)	2.327(3)
Zr–C(16)	2.594(8)	2.562(3)
Zr–C(17)	2.498(8)	2.509(4)
Zr–C(18)	2.477(8)	2.497(4)
Zr–C(19)	2.589(8)	2.560(3)
Zr–C(20)	2.676(7)	2.609(3)
C(1)–Si(2)	1.891(8)	1.879(3)
Si(2)–C(5)	1.916(11)	1.868(5)
Si(2)–C(6)	1.918(12)	1.877(5)
Si(2)–C(7)	1.937(10)	1.886(4)
C(16)–C(17)	1.381(13)	1.399(6)
C(16)–C(20)	1.396(11)	1.413(5)
C(17)–C(18)	1.412(14)	1.402(6)
C(18)–C(19)	1.413(12)	1.395(5)
C(19)–C(20)	1.419(11)	1.420(5)
X(2)–C(20)	1.536(11)	1.872(4)
X(2)–C(21)	1.520(13)	1.840(5)
X(2)–C(22)	1.555(12)	1.857(4)
X(2)–C(23)	1.537(13)	1.854(5)
Zr–Cent(1)	2.26	2.24
Zr–Cent(2)	2.27	2.25

(b) Bond angles

	X = C	X = Si
Cl–Zr–C(1)	98.2(2)	99.9(1)
Zr–C(1)–Si(2)	121.0(4)	121.0(2)
Si(1)–C(1)–Si(2)	111.4(4)	112.4(2)
Si(2)–C(1)–H(11)	103	101
C(1)–Si(1)–C(2)	117.2(5)	116.0(2)
C(1)–Si(1)–C(3)	115.4(4)	116.1(2)
C(1)–Si(1)–C(4)	109.6(4)	110.3(2)
C(2)–Si(1)–C(3)	103.8(6)	103.5(3)
C(2)–Si(1)–C(4)	102.1(6)	102.5(2)
C(3)–Si(1)–C(4)	107.4(6)	107.2(3)
C(8)–C(9)–C(10)	107.0(9)	107.3(4)
C(9)–C(10)–C(11)	106.5(10)	108.1(4)
C(10)–C(11)–C(12)	110.5(9)	109.4(4)
C(11)–C(12)–C(8)	104.2(9)	104.9(3)
C(12)–C(8)–C(9)	111.7(9)	110.3(4)
C(8)–C(12)–X(1)	128.3(9)	126.2(3)
C(11)–C(12)–X(1)	126.1(9)	127.3(3)
C(12)–X(1)–C(13)	111.4(9)	112.4(2)
C(12)–X(1)–C(14)	112.0(9)	105.7(2)
C(12)–X(1)–C(15)	105.9(10)	110.0(2)
C(13)–X(1)–C(14)	108.3(11)	110.0(3)
C(13)–X(1)–C(15)	109.6(11)	109.5(3)
C(14)–X(1)–C(15)	109.6(11)	109.1(3)
Zr–C(1)–Si(1)	118.9(4)	117.2(2)
Zr–C(1)–H(11)	90	93
Si(1)–C(1)–H(11)	107	107

TABLE 5 *(continued)*

(b) Bond angles *(continued)*

	X = C	X = Si
C(1)–Si(2)–C(5)	111.9(4)	113.2(2)
C(1)–Si(2)–C(6)	110.2(5)	110.2(2)
C(1)–Si(2)–C(7)	116.5(4)	117.2(2)
C(5)–Si(2)–C(6)	109.4(6)	108.8(2)
C(5)–Si(2)–C(7)	105.0(5)	103.9(2)
C(6)–Si(2)–C(7)	103.4(5)	102.7(2)
C(16)–C(17)–C(18)	108.2(8)	107.4(3)
C(17)–C(18)–C(19)	107.2(8)	108.1(3)
C(18)–C(19)–C(20)	108.0(8)	109.3(3)
C(19)–C(20)–C(16)	106.9(7)	105.4(3)
C(20)–C(16)–C(17)	109.6(8)	109.8(4)
C(16)–C(20)–X(2)	126.6(8)	125.5(3)
C(19)–C(20)–X(2)	125.1(7)	126.4(3)
C(20)–X(2)–C(21)	113.4(7)	112.3(2)
C(20)–X(2)–C(22)	105.2(7)	104.9(2)
C(20)–X(2)–C(23)	111.7(8)	110.4(2)
C(21)–X(2)–C(22)	108.5(8)	108.9(2)
C(21)–X(2)–C(23)	108.9(9)	110.5(3)
C(22)–X(2)–C(23)	109.1(8)	109.7(2)
Cent(1)–Zr–Cl	106.8	105.5
Cent(1)–Zr–C(1)	107.1	107.8
Cent(2)–Zr–Cl	105.3	105.4
Cent(2)–Zr–C(1)	106.7	106.6
Cent(1)–Zr–Cent(2)	128.1	129.1

