

Synthesis and Absolute Configuration of a Series of Chiral Ruthenium Complexes; Crystal Structure of (R) - $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{I}]$ ($\text{R}^* = \text{Neomenthyl}$) †

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The syntheses of $[\{\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})_2\}_2]$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})_2\text{X}]$ ($\text{R}^* = \text{menthyl}$ or neomenthyl ; $\text{X} = \text{Cl}$, Br , or I) are reported. Phosphines and phosphites react with the halide complexes to give the diastereoisomers $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})\text{LX}]$ [$\text{R}^* = \text{menthyl}$, $\text{X} = \text{Cl}$, $\text{L} = \text{PPh}_2\text{Me}$ or $\text{PPh}_2(\text{CH}_2\text{OMe})$; $\text{X} = \text{Br}$, $\text{L} = \text{PBU}^n_3$ or $\text{P}(\text{OPh})_3$; $\text{R}^* = \text{neomenthyl}$, $\text{X} = \text{I}$, $\text{L} = \text{PPh}_3$] containing a chiral ruthenium atom. These diastereoisomers have been resolved and their circular dichroism (c.d.) spectra are reported. An X -ray analysis of c.d. $(-)$ $_{325}[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{I}]$ ($\text{R}^* = \text{neomenthyl}$) has been carried out which established the absolute configuration of the ruthenium centre to be R . The crystals are monoclinic, space group $P2_1$ (no. 4) with $a = 12.833(6)$, $b = 15.186(6)$, $c = 7.972(5)$ Å, $\beta = 101.50(4)^\circ$, and $Z = 2$. On the basis of 1 773 observed reflections, the structure was refined to $R = 0.054$. It is proposed that the c.d. spectrum in the region 300–400 nm can be used to establish the configuration of the ruthenium atom in complexes of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})\text{-LX}]$ described.

In recent years there has been considerable interest in the stereochemical course of stoichiometric or catalytic reactions involving a chiral metal centre of an organotransition-metal complex.¹ Such studies require a knowledge of the absolute configurations of the chiral metal centres involved and at present the only unambiguous method of determining this is by X -ray crystallographic studies. It would obviously be desirable to correlate the known absolute configurations of organotransition-metal complexes with their chiroptical properties. In this way the unambiguous assignments of absolute configurations from X -ray studies on a few stable key organotransition-metal compounds could be readily extended to a large number of less stable related compounds using circular dichroism (c.d.) spectroscopy.

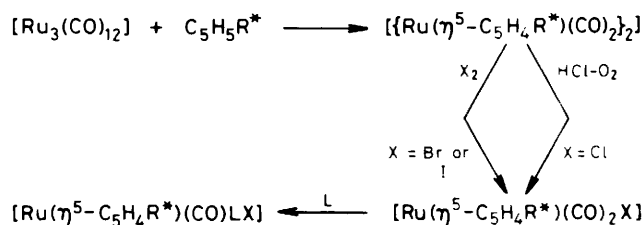
An attempt to do this for pseudo-tetrahedral complexes of the type $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{X}]$ found that there was a lack of correspondence between the u.v. and c.d. spectra and that it was feasible to correlate the chiroptical properties of these compounds with their absolute configurations only when the nature of the X group did not differ significantly.²

In the course of an investigation into the catalytic properties of cyclopentadienyl compounds³ we have investigated a number of chiral complexes and report herein the preparation and X -ray crystal structure of (R) -c.d. $(-)$ $_{325}[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$.[†] We have also examined the possibility of using the c.d. spectrum of this compound together with that of (S) -c.d. $(-)$ $_{310}[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_3)\text{Cl}]$ as a basis for assigning the configuration of the metal centre of a compound of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})\text{LX}]$ (where $\text{R}^* = \text{menthyl}$ or neomenthyl , $\text{X} = \text{halide}$, and $\text{L} = \text{phosphine}$ or phosphite ligand) by c.d. spectroscopy alone.

† (R) -Carbonyliodo $[\eta\text{-}(c\text{-}2\text{-isopropyl-}t\text{-}5\text{-methylcyclohexan-}r\text{-}1\text{-yl)cyclopentadienyl}]$ triphenylphosphineruthenium.

Supplementary data available (No. SUP 23832, 17 pp.): structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

‡ Throughout this paper menthylcyclopentadienyl and neomenthylcyclopentadienyl are abbreviated as mcp and nmcp, respectively; menthyl and neomenthyl are t -2-isopropyl- c -5-methylcyclohexan- r -1-yl and c -2-isopropyl- t -5-methylcyclohexan- r -1-yl, respectively.



Scheme. $\text{R}^* = \text{Menthyl}$ or neomenthyl , $\text{L} = \text{phosphine}$ or phosphite ligand

Results and Discussion

The menthyl- and neomenthyl-cyclopentadienylruthenium complexes were synthesised by the procedures outlined in the Scheme which are analogous to those reported for the corresponding cyclopentadienyl compounds. Spectroscopic and analytical data are given in Tables 1–3.

The structure of the complex c.d. $(-)$ $_{325}[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$ (14a)§ is shown in Figure 1 and the environment around the ruthenium atom is shown in detail in Figure 2. According to the sequence rules for organometallic compounds⁴ the absolute configuration of the ruthenium in this compound is R . Selected bond distances and angles are reported in Table 4. The angles between the monodentate ligands range from $92.3(1)^\circ$ (I-Ru-P) to $86.2(4)^\circ$ (I-Ru-C) and indicate an almost octahedral environment around the ruthenium atom. The Ru-I bond distance of $2.708(1)$ Å agrees well with that found in $[\text{Ru}(\text{CO})_4\text{I}_2]$ [$2.719(7)$ Å]⁵ whereas the Ru-cp (mean 2.234 Å), C(cp)-C(cp) (mean 1.40 Å), Ru-C(CO) , and Ru-P bond lengths are very similar to those previously found in the complex $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_3)\text{Cl}]$.⁶ Thus changing the nature of the halide has no significant effect upon

§ The optically pure diastereoisomers are designated by the sign of the defined maximum of the c.d. spectrum in the 300–325 nm region rather than by the optical rotatory dispersion (o.r.d.) sign at 578 nm in order to avoid the confusion generated by the fact that some pairs of diastereoisomers have the same o.r.d. sign at 578 nm.

