Synthesis, Properties and Crystal Structures of Diastereomeric Areneruthenium(II) Chiral Schiff-base Complexes†

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Diastereomers (S_{Ru},S_C)-**1a** and (R_{Ru},S_C)-**1b**, in a ratio of 85:15 and formulated as [Ru(η-MeC$_6$H$_4$Pr^i-*p*)Cl(L*)], have been prepared by treating [{Ru(η-MeC$_6$H$_4$Pr^i-*p*)Cl$_2$}$_2$] with the sodium salt of (*S*)-α-methylbenzylsalicylaldimine (HL*) in tetrahydrofuran at −70 °C. The reaction of **1** (**1a** + **1b**) with AgClO$_4$ in acetone followed by an addition of PPh$_3$ or 4-methylpyridine (4Me-py) leads to the formation of adducts [Ru(η-MeC$_6$H$_4$Pr^i-*p*)(PPh$_3$)(L*)]ClO$_4$ **2** [(S_{Ru},S_C) **2a**, (R_{Ru},S_C) **2b**] and [Ru(η-MeC$_6$H$_4$Pr^i-*p*)(4Me-py)(L*)]ClO$_4$ **3** [(S_{Ru},S_C) **3a**, (R_{Ru},S_C) **3b**] in the diastereomeric ratios (S_{Ru},S_C):(R_{Ru},S_C) of 2:98 and 76:24, respectively. Complex **1** crystallises with equal numbers of **1a** and **1b** molecules in an asymmetric unit of monoclinic space group $P2_1$ with a = 10.854(1), b = 17.090(1), c = 12.808(4) Å, β = 110.51(1)°, and Z = 4. The structure was refined to R = 0.0552 and R' = 0.0530 with 2893 reflections having $I \geqslant 1.5\sigma(I)$. The absolute configurations of the chiral centres in the optically pure single crystal of the PPh$_3$ adduct have been obtained from an X-ray study. Crystals of formulation [Ru(η-MeC$_6$H$_4$Pr^i-*p*)(PPh$_3$)(L*)]$_2$[ClO$_4$][PF$_6$]·1.5 CHCl$_3$, obtained in presence of both ClO$_4$ and PF$_6$ anions, belong to the non-centric triclinic space group $P1$ with a = 10.852(2), b = 14.028(1), c = 15.950(2) Å, α = 91.51(1), β = 105.97(1), γ = 106.11(1)°, and Z = 2. The final residuals were R = 0.0713, R' = 0.0752 with 7283 reflections having $I \geqslant 2.5\sigma(I)$. The crystal structures of **1a**,**1b**, and the PPh$_3$ adduct (**2b**,**2b′**) consist of a ruthenium(II) centre bonded to a η-*p*-cymene, a bidentate chelating Schiff base, and a unidentate ligand (Cl or PPh$_3$). The chirooptical properties of the complexes have been studied using ^{1}H NMR and CD spectral data. The presence of a low-energy barrier for the intermediate involved in these reactions, showing both retention as well as inversion of the metal configuration, is discussed.

Stereochemical aspects of reactions involving chiral half-sandwich transition-metal complexes have attracted[1–3] considerable interest in the areas of asymmetric catalysis and for the development of enantioselective reactions involving chiral intermediates. Cyclopentadienylruthenium(II) chiral complexes have been studied extensively.[4] Significant progress has been made towards understanding stereoselective transformation reactions involving diastereomeric complexes[5,6] containing uni- or bi-dentate chelating chiral phosphine ligands. Chiral Schiff-base complexes are also known[1,7] to be useful in stereochemical investigations on half-sandwich cyclopentadienyl complexes. In contrast an analogous chemistry of monoarene transitional-metal complexes is virtually unknown.[4] The present work stems from our interest to develop the chemistry of areneruthenium chiral Schiff-base complexes.

In this paper we report the syntheses and chiroopticai properties of [Ru(η-MeC$_6$H$_4$Pr^i-*p*)Cl(L*)] **1** and its triphenylphosphine and 4-methylpyridine adducts [HL* = (*S*)-α-methylbenzylsalicylaldimine, 2-HOC$_6$H$_4$CH=NCHMePh]. The crystal structures of a diastereomeric mixture of (S_{Ru},S_C)-**1a** and (R_{Ru},S_C)-**1b** and of an optically pure phosphine adduct **2b**,**2b′** with a R_{Ru},S_C configuration at the chiral centres have been determined. A preliminary communication of this work has been made.[8]

Experimental

Materials and Physical Measurements.—Reactions were carried out under a dinitrogen atmosphere using the Schlenk technique. The precursor complex [{Ru(η-MeC$_6$H$_4$Pr^i-*p*)Cl$_2$}$_2$] and AgClO$_4$ were prepared by following literature procedures.[9,10] Triphenylphosphine (Fluka) and 4-methylpyridine (Fluka) were used as received. The chiral ligand, (*S*)-α-methylbenzylsalicylaldimine (HL*), was synthesised by a modified procedure[11] in which diethyl ether was used as a solvent and the product was crystallised by slow evaporation of a diethyl ether solution at 5 °C. Crystals were washed rapidly with cold diethyl ether and dried *in vacuo*.

Elemental analysis was performed on a Heraeus CHN-O Rapid analyser. Proton NMR spectra in CDCl$_3$, containing tetramethylsilane as an internal standard, were recorded on Bruker WH-270 and ACF 200 MHz spectrometers. Polarimetric measurements were done using a Roussel Jouan type 71 instrument. Circular dichroism (CD) spectra were recorded in acetone solutions using a JASCO J-500A spectrophotometer.

Preparations.—[Ru(η-MeC$_6$H$_4$Pr^i-*p*)Cl(L*)] **1**. To a sodium salt of the Schiff-base ligand, prepared by treating HL* (240 mg, 1.0 mmol) with NaH (25 mg, 1.0 mmol) in tetrahydrofuran (thf, 20 cm^3), was added [{Ru(η-MeC$_6$H$_4$Pr^i-*p*)Cl$_2$}$_2$] (200 mg, 0.3 mmol). The mixture was stirred for 24 h at −70 °C, followed by warming to room temperature. The solvent was then removed and the solid residue was dissolved in CHCl$_3$ (5 cm^3). The solution was chromatographed on a silica column in CHCl$_3$. A reddish band, eluted with CHCl$_3$–thf (5:3 v/v), was collected. Evaporation of the solvent afforded the red, crystalline, air-stable complex **1** in *ca.* 70% yield. The product was found to be a mixture of **1a** and **1b** in 85:15 ratio (Found: C, 60.1; H, 5.9; N, 3.0, C$_{25}$H$_{28}$ClNORu requires C, 60.6; H, 5.7; N, 2.8%).

