Diastereomeric Chiral Diphosphine Chloro(η^5-cyclopentadienyl)ruthenium(II) Complexes and the Crystal Structure of [(*S*)RuCl(η^5-C_5H_5){(*R*)$Ph_2PCH(Me)CH_2PPh_2$}] †

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Diastereomeric [RuCl(η^5-C_5H_5){$Ph_2PCH(R)CH_2PPh_2$}] chelate complexes (where R = CH_3, cyclo-C_6H_{11}, or C_6H_5) form in nearly equimolar amounts in the displacement reaction of triphenylphosphine from [RuCl(η^5-C_5H_5)(PPh_3)$_2$]. The diastereomers were separated by fractional crystallization. Diastereomeric composition at the equilibrium showed a low asymmetric induction (28—41%) by the optically active diphosphine ligand on the chiral ruthenium atom. The absolute configuration at the ruthenium atom has little influence on the chiroptical properties of the complexes, which appear to be dominated, at least in the visible region, by the chiral conformation of the chelate ligand. The crystal structure of the title diastereomer, [(*S*)RuCl(η^5-C_5H_5){(*R*)$Ph_2PCH(Me)CH_2PPh_2$}], has been investigated. It is monoclinic, space group $P2_1$, with a = 9.688(3), b = 15.037(4), c = 10.556(2) Å, β = 113.54(2)°, and Z = 2. The structure was solved by Patterson and Fourier methods, and refined by least squares on the basis of 2 000 significant counter data, to a final R value of 0.042. The complex shows a distorted λ conformation of the diphosphine ligand in the chelate five-membered ring, in the solid state. The Ru–Cl and Ru–P interactions are 2.444(2) and 2.277 Å (mean value), respectively.

Chiral diphosphines of the dppe type [dppe = 1,2-bis(diphenylphosphino)ethane] have been successfully used in asymmetric hydrogenation [1] and asymmetric allylation reactions.[2,3] Less brilliant but still interesting results have also been obtained when these ligands have been used in other asymmetric reactions, such as cross-coupling [4] and hydroformylation.[5] In spite of this, model studies using the above ligands for a better understanding of the nature of the diastereotopic interactions responsible for asymmetric induction are rare.[6]

We have recently reported [7] that in the displacement reaction of triphenylphosphine from [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (1) by 1,2-bis(diphenylphosphino)propane [(*R*)dppp],[8] 1,2-bis(diphenylphosphino)-1-phenylethane [(*R*)dpppe],[9] and 1-cyclohexyl-1,2-bis(diphenylphosphino)ethane [(*S*)cdppe] [10] carried out at 80 °C, two diastereomers form in nearly equal amounts, which differ in configuration at the ruthenium atom (Scheme). In view of the interest of diastereomeric metal complexes in which the metal is a chiral centre for investigations of the stereochemistry of reactions occurring at metal–ligand bonds,[11,12] and of the possibility to use these compounds for the preparation of olefin complexes in which enantioface discrimination can be investigated,[13] we have pursued our investigation with the separation of the above diastereomers. We discuss in this paper the configurational stabilities at the metal atoms, the chiroptical properties as compared with those of the corresponding complexes containing (*S,S*)-2,3-bis(diphenylphosphino)butane [(*S,S*)dppb] [14] and (*R,R*)-1,2-bis{(*o*-methoxyphenyl)phenylphosphino}ethane [(*R,R*)-mpppe] [15] and the crystal structure of the less soluble diastereomer which contains (*R*)dppp. A brief description of this latter structure has been reported in connection with the determination of the stereochemistry of the insertion of $SnCl_2$ to form the corresponding trichlorostannato-complex.[12]

Experimental

The solvents were dried and degassed before use. The diphosphines (*R*)dppp,[8] (*R*)dpppe,[9] (*S*)cdppe,[10] (*S,S*)dppb,[14] and the complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (1) [16] were prepared according to the methods described in the literature. The diphosphine (*R,R*)mpppe [15] was a generous gift by Dr. W. S. Knowles.

Proton and ^{31}P n.m.r. spectra were recorded on a Bruker WP-60 FTNMR spectrometer in C_6D_6, C_7D_8, or C_6D_5Cl solutions. The chemical shifts for the ^{31}P n.m.r. spectra were measured from 85% H_3PO_4 (downfield positive). Circular dichroism (c.d.) spectra were obtained using a JASCO J-40 AS dichrograph with CH_2Cl_2 solutions. Ultraviolet and visible spectra with the same solvent were obtained on a Cary 14 spectrometer.

