Preparation, Characterization and Thermal Reactions of 1-Oxa-2-zirconacyclopentanes and 1-Oxa-2-zirconacyclohexane: Crystal Structures of $[\{Zr(C_5H_5)_2(OCH_2CH_2CHMe)\}_2]$ and $[Zr(C_5Me_5)_2\{OCH_2(CH_2)_2CH_2\}]$ ‡

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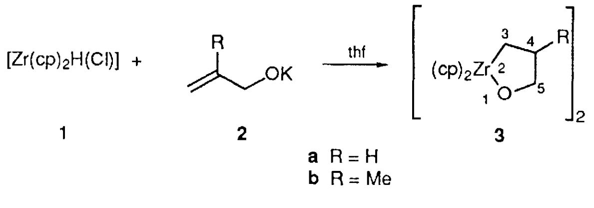
1-Oxa-2-zirconacyclopentanes $[\{Zr(cp)_2(OCH_2CHRCH_2)\}_2]$ (R = H, **3a**: or Me, **3b**) and $[\{Zr(cp)_2(OCH_2CH_2CHMe)\}_2]$ **3c** (cp = η-C_5H_5) formed from the intramolecular hydrozirconation of $[Zr(cp)_2H(Cl)]$ with potassium allyl or homoallyl alcoholates have been characterized as dimeric five-co-ordinated metallocene structures. Complex **3c** crystallizes in space group $P2_1/n$ ($Z = 2$) with a = 17.090(4), b = 8.345(3), c = 8.841(3) Å, β = 102.90(2)°, and R = 0.039 for 2030 reflections. Monomeric $[Zr(C_5Me_5)_2(OCH_2CH_2CH_2)]$ **9** and $[Zr(C_5Me_5)_2\{OCH_2(CH_2)_2CH_2\}]$ **12** have been prepared by the reaction of appropriate Grignard reagents with $[Zr(C_5Me_5)_2Cl_2]$. Complex **12** crystallizes in space group $Pnn2$ ($Z = 4$) with a = 15.634(2), b = 15.024(3), c = 9.571(1) Å, and R = 0.074 for 1336 reflections. Remarkable differences in the thermal stability and modes of decomposition have been observed among these complexes depending on the co-ordination numbers of the zirconium atoms and the size of the metallacycles. The mechanisms of thermal reaction of **3** are discussed on the basis of the product analysis and by use of the deuteriated derivatives.

Recently, oxametallacyclic compounds have been attracting considerable interest in organometallic and synthetic organic chemistry.[1] Only a limited number of oxametallacycles, however, have been isolated and characterized.[2–4] Some oxametallacyclopentanes and oxametallacyclopentenes of Group 4 transition metals have been prepared by the reaction of olefin- or acetylene-metal complexes with carbonyl compounds.[3,4] In this paper we report the preparation, structural characterization, and thermal reactions of several mono- and di-meric 1-oxa-2-zirconacyclopentanes and a monomeric 1-oxa-2-zirconacyclohexane. The modes of thermal decomposition of five-membered zirconacycles depend on the co-ordination number, four or five, of the zirconium atom. Part of this work has been communicated.[5]

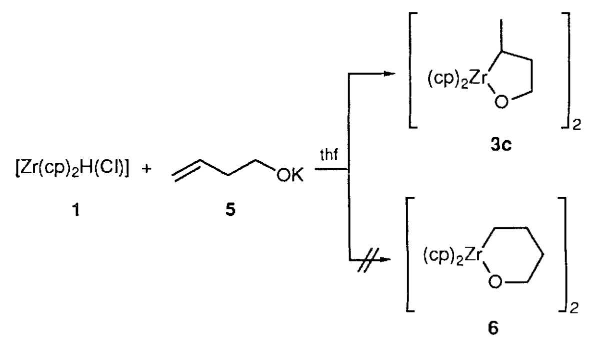
Results and Discussion

Preparation of Dimeric 2,2-*Di(cyclopentadienyl)*-1-*oxa*-2-*zirconacyclopentanes*.—Addition of a solution of potassium prop-2-enolate **2a** in tetrahydrofuran (thf) to a suspension of $[Zr(cp)_2H(Cl)]$ **1** (cp = η-cyclopentadienyl) in thf at 45–50 °C resulted in a pale yellow solution. After removal of the solvent, the residue was dissolved in the minimum amount of hot toluene. Addition of a small volume of chloroform caused precipitation of 1-oxa-2-zirconacyclopentane **3a** as a microcrystalline solid in a few minutes [equation (1)]. When toluene was used as a solvent for the above reaction, complex **3a** could not be obtained. Addition of **2a** at −70 °C in thf followed by stirring the mixture at room temperature did not give the desired product, either. Thus, use of thf as solvent and reaction at 45–50 °C are requisite for a good yield of **3a**. Compound **3a** could also be prepared by the reaction of zirconocene dichloride with the Normant Grignard reagent $XMgCH_2(CH_2)_2OMgX$ (X = Cl and/or Br) **4**.[6] This procedure, however, was found not to be suitable for the preparation of an analytically pure sample of **3a** because of contamination with the complex of the magnesium salt and the corresponding monomeric 1-oxa-2-zirconacyclopentane.



(1)

An analogous reaction of compound **1** with potassium 2-methylprop-2-enolate **2b** gave the 3-methyl-substituted derivative **3b**. As shown in equation (2), reaction of **1** with potassium



(2)

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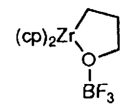
† *Present address*: see *a*.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.



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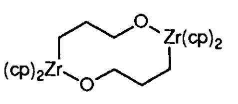

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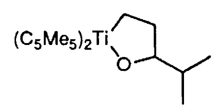

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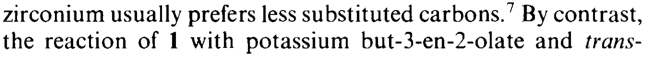
but-3-enolate **5** gave the kinetically favoured five-membered **3c** instead of six-membered 1-oxa-2-zirconacyclohexane **6**. This is in contrast to the fact that, in intermolecular hydrozirconation, zirconium usually prefers less substituted carbons.[7] By contrast, the reaction of **1** with potassium but-3-en-2-olate and *trans*-but-2-enolate did not afford the cyclic products.

