Synthesis of 5-*ansa*-Zirconocene Complexes and Crystal Structure of $[Zr\{C_6H_4(CH_2C_5H_4)_2\text{-}1,3\}Cl_2]$†

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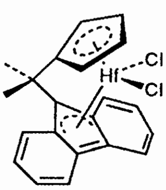
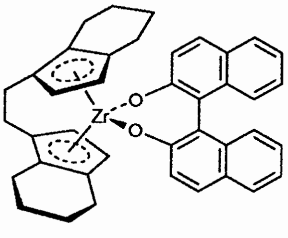
Zirconocene derivatives with interannular $MeN(CH_2CH_2)_2$, $C_5H_3N(CH_2)_2\text{-}2,6$ or $C_6H_4(CH_2)_2\text{-}1,3$ bridges were synthesised by the reaction of the corresponding disodium salts with $ZrCl_4$. The crystal structure of dichloro[*m*-phenylenedimethylenebis(η^5-cyclopentadienyl)]zirconium was determined by X-ray crystallography. The compound crystallizes in space group $P2_12_12_1$ with cell parameters: $a = 13.519(4)$, $b = 13.671(3)$, $c = 8.557(2)$ Å, $Z = 4$, $R = 0.034$ and $R' = 0.039$.

Recently, the study of Group 4 metallocene complexes used for homogeneous Ziegler–Natta polymerization of olefins has attracted the attention of many chemists.[1,2] The homogeneous system is undoubtedly the most versatile route to polymers with controlled structures: the broad electronic and steric variability of cyclopentadienyl-type ligands allows the design of catalyst precursors that are able to form regio- and stereo-regular polyolefins. At present, many research groups are engaged in evaluating the critical parameters for the stereoregularity of α-olefin polymerization and finding an explicit relationship between ligand properties of the catalysts and polymer structures.[3–15] Many *ansa*-metallocene complexes have been tested as catalyst precursors, and a large number of them showed excellent features. For example, with poly(aluminoxanes) as co-catalyst, dichloro{(*R*,*S*)-[1,1′-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]}zirconium leads to highly isotactic polypropylene,[16] while the hafnium complex **A** leads to syndiotactic polypropylene,[17] and optically active poly(cyclopentane-1,3-diylmethylene) was obtained with hexa-1,5-diene in the presence of the chiral zirconium complex **B**.[18] However, compared with 1- or 2-*ansa* metallocene compounds, *ansa*-metallocene compounds with longer bridge chains (three or more atoms in the bridge chains) have been paid little attention up to now.[19–26] Herein we report the synthesis of 5-*ansa*-zirconocene complexes and the crystal structure of dichloro[*m*-phenylenedimethylenebis(η^5-cyclopentadienyl)]zirconium $[Zr\{C_6H_4(CH_2C_5H_4)_2\text{-}1,3\}Cl_2]$.

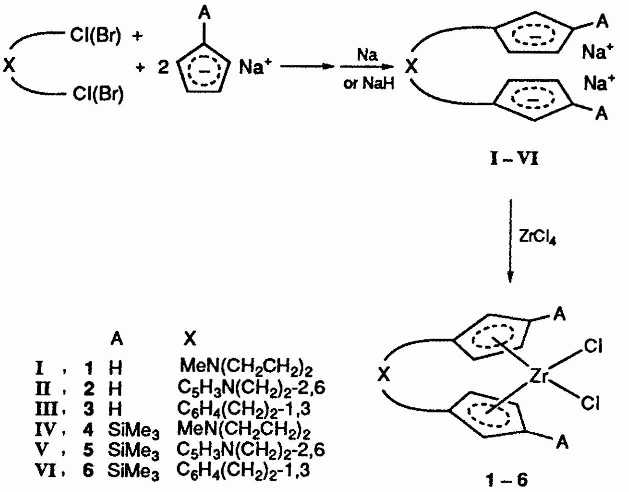
These compounds show two special features; the presence of five-atom bridge chains and incorporation of nitrogen atoms in the bridge chains for four of them.



A



B



		A	X
I ,	**1**	H	$MeN(CH_2CH_2)_2$
II ,	**2**	H	$C_5H_3N(CH_2)_2\text{-}2,6$
III ,	**3**	H	$C_6H_4(CH_2)_2\text{-}1,3$
IV ,	**4**	$SiMe_3$	$MeN(CH_2CH_2)_2$
V ,	**5**	$SiMe_3$	$C_5H_3N(CH_2)_2\text{-}2,6$
VI ,	**6**	$SiMe_3$	$C_6H_4(CH_2)_2\text{-}1,3$

Scheme 1

Results and Discussion

Synthetic Procedures.—The disodium salts (**I**–**VI**) and corresponding complexes (**1**–**6**) were synthesised as shown in Scheme 1.

