Halogeno, Hydrido, and Hydrocarbyl Derivatives of (η-Cyclo-octatetraene)-(η-pentamethylcyclopentadienyl)zirconium(IV): *X*-Ray Crystal Structure of $[Zr(\eta-C_5Me_5)(\eta-C_8H_8)H]$ ‡

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The sequential addition of $K_2(C_8H_8)$ and $Li(C_5Me_4R)$ (R = Me or Et) to $ZrCl_4$ affords $[Zr(\eta-C_5Me_4R)(\eta-C_8H_8)Cl]$ which further reacts with MR′ (M = MgCl or Li; R′ = Me, Et, CH_2Ph, C_6H_4Me-4, CMe=CHMe, C_2Me, or C_2Ph) to afford the corresponding hydrocarbyl derivatives $[Zr(\eta-C_5Me_4R)(\eta-C_8H_8)R']$. Reaction of $[Zr(\eta-C_5Me_4R)(\eta-C_8H_8)Cl]$ with $LiAlH_4$ or $Mg(Cl)CHMe_2$ affords $[Zr(\eta-C_5Me_4R)(\eta-C_8H_8)H]$. Both i.r. and n.m.r. data suggest that the compounds $[Zr(\eta-C_5Me_4R)(\eta-C_8H_8)X]$ (X = Cl, H, or R′) have a 'planar' 1—8-η-C_8H_8 ligand and should therefore be regarded as 18-electron complexes of Zr^{IV}. An *X*-ray diffraction study of $[Zr(\eta-C_5Me_5)(\eta-C_8H_8)H]$ has shown that the molecule is monomeric and has one terminal hydride ligand. All eight carbon atoms of the C_8 ring are within bonding distance of the Zr atom, with Zr–C varying from 2.43(4) to 2.68(4) Å and the ring itself slightly folded into an envelope conformation. It is bonded to the metal atom on the convex face. Crystals of $[Zr(\eta-C_5Me_5)(\eta-C_8H_8)H]$ are orthorhombic, space group $Pbc2_1$, with two crystallographically distinct molecules in the asymmetric unit. Surprisingly, although the two molecules appear to be related by a pseudo-glide plane, in fact one molecule is twisted in its crystal siting relative to the other, though their molecule symmetry is identical. The structure could not be very accurately determined; it has been refined to *R* 0.066 (*R′* 0.055) for 1 019 reflections measured at 210 K to 2θ = 50°.

The organometallic chemistry of zirconium has principally evolved about the 4+ oxidation state of the metal.[1] However, it is apparent from several recent reports[2] that the lower oxidation states of zirconium offers intriguing possibilities in terms of bonding and reactivity. The objective of the work to be described in this and subsequent papers was the synthesis of a class of organozirconium complexes in which the metal would be capable of facile transition between the 2+ and 4+ oxidation states, through the formal transfer of an electron pair between the metal and a suitable ligand. In this context, cyclo-octatetraene was thought to be a particularly interesting ligand[3] as it is known to co-ordinate to *d*- and *f*-block elements in a planar 1—8-η mode in which it is formally regarded as the 10 π-electron species $C_8H_8^{2-}$, as well as in a variety of other, non-planar modes, such as 1—4-η, 1—6-η, and 1—2,5—6-η which are regarded as being derived from the neutral non-aromatic 8 π-electron molecule. Thus a rearrangement of co-ordinated cyclo-octatetraene from 1—8-η to, for example, 1—4-η is tantamount to a reduction of two units in the formal oxidation state of the metal. Only the more electropositive metals will stabilize the planar 1—8-η form of cyclo-octatetraene, and there are no examples of this type of co-ordination with the transition metals to the right of Group 6.[3] On the other hand, 1—8-η co-ordination appears to be particularly stable for the *f*-block elements. There already exist several well documented[4—7] examples of 1—8-η-C_8H_8 complexes of zirconium and at least one[4] in which the C_8H_8 ligand adopts a different co-ordination mode. It was our intention therefore to synthesize a series of 1—8-η-C_8H_8 complexes of zirconium(IV) which were sufficiently robust to allow easy storage and handling but which would nevertheless prove to be reactive towards a range of attacking groups which were able to induce a change in the cyclo-octatetraene co-ordination mode. In this paper we describe the synthesis of such a group of complexes containing, in addition to cyclo-octatetraene and the versatile pentamethylcyclopentadienyl group, a series of two-electron anionic ligands. Subsequent papers will deal with the reactivity of these compounds.

Results and Discussion

The reaction of $ZrCl_4$ with one equivalent of $K_2(C_8H_8)$ in tetrahydrofuran (thf) afforded an orange crystalline precipitate, presumably of $[Zr(\eta-C_8H_8)Cl_2(thf)]$, a compound previously made by the reaction of $[Zr(\eta-C_8H_8)(1—6-\eta-C_8H_8)(thf)]$ with HCl,[8] and by the electrolysis of $ZrCl_4$ in the presence of cyclo-octatetraene.[9] Subsequent treatment of the reaction mixture with $Li(C_5Me_4R)$ (R = Me or Et) yielded $[Zr(\eta-C_5Me_4R)(\eta-C_8H_8)Cl]$ [(**1**), R = Me; (**2**), R = Et] as a bright yellow crystalline solid after recrystallization. Both (**1**) and (**2**) are air sensitive in the solid state and in solution but they may be stored indefinitely at room temperature under nitrogen. When the order of addition was reversed by adding $Li(C_5Me_5)$ to the zirconium halide prior to the $K_2(C_8H_8)$, a large proportion of the product isolated was dichlorobis(η-pentamethylcyclopentadienyl)zirconium, previously prepared by Bercaw and co-workers.[2b] Only a small quantity of (**1**) was recovered.

The general synthetic method may be extended to other cyclo-octatetraenes and to hafnium. For instance, $[Zr(\eta-C_5Me_5)(\eta-C_8H_7Me)Cl]$ and $[Hf(\eta-C_5Me_5)(\eta-C_8H_8)Cl]$[10] have been isolated in good yield, and shown to have properties similar to those of (**1**) and (**2**). Kablitz and Wilke[8] reported the synthesis of $[Zr(\eta-C_5H_5)(\eta-C_8H_8)Cl]$ as a red crystalline material but have not described its chemistry further.

