Dinuclear Zirconium Complexes with $Me_2Si(C_5H_4)_2$ as Bridging Ligand. Molecular Structure of $[\{Zr(\eta^5\text{-}C_5H_3Bu^t{}_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$†

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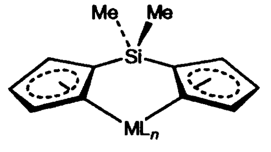
The reaction of $Li_2[Me_2Si(C_5H_4)_2]$ with 2 equivalents of $[ZrLCl_3]$ ($L = C_5Me_5$ or $C_5H_3Bu^t{}_2$) in toluene under reflux gave the known $[\{Zr(C_5Me_5)Cl_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **1** and the new chloro derivative $[\{Zr(C_5H_3Bu^t{}_2)Cl_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **2** in good yields. Addition of 4 equivalents of LiMe (or MgMeCl) to a pentane solution of **1** or **2** afforded the tetramethyl derivatives $[\{Zr(C_5Me_5)Me_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **3** and $[\{Zr(C_5H_3Bu^t{}_2)Me_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **4**. Compound **3** is extremely moisture sensitive leading to the μ-oxo dinuclear complex $[\{Zr(C_5Me_5)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **5**, as demonstrated by ^1H NMR spectroscopy. Compound **4** reacted with water, in pentane or toluene, to give the μ-oxo dimethyl complex $[\{Zr(C_5H_3Bu^t{}_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **6**. Further reaction of **6** with water in toluene gave an unidentified insoluble yellow powder through the intermediate formation of a μ-dioxo methyl complex **7**, identified by ^1H NMR spectroscopy. The crystal structure of **6** has been determined by X-ray diffraction methods: monoclinic, space group $P2_1/n$, $a = 15.494(4)$, $b = 13.338(3)$, $c = 19.933(4)$ Å, $\beta = 107.19(1)°$ and $Z = 4$. Complex **6** is a dimer produced by the interaction of two $Zr(\eta^5\text{-}C_5H_3Bu^t{}_2)Me$ units bridged by one oxygen atom and the $Me_2Si(C_5H_4)_2$ group.

The bis(cyclopentadienediyl)dimethylsilicon anion $[Me_2Si(C_5H_4)_2]^{2-}$ is known[1] to bond to transition metals as a chelating **I** or as a bridging ligand **II**. The synthesis of dinuclear Group 4 transition-metal complexes by using bridging bis(cyclopentadienediyl)dimethylsilicon and fulvalene [5-cyclopenta-2,4-dien-1-ylidene)cyclopenta-1,3-diene] ligands has received considerable attention[2,3] as these systems offer the opportunity to observe co-operative chemical reactivity. These compounds containing two proximal electron-deficient metal centres are thus potential model systems to evaluate how the mutual participation of both metal centres can modify the reactivity patterns exhibited by the corresponding mononuclear compounds, as we have recently reported in relation to reduction processes.[4]

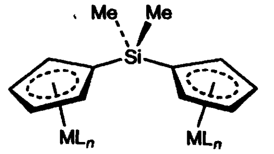
In this paper we report the synthesis and characterization of $[(ZrLX_2)_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ ($L = C_5Me_5$ or $C_5H_3Bu^t{}_2$, X = Cl or Me). Hydrolysis of the methyl derivatives leads to the μ-oxo dimethyl dinuclear compounds $[\{ZrL(Me)\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$. All the compounds reported were characterized by the usual analytical and spectroscopic methods and the molecular structure of $[\{Zr(\eta^5\text{-}C_5H_3Bu^t{}_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ has been fully elucidated by X-ray diffraction studies. Comparisons are made with the solid-state structures of other bis(cyclopentadienediyl)dimethylsilyl complexes.

Results and Discussion

Overnight reaction of $Li_2[Me_2Si(C_5H_4)_2]$ with 2 equivalents of $[ZrLCl_3]$ ($L = C_5Me_5$ or $C_5H_3Bu^t{}_2$) under refluxing toluene was found to be a suitable method to obtain the chloro derivatives $[\{Zr(C_5Me_5)Cl_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]^5$ **1** and $[\{Zr(C_5H_3Bu^t{}_2)Cl_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **2** in good yields (Scheme 1).



I



II

The ^1H NMR spectrum of compound **2** shows the expected resonances for the bridging $Me_2Si(C_5H_4)_2$ with two sets of pseudo-triplets due to an AA′BB′ system for the cyclopentadienyl protons (δ 6.62 and 6.49 in $CDCl_3$, 6.62 and 6.14 in C_6D_6) and one singlet for the methyl protons [δ 0.66 ($CDCl_3$), 0.96 (C_6D_6)]. The proton resonances for the *tert*-butyl and ring protons of the $C_5H_3Bu^t{}_2$ group are readily assignable as one singlet at δ 1.24 ($CDCl_3$) (1.20 in C_6D_6) and one triplet [δ 6.39 ($CDCl_3$), 6.31 (C_6D_6)] and one doublet [δ 6.08 ($CDCl_3$), 5.81 (C_6D_6)] respectively.

