

The X-ray crystal structures of the *ansa*-metallocenes, $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ (M = Ti, Zr and Hf)

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Abstract

Group 4 metallocenes and *ansa*-metallocenes are known for their role in the Ziegler–Natta catalysis of olefins and in the catalytic dehydrocoupling of hydrosilanes to form polysilanes. This report describes the crystal structures of three carbon-bridged *ansa*-metallocene dichlorides, $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ (M = Ti (1), Zr (2) and Hf (3)). Comparisons of the structures of the molecules with previously characterized systems is made; in particular, the $\text{Cp}_{\text{centroid}}\text{--M--Cp}_{\text{centroid}}$ angle, the position of the metal relative to the cyclopentadienyl rings and the uniformity of the C–C bond lengths in the Cp rings are discussed. Comparisons between structure and reactivity in the dehydrocoupling of hydrosilanes are described.

Keywords: Titanium; Zirconium; Hafnium; *ansa*-Metallocenes; Dehydrogenative coupling

1. Introduction

A Ziegler–Natta catalyst is made from the combination of a transition metal compound (Groups 4 to 8) and an organometallic derived from groups 1, 2 or 13 with the best known probably derived from TiCl_4 or TiCl_3 with R_3Al . The metallocenes of Group 4, Cp_2MCl_2 , belong to a class of bent-sandwiches and have been utilized as precursors to homogeneous catalysts for polymerization of olefins [1]. Attempts to relate structural characteristics to reactivity continue as the understanding of the catalytic process increases [2–5].

ansa-Metallocenes are “sandwich” molecules where the two rings are connected by a chelate bridge. The introduction of the chelate bridge leads to a more fixed ligand geometry about the metal center. *ansa*-Zirconocene derivatives can produce both isotactic [6] and syndiotactic polypropylenes [7] and the bridge conformation can influence the stereoselectivity of the catalyst [3].

A less common use for the Group 4 metallocenes is as catalysts for the dehydrocoupling of hydrosilanes to form polysilanes [8]. The first generation catalyst sys-

tems were derived from Cp_2MR_2 (Cp = $\eta^5\text{-C}_5\text{H}_5$; M = Ti, Zr; R = Me, Ph) [8b], $\text{CpCp}^*\text{M}[\text{Si}(\text{SiMe}_3)_3]\text{R}$ (Cp* = $\eta^5\text{-C}_5\text{Me}_5$; M = Zr, Hf; R = H, Cl Me) [8a,e], and $\text{Cp}_2\text{MCl}_2/\text{nBuLi}$ (M = Ti, Zr, Hf) [8c,f], which have been utilized to convert PhSiH_3 to $\text{H}(\text{PhSiH})_x\text{H}$ with average molecular weights ranging from 1000 to about 5000 and in most cases also produce undesired cyclopolysilane by-products. The basic steps leading to silicon–silicon bond formation have been shown to be consistent with σ -bond metathesis steps [8a,e]. Structural modifications have led to a marginal improvement in the average molecular weights of the $\text{H}(\text{PhSiH})_x\text{H}$ produced to about 14 000 [9]. When comparable parent and *ansa*-metallocenes are compared as precursor catalysts for the polymerization of PhSiH_3 , the *ansa*-metallocenes produce lower molecular weight polymers [9,10]. Unlike the studies of the Ziegler–Natta catalysts where structure–activity studies are at a more advanced level, the effect of structural modifications on the σ -bond metathesis steps leading to silicon–silicon bond formation is less well understood and less obvious but may involve a more severe steric requirement for the bond formation step than appears to be the case for olefin polymerization. Detailed structural information concerning the catalyst precursors may provide information about the metal center that will guide the selection of modifications that will lead to an increase in the

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molecular weight of the polysilane and an elimination of cyclic formation, both of which are desirable for materials applications.

In this report, the X-ray crystal structures of three Group 4 *ansa*-metallocene dichlorides, $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ (M = Ti (**1**), Zr (**2**) and Hf (**3**)), are described and a comparison of the structural parameters to other crystallographically characterized Group 4 systems is reported.

2. Experimental details

2.1. General

All operations were conducted under an N_2 atmosphere. Solvents were dried by standard techniques. Compounds **1** and **2** were prepared by literature methods [11] and **3** was prepared in a similar fashion [10]. Single crystals of **1**, **2** and **3** were obtained by slow evaporation of a methylene chloride solution at room temperature.