Both (**1**) and (**2**) proved to be good starting materials for a range of derivatives *via* simple metathetical routes, as shown in

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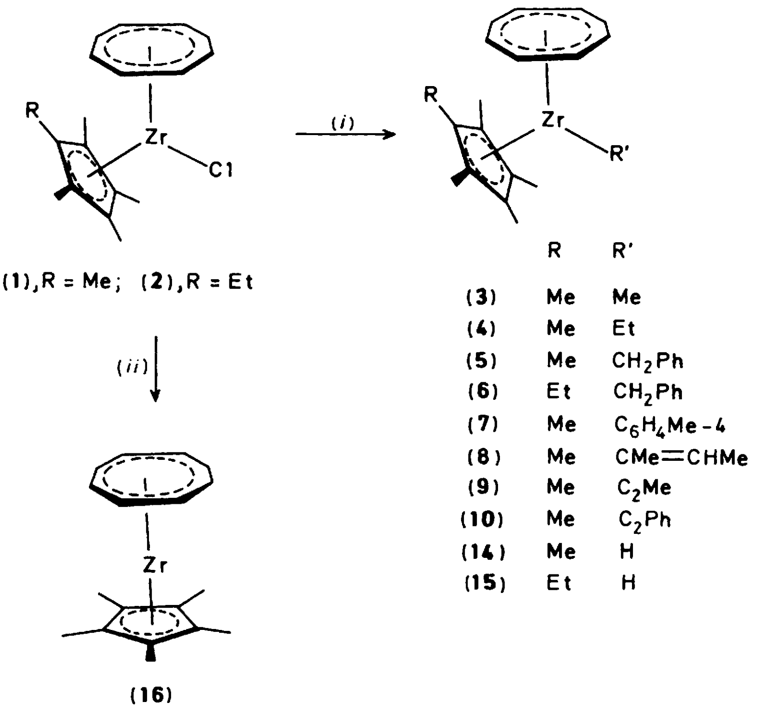
‡ (η-Cyclo-octatrienedi-ido)hydrido(η-pentamethylcyclopentadienyl)zirconium(IV).

Supplementary data available (No. SUP 56450, 6 pp.): H-atom co-ordinates, thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non S.I. units employed: atm = 101 325 Pa, eV ≈ 1.60 × 10^{-19} J.



(1), R = Me; (2), R = Et

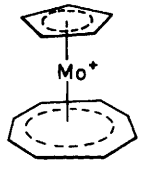
	R	R'
(3)	Me	Me
(4)	Me	Et
(5)	Me	CH_2Ph
(6)	Et	CH_2Ph
(7)	Me	C_6H_4Me-4
(8)	Me	CMe=CHMe
(9)	Me	C_2Me
(10)	Me	C_2Ph
(14)	Me	H
(15)	Et	H

(16)

Scheme. (*i*) Mg(Cl)R′ or LiR′ [(3)—(10)], Mg(Cl)Pr^i [(14) and (15)]; Et_2O, 20 °C; (*ii*) Na/Hg, toluene, 20 °C

the Scheme. Reactions with organo-lithium and -magnesium reagents were very rapid and generally afforded the expected products in good yield and purity. Particularly good results were obtained with chloro-Grignard reagents and halide-free methyl-lithium. The compounds (**1**)—(**10**) were characterized by elemental analysis (Table 1) and/or ^1H and ^{13}C n.m.r. spectroscopy (Table 2).

An 18-electron Zr^{IV} configuration with planar cyclo-octatetraene is proposed for complexes (**1**)—(**10**) from the following evidence. Firstly, singlet resonances are observed for the cyclo-octatetraene ligand in the ^1H n.m.r. spectrum at shifts between δ 5.97 and 5.79 p.p.m. (C_6D_6), appreciably downfield of that observed for free C_8H_8 measured under identical conditions (δ 5.63 p.p.m.).* Generally a pronounced upfield shift is observed in the olefinic proton resonance on co-ordination to a transition metal. This is true of mono-olefins as well as cyclic and acyclic polyolefins. The downfield shift observed for (**1**)—(**10**) is interpreted as reflecting increased ring current in a planar C_8H_8 ring system. Unfortunately, the literature offers no unequivocal evidence to substantiate this proposal. The complexes $[M(C_8H_8)_2R]$ (M = Nb or Ta, R = Me or Ph) which are each presumed to have both a 1—8-η- and a 1—4-η-C_8H_8 ligand display two well separated signals in the ^1H n.m.r. spectrum (*ca.* δ 5.9 and 5.4 p.p.m. in CD_2Cl_2).[11] However, the signals are not assigned. Another interesting sequence of related cyclo-octatetraene complexes, (**11**)—(**13**), has been prepared by Segal *et al.*[12] Application of the 18-electron rule suggests that these should have 1—8-η-, 1—6-η-, and 1—4-η-cyclo-octatetraene ligands respectively and although this has not been confirmed by, for example, *X*-ray crystallography, the proposed structures are entirely reasonable. In keeping with the relative degree of delocalization about the C_8H_8 ring in (**11**) and (**13**) the observed ^1H n.m.r. signals are singlets at δ 7.4 and 5.00 p.p.m., respectively.[12] Compound (**12**) has a rigid 1—6-η-C_8H_8 ligand, as predicted by the application of orbital symmetry rules to polyene complexes,[13] and therefore displays a complex ^1H n.m.r. pattern. However, the mean chemical shift of δ 5.4 p.p.m. is as expected for a partially delocalized ring system.



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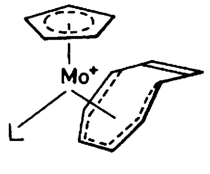

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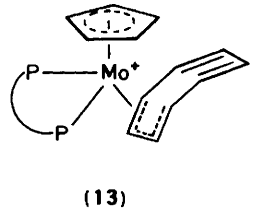

(13)

Perhaps the best n.m.r. evidence for the 1—8-η structure of complexes (**1**)—(**10**) comes from the compound [Zr(η-C_5Me_5)(1—4-η-C_8H_8)(η-C_3H_5)] which is described in detail elsewhere.[14] The ^1H n.m.r. spectra of this and other related complexes in which it is reasonable to assume 1—4-η co-ordination of the C_8H_8 ring display ^1H n.m.r. signals at *ca.* δ 5.5 p.p.m., upfield of those for free cyclo-octatetraene.

