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Enantiospecific synthesis of a planar chiral fluorenylzirconium *ansa*-metallocene: synthesis and structures of [1-(9-fluorenyl)- and [1-(1-methyl-9-fluorenyl)-2-(2-indenyl)naphthalene]zirconium dichloride

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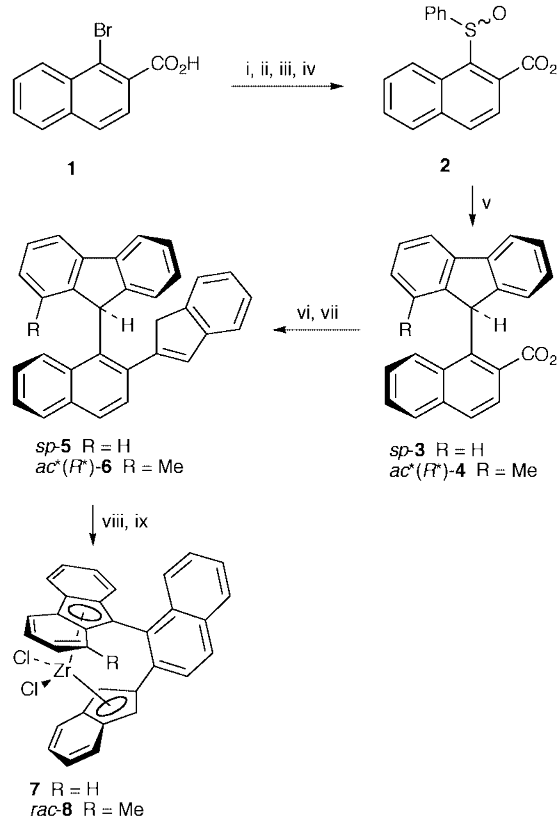
Di-lithiation of +*ac*(*R*)-1-methyl-9-[2-(2-indenyl)-1-naphthyl]fluorene, +*ac*(*R*)-6, generates an axially chiral fluorenyl ligand, (a-*S*)-10, which on reaction with $ZrCl_4$ enantiospecifically provides the planar chiral *ansa*-zirconocene (p-*S*)-[1-(1-methyl-9-fluorenyl)-2-(2-indenyl)-naphthalene]zirconium dichloride, (p-*S*)-8; single crystal X-ray structures have been determined for the racemic *ansa*-zirconocene *rac*-8 and the related C_s-symmetric *ansa*-zirconocene 7.

Planar chiral group IV metallocenes in which the cyclopentadienyl ligands are bridged (*ansa*-metallocenes) continue to attract great interest in the areas of stereoregular α-olefin polymerisation[1] and asymmetric organic synthesis.[2] In the search for new complexes with desirable reactivity and stereoselectivity, considerable effort has been directed at the challenges associated with obtaining stereochemically pure metal complexes.[3] In the case of polymerisation catalysts, the emphasis has been on the selective synthesis of racemic C_2-symmetric *ansa*-metallocenes at the expense of *meso* diastereoisomers. Applications in the area of asymmetric organic synthesis impose the additional requirement of enantiomeric purity. Recently, we demonstrated that a new ligand design—axially chiral cyclopentadienyl ligands—has the potential to allow the enantiospecific synthesis of planar chiral cyclopentadienylmetal complexes containing pendant donor atoms.[4] Here we describe the enantiospecific synthesis of a planar chiral fluorenylzirconium *ansa*-metallocene, linked through a 1,2-naphthalene bridge, using an axially chiral fluorenyl ligand. While fluorenylzirconium *ansa*-metallocenes have been extensively studied as catalysts for olefin polymerisation,[5] chiral complexes have only ever been prepared as the racemates and complexes with a C(sp^2)–C(sp^2) bridge are unprecedented.[6]

