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Sterically demanding cyclopentadienyl chemistry: synthesis of iron and zirconium complexes of 1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl

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Abstract

Reaction of phenyl magnesium bromide with the α,β-unsaturated ketone 3-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one, followed by an aqueous work-up, generates the pro-chiral tetra-substituted cyclopentadiene, 1-phenyl-3-methyl-4,5,6,7-tetrahydroindene, Cp‡H, a precursor to the η^5-cyclopentadienyl ligand in $(Cp^{‡})_2Fe$ and $[(Cp^{‡})Fe(CO)]_2(\mu\text{-}CO)_2$. Both complexes were generated as mixtures of *rac*-(*RR* and *SS*)- and *meso*-(*RS*)-isomers, and in either case pure *meso*-isomer was isolated by crystallisation and characterised by single crystal X-ray structure, both molecules having crystallographic C_i symmetry. Reduction with Na/Hg cleaves *meso*-(*RS*)-$[(Cp^{‡})Fe(CO)]_2(\mu\text{-}CO)_2$ and the resulting mixture of (*R*)- and (*S*)-$[(Cp^{‡})Fe(CO)_2]^-$ anions reacts with MeI to give racemic $(Cp^{‡})Fe(CO)_2Me$, which was characterised by the X-ray crystal structure. The Cp‡ ligand is more electron donating than (η-C_5H_5) as revealed by the reduction potential of the $(Cp^{‡})_2Fe^+/(Cp^{‡})_2Fe$ couple, $E° = -0.127$ V (vs. Ag | AgCl). Reaction of LiCp‡ with $ZrCl_4$ yields the zirconocene dichloride $[Zr(Cp^{‡})_2Cl_2]$ as mixture of *rac*- and *meso*-isomers, from which pure *rac*-isomer is obtained as a mixture of *RR* and *SS* crystals by recrystallisation. The reaction of *rac*-$[Zr(Cp^{‡})_2Cl_2]$ with LiMe gives *rac*-$[Zr(Cp^{‡})_2Me_2]$. The structures of *RR*-$[Zr(Cp^{‡})_2Cl_2]$ and *rac*-$[Zr(Cp^{‡})_2Me_2]$ have been determined by X-ray diffraction. The structural studies reveal the influence of the bulky substituted cyclopentadienyl ligand on the metal–Cp‡ distances and other metric parameters. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Ferrocene; Iron carbonyls; Zirconium; Chiral metallocene

1. Introduction

The cyclopentadienyl ligand (η-C_5H_5) is one of the most ubiquitous ligands of organotransition-metallic chemistry [1]. The importance of this ligand is primarily due to the ease of synthesis of complexes incorporating one or more cyclopentadienyl rings, the fact that the ligand produces stable complexes by effectively occupying three coordination sites at the metal and the wide variation possible in the steric and electronic properties of these complexes associated with substitution of one of more of the hydrogen atoms in the C_5H_5 ring. Thus, the peralkylated ligand, C_5Me_5, is more electron donating, as revealed in the oxidation potentials of the ferrocenes $[Fe(\eta\text{-}C_5R_5)_2]$ (R = H, Me) [2]. The greater steric size (Tolman angle) of the η-C_5Me_5 ligand is vital to the stabilisation of monomeric complexes of the lanthanides [3]. Two recent areas of development in cyclopentadienyl chemistry have been the design and synthesis of dicyclopentadienyl ligands for the synthesis of ansa-metallocenes [4], and the synthesis of chiral and pro-chiral metallocenes [5], and half-sandwich compounds [6].

This paper describes the synthesis of a bulky pro-chiral cyclopentadiene from a well-established cyclopentenone precursor. The ligand system described here was selected as being the product of a flexible synthesis, where changes to the ligand could be made by varying one of several reagents (cyclohexene, crotonic acid, PhMgBr). Our initial exploration of the coordination chemistry of this ligand has involved the synthesis and

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structural characterisation of some representative examples of iron and zirconium complexes, and these are described here.

Nile and co-workers have reported the synthesis of alkylated 4,5,6,7-tetrahydroindenes via methylation of the corresponding cyclopentenones [7]. The synthesis of cyclopentenones by the Nazarov cyclization [8], and subsequent alkylation is a route to 4,5,6,7-tetrahydroindenes [9] that is significantly more facile and versatile than hydrogenation of metallated indenyl ligands [10]. Reported here is the synthesis and complexation of a more sterically demanding 4,5,6,7-tetrahydroindene, 1-phenyl-3-methyl-4,5,6,7-tetrahydroindene (**1**), from the same ketone precursor utilised by Nile.

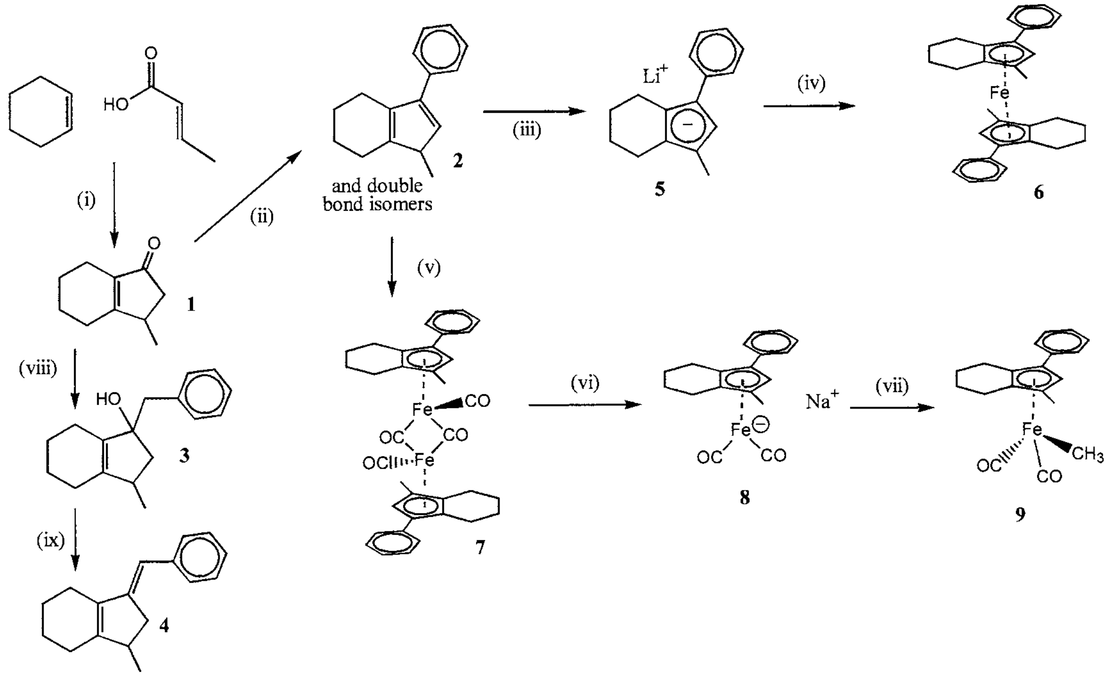
2. Results and discussion

The synthesis of 3-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one (**1**) (Scheme 1) follows the Nazarov cyclization reaction between crotonic acid and cyclohexene in polyphosphoric acid reported originally by Dev [11] and later by Nile and co-workers [12]. In our hands, the yield was optimised by efficiently mixing the crotonic acid and polyphosphoric acid by mechanical stirring at 60°C for ca. 30 min before adding the cyclohexene. Addition of the cyclohexene was carried out over 30 min and the complete mixture was then stirred at 60°C for 2 h. This appears to prevent the occurrence of an exothermic initiation of the cyclization reported by Nile. The second alteration was the use of 10% NaOH solution in water to facilitate the decomposition of the polyphosphoric acid rather than solid ammonium sulphate, the combination of these two changes increases the yield from 36 to 55%.