compounds, whose molecular structures are shown in Figure 4, are isostructural even though the substituent on the cyclopentadienyl moiety is in one case the t-butyl group and in the other the trimethylsilyl unit. Bond angles and bond lengths are shown in Table 5. The presence of only one bulky substituent on the cyclopentadienyl group facilitates orientation of the two rings in such a manner as to minimise interligand steric repulsion. The effect of this is such that the metal–carbon σ-bond length is virtually identical in the two compounds, 2.324(8) and 2.327(3) Å for R = CMe$_3$ and SiMe$_3$, respectively, and is near the 2.329(6) Å observed in [Zr(η-C$_5$H$_5$)$_2${CH(SiMe$_3$)$_2$}Ph].[5] We note also that the increased size of the π-bonded ligands does not effect any change in the preferred Zr–CH(SiMe$_3$)$_2$ conformation
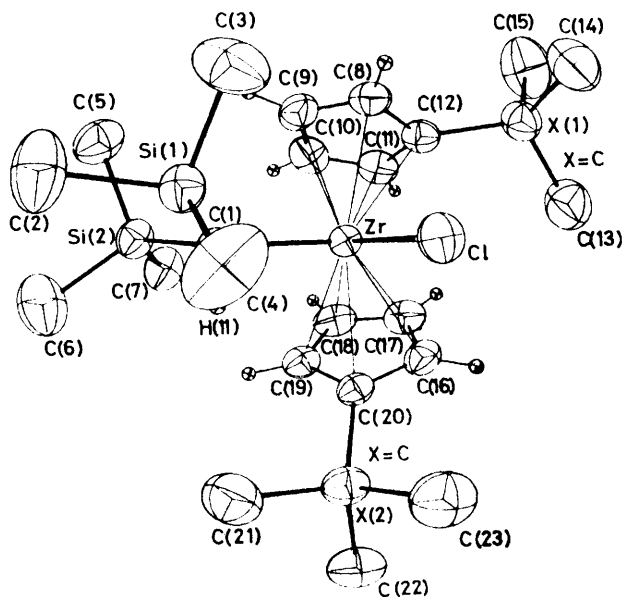

FIGURE 4 Molecular structure and atom-numbering scheme for [Zr(η-C$_5$H$_4$R)$_2${CH(SiMe$_3$)$_2$}Cl] (R = CMe$_3$ or SiMe$_3$)

TABLE 6

Least-squares plane calculations *

Plane (a): C(8), C(9), C(10), C(11), C(12)

X = Si: $-0.2121X - 0.3659Y - 0.9062Z = -3.0349$
X = C: $-0.1994X - 0.3898Y - 0.8990Z = -2.6561$

Deviations:

	X = C	X = Si
C(8)	0.004	0.001
C(9)	−0.005	0.004
C(10)	0.004	−0.007
C(11)	−0.002	0.007
C(12)	0.000	−0.005
X(1)	0.336	0.259
Zr	−2.252	−2.238

Plane (b) C(16), C(17), C(18), C(19), C(20)

X = Si: $-0.6137X + 0.4346Y - 0.6592Z = -5.5672$
X = C: $-0.5962X + 0.4385Y - 0.6725Z = -5.4594$

Deviations:

	X = C	X = Si
C(16)	−0.008	−0.001
C(17)	0.008	−0.002
C(18)	0.004	0.004
C(19)	0.001	−0.005
C(20)	−0.006	0.004
X(2)	−0.449	−0.296
Zr	2.263	2.247

* The right-hand orthogonal Å frame is defined with X parallel to a, Z being in the ac plane.

over the aforementioned unsubstituted cyclopentadienyl compound, corresponding to that shown in (I).

