Synthesis and Stereochemical Studies of the Chiral Ruthenium Complexes [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}X] [dpompyr = *N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidine, X = H or Cl]. Crystal Structure of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl]†

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A simple procedure for the preparation of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] [dpompyr = *N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidine] from [$Ru_3(CO)_{12}$] is described. The hydride reacts stereospecifically with chloroform or carbon tetrachloride to give [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] whose structure is reported. The crystals are monoclinic, space group $P2_1$ with a = 11.076(2), b = 10.908(2), c = 12.825(3) Å, β = 92.26(2), and Z = 2. The structure was solved by the heavy-atom method and refined to R = 0.0322 using 2 306 diffractometer data with $I > 3\sigma(I)$. Synthesis of this chloro-complex from [Ru(η-C_5H_5)(PPh_3)$_2$Cl] and (*S*)dpompyr proceeds with only modest diastereoselectivity whereas reduction of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] using $LiAlH_4$ regenerates 88% [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H]. Mechanisms are proposed to explain the observed diastereoselectivities. Circular dichroism and ^1H, ^{13}C, and ^{31}P n.m.r. spectra of all new compounds are also reported.

Organometallic compounds containing a chiral metal centre have attracted considerable interest since 1969 when the first such compound was prepared in an optically pure form.[1] This interest has been stimulated by the use of such compounds to obtain valuable mechanistic information from stereochemical studies[2] and their application as reagents in asymmetric synthesis.[3] Unfortunately, the synthesis and resolution of such chiral organometallic compounds is often not trivial. For example, chiral ruthenium complexes of the type [Ru(η-C_5H_5)(L–L)X] (where L–L = chelating diphosphine without C_{2v} symmetry) have proved to be convenient model compounds for stereochemical studies because of the configurational stability of the chiral ruthenium centre. However, the reported synthesis is *via* the displacement of the triphenylphosphine ligands from [Ru(η-C_5H_5)(PPh_3)$_2$Cl] by the appropriate chiral chelating diphosphine in refluxing benzene or toluene.[4] This procedure leads to a diastereoisomeric mixture in *ca.* 1:1 ratio with subsequent tedious separation of the diastereoisomers by various analytical methods. In contrast, we report herein a simple procedure which leads directly in high yield to optically pure [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] [dpompyr = *N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidine, $Ph_2POCH_2CH(CH_2)_3NPPh_2$]. Further, we illustrate how this readily accessible complex is amenable for stereochemical studies.

Results and Discussion

We have previously demonstrated that [Ru(η-C_5H_5)$(CO)_2$H] is, because of the strong labilising effect of the hydride ligand, a useful starting material, reacting smoothly with a chelating diphosphine to displace both carbonyl ligands.[5] We have now found that when the chiral diphosphine (*S*)dpompyr is refluxed in heptane with [Ru(η-C_5H_5)$(CO)_2$H], generated *in situ* from cyclopentadiene and [$Ru_3(CO)_{12}$], optically pure [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] precipitates from the reaction mixture. Thus, by this simple 'one-pot' procedure optically pure [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] may be prepared in 70% yield from [$Ru_3(CO)_{12}$].

Several interesting features were revealed when the reaction was monitored by ^1H and ^{31}P n.m.r.; this was carried out by periodically withdrawing samples from the reaction mixture, evaporating off the heptane under high vacuum and dissolving the residue in degassed C_6D_6. The ^{31}P n.m.r. spectrum of the free ligand (*S*)dpompyr consists of two singlets at δ 113.7 and 46.7 p.p.m. [Figure 1 (*a*)]; these may be assigned to the diphenylphosphino-groups co-ordinated to oxygen and nitrogen respectively.[6] After reaction with [Ru(η-C_5H_5)$(CO)_2$H] for 5 min at room temperature, the $-OPPh_2$ signal at δ 113.7 p.p.m. is replaced by two signals at δ 160.5 and 160.3 p.p.m. whereas the $-NPPh_2$ signal at δ 46.7 p.p.m. is shifted slightly to give two signals at δ 45.8 and 45.5 p.p.m. [Figure 1(*b*)]. The doubling of the signals together with the large shift of the $-OPPh_2$ signal clearly indicate that the initial product formed after reaction for 5 min at room temperature is a diastereoisomeric mixture of [Ru(η-C_5H_5)(CO){(*S*)dpompyr-*P*}H] containing a unidentate diphosphine ligand (dpompyr-*P*) co-ordinated exclusively through the phosphorus bound to the oxygen atom. In keeping with this proposal the i.r. spectrum of the initial product contained a single strong carbonyl absorption at 1 941 cm^{-1}.

In addition to the chiral phosphorus ligand the initial product also contains a chiral ruthenium centre; however, this is formed with little stereochemical control since an almost equimolar mixture of the monosubstituted diastereoisomers was obtained. This was also evident from the ^1H n.m.r. spectrum which

† Chloro(η-cyclopentadienyl)[(*S*)-*N*-diphenylphosphino-2-(diphenylphosphinoxymethyl)pyrrolidine-*PP'*](*S*)ruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

