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Zirconium bis-indenyl compounds. Synthesis and X-ray crystallography study of 1- and 2-substituted bis(R-indenyl)zirconium dichloride metallocenes

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Abstract

A series of 1- and 2-substituted indenyl ligands were prepared and used in the synthesis of $[1\text{-R-Ind}]_2ZrCl_2$ [R = Me (**2b**), Et (**4b**), ^{i}Pr (**5b**), ^{t}Bu (**6b**), $SiMe_3$ (**8b**), Ph (**10b**), Bz (**12b**), 1-Naph (**14b**)] and $[2\text{-R-Ind}]_2ZrCl_2$ [R = Me (**1b**), Et (**3b**), $SiMe_3$ (**7b**), Ph (**9b**), Bz (**11b**), 1-Naph (**13b**)] metallocenes. An X-ray crystallographic study of **4b** and **10b** showed the complexes to be the *racemic* diastereomers (**4b**, both the *R*,*R* and *S*,*S*-enantiomers and **10b**, the *S*,*S*-enantiomer). The X-ray data together with NMR spectral data revealed that the size of the substituent influenced the orientation the two indenyl ligands of the metallocenes. The **4b** diastereomers are both found to crystallize with their ethyl groups *syn* (bis-central) with respect to each other whereas the larger phenyl groups in **10b** results in an *anti* (bis-lateral) orientation of the indenyl ligands. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zirconium; Indenyl; Metallocene complexes

1. Introduction

The importance of single-center catalysts (SCC) is reflected by the recent series of reviews on the topic [1–10]. The major advantage of SCCs lies in the fact that subtle changes in their molecular architecture lead to polymers with vastly different properties. For example, Waymouth has recently developed a novel catalyst system in which ligand orientation effects can be controlled resulting in a catalyst that is capable of polymerizing propene into elastomeric polypropylene [11–15]. These catalysts consist of zirconium dichloride bonded to two unconnected, oscillating indene ligands substituted at the 2-position. Bulky substituents enable these metallocenes to polymerize sections of atactic and isotactic polypropylene in the same polymer chain. Not only are these highly effective polymerization catalysts, but substitution at the 2-position is easily and relatively cheaply achieved. This result indicates that other 1- or 2-substituted, *unbridged* bis-indenyl Group 4 metallocenes may also have interesting properties. It is to be noted that reports on the synthesis and application of such compounds in the synthesis of polymers have been limited to the papers by Waymouth (vide supra) and a few other relevant publications that have appeared in the open literature [16–21].

In this paper we describe the *systematic* synthesis and characterization of a series of 1- and 2-substituted bis(R-indenyl)zirconium dichloride compounds (R = alkyl or aryl). A paper on the use of these metallocenes in the polymerization of ethene and propene is in preparation [22].

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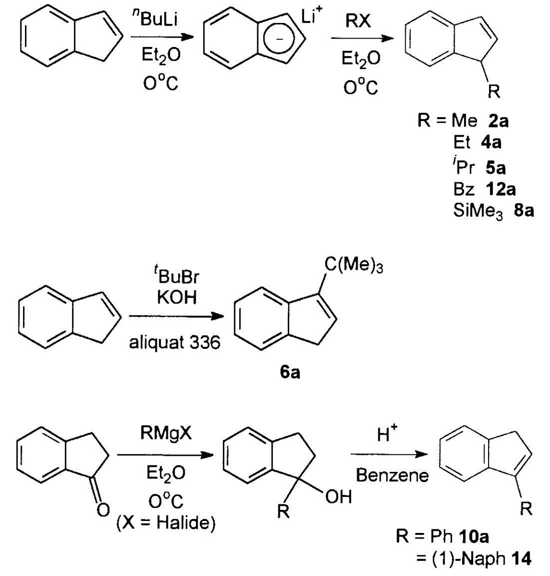
2. Results and discussion

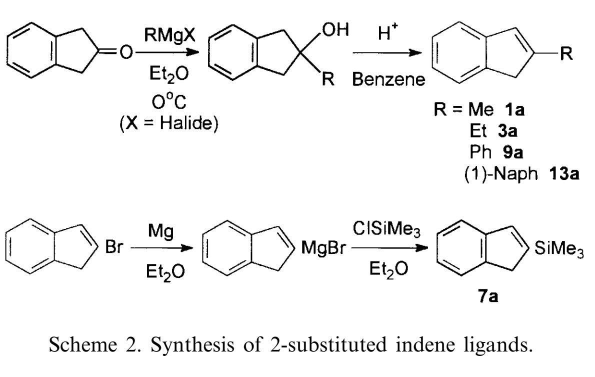
2.1. Synthesis of the substituted indene ligands

The synthesis of substituted indene ligands may be approached via several synthetic routes. Many of these reactions involve the formation of the five membered ring as a last step from a suitably substituted benzene precursor (e.g. via Friedel Crafts methodology), followed by a reduction step to form the indene [23–26] or the cyclization of phenyl substituted allylic cations [27,28]. We have however preferred to use indene and 1- and 2-indanone as our starting materials for the synthesis of the substituted indenes described in this paper. A number of approaches may be followed and these are summarized in Schemes 1 and 2, which depict synthetic routes to 1- (and 3-) and 2-substituted indene compounds respectively. The substituted indene compounds synthesized in this paper are included in these two schemes.

The synthesis of the 1-indene [R = Et (**4a**) and ^{i}Pr (**5a**)], 3-indene [R = ^{t}Bu (**6a**) and Ph (**10a**)] and 2-indene [R = Me (**1a**), Ph (**9a**) and Bz (**11a**)] ligands have been described elsewhere [20,29,31–33]. 2-Ethylindene (**3a**) was synthesized by the addition of the Grignard reagent of 2-ethylbromide to 2-indanone, followed by dehydration. Similarly, 2- and 3-(1)-naphthyl-indene (**13a** and **14a**) were synthesized by nucleophilic addition of the Grignard reagent of 1-bromonaphthalene to either 2- or 1-indanone, respectively, followed by dehydration. The synthesis of 1-methylindene and (**2a**) and 1-benzylindene (**12a**) were accomplished by addition of indenyllithium to the electrophiles methyliodide and benzylbromide, respectively.



Scheme 1. Synthesis of 1- and 3-substituted indene ligands.



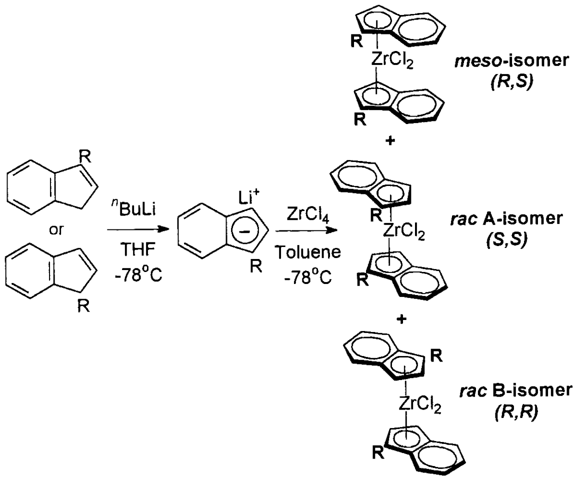
Scheme 2. Synthesis of 2-substituted indene ligands.

2.2. Synthesis of the metallocenes

The substituted ligands **1a**–**14a** were used as precursors in the successful synthesis of a series of bis(1-R-indenyl)zirconium dichloride [R = Me (**2b**), Et (**4b**), ^{i}Pr (**5b**), ^{t}Bu (**6b**), SiMe$_3$ (**8b**), Ph (**10b**), Bz (**12b**), and 1-Naph (**14b**)] and bis(2-R-indenyl)zirconium dichloride [R = Me (**1b**), Et (**3b**), SiMe$_3$ (**7b**), Ph (**9b**), Bz (**11b**) and 1-Naph (**13b**)] complexes. The synthetic procedure is illustrated in Scheme 3, the reaction scheme for the synthesis of the 1-subsituted metallocenes. In this procedure, *n*-butyllithium was allowed to react with the appropriate indene ligand in THF. The solvent was then removed in vacuo from the resulting salt, replaced with toluene, and the metallocene formed by the addition of $ZrCl_4$, also in toluene.

The 1-substituted indene ligands are prochiral and can yield two diastereomers. A *re*, *re* or *si*, *si* attachment gives rise to the two *racemic* (*rac*) enantiomers (i.e. these make up the *rac*-diasteomer) whereas a *re*, *si* attachment gives the *meso* diastereomer (Scheme 3). The synthetic approach employed in this study gave the statistical 50:50 *rac*:*meso* isomer ratio. Use of $ZrCl_4(THF)_2$, as the zirconium source, has been suggested to modify the ratio of the diastereomers formed [17], but this reagent did not influence our ratios for the synthesis of **4b** and **5b**. The most probable reason for this lack of isomer selectivity may relate to the small size of the indene ligand R-groups (R = ethyl and *iso*-propyl). This proposal is reinforced by the observation that even with the use of $ZrCl_4$, the bulky naphthyl substituted ligand (**14a**) attached to the metal to give a 60:40 *rac*:*meso* isomeric mixture of **14b**. However no attempt was made to synthesize **14b** using $ZrCl_4(THF)_2$ to see if this ratio could be improved.

Depending on the nature of the ligand substituent, different solvents had to be used to achieve successful purification of the metallocenes and separation of their diastereomers. There appears to be a relationship between the size of the indenyl ligand substituent and the solubility of these metallocenes. Complexes with substituents smaller than *tert*-butyl can easily be dissolved and recrystallized from toluene. More polar solvents, such as dichloromethane, had to be employed for the



Scheme 3. The prochiral 1- and 3-substituted indene precursors result in the formation of *rac*- and *meso*-metallocene compounds. The 2-substituted metallocenes were synthesized according to the same route.

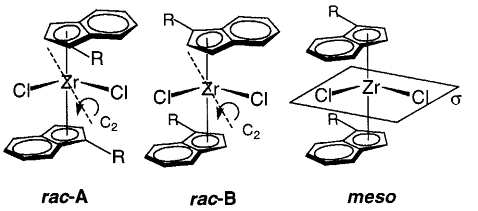


Fig. 1. Representation of the symmetry elements of the *rac*- and *meso*-diastereomers.

other metallocenes. The exception to this rule was the benzyl substituted metallocenes (**11b** and **12b**), which could also be successfully purified from toluene.

The many fractional-crystallization steps undertaken for the purification of most of the metallocenes incurred a heavy product-loss penalty. For **2b**, the methyl substituted metallocene, no separation of the diastereomers could be achieved. The compound was instead purified as a 50:50 mixture of the *rac*:*meso* isomers.