2.2. Data collection

A single crystal of the appropriate dimensions was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed using a Siemens R3 automated single crystal X-ray diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(5) K. Autoindex-

ing of 10 centered reflections from the rotation photograph indicated a monoclinic lattice. Axial photographs were taken to confirm the Laue symmetry and cell lengths. Final cell constants and the orientation matrix for data collection were calculated by least squares refinement of the setting angles: 15 reflections ($50^\circ < 2\theta < 55^\circ$) for **1**; 20 reflections ($15^\circ < 2\theta < 30^\circ$) for **2**; 15 reflections ($25^\circ < 2\theta < 53^\circ$) for **3**. Intensity data were collected using θ - 2θ scans with variable scan speed. Four representative reflections for **1** and three representative reflections for **2** and **3**, which were measured every 50 reflections, showed less than 4% variation during data collection. Crystal data and intensity data collection parameters are listed in Table 1.

2.3. Structure solution and refinement

Data reduction and structure solution and refinement were carried out using the SHELXTL-PLUS (VMS) software package (G.M. Sheldrick, Siemens Analytical X-Ray Division, Madison, WI, 1991). Empirical absorption correction was applied to the data using ψ -scan (XEMP, SHELXTL-PLUS) for **2**, and using equivalent reflections (SHELXA, G.M. Sheldrick, 1993, Universität Göttingen, Germany) for **3**. No absorption correction was applied to the data for **1**. The structures were solved by the Patterson method and refined successfully in the monoclinic space group $P2_1/m$. Full matrix least squares refinement was carried out by minimizing $\sum w(F_o - F_c)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were

Table 1
Summary of the crystal structure data for $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ M = Ti, Zr, Hf

	M = Ti(1)	M = Zr(2)	M = Hf(3)
Formula weight	289.0	332.4	419.6
Cryst. size, mm	0.4 × 0.3 × 0.3	0.55 × 0.4 × 0.4	0.5 × 0.3 × 0.05
Cryst. system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$
a (Å)	7.122(2)	7.145(2)	7.104(2)
b (Å)	8.629(2)	8.853(2)	8.875(2)
c (Å)	9.973(2)	10.158(2)	10.145(3)
β (deg)	90.47(2)	90.56(2)	90.54(2)
Vol (Å ³)	612.89(13)	642.50(12)	639.6(3)
Z	2	2	2
d_{calcd} (g cm ⁻³)	1.566	1.718	2.179
Temp. (°C)	25	25	25
Radiation	graphite monochromator, Mo K α ($\lambda = 0.71073 \text{ \AA}$)		
2 θ range (deg)	3.0 to 60.0	3.0 to 60.0	3.0 to 65.0
Scan type	2 θ - θ	2 θ - θ	2 θ - θ
Index ranges for data collection	-10 < h < 10 0 < k < 12 -6 < l < 14	-10 < h < 10 0 < k < 12 -14 < l < 12	-10 < h < 10 -12 < k < 13 -14 < l < 15
No. of refls colled	2202	4040	6609
No. of indep. refls	1910 ($R_{\text{int}} = 1.42\%$)	2000 ($R_{\text{int}} = 2.06\%$)	2459 ($R_{\text{int}} = 6.96\%$)
R	3.25%	2.69%	3.39%
wR	3.76%	3.73%	4.82%
gof	1.02	1.22	1.03

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ (M = Ti (1), Zr (2), Hf (3))

