Chiral Tetraphenylcyclopentadienyl Complexes of Ruthenium and Palladium; Crystal Structure of $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2Br]$ (R^{1*} = Menthyl)†

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The compound (−)-bromomenthyltetraphenylcyclopentadiene has been synthesised. It reacts with $[Ru_3(CO)_{12}]$ to give $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_3]Br$ (R^{1*} = menthyl) which on heating yields $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2Br]$ **1**. Alternatively complex **1** may be prepared by treating bromoform with $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2H]$, generated from $[Ru_3(CO)_{12}]$ and $C_5Ph_4R^{1*}H$. A crystal structure of complex **1** shows that the crystals are monoclinic, space group $P2_1$ (C_2^2, no. 4), $Z = 4$, with $a = 13.783(4)$, $b = 17.799(5)$, $c = 14.974(3)$ Å, $\beta = 107.05(2)°$, $U = 3512.0$ Å^3; the structure has been refined to R 0.0777 for 3931 unique reflections in the range $3.5 < 2\theta < 45°$ (Mo-Kα radiation). The corresponding complex $[Pd(\eta^5\text{-}C_5Ph_4R^{2*})(\eta^3\text{-}C_3H_5)]$ (R^{2*} = neomenthyl) **2** has been synthesised by the reaction of $Li[C_5Ph_4R^{2*}]$ with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$.

Chiral cyclopentadienyl ligands have attracted considerable interest in recent years since they could prove to be attractive alternatives to chiral phosphine ligands in enantioselective synthesis.[1] This would be particularly valuable for substrates such as non-functionalised alkenes where the use of chiral phosphines leads to poor stereoselectivity.[2] We have therefore initiated a research programme to develop effective chiral cyclopentadienyl ligands.[3] One approach to this has been the synthesis of chiral tetra-aryl cyclopentadienyl ligands since, by analogy with the structures of pentaphenylcyclopentadienyl complexes,[4] the four aryl groups cannot lie coplanar and therefore must adopt a chiral array; it was hoped 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.

With this objective in mind we recently synthesised and determined the structures of a number of rhodium menthyl- and neomenthyl-tetraphenylcyclopentadienyl complexes.[5] We report herein our attempts to synthesise other transition-metal compounds containing such chiral tetraphenylcyclopentadienyl ligands.

Results and Discussion

Bromomenthyltetraphenylcyclopentadiene is readily made by bromination of menthyltetraphenylcyclopentadiene with *N*-bromosuccinimide using a procedure similar to that reported for 5-bromopentaphenylcyclopenta-1,3-diene.[6] Heating $C_5Ph_4R^{1*}Br$ (R^{1*} = menthyl) with dodecacarbonyltriruthenium in xylene under reflux gave bromodicarbonyl(η^5-menthyltetraphenylcyclopentadienyl)ruthenium in moderate (35%) yield. When the reaction was carried out in a more polar solvent, tetrahydrofuran (thf), the yield of the bromodicarbonyl complex was much higher (97%) and the reaction proceeded at a much lower temperature. This suggests that a highly polar intermediate is involved and support for this suggestion came from monitoring the reaction in xylene by IR spectroscopy. An intermediate with ν_{CO} 2135 (br), 2078 and 2067 cm^{-1} was detected which was observed to be converted to the product $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2Br]$ having ν_{CO}(xylene) at 2043 and 1996 cm^{-1}. The IR spectrum of the intermediate is similar to that reported for $[Ru(C_5H_5)(CO)_3]BF_4$ [ν_{CO} 2137, 2091 and 2077 cm^{-1} (CH_2Cl_2)][7] and we propose that the observed intermediate is $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_3]Br$ formed by oxidative addition from the initial cyclopentadiene complex $[Ru(\eta^4\text{-}C_5Ph_4R^{1*}Br)(CO)_3]$. The final step in the reaction is then loss of CO from $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_3]Br$ followed by co-ordination of the outer-sphere bromide ion.

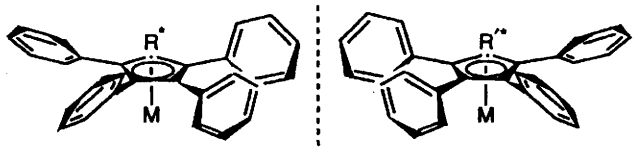

Fig. 1 Chiral array of four aryl substituents. R*, R'* = bulky chiral substituent; R'* has the opposite configuration to R*

The reaction of $[Ru_3(CO)_{12}]$ with cyclopentadiene in heptane under reflux in air is known to lead to $[Ru(C_5H_5)(CO)_2H]$[7] which reacts with halogenated solvents to give the corresponding halide complex.[8] This sequence formed the basis of an alternative, but inferior, synthesis of complex **1**. Thus, heating $[Ru_3(CO)_{12}]$ with $C_5Ph_4R^{1*}H$ in xylene under reflux resulted in significant decomposition but did generate $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2H]$ which on treatment with bromoform gave complex **1** in 25% overall yield.