Sodium cyclopentadienide or $Na(C_5H_4SiMe_3)$ were treated with organohalides to produce the corresponding ring-bridged bis-cyclopentadienes). The resulting solutions were then treated with Na or NaH to yield the disodium salts (**I**–**VI**).

The purity of the disodium salts was critical in the following reactions. However we found that the ring-bridged bis(cyclopentadienes) could not be distilled even under high vacuum. Recrystallization was suitable only for some of the disodium salts. If however a small excess of organohalide was used and the reaction time extended, sufficiently pure disodium salts were obtained.

Addition of tetrahydrofuran solutions of the disodium salts to $ZrCl_4$ suspended in toluene at 0 °C and stirring overnight at room temperature followed by reflux for *ca.* 4 h prior to removal of solvent led to complexes **1**–**6**. The residues were washed with small portions of *n*-hexane and then extracted with CH_2Cl_2. Compounds **1** and **2** (poorly soluble in CH_2Cl_2) were extracted with boiling CH_2Cl_2, while the remainder (well soluble) were extracted at room temperature.

Analytically pure samples of **1**–**6** were obtained by recrystallization from thf–*n*-hexane or CH_2Cl_2–*n*-hexane. Attempts to

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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

Table 1 Bonding energy (b.e.) data (eV)*

	N 1s		Zr $3d_{\frac{5}{2}}$	
Compound	b.e.	ΔE_1	b.e.	ΔE_2
$[Zr(C_5H_5)_2Cl_2]$			184.3	
I	402.0			
1	401.5	−0.5	183.6	−0.7
II	399.9			
2	399.4	−0.5	183.5	−0.8

* ΔE_1 = b.e. N 1s (**1**) − b.e. N 1s (**I**) or b.e. N 1s (**2**) − b.e. N 1s (**II**); ΔE_2 = b.e. Zr $3d_{\frac{5}{2}}$ (**1** or **2**) − b.e. Zr $3d_{\frac{5}{2}}$ $\{[Zr(C_5H_5)_2Cl_2]\}$.

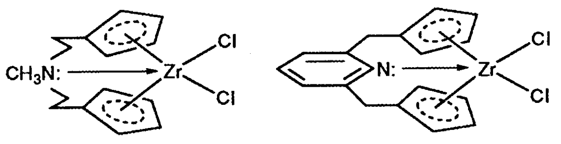

Fig. 1

separate the *rac* and *meso* forms of **4**–**6** by recrystallization however were not successful.

Spectroscopy.—The ^1H NMR spectra of the disodium salts **I**–**III** and zirconocene complexes **1**–**3** exhibit A_2B_2 patterns for the cyclopentadienyl protons. Multiplets were observed for these protons at δ *ca.* 5.5 [similar to those in $Na(C_5H_5)$] for the disodium salts and at δ 6.5 $\{$similar to those in $[Zr(C_5H_5)_2Cl_2]\}$ for the zirconocene complexes. The corresponding data of disodium salts **IV**–**VI** and zirconocene complexes **4**–**6** were similar but the spectra were more complicated owing to the $SiMe_3$ substituent groups. Since complexes **4**–**6** are mixtures of the *rac* and *meso* forms, the protons of $SiMe_3$ groups exhibit multiplets instead of singlets in the ^1H NMR spectra. Compared with the corresponding disodium salts, the chemical shifts of the protons in the bridge chains of compounds **1** and **2** are shifted significantly downfield. The chemical shift of the N-methyl protons in compound **1** are shifted downfield by 0.47 ppm in $[^2H_8]$tetrahydrofuran while the chemical shifts of the protons in the bridge chain of compound **2** are shifted downfield by *ca.* 0.25–0.45 ppm. These shifts indicate co-ordination of the N atoms to zirconium.

In IR spectra, identical absorptions of the cyclopentadienyl groups are evident for all six compounds, occurring at *ca.* 3080, 1450, 1040 and 830 cm^{-1}. For compounds **4**–**6**, two strong absorption peaks appear at *ca.* 757 and 1247 cm^{-1} attributed to the presence of Si–C bonds. For compounds containing phenyl or pyridyl rings (**2**, **3**, **5** and **6**), strong absorption peaks appear in the region 1400–1600 cm^{-1}. The IR spectra of **1** and **2** are also indicative of the co-ordination mode of the ligands. The absorption peaks of the C–N stretching vibration for **1** are assigned at *ca.* 1206 and 1071 cm^{-1} and are shifted to a lower frequency compared with those of the disodium salt **I** (1216, 1096 cm^{-1}). This implies the co-ordination of the N atom to zirconium.[27] Similarly, for compound **2**, a strong band at 1607 cm^{-1} assigned to ν(C=N) is shifted to higher wavenumber [relative to the sodium salt **II** (1584 cm^{-1})] due to co-ordination of the N atom to zirconium.[28,29]

