(η^6-Arene)ruthenium(II) complexes containing enantiomerically pure (β-aminoalkyl)phosphines or a (β-aminoalkyl) phosphinite: synthesis, stereochemical and kinetic studies

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The chiral P–N* ligands [(*S*)-2-(dimethylamino)-3-phenylpropyl]diphenylphosphine, (*S*)-phephos, **1**, [(*S*)-2-(dimethylamino)-2-phenylethyl]diphenylphosphine, (*S*)-phglyphos, **2**, [(*S*)-2-(dimethylamino)-3-methylbutyl]-diphenylphosphine, (*S*)-valphos, **3**, and [(+)-(2*S*,3*R*)-4-(dimethylamino)-3-methyl]-2-diphenylphosphinoxy-1,2-diphenylbutane, (+)-(2*S*,3*R*)-chiraldphos, **4**, reacted with [Ru(η^6-arene)Cl₂]₂ (arene = *p*-cymene, benzene or hexamethylbenzene), in dichloromethane or tetrahydrofuran solution, affording the corresponding [Ru(η^6-arene)-(P–N*)Cl₂] complexes, **5**, in which the P–N* acts as a monodentate P-bonded ligand. In methanol the same reactions easily afforded the corresponding chelate complexes [Ru(η^6-arene)(P–N*)Cl]Cl. Using ligands **1**–**3**, when the arene is *p*-cymene, 90:10 diastereomeric mixtures of the cationic complexes have been obtained while only one diastereomer was formed in the corresponding reactions when the arene is benzene or hexamethyl-benzene. The determination of the absolute configuration of the major products as R_{Ru},S_C diastereoisomers was made from the crystal structure and CD spectra comparison of the complex (R_{Ru},S_C)-[Ru(η^6-*p*-MeC₆H₄Pr^i)-(*S*-phglyphos)Cl]BF₄. Complexes [Ru(η^6-arene)(P–N*)Cl]Cl were also obtained by adding small amounts of methanol to solutions of [Ru(η^6-arene)(P–N*)Cl₂] in chloroform. A kinetic study, in CDCl₃ solution containing variable amounts of methanol, on the chelation process in the neutral species [Ru(η^6-arene)(P–N*)Cl₂] showed first-order behaviour of the k_{obs} values with the nucleophile (methanol) concentration. The pseudo-first-order rate constants are ascribed to replacement of Cl⁻ by a molecule of methanol. A reaction mechanism is proposed.

Introduction

Pseudo-tetrahedral transition metal complexes in which the metal is a stereogenic centre that contain optically active ligands are important in determining the role that the metal plays in the stereochemical course of reactions such as ligand substitution or migratory insertion.[1] This information could be useful for understanding the stereochemical course of homogeneous asymmetric reactions catalysed by transition metal complexes.[2] A literature search revealed that extensive studies have been performed on half-sandwich η^5-C₅H₅ complexes. Especially relevant are the stereochemical studies performed by Consiglio and Morandini[2a] on ruthenium complexes of the type [Ru(η^5-C₅H₅)X(prophos)] [prophos = (*R*)-1,2-propanediyl-bis(diphenylphosphine)]. Analogous η^6-areneruthenium complexes have been studied to a lesser extent. There is renewed interest in η^6-areneruthenium(II) complexes owing to the great stability of the metal–arene bond in these compounds[3] and their ability to act as effective precursors for catalytic asymmetric hydrogenation[4] and to promote the synthesis of complex organic compounds.[5] In addition, studies on the kinetics of CH₃CN–CD₃CN exchange equilibria in the isoelectronic complexes [Ru(η^5-C₅η₅)(CH₃CN)₃]⁺ and [Ru(η^6-C₆η₆)(CH₃CN)₃]²⁺ have evidenced different pathways for these two simple substitution reactions.[6]