The isolation yields of **3a**–**3c** were variable (10–64%) depending on the work-up conditions, because the solubility of these complexes is changed to a large extent by the presence of trace amounts of thf which keeps the complex monomeric by co-ordination to zirconium. Interestingly, addition of a small amount of chloroform to the solution of the product in toluene facilitates the formation of crystalline dimer **3**. The dimeric complexes **3**, once crystallized, have low solubility in most common organic solvents.

The structure of complexes **3a**–**3c** was determined based mainly on their spectral data. Mass spectra of these complexes afforded $2M^+$ peaks, which supported the assigned dimeric structures. Addition of BF_3 (0.25 equivalent) to a solution of **3a** in $CDCl_3$ resulted in ^1H NMR signals due to BF_3 adduct **7** in addition to signals due to free **3a**, which supports the dimeric structure **3** and excludes the ten-membered structure **8**.

Preparation of Monomeric 1-*Oxa*-2-*zirconacyclopentane* **9**.—Monomeric compound **9** was prepared by the reaction of $[Zr(C_5Me_5)_2Cl_2]$ with the Normant Grignard reagent **4** in thf at 35–50 °C [equation (3)]. Removal of the solvent under reduced

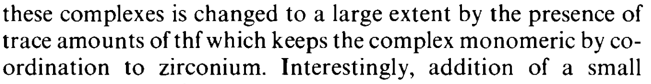


(3)

4 9

pressure followed by extraction of the residue with hexane and concentration of the extract afforded **9** as an off-white solid in 26% yield. Proton and ^{13}C NMR and mass spectra supported the monomeric structure. Complex **9** is quite unstable in the absence of a co-ordinating solvent such as thf. 5-Isopropyl-1-oxa-2-titanacyclopentane **10**, a titanium analogue of **9**, had been synthesised by the reaction of $[Ti(C_5Me_5)_2(CH_2{=}CH_2)]$ with 2-methylpropanal.[3a,8]

Preparation of Monomeric 1-*Oxa*-2-*zirconacyclohexane* **12**.—Treatment of $[Zr(C_5Me_5)_2Cl_2]$ with compound **11** in thf at 60–70 °C followed by recrystallization from hexane afforded **12** as colourless plates in 84% yield [equation (4)]. The structure of



(4)

11 12

12 was supported by ^1H and ^{13}C NMR spectra, and an X-ray crystal structure determination (see below). In sharp contrast to **9**, complex **12** does not decompose in air and is thermally stable even at the melting point (250 °C).

X-Ray Structural Studies of Compounds **3c** *and* **12**.—An ORTEP drawing of the dimeric molecule **3c** is shown in Fig. 1. Selected bond distances and angles shown in Table 1 appear normal. The cyclopentadienyl rings are eclipsed. Each zirconium atom has a five-co-ordinated bent metallocene structure (18-electron complex) surrounded by a carbon atom, two oxygens and two cp ligands. Five-co-ordinated bent metallocene complexes $[Zr(cp)_2(\eta^2\text{-}COMe)Me]$,[9] $[\{Zr(cp)_2(O{=}C{=}CPh_2)\}_2]$,[10] $[\{Zr(cp)_2(CH_2{=}O)\}_3]$,[11] $[Zr(cp)_2Cl(O_2NCMe_2)]$,[12] and $[\{Zr(cp)_2[OC{=}\underline{C(CH_2)_3C}H_2]\}_2]$[2g] have been reported. In these complexes the angle X–Zr–Y (X, Y = C, O or Cl) defined by the two outer ligands and zirconium is very similar to that of **3c** [136.7(4)°] and comparable to the value (130°) calculated for imaginary $[Ti(cp)_2H_3]$ by the extended-Hückel molecular orbital (EHMO) method.[13]

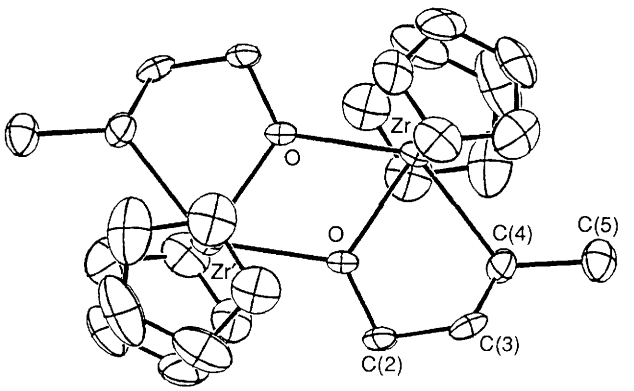


Fig. 1 An ORTEP view of compound **3c**. Two zirconocene moieties are related by the centrosymmetry. Atoms C(2)–C(5) have an occupancy of 0.5 owing to positional disorder. Hydrogen atoms are omitted for simplicity

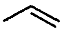
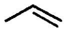
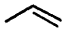
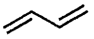
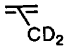
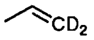
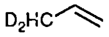
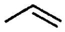
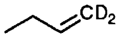
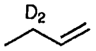
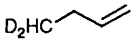
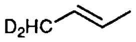
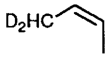
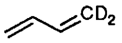
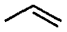
Table 1 Selected bond distances (Å) and angles (°) of compounds **3c** and **12**[a]

	3c		**12**
Zr–O(1)	2.190(3)		2.008(13)
Zr–O(1′)	2.234(7)		
Zr–Zr′	3.740(10)		
Zr–C(4)	2.382(11)	[2.452(12)][b]	
Zr–C(5)			2.264(18)
O(1)–C(2)	1.427(10)	[1.473(11)]	1.428(25)
C(2)–C(3)	1.506(16)	[1.515(15)]	1.447(41)
C(3)–C(4)	1.503(17)	[1.479(13)]	1.605(41)
C(4)–C(5)	1.559(17)	[1.501(16)]	1.488(27)
O(1)–Zr–C(4)	72.2(4)	[70.0(5)][b]	
O(1)–Zr–C(5)			86.1(6)
O(1)–Zr–O(1′)	64.5(4)		
Zr–O(1)–C(2)	119.6(5)	[123.5(5)]	141.1(12)
Zr′–O(1)–C(2)	124.3(4)	[120.2(4)]	
Zr–O(1)–Zr′	115.5(4)		
O(1)–C(2)–C(3)	105.6(6)	[105.7(7)]	110.3(21)
C(2)–C(3)–C(4)	105.5(9)	[107.8(8)]	114.5(25)
C(3)–C(4)–C(5)	114.9(9)	[115.3(9)]	115.2(19)
Zr–C(4)–C(3)	102.2(7)	[107.6(8)]	
Zr–C(4)–C(5)	123.7(6)	[124.3(7)]	
Zr–C(5)–C(4)			114.9(12)

[a] Complex **3c** has a dimeric structure with a crystallographic centre of symmetry and independent atoms comprise half of the dimeric structure; Zr and O are related by the centre of symmetry to Zr′ and O′, respectively. [b] Distances and angles due to C(2*)–C(5*), which are disordered atoms C(2)–C(5); occupancies of C(2)–C(5) and C(2*)–C(5*) are 0.5.

