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Chiral annulated cyclopentadienyl ligands: Synthesis and crystal structure of both *exo* and *endo* Rh{η^5-Cp′}(cod) [Cp′ = (4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl] [1]

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Abstract

The title homochiral cyclopentadiene ligand $C_{31}H_{30}$ (i.e., Cp′H, **5**) has been synthesised from camphor in four steps. The lithium salt of this ligand reacted with $[Rh(cod)Cl]_2$ to give predominantly racemic (η^4-cycloocta-1,5-diene)[η^5-1,2,3-triphenyl-4-methyl-7-isopropyl-1H-indenyl]rhodium although the desired RhCp′(cod) complex was formed in 20% yield as an equal mixture of *endo* **7a** and *exo* **7b** isomers. The X-ray structures of **7a** and **7b** have been determined at room temperature with use of Mo-K_α radiation ($\lambda = 0.71069$ Å). Both compounds crystallise in the orthorhombic space group $P2_12_12_1$ (D_2^4, No. 19); for compound **7a**, $a = 13.549(23)$ Å, $b = 14.490(25)$ Å, $c = 15.909(14)$ Å, $V = 3123(8)$ Å^3, $Z = 4$ and $D_c = 1.303$ g cm^{-3} and the structure was refined to $R = 0.0488$ on the basis of 2545 independent reflections. For the *exo* isomer **7b**, $a = 13.301(18)$ Å, $b = 15.599(32)$ Å, $c = 14.436(19)$ Å, $V = 2995(10)$ Å^3, $Z = 4$ and $D_c = 1.359$ g cm^{-3}; the structure was refined to $R = 0.0362$ on the basis of 4620 independent reflections. Bromine reacts with the compounds **7a** and **7b** to give the corresponding $[\{Rh(Cp')\}_2(\mu\text{-}Br_3)]Br_3$. © 1998 Elsevier Science S.A.

Keywords: Chiral annulated cyclopentadienyl; Rhodium complexes; Fused camphor derivatives

1. Introduction

In the last ten years there has been considerable interest in the development of chiral cyclopentadienyl ligands [1–5], which has been primarily motivated by the belief that such ligands could play a valuable role in catalytic enantioselective synthesis, particularly for reactions or substrates where chiral phosphine ligands are ineffective. To date, considerable success has been achieved with chiral metallocene complexes that catalyse the polymerization of alkenes [6–8], the hydrogenation of nonfunctionalised alkenes [9–11] and C=N bonds [12], the hydrosilylation of ketones [13,14] or act as chiral Lewis acid catalysts [15,16]; all of these reactions take place with high enantioselectivities, often approaching $\geq$ 95% e.e. Less success has been achieved with monocyclopentadienyl catalysts [2,17]; the only chiral monocyclopentadienyl complex that has given impressive results is $ZrCp^{**}Cl_3$ (where Cp^{**} is a cyclopentadienyl ligand having fused bornyl substituents) [18]. Clearly, having fused chiral substituents is one of the features that contributes to the effectiveness of this ligand.

Having embarked on a programme to synthesise an effective chiral monocyclopentadienyl ligand to develop chiral analogues of $[Rh(C_5Me_5)Cl_2]_2$ and other attractive monocyclopentadienyl catalysts [19–23], we decided to incorporate a fused camphor substituent into a cyclopentadienyl ring. Further, since we and others have shown that phenyl substituents on a cyclopentadienyl ring adopt a chiral array [24,25], we were also attracted to the idea of having phenyl substituents on the other positions of the cyclopentadienyl ring because of the possibility that the fused chiral substituent would dictate

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[1] Dedicated to Peter Maitlis on the occasion of his 65th birthday.

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the chiral array of the phenyl substituents, and in this way transmit the chirality to the metal environment. Thus, our target chiral cyclopentadiene ligand containing all these desirable features was (4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindene, **5**. The synthesis and reactions of this ligand are described herein.

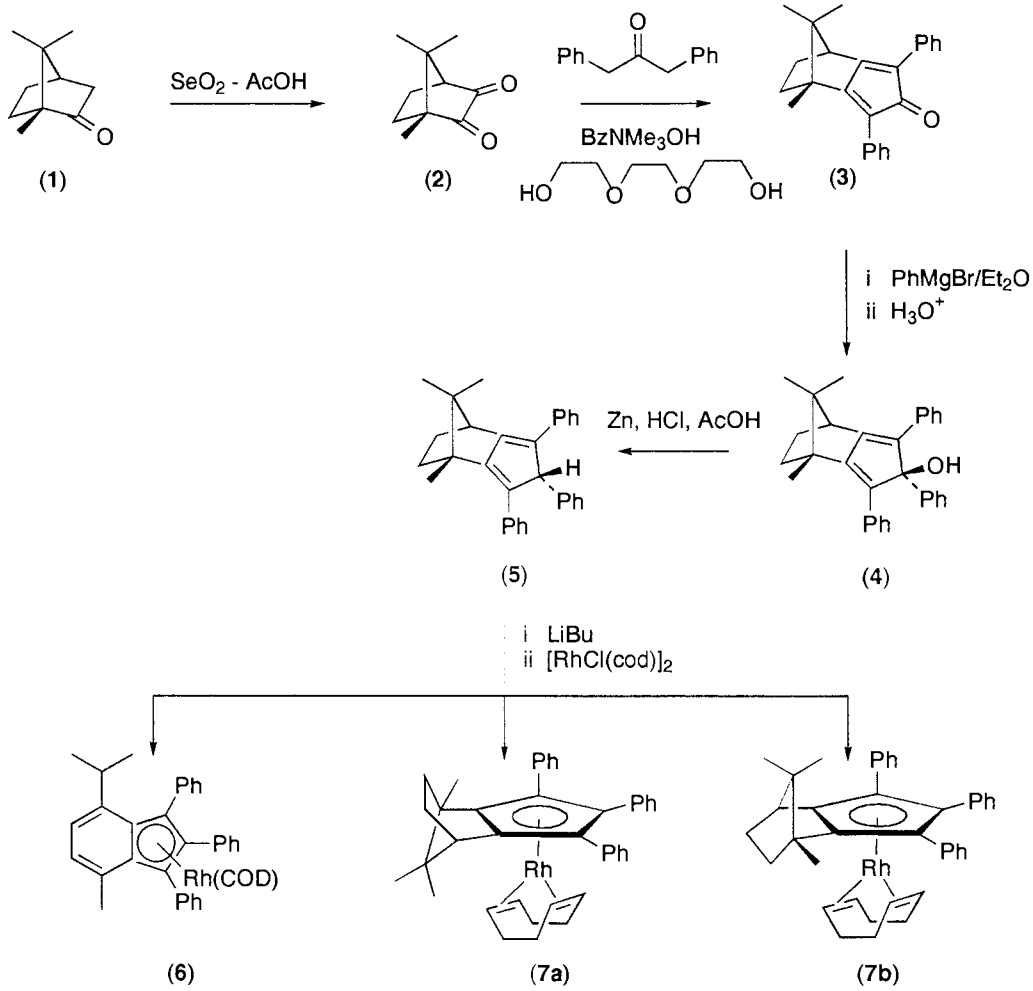
2. Results and discussion

2.1. Ligand synthesis

Although initially we thought we were being somewhat ambitious in targeting (4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindene, we were delighted to find that this ligand could be synthesised in just four steps from readily available camphor as illustrated in Scheme 1. The relative simplicity of this synthesis compared to the syntheses of most other chiral cyclopentadienes is another attractive feature of this ligand. The first two steps involved a slight modification of a literature procedure to give (4*S*,7*R*)-1,3-diphenyl-4,8,8-trimethyltetrahydro-4,7-methanoindenone [26]. Addition of phenyl magnesium bromide to a solution of this indenone gave the corresponding carbinol, **4**. From the $^{1}H\{^{13}C\}$ NMR spectra of the product, it was apparent that there is only one isomer of the carbinol present, and this presumably arises from the Grignard attacking the carbonyl on the less hindered face; the ability of the *syn*-7 methyl group of camphor to block the *exo* attack of nucleophiles is well documented [27,28]. The required cyclopentadiene (**5**) was obtained by treatment of the alcohol, **4** with hydrochloric acid and zinc in acetic acid although $^{1}H\{^{13}C\}$ NMR spectroscopy showed the product to be a mixture of structural and stereo-isomers due to the rearrangement of the double bonds and epimerisation at C_1, C_2, and C_3.