Diastereomeric η^6-areneruthenium(II) chelate complexes of the type [Ru(η^6-arene)(L–L*)X]⁺ (L–L* = chiral chelating ligand; X = halide) are easily prepared from [Ru(η^6-arene)Cl₂]₂ by reaction with one equivalent of the bidentate chiral ligand;[1,2] in some cases the neutral species [Ru(η^6-arene)(L–L*)X₂], containing the L–L* as a monodentate ligand, were also isolated.[7] Neutral diastereomeric η^6-areneruthenium(II) chelate complexes were also obtained, in these reactions, using chiral chelating anions. Among the complexes of the latter group are diastereomeric ruthenacycles.[8] Diastereomeric pseudo-tetrahedral η^6-areneruthenium(II) complexes are often configurationally unstable at the stereogenic metal centre and epimerization at this centre can occur.[9]

We report here the synthesis of η^6-areneruthenium(II) complexes of the type [Ru(η^6-arene)(P–N*)Cl₂] (P–N* = [(*S*)-2-(dimethylamino)-3-phenylpropyl]diphenylphosphine, (*S*)-phephos, **1**; [(*S*)-2-(dimethylamino)-2-phenylethyl]diphenyl-phosphine, (*S*)-phglyphos, **2**; [(*S*)-2-(dimethylamino)-3-methyl-butyl]diphenylphosphine, (*S*)-valphos, **3**; or (+)-(2*S*,3*R*)-4-(dimethylamino)-3-methyl-2-diphenylphosphinoxy-1,2-di-phenylbutane, (+)-(2*S*,3*R*)-chiraldphos, **4**), in which the P–N* ligand is monodentate P-bonded (see Chart 1). The ring closure processes affording the diastereomeric ionic complexes [Ru(η^6-arene)(P–N*)Cl]Cl are studied. On the basis of kinetic data the Cl⁻ replacement can be considered as a bimolecular solvolytic process due to the attack of methanol at co-ordinated chloride. The kinetic control of the asymmetric induction in the formation of the chelate complexes [Ru(η^6-arene)(P–N*)Cl]Cl is discussed. The crystal structure of [Ru(η^6-*p*-MeC₆H₄Pr^i)(*S*-

(S)-Phephos **1**

(S)-Phglyphos **2**

(S)-Valphos **3**
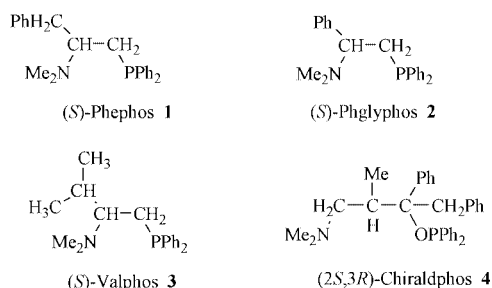
(2S,3R)-Chiraldphos **4**

Chart 1

phephos)Cl$_2$], **5a**, is also reported. In order to assign the absolute configuration of the diastereomer formed as the only or major product in the ring closure process, the structure of [Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(*S*-phglyphos)Cl]BF$_4$ was determined by X-ray methods.

Experimental

An established method was used to prepare the compound [Ru(η^6-C$_6$Me$_6$)Cl$_2$]$_2$.[10] (+)-(2S,3R)-chiraldphos, **4**, was prepared starting from the corresponding chiral aminoalcohol by a previously described procedure.[11] All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. IR spectra were obtained as Nujol mulls on KBr plates using a Perkin-Elmer FTIR 1720 spectrometer, ^{1}H and ^{31}P-{^{1}H} NMR spectra on a Bruker AMX R300. ^{1}H NMR spectra were referenced to internal tetramethylsilane and ^{31}P-{^{1}H} spectra to external 85% H$_3$PO$_4$; positive chemical shifts for all nuclei are to higher frequency. NMR data for complexes **5**–**13** are reported in Tables 1 and 2. Circular dichroism (CD) spectra were recorded on a JASCO J-500 spectrophotometer. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