Secondly, the compounds described in this paper show no i.r. absorptions in the region 1 680—1 500 cm^{-1}, other than those which may reasonably be ascribed to the vibrations of the R′ group (*e.g.* phenyl vibrations). Bands assigned to the vibration of

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* Compounds (5)—(7) cannot be included in this argument because of the proximity of the C_8H_8 protons to the anisotropic magnetic field of the aromatic ring.

Table 1. Analytical data,[a] yields, and melting points

Compound	Yield (%)	M.p. (θ_c/°C)	Analysis C	Analysis H
(1) [Zr(η-C_5Me_5)(η-C_8H_8)Cl]	80	244—245	59.6 (59.1)	6.4 (6.3)
(2) [Zr(η-C_5Me_4Et)(η-C_8H_8)Cl]	68	179	60.2 (60.1)	7.5 (6.6)
(3) [Zr(η-C_5Me_5)(η-C_8H_8)Me]	87	220	65.5 (66.1)	8.9 (7.6)
(4) [Zr(η-C_5Me_5)(η-C_8H_8)Et]	74	90[b]	66.8 (66.8)	7.8 (7.8)
(5) [Zr(η-C_5Me_5)(η-C_8H_8)(CH_2Ph)]	75	139[b]	70.8 (71.2)	7.5 (7.1)
(6) [Zr(η-C_5Me_4Et)(η-C_8H_8)(CH_2Ph)]		100[b]	71.6 (71.7)	7.5 (7.4)
(7) [Zr(η-C_5Me_5)(η-C_8H_8)(C_6H_4Me-4)]	95	181	71.0 (71.2)	7.6 (7.1)
(9) [Zr(η-C_5Me_5)(η-C_8H_8)(C_2Me)]		158	67.8 (68.2)	6.5 (7.1)
(10) [Zr(η-C_5Me_5)(η-C_8H_8)(C_2Ph)]		166	70.9 (72.3)	7.5 (6.5)
(14) [Zr(η-C_5Me_5)(η-C_8H_8)H]	87	130[b]	64.9 (65.2)	7.3 (7.3)
(16) [Zr(η-C_5Me_5)(η-C_8H_8)]	58	202	66.0 (65.4)	7.1 (7.0)

[a] Calculated values are given in parentheses. [b] With decomposition.

Table 2. Proton and ^{13}C n.m.r. data[a]

	$^1H(\delta)$			$^{13}C(\delta)$			
Compound	C_8H_8	$C_5\mathit{Me}_4R$	Other	C_8H_8	C_5Me_4R	$C_5\mathit{Me}_4R$	Other
(1)	5.92	1.65		96.6	119.6	12.2	
(2)	5.91	1.65, 1.67	2.07 [q, 2 H, $C\mathit{H}_2CH_3$, *J*(HH) 8], 0.70 (t, 3 H, $CH_2C\mathit{H}_3$)	96.5	118.8, 120.1, 122.3	12.0, 12.2	20.8 (–CH_2–), 14.7 ($CH_2\mathit{C}H_3$)
(3)	5.84	1.58	−0.36 (ZrMe)	95.1	116.7	11.7	22.0 (Zr–Me)
(4)	5.83	1.59	1.41 [t, 3 H, Zr–$CH_2C\mathit{H}_3$, *J*(HH) 8.5], 0.11 (q, 2 H, Zr–$C\mathit{H}_2CH_3$)	94.7	116.8	11.7	30.5 (CH_2), 21.0 ($CH_2\mathit{C}H_3$)
(5)	5.64	1.53	7.32 (m, 2 H, Ph), 6.92 (m, 3 H, Ph), 1.45 (s, 2 H, $C\mathit{H}_2Ph$)	94.9	117.9	11.9	159.4 (CH_2–*C*), 127.7, 126.0, 119.9 (Ph), 46.5 (CH_2)
(6)	5.65	1.53, 1.58	7.35 (m, 2 H, Ph), 7.0 (m, 3 H, Ph), 1.98 [q, 2 H, $C\mathit{H}_2CH_3$, *J*(HH) 8], 1.44 (s, 2 H, $C\mathit{H}_2Ph$), 0.71 (t, 3 H, $CH_2C\mathit{H}_3$)	94.7	116, 117.5, 122.8	11.8	159.4 (CH_2–*C*), 127.6, 125.9, 119.7 (Ph), 46.4 (CH_2)
(7)	5.72	1.43	7.2 [d, 2 H, Ph, *J*(HH) 8.5], 6.95 (d, 2 H, Ph), 2.34 (s, 3 H, $C_6H_4\mathit{Me}$)	95.6	117.8	12.0	186.4 (Zr–C), 136.0, 131.6, 126.3 (2-, 3-, and 4-C), 21.7 ($C_6H_4\mathit{Me}$)
(8)[b]	5.79, 5.82	1.56, 1.58	5.93 (m, 1 H, C*H*Me), 5.23 (m, 1 H, C*H*Me), 1.77 (s br, 6 H, Zr–CCH_3, both isomers), 1.68 and 1.93 (s br, 3 H each, CH*Me*)	94.9, 95.0	117.4, 118.1	11.9, 12.3	186.7, 186.4 (Zr–C), 123.9, 120.7 (=*C*HMe), 33.5, 23.8, 23.3, 14.7 (Me)
(9)	5.96	1.72	1.89 (s, 3 H, Me)	95.7	118.4	12.5	5.0 (Me)
(10)	5.97	1.69	6.8—7.6 (m, 5 H, Ph)	95.8	118.5	12.4	131.5, 128.4, 125.5 (Ph), 100.9 (Zr–C≡), 76.7 (≡*C*–Ph)
(14)	5.93[c]	1.72	5.18 (br, 1 H, Zr–H)	94.2	116.7	12.7	
(15)[d]	5.90[c]	1.70, 1.71	5.09 (br, 1 H, Zr–H)	94.1	116.9, 118.1	12.7, 12.4	21.2 (CH_2), 15.8 ($CH_2\mathit{Me}$)

