

STEREOCHEMISTRY OF SUBSTITUTION REACTIONS AT A CHIRAL RUTHENIUM ATOM: THE CRYSTAL STRUCTURE OF (*R*)-[Ru(η^5 -C₅H₄R*)(CO)(PPh₃)NCCH₃]PF₆ (R* = NEOMENTHYL) ‡

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Summary

The stereochemistry of substitution reactions of complexes of the type [Ru(η^5 -C₅H₄R*)(CO)(PPh₃)L]ⁿ⁺ (R* = menthyl or R = neomenthyl; n = 0, L = Cl or I; n = 1, L = NCCH₃ or NCCD₃) has been studied by X-ray crystallography, Circular Dichroism and ¹H, ¹³C and ³¹P NMR spectroscopy. All the reactions investigated have been unequivocally proved to occur with $\geq 94\%$ retention of configuration at the ruthenium atom. Thus (*S*)-Ru(η^5 -C₅H₄R*)(CO)(PPh₃)Cl reacts with NaI to give (*R*)-Ru(η^5 -C₅H₄R*)(CO)(PPh₃)I (R* = menthyl or neomenthyl) and reaction of Ru(η^5 -C₅H₄R*)(CO)(PPh₃)X (R* = menthyl, (*S*)_{Ru}, X = Cl; R* = neomenthyl, (*R*)_{Ru}, X = I) with AgY in acetonitrile yields the corresponding complex (*R*)-[Ru(η^5 -C₅H₄R*)(CO)(PPh₃)(NCCH₃)]Y (Y = PF₆ or BF₄). An X-ray structure determination of [Ru(η^5 -C₅H₄R*)(CO)(PPh₃)NCCH₃]PF₆ (R* = neomenthyl) has confirmed that the absolute configuration of the ruthenium centre is *R*. The crystals are orthorhombic, space group *P*2₁2₁2₁ (No. 19) with *a* 10.400(2), *b* 15.850(4), *c* 24.740(5) Å and *Z* = 4. The structure was solved via the heavy-atom method and refined to *R* = 0.036 using 4183 diffractometer data with *I* $\geq 1.56(I)$. CD₃CN undergoes exchange with the coordinated acetonitrile in (*R*)-[Ru(η^5 -C₅H₄R*)(CO)(PPh₃)(NCCH₃)]BF₄ (R* = neomenthyl) with retention of configuration at ruthenium and reaction of (*R*)-[Ru(η^5 -C₅H₄R*)(CO)(PPh₃)NCCD₃]BF₄ with NaI regenerates (*R*)-[Ru(η^5 -C₅H₄R*)(CO)(PPh₃)I] (R* = neomenthyl).

‡ (*R*)-Acetonitrilecarbonyl(*c*-2-isopropyl-*t*-5-methylcyclohexan-*r*-1-yl)-triphenylphosphineruthenium-(1+) hexafluorophosphate(1-).

Introduction

The classical studies of the stereochemistry of organic reactions have contributed significantly to the detailed understanding of the mechanisms of organic chemistry [1]. More recently, the stereochemical course of reactions involving chiral inorganic and organometallic compounds has been increasingly studied in order to gain a similar detailed knowledge of reaction pathways, especially those common in catalytic reactions [2].

As a contribution to this area we report herein stereochemical studies of reactions involving substitution at a chiral ruthenium centre in molecules of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)_n\text{L}]^{n+}$ ($\text{C}_5\text{H}_4\text{R}^* = \text{mcp} = \eta^5\text{-menthylcyclopentadienyl}$ or $\text{C}_5\text{H}_4\text{R}^* = \text{nmcp} = \eta^5\text{-neomenthylcyclopentadienyl}$; $n = 0$, $\text{L} = \text{Cl}$ or I ; $n = 1$, $\text{L} = \text{MeCN}$)[‡]. Such complexes have several features which make them particularly attractive for stereochemical studies. Not only can they be readily prepared but more significantly the diastereoisomers can readily be separated by chromatography or crystallisation; a striking example is that of $(R)\text{-Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ which crystallises out $\geq 99\%$ optically pure upon cooling a dichloromethane/ether solution of the mixture of diastereomers. Further, such complexes are exceedingly configurationally stable; thus ³¹P NMR spectroscopy indicates that $(R)\text{-Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ shows no sign of racemisation of the ruthenium centre after heating at 80°C in toluene for 24 h. Also we have shown that the ¹H and ¹³C NMR chemical shifts of the substituted-cyclopentadienyl ring and the Circular Dichroism (CD) spectra of the complexes in the region 300–400 nm may be used to diagnose the stereochemistry of complexes of the type discussed herein [3]. In addition, related cyclopentadienyl complexes catalyse hydroformylation [4] and promote the cyclopropanation of olefins [5], and we intend to extend our stereochemical studies to include an investigation of the individual steps in such reactions.

The stereochemical studies described here complement those recently reported on $\text{Ru}(\text{C}_5\text{H}_5)[(R)\text{-Ph}_2\text{PCH}(\text{Me})\text{CH}_2\text{PPh}_2]\text{Cl}$ which reacts with SnCl_2 [6a] and Me-MgBr [6b] with net retention of configuration at the ruthenium atom.

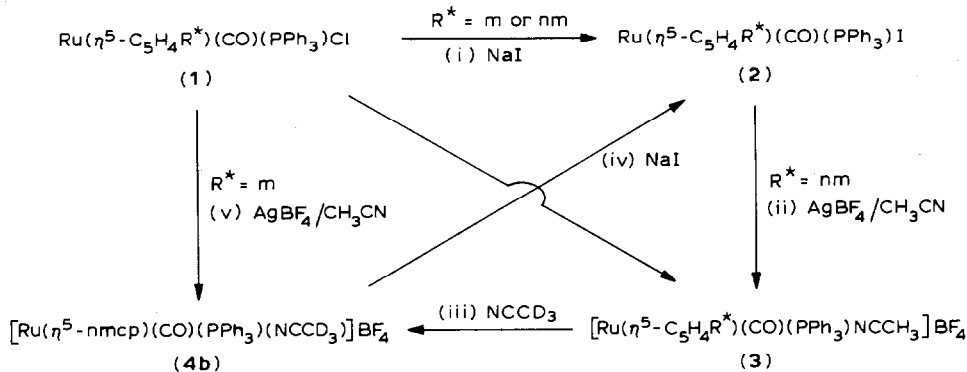
Results and discussion

The reactions studied are outlined in Scheme 1.

Reaction (i)

The chloro complexes $\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{Cl}$ (**1a**, $\text{R}^* = \text{menthyl}$; **1b**, $\text{R}^* = \text{neomenthyl}$) readily undergo a metathesis reaction when treated with sodium iodide in dichloromethane to give the corresponding iodo complexes. Obviously in order to ascertain the stereochemical course of this reaction one must know the configuration of the starting complex and that of the product. For $(S)\text{-Ru}(\text{mcp})(\text{CO})(\text{PPh}_3)\text{Cl}$ [7] and $(R)\text{-Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ [3] we have established the absolute configuration by X-ray crystallography, and this has allowed us to unambiguously assign the ¹H, ¹³C and ³¹P NMR spectra and the CD spectra of

[‡] 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*-methylcyclohexan-*r*-1-yl, respectively.



Scheme 1. Menthyl complexes (i.e. $\text{R}^* = \text{m}$) labelled a. The corresponding neomenthyl complexes (i.e. $\text{R}^* = \text{nm}$) labelled b.