The reaction of **1** with an excess of phenyl magnesium bromide, followed by acid-catalysed dehydration, yields readily the substituted cyclopentadiene 1-phenyl-3-methyl-4,5,6,7-tetrahydroindene, ($Cp^{\ddagger}H$) **2**. The product was shown by ^{1}H-NMR, ^{13}C-NMR and GC mass spectra to be a mixture of four isomers (one of which is depicted in Scheme 1), differing by the positions of double bonds within the five-membered ring. **2** could be purified by distillation, although with a substantial loss, presumably due to pyrolysis of the diene in the distillation flask.

The synthesis of a range of cyclopentadienes can be achieved by varying the Grignard used in the reaction with **1**, although the limit of this flexibility is demonstrated by $PhCH_2MgBr$, which reacts cleanly with the α,β-unsaturated ketone **1**, to generate, after an acid-catalysed elimination reaction, a benzylidene substituted cyclopentene, **4**, in which the double bond has been generated in conjugation with the aromatic ring.

The $(Cp^{\ddagger})^-$ anion (**5**), can be generated from $Cp^{\ddagger}H$ (**2**), by reaction with one equivalent of BuLi in diethyl ether, and thorough washing to remove any unreacted BuLi. The planar anion **5** is pro-chiral, and its coordination to a metal atom can generate either an *R* or *S* enantiomer (the notation [13,14] is illustrated in Fig. 1). In a non-enantioselective synthesis three isomers are formed the enantiomers *RR* (25%) and *SS* (25%) (com-



Scheme 1. Preparation of 1-phenyl-3-methyl-4,5,6,7-tetrahydroindene and iron complexes. Reagents: (i) PPA; (ii) PhMgBr, then H_2O; (iii) BuLi; (iv) $FeCl_2$; (v) $Fe_2(CO)_9$; (vi) Na/Hg; (vii) MeI; (viii) $PhCH_2MgBr$; then H_2O; (ix) HCl.

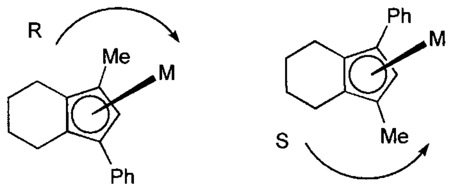


Fig. 1. Absolute configuration of a Cp‡ ligand coordinated to a transition metal.

prising collectively the *rac* diastereomer) and the *meso* diastereomer *SR* (50%). Due to different packing requirements of chiral and centrosymmetric molecules [15], *rac*- and *meso*-diastereomers crystallise under different thermodynamic conditions and can be separated by selective crystallisation. Resolution of the *RR* and *SS* enantiomers, indistinguishable by most methods, is a much more difficult task. Chemically, enantiomers can be separated in the form of their diastereomeric (e.g. alkoxide) derivatives [16], i.e. through the introduction of an additional chiral centre. A racemic mixture of enantiomers can crystallise either together in a racemic crystal (possessing inversion elements of symmetry) or separately in right- and left-handed crystals consisting each of one enantiomer only. Although centrosymmetric crystal structures are much more numerous than chiral [17], such spontaneous resolution is not as rare as is sometimes believed. However, factors directing crystallisation towards chiral or racemic structure, are subtle and by no means fully understood to the present day [18], even though the spontaneous resolution of *rac*-tartaric acid was the starting point of the whole modern stereochemistry [19].

The addition of half an equivalent of $FeCl_2$ to a solution of **5** in THF at 0°C gave the orange substituted ferrocene $(Cp^‡)_2Fe$ (**6**), in moderate yield. The ^{1}H-NMR spectrum of the crude, unpurified, **6** shows two sharp singlets characteristic of a cyclopentadienyl proton, at 3.77 and 3.80 ppm. Since each Cp‡ ligand contains only one such hydrogen (in position 2), the *SS* and *RR* enantiomers are indistinguishable in NMR and either has a molecular symmetry C_2, the entire *rac* isomer should produce only one such resonance. The same is true for the *meso* isomer, which has a C_i molecular symmetry. Crystallisation of crude **6** from alkane solvents gave two crops of microcrystalline powder (total yield 30%), exhibiting only the δ 3.80 ppm resonance. The first crop contained a small number of single crystals suitable for X-ray structure determination (vide infra), which identified the *meso* isomer. The X-ray diffraction pattern of the powder proved identical with the one calculated from the single crystal X-ray structure. On the basis of all this evidence, **6** was synthesised as a mixture of the *rac* and *meso* isomers in a ratio (from NMR intensities) of ca. 45:55, although we could not isolate, in a pure state, the considerably more soluble *rac* isomer.

The crystal structure of **6** is centrosymmetric (space group $P2_1/c$). The molecule (see Fig. 2 and for metric data, Table 1) is located at a crystallographic inversion centre, thus having the *meso* (*RS*) configuration, with the molecular and crystallographic inversion centres co-incident, and a distal mutual orientation of the cyclopentadienyl ligands. Although this conformation reduces ligand–ligand repulsions, the distance between the iron atom and the cyclopentadienyl ring plane, 1.672 Å is still relatively long (cf. 1.648 Å in the triclinic [20] and 1.658 Å in the orthorhombic [21] phases of $Fe(\eta\text{-}C_5H_5)_2$, 1.657 Å in $Fe(\eta\text{-}C_5Me_5)_2$ [22]).

In order to clarify the electronic properties of **6**, its electrochemistry was investigated. The ease of oxidation of substituted ferrocenes relative to the parent $Fe(\eta\text{-}C_5H_5)_2$, can be expressed in terms of $\Delta E_{1/2}$, which is the difference between $E_{1/2}$ for the substituted ferrocene and $Fe(\eta\text{-}C_5H_5)_2$. Cyclic voltammetry of **6** and a mixture of **6** plus $Fe(\eta\text{-}C_5H_5)_2$ as an internal calibrant, gave a value for $\Delta E_{1/2}$ of -0.314 V. It is well established that, for substituted ferrocenes, $E_{1/2}$ decreases upon the introduction of an alkyl group, and increases when a phenyl substituent is introduced [23]. Therefore, the value of $\Delta E_{1/2}$ for **6** is expected to be less negative than that for a ferrocene with three alkyl substituents on each cyclopentadienyl ring and more negative than a ferrocene with only two alkyl substituents per cyclopentadienyl ring. This is confirmed by comparison with values of $\Delta E_{1/2} = -0.340$ V for bis(1-methyl-4,5,6,7-tetrahydroindenyl)iron(II) and $\Delta E_{1/2} = -0.249$ V for bis(4,5,6,7-tetrahydroindenyl)iron(II) [2,24].