[a] Measured in [$^2H_6$]benzene; chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] [Zr(η-C_5Me_5)(η-C_8H_8)(CMe=CHMe)]; a 1:1 mixture of *E* and *Z* isomers. [c] Doublet, *J*(HH) 1.5 Hz. [d] [Zr(η-C_5Me_4Et)(η-C_8H_8)H].

free C=C bonds have been reported at 1 680—1 660 cm^{-1} for 1—6-η co-ordination and at 1 575—1 500 cm^{-1} for 1—4-η co-ordination.[15,4]

Thirdly, in common with the majority of Zr^{IV} complexes with carbocyclic ligands, compounds **(1)**—**(10)** are pale in colour, whereas the lower oxidation states of Zr are represented by highly coloured compounds such as [Zr(C_5H_5)$_2$(dmpe)] [dmpe = 1,2-bis(dimethylphosphino)ethane][2c] and [ZrH(1—5-η-C_6H_7)(dmpe)$_2$],[2d] and [Zr(η-C_5Me_5)(1—4-η-C_8H_8)(η-C_3H_5)].[14]

Of some interest in terms of the arguments put forward in the introduction to this paper was the stability of the ethyl compound **(4)**. As a crystalline solid **(4)** showed no evidence of decomposition over a period of months when stored under an atmosphere of dry N_2 at 20 °C. Furthermore, a solution of **(4)** in toluene showed no significant decomposition after 8 h at 100 °C. In contrast it is suggested that [ZrCl(Et)(η-C_5H_5)$_2$] be stored at 0 °C[16] and it is reported that [Zr(η-C_8H_8)(Et)$_2$(OEt_2)][8] decomposes at 60 °C. The thermal stability of **(4)** can be understood in terms of the mechanism of β-elimination which requires a vacant co-ordination site adjacent to the alkyl group. No such site is available in **(4)** which is an 18-electron complex.

Table 3. Selected bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for [Zr(η-C_5Me_5)(η-C_8H_8)H] (**14**)

Zr–C(1)	2.44(4)	Zr–C(2)	2.48(3)
Zr–C(3)	2.54(3)	Zr–C(4)	2.44(3)
Zr–C(5)	2.43(4)	Zr–C(6)	2.46(3)
Zr–C(7)	2.48(4)	Zr–C(8)	2.49(5)
Zr–C(11)	2.51(2)	Zr–C(12)	2.55(2)
Zr–C(13)	2.56(2)	Zr–C(14)	2.51(2)
Zr–C(15)	2.48(2)	Zr–H	1.81
Zr(50)–C(51)	2.44(4)	Zr(50)–C(52)	2.50(3)
Zr(50)–C(53)	2.53(2)	Zr(50)–C(54)	2.55(3)
Zr(50)–C(55)	2.45(3)	Zr(50)–C(56)	2.58(3)
Zr(50)–C(57)	2.68(4)	Zr(50)–C(58)	2.51(5)
Zr(50)–C(61)	2.50(2)	Zr(50)–C(62)	2.48(2)
Zr(50)–C(63)	2.48(2)	Zr(50)–C(64)	2.49(2)
Zr(50)–C(65)	2.51(2)	Zr(50)–H(50)	1.78
C–C in C_8 (mean)	1.41(6)		
C–H fixed at	0.96		
C(1)–C(2)–C(3)	138(3)	C(2)–C(3)–C(4)	136(3)
C(3)–C(4)–C(5)	138(4)	C(4)–C(5)–C(6)	143(4)
C(5)–C(6)–C(7)	119(4)	C(6)–C(7)–C(8)	142(4)
C(7)–C(8)–C(1)	134(4)	C(8)–C(1)–C(2)	118(3)
C(51)–C(52)–C(53)	134(3)	C(52)–C(53)–C(54)	138(3)
C(53)–C(54)–C(55)	128(3)	C(54)–C(55)–C(56)	129(3)
C(55)–C(56)–C(57)	139(3)	C(56)–C(57)–C(58)	131(4)
C(57)–C(58)–C(51)	133(5)	C(58)–C(51)–C(52)	144(2)

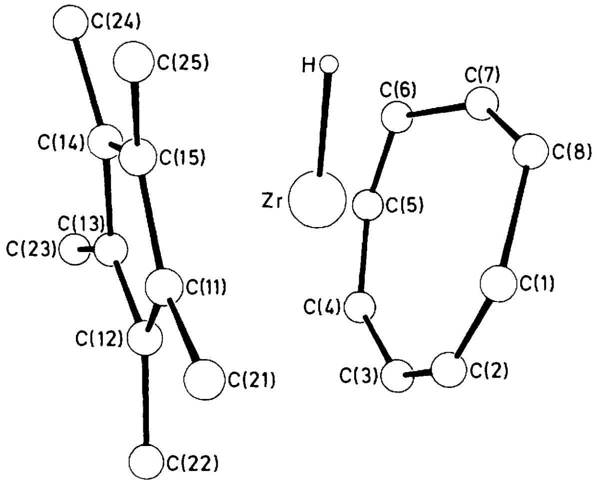

Figure 1. Molecular structure of [Zr(η-C_5Me_5)(η-C_8H_8)H] (**14**) showing the atom numbering. Hydrogen atoms have been omitted for clarity (except the hydride ligand)

Also it appears from this evidence that the 1—8-η co-ordination mode of the cyclo-octatetraene is sufficiently stable not to permit β-elimination to proceed *via* a 1—6-η- or a 1—4-η-C_8H_8 intermediate. An n-propyl[10,14] derivative has also been synthesized and shown to have thermal stability similar to that of the ethyl compound. However, when (**1**) was reacted with an equimolar quantity of 2-propylmagnesium chloride the isolated product was [Zr(η-C_5Me_5)(η-C_8H_8)H] (**14**). The presence of the hydride ligand was evident from the i.r. spectrum which showed a peak at 1 500 cm^{-1}, close to the range of previously observed terminal ν(Zr–H) frequencies (1 540—1 565 cm^{-1}),[8,17] and from a signal in the ^1H n.m.r. spectrum at δ 5.18 p.p.m. In the latter spectrum the signal due to the cyclo-octatetraene protons appeared as a doublet [Table 2; *J*(HH) 1.5 Hz]. Irradiation of the signal at δ 5.18 p.p.m. reduced the C_8H_8 signal to a sharp singlet.