For our initial studies, racemic isopropyl 1-(phenylsulfinyl)-naphthalene-2-carboxylate (**2**) was prepared in an overall yield of 73% from 1-bromo-2-naphthoic acid (**1**), as outlined in Scheme 1.† Reaction of the sulfoxide **2** with fluorenyllithium or 1-methylfluorenyllithium afforded the coupled products *sp*-**3** and *ac**(*R**)-**4** in 91 and 88% yields, respectively. Following the precedence of Bosnich and co-workers,[7] reaction of *sp*-**3** and *ac**(*R**)-**4** with the di-Grignard reagent derived from 1,2-bis-(chloromethyl)benzene, followed by acid-catalysed dehydration of the intermediate 2-indanols, provided the 2-indenyl ligands *sp*-**5** and *ac**(*R**)-**6** in 70 and 49% overall yields, respectively. Metallation of both *sp*-**5** and *ac**(*R**)-**6** was achieved by di-lithiation with BuLi in THF solution, followed by replacement of the solvent with benzene and reaction of the dianions with $ZrCl_4$. After removal of inorganic salts and concentration, the *ansa*-zirconocene complexes **7**‡ and *rac*-**8**§ crystallised in 55 and 57% yields, respectively. The complexes **7** (Fig. 1)¶ and *rac*-**8** (Fig. 2)|| were characterised by single crystal X-ray analysis; the geometry about zirconium is within expected values for both complexes,[8] with (η^5-centroid)–Zr–(η^5-centroid) angles of 127.94(4) and 126.8(1)°, and Cl–Zr–Cl angles of 99.05(5) and 97.9(3)°, for **7** and *rac*-**8**, respectively. For both complexes, the indenyl and fluorenyl Zr–C distances vary considerably; those for the indenyl groups vary from 2.467(4) to 2.630(4) Å, and 2.45(2) to 2.69(2) Å, for **7** and *rac*-**8**, respectively; the Zr–C distances for the fluorenyl groups vary from 2.406(3) to 2.713(4) Å, and 2.43(2) to 2.69(3) Å, for **7** and *rac*-**8**, respectively. While the crystal structure of **7** shows only minor deviations from C_s-symmetry, in complex *rac*-**8** the cyclopentadienyl moieties display consymmetric rotations,[9] with respect to the $ZrCl_2$ bisector, of −14.5 and +11.5° for the fluorenyl and indenyl groups, repectively (for the enantiomer illustrated in Fig. 2); the mean plane of the naphthalene is also rotated from the orthogonal, with respect to the mean plane of the fluorenyl group, by 9.4° (the indenyl group rotated away from the fluorenyl 1-methyl substituent).



Scheme 1 *Reagents and conditions*: i, $SOCl_2$ (10 equiv.), pyridine (1 equiv.), benzene, 25 °C, 16 h; ii, Pr^{i}OH (2 equiv.), pyridine (2 equiv.), CH_2Cl_2, 25 °C, 30 min; iii, PhSNa (1.2 equiv.), DMF, 70 °C, 16 h; iv, OXONE® (2 equiv.), acetone (12 equiv.), MeCN/aqueous $NaHCO_3$, 25 °C, 7 h; v, fluorenyllithium or 1-methylfluorenyllithium (1.2 equiv.), THF, 0 °C, 30 min; vi, 1,2-$C_6H_4(CH_2MgCl)_2$ (1.5 equiv.), THF, −78 to 25 °C, 16 h; vii, TsOH (0.05 equiv.), benzene, reflux, 20 min; viii, BuLi (2.4 equiv.), THF, 0 °C, 60 min; ix, $ZrCl_4$ (1.1 equiv.), benzene, 25 °C, 90 min.

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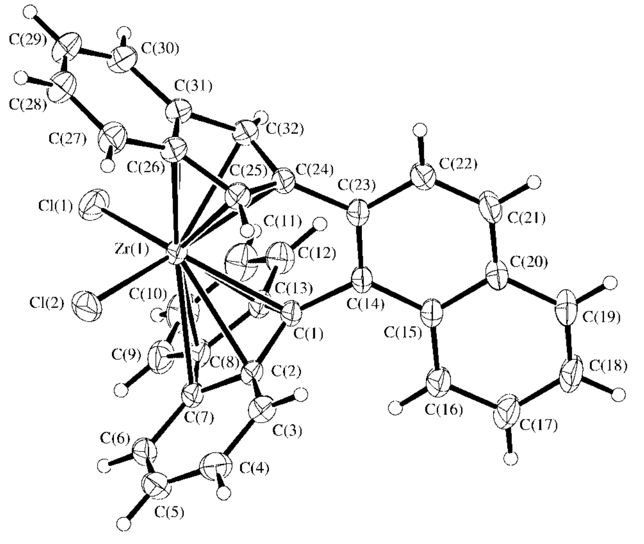


Fig. 1 ORTEP plot of **7**, with crystallographic numbering; 25% thermal ellipsoids are shown for non-hydrogen atoms. Selected distances (Å) and angles (°): Zr(1)–Cl(1) 2.407(1), Zr(1)–Cl(2) 2.412(1), Zr(1)–C(1) 2.406(3), Zr(1)–C(2) 2.580(3), Zr(1)–C(7) 2.704(4), Zr(1)–C(8) 2.713(4), Zr(1)–C(13) 2.552(3), Zr(1)–C(24) 2.479(3), Zr(1)–C(25) 2.467(4), Zr(1)–C(26) 2.620(4), Zr(1)–C(31) 2.630(4), Zr(1)–C(32) 2.496(4); Cl(1)–Zr(1)–Cl(2) 99.05(5), centroid(1)–Zr(1)–centroid(2) 127.94(4).

