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Journal of Organometallic Chemistry 495 (1995) 215–220

Journal of Organometallic Chemistry

Chiral tetraphenylcyclopentadienyl complexes of rhodium: synthesis and crystal structure of [Rh{η^5-$C_5Ph_4CH(Me)Ph$}(cod)]

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Received 11 January 1995

Abstract

Phenethyltetraphenylcyclopentadiene has been made from (*R*)-1-phenethyl bromide (43.8% e.e.) and lithium tetraphenylcyclopentadienide. The syntheses of the hydrogenation catalyst $[Rh\{C_5Ph_4CH(Me)Ph\}Br_2]_2$ and of $Rh\{C_5Ph_4CH(Me)Ph\}(C_8H_{12})$ are also reported along with the crystal structure of the latter.

Keywords: Rhodium; Tetraphenylcyclopentadienyl; Chirality; Crystal structure; Hydrogenation; Catalysis

1. Introduction

Over the last ten years chiral cyclopentadienyl ligands have found increasing applications in enantioselective synthesis [1], including stereoregular polymerisation [2]. To date, however, the most stereospecific catalysts have been metallocenes containing two cyclopentadienyl ligands [3], usually linked together [4] to prevent rotation about the metal cyclopentadienyl bond. Consequently, such catalysts have been limited to Group 4 or lanthanide metals. Given that monocyclopentadienyl complexes of the softer transition metals to the right of the Periodic Table are active catalysts for a wide range of reactions, including those such as hydroformylation [5] for which Group 4 or lanthanide metals show little activity, then there are considerable advantages to be gained from developing effective chiral monocyclopentadienyl catalysts. With this objective in mind we have recently synthesised and determined the structures of a range of menthyl-and neomenthyl-tetraphenylcyclopentadienyl complexes [6]. The attractive feature of such compounds is that the four aryl groups cannot lie coplanar and therefore must adopt a chiral array; it was reasoned that by having a bulky chiral group in the fifth position of the cyclopentadienyl ligand this would dictate the chiral orientation of the four aryl groups (Fig. 1). This would produce a chiral "umbrella" over the metal and in this way transmit the chirality to the metal environment.

It was found that the orientation of the phenyl groups was indeed influenced by the menthyl or neomenthyl substituent. We were therefore interested to investigate how other chiral substituents on the cyclopentadienyl ring influenced the orientation of the four phenyl substituents and we report here the synthesis of 1-phenylethyltetraphenylcyclopentadienyl complexes of rhodium and the crystal structure of one of them.

2. Results and discussion

2.1. Synthetic and catalytic studies

Our previous route to homochiral tetraphenylcyclopentadienes by nucleophilic attack of the tetraphenylcyclopentadienide anion on the corresponding chiral tosylate was inappropriate because of the instability of benzyl tosylates [7]. We were, however, able to employ a similar strategy using 1-bromoethylbenzene (Eq. (1))

$$Li[C_5Ph_4H] + PhCH(Me)Br \rightarrow C_5Ph_4H\{CH(Me)Ph\} + LiBr \quad (1)$$

Unfortunately, although 1-bromoethylbenzene can be readily synthesized, its tendency to racemise is well documented [8], and after purification our sample was found to have an optical purity of only 43.8% (*R*).

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SSDI 0022-328X(95)05464-2

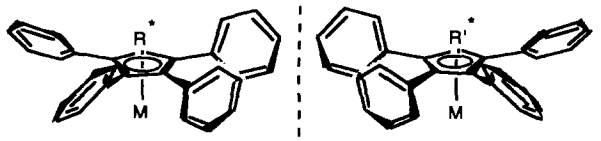

Fig. 1. Chiral arrays of tetraphenyl substituents.

Treatment of this partially racemised (*R*)-phenethyl bromide with lithium tetraphenylcyclopentadienide gave optically active phenethyltetraphenylcyclopentadiene as a mixture of the 1,3-, 2,4-, and 1,4-isomers. Although disappointed that we failed to obtain the optically pure product, we note that a previous method of introducing a CH(Me)Ph substituent into a cyclopentadiene ring, involving hydride transfer from optically active alkyllithium reagents to 6-methyl-6-phenylfulvene, failed to yield any optically active lithium 1-phenylethylcyclopentadienide [9].