As prepared, crystals of (**14**) were invariably pale green.

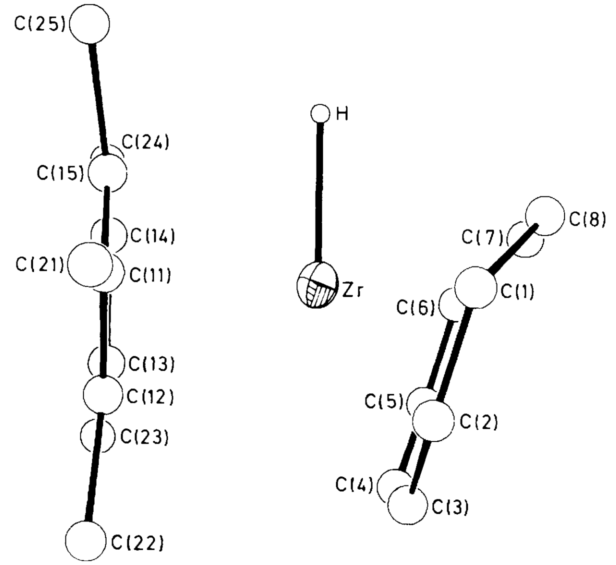

Figure 2. Cross-section through the molecule perpendicular to the mean planes of the two ring systems and including the Zr–H bond, for molecule 1 of the crystallographic asymmetric unit. In molecule 2 the C_5 ring adopts a staggered orientation relative to that of molecule 1

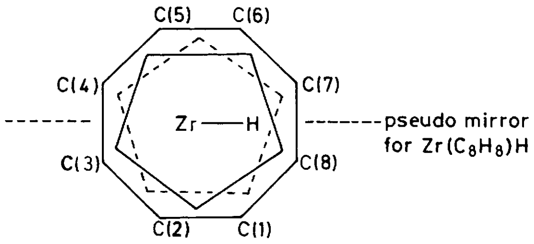

Figure 3. Diagrammatic projection of (**14**) onto the mean plane of the C_8 ring, showing the relationship of the C_5 ring to the mirror symmetry of the Zr(C_8H_8)H moiety.

However, repeated crystallization afforded pale yellow crystals, identical in all other respects with the green crystals which presumably contained traces of a highly coloured impurity. Thus as all the data suggested that (**14**) was a compound of the same type as compounds (**1**)—(**10**), and because suitable crystals were available, it was selected for an *X*-ray crystallographic study.

The results of the *X*-ray diffraction study on (**14**) are summarized in Table 3 and illustrated in Figure 1 (which also includes the atom numbering for molecule 1 of the crystallographic asymmetric unit). The terminally-bound hydride ligand lies between the two ring systems, and these both tilt away from the molecular centre to accommodate the hydride. A cross section through the molecule, perpendicular to the ring systems and including the Zr–H bond, is given in Figure 2.

The molecular geometry is not very accurately determined, for reasons given in the Experimental section. The two Zr–H bond lengths (1.81 and 1.78 Å) are comparable with those found in [ZrH(η^5-C_8H_{11})(dmpe)$_2$] [1.67(2) Å][2c] and in [{ZrH(μ-H)(η-C_5H_4Me)$_2$}$_2$] [1.78(2) Å].[17c] The pentamethylcyclopentadienyl ligands were constrained during refinement to have C–C bond lengths in the ring of 1.420 Å, but the individual Zr–C distances do not deviate significantly from their mean value of 2.51(2) Å. Likewise, the C–C(methyl) distances show no significant deviation from their mean value of 1.52(3) Å, though

Table 4. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for [Zr(η-C_5Me_5)(η-C_8H_8)H] (**14**)

Atom	*x*	*y*	*z*
Zr	0.567 0(5)	0.861 4(3)	0.750 00
C(1)	0.330(5)	0.801(3)	0.733 6(15)
C(2)	0.402(4)	0.723(2)	0.750 6(12)
C(3)	0.501(4)	0.699(2)	0.791 8(11)
C(4)	0.584(5)	0.748(2)	0.828 0(10)
C(5)	0.592(5)	0.838(3)	0.851 3(15)
C(6)	0.545(5)	0.921(3)	0.847 0(12)
C(7)	0.411(5)	0.935(3)	0.822 0(15)
C(8)	0.322(5)	0.899(3)	0.780(2)
C(11)	0.660(3)	0.808 3(14)	0.655 9(7)
C(12)	0.737(3)	0.753 4(14)	0.695 7(7)
C(13)	0.822(3)	0.817 9(14)	0.727 4(7)
C(14)	0.797(3)	0.912 5(14)	0.707 1(7)
C(15)	0.697(3)	0.906 6(14)	0.663 0(7)
C(21)	0.560(4)	0.756(2)	0.611 1(11)
C(22)	0.751(4)	0.645(2)	0.703 8(9)
C(23)	0.941(4)	0.805(2)	0.774 1(10)
C(24)	0.858(4)	1.010(2)	0.721 1(11)
C(25)	0.641(3)	0.980 0(14)	0.618 9(9)
Zr(50)	0.079 2(5)	0.857 6(3)	0.467 81(10)
C(51)	−0.139(5)	0.769(3)	0.452 3(14)
C(52)	−0.038(3)	0.705(2)	0.437 8(9)
C(53)	0.089(3)	0.711 2(13)	0.404 5(7)
C(54)	0.164(4)	0.779(2)	0.377 0(11)
C(55)	0.126(4)	0.881(2)	0.367 1(11)
C(56)	−0.027(4)	0.938(2)	0.379 1(11)
C(57)	−0.142(4)	0.926(3)	0.410 0(12)
C(58)	−0.179(6)	0.855(4)	0.446(2)
C(61)	0.166(3)	0.779 0(11)	0.555 8(8)
C(62)	0.270(3)	0.764 0(11)	0.513 5(8)
C(63)	0.328(3)	0.854 9(11)	0.499 1(8)
C(64)	0.260(3)	0.926 0(11)	0.532 5(8)
C(65)	0.160(3)	0.879 1(11)	0.567 5(8)
C(71)	0.086(4)	0.697(2)	0.585 3(10)
C(72)	0.319(4)	0.668(2)	0.497 8(10)
C(73)	0.447(4)	0.878(2)	0.463 3(13)
C(74)	0.290(4)	1.032(2)	0.536 0(13)
C(75)	0.071(4)	0.922(2)	0.611 3(11)
H	0.518	0.974	0.717
H(50)	0.048	0.976	0.492

