Allyl Derivatives of (Cyclo-octatetraene)(η-pentamethylcyclopentadienyl)-zirconium: *X*-Ray Crystal Structure of $[Zr(\eta\text{-}C_5Me_5)(1\text{—}4\text{-}\eta\text{-}C_8H_8)(\eta\text{-}C_3H_5)]$ ‡

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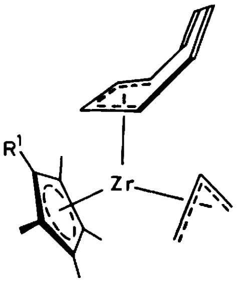
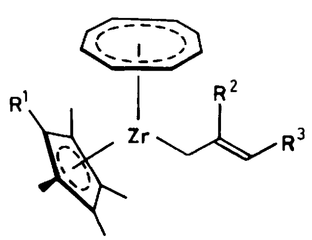
Reaction of $[Zr(\eta\text{-}C_5Me_4R^1)(\eta\text{-}C_8H_8)Cl]$ with $MgCl(CH_2CR^2CHR^3)$ (R^1 = Me, $R^2 = R^3$ = H; R^2 = H, R^3 = Me or Ph; R^2 = Me, R^3 = H; R^1 = Et, $R^2 = R^3$ = H; R^2 = Me, R^3 = H) affords a series of complexes of general formula $[Zr(C_5Me_4R^1)(C_8H_8)(CH_2CR^2CHR^3)]$. Both the C_3H_5 complexes are intense purple and the pentamethylcyclopentadienyl derivative is shown by a single crystal *X*-ray diffraction study to have an $\eta\text{-}C_3H_5$ ligand and a $1\text{—}4\text{-}\eta\text{-}C_8H_8$ ligand attached to zirconium [mean Zr–C: C_3H_5, 2.480; C_8H_8 (co-ordinated C), 2.457; C_5Me_5, 2.510 Å] and is therefore formally a complex of zirconium(II). This complex undergoes rapid interchange of *syn* and *anti* allyl hydrogen atoms at 20 °C (from n.m.r. measurements) and reacts readily with H_2 (1 atm) affording a mixture of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)(\sigma\text{-}C_3H_7)]$ and $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)H]$. Those complexes with substituted allyl ligands are pale yellow and have $\sigma\text{-}CH_2CR^2CHR^3$ and $\eta\text{-}C_8H_8$ ligands and are formally derivatives of Zr^{IV}. Despite the formal co-ordinative saturation of the yellow complexes, the 2-methylallyl derivatives undergo a rapid 1,3 shift.

In a previous paper [1] we reported the synthesis of a range of 18-electron zirconium(IV) complexes containing the planar $\eta\text{-}C_8H_8$ ligand, and discussed the possibility that this ligand might be induced to undergo a reductive ring slippage under the influence of an attacking electron donor, thus simultaneously creating co-ordination sites on the metal and reducing the formal oxidation state from zirconium(IV) to zirconium(II). This paper describes a group of complexes $[Zr(\eta\text{-}C_5Me_4R^1)(C_8H_8)A]$ where A^- is an allyl ligand which may function as a two-electron or a four-electron donor, thus allowing the observation of the relative abilities of the C_8 and C_3 ligands to achieve their maximum degree of co-ordination to the metal.



	R^1
(1)	Me
(2)	Et



	R^1	R^2	R^3
(3)	Me	H	Me
(4)	Me	H	Ph
(5)	Me	Me	H
(6)	Et	Me	H

Results and Discussion

On the addition of a tetrahydrofuran (thf) solution of $MgCl(C_3H_5)$ to a suspension of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)Cl]$ in diethyl ether, an intense purple solution formed. Evaporation of the solvent and recrystallization from hexane afforded purple-black crystals of $[Zr(C_5Me_5)(C_8H_8)(C_3H_5)]$ (**1**) in good yield (Table 1). The intense and characteristic colour of (**1**) suggested a molecule with an electronic structure quite different from the pale yellow $\eta\text{-}C_8H_8$ derivatives of Zr^{IV} which we have previously described.[1,2] Strong absorptions at visible wavelengths are frequently observed for compounds of zirconium(II) such as $[Zr(\eta\text{-}C_5H_5)_2(dmpe)]$ [dmpe = 1,2-bis(dimethylphosphino)ethane],[3] $[Zr(\eta\text{-}C_8H_8)(1\text{—}4\text{-}\eta\text{-}C_8H_8)(thf)]$,[4] and $[Zr(\eta\text{-}C_5Me_5)(\eta^3\text{-}CH_2CHCHMe)(\eta\text{-}C_4H_6)]$.[5] In an analogous reaction purple $[Zr(C_5Me_4Et)(C_8H_8)(C_3H_5)]$ (**2**) was prepared from $[Zr(\eta\text{-}C_5Me_4Et)(\eta\text{-}C_8H_8)Cl]$ and $MgCl(CH_2CHCH_2)$.