Table 1. Physical and analytical data

Complex	I.r. ^a /cm ⁻¹	M ⁺ (m/e)	Analysis ^b (%)		α_{D-20} ^c
			C	H	
(1) [$\{\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\}_2$]	2 010, 2 000, 1 965, 1 955, 1 935, 1 785	722	56.25 (56.65)	6.65 (6.40)	—
(2) [$\{\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\}_2$]	2 000, 1 965, 1 955, 1 935, 1 785	722	55.85 (56.65)	6.15 (6.40)	+
(3) [$\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\text{Cl}$]	2 050, 2 000	396	50.60 (51.60)	5.55 (5.85)	—
(4) [$\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\text{Br}$]	2 055, 2 000	440	45.80 (46.40)	5.05 (5.25)	—
(5) [$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{Cl}$]	2 050, 2 002	396	53.50 (51.60)	6.40 (5.85)	+
(6) [$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{Br}$] ^d	2 049, 2 001	440	47.50 (46.40)	5.20 (5.25)	+
(7) [$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{I}$] ^e	2 049, 2 000	488	41.50 (41.90)	4.95 (4.70)	+
(8) c.d. (\pm) ₃₁₀ [$\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_2\text{Me})\text{Cl}$]	1 950 ^f	568	60.10 (61.30)	5.70 (6.35)	—
(9) c.d. (\pm) ₃₁₀ [$\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_2(\text{CH}_2\text{OMe})\text{Cl})$]	1 950 ^f	598	59.15 (60.25)	6.00 (6.35)	—
(10) c.d. (\pm) ₃₀₅ [$\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{P}(\text{OPh})_3)\text{Br}$]	1 985 ^f	722	55.90 (56.50)	5.05 (5.25)	—
(11) c.d. (\pm) ₃₂₀ [$\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PBu}^n_3)\text{Br}$]	1 945 ^f	614	55.95 (54.70)	7.85 (8.15)	—
(12) (<i>RS</i>)-[$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{Cl}$] ^f	1 944 ^f	630	65.70 (64.80)	6.00 (6.00)	—
(13) (<i>RS</i>)-[$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{Br}$] ^g	1 952	674	62.50 (60.45)	5.70 (5.60)	—
(14) c.d. (\pm) ₃₂₅ [$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}$] ^h	1 950 ^f	722	56.50 (56.60)	4.80 (5.30)	—

^a Pentane solution unless otherwise stated. ^b Calculated values are given in parentheses. ^c CHCl₃ solution. ^d Br: 18.05 (18.15%), ^e I: 26.10 (26.05%), ^f Cl: 6.20 (5.60%), ^g Br: 11.80 (11.80%), ^h I: 17.15 (17.60%).

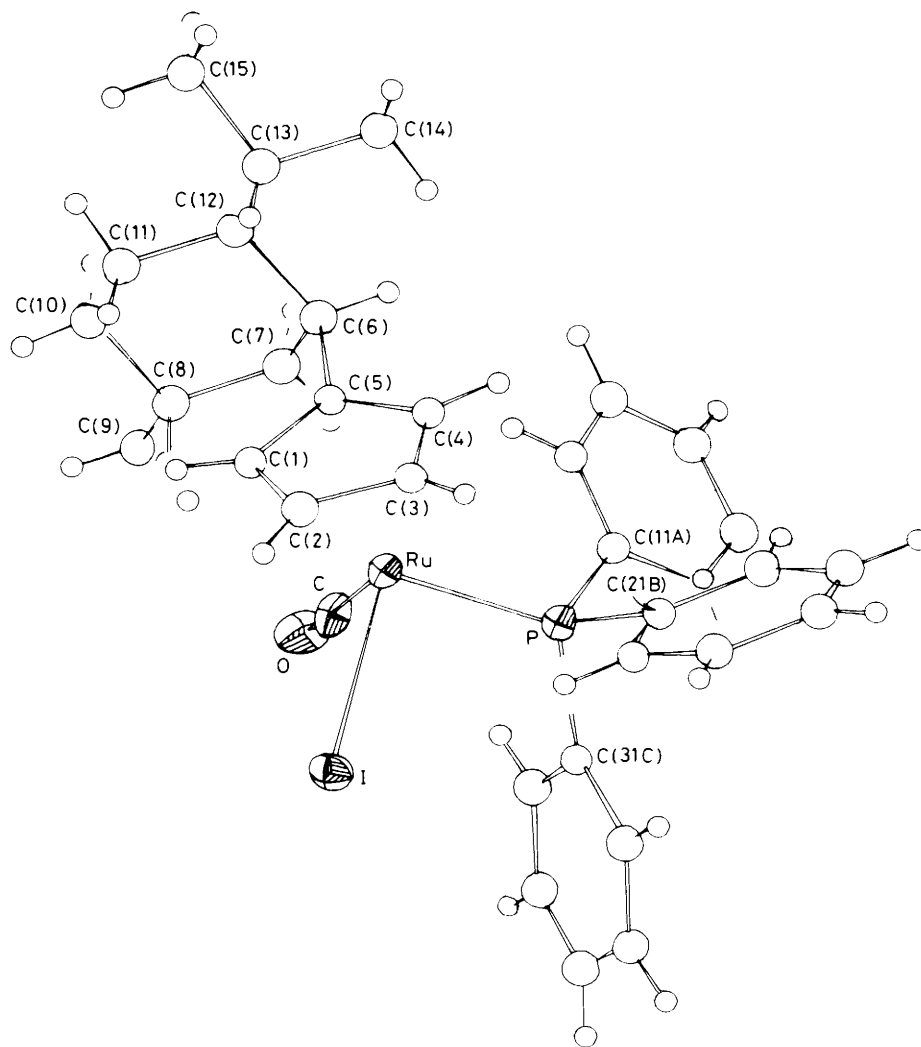
**Figure 1.** The absolute configuration of (*R*)-c.d.(-)₃₂₅[$\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}$] (14a)

Table 2. ^1H N.m.r. data ^a ($\delta/\text{p.p.m.}$, J/Hz)

Complex	Cyclopentadienyl	Menthyl or neomenthyl	Others
$[\{\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\}_2]$	5.33 (m), 5.11 (m), 4.89 (m), 4.81 (m)	2.22 (H^6 , t, $J = 12$), 2.06 (1 H, d, $J = 12$), 1.85—1.35 (4 H, m), 1.15 (1 H, q, $J = 12$), 1.04 (2 H, d, $J = 9$), 0.9 (1 H, m), 0.95 (3 H, d, $J = 7$), 0.80 (3 H, d, $J = 12$), 0.77 (3 H, d, $J = 12$)	
$[\{\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\}_2]$	5.58 (m), 5.25 (m), 4.89 (m), 4.80 (m)	2.98 (H^6 , br s), 2.09 (1 H, d, $J = 12$), 2.0—1.0 (8 H, m), 0.90 (6 H, m), 0.75 (3 H, d, $J = 7$)	
$[\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\text{Cl}]$	5.42 (m), 5.31 (m), 5.26 (m), 5.09 (m)	2.10 (H^6 , t, $J = 12$), 1.9—1.0 (8 H, m), ~ 0.9 (1 H), 0.90 (3 H, d, $J = 12$), 0.87 (3 H, d, $J = 12$), 0.78 (3 H, d, $J = 7$)	
$[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{Cl}]$	5.50 (m), 5.09 (t, $J = 2.5$), 5.45—5.20 (2 H, m)	2.92 (H^6 , br s), 2.0—1.0 (8 H, m), 0.90—0.65 (10 H, m)	
$[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{Br}]$	5.53 (m), 5.13 (t, $J = 2$), 5.45—5.20 (2 H, m)	2.95 (H^6 , br s), 2.0—0.70 (18 H, m)	
$[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{I}]$	5.62 (br s), 5.50 (br s), 5.30 (br s), 5.22 (br s)	2.90 (H^6 , br s), 2.0—1.0 (9 H, m) 1.0—0.85 (6 H, m), 0.8 (3 H, br s)	
c.d.(+) ₃₁₀ $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_2\text{Me})\text{Cl}]$ ^b	4.98, 4.68, 4.60, 4.56	2.16 (H^6 , m), 1.77—0.7 (9 H, m), 0.85 (3 H, d, $J = 7$), 0.80 (3 H, d, $J = 7$), 0.68 (3 H, d, $J = 7$)	7.65—7.37 (10 H, m), 2.16 (3 H, d, $J = 10$)
c.d.(−) ₃₁₀ $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_2\text{Me})\text{Cl}]$ ^b	5.00, 4.67, 4.55, 4.21	2.09 (H^6 , m), 1.79—0.8 (9 H, m), 0.89 (3 H, d, $J = 7$), 0.82 (3 H, d, $J = 7$), 0.73 (3 H, d, $J = 7$)	7.65—7.35 (10 H, m), 2.16 (3 H, d, $J = 10$)
(<i>RS</i>)- $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{Cl}]$	5.40, 5.30, 5.00, 4.70, 4.61, 4.50, 4.20, 3.60	3.05 (H^6 , s), 2.75 (H^6 , s), 2.5—2.0 (2 H, m), 1.9—1.0 (16 H, m), 1.0—0.8 (12 H, m), 0.80—0.76 (6 H, m)	7.1—7.7 (30 H, m)
(<i>RS</i>)- $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{Br}]$	5.46, 5.34, 5.00, 4.62, 4.52, 4.49, 4.20, 3.65	3.09 (H^6 , s), 2.80 (H^6 , s), 2.5—2.0 (2 H, m), 1.9—1.0 (16 H, m), 1.0—0.8 (12 H, m), 0.8—0.74 (6 H, m)	7.10—7.32 (30 H, m)
(<i>R</i>)- $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$ ^{b,c}	5.63, 4.60, 4.55, 4.29	2.87 (H^6 , br s), 2.23 (H, d, $J = 13$), 1.80 (2 H, m), 1.60 (H, m), 1.36 (H, m), 1.3—1.0 (4 H, m), 0.89 (Me, d, $J = 7$), 0.87 (Me, d, $J = 7$), 0.76 (Me, d, $J = 7$)	7.60—7.35 (15 H, m)
(<i>S</i>)- $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$ ^b	5.52, 5.10, 4.00, 3.90	3.10 (H^6 , br s), 2.28 (H, d, $J = 13$), 1.83 (H^6 , d, $J = 13$), 1.70 (2 H, m), 1.39 (H, m), 1.23 (3 H, m), 1.10 (H, m), 0.96 (Me, d, $J = 7$), 0.90 (Me, d, $J = 7$), 0.76 (Me, d, $J = 7$)	7.78—7.64 (3 H, m), 7.60—7.44 (8 H, m), 7.44—7.30 (4 H, m)