An attempt was made to isolate the $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2H]$ formed in the above reaction but, although this compound appears to be somewhat less air-sensitive than the corresponding C_5H_5 complex, it still proved impossible to isolate an analytically pure sample. However, the spectroscopic properties of the product isolated [ν_{CO} 2018 and 1957 cm^{-1} (hexane), δ_H −9.8 (RuH, $CDCl_3$)] closely resemble those of $[Ru(C_5H_5)(CO)_2H]$[9] [ν_{CO} 2025 and 1966 cm^{-1} (CS_2), δ_H −10.9 (RuH, C_6H_{12})]; this, together with its FAB mass spectrum {*m*/*z* (argon) 665 ($[Ru(C_5Ph_4R^{1*})(CO)_2]^+$, 24), 635 ([Ru(C$_5$-

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Menthyl and neomenthyl are *t*-2-isopropyl-*c*-5-methylcyclohexan-*r*-1-yl and *c*-2-isopropyl-*t*-5-methylcyclohexan-*r*-1-yl, respectively.

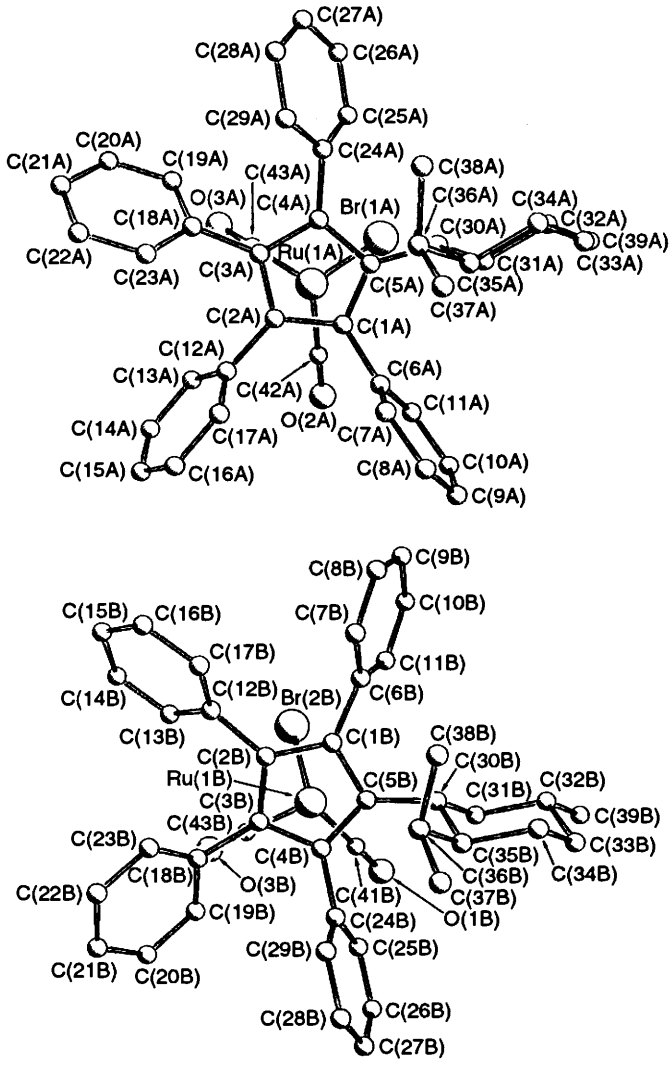

Fig. 2 Structure of the two crystallographically independent molecules of $[Ru(\eta^5\text{-}C_5Ph_4R^{1*})(CO)_2Br]$ **1**

$Ph_4R^{1*})CO]^+$, 32) and 605 ($[Ru(C_5Ph_4R^{1*})]^+$, 100%)} and its reaction with bromoform to give **1** leave no doubt as to its identity.

Reaction of $Li[C_5Ph_4R^{2*}]$ (R^{2*} = neomenthyl) with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ in thf at room temperature rapidly led to the formation of $[Pd(\eta^5\text{-}C_5Ph_4R^{2*})(\eta^3\text{-}C_3H_5)]$. The product was isolated as a purple air-sensitive powder which proved to be unstable in solution over a period of hours, frustrating attempts to grow crystals for X-ray analysis. Such instability was not reported for the corresponding pentaphenylcyclopentadienyl compound[10] and may arise from the considerable steric bulk of the neomenthyltetraphenylcyclopentadienyl ligand. In the ^1H and ^{13}C NMR spectra of this compound, the methylene groups of the η^3-allyl ligand are inequivalent reflecting the chirality of the cyclopentadienyl ligand.