X-Ray photoelectron spectra were used to measure the electronic energy level of the Zr and N atoms in **1** and **2**. The results (in Table 1) show that the binding energies of Zr $3d_{\frac{5}{2}}$ in **1** and **2** decrease relative to those in $[Zr(C_5H_5)_2Cl_2]$. This further confirms the existence of intramolecular co-ordination bonds from the nitrogen atoms in the bridge chains to the zirconium atoms in **1** and **2** (Fig. 1). Moreover, the binding energies of N 1s in **1** and **2** also decrease as compared with the disodium salts **I** and **II**. Chen *et al.*[24] found similar behaviour for O 1s in $[Ti\{C_5H_4(CH_2)_2O(CH_2)_2C_5H_4\}Cl_2]$ and $[Ti_2\{C_5H_4(CH_2)_2O(CH_2)_2C_5H_4\}(C_5H_5)_2Cl_4]$.

Table 2 Crystallographic data for compound **3**

Formula	$C_{18}H_{16}Cl_2Zr$
M	394.428
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	13.519(4)
b/Å	13.671(3)
c/Å	8.557(2)
U/Å^3	1581.5
Z	4
D_c/g cm^{-3}	1.640
F(000)	776
μ(Mo-Kα)/cm^{-1}	10.14
λ/Å	0.709 30
Crystal dimensions/mm	0.20 × 0.18 × 0.14
2θ/°	2–50
Total reflections measured	1620
Unique data used [$I \geq 3\sigma(I)$]	1330
R'	0.039
R	0.034
S	1.436

Table 3 Bond distances (Å) for $[Zr\{C_6H_4(CH_2C_5H_4)_2\text{-}1,3\}Cl_2]$ **3** with estimated standard deviations (e.s.d.s) in parentheses*

Zr–Cl(1)	2.446(2)	C(13)–C(14)	1.40(1)
Zr–Cl(2)	2.431(2)	C(14)–C(15)	1.43(2)
Zr–C(11)	2.599(8)	C(21)–C(22)	1.41(1)
Zr–C(12)	2.570(6)	C(21)–C(25)	1.40(1)
Zr–C(13)	2.51(1)	C(21)–C(38)	1.56(1)
Zr–C(14)	2.470(9)	C(22)–C(23)	1.42(1)
Zr–C(15)	2.524(9)	C(23)–C(24)	1.47(2)
Zr–C(21)	2.619(9)	C(24)–C(25)	1.44(2)
Zr–C(22)	2.53(1)	C(31)–C(32)	1.38(1)
Zr–C(23)	2.47(2)	C(31)–C(36)	1.39(1)
Zr–C(24)	2.53(2)	C(31)–C(37)	1.53(1)
Zr–C(25)	2.604(8)	C(32)–C(33)	1.35(1)
C(11)–C(12)	1.41(1)	C(33)–C(34)	1.38(1)
C(11)–C(15)	1.41(1)	C(34)–C(35)	1.43(1)
C(11)–C(37)	1.55(1)	C(35)–C(36)	1.43(1)
C(12)–C(13)	1.41(1)	C(35)–C(38)	1.49(1)
Zr–Cp(1)	2.233(9)	Zr–Cp(2)	2.25(2)

* Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings C(11)–C(15) and C(21)–C(25) respectively.

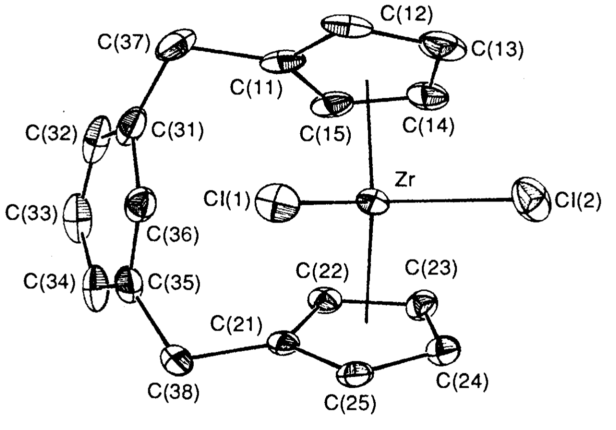

Fig. 2 Crystal structure of $[Zr\{C_6H_4(CH_2C_5H_4)_2\text{-}1,3\}Cl_2]$ **3**

The mass spectra of complexes **1**–**6** showed the molecular ion peaks and fragments corresponding to *M* − Cl or/and *M* − 2Cl. For complexes **4**–**6**, fragments (*m*/*z* 73) attributed to $SiMe_3$ were prominent.