The bulkiness of the substituents does, however, produce considerable strain within the π-bonded ligands, which is manifested in two ways. Firstly, the central atom of the $-XMe_3$ substituent is forced to reside considerably out of the plane of the cyclopentadienyl carbon atoms and away from the zirconium atom. The least-squares plane calculations shown in Table 6 indicate that for both X = C and X = Si the carbon atoms of the ring are planar to within 0.008 Å, whereas the atom X lies 0.259 and 0.296 Å out of plane for X = Si, and an even greater 0.336 and 0.449 Å for X = C. The larger deviation for X = C is a result of the relative

shortness of a C–C bond compared to that of a C–Si bond which would naturally lead to greater strain in the t-butyl analogue. The second way in which the steric strain caused by the substituent is evidenced concerns the Zr–C(π) bond distances shown in Table 5. For X = C the Zr–C(π) length shows ranges of 2.500(9)—2.633(8) Å and 2.477(8)—2.676(7) Å, while for X = Si the range is 2.517(4)—2.558(4) Å and 2.497(4)—2.609(3) Å. Once more the more pronounced effect is for the t-butyl case. In each example the distortion is such that a trend is followed whereby the cyclopentadienyl carbon that is bonded to the $-XMe_3$ species [C(12)] is furthest from zirconium, while carbons 9 and 10 of the ring are closest. There is no suggestion that this is anything but a steric effect since the cyclopentadienyl C–C distances are roughly equivalent.

As expected, the Zr–C(π) average distances, of 2.56 and 2.54 Å for X = C and Si respectively, are slightly longer compared to those determined for unsubstituted cyclopentadienyl compounds: 2.52(2) Å for [Zr(η-$C_5H_5)_2(CH_2SiMe_3)_2$],[12] 2.494(4) Å for [Zr{(η-$C_5H_4)_2$-$(CH_2)_3$}Cl_2],[13] and 2.52(1) Å for [Zr(η-$C_5H_5)_2Me_2$].[14] It is interesting to note, however, that the Zr–C(π) average distances do agree more closely with the 2.55(3) Å average found for [Zr(η^5-$C_9H_7)_2Me_2$].[15]

The Zr–Cl distances, at 2.452(2) and 2.447(1) Å for X = C and Si respectively, are close to the 2.441(10) Å observed for [Zr{(η-$C_5H_4)_2(CH_2)_3$}Cl_2].[13] All other distances are within normal ranges, and there are no intermolecular contacts of significance. The unit-cell packing view is shown in Figure 5.

EXPERIMENTAL

General Procedures.—These have been described in Parts 1 [16] and 2.[1] The zirconocene(IV) dichloro-complexes [Zr-(η-$C_5H_4R)_2Cl_2$] were prepared by the procedures reported previously.[1] The variable-temperature ^{1}H n.m.r. measurements were carried out on a Perkin-Elmer R12 spectrometer.
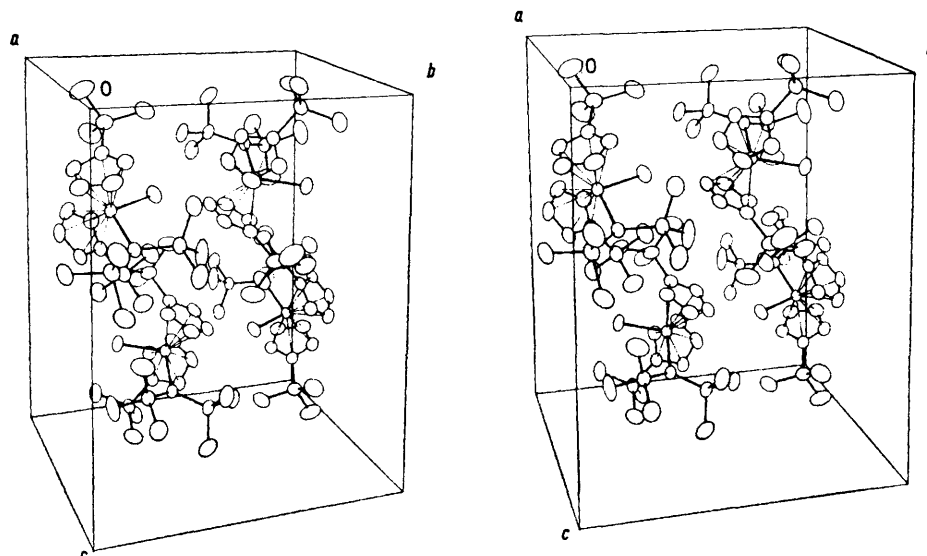

FIGURE 5   Stereoscopic view of the unit-cell packing for [Zr(η-$C_5H_4SiMe_3)_2${CH(SiMe_3)_2}Cl]