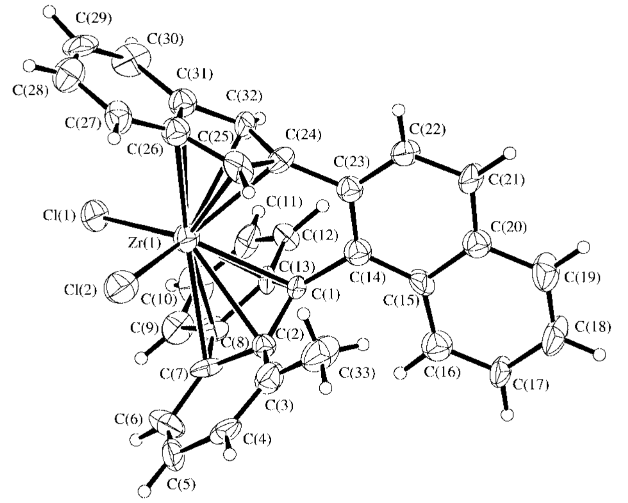
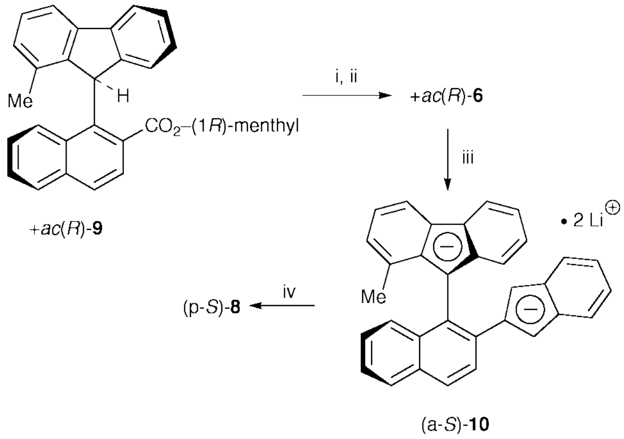


Fig. 2 ORTEP plot of *rac*-**8**, with crystallographic numbering; 25% thermal ellipsoids are shown for non-hydrogen atoms. Selected distances (Å) and angles (°): Zr(1)–Cl(1) 2.383(6), Zr(1)–Cl(2) 2.424(8), Zr(1)–C(1) 2.43(2), Zr(1)–C(2) 2.63(3), Zr(1)–C(7) 2.69(3), Zr(1)–C(8) 2.67(2), Zr(1)–C(13) 2.54(3), Zr(1)–C(24) 2.49(3), Zr(1)–C(25) 2.45(2), Zr(1)–C(26) 2.59(2), Zr(1)–C(31) 2.69(2), Zr(1)–C(32) 2.54(2); Cl(1)–Zr(1)–Cl(2) 97.9(3), centroid(1)–Zr(1)–centroid(2) 126.8(1).



Scheme 2 *Reagents and conditions*: i, 1,2-$C_6H_4(CH_2MgCl)_2$ (1.5 equiv.), THF, −78 to 25 °C, 16 h; ii, TsOH (0.05 equiv.), benzene, reflux, 15 min; iii, BuLi (2.4 equiv.), THF, 0 °C, 60 min; iv, $ZrCl_4$ (1.1 equiv.), benzene, 25 °C, 90 min.

We have described the asymmetric synthesis of +*ac*(*R*)-**9** (Scheme 2†), in 75% de, through a coupling reaction of (1*R*)-menthyl (*S*)-1-(*p*-tolylsulfinyl)naphthalene-2-carboxylate with 1-methylfluorenyllithium at 0 °C; recrystallisation furnishes +*ac*(*R*)-**9** in ⩾96% de.[10] Reaction of +*ac*(*R*)-**9** with the di-Grignard reagent derived from 1,2-bis(chloromethyl)benzene, followed by acid-catalysed dehydration of the intermediate 2-indanol, then recrystallisation, provided the 2-indenyl ligand +*ac*(*R*)-**6** in 64% overall yield, $[\alpha]_{549}$ −382 (*c* 1.9, benzene). The enantiomeric excess of +*ac*(*R*)-**6** was determined to be >99% by HPLC analysis.** Metallation of +*ac*(*R*)-**6**, as described above for the racemate, provided the *ansa*-zirconocene complex (p-*S*)-**8** in 35% yield, $[\alpha]_{549}$ +30.4 (*c* 3.0, C_6D_6). While the enantiomeric excess of (p-*S*)-**8** was not determined directly, treatment of a benzene solution of (p-*S*)-**8** with glacial acetic acid led to the quantitative recovery of +*ac*(*R*)-**6** in >99% ee,** confirming the enantiomeric purity of (p-*S*)-**8**. We have previously demonstrated that the fluorenyllithium derived from an asymmetrically substituted 9-(1-naphthyl)fluorene retains an axial chiral element.[10] Di-lithiation of +*ac*(*R*)-**6** therefore generates the fluorenyllithium (a-*S*)-**10**, where the descriptor for absolute configuration refers to the fluorenyl–naphthyl axis. In the case of the *ansa*-zirconocene (p-*S*)-**8** derived from (a-*S*)-**10**, the single descriptor for absolute configuration refers to the planar chirality of the fluorenyl–zirconium moiety as the axial chirality of the precursor fluorenyllithium is considered to be latent in the complex.