Having established the reactivity of the $(Cp^‡)^-$ anion **5**, derived by deprotonation of the cyclopentadiene **2**,

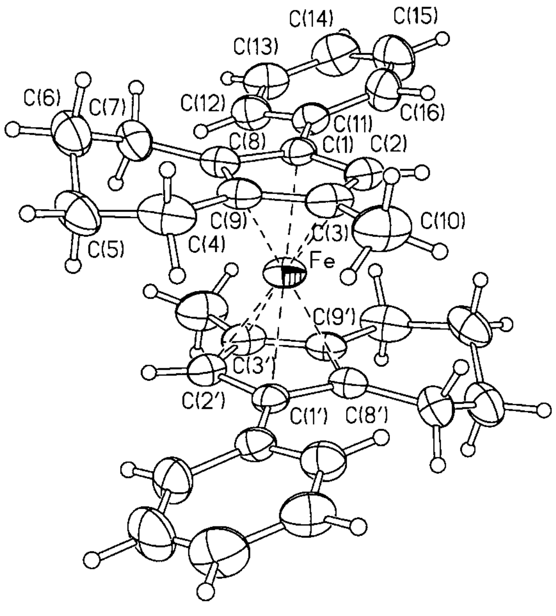


Fig. 2. Molecular structure of **6** (50% displacement ellipsoids). Primed atoms are symmetrically related via the inversion centre.

Table 1
Geometry of metal–$Cp^{\ddagger}$ coordination

	6	**7**	**9**	**10** [b]	**10** [c]	**11** [b]	**11** [c]
Bond distances (Å)							
M [a]–C(1)	2.054(5)	2.123(1)	2.113(2)	2.504(2)	2.501(2)	2.521(2)	2.527(2)
M–C(2)	2.070(5)	2.146(1)	2.109(2)	2.492(2)	2.467(2)	2.448(2)	2.483(2)
M–C(3)	2.087(5)	2.188(1)	2.153(2)	2.569(2)	2.543(2)	2.570(2)	2.560(2)
M–C(8)	2.066(5)	2.104(1)	2.118(2)	2.601(2)	2.605(2)	2.623(2)	2.621(2)
M–C(9)	2.058(5)	2.153(1)	2.129(2)	2.607(2)	2.604(2)	2.631(2)	2.625(2)
C(1)–C(2)	1.450(7)	1.434(2)	1.445(3)	1.442(3)	1.440(3)	1.432(2)	1.433(2)
C(2)–C(3)	1.405(7)	1.426(2)	1.419(3)	1.406(3)	1.407(3)	1.409(2)	1.414(2)
C(3)–C(9)	1.397(8)	1.425(2)	1.428(3)	1.421(3)	1.424(3)	1.420(2)	1.423(2)
C(9)–C(8)	1.438(7)	1.435(2)	1.438(3)	1.410(3)	1.429(3)	1.418(2)	1.416(2)
C(8)–C(1)	1.452(7)	1.445(2)	1.421(3)	1.441(3)	1.426(3)	1.435(2)	1.429(2)
C(1)–C(11)	1.474(7)	1.479(2)	1.487(3)	1.478(3)	1.480(3)	1.479(2)	1.478(2)
τ [d] (°)	17.4	39.4	54.4	15.9	25.1	27.7	26.3
Distances of atoms (Å) from the mean plane of C(1), C(2), C(3), C(9) and C(8) [η-Cp moiety]							
M	1.672	1.761	1.741	2.245	2.232	2.258	2.254
C(4)	−0.01	−0.09	−0.16	−0.10	−0.11	−0.18	−0.16
C(7)	−0.14	−0.16	−0.13	−0.19	−0.19	−0.11	−0.26
C(10)	−0.08	−0.14	−0.10	−0.13	−0.12	−0.12	−0.13
C(11)	−0.08	−0.14	−0.19	−0.04	−0.09	−0.11	−0.12
Distances of atoms (Å) from the mean plane of C(4), C(9), C(8) and C(7)							
C(5)	0.37	0.39	0.25	0.41	0.44	0.32	0.22
C(6)	−0.44	−0.36	−0.47	−0.36	−0.35	−0.45	−0.53

[a] M = Fe (**6**, **7**, **9**), Zr (**10**, **11**).

[b] Atoms C(1) to C(16).

[c] Atoms C(17) to C(32) in the same order.

[d] Dihedral angle between Cp and Ph ring planes.

with metal halide salts, we sought to investigate the reactivity of the free diene **2** towards metallation reactions. Prolonged reflux of **2** with $Fe_2(CO)_9$ in toluene gave a red–brown solution, from which a dark brown powder was precipitated by partial removal of the solvent under reduced pressure. Recrystallisation of this material from CH_3CN gave red–brown crystals identified by a single-crystal X-ray diffraction study as the dimer *meso*-*trans*-bis(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)tetracarbonyldi-iron, $[Fe(Cp^{\ddagger})(CO)_2]_2$ (**7**). Using $Fe(CO)_5$ as the iron source instead of $Fe_2(CO)_9$, produced a significantly lower yield of **7**.

The solution infrared spectrum of **7** contains two bands at 1974 and 1933 cm^{-1} assigned to terminal CO, and a single band at 1759 cm^{-1} assigned to a bridging CO stretch. This pattern of peaks, together with a weak shoulder at 1796 cm^{-1}, is well documented to be characteristic of a solution-phase equilibrium between *cis* and *trans* isomers of a $[CpFe(CO)_2]_2$ dimer [25].

Only one set of ^{1}H- and ^{13}C-NMR resonances is observed for the methyl, phenyl and tetramethylene moieties, indicating that **7** was isolated as a single isomer. The geometry of compound **7** was established by a single-crystal X-ray structural study. In common with compound **6**, compound **7** proved to be a *meso* isomer, the dinuclear molecule lying at a crystallographic inversion centre coincident with the molecular inversion centre (Fig. 3, Table 1). The Fe–Fe distance of 2.5541(5) is intermediate between 2.534(2) Å in *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ [26], and 2.560(1) Å in *trans*-$[Fe(\eta\text{-}C_5Me_5)(CO)_2]_2$ [27] and characteristic for a carbonyl-bridged single bond. The bridging is symmetrical: Fe–C(02) 1.930(1) and Fe–C(02′) 1.939(1) Å, cf. Fe–C(01) 1.753(2) Å for the terminal CO group. The iron atom to cyclopentadienyl ring plane distance of 1.761 Å in **7** is close to the corresponding distances in *trans*-$[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ (1.754 Å) [28] and in *trans*-$[Fe(\eta\text{-}C_5Me_5)(CO)_2]_2$ (1.765 Å) [29].

The dimer **7** can be cleaved using well-established methodology, and the reductive cleavage with Na/Hg amalgam gives the sodium salt of the $[Fe(Cp^{\ddagger})(CO)_2]^-$ anion, **8**. This salt has not been isolated but was reacted directly with MeI to yield $[Fe(Cp^{\ddagger})(CO)_2Me]$ (**9**). Since the di-iron starting material is the achiral *RS* (*meso*) isomer, cleavage of the iron–iron bond will give a racemic mixture of iron anions, **8** and hence a racemic mixture of iron methyl complexes, **9**.