The bond lengths of Zr–O(1) and Zr–O(1′) are 2.190(3) Å and 2.234(7) Å, respectively, consistent with the value (2.11–2.14 Å) estimated from the sum of the covalent radii for Zr (1.45–1.48 Å) and oxygen (0.66 Å).[14] Donation of the p_π orbital of O(1′) of a neighbouring 1-oxa-2-zirconacyclopentane to the empty d_π

Table 2 Thermal decomposition of zirconaoxacyclopentanes[a]

Compound	Products due to fission A (%)			Products due to fission B (%)			
3a	CH_4 (2)		(19)		(79)		
3b	CH_4 (7)		(89)		(4)		
3c	CH_4 (7)		(21)		(50)		(5)
					(5)		(9)
					(2)		
18	CH_4 (11)		(13)		(31)		(45)
19	CH_4 (4)[b]		(20)		(33)		(7)
					(8)		(7)
					(7)		(11)
					(2)		
9	CH_4[c]		(83)		(17)		

[a] Yields of the volatile products except those of cyclopentadiene are given in mol %. Good mass balances were obtained. [b] The deuterium content of methane was not determined, though the ^2D NMR spectrum contained signals due to $[^2H_x]$methane. [c] The yield of methane varied in each experiment.

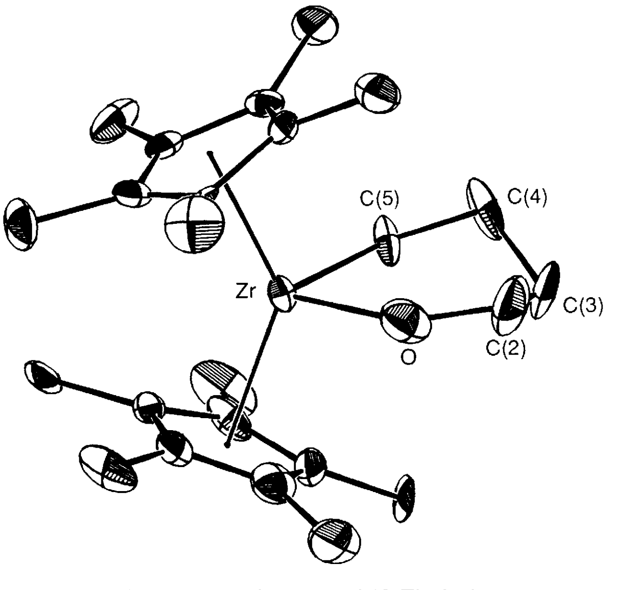


Fig. 2 Molecular structure of compound **12**. The hydrogen atoms are omitted for simplicity

orbital of zirconium can be considered to diminish the double-bond character between Zr and O(1) (see below).

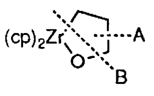
The crystal structure of compound **12** was also determined by X-ray analysis. An ORTEP drawing with labelling scheme is shown in Fig. 2. The molecule is monomeric and there is no short intermolecular interaction. The central zirconium atom has pseudo-tetrahedral geometry with two C_5Me_5 ligands, an oxygen and C(5). The angle O–Zr–C(5) [86.1(6)°] is much smaller than that calculated (110°) for $[Ti(cp)_2H_2]$,[13] but is comparable to that [80.9(2)°] of **10**.[8] The Zr–O bond length [2.008(13) Å] is rather shorter than the single-bond distance of **3c**. Similar short bond lengths have been reported in other four-co-ordinated zirconium complexes: $[\overline{Zr(C_5Me_5)_2\{OC(CHMe_2)_2CH_2CH=CHCH_2}\}]$ [1.961(7) Å],[15] $[\overline{Zr(cp)_2(OCH_2CH_2SiMe_2CH_2})]$ [1.941(2) Å],[16] and $[\{Zr(cp)_2Me\}_2(\mu\text{-}O)]$ [1.948(1) Å].[17] The double-bond character of the Zr–O bonds in these monomeric complexes are ascribable to π donation from the oxygen atom to the empty orbital ($1a_1$) of zirconium. Such p_π–d_π overlap is also found for compound **10**.[8]

Thermal Reactions of 1-*Oxa*-2-*zirconacyclopentanes*.—Complexes **3a**–**3c** were decomposed at 240–250 °C under reduced pressure and the results are given in Table 2. The products can be considered to arise from two kinds of bond fission, modes A and B (see **13**). Thermal decomposition of **3a** afforded mainly propene. Ethylene (19%) and a small amount of methane were also obtained. The yield of cyclopentadiene depends on the reaction conditions. The major product of thermolysis of **3b** was propene accompanied by a small amount of 2-methylpropene, while the decomposition of **3c** produced rather complicated products, propene, but-1-ene, (*Z*)-but-2-ene, (*E*)-but-2-ene, buta-1,3-diene and butane. The residues obtained from the thermal decomposition of **3** contain the oxygen-bridged oligomer $[\{Zr(cp)_2O\}_x]$, which was characterized by its IR absorption between 720 and 780 cm^{-1} assigned to ν(Zr–O–Zr) and ^1H NMR signals at δ 6.34 due to the $\eta\text{-}C_5H_5$ ligand.[18]

The mode A reaction involving C_β–$C_{\beta'}$ bond fission would proceed *via* a mixed-ligand complex **14**. It corresponds to the reverse reaction of the formation of 1-oxa-2-metallacyclopentanes in which an olefin adds to complexes of the type **15** or a carbonyl compound reacts with olefinmetal complexes.[3,4] Further thermal decomposition of complex **15** (M = Zr, R^1 = R^2 = H) possibly formed from a complex of the type **14** under reaction conditions will give methane, as has been reported for the decomposition of $[Zr(cp)_2(CH_2{=}O)\}_3]$.[11]