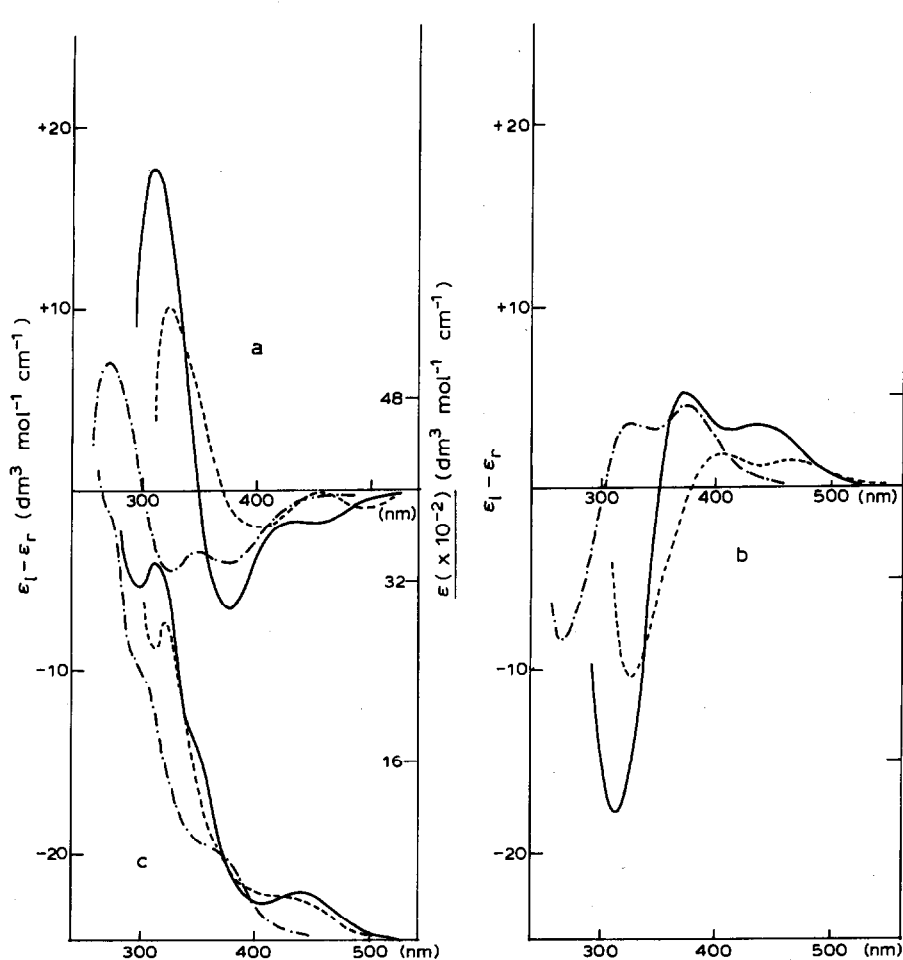


Fig. 1. (a) CD spectra of $(R)\text{-CD}(+)\text{-}_{310}\text{-Ru(mcp)CO(PPh}_3\text{)Cl}$ [(R)-**1a**] (—), $(S)\text{-CD}(+)\text{-}_{325}\text{-Ru(mcp)CO(PPh}_3\text{)I}$ [(S)-**2a** from (R)-**1a**] (-----) and $(S)\text{-CD}(+)\text{-}_{270}\text{-[Ru(mcp)CO(PPh}_3\text{)NCMe]BF}_4$ [(S)-**3a** from (S)-**2a**] (-·-·-·-); (b) CD spectra of $(S)\text{-CD}(-)\text{-}_{310}\text{-Ru(mcp)CO(PPh}_3\text{)Cl}$ [(S)-**1a**] (—), $(R)\text{-CD}(-)\text{-}_{325}\text{-Ru(mcp)CO(PPh}_3\text{)I}$ [(R)-**2a** from (S)-**1a**] (-----) and $(R)\text{-CD}(-)\text{-}_{270}\text{-[Ru(mcp)CO(PPh}_3\text{)NCMe]BF}_4$ [(R)-**3a** from (R)-**2a**] (-·-·-·-); (c) UV spectra of (R)-**1a** (—), (S)-**2a** (-----) and (S)-**3a** (-·-·-·-). Solvent CH_2Cl_2 , concentration ca. 10^{-3} M.

these two compounds and also the corresponding spectra of their respective epimers. This is an important result, since the region 270–400 nm of the CD spectra of the epimeric pairs (*R*)- and (*S*)-Ru(η^5 -C₅H₄R*)(CO)(PPh₃)X (R* = menthyl, X = Cl or I; R* = neomenthyl, X = Cl or I) is particularly sensitive to the stereochemistry of the metal (Figs. 1 and 2). Similarly the NMR spectra of these complexes are strongly dependent upon the stereochemistry of the metal (Tables 1 and 2).

As the halide is changed from chloride to iodine one would expect only slight shifts in the CD and NMR spectra. Indeed, comparison of the CD spectra of the two epimers of Ru(mcp)(CO)(PPh₃)I shows that whereas each epimer gives rise to very different CD spectra due to the different configurations of the metal centres, each

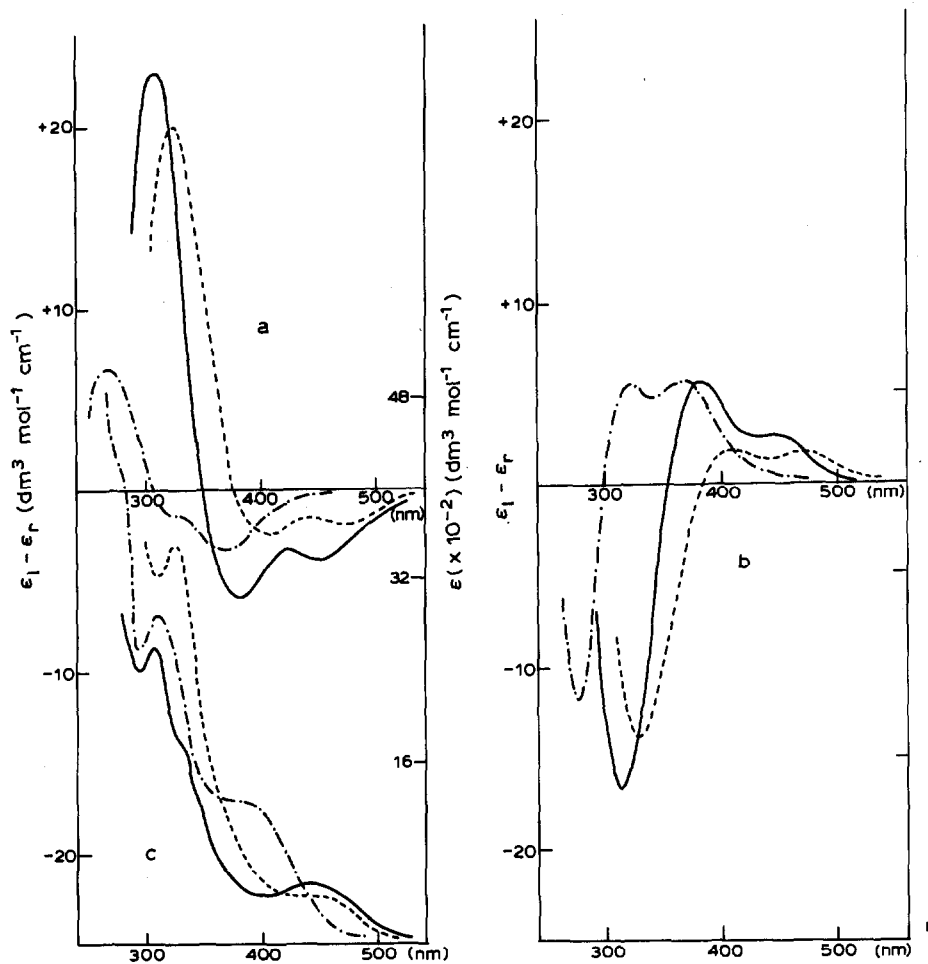


Fig. 2. (a) CD spectra of (*R*)-CD(+)₃₁₀-Ru(nmcp)CO(PPh₃)Cl [(*R*)-1b] (—), (*S*)-CD(+)₃₂₅-Ru(nmcp)CO(PPh₃)I [(*S*)-2b from (*R*)-1b] (-----) and (*S*)-CD(+)₂₇₀-[Ru(nmcp)CO(PPh₃)NCMe]BF₄ [(*S*)-3b from (*S*)-2b] (-·-·-·); (b) CD spectra of (*S*)-CD(-)₃₁₀-Ru(nmcp)CO(PPh₃)Cl [(*S*)-1b] (—), (*R*)-CD(-)₃₂₅-Ru(nmcp)CO(PPh₃)I [(*R*)-2b from (*S*)-1b] (-----) and (*R*)-CD(-)₂₇₀-[Ru(nmcp)CO(PPh₃)NCCH₃]BF₄ [(*R*)-3b from (*R*)-2b] (-·-·-·); (c) UV spectra of (*R*)-1b (—), (*S*)-2b (-----) and (*S*)-3b (-·-·-·). Solvent CH₂Cl₂, concentration ca. 10⁻³ M.

spectrum closely resembles the CD spectrum of either *R*- or *S*-Ru(mcp)(CO)(PPh₃)Cl (see Fig. 1). Similarly, although the NMR spectra of the epimers of Ru(nmcp)CO(PPh₃)X (X = I or Cl) are very different there is a close correspondence between the spectra of the chloro and iodo complexes. For example, in the ¹H NMR spectrum of (*S*)-Ru(nmcp)CO(PPh₃)I [3] one of the cyclopentadienyl resonances occurs at δ 3.90 at significantly higher field than the corresponding signal of the (*R*)_{Ru}-epimer (at δ 4.29); also H(6) occurs at δ 3.10 in the spectrum of (*S*)-Ru(nmcp)CO(PPh₃)I whereas the corresponding signal in the (*R*)_{Ru}-epimer is at δ 2.87. These features are also observed in the ¹H NMR of the two epimers of Ru(nmcp)CO(PPh₃)Cl (Table 1).