Table 4 Bond angles (°) for $[Zr\{C_6H_4(CH_2C_5H_4)_2\text{-}1,3\}Cl_2]$ **3** with e.s.d.s in parentheses

Cl(1)–Zr–Cl(2)	89.55(8)	C(13)–Zr–C(21)	149.1(3)	C(11)–Zr–C(14)	53.1(3)	C(21)–Zr–C(23)	53.4(3)
Cl(1)–Zr–C(11)	89.7(2)	C(13)–Zr–C(22)	119.3(3)	C(11)–Zr–C(15)	31.7(3)	C(21)–Zr–C(24)	53.2(3)
Cl(1)–Zr–C(12)	83.9(2)	C(13)–Zr–C(23)	109.7(3)	C(25)–C(21)–C(38)	124.9(8)	C(21)–Zr–C(25)	31.3(3)
Cl(1)–Zr–C(13)	110.9(2)	C(13)–Zr–C(24)	129.8(3)	C(21)–C(22)–C(23)	108(2)	C(22)–Zr–C(23)	33.0(3)
Cl(1)–Zr–C(14)	137.7(2)	C(13)–Zr–C(25)	162.1(3)	C(22)–C(23)–C(24)	109(2)	C(22)–Zr–C(24)	55.0(4)
Cl(1)–Zr–C(15)	119.8(2)	C(14)–Zr–C(15)	33.1(2)	C(23)–C(24)–C(25)	106(1)	C(22)–Zr–C(25)	53.2(3)
Cl(1)–Zr–C(21)	92.4(2)	C(14)–Zr–C(21)	117.0(3)	C(21)–C(25)–C(24)	108.7(9)	C(23)–Zr–C(24)	34.0(4)
Cl(1)–Zr–C(22)	123.2(2)	C(14)–Zr–C(22)	86.5(3)	C(32)–C(31)–C(36)	120.9(9)	C(23)–Zr–C(25)	54.3(3)
Cl(1)–Zr–C(23)	138.8(2)	C(14)–Zr–C(23)	82.8(4)	C(11)–Zr–C(21)	110.0(3)	C(24)–Zr–C(25)	32.4(4)
Cl(1)–Zr–C(24)	109.2(3)	C(14)–Zr–C(24)	112.7(4)	C(11)–Zr–C(22)	99.8(3)	C(12)–C(11)–C(15)	109.7(7)
Cl(1)–Zr–C(25)	84.6(2)	C(32)–C(31)–C(37)	126.2(9)	C(11)–Zr–C(23)	121.0(3)	C(12)–C(11)–C(37)	123.6(7)
Cl(2)–Zr–C(11)	124.6(2)	C(36)–C(31)–C(37)	111.9(8)	C(11)–Zr–C(24)	153.9(3)	C(15)–C(11)–C(37)	126.7(7)
Cl(2)–Zr–C(12)	93.3(2)	C(31)–C(32)–C(33)	119(2)	C(11)–Zr–C(25)	139.9(3)	C(11)–C(12)–C(13)	106.8(7)
Cl(2)–Zr–C(13)	76.4(2)	C(32)–C(33)–C(34)	122(1)	C(12)–Zr–C(13)	32.3(3)	C(12)–C(13)–C(14)	108.6(7)
Cl(2)–Zr–C(14)	96.0(3)	C(33)–C(34)–C(35)	120.8(9)	C(12)–Zr–C(14)	53.9(3)	C(13)–C(14)–C(15)	108.2(8)
Cl(2)–Zr–C(15)	128.1(2)	C(34)–C(35)–C(36)	115.1(9)	C(12)–Zr–C(15)	53.6(3)	C(11)–C(15)–C(14)	106.7(8)
Cl(2)–Zr–C(21)	125.4(2)	C(14)–Zr–C(25)	136.2(4)	C(12)–Zr–C(21)	141.1(3)	C(22)–C(21)–C(25)	109.6(9)
Cl(2)–Zr–C(22)	125.8(2)	C(15)–Zr–C(21)	97.1(3)	C(12)–Zr–C(22)	128.5(3)	C(22)–C(21)–C(38)	125(1)
Cl(2)–Zr–C(23)	93.4(3)	C(15)–Zr–C(22)	75.1(3)	C(12)–Zr–C(23)	136.8(3)	C(34)–C(35)–C(38)	130(1)
Cl(2)–Zr–C(24)	74.9(3)	C(15)–Zr–C(23)	89.8(3)	C(12)–Zr–C(24)	161.9(3)	C(36)–C(35)–C(38)	114.5(9)
Cl(2)–Zr–C(25)	95.1(3)	C(15)–Zr–C(24)	123.7(3)	C(12)–Zr–C(25)	165.6(3)	C(31)–C(36)–C(35)	121.1(8)
C(11)–Zr–C(12)	31.7(3)	C(15)–Zr–C(25)	126.9(3)	C(13)–Zr–C(14)	32.7(4)	C(11)–C(37)–C(31)	106.6(7)
C(11)–Zr–C(13)	52.6(2)	C(21)–Zr–C(22)	31.8(3)	C(13)–Zr–C(15)	54.1(3)	C(21)–C(38)–C(35)	108.1(7)