Preparation of the Zirconocene(IV) *Chloro-alkyls*, [Zr(η-C$_5$H$_4$R)$_2${CH(SiMe$_3$)$_2$}Cl].—This is illustrated by a typical example; further details are in Tables 1—3. Bis(trimethylsilyl)methyl-lithium (1.0 mmol) in diethyl ether was added dropwise to a suspension of dichlorobis(η-methyl-cyclopentadienyl)zirconium(IV) (0.33 g, 1 mmol) in diethyl ether (20 cm³). The mixture was stirred for 14 h and the volatiles were removed *in vacuo*. The residue was extracted with warm hexane (40 cm³) and filtered to give a pale yellow solution. Concentration of the filtrate and cooling to −30 °C gave *chlorobis*(η-*methylcyclopentadienyl*)*bis*(*trimethylsilylmethyl*)*zirconium*(IV) (0.31 g, 68%) as pale yellow crystals.

Crystal Data.—C$_{23}$H$_{45}$ClSi$_2$X$_2$Zr, X = C(X = Si), *M* = 528.5 (560.6), Monoclinic, *a* = 10.496(6) [10.525(5)], *b* = 15.250(8) [15.320(7)], *c* = 18.272(9) [19.064(8)] Å, β = 100.48(5) [98.73(4)]°, *U* = 2 876 (3 038) Å³, *D*$_c$ = 1.22 (1.23) g cm⁻³, *Z* = 4 (4), μ(Mo-*K*$_α$) = 5.59 (6.07) cm⁻¹, *F*(000) = 1 120 (1 184), λ(Mo-*K*$_α$) = 0.710 69 Å, space groups *P*2$_1$/*n*. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections (2θ > 30°) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

X-Ray Data Collection for [Zr(η-C$_5$H$_4$Bu^t)$_2${CH(SiMe$_3$)$_2$}Cl].—A crystal of dimensions 0.15 × 0.25 × 0.30 mm was sealed in a thin-walled capillary under a dinitrogen atmosphere. Data were taken on the diffractometer using graphite-monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique in a manner similar to that described previously.[17] All the reflections in one independent quadrant out to 2θ = 50° were measured, 3 394 being considered observed [*I* > 3σ(*I*)]. The intensities were corrected for Lorentz and polarisation effects, but not for absorption (μ = 5.59 cm⁻¹). Full-matrix least-squares refinement was carried out using the SHELX program by G. M. Sheldrick.* The function *w*(|*F*$_o$| − |*F*$_c$|)² was minimised. No corrections were made for extinction. Atomic scattering factors for Zr, Cl, Si, and C were taken from Cromer and Waber,[18] whereas those for H were taken from ref. 19. Corrections for the real and imaginary components of anomalous dispersion were used only for Zr, the values being those of Cromer and Liberman.[20]

X-Ray Data Collection for [Zr(η-C$_5$H$_4$SiMe$_3$)$_2${CH(SiMe$_3$)$_2$}Cl].—Following the data collection procedures given above, 4 214 independent reflections were observed from a yellow crystal of dimensions 0.25 × 0.30 × 0.35 mm. Refinement was also carried out by the methods outlined above.

Structure Determination and Refinement for [Zr(η-C$_5$H$_4$Bu^t)$_2${CH(SiMe$_3$)$_2$}Cl].—The position of the zirconium atom was revealed *via* Patterson-map inspection, and calculation of a Fourier map phased on the metal atom led to the co-ordinates of the remaining 28 non-hydrogen atoms. After several cycles of least-squares refinement with at first isotropic and then anisotropic thermal parameters, the cyclopentadienyl hydrogens and the hydrogen atom on the α-carbon atom of the σ-bound ligand were placed in calculated positions. Further refinement led to final values of *R* = Σ(||*F*$_o$| − |*F*$_c$||)/Σ|*F*$_o$| = 0.060 and *R′* = [Σ(|*F*$_o$| − |*F*$_c$|)²/Σ(*F*$_o$)²]$^{\frac{1}{2}}$ = 0.072. The estimated standard deviation of an observation of unit weight was 3.01. Unit weights were used throughout the refinement. The

* Other crystallographic programs used on a UNIVAC 1110 include ORTEP (thermal ellipsoid drawings, by C. K. Johnson) and BPL (least-squares planes, by W. E. Hunter).