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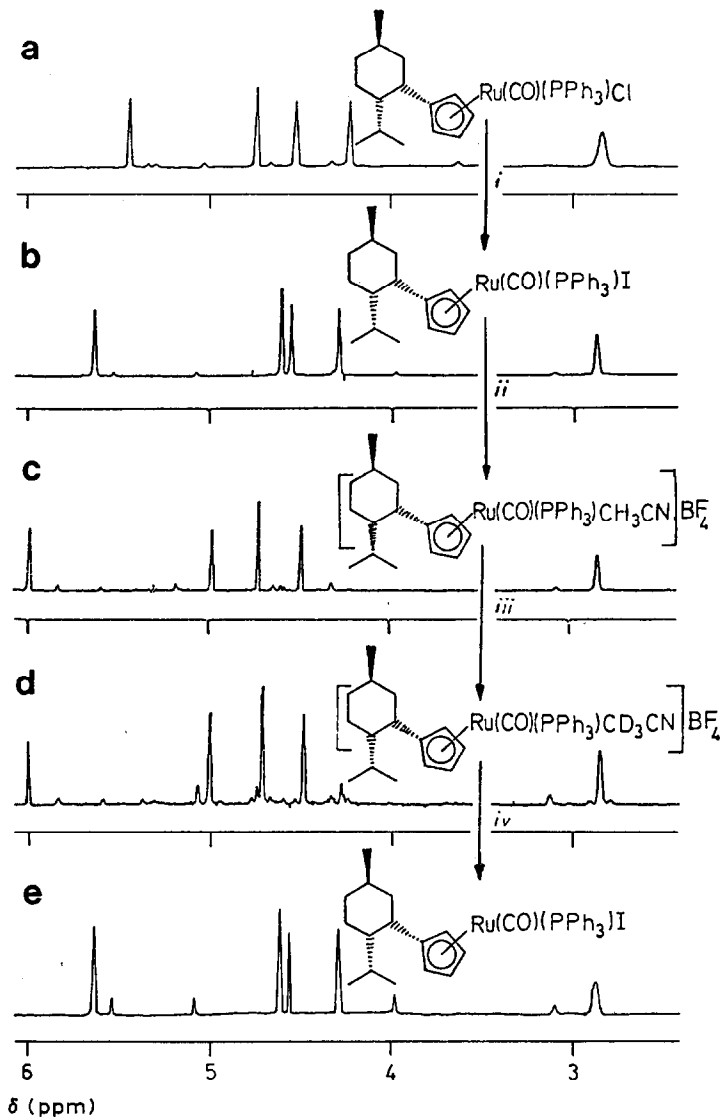


Fig. 3. 400 MHz ¹H NMR spectra. (i) NaI, (ii) AgBF₄ + MeCN, (iii) CD₃CN, (iv) NaI.

TABLE I
 ^1H AND $^{31}\text{P}\{^1\text{H}\}$ NMR DATA^a (CDCl_3) (δ (ppm); J in Hz) AND INFRARED DATA (cm^{-1})

Complex	cp	Menthyl or neomenthyl	Other	$^{31}\text{P}\{^1\text{H}\}$
(R) -Ru(mcp)CO(PPh ₃)I ^b	5.31, 4.76	2.32 (H(7); dt, J 11, 2J 3),	7.70-7.30 (PPh ₃)	48.9
	4.43, 3.96	2.20 (H(6); dq, J 12, 2J 3),		
		1.85-0.96 (8H); 0.92 (Me, d, J 7)		
(S) -Ru(mcp)CO(PPh ₃)I ^b	5.26, 4.74,	0.83 (Me, d, J 7), 0.78 (Me, d, J 7)	7.70-7.30 (PPh ₃)	49.7
	4.43, 4.37	2.10 (H(6); dq, J 13, 2J 2),		
		1.94-1.01 (9H); 0.92 (Me, d, J 7),		
(R) -[Ru(mcp)CO(PPh ₃)NCMe]BF ₄ ^c	5.60, 4.87,	0.80 (Me, d, J 7), 0.68 (Me, d, J 7)	2.06 (MeCN)	50.1
	4.70, 4.35	2.32 (H(7); dt, J 12, 2J 3),		
		1.85-0.98 (8H); 0.93 (Me, d, J 7),		
(S) -[Ru(mcp)CO(PPh ₃)NCMe]BF ₄ ^c	5.84, 5.13,	0.83 (2Me, d, J 7)	2.06 (MeCN) 7.80-7.30 (PPh ₃)	50.4
	4.49 (2H)	2.04 (H(6); m), 1.90-0.76 (9H),		
		0.96 (Me, d, J 7),		
(R) -Ru(nmcp)CO(PPh ₃)Cl ^d	5.30, 4.98,	0.83 (Me, d, J 7), 0.73 (Me, d, J 7)	7.59-7.52 (6H, m) 7.43-7.35 (9H, m)	49.2
	4.63, 3.60	3.06 (H(6); m), 2.30 (H, m),		
		1.85-0.97 (8H); 0.95 (Me, d, J 7)		
(S) -Ru(nmcp)CO(PPh ₃)Cl ^d	5.41, 4.69,	0.93 (Me, d, J 7), 0.78 (Me, d, J 7)	7.59-7.52 (6H, m) 7.43-7.35 (9H, m)	49.9
	4.48, 4.19	2.76 (H(6); bs), 2.19 (H, m),		
		1.84-0.90 (8H); 0.88 (Me, d, J 7)		
(R) -[Ru(nmcp)CO(PPh ₃)NCCH ₃]BF ₄ ^c	6.04, 5.01	0.87 (Me, d, J 7), 0.77 (Me, d, J 7)	2.04 (MeCN) 7.60-7.45 (5H) 7.45-7.30 (9H)	50.0
	4.68, 4.46	2.83 (H(6); bs), 1.95-0.92 (9H)		
		0.88 (Me, d, J 7), 0.82 (Me; d, J 7)		
(S) -[Ru(nmcp)CO(PPh ₃)NCCH ₃]BF ₄ ^{c,e}	5.78, 5.23,	0.76 (Me, d, J 7)	2.09 (MeCN) 7.70-7.20 (PPh ₃)	49.2
	4.67, 4.40	3.10 (H(6); bs), 1.90-0.7 (18H)		

^a ^1H NMR recorded at 400 MHz on a Bruker WH spectrometer unless specified and ^{31}P NMR recorded on a JEOL PFT-100 spectrometer at 40.48 MHz using 85% H_3PO_4 as an external reference; bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ^b $\nu(\text{CO})$ 1953 cm^{-1} (CHCl_3). ^c $\nu(\text{CN})$ 2260w, $\nu(\text{CO})$ 1990br cm^{-1} (CHCl_3). ^d $\nu(\text{CO})$ 1953 cm^{-1} (CHCl_3). ^e Recorded at 220 MHz.