The rhodium cyclooctadiene complex $Rh\{C_5Ph_4CH(Me)Ph\}(C_8H_{12})$ was readily made by treatment of the cyclopentadiene $C_5Ph_4H\{CH(Me)Ph\}$ with butyllithium at 125 °C in xylene followed by the addition of $[RhCl(C_8H_{12})]_2$. The product was obtained in 86% yield as a bright yellow powder and was characterised by ^1H and ^{13}C NMR spectroscopy. We [10], and others [10], have previously noted that the chiral phenyl array in pentaphenylcyclopentadienyl compounds can, in the presence of another chiral centre in the molecule, give rise to diastereoisomers which can be detected by NMR spectroscopy. Given that the chiral CH(Me)Ph unit was not homochiral, one might have similarly expected the NMR spectra to indicate the presence of diastereoisomers resulting from two chiral phenyl arrays each of which was favoured by different enantiomers of the CH(Me)Ph ring substituent. Even at −70 °C, however, there was no indication of the presence of diastereoisomers in either the ^1H or the ^{13}C NMR spectra, suggesting that the 1-phenylethyl substituent has little to no influence on the orientation of the tetraphenyl array. In order to gain further information on this point the compound was studied by X-ray diffraction and the structure is described below.

Treatment of $Rh\{C_5Ph_4CH(Me)Ph\}(C_8H_{12})$ with a solution of bromine in pentane yielded the compound $[Rh\{C_5Ph_4CH(Me)Ph\}Br_2]_2$ as a dull red powder, which