The mechanism of formation of the three-carbon unit from compound **3a** and four-carbon products from **3b** and **3c** by mode B decomposition might involve initial retrohydrozirconation of **3** to form the alkoxozirconium hydride species **16**. A possible route giving C_3 hydrocarbon from **16** involves cleavage of the allylic C–O bond giving an allylmetal hydride complex, whose reductive elimination produces propene. Another possibility is the intramolecular hydrozirconation of **16** to four-membered metallacycle **17**, which in turn decomposes by a metathesis-like reaction to give propene and oxozirconium species. A mechanism involving generation of trimethylene diradical can be ruled out, because this species is known to give predominantly cyclopropane.[19]

In order to get more insight into the mechanism of the mode B decomposition we carried out deuterium-labelling experi-



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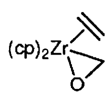

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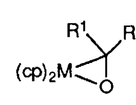

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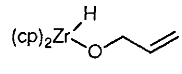
M = Ti or Zr



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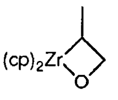

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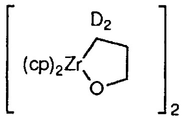

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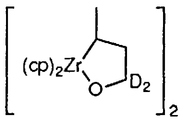

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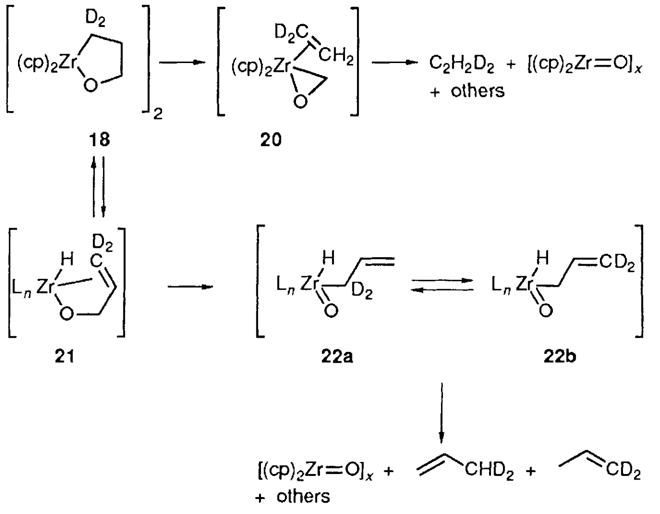


Scheme 1

ments. The deuteriated complexes **18** and **19** were prepared according to equations (1) and (2) using the corresponding deuterium-labelled substrates. The thermal decomposition of **18** followed by analyses of the products by ^1H, ^2H and ^{13}C NMR spectroscopy revealed the formation of $[^2H_2]$ethylene, $[1,1\text{-}^2H_2]$propene, and $[3,3\text{-}^2H_2]$propene (see Table 2). The deuterium content of methane was not determined. The thermal decomposition of **19** afforded $[1,1\text{-}^2H_2]$but-1-ene, $[4,4\text{-}^2H_2]$but-1-ene, and (*Z*)- and (*E*)-$[1,1\text{-}^2H_2]$but-2-ene. There was no deuteriated propene. These results might reasonably be understood by the mechanism shown in Schemes 1 and 2,[20–22] and a path involving metathetic cleavage of complex **17** can be ruled out.

The deuterium scrambling found in the thermal reaction of compound **18** can be best explained by the intervention of allylhydridozirconium species **22** (Scheme 1). Here, an allylic rearrangement between **22a** and **22b** causes deuterium scrambling. As shown in Scheme 2, the deuterium distribution observed in the thermal decomposition of **19** can be reasonably understood by a mechanism involving intermediary species **25** and **27**, in which the allylic rearrangement **25a** $\rightleftharpoons$ **25b** and the cyclopropylcarbinyl–homoallyl interconversion **27a** $\rightleftharpoons$ **27b** $\rightleftharpoons$ **27c** have been proposed.[23]

In contrast to the above results for the dimeric complexes **3**, thermal decomposition of monomeric complex **9** proceeded smoothly at 250 °C to give ethylene (83%) and propene (17%). Methane was also detected, but the yield varied in each experiment. Thus, β-carbon–carbon bond fission (mode A) occurred predominantly.

The observed remarkable differences in the reaction modes between dimeric complex **3** and monomeric **9** might be attributed to the difference in the co-ordination number of zirconium. For the four-co-ordinated complex **9** (16-electron complex) the mode A reaction can be considered to be a symmetry-allowed process,[24] though support based on MO calculations for the present system is still lacking. On the other hand, for the five-co-ordinated complexes **3** (18-electron complexes) two modes of ring fission, A and B, have been observed, which suggests that the activation energies of the mode A reaction of **3** are little higher than that of **9**. It is noteworthy that the six-membered monomeric complex **12**, for which the mode A reaction is impossible, is thermally quite stable.