^a Recorded in CDCl_3 at 220 MHz unless otherwise specified; numbering system shown in Figure 1; br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ^b Recorded at 400 MHz. ^c c.d.(−)₃₂₅ isomer.

the structure. These two complexes do, however, have different packings and belong to different space groups because the cyclopentadienyl moiety in the nmcp ligand is an axial rather than an equatorial substituent as found in mcp. This also influences the torsion angle around the C(12)–C(13) bond, *i.e.* in spite of the fact that the isopropyl is a staggered equatorial substituent in both nmcp and mcp the hydrogen atoms bond to C(12) and C(13) are '*anti*' in nmcp but *syn* in mcp. The three chiral centres C(6), C(8), and C(12) in the neomenthyl moiety have *S*, *R*, and *S* configurations respectively as previously reported.^{7,8}

The complex (*R*)- $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$ proved to be exceedingly configurationally stable and showed no sign of racemization after 24 h in toluene at 80 °C. It was therefore possible to measure the optical yield of its synthesis by monitoring the ^{31}P n.m.r. spectrum of the reaction mixture. In toluene at 100 °C this was found to be 19% enantiomeric excess (*R*); this compares with 6% enantiomeric excess for the formation of $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{Cl}]$ under identical conditions. These modest optical yields are in keeping with those observed in asymmetric catalytic

hydrogenations with complexes of the type $[\text{Ti}(\eta^5\text{-nmcp})(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]$ ³ and are not unexpected given the relatively high temperature of the syntheses and the probable rotational mobility of the chiral cyclopentadienyl substituent.

Differences between the menthyl- and neomenthyl-cyclopentadienyl complexes are clearly evident in the n.m.r. spectra. For example, in the menthyl complexes H^6 , the proton adjacent to the cyclopentadienyl substituent, appears at significantly higher field than the corresponding proton in the neomenthyl analogues (Table 2). In contrast, in the ^{13}C n.m.r. spectra (Table 3), C^6 , the carbon bearing the cyclopentadienyl substituent, occurs at lower field in the menthyl epimer. The assignment of the cyclopentadienyl carbon signals in (*S*)- $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$ is based on the observed coupling of the ring carbons 1 and 4 to the neomenthyl proton, H^6 , in addition to the cyclopentadienyl protons. Both the ^1H and ^{13}C chemical shifts of the cyclopentadienyl ring are sensitive to the stereochemistry of the ring substituent. More significantly, in complexes of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})\text{LX}]$ these shifts are also very sensitive to the stereochemistry of the

ruthenium atom so that the $C_5H_4R^*$ (R^* = menthyl or neomenthyl) ligand acts as an excellent probe for investigating the stereochemistry of the metal atom by n.m.r. spectroscopy. This is especially true when such experiments are combined with the results from the more powerful technique of c.d. spectroscopy described below.

Figure 3(a) shows the c.d. spectra of the dimers $[(Ru(\eta^5-C_5H_4R^*)(CO)_2)_2]$ [R^* = menthyl (1) or neomenthyl (2)]; in Figure 3(b) the corresponding spectra of the monomers, $[Ru(\eta^5-C_5H_4R^*)(CO)_2X]$, are shown. In spite of the fact that the chiral ligands are epimers, the c.d. spectra of the menthyl and neomenthyl complexes are essentially enantiomeric as

Table 3. ^{13}C - $\{^1H\}$ and ^{31}P - $\{^1H\}$ N.m.r. data ^a ($CDCl_3$) ($\delta/p.p.m.$, J/Hz)