Preparations

[β-(Dimethylamino)alkyl]diphenylphosphines 1–3. The procedure previously reported was modified.[12] The procedure for the preparation of (*S*)-phephos **1** is typical. Triphenylphosphine (2.29 g, 8.75 mmol) was slowly added to a stirred solution of sodium (0.443 g, 18.8 mmol) in liquid ammonia (70 mL) at −78 °C. An immediate reaction took place and the solution became deep orange. After about 2 h, (*S*)-2-(dimethylamino)-3-phenylpropyl chloride hydrochloride (2.05 g, 8.75 mmol) was added at − 78 °C. The resulting mixture was stirred for 12 h. During this time the ammonia evaporated and a white solid was obtained. It was extracted 3 times with a total of 30 mL of hexane. Removal of the hexane left a white solid in 50% yield. The compound (*S*)-phglyphos **2**, white solid, 20% yield, and (*S*)-valphos **3**, colorless syrup, 95% yield, were obtained similarly.

[Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(*S*-phephos)Cl$_2$] 5a. The following procedure for the preparation of **5a** is typical and was used for all [Ru(η^6-*p*-MeC$_6$H$_4$Pr)(1–3)Cl$_2$] complexes. A solution of 0.113 g (0.326 mmol) of (*S*)-phephos in dichloromethane (10 mL) was added to a stirred solution of [Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) in the same solvent (25 mL). During the addition the orange solution changed to a deep red. After 15 min the reaction mixture was concentrated to *ca.* 5 mL and by slow addition of hexane (30 mL) a red-orange microcrystalline powder precipitated. It was separated by filtration, washed with hexane (3 × 5 mL) and dried. Yield 85%. Calc. for C$_{33}$H$_{40}$Cl$_2$NPRu: C, 60.64; H, 6.17; Cl, 10.85; N, 2.14. Found: C, 60.78, H, 6.26; Cl, 11.02; N, 2.18%.

[Ru(η^6-C$_6$H$_6$)(*S*-phephos)Cl$_2$] 5b. The following procedure for the preparation of **5b** is typical and was used for all [Ru(η^6-C$_6$H$_6$)(1–3)Cl$_2$] complexes. (*S*)-phephos (0.111 g, 0.320 mmol) was added to a suspension of [Ru(η^6-C$_6$H$_6$)Cl$_2$]$_2$ (0.080 g, 0.16 mmol) in dichloromethane (30 mL). The reaction mixture was then stirred for approximately 2 h at room temperature until no brown solid remained. The resulting red-orange solution was reduced to *ca.* 5 mL and by addition of hexane (30 mL) an orange powder precipitated. It was separated by filtration, washed with hexane (3 × 5 mL) and dried. Yield 80%. Calc. for C$_{29}$H$_{32}$Cl$_2$NPRu: C, 58.29; H, 5.4; Cl, 11.87; N, 2.34. Found: C, 58.31, H, 5.45; Cl, 11.90; 5.45%.

[Ru(η^6-C$_6$Me$_6$)(*S*-phephos)Cl$_2$] 5c. The following procedure for the preparation of **5c** is typical and was used for all [Ru(η^6-C$_6$Me$_6$)(1–3)Cl$_2$] complexes. [Ru(η^6-C$_6$Me$_6$)Cl$_2$]$_2$ (0.096 g, 0.144 mmol) was dissolved in 20 mL of chloroform and a solution of (*S*)-phephos (0.100 g, 0.288 mmol) in the same solvent (5 mL) was added. The resulting orange solution was stirred at room temperature for 30 min then, the solvent was reduced to *ca.* 5 mL and by addition of hexane (40 mL) an orange powder was obtained. It was separated by filtration, washed with hexane (4 × 5 mL) and dried. Yield: 88%. Calc. for C$_{35}$H$_{44}$Cl$_2$NPRu: C, 61.67; H, 6.51; Cl, 10.40; N, 2.05. Found: C, 61.52, H, 6.40; Cl, 10.60; N, 2.01.

[Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(*S*-phglyphos)Cl$_2$] 6a. Red-orange powder. Yield: 83%. Calc. for C$_{32}$H$_{38}$Cl$_2$NPRu: C, 60.09; H, 5.99; Cl, 11.09; N, 2.19. Found: C, 60.20; H, 6.05; Cl, 11.21; N, 2.15%.

[Ru(η^6-C$_6$H$_6$)(*S*-phglyphos)Cl$_2$] 6b. Orange powder. Yield 78%. Calc. for C$_{28}$H$_{30}$Cl$_2$NPRu: C, 57.64; H, 5.18; Cl, 11.15; N, 2.40. Found: C, 57.75, H, 5.19; Cl, 12.18; N, 2.38%.

[Ru(η^6-C$_6$Me$_6$)(*S*-phglyphos)Cl$_2$] 6c. Orange powder. Yield 86%. Calc. for C$_{34}$H$_{42}$Cl$_2$NPRu: C, 61.16; H, 6.34; Cl, 10.62; N, 2.10. Found: C, 61.30, H, 6.40; Cl, 10.79; N, 2.06%.

[Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(*S*-valphos)Cl$_2$] 7a. Red-orange powder. Yield 88%. Calc. for C$_{29}$H$_{40}$Cl$_2$NPRu: C, 57.52; H, 6.66; Cl, 11.71; N, 2.31. Found: C, 57.59, H, 6.68; Cl, 11.69; N, 2.29%.

[Ru(η^6-C$_6$H$_6$)(*S*-valphos)Cl$_2$] 7b. Orange powder. Yield: 79%. Calc. for C$_{25}$H$_{32}$Cl$_2$NPRu: C, 54.65; H, 5.87; Cl, 12.90; N, 2.55. Found: C, 54.80, H, 5.96; Cl, 12.69; N, 2.50%.

[Ru(η^6-C$_6$Me$_6$)(*S*-valphos)Cl$_2$] 7c. Orange powder. Yield: 86%. Calc. for C$_{31}$H$_{44}$Cl$_2$NPRu: C, 58.76; H, 7.00; Cl, 11.19; N, 2.21. Found: C, 58.90, H, 7.10; Cl, 11.10; N, 2.18%.

[Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(chiraldphos)Cl$_2$] 8a. A solution of chiraldphos (0.153 g, 0.326 mmol) in tetrahydrofuran (10 mL) was added to a stirred solution of [Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) in the same solvent (25 mL). During the addition the orange solution changed to a deep red. After 10 min the reaction mixture was concentrated to *ca.* 5 mL and by slow addition of hexane (30 mL) a red-orange microcrystalline powder precipitated. It was separated by filtration, washed with cold toluene (3 mL) and dried. Yield 75%. Calc. for C$_{48}$H$_{40}$Cl$_2$NOPRu: C, 63.64; H, 6.25; Cl, 9.12; N, 1.81. Found: C, 63.79, H, 6.30; Cl, 9.19; N, 1.79%.

[Ru(η^6-*p*-MeC$_6$H$_4$Pr^i){PhPCH$_2$CH(CH$_2$Ph)NHMe$_2$}Cl$_2$]PF$_6$ 9. NH$_4$PF$_6$ (0.019 g, 0.12 mmol) was added under stirring to a solution of [Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)(*S*-phephos)Cl$_2$] (0.080 g, 0.12 mmol) in dichloromethane (10 mL). After 1 h the solvent was reduced to *ca.* 3 mL and by addition of hexane (20 mL) an orange powder was obtained. It was separated by filtration, washed with hexane (5mL) and dried. Yield: 88%. IR (KBr, Nujol): *ν*(PF$_6$) 840 cm^{-1}. Calc. for C$_{33}$H$_{41}$Cl$_2$F$_6$NP$_2$Ru: C, 49.57; H, 5.17; Cl, 8.87; N, 1.75. Found: C, 49.51, H, 5.15; Cl, 8.89;