Table 7

Atomic positions in fractional co-ordinates for
[Zr(η-C$_5$H$_4$Bu^t)$_2${CH(SiMe$_3$)$_2$}Cl]

Atom	*x*	*y*	*z*
Zr	0.190 55(7)	0.088 51(5)	0.257 10(4)
Cl	0.249 1(2)	0.241 7(1)	0.240 4(1)
Si(1)	−0.087 1(2)	0.216 3(2)	0.287 5(1)
Si(2)	−0.097 3(2)	0.018 9(2)	0.330 3(2)
C(1)	0.009 7(7)	0.112 8(5)	0.311 2(4)
C(2)	−0.254(1)	0.221 8(8)	0.315 2(7)
C(3)	−0.119(1)	0.247 2(8)	0.186 0(6)
C(4)	0.001(1)	0.312 3(6)	0.341 4(7)
C(5)	−0.238(1)	−0.000 0(8)	0.249 2(7)
C(6)	−0.164(1)	0.041 0(9)	0.419 5(7)
C(7)	−0.014(1)	−0.094 3(6)	0.348 7(7)
C(8)	0.089 7(9)	0.105 5(6)	0.118 6(5)
C(9)	0.012 8(9)	0.050 6(7)	0.150 6(5)
C(10)	0.085(1)	−0.027 7(7)	0.170 3(6)
C(11)	0.206(1)	−0.015 2(7)	0.149 7(5)
C(12)	0.211 8(9)	0.067 9(6)	0.116 8(5)
X(1)	0.313(1)	0.098 3(8)	0.074 6(5)
C(13)	0.450(1)	0.088(1)	0.121 1(7)
C(14)	0.294(1)	0.198(1)	0.050 2(8)
C(15)	0.298(2)	0.039(1)	0.003 4(7)
C(16)	0.425 4(7)	0.084 6(6)	0.332 2(5)
C(17)	0.394 3(9)	0.004 0(7)	0.299 6(5)
C(18)	0.297 0(9)	−0.034 2(5)	0.333 4(5)
C(19)	0.271 5(8)	0.024 7(5)	0.388 6(4)
C(20)	0.352 8(7)	0.098 8(5)	0.388 0(4)
X(2)	0.376 9(9)	0.169 5(6)	0.448 7(5)
C(21)	0.256(1)	0.193 5(8)	0.479 2(6)
C(22)	0.477(1)	0.128 7(7)	0.512 7(5)
C(23)	0.434(1)	0.253 1(7)	0.421 1(6)
H(1)[C(1)]	0.071 9	0.123 3	0.365 4
H(1)[C(8)]	0.062 7	0.166 4	0.098 7
H(1)[C(9)]	−0.079 1	0.063 2	0.159 3
H(1)[C(10)]	0.054 3	−0.083 0	0.195 5
H(1)[C(11)]	0.280 0	−0.059 7	0.157 5
H(1)[C(16)]	0.491 5	0.127 2	0.317 8
H(1)[C(17)]	0.434 8	−0.022 6	0.257 7
H(1)[C(18)]	0.253 5	−0.093 2	0.320 5
H(1)[C(19)]	0.205 1	0.015 7	0.422 8

largest parameter shifts in the final cycle were less than 0.05 of their estimated standard deviation and no unaccountable electron density was shown by the final difference Fourier. No systematic variation of *w*(|*F*$_o$| − |*F*$_c$|) against |*F*$_o$| or (sinθ)/λ was noted. The final values of the positional parameters are given in Table 7, while bond lengths and angles are given in Table 5. The observed and calculated structure-factor amplitudes, hydrogen-atom co-ordinates, and thermal parameters are given in Supplementary Publication No. SUP 22939 (49 pp.).†

Structure Determination and Refinement for [Zr(η-C$_5$H$_4$-SiMe$_3$)$_2${CH(SiMe$_3$)$_2$}Cl].—The procedure was the same as for the t-butyl compound except for hydrogen-atom location. Cyclopentadienyl hydrogen atoms were placed in calculated positions and were not subsequently varied, whereas all other hydrogen atoms were located from a difference-Fourier map and their parameters were refined for three cycles and then fixed. This led to final values of *R* = 0.030 and *R′* = 0.036 with unit weights being used throughout the refinement. The estimated standard deviation of an observation of unit weight was 1.50. The largest parameter shifts in the last cycle were less than 0.01 of their estimated standard deviations. Final observations were the same as for the t-butyl compound and all resulting information is given in the corresponding tables and Supplementary Publication.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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