	CO	C_5 ring	Menthyl or neomenthyl	Others
$[(Ru(\eta^5-mcp)(CO)_2)_2]$	221.6	117.2 (C^5) 90.8, 89.4, 87.6 ^b } C^{1-4}	50.7 (C^{12}), 45.2 (C^7), 39.1 (C^6), 35.1 (C^{10}), 33.3 (C^8), 27.6 (C^{13}), 24.6 (C^{11}), 22.5 (C^9), ^c 21.6 (C^{14}), ^c 15.5 (C^{15}) ^c	
$[(Ru(\eta^5-nmcp)(CO)_2)_2]$	220.5	114.2 (C^5) 93.0, 91.6, 88.8, 88.3 } C^{1-4}	47.9 (C^{12}), 45.3 (C^7), 35.9 (C^6), 35.4 (C^{10}), 29.8 (C^8), 27.8 (C^{13}), 24.6 (C^{11}), 22.6 (C^9), ^c 21.8 (C^{14}), ^c 20.5 (C^{15}) ^c	
$[Ru(\eta^5-mcp)(CO)_2Cl]$	197.4	117.0 (C^5) 89.3, 88.7, 86.5, 80.5 } C^{1-4}	50.4 (C^{12}), 43.9 (C^7), 38.3 (C^6), 34.7 (C^{10}), 32.9 (C^8), 27.6 (C^{13}), 24.4 (C^{11}), 22.3 (C^9), ^c 21.5 (C^{14}), ^c 15.4 (C^{15}) ^c	
c.d.(+) ₃₁₀ $[Ru(\eta^5-mcp)(CO)(PPh_2Me)Cl]$ ^{e,f}	203.8 (d, $J = 21$ °)	113.6 (C^5) 90.3 (d, $J = 4$ °), 83.7, 82.8, 80.4 } C^{1-4}	50.7 (C^{12}), 42.9 (C^7), 38.8 (C^6), 35.1 (C^{10}), 33.0 (C^8), 27.5 (C^{13}), 24.8 (C^{11}), 22.4 (C^9), ^c 21.6 (C^{14}), ^c 15.5 (C^{15}) ^c	137.8 (d, $J = 48$ °), 137.3 (d, $J = 48$ °), 132.4 (d, $J = 11$ °), 131.7 (d, $J = 10$ °), 130.2, 129.9, 128.4 (d, $J = 9$ °), 128.3 (d, $J = 9$ °) 16.9 (Me, d, $J = 33$ °)
c.d.(-) ₃₁₀ $[Ru(\eta^5-mcp)(CO)(PPh_2Me)Cl]$ ^{e,h}	203.8 (d, $J = 21$ °)	113.6 (C^5 , d, $J = 7$ °) 93.5, 87.4, 79.3 (d, $J = 2$ °), 75.9 } C^{1-4}	50.5 (C^{12}), 43.7 (C^7), 38.4 (C^6), 35.2 (C^{10}), 33.0 (C^8), 27.5 (C^{13}), 24.8 (C^{11}), 22.4 (C^9), ^c 21.6 (C^{14}), ^c 15.5 (C^{15}) ^c	137.8—128.3 (Ph) 17.1 (Me, d, $J = 33$ °)
(<i>RS</i>)- $[Ru(\eta^5-nmcp)(CO)(PPh_3)Cl]$ ^f	204.1 (d, $J = 21$ °)	110.7 (C^5 , d, $J = 6$ °), 109.8 (C^5 , d, $J = 8$ °) 98.6, 87.7, 86.8, 80.7 } C^{1-4} 95.0 (d, $J = 3$ °), 82.5, 80.3, 75.2 } C^{1-4}	48.3, 47.7 (C^{12}), 42.9 (C^7), 35.3, 35.2 (C^{10}), ^d 34.6 (C^6), ^d 29.4 (C^8), 28.1, ^f 27.7 (C^{13}), 24.6, 24.3 (C^{11}), 22.6 (C^9), ^c 21.9 (C^{14}), ^c 20.7, 20.6 (C^{15}) ^c	135.9—127.8 (Ph)
$[Ru(\eta^5-nmcp)(CO)_2Cl]$	196.7	113.7 (C^5) 92.5, 90.8, 85.7, 81.3 } C^{1-4}	47.7 (C^{12}), 43.6 (C^7), 35.1 (C^6 , C^{10}), 29.6 (C^8), 27.8 (C^{13}), 24.6 (C^{11}), 22.4 (C^9), ^c 21.8 (C^{14}), 20.7 (C^{15}) ^c	
$[Ru(\eta^5-nmcp)(CO)_2Br]$	196.27, 196.08	112.5 (C^5) 92.5, 91.2, 85.7, 82.0 } C^{1-4}	47.7 (C^{12}), 44.3 (C^7), 35.3 (C^6), ^d 35.0 (C^{10}), ^d 29.7 (C^8), 27.9 (C^{13}), 24.6 (C^{11}), 22.4 (C^9), ^c 21.8 (C^{14}), 20.7 (C^{15}) ^c	
$[Ru(\eta^5-nmcp)(CO)_2I]$	196.15, 195.96	111.9 (C^5) 92.6, 91.2, 85.1, 82.7 } C^{1-4}	47.9 (C^{12}), 45.1 (C^7), 35.6 (C^6), 35.0 (C^{10}), 29.7 (C^8), 27.9 (C^{13}), 24.6 (C^{11}), 22.4 (C^9), ^c 21.8 (C^{14}), 20.6 (C^{15}) ^c	
(<i>RS</i>)- $[Ru(\eta^5-nmcp)(CO)(PPh_3)Br]$ ^k	l	110.1, 108.7 (C^5) 99.4, 95.8, 87.4, 86.6, } C^{1-4} 83.0, 82.3, 80.6, 76.9 }	48.5, 47.9 (C^{12}), 43.6 (C^7), 35.6 (C^{10}), 35.0 (C^6), 29.6 (C^8), 28.3, 27.8 (C^{13}), 24.8, 24.5 (C^{11}), 22.6 (C^9), ^c 22.1 (C^{14}), ^c 21.7, 21.4 (C^{15}) ^c	136.1—128.0 (Ph)
(<i>R</i>)- $[Ru(\eta^5-nmcp)(CO)(PPh_3)I]$ ^{e,m}	203.6 (d, $J = 21$ °)	109.8 (C^5 , d, $J = 5$ °) 94.4 (d, $J = 4$ °), 85.4, 84.7, 82.0 } C^{1-4}	48.4 (C^{12}), 44.1 (C^7), 36.0 (C^{10}), 35.4 (C^6), 29.6 (C^8), 27.9 (C^{13}), 24.3 (C^{11}), 22.6 (C^9), ^c 22.1 (C^{14}), ^c 20.6 (C^{15}) ^c	136.1—128.0 (Ph)

Table 3 (continued)

	CO	C ₅ ring	Menthyl or neomenthyl	Others
<i>(S)</i> -[Ru(η^5 -nmcp)(CO)(PPh ₃)I] ^{e, a}	203.7	107.1 (C ⁵ , d, <i>J</i> = 8 °)	48.0 (C ¹² , <i>J</i> = 124 °),	136.1 (d, <i>J</i> = 48 °),
	(d, <i>J</i> = 21 °)	98.4 (<i>J</i> = 177 °),	44.1 (C ⁷ , <i>J</i> = 126 °),	133.8 (d, <i>J</i> = 11 °),
		83.5 (<i>J</i> = 175 °),	35.5 (C ¹⁰ , <i>J</i> = 124 °),	130.0,
		86.1 (<i>J</i> = 179 °),	35.4 (C ⁶ , <i>J</i> = 128 °),	128.0 (d, <i>J</i> = 10 °)
		80.4 (<i>J</i> = 179 °)	29.6 (C ⁸ , <i>J</i> = 125 °),	
			28.2 (C ¹³ , <i>J</i> = 125 °),	
			24.7 (C ¹¹ , <i>J</i> = 125 °),	
			22.5 (C ⁹ , <i>J</i> = 125 °),	
			22.0 (C ¹⁴ , <i>J</i> = 125 °),	
			20.6 (C ¹⁵ , <i>J</i> = 125 °)	

^a Recorded on a JEOL PFT-100 instrument at 40.48 MHz unless otherwise specified; numbering system shown in Figure 1. ^b Overlapping signals. ^{c, d} These assignments may be interchanged. ^e ¹³C N.m.r. recorded at 100.62 MHz. ^f ³¹P-¹H: δ 35.6 p.p.m. ^g ³¹P-¹³C: δ 35.8 p.p.m. ^h ³¹P-¹H: δ 50.8 and 50.0 p.p.m. ⁱ ³¹P-¹H: δ 50.8 and 50.0 p.p.m. ^j Tentatively assigned to one diastereoisomer. ^k ³¹P-¹H: δ 46.8 and 45.7 p.p.m. ^l Not observed. ^m ³¹P-¹H: δ 49.8 p.p.m. ⁿ ³¹P-¹H: δ 49.4 p.p.m. ^o ¹J(¹³C-¹H).