Compound (**1**) displayed a strong absorption in the i.r. spectrum at 1 524 cm^{-1}, indicative of an $\eta\text{-}C_3H_5$ group,[6] and a weaker band at 1 509 cm^{-1} suggesting 1—4-η co-ordination of the C_8H_8 ligand.[7,8] The ^1H n.m.r. spectrum (Table 2) of the allyl moiety at temperatures above −40 °C was of the AX_4 type consistent with an $\eta\text{-}C_3H_5$ group undergoing *syn–anti* exchange, though by no means establishing this mode of co-ordination. At temperatures below −40 °C the allyl signals broaden and collapse and are not observed at −96 °C whereas the resonances due to the C_5Me_5 and C_8H_8 groups remain unchanged over this temperature range. The C_8H_8 resonance was observed as a sharp singlet at δ 5.52 p.p.m., upfield of the signal for free C_8H_8 measured under the same conditions (δ 5.63 p.p.m.). As previously discussed [1] the observed downfield shift of the $\eta\text{-}C_8H_8$ resonance of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)H]$ and related species may be interpreted as arising from increased aromatization of the C_8 ring on co-ordination to the metal in a planar, 1—8-η mode. Conversely the upfield shift observed for (**1**) and (**2**) suggests a non-planar C_8H_8 ligand with a low degree of delocalization about the ring. Significantly the ^{13}C chemical shift (Table 3) of the C_8H_8 carbon nuclei in (**1**) is approximately 4 p.p.m. higher than is observed for the $\eta\text{-}C_8H_8$ complexes.

In order to define unambiguously the molecular structure of (**1**) a single-crystal *X*-ray diffraction study was undertaken. The results are summarised in Table 4 and illustrated in Figure 1 (which also includes the atom numbering scheme). The mol-

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‡ (η-Allyl)(1—4-η-cyclo-octatetraene)(η-pentamethylcyclopentadienyl)zirconium(II).

Supplementary data available (No. SUP 56453, 7 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.

Table 1. Analytical data,[a] yields, and melting points for the zirconium complexes

Complex	Yield (%)	M.p.[b] (θ_c/°C)	Analysis (%) C	H
(1) [Zr(η-C_5Me_5)(1—4-η-C_8H_8)(η-C_3H_5)]	80	115	68.2 (67.9)	7.5 (7.9)
(2) [Zr(η-C_5Me_4Et)(1—4-η-C_8H_8)(η-C_3H_5)]	81	90	69.0 (68.5)	7.6 (7.8)
(3) [Zr(η-C_5Me_5)(η-C_8H_8)(σ-$CH_2CHCHMe$)]			68.4 (68.5)	8.4 (7.8)
(4) [Zr(η-C_5Me_5)(η-C_8H_8)(σ-$CH_2CHCHPh$)]		85	72.8 (72.5)	7.8 (7.2)
(5) [Zr(η-C_5Me_5)(η-C_8H_8)(σ-CH_2CMeCH_2)]	85	105	68.0 (68.5)	8.5 (7.8)
(6) [Zr(η-C_5Me_4Et)(η-C_8H_8)(σ-CH_2CMeCH_2)]	82	105	69.0 (69.1)	8.5 (8.0)