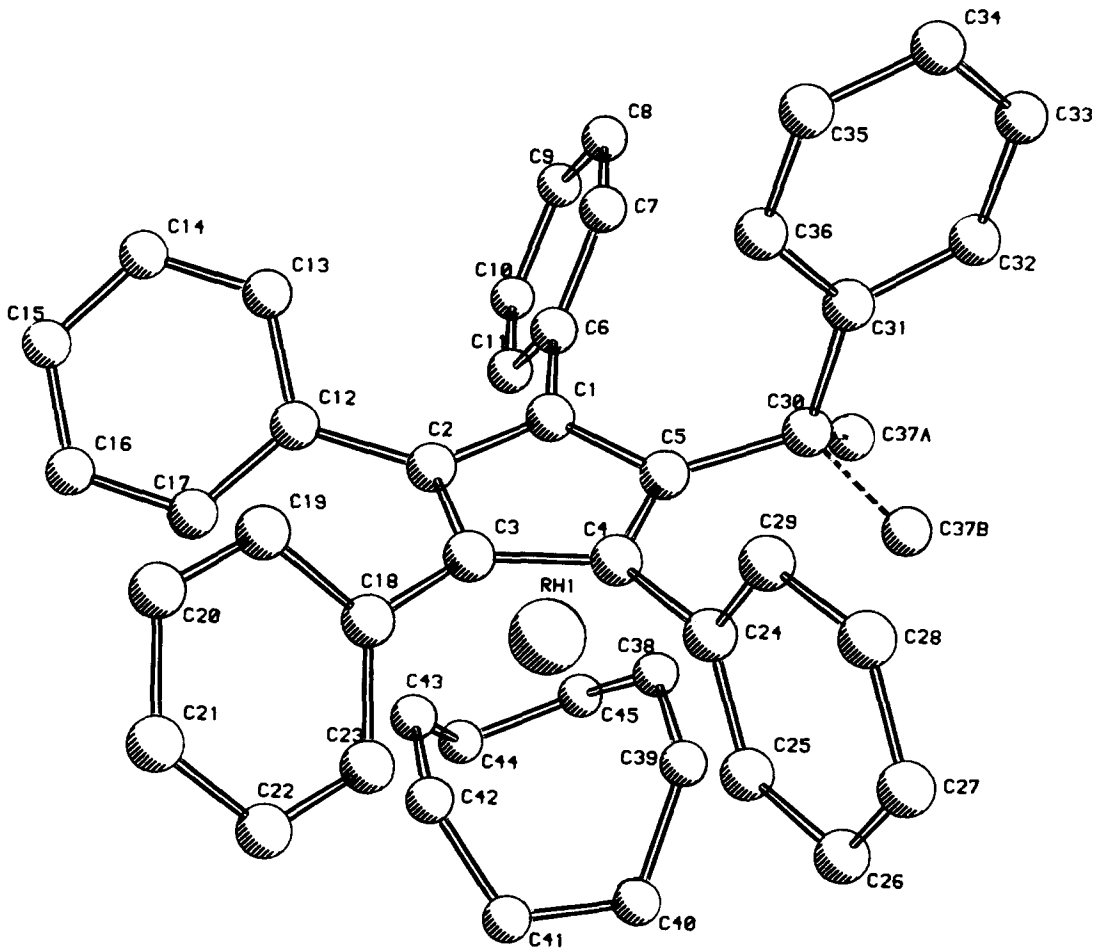

Fig. 2. Structure of $Rh\{C_5Ph_4CH(Me)Ph\}cod$.

was characterised by elemental analysis, ^{1}H and ^{13}C NMR and mass spectrometry. Preliminary experiments revealed that at 20 °C and 4.5 atm hydrogen pressure, $[Rh\{C_5Ph_4CH(Me)Ph\}Br_2]_2$, in dichloromethane and in the presence of 20 equivalents of triethylamine, catalysed the hydrogenation of α-ethylstyrene to give (*R*)-2-phenylbutane in 5% e.e. Allowing for the 43.8% optical purity of the initial phenethyl bromide ligand this suggests a true optical yield of 11.5% e.e. Although clearly modest, it should be noted that this exceeds the optical yield reported for the reduction of α-ethylstyrene using chiral phosphine ligands such as diop. [11]. It is also superior to the performance of simple chiral cyclopentadienyl catalysts [12]; we believe that the reasons for this, given the evidence that the 1-phenylethyl substituent has little to no influence on the orientation of the tetraphenyl array, are twofold. The first is that the 1-phenylethyl substituent in the tetraphenylcyclopentadienyl moiety has less mobility than a single chiral substituent in a cyclopentadienyl or even tetramethylcyclopentadienyl moiety. Secondly, in a simple chiral cyclopentadienyl catalyst there will be a strong preference for a conformation which places the bulky olefinic substrate and the bulky chiral substituent far apart, whereas in the $C_5Ph_4CH(Me)Ph$ case there is less reason for the substrate to avoid the chiral group since all the substituents are bulky.

2.2. Description of structures

The molecular structure is illustrated in Fig. 2; bond lengths and angles with estimated standard deviations are listed in Table 1.

The molecule comprises a rhodium(I) bonded to a cycloocta-1,5-diene ligand, and to a tetraphenyl(1-phenethyl)cyclopentadienyl ligand. The cyclopentadienyl fragment is planar (rms deviation from mean plane 0.013 Å; distance of rhodium from mean plane 1.935 Å) and the five rhodium–carbon distances are similar (2.26–2.32 Å). The four substituent phenyl rings are planar (rms deviations 0.004, 0.011, 0.006 and 0.003 Å) and their bonded carbon atoms deviate by 0.029, 0.093, 0.186 and 0.176 Å from the cyclopentadienyl plane in directions away from the metal; the bonded carbon atom of the 1-phenethyl group deviates by 0.25 Å in the same sense.