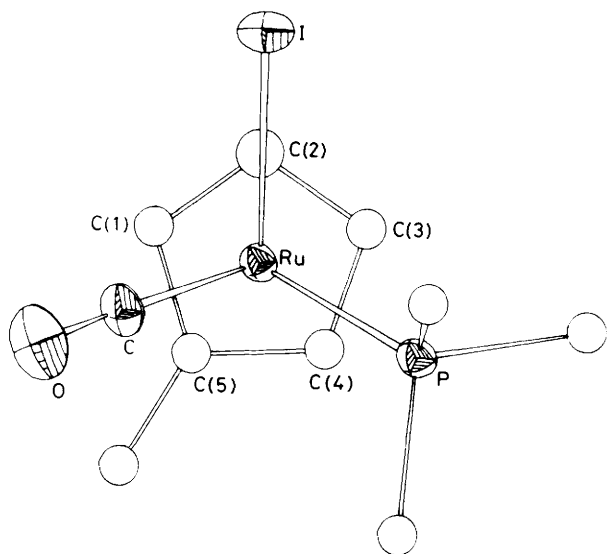


Figure 2. The co-ordination about the Ru atom in *(R)*-c.d.(-)₃₂₅-[Ru(η^5 -nmcp)(CO)(PPh₃)I] (14a)

already observed in Ti^{IV} and Zr^{IV} complexes with the same ligands.⁹ Hence the c.d. spectra of these compounds are determined mainly by the chirality of the carbon atom directly bound to the five-membered ring, *i.e.* the local environments of the cyclopentadienyl moieties can be considered to be enantiomeric. This is also reflected in the sign of the optical rotation, α_{5-8} , for [(Ru(η^5 -C₅H₄R*)(CO)₂)₂] and [Ru(η^5 -C₅H₄R*)(CO)₂X] which is always negative for R* = menthyl but positive for R* = neomenthyl.

Complexes of the type [Ru(η^5 -C₅H₄R*)(CO)LX] contain a chiral ruthenium atom and the epimeric pairs (8a),(8b); (9a),(9b); (10a),(10b); and (11a),(11b) differ only in the configuration of the ruthenium atom; their c.d. spectra are illustrated in Figure 4(a)–(d) respectively. Figure 4(e) and (f) show the c.d. spectra of the epimers of [Ru(η^5 -nmcp)(CO)-(PPh₃)I] [*(R)*-c.d.(-)₃₂₅(14a); *(S)*-c.d.(+)₃₂₅(14b)] and [Ru(η^5 -mcp)(CO)(PPh₃)Cl] [*(S)*-c.d.(-)₃₁₀(15a); *(R)*-c.d.(+)₃₁₀(15b)]; the absolute configurations of these complexes have been defined by X-ray crystallography.⁶

All the c.d. spectra show a well defined morphology in the region 300–500 nm: a maximum between 305 and 325 nm, a maximum of opposite sign between 350 and 380 nm, and another maximum over 400 nm of either sign. The corresponding visible and u.v. spectra [Figure 4(a)–(f)] also all show

three transitions, one of which appears as a shoulder around 350 nm; thus there appears to be a clear relationship between the positions of the c.d. bands and the absorption maxima. The c.d. spectra of all the diastereoisomeric pairs show an almost enantiomeric shape, at least in the region below 400 nm, which arises from the enantiomeric relationship between the two ruthenium atoms. Thus for the ruthenium complexes [Ru(η^5 -C₅H₄R*)(CO)LX] described herein, *the maxima of the c.d. spectra in the range 300–400 nm, especially those localised in the 305–325 nm region, appear to be diagnostic of the absolute configuration of the metal centre.* This undoubtedly arises because of the similarity of the X-groups (Cl, Br, or I) and the absence of an intense bathochromic shift due to the different ligands L or substituent X. Therefore, based on the c.d. spectra of the complexes of known absolute configuration, (*R*)-c.d.(-)₃₂₅(14a) and (*S*)-c.d.(-)₃₁₀(15a), the negative c.d. effect in the 300–325 nm region is associated with an *S* configuration in the complexes c.d.(-)₃₁₀(8a) and c.d.(-)₃₁₀(9a). Similarly the positive c.d. effect in the same region signifies an *R* configuration in the complexes c.d.(+)₃₁₀(8b) and c.d.(+)₃₁₀(9b). On going from the complexes (8) and (9) to compounds (10) and (11) the halide changes its position in the ligand priority sequence, *i.e.* mcp (or nmcp) > Cl > phosphine or phosphite > CO but Br (or I) > mcp (or nmcp) > phosphine or phosphite > CO. Therefore the negative c.d. effect in the 300–325 nm region is now associated with an *R* configuration in the complexes c.d.(-)₃₀₅(10a) and c.d.(-)₃₂₀(11a); the corresponding complexes (10b) and (11b) which show a positive c.d. effect in this region have an *S* configuration.

For other complexes of the type [Ru(η^5 -C₅H₄R*)(CO)LX] (R* = menthyl or neomenthyl) it is obviously of interest to determine the range of ligands L and X for which it is still possible to apply the above correlation between the c.d. spectrum and the ruthenium configuration; we are currently investigating this.

Finally, an interesting experimental point that we have noted is that each of the above diastereoisomers which exhibits a negative c.d. effect in the region 305–325 nm is eluted more rapidly in the thin-layer chromatography (t.l.c.) separation than the corresponding diastereoisomer with a positive c.d. effect in this region.

Experimental

Circular dichroism spectra in the region 280–550 nm were recorded on a Jobin-Yvon Dichrographe III using chloroform as a solvent and generally with concentrations of 0.5 mg ml⁻¹; the short wavelength limit was determined by the strong