[Ru(η-MeC$_6$H$_4$Pr^i-*p*)(PPh$_3$)(L*)]ClO$_4$ **2**. Complex **1** (100 mg, 0.2 mmol) was taken in acetone (20 cm^3). Silver perchlorate (42 mg, 0.2 mmol) was added and the mixture stirred for 30 min at −5 °C followed by filtration through Celite under cold conditions. To the filtrate was added PPh$_3$ (80 mg, 0.3 mmol).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

The mixture was stirred for 30 min at 0 °C. The resulting yellow solution was concentrated to *ca.* 3 cm^3 and hexane (10 cm^3) was added. The air-stable solid residue thus formed was filtered off, washed with hexane and finally dried over P_4O_{10} *in vacuo* (yield: *ca.* 80%). The complex was isolated in crystalline form on slow evaporation of a solution in $CHCl_3$–hexane at 5 °C (Found: C, 62.5; H, 5.0; N, 1.8. $C_{43}H_{43}ClNO_5Ru$ requires C, 62.8, H, 5.2; N, 1.7%). The product is a mixture of two diastereomers **2a** and **2b** in a 2:98 ratio. The optically pure complex with a R_{Ru},S_C configuration can be obtained by a combination of column chromatographic and fractional crystallisation methods. The chromatography was carried out on an alumina column (deactivated by thf) using thf–$CHCl_3$ (5:3 v/v) eluent. A yellow band eluted with thf was collected and evaporated to dryness. The resulting solid was dissolved in $CHCl_3$–light petroleum (b.p. 60–80 °C) (1:1) and NBu_4PF_6 was added. Slow evaporation of the solution at 5 °C afforded optically pure diastereomers containing (R_{Ru},S_C)-[Ru(η-$MeC_6H_4Pr^i$-*p*)(PPh_3)(L*)]ClO_4 **2b** and (R_{Ru},S_C)-[Ru(η-$MeC_6H_4Pr^i$-*p*)(PPh_3)(L*)]PF_6 **2b′** in a 1:1 proportion in the unit cell (see below). Yield *ca.* 40%. Polarimetric data on the single crystals containing **2a** and **2b′**: α(25 °C, 589 nm) = −516°, (25 °C, 546 nm) = −950° (*c* = 0.6 mg cm^{-3}).

[Ru(η-$MeC_6H_4Pr^i$-*p*)(4Me-py)(L*)]ClO_4 **3**. The 4-methylpyridine adduct was synthesised as a mixture of (S_{Ru},S_C)-**3a** and (R_{Ru},S_C)-**3b** in a ratio of 76:24 following the above procedure using 4Me-py instead of PPh_3. The diastereomeric mixture was obtained in crystalline form in *ca.* 80% yield (Found: C, 57.1; H, 5.7; N, 4.5. $C_{31}H_{35}ClN_2O_5Ru$ requires C, 57.1; H, 5.4; N, 4.3%).

CAUTION: Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

X-Ray Structure Determinations of [Ru(η-$MeC_6H_4Pr^i$-*p*)-Cl(L*)] *and* [Ru(η-$MeC_6H_4Pr^i$-*p*)(PPh_3)(L*)]$_2$[ClO_4][PF_6]·1.5$CHCl_3$. *Crystal data for complex* **1** (**1a**,**1b**) $C_{25}H_{28}ClNORu$, *M* = 494.54, monoclinic, space group $P2_1$, *a* = 10.854(1), *b* = 17.090(1), *c* = 12.808(4) Å, β = 110.51(1)°, *U* = 2225(1) Å^3, *F*(000) = 988, *Z* = 4, D_c = 1.47 g cm^{-3}, Mo-Kα radiation, λ = 0.7107 Å, μ(Mo-Kα) = 6.88 cm^{-1}, *T* = 293 K.

Crystal data for complex **2b**,**2b′** $C_{86}H_{86}ClF_6N_2O_6P_3Ru_2$·1.5 $CHCl_3$, *M* = 1901.6, triclinic, space group *P*1, *a* = 10.852(2), *b* = 14.028(1), *c* = 15.950(2) Å, α = 91.51(1), β = 105.97(1), γ = 106.11(1)°, *U* = 2228(1) Å^3, *F*(000) = 961, *Z* = 2, D_c = 1.41 g cm^{-3}, Mo-Kα radiation, μ(Mo-Kα) = 5.33 cm^{-1}, *T* = 290 K.

Data collection and processing. A red crystal of complex **1** (0.2 × 0.2 × 0.1 mm) was mounted on a glass fibre. Unit-cell parameters were obtained by least-squares treatment of 25 reflections in the range $16 \leqslant 2\theta \leqslant 32°$. Intensity data in the ranges $0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 20$ and $-14 \leqslant l \leqslant 14$ within the range $4 \leqslant 2\theta \leqslant 50°$ were measured using a ω–2θ mode on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation. They were corrected for Lorentz and polarisation effects and for absorption[12] (transmission coefficient range: 0.85–1.00). 2893 Reflections, out of 4036 unique data, with $I \geqslant 1.5\sigma(I)$ were used in the structure solution and refinement.

A red crystal of complex **2b**,**2b′** with approximate dimensions 0.5 × 0.2 × 0.2 mm was mounted on a glass fibre. Unit-cell dimensions were determined from setting angles of 25 reflections in the range of $16 \leqslant 2\theta \leqslant 34°$ in a similar manner as for **1**. Data were collected in the ranges $0 \leqslant h \leqslant 12$, $-16 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 18$ and corrected for Lorentz and polarisation effects and for absorption[12] (transmission coefficient range: 0.98–1.00). Of 8258 unique reflections, 7283 with $I \geqslant 2.5\sigma(I)$ were used for the structure solution and least-squares refinement

Structure solution and refinement. The structures of isomers **1a** and **1b** were solved by the Patterson method which revealed the positions of two ruthenium atoms in the crystallographic asymmetric unit. The remaining atoms were located in successive Fourier difference maps and refined by least-squares techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the chiral carbon atoms were located from the Fourier map and were left unrefined by fixing the thermal parameter obtained by adding 0.015 to the thermal parameter of the corresponding carbon atoms. The final full-matrix least-squares refinement converged to *R* = 0.0552 and *R′* = 0.0530 with a weighting scheme $w = 1.00/[\sigma^2(F_o) + 0.000\,966(F_o)^2]$ using 522 parameters. The highest shift/e.s.d. was 0.12:1. The final Fourier difference map showed a peak of 0.72 e Å^{-3} situated near a ruthenium atom. All calculations were carried out using a VAX 88 computer and the SHELX[13] system of programs at the computer centre of the Indian Institute of Science. Atomic scattering factors were taken from ref. 14.

The procedures adopted for isomers **2b** and **2b′** were similar, using 7283 reflections with $I \geqslant 2.5\sigma(I)$ out of 8258 unique data and 538 parameters. The atoms in the co-ordination sphere, chlorine and phosphorus atoms of the anions were refined anisotropically leaving the remaining atoms at the isotropic stage. Hydrogen atoms bonded to the chiral carbon centres were fixed (C–H 0.9 Å) at the calculated positions and were not refined. The final convergence was obtained with *R* = 0.0713 and *R′* = 0.0752 using a weighting scheme $w = 1.00/[\sigma^2(F_o) + 0.005\,595(F_o)^2]$. The final Fourier difference map showed no peaks above 1.2 e Å^{-3}. The maximum shift/e.s.d. was 0.10:1. The oxygen atoms of the ClO_4 anion were found to be positionally disordered and were refined with a site occupancy factor of 0.5. The lattice $CHCl_3$ molecules were found to be thermally disordered and were refined with site occupancy factors of 1.0 and 0.5. Further disorder was noticed in the carbon atoms of the isopropyl group of the second molecule. The disordered atoms were modelled with two sets of site occupancy factors of 0.7 and 0.3 (see Table 4).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Absolute Configuration of Ruthenium in Isomers **2b** *and* **2b′**.—Using the methodology adopted by Consiglio and co-workers[15] for analogous half-sandwich complexes, the absolute configurations of the chiral centres in isomers **2b** and **2b′** have been determined on the basis of Hamilton's *R*-factor significant test[16] and with reference to a known[17] absolute configuration S_C of the chiral carbon atom. The residuals *R* and *R′* were 0.0713 and 0.0752, respectively, for the R_{Ru},S_C configuration of the chiral centres. For the corresponding enantiomer with an S_{Ru},R_C configuration, *R* = 0.0718 and *R′* = 0.0758. From the co-ordination geometry of the metal and the S_C configuration of the carbon centre, the absolute configuration of the ruthenium centres in **2b** and **2b′** was unequivocally assigned as R_{Ru}.