N, 1.74%. ^{1}H NMR (CDCl$_3$): δ 0.85 and 1.1 (2 d, 6 H, $J = 7$, CHCH$_3$), 1.84 (s, 3 H, CH$_3$), 2.11 (m, 1 H, CH), 2.52 (sept, 1 H, $J = 7$, CHCH$_3$), 2.65–2.85 (m, 4 H, 2CH$_2$), 2.90 and 2.95 (s, 6 H, NCH$_3$), 4.86 (d, 1 H, $J = 5.9$, CH$_{cy}$), 5.03 (d, 1 H, $J = 5.9$, CH$_{cy}$), 5.08 (d, 1 H, $J = 5.9$, CH$_{cy}$), 5.28 (d, 1 H, $J = 5.9$, CH$_{cy}$), 6.99–7.21 (m, 5 H, CH$_{Ar}$), 7.37–7.47 (m, 6 H, CH$_{Ar}$), 7.69 (t, 2 H, $J = 9$ Hz, CH$_{Ar}$), 8.07 (m, 2 H, CH$_{Ar}$) and 8.35 (br s, 1 H, NH$^+$). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 22.1 (s) and -143.8 (sept, J(PF) = 717 Hz, PF$_6^-$). $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 90 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-p-MeC$_6$H$_4$Pr^i)(S-phephos)Cl]Cl 10a. The following procedure for the preparation of **10a** is typical and was used for all chelate complexes. (S)-phephos (0.135 g, 0.389 mmol) was added to a stirred solution of [Ru(η^6-p-MeC$_6$-H$_4$Pr^i)Cl$_2$]$_2$ (0.120 g, 0.195 mmol) in CH$_3$OH (25 mL) at room temperature. After 1 h the solvent was removed under reduced pressure and the residue recrystallized from CH$_2$Cl$_2$–hexane to give an orange powder. ^{1}H and ^{31}P-{^{1}H} NMR spectra (see Table 2) showed that the orange solid was a diastereomeric mixture of **10a** and **10a′** in the ratio 90 : 10. From a solution of the diastereomeric mixture left for 72 h at ambient temperature in chloroform **10a** was obtained as pure sample. Yield 70%. Calc. for C$_{33}$H$_{40}$Cl$_2$NPRu: C, 60.64; H, 6.17; Cl, 10.85; N, 2.14. Found: C, 60.75, H, 6.19; Cl, 10.79; N, 2.16%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 91 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-C$_6$H$_6$)(S-phephos)Cl]Cl 10b. Orange powder. Yield 81%. Calc. for C$_{29}$H$_{32}$Cl$_2$NPRu: C, 58.29; H, 5.4; Cl, 11.87; N, 2.34. Found: C, 58.33, H, 5.43; Cl, 11.90; N, 2.30%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 95.4 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-C$_6$Me$_6$)(S-phephos)Cl]Cl 10c. Orange microcrystalline solid. Yield: 80%. Calc. for C$_{35}$H$_{44}$Cl$_2$NPRu: C, 61.67; H, 6.51; Cl, 10.48; N, 2.05. Found: C, 61.73, H, 6.58; Cl, 10.58; N, 2.07%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 98 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-p-MeC$_6$H$_4$Pr^i)(S-phglyphos)Cl]Cl 11a. Red-orange powder. Yield 69%. Calc. for C$_{32}$H$_{38}$Cl$_2$NPRu: C, 60.09; H, 5.99; Cl, 11.09; N, 2.19. Found: C, 60.15; H, 6.03; Cl, 11.11; N, 2.15%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 94.7 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-p-MeC$_4$H$_4$Pr^i)(S-phglyphos)Cl]BF$_4$ 11a″. NaBF$_4$ (0.014 g, 0.125 mmol) was added to a solution of complex **10a** (0.080 g, 0.125 mmol) in 5 mL of methanol. The reaction mixture was stirred for 12 h, and the orange microcrystalline compound that precipitated filtered off and washed with water and diethyl ether. Yield: 70%. The mother liquors were vacuum-evaporated to dryness. The residue was dissolved in dichloromethane and by addition of hexane an orange solid was obtained. Yield: 15%. Both reaction products showed only one resonance at δ 48.03 in their ^{31}P-{^{1}H} NMR spectra (CDCl$_3$). Calc. for C$_{32}$H$_{38}$BClF$_4$NPRu: C, 55.63; H, 5.54; Cl, 5.13; N, 2.03. Found: C, 55.70, H, 5.59; Cl, 5.30; N, 1.99%. ^{1}H NMR (CDCl$_3$): δ 1.26 and 1.30 (2 d, 6 H, $J = 7$, CHCH$_3$), 1.36 (s, 3 H, CH$_3$), 2.85 (m, 4 H, 2CH$_2$), 2.96 and 3.11 (s, 6 H, NCH$_3$), 3.50 (m, 1 H, CHCH$_3$), 4.48 (m, 1 H, CH), 5.17 (d, 1 H, $J = 6$, CH$_{cy}$), 5.29 (m, 1 H, CH$_{cy}$), 5.97 (d, 1 H, $J = 6$, CH$_{cy}$), 6.17 (d, 1 H, $J = 6$ Hz, CH$_{cy}$) and 7.35–7.62 (m, 15 H, CH$_{Ar}$). $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 97 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-C$_6$H$_6$)(S-phglyphos)Cl]Cl 11b. Red-orange powder. Yield: 78%. Calc. for C$_{28}$H$_{30}$Cl$_2$NPRu: C, 57.64; H, 5.18; Cl, 12.15; N, 2.40. Found: C, 57.71, H, 5.21; Cl, 12.27; N, 2.35%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 96 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-C$_6$Me$_6$)(S-phglyphos)Cl]Cl 11c. Orange powder. Yield 86%. Calc. for C$_{34}$H$_{42}$Cl$_2$NPRu: C, 61.16; H,