Table 4. Distances (Å) and angles (°) in *c.d.*(-)₃₂₅[Ru(η⁵-nmcp)(CO)(PPh₃)I] •

Ru-I	2.708(1)	C(1)-C(2)	1.39(2)	C(10)-C(11)	1.51(2)	C(21B)-C(22B)	1.38(2)
Ru-P	2.313(4)	C(1)-C(5)	1.40(2)	C(11)-C(12)	1.50(2)	C(21B)-C(26B)	1.40(2)
Ru-C	1.866(13)	C(2)-C(3)	1.42(2)	C(12)-C(13)	1.54(2)	C(22B)-C(23B)	1.41(2)
Ru-C(1)	2.257(12)	C(3)-C(4)	1.37(2)	C(13)-C(14)	1.51(2)	C(23B)-C(24B)	1.36(2)
Ru-C(2)	2.226(12)	C(4)-C(5)	1.44(2)	C(13)-C(15)	1.49(2)	C(24B)-C(25B)	1.32(2)
Ru-C(3)	2.237(14)	C(5)-C(6)	1.51(2)	C(11A)-C(12A)	1.35(2)	C(25B)-C(26B)	1.41(2)
Ru-C(4)	2.189(12)	C(6)-C(7)	1.54(2)	C(11A)-C(16A)	1.41(2)	C(31C)-C(32C)	1.39(2)
Ru-C(5)	2.261(12)	C(6)-C(12)	1.56(2)	C(12A)-C(13A)	1.38(2)	C(31C)-C(36C)	1.40(2)
C-O	1.12(1)	C(7)-C(8)	1.52(2)	C(13A)-C(14A)	1.40(2)	C(32C)-C(33C)	1.37(2)
P-C(11A)	1.84(1)	C(8)-C(9)	1.54(2)	C(14A)-C(15A)	1.35(2)	C(33C)-C(34C)	1.39(2)
P-C(21B)	1.83(1)	C(8)-C(10)	1.52(2)	C(15A)-C(16A)	1.36(2)	C(34C)-C(35C)	1.34(2)
P-C(31C)	1.82(1)					C(35C)-C(36C)	1.36(2)
I-Ru-cp †	120.5(4)	C(2)-C(3)-C(4)	106(1)	C(9)-C(8)-C(10)	110(1)		
P-Ru-cp †	126.7(4)	C(3)-C(4)-C(5)	111(1)	C(8)-C(10)-C(11)	112(1)		
C-Ru-cp †	128.2(4)	C(4)-C(5)-C(1)	105(1)	C(10)-C(11)-C(12)	116(1)		
I-Ru-P	92.3(1)	C(5)-C(1)-C(2)	108(1)	C(11)-C(12)-C(13)	114(1)		
I-Ru-C	86.2(4)	C(1)-C(5)-C(6)	130(1)	C(11)-C(12)-C(6)	112(1)		
P-Ru-C	91.5(4)	C(4)-C(5)-C(6)	123(1)	C(12)-C(13)-C(14)	113(1)		
Ru-C-O	178(1)	C(5)-C(6)-C(7)	116(1)	C(12)-C(13)-C(15)	113(1)		
Ru-P-C(11A)	114.0(5)	C(5)-C(6)-C(12)	112(1)	C(14)-C(13)-C(15)	110(1)		
Ru-P-C(21B)	114.5(4)	C(6)-C(7)-C(8)	115(1)	C(11A)-P-C(21B)	105.4(6)		
Ru-P-C(31C)	117.9(4)	C(7)-C(8)-C(9)	113(1)	C(11A)-P-C(31C)	101.2(6)		
C(1)-C(2)-C(3)	110(1)	C(7)-C(8)-C(10)	111(1)	C(21B)-P-C(31C)	102.2(5)		

• Atoms C(22A)—C(16A), C(21B)—C(26B), and C(31C)—C(36C) refer to the carbon atoms of the phenyl groups. † cp indicates the centre of the cyclopentadienyl ring.

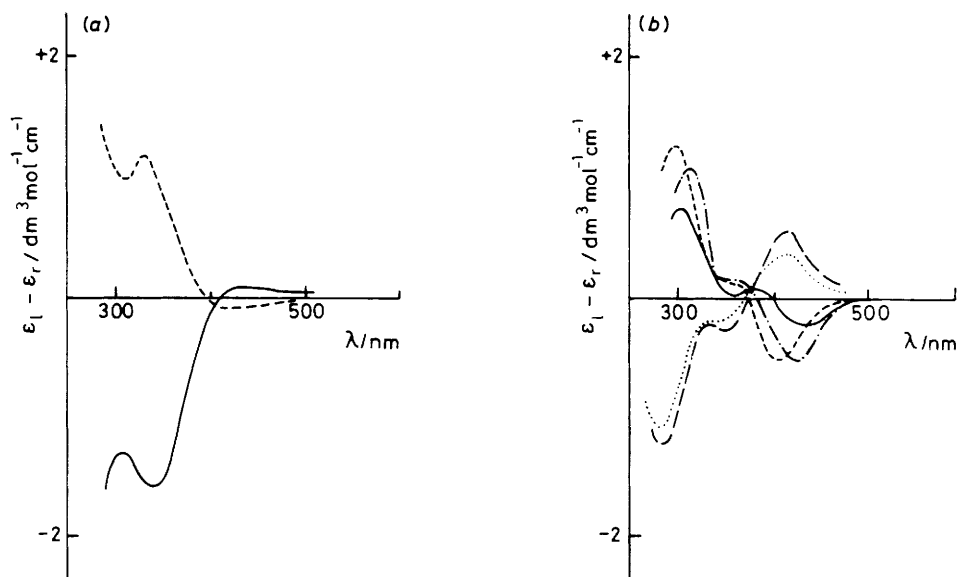


Figure 3. (a) C.d. spectra of $[\{\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\}_2]$ (—) and $[\{\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\}_2]$ (---); (b) c.d. spectra of $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\text{Cl}]$ (—), $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\text{Br}]$ (.....), $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{Cl}]$ (---), $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{Br}]$ (-·-·-·), and $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\text{I}]$ (—)

absorption of the compounds. All the complexes chiral at the metal are stable in solution for several days without any sign of racemisation. Mass spectra were recorded on a MAAT 112 mass spectrometer and the quoted M^+ is that peak in the parent multiplet which arises from the most abundant ruthenium and halogen isomers. This peak was generally 6–10% of the intensity of the strongest peak in the spectrum.

The preparations of (*R*)-(–)menthylcyclopentadiene and (*S*)-(+)-neomenthylcyclopentadiene have been reported.⁹

Preparation of $[\{\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})_2\}_2]$ [$\text{R}^* = \text{Menthyl}$ (1) or *Neomenthyl* (2)].—(a) Freshly distilled (*R*)-(–)menthyl-

cyclopentadiene or (*S*)-(+)-neomenthylcyclopentadiene (0.55 g, 2.45 mmol) and $[\text{Ru}_3(\text{CO})_{12}]$ (0.2 g, 0.36 mmol) in iso-octane (10 cm³) were placed in a sealed tube under argon at 120 °C for 5 d. On standing at room temperature for 1 d well formed bright orange crystals of $[\{\text{Ru}(\eta^5\text{-mcp})(\text{CO})_2\}_2]$ or $[\{\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\}_2]$ were obtained in 75% and 45% yield respectively.

(b) A mixture of (*S*)-(+)-neomenthylcyclopentadiene (612 mg, 3 mmol), $[\text{Ru}_3(\text{CO})_{12}]$ (500 mg, 0.78 mmol), and heptane (100 cm³) was refluxed in air for 24 h. The yellow solution gradually darkened and became black. Solvent was removed on a rotary evaporator to leave yellow-brown crystals which were purified by passing down an alumina