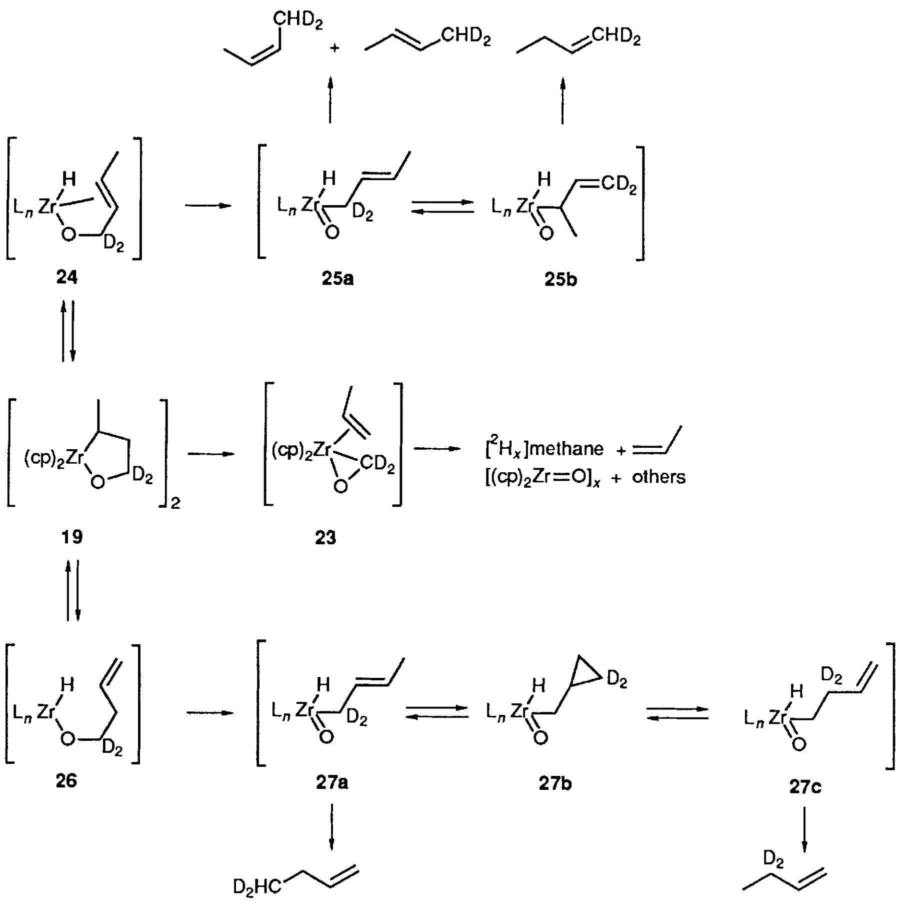
Experimental

General.—All manipulations of oxygen- and moisture-sensitive materials were conducted under an argon atmosphere purified by passing through a column packed with BASF-Catalyst R3-11 by the use of standard Schlenk techniques and a glove-box. Tetrahydrofuran and diethyl ether were freshly distilled from sodium diphenylketyl or Na–K alloy. Hexane, toluene and dichloromethane were distilled from finely powdered calcium hydride. Chloroform was treated with concentrated H_2SO_4 and distilled after being dried over P_2O_5 under argon. $[^2H_6]$benzene and $[^2H_8]$toluene were dried over Na–K alloy and $[^2H_1]$chloroform was dried over P_2O_5. They were freshly distilled before use. The compounds $[Zr(cp)_2Cl_2]$, $[Zr(cp)_2H(Cl)]$ and $[Zr(C_5Me_5)_2Cl_2]$ were prepared by the literature method with some modification.[25,26] Magnesium (99.99% purity) was obtained from Rare Metallic Co., Ltd. Gaseous BF_3 (99.8%) was used as obtained from Hashimoto Kasei Co.

Apparatus.—Proton NMR spectra were recorded with Varian EM 390 (90 MHz), JEOL FX100 (100 MHz) or JEOL GX400 (400 MHz) spectrometers, ^{13}C and ^2D NMR spectra on a JEOL GX400 spectrometer (100 MHz for ^{13}C and 60 MHz for ^2D), mass spectra on a JEOL-D300 spectrometer at the ionization voltage of 70 eV for organic compounds and 20 eV for zirconium complexes and IR spectra on a Hitachi 295 spectrometer. All melting points were uncorrected. Elemental analyses were performed at Wako Pure Chemical Industry Ltd. Gas chromatography was carried out on a Hitachi 263-30 instrument equipped with a flame ionization detector and a glass capillary.

Preparations.—Compound **3a**. To a suspension of $[Zr(cp)_2H(Cl)]$ (1.0 g, 3.8 mmol) in thf (100 cm^3) at 45 °C was added a solution of potassium prop-2-enolate (3.8 mmol) in the same solvent, prepared by the reaction of allyl alcohol (0.26 cm^3, 3.8 mmol) with potassium hydride (0.15 g, 3.8 mmol) in thf (100 cm^3). The reaction mixture was stirred for 5 h at 45 °C giving a pale yellow solution containing off-white precipitates. Solvent was removed under reduced pressure to give a yellow residue, which was extracted with two (50 cm^3) portions of toluene. The combined toluene solution was concentrated under reduced pressure to give a white solid, which was washed with hexane and dried *in vacuo* (0.34 g, 33%). The complex had very poor solubility in chloroform. NMR: ^1H ($CDCl_3$), δ 1.03 [t, H^3, $J(H^3H^4)$ = 6.1], 1.85 (m, H^4), 3.52 [t, H^5, $J(H^4H^5)$ = 5.4] and 5.83 (s, cp); ^{13}C (CD_2Cl_2), δ 33.1 [C^4, J(CH) = 124], 44.9 (C^3, 124), 76.9 (C^5, 139) and 109.9 (cp, 164 Hz). IR (KBr): 2846m, 2798m, 1448s, 1362w, 1314w, 1260w, 1209w, 1162w, 1069s, 1046s, 1028s, 956s, 908w, 864w, 793vs, 666w, 619w, 590s, 471s, 407s and 323s cm^{-1}. Mass spectrum (^{90}Zr): *m/z* 556 ($2M^+$), 514 ($2M^+ - C_3H_6$), 472 ($2M^+ - C_6H_{12}$), 456 ($2M^+ - C_6H_{12}O$), 278 (M^+), 250 ($M^+ - C_2H_4$) and 220 ($M^+ - C_3H_6O$) (Found: C, 54.90; H, 5.60. Calc. for $C_{13}H_{16}OZr$: C, 55.85; H, 5.75%).

Complex **3a** (18 mg, 0.07 mmol) was hydrolysed by the addition of 1 mol dm^{-3} H_2SO_4. Propan-1-ol was obtained in



Scheme 2

96% yield by GLC [5% Diisodecyl phthalate on Celite 545 (DIDP), 2 m]. Decomposition of **3a** in $CDCl_3$ by the addition of 1 mol dm^{-3} D_2SO_4–D_2O at 50 °C for 1 h gave [3-^{2}H]-propan-1-ol quantitatively.

The BF_3 *adduct of* **3a**.—To a dispersed suspension of complex **3a** (50 mg, 0.085 mmol) in dichloromethane (10 cm^3) was added a solution of BF_3 (0.04 mmol) in dichloromethane (10 cm^3) at −40 °C. Complex **3a** dissolved completely in 30 min. The solvent was removed under reduced pressure to give an oily substance, whose ^{1}H NMR spectrum in $CDCl_3$ showed signals due to the starting complex and only one set of three methylene signals assignable to the BF_3 adduct of **3a**. ^{1}H NMR of adduct ($CDCl_3$): δ 1.28 (t, 2 H, J = 6.2), 2.10 (m, 2 H), 3.74 (t, 2 H, J = 5.5 Hz) and 5.99 (s, cp).