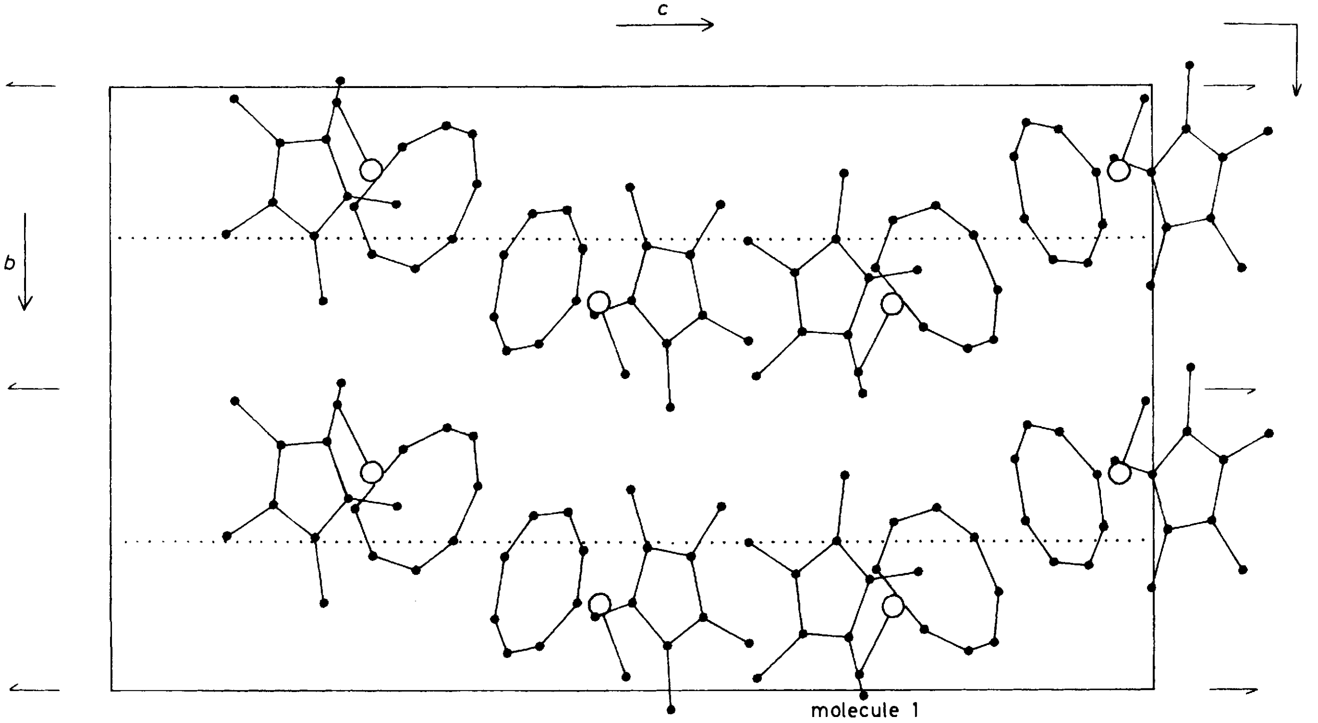

Figure 4. Contents of the orthorhombic unit cell ($Pbc2_1$) viewed in projection down *a* looking towards the origin; hydrogen atoms (except the hydride) have been omitted. The *z* co-ordinate of the Zr atom of molecule 1 has been arbitrarily fixed at 0.75; the pseudo-glide relationship between molecules 1 and 2 is apparent

the methyl groups themselves bend away from the Zr atom, the C–C(methyl) vectors lying between 3 and 8° out of the plane of the C_5 ring. All eight atoms of the C_8H_8 ring are within bonding distance of the Zr atom, giving the latter an overall 18-electron configuration. As Figure 2 shows, the C_8 ring has a shallow 'envelope' configuration, and is bonded on its convex side to the Zr atom. The Zr–C distances for molecule 1 vary between 2.43(4) and 2.54(3) Å, *i.e.* probably not significantly. The fold of the ring lies along the C(1) ⋯ C(6) vector with an interplanar angle of 153°, and the mean C–C bond length in the C_8 ring is 1.41(6) Å. These distances may be compared with mean Zr–C and C–C distances of 2.46(7) and 1.374(15) Å in [Zr(η^4-C_8H_8)(η-C_8H_8)(thf)],[4] of 2.461(15) and 1.398(7) in [Zr(η-C_8H_8)(thf)Cl_2],[5] of 2.479(6) and 1.383(10) Å in [Zr(η-C_3H_5)(η-C_8H_8)(thf)],[6] and of 2.499(2) and 1.398(2) Å, respectively, in [Zr(η-C_8H_8)(η^3,η'^3-$C_{10}H_{16}$)].[7]

As discussed in the Experimental section, the two crystallographically distinct molecules are related to one another by a very approximate glide-plane relationship; on the basis of this, molecule 2 was given crystallographic numbering similar to that of molecule 1 but with atom numbers *n* replaced by (50 + *n*). This numbering sequence is used in the list of atom co-ordinates in Table 4. It turns out, however, that with this numbering, the fold in the C_8 ring occurs between atoms 'C(5)' and 'C(8)', *i.e.* along the C(55) $\cdots$ C(58) vector, rather than as in molecule 1 along the C(6) $\cdots$ C(1) vector. The position of the Zr–H bond is also approximately perpendicular to the fold in the ring, which is also the case for molecule 1. If, however, the moiety comprising the C_8 ring and the Zr–H bond is superimposed on the corresponding moiety for molecule 1, it is then found that the C_5 ring for molecule 2 is in a staggered orientation with respect to that adopted in molecule 1. This can be understood on inspection of Figure 3, which shows a diagrammatic projection of molecule 1 onto the mean plane of the C_8 ring. The Zr–H bond lies in a plane perpendicular to the mean plane of the C_8 ring, and this plane is a mirror plane for the C_8 ring: C(3) and C(4), C(2) and C(5), C(1) and C(6), C(8) and C(7), are mirror-related pairs of atoms. The C_5 ring is, however, skewly related to this mirror plane in such a way that its mirror image is in a staggered orientation relative to itself. Molecule 2 of the crystallographic asymmetric unit is therefore the enantiomorph of molecule 1, but the crystal symmetry ($Pbc2_1$) ensures that in the unit cell the molecules occur as four enantiomorphous pairs. In molecule 2 the Zr–C(C_8) distances vary between 2.44(4) and 2.68(4), and the interplanar angle at the fold in the C_8 ring is 164°. The crystal packing is illustrated in Figure 4.