2.2. Rhodium complexes

Treatment of the cyclopentadiene **5** with butyl lithium and di-μ-chlorobis(cyclooctadiene)dirhodium gave a mixture of products of which the major component (70%) was a rhodium cyclooctadiene complex. However, the $^{1}H\{^{13}C\}$ NMR spectra, the elemental analysis and mass spectrum were all at variance with a bornylcy-



Scheme 1.

clopentadienyl complex, whereas, all the data were consistent with an indenyl complex **6**. The indenyl complex **6** is chiral by virtue of the substituted indenyl ligand possessing prochiral faces, although the product obtained was the racemic modification and showed no overall optical activity.

The formation of this new ring system from the cyclopentadiene **5** is unusual, but related rearrangements have been reported. For example, when α-fenchyl tosylate is heated under reflux with acid it gives rise to the α-fenchyl cation; this proceeds through a series of rearrangements via the bornyl cation to 4-methyl isopropylbenzene [29,30]. In our case, we believe that the rhodium is involved in the formation of **6** that entails a dehydrogenation of the anion of **5**. However, we cannot rule out a radical pathway as proposed for the related rearrangement of bornyls to give olefinic products [31,32].

The minor product (20%) of the complexation of the cyclopentadiene **5** to rhodium was shown by $^{1}H\{^{13}C\}$ NMR spectroscopy to consist of a 1:1 mixture of the *endo*- and *exo*- form of the desired cyclopentadienyl complex, **7a** and **7b**, respectively. The presence of the methyl group on the 4-position of the bornyl fragment confers planar chirality on the cyclopentadienyl ligand. Thus, the *endo* and the *exo* complexes may be designated 1*S* and 1*R*, respectively [33]. It is interesting that no face selectivity was observed; whereas, in the case of monocyclopentadienyl metal complexes of the non-phenylated fused bornylcyclopentadiene, a moderate face selectivity of ca. 3:1 was found on complexation to $Co(CO)_2$ [34]. We attribute the lack of face selectivity to the much high temperature utilised in the synthesis of these triphenyl substituted cyclopentadienyl complexes coupled with the fact that the longer rhodium–cyclopentadienyl bond distance, compared to that of cobalt, allows the rhodium to be less discriminating between the steric demands of the two faces of the ligand.

Attempts were made to separate the *endo* and *exo* isomers by a variety of chromatographic techniques LPLC, TLC, and HPLC, but the mixture remained intractable. The isomers were fortuitously separated by a series of crystallisations from heptane and diisopropyl ether.

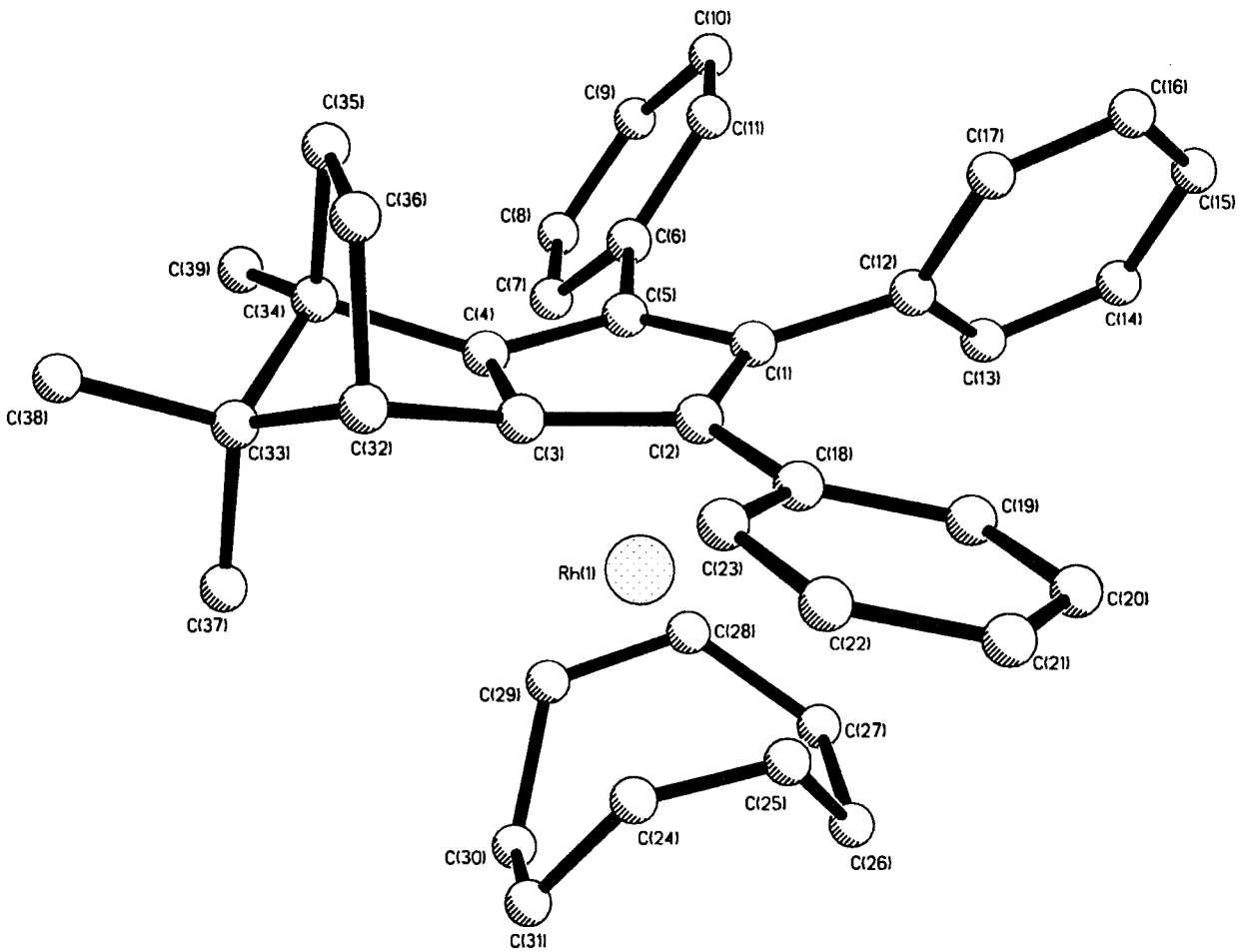


Fig. 1. Molecular structure of Rh{η^5-Cp′}(cod)} **7a** [Cp′ = *endo*-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl] showing the atomic numbering system.

Both the $^{1}H\{^{13}C\}$ NMR spectra of the *endo*-**7a** and *exo*-**7b** forms of the rhodium complex showed interesting differences. The most striking feature of the ^{1}H NMR spectra is the difference in the ^{1}H resonance frequencies of the methyl groups of the bornyl unit. The methyl groups of the *exo*-complex give rise to signals at δ_H 0.72, 0.75, and 0.95 ppm whereas the *endo*-complex gives signals at δ_H 0.96, 1.11, and 2.07 ppm. Selective decoupling, NOE and two-dimensional NMR experiments indicated that the high-frequency shift of one of the methyl groups in the *endo*-complex (**7a**) is due to shielding of the protons attached to C(37) (Fig. 1) from the olefinic double bonds of the cycloocta-1,5-diene ligand.