The complex [RuCl(η^5-C_5H_5){(*S,S*)dppb}] (2d) was prepared as reported elsewhere.[7]

[RuCl(η^5-C_5H_5){(*R*)dppp}] (2a) *and* (2a′).—A solution of (1) (2 g, 2.75 mmol) and (*R*)dppp (1.2 g, 2.9 mmol) in benzene (100 cm^3) was refluxed for 4 h. The volume was then reduced to 20 cm^3 and n-hexane added until an orange precipitate formed, which was filtered off, washed with n-hexane and dried. The ^1H n.m.r. spectrum in C_6D_6 showed the two singlets due to the cyclopentadienyl protons (δ 4.38 and 4.35) in a *ca.* 60 : 40 ratio. After recrystallizing twice from CH_2Cl_2–n-hexane (1 : 2, 30 cm^3), the optically pure less soluble diastereomer (2a′) was obtained (0.6 g, 36%). By addition of n-hexane to the mother-liquor of the first recrystallization, an orange-yellow compound was obtained which contained the

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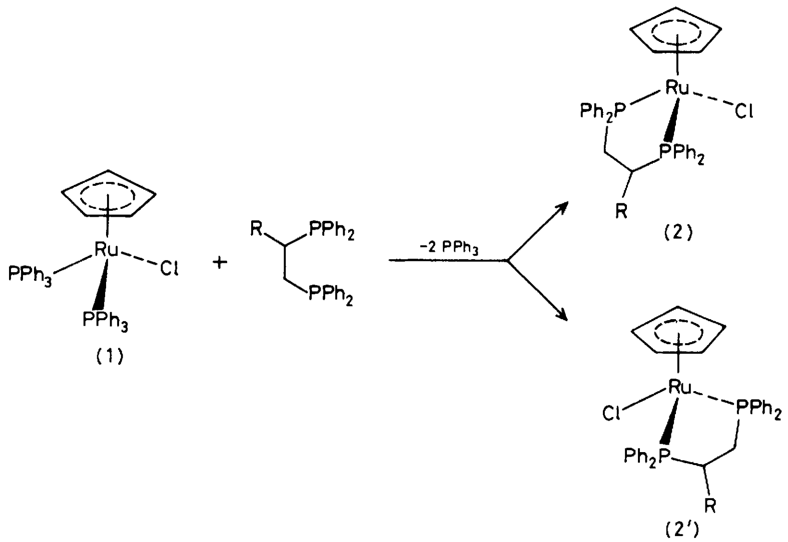
† [(*R*)-1,2-Bis(diphenylphosphino)propane-*PP′*]chloro(η^5-cyclopentadienyl)(*S*)ruthenium.

Supplementary data available (No. SUP 23689, 17 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme. R = CH_3, (*R*)dppp; C_6H_5, (*R*)dpppe; or cyclo-C_6H_{11}, (*S*)cdppe

more soluble diastereomer in an enrichment of 73%. Further recrystallization from CH_2Cl_2–n-hexane yielded the pure more soluble diastereomer (2a) (0.4 g, 24%) [Found (2a): C, 61.85; H, 5.05; Cl, 5.75. Found (2a′): C, 61.55; H, 4.85. $C_{32}H_{31}ClP_2Ru$ requires C, 62.55; H, 5.10; Cl, 5.75%]. ^1H N.m.r. (in C_6D_6): (2a): δ 0.91 (dd, 3 H, CH_3, J_{P-H} 11.9, J_{H-H} 6.6 Hz), 2.66 (complex m, 3 H), 4.35 (s, 5 H, C_5H_5), 7.15 (complex m, 20 H, C_6H_5); (2a′): δ 0.91 (dd, 3 H, CH_3, J_{P-H} = 11.9, J_{H-H} = 6.6 Hz), 2.66 (complex m, 3 H), 4.38 (s, 5 H, C_5H_5), 7.14 (complex m, 20 H, C_6H_5). ^{31}P n.m.r. (in C_7D_8): (2a): δ 80.9 and 74.1 (J_{P-P} = 30.2 Hz); (2a′): δ 86.4 and 61.3 (J_{P-P} = 36.7 Hz).