The phenyl rings are twisted into a propeller conformation around the cyclopentadienyl ring with dihedral angles relative to the latter plane of 66°, 47°, 53° and 96°. Thus, the environment for the 1-phenethyl group is

Table 1
Selected bond lengths (Å) and bond angles (°) for $Rh\{\eta^5\text{-}C_5Ph_4CH(Me)Ph\}cod$

(a) Selected bond lengths			
Rh(1)–C(1)	2.315(9)	Rh(1)–C(2)	2.301(8)
Rh(1)–C(3)	2.311(7)	Rh(1)–C(4)	2.281(8)
Rh(1)–C(5)	2.265(8)	Rh(1)–C(38)	2.312(8)
Rh(1)–C(39)	2.130(9)	Rh(1)–C(42)	2.128(13)
Rh(1)–C(43)	2.125(12)	C(1)–C(2)	1.443(9)
C(1)–C(5)	1.451(9)	C(2)–C(3)	1.465(9)
C(3)–C(4)	1.423(9)	C(4)–C(5)	1.464(9)
C(5)–C(30a)	1.509(19)	C(5)–C(30b)	1.507(19)
C(30a)–C(31)	1.512(18)	C(30a)–C(37a)	1.446(16)
C(30b)–C(31)	1.511(20)	C(30b)–C(37b)	1.441(24)
C(38)–C(39)	1.389(13)	C(38)–C(45)	1.529(15)
C(39)–C(40)	1.584(17)	C(40)–C(41)	1.481(16)
C(41)–C(42)	1.497(18)	C(42)–C(43)	1.427(15)
C(43)–C(44)	1.536(14)	C(44)–C(45)	1.482(20)
(b) Selected bond angles (°)			
C(2)–C(1)–C(5)	108.0(5)	C(2)–C(1)–C(6)	126.2(6)
C(5)–C(1)–C(6)	125.8(6)	C(1)–C(2)–C(3)	108.2(5)
C(1)–C(2)–C(12)	125.0(6)	C(3)–C(2)–C(12)	126.4(6)
C(2)–C(3)–C(4)	107.6(6)	C(2)–C(3)–C(18)	125.3(6)
C(4)–C(3)–C(18)	126.6(6)	C(3)–C(4)–C(5)	108.9(5)
C(3)–C(4)–C(24)	124.8(6)	C(5)–C(4)–C(24)	125.9(6)
C(1)–C(5)–C(4)	107.2(5)	C(1)–C(5)–C(30a)	125.9(8)
C(4)–C(5)–C(30a)	125.2(8)	C(1)–C(5)–C(30b)	125.0(8)
C(4)–C(5)–C(30b)	126.0(8)	C(5)–C(30a)–C(31)	112.2(8)
C(5)–C(30a)–C(37a)	118.2(15)	C(31)–C(30a)–C(37a)	115.3(14)
C(5)–C(30b)–C(31)	112.5(8)	C(5)–C(30b)–C(37b)	116.5(16)
C(31)–C(30b)–C(37b)	114.3(15)	C(39)–C(38)–C(45)	124.1(11)
C(38)–C(39)–C(40)	125.1(9)	C(39)–C(40)–C(41)	111.0(9)
C(40)–C(41)–C(42)	116.6(11)	C(41)–C(42)–C(43)	123.1(9)
C(42)–C(43)–C(44)	123.6(10)	C(43)–C(44)–C(45)	111.6(11)
C(38)–C(45)–C(44)	114.0(9)		

approximately symmetric, with the two end phenyl groups asymmetrically "cupping" the site for the methyl and hydrogen substituents. The four phenyl ring-substituents show no disorder, whereas the planes of the two components of the disordered 1-phenethyl [C(5), C(30), C(31)], and of its phenyl fragment (rms deviation 0.015 Å), are inclined at 87°, 89° and 90° to the cyclopentadienyl plane, showing how symmetrically it occupies its substitution site. This, together with the failure to detect diastereoisomers in the NMR spectra, suggests that the phenethyl substituent has no significant effect upon the tetraphenyl array and that the crystal is a racemic mixture of the two enantiomers in the centro-symmetric space group.

The four rhodium–carbon distances to the cycloocta-1,5-diene ligand are also very similar (2.12–2.13 Å), and the ligand adopts a familiar boat conformation, with only a small twist (rms deviation from mean plane through four bonded carbon atoms 0.042 Å).

Bond lengths and angles seem normal and there are no significant intermolecular contacts.