Results and Discussion

Synthesis and ^{1}H *NMR Spectra of Complex* **1**.—Complex **1** is isolated from the reaction of [{Ru(η-$MeC_6H_4Pr^i$-*p*)Cl_2}$_2$] with the sodium salt of the chiral Schiff-base ligand (*S*)-α-methyl-

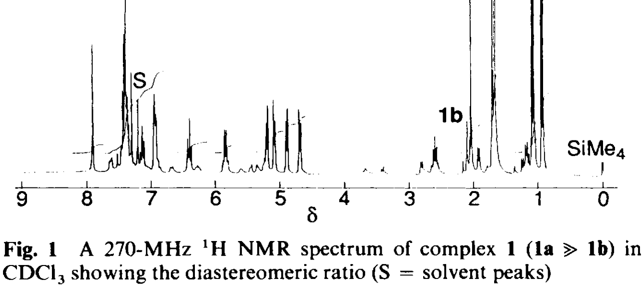


Fig. 1 A 270-MHz ^{1}H NMR spectrum of complex **1** (**1a** ≫ **1b**) in $CDCl_3$ showing the diastereomeric ratio (S = solvent peaks)

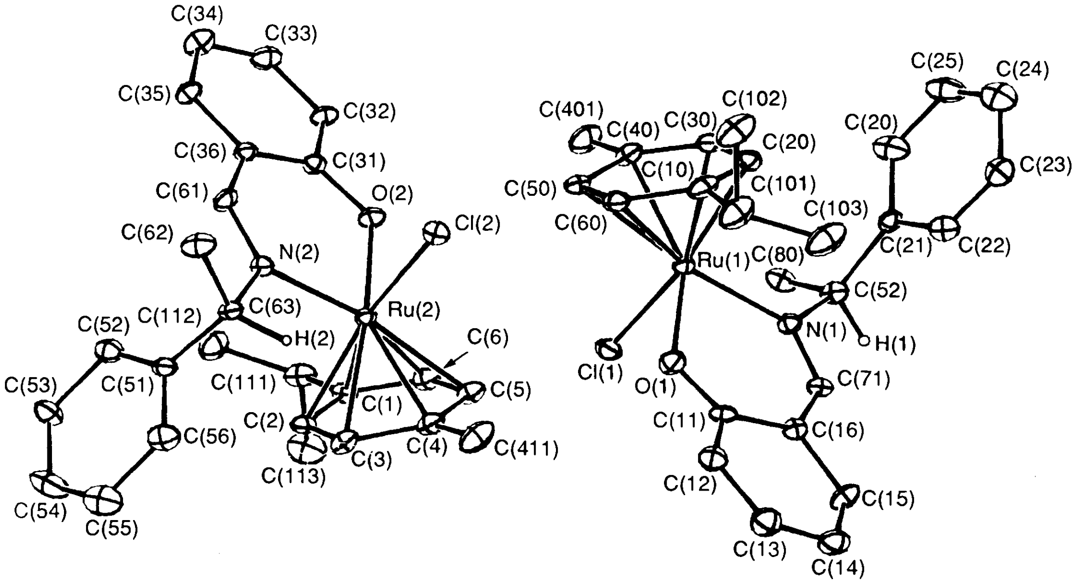


Fig. 2 The ORTEP views of isomers (S_{Ru},S_C)-**1a** and (R_{Ru},S_C)-**1b** in $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)Cl(L^*)]$ with the atom numbering schemes

Table 1 Proton NMR data[a] of complexes **1** (**1a** ≫ **1b**), **2** (**2b** ≫ **2a**) and **3** (**3a** > **3b**) in $CDCl_3$

Complex	L and L*[b]	η-*p*-Cymene
1a	1.75 (d, 3 H, 7), 5.9 (q, 1 H, 7), 6.35–7.71 (m, 10 H), 7.99 (s, 1 H)	0.99, 1.15 (6 H, 7), 2.11 (s, 3 H),[c] 2.68 (spt, 1 H, 6), 4.85 (q, 2 H, 6), 5.20 (q, 2 H, 6)
2b	1.30 (d, 3 H, 7), 5.50 (q, 1 H, 7), 6.35–7.30 (m, 26 H)	0.85, 1.07 (d, 6 H, 7), 1.59 (s, 3 H),[d] 2.39 (spt, 1 H, 6), 5.02 (q, 2 H, 6), 5.25 (q, 2 H, 6)
3a	2.37 (s, 3 H, L), 2.15 (d, 3 H, 6), 6.0–7.5 (m, 12 H), 8.10 (s, 1 H)	0.82, 1.04 (d, 6 H, 7), 1.79 (s, 3 H),[e] 2.50 (spt, 1 H, 6), 5.05 (q, 2 H, 7), 5.60 (q, 2 H, 7)

[a] δ with *J* in Hz; s = singlet, d = doublet, q = quartet, spt = septet and m = multiplet. [b] L = PPh_3 or 4Me-py. [c] For **1b**: δ 2.16 (s, 3 H). [d] For **2a**: δ 1.70 (s, 3 H). [e] For **3b**: δ 1.83 (s, 3 H).