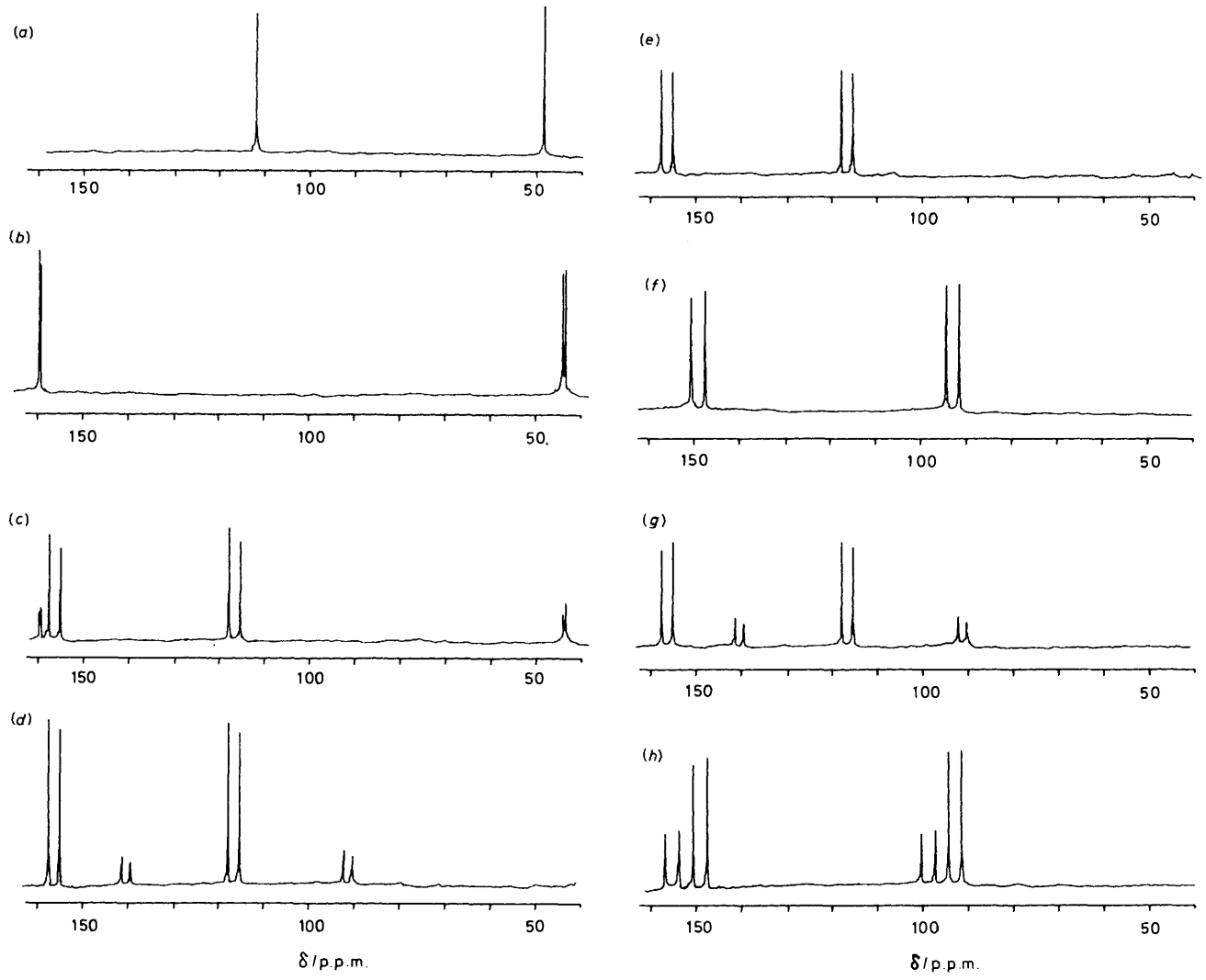

Figure 1. ^{31}P N.m.r. spectra: (*a*) (*S*)dpompyr; [Ru(η-C_5H_5)$(CO)_2$H] and (*S*)dpompyr, (*b*) after 5 min at room temperature (r.t.), (*c*) after 5 min at 98 °C, (*d*) after 4 h at 98 °C; (*e*) [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] which crystallises from the reaction mixture; (*f*) [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] obtained by reaction of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] with $CHCl_3$; (*g*) [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] obtained by reaction of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] with $LiAlH_4$; (*h*) [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] obtained from [Ru(η-C_5H_5)$(PPh_3)_2$Cl] and (*S*)dpompyr

contains two cyclopentadienyl resonances of similar intensity at δ 4.85 and 4.86 p.p.m. while in the hydridic region there are two doublets, again of approximately equal intensities, which are located at δ −11.26 and −11.28 p.p.m. (J_{P-H} = 32 Hz) [Figure 2(*a*)].

Upon heating the reaction mixture, the ^{31}P n.m.r. spectra show a progressive decrease in the signals assigned to the monosubstituted complex with a concomitant formation of two sets of signals which differ greatly in intensity; these are assigned to the two diastereoisomers of [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] which differ in their chirality at ruthenium. Each set of signals consists of two doublets with the major signals located at δ 156 and 116 p.p.m. ($J_{P-P'}$ = 60 Hz) and the minor signals at δ 147.6 and 93.2 p.p.m. ($J_{P-P'}$ = 76 Hz) [Figure 1(*c*) and (*d*)]. After reflux for 4 h in heptane, the i.r. spectrum of the reaction mixture no longer contained a carbonyl absorption, indicating that all the monosubstituted complex [Ru(η-C_5H_5)(CO){(*S*)-dpompyr-*P*}H] had been consumed. The ^{31}P n.m.r. spectrum of the final product consisted of the two sets of doublets of the diastereoisomers in the ratio 9:1. Upon cooling the reaction mixture, pale yellow crystals were deposited. Elemental analysis and mass spectroscopy confirmed that these were [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] and their optical purity was shown by ^{31}P and ^{1}H n.m.r. [Figures 1(*e*) and 2(*c*) respectively]. The n.m.r. spectra of the crystals correspond to those of the major diastereoisomer formed in the reaction.