2.3. Characterization of the metallocenes

The *rac*- and *meso*-diastereomers are readily distinguished from one another by the differing positions of their H-2 and H-3 ^{1}H-NMR spectroscopy signals (refer to Table 1 for numbering schemes). Since both *rac*-enantiomers have C_2-symmetry this results in the H-2 as well as the H-3 protons on each ring being equivalent. In the *meso*-diastereomer these protons can be related by a mirror-plane bisecting the Cl–Zr–Cl plane (Fig. 1). This results in the two H-2 protons and two H-3 protons in each diastereomer giving rise to one signal each.

The *absolute* stereochemical assignment for two of these metallocenes viz. **4b** and **10b**, was made possible by X-ray crystallography (vide infra). For the remaining 1-substituted metallocenes (**5b**, **6b**, **8b** and **14b**), the *rac*- and *meso*- diastereomers could be differentiated by reaction of the isolated diastereomers with methyllithium, replacing the chloride ligands with methyl groups. As the *rac*-diastereomer has C_2-symmetry, only one methyl resonance is expected (and observed). However, as the *meso*-diastereomer has C_s-symmetry, two methyl resonances of equal intensity are expected (and observed).

Attempts at methylating the 1-benzyl substituted metallocene **12b** were not successful, presumably due to the methyllithium preferentially reacting with the acidic benzylic methylene protons, even when an excess of methyllithium was used. The diastereomers of **12b** were therefore assigned using an alternative procedure, which will be discussed later.

For all of the metallocenes, the H-3 signal was identified as a doublet of doublets through its coupling to protons H-2 and H-4. H-2 however showed only vicinal coupling to H-3 and was thus observed as a simple doublet. For both diastereomers, the H-2 signal is downfield from H-3 with their corresponding ^{13}C-NMR spectral data yielding equivalent positions in the ^{13}C-NMR spectra. An exception to this ordering was found for *one* of the **6b** (R = ^{t}Bu) diastereomers. In this case the H-3 resonance (δ 6.48) is found downfield from that of H-2 (δ 5.89). Interestingly, C–H correlation showed that C-3 (δ 96.62) is upfield from C-2 (δ 117.65), i.e. opposite to the ^{1}H-NMR signal order. The NMR spectral data for the other diastereomer was consistent with that found for the other metallocenes.

Together with the stereochemical assignments made earlier, it was possible to assign the H-2 and H-3 signals to a particular diastereomer. An interesting observation is that for a sample containing a mixture of *rac*- and *meso*- diastereomers, the 'inner pair' of H-2 and H-3 resonances can be assigned to the *rac*-diastereomer. Also, the separation between the H-2 and H-3 signals, $\Delta\delta$, was found to be dependent on the R-group (Table 2). For the *rac*-diastereomer, $\Delta\delta$ becomes smaller as the electron donating strength of the indenyl substituent increases and eventually the signal positions interconvert as observed for **6b** (R = ^{t}Bu) where $\Delta\delta = -0.59$. No linear relationship between $\Delta\delta$ and the electronic properties of the R-substituents could be found (the Hammett substituent functions σ_m, σ_p and F were considered [34]), which suggests that $\Delta\delta$ is also influenced by steric factors.

Using the knowledge of the positioning of the H-2 and H-3 resonances we have tentatively assigned the stereochemistry for the 1-methyl (**2b**) and 1-benzyl substituted metallocene (**12b**) diastereomers. Thus, for **12b** the *rac*-isomer has its H-2 and H-3 resonances at δ 6.05 and 5.83 ('inner-pair'), whereas the *meso*-diastereomer resonances for the protons are at δ 6.29 and 5.29 ('outer-pair').

Table 1
NMR spectral data for the bis(R-indenyl)zirconium dichloride metallocenes [a]

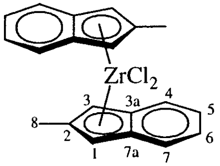
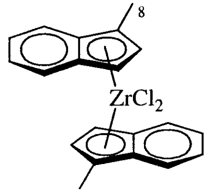
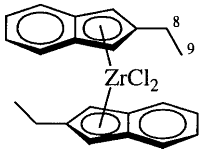
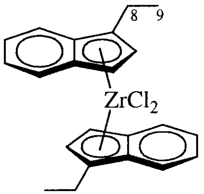
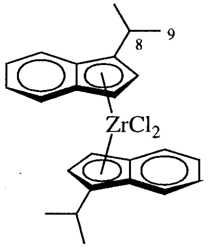
Metallocene [b]	Code	^{1}H-NMR spectra [c]	Assignment [d]	^{13}C-NMR spectra	Assignment [d]
	**1b**	2.04 (s, 6H)	H_8	16.89	C_8
		5.83 (s, 4H)	H_1, H_3	106.18	C_1, C_3
		7.24 (m, 4H)	H_5, H_6	125.14, 125.20	$C_{4–7}$
		7.64 (m, 4H)	H_4, H_7	126.17	C_2
				138.12	C_{3a}, C_{7a}
	**2b**	*Isomer 1:*		*Isomer 1:*	
		2.35 (s, 6H)	H_8	12.93	C_8
		5.83 (dd, $J = 2.8$, $J_{3–4} = 0.7$ Hz, 2H)	H_3	*Isomer 2:*	
		6.07 (d, $J = 3.1$, 2H)	H_2	13.35	C_8
		Isomer 2:		*Both Isomers:*	
		2.42 (s, 6H)	H_8	98.95, 99.14, 118.17, 121.50,	$C_{1–7a}$
		5.70 (dd, $J = 3.2$, $J_{3–4} = 0.7$ Hz, 2H)	H_3	123.03, 123.72, 123.73, 125.41,	
		6.31 (d, $J = 3.1$ Hz, 2H)	H_2	125.44, 125.48, 125.54, 125.84,	
		Both Isomers:		125.96, 126.03, 126.76, 127.17	
		7.22–7.32, 7.44–7.47, 7.55–7.64 (m, 8H)	$H_{4–7}$		
	**3b**	0.97 (t, $J = 7.6$ Hz, 6H)	H_9	14.24	C_9
		2.43 (q, $J = 7.5$, Hz 4H)	H_8	24.27	C_8
		5.81 (s, 4H)	H_1, H_3	104.63	C_1, C_3
		7.24 (m, 4H)	H_5, H_6	125.04	C_5, C_6
		7.67 (dd, $J = 6.5$ $^4J = 3.1$ Hz, 4H)	H_4, H_7	125.44	C_4, C_7
				126.10	C_2
				145.02	C_{3a}, C_{7a}
	**4b**	*Isomer 1 (rac)* [e]:		*Isomer 1:*	
		1.15 (t, $J = 7.5$ Hz, 6H)	H_9	13.86	C_9
		2.84 (m, 4H)	H_8	20.99	C_8
		5.82 (dd, $J_{3–2} = 3.2$, $^4J_{3–4} = 0.7$ Hz, 2H)	H_3	98.81	C_3
		6.04 (d, $J = 3.3$ Hz, 2H)	H_2	121.27	C_2
		7.23–7.32 (m, 4H)	H_5, H_6	123.81, 125.72	C_4, C_7
		7.54–7.68 (m, 4H)	H_4, H_7	125.35, 126.22	C_5, C_6
		Isomer 2 (meso):		125.30, 125.75	
		1.23 (t, $J = 7.5$ Hz, 6H)	H_9		
		2.92 (q, $J = 7.5$ Hz, 4H)	H_8		
		5.62 (dd, $J_{3–2} = 3.2$ Hz, $^4J_{3–4} = 0.8$ Hz, 2H)	H_3		
		6.32 (d, $J = 3.2$ Hz, 2H)	H_2		
		7.19–7.49, 7.56–7.57, 7.60–7.62 (m, 8H)	$H_{4–7}$		
	**5b**	*Isomer 1 (rac)* [f]:		*Isomer 1:*	
		1.10 (d, $J = 6.9$ Hz, 6H)	H_9	20.03	C_{3a}, C_{7a}
		1.17 (d, $J = 6.7$ Hz, 6H)	H_9	24.35	C_9
		3.51 (dt, $J = 6.8$ Hz, 2H)	H_8	27.10	C_8
		5.90 (dd, $J_{3–2} = 3.2$ Hz, $^4J_{3–4} = 0.5$ Hz, 2H)	H_3	96.48, 123.99	C_2, C_3
		5.91 (d, $J = 3.3$ Hz, 2H)	H_2	124.28, 125.20, 125.89, 126.74	$C_{4–7}$
		7.19, 7.34 (m, 4H)	H_5, H_6	123.99	C_1
		7.54 (d, $J_{4–5} = 8.5$ Hz, 2H)	H_4	127.83, 132.28	C_{3a}, C_{7a}

Table 1 (*Continued*)