The 16-electron hydride $[Zr(\eta\text{-}C_5H_5)_2(H)Cl]$ is very reactive towards alkenes and has found some applications in stoicheiometric organic synthesis.[18] In contrast **(14)** did not react with ethylene (100 atm) at 18 °C over 18 h. Under similar conditions other simple alkenes were also unreactive, as were the disubstituted alkynes, but-2-yne and 3-phenylprop-2-yne. However, reaction with buta-1,3-diene afforded quantitatively a mixture of *E* and *Z* isomers of the but-2-en-1-yl compound $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(CH_2CH{=}CHMe)]$ corresponding to 1,4-addition to the diene.[14] Some terminal alkynes also proved reactive: phenylethyne gave the corresponding phenylethynyl complex **(10)** in high yield and ethyne apparently afforded a mixture of the ethynyl and ethenyl compounds. However, no reaction was observed with 3,3-dimethylbutyne under similar reaction conditions.

Reduction of **(1)** dissolved in toluene with sodium amalgam formed a dark brown solution from which black pyrophoric crystals of **(16)** were isolated. The i.r. spectrum of **(16)** showed bands consistent with the presence of $C_8H_8^{2-}$ and a pentamethylcyclopentadienyl group. Toluene solutions of **(16)** were paramagnetic with a single resonance in the e.s.r. spectrum at $g = 1.982$. When **(16)** was dissolved in chlorinated solvents a rapid reaction took place forming **(1)**, whereas thf led to intractable products. It is tentatively suggested that **(16)** is the Zr^{III} complex $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)]$ which is also claimed to be the product of the reduction of $[Zr(\eta\text{-}C_5Me_5)Cl_3]$ in the presence of cyclo-octatetraene.[19]

Experimental

All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were dried and distilled under nitrogen immediately prior to use. Infrared spectra in the range 4 000—600 cm^{-1} were recorded on a Perkin-Elmer 297 grating spectrophotometer as a Nujol mull of the solid held between NaCl discs. The i.r. samples were prepared in a nitrogen-filled glove box (Vacuum Atmospheres HE43) containing < 5 p.p.m. oxygen. Hydrogen-1 n.m.r. spectra were recorded on a JEOL PS100 spectrometer (continuous wave) or JEOL FX 90Q or JEOL FX 200 (Fourier transform) spectrometers operating at 100, 90, and 199.5 MHz, respectively. Carbon-13 n.m.r. spectra were recorded on a JEOL FX 90Q spectrometer at 22.5 MHz. Tetramethylsilane was used as internal reference for both ^1H and ^{13}C n.m.r. spectra unless otherwise stated. Samples were prepared under nitrogen or argon in dry, deoxygenated deuteriated solvents. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument in toluene as solvent, and were calibrated against a solid sample of diphenylpicrylhydrazyl radical. Mass spectra were recorded on a A.E.I. MS 9 mass spectrometer fitted with VG 3D8 electronics and VG ZAB ion source operating at 70 eV in electron impact mode. Samples for microanalysis were presealed in aluminium capsules in the glove box. Melting points were measured under vacuum in sealed capillary tubes.

Synthesis of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)Cl]$ **(1)**.—Zirconium tetrachloride (15 g, 64.4 mmol) was added to thf (50 cm^3) at −78 °C with rapid stirring. The cold slurry was treated with a solution of $K_2(C_8H_8)$ [from potassium (5.4 g) and C_8H_8 (6.9 g)] in thf (100 cm^3). The mixture was then heated under reflux for 18 h affording a fine orange precipitate and a red solution. After cooling to 20 °C a suspension of $Li(C_5Me_5)$ (65.5 mmol) in thf (125 cm^3) was added with rapid stirring, and the mixture was warmed to the point where a gentle reflux was maintained. Over 2 d a pale off-white solid and a yellow solution formed. The reaction mixture was cooled to room temperature and filtered through a pad of kieselguhr. Solvent was removed from the filtrate *in vacuo* and the oily orange solid residue was washed with diethyl ether (2 × 20 cm^3). The solid was dissolved in dichloromethane (*ca.* 200 cm^3) and filtered through kieselguhr. Subsequent cooling of the filtrate (−20 °C) yielded bright yellow crystals of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)Cl]$ **(1)** (18.7 g, 51.2 mmol, 80%); $\nu_{max.}$ 3 010s, 1 260m, 1 080m,br, 1 020m, 915s, 805s, 775s, 745vs, 700m, 675m, and 640s cm^{-1}. Other experimental data are presented in Tables 1 and 2.

Similarly, $[Zr(\eta\text{-}C_5Me_4Et)(\eta\text{-}C_8H_8)Cl]$ **(2)** was prepared in 68% yield; $\nu_{max.}$ 3 010m, 1 314w, 1 258m, 1 094m,br, 1 022m, 962w, 948w, 922m, 906m, 814m, 798m, 735s, and 722m cm^{-1}.

Synthesis of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)Me]$ **(3)**.—To a stirred suspension of **(1)** (0.82 g, 2.24 mmol) in diethyl ether (20 cm^3) was slowly added a solution of LiMe (1.96 mol dm^{-3} in Et_2O, 1.15 cm^3, 2.25 mmol) using a syringe. Addition of the lithium reagent was halted when all the starting material had dissolved. After 1 h solvent was removed *in vacuo* and the solid yellow residue was extracted with hexane (40 cm^3). The solution was filtered through a kieselguhr pad and the solution reduced in volume *in vacuo* until saturated. The complex $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)Me]$ **(3)** was isolated as yellow needles on cooling the solution to −20 °C over 18 h. Further crops were obtained from the mother-liquor (0.68 g, 1.97 mmol, 87%).