	M = Ti (1)				M = Zr (2)				M = Hf (3)			
	x	y	z	$U(\text{eq})^a$	x	y	z	$U(\text{eq})$	x	y	z	$U(\text{eq})$
M	1870(1)	2500	3293(1)	23(1)	8198(1)	2500	3326(1)	27(1)	1817(1)	2500	1690(1)	26(1)
Cl(1)	-1357(1)	2500	3766(1)	40(1)	11544(1)	2500	3817(1)	48(1)	-1502(1)	2500	1162(1)	45(1)
Cl(2)	2992(1)	2500	5494(1)	41(1)	6959(1)	2500	5541(1)	49(1)	3038(2)	2500	-513(1)	46(1)
C(1)	3103(2)	1181(2)	1464(1)	28(1)	6887(2)	1186(2)	1411(2)	32(1)	3125(4)	1187(3)	3598(3)	29(1)
C(2)	4130(2)	686(2)	2616(1)	31(1)	8749(3)	640(2)	1571(2)	39(1)	4143(4)	661(3)	2485(3)	34(1)
C(3)	2922(2)	-202(2)	3436(2)	38(1)	8841(3)	-255(2)	2720(2)	45(1)	2928(5)	-220(3)	1697(4)	41(1)
C(4)	1144(2)	-216(2)	2838(2)	39(1)	7081(3)	-251(2)	3299(2)	45(1)	1156(5)	-229(3)	2275(4)	43(1)
C(5)	1233(2)	657(2)	1634(1)	34(1)	5884(3)	648(2)	2518(2)	37(1)	1255(5)	655(3)	3434(3)	36(1)
C(6)	3698(3)	2500	546(2)	31(1)	6284(4)	2500	541(2)	34(1)	3733(6)	2500	4478(4)	33(1)
C(7)	2626(4)	2500	-782(2)	49(1)	7310(6)	2500	-784(3)	56(1)	5827(8)	2500	4745(5)	47(1)
C(8)	5822(4)	2500	295(3)	43(1)	4173(5)	2500	276(4)	50(1)	2690(11)	2500	5796(5)	51(2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

located from the difference Fourier synthesis and were refined isotropically. The final residual values and structure refinement parameters are listed in Table 1. The atomic coordinates for the non-hydrogen atoms and selected bond distances and angles are listed in Tables 2 and 3 respectively. A projection view of the molecule with non-hydrogen atoms represented by 50% probability ellipsoids for **1** is presented in Fig. 1 (the structures of compounds **1**, **2** and **3** are isomorphous).

A complete list of bond distances and bond angles, positional and isotropic displacement coefficients for the hydrogen atoms and a list of the anisotropic displacement coefficients for the non-hydrogen atoms and calculated and observed structure factors are available from N.P.R. and will be deposited in the Cambridge Crystallographic Data Center.

3. Results and discussion

3.1. Molecular structures of **1**, **2** and **3**

The incorporation of a bridging unit into the metallocene dichloride has geometrical consequences that depend on the number of atoms in the bridge. For the purpose of discussion only systems that contained a bridging unit and no other ring substituents were chosen for comparison. Table 4 lists three pertinent structural parameters for the parent $(\text{C}_5\text{H}_5)_2\text{MCl}_2$ and the two one-atom bridge systems for which data are available for all three metals (Ti, Zr and Hf). Table 4 demonstrates that the major effect of the presence of a bridging atom is a change in the $\text{Cp}_{(\text{centroid})}\text{-M-Cp}_{(\text{centroid})}$ angle. A bridge containing a single silicon center reduces this angle by approximately $3\text{--}4^\circ$ for M = Ti, Zr but has only a marginal effect when M = Hf. However, a one carbon atom bridge reduces the angle by about $10\text{--}13^\circ$. Data for all three metals are not available for two or three atom bridges, at least for these simpler

systems, but the $\text{Cp}'\text{-M-Cp}'$ angle in $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{-TiCl}_2$ is 128.4° [17]; thus the one atom silicon bridge and the ethano bridge systems appear to alter the $\text{Cp}'\text{-M-Cp}'$ angle in a similar manner. The $\text{M-Cp}_{(\text{centroid})}$ and $\text{M-Cl}_{(\text{av})}$ distances do not vary significantly from the parent to the *ansa*-metallocenes listed in Table 4.

Table 3

Selected bond distances (\AA) and angles (deg) for $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ M = Ti, Zr, Hf