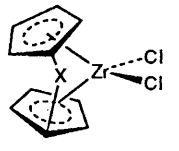

Fig. 3

Crystal and Molecular Structure.—The crystal structure of dichloro[*m*-phenylenedimethylenebis(η^5-cyclopentadienyl)]-zirconium **3** was determined by means of X-ray diffraction. The crystallographic data are listed in Table 2, individual interatomic distances and angles are collected in Tables 3 and 4. Fig. 2 shows a general view of the structure and also contains the numbering scheme used throughout the following discussion.

The co-ordination geometry about the zirconium is the familiar distorted tetrahedron (the four ligands being two cyclopentadienyl rings and two halogen atoms) found for zirconocene derivatives of this type.[30] The C–C distances within the two cyclopentadienyl rings range from 1.40(1) to 1.47(2) Å. The bond angles within the cyclopentadienyl rings range from 106° at the proximal or distal carbons to 109° at the bridgehead carbons. The maximum deviation of the cyclopentadienyl carbons from their least-squares planes is ± 0.016 A.

The Zr–Cl distances, 2.44 Å (av.), are similar to those observed in similar structures (see Table 5). However, the Zr–Cp distances, 2.24 Å (av.), and the average Zr–C(Cp) distance of 2.54 Å, are longer than in the other compounds in Table 5. The most significant difference is however the very small Cl–Zr–Cl angle of 89.55(8)°. These effects are caused by the longer, five-atom bridge in **3**. The existence of the rigid, five-atom bridge causes the distance between the two bridgehead atoms, C(11) and C(21), to be long, and so enlarges the Zr–C(Cp) distances. The distances between Zr and the bridgehead atoms, Zr–C(11) 2.599(8), Zr–C(21), 2.619(9) Å, are much longer than typical values for Zr–C. The long, rigid bridge also leads to an unsymmetrically distorted metallocene geometry in order to accommodate the large separation between the bridgehead atoms. As depicted in Fig. 3, the bridge is asymmetrically disposed with respect to the bisector of the Cl–Zr–Cl angle. For 1- and 2-*ansa*-zirconocene complexes, the bridges lie directly opposite to the $ZrCl_2$ moiety in the solid state and so many are C_2-axial symmetric (though some of them are not).[14] However, in the 5-*ansa*-zirconocene compound **3** the bridge lies adjacent to the $ZrCl_2$ moiety (Fig. 2) so leading to a significant interaction and steric crowding about the Zr atom. The Cl–Zr–Cl angle is compelled to contract owing to the presence of the bulky bridge chain while the Cp–Zr–Cp angle is slightly enlarged. The shortest distance between the carbon atoms of the phenyl ring and the zirconium atom at 3.35 Å [Zr $\cdots$ C(36)] precludes any significant Zr–π interactions.

The length of the bridge is also reflected by the angle at which the two mean ring-planes intersect. Brintzinger and co-workers[34] found that in the crystal structures of $[Ti\{C_5H_4(CH_2)_nC_5H_4\}Cl_2]$ (n = 1–3) the dihedral angles between the two cyclopentadienyl planes were reduced when the number of atoms in the bridge increased. For *ansa*-zirconocene complexes, a similar situation is found as shown in Table 5 for $[Zr\{C_5H_4(SiMe_2)C_5H_4\}Cl_2]$ and $[Zr\{C_5H_4(CH_2)_3C_5H_4\}Cl_2]$. In **3** this angle is 54.1(3)°, almost equal to that found in $[Zr(C_5H_4Me)_2Cl_2]$. This suggests that the position adopted by the bridge causes no (or very little) tilting of the rings away from the position adopted in $[Zr(C_5H_4Me)_2Cl_2]$.

The corresponding data for the phenyl ring are not significantly different from those in other compounds. To minimize the interaction between $ZrCl_2$ and the bridge chain, the phenyl ring lies *trans* the $ZrCl_2$ bisector.

Thus, through determination of the X-ray crystal structure of **3**, together with spectral studies, we have found that these 5-*ansa* zirconocene complexes are different from 1- or 2-*ansa*-zirconene complexes in two main ways: (1) a hetero atom in the middle of the five-atom bridge can co-ordinate to the metal atom; (2) the long bridge chain in **3** is disposed asymmetrically adjacent to the $ZrCl_2$ moiety in the molecule and so causes steric crowding. The special steric and electronic properties caused by these differences may have significant effects on catalysis. The study of olefin polymerization with these compounds as catalyst precursors is on hand.