The most remarkable feature of the ^{13}C NMR spectra of the two complexes is the range of resonance frequencies displayed by the *exo*-complex. Thus, whereas in the *endo*-complex the signals for the CH_2 carbon atoms appear at δ_C 27.2 and 34.3 ppm, the corresponding signals are at δ_C 29.0 and 38.6 ppm in the *exo*-complex. Similarly, in the *endo*-complex, the nonproton bearing carbon atoms of the chiral group, C(33) and C(34), are located at δ_C 51.6 and 54.6 ppm, whereas in the *exo*-complex these signals appear at δ_C 51.4 and 68.4 ppm. Further, the signals associated with the cyclopentadienyl carbon atoms occur in the range δ_C 91–117 ppm for the *endo*- complex, which is typical for a cyclopentadienylrhodium(I) complex [35]; whereas, the signals for the *exo*-complex are spread over a much larger range with one signal at δ_C 127 ppm.

Oxidation of the rhodium cyclooctadiene complexes **7a** and **7b** with bromine gave the corresponding rhodium (III) complexes $[\{Rh(Cp')\}_2(\mu\text{-}Br_3)]Br_3$ **8a** and **8b**. These were characterised by elemental analysis, NMR and mass spectroscopy. Both **8a** and **8b** are active hydrogenation catalysts, and their use as enantioselective hydrogenation catalysts will be reported together with studies using related chiral cyclopentadienyl rhodium complexes [36].

*2.3. X-ray crystallographic structures of **7a** and **7b***

It is an interesting crystallographic nicety that the *endo*- and *exo*-fused (4*S*)-bornyl structures crystallise in the same space group, and with *very* similar unit cell

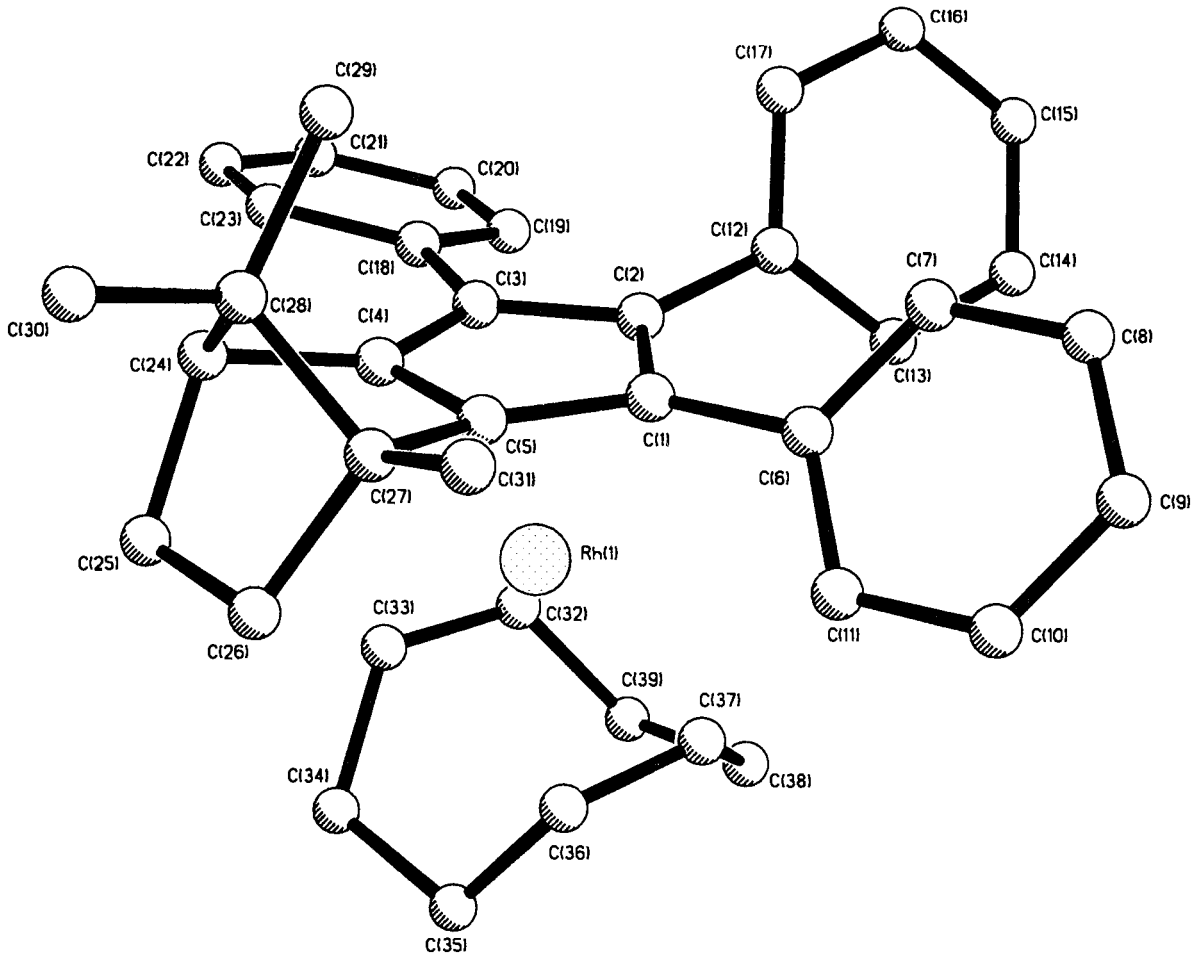


Fig. 2. Molecular structure of Rh{η^5-Cp′}(cod)} **7b** [Cp′ = *exo*-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl] showing the atomic numbering system.

constants—to such an extent that initial thoughts were that the two structures were identical. However, the structures are in no way isomorphous, since the sites of the two rhodium atoms are entirely different with respect to the internal symmetry elements. The two structures are shown in Figs. 1 and 2. Table 1a and b list the positional parameters with estimated standard deviations for the *endo*- and *exo*- isomers, respectively, and the corresponding selected bond distances and bond angles are presented in Table 2a and b.

Both the *exo*- and *endo*-forms of the complex consist of planar C_5 rings with three phenyl substituents inclined to the cyclopentadienyl ring in a similar propeller array, i.e., at angles of 50, 62 and 15° for the *exo*- and at angles of 49, 63 and 16° for the *endo*-isomer. The small inclination of the phenyl adjacent to the side of the (4*S*)-bornyl fragment which does *not* carry a methyl substituent is noteworthy. Also, unlike the other phenyl substituents, this phenyl is displaced out of the cyclopentadienyl plane towards the metal with the *ipso* carbon atoms of phenyl groups deviating from the mean plane by 0.063 Å and 0.054 Å for the *exo*- and *endo*-isomers, respectively. In both complexes, the conformation of the phenyl propellers appears to be dictated by the methyl group on the bornyl fragment. Thus, in the *exo*- and *endo*-isomers, the shortest carbon–carbon distance between this carbon and the adjacent phenyl ring is an acceptable 3.37 and 3.38 Å respectively, whereas in both isomers this would have been unacceptably short if the phenyl groups had adopted the alternative propeller conformation.

The distance of the rhodium atom from the cyclooctadiene ligand is essentially the same in both isomers, but the distance of the rhodium atom from the cyclopentadienyl plane is 1.917 Å in the *exo*- isomer and 1.933 Å in the *endo*-isomer. In both cases, the cyclopentadienyl ring is bonded slightly asymmetrically to the rhodium, with the two carbons forming a junction with the (4*S*)-bornyl fragment somewhat more remotely sited. This is more pronounced in the case of the *endo*-isomer with deviations of 0.52 and 0.57 Å in the Rh–C distances compared to 0.34 and 0.33 Å for the *exo*-structure.