The NMR spectra of **9** reveal the presence of a metal-bound methyl ligand, by a sharp singlet at $\delta = 0.01$ ppm in the ^{1}H spectrum, and at $\delta = -13.4$ ppm in the ^{13}C spectrum. The solution infrared spectrum shows the presence of a *cis*-dicarbonyl fragment with two bands at 2025 and 1979 cm^{-1}. Compound **9** is a low melting solid and was purified by sublimation; the sublimed material usually melted to a red oil (distillation), but a dark red solid was obtained by careful, slow sublimation and provided single crystals of suitable quality to determine the X-ray crystal structure (see Fig. 4, Table 1).

The crystal of **9** is racemic, containing both the *R* and *S* enantiomers. The iron atom lies substantially closer to the cyclopentadienyl ring plane (1.741 Å) than in **7**. The difference can be due to different π acceptor strengths of the opposing ligands, competing with the cyclopentadienyl for the d electrons of Fe. Thus, strong iron–carbonyl d–π* backbonding weakens the iron–cyclopentadienyl bond in **7** relative to **6**, while in **9** the substitution of a σ-methyl ligand (with no π-acceptor capacity) for a carbonyl group partially relieves the competition. The iron–methyl σ-bond length of 2.062(2) Å is in agreement with the values of 2.04–2.07 Å in the three previously known structures containing $CpFe(CO)_2Me$ moieties [30]. The Fe–CO distances of 1.757(2) and 1.748(2) Å are unexceptional.

Having established the metallation chemistry of both the neutral tetrahydroindene and lithium tetrahydroindenide salt through the synthesis and characterisation of iron complexes, we explored the chemistry of two representative examples of Group 4 metallocenes, $[Zr(Cp^{‡})_2X_2]$ (X = Cl, Me). The zirconocene dichloride, **10**, was prepared by the reaction of freshly sublimed $ZrCl_4$ with $LiCp^{‡}$ in diethyl ether. The ^{1}H-NMR spectrum of the crude reaction mixture shows two sharp resonances at $\delta = 6.32$ and 5.88 ppm, which are assigned to the single hydrogen atom attached to the cyclopentadienyl ring in the *rac* and *meso* isomers, respectively. Crystallisation from toluene followed by recrystallisation from dichloromethane gave yellow crystals of the pure (by NMR spectra) *rac* isomer, characterised by X-ray crystallography (vide infra). Attempts to isolate pure *meso* isomer by fractional recrystallisation were unsuccessful, yielding either the pure *rac* isomer or a mixture of the *rac* and *meso*. The ^{1}H- and ^{13}C-NMR spectra of the *rac*-**10** were fully assigned using ^{1}H–^{1}H COSY and ^{13}C–^{1}H HETCOR 2-D techniques.

The X-ray study of **10** proved that it crystallises in a chiral space group ($P2_12_12_1$) that possesses no inversion symmetry elements and that both $Cp^{‡}$ ligands in the molecule have the same absolute configuration. Thus, *rac*-**10** undergoes a spontaneous resolution upon crystallisation, forming crystals of pure *SS* and pure *RR* enantiomers. The sample chosen for the X-ray study, has the absolute *RR* configuration of the molecule, which was determined directly from the anomalous X-ray scattering of zirconium atoms.

The molecule (see Fig. 5) has a typical non-bridged Group 4 bent metallocene structure, with two planar η^5-cyclopentadienyl systems forming a dihedral angle of 56.0° and two chloride ligands lying in the bisectral plane of this angle. The Zr–$Cp^{‡}$ distances (Table 1), Zr–Cl(1) and Zr–Cl(2) bond lengths [2.4470(5) and 2.4477(5) Å, respectively] are comparable with those typically found in $Zr(\eta\text{-}C_5H_5)_2X_2$ and $Zr(\eta\text{-}C_5Me_5)_2X_2$ complexes [31]. The $Cp^{‡}$ ligands do not adopt a distal configuration as seen in the ferrocene **6**, rather the bulky cyclohexyl groups of both ligands are directed in the same direction, and the phenyl groups nearly eclipse the methyl groups.

The dimethyl zirconocene, $[Zr(Cp^{‡})_2Me_2]$ (**11**), was readily prepared via the addition of methyl lithium to *rac*-**10** (see Scheme 2 for preparation of zirconium complexes). The ^{1}H-NMR spectrum of the crude reaction mixture possesses a single sharp resonance in the cyclopentadienyl–CH region at $\delta = 4.96$ ppm, indicating the presence of only one isomer in solution. This

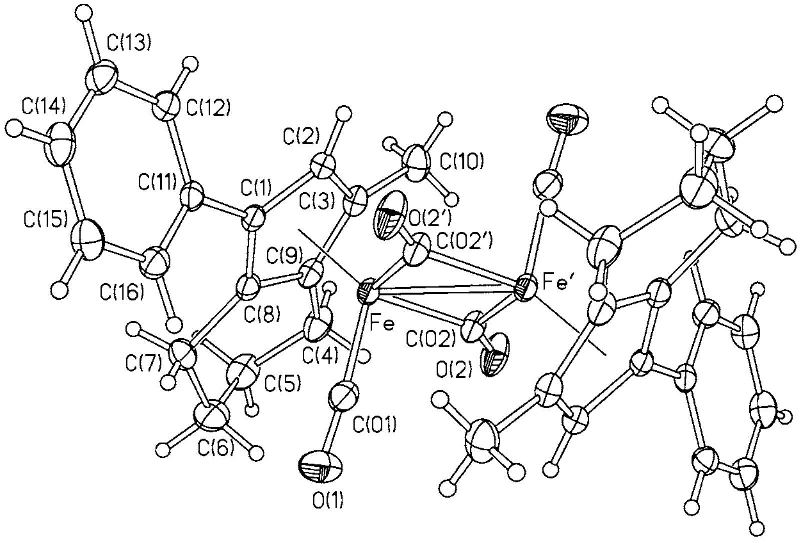


Fig. 3. Molecular structure of **7** (50% displacement ellipsoids). Primed atoms are symmetrically related via the inversion centre.