Experimental

All manipulations were performed under pre-purified argon by use of Schlenk techniques or a glove-box. All hydrocarbon and ether solvents were refluxed and distilled over finely divided $LiAlH_4$ or blue sodium–benzophenone under argon immediately before use. Dichloromethane was distilled from P_2O_5. $[^2H_8]$Tetrahydrofuran was dried over Na/K alloy and degassed and transferred under high vacuum. Deuteriochloroform was dried over Linde 4A molecular sieves and degassed and transferred under high vacuum. Zirconium tetrachloride was

Table 5 Structural data (lengths Å, angles °) for complexes $[ZrLCl_2]$

L	Zr–Cl (av.)	Zr–Cp[a] (av.)	Zr–C(Cp)[a] (av.)	Cl–Zr–Cl	Cp–Zr–Cp	Cp–Cp[b]	Ref.
$C_5H_4(SiMe_2)C_5H_4$	2.435(1)	2.197	2.50	97.98	125.4	56.8	31
$(C_5H_4Me)_2$	2.443(1) 2.442(1)	2.206		95.10	128.9	54.2	32
$C_5H_4(CH_2)_3C_5H_4$	2.431(2) 2.451(2)	2.192	2.49	96.92	129.5	50.2	33
$C_6H_4(CH_2C_5H_4)_2$-1,3	2.446(2) 2.431(2)	2.24	2.54	89.55	130.3	54.11	This work

[a] C(Cp) refers to ring carbon atoms of the cyclopentadienyl rings. [b] Cp–Cp refers to the dihedral angles between the cyclopentadienyl rings.

sublimed before use. Sodium cyclopentadienide was prepared by treating the freshly distilled monomer with sodium sand or NaH in tetrahydrofuran. Sodium trimethylsilylcyclopentadienide,[35] $MeN(CH_2CH_2Cl)_2$[36] and $C_5H_3N(CH_2Cl)_2$-2,6[37] were prepared according to the literature methods.

Infrared spectra were recorded on a Perkin Elmer 983 spectrometer in Nujol and Fluorolube mulls and were examined between disc-shaped CsI and NaCl crystals; the mulls were prepared in an argon-filled glove-box. Mass spectra were obtained with a Finnigan 4201 spectrometer. Proton NMR spectra were measured on a Varian XL-200 (200 MHz) or a FX-90Q (90 MHz) spectrometer, referenced to external $SiMe_4$ or internal $[^2H_8]$thf. X-Ray photoelectron spectra were recorded on a Perkin Elmer φ550 spectrometer equipped with a Mg-Kα X-ray source.

Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Preparation of Disodium Salts.—$Na(C_5H_5)$ or $Na(C_5H_4SiMe_3)$ (19 mmol) was added to an organohalide (10 mmol) in thf (20 cm^3) at 0 °C and left for 1 h. The reaction mixture was then stirred for 5 h at room temperature and the resultant NaCl was filtered off. The solution was transferred to a suspension of NaH (30 mmol) in thf (20 cm^3) and stirred overnight at room temperature. After centrifugation, an orange solution of the disodium salt was obtained in nearly quantitative yield. NMR spectra were obtained in $[^2H_8]$thf.

$MeN(CH_2CH_2C_5H_4Na)_2$ **I**. δ_H 5.40 (8 H, m, C_5H_4), 2.60–2.50 (8 H, m, CH_2CH_2) and 2.12 (3 H, s, CH_3). IR: 3055m, 2922s, 2840m, 2768m, 1460m, 1455m, 1374s, 1216m, 1160w, 1096s, 1021s, 933s, 896s, 784vs, 719s, 675m, 630m, 597m and 300s cm^{-1}.

$C_5H_3N(CH_2C_5H_4Na)_2$-2,6 **II**. δ_H 7.53–6.88 (3 H, m, C_5H_3N), 5.51–5.29 (8 H, m, C_5H_4) and 3.95 (4 H, s, CH_2). IR: 3070m, 2916s, 1584m, 1571s, 1450s, 1420w, 1375s, 1153w, 1022m, 994w, 897s, 721s and 674m cm^{-1}.

$C_6H_4(CH_2C_5H_4Na)_2$-1,3 **III**. δ_H 7.18–6.86 (4 H, m, C_6H_4), 5.70–5.44 (8 H, m, C_5H_4) and 3.67 (4 H, s, CH_2).

$MeN[CH_2CH_2C_5H_3(SiMe_3)Na]_2$ **IV**. δ_H 5.78–5.54 (6 H, m, C_5H_3), 2.70–2.50 (8 H, m, CH_2CH_2), 2.14 (3 H, s, CH_3) and 0.19 (18 H, s, $SiMe_3$).