2.4. Circular dichroism studies

Polarimetry studies of the *endo*- and *exo*-complexes **7a** and **7b** respectively, showed that the *endo*-form is dextrorotatory and the *exo*- form is levorotatory. Thus, the optical activity of the complex is not only dependent upon the fused chiral substituent but also depends upon the planar chirality of the complex, i.e., which face of the C_5 ring is bound to the rhodium atom. This marked difference in the chiro-optical behaviour of the complexes is also reflected in their circular dichroism spectra. The UV spectrum of the *endo*-form has λ_{max} at 264 nm ($\varepsilon = 32\,300$) while the maximum Cotton effect are at 216 nm ($\Delta\varepsilon - 22$), 230 nm ($\Delta\varepsilon + 36$), 258 nm ($\Delta\varepsilon + 9$), and 303 nm ($\Delta\varepsilon + 19$). The *exo*-form has λ_{max} 254 nm ($\varepsilon = 38\,400$) with Cotton effect maxima at 220 nm ($\Delta\varepsilon + 22$), 237 nm ($\Delta\varepsilon - 7$), 263 nm ($\Delta\varepsilon - 18$), and 290 nm ($\Delta\varepsilon - 26$).

These two CD spectra (Fig. 3) display pseudo enantiomorphic behaviour at longer wavelengths. It should be noted that similar behaviour was observed for the chiral tetraphenylcyclopentadienyl complexes $Rh(C_5Ph_4R^*)(C_8H_{12})$ where R^* = menthyl or neomenthyl [23]. In the case of the tetraphenylcyclopentadienyl complexes, the metal is complexed to the same face, and the pseudo-enantiomorphic behaviour observed in the circular dichroism spectra is due to the effect of the chiral-directing groups menthyl and neomenthyl. The bornylcyclopentadienyl complexes contain identical chiral ligands; consequently, the pseudo-enantiomorphic behaviour in the CD spectra is due to the fact that the rhodium is complexed to opposite faces of the C_5 ring.

3. Experimental

3.1. General

All reactions of moisture-sensitive reagents were performed under nitrogen. THF was heated under reflux over sodium benzophenone ketyl and distilled under nitrogen. Benzene, xylene and diethyl ether were heated under reflux over sodium and distilled under nitrogen whereas triethylene glycol was dried over calcium sulphate. All other solvents and reagents were used without purification. NMR spectra were recorded on a Bruker AM250 spectrometer. Low-resolution mass spectra were obtained on a Kratos MS80 fitted with a FAB source operating through a DS55 data system. UV spectra were recorded on a Perkin Elmer 559 UV/VIS spectrophotometer. Optical rotations were measured on a Perkin Elmer 141 polarimeter, and CD spectra were obtained by the National CD Service SERC Birkbeck College, University of London. Elemental analysis were performed by the University of Sheffield microanalysis service.

3.2. Synthesis of (−)-camphorquinone, **2**

This was prepared in 65% yield by the literature method [37]. M.p. 194–195°C lit. 198°C. (Found: C, 72.9; H, 8.3. Calc. for $C_{10}H_{14}O_2$ C, 72.3; H, 8.5%); $[\alpha]_D$ (20°C, $l = 0.1$, $c = 1.270$, $CHCl_3$) −107.9d; δ_H (250 MHz; solvent $CDCl_3$; standard $SiMe_4$) 0.94 (3H, s, CH_3), 1.07 (3H, s, CH_3), 1.11 (3H, s, CH_3), 1.64 (2H, m, CH_2), 1.93 and 2.16 (2H, m, CH_2), 2.64 (1H, d, J_{HH} 5.5 Hz); δ_C (63 MHz; solvent $CDCl_3$, standard $SiMe_4$) 8.4, 17.0, and 20.6 (CH_3), 29.6 and 21.9 (CH_2), 57.7 (CH), 42.2 and 58.3 (C), 202.4 and 204.4 (C, carbonyl).

Table 1

(a) Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for (η^4-cycloocta-1,5-diene)[*endo*-η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7a**

Atom	*x*	*y*	*z*	U_{eq}^a
Rh(1)	2389(1)	1579(1)	1723(1)	34(1)
C(1)	1856(5)	869(5)	2913(4)	35(2)
C(2)	2423(4)	1686(4)	3135(3)	33(2)
C(3)	3447(5)	1492(5)	2867(4)	39(2)
C(4)	3467(5)	626(5)	2476(5)	41(3)
C(5)	2482(5)	237(4)	2463(4)	37(2)
C(6)	2220(5)	−705(5)	2146(5)	45(3)
C(7)	2523(7)	−988(4)	1347(4)	55(3)
C(8)	2274(7)	−1866(5)	1058(5)	74(4)
C(9)	1739(7)	−2463(5)	1556(7)	85(4)
C(10)	1445(7)	−2197(6)	2353(7)	80(4)
C(11)	1693(5)	−1321(5)	2638(6)	58(3)
C(12)	823(4)	646(4)	3172(5)	38(2)
C(13)	84(5)	440(6)	2600(6)	49(3)
C(14)	−844(6)	165(6)	2870(5)	59(3)
C(15)	−1055(6)	81(5)	3716(6)	62(3)
C(16)	−327(6)	276(6)	4292(6)	71(4)
C(17)	591(6)	572(5)	4030(5)	51(3)
C(18)	2083(5)	2545(5)	3569(4)	42(3)
C(19)	1079(6)	2789(5)	3617(5)	48(3)
C(20)	777(6)	3595(5)	4008(5)	57(3)
C(21)	1448(7)	4203(6)	4335(5)	67(4)
C(22)	2436(8)	3973(6)	4299(5)	77(4)
C(23)	2761(6)	3154(6)	3929(5)	60(3)
C(24)	2548(7)	2981(5)	1350(4)	54(3)
C(25)	1528(5)	2770(5)	1456(4)	46(3)
C(26)	830(7)	2670(6)	718(5)	66(3)
C(27)	761(6)	1679(6)	398(5)	74(3)
C(28)	1670(6)	1128(5)	619(5)	56(3)
C(29)	2644(7)	1387(5)	413(4)	61(3)
C(30)	2879(7)	2278(7)	−78(5)	77(4)
C(31)	3035(7)	3098(6)	499(5)	75(4)
C(32)	4503(5)	1711(6)	3129(4)	54(3)
C(33)	5115(6)	1219(6)	2429(6)	58(3)
C(34)	4549(6)	286(6)	2510(6)	55(3)
C(35)	4644(7)	86(6)	3484(6)	77(4)
C(36)	4645(7)	1063(7)	3902(5)	76(4)
C(37)	5075(5)	1676(6)	1562(5)	70(3)
C(38)	6234(6)	1159(8)	2674(7)	97(5)
C(39)	4861(6)	−499(6)	1935(6)	82(4)

(b) Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for (η^4-cycloocta-1,5-diene)[*exo*-η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7b**

Atom	*x*	*y*	*z*	U_{eq}^a
Rh(1)	−146(1)	−879(1)	−838(1)	27(1)
C(1)	21(4)	−161(3)	−2185(3)	30(1)
C(2)	−615(3)	331(3)	−1574(3)	29(1)
C(3)	−27(3)	543(2)	−763(3)	27(1)
C(4)	976(3)	243(3)	−930(4)	29(1)
C(5)	1003(3)	−177(3)	−1781(3)	28(1)
C(6)	−241(4)	−478(3)	−3125(3)	35(1)
C(7)	−721(4)	55(4)	−3757(4)	47(2)
C(8)	−934(5)	−243(5)	−4640(4)	60(2)
C(9)	−688(5)	−1061(5)	−4891(4)	62(2)
C(10)	−201(5)	−1586(4)	−4290(4)	61(2)
C(11)	14(5)	−1301(3)	−3397(3)	49(2)
C(12)	−1634(3)	629(3)	−1821(3)	30(1)
C(13)	−2410(4)	64(4)	−2001(4)	39(2)
C(14)	−3350(4)	379(4)	−2270(4)	51(2)
C(15)	−3506(5)	1240(5)	−2347(4)	54(2)