[RuCl(η^5-C_5H_5){(*R*)dpppe}] (2b) *and* (2b′).*—A mixture of (1) (2 g, 2.75 mmol) and (*R*)dpppe (1.4 g, 2.95 mmol) was refluxed in benzene (100 cm^3) for 4 h. The volume was reduced to 20 cm^3 and then by addition of n-hexane a yellow-orange compound was precipitated, which was separated by filtration. The ^1H n.m.r. spectrum of the crude product showed two singlets due to the cyclopentadienyl protons in a 85 : 15 ratio. Therefore, after two recrystallizations from CH_2Cl_2–n-hexane the pure less soluble diastereomer (2b′) was obtained (0.5 g, 32%). By addition of n-hexane to the mother-liquor, the pure more soluble diastereomer (2b) was obtained (0.5 g, 27%) [Found (2b): C, 65.65; H, 4.90; Cl, 5.05; P, 9.30. Found (2b′): C, 66.10; H, 5.30. $C_{37}H_{33}ClP_2Ru$ requires C, 65.65; H, 4.90; Cl, 5.25; P, 9.15%]. ^1H N.m.r. (in C_6D_6): (2b): δ 2.20 (complex m, 3 H), 4.20 (s, 5 H, C_5H_5), 6.86 (complex m, 25 H, C_6H_5); (2b′): δ 2.49 (complex m, 3 H), 4.15 (s, 5 H, C_5H_5), 6.87 (complex m, 25 H, C_6H_5). ^{31}P N.m.r. (in C_7D_8): (2b): δ 83.9 and 66.4 (J_{P-P} = 35.7 Hz); (2b′): δ 90.2 and 58.1 (J_{P-P} = 40.0 Hz).

[RuCl(η^5-C_5H_5){(*S*)cdppe}] (2c) *and* (2c′).*—A solution of (1) (2 g, 2.75 mmol) and (*S*)cdppe (1.4 g, 2.91 mmol) in toluene (100 cm^3) was refluxed for 6 h. After cooling, the volume was reduced to 20 cm^3 and n-hexane added. An orange compound precipitated, which was filtered off and washed with n-hexane. The ^1H n.m.r. spectrum showed two peaks due to the cyclopentadienyl protons in a 1 : 1 ratio. The crude product was dissolved in benzene (10 cm^3) and the same ammount of n-hexane was added. After standing at room temperature, a yellow-orange precipitate was found, which was the pure less soluble diastereomer (2c′) (0.5 g, 27%). The more soluble diastereomer (2c) was precipitated from the mother-liquor of the second crystallization step at −20 °C in the ratio 85 : 15 (0.4 g, 21%) [Found (2c): C, 65.70; H, 6.10. Found (2c′): C, 64.45; H, 5.70; Cl, 4.75. $C_{37}H_{39}ClP_2Ru$ requires C, 65.10; H, 5.75; Cl, 5.20%]. ^1H N.m.r. (in C_6D_6): (2c): δ, 1.00 (complex m, 11 H, C_6H_{11}), 2.80 (complex m, 3 H), 4.30 (s, 5 H, C_5H_5), 7.05 (complex m, 20 H, C_6H_5); (2c′): δ 1.00 (complex m, 11 H, C_6H_{11}), 2.80 (complex m, 3 H), 4.30 (s, 5 H, C_5H_5), 7.05 (complex m, 20 H, C_6H_5). ^{31}P N.m.r. (in C_7D_8): (2c): δ 71.1 and 67.4 (J_{P-P} = 36.8 Hz); (2c′): δ 90.0 and 61.9 (J_{P-P} = 36.8 Hz).

[RuCl(η^5-C_5H_5){(*R*,*R*)mpppe}] (2e).—A mixture of (1) (0.5 g, 0.69 mmol) and (*R*,*R*)mpppe (0.35 g, 0.76 mmol) was refluxed in benzene (50 cm^3) for 6 h. The volume was reduced to 10 cm^3 and n-hexane added until a yellow precipitate formed, which was filtered off, washed with n-hexane, and dried. The crude product was purified through recrystallization from benzene–n-hexane (Found: C, 61.0; H, 5.10. $C_{33}H_{33}ClO_2P_2Ru$ requires C, 60.05; H, 5.05%). ^1H N.m.r. (in CD_2Cl_2): δ 2.52 (complex m, 4 H), 3.34 (s, 3 H, CH_3), 3.54 (s, 3 H, CH_3), 4.42 (s, 5 H, C_5H_5), 7.19 (complex m, 18 H). ^{31}P N.m.r. (in C_6D_8): δ 77.7 and 72.0 (J_{P-P} = 17.9 Hz).

X-*Ray Crystal Structure of* [(*S*)RuCl(η^5-C_5H_5){(*R*)dppp}] (2a′).—*Crystal data.* $C_{32}H_{31}ClP_2Ru$, *M* = 614.1, Monoclinic, space group $P2_1$ (no. 4), *a* = 9.688(3), *b* = 15.037(4), *c* = 10.556(2) Å, β = 113.54(2)°, *U* = 1 409.8 Å^3, *Z* = 2, D_c = 1.45 g cm^3, *F*(000) = 628, monochromatic Mo-K_α radiation, λ = 0.710 73 Å, μ(Mo-K_α) = 7.721 cm^{-1}.