Addition of 4 equivalents of LiMe or MgMeCl to a pentane solution of compound **1** or **2** affords the tetramethyl derivatives $[\{Zr(C_5Me_5)Me_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **3** and $[\{Zr(C_5H_3Bu^t{}_2)Me_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **4**. Compound **3** is extremely moisture sensitive and must be manipulated under rigorous anhydrous conditions to avoid the formation of the μ-oxo dinuclear complex $[\{Zr(C_5Me_5)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **5**, which could not be isolated by addition of the stoichiometric amount of water to **3**. When the synthesis of **3** is carried out under insufficiently dry conditions, the final product always contains variable amounts of the μ-oxo complex, as demonstrated by NMR spectroscopic studies. The ^1H NMR spectrum of pure **3**, in C_6D_6 at room temperature, shows the expected two pseudo-triplets for the cyclopentadienyl protons of the bridging ligand corresponding to an AA′BB′ spin system. The dimethylsilyl, the metal-bonded methyl and the C_5Me_5 ring protons appear as singlets and are readily assignable. This is consistent with a dinuclear structure with a C_s symmetry

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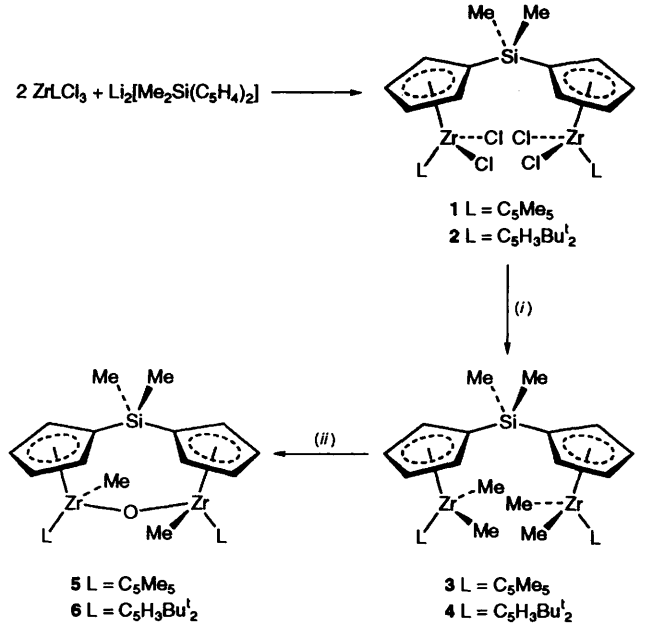
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

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



Scheme 1 (*i*) LiMe or MgMeCl; (*ii*) water

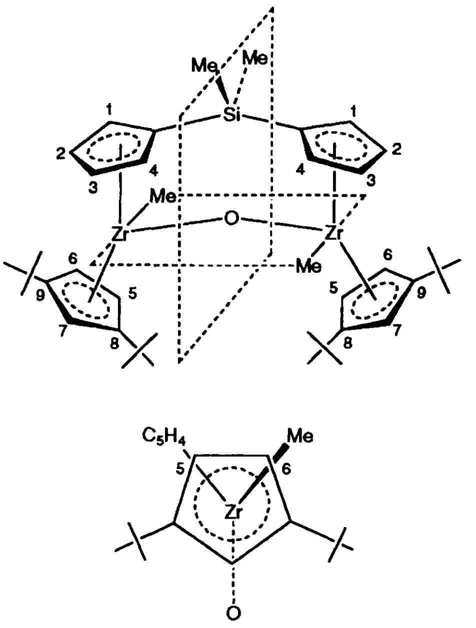
around each zirconium centre. When partial hydrolysis takes place an additional group of resonances is observed, corresponding to the μ-oxo derivative **5**.

Compound **4** is more resistant to hydrolysis and can easily be obtained by reaction of **2** with LiMe or MgMeCl. The ^1H NMR spectrum shows the same spectral features as observed for **3** and the expected resonances are readily assignable (see Experimental section). Compound **4** reacts with water, in pentane or toluene, to give a solution from which a yellow crystalline solid can be isolated and identified as the μ-oxo complex $[\{Zr(C_5H_3Bu^t_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **6**. Complex **6** shows a C_1 symmetry with a chiral arrangement around each zirconium centre and therefore the cyclopentadienyl protons of the bridging ligand appear as a more complex ABCD system characterized by four multiplets in the aromatic region. The ^1H NMR spectrum in C_6D_6 shows four multiplets (δ 5.58, 6.29, 6.43 and 6.80) for the cyclopentadienyl protons of the bridging group, three pseudo-triplets (δ 5.44, 6.16 and 6.29) for the cyclopentadienyl protons of the $C_5H_3Bu^t_2$ rings, two singlets (δ 1.17 and 1.32) for the *tert*-butyl protons and two singlets assignable to methyl groups bonded to the silicon and zirconium atoms.

The presence of the μ-oxo bridge in $[\{Zr(C_5H_3Bu^t_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **6** generates a chiral metal centre. As a result the distal and proximal protons of the cyclopentadienyl bridging group form diastereotopic pairs which produce an ABCD spin system giving four multiplets. Similarly this effect produces an ABC spin system for the cyclopentadienyl protons of the $C_5H_3Bu^t_2$ ring.

Attempts to obtain pure samples of compound **5** by reaction of **3** with stoichiometric amounts of water were unsuccessful, although its formation has been demonstrated by ^1H NMR spectroscopy. The spectral behaviour of **5** is similar to that observed for **6** and its ^1H NMR spectrum (C_6D_6) shows four multiplets (δ 5.21, 5.47, 5.97 and 6.33) and one singlet (δ 0.53) respectively due to the cyclopentadienyl and dimethylsilyl bridging ligand, along with two singlets for pentamethylcyclopentadienyl (δ 1.77) and the methylzirconium protons (δ 0.07).