Compound **3b**. To [Zr(cp)$_2$H(Cl)] (0.72 g, 2.8 mmol) suspended in thf (100 cm^3) at 50 °C was added dropwise a solution of freshly prepared potassium 2-methylprop-2-enolate (2.8 mmol) in thf (100 cm^3) for a period of 1 h. The mixture was stirred at 50 °C for 5 h, then all volatiles were removed under reduced pressure to give an off-white residue, which was extracted with two (35 cm^3) portions of toluene. The toluene solution was concentrated under reduced pressure to 30 cm^3. To this pale yellow solution was carefully added chloroform (30 cm^3) without disturbing the toluene layer. After several minutes, a colourless crystalline precipitate appeared. The mixture was cooled to −20 °C to give compound **3b** as colourless crystals (0.2 g, 25%). The isolated complex had very poor solubility in all common organic solvents such as toluene, thf, and chloroform. NMR ($CDCl_3$): ^{1}H, δ 1.40 (d, CH_3, J = 6.8), 1.5–1.8 (m, H^4, H^{3a}, and H^{3b}), 3.3–3.4 (m, H^{5a}), 3.7–3.8 (m, H^{5b}), 5.78 (cp) and 5.79 (cp); ^{13}C, δ 20.00 [CH_3, J(CH) = 124], 37.35 (C^4, 126), 54.36 (C^3, 122), 81.72 (C^5, 136), 109.31 (cp, 160) and 109.70 (cp, 160 Hz). Mass spectrum (^{90}Zr): m/z 584 ($2M^+$), 528 ($2M^+$ − C_4H_8), 512 ($2M^+$ − C_4H_8O), 497 ($2M^+$ − C_4H_8O − CH_3), 470 ($2M^+$ − C_4H_8O − C_3H_6), 456 ($2M^+$ − $C_8H_{16}O$), 292 (M^+), 250 (M^+ − C_3H_6) and 220 (M^+ − C_4H_8O, base peak). IR (KBr): 2930m, 2860m, 2815m, 1418m, 1360w, 1253w, 1008s 800s, 782s, 583s, 535w, 418s and 306w cm^{-1} (Found: C, 56.30; H, 6.15. Calc. for $C_{14}H_{18}OZr$: C, 57.30; H, 6.20%).

Compound **3c**. A solution of potassium but-3-enolate (9.3 mmol) in thf (100 cm^3), freshly prepared by the reaction of but-3-en-1-ol (0.78 cm^3, 9.3 mmol) with potassium hydride (0.41 g, 10.2 mmol), was added dropwise to a suspension of [Zr(cp)$_2$H(Cl)] (2.4 g, 9.3 mmol) in thf (100 cm^3) kept at 50 °C. The reaction mixture was stirred at this temperature for 10 h. Removal of all volatiles gave an off-white residue, which was extracted with two (50 cm^3) portions of toluene. The combined organic layer was concentrated to *ca.* 30 cm^3, and then chloroform (20 cm^3) was added. White solids were separated (1.7 g, 64%) after keeping the temperature at 20 °C for 22 h. The product was contaminated with some impurities. An analytically pure sample (0.4 g, 15% yield) was obtained by recrystallization from hot chloroform (80 cm^3). NMR ($CDCl_3$): ^{1}H, δ 1.40 (d, CH_3, J = 6.8), 1.51–1.60 (m, H^3), 1.65–1.77 (m, H^{4a} and H^{4b}), 3.30–3.36 (m, H^{5a}), 3.69–3.79 (m, H^{5b}), 5.89 (cp) and 5.90 (cp); ^{13}C, δ 23.34 [CH_3, J(CH) = 121], 40.46 (C^4, 124), 51.87 (C^3, 123), 72.91 (C^5, 138), 107.66 (cp, 159), and 108.15 (cp, 160 Hz). Mass spectrum (^{90}Zr): m/z 292 (M^+), 250 (M^+ − C_3H_6) and 220 (M^+ − C_4H_8O, base peak). IR (KBr): 2850m, 2790m, 1427m, 1048m, 1010m, 800s, 792s, 778s, 618s, 600m, 471s and 370w cm^{-1} (Found: C, 57.30; H, 6.15. Calc. for $C_{14}H_{18}OZr$: C, 57.30; H, 6.20%).

[3,3-$^2H_2$]*Prop*-2-*en*-1-*ol*. Prop-2-ynyl acetate (47 g, 0.48 mol) was deuteriated by $NaCO_3$–D_2O (three times). The deuteriated compound propargyl acetate-*d* (97% deuterium content) was obtained in 63% yield. Reaction of this acetate (24 g, 0.25 mol) with $LiAlH_4$ (18.8 g, 0.49 mol) in diethyl ether (250

Table 3 Crystal data and data collection parameters *

Complex	**3c**	**12**
Formula	$C_{28}H_{36}O_2Zr_2$	$C_{24}H_{38}OZr$
M	587.04	433.79
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pnn2$
a/Å	17.090(4)	15.634(2)
b/Å	8.345(3)	15.024(3)
c/Å	8.841(3)	9.574(1)
β/°	102.90(2)	
Z	2	4
U/Å^3	1228.9(6)	2248.7(6)
D_c/g cm^{-3}	1.59	1.28
Reflections measured	$\pm h, +k, +l$	$+h, +k, +l$
μ/cm^{-1}	8.56	4.93
Data collected	4305	3906
Unique data	2400	1739
Unique data [$\lvert F_o\rvert > 3\sigma(F_o)$]	2030	1336
No. of variables	286	236
R	0.039	0.074
R	0.044	0.065

* Details in common: scan mode 2θ–θ; 25 °C; scan speed 3° min^{-1}; scan width 1.1 + 0.5 tanθ; background count 8s; $2\theta_{max}$ = 60.0°.

cm^3) according to the literature method[27] followed by addition of D_2O gave a mixture of ethanol and [3,3-$^2H_2$]prop-2-en-1-ol. Spinning band distillation (150 theoretical plates) gave the latter compound (4.2 g, 28% yield), whose deuterium content was 93%. ^{1}H NMR ($CDCl_3$): δ 4.2 (d, 2 H, CH_2O), 5.16 (t, 0.14 H, =CHD) and 5.90 (br s, 1 H, =CH).

Compound **18**. The reaction of [Zr(cp)$_2$H(Cl)] (2.0 g, 7.7 mmol) with potassium [3,3-$^2H_2$]prop-2-en-1-olate (7.7 mmol) in thf (250 cm^3) was conducted according to the preparation of **3a**. Complex **18** (0.2 g, 10% yield) was obtained.