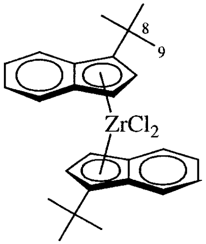
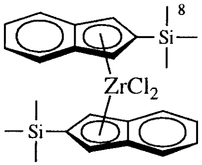
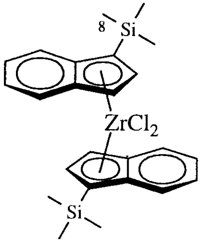
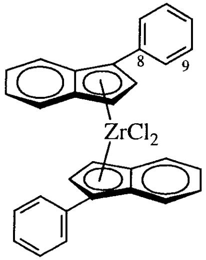
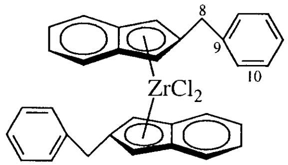
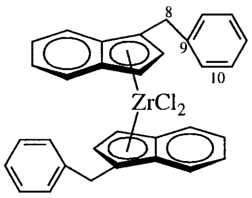
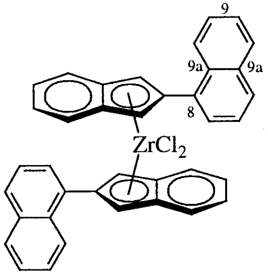
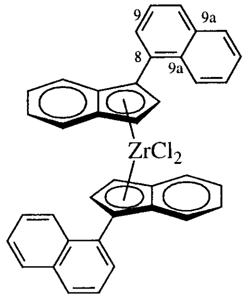
Metallocene [b]	Code	^{1}H-NMR spectra [c]	Assignment [d]	^{13}C-NMR spectra	Assignment [d]
		7.65 (m, $J = 8.5$ Hz, 2H)	H_7		
		Isomer 2 (meso):			
		1.15 (d, $J = 6.9$ Hz, 6H)	H_9		
		1.32 (d, $J = 6.8$ Hz, 6H)	H_9		
		3.55 (dq, $J = 6.8$ Hz, 2H)	H_8		
		5.37 (dd, $J = 3.2$ Hz, $J_{3-4} = 0.7$ Hz, 2H)	H_3		
		6.33 (d, $J = 3.2$ Hz, 2H)	H_2		
		7.23, 7.32 (m, 4H)	H_5, H_6		
		7.44 (dd, $J = 8.5$ Hz, $^4J = 0.7$ Hz, 2H), 7.60 (dd, $J = 8.6$ Hz, $^4J = 0.8$ Hz, 2H)	H_4, H_7		
	**6b**	*Isomer 1 (rac)* [f]:			
		1.42 (s, 18H)	H_9	30.6	C_9
		5.89 (d, $J = 3.0$ Hz, 2H)	H_2	34.32	C_8
		6.48 (dd, $J_{3-2} = 3.4$ Hz, $^4J_{3-4} = 0.5$ Hz, 2H)	H_3	96.62	C_3
		7.17 (m, 2H), 7.31 (m, 2H)	H_5, H_6	117.65	C_2
		7.67 (d, $J = 8.5$ Hz, 2H), 7.89 (d, $J = 8.6$ Hz, 2H)	H_4, H_7	121.82	C_1
		Isomer 2 (meso):		124.07, 125.11, 125.33, 125.97	C_{4-7}
		1.49 (s, 18H)	H_9	131.04, 132.98	C_{7a}, C_{3a}
		6.05 (dd, $J_{3-2} = 3.3$ Hz, $^4J_{3-4} = 0.8$ Hz, 2H)	H_3		
		6.43 (d, $J = 6.5$ Hz, 2H)	H_2		
		7.25, 7.50, 7.90 (m, 8H)	H_{4-7}	−0.46	C_9
	**7b**	0.074 (s, 18H)	H_8	111.73	C_1, C_3
		5.97 (s, 4H)	H_1, H_3	125.38	C_5, C_6
		7.29 (m, 4H)	H_5, H_6	125.78	C_4, C_7
		7.80 (m, 4H)	H_4, H_7	129.36	C_2
				141.09	C_{3a}, C_{7a}
	**8b**	*Isomer 1 (rac)* [f]:		*Isomer 1:*	
		0.35 (s, 18H)	H_8	−2.53	C_8
		6.37 (dd, $J = 3.2$ Hz, $^4J_{3-4} = 0.8$ Hz, 2H)	H_3	46.51	C_1
		6.43 (d, $J = 3.2$ Hz, 2H)	H_2	104.78, 125.02, 125.87, 126.21, 127.09, 127.57	C_2, C_3, C_{4-7}
		7.28 (m, 4H), 7.67–7.73 (m, 4H)	H_{4-7}	128.83, 135.75	C_{3a}, C_{7a}
		Isomer 2 (meso):			
		0.40 (s, 18H)	H_8		
		6.17 (dd, $J = 3.2$ Hz, $^4J_{3-4} = 0.8$ Hz, 2H)	H_3		
		6.58 (d, $J = 3.2$ Hz, 2H)	H_2		
		7.07 (m, 2H), 7.70 (m, 2H)	H_{4-7}		
	**10b**	*Isomer 1 (rac)* [e]:		*Isomer 1:*	
		5.93 (dd, $J_{2-1} = 3.6$ Hz, $^4J_{2-4} = 0.8$ Hz, 2H)	H_3	103.42, 118.94	C_2, C_3
		6.36 (d, $J = 3.5$ Hz, 2H)	H_2	123.47, 126.09, 126.16, 127.73, 127.84, 127.94, 129.29	C_{4-7}, C_9
		7.17 (m, 2H), 7.32–7.65 (m, 14H), 7.77–7.82 (m, 2H)	H_{4-7}, H_9	117.19, 126.80, 128.80, 134.55	C_1, C_{3a}, C_{7a}, C_8
		Isomer 2 (meso):			
		5.99 (dd, $J_{2-1} = 3.5$ Hz, $^4J_{2-4} = 0.8$ Hz, 2H)	H_3		
		6.57 (d, $J = 3.5$ Hz, 2H)	H_2		
		7.12–7.66, 7.84–7.89 (m, 18H)	H_{4-7}, H_9		

Table 1 (*Continued*)

Metallocene [b]	Code	^{1}H-NMR spectra [c]	Assignment [d]	^{13}C-NMR spectra	Assignment [d]
	**11b**	3.70 (s, 4H)	H_8	37.44	C_8
		5.86 (s, 4H)	H_1, H_3	105.74	C_1, C_2
		7.00 (m, 4H)	H_4, H_7	125.35, 125.49, 126.34, 128.44,	C_{4-7}, C_{10}
		7.14–7.25 (m, 10H)	H_{10}	128.62	
		7.64 (m, 4H)	H_5, H_6	126.26, 139.82, 141.25	C_2, C_{3a}, C_{7a}, C_9
	**12b**	*Isomer 1 (meso):*		*Isomer 1:*	
		4.18 (d, $J = 15.9$ Hz, 2H)	H_8	34.11	C_8
		4.26 (d, $J = 15.9$ Hz, 2H)	H_8	99.18	C_3
		5.29 (dd, $J_{3-1} = 3.2$ Hz, $^4J_{3-4} = 0.8$ Hz, 2H)	H_3	120.78, 121.74	C_2
					C_1
		6.29 (d, $J = 3.2$ Hz, 2H)	H_2	123.80, 125.64, 126.38, 126.49,	C_{4-7}, C_{10}
		7.19–7.30 (m, 14H)	H_5, H_6, H_{10}	128.51, 128.90	
		7.38 (m, 2H), 7.62 (m, 2H)	H_4, H_7	125.97, 127.48, 139.48	C_{3a}, C_{7a}, C_9
		Isomer 2 (rac):		*Isomer 2:*	C_8
		4.04 (d, $J = 15.9$ Hz, 2H)	H_8	33.96	C_3
		4.23 (d, $J = 15.9$ Hz, 2H)	H_8	99.07	C_2
		5.83 (dd, $J_{3-1} = 3.2$ Hz, $^4J_{3-4} = 0.7$ Hz, 2H)	H_3	122.06	C_{4-7}, C_{10}
				123.62, 125.62, 125.76, 126.31,	C_1, C_{3a}, C_{7a}, C_9
		6.05 (d, $J = 3.3$ Hz, 2H)	H_2	126.44, 128.43, 128.67, 121.63,	
		7.11–7.32 (m, 14H)	H_5, H_6, H_{10}	126.57, 139.76	
		7.6 (m, 4H)	H_4, H_7		
	**13b**	6.37 (s, 4H)	H_1, H_3	107.82	C_1, C_3
		7.21(m. 1H), 7.37–7.41 (m, 1H), 7.46–7.52	H_{4-7}, H_9	125.08, 125.28, 125.35, 126.21,	C_{4-7}, C_9
		(m, 2H), 7.54–7.59 (m, 1H), 7.95 (m, 1H),		126.79, 126.99, 127.28, 128.55,	C_2, C_{3a}, C_{7a},
		7.97–8.00 (m, 1H), 8.18 (m, 20H)		129.01, 129.51	C_8, C_{9a}
				130.52, 131.35, 132.09, 134.31	
	**14b**	*Isomer 1 (rac):*			
		6.30 (dd, $J_{3-2} = 3.4$ Hz, $^4J_{3-4} = 0.5$ Hz, 2H)	H_3		
		6.43 (d, $J = 3.5$ Hz, 2H)	H_2		
		7.15–7.94 (m, 22H)	H_{4-7}, H_9		
		Isomer 2 (meso) [f]*:*			
		6.06 (dd, $J_{3-2} = 3.4$ Hz, $^4J_{3-4} = 0.7$ Hz, 2H)	H_3		
		6.91 (d, $J = 3.4$ Hz, 2H)	H_2		
		7.21–7.95 (m, 22H)	H_{4-7}, H_9		

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[a] NMR spectra were recorded in $CDCl_3$ with chemical shifts relative to TMS, δ scale. For the 1-substituted metallocenes, the NMR spectral data given in the table are ordered such that the first diastereomer isolated by the crystallization process is listed first.

[b] The numbering scheme employed for all the metallocenes is the same as that used for bis(2-methyl-indenyl)zirconium dichloride, **2b**.

[c] All J-values are ^3J, unless specified otherwise.

2.4. Crystal structures of 4b and 10b

X-ray quality crystals were obtained for bis(1-ethylindenyl)zirconium dichloride (**4b**) and bis(1-phenyl-indenyl)zirconium dichloride (**10b**) and the crystal structures of these compounds were determined at 173 K. Selected structural parameters are listed in Table 3 and molecular diagrams for these two structures are depicted in Figs. 2–4.

The crystal structure complex of **4b** reveals two unique molecules in a 1:1 ratio *i.e.* the *R*,*R* (**4b-*R*,*R***) and *S*,*S* (**4b-*S*,*S***) *racemic* enantiomers respectively, which are similar in many respects. The metal atoms in these structures are in a pseudotetrahedral environment formed by the two chlorine ligands and two η^5-bonded indenyl ligands. A slight asymmetry is observed in the attachment of the indenyl ligands to the zirconium atoms.

Erker et al. have proposed three possible solid state conformers for unbridged, *rac*-bis(1-R-indenyl)-zirconium dichloride metallocenes [16,17]. These are depicted in Fig. 5, with the size of the R-substituent dictating which ligand conformation is adopted. These workers predicted that metallocenes with small, intermediate and large substituents would adopt the *syn*-(**A**), *gauche*-(**B**) and *anti*-(**C**) conformations, respectively.

Table 2
Selected ^{1}H-NMR spectral data for the bis(1-R-indenyl)zirconium dichloride metallocenes

Metallocene	R	Isomer	H-2	H-3	Δδ [a]
2b [b]	Me	*rac*	6.07	5.83	0.24
		meso	6.31	5.70	0.61
4b [c]	Et	*rac*	6.04	5.82	0.22
		meso	6.32	5.62	0.70
5b [d]	^{i}Pr	*rac*	5.91	5.90	0.01
		meso	6.33	5.37	0.96
6b [d]	^{t}Bu	*rac*	5.89	6.48	−0.59
		meso	6.43	6.05	0.38
8b [d]	SiMe$_3$	*rac*	6.43	6.37	0.06
		meso	6.52	6.17	0.35
10b [c]	Ph	*rac*	6.36	5.93	0.43
		meso	6.57	5.99	0.58
12b [a]	Bz	*rac*	6.05	5.83	0.22
		meso	6.29	5.29	1.00
14b [d]	(1)-Naph	*rac*	6.43	6.30	0.13
		meso	6.91	6.06	0.85
	Cy [c,e]	*rac*	5.90	5.83	0.07
		meso	6.30	5.81	0.49

[a] H-2–H-3.