It has been reported that reaction of $Li[C_5Ph_5]$ with $TiCl_4$ leads to $[Ti(\eta^5\text{-}C_5Ph_5)_2Cl_2]$, although only brief experimental details have been published.[11] We therefore had several attempts to synthesise $[Ti(\eta^5\text{-}C_5Ph_4R^{1*})_2Cl_2]$ by reaction of $Li[C_5Ph_4R^{1*}]$ with either $TiCl_4$ or $TiCl_3$, but even under quite forcing conditions, *e.g.* xylene at 140 °C for 3 h, none of the desired complex was formed. We conclude that the steric bulk of the menthyltetraphenylcyclopentadienyl ligand inhibits the complexation of two such ligands to a single titanium atom.

Crystal Structure of Complex **1**.—The structures of the two crystallographically independent molecules are illustrated in Fig. 2, Table 1 gives bond lengths and angles with estimated standard deviations.

The structure comprises two molecules, each of which contains a ruthenium atom bonded to a bromine, two carbonyls and to an η^5-menthyltetraphenylcyclopentadienyl ligand; the bromine and carbonyl ligands are unevenly disordered between the three basal sites of each molecule. With the exception of the menthyl substituents, the molecules are closely centrosymmetrically related through [−0.25, 0, 0.25], which would be the site of the inversion centre in space group $P2_1/n$ with 2_1 coincident with the crystallographic y axis. In contrast to the normal conformation adopted by a phenyl-substituted cyclopentadienyl,[4,12] the phenyl groups do not adopt a full propeller arrangement; the direction of tilt changes after the first phenyl group. Thus, the two phenyls adjacent to the menthyl site are tilted in opposite directions to form a 'cup' with its open side directed away from the metal, within which is encapsulated the menthyl substituent, of which the isopropyl group is situated on the side of the cyclopentadienyl away from the ruthenium. A similar orientation of the phenyl groups was found for the related $[Rh(\eta^5\text{-}C_5Ph_4R^{1*})(cod)]$ (cod = cycloocta-1,5-diene) complex[5] and supports the view that the chiral orientation of the phenyl groups can be influenced by the chirality of the fifth ring-substituent. The two menthyl substituents differ only in their rotational orientations; torsion angles C(1)–C(5)–C(30)–C(35) and C(4)–C(5)–C(30)–C(35) are, respectively, −57 and +110° for molecule A, and +120 and −44° for molecule B, showing that equivalent (but not pseudo-symmetry related) torsion angles differ by only about 13°. Similarly, the interplanar angles between the phenyl rings and the cyclopentadienyl ring are 96, 58, 48 and 63° for molecule A, and 110, 69, 49 and 72° for molecule B. The ruthenium atoms are rather asymmetrically bonded to the five-membered ring and lie respectively 1.899 and 1.900 Å from the cyclopentadienyl planes for molecules A and B.

Compared with related ruthenium cyclopentadienyl complexes, the ruthenium–cyclopentadienyl bond lengths in complex **1** are not exceptional but tend to be long, *i.e.* mean Ru–C distance is 2.252(11) compared to 2.219(19) and 2.229(12) Å in $[Ru(C_5H_5)(CO)_2Br]$ and $[Ru(C_5Me_4Et)(CO)_2Br]$[13] respectively. This may indicate steric congestion in **1** but we note that the sterically crowded complex $[Ru(C_5Ph_5)(CO)(PPh_3)Br]$ has a significantly larger ruthenium–cyclopentadienyl bond length [mean Ru–C distance = 2.277(11) Å].[4c] Given the constraints applied, it is not appropriate to comment upon the Ru–CO and Ru–Br distances in complex **1**.

Conclusion

Clearly the menthyl- and neomenthyl-tetraphenylcyclopentadienyl ligands are bulky and the failure to prepare $[Ti(\eta^5\text{-}C_5Ph_4R^{1*})_2Cl_2]$ with two such bulky ligands bound to the same metal is not too surprising. It is also clear, however, from the work described herein and our previous syntheses of rhodium complexes, that binding one of these ligands to a metal presents no inherent difficulties. This, together with the fact that bulky ligands are often most effective in enantioselective synthesis[14] and the observation that the chiral orientation of the phenyl groups is influenced by the chirality of the fifth ring-substituent thus transmitting the chirality over the whole metal, encourages us to extend our studies to developing enantioselective transition metal catalysts bearing chiral tetraarylcyclopentadienyl ligands.