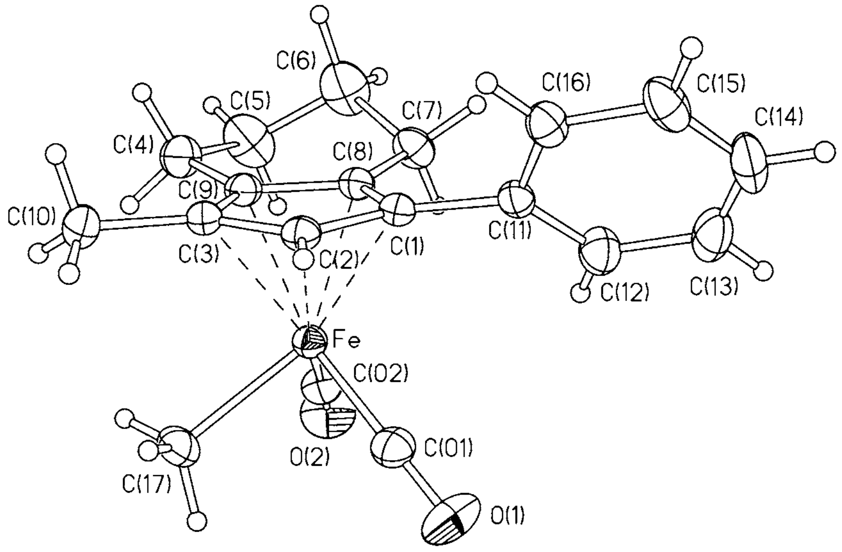


Fig. 4. Molecular structure of **9** (50% displacement ellipsoids).

could be expected to be *rac*-**11**, given that the parent compound was a pure *rac* isomer and that the optical inversion (through breaking and reforming of the metal–cyclopentadienyl bond) would require much harsher reaction conditions [32]. Recrystallization of **11** from hexanes at −20°C gave colourless single crystals suitable for an X-ray structure determination, which confirmed the above expectations. However, unlike the parent compound, *rac*-**11** does *not* spontaneously resolve into left- and right-hand crystals, but crystallises instead in a centrosymmetric structure (space group $P\bar{1}$) comprising equal amounts of the *SS* and *RR* enantiomers.

The asymmetric unit contains one molecule **11** (Fig. 6) and half of a *n*-hexane molecule of crystallisation. The latter is situated at an inversion centre, with each carbon atom disordered over two positions with equal occupancies. Molecule **11** is essentially isostructural with **10**, chlorine atoms being replaced by two methyl groups, which form σ-bonds Zr–C(33) 2.264(2) and Zr–C(34) 2.270(2) Å. The Cp‡ ligands in **11** are slightly more distant from the metal atom than in **10**, probably due to smaller positive charge on the metal atom resulting from lower electronegativity of the methyl group compared to the chloride ligand (2.4 vs. 3.0 on the Pauling's scale) [33]. The alternative, steric, explanation is less plausible, as although the effective van der Waals radius of a methyl group (2.0 Å) is larger than that of a Cl atom (1.8 Å) [34], the dihedral angle between the cyclopentadienyl rings in **11** does not widen (56.1°, cf. 56.0° in **10**), while the Me–Zr–Me angle of 96.64(8)° in **11** is actually smaller than the Cl–Zr–Cl angle 97.78(2)° in **10**.

Both **10** and **11** display approximate (non-crystallographic) molecular symmetry C_2, distorted in the former by slightly different orientations of the phenyl rings. Thus the methyl group of one Cp‡ ligand approaches the phenyl substituent of the other, and vice versa. The mutual orientation of the two cyclopentadienyl rings is somewhat staggered: the projections of the C(2)–H and C(18)–H bonds on the XZrX plane form an angle of 17.5° in **10** and 43.3° in **11**.

The conformation of the Cp‡ ligand in all five structures displays certain similarities (see Table 1). All the substituents on the η^5-ring are tilted out of the ring plane and away from the metal atom; this is common for substituted cyclopentadienyl ligands. The tetrahydrobenzene ring adopts a twisted conformation: the

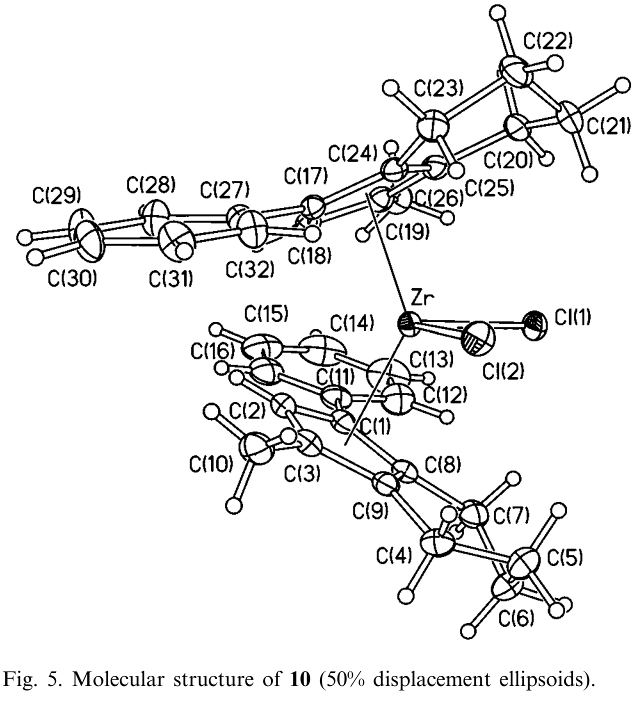
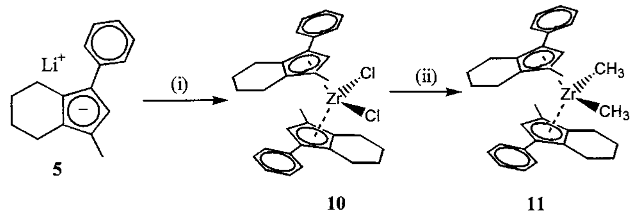


Fig. 5. Molecular structure of **10** (50% displacement ellipsoids).



Scheme 2. Preparation of zirconium complexes. Reagents: (i) $ZrCl_4$; (ii) MeLi.

carbon atoms C(4), C(7), C(8) and C(9) are co-planar, as required by the sp^2-hybridisation of C(8) and C(9); the C(5) atom is displaced from this plane towards the metal atom and C(6) to the opposite side. Such a (relatively stable) conformation may offer some opportunities for stereo- or enantioselective reactions. On the other hand, the phenyl ring rotates easily around the C(1)–C(11) bond, the torsion angle τ increasing with the increase of steric congestion within the metal coordination sphere.

3. Conclusions

We have synthesised a bulky cyclopentadiene which is deprotonated to yield a cyclopentadienyl ligand with enantiotopic faces. The complexation of this ligand with iron and zirconium has demonstrated that its steric demands cause only a relatively small weakening of the η^5-bonding, but at the same time provides interesting possibilities to control the stereochemistry on the metal centre or to screen an electron-poor metal atom. To investigate the latter opportunities, further studies of early transition metal (Groups 3 and 4) complexes of these ligands are in progress.

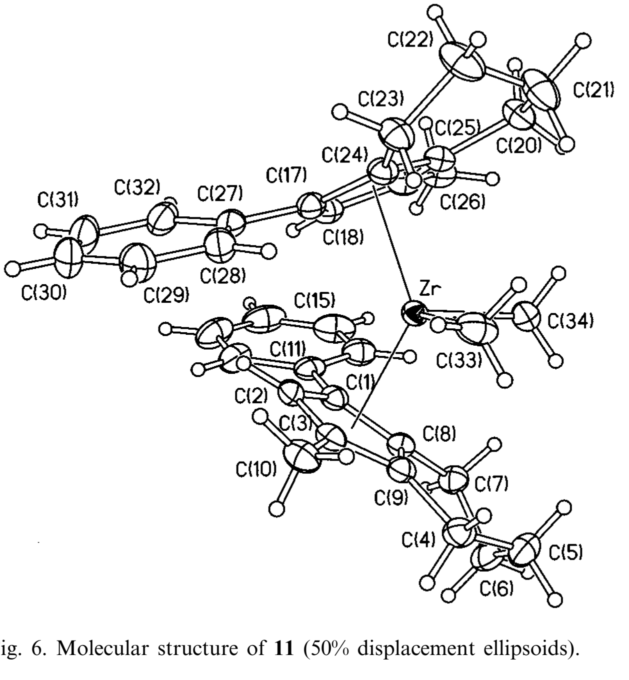


Fig. 6. Molecular structure of **11** (50% displacement ellipsoids).