Table 2 Positional parameters for isomers **1a** and **1b** with their estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	−0.5021(1)	−0.2828	−0.1334(1)	Ru(2)	−0.9785(1)	−0.1286(1)	−0.3393(1)
Cl(1)	−0.6784(3)	−0.3774(2)	−0.2163(3)	Cl(2)	−0.8080(4)	−0.0307(2)	−0.2596(3)
O(1)	−0.6005(9)	−0.2551(6)	−0.0253(8)	O(2)	−0.8848(9)	−0.1501(6)	−0.4511(7)
N(1)	−0.4084(10)	−0.3789(6)	−0.0249(9)	N(2)	−1.0752(10)	−0.0352(6)	−0.4397(9)
C(10)	−0.4052(17)	−0.1717(9)	−0.1007(12)	C(1)	−1.0762(12)	−0.2432(7)	−0.3793(11)
C(20)	−0.3203(12)	−0.2275(8)	−0.1184(11)	C(2)	−1.1589(12)	−0.1879(8)	−0.3502(11)
C(30)	−0.3597(12)	−0.2676(8)	−0.2170(11)	C(3)	−1.1176(15)	−0.1461(8)	−0.2485(11)
C(40)	−0.4803(15)	−0.2622(8)	−0.2992(11)	C(4)	−0.9834(15)	−0.1593(9)	−0.1740(12)
C(50)	−0.5749(13)	−0.2028(9)	−0.2805(11)	C(5)	−0.9014(15)	−0.2102(8)	−0.1995(11)
C(60)	−0.5359(14)	−0.1581(9)	−0.1798(12)	C(6)	−0.9509(14)	−0.2507(8)	−0.3010(12)
C(80)	−0.3841(14)	−0.4753(9)	−0.1584(13)	C(111)	−1.1215(14)	−0.2861(10)	−0.4866(12)
C(101)	−0.3808(21)	−0.1204(12)	0.0087(13)	C(112)	−1.2143(19)	−0.2417(11)	−0.5861(13)
C(102)	−0.3099(22)	−0.0419(9)	−0.0140(15)	C(113)	−1.1794(21)	−0.3659(11)	−0.4679(18)
C(103)	−0.2835(25)	−0.1594(11)	0.1116(15)	C(411)	−0.9309(21)	−0.1057(11)	−0.0603(13)
C(401)	−0.5270(19)	−0.3051(12)	−0.4022(12)	C(31)	−0.9164(11)	−0.1214(8)	−0.5528(9)
C(11)	−0.5767(12)	−0.2753(8)	0.0745(10)	C(32)	−0.8619(14)	−0.1628(9)	−0.6249(11)
C(12)	−0.6287(15)	−0.2318(10)	0.1426(13)	C(33)	−0.8915(14)	−0.1365(10)	−0.7331(11)
C(13)	−0.6111(18)	−0.2571(11)	0.2513(14)	C(34)	−0.9685(18)	−0.0716(10)	−0.7765(13)
C(14)	−0.5372(17)	−0.3277(12)	0.2941(14)	C(35)	−1.0256(14)	−0.0303(9)	−0.7040(10)
C(15)	−0.4846(16)	−0.3645(8)	0.2323(11)	C(36)	−0.9990(12)	−0.0581(8)	−0.5972(10)
C(16)	−0.4939(13)	−0.3422(8)	0.1207(11)	C(61)	−1.0674(13)	−0.0159(9)	−0.5364(10)
C(71)	−0.4227(12)	−0.3897(8)	0.0684(11)	C(62)	−1.1418(17)	0.1091(9)	−0.4192(14)
C(52)	−0.3224(13)	−0.4359(8)	−0.0495(11)	C(63)	−1.1555(12)	0.0153(7)	−0.3912(10)
C(21)	−0.1830(13)	−0.4005(8)	−0.0272(10)	C(51)	−1.2961(12)	−0.0113(8)	−0.4342(12)
C(22)	−0.1151(16)	−0.3656(10)	0.0747(13)	C(52)	−1.3583(15)	−0.0368(9)	−0.5395(13)
C(23)	0.0094(19)	−0.3388(12)	0.1042(15)	C(53)	−1.4968(16)	−0.0651(12)	−0.5701(17)
C(24)	0.0724(19)	−0.3455(10)	0.0200(20)	C(54)	−1.5580(16)	−0.0597(12)	−0.4899(23)
C(25)	0.0068(17)	−0.3803(10)	−0.0794(18)	C(55)	−1.4972(21)	−0.0302(12)	−0.3860(21)
C(26)	−0.1191(16)	−0.4054(8)	−0.1061(16)	C(56)	−1.3592(16)	−0.0057(10)	−0.3562(14)

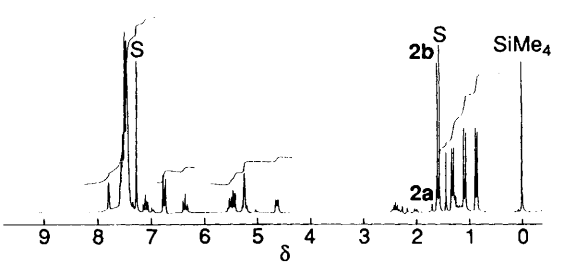


Fig. 3 A 200 MHz ^{1}H NMR spectrum of complex **2** in $CDCl_3$ (S = solvent peaks)

Table 3 Selected bond distances (Å) and angles (°) for isomers **1a** and **1b** with their e.s.d.s in parentheses

Ru(1)–Cl(1)	2.445(3)	Cl(1)–Ru(1)–C_0	126.3
Ru(1)–O(1)	2.078(11)	O(1)–Ru(1)–C_0	121.2
Ru(1)–N(1)	2.161(9)	N(1)–Ru(1)–C_0	135.2
Ru(1)–C_0	1.625	Cl(2)–Ru(2)–C'_0	129.2
Ru(2)–C'_0	1.672	O(2)–Ru(2)–C'_0	123.2
Ru(2)–Cl(2)	2.437(3)	N(2)–Ru(2)–C'_0	132.1
Ru(2)–O(2)	2.059(10)	Cl(1)–Ru(1)–N(1)	84.1(2)
Ru(2)–N(2)	2.087(10)	O(1)–Ru(1)–N(1)	88.8(4)
Ru(1)–C(10)	2.139(15)	Cl(1)–Ru(1)–O(1)	86.1(3)
Ru(1)–C(20)	2.135(13)	Cl(2)–Ru(2)–N(2)	82.9(3)
Ru(1)–C(30)	2.182(15)	Cl(2)–Ru(2)–O(2)	85.7(3)
Ru(1)–C(40)	2.245(15)	O(2)–Ru(2)–N(2)	88.4(4)
Ru(1)–C(50)	2.236(13)	Ru(1)–N(1)–C(71)	121.9(9)
Ru(1)–C(60)	2.208(15)	C(1)–C(16)–C(71)	128(1)
Ru(2)–C(1)	2.200(12)	O(1)–C(11)–C(16)	120(1)
Ru(2)–C(2)	2.165(13)	Ru(1)–O(1)–C(11)	130.0(9)
Ru(2)–C(3)	2.225(17)	Ru(2)–N(2)–C(61)	126.0(9)
Ru(2)–C(4)	2.199(16)	C(31)–C(36)–C(61)	123(1)
Ru(2)–C(5)	2.191(13)	O(2)–C(31)–C(36)	127(1)
Ru(2)–C(6)	2.140(13)	Ru(2)–O(2)–C(31)	126.8(8)
		Ru(1)–N(1)–C(52)	124.1(8)
		Ru(2)–N(2)–C(63)	115.0(7)

C_0 and C'_0 are the centroids of the η-*p*-cymene rings.

benzylsalicylaldimine (HL*) in thf at −70 °C. The air-stable product, formulated as $[Ru(\eta\text{-}MeC_6H_4Pr^i\text{-}p)Cl(L^*)]$ from the analytical data, shows the presence of two diastereomers, **1a** and **1b**, in a ratio of 85:15 according to the ^{1}H NMR spectrum in $CDCl_3$ (Fig. 1). The isomer ratio was obtained from the peak intensities of two sets of methyl signals of the *p*-cymene ligand appearing at δ 2.11 and 2.16. Relevant ^{1}H NMR data are presented in Table 1.

The ^{1}H NMR spectrum of complex **1** suggests the presence of η-*p*-cymene, Cl and L* ligands in a 1:1:1 ratio. The $CHMe_2$ group of the *p*-cymene ligand in **1a** appears as two sets of doublets in the range δ 0.99–1.22 and a septet at δ 2.68. This indicates a non-equivalence of the two methyl groups in this moiety. The arene ring protons appear as two AB quartets in the range δ 4.75–5.51. The benzylic proton of the chiral Schiff-base ligand shows a quartet near δ 5.9 and the methyl protons of the CHMe group display a doublet at δ 1.75. The spectral pattern in the range δ 6.35–7.71 is complex but corresponds to the phenyl ring protons of the Schiff base. A singlet at δ 7.99 is assignable to the imino proton. The spectral data suggest a bidentate chelating mode of bonding of the Schiff-base ligand through the phenolic oxygen and the imine nitrogen.