3. Experimental details

All reactions were carried out under nitrogen. THF was heated under reflux over sodium benzophenone ketyl and distilled under nitrogen whereas xylene was heated under reflux over sodium and distilled under nitrogen. All other solvents and reagents were used without purification. Di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium was prepared by the published procedure [13].

NMR spectra were recorded on a Bruker AM250 spectrometer and optical rotations were measured on a Perkin Elmer 141 polarimeter. Microanalytical data were obtained by the University of Sheffield Microanalytical service.

3.1. (R)-(+)-1-Phenylethyl bromide

(−)-1-Phenylethanol (1.01 g, 8.2 mmol) was converted to (*R*)-(+)-1-phenylethyl bromide by the method of Gerrard [14] (0.9 g, 59%). $[\alpha]_D = +75°$ (neat = 1 dm) corresponds to 43.8% optical purity (based on a value of 171°) [15].

3.2. (S)-Phenethyltetraphenylcyclopentadiene

Tetraphenylcyclopentadiene (1.11 g, 3 mmol) in THF (60 cm^3) was treated under nitrogen with a solution of methyllithium in hexanes (Aldrich 1.4 M, 2.2 cm^3, 3.1 mmol) and stirred at room temperature for 30 min. A solution of (*R*)-1-phenylethyl bromide (3 mmol) in THF was then added over 30 min. Stirring was continued for a further 20 h; then water (10 cm^3) was added and the mixture was extracted with ether (3×25 cm^3). The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo to leave a pale yellow oil $[\alpha]$ ($l = 1.0$, $c = 2.86$, $t = 20$ °C, $CHCl_3$) (589 nm) +19.1, (578 nm) +20.7, (546 nm) +23.9, and (436 nm) +47.6 d; δ_H (250 MHz; solvent $CDCl_3$; standard $SiMe_4$) 1.02–1.51 (3 H, m, CH_3), 3.33–3.50, 3.88–4.01, and 4.10–4.27 (1 H, m, CH), 4.41, 4.62, and 5.06 (1 H, m CpH), 6.76–7.38 (25 H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 16.3 and 17.3 (CH_3), 38.6, 40.7, and 43.3 (CH), 60.3, 59.8, and 68.7 (CH cyclopentadienyl), 125.8–130.3 (CH aromatic), 135.4–150.5 (C aromatic).

3.3. (−)-(η^4-Cycloocta-1,5-diene)[(S)-η^5-phenethyltetraphenylcyclopentadienyl]rhodium

A solution of (+)-phenethyltetraphenylcyclopentadiene (0.5 g, 1.05 mmol) in xylene (25 cm^3) was heated under nitrogen to 135 °C and treated with a solution of methyllithium in hexanes (Aldrich 1.4 M, 0.75 cm^3, 1.1 mmol). The mixture was kept at 135 °C for 1.5 h and the solution of lithium phenethyltetraphenylcyclopentadienide thus obtained was treated with di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium (0.30 g, 0.61 mmol). The mixture was stirred at 135 °C for a further 1 h then cooled to room temperature and filtered, and the solvent was removed in vacuo. Chromatography (alumina, petrol–petrol : ether 1 : 1) gave the product as a yellow powder (0.6 g, 84%) m.p. 167–170 °C (Found C, 78.6; H, 6.2; $C_{45}H_{41}Rh$ requires C, 78.9; H, 6.0%); $[\alpha]$ ($l = 1.0$, $c = 1.532$, $t = 20$ °C, $CHCl_3$) (589 nm) −25.2°, (578 nm) −26.6°, and (546 nm) −30.8°; δ_H (220 MHz; solvent $CDCl_3$; standard $SiMe_4$) 1.13 (3 H, d $J_{HH} = 8$ Hz, CH_3), 1.91–2.52 and 2.56–2.70 (8 H, m, CH_2 COD), 3.70–3.96 (5 H, m, CH), 6.63–7.35 and 7.47–7.61 (25 H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 22.2 (CH_3), 37.8 (CH), 31.7 and 32.9 (CH_2 COD), 72.3 and 72.5 (CH COD), 104.5 ($J_{RhC} = 3.8$ Hz), 105.9 ($J_{RhC} = 4.6$ Hz), 106.1 ($J_{RhC} = 3.8$ Hz), 107.9 ($J_{RhC} = 4.1$ Hz), and 109.0 ($J_{RhC} = 4.5$ Hz), (C cyclopentadienyl), 125.5–128.7 and 131.3–133.8 (CH aromatic), 133.9–135.7 and 147.3 (C aromatic).