Structure determination. A well formed prismatic crystal of the diastereomer (2a′) of dimensions 0.08 × 0.22 × 0.28 mm was mounted on an Enraf-Nonius CAD-4 automated diffractometer, where automatic location and centring of 25 reflections ($20 \leqslant 2\theta \leqslant 26°$) provided the unit-cell parameters. A preliminary study showed systematic absences in (0*k*0, $k \neq 2n$), indicating the presence of a 2_1 axis. Intensities were collected in the range $6 \leqslant 2\theta \leqslant 50°$ by using the ω scan method and a scan range of (1.4 + 0.35 tanθ) ° with a 25% extension at each end for background determination. The reflections were measured with a constant speed of 3.3° min^{-1}. A total of 2 580 independent intensities, corresponding to the ±*h*, *k*, *l* indices (referred to right-handed axes) were measured. Lorentz and polarization corrections were applied. Three

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* For diastereomers (2b), (2b′), (2c), and (2c′) (Scheme) the configuration at the ruthenium atom is arbitrarily assigned.

Table 1. Final positional parameters for [(S)RuCl(η^5-C_5H_5){(R)-dppp}] (2a′)

Atom *	x	y	z
Ru	0.233 41(6)	0.000 0(0)	0.204 35(6)
Cl	0.079 8(3)	0.066 8(2)	−0.018 8(2)
P(1)	0.401 8(2)	0.114 1(2)	0.264 3(2)
P(2)	0.376 1(2)	−0.049 9(2)	0.092 0(2)
C(1)	0.525 0(9)	0.105 9(6)	0.169 6(9)
C(2)	0.456 0(9)	0.049 3(7)	0.039 5(8)
C(3)	0.567 7(10)	0.033 6(7)	−0.025 5(9)
cp(1)	0.109 1(9)	0.008 9(10)	0.339 4(10)
cp(2)	0.246 9(11)	−0.030 8(8)	0.408 8(9)
cp(3)	0.249 9(10)	−0.110 1(7)	0.341 3(10)
cp(4)	0.109 6(11)	−0.119 3(8)	0.228 7(11)
cp(5)	0.028 1(10)	−0.044 5(9)	0.229 6(12)
C(111)	0.339 3(8)	0.231 0(6)	0.237 6(8)
C(112)	0.188 1(9)	0.252 1(6)	0.175 1(9)
C(113)	0.143 0(10)	0.341 1(7)	0.158 8(10)
C(114)	0.248 9(10)	0.408 2(7)	0.205 2(10)
C(115)	0.397 2(11)	0.386 5(8)	0.269 5(10)
C(116)	0.446 0(10)	0.297 8(7)	0.285 7(9)
C(121)	0.533 4(9)	0.124 2(6)	0.447 0(8)
C(122)	0.476 5(10)	0.155 3(7)	0.538 4(9)
C(123)	0.566 3(10)	0.166 9(7)	0.679 3(10)
C(124)	0.712 7(10)	0.144 5(7)	0.725 0(9)
C(125)	0.774 1(11)	0.115 5(8)	0.640 5(10)
C(126)	0.685 9(10)	0.102 9(7)	0.498 8(10)
C(211)	0.544 0(8)	−0.119 0(6)	0.182 7(8)
C(212)	0.607 7(9)	−0.169 6(7)	0.113 7(9)
C(213)	0.738 2(10)	−0.219 9(7)	0.185 3(10)
C(214)	0.802 5(10)	−0.214 9(7)	0.329 2(10)
C(215)	0.741 5(10)	−0.163 9(7)	0.398 2(10)
C(216)	0.611 5(9)	−0.116 9(6)	0.326 8(9)
C(221)	0.281 6(8)	−0.115 1(6)	−0.065 3(8)
C(222)	0.226 1(10)	−0.079 1(7)	−0.198 8(10)
C(223)	0.152 3(11)	−0.133 2(7)	−0.312 6(11)
C(224)	0.128 8(11)	−0.219 1(8)	−0.295 5(11)
C(225)	0.173 4(11)	−0.257 1(7)	−0.167 7(10)
C(226)	0.251 2(10)	−0.203 7(7)	−0.051 4(9)

* cp(1)—cp(5) are the carbon atoms of the η^5-C_5H_5 ligand.

standard reflections were periodically measured during the data collection and no decay was observed. Absorption correction was made by using an empirical method based on ψ scans (ψ 0—360°, every 10°) on two reflections with χ values near to 90°; the maximum, minimum, and average relative transmission values were 1.00, 0.88, and 0.93, respectively. The structure was solved by conventional Patterson and Fourier methods, on the basis of 2 000 unique intensities with $I > 3\sigma(I)$, 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 the non-hydrogen atoms and after five preliminary cycles of refinement, all the non-phenyl group atoms were treated anisotropically and the absolute configuration was tested by refining (three cycles) both the enantiomers. The results were $R = 0.0498$ and $R' = 0.0549$ for the (R)Ru,(S)C enantiomer and $R = 0.0495$ and $R' = 0.0547$ for the (S)Ru,(R)C enantiomer. Taking into account both the Hamilton's R factors significance test,[17] and that the (R) configuration of the asymmetric carbon atom of the ligand dppp was previously known,[8] there is no doubt that the enantiomer (S)Ru,(R)C [18] is the correct one.