[b] Tentative assignment of stereochemistry (see text).

[c] Assignment of stereochemistry made by X-ray crystallography.

[d] Assignment of stereochemistry made by converting dichlorometallocenes to their dimethyl derivatives.

[e] Bis(1-cyclohexyl-indenyl)zirconium dichloride. Metallocene synthesized Krüger et al. [16].

Fig. 3 (top view of the two enantiomers, looking down the two five-membered rings of the indenyl ligands) reveals that both **4b** enantiomers adopt the *syn* conformation with the two ethyl substituents positioned over the open sector of the metallocene. This conformation is similar to **A** in Fig. 5, the structure predicted for metallocenes with small substituents. In this conformation there is less steric interaction between the ethyl substituents and the chloride ligands than if the annelated indenyl six-membered ring were positioned over them.

Metallocene **10b** has C_2 symmetry, with the zirconium atom in a pseudotetrahedral environment formed by the two chlorine ligands and two η^5-coordinated indenyl ligands. The *si*-faces of the two indenyl ligands are attached to the metal, creating a metallocene that has *S*,*S* stereochemistry. The Zr–Cl bond lengths are 2.429(7) Å, which is typical for this class of metallocene. However, the Cl–Zr–Cl angle is 98.98(2)°, which is notably larger than the mean value of 94.77° for similar 1- or 2-substituted bis(indenyl)zirconium dichloride metallocenes (determined from the Cambridge Structural Database [35,36]). This implies that there may be less steric strain in the Cl–Zr–Cl bond angle in this compound (vide infra). The Cp_{cen}–Zr–Cp_{cen} bending angle of 128.66(6)° does, however, fall within the expected range. Of the Zr–C_{Cp} bond lengths, the two bonds to the bridgehead carbons of the indenyl ligand are the longest. Of the remaining three, the bond to the five-membered ring carbon atom to which the substituent is attached, is the longest. This is most probably a result of the steric strain imposed by the phenyl groups upon the structure. The difference between the longest and shortest Zr–C_{Cp} bond is 0.163 Å. Although not out of the ordinary, this is larger than that of the analogous 1-neomenthyl substituted metallocene, the difference here being 0.103 Å [17]. This phenomenon illustrates the size effect of the large and inflexible phenyl group.

A top view of **10b** (Fig. 4b) indicates that an *anti*-type structure is adopted, but this conformation is slightly different from that depicted in Fig. 5. The crystal structure indicates that the indenyl ligands are orientated so as to keep the large phenyl substituents away from each other with the C(1)–Cp_{cen}–Cp_{cen}–C(1A) torsional angle equal to 113.7(8)°. However, this is significantly smaller than the values of close to 180° for the analogous bis(1-cyclohexyl-tetrahydroindenyl)zirconium dichloride [16] and bis(1-neomenthyl-indenyl)zirconium dichloride [17] zirconocenes. Placement of the phenyl substituents in the crowded back section of the bent metallocene is most likely a result of the greater steric strain placed upon the metallocene by the more rigid phenyl ring compared to the

Table 3
Selected crystallographic structural data for **4b** and **10b**

Parameter	**4b**-*S*,*S*		**4b**-*R*,*R*		**10b** [a]	
Bond lengths						
Zr–Cl	Zr(1A)–Cl(1A)	2.449(5)	Zr(1)–Cl(1)	2.442(5)	Zr(1)–Cl(1)	2.429(7)
	Zr(1A)–Cl(2A)	2.434(4)	Zr(1)–Cl(2)	2.441(4)	Zr(1)–Cl(2)	2.429(7)
Zr–C_{Cp} [b]	Zr(1A)–C(3A)	2.571(10)	Zr(1)–C(3)	2.556(10)	Zr(1)–C(1)	2.532(1)
	Zr(1A)–C(4A)	2.462(9)	Zr(1)–C(4)	2.468(9)	Zr(1)–C(2)	2.493(2)
	Zr(1A)–C(5A)	2.411(7)	Zr(1)–C(5)	2.453(8)	Zr(1)–C(3)	2.473(2)
	Zr(1A)–C(6A)	2.492(10)	Zr(1)–C(6)	2.533(10)	Zr(1)–C(4)	2.564(2)
	Zr(1A)–C(7A)	2.589(11)	Zr(1)–C(7)	2.595(11)	Zr(1)–C(9)	2.636(2)
	Zr(1A)–C(14A)	2.593(10)	Zr(1)–C(14)	2.582(11)		
	Zr(1A)–C(15A)	2.532(8)	Zr(1)–C(15)	2.541(8)		
	Zr(1A)–C(16A)	2.520(10)	Zr(1)–C(16)	2.542(8)		
	Zr(1A)–C(17A)	2.574(12)	Zr(1)–C(17)	2.584(9)		
	Zr(1A)–C(18A)	2.618(11)	Zr(1)–C(18)	2.608(11)		
	Zr(1A)–C_{Cp}(1) (avg)	2.505	Zr(1)–C_{Cp}(1) (avg)	2.521	$Zr(1)_{avg}$–C_{Cp} (avg)	2.539
	Zr(1A)–C_{Cp}(2) (avg)	2.567	Zr(1)–C_{Cp}(2) (avg)	2.571		
Zr–Cp_{cen} [c]	Zr(1A)–Cp_{cen}	2.224	Zr(1)–Cp_{cen}	2.241	Zr(1)–Cp_{cen}	2.231(0)
C_{Cp}–C(R) [d]	C(3A)–C(2A)	1.465(18)	C(3)–C(2)	1.484(16)	C(1)–C(10)	1.476(7)
	C(14A)–C(13A)	1.534(15)	C(14)–C(13)	1.558(16)		
Bond angles						
Cl–Zr–Cl	Cl(1A)–Zr(1A)–Cl(2A)	96.45(16)	Cl(1)–Zr(1)–Cl(2)	96.18(17)	Cl(1)–Zr(1)–Cl(1A)	98.98(2)
Cp_{cen}–Zr–Cp_{cen} [e]	Cp_{cen}–Zr(1A)–Cp_{cen}	132.72	Cp_{cen}–Zr(1)–Cp_{cen}	131.98	Cp_{cen}–Zr(1)–Cp_{cen}	128.66(6)
Cp(R1)–Cp_{cen}–Cp_{cen} –Cp(R2) [f]	C(3A)–Cp_{cen}–Cp_{cen} –C(14A)	–27.5(9)	C(3)–Cp_{cen}–Cp_{cen} –C(14)	29.3(8)	C(1A)–Cp_{cen}–Cp_{cen} –C(1)	113.7(8)

[a] As the zirconium atom resides on a point of symmetry, the second indenyl ligand was generated by a C_2 symmetry operation.

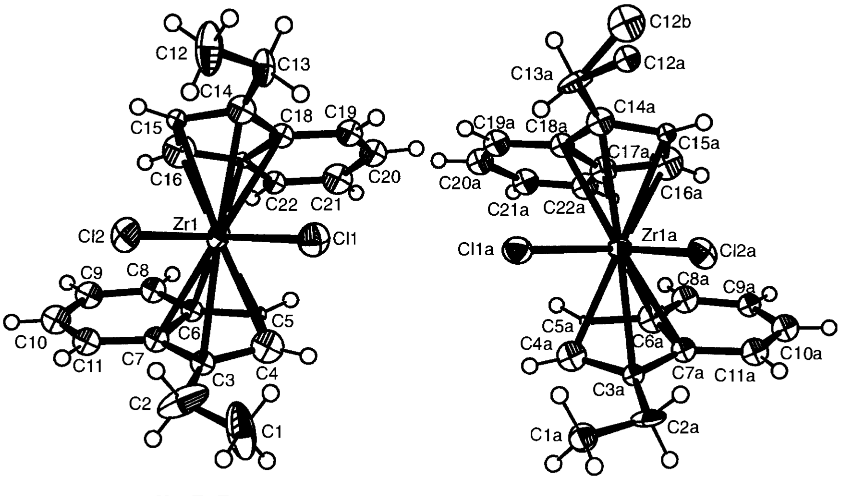
[b] The distance from the zirconium atom to the carbon atoms in the five-membered ring in the indenyl ligand.

[c] The average of the two vectors drawn from the metal to the centroid of the five-membered ring in the indenyl ligand.

[d] The length of the bond that connects the substituent to the indenyl ligand.

[e] The angle formed between the two ring centroids and the zirconium atom.

[f] The torsional angle between the R-substituents on the two indenyl ligands when looking along an imaginary line connecting the two indenyl ring centroids.



4b-*R,R* **4b-*S,S***

Fig. 2. ORTEP diagram of the two *racemic* enantiomers of bis(1-ethyl-indenyl)zirconium dichloride (**4b**) with 50% probability thermal ellipsoids (H-atoms on C12a and C12b omitted for clarity).

more flexible cyclohexyl and neomenthyl entities. A possible concomitant effect of the phenyl rings being placed further away from the open face of the metallocene is the larger Cl–Zr–Cl bond angle observed. To relieve any overbearing steric strain, the dihedral angle formed between the least squares planes through the phenyl ring and the indenyl ligands is 34.93(4)° (the dihedral angle to the five-membered ring is 32.21(5)°). This angle is considerably larger than the same angle in the 2-phenyl substituted metallocene bis(2-phenyl-indenyl)zirconium dichloride, which is only 10.44° for the '*meso*-like' structure and 11.54° for the '*rac*-like' structures [11,13]. Even in the di-substituted metallocene, bis(1-methyl-2-phenyl-indenyl)zirconium dichloride, this dihedral angle is only 26.4(8)° ('*meso*-like') and 31.4(8)° ('*rac*-like') [13]. A distinct feature of the latter two metallocenes, synthesized by the Waymouth group, is that both the '*meso*-like' and '*rac*-like' structures are found in the same crystal structure implying that they are similar in energy (Scheme 4). However, only one stereoisomer of **10b** is found in the solid state, implying unfavorably high steric energies in all other conformers.

The size of the ligand substituents and eventual conformation adopted by these ligands has a direct impact on the space available to reactant molecules in the reaction sphere of the metallocene during an olefin polymerization reaction. This issue will be more fully discussed in a related paper [22].