Experimental

General experimental details together with the syntheses of menthyl- and neomenthyl-tetraphenylcyclopentadiene have been reported previously.[6]

Table 1 Bond lengths (Å) and angles (°) for complex **1***

Ru(1A)–Br(1A)	2.529(5)	Ru(1A)–Br(2A)	2.527(13)	C(33A)–C(34A)	1.540(9)	C(34A)–C(35A)	1.540(13)
Ru(1A)–Br(3A)	2.526(10)	Ru(1A)–C(1A)	2.235(12)	C(35A)–C(36A)	1.539(8)	C(36A)–C(37A)	1.540(15)
Ru(1A)–C(2A)	2.199(11)	Ru(1A)–C(3A)	2.238(10)	C(36A)–C(38A)	1.539(16)	C(1B)–C(6B)	1.492(18)
Ru(1A)–C(4A)	2.296(11)	Ru(1A)–C(5A)	2.295(13)	C(2B)–C(12B)	1.507(17)	C(3B)–C(18B)	1.507(17)
Ru(1B)–Br(1B)	2.527(9)	Ru(1B)–Br(2B)	2.527(5)	C(4B)–C(24B)	1.497(17)	C(5B)–C(30B)	1.536(16)
Ru(1B)–Br(3B)	2.526(9)	Ru(1B)–C(1B)	2.312(12)	C(30B)–C(31B)	1.540(11)	C(30B)–C(35B)	1.540(12)
Ru(1B)–C(2B)	2.271(11)	Ru(1B)–C(3B)	2.205(10)	C(31B)–C(32B)	1.540(13)	C(32B)–C(33B)	1.540(13)
Ru(1B)–C(4B)	2.207(11)	Ru(1B)–C(5B)	2.274(12)	C(32B)–C(39B)	1.540(11)	C(33B)–C(34B)	1.540(12)
C(1A)–C(6A)	1.524(18)	C(2A)–C(12A)	1.525(17)	C(34B)–C(35B)	1.540(12)	C(35B)–C(36B)	1.539(10)
C(3A)–C(18A)	1.496(17)	C(4A)–C(24A)	1.507(17)	C(36B)–C(37B)	1.540(15)	C(36B)–C(38B)	1.539(17)
C(5A)–C(30A)	1.533(16)	C(30A)–C(31A)	1.540(10)	Ru–C(O)	1.930	C–O	1.150
C(30A)–C(35A)	1.540(10)	C(31A)–C(32A)	1.540(14)	C–C(Cp)	1.420	C–C(phenyl)	1.395
C(32A)–C(33A)	1.540(12)	C(32A)–C(39A)	1.540(9)				
Br(1A)–Ru(1A)–Br(2A)	80.4(3)	Br(1A)–Ru(1A)–Br(3A)	86.8(3)	C(31A)–C(30A)–C(35A)	109.5(6)	C(30A)–C(31A)–C(32A)	109.5(8)
Br(2A)–Ru(1A)–Br(3A)	71.0(5)	C(41A)–Ru(1A)–Br(1A)	5.5(2)	C(31A)–C(32A)–C(33A)	109.5(7)	C(31A)–C(32A)–C(39A)	109.5(8)
C(42A)–Ru(1A)–Br(1A)	89.9(2)	C(43A)–Ru(1A)–Br(1A)	77.1(1)	C(33A)–C(32A)–C(39A)	109.5(7)	C(32A)–C(33A)–C(34A)	109.5(7)
C(41A)–Ru(1A)–Br(2A)	85.5(3)	C(42A)–Ru(1A)–Br(2A)	13.0(3)	C(33A)–C(34A)–C(35A)	109.5(8)	C(36A)–C(35A)–C(30A)	109.6(6)
C(43A)–Ru(1A)–Br(2A)	85.6(4)	C(41A)–Ru(1A)–Br(3A)	90.5(3)	C(36A)–C(35A)–C(34A)	109.6(7)	C(30A)–C(35A)–C(34A)	109.4(7)
C(42A)–Ru(1A)–Br(3A)	80.2(4)	C(43A)–Ru(1A)–Br(3A)	18.9(4)	C(35A)–C(36A)–C(37A)	109.5(7)	C(35A)–C(36A)–C(38A)	109.6(7)
C(41A)–Ru(1A)–C(42A)	94.5	C(41A)–Ru(1A)–C(43A)	79.5	C(37A)–C(36A)–C(38A)	109.5(9)	C(2B)–C(1B)–C(6B)	128.2
C(42A)–Ru(1A)–C(43A)	96.4	Br(1B)–Ru(1B)–Br(2B)	83.2(3)	C(5B)–C(1B)–C(6B)	123.8	C(1B)–C(2B)–C(12B)	125.7
Br(1B)–Ru(1B)–Br(3B)	77.5(4)	Br(2B)–Ru(1B)–Br(3B)	86.3(3)	C(3B)–C(2B)–C(12B)	126.3	C(2B)–C(3B)–C(18B)	126.5
C(41B)–Ru(1B)–Br(1B)	9.3(3)	C(42B)–Ru(1B)–Br(1B)	86.2(3)	C(4B)–C(3B)–C(18B)	124.1	C(3B)–C(4B)–C(24B)	121.1
C(43B)–Ru(1B)–Br(1B)	88.5(3)	C(41B)–Ru(1B)–Br(2B)	81.6(1)	C(5B)–C(4B)–C(24B)	130.2	C(1B)–C(5B)–C(30B)	122.8(6)
C(42B)–Ru(1B)–Br(2B)	4.1(1)	C(43B)–Ru(1B)–Br(2B)	82.4(1)	C(4B)–C(5B)–C(30B)	127.5(6)	C(1B)–C(6B)–C(7B)	119.4
C(41B)–Ru(1B)–Br(3B)	86.6(3)	C(42B)–Ru(1B)–Br(3B)	84.3(3)	C(1B)–C(6B)–C(11B)	120.6	C(2B)–C(12B)–C(13B)	122.2
C(43B)–Ru(1B)–Br(3B)	12.1(3)	C(41B)–Ru(1B)–C(42B)	85.0	C(2B)–C(12B)–C(17B)	117.7	C(3B)–C(18B)–C(19B)	121.0
C(41B)–Ru(1B)–C(43B)	97.3	C(42B)–Ru(1B)–C(43B)	79.7	C(3B)–C(18B)–C(23B)	118.9	C(4B)–C(24B)–C(25B)	123.3
C(2A)–C(1A)–C(6A)	124.9	C(5A)–C(1A)–C(6A)	126.6	C(4B)–C(24B)–C(29B)	116.7	C(5B)–C(30B)–C(31B)	113.4(7)
C(1A)–C(2A)–C(12A)	126.7	C(3A)–C(2A)–C(12A)	125.2	C(5B)–C(30B)–C(35B)	115.2(7)	C(31B)–C(30B)–C(35B)	109.5(8)
C(2A)–C(3A)–C(18A)	126.8	C(4A)–C(3A)–C(18A)	124.6	C(30B)–C(31B)–C(32B)	109.5(6)	C(31B)–C(32B)–C(33B)	109.5(7)
C(3A)–C(4A)–C(24A)	125.6	C(5A)–C(4A)–C(24A)	126.2	C(31B)–C(32B)–C(39B)	109.5(7)	C(33B)–C(32B)–C(39B)	109.4(9)
C(1A)–C(5A)–C(30A)	126.1(6)	C(4A)–C(5A)–C(30A)	124.8(6)	C(32B)–C(33B)–C(34B)	109.5(9)	C(33B)–C(34B)–C(35B)	109.5(6)
C(1A)–C(6A)–C(7A)	116.2	C(1A)–C(6A)–C(11A)	123.6	C(36B)–C(35B)–C(30B)	109.6(7)	C(36B)–C(35B)–C(34B)	109.6(6)
C(2A)–C(12A)–C(13A)	119.8	C(2A)–C(12A)–C(17A)	120.2	C(30B)–C(35B)–C(34B)	109.4(7)	C(35B)–C(36B)–C(37B)	109.5(8)
C(3A)–C(18A)–C(19A)	120.3	C(3A)–C(18A)–C(23A)	119.7	C(35B)–C(36B)–C(38B)	109.6(7)	C(37B)–C(36B)–C(38B)	109.5(9)
C(4A)–C(24A)–C(25A)	122.6	C(4A)–C(24A)–C(29A)	117.3	Ru–C–O	180.0	C–C–C(Cp)	108.0
C(5A)–C(30A)–C(31A)	113.6(8)	C(5A)–C(30A)–C(35A)	115.5(8)	C–C–C(phenyl)	120.0		