Unfortunately, the crystals proved unsuitable for *X*-ray crystallography and therefore it was not possible to assign their absolute configuration directly. This was done indirectly by converting crystalline [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] into the corresponding chloro-complex [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] with chloroform; this reaction proceeded with complete stereospecificity as measured by ^{1}H and ^{31}P n.m.r. spectroscopy [Figure 1(*f*)]. A similar stereospecific reaction occurred when [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] was treated with carbon tetrachloride.

The chloro-complex was obtained as yellow-orange crystals which proved suitable for *X*-ray study and a view of the molecule is shown in Figure 3. Selected bond distances and angles are given in Table 1. In accordance with the

Table 1. Selected bond distances (Å) and angles (°) in [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl]*

P(1)–Ru–P(2)	88.74(6)	Ru–P(1)–N	117.9(2)	Ru–P(2)–O	122.1(2)
P(1)–Ru–Cl	92.60(6)	Ru–P(1)–C(111)	116.7(2)	Ru–P(2)–C(211)	118.9(2)
P(1)–Ru–Cp	127.1	Ru–P(1)–C(121)	112.8(2)	Ru–P(2)–C(221)	113.0(2)
P(2)–Ru–Cl	96.51(5)	N–P(1)–C(111)	103.3(3)	O–P(2)–C(211)	102.4(3)
P(2)–Ru–Cp	124.8	N–P(1)–C(121)	102.3(3)	O–P(2)–C(221)	95.4(3)
C(1)–Ru–Cp	118.4	C(111)–P(1)–C(121)	101.7(3)	C(211)–P(2)–C(221)	100.8(3)
P(1)–N–C(10)	124.6(4)	P(2)–O–C(6)	123.9(3)	P(1)–N–C(7)	124.5(4)
O–C(6)–C(7)	114.8(5)	C(7)–N–C(10)	110.4(5)	C(6)–C(7)–C(8)	109.3(5)
C(6)–C(7)–N	113.7(5)	N–C(7)–C(8)	103.8(5)	C(7)–C(8)–C(9)	103.6(6)
C(8)–C(9)–C(10)	102.1(6)	N–C(10)–C(9)	105.1(5)		

Ru–Cl	2.444(1)	Ru–C(5)	2.235(8)	C(6)–C(7)	1.517(9)	C(1)–C(2)	1.418(11)
Ru–P(1)	2.269(2)	P(1)–N	1.670(5)	C(7)–C(8)	1.547(8)	C(1)–C(5)	1.425(11)
Ru–P(2)	2.242(1)	P(1)–C(111)	1.846(6)	C(8)–C(9)	1.543(11)	C(2)–C(3)	1.408(13)
Ru–C(1)	2.184(7)	P(1)–C(121)	1.850(6)	P(2)–O	1.641(4)	C(3)–C(4)	1.419(12)
Ru–C(2)	2.233(7)	O–C(6)	1.449(8)	P(2)–C(211)	1.837(6)	C(4)–C(5)	1.397(12)
Ru–C(3)	2.231(7)	N–C(7)	1.483(8)	P(2)–C(221)	1.821(6)	C(9)–C(10)	1.500(10)
Ru–C(4)	2.249(7)	N–C(10)	1.464(8)				

Deviations (Å) from the Rh–P(1)–P(2) plane

C(111)	1.518	N	−1.238	C(211)	−1.148	C(6)	−1.339
C(121)	−0.122	C(7)	−2.072	C(221)	1.598	O	−0.122

* Cp Indicates the centre of the cyclopentadienyl ring.

stereochemical convention adopted for organometallics[7] the ligand priority sequence is C_5H_5 > Cl > P(O) > P(N). The ligand environment about the ruthenium is shown in detail in Figure 4 from which it can be seen that the ruthenium centre has an (*S*) configuration.

The ruthenium atom is almost at the centre of an octahedron having the C_5H_5 ligand at one face and the Cl, P(O), P(N) ligands at another. The metal–ligand interactions are similar to those found in related complexes such as [Ru(η^5-C_5H_5){$Ph_2PCH_2CH(Me)PPh_2$}Cl].[4] Similarly, the conformation of the diphosphine ligand is close to that found in the cation [Rh(cod){(*S*)dpompyr-*PP'*}]$^+$ (cod = cyclo-octa-1,5-diene)[8] except that the P–Rh–P' angle is 93.0(1)° in the square-planar rhodium derivative but only 88.7(1)° in the more crowded octahedral complex. This difference is gradually absorbed by the other degrees of freedom of the two metallocycles both of which have a boat conformation with the oxygen atom in the PRhP' plane; the orientation of the phenyl rings is also similar in the two species.