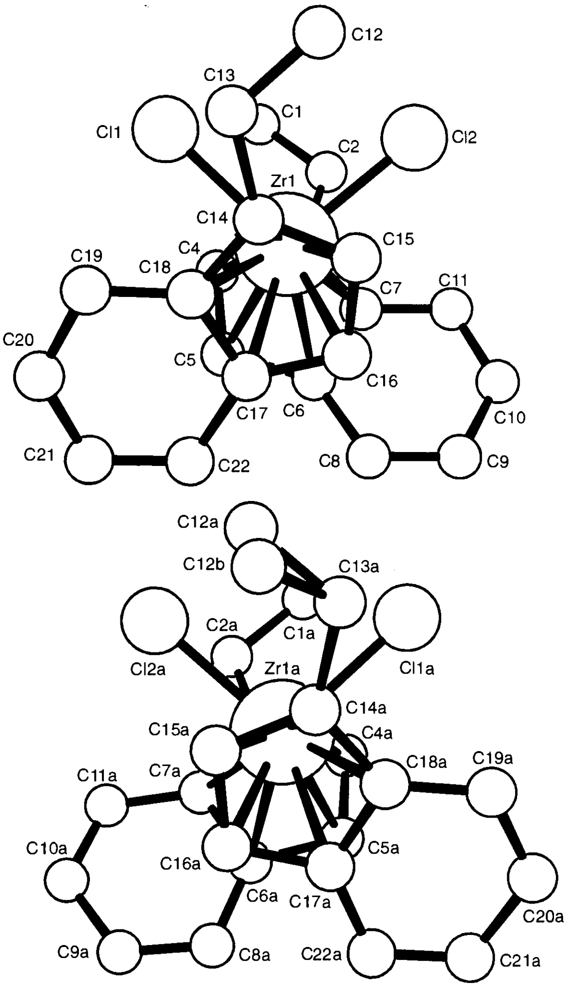


Fig. 3. Molecular geometry of **4b** viewed down the five-membered rings of the indenyl ligands (a) *R*,*R*-enantiomer (top) and (b) *S*,*S*-enantiomer (bottom).

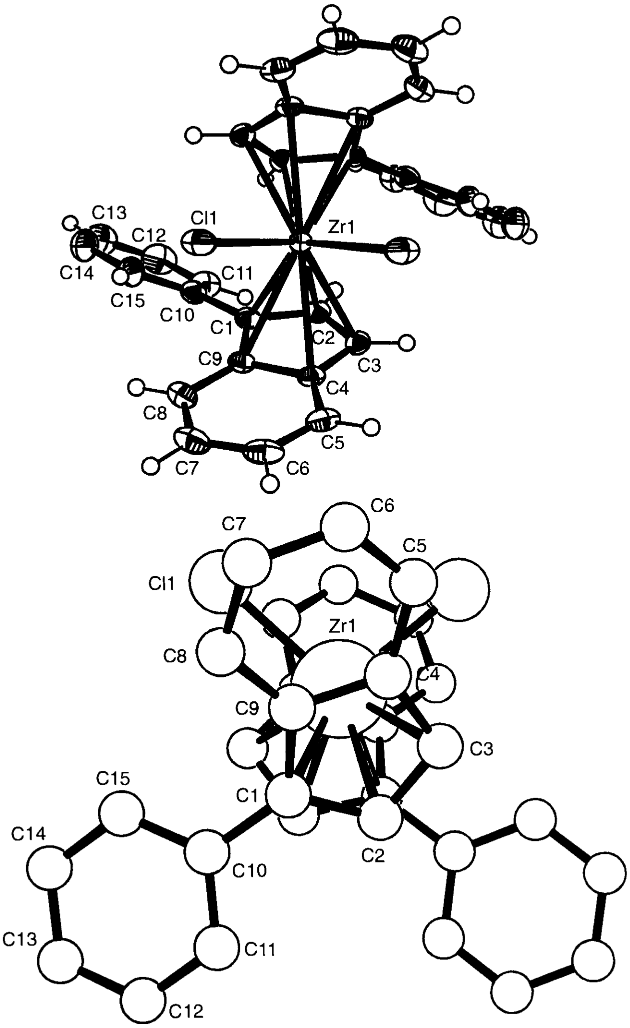


Fig. 4. (a) ORTEP diagram of bis(1-phenyl-indenyl)zirconium dichloride (**10b**) with 40% probability thermal ellipsoids (top) and (b) **10b** viewed down the five-membered rings of the indenyl ligands (bottom). As the second ligand is generated by symmetry, it is not numbered.

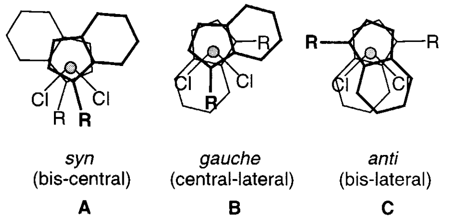


Fig. 5. The ligands in unbridged Group 4 metallocenes can adopt three conformations with respect to each other. These conformers are dictated by the size of the substituents on the indenyl ligands.

3. Conclusions

A series of 1- (and 3-) and 2-substituted indene ligands were synthesized and their lithiated salts reacted with $ZrCl_4$ to give the corresponding 1- and 2-bis(R-indenyl)zirconium dichloride metallocenes. The 1- and 3-substituted indenes are prochiral resulting in two diastereomers being formed, viz. one *meso*- and two *rac*-enantiomers making up the other diastereomer. These could be separated and purified by fractional crystallization.

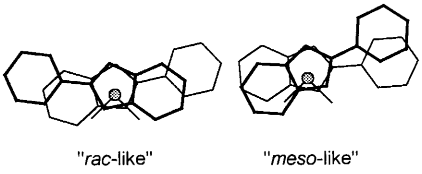
The crystal structures of two 1-substituted metallocenes, **4b** and **10b**, were successfully determined by X-ray diffraction at 173 K. The indenyl ligands in **4b** are orientated so as to place the ethyl groups *syn* with respect to each other, over the open sector of the metallocene, pointing between the two chloride atoms. In **10b**, due to the larger size of the phenyl ligand, the indenyl ligands are orientated to place these substituents *anti* to each other towards the back sector of the bent metallocene.

What is clear from these and related crystal structures are that the two substituents on the different rings in the metallocene interact with each other and depending on their size adopt a specific conformation in the solid state. This should have implications on the use of these metallocenes in olefin polymerization studies [22].

4. Experimental

4.1. General procedures

All experimental procedures, unless specified otherwise, were performed under an argon atmosphere employing standard Schlenk techniques and apparatus. Solvents employed in reactions were distilled under a nitrogen atmosphere from an appropriate drying agent. Tetrahydrofuran and ether were first pre-dried over 4 Å molecular sieves and then distilled from sodium wire/benzophenone. Toluene was dried by heating under reflux over molten sodium. Dichloromethane, benzene, hexane and pentane were distilled from calcium hydride. All solvents were transferred to reaction vessels via a cannula from solvent collection flasks. The solvents chloroform-*d* and benzene-d_6, employed in the NMR spectroscopic analyses of the metallocenes, were first dried over calcium hydride, subjected to three freeze–pump–thaw deoxygenating cycles and then collected for use by a trap-to-trap distillation at reduced pressure. The latter procedures were carried out in an all-glass manifold. Technical grade indene (Aldrich, 90%) was purified according to the procedure outlined by Perrin [37]. All indene ligands were distilled under reduced pressure, from calcium hydride, before use in the synthesis of the metallocenes. 1-Indanone [38], 2-indanone [39], 2-methylindene (**1a**) [33], 1-ethylindene (**4a**) [29], 1-*iso*-propylindene (**5a**) [29], 3-*tert*-butylindene (**6a**) [32], 2-trimethylsilylindene (**8a**) [31], 1-trimethylsilylindene (**7a**) [33], 2-phenylindene (**9a**) [11,30], 3-phenylindene (**10a**) [30], 2-benzylindene (**11a**) [20] and bis(2-phenyl-indenyl)zirconium dichloride (**9b**) [11] were synthesized according to literature procedures. NMR spectra were recorded on either a Bruker AC 200 MHz or Bruker DRX 400 MHz spectrometer. Elemental analysis was performed by the Agricultural Research Council (Pretoria, South Africa) and high-resolution mass spectrometry (HR-MS) by the Cape Technikon (Cape Town, South Africa).



Scheme 4. Both the *anti*-‘*rac*-like’ and *syn*-‘*meso*-like’ structures are found in the crystal structure of bis[2-phenylindenyl]zirconium dichloride.

4.2. 1-Methylindene (**2a**)

n-Butyllithium (14.3 ml, 2.4 M, 34.4 mmol) was added drop-wise to a solution of indene (4.00 g, 34.4 mmol, 4.0 ml) in 80 ml diethyl ether at 0°C. This was slowly allowed to warm to room temperature and stirred for 3 h in total. This orange–yellow solution was then added drop-wise via cannula to iodomethane (9.6 g, 8.61 ml, 0.138 mol) in 50 ml diethyl ether at 0°C. This was stirred overnight and the reaction terminated by the addition of 50 ml of a saturated aqueous NH_4Cl solution. The organic material was extracted into diethyl ether, separated, dried ($MgSO_4$), filtered and the solvent removed at a rotary-evaporator. The remaining product was distilled at reduced pressure to give a colorless oil (**2a**, 4.34 g, 75%), which turned yellow on standing at room temperature (r.t.). ^1H-NMR (200 MHz, $CDCl_3$): δ 7.15–7.43 (m, 4H, arom. H), 6.77 (dd, $^3J = 5.5$ Hz, $^4J = 1.9$ Hz, 1H, 3-CH), 6.47 (dd, $^3J = 5.5$ Hz, $^4J = 1.9$ Hz, 1H, 2-CH), 3.48 (m, 1H, 1-CH), 1.31 (d, $^3J = 7.6$ Hz, 3H, CH_3). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 149.14, 143.26 (C-3a and C-7a), 141.26, 130.11, 126.35, 124.72 (arom. C), 122.56 (C-3), 120.96 (C-2), 45.06 (C-1), 15.95 (CH_3).