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

Table 2. Proton n.m.r. data[a] for the zirconium complexes

Complex	C_8H_8	C_5Me_4R	H^1	R^2	H^3	R^3
(1)[b]	5.52	1.50	2.72	6.67		
(2)[c]	5.55	1.42, 1.48	2.71	6.69		
E-(3)[d]	5.77	1.52	1.10	5.96	4.70	2.00
Z-(3)[e]	5.83	1.53	0.93			1.93
(4)[f]	5.77	1.54	1.20	6.76	6.04	7.22—7.58
(5)[g]	5.80	1.52	0.88	1.84	4.58	4.84
(6)[g]	5.79	1.48, 1.54	0.95	1.83	4.55	4.80

[a] Chemical shifts, δ, in p.p.m. to high frequency of $SiMe_4$, measured in [$^2H_6$]benzene or [$^2H_8$]toluene, 30 °C unless stated. [b] $^3J(H^1H^2)$ 11 Hz. [c] $^3J(H^1H^2)$ 12 Hz. [d] $^3J(H^1H^2)$ 8.8, $^4J(H^1H^3)$ 1.3, $^5J(H^1Me)$ 1.3, $^3J(H^2H^3)$ 14.5, $^4J(H^2Me)$ 1.5, $^3J(H^3Me)$ 6.4 Hz. [e] Crotyl protons H^2 and H^3 could not be positively identified. [f] $^3J(H^1H^2)$ 12 Hz. [g] −90 °C.

ecule has approximate (non-crystallographic) mirror symmetry with atoms Zr, C(2), C(22), and C(32) lying on the pseudo-mirror plane which also bisects the bonds between atoms C(12)–C(13), C(16)–C(17), and C(24)–C(25). The metal is equivalently bonded to all three allyl carbon atoms in 1—3-η co-ordination mode [Zr–C *ca.* 2.48 Å, see Table 4] and the two allyl carbon–carbon bonds are equal (*ca.* 1.39 Å) within experimental error. Whereas this equivalence in C–C bond lengths is similar to that observed[9] in two independent molecules of [Zr(η-C_8H_8)(η-C_3H_5)(thf)] (mean C–C 1.358 Å) the Zr–C(allyl) bonds in the latter compound vary over a range from 2.448(5) to 2.517(5) Å (mean Zr–C 2.481 Å). The pentamethylcyclopentadienyl ligand in (1) shows no significant deviation from the idealized pentagonal geometry with a mean C–C bond length of 1.418(4) Å and a mean Zr–C distance of 2.510(12) Å. As expected the methyl groups lie between 3 and 10° out of the C_5 plane, bending away from the metal atom.

The cyclo-octatetraene ligand is co-ordinated in a 1—4-η mode with atoms C(15)—C(18) more than 3.25 Å from the metal. Atoms C(11)—C(14) are bonded to zirconium but with a marked distinction between the inner and outer Zr–C bond lengths (mean 2.388 and 2.530 Å respectively). Brauer and Krüger[7] noted an even greater difference in the inner and outer Zr–C distances of the 1—4-η-C_8H_8 ligand in [Zr(η-C_8H_8)(1—4-η-C_8H_8)(thf)] but ascribed the effect, at least in part, to the imperfections of their least-squares model. However, the effect appears to be both real and general for 1—4-η-C_8H_8 complexes of the early transition metals[10,11] and is rather more pronounced for these elements than for later transition elements.[8,12] Interestingly there is evidence that 1—4-η-butadiene ligands also have a pronounced tendency towards a strong 1,4 interaction with the metal.[13]

Carbon–carbon bond distances within the co-ordinated portion of the C_8H_8 ligand are approximately equal whereas those not involved with the metal alternate in length with localized double bonds between C(15) and C(16), and between C(17) and C(18).

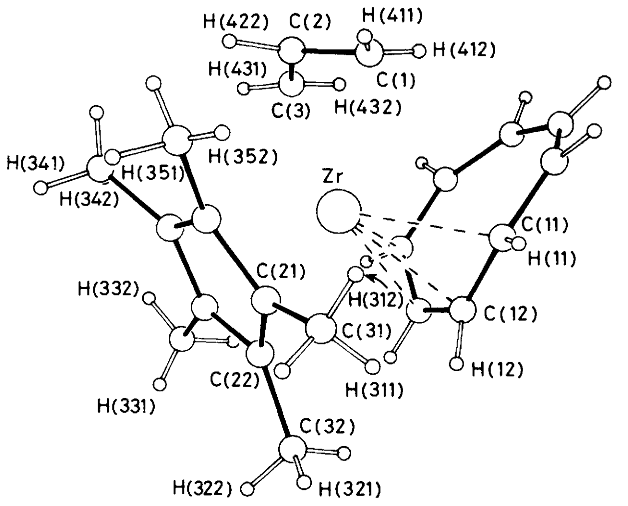

Figure 1. Molecular structure of [Zr(η-C_5Me_5)(1—4-η-C_8H_8)(η-C_3H_5)] (1) showing the atom numbering