$C_5H_3N[CH_2C_5H_3(SiMe_3)Na]_2$-2,6 **V**. δ_H 7.51–7.03 (3 H, m, C_5H_3N), 5.85–5.46 (6 H, m, C_5H_3), 4.04 (4 H, s, CH_2) and 0.18 (18 H, s, $SiMe_3$).

$C_6H_4[CH_2C_5H_3(SiMe_3)Na]_2$-1,3 **VI**. δ_H 7.25–6.96 (4 H, m, C_6H_4), 5.89–5.63 (6 H, m, C_5H_3), 3.78 (4 H, s, CH_2) and 0.14 (18 H, s, $SiMe_3$).

Preparation of 5-*ansa*-*Zirconocene Dichlorides.*—To a suspension of $ZrCl_4$ (10 mmol) in toluene (20 cm^3), a thf solution of disodium salt (10 mmol) was slowly added over 1 h at 0 °C. The solvent was removed under vacuum. The solid residue was washed with small portions of *n*-hexane and then extracted with CH_2Cl_2. Upon concentrating the extract a pale yellow powder was obtained. Recrystallization from thf–*n*-hexane or CH_2Cl_2–*n*-hexane yielded a white solid.

$[Zr\{MeN(CH_2CH_2C_5H_4)_2\}Cl_2]$ **1**. Yield 2.3 g, 61% (Found: C, 48.5; H, 5.2; Cl, 19.0; Zr, 23.9. $C_{15}H_{19}Cl_2NZr$ requires C, 48.0; H, 5.1; Cl, 18.9; Zr, 24.3%). IR: 3079m, 2935m, 2847m, 1492m, 1450s, 1390w, 1337m, 1281m, 1206m, 1071s, 1034s, 1014m, 807vs, 739s, 465m, 389m and 331s cm^{-1}; $\delta_H([^2H_8]thf)$ 6.57–6.34 (8 H, m, C_5H_4), 3.03 (4 H, t, CH_2), 2.81–2.78 (4 H, m, CH_2) and 2.57 (3 H, s, CH_3). Mass spectrum: *m*/*z* 373 (M^+), 338 (*M* − Cl).

Table 6 Final positional parameters for $[Zr\{C_6H_4(CH_2C_5H_4)_2$-1,3$\}Cl_2]$ **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Zr	0.316 83(5)	0.211 11(5)	0.009 9(1)
Cl(1)	0.167 5(2)	0.161 7(2)	−0.130 7(3)
Cl(2)	0.226 5(2)	0.200 1(2)	0.254 8(3)
C(11)	0.412 6(6)	0.067 2(6)	−0.118(1)
C(12)	0.356 5(6)	0.027 3(5)	0.005(1)
C(13)	0.394 8(7)	0.067 3(6)	0.145(1)
C(14)	0.470 1(6)	0.133 7(7)	0.107(1)
C(15)	0.481 1(6)	0.134 5(6)	−0.059(1)
C(21)	0.336 7(7)	0.369 6(6)	−0.159(1)
C(22)	0.425 0(7)	0.352 7(6)	−0.075(1)
C(23)	0.403 2(7)	0.363 2(6)	0.087(1)
C(24)	0.297 6(9)	0.386 3(6)	0.102(1)
C(25)	0.259 1(8)	0.388 2(6)	−0.054(1)
C(31)	0.430 9(7)	0.125 4(7)	−0.390(1)
C(32)	0.521 4(7)	0.138 4(9)	−0.462(1)
C(33)	0.545 6(7)	0.228 5(9)	−0.515(1)
C(34)	0.487 4(7)	0.309 9(7)	−0.487(1)
C(35)	0.393 7(8)	0.300 6(7)	−0.411(1)
C(36)	0.364 9(7)	0.202 4(7)	−0.375(1)
C(37)	0.400 0(8)	0.036 9(7)	−0.291(1)
C(38)	0.329(1)	0.377 6(7)	−0.341(1)
Cp(1)	0.423 0	0.086 0	0.016 0
Cp(2)	0.344 3	0.372 0	−0.020 0

$[Zr\{C_5H_3N(CH_2C_5H_4)_2$-2,6$\}Cl_2]$ **2**. Yield 2.7 g, 65% (Found: C, 52.2; H, 4.1; Cl, 17.9; Zr, 23.0. $C_{17}H_{15}Cl_2NZr$ requires C, 51.6; H, 3.8; Cl, 17.9; Zr, 23.1%). IR: 3079m, 2940m, 1607s, 1569m, 1492m, 1460s, 1424m, 1375s, 1039s, 826vs, 721m, 478s and 400m cm^{-1}. $\delta_H([^2H_8]thf)$ 7.78–7.13 (3 H, m, C_5H_3N), 6.60–6.42 (8 H, m, C_5H_4) and 4.41–4.22 (4 H, dd, CH_2). Mass spectrum: *m*/*z* 393 (M^+), 358 (*M* − Cl).