4.3. 2-Ethylindene (**3a**)

Bromoethane (4.12 g, 37.8 mmol; 2.82 ml) was added dropwise, from a pressure-equalizing dropping funnel to magnesium (0.920 g, 37.8 mmol) suspended in 100 ml of diethyl ether at a rate to effect gentle reflux. Once all the magnesium had been consumed, 2-indanone

(5.00 g, 37.8 mmol) dissolved in 50 ml of diethyl ether, was slowly added drop-wise at 0°C via cannula. A white mixture was formed by the end of the addition, which was slowly allowed to warm to r.t. and then stirred overnight. The reaction mixture was cooled to 0°C and the reaction terminated by the addition of 50 ml of a saturated aqueous NH_4Cl solution. The organic layer was extracted with diethyl ether, dried ($MgSO_4$), filtered and the solvent removed on a rotary-evaporator. The product was taken up in 200 ml of benzene, *p*-toluenesulfonic acid hydrate (0.5 g) added and the solution heated under reflux overnight in a Dean–Stark apparatus. A saturated aqueous Na_2CO_3 solution was added to the remaining benzene, the organic layer extracted with diethyl ether, separated, dried ($MgSO_4$), filtered and the solvent removed at the rotary-evaporator. The remaining product was distilled at reduced pressure to give a colorless oil (**3a**, 3.2 g, 59%), which turned yellow on standing at r.t. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.05–7.35 (m, 4H, arom. H), 6.48 (t, $^4J = 0.6$ Hz, 1H, 3-CH), 3.28 (d, $^4J = 0.5$ Hz, 2H, 1-CH_2), 2.48 (q, $^3J = 7.4$ Hz, 2H, CH_2), 1.20 (t, $^3J = 7.5$ Hz, 3H, CH_3). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 152.40, 145.71 (C-3a and C-7a), 126.22, 125.17, 123.49, 123.35 (arom. C), 143.06 (C-2) 119.84 (C-3), 40.92 (C-1), 24.78 (CH_2), 14.09 (CH_3).

4.4. *1-Benzylindene (**12a**)*

The procedure followed in the synthesis of 1-methylindene (**3a**) was followed except that ^{n}BuLi (43 ml, 2.0 M, 86.1 mmol) was added to indene (10.0 g, 10.0 ml, 86.1 mmol) in 100 ml of diethyl ether. This solution was then added drop-wise via cannula to benzylbromide (14.7 g, 10.2 ml, 86.1 ml) in 50 ml of diethyl ether. After work-up, the desired product was obtained as a colorless oil (**13a**, 10.8 g, 61%), which turned yellow on standing at r.t. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.09–7.35 (m, 9H, arom. H), 6.76 (dd, $^3J = 5.5$ Hz, $^4J = 1.8$ Hz, 1H, 3-CH), 6.41 (dd, $^3J = 5.6$ Hz, $^3J = 1.9$ Hz, 1H, 2-CH), 3.69 (m, 1H, 1-CH), 3.09 (dd, $^2J = 13.5$ Hz, $^3J = 6.8$ Hz, 1H, C*H*H), 2.68 (dd, $^2J = 13.5$ Hz, $^3J = 9.2$ Hz, 1H, CH*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 147.03, 144.27, 140.32 (C-3a, C-7a and C-1'), 138.89, 130.92, 129.00, 128.27, 126.64, 126.20, 124.61 (arom. C), 123.14 (C-3), 121.09 (C-2), 51.75 (C-1), 37.96 (CH_2).

4.5. *2-(1)-Naphthylindene (**13a**)*

To magnesium (1.01 g, 41.6 mmol) suspended in 500 ml of diethyl ether, 1-bromonaphthalene (7.83 g, 5.26 ml, 37.8 mmol) in 50 ml of diethyl ether was added dropwise from a pressure-equalizing dropping funnel. After all the magnesium had been consumed, 2-indanone (5.00 g, 37.8 mmol), in 100 ml of diethyl ether, was added dropwise over 5 h. A white precipitate formed during the addition and the reaction stirred overnight after which a 50 ml saturated aqueous NH_4Cl solution was added, at 0°C, to terminate the reaction. The organic material was extracted into diethyl ether, dried ($MgSO_4$), filtered and the solvent removed at the rotary-evaporator. The remaining product was purified by passage through a short silica column using hexane eluent to remove all non-polar products. An ethyl acetate:hexane (1:1) mixture was then employed to retrieve the desired product, which was taken up in benzene (200 ml) and heated under reflux overnight together with *p*-toluenesulfonic acid hydrate (0.6 g) in a Dean–Stark apparatus. A 50 ml saturated aqueous Na_2CO_3 solution was added, the organic layer extracted into diethyl ether, separated, dried ($MgSO_4$), filtered and the solvent removed at the rotary-evaporator to leave a yellow–white solid (**14a**, 6.4 g, 70%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.25 (m, 1H, arom. H), 7.83 (m, 1H, arom. H), 7.75 (m, 1H, arom. H), 7.40–7.48 (m, 6H, arom. H), 7.30 (m, 1H, arom. H), 7.20 (m, 1H, arom. H), 7.09 (d, $^4J = 0.5$ Hz, 1H, 3-CH), 3.83 (d, $^4J = 0.6$ Hz, 2H, 1-CH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 145.88, 145.29, 143.22, 135.64, 133.99 (C-3a, C-7a, C-1′, C-4′ and C-8′), 131.53, 128.43, 127.63, 126.62, 126.10, 125.96, 125.80, 125.22, 124.71, 123.59, 121.02 (arom. C, C-2 and C-3), 42.91 (C-1). Anal. Calc. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 93.79; H, 5.84%. HR-MS (*m*/*z*): Calc. for $C_{19}H_{14}$ (M^+), 242.1096; found (EI), 242.1091.

4.6. *3-(1)-Naphthylindene (**14a**)*

1-Bromonaphthalene (8.62 g, 5.78 ml, 41.6 mmol), in 50 ml of diethyl ether, was added from a pressure-equalizing dropping funnel to magnesium (1.01 g, 45.8 mmol) suspended in 500 ml of diethyl ether. After all the magnesium had been consumed, 1-indanone (5.00 g, 37.8 mmol) in 100 ml of diethyl ether was slowly added drop-wise via a cannula, at 0°C. The white mixture that formed was stirred overnight at r.t. and the reaction terminated by the addition of 50 ml of a saturated aqueous NH_4Cl solution at 0°C. The organic material was extracted into diethyl ether, separated, dried ($MgSO_4$), filtered and the solvent removed on a rotary-evaporator to leave an orange oil. This was purified by passage through a short silica column. Hexane eluent was first used to remove non-polar side-products and then an ethyl acetate–hexane (1:1) solvent mixture was used to retrieve the desired product as a viscous orange oil. This was taken up in 200 ml of benzene and refluxed overnight in a Dean–Stark apparatus together with *p*-toluenesulfonic acid hydrate (0.6 g). The acid was neutralized by the addition of a 50 ml saturated aqueous Na_2CO_3 solution. The organic material was extracted into diethyl ether, separated, dried ($MgSO_4$), filtered and the solvent removed at the rotary-evaporator to yellow solid. This was purified by passage through a short silica column, using hexane as the eluent to obtain the desired product as a white–yellow solid (**14a**, 6.38 g, 67%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.81–7.93 (m, 3H, arom. H), 7.05–7.57 (m, 8H, arom. H), 6.61 (t, $^3J = 2.1$ Hz, 1H, 2-CH), 3.60 (d, $^3J = 1.9$ Hz, 2H, 1-CH_2). ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 145.71, 144.13, 143.93, 134.10, 133.71 (C-3a, C-7a, C-1′, C-4′ and C-8′), 132.99, 128.22, 127.92, 126.51, 126.25, 126.14, 125.81, 125.72, 125.46, 124.83, 123.86 (arom. C), 131.87 (C-3), 120.83 (C-2), 38.55 (C-1). Anal. Calc. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 93.77; H, 5.82%. HR-MS (*m*/*z*): Calc. for $C_{19}H_{14}$ (M^+), 242.1096; found (EI), 242.1106.

4.7. *Bis[2-methyl-indenyl]zirconium dichloride (**1b**)*

n-Butyllithium (6.4 ml, 1.8 M, 11.5 mmol) was added drop-wise to **1a** (1.50 g, 11.5 mmol) in 50 ml of THF at −78°C. This was slowly allowed to warm to r.t. and stirred for 4 h in total. The solvent was removed in vacuo to leave a white–yellow solid to which 70 ml of toluene was added. The resulting slurry was cooled to −78°C and $ZrCl_4$ (1.34 g, 5.76 mmol) in 50 ml of toluene added drop-wise via a cannula. This mixture was slowly allowed to warm to r.t., developing a canary-yellow color, and stirred for 18 h. The reaction mixture was filtered through a 2 cm celite pad in an inert-air filtration apparatus. The pad was washed with toluene until the washings were clear. The volume of clear filtrate solution was reduced in vacuo and crystallization effected at −18°C. The pure product was collected as yellow needle-like crystals of **1b** (0.21 g, 10%). Anal. Calc. for $C_{20}H_{18}Cl_2Zr$: C, 57.13; H, 4.37. Found: C, 55.93; H, 4.37%. HR-MS (*m*/*z*): Calc. for $C_{20}H_{18}^{35}Cl_2^{90}Zr$ (M^+), 417.9833; found (EI), 417.9835.

4.8. *rac- and meso-Bis[1-methyl-indenyl]zirconium dichloride (**2b**)*

The same synthetic procedure employed in the synthesis of **1b** were followed except that *n*-butyllithium (11.5 ml, 2.0 M, 23.0 mmol) was added to **2a** (3.00 g, 23.0 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 60 ml of toluene was added followed by $ZrCl_4$ (2.68 g, 11.5 mmol) in 60 ml of toluene, this yielding an orange mixture. NMR spectral analysis (not shown) of this crude material revealed a 50:50 *rac*:*meso* isomer mix. The clear orange filtrate from the filtration concentrated in vacuo and crystallization effected at −18°C. The pure product (**2b**) was collected as a 1:1 mixture of *rac*:*meso* isomers in the form of a yellow powder (1.1 g, 23%). Anal. Calc. for $C_{20}H_{18}Cl_2Zr$: C, 57.13; H, 4.31. Found: C, 55.97; H, 4.43%. HR-MS (*m*/*z*): Calc. for $C_{20}H_{18}^{35}Cl_2^{90}Zr$ (M^+), 417.9833; found (EI), 417.9866.

4.9. *Bis[2-ethyl-indenyl]zirconium dichloride (**3b**)*

The same synthetic procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (6.3 ml, 2.2 M, 13.9 mmol) was added to **3a** (3.00 g, 23.0 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 60 ml of toluene was added followed by $ZrCl_4$ (1.62 g, 6.93 mmol) in 60 ml of toluene to give a yellow mixture. The clear yellow filtrate from the filtration was concentrated and crystallization effected at −18°C. The pure product (**3b**) was collected as orange–yellow needle-like crystals (1.4 g, 43%). Anal. Calc. for $C_{22}H_{22}Cl_2Zr$: C, 58.91; H, 4.94. Found: C, 59.62; H, 5.11%. HR-MS (*m*/*z*): Calc. for $C_{22}H_{22}^{35}Cl_2^{90}Zr$ (M^+), 446.0146; found (EI), 446.0141.