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 0.042 and 0.045 respectively. The weights were computed according to the formula $w = 4F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{\frac{1}{2}}/Lp$ [I and Lp are the integrated intensity and the Lorentz-polarization correction, respectively]. The p ' fudge-factor ' was assumed equal to 0.04. The final difference-Fourier map was flat, showing only random residual peaks not exceeding 0.4 e Å^{-3}. The final positional parameters are reported in Table 1.

Results and Discussion

(*a*) *Preparation and Epimerization of the Complexes.*—The exchange reaction between (1) and the diphosphine in boiling benzene leads to the formation of the chelate complexes in a few hours.[7] When (R)dppp, (R)dpppe, or (S)cdppe are used, the two possible diastereomers (2) and (2′) form in a ratio close to 1 : 1. This ratio, however, does not correspond to the thermodynamic ratio and is probably a consequence of a low enantiosite selection in the stepwise displacement [7] of the two triphenylphosphine molecules by the diphosphine from (1). In fact, (2) and (2′) do not show any epimerization when heated in toluene at 80 °C for 96 h. However, epimerization takes place at the same temperature in C_6D_5Cl, the epimerization rate decreasing in the order (2a) > (2c) > (2b). The epimeric composition at the equilibrium under the above conditions is (2a′)–(2a) and (2c′)–(2c) *ca.* 2.4 : 1 and (2b)–(2b′) *ca.* 1.8 : 1. Thus it appears that the thermodynamic asymmetric induction of the chiral ligand on the pseudo-tetrahedral ruthenium atom is rather low.

In the case of complex (2), where the crystal structure of (2a′) has been determined (see later) the (S)Ru,(R)C diastereomer predominates over the (R)Ru,(R)C one.

(*b*) *Chiroptical Properties.*—In Figure 1 the c.d. spectra of diastereomeric (2a) and (2a′) are compared with the corresponding spectra of the (S,S)dppb [(2d)] and (R,R)mpppe [(2e)] containing complexes. Figure 2 reports the c.d. and u.v. spectra of the diastereomeric (S)cdppe containing complexes (2c) and (2c′) and in Figure 3 the c.d. spectra of the diastereomeric (R)dpppe containing complexes (2b) and (2b′) are shown. In each case the sign of the c.d. band at *ca.* 400—410 nm appears to be correlated to the absolute configuration of the chiral ligand, being positive for (S) and negative for (R) absolute configuration. The spectra of (2a) and (2a′) are not very different, although a low-intensity positive band is detectable at *ca.* 480 nm for (2a) which does not appear (and therefore it is probably negative) in the spectrum of (2a′). The spectra of diastereomeric (2b) and (2b′) and of (2c) and (2c′) differ even less from each other. The c.d. spectrum of (2a′) in which the metal has an (S) absolute configuration, is almost the mirror image of (2d) in which the metal is achiral (the two ligands have opposite absolute configurations); furthermore the spectrum of (2e) shows bands with the lowest ellipticity. Diastereomeric metal complexes having opposite chiralities at the metal normally exhibit c.d. spectra which are practically mirror images of each other, at least in the visible region,[11] with the remarkable exception of diastereomeric {(R,R)-2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene}carbonyl(η^5-cyclopentadienyl)iron hexafluorophosphate, differing in configuration at the iron atom.[6] Therefore we interpret the above results by assuming that the c.d. spectra of complexes (2) are predominantly influenced by the chiral conformation of the chiral ligand. This conformation is forced by the substituent(s) on the C_2 moiety of the diphosphine ligand and is the λ conformation for ligands having an (R) absolute configuration and the δ conformation for ligands having an (S) absolute configuration. There should be less difference in energy for both the conformations in the complex containing the ligand (R,R)mpppe (which does not have