Synthesis of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)H]$ **(14)**.—To a solution of **(1)** (0.75 g, 2.05 mmol) in toluene (60 cm^3) was slowly added a solution of $Mg(Cl)CHMe_2$ (0.93 mol dm^{-3} in Et_2O, 2.2 cm^3, 2.05 mmol). The mixture was stirred for 4 h during which time the colour changed from yellow to pale green and an insoluble off-white precipitate formed. After filtration the solution was partially evaporated *in vacuo* until the product began to precipitate. Cooling to −20 °C afforded $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)H]$ **(14)** as pale green plates (0.59 g, 1.78 mmol, 87%); $\nu_{max.}$ 3 048w, 3 020w, 1 780w,br, 1 650w,br, 1 550—1 450m,br, 1 264m, 1 090m,br, 1 023m, 916m, 904m, 862w, 794m, 772w, 761w, and 728s cm^{-1}.

The colour evidently results from a trace impurity which could be eliminated only by repeated crystallization. The pure material was very pale yellow.

In an alternative synthesis, $LiAlH_4$ (0.07 g, 1.79 mmol) was added to a stirred suspension of (**1**) (0.25 g, 0.68 mmol) in diethyl ether (60 cm^3). After 5 min the solution turned green and in a recovery procedure similar to that described above, crystals of (**14**) were isolated (0.092 g, 40%). The material was identified by comparison of the n.m.r. spectra with those of a sample prepared as above.

In an analogous reaction $[Zr(\eta\text{-}C_5Me_4Et)(\eta\text{-}C_8H_8)H]$ was prepared from (**2**) and $Mg(Cl)CHMe_2$ as pale green crystals (57%); $\nu_{max.}$ 3 060m, 3 020m, 2 805m, 1 570—1 500m,br, 1 492m, 1 482m, 1 310w,br, 1 264s, 1 191w, 1 152w, 1 094s, 1 040s, 1 026s, 915w, 908m, 858w, 804m, and 749s cm^{-1}.

Synthesis of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)]$ (**16**).—To a rapidly stirred amalgam (0.5 g Na in 50 cm^3 Hg) was added a toluene solution of (**1**) (1.50 g, 4.11 mmol in 100 cm^3). After 36 h the dark green-brown solution was filtered through kieselguhr. The amalgam was washed with toluene (2 × 10 cm^3) and the washings were also passed through kieselguhr. Partial evaporation *in vacuo* of the combined filtrates gave a saturated solution which afforded brown-black pyrophoric crystals of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)]$ (**16**) on cooling to −20 °C (0.79 g, 2.4 mmol, 58%); $\nu_{max.}$ 3 012m, 3 004s, 1 868w,br, 1 782w,br, 1 672w,br, 1 259m, 1 100m,br, 1 022m, 907m, 899m, 808m, 788m, 760m, 745vs, 678m, and 642m cm^{-1}; e.s.r. (toluene, 18 °C), $g = 1.982$ (singlet).

Reaction of (**14**) *with Phenylethyne.*—To a rapidly stirred solution of (**14**) (0.3 g, 0.91 mmol) in toluene (20 cm^3) at 0 °C was added a solution of PhC_2H (0.19 g, 1.86 mmol) in toluene (10 cm^3). After 1 h solvent was removed *in vacuo* and the yellow oily residue was crystallized from hexane at −20 °C, affording yellow crystals (0.33 g, 0.78 mmol, 86%) which had identical spectroscopic properties to those of (**10**) prepared from (**1**) and $Mg(Cl)C_2Ph$.

Crystal Structure Determination of (**14**).—Crystals of (**14**) were obtained as thin pale green needles by recrystallization from a diethyl ether solution which was slowly cooled from 25 to 0 °C. The data crystal, of approximate dimensions 0.25 × 0.15 × 0.08 mm, was mounted under argon in a Lindemann capillary tube. Intensities were recorded at 210 K ($\theta/2\theta$ scan) in the range $2.9 \leqslant 2\theta \leqslant 50°$: a 1.5-kW *X*-ray tube was used at first, but this failed after *ca.* 1 000 intensities had been measured and had to be replaced with a 1.0-kW tube which gave intensities some 70% lower than those from the 1.5-kW tube. Of the 1 875 unique intensities measured on a Nicolet *P*3*m* four-circle diffractometer, only 1 019 were used in the solution and refinement of the structure. No correction was applied for *X*-ray absorption effects.

Crystal data. $C_{18}H_{24}Zr$, $M = 331.6$, orthorhombic, $a = 9.518(5)$, $b = 13.956(5)$, $c = 23.753(10)$ Å, $U = 3\,155(3)$ Å^3, $Z = 8$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\,376$, space group $Pbc2_1$ (non-standard setting of $Pca2_1$, no. 29), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.8 cm^{-1}.

The structure was solved by heavy-atom methods and was refined using blocked-cascade least-squares methods. The zirconium atoms were refined anisotropically and the other non-hydrogen atoms isotropically. The hydrogen atoms were all located on electron density maps, but because of the paucity of data, all except the hydride were included in calculated positions and refined in a 'riding' mode with thermal parameters fixed at 1.2 times that of the bonded carbon atom. The C_5 rings were refined as rigid groups of ideal pentagonal symmetry. The hydride ligands were located unequivocally but proved unstable on refinement; they were therefore included at the positions of maximum electron density with fixed positional and thermal parameters. The Zr–H bond lengths thus carry no meaningful standard deviations. Individual weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.000\,25|F_o|^2]^{-1}$, and the refinement converged at R 0.066 (R' 0.055). The final electron density difference synthesis showed no features > 0.7 or < −0.6 e Å^{-3}. Atomic scattering factors were taken from ref. 20. All computations were carried out within the Laboratory on a Date General 'Eclipse' minicomputer using the SHELXTL system of programs.[21] The atomic co-ordinates for (**14**) are in Table 4.

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