* Cp = the centroid of the cyclopentadienyl ring of $C_5Ph_4R^1$ *.

Syntheses.—(−)-*Bromomenthyltetraphenylcyclopentadiene.* Menthyltetraphenylcyclopentadiene (2.0 g, 4.5 mmol) and *N*-bromosuccinimide (0.8 g, 4.5 mmol) were suspended in carbon tetrachloride (40 cm^3) and the mixture heated to reflux under nitrogen whilst being irradiated with a UV lamp for 2.5 h. After cooling to room temperature, the solvent was removed *in vacuo* and the crude product recrystallized from light petroleum (b.p. 40–60 °C) to give a yellow powder (1.9 g, 81%), m.p. 192–195 °C (Found: C, 79.8; H, 7.1; Br, 13.5. $C_{39}H_{39}Br$ requires C, 79.7; H, 6.7; Br, 13.5%): $[\alpha]_D^{20}$ (= $100\alpha/lc$, where α is the observed rotation in degrees, l is the path length in dm and c is the concentration in g per 100 cm^3 solution) (c = 1.180, $CHCl_3$) (589 nm) −593, (578 nm) −65.3, and (546 nm) −78.0° dm^{-1} g^{-1} cm^3. Electron impact mass spectrum: m/z 588 ($[M]^+$, 38), 508 ($[M - Br]^+$, 93%): NMR ($CDCl_3$, reference $SiMe_4$): δ_H(250 MHz) 0.27–2.80 (19 H, m), 6.50–7.50 (20 H, m); δ_C(63 MHz) 14–16 and 21–22.5 (CH_3), 24–27, 33–34 and 39–44 (menthyl CH), 22–25, 35–36 and 41–43 (menthyl CH_2), 126–132 (aromatic CH), 133–138 and 143–150 (aromatic C).