3.4. (−)-Di-μ-bromodibromobis[(S)-η^5-phenethyltetraphenylcyclopentadienyl]dirhodium

A solution of (−)-(η^4-cycloocta-1,5-diene)[(*S*)-η^5-phenethyltetraphenylcyclopentadienyl]rhodium (0.34 g, 0.5 mmol) in pentane (5 cm^3) was treated with a solution of bromine in pentane (0.5 mmol). The dark red precipitate formed was collected and dried (0.22 g, 60%). (Found C, 59.5; H, 3.9; $C_{74}H_{58}Br_4Rh_2$ requires C, 60.3; H, 4.0%); $[\alpha]_{436}$ ($l = 0.1$, $c = 0.056$, $CHCl_3$) +536°; δ_H (220 MHz, solvent $CDCl_3$; standard $SiMe_4$)

1.50 (3 H, d J_{HH} 6 Hz, CH_3), 4.30 (1 H, q J_{HH} 6 Hz, CH), 6.75–8.09 (25 H, m, CH aromatic); δ_C (63 MHz; solvent $CDCl_3$; standard $SiMe_4$) 21.4 (CH_3), 38.1 (CH), 101.0, 101.3, and 101.5 (C cyclopentadienyl), 126.7–132.8 (CH aromatic), 126.9–128.6 and 141.1–142.1 (C aromatic).

Table 2
Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for Rh{η^5-$C_5Ph_4CH(Me)Ph$}cod

Atom	x	y	z	U_{eq}
Rh(1)	4525(1)	2081(1)	2596(1)	50(1) [a]
C(1)	3098(8)	817(6)	2795(4)	48(3) [a]
C(2)	2269(7)	2042(6)	3097(4)	45(3) [a]
C(3)	1995(7)	3010(7)	2453(4)	46(3) [a]
C(4)	2692(8)	2382(7)	1773(4)	48(3) [a]
C(5)	3413(7)	1018(6)	1975(4)	48(3) [a]
C(6)	3608(8)	−461(7)	3259(4)	57(3) [a]
C(7)	3046(13)	−1401(8)	3132(5)	82(5) [a]
C(8)	3500(16)	−2556(9)	3554(7)	111(6) [a]
C(9)	4489(16)	−2787(12)	4107(8)	122(7) [a]
C(10)	5064(12)	−1851(13)	4250(7)	108(6) [a]
C(11)	4616(10)	−698(10)	3816(5)	78(4) [a]
C(12)	1636(8)	2248(7)	3917(4)	50(3) [a]
C(13)	923(9)	1453(8)	4287(4)	65(4) [a]
C(14)	279(11)	1665(10)	5026(5)	83(5) [a]
C(15)	374(11)	2624(10)	5426(5)	89(5) [a]
C(16)	1076(10)	3410(9)	5078(5)	76(4) [a]
C(17)	1685(9)	3235(7)	4320(4)	59(3) [a]
C(18)	985(9)	4373(7)	2495(4)	54(3) [a]
C(19)	−459(9)	4650(8)	2837(5)	63(3) [a]
C(20)	−1416(11)	5895(9)	2860(6)	90(4) [a]
C(21)	−993(13)	6889(9)	2574(6)	101(5) [a]
C(22)	422(14)	6642(8)	2248(5)	93(5) [a]
C(23)	1414(11)	5388(7)	2207(4)	71(4) [a]
C(24)	2539(8)	3008(7)	963(4)	51(3) [a]
C(25)	3488(9)	3610(8)	650(4)	68(4) [a]
C(26)	3360(11)	4190(9)	−101(5)	78(4) [a]
C(27)	2247(12)	4162(9)	−544(5)	79(4) [a]
C(28)	1302(13)	3586(10)	−242(5)	92(5) [a]
C(29)	1439(11)	3001(9)	508(5)	78(4) [a]
C(30a) [b]	4013(11)	−5(16)	1403(11)	66(2)
C(30b) [b]	4015(13)	−19(17)	1414(10)	66(2)
C(31)	2824(7)	−447(7)	1161(4)	58(3) [a]
C(32)	3162(13)	−1474(9)	690(5)	89(5) [a]
C(33)	2058(15)	−1836(11)	436(6)	108(7) [a]
C(34)	607(14)	−1254(10)	668(6)	100(6) [a]
C(35)	247(12)	−274(10)	1137(5)	83(5) [a]
C(36)	1299(9)	103(7)	1400(4)	60(3) [a]
C(37a) [b]	5436(14)	−1003(15)	1533(11)	88(6)
C(37b) [b]	5015(18)	161(19)	796(10)	90(6)
C(38)	6805(8)	882(10)	2478(5)	79(4) [a]
C(39)	6526(8)	1896(8)	1928(5)	68(4) [a]
C(40)	7053(11)	3063(11)	1957(7)	97(5) [a]
C(41)	5987(12)	4060(11)	2433(9)	125(7) [a]
C(42)	4923(11)	3667(10)	2970(7)	90(5) [a]
C(43)	5387(10)	2627(11)	3535(6)	90(5) [a]
C(44)	7021(12)	1859(15)	3694(8)	137(8) [a]
C(45)	7652(11)	755(13)	3204(6)	111(6) [a]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Atoms C(30a), C(30b), C(37a), C(37b) each have 50% occupancy: refined positions of atoms C(30a) and C(30b) are almost coincident.