It appears from the spectral data that the formation of isomers **1a** and **1b** is a highly stereoselective process induced by the chiral Schiff-base ligand. The absolute configurations of the chiral centres, however, cannot be determined from the ^{1}H NMR data. Attempts to separate the diastereomers from the mixture by a combination of column chromatography and fractional crystallisation remain unsuccessful.

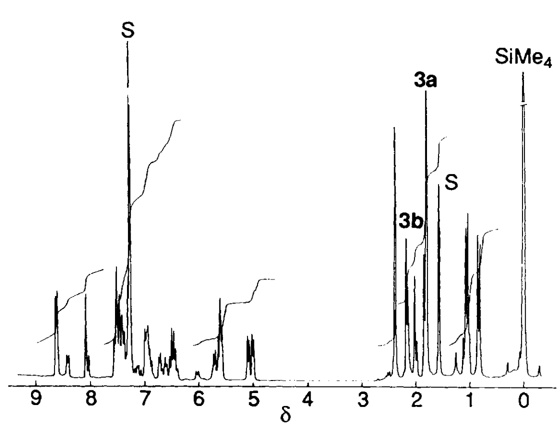
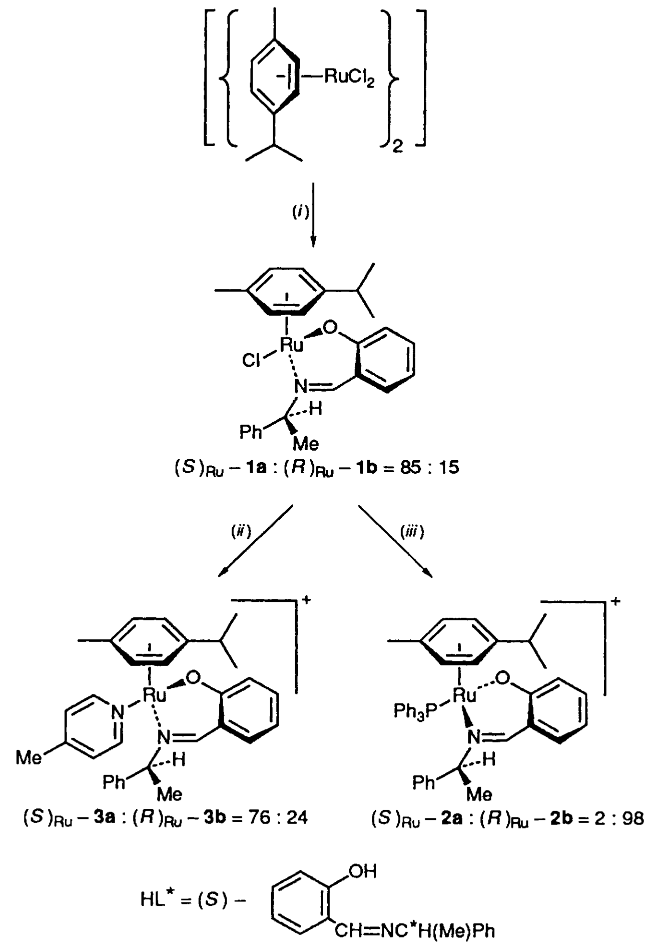


Fig. 4 A 200-MHz ^{1}H NMR spectrum of complex **3** (**3a** > **3b**) showing a 74:26 ratio of the diastereomers in $CDCl_3$ (S = solvent peaks)



Scheme 1 (*i*) NaL*, thf, −70 °C; (*ii*) Me_2CO, −5 °C, (*a*) $AgClO_4$, (*b*) 4Me-py; (*iii*) Me_2CO_2, −5 °C, (*a*) $AgClO_4$, (*b*) PPh_3

Crystal Structures of Isomers **1a** *and* **1b**.—Single crystals obtained from the mixture and subjected to structural studies show the presence of both isomers **1a** and **1b** in the crystallographic asymmetric unit. The ORTEP [18] views of the molecules are displayed in Fig. 2. Atomic coordinates and selected bond distances and angles are given in Tables 2 and 3, respectively. The crystalline mass was found to be uniform and this was verified from the unit-cell parameters obtained from several crystals. However, the ^{1}H NMR spectrum of the crystals in $CDCl_3$ show a 85:15 ratio of **1a** and **1b** instead of the expected 1:1 ratio.

The molecules **1a** and **1b** differ in chirality at the metal centre. The geometry of the ruthenium atom is essentially octahedral having the *p*-cymene group at one face. The chiral

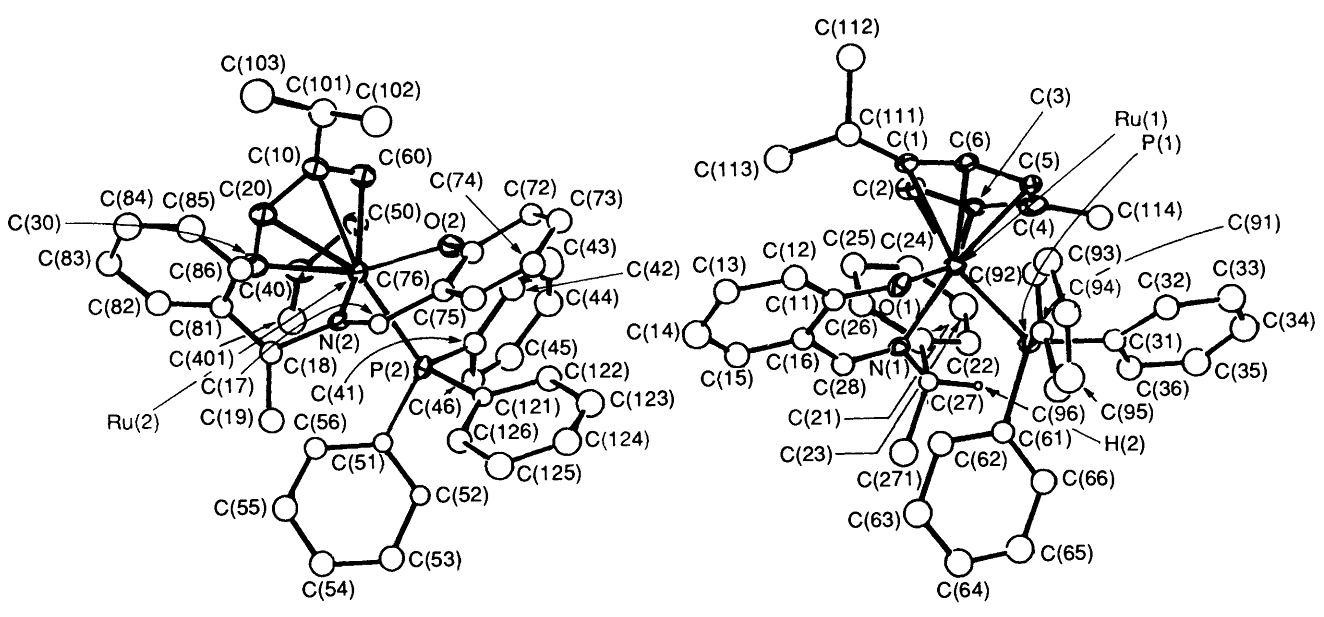


Fig. 5 The ORTEP views of the cations (R_{Ru},S_C)-[Ru(η-MeC$_6$H$_4$Pr^i-*p*)(PPh$_3$)(L*)]$^+$ in **2b** and **2b′** along with the atom numbering schemes