Table 1 (continued)

(b) Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for (η^4-cycloocta-1,5-diene)[*exo*-η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7b**

Atom	*x*	*y*	*z*	U_{eq}^a
C(16)	−2750(5)	1804(4)	−2171(4)	56(2)
C(17)	−1804(4)	1501(4)	−1911(4)	45(2)
C(18)	−377(3)	1007(3)	76(3)	31(1)
C(19)	−1394(4)	1096(4)	290(4)	43(2)
C(20)	−1704(4)	1491(4)	1094(4)	52(2)
C(21)	−1019(5)	1811(4)	1707(4)	54(2)
C(22)	−13(5)	1729(4)	1512(4)	61(2)
C(23)	298(4)	1344(4)	708(4)	47(2)
C(24)	2077(4)	363(4)	−647(4)	41(2)
C(25)	2498(4)	−541(4)	−410(4)	47(2)
C(26)	2525(4)	−1001(4)	−1354(4)	50(2)
C(27)	2106(4)	−329(4)	−2039(4)	37(2)
C(28)	2531(4)	529(4)	−1626(4)	45(2)
C(29)	2116(5)	1353(4)	−2081(5)	61(2)
C(30)	3688(4)	584(5)	−1613(5)	65(3)
C(31)	2337(4)	−494(5)	−3061(4)	56(2)
C(32)	−1049(4)	−1099(3)	344(4)	41(2)
C(33)	−40(4)	−1230(4)	573(3)	42(2)
C(34)	427(5)	−2102(4)	714(5)	64(2)
C(35)	271(6)	−2695(4)	−98(5)	69(2)
C(36)	69(5)	−2221(3)	−1003(4)	50(2)
C(37)	−905(5)	−1980(4)	−1287(4)	48(2)
C(38)	−1844(5)	−2170(4)	−729(5)	64(2)
C(39)	−1793(5)	−1836(4)	241(4)	60(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised U_{ij} tensor.

3.3. Synthesis of (−)-(4S,7R)-1,3-diphenyl-4,8,8-trimethyl-2H,4,5,6,7-tetrahydro-4,7-methanoinden-2-one, *3*

This was synthesised by a modification of the literature procedure [26]. (−)-Camphorquinone (20 g, 0.12 mol) and dibenzylketone (25.3 g, 0.12 mol) were dissolved in hot triethylene glycol (100 cm^3) and heated to 130°C under nitrogen. Benzyltrimethylammonium hydroxide in methanol (40%) (Triton B, Aldrich) (13 cm^3) was added via a hypodermic syringe and the reaction was stirred at 125°C for 90 h. The mixture was allowed to cool, poured into water (400 cm^3) and then extracted into ether (400 cm^3); salt was required to break down the emulsion. The combined organic phase was washed with water, HCl (2 M), 5% NaOH, and saturated NaCl solution then dried over $CaCl_2$. Removal of the solvent in vacuo yielded a red oil. This was chromatographed twice (silica, petrol b.p. 60–80°C) to give the product as a red oil which crystallised on standing (22 g, 54%), m.p. 110°C lit. [37] 111–112°C. (Found: C, 88.4; H, 7.4. Calc. for $C_{25}H_{24}O$ C, 88.2; H, 7.1); i.r. ν_{CO} at 1718 cm^{-1} (petrol); [α] (20°C, $l = 0.1$, $c = 0.0692$, $CDCl_3$) (589 nm) −28.9, (578 nm) −57.8, (546 nm) −72.3, and (436 nm) +794.8d; *m/z* EI 340 [$(M)^+$ (100%)]; δ_H (250 MHz, solvent $CDCl_3$, standard $SiMe_4$) 0.97 (3H, s, CH_3), 1.07 (3H, s, CH_3), 1.15 (3H, s, CH_3), 1.64–2.29 (4H, m, CH_2), 350 (1H, d, J_{HH} 4.6 Hz, CH), 7.17–7.43 and 7.69–7.71 (10H, m, aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 12.1, 17.2, and 21.4 (CH_3), 25.9 and 34.7 (CH_2); 48.6 (CH); 50.2 and 51.2 (C), 126.0–130.2 (CH, aromatic), 115.6, 118.6, 130.9, 132.0, 164.6, and 165.8 (C, aromatic), 202.9 (C, carbonyl).

3.4. Synthesis of (−)-(2R,4S,7R)-1,2,3-triphenyl-4,8,8-trimethyl-2H,4,5,6,7-tetrahydro-4,7-methanoinde-2-ol, *4*

A solution of phenyl magnesium bromide, prepared from bromobenzene (4 g, 25.2 mmol) in ether (80 cm^3) and magnesium (6 g) in ether (20 cm^3), was added under nitrogen through a dropping funnel to a stirred solution of (−)-(4*S*,7*R*)-1,3-diphenyl-4,8,8-trimethyl-2*H*,4,5,6,7-tetrahydro-4,7-methanoinden-2-one (4.3 g, 12.6 mmol) in benzene (100 cm^3). When addition was complete, the mixture was heated to 40°C for 3 h. After cooling, sulphuric acid was added slowly (100 cm^3 0.5 M) followed by ether (100 cm^3). The mixture was then transferred to a separating funnel and the aqueous layer removed. The organic phase was washed with water (2×200 cm^3), dried over $MgSO_4$ and the solvent removed in vacuo. The crude product was chromatographed (silica, petrol b.p. 60–80°C: 5% ether) to give the carbinol as a pale yellow foam (4.3 g, 82%). (Found: C, 88.4; H, 7.4. $C_{31}H_{30}O$ requires C, 88.9; H, 7.2%); [α] (20°C, $l = 1.0$, $c = 0.604$, $CHCl_3$) (589 nm)

−7.95, (578 nm) −9.3, (546 nm) −13.6, and (436 nm) −69.0°; *m/z* EI 418 [$(M)^+$ (58%)], 403 [$(M-CH_3)^+$ (23%)], 342 [$(M-Ph)^+$ (100%)]; δ_H (250 MHz, solvent $CDCl_3$, standard $SiMe_4$) 0.96 (3H, s, CH_3), 0.99 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.61–1.80, 1.85–1.95, and 2.15–2.34 (1H, 1H, and 2H, m, CH_2), 1.70 (1H, s, COH), 3.06 (1H, d, J_{HH} 4.4 Hz, CH), 7.01–7.34 (15H, m, aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 12.3, 17.7, and 21.0 (CH_3), 26.3 and 34.7 (CH_2), 48.9 (CH), 49.8 and 52.3 (C), 95.3 (PhCOH),

Table 2

(a) Selected bond lenghts (Å) and bond angles (deg) for (η^4 − cycloocta-1,5-diene)[*endo*-η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7a**

Selected bond lengths (Å)			
Rh(1)–C(1)	2.271(7)	Rh(1)–C(2)	2.252(6)
Rh(1)–C(3)	2.320(7)	Rh(1)–C(4)	2.340(8)
Rh(1)–C(5)	2.276(7)	Rh(1)–C(24)	2.127(7)
Rh(1)–C(25)	2.126(8)	Rh(1)–C(28)	2.112(9)
Rh(1)–C(29)	2.131(7)	C(1)–C(2)	1.455(9)
C(1)–C(5)	1.439(9)	C(2)–C(3)	1.478(9)
C(3)–C(4)	1.401(11)	C(4)–C(5)	1.449(10)
C(30)–C(31)	1.516(13)	C(24)–C(25)	1.425(12)
C(24)–C(31)	1.516(12)	C(25)–C(26)	1.515(11)
C(26)–C(27)	1.527(12)	C(27)–C(28)	1.510(12)
C(28)–C(29)	1.410(13)	C(29)–C(30)	1.542(12)
Selected bond angles (deg)			
C(2)–C(1)–C(5)	109.2(6)	C(2)–C(1)–C(12)	127.1(6)
C(5)–C(1)–C(12)	123.4(6)	C(1)–C(2)–C(3)	105.7(5)
C(1)–C(2)–C(18)	128.8(6)	C(3)–C(2)–C(18)	125.5(6)
C(2)–C(3)–C(4)	108.5(6)	C(2)–C(3)–C(32)	139.7(6)
C(4)–C(3)–C(32)	106.8(6)	C(3)–C(4)–C(5)	109.7(6)
C(3)–C(4)–C(34)	106.8(6)	C(5)–C(4)–C(34)	138.5(7)
C(1)–C(5)–C(4)	106.7(5)	C(1)–C(5)–C(6)	127.4(6)
C(4)–C(5)–C(6)	125.3(6)	C(25)–C(24)–C(31)	123.5(7)
C(24)–C(25)–C(26)	122.3(7)	C(25)–C(26)–C(27)	112.8(7)
C(26)–C(27)–C(28)	111.7(7)	C(27)–C(28)–C(29)	124.6(7)
C(28)–C(29)–C(30)	122.2(7)	C(29)–C(30)–C(31)	112.3(7)
C(24)–C(31)–C(30)	113.1(7)		