We have previously demonstrated that the region around 300 nm in the c.d. spectra of related chiral complexes of the type [Ru(η-C_5H_4R)(L)L'X] is diagnostic of the stereochemistry about the ruthenium atom.[9] Inspection of the c.d. spectrum of [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}X] (X = Cl) reveals that the maximum at 300 nm has the same sign as the maximum at 305 nm which appears in the c.d. spectrum of the hydride precursor (X = H) which crystallises optically pure from the original reaction mixture [see Figure 5(*a*)]. This implies that the reaction of (*S*)dpompyr with [Ru(η-C_5H_5)(CO)$_2$H] gives predominantly [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] which reacts stereospecifically with chloroform to give [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl]. In support of this other workers have shown that the conversion of a ruthenium hydride complex to a ruthenium chloride complex by chlorinated solvents proceeds with retention of configuration at ruthenium.[10]

The hydride complex was also prepared by reduction of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] with $LiAlH_4$ in tetrahydrofuran (thf) and again characterised by elemental analysis and mass spectroscopy. Examination of the ^{31}P n.m.r. spectrum of the product revealed that this reduction also proceeded with high stereospecificity to give the two previously identified diastereoisomers of [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] in the ratio 88:12 [Figure 1(*g*)]. It is particularly significant that the major diastereoisomer of the hydride formed by reduction of the chloro-complex has the same ^{1}H and ^{31}P n.m.r. spectra as the diastereoisomer of the hydride used to prepare the chloro-complex, *i.e.* the reaction sequence shown below, {Ru} = Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}, occurs with overall retention of con-

$$[\{Ru\}H] \xrightarrow{CHCl_3} [\{Ru\}Cl] \xrightarrow{LiAlH_4} [\{Ru\}H]$$

figuration at ruthenium. Given that we have shown that the first step proceeds with retention it follows that the reduction step also proceeds with retention.

The remarkable feature of this work, apart from the ease with which optically pure [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] is obtained, is the high diastereoselectivity with which this hydride is formed. This contrasts markedly with the synthesis of [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl], prepared by displacement of triphenylphosphine in [Ru(η-C_5H_5)(PPh_3)$_2$Cl] with (*S*)-dpompyr. The ^{31}P n.m.r. spectrum of this reaction mixture [Figure 1(*h*)] revealed that the two diastereoisomers of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] were formed in an approximately 60:40 ratio [major isomer: δ 149.4 (d), 92.9 (d, $J_{P-P'}$ = 76 Hz); minor isomer: δ 154.1 (d), 99.2 (d, $J_{P-P'}$ = 72 Hz)]. Similar ratios have been obtained by others for analogous chloro-complexes containing different chiral chelating phosphines.[4]

The obvious question raised by these results is why is the hydride complex, but not the chloro-complex formed diastereoselectively? In attempting to answer this it is important to bear in mind the result discussed earlier that very little, if any, stereoselectivity is shown in the initial step, the formation of [Ru(η-C_5H_5)(CO){(*S*)dpompyr-*P*}H] containing a unidentate diphosphine ligand. It follows that in the subsequent step, the displacement of CO and chelation of the dpompyr, the initial chiral centre must be destroyed. In the case of the hydride complex this could occur by migration of the hydride ligand from the ruthenium onto the cyclopentadienyl group to give a