3.5. Crystal data

Ru{C_5Ph_4(CH(Me)Ph}cod; $C_{45}H_{41}Rh$; $M = 684.72$; crystallises from ethanol/water/heptane as small yellow blocks; crystal dimensions $0.325 \times 0.175 \times 0.175$ mm. Triclinic, $a = 9.688(11)$, $b = 11.299(16)$, $c = 17.396(12)$ Å, $\alpha = 85.06(9)$, $\beta = 85.38(8)$, $\gamma = 68.54(9)^0$, $U = 1763(3)$ Å^3; $D_c = 1.290$ g cm^{-3}, $Z = 2$. Space group $P\bar{1}$ (C_i^1, No. 2), Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 5.04 cm^{-1}, $F(000) = 711.92$.

3.6. Structure analysis and refinement

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 4-circle diffractometer by the omega scan method. The 4457 independent reflections (of 6035 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects; no correction was made for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Since the original mixture from which the crystal was obtained had an enantiomeric excess of one optical isomer of the 2-phenethyl ligand, it had been anticipated that a non-racemic space group might have arisen. The interpretation in space group $P\bar{1}$ reveals a disorder of the methyl substituent C(37) into two sites with equal occupancy, but no apparent disorder of the remainder of the structure as evidenced by thermal vibrational parameters and molecular geometry. Structure factor calculations in space group $P\bar{1}$ for two enantiomeric models, each comprising two independent molecules of the same chirality gave (not surprisingly) indistinguishable values of R. No refinement in the lower symmetry space group was attempted, since the high correlation coefficients for almost all pairs of parameters would have precluded a well-determined refinement. Thus, it is impossible to determine whether the crystals actually consist of equal numbers of each enantiomer, or whether the existing proportions of the two enantiomers are statistically disordered over the lattice sites, differing only in the interchange of methyl and hydrogen in the 1-phenethyl ligand. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement in $P\bar{1}$ converged at a final R 0.0835 (R_w 0.0847, 412 parameters, mean and maximum δ/σ 0.017, 0.061), with allowance for the thermal anisotropy of all non-hydrogen atoms with the exception of the disordered carbon atoms. The final minimum and maximum difference electron density were −1.08 and 1.27 eÅ^{-3}. Complex scattering factors were taken from the international tables [16] and from the program package SHELXTL [17] as implemented on the Data General Nova 3 com-

puter. A weighting scheme $w^{-1} = [\sigma^2(F) + g(F)^2]$ with $g = 0.00268$ was used in the latter stages of the refinement.