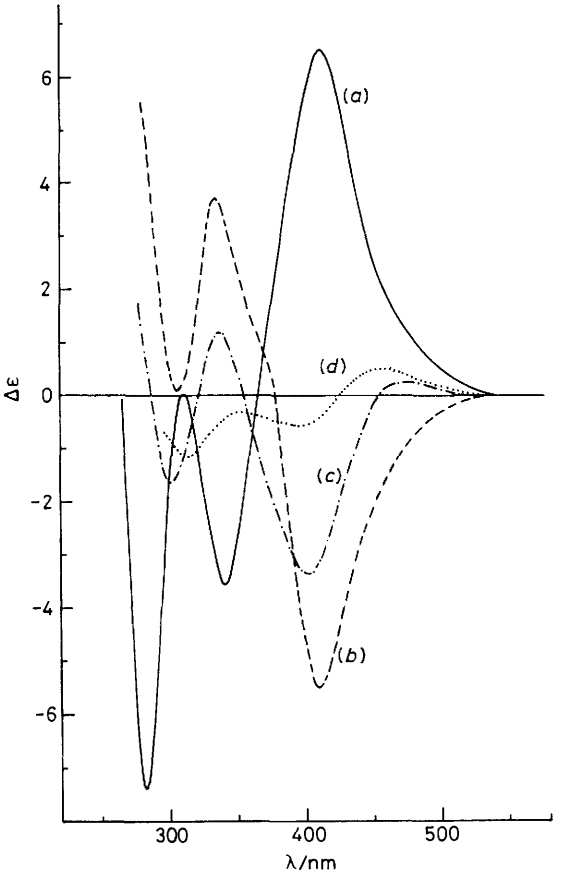

Figure 1. C.d. spectra of (*a*) (2d), (*b*) (2a′), (*c*) (2a), and (*d*) (2e)

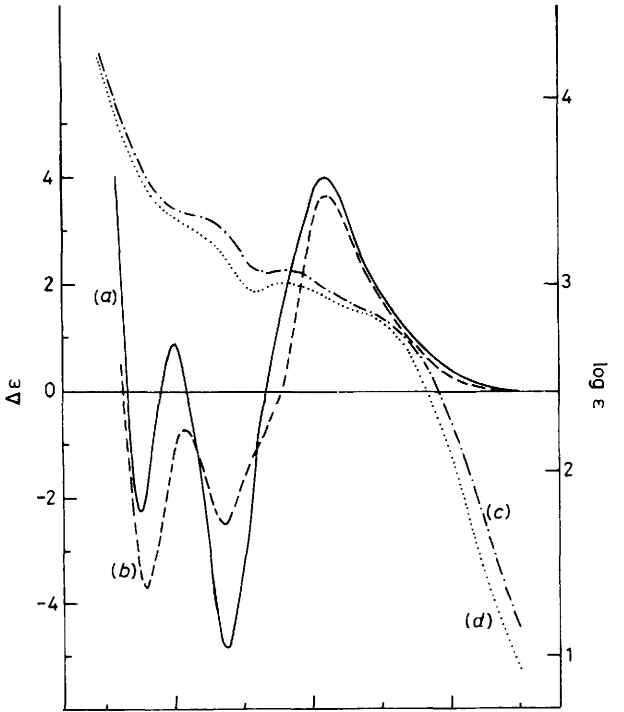

Figure 2. C.d. spectra of (*a*) (2c) and (*b*) (2c′); visible and u.v. spectra (right-hand scale) of (*c*) (2c′) and (*d*) (2c)

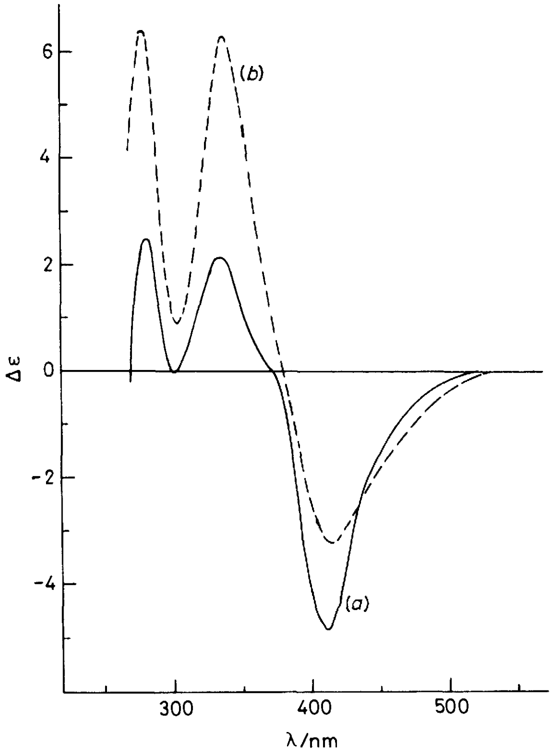

Figure 3. C.d. spectra of (*a*) (2b) and (*b*) (2b′)

substituents on the C_2 moiety) therefore producing less intense c.d. bands (at least in the visible region). Some distortions of the above conformation can be expected that would alleviate non-bonded interaction,[19] which could be different for each of the diastereomers.