(b) Selected bond lengths (Å) and bond angles (deg) for (η^4-cycloocta-1,5-diene)[*exo*-η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7b**

Selected bond lengths (Å)			
Rh(1)–C(1)	2.255(5)	Rh(1)–C(2)	2.254(6)
Rh(1)–C(3)	2.227(5)	Rh(1)–C(4)	2.304(6)
Rh(1)–C(5)	2.320(6)	Rh(1)–C(32)	2.115(6)
Rh(1)–C(33)	2.114(6)	Rh(1)–C(36)	2.126(6)
Rh(1)–C(37)	2.095(7)	C(1)–C(2)	1.444(7)
C(1)–C(5)	1.430(7)	C(2)–C(3)	1.447(7)
C(3)–C(4)	1.435(6)	C(4)–C(5)	1.393(7)
C(32)–C(33)	1.398(8)	C(33)–C(34)	1.508(9)
C(34)–C(35)	1.508(10)	C(35)–C(36)	1.525(9)
C(36)–C(37)	1.410(9)	C(37)–C(38)	1.517(9)
C(38)–C(39)	1.495(10)	C(32)–C(39)	1.524(9)
Selected bond angles (deg)			
C(2)–C(1)–C(5)	107.2(4)	C(2)–C(1)–C(6)	126.7(4)
C(5)–C(1)–C(6)	125.6(4)	C(1)–C(2)–C(3)	107.4(4)
C(1)–C(2)–C(12)	123.9(4)	C(3)–C(2)–C(12)	128.3(4)
C(2)–C(3)–C(4)	107.0(4)	C(2)–C(3)–C(18)	127.0(4)
C(4)–C(3)–C(18)	126.0(4)	C(3)–C(4)–C(5)	109.0(4)
C(3)–C(4)–C(24)	143.6(4)	C(5)–C(4)–C(24)	105.6(4)
C(1)–C(5)–C(4)	109.2(4)	C(1)–C(5)–C(27)	141.0(4)
C(4)–C(5)–C(27)	108.2(4)	C(32)–C(33)–C(34)	124.0(5)
C(33)–C(34)–C(35)	113.1(5)	C(34)–C(35)–C(36)	113.1(5)
C(35)–C(36)–C(37)	122.7(6)	C(36)–C(37)–C(38)	123.4(5)
C(37)–C(38)–C(39)	113.0(5)	C(32)–C(39)–C(38)	112.6(5)
C(33)–C(32)–C(39)	122.4(5)		

124.8–129.4 (CH, aromatic), 134.2, 134.3, 135.3, 139.9, 141.2, 150.9, and 151.4 (C aromatic).

*3.5. Synthesis of (−)-(2RS,4S,7R)-1,2,3-triphenyl-4,8,8-trimethyl-2H,4,5,6,7-tetrahydro-4,7-methanoindene, **5***

(−)-(2*R*,4*S*,7*R*)-1,2,3-Triphenyl-4,8,8-trimethyl-2*H*,4,5,6,7-tetrahydro-4,7-methanoinden-2-ol (4.3 g, 10 mmol) in glacial acetic acid (100 cm^3) was heated under reflux and concentrated hydrochloric acid (10 cm^3) was carefully added. After 4 h under reflux, zinc (1.3 g) was carefully added and heating was continued for 4 h. After cooling to room temperature, the mixture was partitioned between ether (300 cm^3) and water (500 cm^3); the organic phase was washed with water (3 × 200 cm^3), saturated $NaHCO_3$ (2 × 200 cm^3), and water

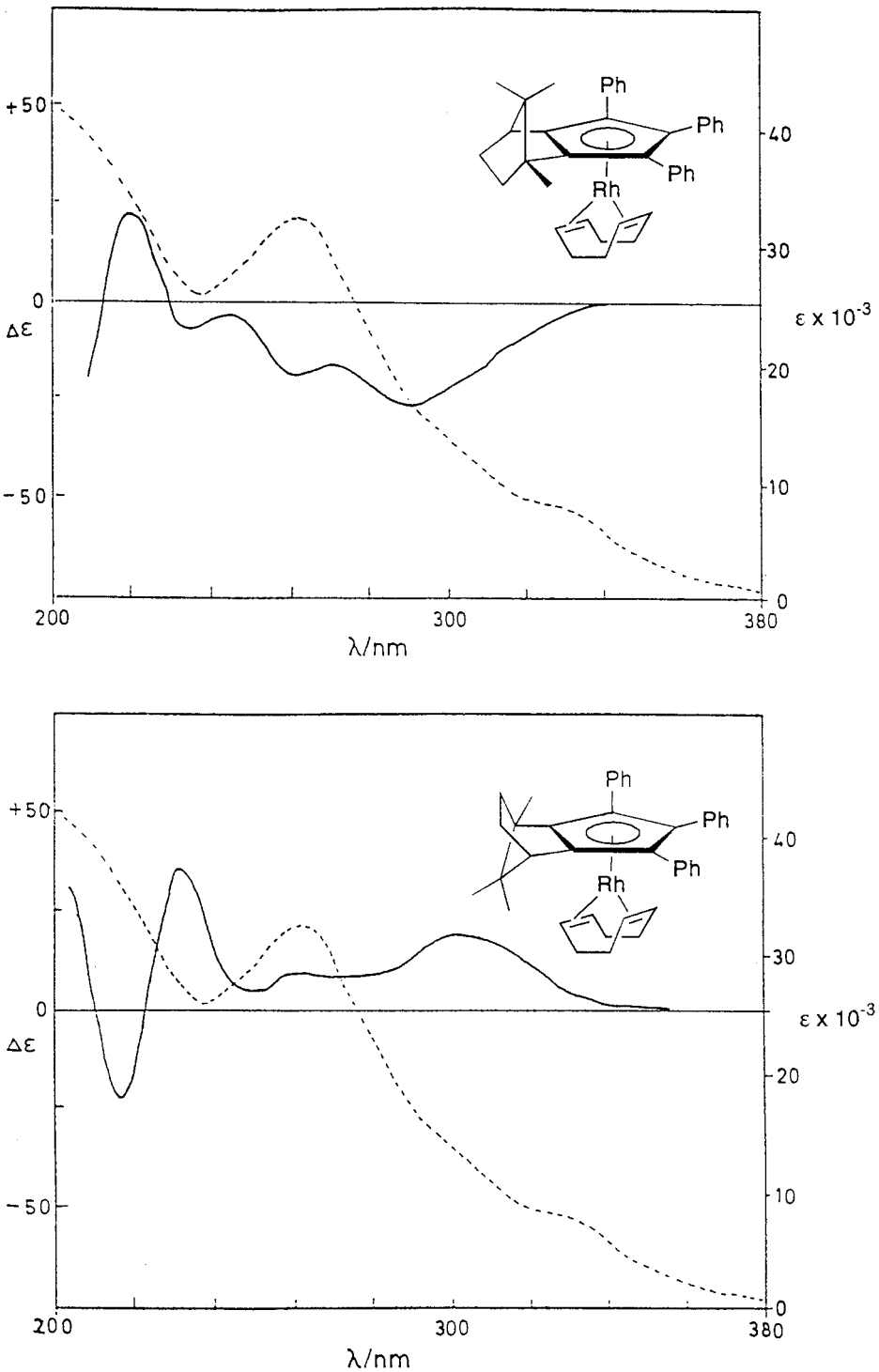


Fig. 3. UV (- - -) and c.d. (————) spectra of *endo*-**7a** and -**7b**.