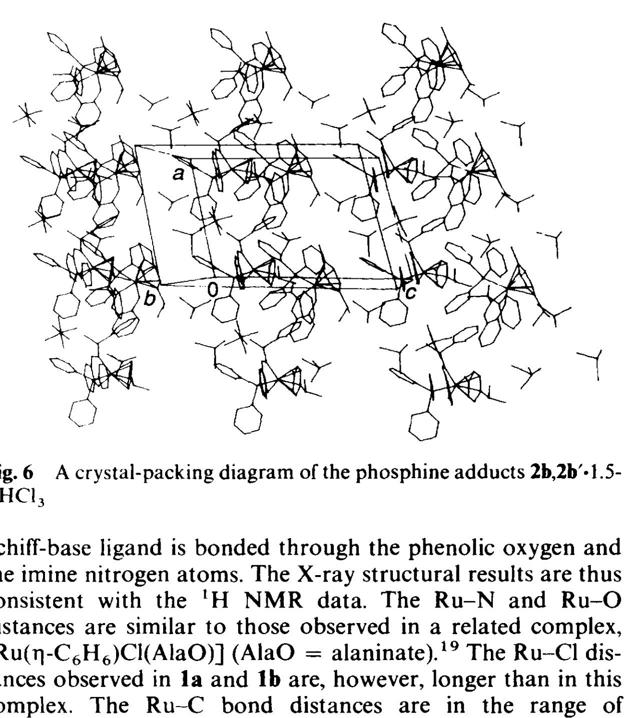


Fig. 6 A crystal-packing diagram of the phosphine adducts **2b**,**2b′**·1.5-CHCl$_3$

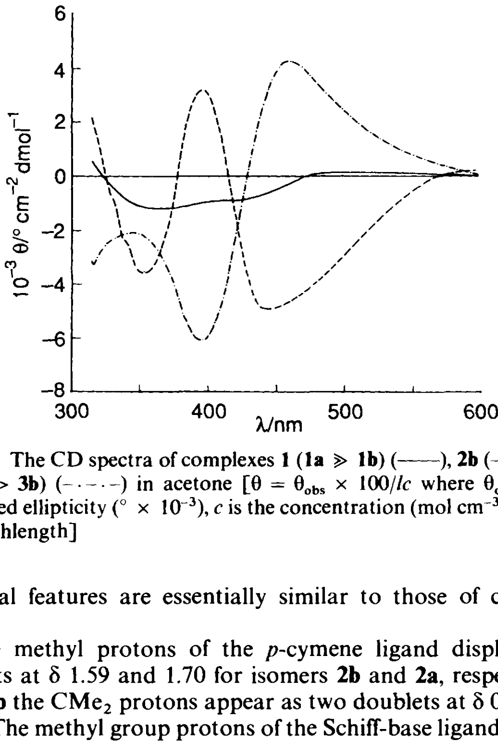


Fig. 7 The CD spectra of complexes **1** (**1a** ≫ **1b**) (——), **2b** (– – –) and **3** (**3a** > **3b**) (- · - · -) in acetone [$\theta = \theta_{obs} \times 100/lc$ where θ_{obs} is the observed ellipticity (° × 10^{-3}), c is the concentration (mol cm^{-3}) and l is the pathlength]

Schiff-base ligand is bonded through the phenolic oxygen and the imine nitrogen atoms. The X-ray structural results are thus consistent with the ^{1}H NMR data. The Ru–N and Ru–O distances are similar to those observed in a related complex, [Ru(η-C$_6$H$_6$)Cl(AlaO)] (AlaO = alaninate).[19] The Ru–Cl distances observed in **1a** and **1b** are, however, longer than in this complex. The Ru–C bond distances are in the range of 2.135(13)–2.245(15) Å (mean 2.18 Å). The arene rings are essentially planar showing a maximum deviation of 0.06 Å from the mean plane.

Reactivity of Complex **1**.—The reactivity of [Ru(η-MeC$_6$H$_4$-Pr^i-*p*)Cl(L*)] **1** toward PPh$_3$ and 4-methylpyridine has been studied. With AgClO$_4$ in acetone complex **1** forms a yellow solution which on subsequent treatment with PPh$_3$ leads to the formation of a triphenylphosphine adduct, [Ru(η-MeC$_6$H$_4$Pr^i-*p*)(PPh$_3$)(L*)]ClO$_4$ **2**. A similar reaction with 4-methylpyridine forms [Ru(η-MeC$_6$H$_4$Pr^i-*p*)(4Me-py)(L*)]ClO$_4$ **3**. Both **2** and **3** are ionic in nature and are soluble in polar organic solvents but insoluble in hexane.

The ^{1}H NMR spectrum of complex **2** (Fig. 3), indicates the presence of two diastereomers **2a** and **2b** in a 2:98 ratio. In contrast, that of **3** shows the presence of **3a** and **3b** in a 76:24 ratio (Fig. 4). The relevant data are given in Table 1. The spectral features are essentially similar to those of complex **1**.

The methyl protons of the *p*-cymene ligand display two singlets at δ 1.59 and 1.70 for isomers **2b** and **2a**, respectively. For **2b** the CMe$_2$ protons appear as two doublets at δ 0.85 and 1.07. The methyl group protons of the Schiff-base ligand show a doublet at δ 1.30. The arene ring displays two AB quartets in the range δ 4.6–5.6. For **3** the methyl groups of the arene ligand appear as two singlets located at δ 1.79 and 1.83 for **3a** and **3b**, respectively. The CMe$_2$ group exhibits two doublets at δ 0.82 and 1.04. The methyl protons of 4-methylpyridine and the Schiff base in **3a** appear as a singlet at δ 2.37 and a doublet at δ 2.15, respectively. The imine proton appears as a singlet at δ 8.10. A doublet at δ 8.61 is assigned to the *ortho*-proton of the phenolic ring.