	M = Ti (1)	M = Zr (2)	M = Hf (3)
A. Interatomic distances			
M-C1(1)	2.350(1)	2.438(1)	2.413(1)
M-C1(2)	2.330(1)	2.426(1)	2.404(1)
M-C1	2.328(1)	2.445(1)	2.436(3)
M-C2	2.348(1)	2.462(2)	2.454(3)
M-C3	2.452(2)	2.558(2)	2.540(3)
M-C4	2.442(2)	2.563(2)	2.538(3)
M-C5	2.336(2)	2.463(2)	2.447(3)
M-Cp ^a	2.056	2.192	2.174
C6-C7	1.527(3)	1.539(4)	1.510(7)
C6-C8	1.535(3)	1.529(4)	1.535(7)
C6-C1	1.523(2)	1.521(2)	1.528(4)
C1-C2	1.422(2)	1.423(3)	1.425(4)
C2-C3	1.416(2)	1.411(3)	1.408(5)
C3-C4	1.396(2)	1.393(3)	1.394(5)
C4-C5	1.419(2)	1.408(3)	1.415(5)
C5-C1	1.418(2)	1.422(3)	1.418(4)
B. Bond angles			
C1-M-C1	98.0(1)	100.1(1)	98.9(1)
Cp'-M-Cp'	121.5	116.6	117.1
C1-C6-C1 ^{a,b}	96.7(1)	99.8(2)	99.4(3)
C7-C6-C8	110.1(2)	108.9(3)	109.1(4)
C1-C6-C7	112.6(1)	111.9(2)	112.2(2)
C2-C1-C6	124.5(1)	125.8(2)	124.7(3)
C5-C1-C6	125.2(1)	125.0(2)	125.6(3)
C2-C1-C5	106.5(1)	105.9(2)	106.3(2)
C1-C2-C3	108.6(1)	108.7(2)	108.6(3)
C2-C3-C4	108.2(1)	108.3(2)	108.4(3)
C3-C4-C5	108.0(1)	108.0(2)	108.0(3)
C1-C5-C4	108.6(1)	109.1(2)	108.7(3)

^a Cp' denotes the centroid of the cyclopentadiene ring.^b Symmetry operation for generating equivalent atom = $x\ 0.5 - y\ z$.

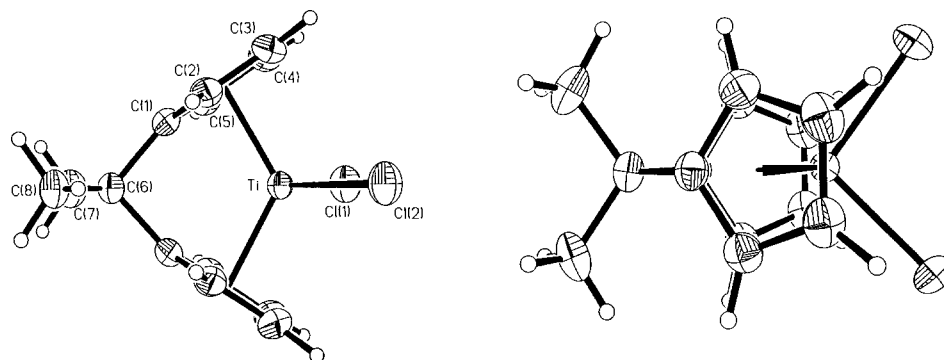


Fig. 1. Two perpendicular views of the molecular structure of **1** showing atom numbering schemes. Non-hydrogen atoms represented by 50% probability ellipsoids.

Fig. 2 shows the bond distances associated with the Cp rings in $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$, $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. Petersen has attributed the relative shortness of the C3–C4 bond in $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ to a small but significant π -bonding contribution from an

η^3 -allyl or η^2 -olefin resonance structure [13]. This bond shortening is observed in the other structures shown in Fig. 2. The difference between the shortest C–C Cp bond and the average of the four remaining C–C bonds decreases in the order $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2 > \text{Me}_2\text{C}$ -

Table 4
Geometric parameters around the metal center for various metallocene dichlorides

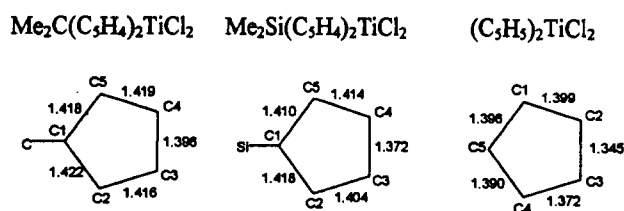
Compound	Cp'–M–Cp' (°)	M–Cl ^a (Å)	M–Cp ^a (Å)	Ref.
$(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ ^b	131.0	2.364(1)	2.059	12
$\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$	128.7	2.356(1)	2.075	13
$\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$	121.5	2.340(10)	2.056	This work
$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ ^b	129.3	2.447(1)	2.203	14
$\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$	125.4	2.435(1)	2.197	13
$\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$	116.6	2.432(6)	2.192	This work
$(\text{C}_5\text{H}_5)_2\text{HfCl}_2$ ^b	127.1	2.423(2)	2.18	15
$\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{HfCl}_2$	126.8	2.424(2)	2.191 ^c	16
$\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{HfCl}_2$	117.1	2.409(5)	2.174	This work

^a Average distance.

^b Average data for both molecules in the asymmetric unit.