TABLE 2
 ^{13}C (^1H) NMR DATA (CDCl_3) (δ ppm; J in Hz)^a

Complex	CO	C ₅ -ring	Menthyl or neomenthyl	Others
<i>(R)</i> -Ru(mcp)CO(PPh ₃)I	203.9	110.8 (C(1), d, J 6.3 ^b)	50.8 (C(12)), 44.4 (C(7)), 38.5 (C(6)),	136.5–128.1 (Ph)
	d, J 21 ^b	94.6, 87.9	35.3 (C(10)), 33.1 (C(8)), 27.6 (C(13)),	
		80.7, 79.3	24.8 (C(11)), 22.5 (C(9)) ^c , 21.7 (C(14)),	
			15.7 (C(15)) ^c	
<i>(S)</i> -Ru(mcp)CO(PPh ₃)I	203.7	112.9 (C(1), d, J 4.4)	50.9 (C(12)), 44.1 (C(7)), 39.2 (C(6)),	136.2–128.1 (Ph)
	d, J 20.3 ^b	88.8 (d, J 4.7 ^b)	35.1 (C(10)), 33.2 (C(8)), 27.5 (C(13)),	
		86.0, 85.8	24.8 (C(11)), 22.4 (C(9)) ^c , 21.6 (C(14)) ^c ,	
		81.0	15.5 (C(15)) ^c	
<i>(R)</i> -[Ru(mcp)CO(PPh ₃)NCMe]BF ₄	201.2	117.9 (C(1), d, J 6 ^b)	50.5 (C(12)), 44.7 (C(7)), 38.3 (C(6)),	133.4–129.0 (Ph)
	d, J 18.5 ^b	93.4, 89.7	34.9 (C(10)), 32.9 (C(8)), 27.6 (C(13)),	3.5 MeCN
		79.2, 77.5	24.6 (C(11)), 22.5 (C(9)) ^c	129.6 MeCN
			21.6 (C(14)), 15.5 (C(15)) ^c	
<i>(S)</i> -[Ru(mcp)CO(PPh ₃)NCMe]BF ₄	201.3	114.7 (C(1), d, J 5 ^b)	50.6 (C(12)), 44.6 (C(7)), 39.1 (C(6)),	133.3–129.0 (Ph)
	d, J 18.5 ^b	93.7, 87.4	34.7 (C(10)), 33.2 (C(8)), 27.7 (C(13)),	3.6 MeCN
		85.4, 78.3	24.6 (C(11)), 22.4 (C(9)) ^c , 21.4 (C(14)) ^c ,	129.8 MeCN
			15.5 (C(15)) ^c	
<i>(S)</i> -Ru(nmcp)CO(PPh ₃)Cl	204.2	111.3 (C(1), d, J 4.9 ^b)	48.7 (C(12), 43.0 (C(7)), 35.6 (C(10)) ^d ,	135.6–128.1 (Ph)
	d, J 21.4 ^b	95.2, 87.0,	35.5 (C(6)) ^d , 29.6 (C(8)), 27.9 (C(13)),	
		80.8, 80.3	24.6 (C(11)), 22.6 (C(9)) ^c , 22.1 (C(14)) ^c ,	
			20.8 (C(15)) ^c	
<i>(R)</i> -Ru(nmcp)CO(PPh ₃)Cl	204.2	110.6 (C(1), d, J 8.0 ^b)	48.1 (C(12)), 42.8 (C(7)), 35.6 (C(10)),	135.6–128.1 (Ph)
	d, J 21.1 ^b	98.4, 87.9,	34.9 (C(6)), 29.6 (C(8)), 28.3 (C(13)),	
		82.5, 75.5	24.8 (C(11)), 22.6 (C(9)) ^c , 22.0 (C(14)) ^c ,	
			20.7 (C(15)) ^c	

^a Recorded on a Bruker WH spectrometer at 100.6 MHz; numbering system shown in Fig. 4. ^b $J(^{31}\text{P}-^{13}\text{C})$. ^{c,d} These assignments may be interchanged.

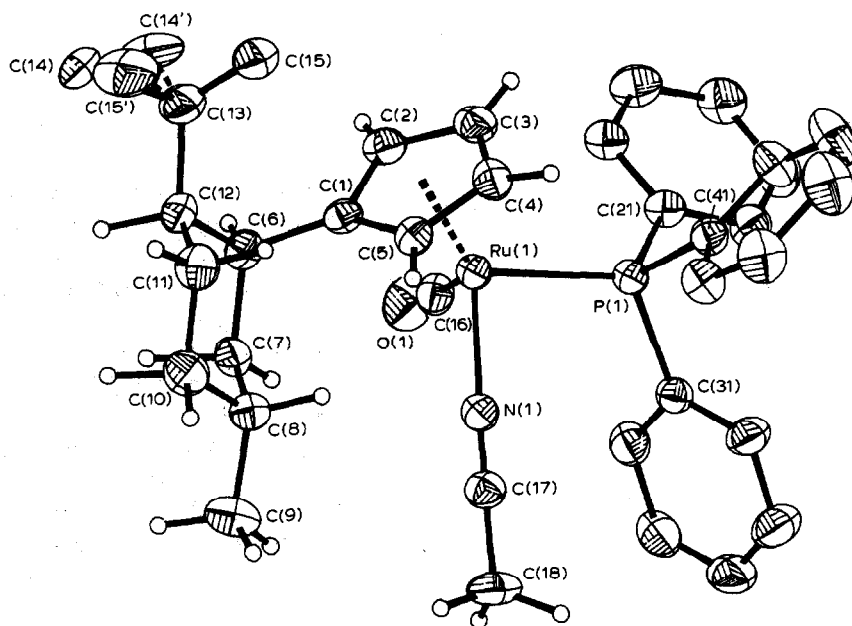


Fig. 4. The molecular structure of $(R)\text{-Ru-[Ru(nmcp)CO(PPh}_3\text{)NCMe]PF}_6$.

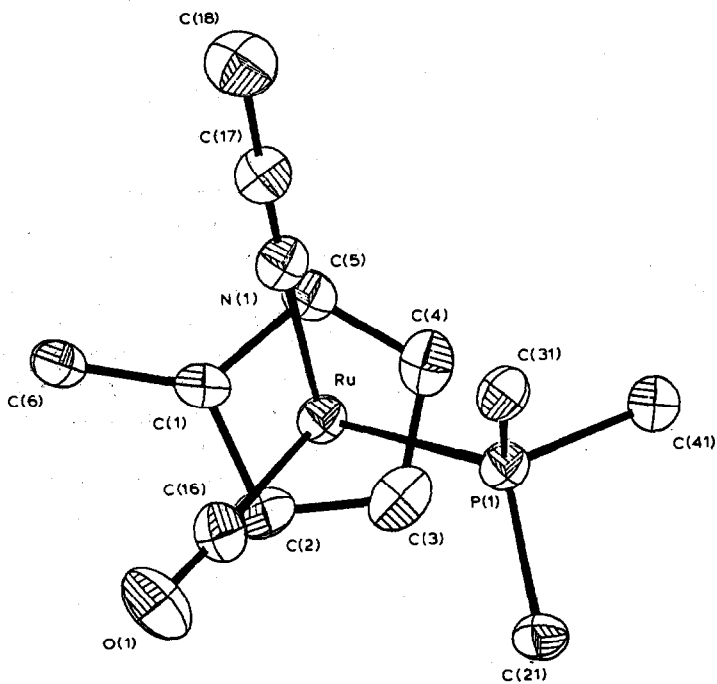


Fig. 5. The environment about the chiral ruthenium centre.

Considering the close similarity of these compounds the matching sets of ^1H , ^{13}C and ^{31}P NMR spectra and CD spectra must arise from the chloro and iodo complexes with the same configuration at the metal. Thus it is possible to assign unambiguously the stereochemistry of any epimer of $\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{X}$ ($\text{R}^* = \text{menthyl}$ or neomenthyl , $\text{X} = \text{Cl}$ or I) from either the CD or NMR spectrum.

When the metathesis reaction (i) is carried out with (*S*)- $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{Cl}$, ^1H and ^{31}P NMR spectroscopy indicate that the product is exclusively (*R*)- $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ (Fig. 3(a) and (b)). It should be appreciated that both (*S*)- $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{Cl}$ and (*R*)- $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ have the same absolute stereochemical arrangement, and the change in the formal designation of configuration merely arises from the change of the position of the halide in the ligand priority sequence, [8] i.e. nmcp (or mcp) $>$ Cl $>$ PPh_3 $>$ CO but I $>$ nmcp (or mcp) $>$ PPh_3 $>$ CO . Thus reaction (i) is totally stereospecific ($\geq 99\%$) and occurs with retention of configuration at the ruthenium atom. The same result is found when the reaction is repeated with (*R*)- $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{Cl}$ or with either of the corresponding resolved menthylcyclopentadienyl chloro epimers. Further, CD spectroscopy confirms that reaction (i) occurs with retention of configuration at the ruthenium atom (Figs. 1 and 2).