(−)-*Bromodicarbonyl*(η^5-*menthyltetraphenylcyclopentadienyl*)*ruthenium* **1**. *Method* (*i*). (−)-Bromomenthyltetraphenylcyclopentadiene (300 mg, 0.51 mmol) and dodecacarbonyltriruthenium (110 mg, 0.17 mmol) were heated at reflux under nitrogen in thf (15 cm^3) for 17 h. The mixture was allowed to cool to room temperature and the solvent removed *in vacuo*. The residue was chromatographed on alumina and a yellow band eluted with hexane–CH_2Cl_2–Et_2O; removal of the eluent *in vacuo* gave the pure yellow product (370 mg, 97%), m.p. 180 °C (decomp.) (Found: C, 65.8; H, 5.4; Br, 9.8. $C_{41}H_{39}BrO_2Ru$ requires C, 66.1; H, 5.3; Br, 10.7%): $[\alpha]_D^{20}$ (c = 1.00, $CHCl_3$) (589 nm) −253, (578 nm) −265.0, (546 nm) −304.0, and (436 nm) −659.0° dm^{-1} g^{-1} cm^3: IR. ν_{CO}(CH_2Cl_2) at 1997 and 2045 cm^{-1}. FAB mass spectrum: (argon) 687 {$[Ru(C_5Ph_4R^{1*})Br]^+$, 18}, 665 {$[Ru(C_5Ph_4R^{1*})(CO)_2]^+$, 27}, 635 {$[Ru(C_5Ph_4R^{1*})(CO)]^+$, 27} and 605 {$[Ru(C_5Ph_4R^{1*})]^+$, 100%}. NMR ($CDCl_3$, reference $SiMe_4$): δ_H(250 MHz) −0.70 (3 H, d, J_{HH} 7, CH_3), 0.69 (3 H, d, J_{HH} 7, CH_3), 0.75 (3 H, d, J_{HH} 7 Hz, CH_3), 0.16–1.67 (9 H, m, menthyl CH_2 and CH), 2.19 (1 H, m, menthyl CH), 6.89–7.45 (20 H, m, aromatic CH); δ_C(63 MHz) 16.1, 21.6, 22.1 (menthyl CH_3), 24.6, 34.3 and 48.6 (CH_2), 27.9, 33.7, 38.2 and 45.2 (CH), 104.8, 105.0, 110.0, 110.9 and 115.7 (cyclopentadienyl C), 127.3–128.5 and 132.6–133.6 (aromatic CH), 129.3–133.0 (aromatic C), 196.9 and 197.0 (CO).

Method (*ii*) A mixture of menthyltetraphenylcyclopentadiene (110 mg, 0.216 mmol) and dodecacarbonyltriruthenium (43 mg, 0.067 mmol) was heated at reflux under nitrogen in xylene (12 cm^3) and the reaction monitored by IR spectroscopy. Heating was stopped when the IR spectrum showed that all the $[Ru_3(CO)_{12}]$ had been converted into $[Ru(C_5Ph_4R^{1*})(CO)_2H]$ (ν_{CO} at 1960 and 2019 cm^{-1}), *ca.* 100 min. The solution was allowed to cool to room temperature, bromoform (1 cm^3) was added and the mixture heated at 100 °C for 10 min. Work-up of the reaction mixture as described above gave the desired product (38 mg, 25%).

(+)-(η^5-*Neomenthyltetraphenylcyclopentadienyl*)(η^3-*propenyl*)*palladium* **2**. Neomenthyltetraphenylcyclopentadiene (500 mg, 1 mmol) was dissolved in dry toluene (8 cm^3) and heated to 98 °C under nitrogen. Butyllithium solution (2.5 mol dm^{-3} in hexanes, 1 mmol) was added over 15 min and the mixture stirred for 1 h at 95 °C. After cooling to room temperature, the solution of $Li[C_5Ph_4R^{2*}]$ was added dropwise over 10 min to a solution of freshly prepared di-μ-chloro-bis(η^3-propenyl)-dipalladium (200 mg, 1.1 mmol) in thf (30 cm^3) under nitrogen. The mixture was stirred at room temperature for 35 min and the solvent then removed *in vacuo*. The residue was extracted into dichloromethane, filtered and, after removing the dichloromethane *in vacuo*, the product was chromatographed [alumina; 2% ether, 98% light petroleum (b.p. 60–80 °C)] to give a purple powder (170 mg, 28%), m.p. 65–67 °C (Found: C, 77.8; H, 7.0. $C_{42}H_{44}Pd$ requires C, 77.0; H, 6.8%). $[\alpha]_D^{20}$ (c = 0.82, 589 nm, $CHCl_3$) +419° dm^{-1} g^{-1} cm^3. FAB mass spectrum: m/z (argon) 654 ($[M]^+$, 100), 611 ($[M - allyl]^+$, 20%). NMR ($CDCl_3$, reference $SiMe_4$): δ_H(250 MHz) 0.68–1.98 (18 H, m, menthyl), 2.71 (2 H, m, allyl), 3.46 (1 H, m, menthyl), 3.71 and 3.65 (2 H, m, allyl), 5.29 (1 H, m, allyl), 6.8–7.4 (20 H, m, aromatic); δ_C(63 MHz) 18.8, 21.6, 24.7, 25.6, 27.2, 35.1 and 44.0 (menthyl CH and CH_3), 23.6, 29.7 and 37.8 (CH_2), 50.3 and 50.8 (allylic CH_2), 97.9 (allylic CH), 115.8, 116.1, 116.8, 117.5 and 118.0 (cyclopentadienyl C), 125–133 (aromatic CH), 135–137 (aromatic C).