^c Calculated from *xyz* coordinates in indicated reference.

Bond distances (Å) in the Cp rings[†] of $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ (**1**) and $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ (**8**), $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (**4**).



[†] Bond lengths for one Cp ring only. In Compounds **1** and **8** the metal lies between C3 and C4, while in compound **4** the metal lies between C2 and C3. For compound **4** only one of the 4 unique Cp rings is shown (see text).

Fig. 2. Bond distances (Å) in the Cp rings of $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ (**1**) and $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ (**8**), $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ (**4**). $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$, $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$, $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$.

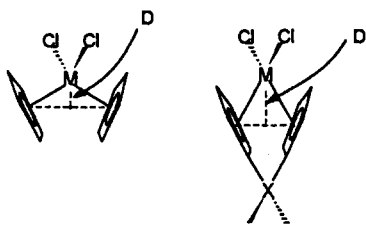


Fig. 3. Position of metal in metallocene and *ansa*-metallocene dichlorides.

(C_5H_4)₂TiCl₂ (0.040 and 0.023 Å, respectively). In the parent system, (C_5H_5)₂TiCl₂, there are four independent Cp-rings with a difference between the shortest and the average of the four remaining C–C bonds that ranges from 0.014 to 0.042.

Another consequence of the bridging unit is the change in position of the metal relative to an imaginary line connecting the Cp rings (Fig. 3). The perpendicular distance of the metal from this line connecting the centroids of the two Cp rings is represented by *D* and the values calculated for a variety of *ansa*-metallocene dichlorides that contain no additional ring substituents are listed in Table 5. The percentage change of position of the metal in going from the parent metallocene to the *ansa*-metallocene (Δ in Table 5) may be a useful parameter for demonstrating how far the metal protrudes from the umbrella created by the Cp rings. The larger the distance *D* the more vulnerable the metal may be to reaction chemistry.

The largest change of position of the metal is observed when the Cp rings are connected by a single carbon bridge (16–23% change dependent on the metal). A single silicon bridge results in approximately the same structural effect as a two carbon bridge as indicated earlier in the discussion of the Cp'–M–Cp' angle. The smallest change in the relative position of the metal occurs in the three atom bridge systems **16**, **18** and **19** where the Cp'–M–Cp' angles of 129.6, 132.5 and 130.2°

respectively differ little from the parent metallocene. With compound **17** the % change in position is –4, indicating that the metal is actually pulled slightly back under the Cp ring (the Cp'–M–Cp' angle for this complex is 129.5°, 2.4° larger than the parent hafnocene dichloride). The difference in metal position between the single carbon bridged Me₂C(C₅H₄)₂HfCl₂ (**3**) and the *n*-propyl bridged (H₂C)₃(C₅H₄)₂HfCl₂ (**17**) is shown diagrammatically in Fig. 4.

3.2. Comments on structure / activity of *ansa*-metallocenes as dehydrocoupling catalysts

The reaction of Cp₂ZrCl₂ with *n*BuLi has been shown to generate Cp₂Zr(CH₂=CH₂) [23] and we have proposed that H₂SiPhR reacts with this olefin complex to produce Cp₂Zr(H)SiPhRH which initiates the catalytic cycle [24]. It is probable that the reactions of Cp₂HfCl₂/*n*BuLi resemble those of zirconium but it is not yet clear that the titanium system follows the same reaction pathway. The most likely mechanism for silicon–silicon bond formation involves σ -bond metathesis [8a,e]. That considerable steric hindrance in the bond forming step must exist is indicated in the rate and relative conditions required for primary silanes, which produce polymers at room temperature, and secondary silanes which produce only short chains and usually at useful rates only above 80 °C.

We have carried out a comparison of compounds **4** with **1** and **8**, **5** with **2** and **9** as well as **6** with **3** and **10** (parent metallocene dichlorides compared to the one atom bridge *ansa*-metallocene dichlorides) as catalyst precursors for the dehydrogenative coupling of hydrosilanes. The rate of dehydrocoupling is slower with **1**, **2**, **3**, **8**, **9** and **10** compared to the parent metallocenes and the molecular weights of H(PhSiH)_{*x*}H produced from the *ansa*-systems, Me₂El(C₅H₄)₂MCl₂/*n*BuLi, are all lower than those obtained from the parent metallocene combination, Cp₂MCl₂/*n*BuLi. All product mixtures