Compound **6** reacts in toluene by further addition of water to give a yellow precipitate which is completely insoluble in all common solvents, preventing its structural characterization. However, in this reaction the intermediate formation of a μ-dioxo methyl complex **7** has been observed by NMR studies.



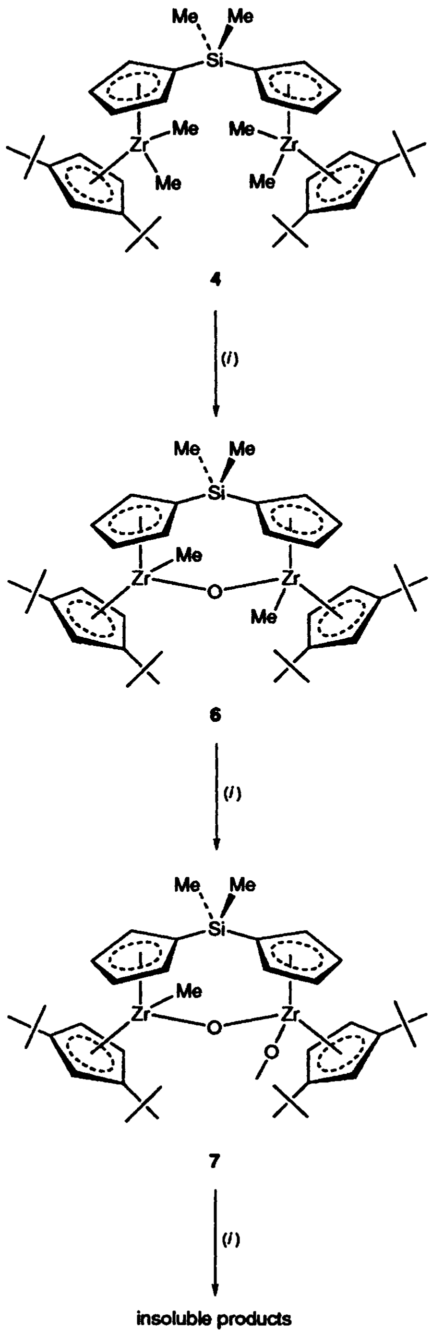
The ^1H NMR spectrum of complex **7** in C_6D_6 shows the presence of fourteen signals for the cyclopentadienyl ring protons. The ^1H–^1H NMR two-dimensional correlation (COSY) spectrum clearly shows the correlation between eight of these signals (δ 6.80, 6.69, 6.43, 6.34, 6.31, 6.04, 5.78 and 5.59), which are assignable to eight protons of the two cyclopentadienyl rings of the bridging ligand and the correlation between the other six signals (δ 6.29, 6.19, 6.16, 5.95, 5.45 and 5.38) corresponding to the $C_5H_3Bu^t_2$ ring protons. Four signals (δ 1.38, 1.32, 1.17 and 1.16) are also observable for the *tert*-butyl protons and three resonances (δ 0.59, 0.53 and 0.52) appear for the methyl protons. These spectral data are indicative of the formation of a dinuclear zirconium species in which the chiral ligand arangement about each zirconium centre, observed for **6**, is maintained and both zirconium centres show different co-ordination environments. This disposition makes the two metal atoms inequivalent, generating two sets of ABCD and ABC spin system signals for the cyclopentadienyl protons of the bridging group and $C_5H_3Bu^t_2$ respectively. The presence of three resonances for the methyl protons indicates the loss of one of the methyl groups bonded to zirconium in the starting compound **6**.

All these data are in agreement with the reaction pathway shown in Scheme 2, indicating that compound **6** reacts with 1 equivalent of water, resulting in the hydrolysis of one of the methyl groups bonded to zirconium to give the species **7**, which then reacts with more water to yield the final product as an insoluble yellow powder.

A feature associated with the ^{13}C NMR spectra of all the dinuclear compounds described here, with the $Me_2Si(C_5H_4)_2$ bridging ligand, is the resonance for the bridgehead carbon of the latter, which is, always, shifted downfield from the proximal and distal carbon resonances corresponding to the bridging co-ordination of this ligand.[2,5]

Crystal Structure of Complex **6**.—The crystal structure of compound **6** is shown in Fig. 1 with the atomic labelling scheme. Final atomic parameters for non-hydrogen atoms are displayed in Table 1, selected bond distances and angles in Table 2.

The structure of complex **6** consists in two $Zr(\eta^5\text{-}C_5H_3Bu^t_2)Me$ units bonded by one bridging oxygen atom and the bridging $Me_2Si(C_5H_4)_2$ ligand. Each zirconium centre shows a metallocene-type pseudo-tetrahedral geometry assuming that the ring centroids occupy a unique co-ordination position, comparable to the structures found for $Zr(C_5H_5)_2X_2$.[6]



Scheme 2 (*i*) Water

The structure of this zirconium compound compares very well with that previously reported for the similar titanium derivative $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$[2], although important differences with respect to the structure found by Reddy and Petersen[5] for the analogous zirconium complex $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ can be observed. The structure of **6** shows a non-symmetric disposition of the bridging ligand, with one of the C_5H_4 rings twisted with respect to the other around the line defined by the silicon and the bridgehead carbon atoms.