4. Experimental

4.1. General remarks

Air-sensitive compounds were manipulated under a nitrogen atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on Varian XL-200 (^1H), Varian Gemini-200 (^1H and ^{13}C), Bruker AC-250 (^1H and ^{13}C) or Varian VXR-400 (^1H-^1H COSY and ^1H-^{13}C HETCOR) instruments. Infrared spectra were run as liquid films on a Perkin–Elmer 1615 FTIR spectrometer or as solid samples on a Graseby Specac 10500 Golden Gate coupled to a Perkin–Elmer 1000 series Paragon spectrometer. Mass spectroscopy was undertaken on a VG Micromass 7070E instrument operating in EI mode. Gas chromatography–mass spectroscopy was carried out using a Hewlett–Packard 5890 series gas chromatograph coupled to a Finnegan Mass Lab Trio 1000 mass spectrometer operating in EI mode, using a 1.25 m HP methyl silicone column; column temperature 40°C for 1 min, then 10°C min^{-1} to 270°C. CHN analysis was performed on a EAI CE-440 Elemental Analyser. Cyclic voltammetry was carried out with a EG&G PAR Potentiostat/Galvanostat model 263 using a platinum bead electrode, an Ag | AgCl non-aqueous reference electrode, lithium perchlorate as the supporting electrolyte and acetonitrile as the solvent. Solvents were predried and distilled from appropriate drying agents. Unless indicated otherwise all reagents were used as received. Diiron nonacarbonyl, $Fe_2(CO)_9$, was purified by washing under N_2 with, in order, 25% hydrochloric acid in water, water, ethanol, and diethyl ether, followed by drying under reduced pressure.

4.2. 3-Methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one (1)

Cyclohexene (27.3 g, 0.332 mol) was added dropwise to a mechanically stirred mixture of crotonic acid (28.7 g, 0.333 mol) and polyphosphoric acid (200 g) maintained at 60°C. The mixture was stirred at 60°C for 2 h. A solution of NaOH (10% by mass, 100 cm^3) was added and the slurry stirred for 16 h to facilitate decomposition of the polyphosphoric acid. The mixture was extracted with 40–60°C petroleum ether (3 × 100 cm^3), and the combined organic extracts were washed with 5% ammonia solution in water (50 cm^3), followed by saturated sodium chloride solution (2 × 50 cm^3). The solution was dried over magnesium sulphate and concentrated. Distillation under reduced pressure (b.p. = 58–60°C, ~1 mmHg) afforded **1** as a colourless oil.

Yield 27.4 g, 55%. ^{1}H-NMR: δ (ppm, $CDCl_3$) 1.11 (d, 3H, $J = 6.2$ Hz, CH_3); 1.30–2.80 (series of overlapping m, 11H). $^{13}C\{^1H\}$-NMR; δ (ppm, $CDCl_3$) 19.2, 20.4, 22.1, 22.6, 26.4, 36.7, 43.9 (CH_3, CH, $5CH_2$); 138.3, 177.9, 208.7 (3 quat. C). MS (EI): m/z 150 [M^+]. IR: (cm^{-1}) 1700, 1647 (CO).

4.3. 1-Phenyl-3-methyl-4,5,6,7-tetrahydroindene (**2**)

Phenyl magnesium bromide was prepared from bromobenzene (5.50 g, 35 mmol) and magnesium turnings (0.97 g, 40 mmol) in diethyl ether (100 cm^3). The Grignard solution was cooled to 0°C and 3-methyl-2,3,4,5,6,7-hexahydroind-8(9)-en-1-one (5 g, 33 mmol) was slowly added with stirring. The mixture was allowed to warm to room temperature (r.t.) and stirred for 15 h. After filtration from the excess Mg the solution was quenched with water (50 cm^3) and the organic layer was extracted with diethyl ether (2 × 50 cm^3). The combined organic extracts were dried over magnesium sulphate and filtered. Aqueous HCl (6 M, 0.5 cm^3) was then added and the solution stirred for 2 h. After washing with water and drying with magnesium sulphate the solution was concentrated on a rotary evaporator. Distillation at reduced pressure (b.p. = 80–81°C, ~ 1 mmHg) provided **1** as an orange–red oil. Yield 3.6 g, 52%. ^{1}H-NMR, $^{13}C\{^1H\}$-NMR and GC–MS indicated the presence of several isomers. GC–MS: 4 isomers detected with base $m/z = 210$ [M^+] at retention times 15.78, 16.35, 17.20 and 17.65 min. Anal. Calc. for $C_{16}H_{18}$ (210.32): C, 91.3; H, 8.6. Found: C, 85.7; H, 8.1%. Many samples, including those pure by GC–MS, consistently gave this low analysis.

4.4. 1-Benzylidene-3-methyl-2,3,4,5,6,7-hexahydroind-8(9)-ene (**4**)

Benzyl magnesium chloride was prepared from benzylchloride (4.43 g, 35 mmol) and magnesium turnings (0.97 g, 40 mmol) in diethyl ether (100 cm^3). The Grignard solution was cooled to 0°C and neat **1** (5.00 g, 33.3 mmol) was slowly added with stirring. The mixture was allowed to warm to r.t. and was stirred for 15 h. After filtration from the excess Mg, the solution was quenched with water (50 cm^3) and the organic layer was extracted with diethyl ether (2 × 50 cm^3). The combined organic extracts were dried over magnesium sulphate and then filtered. Aqueous HCl (6 M, 0.5 cm^3) was then added and the solution was stirred for 2 h. After washing with water and drying over $MgSO_4$ the solution was concentrated on a rotary evaporator. Distillation at reduced pressure (b.p. = 105–107°C, ~ 1 mmHg) provided **4** as an orange–red oil. Yield 4.8 g, 64%. ^{1}H-NMR: δ ($CDCl_3$) 1.14 (d, 3H, CH_3); 1.60–2.60 (series of br m, 8H, CH_2); 2.45 (m, 1H, $CH\mathit{H}$); 2.80 (br m, 1H, C(Me)H); 3.18 (m, 1H, $C\mathit{H}H$); 6.16 (s, 1H, =C(Ph)H); 7.10–7.5 (series of m, 5H, phenyl CH's). $^{13}C\{^1H\}$-NMR: δ ($CDCl_3$) 20.2 ($\mathit{C}H_3$); 22.8, 23.1, 23.5, 25.3 (4 × $\mathit{C}H_2$); 39.4 (C(Me)H or cyclopentenyl $\mathit{C}H_2$); 41.6 (cyclopentenyl $\mathit{C}H_2$ or C(Me)H); 114.9 (=C(Ph)H); 125.7 (*para*-CH); 128.4 (*meta*-CH or *ortho*-CH); 128.8 (*ortho*-CH or *meta*-CH); 137.0, 139.8, 149.3, 151.4 (quat. C and *ipso*-C). MS (EI): m/z 224 [M^+].