(*c*) *Crystal Structure of* [(*S*)RuCl(η^5-C_5H_5){(*R*)dppp}] (2a′).—A view of the molecule in its absolute configuration is shown in Figure 4. Figure 5 depicts the co-ordination around the ruthenium atom. Bond parameters are reported in Table 2. The ruthenium atom is in an octahedral environment and is bound to the cyclopentadienyl ring (formally three *fac* positions), to the two phosphorus atoms of the dppp ligand, and to a chlorine atom. The cyclopentadienyl ring is essentially planar, the maximum out-of-plane displacement being 0.010 Å, with C–C bond lengths in the range 1.370(17)—1.410(14) Å, mean value 1.386 Å. The Ru–C interactions, ranging from 2.159(9) to 2.230(10) Å (mean 2.194 Å), are close to those found for complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (1) [20] (mean 2.207 Å) which has the same co-ordination around the ruthenium atom. Complex (1) also has a similar Ru–Cl bond length of 2.453(2), compared with the value reported here of 2.444(2) Å, but has different Ru–P interactions, which are longer (mean 2.336 Å) than in our compound (mean 2.277 Å). These differences are clearly due to steric effects, the M–P distances being sensitive to the bulkiness of the phosphine ligand.[21] The chelating dppp has a lower steric hindrance than two triphenylphosphine ligands and, from this point of view, it can be compared with two PMe_3 ligands; in fact in the complex [RuCl(η^5-C_5H_5)(PMe_3)$_2$] (1)[20] the Ru–P interactions have a mean value of 2.27 Å. However, the different acidities of the ligands involved must be taken into account; the π back-donation plays a fundamental role in determining such distances, as suggested by the value of the estimated Ru–P ' single bond ' of *ca.* 2.43 Å.[22] The angles around the ruthenium atom are in the sequence cp*–Ru–P (mean 130.4) >

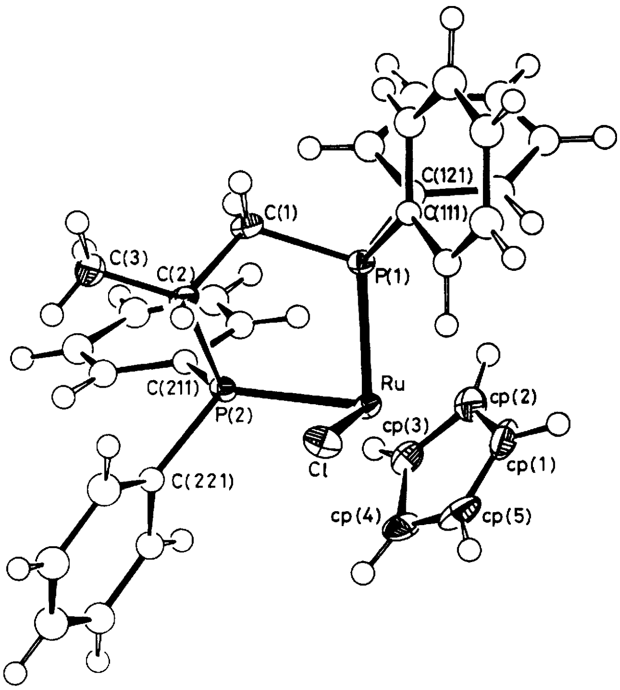

Figure 4. A view of the complex [(*S*)RuCl(η^5-C_5H_5){(*R*)dppp}] (2a′) in its absolute configuration

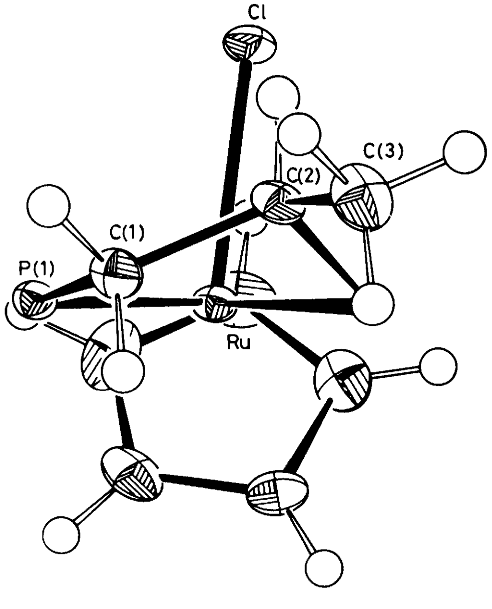

Figure 5. A view of the co-ordination around the ruthenium atom within the complex [(*S*)RuCl(η^5-C_5H_5){(*R*)dppp}] (2a′). The plane P(1),Ru,P(2) is normal to the plane of the drawing. The conformation of the Ru(dppp) ring is λ