The (centroid)–Zr–(centroid) (129.1 and 129.6°) and the C_{methyl}-Zr-O angles [92.7(1) and 93.9(1)°] are within the expected range.[7] The Zr–C(ring) distances are fairly uniform in each ring and the C–C ring distances show very small differences, corresponding to η^5 co-ordination of the cyclopentadienyl ring. This behaviour is opposite to that observed for similar mononuclear complexes with the *ansa*-$Me_2Si(C_5H_4)_2$ group.[8]

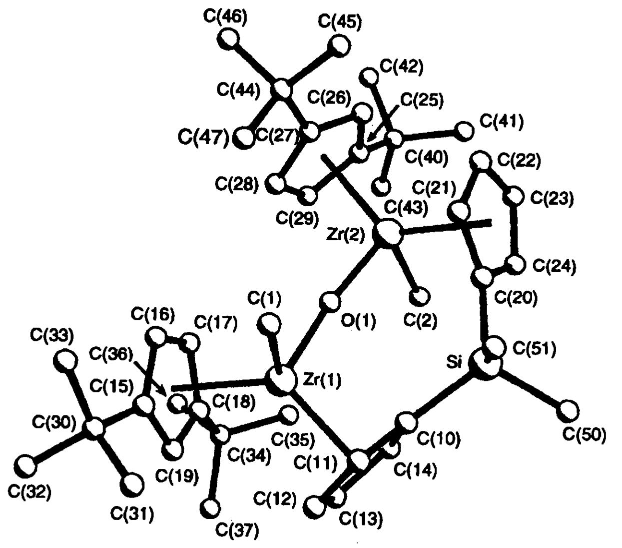


Fig. 1 Perspective view of the molecular structure of $[\{Zr(C_5H_3Bu^t{}_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **6** with the atom-numbering scheme

A small difference between the Zr–centroid distances for both rings of the bridging ligand is observed [Zr(1)–Cp(1) 2.248 and Zr(2)–Cp(3) 2.279 Å].

The Zr(1)–O–Zr(2) angle of 171.8(1)° shows a nearly linear disposition. The Zr–O bond lengths are 1.955(2) and 1.946(3) Å for Zr(1) and Zr(2) respectively. Average values for single and double Zr–O bonds are 2.15–2.20 and 1.95 Å.[6,9] The short Zr–O distances indicate a multiple-bond character commonly observed in structures of type $[\{Zr(C_5H_5)_2X\}_2(\mu\text{-}O)]$.[5] This interaction reduces the electrophilic character of the metal centre increasing the Zr–centroid and the Zr–Me distances. Thus, these distances, 2.277 and 2.328 Å (average), are larger for compound **6** than those observed for $[Zr(\eta^5\text{-}C_5H_5)_2Me_2]$, 2.23 and 2.276 Å (average),[10] respectively. Both methyl groups are located in *trans* positions with respect to the Zr–Zr line, thus making the C_5H_4 rings *trans* with respect to the same line. A value of 90° for the dihedral angle (φ) between the two L–Zr–O planes, calculated from structures of $[\{Zr(C_5H_5)_2X\}_2(\mu\text{-}O)]$ compounds, has been found to optimize the π donation between oxygen p_π orbitals and the metal d_{z^2} lowest unoccupied molecular orbital (LUMO). However, for the known $[\{Zr(C_5H_5)_2X\}_2(\mu\text{-}O)]$ structures this angle differs significantly from the ideal value, ranging between 45 and 75°.[5] The φ angle for compound **6**, 17.4°, is very small in comparison to those found for the other complexes. The distance between the ring centroids is another interesting structural parameter in this type of complex. Several examples confirm Petersen's proposal[5] that a decrease in this distance implies a reduction of the Zr–O–Zr angle. The structure of compound **6** is again an exception to this rule. The centroid–centroid distance for the bridging ligand, 5.34 Å for **6**, is larger than those observed in $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ [4.95(1) Å],[5] $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}CH_2(C_5H_4)_2\}]$ [4.82(1) Å][5] and 3.84 Å (estimated) in $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}C_{10}H_8)]$,[11] while the corresponding Zr–O–Zr angle (171.8°) is substantially smaller, *cf.* 178.6(2)° for $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$, 174.3(2)° for $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}CH_2(C_5H_4)_2\}]$ and 156.0(2)° for $[\{Zr(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)(\mu\text{-}C_{10}H_8)]$. These structural parameters for complex **6** must be due to the twisted C_5H_4 rings of the bridging ligand. The magnitude of this rotation can be estimated by Petersen's proposal[5] from the dihedral angle, θ, between the corresponding lines passing through each pair of proximal carbon atoms of the linked five-membered rings. The value is 33.4° for **6**, whereas for the more symmetrical disposition found for the Petersen compound it is 4.2°. Another