(2×200 cm^3). The organic phase was then dried over $MgSO_4$ and the solvent removed in vacuo to give a dark tan oil. Repeated chromatography (silica, petrol b.p. 60–80°C) gave the product as a pale foam (2.8 g, 70%), m.p. 41–45°C; (Found: C, 92.5; H, 7.3. $C_{31}H_{30}$ requires C, 92.5; H, 7.5%); $[\alpha]$ (20°C, $l = 1.0$, $c = 1.085$, $CHCl_3$) (589 nm) −553.9, (578 nm) −608.3, (546 nm) −815.7, and (436 nm) −3580°; m/z EI 402 [$(M)^+$ (60%)]; δ_H (250 MHz, solvent $CDCl_3$, standard $SiMe_4$) 0.55–2.40 (13H m), 2.70–3.50 (1H, m, CH), 4.50–5.18 (1H, m, CpH), 6.90–7.70 (15H, m, aromatic); δ_C (63 MHz, solvent $CDCl_3$, standard $SiMe_4$) 12.2, 18.5, 20.0, 21.0, 22.8, and 23.5 (CH_3), 26.4, 26.6, 34.9, and 35.3 (CH_2), 57.2 and 64.6 (C), 125.2–131.2 (CH, aromatic), 133.7–153.3 (C, aromatic).

3.6. Synthesis of (η^4-Cycloocta-1,5-diene)[rac(RS)-η^5-1,2,3-triphenyl-4-methyl-7-isopropyl-1H-indenyl]rhodium, ***6****, (+)-(η^4-cycloocta-1,5-diene)[endo-η^5-(4S,7R)-1,2,3-triphenyl-4,8,8-trimethyl-1H,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium,* ***7a****, and (−)-(η^4-cycloocta-1,5-diene)[exo-η^5-(4S,7R)-1,2,3-triphenyl-4,8,8-trimethyl-1H,4,5,6,7-tetrahydro-4,7-methanoindenyl]-rhodium,* ***7b***

A solution of (−)-(2*RS*,4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-2H,4,5,6,7-tetrahydro-4,7-methanoindene (4.73 g, 11.8 mmol) in xylene (200 cm^3) was heated to 125°C under nitrogen. Butyl lithium in hexane (Aldrich) (4.6 cm^3, 2.59 M, 11.9 mmol) was added via a hypodermic syringe and, after stirring for 2 h, di-μ-chlorobis(η^4-cyclooctadiene)dirhodium (2.95 g, 6 mmol) was added. The mixture was stirred for a further 2 h, allowed to cool and filtered. After removal of the solvent in vacuo, chromatography (silica, petrol b.p. 60–80°C) of the residue gave two products. The major, slower moving component was recrystallised from diisopropyl ether to give small yellow crystals of (η^4-cycloocta-1,5-diene)-*rac*(*RS*)(η^5-1,2,3-triphenyl-4-methyl-7-isopropyl-1*H*-indenyl)rhodium, **6** (5.0 g, 70%), m.p. > 210°C (decomp.); (Found: C, 76.6; H, 6.2. $C_{39}H_{39}Rh$ requires C, 76.7; H, 6.4%); m/z + FAB argon 610 [$(M)^+$ (100%)], 500 [$(M–COD)^+$ (23%)]; δ_H (250 MHz, solvent $CDCl_3$, standard $SiMe_4$) 1.02 (3H, d, J_{HH} 6.5 Hz CH_3), 1.15 (3H, d, J_{HH} 6.5 Hz, CH_3), 1.99 (3H, s, CH_3), 2.87 (1H, septet, J_{HH} 6.5 Hz, C*H*Me_2), 1.76–2.33 (8H, m, CH_2 COD), 3.85–4.09 (4H, m, CH COD), 6.85–7.40 (15H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 22.0, 24.0, and 27.9 (CH_3), 24.8 (CH), 31.5–31.7 (CH_2 COD), 71.2 (J_{CRh} 13.9 Hz) and 72.2 (J_{CRh} 13.5 Hz)(CH COD), 96.2, 98.3, 107.2, 108.6, and 118.8 (C cyclopentadienyl), 119.1 and 124.8–132.7 (CH aromatic), 134.7–140.0 (C aromatic).

The minor, faster moving product was an *endo*:*exo* 1:1 mixture of (η^4-cycloocta-1,5-diene)[η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7a** and **7b** (1.5 g, 20%) m.p. 201–205°C; (Found: C, 76.9; H, 6.9. $C_{39}H_{41}Rh$ requires C, 76.5; H, 6.8%). These were separated as follows: repeated crystallisation from heptane gave the *exo*-form and repeated crystallisation from diisopropyl ether of the mother liquid from the first heptane crystallisation gave the *endo*-form.

(+)-(η^4-Cycloocta-1,5-diene)[*endo* η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7a**. $[\alpha]$ (20°C, $l = 0.1$, $c = 1.043$, $CHCl_3$) (589 nm) + 413.8, (578 nm) + 438.2, and (546 nm) +518.7d; m/z + FAB argon 612 [$(M)^+$ (100%)]; δ_H (250 MHz; solvent $CDCl_3$; standard $SiMe_3$) 0.95 (3H, s, CH_3), 1.11 (3H, s, CH_3), 2.07 (3H, s, CH_3), 1.59–2.48 (10H, m, CH_2), 3.10 (1H, d, CH), 3.62 (4H, m, CH COD), 6.65–7.45 (15H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 13.8, 20.1, and 20.8 (CH_3), 27.2 and 34.3 (CH_2), 30.9 and 32.3 (CH_2 COD), 49.6 (CH), 51.6 and 54.6 (C), 69.5 and 70.1 (J_{CRh} 14 Hz), 91.2 (J_{CRh} 3.5 Hz), 96.9 (J_{CRh} 3.2 Hz), 108.8 (J_{CRh} 4.9 Hz), 114.9 (J_{CRh} 4.8 Hz), and 116.9 (J_{CRh} 4.5 Hz)(C cyclopentadienyl), 125.6, 125.7, and 126.0 (CH *p* aromatic), 127.2, 127.5, 127.6, 128.5, 130.4, and 133.1 (CH *m* and *o* aromatic), 134.6, 134.9, and 136.3 (C aromatic).

(−)-(η^4-Cycloocta-1,5-diene)[*exo* η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7b**. $[\alpha]$ (20°C, $l = 0.1$, $c = 1.043$, $CHCl_3$) (589 nm) −466.0, (578 nm) −492.8, and (546 nm) −589.6d; m/z + FAB argon 612 [$(M)^+$ (100%)]; δ_H (250 MHz; solvent $CDCl_3$; standard $SiMe_4$) 0.72 (3H, s, CH_3), 0.75 (3H, s, CH_3), 0.95 (3H, s, CH_3), 1.75–1.89 and 1.98–2.48 (10H, m, CH_2), 2.82 (1H, d, CH), 3.51–3.68 (4H, m, CH COD), 6.90–6.97, 7.02–7.24, and 7.32–7.38 (15H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 13.0, 20.8, and 21.9 (CH_3), 29.0 and 38.6 (CH_2) 31.1 and 33.1 (CH_2 COD), 48.5 (CH), 51.4 and 68.4 (C), 70.0 (J_{CRh} 13.6 Hz) and 70.2 (J_{CRh} 13.8 Hz)(CH COD), 98.7 (J_{CRh} 5.4 Hz), 98.9 (J_{CRh} 3.8 Hz), 102.7 (J_{CRh} 3.6 Hz), 120.7 (J_{CRh} 3.9 Hz), and 127.0 (J_{CRh} 3.7 Hz)(C cyclopentadienyl), 125.7, 125.8, and 126.0 (CH *p* aromatic), 127.1, 127.4, 127.7, 129.7, 130.9, and 132.0 (CH *o* and *m* aromatic), 134.6, 135.5, and 135.8 (C aromatic).