The C_8 rings in 1—4-η-cyclo-octatetraene complexes are non-planar and may in general be described by two planes.[11] In complex (1) the atom sequences C(11)—C(14) and C(11),-C(14)—C(18) are each approximately coplanar and make an interplanar angle of 149°. This may be compared with the values of 159° found[7] for the 1—4-η-C_8H_8 ring of [Zr(η-C_8H_8)(1—4-η-C_8H_8)(thf)] and 136—147° found for 1—4-η-C_8H_8 complexes of iron and ruthenium.[8,12,*] There are three idealized conformations of the C_8H_8 ligand (C_s, D_{2d}, and C_{2v}) which are accessible by slight distortions of the planar conformation,[11] and it has been proposed that a near continuum of closely related structures exists because the three basic conformations are close in terms of atom movement. In fact in (1) the C_8H_8 ligand may be described more accurately by three planes, C(11)—C(14), C(11),C(14),C(15),C(18), and C(15)—C(18) (interplanar angles 152 and 170°) implying a geometry between the simple C_s structure (one fold) and the C_{2v} form (two folds) (Figure 2). The metal atom lies 2.05 Å from the plane C(11)—C(14) on the convex side of the shallow tub.

Thus the crystallographic results establish (1) as a 16-electron complex of zirconium(II). The affinity of the metal for an η-C_3H_5 moiety is evidently sufficient to displace the cyclo-octatetrene from the 1—8-η co-ordination mode and thereby to bring about a formal reduction of the metal.

In contrast to the results obtained with the C_3H_5 ligand, reaction of [Zr(η-$C_5Me_4R^1$)(η-C_8H_8)Cl] with 2- or 3-

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* See discussion in ref. 11.

Table 3. Carbon-13 n.m.r. data[a] for the zirconium complexes

Complex	C_8H_8	$C_5Me_4R^1$	$C_5\mathit{Me}_4R^1$	R^2/R^3	C^1	C^2	C^3	Other
(1)	99.3	115.0	11.2		75.8	144.3	75.8	
(2)	99.3	118.4, 120.1	11.1		75.7	144.2	75.7	19.9 (CH_2), 14.9 (Me)
E-**(3)**	95.9	116.6	11.7	18.6	43.9	143.4	109.5	
Z-**(3)**	95.0	117.0	11.7	13.1	37.3	144.2	108.6	
(4)	95.3	117.0	11.7	141.9	43.5	144.5	115.9	123.9, 124.8, 128.8 (Ph)
(5)[b]	94.9	116.5			46.7	158.9	100.6	
(5)[c]	95.2	117.0	11.8	25.7	74.3	158.5	74.3	
(6)[b]	94.8	115.9, 116.8	11.5, 11.6	25.8	46.6	159.0	100.5	20.3 (CH_2), 15.2 (Me)

[a] Chemical shifts in p.p.m. to high frequency of $SiMe_4$, measured in $[^2H_6]$benzene or $[^2H_6]$toluene. [b] −70 °C. [c] 50 °C.

Table 4. Selected bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for $[Zr(\eta\text{-}C_5Me_5)(1\text{—}4\text{-}\eta\text{-}C_8H_8)(\eta\text{-}C_3H_5)]$ **(1)**