Table 2 lists atomic positional parameters with estimated standard deviations. A full list of bond lengths and bond angles, anisotropic thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We wish to record our sincere thanks to the S.E.R.C. for a CASE studentship (to J.A.R.), to Johnson Matthey for the generous loan of ruthenium trichloride (to C.W.) and to the Royal Society and the S.E.R.C. for funds for the X-ray and computing equipment.

References

[1] (a) R.L. Halterman, *Chem. Rev., 92* (1992) 965; (b) G. Erker and A.A.H. van der Zeijden, *Angew. Chem., Int. Ed. Engl., 29* (1990) 512, and references therein.

[2] (a) K.B. Sinclair and R.B. Wilson, *Chem. Ind.,* (1994) 857; (b) X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc., 116* (1994) 10015, and references therein.

[3] R.L. Haltermann, K.P.C. Vollhardt, M.E. Welker, D. Bläser and R. Boese, *J. Am. Chem. Soc., 109* (1987) 8105.

[4] (a) V.P. Conticello, L. Brard, M.A. Giarrdello, Y. Tsuji, M. Sabat, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc., 114* (1992) 2761; (b) Z. Chen and R.L. Haltermann, *J. Am. Chem. Soc., 114* (1992) 2276; (c) J.A. Ewen, R.L. Jones, A. Razavi and J.D. Ferrara, *J. Am. Chem. Soc., 110* (1988) 6255; (d) P. Pino, P. Cioni and J.J. Wei, *J. Am. Chem. Soc., 109* (1987) 6189.

[5] A. Fusi, E. Cesarotti and R. Ugo, *J. Mol. Catal., 10* (1981) 213.

[6] (a) J.A. Ramsden, D.J. Milner, H. Adams, N.A. Bailey, A.J. Smith and C. White, *Organometallics,* in press; (b) J.A. Ramsden, D.J. Milner, P.D. Hempstead, N.A. Bailey and C. White, *J. Chem. Soc., Dalton Trans.,* in press.

[7] J.K. Kochi and G.S. Hammond, *J. Am. Chem. Soc., 75* (1953) 3443.

[8] H.J. Dauben and L.L. McCoy, *J. Am. Chem. Soc., 81* (1959) 5408.

[9] G. Erker, R. Nolte, R. Aul, S. Wilker, C. Kruger and R. Noe, *Organometallics, 113* (1991) 7594.

[10] (a) H. Adams, N.A. Bailey, A.F. Browning, J.A. Ramsden and C. White, *J. Organomet. Chem., 387* (1990) 305; (b) L. Li, A. Decken, M.J. McGlinchey, P. Brégaint, J.-Y. Thépot, L. Toupet, J.-R. Hamon and C. Lapinte, *Organometallics, 13* (1994) 682.

[11] W. Dumont, J.C. Poulin, T.P. Dang and H.B. Kagan, *J. Am. Chem. Soc. 95* (1973) 8295.

[12] (a) P.A. Schofield, H. Adams, N.A. Bailey, E. Cesarotti and C. White, *J. Organomet. Chem., 412* (1991) 273; (b) H. Adams, N.A. Bailey, M. Colley, P.A. Schofield and C. White, *J. Chem. Soc., Dalton Trans.,* (1994) 1445.

[13] G. Giordano and R.H. Crabtree, *Inorg. Synth., 28* (1990) 88.

[14] W. Gerrard, *J. Chem. Soc.,* (1945) 848.

[15] R.O. Hutchins, D. Masilamani and C.A. Maryanoff, *J. Org. Chem., 41* (1976) 1071, and references therein.

[16] *International Tables for X-ray Crystallography, Vol. 4,* Kynoch, Birmingham, UK, 1974.

[17] G.M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 5.1), University of Göttingen, Germany 1985.