Table 1 Positional parameters and their estimated standard deviations for compound **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zr(1)	0.3952(1)	0.1267(1)	0.2815(1)	C(26)	0.7253(2)	−0.1356(2)	0.3400(1)
Zr(2)	0.6171(1)	0.0027(1)	0.2687(1)	C(27)	0.6441(2)	−0.1405(2)	0.3594(1)
Si	0.4148(1)	0.0693(1)	0.0922(1)	C(28)	0.6391(2)	−0.0504(2)	0.3947(1)
O(1)	0.5095(1)	0.0638(2)	0.2824(1)	C(29)	0.7139(2)	0.0089(2)	0.3963(2)
C(1)	0.3153(2)	−0.0228(2)	0.2516(2)	C(30)	0.2200(2)	0.1126(3)	0.3785(2)
C(2)	0.6879(2)	0.1556(2)	0.2650(2)	C(31)	0.1531(2)	0.1385(4)	0.3079(2)
C(10)	0.3737(2)	0.1540(2)	0.1503(2)	C(32)	0.1947(2)	0.1718(3)	0.4362(2)
C(11)	0.2860(2)	0.1585(3)	0.1586(2)	C(33)	0.2131(3)	0.0020(3)	0.3944(2)
C(12)	0.2803(2)	0.2418(3)	0.1996(2)	C(34)	0.5082(2)	0.3305(3)	0.4054(2)
C(13)	0.3636(2)	0.2912(2)	0.2168(2)	C(35)	0.5711(3)	0.3255(4)	0.3596(2)
C(14)	0.4204(2)	0.2389(2)	0.1863(1)	C(36)	0.5649(3)	0.3279(4)	0.4813(2)
C(15)	0.3169(2)	0.1405(2)	0.3814(1)	C(37)	0.4526(3)	0.4269(3)	0.3933(3)
C(16)	0.3950(2)	0.0792(2)	0.4057(1)	C(40)	0.8680(2)	−0.0212(2)	0.3665(2)
C(17)	0.4723(2)	0.1393(2)	0.4130(1)	C(41)	0.8852(2)	−0.0364(3)	0.2965(2)
C(18)	0.4435(2)	0.2377(2)	0.3928(1)	C(42)	0.9271(2)	−0.0958(3)	0.4189(2)
C(19)	0.3480(2)	0.2371(2)	0.3729(1)	C(43)	0.8946(2)	0.0846(3)	0.3931(2)
C(20)	0.5205(2)	−0.0004(2)	0.1366(1)	C(44)	0.5864(2)	−0.2331(2)	0.3592(2)
C(21)	0.5278(2)	−0.0997(2)	0.1631(2)	C(45)	0.5872(3)	−0.3066(3)	0.3012(2)
C(22)	0.6189(3)	−0.1306(3)	0.1779(2)	C(46)	0.6261(3)	−0.2861(3)	0.4297(2)
C(23)	0.6685(2)	−0.0513(4)	0.1630(2)	C(47)	0.4888(2)	−0.2056(3)	0.3515(2)
C(24)	0.6088(2)	0.0284(3)	0.1376(2)	C(50)	0.4383(3)	0.1484(3)	0.0226(2)
C(25)	0.7700(2)	−0.0439(2)	0.3633(1)	C(51)	0.3241(3)	−0.0226(3)	0.0516(2)

Table 2 Selected bond distances (Å) and angles (°) for compound **6**

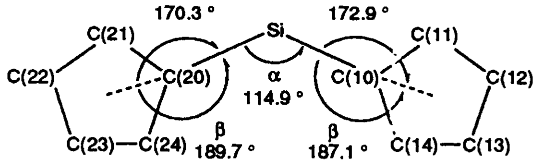
Zr(1)–O(1)	1.955(2)	Zr(1)–C(1)	2.330(1)
Zr(1)–Cp(1)	2.248	Zr(1)–Cp(2)	2.299
Zr(2)–O(1)	1.946(3)	Zr(2)–C(2)	2.327(3)
Zr(2)–Cp(3)	2.279	Zr(2)–Cp(4)	2.283
Si–C(10)	1.860(4)	Si–C(20)	1.864(3)
Si–C(50)	1.862(5)	Si–C(51)	1.860(4)
Cp(1)–Zr(1)–Cp(2)	129.1	C(1)–Zr(1)–Cp(2)	107.2
C(1)–Zr(1)–Cp(1)	102.3	O(1)–Zr(1)–Cp(2)	110.6
O(1)–Zr(1)–Cp(1)	108.4	Cp(3)–Zr(2)–Cp(4)	129.6
C(2)–Zr(2)–Cp(4)	105.7	C(2)–Zr(2)–Cp(3)	101.4
O(1)–Zr(2)–Cp(4)	109.2	O(1)–Zr(2)–Cp(3)	110.4
O(1)–Zr(1)–C(1)	92.7(1)	O(1)–Zr(2)–C(2)	93.9(1)
C(10)–Si–C(20)	114.9(2)	Zr(1)–O(1)–Zr(2)	171.8(1)

Numbers in parentheses are estimated standard deviations in the least significant digits. Centroids: Cp(1), C(10)–C(11)–C(12)–C(13)–C(14), Cp(2) C(15)–C(16)–C(17)–C(18)–C(19), Cp(3) C(20)–C(21)–C(22)–C(23)–C(24), Cp(4) C(25)–C(26)–C(27)–C(28)–C(29).

parameter employed to evaluate this rotation is based on the distances from the proximal carbon atoms to the Si–C(50)–C(51) plane. These distances are 2.363(3) for C(21), 2.334(3) for C(24), 2.677(4) for C(11) and 1.992(3) Å for C(14), showing that only ring Cp(1) is rotated, Cp(3) remaining in a symmetrical disposition. In contrast, an asymmetrical arrangement for both C_5H_4 rings is found for the compound $[\{Ti(\eta^5\text{-}C_5H_5)Cl\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$.[2]

These effects must be produced by the presence of the di-*tert*-butylcyclopentadienyl ligand which exerts an important steric constraint with a strong influence on the orientation of the oxygen and zirconium orbitals. Thus not only the size/length of the bridging ligand, but also the complete zirconium environment, must exhibit an influence on the central geometry of these oxo-bridged zirconocene complexes.