Zr–C(1)	2.467(6)	Zr–C(2)	2.485(5)
Zr–C(3)	2.488(6)	Zr–C(11)	2.521(4)
Zr–C(12)	2.386(5)	Zr–C(13)	2.382(6)
Zr–C(14)	2.540(6)	Zr–C(21)	2.499(4)
Zr–C(22)	2.511(4)	Zr–C(23)	2.494(4)
Zr–C(24)	2.525(4)	Zr–C(25)	2.523(5)
C(1)–C(2)	1.380(7)	C(2)–C(3)	1.388(9)
C(11)–C(12)	1.404(7)	C(11)–C(18)	1.441(6)
C(12)–C(13)	1.402(8)	C(13)–C(14)	1.418(6)
C(14)–C(15)	1.444(6)	C(15)–C(16)	1.360(8)
C(16)–C(17)	1.413(8)	C(18)–C(17)	1.373(7)
C(21)–C(22)	1.420(8)	C(21)–C(25)	1.421(6)
C(21)–C(31)	1.504(7)	C(22)–C(23)	1.415(6)
C(22)–C(32)	1.501(7)	C(23)–C(24)	1.423(7)
C(23)–C(33)	1.501(9)	C(24)–C(25)	1.413(7)
C(24)–C(34)	1.505(6)	C(25)–C(35)	1.501(8)
C(11)–C(12)–C(12)	130.9(4)	C(12)–C(13)–C(14)	131.7(5)
C(13)–C(14)–C(15)	131.8(5)	C(14)–C(15)–C(16)	135.0(5)
C(15)–C(16)–C(17)	134.5(4)	C(16)–C(17)–C(18)	132.9(4)
C(17)–C(18)–C(11)	134.5(5)	C(18)–C(11)–C(12)	132.6(5)
C(1)–C(2)–C(3)	123.4(6)		

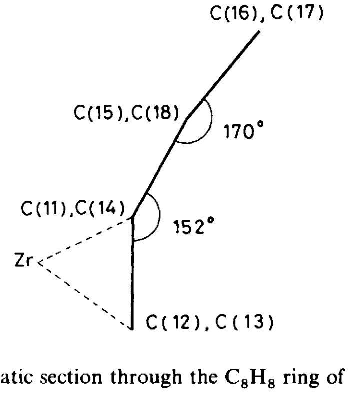
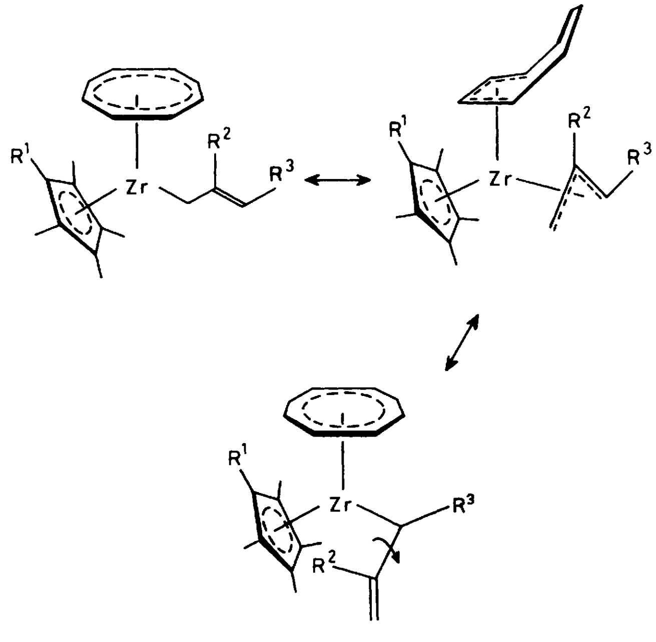


Figure 2. Schematic section through the C_8H_8 ring of **(1)** showing the interplanar angles



Scheme.