[1,1-$^2H_2$]*But*-3-*en*-1-*ol*. To $LiAlD_4$ (1.54 g, 0.037 mol) in ether (30 cm^3) was added a solution of methyl but-3-enolate (6.0 g, 0.06 mol) in ether (20 cm^3) *via* a syringe. The reaction mixture was heated at reflux over 2 h, and then water (1.5 cm^3) was added carefully. Distillation gave [1,1-$^2H_2$]-but-3-en-1-ol, whose deuterium content was 89%. ^{1}H NMR ($CDCl_3$): δ 2.31 (d, 2 H, CH_2CD_2O, J = 6.9 Hz), 3.45 (br s, CHDO, 0.22 H), 4.9–5.2 (m, 1 H, =CH) and 5.5–6.0 (m, 2 H, $=CH_2$).

Compound **19**. Reaction of [Zr(cp)$_2$H(Cl)] (1.81 g, 7.1 mmol) with potassium [1,1-$^2H_2$]but-3-en-1-olate (7.1 mmol) in thf (150 cm^3) was carried out according to the preparation of **3c** to give complex **19** (0.2 g, 10% yield).

[$\overline{\text{Zr}(C_5Me_5)_2(OCH_2CH_2CH_2})$] **9**. To a solution of [Zr(C_5Me_5)$_2Cl_2$](0.60 g, 1.4 mmol) in thf (40 cm^3) was added a solution of Normant reagent **4**[6] (1.2 equivalents) in thf (30 cm^3) *via* a syringe. The reaction mixture was stirred at 40 °C for 12 h to give a pale yellow solution. After the removal of all volatiles under reduced pressure, the residue was extracted with two (20 cm^3) portions of hexane. The combined hexane solution was concentrated to give compound **9** as a pale yellow solid (0.15 g, 26%). Some impurities were detected by ^{1}H NMR spectroscopy. Further purification by recrystallization failed due to the considerable decomposition of **9**. When the above reaction was carried out under reflux even trace amounts of **9** could not be detected. NMR (C_6D_6): ^{1}H, δ 1.06 [t, H^3, $J(H^3H^4)$ = 7.1], 1.92 (s, C_5Me_5), 2.84 (m, H^4) and 4.26 [t, H^5, $J(H^4H^5)$ = 6.0]; ^{13}C, δ 11.22 [C_5*Me*$_5$, J(CH) = 125], 43.02 (C^4, 122), 44.72 (C^3, 121), 71.72 (C^5, 140 Hz) and 118.79 (*C*$_5$Me$_5$). Mass spectrum (^{90}Zr): m/z 418 (M^+, very weak) and 360 ($M^+ - C_3H_6O$, base peak).

[$\overline{\text{Zr}(C_5Me_5)_2\{OCH_2(CH_2)_2CH_2}\}$] **12**. To a solution of [Zr(C_5Me_5)$_2Cl_2$] (2.03 g, 4.7 mmol) in thf (30 cm^3) was added a solution of compound **11** (0.18 mol dm^{-3}, 31 cm^3, 5.6 mmol, 1.2 equivalents) in the same solvent *via* a syringe. The reaction mixture was stirred at 60 °C for 15 h. During this period the colour of the mixture turned to pale yellow. All volatiles were removed under reduced pressure and the residue was extracted with two (30 cm^3) portions of hexane. The combined hexane solution was filtered through a Celite pad, concentrated to *ca*. 10 cm^3, and kept at −20 °C overnight. Cream-yellow crystalline solids (1.71 g, 84%) were collected. An analytically pure sample was obtained by recrystallization from toluene at −20 °C as colourless plates, m.p. 248–252 °C. NMR (C_6D_6): ^{1}H, δ 0.70 [t, 2 H^3, $J(H^3H^4)$ = 6.5], 1.53 (m, 2 H^5), 1.88 (s, 2 C_5Me_5), 2.01 (m, 2 H^4), 4.27 [t, 2 H^6, $J(H^5H^6)$ = 5.9]; ^{13}C, δ 11.41 [C_5*Me*$_5$, J(CH) = 127], 29.94 (C^5, 125), 33.90 (C^4, 123), 43.48 (C^3, 118), 71.01 (C^6, 147 Hz) and 117.83 (C_5Me_5). IR (KBr): 2931s, 2900s, 2852s, 2832s, 1438m, 1381m, 1212w, 1102s, 1042m, 928w, 873w, 476m, 447m and 342m cm^{-1}. Mass spectrum (^{90}Zr): m/z 432 (M^+), 376 ($M^+ - C_4H_8$) and 360 ($M^+ - C_4H_8O$, base peak). Exact mass spectrum: Found 432.1951; Calc. for $C_{24}H_{38}OZr$ 432.1965.

Thermal Decompositions.—Compounds **3** *and* **9**. The isolated complex **3a** (70 mg, 0.07 mmol) was placed in a Schlenk tube and evacuated. The tube was rapidly heated to 250 °C in a silicone oil-bath. After 5 min the tube was cooled to room temperature. To this were introduced butane (5 cm^3, 0.22 mmol) and then argon. The GLC analysis (Durapak, 2 m and DIDP, 5 m) of the organic products indicated that methane (2%), ethylene (19%) and propene (79%) were formed. The combined chemical yield was 80%. The structures of these products were confirmed by ^{1}H NMR and GC–MS spectra. The IR spectrum of the residue upon thermal decomposition (KBr) exhibited broad absorption between 720 and 780 cm^{-1}. The ^{1}H NMR ($CDCl_3$) spectrum displayed complex signals, including an intense singlet at δ 6.34. The thermal decompositions of compounds **3b**, **3c** and **9** were also carried out under identical conditions. The results are compiled in Table 2.

Compounds **18** *and* **19**. The location of deuterium in the organic products derived from compounds **18** and **19** was determined by careful analysis of their ^{1}H and ^{2}D NMR spectra. The ^{2}D NMR spectrum of the decomposition products of **18** indicated that [$^2H_2$]ethylene (14%), [1,1-$^2H_2$]propene (35%) and [3,3-$^2H_2$]propene (51%) were formed. Proton NMR and GC–MS spectra also supported the formation of those products. ^{2}D NMR ($CDCl_3$): δ 1.0 ([^2H_x]methane, trace), 1.7 ($CD_2HCH{=}CH_2$, relative intensity 3.8), 4.9 and 5.0 ($CD_2{=}CHCH_3$, 2.6) and 5.5 ($C_2H_2D_2$, 1.0).