For compounds with $Me_2Si(C_5H_4)_2$, Fischer and co-workers[12] justified, from a geometric point of view, the chelating or the bridging disposition of this group. This can be done by evaluating the distortion of the $C_{ipso}(C_5H_4)$–Si–$C_{ipso}(C_5H_4)$ and centroid–$C_{ipso}(C_5H_4)$–Si angles, α and β respectively. For compound **6** these angles are 114.9(2) and 188.4° respectively. These values are in agreement with the predictions for a bridging disposition, involving an enlargement with respect to the theoretical values (109.5 and 180° for α and β respectively).



Experimental

All operations were performed under an inert atmosphere of dinitrogen or argon using Schlenk and vacuum-line techniques or a VAC model HE-63-P glove-box. The following solvents were dried and purified by distillation under argon before use by employing the appropriate drying/deoxygenating agents: toluene (sodium), pentane (sodium–potassium alloy). The compounds $[Zr(\eta^5\text{-}C_5Me_5)Cl_3]$,[13] $[Zr(\eta^5\text{-}C_5H_3Bu^t{}_2)Cl_3]$[14] and $Li_2[Me_2Si(C_5H_4)_2]$[5,15] were prepared according to literature procedures; MgMeCl and LiMe in diethyl ether solution (Aldrich) were used without further purification. Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on Varian 300 Unity and 500 Unity Plus instruments; the chemical shifts are reported in δ (positive chemical shifts to higher frequency) relative to $SiMe_4$ as standard. Mass spectra were recorded on a Hewlett-Packard 5890 spectrometer. Elemental C, H and N analyses were performed with a Perkin-Elmer 240B microanalyser.

Preparations.—$[\{Zr(\eta^5\text{-}C_5H_3Bu^t{}_2)Cl_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}]$ **2**. Toluene (70 cm^3) was added to a mixture of $[Zr(\eta^5\text{-}C_5H_3Bu^t{}_2)Cl_3]$ (3.6 g, 9.60 mmol) and $Li_2[Me_2Si(C_5H_4)_2]$ (0.96 g, 4.80 mmol) and the mixture stirred under reflux overnight. After cooling at room temperature the resulting solution was evaporated *in vacuo* to *ca.* 20 cm^3. By addition of pentane to form two phases and cooling to −30 °C a pale brown solid was obtained. Recrystallization from toluene–pentane at −30 °C gave a crystalline pale brown solid which was characterized as compound **2**. Yield 3.32 g (80%) (Found: C, 49.95; H, 6.35. Calc. for $C_{34}H_{56}Cl_4SiZr_2$: C, 50.00; H, 6.45%). NMR (25 °C): ^1H ($CDCl_3$, 300 MHz); δ 0.66 (s, 6 H, $SiMe_2$), 1.24 [s, 36 H, $C(CH_3)_3$], 6.08 (d, 4 H, *J* = 2.7, $C_5H_3Bu^t{}_2$), 6.39 (t, 2 H, *J* = 2.6, $C_5H_3Bu^t{}_2$), 6.49 (t, 4 H, *J* = 2.4, C_5H_4) and 6.62 (t, 4 H, *J* = 2.6, C_5H_4); (C_6D_6, 300 MHz); δ 0.96 (s, 6 H, $SiMe_2$), 1.20 [s, 36 H, $C(CH_3)_3$], 5.81 (d, 4 H, *J* = 2.7, $C_5H_3Bu^t{}_2$), 6.14 (t, 4 H, *J* = 2.4, C_5H_4), 6.31 (t, 2 H, *J* = 2.7, $C_5H_3Bu^t{}_2$) and 6.62 (t, 4 H, *J* = 2.6 Hz, C_5H_4); $^{13}C\text{-}\{^1H\}$

Table 3 Crystal and X-ray structural analysis data for compound **6**

Empirical formula	$C_{40}H_{62}OSiZr_2$
M	769.47
Crystal colour, habit	Colourless, prism
Crystal system, space group	Monoclinic, $P2_1/n$
Unit-cell determination	Least-squares fit from 25 reflections $\theta < 12°$
a, b, c/Å	15.494(4), 13.338(3), 19.933(4)
β/°	107.19(1)
U/Å^3, Z	3935(3), 4
D_c/g cm^{-3}	1.299
μ(Mo-Kα)/cm^{-1}	5.772
F(000)	1616
Technique	ω–2θ scan mode
Reflections measured	9266
Unique observed reflections [$I > 2\sigma(I)$]	5598
hkl ranges	-19 to 0, -17 to 0, -25 to 25
Standard reflections	2 every 120 min; no variation
Parameters refined	398
Goodness of fit	1.372
R	0.033
R'	0.042
Weighting scheme, w	$4F^2/\sigma(F^2)^2$; $\sigma(F^2) = [\sigma(I)^2 + (0.04F^2)^2]$
Maximum and minimum peaks in final difference map/e Å^{-3}	1.145, -0.395

($CDCl_3$, 75.5 MHz); δ 0.8 ($SiMe_2$), 31.2 [$C(\mathit{C}H_3)_3$], 33.9 [$\mathit{C}(CH_3)_3$], 110.7, 114.8 (C_5H_4), 115.6 (C_a, $C_5H_3Bu^t_2$), 125.3 (C_{ipso}, C_5H_4), 125.9 (C_b, $C_5H_3Bu^t_2$) and 144.2 (C_{ipso}, $C_5H_3Bu^t_2$).