Crystal-structure Determination of [Ru(η^5-$C_5Ph_4R^{1*}$)-$(CO)_2Br$].—*Crystal data.* $C_{41}H_{39}BrO_2Ru$, M = 744.74 (crystallises from dichloromethane–pentane as yellow–orange elongated plates; crystal dimensions 0.72 × 0.50 × 0.40 mm), monoclinic, space group $P2_1$ (C_2^2, no. 4), a = 13.783(4), b = 17.799(5), c = 14.974(3) Å, β = 107.05(2)°, U = 3512.0 $Å^3$, D_m = 1.40, D_c = 1.409 g cm^{-3}, Z = 4, λ(Mo-Kα) = 0.710 73 Å), μ(Mo-Kα) = 1.62 mm^{-1}, $F(000)$ = 1520.

Structure analysis and refinement. Three-dimensional, room temperature X-ray data of good quality were collected on a Siemens P4 diffractometer in the range $3.5 < 2\theta < 45°$ by the ω-scan method. Of the 5853 reflections measured, the 3931 independent reflections for which $|F|/\sigma(|F|) > 5.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 24 azimuthal scans. The maximum and minimum transmission coefficients were 0.182 and 0.150 respectively.

The positions of the ruthenium atoms were determined by standard Patterson techniques and found to be consistent with space group $P2_1/n$ (of which $P2_1$ is a sub-group). Three positions were found for bromine atoms in the basal sites. Initially, structure solution was continued in this higher symmetry space group, since the positions of the phenyl groups also seemed to be consistent with it. The relative occupancies of the three bromine sites were determined. At this stage, the atoms of the chiral menthyl group were ill-defined, but an acceptable model was derived which accounted well for the electron density and showed disorder of the two optical isomers in different rotational conformations about the bond linking the group to the cyclopentadienyl ring. The geometries of the menthyl groups were constrained with only the isopropyl substituent allowed some rotational freedom. The space group symmetry was lowered to the non-centrosymmetric $P2_1$ and two independent (disordered Br)Ru($C_5Ph_4R^{1*}$) fragments, each containing a menthyl of the correct chirality, were inserted. The omitted phenyl rings were redetermined from difference electron density syntheses: their positions were little changed. The overall structure still possessed approximate $P2_1/n$ symmetry with the two crystallographically independent molecules approximately centrosymmetrically related, and correlation coefficients were very high. The occupancies of the six disordered bromine atoms were now refined with a common isotropic thermal parameter, converging at 0.645, 0.169, 0.186 and 0.253, 0.534, 0.213 for molecules A and B respectively: these values were then constrained. The disordered carbonyl components were detected and inserted with idealised, linear geometries, and appropriate occupancies; optimisation of their angular positions around the ruthenium atoms was permitted. Sensible and controlled refinement could only be achieved after all phenyl groups had been given constrained D_{6h} symmetry, and the cyclopentadienyl ligands had been constrained to D_{5h}. Refinement on $|F|$ then proceeded by blocked cascade least squares methods. Hydrogen atoms were placed in predicted positions, and refined in riding mode, with isotropic thermal parameters related to those of the supporting carbon atoms. Refinement converged at a final R 0.0777 (R' 0.0921, wR 0.1152, 189 parameters, maximum δ/σ 0.021) with allowance for coupled anisotropic thermal motion of ruthenium atoms, and independent anisotropic thermal motion of the (non-