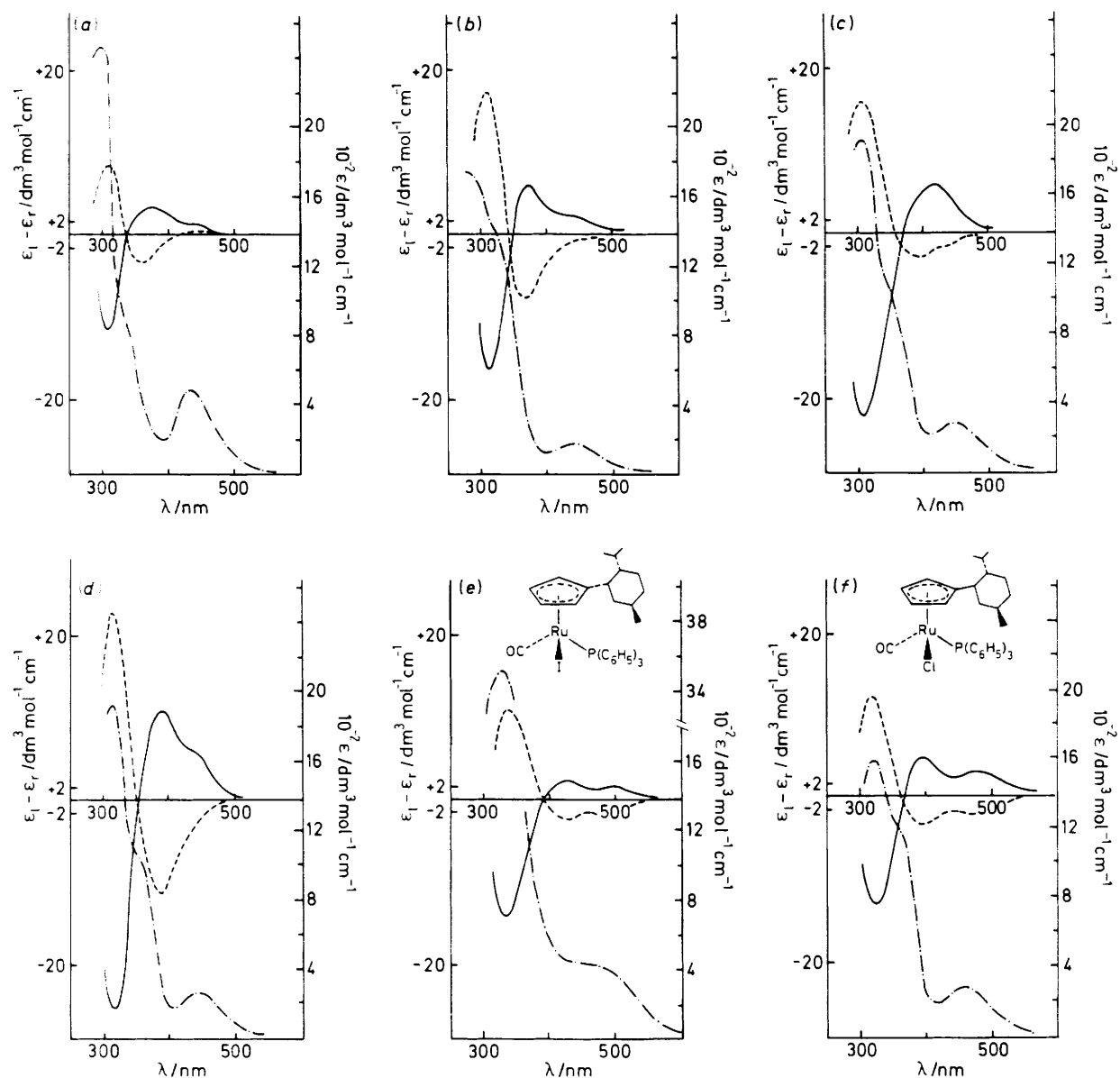


Figure 4. C.d. and absorption spectra of (a) $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_2\text{Me})\text{Cl}]$: c.d.(-) $_{310}$ (8a) (—), c.d.(+) $_{310}$ (8b) (---), absorption (— · — ·); (b) $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_2(\text{CH}_2\text{OMe}))\text{Cl}]$: c.d.(-) $_{310}$ (9a) (—), c.d.(+) $_{310}$ (9b) (---), absorption (— · — ·); (c) $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{P}(\text{OPh})_3)\text{Br}]$: c.d.(-) $_{305}$ (10a) (—), c.d.(+) $_{305}$ (10b) (---), absorption (— · — ·); (d) $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PBU}^a_3)\text{Br}]$: c.d.(-) $_{320}$ (11a) (—), c.d.(+) $_{320}$ (11b) (---), absorption (— · — ·); (e) $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$: (*R*)-(14a) (—), (*S*)-(14b) (---), absorption (— · — ·); (f) $[\text{Ru}(\eta^5\text{-mcp})(\text{CO})(\text{PPh}_3)\text{Cl}]$: (*S*)-(15a) (—), (*R*)-(15b) (---), absorption (— · — ·)

column (20 cm) using light petroleum (b.p. 40–60 °C) as eluant. Removal of the solvent *in vacuo* gave yellow-orange crystals of $[\{\text{Ru}(\eta^5\text{-nmcp})(\text{CO})_2\}_2]$ (495 mg, 86% yield), m.p. 141 °C.

Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})_2\text{X}]$ [$\text{R}^* = \text{Menthyl}$, $\text{X} = \text{Cl}$ (3) or Br (4); $\text{R}^* = \text{Neomenthyl}$, $\text{X} = \text{Cl}$ (5), Br (6), or I (7)].—These complexes were prepared from $[\{\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})_2\}_2]$ ($\text{R}^* = \text{menthyl}$ or neomenthyl) using identical procedures as those reported for the corresponding cyclopentadienyl complexes.¹⁰ Complex (3) was obtained as a pale microcrystalline product (yield 54%), (4) as a yellow powder (yield 65%), (5) as a yellow oil (yield 66%), (6) as a yellow oil (yield 79%), and (7) as orange crystals (yield 71%).

Preparation and Resolution of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})\text{LX}]$ [$\text{R}^* = \text{Menthyl}$, $\text{X} = \text{Cl}$, $\text{L} = \text{PPh}_2\text{Me}$ or $\text{PPh}_2(\text{CH}_2\text{OMe})$; $\text{X} = \text{Br}$, $\text{L} = \text{PBU}^a_3$; $\text{R}^* = \text{Neomenthyl}$, $\text{X} = \text{I}$, $\text{L} = \text{PPh}_3$].—**General procedure.** Complex (3) [or (4) or (7)] (0.25 mmol) was refluxed in xylene (10 cm³) under nitrogen with a stoichiometric amount of the appropriate ligand, L. The mixture was refluxed until the two strong carbonyl bands of the starting complex were replaced by a single broad band (*i.e.* $\text{X} = \text{Cl}$, 3 h; $\text{X} = \text{Br}$, 4 h; and $\text{X} = \text{I}$, 24 h). Removal of the solvent *in vacuo* gave a microcrystalline yellow mixture of the two diastereoisomers which were quantitatively separated by preparative t.l.c. on silica gel with cyclohexane–ethyl acetate (9.5 : 0.5) as eluant. In the case of $[\text{Ru}(\eta^5\text{-nmcp})(\text{CO})(\text{PPh}_3)\text{I}]$ slow addition of diethyl ether to a dichloromethane solution of