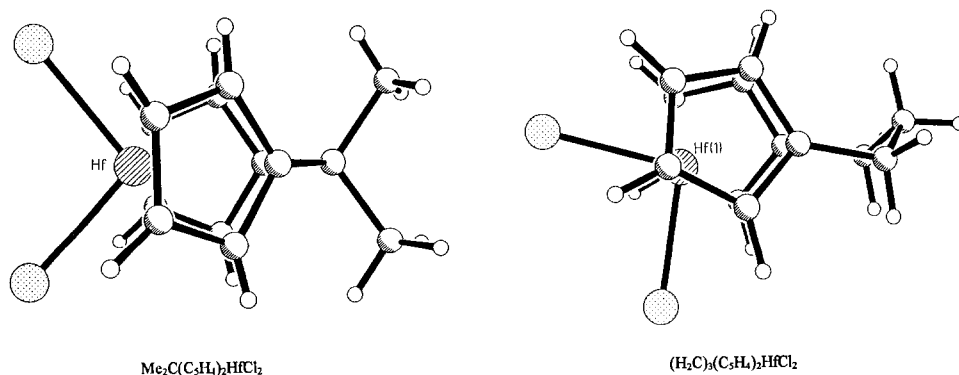








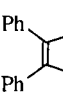

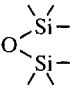
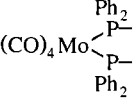
Fig. 4. Ball and stick representations of Me₂C(C₅H₄)₂HfCl₂ and (H₂C)₃(C₅H₄)₂HfCl₂ (Ref. [16]) showing difference in metal position relative to cyclopentadiene rings.

contained cyclic byproducts [10]. In the early stages of the condensation reaction of PhSiH_3 with $\text{Cp}_2\text{HfCl}_2/n\text{BuLi}$ oligomers with Ph_2Si units are formed, which suggests that a minor side reaction that occurs with the hafnium catalyst is disproportionation of the starting primary silane [26]. However, with $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{-HfCl}_2/n\text{BuLi}$, this side reaction is suppressed and the oligomers observed in the early stages of the condensation all had the composition $\text{H}(\text{PhSiH})_3\text{H}$.

The effect of the bridge between the two Cp rings of

Cp_2MCl_2 can be both geometric and electronic. As shown in the structural data reported here for $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{MCl}_2$ the Cp-rings are drawn back from the metal center (Table 5) (lower $\text{Cp}'\text{-M-Cp}'$ angle), thus opening up the coordination site of the metal. This change is also expected to increase the electron deficiency of the metal center [4b]. It was anticipated that opening the coordination site might lead to a decrease in the silicon–silicon bond forming step. However, this was not observed. A possible outcome of the opening of

Table 5
The position of the metal relative to the Cp rings for various *ansa* metallocenes

Bridging unit (X) in $\text{X}(\text{C}_5\text{H}_4)_2\text{MCl}_2$	M	D (Å) ^a	Δ (Å) ^b	% change ^c	Ref.
None	Ti (4)	0.853			12
	Zr (5)	0.933			14
	Hf (6)	0.971			15
	Ti (1)	1.005	0.152	18	this work
	Zr (2)	1.152	0.219	23	this work
	Hf (3)	1.135	0.164	17	this work
<	Ti (7)	0.986	0.133	16	18
	Ti (8)	0.898	0.045	5	13
	Zr (9)	1.008	0.075	8	13
	Hf (10)	1.020	0.049	5	16
	Ti (11)	0.897	0.044	5	18
	Ti (12)	0.896	0.043	5	17a
	Ti (13)	0.898	0.045	5	19
	Ti (14)	0.895	0.042	5	19
	Ti (15)	0.904	0.051	6	19
	Zr (16)	0.939	0.006	0.6	20
	Hf (17)	0.928	-0.043	-4	21
	Ti (18)	0.833	-0.03	-2	22
	Ti (18)	0.833	-0.03	-2	22
	Zr (19)	0.934	0.001	0.1	23

^a See Fig. 2. D is calculated from the published M–Cp distance and $1/2(\text{Cp-M-Cp})$ angle. In compound 10 the M–Cp distance was determined from the reported xyz coordinates in the reference.

^b D for *ansa-D* for parent metallocene).

^c $(\Delta/D_{\text{parent}}) \times 100$.