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-p-MeC$_6$H$_4$Pr^i)(S-valphos)Cl]Cl 12a. Red-orange powder. Yield 88%. Calc. for C$_{29}$H$_{40}$Cl$_2$NPRu: C, 57.52; H, 6.66; Cl, 11.71; N, 2.31. Found: C, 57.63, H, 6.71; Cl, 11.77; N, 2.25%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 92.7 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-C$_6$H$_6$)(S-valphos)Cl]Cl 12b. Orange powder. Yield 79%. Calc. for C$_{25}$H$_{32}$Cl$_2$NPRu: C, 54.65; H, 5.87; Cl, 12.90; N, 2.55. Found: C, 54.76, H, 5.95; Cl, 12.70; N, 2.56%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 99 (ohm^{-1} cm^2 mol^{-1}).

($R_{\mathbf{Ru}}$,$S_{\mathbf{C}}$)-[Ru(η^6-C$_6$Me$_6$)(S-valphos)Cl]Cl 12c. Orange powder. Yield 86%. Calc. for C$_{31}$H$_{44}$Cl$_2$NPRu: C, 58.76; H, 7.00; Cl, 11.19; N, 2.21. Found: C, 58.88, H, 7.09; Cl, 11.09; N, 2.17%. $\varLambda$ (5 × 10^{-4}–10^{-3} M, CH$_3$OH) 101 (ohm^{-1} cm^2 mol^{-1}).

[Ru(η^6-p-MeC$_6$H$_4$Pr^i)(chiraldphos)Cl]Cl 13a and 13a′. Red-orange microcrystalline solid, 60 : 40 diastereomeric mixture. Yield 75%. Calc. for C$_{48}$H$_{40}$Cl$_2$NOPRu: C, 63.64; H, 6.25; Cl, 9.12; N, 1.81. Found: C, 63.77, H, 6.31; Cl, 9.20; N, 1.77%.