$[Zr\{C_6H_4(CH_2C_5H_4)_2$-1,3$\}Cl_2]$ **3**. Yield 2.1 g, 53% (Found: C, 55.2; H, 4.4; Cl, 17.9; Zr, 22.7. $C_{18}H_{16}Cl_2Zr$ requires C, 54.8; H, 4.1; Cl, 18.0; Zr, 23.1%). IR: 3094m, 2916m, 2860w, 1602vs, 1584s, 1484s, 1427s, 1303w, 1152w, 1086m, 1049m, 934m, 813vs, 720s, 430m and 322m cm^{-1}. $\delta_H(CDCl_3)$ 7.20–7.03 (4 H, m, C_6H_4), 6.24–5.95 (8 H, m, C_5H_4) and 3.99–3.73 (4 H, m, CH_2). Mass spectrum: *m*/*z* 392 (M^+), 357 (*M* − Cl).

$[Zr\{MeN[CH_2CH_2C_5H_3(SiMe_3)]_2\}Cl_2]$ **4**. Yield 3.0 g, 57% (Found: C, 49.2; H, 6.7; Cl, 14.3; N, 2.5; Zr, 17.3. $C_{21}H_{35}Cl_2NSi_2Zr$ requires C, 48.5; H, 6.8; Cl, 13.6; N, 2.7; Zr, 17.55%). IR: 3070m, 2949s, 2910m, 1466m, 1424s, 1375m, 1310m, 1247s, 1174m, 1105s, 1043m, 1020w, 920s, 839vs, 756s, 634m, 469m, 419m and 286m cm^{-1}. $\delta_H(CDCl_3)$ 6.60–6.22 (6 H, m, C_5H_3), 3.24–2.80 (8 H, m, CH_2CH_2), 2.69 (3 H, s, CH_3N) and 0.20 (18 H, m, $SiMe_3$). Mass spectrum: *m*/*z* 517 (M^+), 447 (*M* − 2Cl), 444 (*M* − $SiMe_3$) and 73 ($SiMe_3$).

$[Zr\{C_5H_3N[CH_2C_5H_3(SiMe_3)]_2$-2,6$\}Cl_2]$ **5**. Yield 3.2 g, 60% (Found: C, 51.7; H, 5.9; Cl, 13.6; N, 2.6; Zr, 17.0.

$C_{23}H_{31}Cl_2NSi_2Zr$ requires C, 51.2; H, 5.8; Cl, 13.1; N, 2.6; Zr, 16.9%). IR: 3079m, 2946s, 1628m, 1586m, 1571m, 1451m, 1414s, 1247vs, 1069s, 1045s, 1008s, 840vs, 757vs, 630m, 419m and 297m cm^{-1}. δ_H($CDCl_3$) 7.56–7.10 (3 H, m, C_5H_3N), 6.58–6.30 (6 H, m, C_5H_3), 4.34–4.04 (4 H, m, CH_2) and 0.18 (18 H, m, $SiMe_3$). Mass spectrum: m/z 537 (M^+), 502 (M − Cl) and 73 ($SiMe_3$).

[$Zr\{C_6H_4[CH_2C_5H_3(SiMe_3)]_2$-1,3$\}Cl_2$] **6**. Yield 2.6 g, 49% (Found: C, 53.8; H, 5.75; Cl, 13.3; Zr, 17.4. $C_{24}H_{32}Cl_2Si_2Zr$ requires C, 53.5; H, 6.0; Cl, 13.2; Zr, 16.9%). IR: 3060w, 2949m, 2910m, 1602vs, 1586m, 1485m, 1437m, 1370m, 1248vs, 1100s, 1045s, 963m, 839vs, 756s, 421w, 364m and 331s cm^{-1}. δ_H($CDCl_3$) 7.20–7.00 (4 H, m, C_6H_4), 6.59–6.17 (6 H, m, C_5H_3), 3.92 (4 H, m, CH_2) and 0.24 (18 H, m, $SiMe_3$). Mass spectrum: m/z 536 (M^+), 501 (M − Cl), 466 (M − 2Cl) and 73 ($SiMe_3$).

X-Ray Crystal Structure Determination.—A colourless single crystal was sealed in a thin-walled glass capillary under argon. Intensity data were collected at 20 °C with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. Corrections for Lorentz–polarization and absorption were applied for the reflection data. The structure was solved by the Patterson method and Fourier difference synthesis and unit weights were applied. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least-squares techniques. All calculations were performed on a MICROVAX II computer with SDP[38] and ORTEP[39] programs. Scattering factors were taken from ref. 40. Table 6 lists the final atomic coordinates.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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