It is important to consider the influence of the chiral cyclopentadienyl ligand upon these reactions since it may have a strong directing effect upon the reactions at the ruthenium centre. However, the fact that total retention of configuration is observed with both the (*R*) and (*S*) epimers and also with both the menthyl- and neomenthyl-substituted ligands indicates that the chiral cyclopentadienyl ligand may be considered to act merely as a convenient stereochemical NMR probe.

Reactions (ii) and (v). Formation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^)(\text{CO})(\text{PPh}_3)\text{NCCH}_3]\text{Y}$ ($\text{Y} = \text{BF}_4$ or PF_6 ; **3a**, $\text{R}^* = \text{menthyl}$; **3b**, $\text{R}^* = \text{neomenthyl}$)*

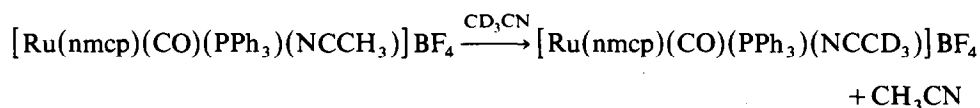
Reaction of (*R*)- $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ ($98.5 \pm 0.5\%$ optically pure) with AgBF_4 in acetonitrile yields the complex $[\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{NCCH}_3]\text{BF}_4$ $93.2 \pm 0.4\%$ optically pure (Fig. 3(b) and (c)). The CD spectrum of the product has the same general shape as the starting iodo complex although shifted to lower wavelength. This indicates that the acetonitrile complex has an (*R*)-configuration and that reaction (ii) proceeds with net retention at the ruthenium. An X-ray structure confirmed this although it should be pointed out that it proved impossible to grow suitable crystals of the tetrafluoroborate salt and so the structure determined was that of $[\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{NCCH}_3]\text{PF}_6$ prepared by the corresponding reaction of $\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{I}$ with silver hexafluorophosphate. However, ^1H and ^{31}P NMR spectroscopy showed that the stereochemical course of the reactions with AgBF_4 and AgPF_6 were identical. Further, the CD spectrum of the crystal used for the structure determination confirmed that this crystal had the same stereochemistry as the predominant diastereoisomer present in the product mixture.

The molecular structure of (*R*)- $[\text{Ru}(\text{nmcp})\text{CO}(\text{PPh}_3)\text{NCCH}_3]\text{PF}_6$ and the atom numbering system used is shown in Fig. 4; the environment about the ruthenium is shown in Fig. 5. Selected bond distances and bond angles are reported in Table 3. The angles between the monodentate ligands range from $92.2(3)^\circ$ (N-Ru-C) to $89.0(2)^\circ$ (P-Ru-N) indicating an essentially octahedral environment around the ruthenium atom. Bond distances are very similar to those previously reported for (*R*)- $\text{Ru}(\text{nmcp})\text{CO}(\text{PPh}_3)\text{I}$ [3] although these two molecules differ in one major

respect. In the iodo complex the carbonyl ligand is almost eclipsed to the neomenthyl-cyclopentadienyl bond presumably so as to allow the maximum separation between the bulky substituents, i.e. I, PPh₃ and neomenthyl. However, in (*R*)-[Ru(nmcp)CO(PPh₃)NCMe]PF₆ the carbonyl and acetonitrile ligands are staggered about the neomenthyl-cyclopentadienyl bond. Presumably this is so as to allow the bulky triphenylphosphine to be *trans* to the bulky neomenthyl substituent.

An analogous reaction with AgBF₄ was carried out with the corresponding epimers of Ru(mcp)(CO)(PPh₃)Cl (**1a**) (i.e. reaction (v)) and the similarity of the CD spectrum of the starting complex with that of the product ion (see Fig. 1) indicated that this reaction also occurred with retention of configuration at the ruthenium. The stereoselectivities of these reactions as measured by ¹H NMR spectroscopy were similar to that measured for the corresponding reaction of AgBF₄ with Ru(nmcp)(CO)(PPh₃)I i.e. 99% (*R*)-**1a** gave 94.0 ± 0.5% (*S*)-**3a** and 99% (*S*)-**1a** gave 93.3 ± 0.5% (*R*)-**3a**.

Reaction (iii). Exchange of coordinated acetonitrile



(*R*)-[Ru(nmcp)(CO)(PPh₃)(NCCH₃)]BF₄, the product obtained from reaction (ii), was dissolved in CD₃CN in an NMR tube and heated. Complete exchange of coordinated NCCH₃ with NCCD₃ occurred after 8 h at 85°C and the reaction was conveniently followed by ¹H NMR by monitoring the disappearance of the coordinated NCCH₃ resonance at δ 2.05. The deuteriated product was obtained with an optical purity of 85.0% whereas the original acetonitrile complex was 93.2% optically

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR [Ru(nmcp)CO(PPh₃)NCMe]PF₆

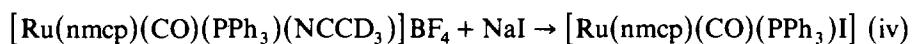
Ru-C(1)	2.262(6)	C(1)-C(2)	1.433(7)
Ru-C(2)	2.187(7)	C(2)-C(3)	1.421(9)
Ru-C(3)	2.180(7)	C(3)-C(4)	1.410(9)
Ru-C(4)	2.241(8)	C(4)-C(5)	1.392(7)
Ru-C(5)	2.251(7)	C(1)-C(5)	1.442(7)
Ru-cp ^a	1.868(7)	C(1)-C(6)	1.498(7)
Ru-N(1)	2.050(6)	N(1)-C(17)	1.136(8)
Ru-C(16)	1.870(7)	O(1)-C(16)	1.139(7)
Ru-P(1)	2.324(3)	C(18)-C(17)	1.449(8)
C(16)-Ru-cp ^a	125.0(3)	C(5)-C(1)-C(2)	105.0(5)
N(1)-Ru-cp ^a	124.4(3)	C(1)-C(2)-C(3)	109.0(6)
P(1)-Ru-cp ^a	124.7(3)	C(2)-C(3)-C(4)	107.8(6)
N(1)-Ru-C(16)	92.2(3)	C(3)-C(4)-C(5)	108.3(6)
P(1)-Ru-C(16)	91.3(2)	C(4)-C(5)-C(1)	109.8(5)
P(1)-Ru-N(1)	89.0(2)	C(5)-C(1)-C(6)	130.8(4)
Ru-C(16)-O(1)	175.9(5)	C(2)-C(1)-C(6)	123.9(5)
Ru-P(1)-C(21)	117.5(3)	C(1)-C(6)-C(7)	114.7(5)
Ru-P(1)-C(31)	114.8(2)	C(1)-C(6)-C(12)	113.4(5)
Ru-P(1)-C(41)	112.8(2)	N(1)-C(17)-C(18)	178.8(6)
Ru-N(1)-C(17)	178.5(4)		

^a cp denotes the centre of the cyclopentadienyl ring.

pure. At first sight this exchange may not appear to be a very stereospecific reaction. However, it should be appreciated that the deuteriated product **4b** will itself exchange with free CD₃CN; indeed this latter exchange will predominate when the deuteriated product is the major complex in solution. Thus, when complete exchange of CH₃CN has occurred the product **4b** will have undergone many exchange reactions and a final optical purity of 85.0% indicates that each individual exchange must indeed be very stereospecific (i.e. $\geq 95\%$).