4.10. *rac- and meso-Bis[1-ethyl-indenyl]zirconium dichloride (**4b**)*

The same synthetic procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (7.7 ml, 1.8 M, 13.9 mmol) was added to **4a** (2.00 g, 13.9 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 80 ml of toluene was added followed by $ZrCl_4$ (1.62 g, 6.93mmol), in 60 ml of toluene, to give an orange colored reaction mixture. NMR spectral analysis (not shown) of this crude material revealed a 50:50 *rac*:*meso* isomer mixture. The clear orange filtrate from the filtration was concentrated and repeated crystallization from toluene at −18°C gave the two isomers of **4b** viz. the *rac*-isomer as yellow needle-like crystals (determined by X-ray crystallography) and *meso*-isomer as an amorphous yellow solid. Total yield of **4b** was 0.60 g (19%). Anal. Calc. for $C_{22}H_{22}Cl_2Zr$: C, 58.91; H, 4.94. Found: C, 58.39, H, 4.94%. HR-MS (*m*/*z*): Calc. for $C_{22}H_{22}^{35}Cl_2^{90}Zr$ (M^+), 446.0146; found (FAB), 446.01.

4.11. *rac- and meso-Bis[1-iso-propyl-indenyl]zirconium dichloride (**5b**)*

The same synthetic procedures employed in the synthesis of **1b** were followed except that *n*-butyllithium (8.62 ml, 2.2 M, 19.0 mmol) was added to **5a** (3.00 g, 19.0 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 80 ml of toluene was added followed by $ZrCl_4$ (2.2 g, 9.48 mmol) in 50 ml of toluene to give an orange–yellow reaction mixture. The clear yellow–orange filtrate from the filtration was concentrated in vacuo with analysis by NMR spectroscopy (not shown) revealing a 50:50 *rac*:*meso* isomer ratio. The first isomer was recrystallized from toluene, layered with pentane, as an amorphous yellow powder at −18°C. Continued crystallization from toluene gave the second isomer as needle-like yellow crystals. Total yield of **5b** was 1.6 g (35%). Anal. Calc. for $C_{24}H_{26}Cl_2Zr$: C, 60.48; H, 5.50.

Found: C, 61.10; H, 5.61%. HR-MS (m/z): Calc. for $C_{24}H_{26}^{35}Cl_2^{90}Zr$ (M^+), 474.0459; found (EI), 474.0467.

The first diastereomer (0.020 g; 0.0419 mmol), suspended in 10 ml of pentane, was quantitatively converted to its dimethyl analogue by adding methyllithium (0.084 mmol, 1 M, 0.084 ml) and stirring at r.t. for 12 h. The solvent was removed in vacuo, taken up in benzene-d_6, and filtered via a glass-filter paper-tipped cannula into an argon filled NMR tube. The product was confirmed to have C_2-symmetry and hence the *rac*-diastereomer due a single Zr–CH_3 below 0 ppm. ^{1}H-NMR (400 MHz, C_6D_6): δ 6.88–7.37 (m, 8H, arom. H), 5.51 (d, $^3J = 3.3$ Hz, 2H, 3-CH), 5.47 (d, $^3J = 3.2$ Hz, 2H, 2-CH), 3.20 (m, $^3J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 1.18 (d, $^3J = 6.8$ Hz, 6H, $CH(CH_3)(CH_3)$), 1.04 (d, $^3J = 6.8$ Hz, 6H, $CH(CH_3)(CH_3)$) and -1.10 (s, 6H, Zr–$(CH_3)_2$).

4.12. rac- and meso-Bis[1-tert-butyl-indenyl]zirconium dichloride (6b)

The same synthetic procedure employed in the synthesis of **1b** were followed except that *n*-butyllithium (4.6 ml, 2.0 M, 9.3 mmol) was added to **6a** (1.60 g, 9.29 mmol) in 70 ml of THF. After removal of the solvent in vacuo, 80 ml of toluene was added followed by $ZrCl_4$ (1.08 g, 4.64 mmol) in 50 ml of toluene to give an orange–yellow reaction mixture. The clear yellow–orange filtrate from the filtration was concentrated in vacuo with analysis by NMR spectroscopy (not shown) revealing a 50:50 *rac*:*meso* isomer ratio. Crystallization from a toluene solution at −18°C gave the first isomer as an amorphous yellow powder. Dissolving this powder in CH_2Cl_2 and crystallization at −18°C gave fine yellow crystals of **6b** (0.68 g, 29%). These slowly darkened (> 1month) on standing at r.t. to give a dirty-yellow product. However, analysis by NMR spectroscopy indicates that this material still contained substantial amounts of pure **6b**. Due to decomposition in the mother-liquor none of the second isomer could be obtained. Anal. Calc. for $C_{26}H_{30}Cl_2Zr$: C, 61.88; H, 5.99. Found: C, 61.11; H, 5.91%. HR-MS (m/z): Calc. for $C_{26}H_{30}^{35}Cl_2^{90}Zr$ (M^+), 502.0772; found (EI), 502.0753.

The first diastereomer (0.020 g; 0.0396 mmol), suspended in 10 ml of pentane, was quantitatively converted to its dimethyl analogue by adding methyllithium (0.079 mmol, 1 M, 0.08 ml) and stirring at r.t. for 12 h. The solvent was removed in vacuo, taken up in benzene-d_6, and filtered via a glass-filter paper-tipped cannula into an argon filled NMR tube. The product was confirmed to have C_2-symmetry and hence the *rac*-diastereomer due a single Zr–CH_3 resonance below 0 ppm. ^{1}H-NMR (400 MHz, C_6D_6): δ 6.57–7.45 (m, 8H, arom. H), 5.47 (d, $^3J = 3.3$ Hz, 2H, 3-CH), 5.4 (d, $^3J = 3.2$ Hz, 2H, 2-CH), 1.04 (s, 18H, $C(CH_3)_3$), and -1.08 (s, 6H, Zr–$(CH_3)_2$).

4.13. Bis[2-trimethylsilyl-indenyl]zirconium dichloride (7b)

The same synthetic procedure employed in the synthesis of **1b** were followed except that *n*-butyllithium (2.89 ml, 2.2 M, 6.37 mmol) was added to **7a** (1.20 g, 6.37 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 40 ml of toluene was added followed by $ZrCl_4$ (0.74 g, 3.18 mmol) in 40 ml of toluene to give a yellow reaction mixture. The clear yellow–orange filtrate from the filtration was concentrated in vacuo and crystallization effected at −18°C from toluene to give the product as yellow rectangular crystals of **7b** (0.53 g, 31%). Anal. Calc. for $C_{24}H_{30}Cl_2Si_2Zr$: C, 53.70; H, 5.63. Found: C, 53.95; H, 5.62%. HR-MS (m/z): Calc. for $C_{24}H_{30}^{35}Cl_2Si_2^{90}Zr$ (M^+), 534.0310; found (EI), 534.0307.

4.14. rac- and meso-Bis[1-trimethylsilyl-indenyl]zirconium dichloride (8b)

The same synthetic procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (7.53 ml, 1.48 M, 11.2 mmol) was added to **8a** (2.10 g, 11.2 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 80 ml of toluene was added followed by $ZrCl_4$ (1.29 g, 5.57 mmol) in 50 ml of toluene giving a yellow mixture. After stirring for 18 h, the toluene was removed in vacuo and 100 ml of CH_2Cl_2 added to the remaining solid, which was then filtered through a 2 cm celite pad in an inert-air filtration apparatus. The pad was washed with CH_2Cl_2 until the washings were clear, a small aliquot was taken from the filtrate and the solvent removed in vacuo. NMR spectral analysis (not shown) on this sample revealed a 50:50 *rac*:*meso* isomer mix. The clear orange filtrate was placed in the freezer and crystallization effected at −18°C to give yellow needle-like crystals of **8b** (0.84 g, 28%). Anal. Calc. for $C_{24}H_{30}Cl_2Si_2Zr$: C, 53.70; H, 5.63. Found: C, 53.16; H, 5.65%. HR-MS (m/z): Calc. for $C_{24}H_{30}^{35}Cl_2Si_2^{90}Zr$ (M^+), 534.0310; found (EI), 534.0321.

The first diastereomer (0.020 g; 0.037 mmol), suspended in 10 ml of toluene, was quantitatively converted to its dimethyl analogue by adding methyllithium (0.075 mmol, 1 M, 0.075 ml) and stirring at r.t. for 12 h. The solvent was removed in vacuo, taken up in benzene-d_6, and filtered via a glass-filter paper-tipped cannula into an argon filled NMR tube. The product was confirmed to have C_2-symmetry and hence the *rac*-diastereomer due a single Zr–CH_3 resonance below 0 ppm. ^{1}H-NMR (400 MHz, C_6D_6): δ 7.17–7.62 (m, 8H, arom. H), 6.05 (d, $^3J = 2.69$ Hz, 2H, 3-CH), 5.39 (d, $^3J = 3.07$ Hz, 2H, 2-CH), −0.16 (s, 18H, $Si(CH_3)_3$), and −1.08 (s, 6H, Zr–$(CH_3)_2$).

4.15. *rac*- and *meso*-Bis[1-phenyl-indenyl]zirconium dichloride (**10b**)

The same synthetic procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (4.86 ml, 1.85 M, 9.00 mmol) was added to **10a** (1.73 g, 9.00 mmol) in 100 ml of THF. After removal of the solvent in vacuo, 60 ml of toluene was added followed by $ZrCl_4$ (1.05 g, 4.50 mmol) in 60 ml of toluene giving a orange mixture on warming to r.t. and stirring for 18 h. The solvent from the clear red filtrate was removed in vacuo and crystallization effected from CH_2Cl_2 at −18°C. A small aliquot was taken from the filtrate before crystallization and its solvent removed in vacuo. NMR spectral analysis (not shown) of this sample revealed a 54:46 *rac*:*meso* isomer mixture. The *R*,*R*-enantiomer (as determined by X-ray crystallography) was obtained as orange rectangular crystals of **10b** (0.96 g, 40%). No *meso*-isomer was obtained due to degradation of the crystallization liquor during the repeated crystallisations. Anal. Calc. for $C_{30}H_{22}Cl_2Zr$: C, 65.67; H, 4.04. Found: C, 65.67; H, 4.13%. HR-MS (*m*/*z*): Calc. for $C_{30}H^{35}_{22}Cl^{90}_2Zr$ (M^+), 542.0146; found (EI), 542.0180.