substituted allyl Grignard reagents $MgCl(CH_2CR^2CHR^3)$ afforded a series of yellow compounds $[Zr(\eta\text{-}C_5Me_4R^1)(\eta\text{-}C_8H_8)(\sigma\text{-}CH_2CR^2CHR^3)]$ **(3)**—**(6)**. The ^1H and ^{13}C n.m.r. parameters of the C_8H_8 ligands in **(3)**—**(6)** (Tables 2 and 3) are very similar to those observed[1] for simple alkyl and hydrido derivatives, *e.g.* $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)H]$ for which the 1—8-η co-ordination of cyclo-octatetraene is established. The σ co-ordination of the 3-substituted allyls **(3)** and **(4)** was apparent from the ^1H n.m.r. spectra which were invariant over the temperature range ±90 °C, and which displayed resonances between δ 4.70 and 6.76 p.p.m., typical of 'free' olefinic hydrogens. Similarly ^{13}C n.m.r. showed resonances typical of free olefinic carbon atoms at between δ 108 and 145 p.p.m. The crotyl compound **(3)** was always isolated as a 2:1 mixture of *E* and *Z* forms, regardless of whether it was prepared by the Grignard method or by 1,4 insertion of buta-1,3-diene into the Zr–H bond of $[Zr(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_8)H]$.[1] Kormer *et al.*[14] found that the *E*:*Z* ratio for $[Mn(\sigma\text{-}CH_2CHCHMe)(CO)_5]$ was determined by the method of synthesis, being *ca.* 15:85 for 1,4 addition of $[MnH(CO)_5]$ to buta-1,3-diene and *ca.* 80:20 from the reaction of $Na[Mn(CO)_5]$ and 1-chlorobut-1-ene. The observation of a constant 2:1 ratio for the zirconium complexes regardless of the synthetic route suggests the two isomers are isolated as an equilibrium mixture which in turn requires that a rearrangement pathway exists for **(3)** which is unavailable to co-ordinatively saturated species such as $[Mn(\sigma\text{-}CH_2CHCHMe)(CO)_5]$ (Scheme).

The behaviour of the 2-methylallyl complexes **(5)** and **(6)** is different. At room temperature only two allyl signals are observed in the ^1H n.m.r. spectrum, corresponding to the Me group and the four methylene protons [δ 1.78 and 2.70 respectively for **(5)**]. However the methylene proton signal is broad at 26 °C and on cooling it collapses and is replaced (−90 °C) by three signals in the ratio 1:1:2 (Table 2) confirming σ co-ordination. Similar temperature-dependent effects are observed in the ^{13}C n.m.r.: the two signals observed at 46.7 and 100.6

Table 5. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for [Zr(η-C$_5$Me$_5$)(1—4-η-C$_8$H$_8$)(η-C$_3$H$_5$)] (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr	0.191 11(3)	0.236 24(4)	0.127 40(1)	C(18)	0.253 6(5)	−0.078 9(5)	0.165 5(2)
C(1)	0.202 2(6)	0.191 3(5)	0.213 2(2)	C(21)	−0.003 8(4)	0.280 7(5)	0.074 4(2)
C(2)	0.240 4(4)	0.322 1(5)	0.214 6(2)	C(22)	0.052 4(4)	0.314 0(5)	0.043 8(2)
C(3)	0.326 3(5)	0.354 7(8)	0.202 1(3)	C(23)	0.119 7(4)	0.426 9(5)	0.066 0(2)
C(11)	0.175 9(4)	−0.019 1(5)	0.119 9(2)	C(24)	0.101 4(4)	0.466 8(4)	0.109 2(2)
C(12)	0.185 2(4)	0.040 4(5)	0.077 7(2)	C(25)	0.025 8(4)	0.376 2(5)	0.114 6(2)
C(13)	0.263 5(4)	0.128 2(5)	0.074 2(2)	C(31)	−0.089 0(5)	0.172 8(6)	0.063 6(3)
C(14)	0.358 7(4)	0.184 3(6)	0.111 6(2)	C(32)	0.030 9(5)	0.259 0(6)	−0.007 8(2)
C(15)	0.438 2(4)	0.128 4(6)	0.157 7(3)	C(33)	0.189 1(5)	0.499 2(6)	0.044 4(2)
C(16)	0.441 7(4)	9.019 8(6)	0.187 5(2)	C(34)	0.145 1(5)	0.593 9(5)	0.139 5(3)
C(17)	0.363 7(5)	−0.070 5(5)	0.190 9(2)	C(35)	−0.027 2(5)	0.388 7(6)	0.151 0(2)

p.p.m. [(**5**), −70 °C], assigned to the carbon atoms in the 1 and 3 positions of a static σ-allyl group, coalesce to a single peak at 74.3 p.p.m. as the temperature is raised to 50 °C.

As 18-electron complexes, (**5**) and (**6**) would not be expected to undergo facile 1,3 exchange. However, it is not unreasonable to suppose that the (η-C$_3$H$_4$Me)(1—4-η-C$_8$H$_8$) isomers of (**5**) and (**6**), analogous to (**1**), are only a little less stable than the σ-C$_3$H$_4$Me forms. This suggests a mechanism (Scheme) in which reversible slippage of the η-C$_8$H$_8$ ring allows the ends of the allyl group to exchange. A similar process would equilibrate *E* and *Z* forms of the crotyl complex (**3**).