[$\{Zr(\eta^5\text{-}C_5Me_5)Me_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}$] **3**. A 3 mol dm^{-3} solution of MgMeCl in diethyl ether (1.70 cm^3, 5.12 mmol) [or a 1.6 mol dm^{-3} solution of LiMe in diethyl ether (3.2 cm^3, 5.12 mmol)] was added to a pentane solution (50 cm^3) containing [$\{Zr(\eta^5\text{-}C_5Me_5)Cl_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}$] (1.0 g, 1.28 mmol) at −78 °C. The reaction mixture was stirred for 30 min and then slowly warmed to room temperature and stirred overnight. After filtration, the solvent was evaporated to dryness *in vacuo* to give a yellow solid. Recrystallization from pentane at −30 °C gave a white-yellow crystalline solid which was characterized as compound **3**. Yield 0.61 g (68%). NMR (C_6D_6, 25 °C); ^1H (300 MHz), δ −0.27 (s, 12 H, ZrMe), 0.68 (s, 6 H, $SiMe_2$), 1.71 (s, 30 H, C_5Me_5), 5.61 (t, 4 H, J = 2.6, C_5H_4) and 6.20 (t, 4 H, J = 2.6 Hz, C_5H_4); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 0.2 ($SiMe_2$), 11.7 [$C_5(\mathit{C}H_3)_5$], 33.2 (ZrMe), 113.4, 118.8 (C_5H_4) and 117.4 [$\mathit{C}_5(CH_3)_5$]; C_{ipso} of C_5H_4 not observed. Electron impact mass spectrum (70 eV): m/z = 666, [M − 2Me]$^+$.

[$\{Zr(\eta^5\text{-}C_5H_3Bu^t_2)Me_2\}_2\{\mu\text{-}Me_2Si(C_5H_4)_2\}$] **4**. A 3 mol dm^{-3} solution of MgMeCl in diethyl ether (0.92 cm^3, 2.76 mmol) [or a 1.6 mol dm^{-3} solution of LiMe in diethyl ether (1.72 cm^3, 2.76 mmol)] was added to a pentane solution (50 cm^3) containing compound **2** (0.6 g, 0.69 mmol) at −78 °C. The reaction mixture was stirred for 30 min and then slowly warmed to room temperature and stirred overnight. After filtration, the solvent was evaporated to dryness *in vacuo* to give a yellow solid. Recrystallization from pentane at −30 °C gave a clear yellow crystalline solid which was characterized as compound **4**. Yield 0.43 g (80%) (Found: C, 64.00; H, 8.30. Calc. for $C_{42}H_{68}SiZr_2$; C, 64.80; H, 8.75%). NMR (C_6D_6, 25 °C): ^1H (300 MHz), δ 0.08 (s, 12 H, ZrMe), 0.69 (s, 6 H, $SiMe_2$), 1.12 [s, 36 H, $C(CH_3)_3$], 5.72 (t, 2 H, J = 2.4, $C_5H_3Bu^t_2$), 5.87 (d, 4 H, J = 2.6, $C_5H_3Bu^t_2$), 5.95 (t, 4 H, J = 2.6, C_5H_4) and 6.41 (t, 4 H, J = 2.6 Hz, C_5H_4); $^{13}C\text{-}\{^1H\}$ (75.5 MHz), δ 0.0 ($SiMe_2$), 31.9 [$C(\mathit{C}H_3)_3$], 32.1 (ZrMe), 33.1 [$\mathit{C}(CH_3)_3$], 106.1 [C_a, $C_5H_3Bu^t_2$), 108.6 (C_b, $C_5H_3Bu^t_2$), 111.5, 120.2 (C_5H_4), 120.5 (C_{ipso}, C_5H_4) and 137.1 (C_{ipso}, $C_5H_3Bu^t_2$). Electron impact mass spectrum: m/z = 750, [M − 2Me]$^+$.

[$\{Zr(\eta^5\text{-}C_5H_3Bu^t_2)Me\}_2(\mu\text{-}O)\{\mu\text{-}Me_2Si(C_5H_4)_2\}$] **6**. Deoxygenated water (6.9 × 10^{-3} cm^3, 0.38 mmol) was added to a pentane solution (50 cm^3) containing compound **4** (0.3 g, 0.38 mmol) at room temperature. The reaction mixture was stirred overnight and the formation of a yellow precipitate was observed. After filtration the resulting yellow solution was evaporated to *ca.* 15 cm^3 *in vacuo*. By cooling at −30 °C a crystalline yellow solid was obtained which was characterized as compound **6**. Yield 0.12 g (40%). Suitable crystals for X-ray diffraction studies were obtained from a saturated solution of **6** in pentane at −30 °C (Found: C, 62.00; H, 7.95. Calc. for $C_{40}H_{62}OSiZr_2$: C, 62.45; H, 8.15%). NMR (C_6D_6, 25 °C): ^1H (300 MHz), δ 0.53 (s, 6 H, ZrMe), 0.59 (s, 6 H, $SiMe_2$), 1.17 [s, 18 H, $C(CH_3)_3$], 1.32 [s, 18 H, $C(CH_3)_3$], 5.44 (t, 2 H, $C_5H_3Bu^t_2$), 5.58 (m, 2 H, C_5H_4), 6.16 (t, 2 H, $C_5H_3Bu^t_2$), 6.29 [m, 4 H (2 H of C_5H_4 + 2 H of $C_5H_3Bu^t_2$)], 6.43 (m, 2 H, C_5H_4) and 6.80 (m, 2 H, C_5H_4); ^{13}C (75.5 MHz), δ 0.1 (q, J = 123, $SiMe_2$), 23.8 (q, J = 122, ZrMe), 32.3 [q, J = 123, $C(\mathit{C}H_3)_3$], 32.6 [s, $\mathit{C}(CH_3)_3$], 32.8 [q, J = 125, $C(\mathit{C}H_3)_3$], 33.1 [s, $\mathit{C}(CH_3)_3$], 105.6, 109.2, 110.5, 111.5, 112.2, 118.5, 127.5 (d, J = 165.5–170 Hz, C_5H_4 + $C_5H_3Bu^t_2$), 122.8 (s, C_{ipso}, C_5H_4), 132.7 (C_{ipso}, $C_5H_3Bu^t_2$) and 133.9 (C_{ipso}, $C_5H_3Bu^t_2$).