The ^{1}H and ^{2}D NMR and mass spectra of the decomposition products of compound **19** indicated that [1,1-$^2H_2$]but-1-ene (51%), [3,3-$^2H_2$]but-1-ene (9%), [4,4-$^2H_2$]but-1-ene (13%), (*E*)- and (*Z*)-[1,1-$^2H_2$]but-2-ene (14%) and [1,1-$^2H_2$]buta-1,3-diene (13%) were produced. The ^{2}D NMR and GC–MS spectra indicated that propene did not contain deuterium. ^{2}D NMR ($CDCl_3$): δ 1.0 [4,4-$^2H_2$]but-1-ene, relative intensity 1.0), 1.6 [1,1-$^2H_2$]but-2-ene, 1.4), 2.1 [3,3-$^2H_2$]but-1-ene, 0.6) and 5.0 (br, $CD_2{=}$, 4.9).

Crystal Structure Determination.—Compound **3c**. Well formed colourless plates of compound **3c** were obtained by recrystallization from a saturated chloroform solution. They were cut by a razor and mounted in thin-walled glass capillaries in a glove-box filled with argon, and then flame sealed. A suitable small (0.48 × 0.14 × 0.10 mm) single crystal was centred on the beam of a Rigaku AFC-5 automated diffractometer. Automatic peak search and indexing methods yielded a monoclinic reduced primitive cell. Final cell dimensions and details of the data collection procedures are given in Table 3. The data were corrected for Lorentz and polarization factors.

The structure was solved by analysis of the three-dimensional Patterson synthesis.[28] Several cycles of block diagonal least-squares refinements and Fourier difference syntheses gave the positions of the non-hydrogen atoms. The thermal parameters

Table 4 Atomic coordinates (× 10^4) of compound **3c***

Atom	*x*	*y*	*z*
Zr	4082(1)	4311(1)	5632(1)
O(1)	5382(2)	4095(3)	5897(3)
CP(1)	3937(4)	7197(7)	6541(8)
CP(2)	4298(4)	6386(9)	7838(7)
CP(3)	3768(6)	5275(10)	8162(8)
CP(4)	3075(5)	5397(10)	7068(11)
CP(5)	3171(4)	6613(10)	6002(9)
CP(11)	2800(3)	2768(8)	4575(8)
CP(12)	3388(4)	1657(7)	4738(8)
CP(13)	3842(4)	1996(8)	3645(7)
CP(14)	3519(4)	3336(8)	2836(6)
CP(15)	2875(4)	3827(8)	3410(8)
C(2)	5837(5)	3160(11)	7138(10)
C(3)	5278(6)	1858(13)	7429(13)
C(4)	4587(6)	2712(12)	7868(11)
C(5)	4049(7)	1637(14)	8662(12)
C(2*)	5866(5)	2813(11)	6798(10)
C(3*)	5437(6)	2371(15)	8064(12)
C(4*)	4589(6)	2034(13)	7320(11)
C(5*)	4119(7)	1182(13)	8323(12)

* CP refers to the atoms of the cyclopentadienyl rings.

Table 5 Atomic coordinates (× 10^4) of compound **12***

Atom	*x*	*y*	*z*
Zr	7 717(1)	2 563(1)	2 924(5)
O	7 203(7)	1 557(7)	4 021(13)
C(2)	6 596(12)	852(15)	3 888(21)
C(3)	5 943(10)	1 087(12)	2 883(36)
C(4)	6 303(11)	1 388(11)	1 385(22)
C(5)	6 675(9)	2 299(8)	1 334(18)
CP(1)	6 985(8)	4 130(9)	3 030(27)
CP(2)	7 847(9)	4 233(9)	3 440(14)
CP(3)	7 978(9)	3 801(9)	4 714(16)
CP(4)	7 177(11)	3 407(10)	5 089(18)
CP(5)	6 531(9)	3 605(9)	4 046(20)
CP(6)	6 587(13)	4 586(11)	1 699(20)
CP(7)	8 472(10)	4 919(9)	2 743(22)
CP(8)	8 739(11)	3 839(12)	5 698(20)
CP(9)	6 943(14)	2 936(12)	6 442(19)
CP(10)	5 618(9)	3 417(12)	4 081(26)
CP(11)	9 212(7)	1 873(8)	3 040(24)
CP(12)	9 297(9)	2 700(10)	2 266(16)
CP(13)	8 894(8)	2 704(9)	992(16)
CP(14)	8 520(8)	1 788(9)	868(16)
CP(15)	8 738(8)	1 316(10)	2 007(17)
CP(16)	9 642(11)	1 581(13)	4 282(23)
CP(17)	10 008(9)	3 401(10)	2 717(28)
CP(18)	8 851(11)	3 402(13)	−183(19)
CP(19)	8 184(11)	1 439(12)	−497(17)
CP(20)	8 560(11)	294(10)	2 240(17)

* CP refers to the atoms of the pentamethylcyclopentadienyl ligands.

of three carbon atoms of the zirconaoxacycle were very large, which means these atoms occupy disordered positions. Therefore, we arranged these carbons at calculated positions with an occupancy of 0.5. The remaining hydrogen atoms were located on the Fourier difference maps. The final refinement cycle with non-hydrogen atoms having anisotropic and hydrogen atoms isotropic thermal parameters converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.044$. The weighting scheme $1/w = \sigma_c{}^2 + (0.015|F_o|)^2$ was employed. The final Fourier difference maps gave no meaningful peak. Selected bond lengths and angles are shown in Table 1, atomic coordinates in Table 4.

Compound **12**. Colourless prisms were obtained by recrystallization from toluene at −20 °C. A suitable crystal with dimensions of 0.36 × 0.23 × 0.17 mm was sealed in a thin-walled capillary under argon. Data were collected on a Rigaku AFC-5 diffractometer using graphite-monochromated Mo-Kα radiation. The automatic peak search and indexing methods yielded an orthorhombic reduced primitive cell. Final cell dimensions and details of the data collection procedures are given in Table 3. The data were corrected for the systematic crystal damage (maximum correction 10% in $|F_o|$) and also for absorption, Lorentz, and polarization factors.

The structure was solved by using direct methods (MULTAN 78) for 1336 independent reflections.[28] The series of block-diagonal least-squares refinements, and Fourier syntheses gave all 26 non-hydrogen atoms and hydrogen atoms of the six-membered ring. Hydrogen atoms of the C_5Me_5 ligands were not located. The final refinement for all non-hydrogen atoms with anisotropic thermal parameters and hydrogen atoms with isotropic thermal parameters converged at $R = 0.074$ and $R' = 0.065$. Selected bond lengths and angles are compiled in Table 1, atomic coordinates in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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