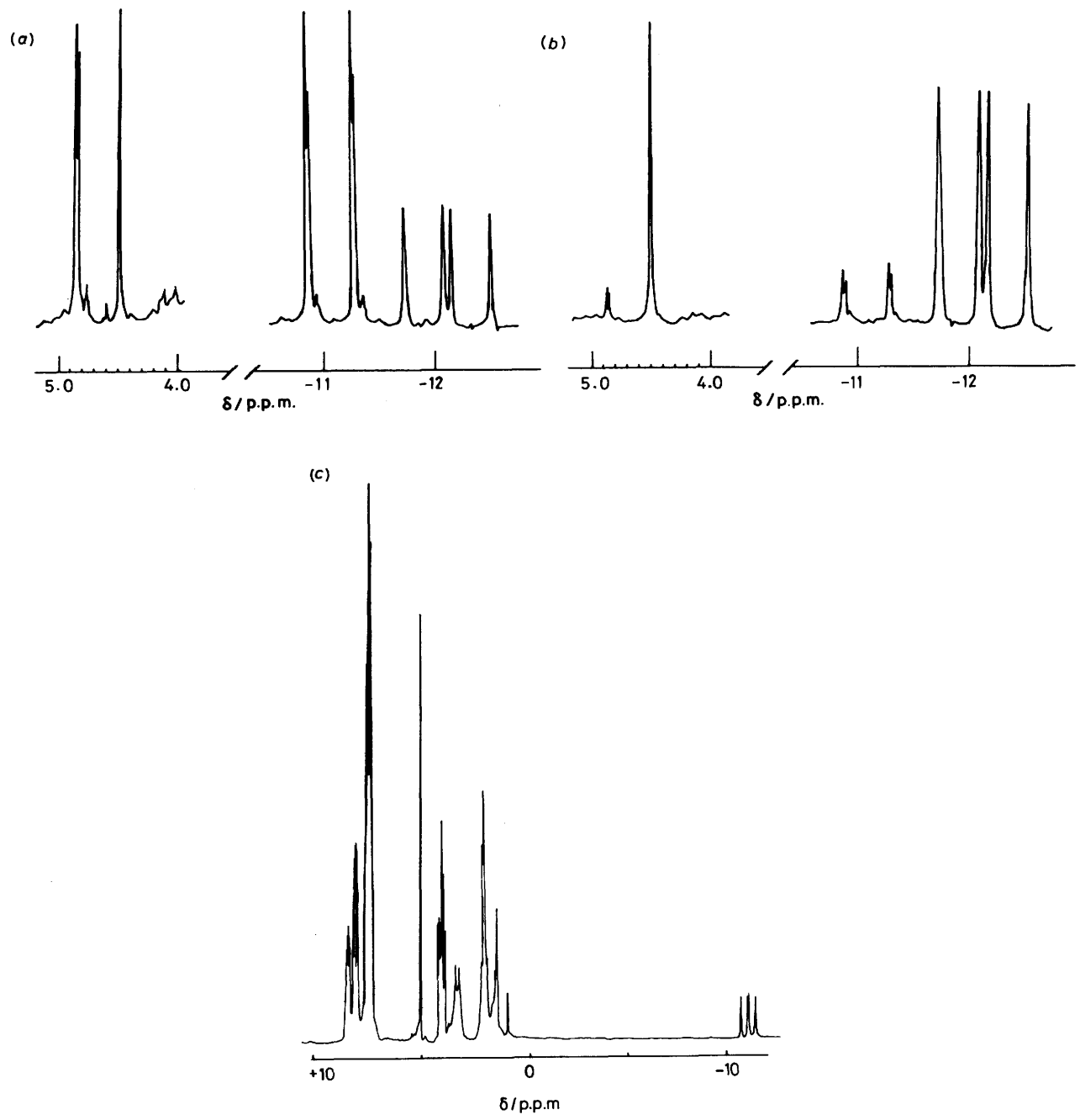

Figure 2. Hydrogen-1 n.m.r. spectra: $[Ru(\eta\text{-}C_5H_5)(CO)_2H]$ and (*S*)dpompyr, (*a*) after 5 min at r.t., (*b*) after 30 min at 98 °C; (*c*) $[(S)Ru(\eta\text{-}C_5H_5)\{(S)dpompyr\text{-}PP'\}H]$ which crystallises from the reaction mixture

co-ordinatively unsaturated cyclopentadiene intermediate. Such a migration is not without precedent[11] and would also explain the observed labilising effect of the hydride ligand,[5] *i.e.* chelation of the (*S*)dpompyr would be promoted by the free co-ordination site on the ruthenium. The final stage in the reaction is then loss of the carbonyl ligand and concomitant migration of the hydride from the cyclopentadiene group to the ruthenium. Given that these steps take place under the influence of the chelating chiral phosphorus ligand one would expect that these would occur with high stereoselectivity as observed.

In the case of the chloro-complex, ^{31}P n.m.r. again shows that the initial formation of the chiral centre in $[Ru(\eta\text{-}C_5H_5)(CO)(L)Cl]$ [L = (*S*)dpompyr-*P*] occurs with little stereoselectivity. Subsequent loss of the carbonyl ligand and closure of the chelate ring occurs with modest stereoselectivity. Thus, the essential difference between the formation of $[Ru(\eta\text{-}C_5H_5)\{(S)dpompyr\text{-}PP'\}X]$ (X = H or Cl) is that in the case of the hydride complex the formation of the final chiral ruthenium centre occurs under the influence of chelated (*S*)dpompyr whereas in the chloride it is formed upon closure of the chelate ring, *i.e.* under the influence of unidentate (*S*)dpompyr. Similarly, the reduction of $[Ru(\eta\text{-}C_5H_5)\{(S)dpompyr\text{-}PP'\}Cl]$ to the corresponding hydride and the reverse reaction, the chlorination of the hydride, both occur with high stereoselectivity since these too take place under the control of chelated (*S*)dpompyr.

Table 2. Final atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	−0.195 29(4)	0.000	−0.158 20(3)	C(115)	−0.655 6(7)	−0.081 1(9)	−0.174 2(6)
Cl	−0.000 9(1)	−0.091 7(2)	−0.105 9(1)	C(116)	−0.535 0(6)	−0.070 4(7)	−0.139 7(6)
P(1)	−0.300 5(1)	−0.158 1(2)	−0.091 3(1)	C(121)	−0.312 4(6)	−0.147 9(6)	0.051 9(5)
P(2)	−0.213 3(1)	−0.090 0(2)	−0.315 2(1)	C(122)	−0.203 9(7)	−0.132 3(7)	0.110 5(6)
O	−0.274 8(4)	−0.225 9(4)	−0.331 5(3)	C(123)	−0.203 3(8)	−0.123 4(9)	0.217 8(7)
N	−0.246 7(5)	−0.299 8(5)	−0.106 6(4)	C(124)	−0.310 7(8)	−0.128 5(9)	0.268 9(7)
C(1)	−0.311 1(7)	0.160 1(7)	−0.184 2(6)	C(125)	−0.419 3(8)	−0.142 8(9)	0.212 1(7)
C(2)	−0.196 5(8)	0.190 2(7)	−0.222 5(6)	C(126)	−0.419 9(7)	−0.153 3(8)	0.102 9(6)
C(3)	−0.111 6(8)	0.184 9(7)	−0.137 9(8)	C(211)	−0.079 7(6)	−0.100 1(7)	−0.395 2(5)
C(4)	−0.174 3(8)	0.158 0(7)	−0.046 3(6)	C(212)	−0.081 4(7)	−0.172 5(8)	−0.484 1(6)
C(5)	−0.296 7(7)	0.144 3(7)	−0.074 1(6)	C(213)	0.019 5(8)	−0.174 4(9)	−0.547 2(7)
C(6)	−0.217 7(7)	−0.339 1(7)	−0.297 0(6)	C(214)	0.118 6(8)	−0.105(1)	−0.520 7(7)
C(7)	−0.161 2(6)	−0.335 6(6)	−0.187 4(5)	C(215)	0.121 2(8)	−0.032 9(9)	−0.432 3(7)
C(8)	−0.121 0(7)	−0.466 3(6)	−0.154 7(6)	C(216)	0.022 9(6)	−0.032 1(6)	−0.367 1(5)
C(9)	−0.227 5(6)	−0.514 1(7)	−0.092 1(6)	C(221)	−0.318 9(5)	−0.011 1(8)	−0.404 6(4)
C(10)	−0.264 4(7)	−0.401 4(7)	−0.034 2(6)	C(222)	−0.280 1(7)	0.083 8(8)	−0.467 7(6)
C(111)	−0.460 7(6)	−0.172 0(6)	−0.135 2(5)	C(223)	−0.361 5(8)	0.150 9(9)	−0.527 9(7)
C(112)	−0.509 3(6)	−0.284 0(7)	−0.165 3(6)	C(224)	−0.483 2(9)	0.127(1)	−0.525 4(8)
C(113)	−0.629 9(7)	−0.294 8(8)	−0.199 8(6)	C(225)	−0.522 3(8)	0.033 1(8)	−0.466 5(6)
C(114)	−0.703 9(7)	−0.192 1(8)	−0.202 3(7)	C(226)	−0.442 1(7)	−0.034 1(7)	−0.402 0(6)