Notes and references

† For simplicity and consistency with Scheme 2, only the +*ac*(*R*)-enantiomers of *ac**(*R**)-**4** and *ac**(*R**)-**6**, and the (p-*S*)-enantiomer of *rac*-**8**, are illustrated in Scheme 1.

‡ *Selected data* for **7**: Found C, 67.4; H, 3.5; Cl, 12.55. $C_{32}H_{20}Cl_2Zr$ requires C, 67.8; H, 3.6; Cl, 12.5%. δ_H (400 MHz, C_6D_6) 6.03 (2H, s, indenyl 1- and 3-H), 6.86–7.04 (8H, m, Ar-H), 7.23 (1H, dd, *J* 7.3, 7.6, Ar-H), 7.31–7.35 (5H, m, Ar-H) and 7.75–7.79 (4H, m, Ar-H).

§ *Selected data* for *rac*-**8**: Found C, 68.2; H, 3.8; Cl, 11.7. $C_{33}H_{22}Cl_2Zr$ requires C, 68.3; H, 3.8; Cl, 12.2%. δ_H (400 MHz, C_6D_6) 1.87 (3H, s, CH_3), 6.04 and 6.08 (each 1H, br s, indenyl 1- and 3-H), 6.80–7.00 (6H, m, Ar-H), 7.10 (1H, d, *J* 8.4, Ar-H), 7.16–7.38 (5H, m, Ar-H), 7.50 (1H, d, *J* 8.1, Ar-H), 7.66–7.73 (3H, m, Ar-H) and 7.83 (1H, d, *J* 8.4 Hz, Ar-H).

¶ *Crystal data* for **7**: $C_{35}H_{23}Cl_2Zr$, $M = 605.69$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.134(2)$, $b = 12.745(2)$, $c = 10.334(2)$ Å, $\alpha = 98.72(1)$, $\beta = 112.29(1)$, $\gamma = 68.47(1)°$, $V = 1375.4(5)$ Å^3, $T = 294$ K, $Z = 2$, μ(Cu-Kα) = 5.336 cm^{-1}, $N = 5673$, N(unique) = 4926 ($R_{int} = 0.048$), $N_{obs} = 3982$ [$I > 3.00\sigma(I)$]. Data collected from a cut twinned crystal. The asymmetric unit contains a complex molecule and a benzene solvate molecule centred on an inversion site; benzene hydrogen atoms were modelled isotropically with restrained bond lengths. Final $R(F) = 0.0353$, $R_w(F) = 0.0398$.

|| *Crystal data* for *rac*-**8**: $C_{33}H_{22}Cl_2Zr$, $M = 580.66$, orthorhombic, space group *Pbca* (no. 61), $a = 20.802(5)$, $b = 29.313(9)$, $c = 8.312(6)$ Å, $V = 5068(3)$ Å^3, $T = 294$ K, $Z = 8$, μ(Cu-Kα) = 5.738 cm^{-1}, $N = 2817$, N(unique) = 2724 ($R_{int} = 0.056$). Data collection was stopped when decay exceeded 50% and data with decay to 30% were subsequently used in the solution and model refinement. A linear decay correction factor was applied to the data, of which 39% were classified as observed with $N_{obs} = 1072$ [$I > 2.50\sigma(I)$]. Atoms C(2), C(14), C(16), C(20), C(23), C(26) and C(31) were modelled with isotropic thermal parameters. Final $R(F) = 0.0820$, $R_w(F) = 0.0733$. CCDC reference number 186/1809. See http://www.rsc.org/suppdata/dt/a9/a910246i/ for crystallographic files in .cif format.

** A 4.6 × 250 mm column [Chiralpak OT(+), Daicel] was used with methanol as eluent at a flow rate of 0.5 ml min^{-1}, column temp. 3 °C, detection 254 nm, t_R: 18.1 min for +*ac*(*R*)-**6** and 22.2 min for −*ac*(*S*)-**6**.

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