Crystal Structure Determination of Compound **6**.—Crystallographic and experimental details of the crystal structure determination are given in Table 3. A suitable crystal of compound **6** was mounted on an Enraf-Nonius CAD-4 automatic four-circle diffractometer with bisecting geometry equipped with a graphite-oriented monochromator and Mo-Kα radiation (λ = 0.710 73 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F) by full-matrix least-squares calculations. All the non-hydrogen atoms were refined anisotropically. In the last cycle of refinement the hydrogen atoms were introduced from geometrical calculations with thermal parameters equivalent to those of the carbon to which they are attached. Final values of R = 0.033 and R' = 0.042 were obtained, where $R' = (\Sigma w||F_o| - |F_c||^2/w|F_o|^2)^{\frac{1}{2}}$ and $w = 4F_o^2/[\sigma|F_o|^2]$.

Anomalous dispersion corrections and atomic scattering factors were taken from ref. 16. Calculations were performed with the SDP package,[17] and the programs MULTAN[18] and DIRDIF[19] on a MicroVax II computer.

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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References

1 K. P. Reddy and J. L. Petersen, *Organometallics*, 1989, **8**, 547.

2 T. Cuenca, J. C. Flores, R. Gómez, P. Gómez-Sal, M. Parra-Hake and P. Royo, *Inorg. Chem.*, 1993, **32**, 3608 and refs. therein.

3 Y. Wielstra, R. Duchateau, S. Gambarota, C. Bensimon and E. Gabe, *J. Organomet. Chem.*, 1991, **418**, 183 and refs. therein; L. M. Alvaro, T. Cuenca, J. C. Flores, P. Royo, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1992, **11**, 3301; A. Cano, T. Cuenca, G. Rodriguez, P. Royo, C. Cardin and D. Wilcock, *J. Organomet. Chem.*, 1993, **447**, 51.

4 T. Cuenca, A. Padilla, M. Parra-Hake, P. Royo, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, in the press.

5 K. P. Reddy and J. L. Petersen, *Organometallics*, 1989, **8**, 2107.

6 D. J. Cardin, M. F. Lappert and C. L. Raston, *Chemistry of Organozirconium and -hafnium Compounds*, Ellis Horwood, London, 1986.

7 K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290; E. L. Lyszak, J. P. O'Brien, D. A. Kort, S. K. Hendges, R. N. Redding, T. L. Busch, M. S. Hermen, K. B. Renkema, M. E. Silver and J. C. Huffman, *Organometallics*, 1993, **12**, 338.

8 R. Gómez, T. Cuenca, P. Royo, W. A. Herrmann and E. Herdweck, *J. Organomet. Chem.*, 1990, **382**, 103; R. Gómez, T. Cuenca, P. Royo, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1991, **10**, 1505; R. Gómez, T. Cuenca, P. Royo and E. Hovestreydt, *Organometallics*, 1991, **10**, 2516; T. Cuenca, R. Gómez, P. Gómez-Sal and P. Royo, *J. Organomet. Chem.*, 1993, **454**, 105.

9 M. E. Silver, H. Y. Chun and R. C. Fay, *Inorg. Chem.*, 1982, **21**, 3765 and refs. therein.

10 W. E. Hunter, D. C. Hrncir, R. V. Bynum, R. A. Penttila and J. L. Atwood, *Organometallics*, 1983, **2**, 750.

11 T. V. Ashworth, T. Cuenca, E. Herdtweck and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 289.

12 T. Akhnoukh, J. Müller, K. Qiao, X.-F. Li and R. D. Fischer, *J. Organomet. Chem.*, 1991, **408**, 47.

13 P. T. Wolczanski and J. E. Bercaw, *Organometallics*, 1982, **1**, 793.

14 J. I. Amor, T. Cuenca and P. Royo, unpublished work.

15 C. S. Bajgur, W. R. Tikkanen and J. L. Petersen, *Inorg. Chem.*, 1985, **24**, 2539.

16 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

17 SDP Structure Determination Package, Enraf-Nonius, Delft, 1985.

18 P. Main, S. J. Fiske, S. E. Hill, L. Lessinger, C. Germain, J.-P. Declerq and M. M. Wolfson, MULTAN, Universities of York and Louvain, 1980.

19 P. T. Beurskens, W. P. Bossman, H. M. Doesburg, R. O. Gould, T. E. M. van der Hark, P. A. S. Prick, J. H. Noordick, G. Beurskens and V. Prathasarathi, DIRDIF, Technical Report 1981/82; Crystallographic Laboratory, Tornooiveld, Nijmegen, 1981.

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