The reaction pathways involved in the formation of complex **2** and **3** are shown in Scheme 1. The reaction of **1** with PPh$_3$ is highly stereospecific [diastereomeric excess (d.e.) 96%] with respect to **1a**. In contrast, the 4-methylpyridine adduct formation proceeds in a stereoselective way (d.e. 52%). The high stereospecificity of the formation of **2b** could be due to the bulk of PPh$_3$ which imposes more steric constraint compared to

Table 4 Positional parameters for isomers **2b**,**2b′**·1.5CHCl$_3$ with their e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.0000	0.0000	0.0000	C(44)	1.1801(18)	0.2923(13)	0.4744(11)
P(1)	−0.0799(3)	−0.0746(2)	−0.1467(2)	C(45)	1.2517(16)	0.3643(11)	0.4391(10)
C(1)	−0.0368(10)	0.0381(9)	0.1299(6)	C(46)	1.1990(13)	0.4353(9)	0.3935(8)
C(2)	0.0930(10)	0.0286(8)	0.1489(6)	C(51)	1.1161(10)	0.6058(7)	0.2912(6)
C(3)	0.1121(11)	−0.0619(8)	0.1178(7)	C(52)	1.1575(11)	0.5648(8)	0.2312(7)
C(4)	0.0055(12)	−0.1434(8)	0.0694(6)	C(53)	1.2469(14)	0.6213(10)	0.1902(9)
C(5)	−0.1258(10)	−0.1322(7)	0.0441(7)	C(54)	1.2984(14)	0.7244(10)	0.2156(9)
C(6)	−0.1468(10)	−0.0411(7)	0.0750(7)	C(55)	1.2552(14)	0.7647(10)	0.2784(9)
C(111)	−0.0702(11)	0.1221(8)	0.1656(7)	C(56)	1.1676(11)	0.7061(8)	0.3155(7)
C(112)	−0.1167(15)	0.0948(11)	0.2474(9)	C(71)	0.6449(11)	0.4490(8)	0.3438(7)
C(113)	0.0500(14)	0.2228(10)	0.1940(9)	C(72)	0.5460(13)	0.3560(9)	0.3421(8)
C(114)	0.0275(13)	−0.2412(9)	0.0499(8)	C(73)	0.4271(14)	0.3280(10)	0.2824(9)
O(1)	−0.0965(7)	0.1017(5)	−0.0531(5)	C(74)	0.3915(15)	0.3906(10)	0.2153(9)
N(1)	0.1733(8)	0.0954(6)	−0.0269(6)	C(75)	0.4830(12)	0.4832(9)	0.2182(8)
C(11)	−0.0366(11)	0.2009(8)	−0.0365(7)	C(76)	0.6081(11)	0.5115(8)	0.2832(7)
C(12)	−0.1165(15)	0.2624(10)	−0.0328(9)	C(17)	0.6909(10)	0.6126(7)	0.2835(6)
C(13)	−0.0643(15)	0.3667(11)	−0.0189(10)	C(18)	0.8621(10)	0.7704(7)	0.3330(7)
C(14)	0.0753(17)	0.4124(12)	−0.0126(11)	C(19)	0.8496(13)	0.7985(9)	0.2358(8)
C(15)	0.1540(14)	0.3505(9)	−0.0160(8)	C(81)	0.7999(10)	0.8346(7)	0.3779(6)
C(16)	0.1021(11)	0.2470(8)	−0.0267(7)	C(82)	0.8839(13)	0.9247(9)	0.4273(8)
C(28)	0.1913(11)	0.1865(8)	−0.0326(7)	C(83)	0.8350(14)	0.9877(10)	0.4693(9)
C(27)	0.2826(11)	0.0524(8)	−0.0343(7)	C(84)	0.6927(15)	0.9608(10)	0.4584(9)
C(271)	0.3690(16)	0.1073(11)	−0.0908(10)	C(85)	0.6137(15)	0.8750(11)	0.4122(9)
C(21)	0.3713(11)	0.0409(8)	0.0555(7)	C(86)	0.6590(13)	0.8074(9)	0.3690(8)
C(22)	0.4238(14)	−0.0386(10)	0.0650(9)	C(121)	0.8655(10)	0.4637(7)	0.2379(6)
C(23)	0.4955(16)	−0.0544(11)	0.1408(10)	C(122)	0.7999(13)	0.3642(9)	0.2241(8)
C(24)	0.5283(15)	0.0120(11)	0.2153(10)	C(123)	0.7026(17)	0.3193(2)	0.1446(11)
C(25)	0.4841(14)	0.0996(10)	0.2101(9)	C(124)	0.6609(17)	0.3762(12)	0.0802(11)
C(26)	0.4050(12)	0.1112(8)	0.1274(7)	C(125)	0.7313(16)	0.4815(12)	0.0883(10)
C(31)	−0.0866(11)	−0.2058(7)	−0.1590(7)	C(126)	0.8287(12)	0.5204(8)	0.1676(7)
C(32)	−0.2051(13)	−0.2821(9)	−0.1725(8)	C(401)	1.2626(18)	0.6805(13)	0.5305(12)
C(33)	−0.2068(15)	−0.3847(11)	−0.1726(10)	C(101)	0.7284(17)	0.6145(12)	0.5873(11)
C(34)	−0.0884(15)	−0.4062(10)	−0.1654(9)	C(102)[a]	0.6036(29)	0.5481(21)	0.5154(18)
C(35)	0.0282(14)	−0.3334(10)	−0.1565(9)	C(102′)[b]	0.6518(94)	0.4852(65)	0.6015(58)
C(36)	0.0336(13)	−0.2312(9)	−0.1499(8)	C(103)[a]	0.6942(33)	0.7152(24)	0.6051(21)
C(61)	0.0092(11)	−0.0112(8)	−0.2229(7)	C(103′)[b]	0.5962(115)	0.6454(79)	0.5317(72)
C(62)	0.0127(13)	0.0886(9)	−0.2271(8)	Cl(1)	0.3018(3)	1.0328(3)	0.4333(2)
C(63)	0.0790(17)	0.1411(12)	−0.2872(10)	O(3)[c]	0.1778(29)	0.9526(20)	0.3621(18)
C(64)	0.1355(18)	0.0914(12)	−0.3372(11)	O(4)[c]	0.3725(28)	1.1428(19)	0.4284(18)
C(65)	0.1268(15)	−0.0062(11)	−0.3311(10)	O(5)[c]	0.2093(23)	1.0584(16)	0.4864(15)
C(66)	0.0625(13)	−0.0585(9)	−0.2751(8)	O(6)[c]	0.3625(29)	1.0064(20)	0.3532(18)
C(91)	−0.2523(12)	−0.0774(8)	−0.2013(7)	O(3′)[c]	0.4248(35)	1.0074(24)	0.4383(22)
C(92)	−0.3434(14)	−0.0826(10)	−0.1585(9)	O(4′)[c]	0.3722(47)	1.0749(31)	0.5336(29)
C(93)	−0.4745(19)	−0.0902(13)	−0.1975(12)	O(5′)[c]	0.3326(35)	0.9406(24)	0.4812(21)
C(94)	−0.5187(17)	−0.0934(12)	−0.2880(11)	O(6′)[c]	0.2182(30)	0.9290(20)	0.4406(18)
C(95)	−0.4314(20)	−0.0828(14)	−0.3381(13)	P(3)	0.4703(4)	0.6823(3)	−0.0085(2)
C(96)	−0.2971(15)	−0.0783(11)	−0.2963(10)	F(1)	0.6032(24)	0.6575(16)	−0.0179(14)
Ru(2)	0.9129(1)	0.5998(1)	0.4418(1)	F(2)	0.3957(16)	0.5685(11)	−0.0105(10)
P(2)	0.9923(3)	0.5274(2)	0.3383(2)	F(3)	0.3937(19)	0.6735(13)	−0.1084(12)
O(2)	0.7617(7)	0.4652(5)	0.4035(5)	F(4)	0.3433(18)	0.7137(13)	0.0099(11)
N(2)	0.8033(8)	0.6605(6)	0.3387(5)	F(5)	0.5465(10)	0.7950(7)	0.0046(6)
C(10)	0.8613(15)	0.6309(8)	0.5683(7)	F(6)	0.5172(15)	0.6896(11)	0.0914(10)
C(20)	0.9283(17)	0.7224(10)	0.5430(8)	C(70)	0.3405(25)	0.4654(17)	0.7844(16)
C(30)	1.0583(15)	0.7387(9)	0.5282(7)	Cl(2)	0.1592(9)	0.4337(6)	0.7563(6)
C(40)	1.1220(16)	0.6629(10)	0.5378(9)	Cl(3)	0.3935(9)	0.3697(6)	0.8236(6)
C(50)	1.0516(15)	0.5697(10)	0.5624(8)	Cl(4)	0.3887(13)	0.5063(9)	0.6908(8)
C(60)	0.9243(19)	0.5535(10)	0.5732(8)	C(99)[c]	0.6512(37)	0.2276(26)	0.6452(23)
C(41)	1.0676(11)	0.4319(8)	0.3893(7)	Cl(5)[c]	0.7516(17)	0.2514(12)	0.5771(10)
C(42)	0.9924(13)	0.3615(9)	0.4273(8)	Cl(6)[c]	0.5657(25)	0 3104(17)	0.6335(15)
C(43)	1.0425(17)	0.2873(12)	0.4721(10)	Cl(7)[c]	0.7285(26)	0.2126(19)	0.7475(17)