4.5. Bis(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl) iron(II) (**6**)

Butyl lithium (1.65 M in hexanes, 2.41 ml, 3.91 mmol) was added at 0°C to a solution of 1-phenyl-3-methyl-4,5,6,7-tetrahydroindene **2** (0.83 g, 3.91 mmol) in diethyl ether (30 cm^3) and the solution was stirred for 4 h at 0°C. The resulting lithium 1-phenyl-3-methyl-4,5,6,7-tetrahydroindenide was isolated on a sintered glass filter and washed with diethyl ether (3 × 10 cm^3) to remove excess butyllithium and organic impurities. The solid was then dissolved in THF (40 cm^3) and the resulting solution was added to a slurry of anhydrous $FeCl_2$ (0.25 g, 1.96 mmol) in THF (10 cm^3) at 0°C. The mixture was allowed to warm to r.t. and stirred for 14 h. After quenching with water (50 cm^3), the organic layer was extracted with diethyl ether (2 × 20 cm^3) and dried over magnesium sulphate. After filtration the solution was concentrated and recrystallised from low boiling petroleum ether to give orange crystals of **6**. Yield 0.10 g, 10%. Further concentration and cooling to −20°C, gave an orange microcrystalline powder, shown to be the same *meso*-isomer as the first crop by powder X-ray diffraction (see text). Yield 0.20 g, 20%. Total yield 0.30 g, 30%. ^{1}H-NMR: δ (ppm, C_6D_6) 1.31 (m, 1H, CH_2); 1.37 (m, 1H, CH_2); 1.54–1.72 (overlapping m, 2H, CH_2); 1.58 (s, 3H, CH_3); 1.91 (m, 1H, CH_2); 2.15 (m, 1H, CH_2); 2.27 (m, 1H, CH_2); 2.58 (m, 1H, CH_2); 3.80 (s, 1H, CH); 7.09–7.47 (series of m, 5H, aromatic CH's). $^{13}C\{^1H\}$-NMR: δ (ppm, C_6D_6) 11.2 (CH_3); 21.9, 23.1, 24.1, 24.7 (CH_2); 70.3 (CH); 81.3, 81.4, 82.6, 86.2 (quat. C); 125.4 (*para*-CH); 127.5 (*meta*-CH); 128.6 (*ortho*-CH); 139.2 (*ipso*-CH). M.p. 191–192°C. MS (EI): m/z 474 [M^+]. Anal. Calc. for $C_{32}H_{34}Fe$ (474.471): C, 81.0; H, 7.2. Found: C, 80.8; H, 7.2%.

4.6. Bis(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)tetracarbonyldiiron (**7**)

A toluene (250 cm^3) solution of 1-phenyl-3-methyl-4,5,6,7-tetrahydroindene (**2**) (6.3 g, 30 mmol) and $Fe_2(CO)_9$ (5.0 g, 13.7 mmol) in toluene was refluxed under nitrogen for 24 h. The solvent was removed under reduced pressure and hexanes (100 cm^3) added. The resulting suspension was filtered through Celite and the residue was washed with hexanes (20 cm^3) to remove any remaining ligand. The product was extracted from the residue with toluene (3×50 cm^3) giving a dark red–brown solution. Reduction of the volume of toluene to ca. 25 cm^3 under reduced pressure followed by filtration gave **7** as a very dark red–brown powder. Yield 2.16 g, 25%. ^1H-NMR δ (ppm, C_6D_6) 1.14–3.00 (series of m, 7H, CH_2); 1.65 (s, 3H, CH_3); 2.74 (m, 1H, CH_2); 3.75 (br s, 1H, η^5-C_5H); 7.11–7.43 (series of m, 5H, phenyl CH's). Selected IR: ν (cm^{-1}) 1974, 1933, 1796 (sh), 1759. MS (EI): m/z 642 [M^+]. Anal. Calc. for $C_{36}H_{34}O_4Fe_2$ (642.358): C, 67.3; H, 5.34. Found: C, 66.8; H, 5.8%.

4.7. (1-Phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)dicarbonyl(methyl)iron (***9***)

A solution of bis(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl) di-iron tetracarbonyl (**7**) (1.5 g, 2.34 mmol) in THF (20 cm^3) was added dropwise to a sodium amalgam (0.2 g of Na) under THF (20 cm^3) and stirred at r.t. for 2 h. The THF solution was decanted away from the amalgam, the amalgam washed with portions of THF (2×20 cm^3) and the THF portions combined. The solution was cooled to 0°C, and iodomethane (0.65 cm^3, 1.4 g, 10 mmol) was added and the reaction mixture was allowed to warm to r.t. and stirred for 1 h. Volatiles were removed under reduced pressure and the residue extracted with hexanes (20 cm^3). The mixture was filtered and the volatiles removed under reduced pressure to leave an orange oily residue. Sublimation onto a liquid nitrogen cooled probe gave **9** as an oily orange solid. Yield 0.67 g, 45%. ^1H-NMR δ (ppm, $CDCl_3$) 0.01 (s, 3H, Fe–CH_3); 1.40–2.80 (series of m, 8H, CH_2); 1.81 (s, 3H, CH_3); 4.85 (s, 1H, CH); 7.28–7.39 (series of m, 5H, phenyl CH's). ^{13}C-NMR (ppm, $CDCl_3$) −13.4 (Fe–CH_3); 10.6 (CH_3); 21.2 (CH_2); 22.0 (CH_2); 22.8 (CH_2); 23.1 (CH_2); 84.0 (CH); 94.2 (quat. C); 94.8 (quat. C); 100.0 (quat. C); 100.5 (quat. C); 127.0 (*para*-phenyl CH); 128.0 (*ortho*-/*meta*-phenyl CH); 128.2 (*meta*-/*ortho*-phenyl CH); 134.1 (*ipso*-phenyl C); 218.0 (CO); 218.1 (CO). Selected IR: ν (cm^{-1}) 1996 (vs), 1943 (vs). MS (EI): m/z 336 [M^+]. Anal. Calc. for $C_{19}H_{20}O_2Fe$ (336.214): C, 67.8; H, 6.0. Found: C, 67.0; H, 5.9%.