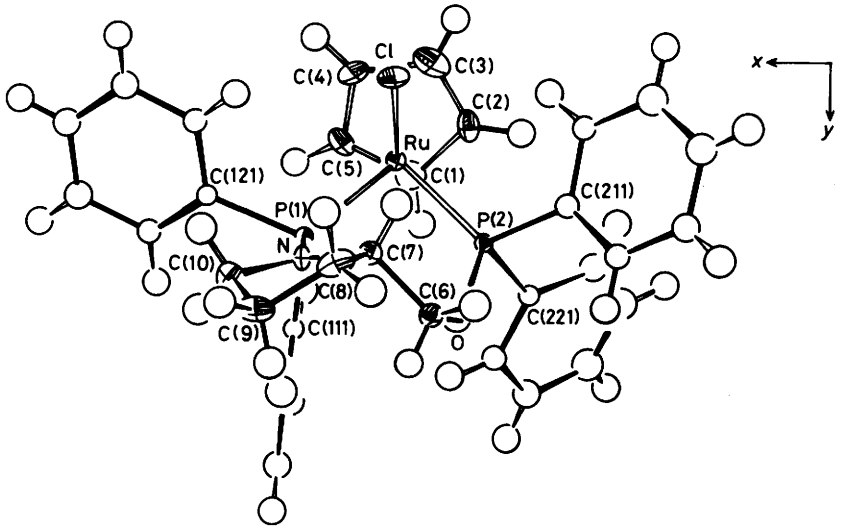

Figure 3. Structure of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl]

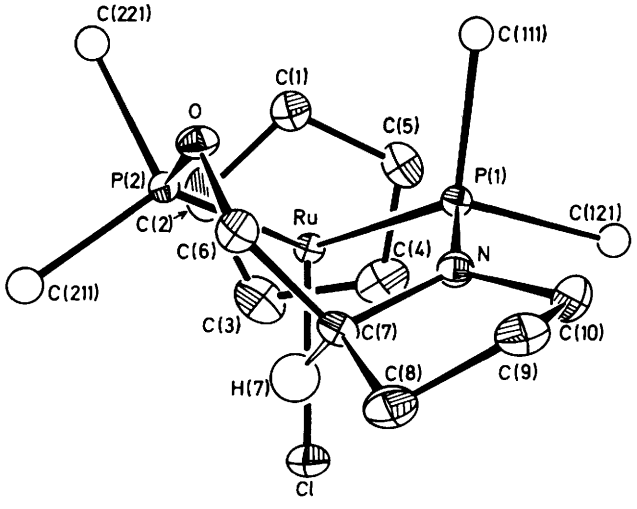

Figure 4. The co-ordination about the Ru atom in [(*S*)Ru(η-C_5H_5){(*S*)-dpompyr-*PP'*}Cl]

Experimental

General Procedures.—Solvents were distilled from $LiAlH_4$ under an inert atmosphere and stored under nitrogen. Elementary analyses were performed by the Mircoanalytical Laboratory of the Dipartimento di Chimica Organica, University of Milan. Hydrogen-1 and ^{31}P n.m.r. were recorded on Varian XL200 and Bruker NS80 spectrometers whereas circular dichroism (c.d.) spectra were recorded on a Jobin-Yvon Dichrographe III instrument using chloroform as a solvent and with concentrations of 0.4—0.5 g dm^{-3}. Mass spectra were recorded on a VG-7070 EQ mass spectrometer and the quoted M^+ is the peak in the parent multiplet which arises from the most abundant ruthenium and chlorine isomers; in general M^+ was 6—10% of the intensity of the strongest peak in the spectrum.

Preparation of (R)-2-*Pyrrolidinemethanol.*—Hydrogen chloride was bubbled over a period of 3 h into a refluxing solution of D-glutamic acid (10 g, 0.068 mol) in absolute methanol (150 cm^3). The solution was cooled to 50 °C and the volume reduced to *ca.* 35 cm^3; a further portion of methanol (25 cm^3) was added and the solution was pumped to dryness to leave a yellow oil.