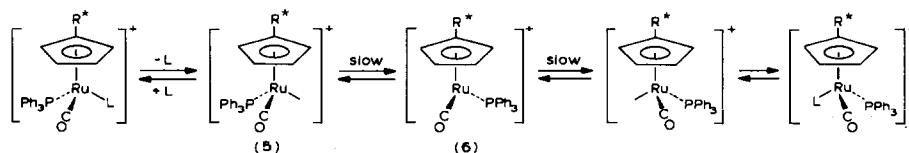
Comparison of the ¹H NMR spectra of the CH₃CN and CD₃CN complexes **3b** and **4b** (Fig. 3(b) and 3(c)) shows that the major diastereoisomers present have almost identical resonances in the cyclopentadienyl region and that the spectra differ radically from that of (*S*)-[Ru(nmcp)(CO)(PPh₃)NCMe]BF₄ (Table 1). This demonstrates conclusively that the exchange reaction (iii) occurs with overall net retention at the ruthenium.

Reaction (iv)



The sample of (*R*)-[Ru(nmcp)(CO)(PPh₃)(NCCD₃)]BF₄ (**4b**) obtained from reaction (iii) was refluxed in acetone with sodium iodide for 48 h. ¹H NMR spectroscopy indicated that the optical purity of the iodo product **2b** obtained was 85.0 ± 0.4% identical to that of the starting complex **4b**. Hence reaction (iv) is totally stereospecific. Further, the ¹H of the major diastereoisomer is identical to that of the original starting complex (*R*)-Ru(nmcp)(CO)(PPh₃)I (**2b**) (Fig. 3) i.e. the reaction sequence **2b** → **3b** → **4b** → **2b** (Scheme 1) results in no change in the configuration of the ruthenium atom. However, the conversions **2b** → **3b** and **3b** → **4b** have been unequivocally proved to occur with retention of configuration at the ruthenium atom by X-ray and ¹H NMR spectroscopy respectively (vide infra). It therefore follows that reaction (iv), the conversion of **4b** to **2b** must also occur with retention of configuration.

The results clearly show that complexes of the type [Ru(η⁵-C₅H₄R*)(CO)(PPh₃)L]ⁿ⁺ exhibit a distinct preference to undergo substitution reactions with retention of configuration at the ruthenium. Although these stereochemical results need to be complemented by kinetic studies in order to make definitive statements concerning the detailed mechanisms of these reactions certain inferences may be made. Kinetic studies on complexes closely related to those discussed herein i.e. M(C₅H₅)(CO)LX (M = Fe, L = P{N(Me)CH(Me)Ph}Ph₂, X = Cl, Br or I [9]; M = Ru, L = CO, X = Br [10]) indicate that they undergo ligand substitution reactions via a dissociative process; such behaviour is indeed typical of diamagnetic octahedral d⁶ compounds [11]. Hence, a plausible pathway for the exchange of acetonitrile in [Ru(nmcp)(CO)(PPh₃)NCCH₃]BF₄ is that shown in Scheme 2.



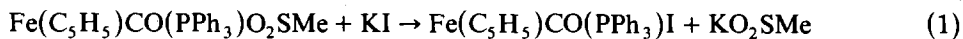
SCHEME 2. L = NCMe.

This is analogous to the proposed mechanism of phosphine exchange in $[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{NO}(\text{PPh}_3)\text{COPh}]$ ($\text{R} = \text{H}$ or Me) [12]. Such a mechanism implies that the coordinatively unsaturated intermediate **5**, (Scheme 2) retains its "pyramidal" geometry and does not rapidly adopt a "planar" geometry as in **6** since this would result in racemisation during the substitution reaction. A theoretical study of the dynamic behaviour of the 16-electron intermediates CpML^1L^2 concluded that such intermediates may indeed be configurationally stable depending upon the metal and the nature of the ligands L^1 and L^2 [13]. Also, earlier kinetic studies of the hydrolysis of *cis*- $[\text{M}(\text{en})_2\text{Cl}_2]^+$ compounds ($\text{M} = \text{Co}$ [14], $\text{M} = \text{Rh}$ [15] or $\text{M} = \text{Cr}$ [16]) concluded that the reactions occurred via a dissociative pathway in which the five-coordinate intermediate retains a tetragonal pyramidal arrangement. This proposal is of course in stark contrast to the classical ideas of organic chemistry where reactions involving coordinatively unsaturated intermediates characteristically occur with racemisation.

A recent study of the mechanism of halide abstraction from $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{I}$ by AgBF_4 concluded that the reaction proceeded via initial formation of the adduct $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{IAg}^+\text{BF}_4^-$ and subsequent formation of coordinatively unsaturated $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]^+$ which rapidly reacted with any available nucleophile [17]. It is therefore reasonable to assume that the analogous reactions (ii) and (v), involving the $\text{Ag}(\text{I})$ -induced removal of halide from $\text{Ru}(\text{C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{X}$ ($\text{X} = \text{Cl}$ or I) proceed via the intermediate **5**, $[\text{Ru}(\text{C}_5\text{H}_4\text{R}^*)(\text{CO})\text{PPh}_3]^+$ followed by rapid coordination of acetonitrile.

Little is known of the mechanism of metathesis reactions with sodium iodide in non-aqueous solvents but reaction (i) involving conversion of $\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})\text{PPh}_3\text{Cl}$ into the corresponding iodide may proceed via the coordinatively unsaturated intermediate **5** or via a four-centred mechanism involving NaI ; either mechanism would account for the observed net retention of configuration.

Our observation that complexes of the type $[\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})\text{PPh}_3\text{L}]^{n+}$ react with net retention of configuration at the metal is in keeping with other stereochemical studies on organometallic complexes. Indeed we know of only one example of an 18-electron organometallic complex which reacts with a Walden-like inversion of configuration at the metal and that involves the substitution of the isocyanide ligand in $\text{Mo}(\text{C}_5\text{H}_5)\text{NO}(\text{CO})\text{CNR}$ ($\text{R} = \text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ or C_6H_{11}) [18]. Photochemical decarbonylation of $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\text{PPh}_3\{\text{C}(\text{O})\text{Me}\}$ also leads to inversion of the iron centre but this is really a special case since it proceeds via migration of the methyl group to the site vacated by the CO ligand which effectively exchanges the position of the CO ligand [19]. Net inversion (10% e.e.) has also been reported for reaction (1).



However, this is proposed to occur via iodide attack on the "16-electron" tight ion pair $[\text{Fe}(\text{C}_5\text{H}_5)\text{CO}(\text{PPh}_3)]^+ \text{O}_2\text{SMe}^-$ [20].

We conclude that substitution reactions of 18-electron organometallic compounds may normally be expected to occur with retention of configuration at the metal and presume that this is a reflection of the fact that inversion arises from an associative mechanism which is a rare reaction pathway for such compounds.

Experimental

General procedures

Circular Dichroism spectra in the region 280–550 nm were recorded on a Jobin-Yvon Dichrographe III using chloroform as a solvent and normally with concentrations of 0.5 mg ml^{-1} ; the short wavelength limit was determined by the strong absorption of the compounds.

The halogeno complexes $\text{Ru}(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{X}$ [$\text{R}^* = \text{menthyl}$, $\text{X} = \text{Cl}$ or I , $\text{R}^* = \text{neomenthyl}$, $\text{X} = \text{Cl}$ (**1b**) or I] were prepared and resolved as previously reported [3] except for **1b** which was resolved by HPLC on 19μ Spherisorbe using EtOAc/petroleum ether (7/93) eluent. ^1H and ^{13}C NMR spectra of new complexes are reported in Tables 1 and 2 respectively.

Stereochemical studies

For each of the reactions studied identical procedures were used for each diastereoisomer and therefore details are only reported for one diastereoisomer.

Conversion of $\text{Ru}(\text{C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{Cl}$ to $\text{Ru}(\text{C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{I}$ ($\text{R}^* = \text{menthyl}$ or neomenthyl)

(*S*)- $\text{Ru}(\text{nmcp})(\text{CO})\text{PPh}_3\text{Cl}$ (100 mg) was stirred with a suspension of NaI (200 mg) in dichloromethane for 80 h and then filtered. Solvent was removed in vacuo and the optical purity of the iodo product determined by ^1H and ^{31}P NMR spectroscopy.