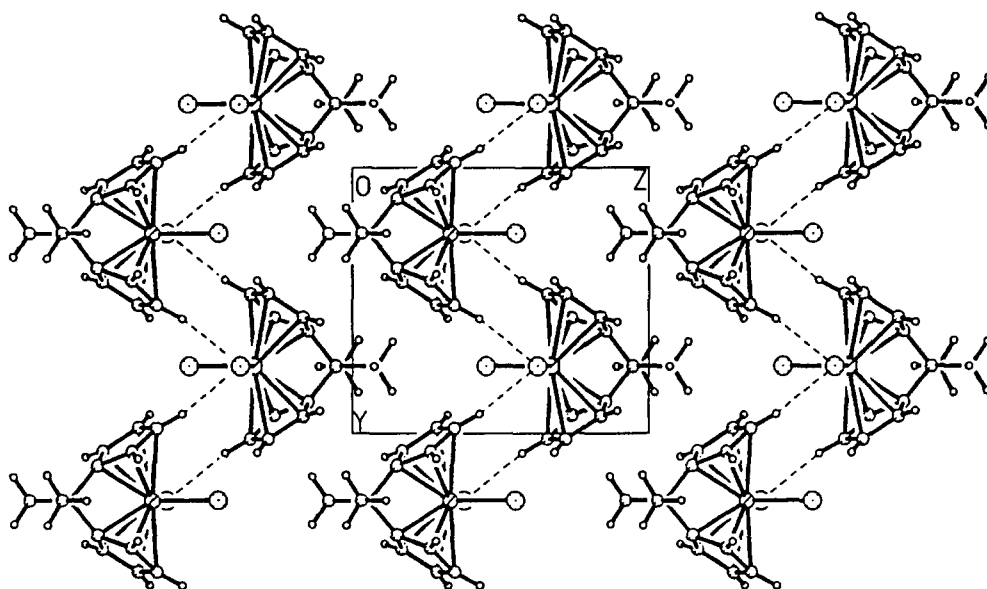


Fig. 5. The crystal packing diagram of **1**, **2** and **3** (viewed down the x axis) showing interatomic hydrogen bonding interactions. Compound: $\text{Me}_2\text{C}[(\text{C}_5\text{H}_4)_2]\text{TiCl}_2$.

the coordination site may be that dimerization of the catalyst species occurs more readily. In the stoichiometric reaction of $\text{Cp}_2\text{ZrCl}_2/n\text{BuLi}$ with H_2SiPh_2 , the products obtained are $n\text{BuPh}_2\text{SiH}$ and $\text{Cp}_2\text{Zr}(\text{H})\text{SiPh}_2\text{H}$, which dimerizes in the absence of a trap [25]. The dimer is usually insoluble and chemically rather inert [25] and may not be catalytically active. The slower rate of dehydrocoupling reactions observed with the *ansa*-metallocene precatalysts may be due to siphoning of the metal species into an inactive form or it could be due to the increased electron deficiency of the metal center. Calculations would be required to assess both the electronic effect and the structural effect that results from opening the coordination site.

3.3. Crystal packing

The crystal packing diagrams of compounds **1**, **2** and **3** reveal short non-bonded distances between a metal chlorine and a Cp hydrogen on an adjacent atom which can be viewed as a hydrogen bonding interaction (Fig. 5). In a neutron diffraction study of $[\text{NPr}_4]_2[\text{PtCl}_4]_2 \cdot \text{cis}[\text{PtCl}_2(\text{NH}_2\text{Me})_2]$, close intermolecular interactions between Pt–Cl and carbon bonded hydrogens with C–H—Cl distances ranging from 2.75 Å to 2.95 Å were observed. These short distances were attributed to weak hydrogen bond interactions. The C–H—Cl angles for these compounds ranged from 118° to 171° [27]. In compounds **1**, **2** and **3** the CH—Cl distances are 2.786 Å, 2.860 Å and 2.850 Å and the C–H—Cl angles are 160.7°, 157.0° and 137.3°, respectively, which is well within this range. Clearfield has reported intermolecular distances as short as 2.749 Å between a chlorine sub-

stituent and a Cp hydrogen in Cp_2TiCl_2 [12]. Interatomic chlorine to cyclopentadienyl hydrogen distances of 2.83 Å were also observed in compound **17**, $(\text{H}_2\text{C})_3(\text{C}_5\text{H}_4)_2\text{HfCl}_2$ [21]. It is probable that short intermolecular distances of this hydrogen bond type may be common in the solid state for metallocene dihalides.

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