Table 5. Atomic co-ordinates for c.d.(-)₃₂₅[Ru(η⁵-nmcp)(CO)(PPh₃)I] with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
I	0.261 95(9)	0.148 5(1)	0.056 0(1)	H(1)	0.574 8(0)	0.062 1(0)	0.274 6(0)
Ru	0.379 46(9)	0.000 0(0)	0.062 3(1)	H(2)	0.412 0(0)	0.067 8(0)	0.400 6(0)
P	0.242 9(3)	-0.073 6(3)	-0.116 1(4)	H(3)	0.317 1(0)	-0.079 6(0)	0.354 1(0)
O	0.457 8(9)	0.074 6(8)	-0.236(1)	H(4)	0.417 3(0)	-0.171 3(0)	0.182 2(0)
C	0.427(1)	0.047 6(10)	-0.125(2)	H(6)	0.593 3(0)	-0.168 4(0)	0.104 3(0)
C(1)	0.525(1)	0.015 7(11)	0.272(1)	H(71)	0.584 5(0)	-0.066 5(0)	-0.114 9(0)
C(2)	0.434(1)	0.018 6(12)	0.343(2)	H(72)	0.695 2(0)	-0.111 3(0)	-0.072 0(0)
C(3)	0.380(1)	-0.063 2(11)	0.316(2)	H(8)	0.650 4(0)	0.056 9(0)	0.022 0(0)
C(4)	0.437(1)	-0.113 7(9)	0.223(2)	H(91)	0.760 8(0)	0.110 8(0)	-0.153 3(0)
C(5)	0.530(1)	-0.067 3(10)	0.197(2)	H(92)	0.775 4(0)	0.015 7(0)	-0.215 8(0)
C(6)	0.621(1)	-0.111 0(10)	0.133(2)	H(93)	0.664 7(0)	0.060 5(0)	-0.259 6(0)
C(7)	0.648(1)	-0.071 7(12)	-0.032(2)	H(101)	0.823 7(0)	0.074 5(0)	0.156 9(0)
C(8)	0.701(1)	0.0180 (11)	-0.010(2)	H(102)	0.853 8(0)	-0.016 6(0)	0.092 4(0)
C(9)	0.728(1)	0.054 8(13)	-0.175(2)	H(111)	0.736 5(0)	0.012 6(0)	0.343 0(0)
C(10)	0.800(1)	0.015 8(12)	0.132(2)	H(112)	0.845 9(0)	-0.034 3(0)	0.368 8(0)
C(11)	0.779(1)	-0.026 6(11)	0.293(2)	H(12)	0.770 6(0)	-0.153 6(0)	0.229 2(0)
C(12)	0.724(1)	-0.114 3(11)	0.272(2)	H(13)	0.668 3(0)	-0.118 3(0)	0.488 8(0)
C(13)	0.712(1)	-0.157 6(11)	0.442(2)	H(141)	0.651 6(0)	-0.269 7(0)	0.524 1(0)
C(14)	0.657(1)	-0.245 9(11)	0.416(2)	H(142)	0.587 8(0)	-0.238 5(0)	0.348 0(0)
C(15)	0.815(1)	-0.165 4(14)	0.567(2)	H(143)	0.696 8(0)	-0.284 9(0)	0.359 9(0)
C(11A)	0.288(1)	-0.155 9(10)	-0.255(2)	H(151)	0.802 2(0)	-0.192 5(0)	0.668 5(0)
C(12A)	0.388(1)	-0.187 4(10)	-0.220(2)	H(152)	0.862 7(0)	-0.200 4(0)	0.519 1(0)
C(13A)	0.427(1)	-0.248 3(11)	-0.321(2)	H(153)	0.844 0(0)	-0.108 5(0)	0.593 0(0)
C(14A)	0.356(1)	-0.277 7(11)	-0.466(2)	H(12A)	0.434 9(0)	-0.166 5(0)	-0.120 5(0)
C(15A)	0.254(1)	-0.250 5(11)	-0.502(2)	H(13A)	0.498 4(0)	-0.268 9(0)	-0.292 9(0)
C(16A)	0.219(1)	-0.190 6(10)	-0.399(2)	H(14A)	0.379 9(0)	-0.317 9(0)	-0.541 6(0)
C(21B)	0.152(1)	-0.132 5(9)	-0.005(2)	H(15A)	0.205 9(0)	-0.273 2(0)	-0.598 8(0)
C(22B)	0.114(1)	-0.087 2(10)	0.121(2)	H(16A)	0.146 9(0)	-0.171 9(0)	-0.424 3(0)
C(23B)	0.040(1)	-0.129 7(12)	0.203(2)	H(22B)	0.137 1(0)	-0.028 9(0)	0.151 0(0)
C(24B)	0.006(1)	-0.212 1(12)	0.154(2)	H(23B)	0.014 9(0)	-0.100 7(0)	0.292 5(0)
C(25B)	0.041(1)	-0.256 9(12)	0.036(2)	H(24B)	-0.046 4(0)	-0.238 4(0)	0.208 2(0)
C(26B)	0.117(1)	-0.218 2(11)	-0.047(2)	H(25B)	0.015 5(0)	-0.314 8(0)	0.006 9(0)
C(31C)	0.152(1)	-0.008 5(10)	-0.273(1)	H(26B)	0.144 2(0)	-0.250 3(0)	-0.131 4(0)
C(32C)	0.048(1)	0.013 8(11)	-0.261(2)	H(32C)	0.019 2(0)	-0.010 8(0)	-0.170 4(0)
C(33C)	-0.013(1)	0.069 8(12)	-0.374(2)	H(33C)	-0.083 4(0)	0.084 0(0)	-0.361 1(0)
C(34C)	0.027(1)	0.105 5(11)	-0.508(2)	H(34C)	-0.014 4(0)	0.144 1(0)	-0.588 1(0)
C(35C)	0.126(1)	0.084 4(10)	-0.522(2)	H(35C)	0.153 9(0)	0.108 5(0)	-0.613 9(0)
C(36C)	0.189(1)	0.029 7(10)	-0.409(2)	H(36C)	0.259 5(0)	0.017 3(0)	-0.423 6(0)

the mixture of diastereoisomers precipitated out the (*R*)-c.d.(-)₃₂₅ isomer selectively ($\geq 95\%$ optically pure).

X-Ray Crystal Structure of (*R*)-[Ru(η⁵-C₅H₅R*)(CO)(PPh₃)I] (R* = Neomenthyl).—*Crystal data.* C₃₄H₃₈IOPRu, $M_r = 721.6$, monoclinic, $a = 12.833(6)$, $b = 15.186(6)$, $c = 7.972(5)$ Å, $\beta = 101.50(4)^\circ$, $U = 1522.4$ Å³, $D_c = 1.574$ g cm⁻³, $Z = 2$, $F(000) = 724$, space group $P2_1$ (no. 4), $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha) = 15.8$ cm⁻¹.

Intensity measurements. The intensity set of data was collected on an Enraf-Nonius CAD-4 automated diffractometer, using graphite-monochromatized Mo- K_α radiation. Intensities were measured using the ω -scan technique with a fixed scan rate of 2.5° min⁻¹. Backgrounds were collected for 25% of the total scan time at each end of the scanning range which was $(0.6 \pm 0.35 \tan \theta)^\circ$. The reliability of the electronics of the instrument and the stability of the crystal were checked by means of three reflections measured every hour and no crystal decay was observed. A total of 2486 reflections with indices $\pm h, k, l$ were collected in the range $6 < 2\theta < 50^\circ$, 1773 of which were found to have $I > 3\sigma(I)$ and after correction for Lorentz and polarization effects were used in the structure determination. An empirical absorption correction was made from data obtained by measuring two reflections with χ values near to 90° at different ψ values (ψ 0– 360° in steps of 10°). The maximum, minimum, and average relative transmission values were 1.00, 0.91, and 0.97 respectively.

Determination and refinement of the structure. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares on a PDP 11/34 computer using the Enraf-Nonius structure determination package. After the location of all non-hydrogen atoms, the non-phenyl atoms were treated anisotropically and the absolute configuration was tested by refining both the enantiomers. The configuration of the neomenthyl moiety is known and hence the absolute configuration of the metal centre could be determined. In addition, both possible enantiomers were refined and $R = R' = 0.054$ for the enantiomer assumed but $R = R' = 0.055$ for the other. In the final refinement the hydrogen atoms were located in their ideal positions (C–H 0.95 Å) after each cycle, but not refined.

The final values of the R and R' conventional agreement indices were 0.046 and 0.041 respectively, the weighting factor being 0.02. The final difference-Fourier map only presented peaks near the Ru and I atoms not exceeding 0.7 e Å⁻³. The final atomic co-ordinates are given in Table 5.

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