Conversion of $\text{Ru}(\text{C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{X}$ to $[\text{Ru}(\text{C}_5\text{H}_4\text{R}^*)(\text{CO})(\text{PPh}_3)\text{NCMe}]\text{BF}_4$ ($\text{R}^* = \text{menthyl}$, $\text{X} = \text{Cl}$; $\text{R}^* = \text{neomenthyl}$, $\text{X} = \text{I}$)

(*R*)- $\text{Ru}(\text{nmcp})(\text{CO})\text{PPh}_3\text{I}$ (85 mg, 0.118 mmol) together with AgBF_4 (24 mg, 0.123 mmol) was dissolved in dry acetonitrile (10 cm^3) and stirred under nitrogen for 50 min. The precipitated silver iodide was then filtered off through a short column (ca. 10 cm long and 1.5 cm diameter) of cellulose and the solvent removed in vacuo to give the product as a green-yellow oil. The optical purity of this acetonitrile complex was measured by ^1H and ^{31}P NMR. Subsequent crystallisation from dichloromethane/petroleum ether gave yellow prisms (55 mg, 65% yield). Found: C, 59.5; H, 5.5; N, 1.8. $\text{C}_{36}\text{H}_{41}\text{BF}_4\text{NOPRu}$ calcd.: C, 59.8; H, 5.7; N, 1.9%.

Exchange of CD_3CN with (*R*)- $[\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{NCCH}_3]\text{BF}_4$

The ruthenium complex (20 mg, 0.0276 mmol) was dissolved in acetonitrile- d_3 (0.5 cm^3) in an NMR tube. After degassing several times the tube was sealed and heated at 85°C for 8 h. The optical purity of the (*R*)- $[\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{NCCD}_3]\text{BF}_4$ was measured by ^1H NMR then the tube broken and the solvent removed in vacuo to give the product as a green-yellow solid (16 mg, 80%).

Conversion of (*R*)- $[\text{Ru}(\text{nmcp})(\text{CO})(\text{PPh}_3)\text{NCCD}_3]\text{BF}_4$ to (*R*)- $\text{Ru}(\text{nmcp})\text{CO}(\text{PPh}_3)\text{I}$

The above sample of (*R*)- $[\text{Ru}(\text{nmcp})\text{CO}(\text{PPh}_3)\text{NCCD}_3]\text{BF}_4$ (16 mg, 0.022 mmol) and sodium iodide (20 mg, 0.13 mmol) were refluxed in acetone (20 cm^3) for 48 h.

(Continued on p. 358)

TABLE 4
 ATOM COORDINATES ($\times 10^4$)

Atom	x	y	z
Ru	-886	-584	-2244
C(1)	73(4)	-315(3)	-3047(2)
C(2)	961(4)	-663(4)	-2644(2)
C(3)	1077(5)	-102(4)	-2219(2)
C(4)	279(5)	600(4)	-2321(2)
C(5)	-347(5)	470(3)	-2811(2)
C(6)	-190(5)	-693(3)	-3591(2)
C(7)	-1615(5)	-872(4)	-3707(2)
C(8)	-2418(6)	-101(5)	-3820(2)
C(9)	-3814(7)	-346(6)	-3960(4)
C(10)	-1808(6)	411(5)	-4289(3)
C(11)	-395(6)	609(5)	-4176(2)
C(12)	399(5)	-182(4)	-4063(2)
C(13)	1851(6)	9(5)	-3996(2)
C(14)	2512(15)	-126(18)	-4553(5)
C(14')	2631(10)	-779(7)	-3965(6)
C(15)	2301(11)	769(8)	-3688(5)
C(15')	2337(16)	619(14)	-4442(7)
C(16)	-1078(5)	-1757(3)	-2235(2)
O(1)	-1125(5)	-2475(2)	-2244(2)
N(1)	-2816(4)	-401(3)	-2363(1)
C(17)	-3885(5)	-284(3)	-2422(2)
C(18)	-5252(5)	-134(5)	-2484(3)
P(1)	-1232(1)	-510(1)	-1318
C(21)	-343(5)	-1245(3)	-890(2)
C(22)	706(5)	-1664(3)	-1095(2)
C(23)	1400(6)	-2205(4)	-754(3)
C(24)	1047(6)	-2314(4)	-226(2)
C(25)	-28(6)	-1900(4)	-29(2)
C(26)	-728(6)	-1370(3)	-361(2)
C(31)	-2898(4)	-693(3)	-1107(2)
C(32)	-3608(6)	-103(4)	-826(2)
C(33)	-4873(7)	-268(6)	-696(3)
C(34)	-5417(7)	-1010(7)	-840(3)
C(35)	-4723(7)	-1608(5)	-1111(2)
C(36)	-3456(6)	-1449(4)	-1247(2)
C(41)	-861(5)	523(3)	-1038(2)
C(42)	-8(6)	659(4)	-624(2)
C(43)	211(9)	1472(5)	-431(3)
C(44)	-425(10)	2134(4)	-646(3)
C(45)	-1278(8)	2017(4)	-1071(3)
C(46)	-1488(6)	1211(3)	-1265(2)
P(2)	-6572(1)	-2655(1)	-2382(1)
F(1)	-6283(4)	-3456(2)	-2740(2)
F(2)	-6880(3)	-1835(2)	-2026(1)
F(3)	-6557(5)	-3202(3)	-1855(2)
F(4)	-6598(4)	-2093(2)	-2907(1)
F(5)	-5103(3)	-2486(3)	-2324(2)
F(6)	-8060(3)	-2813(3)	-2455(2)
C(19)	-720(10)	2996(7)	1364(3)
Cl(1)	-2094(14)	3551(10)	1286(4)
Cl(1')	-2156(9)	3388(6)	1589(3)
Cl(2)	115(9)	2835(6)	779(4)
Cl(2')	-859(9)	2827(6)	647(2)

TABLE 5. ANISOTROPIC TEMPERATURE FACTORS ^a ($\text{\AA}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	43	43	41	5	-1	-4
C(1)	40(2)	44(2)	51(2)	9(2)	3(2)	5(2)
C(2)	44(2)	68(3)	55(2)	20(2)	0(2)	1(3)
C(3)	49(3)	89(4)	53(3)	15(3)	0(3)	-18(3)
C(4)	65(3)	59(3)	52(2)	3(3)	3(2)	-21(3)
C(5)	51(2)	45(2)	52(2)	5(2)	6(2)	0(2)
C(6)	54(3)	45(2)	53(2)	4(2)	5(2)	11(2)
C(7)	56(3)	70(3)	48(2)	-3(2)	-1(2)	-7(2)
C(8)	50(3)	95(4)	62(3)	-7(3)	-1(2)	6(3)
C(9)	61(4)	130(7)	109(5)	-5(5)	-21(4)	-1(4)
C(10)	73(4)	92(5)	63(3)	14(3)	-11(3)	16(3)
C(11)	75(3)	80(4)	53(3)	24(3)	3(3)	-6(4)
C(12)	55(3)	73(3)	47(3)	-3(2)	7(2)	5(3)
C(13)	55(3)	121(6)	66(3)	10(4)	9(3)	-14(4)
C(14)	51(7)	253(25)	71(8)	-41(13)	18(6)	10(12)
C(14')	42(6)	93(10)	132(11)	43(9)	7(6)	8(6)
C(15)	57(6)	131(13)	72(7)	-2(8)	7(6)	-9(8)
C(15')	78(10)	159(17)	105(12)	69(13)	7(9)	-35(13)
C(16)	61(3)	55(3)	54(2)	-4(2)	6(3)	-3(2)
O(1)	107(3)	52(2)	113(3)	-11(2)	19(3)	-3(2)
N(1)	52(2)	52(2)	46(2)	5(2)	0(2)	-8(2)
C(17)	51(3)	55(3)	57(2)	6(2)	1(2)	-8(2)
C(18)	39(3)	86(4)	115(5)	-3(4)	-1(3)	-8(3)
P(1)	44(1)	43(1)	42	5	-1	-4
C(21)	48(2)	44(2)	55(2)	9(2)	-3(2)	1(2)
C(22)	53(3)	53(3)	63(3)	9(2)	-3(2)	0(2)
C(23)	59(3)	58(3)	91(4)	15(3)	-3(3)	11(3)
C(24)	74(4)	69(3)	72(3)	22(3)	-10(3)	9(3)
C(25)	92(4)	76(4)	49(3)	18(3)	-4(3)	8(3)
C(26)	67(4)	65(3)	52(2)	12(2)	1(3)	5(3)
C(31)	47(2)	61(3)	43(2)	4(2)	-2(2)	-7(2)
C(32)	51(3)	82(4)	68(3)	5(3)	10(3)	-1(3)
C(33)	59(4)	111(6)	87(5)	4(4)	18(3)	4(4)
C(34)	57(4)	150(8)	70(4)	14(4)	4(3)	-33(5)
C(35)	81(4)	102(5)	54(3)	13(3)	-1(3)	-45(4)
C(36)	71(4)	78(4)	55(3)	0(3)	9(3)	-25(3)
C(41)	49(2)	52(2)	49(2)	0(2)	3(2)	-5(3)
C(42)	79(4)	58(3)	60(3)	0(3)	-19(3)	-1(3)
C(43)	119(6)	85(5)	75(4)	-9(4)	-28(4)	-26(4)
C(44)	147(8)	51(3)	93(5)	-3(3)	-8(5)	-17(4)
C(45)	105(5)	50(3)	85(4)	5(3)	-1(4)	-2(3)
C(46)	72(3)	53(3)	64(3)	4(2)	-7(3)	1(3)
P(2)	61(1)	52(1)	79(1)	-1(1)	-12(1)	-1(1)
F(1)	137(3)	64(2)	136(3)	-25(2)	-34(3)	19(2)
F(2)	75(2)	78(2)	85(2)	-13(2)	0(2)	2(2)
F(3)	172(4)	98(3)	120(3)	39(2)	0(3)	15(3)
F(4)	130(3)	83(2)	79(2)	6(2)	-2(2)	14(2)
F(5)	58(2)	136(3)	125(3)	-33(3)	-11(2)	6(2)
F(6)	68(2)	113(3)	178(4)	-9(3)	-19(2)	-22(2)
C(19)	136(7)	229(11)	113(6)	-32(7)	6(6)	46(8)
Cl(1)	167(7)	312(12)	239(11)	87(11)	36(9)	50(8)
Cl(1')	118(4)	198(7)	172(6)	-48(6)	33(5)	31(5)
Cl(2)	230(9)	172(6)	199(7)	-71(5)	-35(7)	27(7)
Cl(2')	238(8)	184(6)	107(3)	-46(4)	25(5)	0(7)