4.8. Dichlorobis(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)zirconium (***10***)

A slurry of freshly sublimed $ZrCl_4$ (0.55 g, 2.4 mmol) in Et_2O (20 ml) was added to a slurry of lithium(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenide) (1.0 g, 4.6 mmol) in Et_2O (20 ml) at 0°C under N_2. The reaction mixture was slowly warmed to r.t. and was stirred for 13 h. The Et_2O was removed under reduced pressure and toluene (20 ml) was added. The reaction mixture was filtered to remove LiCl and reduced in volume to ca. 5 ml. Cooling to −20°C for 20 h gave yellow–brown semi-crystalline material, further recrystallization from CH_2Cl_2 at −20°C gave **10** as a yellow crystalline solid. Yield 1.0 g, 72%. ^1H-NMR: δ (ppm, $CDCl_3$) 1.24 (s, 3H, CH_3); 1.44 (m, 1H, –$CH_2CH_2CH_2CH_2$–); 1.75 (overlapping m, 2H, –$CH_2CH_2CH_2CH_2$–); 2.03 (m, 1H, –$CH_2CH_2CH_2CH_2$–); 2.30 (m, 1H, –$CH_2CH_2CH_2CH_2$–); 2.54 (m, 1H, –$CH_2CH_2CH_2CH_2$–); 2.92 (m, 1H, –$CH_2CH_2CH_2CH_2$–); 3.33 (m, 1H, –$CH_2CH_2CH_2CH_2$–). 5.81 (s, 1H, CH); 7.27 (overlapping m, 3H, *ortho*-CH and *para*-CH); 7.43 (t, 2H, *meta*-CH). $^{13}C\{^1H\}$-NMR: δ (ppm, $CDCl_3$) 13.3 (CH_3); 21.2 (–$CH_2CH_2CH_2CH_2$–); 23.0 (–$CH_2CH_2CH_2CH_2$–); 24.0 (–$CH_2CH_2CH_2CH_2$–); 25.4 (–$CH_2CH_2CH_2CH_2$–); 108.9 (CH); 119.9, 125.7, 131.3, 132.5, 134.1 (quat. C or *ipso*-C); 126.8 (*para*-CH); 127.1 (*ortho*-CH); 128.8 (*meta*-CH). Anal. Calc. for $C_{32}H_{34}Cl_2Zr$ (580.754): C, 66.2; H, 5.9. Found: C, 66.0; H, 5.9%.

4.9. Rac-bis(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)dimethylzirconium (***11***)

Methyl lithium (1.6 M in Et_2O, 1.25 ml, 2.0 mmol) was added to a diethyl ether (10 ml) solution of *rac*-**10** (0.23 g, 0.4 mmol) at 0°C. The solution was warmed to r.t. and stirred for 24 h. The Et_2O was removed under reduced pressure and hexanes (20 ml) added. The solution was filtered to remove LiCl and reduced in volume to ca. 5 ml. Cooling to −20°C for 48 h gave colourless crystals of **11**. Yield 0.19 g, 86%. ^1H-NMR: δ (ppm, C_6D_6) −0.20 (s, 3H, Zr–CH_3); 1.46 (s, 3H, CH_3); 1.40, 1.70, 1.85, 2.43, 2.63, 2.78, 2.95 (series of m, 8H, CH_2); 4.96 (s, 1H, CH); 7.27 (overlapping m, 3H, *ortho*-CH and *para*-CH); 7.03 (m, 2H, *meta*-CH). $^{13}C\{^1H\}$-NMR: δ (ppm, C_6D_6) 39.8 (Zr–CH_3); 12.6 (CH_3); 22.3, 23.7, 24.2, 25.0 (CH_2); 104.5 (CH); 119.0, 120.0, 123.3, 126.0 (quat. C); 125.9 (*para*-CH); 126.7 (*ortho*-CH); 128.7 (*meta*-CH); 136.3 (*ipso*-C). Anal. Calc. for $C_{34}H_{40}Zr \cdot (C_6H_{14})_{1/2}$ (583.007): C, 76.2; H, 8.1. Found: C, 76.5; H, 8.1%.

4.10. X-ray crystallography

Single-crystal diffraction experiments were carried out on a Bruker AXS SMART three-circle diffractometer with a 1 K CCD area detector, using graphite-monochromated Mo–K_α radiation ($\bar{\lambda} = 0.71073$ Å) and SMART software [35]. The crystals were cooled using a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat [36]. The data collection nominally covered a hemisphere of reciprocal space, by a combination of three or four sets of ω scans (in steps of 0.3° ω) at different ϕ angles. The reflection intensities were inte-

Table 2
Crystal data and structure refinement

Compound	**6**	**7**	**9**	**10**	**11**
Empirical formula	$C_{32}H_{34}Fe$	$C_{36}H_{34}Fe_2O_4$	$C_{19}H_{20}FeO_2$	$C_{32}H_{34}Cl_2Zr$	$C_{34}H_{40}Zr\cdot\frac{1}{2}C_6H_{14}$
Formula weight	474.44	642.33	336.20	580.71	582.97
T (K)	150	150	150	150	150
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a (Å)	9.021(1)	11.444(1)	10.359(1)	11.342(1)	11.446(3)
b (Å)	13.778(1)	11.211(1)	9.312(1)	14.786(2)	11.451(3)
c (Å)	9.600(1)	11.527(1)	17.635(1)	15.814(2)	13.609(4)
α (°)	90	90	90	90	106.09(4)
β (°)	94.19(1)	103.05(1)	106.95(1)	90	107.57(4)
γ (°)	90	90	90	90	104.00(3)
V (Å^3)	1190.0(2)	1440.7(2)	1627.3(2)	2652(1)	1527(1)
Z	2	2	4	4	2
D_{calc} (g cm^{-3})	1.324	1.481	1.372	1.454	1.268
μ (cm^{-1})	6.5	10.5	9.3	0.636	0.383
$F(000)$	504	668	704	1200	618
Crystal size (mm)	0.30 × 0.30 × 0.15	0.58 × 0.48 × 0.20	0.34 × 0.26 × 0.20	0.38 × 0.18 × 0.16	0.30 × 0.24 × 0.20
Max. 2θ (°)	51	60	55	55	55
Reflections collected	5882	14 599	11 260	21 504	10 043
Unique reflections	1935	3949	3702	6091	6888
R_{int}	0.068	0.036	0.027	0.035	0.012
Observed reflections $I > 2\sigma(I)$	1541	3622	2836	6088	6224
Max./min. transmission	0.9099, 0.7742	0.8189, 0.5728	0.8311, 0.7586	0.8943, 0.8052	0.9317, 0.8199
Refined parameters	167	258	279	453	502
Goodness-of-fit on F^2	1.22	1.10	1.09	1.039	1.146
$R[F^2 > 2\sigma(F^2)]$	0.067	0.027	0.035	0.024	0.027
$wR(F^2)$, all data	0.189	0.075	0.095	0.050	0.061
Residual max., min. $\Delta\rho$ (e Å^{-3})	0.73, −0.52	0.41, −0.40	0.79, −0.35	0.30, −0.29	0.74, −0.38

grated using SAINT software [35]. Absorption corrections were performed by semi-empirical method based on multiple scans of equivalent reflections using SADABS routine [37], or (for **7**) by numerical integration based on face-indexing [38]. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL programs.[37] All non-H atoms were refined in anisotropic approximation, all H atoms were refined in isotropic approximation or (for **6** and the disordered hexane in **11**) were treated as 'riding'. The absolute configuration of **10** was determined by refinement of the Flack parameter [39], which converged at 0.01(2), the expected value being 0 for the correct and 1 for the inverted configuration. Crystal data and experimental details are listed in Table 2.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 116237–116241 for **6**, **7**, **9**, **10** and **11**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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