Refined with site occupancy factors of 0.7 (a), 0.3 (b) and 0.5 (c), respectively

4Me-py. The adduct formation is believed to proceed through a chiral intermediate which is formed upon addition of AgClO$_4$ to the acetone solution of the chloro complex, **1**. Preliminary results[8] show it to contain both *p*-cymene and the Schiff-base ligand (L*). Further investigations aimed towards isolation of this complex in crystalline form for X-ray studies are being made. Since we are unable to isolate single crystals of **1a**, it is difficult to ascertain whether the reactions proceed with retention or inversion of configuration at the metal centre. However, this was done indirectly by an X-ray structure determination of the optically pure PPh$_3$ adduct (**2b**,**2b′**).

Crystal Structure of the PPh$_3$ *Adduct*.—The red prismatic crystals of the phosphine adduct belong to the triclinic space group $P1$. The ORTEP[18] views of two complex cations, present in the unit cell, are shown in Fig. 5. The atomic coordinates are given in Table 4, selected bond distances and angles in **2b** and **2b′** in Table 5. The geometry of the ruthenium atom in the

Table 5 Selected bond distances (Å) and angles (°) for isomers **2b** and **2b** with their e.s.d.s in parentheses

Ru(1)–C$_0$	1.762	P(1)–Ru(1)–C$_0$	130.3
Ru(2)–C$'_0$	1.746	O(1)–Ru(1)–C$_0$	123.3
Ru(1)–P(1)	2.360(3)	N(1)–Ru(1)–C$_0$	129.3
Ru(1)–C(1)	2.292(11)	P(2)–Ru(2)–C$'_0$	130.6
Ru(1)–C(3)	2.275(11)	O(2)–Ru(2)–C$'_0$	122.0
Ru(1)–C(6)	2.208(12)	N(2)–Ru(2)–C$'_0$	130.5
Ru(1)–N(1)	2.142(8)	P(1)–Ru(1)–N(1)	89.7(7)
Ru(1)–C(2)	2.286(8)	P(1)–Ru(1)–O(1)	82.6(2)
Ru(1)–C(4)	2.329(11)	N(1)–Ru(1)–O(1)	86.0(3)
Ru(1)–C(5)	2.233(10)	P(2)–Ru(2)–N(2)	88.5(2)
Ru(1)–O(1)	2.062(7)	P(2)–Ru(2)–O(2)	80.6(2)
Ru(2)–P(2)	2.383(4)	O(2)–Ru(2)–N(2)	88.6(3)
Ru(2)–C(10)	2.299(14)	Ru(1)–N(1)–C(28)	123.2(8)
Ru(2)–O(2)	2.073(6)	N(1)–C(28)–C(16)	129(1)
Ru(2)–N(2)	2.098(8)	C(11)–C(16)–C(28)	119(1)
Ru(2)–C(20)	2.266(14)	O(1)–C(11)–C(16)	124(1)
Ru(2)–C(30)	2.267(10)	Ru(1)–O(1)–C(11)	122.0(7)
Ru(2)–C(40)	2.275(13)	Ru(2)–N(2)–C(17)	125.0(6)
Ru(2)–C(50)	2.224(13)	N(2)–C(17)–C(76)	128.3(9)
Ru(2)–C(60)	2.191(13)	C(17)–C(76)–C(71)	124(1)
		Ru(2)–O(2)–C(71)	126.6(6)
		O(2)–C(71)–C(76)	127(1)

C$_0$ and C$'_0$ are the centroids of the η-*p*-cymene rings.

complex cation is essentially octahedral comprising of a *p*-cymene, a bidentate L* and a unidentate PPh$_3$ ligand. From the geometry of the metal atoms, and on the basis of the known[17] (S_C) configuration of the chiral ligand, the absolute configurations of the chiral centres are unequivocally assigned[15] as R_{Ru} and S_C using the following priority[20] order: η-MeC$_6$H$_4$Pr^i-*p* > PPh$_3$ > O-(*S*)L* > N-(*S*)L*. The bonding features in the two cationic species are essentially the same. Both cations show the same absolute configurations at the chiral centres. The bond distances and angles in **2b**,**2b′** are similar to those found in **1a**,**1b**. A crystal-packing diagram[21] of this complex is shown in Fig. 6. The complexes **2b** and **2b′** differ in their anions. This also accounts for their presence in the unit cell of the non-centric space group *P*1.

Chiroptical Properties and Epimerization.—The chloro diastereomers **1a** and **1b** are configurationally stable in solution showing no significant epimerisation at 70 °C in benzene. The CD spectra of **1** (**1a** ≫ **1b**), **2** (**2b** ≫ **2a**) and **3** (**3a** > **3b**), shown in Fig. 7, reveal that the formation of **2b** takes place stereospecifically with almost complete inversion of configuration at the metal centre. The formation of **3a** and **3b**, proceeds with retention of configuration at the metal centre. The CD spectrum of **2b** with a R_{Ru} configuration is a mirror image of the 4-methylpyridine adduct **3a**. The absolute configuration of **3a** is assigned to S_{Ru}. Complexes which are epimers with an opposite configuration at the metal are known[1] to display CD spectra with a mirror image to each other. The CD spectrum of the chloro complex (**1a** ≫ **1b**) has the same sign as that of the 4Me-py adduct. This indicates a S_{Ru} configuration in the major isomer of **1** and **3** while the configuration is R_{Ru} in the optically pure PPh$_3$ adduct which has been characterised by X-ray analysis.

Conclusion

The present results clearly demonstrate, for the first time, the configurational changes involving half-sandwich chiral arene-ruthenium(II) Schiff-base complexes. The chirooptical properties of the chloro, phosphine and 4-methylpyridine adducts show a significant difference from the properties of closely related cyclopentadienylruthenium(II) chiral complexes. In arene systems the reactions are believed to proceed through an intermediate with a low activation barrier for inversion. In contrast, similar reactions in half-sandwich cyclopentadienyl-transition-metal complexes are known[4] to occur with retention of configuration at the metal centre, and involve an intermediate with a high energy barrier to inversion.

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