4.16. Bis[2-benzyl-indenyl]zirconium dichloride (**11b**)

The same synthetic procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (2.1 ml, 1.85 M, 3.88 mmol) was added to **11a** (0.800 g, 3.88 mmol) in 50 ml of THF. After removal of the solvent in vacuo, 50 ml of toluene was added followed by $ZrCl_4$ (0.451 g, 1.94 mmol) in 50 ml of toluene to give a yellow mixture on warming to r.t. and stirring for 18 h. The clear yellow filtrate from the filtration was concentrated in vacuo and crystallization effected at −18°C. Pure product (**11b**) was obtained as a yellow amorphous solid (0.59 g, 53%). Anal. Calc. for $C_{32}H_{26}Cl_2Zr$: C, 67.11; H, 4.57. Found: C, 67.48; H, 4.62%. HR-MS (*m*/*z*): Calc. for $C_{32}H^{35}_{26}Cl^{90}_2Zr$ (M^+), 570.0459; found (EI), 570.0440.

4.17. *rac*- and *meso*-Bis[1-benzyl-indenyl]zirconium dichloride (**12b**)

The same synthetic procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (9.80 ml, 1.48 M, 14.5 mmol) was added to **12a** (3.00 g, 14.5 mmol) in 100 ml of THF. After removal of the solvent in vacuo, 60 ml of toluene was added followed by $ZrCl_4$ (1.69 g, 7.27 mol) in 60 ml of toluene. This gave an orange mixture on warming to r.t. and stirring for 18 h. The clear orange filtrate from the filtration was concentrated in vacuo. Analysis by NMR spectroscopy (not shown) revealed a 52:48 *rac*:*meso* ratio. Crystallization from toluene at −18°C first gave the *meso*-diastereomer as a yellow amorphous solid. The *rac*-isomer could be obtained as yellow, irregularly shaped crystals from CH_2Cl_2 at −18°C. Total yield of **12b** was 1.34 g (32%). Anal. Calc. for $C_{32}H_{26}Cl_2Zr$: C, 67.11; H, 4.57. Found: C, 66.44; H, 4.62%. HR-MS (*m*/*z*): Calc. for $C_{32}H^{35}_{26}Cl^{90}_2Zr$ (M^+), 570.0459; found (EI), 570.0449.

4.18. Bis[2-(1)-naphthyl-indenyl]zirconium dichloride (**13b**)

The same synthesis procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (2.3 ml, 2.2 M, 4.95 mmol) was added to **13a** (1.2 g, 4.95 mmol) in 80 ml of THF. After removal of the solvent in vacuo, 40 ml of toluene was added followed by $ZrCl_4$ (0.557 g, 2.48 mmol) in 30 ml of toluene to give a yellow mixture reaction mixture on warming to r.t. and stirring for 18 h. The clear yellow filtrate from the filtration procedure was concentrated in vacuo and crystallization from CH_2Cl_2 effected at −18°C. Pure product (**13b**) from the crystallizations was obtained as either a yellow powder or yellow platelets. Total yield was 0.47 g (29%). Anal. Calc. for $C_{38}H_{26}Cl_2Zr$: C, 70.78; H, 4.06. Found: C, 70.48; H, 4.31%. HR-MS (*m*/*z*): Calc. for $C_{38}H^{35}_{26}Cl^{90}_2Zr$ (M^+), 642.0459; found (EI), 642.0475.

4.19. *rac*- and *meso*-Bis[1-(1)-naphthyl-indenyl]-zirconium dichloride (**14b**)

The same synthesis procedure employed in the synthesis of **1b** was followed except that *n*-butyllithium (5.6 ml, 2.2 M, 12.38 mmol) was added to **14a** (3.00 g, 12.38 mmol) in 100 ml of THF. After removal of the solvent in vacuo, 60 ml of toluene was added followed by $ZrCl_4$ (1.44 g, 6.19 mmol) in 50 ml of toluene to give a yellow reaction mixture on warming to r.t. and stirring for 18 h. The solvent was removed in vacuo and replaced with 100 ml of CH_2Cl_2. The slurry was filtered through a 2 cm celite pad in an inert-air filtration apparatus. The solvent was removed from an aliquot taken from this filtrate and analysis by NMR spectroscopy (not shown) revealed a 60:40 *rac*:*meso* isomer ratio. The solvent was removed in vacuo and replaced with a THF–pentane solvent mixture and crystallization effected at −18°C to give a yellow powder. Analysis by NMR spectroscopy revealed this product to be the THF adduct (product:THF = 1:1.5). The product could be freed of solvent by crystallization from toluene. The second diastereomer was obtained by crystallization from toluene. Total yield of **14b** was 0.88 g (22%). Anal. Calc. for $C_{38}H_{26}Cl_2Zr$: C, 70.78; H, 4.06. Found: C, 70.57; H, 4.21%. HR-MS (*m*/*z*): Calc. for $C_{38}H^{35}_{26}Cl^{90}_2Zr$ (M^+), 642.0459; found (EI), 642.0458.

The first diastereomer (0.020 g; 0.031 mmol), suspended in 10 ml of toluene, was quantitatively converted to its dimethyl analogue by adding methyllithium (0.062 mmol, 1 M, 0.062 ml) and stirring at r.t. for 12 h. The solvent was removed in vacuo, taken up in benzene-d_6, and filtered via a glass-filter paper-tipped cannula into an argon filled NMR tube. The product was confirmed to have C_1-symmetry and hence the *meso*-diastereomer due two Zr–CH$_3$ resonances below 0 ppm. ^{1}H-NMR (400 MHz, C$_6$D$_6$): δ 6.87–7.94 (m, 22H, arom. H), 6.20 (d, $^3J = 3.32$ Hz, 2H, 3-CH), 5.73 (d, $^3J = 3.14$ Hz, 2H, 2-CH), -0.41 (s, 3H, Zr–CH$_3$), and -0.52 (s, 3H, Zr–CH$_3$).

4.20. Crystallography

A single crystal (0.28 × 0.16 × 0.12 mm) of **4b** was maneuvered to the end of a 0.30 mm Hilgenberg Mark capillary tube (Glass number 14; Lindemann-glass) and secured in position using a glass fiber. The glass fiber was in turn glued to the walls of the capillary. For **10b** a single crystal (0.74 × 11.5 × 10 mm) was mounted at the end of a glass-fiber using epoxy-glue and protected from the atmosphere by anointing it with a drop of paraffin oil. Both mounted crystals were then secured to a brass-collar before moving them to the goniometer. All of the above procedures were performed in a Schlenk-tube, under a microscope, with a steady stream of Argon gas protecting the system.

Both crystal data sets were collected on a 1K SMART Siemens CCD area detector system using Mo–K$_\alpha$ radiation. X-rays were generated using a regular sealed tube and a Phillips X-ray generator operating at 50 kV and 30 mA. A graphite-monochromator followed by a 0.5 mm collimator was used. The 9 cm wide CCD area detector was mounted 4.5 cm from the crystal and both data sets collected at 173 K. The data collection nominally covered a full hemisphere of reciprocal space, by a combination of three sets of exposures with 1321 and 2169 frames for **4b** and **10b**, respectively.

In order to monitor crystal and instrument stability and to enable crystal decay corrections, the first 50 frames of the first data set were measured again at the end of the data collection. Crystal decay was found to be negligible after analyzing the duplicate reflections.

The determination of the unit cell parameters, crystal orientation and data collection were performed with the SMART system [40]. The data reduction and absorption corrections were performed using the program SAINT [41] and SADABS [42], respectively. The program SHELXTL-PLUS (Version 5.1) was used for the structure solution, refinement and publication preparation [43]. Molecular graphics were prepared using ORTEP-3 for Windows [44]. The structures were solved by direct methods using Fourier techniques and refined by full matrix least-squares methods based on F^2.

Table 4
Crystal data and structure refinement for **4b** and **10b**

Identification code	**4b**	**10b**
Empirical formula	$C_{22}H_{22}Cl_2Zr$	$C_{31}H_{24}Cl_4Zr$
Formula weight	448.52	629.52
Temperature	173(2)	173(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P1n1$	$C2/c$
Unit cell dimensions		
a (Å)	8.1156(4)	90
b (Å)	13.5223(7)	109.188(2)
c (Å)	17.3459(9)	90
α (°)	90	90
β (°)	91.3650(10)	109.188(2)
γ (°)	90	90
Volume (Å^3)	1903.03(17)	2712.5(5)
Z	4	4
D_{calc} (Mg m^{-3})	1.565	1.542
Absorption coefficient (mm^{-1})	0.860	0.819
F(000)	912	1272
Crystal size (mm)	0.28 × 0.16 × 0.12	0.74 × 0.23 × 0.20
Theta range for data collection (°)	1.51–28.30	5.80–28.30
Index ranges	$-10 \leq h \leq 9$; $-16 \leq k \leq 17$; $-22 \leq l \leq 22$	$-14 \leq h \leq 14$; $-24 \leq k \leq 24$; $-18 \leq l \leq 18$
Scan type	ω	ω
Scan width (°)	0.3	0.3
Scan speed	10 s frame exposures	10 s frame exposures
Reflections collected	11 645	14 794
Independent reflections	6497 [$R_{int} = 0.0431$]	3341 [$R_{int} = 0.0175$]
Completeness to $\theta = 28.30$	91.3%	98.8%
Reflections observed ($>2\sigma$)	5211	3088
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6497/15/239	3341/0/164
Goodness-of-fit on F^2	1.076	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0541$, $wR_2 = 0.1053$	$R_1 = 0.0199$, $wR_1 = 0.0532$
R indices (all data)	$R_1 = 0.0759$, $wR_2 = 0.1163$	$R_1 = 0.0224$, $wR_2 = 0.0542$
Largest difference peak and hole (e Å^{-3})	0.701 and -0.716	0.408 and -0.427

The structure of **4b** could be refined as a disorder model in the centrosymmetric space group $P2_1/n$. However, it was possible to resolve the disorder in the space group $P1n1$ with $Z = 4$, where the two independent molecules in the asymmetric unit correspond to two *racemic* enantiomers. There is also a large correlation matrix when the two enantiomers are allowed to refine in the lower symmetry space group. It was only possible to arrive at an acceptable solution for **4b** by making all the indenyl carbon atoms isotropic. When the structure was solved in an anisotropic mode C5, C14, C15, C17 and C15a became non-positive definite. The five-membered ring was also fitted to a regular pentagon (C–C = 1.42 Å) and allowed to refine as a variable metric group. Two alternate positions were found for C12a in the difference electron density map. These were refined isotropically with a 50% occupancy factor each (viz. C12a and C12b). The remaining non-hydrogen atoms were refined anisotropically. The metallocene **10b** was found to inhabit the space group *C*2/*c* and all of its non-hydrogen atoms were refined anisotropically. For both compounds, the hydrogen atoms were allowed to refine, by riding on their parent atoms. The data collection statistics for these two structures are collected in Table 4.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146396 for compound **4b** and CCDC no. 146395 for compound **10b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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