Table 2 Atomic coordinates ($\times 10^4$) for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1A)	−1378(1)	−2582(3)	1491(1)	C(36A)	2438(6)	−1762(6)	2521(4)
Ru(1B)	−3615(1)	2561(2)	3541(1)	C(37A)	3503(8)	−2119(9)	2827(6)
Br(1A)	−2284(4)	−1905(4)	−6(3)	C(38A)	2521(11)	−919(7)	2760(6)
Br(2A)	−2423(11)	−3655(6)	597(11)	C(39A)	365(8)	−1378(8)	−1448(4)
Br(3A)	−3068(5)	−2612(9)	1831(9)	C(41A)	−1963	−1997	378
Br(1B)	−2670(8)	1856(7)	5002(5)	C(42A)	−1895	−3529	916
Br(2B)	−2776(4)	3691	4472(4)	C(43A)	−2621	−2253	1714
Br(3B)	−1920(5)	2306(7)	3271(8)	C(1B)	−5267(9)	2999(7)	3066(7)
O(1A)	−2312	−1649	−286	C(2B)	−4807	3113	2343
O(2A)	−2203	−4092	574	C(3B)	−4524	2401	2074
O(3A)	−3362	−2057	1847	C(4B)	−4809	1846	2631
O(1B)	−2743	1787	5448	C(5B)	−5268	2216	3244
O(2B)	−2562	3981	4550	C(6B)	−5694(9)	3574(7)	3570(7)
O(3B)	−1656	2547	2947	C(7B)	−6586	3949	3097
C(1A)	247(9)	−2941(7)	1910(7)	C(8B)	−7003	4478	3565
C(2A)	−186	−3091	2643	C(9B)	−6528	4634	4505
C(3A)	−446	−2393	2972	C(10B)	−5636	4260	4977
C(4A)	−174	−1812	2441	C(11B)	−5219	3730	4510
C(5A)	254	−2150	1785	C(12B)	−4666(10)	3861(6)	1926(8)
C(6A)	749(8)	−3526(6)	1448(8)	C(13B)	−3709	4169	2030
C(7A)	1731	−3741	1949	C(14B)	−3616	4844	1587
C(8A)	2224	−4306	1603	C(15B)	−4482	5210	1040
C(9A)	1734	−4655	757	C(16B)	−5439	4902	935
C(10A)	752	−4440	256	C(17B)	−5531	4227	1378
C(11A)	260	−3875	602	C(18B)	−4203(9)	2230(8)	1216(6)
C(12A)	−298(10)	−3857(6)	3056(8)	C(19B)	−3440	1708	1245
C(13A)	−1250	−4097	3090	C(20B)	−3194	1529	430
C(14A)	−1352	−4788	3494	C(21B)	−3710	1873	−412
C(15A)	−501	−5239	3863	C(22B)	−4473	2395	−440
C(16A)	451	−4999	3830	C(23B)	−4720	2574	374
C(17A)	553	−4309	3426	C(24B)	−4745(10)	1026(6)	2430(10)
C(18A)	−801(9)	−2269(8)	3813(6)	C(25B)	−4042	541	3011
C(19A)	−1595	−1772	3774	C(26B)	−3996	−209	2755
C(20A)	−1908	−1646	4567	C(27B)	−4652	−473	1918
C(21A)	−1426	−2017	5400	C(28B)	−5355	12	1337
C(22A)	−631	−2513	5439	C(29B)	−5401	761	1593
C(23A)	−318	−2639	4646	C(30B)	−5899(6)	1860(6)	3825(5)
C(24A)	−247(11)	−981(6)	2606(9)	C(31B)	−5249(5)	1530(7)	4760(5)
C(25A)	−870	−503	1944	C(32B)	−5939(6)	1319(6)	5366(4)
C(26A)	−954	253	2158	C(33B)	−6725(7)	732(7)	4848(6)
C(27A)	−414	530	3034	C(34B)	−7373(5)	1064(7)	3913(5)
C(28A)	209	52	3696	C(35B)	−6683(5)	1273(5)	3308(4)
C(29A)	292	−704	3482	C(36B)	−7330(7)	1599(6)	2371(5)
C(30A)	817(5)	−1724(7)	1198(5)	C(37B)	−7955(10)	966(7)	1767(7)
C(31A)	348(5)	−1831(7)	138(5)	C(38B)	−8051(11)	2203(7)	2550(7)
C(32A)	833(6)	−1270(6)	−388(4)	C(39B)	−5288(8)	987(8)	6299(5)
C(33A)	1985(6)	−1410(8)	−124(4)	C(41B)	−3069	2076	4736
C(34A)	2453(5)	−1303(7)	936(5)	C(42B)	−2955	3451	4173
C(35A)	1969(5)	−1865(5)	1461(4)	C(43B)	−2388	2552	3169

pseudo-symmetry-related) highest occupancy disorder component of each bromine: a common isotropic thermal parameter was refined for each pseudo-centrosymmetrically related pair of ligands. Minimum and maximum difference electron densities were −1.41 and +1.37 e Å^{-3} respectively. Complex scattering factors were taken from the program package SHELXTL-PC[15] which, as implemented on the Viglen 486dx, was used for the final refinement; the structure solution was carried out using SHELXTL[16] as implemented on the Data General Nova 3 computer. A weighting scheme $w^{-1} = \sigma^2(F) + 0.001\ 70(F)^2$ was used in the latter stages of refinement. Table 2 lists atomic positional parameters with estimated standard deviations.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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