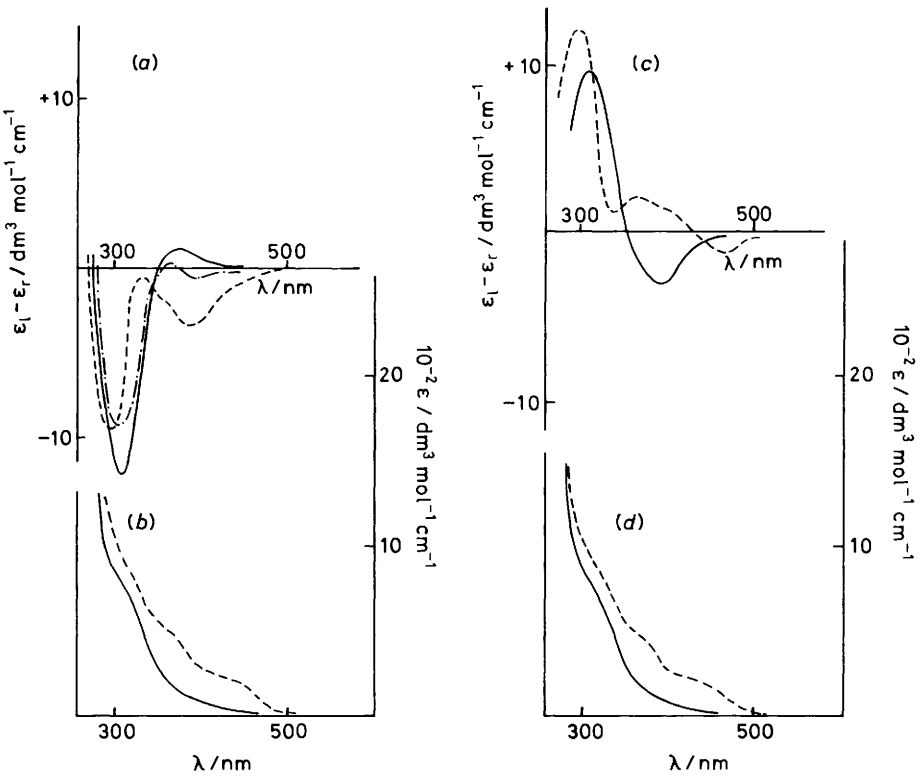

Figure 5. (*a*) C.d. spectra of c.d.$(-)_{300}$[(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] (– – –) obtained by reaction of c.d.$(-)_{305}$[(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] (——) with $CHCl_3$; [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] (— · — · —) obtained by reaction of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] with $LiAlH_4$. (*b*) U.v. spectra of c.d.$(-)_{305}$[Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] (——) and c.d.$(-)_{300}$[(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] (– – –). (*c*) C.d. spectra of c.d.$(+)_{300}$[(*R*)Ru(η-C_5H_5){(*R*)dpompyr-*PP'*}Cl] (– – –) and c.d.$(+)_{305}$[(*R*)Ru(η-C_5H_5){(*R*)dpompyr-*PP'*}H] (——). (*d*) U.v. spectra of c.d.$(+)_{300}$[(*R*)Ru(η-C_5H_5){(*R*)dpompyr-*PP'*}Cl] (– – –) and c.d.$(+)_{305}$[(*R*)Ru(η-C_5H_5){(*R*)dpompyr-*PP'*}H] (——)

This was dissolved in anhydrous diethyl ether (30 cm^3) and the solution stored overnight in a refrigerator to yield D-glutamic acid dimethyl ester hydrochloride as an oily solid (6.6 g, 54%), α (589.3 nm, 20 °C, 5 g dm^{-3} in H_2O) = −20°. D-Glutamic acid dimethyl ester was cyclised to give the D-methyl ester of D-prolin-5-one by heating to 120 °C in an oil-bath under vacuum for 24 h. The crude product was dissolved in thf (40 cm^3) and added dropwise to a stirred suspension of $LiAlH_4$ (2 g) in thf (60 cm^3). When the addition was complete, the mixture was refluxed overnight, cooled to room temperature and then finely crushed $Na_2SO_4 \cdot 10H_2O$ (20 g) was carefully added. The suspension was stirred for 1 h and then filtered; removal of the solvent from the filtrate under vacuum and distillation of the resulting oil gave (*R*)-2-pyrrolidinemethanol (1.2 g, 38% yield based on D-glutamic acid dimethyl ester) α (589.3 nm, 20 °C, 2 g dm^{-3} in MeOH) = −3.0°.

Preparation of (S)- *and* (R)-N-*Diphenylphosphino*-2-(*diphenylphosphinoxymethyl*)*pyrrolidine*.—The diphosphine (*S*)dpompyr was prepared as previously described;[12] (*R*)dpompyr was prepared by a similar procedure from (*R*)-2-pyrrolidinemethanol α (589.3 nm, 20 °C, 1 g dm^{-3} in $CHCl_3$) = +15°.

Preparation of [Ru(η-C_5H_5)(dpompyr-*PP'*)H].—Freshly distilled cyclopentadiene (2 cm^3) was added under nitrogen to a refluxing solution of [$Ru_3(CO)_{12}$] (100 mg, 0.156 mmol) in heptane (30 cm^3) in a two-necked flask. Reflux under nitrogen was continued until the colour of the solution changed from orange to pale yellow (*ca.* 2 h); the i.r. spectrum of the solution confirmed that all the [$Ru_3(CO)_{12}$] (ν_{CO} 2 070, 2 025, and 2 010 cm^{-1}) had been consumed to give [Ru(η-C_5H_5)$(CO)_2$H] (ν_{CO} 2 029 and 1 972 cm^{-1}). Upon addition of (*S*)- or (*R*)-dpompyr (240 mg, 0.511 mmol), dissolved in the minimum of heptane (*ca.* 2 cm^3), the i.r. spectrum showed only one broad carbonyl band at 1 941 cm^{-1} which is assigned to the intermediate [Ru(η-C_5H_5)(CO)(dpompyr-*P*)H]. After further reflux for 12 h (or 24 h at room temperature) a pale precipitate was formed and the solution was almost colourless. Upon standing at room temperature, optically pure [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] (or [(*R*)Ru(η-C_5H_5){(*R*)dpompyr-*PP'*}H]) crystallised out as pale yellow, bright plates {215 mg, 72% yield based upon [$Ru_3(CO)_{12}$]} (Found: C, 63.7; H, 5.15; N, 2.00%; M^+, 637. Calc. for $C_{34}H_{35}NOP_2Ru$: C, 64.15; H, 5.50; N, 2.20%).