3.7. Synthesis of (−)-tri-μ-bromobis[endo η^5-(4S,7R)-1,2,3-triphenyl-4,8,8-tri-methyl-1H,4,5,6,7-tetrahydro-4,7-methanoindenyl]dirhodium tribromide, ***8a***

(+)-(η^4-Cycloocta-1,5-diene)[*endo*-η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8- trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium, **7a** (69 mg, 0.11 mmol) in ether (10 cm^3) was treated with a solution of bromine in ether until no further product precipitated. The dark brick red precipitate was collected and washed with

pentane (61 mg, 81%) m.p. > 240°C (Found: C, 51.9; H, 3.8. $C_{62}H_{58}Br_6Rh_2$ requires C, 50.03; H, 3.93%); [α] (20°C, $l = 0.1$, $c = 0.091$, $CHCl_3$) (589 nm) −110, (578 nm) −55, (546 nm) −55, and (436 nm) −286°; m/z + FAB argon 1247 [$(M-Br)^+$ (100%)], 1168 [$(M-Br_2)^+$ (18%)], 585 [$(CpRhBr)^+$ (87%)]; S_H (250 MHz; solvent $CDCl_3$; standard $SiMe_4$) 0.99 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.64 (3H, s, CH_3), 1.57–1.69 (1H, m), 1.78–1.91 (2H, m), 1.98–2.15 (1H, m) (CH_2CH_2), 2.94 (1H, d, J_{HH} 4 Hz, CH), 7.02–7.17 and 7.26–7.70 (15H, m, CH aromatic); S_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 11.6, 20.5, and 28.2 (CH_3), 25.7 and 32.9 (CH_2), 46.9 (CH), 51.6 and 54.5 (C), 93.0 (J_{CRh} 6 Hz), 94.3 (J_{CRh} 13 Hz), 95.7 (J_{CRh} 7 Hz), 109.7 (J_{CRh} 10 Hz), 110.3 (J_{CRh} 10 Hz)(C cyclopentadienyl), 126.8–127.6 (C aromatic), 127.8–132.1 (CH aromatic).

Table 3
Crystallographic data for diffraction studies of *endo*- and *exo*-(η^4-cycloocta-1,5-diene)[η^5-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium **7a** and **7b**

	7a	**7b**
Crystal parameters		
Empirical formula	$C_{39}H_{41}Rh$	$C_{39}H_{41}Rh$
Molecular weight	$M = 612.66$	$M = 612.66$
Colour	Orange	Orange/yellow
Solvent	Pentane/methanol	Heptane/ether
Crystal size (mm)	$0.35 \times 0.275 \times 0.225$	$0.32 \times 0.36 \times 0.40$
Habit	Blocks	Blocks
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (D_2^4, No. 19)	$P2_12_12_1$ (D_2^4, No. 19)
a (Å)	13.549(23)	13.301(18)
b (Å)	14.490(25)	15.599(32)
c (Å)	15.909(14)	14.436(19)
V (Å^3)	$U = 3123(8)$	$U = 2995(10)$
Z	4	4
D(calcd) (g cm^{-3})	1.303	1.359
μ (cm^{-1})	5.61	5.85
F(000)	1279.86	279.86
Intensity data		
Diffractometer	Nicolet R3 4-circle	Stoe Stadi-2
λ (Mo K_α radiation) (Å)	0.71069	0.71069
Monochromator	Graphite, incident beam	Graphite, incident beam
Reflections measured	$+h, +k, \pm l$	$+h, +k, \pm l$
20 range (deg)	3.5–50	6.5–50
Temperature (°C)	20	20
Scan type	ω	ω
Scan speed (deg min^{-1})	4	0.6
Scan range (deg)	3	Variable
bkgd measurement	50% scan time	50% scan time
Standard reflections	1 in every 200	1 per layer
No. of reflections collected	3140	4840
No. of reflections used	2545	4620
Acceptance criterion	$\|F\|/\sigma(\|F\|) > 3.0$	$\|F\|/\sigma(\|F\|) > 3.0$
R_{merge}	0.0116	
Minimum transmission coefficient	0.612	0.72
Maximum transmission coefficient	0.629	0.83
abs method	Psi scans	Gaussian
Structure solution		
Method	Patterson/Fourier	Patterson/Fourier
Progams	SHELXTL ([38])	SHELXTL ([38])
Computer	Data General Nova 3	Data General Nova 3
Scattering factors	Ref. [39]	Ref. [39]
R	0.0488	0.0362
R_w	0.0413	
Weighting scheme	$w = [\sigma^2(F) + 0.00034F^2]^{-1}$	Unit weights
H refinement	Riding mode	Riding mode

3.8. Synthesis of (−)-tri-μ-bromobis[exo η⁵-(4S,7R)-1,2,3-triphenyl-4,8,8-tri-methyl-1H,4,5,6,7-tetrahydro-4,7-methanoindenyl]dirhodium tribromide, ***8b***

This dark red compound was prepared in 91% yield by an analogous procedure from (−)-(η⁴-cycloocta-1,5-diene)[*exo*-η⁵-(4*S*,7*R*)-1,2,3-triphenyl-4,8,8-trimethyl-1*H*,4,5,6,7-tetrahydro-4,7-methanoindenyl]rhodium, **7b** m.p. > 240°C; (Found: C, 52.0; H, 3.92; Br, 32.2. $C_{62}H_{58}Br_6Rh_2$ requires C, 50.03; H, 3.93; Br, 32.2%); $[\alpha]$ (20°C, $l = 0.1$, $c = 0.097$, $CHCl_3$) (589 nm) −130, (578 nm) −100, (546 nm) −210, and (436 nm) −1160d; m/z + FAB argon 1247 [(M–Br)$^+$ (68%)], 1168 [(M–Br_2)$^+$ (12%)], 585 [(CpRhBr)$^+$ (100%)]; δ_H (250 MHz; solvent $CDCl_3$; standard $SiMe_4$) 1.05 (6H, s, CH_3), 1.09 (6H, s, CH_3), 1.12 (6H, s, CH_3), 2.05–2.19, 2.29–2.44, 2.52–2.67, and 2.78–2.93 (8H, m, CH_2), 2.82 (2H, d, J_{HH} 4.5 Hz, CH), 7.06–7.15, 7.27–7.55, and 7.71–7.79 (30H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 11.8 and 20.9 (CH_3), 27.8 and 36.4 (CH_2), 46.2 (CH), 51.6 and 62.4 (C), 94.0, 97.2, 98.3, 115.5, and 117.4 (C cyclopentadienyl), 126.5–127.1 (C aromatic), 127.7–132.5 (CH aromatic).

3.9. Crystal structure determination

Experimental details of X-ray data collection, and solution and refinement of the structures are summarised in Table 3. The crystal of **7b** contained a disordered half molecule of solvent, Et_2O; the most successful model has this solvent disordered over three sets of positions. Tables of complete bond lengths and angles, anisotropic thermal parameters with e.s.d.'s and hydrogen atom positional parameters together with tables of observed and final calculated structure factors for **7a** and **7b** have been deposited at the Cambridge Crystallographic Data Centre.

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