^a The temperature factor exponent takes the form: $-2\pi^2(U_{11} \cdot h^2 \cdot a^{*2} + \dots + 2U_{12} \cdot h \cdot k \cdot a^* \cdot b^*)$.

After removal of the solvent in vacuo the optical purity of the orange Ru(nmcp)CO(PPh₃)I was measured by ¹H NMR spectroscopy.

X-Ray crystal structure of (R)-[Ru(η⁵-C₅H₄R)(CO)(PPh₃)NCCH₃]PF₆ (R* = neomenthyl)*

The compound was prepared by the procedure described above for the tetrafluoroborate salt but using AgPF₆ in place of AgBF₄. Suitable crystals were obtained by recrystallising the crude material from a mixture of CH₂Cl₂/Et₂O/McCN (2/20/1) at -78°C. The presence of dichloromethane in the crystal lattice necessitated the mounting of the crystal in a Lindemann capillary so that it remained bathed in mother liquor and at a temperature of 0°C.

Crystal data. [C₃₆H₄₁NO₂Ru]⁺ [PF₆]⁻ · CH₂Cl₂, *M* = 865, orthorhombic, *a* 10.400(2), *b* 15.850(4), *c* 24.740(5) Å, *U* 4078.1 Å³, space group *P*2₁2₁2₁ (No. 19), *Z* = 4, *D*_c = 1.41 g cm⁻³, *F*(000) = 1768, λ 0.71069 Å, μ(Mo-K_α) 5.76 cm⁻¹.

Data collection. Unit cell parameters were determined and intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω-scan procedure [21]. Three intensity-control reflections collected every hour showed that no reduction in diffracted intensity occurred during data collection. 5236 Data (1.5 ≤ θ ≤ 27.5°) were measured of which 5205 were unique and 4189 were considered observed (*I* ≥ 1.5σ(*I*)).

Structure solution and refinement

The heavy-atom method was used to solve the structure and the absolute configuration about the Ru atom was determined by obtaining the correct stereochemistry for the neomenthyl substituent; the molecule was found to have the *R* configuration about the metal [8]. An absorption correction using the DIFABS [22] method was applied to the data after refinement with isotropic thermal parameters for all the non-hydrogen atoms. Atoms C(14) and C(15) on the isopropyl constituent of the neomenthyl group were found to be disordered between two sites with equal occupation. A similar disordering occurred for the two chlorine atoms on the dichloromethane molecule present in the crystal lattice. Following refinement with anisotropic thermal parameters for all non-hydrogen atoms (including those at half occupancy), difference Fouriers revealed the positions of all hydrogen atoms with the exceptions of H(13), the methyl hydrogens on C(14), C(14'), C(15) and C(15'), and the two hydrogens on dichloromethane. Hydrogen atoms were refined with isotropic temperature factors and, with the exception of the methyl hydrogens attached to C(9) and C(18), without geometric constraints. The final blocked full-matrix least-squares refinement was carried out with the omission of six strong low angle reflections and a weighting scheme $w = 1/(\sigma^2(F_0) + 0.0006 F_0^2)$. The final *R*-factors were $R = \Sigma|\Delta F|/\Sigma|F_0| = 0.036$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma w|F_0|^2]^{1/2} = 0.043$.

Inverting the structure to give the *S*-enantiomer gave *R*-factors 0.039 and 0.047 respectively, thus confirming the correct choice of absolute configuration.

All computations were made using the SHELX-76 [23] program on a DEC VAX 11/750 computer. Selected bond lengths and bond angles are given in Table 3 and final atomic coordinates are given in Table 4. Isotropic and anisotropic temperature factors are given in Tables 5 and 6. All thermal parameters and structure factor tables may be obtained from the authors.

TABLE 6

HYDROGEN ATOM COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(2)	1338(44)	-1177(30)	-2661(18)	44(12)
H(3)	1607(57)	-256(35)	-1938(24)	76(18)
H(4)	246(45)	1144(29)	-2082(17)	45(12)
H(5)	-933(40)	839(25)	-2936(15)	32(10)
H(6)	216(49)	-1249(34)	-3537(20)	58(14)
H(7A)	-1975(57)	-1172(38)	-3426(23)	74(18)
H(7B)	-1472(72)	-1241(44)	-4148(27)	108(23)
H(8)	-2348(50)	334(29)	-3471(20)	59(14)
H(9A)	-3795(7)	-664(6)	-4345(4)	152(21)
H(9B)	-4360(7)	231(6)	-3995(4)	152(21)
H(9C)	-4259(7)	-750(6)	-3662(4)	152(21)
H(10A)	-2450(75)	952(48)	-4420(30)	126(26)
H(10B)	-1698(48)	97(31)	-4693(21)	50(13)
H(11A)	-296(58)	1027(37)	-3848(23)	75(18)
H(11B)	-94(52)	852(33)	-4468(22)	60(16)
H(12)	318(55)	-579(36)	-4455(22)	74(16)
H(18A)	-5434(5)	117(5)	-2880(3)	193(29)
H(18B)	-5719(5)	257(5)	-2186(3)	193(29)
H(18C)	-5625(5)	-768(5)	-2461(3)	193(29)
H(22)	1069(42)	-1646(27)	-1518(18)	49(12)
H(23)	2064(52)	-2513(32)	-890(19)	55(14)
H(24)	1411(68)	-2574(48)	84(29)	111(23)
H(25)	-259(46)	-1998(29)	361(18)	46(12)
H(26)	-1586(55)	-1125(34)	-325(21)	64(16)
H(32)	-3068(65)	447(43)	-690(26)	100(21)
H(33)	-5335(76)	190(47)	-549(31)	103(26)
H(34)	-6071(82)	-1054(54)	-707(32)	110(31)
H(35)	-5135(59)	-2080(39)	-1291(23)	76(18)
H(36)	-2919(55)	-1826(37)	-1426(22)	73(18)
H(42)	341(51)	261(33)	-518(21)	47(15)
H(43)	927(70)	1608(42)	-182(28)	98(21)
H(44)	-475(65)	2691(42)	-530(26)	91(21)
H(45)	-1679(58)	2515(37)	-1287(23)	77(18)
H(46)	-2066(43)	1188(27)	-1540(17)	38(11)

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