Reactions of [Zr(η-C$_5$Me$_5$)(1—4-η-C$_8$H$_8$)(η-C$_3$H$_5$)].—Compound (**1**) did not react with tertiary phosphine ligands (*e.g.* PMe$_3$, PMe$_2$Ph, and PEt$_3$) despite being a 16-electron compound. This is in contrast to the ability of [Zr(η-C$_4$H$_6$)$_2$(dmpe)] to react readily with phosphines,[15] but is comparable with the inability of [Zr(η-C$_5$Me$_5$)$_2$H$_2$] and analogous species to form stable adducts with phosphine ligands of this type.[16]

Hydrogen (1 atm, *ca.* 10^5 Pa) reacted with a hexane solution of (**1**) at room temperature, affording a yellow solution which was shown to contain a mixture of [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(σ-C$_3$H$_7$)] and [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)H].[1] The former compound is not converted to the latter by prolonged exposure to H$_2$ under these conditions. Compound (**1**), being both co-ordinatively unsaturated and in a low oxidation state, is likely to be susceptible to oxidative addition of H$_2$. Subsequent reductive transfer of one of the hydride ligands to the allyl group would afford a co-ordinated propene which might either be eliminated irreversibly affording [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)H] or undergo a further hydride transfer to give the stable n-propyl complex.

Experimental

General procedures and the syntheses of starting materials have been described previously.[1]

(η-*Allyl*)(1—4-η-*cyclo-octatetraene*)(η-*pentamethylcyclopentadienyl*)*zirconium*(II).—To a rapidly stirred suspension of [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)Cl] (0.40 g, 1.09 mmol) in diethyl ether (20 cm^3) at 0 °C was added dropwise a thf solution of MgCl(CH$_2$CHCH$_2$) (0.81 mol dm^{-3}, 1.35 cm^3) until all of the yellow crystals had dissolved. After 1 h the solvent was removed *in vacuo* and the purple solid extracted with hexane (60 cm^3). The solution was filtered, reduced in volume and cooled to −20 °C yielding large purple-black crystals of (**1**).

The same basic method was used to synthesize compounds (**2**)—(**6**) from (**1**) and the appropriate chloro-Grignard reagent. Analytical and other data are included in Table 1; ^{1}H and ^{13}C n.m.r. data are in Tables 2 and 3 respectively.

Reaction of (**1**) *with Hydrogen.*—Hydrogen was bubbled slowly through a hexane solution of (**1**) (0.4 g, 1.08 mmol) at 18 °C until the colour of the solution changed to yellow. Filtration and cooling to −78 °C afforded a crystalline material (0.22 g) which was shown to be a mixture of [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)H] and [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(σ-C$_3$H$_7$)] by ^{13}C and ^{1}H n.m.r. spectroscopy. The identity of the n-propyl complex was confirmed by alternative synthesis[17] from (**1**) and MgCl(C$_3$H$_7$).

Reactions of [Zn(η-C$_5$Me$_5$)(η-C$_8$H$_8$)H] *with Buta*-1,3-*diene.*—Buta-1,3-diene (0.10 g, 1.85 mmol) was added to a Schlenk tube fitted with a dry-ice condenser and containing a stirred solution of [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)H] (0.31 g, 0.94 mmol) in toluene at 18 °C. After 1 h the toluene was evaporated at reduced pressure and the residue extracted with hexane. On cooling the filtered solution to −20 °C yellow crystals of [Zr(η-C$_5$Me$_5$)(η-C$_8$H$_8$)(σ-CH$_2$CHCHMe)] (**3**) (2:1, *E*:*Z* mixture of isomers) were deposited (0.25 g, 0.66 mmol, 70%).