cp*–Ru–Cl > (122.0) > P–Ru–Cl (mean 88.5) > P–Ru–P (82.9°), as expected for the presence of a chelating diphosphine. The P–Ru–P bite angle is very similar to that found in [$RuCl_2(PhMePCH_2CH_2PMePh)_2$] (82.7°).[23] The chlorine ligand is bent towards the P(2) atom [Cl–Ru–P(1) 92.9, Cl–Ru–P(2) 84.0°] to avoid short non-bonding interactions with one of the phenyl rings bound to P(1) [Cl···H(112) 2.64 Å].

Table 2. Bond parameters for [(*S*)RuCl(η^5-C_5H_5){(*R*)dppp}] (2a′)

Distances (Å)		Angles (°)	
Ru–Cl	2.444(2)	Cl–Ru–cp* [a]	122.0
Ru–P(1)	2.276(2)	P(1)–Ru–cp*	129.5
Ru–P(2)	2.278(2)	P(2)–Ru–cp*	131.3
Ru–cp(1)	2.207(9)	Cl–Ru–P(1)	92.9(1)
Ru–cp(2)	2.159(9)	Cl–Ru–P(2)	84.0(1)
Ru–cp(3)	2.161(9)	P(1)–Ru–P(2)	82.9(1)
Ru–cp(4)	2.230(10)	Ru–P(1)–C(1)	110.2(3)
Ru–cp(5)	2.213(10)	Ru–P(1)–C(111)	121.4(3)
P(1)–C(1)	1.843(10)	Ru–P(1)–C(121)	118.2(3)
P(1)–C(111)	1.843(8)	Ru–P(2)–C(2)	107.6(3)
P(1)–C(121)	1.845(8)	Ru–P(2)–C(211)	120.6(3)
P(2)–C(2)	1.864(9)	Ru–P(2)–C(221)	117.5(3)
P(2)–C(211)	1.843(9)	C(1)–P(1)–C(111)	103.0(4)
P(2)–C(221)	1.828(8)	C(1)–P(1)–C(121)	104.2(4)
C(1)–C(2)	1.525(13)	C(111)–P(1)–C(121)	97.4(4)
C(2)–C(3)	1.514(13)	C(2)–P(2)–C(211)	102.7(4)
cp(1)–cp(2)	1.377(16)	C(2)–P(2)–C(221)	106.0(4)
cp(1)–cp(5)	1.370(17)	C(211)–P(2)–C(221)	100.8(4)
cp(2)–cp(3)	1.395(14)	P(1)–C(1)–C(2)	112.3(6)
cp(3)–cp(4)	1.410(14)	P(2)–C(2)–C(1)	105.3(6)
cp(4)–cp(5)	1.377(16)	P(2)–C(2)–C(3)	117.9(7)
C–C (phenyl) (mean values)		C(1)–C(2)–C(3)	111.1(7)
C(111)—C(116)	1.385		
C(121)—C(126)	1.375		
C(211)—C(216)	1.380		
C(221)—C(226)	1.381		

[a] cp* indicates the centre of the η^5-C_5H_5 ligand.

The presence of an asymmetric carbon atom in dppp differentiates the two phosphorus atoms and as a result the complex is chiral at the ruthenium centre which displays an (*S*) configuration.[18] The Ru(dppp) metallacycle has a λ conformation. In fact, for an (*R*) absolute configuration at the C(2) carbon atom,[8] a δ conformation of the ring would require that the methyl group [C(3)] would be in a crowded axial position, rather than in an equatorial one. Moreover, the two carbon atoms of the ring are both out from the same side of the P(1), Ru,P(2) plane [C(2) 0.89, C(1) 0.25 Å] and, therefore, the λ conformation is distorted. Such distortions are very common in the solid state[24] and, presumably, they are due to intermolecular packing forces. In fact, while in solution only a small energy difference is expected for the possible distorted λ conformers,[25] in the crystal a change of conformation of the cycle causes a displacement of the phenyl rings and, therefore, large variations in the packing energy. We have found some short intramolecular contacts [H(11)···H(126) 2.05, H(2)··· H(222) 2.30 Å; these are rather imprecise values because of the idealized hydrogen atom locations] but, in our opinion, this is a consequence rather than the cause of the chelate ring distortion.

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