Preparation of [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl].—(*i*) *From* [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H]. A solution of [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] (100 mg) in chloroform (20 cm^3) was stirred under nitrogen for 48 h. The resulting orange solution was evaporated to dryness and the residue chromatographed on silica using chloroform. The eluant was concentrated to *ca.* 3 cm^3 and [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] was precipitated in quantitative yield as bright orange, well formed crystals by slow diffusion of light petroleum (b.p. 40—60 °C) (Found: C, 60.5; H, 5.00; N, 2.00%; M^+, 671. Calc. for $C_{34}H_{34}ClNOP_2Ru$: C, 60.85; H, 5.05; N, 2.10%).

(*ii*) *From* [Ru(η-C_5H_5)$(PPh_3)_2$Cl]. The diphosphine (*S*)-dpompyr (170 mg, 0.36 mmol) was added to a refluxing solution of [Ru(η-C_5H_5)$(PPh_3)_2$Cl] (225 mg, 0.31 mmol) in benzene (30 cm^3) under nitrogen. The reflux was continued for 6 h and then the solution allowed to cool; solvent was removed *in vacuo* and

the residue chromatographed and recrystallised as described above.

Reduction of [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] *to* [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H].—Diastereoisomerically pure [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl] (30 mg, 0.045 mmol) was dissolved under nitrogen in a mixture of heptane (20 cm^3) and thf (2 cm^3). A solution of $LiAlH_4$ in thf (0.45 cm^3, 0.1 mol dm^{-3}) was added dropwise and the colour of the mixture rapidly turned from orange to pale yellow. Excess of finely crushed $Na_2SO_4 \cdot 10H_2O$ was added and the suspension stirred for 1 h before filtering. Evaporation of the filtrate afforded pure [Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}H] almost quantitatively.

X-*Ray Crystal Structure of* [(*S*)Ru(η-C_5H_5){(*S*)dpompyr-*PP'*}Cl].—*Crystal data.* $C_{34}H_{34}ClNOP_2Ru$, $M = 671.1$, monoclinic, $a = 11.076(2)$, $b = 10.908(2)$, $c = 12.825(3)$ Å, $\beta = 92.26(2)°$, $U = 1\,548.3$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 1.44$ g cm^{-3}, $F(000) = 688$, λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 7.1 cm^{-1}.

Data collection, structure solution, and refinement. 3 174 Independent reflections ($\pm h$, $+k$, $+l$) were collected on an Enraf-Nonius CAD4 automated diffractometer and corrected for Lorentz, polarization, and absorption effects as previously described.[4] 2 306 Data having $I > 3\sigma(I)$ were retained and, using Patterson and Fourier methods, the structure was resolved and was refined by full-matrix least-squares methods. All the non-hydrogen atoms (except the phenyl carbons) were treated anisotropically and 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 absolute configuration was determined by internal comparison, the starting reagent being (*S*)-2-pyrrolidinemethanol, but we refined, as a test, both the enantiomers. Using the weighting scheme $w = 4|F_o|^2/[\sigma^2(|F_o|^2)]$ the final R factors were $R = (\Sigma\|F_o\| - k|F_c\|)/\Sigma|F_o| = 0.0322$ and $R' = [\Sigma w(|F_o| - k|F_c|)^2/wF_o]^{\frac{1}{2}} = 0.0402$ for (*S*)Ru and (*S*)C(7); in contrast, the corresponding values for (*R*)Ru and (*R*)C(7) were 0.0332 and 0.0415. All the computations were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package.

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References

1 H. Brunner, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 382.
2 E. Cesarotti, M. Angoletta, N. P. C. Walker, M. Hursthouse, R. Vefghi, P. A. Schofield, and C. White, *J. Organomet. Chem.*, 1985, **286**, 343; J. H. Merrifield, J. M. Fernandez, W. E. Buhro, and J. A. Gladysz, *Inorg. Chem.*, 1984, **23**, 4022; H. Brunner and H. Vogt, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 405; H. Brunner, *Adv. Organomet. Chem.*, 1980, **18**, 151.
3 M. T. Reetz, S. H. Kyung, and J. Westermann, *Organometallics*, 1984, **3**, 1716; S. G. Davies and J. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1986, 609 and refs. therein.
4 F. Morandini, G. Consiglio, B. Straub, G. Ciani, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1983, 2293.
5 C. White and E. Cesarotti, *J. Organomet. Chem.*, 1985, **287**, 123.
6 V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 227.
7 K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, 1975, **97**, 6598.
8 E. Cesarotti, A. Chiesa, G. Ciani, and A. Sironi, *J. Organomet. Chem.*, 1983, **251**, 79.
9 E. Cesarotti, A. Chiesa, G. F. Ciani, A. Sironi, R. Vefghi, and C. White, *J. Chem. Soc., Dalton Trans.*, 1984, 653.
10 F. Morandini, G. Consiglio, and V. Lucchini, *Organometallics*, 1985, **4**, 1202.
11 A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1975, 1710; K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc. A*, 1970, 2875; M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753.
12 E. Cesarotti, A. Chiesa, and G. D'Alfonso, *Tetrahedron Lett.*, 1982, **23**, 2995.

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