Crystal Structure Determination of [Zr(η-C$_5$Me$_5$)(1—4-η-C$_8$H$_8$)(η-C$_3$H$_5$)] (**1**).—Crystals of (**1**) grow as deep purple, thin rectangular plates during the slow cooling of a saturated solution of thf–toluene–light petroleum (b.p. 40—60 °C). The data crystal, of dimensions 0.15 × 0.35 × 0.40 mm, was mounted under argon in a Lindemann capillary tube. Intensities were recorded in the range $2.9 < 2\theta < 56°$ at 210 K (ω-scan). Of the 4 248 independent intensities measured on a Nicolet *P*3*m* four-circle diffractometer, 2 303 were used in the solution and refinement of the structure [$I > 2.5\sigma(I)$]. No correction was applied for *X*-ray absorption effects. Standard reflections $\bar{3}2\bar{2}$ and $\bar{2}\bar{2}4$ were monitored every 48 reflections and showed some 5% decay over the 43 h of crystal exposure to *X*-rays. Correction was made for crystal decay.

Crystal data. C$_{21}$H$_{28}$Zr, $M = 371.7$ monoclinic, $a = 13.537(5)$, $b = 9.831(5)$, $c = 28.954(12)$ Å, $\beta = 113.79(3)°$, $U = 3\,523(3)$ Å^3, $Z = 8$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\,552$, space group *A*2/*a* (non-standard setting of *C*2/*c*, no. 15), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 6.1$ cm^{-1}.

The structure was solved by heavy-atom methods and was refined using blocked-cascade least-squares methods. Hydrogen atoms were all located and were refined with isotropic thermal parameters, all other atoms with anisotropic parameters. Individual weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.0007|F_o|^2]^{-1}$, and the refinement converged at *R* 0.042, *R'* 0.036. The final electron density difference synthesis showed no peaks >0.6 or <-0.7 e Å^{-3}. Atomic scattering factors were taken from ref. 18. All computations were carried out within the Laboratory on a Data General 'Eclipse' mini-computer using the SHELXTL system of programs.[19] Atomic co-ordinates for (**1**) are in Table 5.

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References

1 W. J. Highcock, R. M. Mills, J. L. Spencer, and P. Woodward, preceding paper.
2 W. J. Highcock, R. M. Mills, J. L. Spencer, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1982, 128.
3 K. I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 1981, **103**, 2687.
4 H-J. Kablitz and G. Wilke, *J. Organomet. Chem.*, 1973, **51**, 241.
5 J. Blenkers, H. J. de Liefde Meijer, and J. H. Teuben, *J. Organomet. Chem.*, 1981, **218**, 385.
6 H. A. Martin, P. J. Lemaire, and F. Jellinek, *J. Organomet. Chem.*, 1968, **14**, 149.
7 D. J. Brauer and C. Krüger, *J. Organomet. Chem.*, 1972, **42**, 129.
8 M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, and P. A. Tucker, *J. Organomet. Chem.*, 1976, **121**, C18.
9 D. J. Brauer and C. Krüger, *Organometallics*, 1982, **1**, 204.
10 R. R. Schrock, L. J. Guggenberger, and A. D. English, *J. Am. Chem. Soc.*, 1976, **98**, 903; H. Dietrich and M. Soltwisch, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 765.
11 L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6693.
12 F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Am. Chem. Soc.*, 1973, **95**, 4522 and refs. therein; F. A. Cotton and R. Eiss, *ibid.*, 1969, **91**, 6593; I. W. Bassi and R. Scordamaglia, *J. Organomet. Chem.*, 1972, **37**, 353; G. Allegra, A. Colombo, A. Immirzi, and I. W. Bassi, *J. Am. Chem. Soc.*, 1968, **90**, 4455.
13 S. S. Wreford and J. F. Whitney, *Inorg. Chem.*, 1981, **20**, 3918; G. Erker, K. Engel, C. Krüger, and G. Müller, *Organometallics*, 1984, **3**, 128.
14 V. A. Kormer, M. I. Lobach, N. N. Druz, V. I. Klepikova, and N. V. Kiseleva, *Dokl. Akad. Nauk. SSSR*, 1979, **246**, 1372; *Dokl. Chem.* (*Engl. Transl.*), 1979, **246**, 315.
15 R. P. Beatty, S. Datta, and S. S. Wreford, *Inorg. Chem.*, 1979, **18**, 3139.
16 J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 2716.
17 A. C. Bray, W. J. Highcock, C. Pahl, and J. L. Spencer, unpublished work.
18 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
19 G. M. Sheldrick, SHELXTL, University of Cambridge, 1976; updated University of Göttingen, 1981.

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