Kinetics

The reactions were followed in CDCl$_3$ containing variable amounts of methanol, ethanol, 2-propanol or 2-methyl-2-propanol by recording the decrease in intensity of the ^{31}P-{^{1}H} NMR resonance of the starting material. The alcohol solvents were purified and dried by standard methods. The kinetic runs were performed by adding a known volume of methanol (or of alcohol) to a solution of known concentration of [Ru-(η^6-arene)(P–N*)Cl$_2$] in CDCl$_3$. All the concentrations are expressed in moles per kilogram of solvent. The kinetics was studied under pseudo-first-order conditions with the methanol concentration at least 20 times that of the complex. Under these conditions, keeping constant the methanol concentration, no variations in the rate constant were observed when the concentration of the complex was varied. The kinetics are first order with respect to the free methanol concentration and the plots of k_{obs} vs. [CH$_3$OH] were linear with no significant intercepts. The rate constants have been calculated as the means of three kinetic runs. Activation parameters were obtained from the Eyring equation.

Crystal structure determination of complexes 5a and 11a″

The intensity data of complex **5a** were collected at room temperature (293(2) K) on a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and the θ–2θ scan technique. A correction for absorption was made [maximum and minimum value for the transmission coefficient 1.0000 and 0.7519].[13] The intensity data of **11a″** were collected at room temperature (293(2) K) on a Bruker AMX SMART 1000 single-crystal diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) equipped with area detector. The SMART 1000 package was used for data reduction and absorption correction. Crystallographic and experimental details are summarized in Table 3.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into geometrically calculated positions and refined riding on the corresponding carbon atoms.

All calculations were carried out on the DIGITAL Alpha-Station 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del Consiglio Nazionale delle Ricerche, Parma, using the SHELX 97 systems of crystallographic computer programs.[14,15]

Table 1 ^{1}H and ^{31}P-$\{^1$H$\}$ NMR data for the complexes [Ru(η^6-arene) (P–N*)Cl$_2$]^a

Complex	^{31}P-$\{^1$H$\}$ ^{b}	^{1}H ^{c}	
		η^6-arene	P–N*
5a	21.1 (s)	0.67/0.87 (2d, 6 H, J 6.9/6.9, CHCH$_3$), 1.81 (s, 3 H, CH$_3$), 2.49 (sept, 1 H, J 6.9, CHCH$_3$), 4.88 (d, 1 H, J 5.9, CH), 5.05 (br s, 2 H, CH), 5.26 (d, 1 H, J 5.9, CH)	1.89 (s, 6 H, NCH$_3$), 2.09 (m, 1 H, CH), 2.67–2.90 (m, 4 H, CH$_2$), 6.97 (d, 2 H, J 7, CH$_{Ar}$), 7.21 (m, 3 H, CH$_{Ar}$), 7.37 (m, 2 H, CH$_{Ar}$), 7.47 (m, 4 H, CH$_{Ar}$), 7.69 (t, 2 H, J 9 CH$_{Ar}$), 8.07 (m, 2 H, CH$_{Ar}$)
5b	22.2 (s)	5.24 (br s, 6 H, CH)	1.87 (s, 6 H, NCH$_3$), 2.14 (m, 1 H, CH), 2.58–2.70 (m, 4 H, CH$_2$), 6.94 (d, 2 H, J 7, CH$_{Ar}$), 7.14 (m, 3 H, CH$_{Ar}$), 7.30–7.51 (m, 6 H, CH$_{Ar}$), 7.65 (t, 2 H, J 9 CH$_{Ar}$), 7.96 (m, 2 H, CH$_{Ar}$)
5c	23.0 (s)	1.67 (s, 18 H, CH$_3$)	1.88 (s, 6 H, NCH$_3$), 2.15 (m, 1 H, CH), 2.51–2.80 (m, 4 H, CH$_2$), 6.87 (d, 2 H, J 7, CH$_{Ar}$), 6.96–7.20 (m, 4 H, CH$_{Ar}$), 7.39 (m, 4 H, CH$_{Ar}$), 7.66 (m, 1 H, CH$_{Ar}$), 7.86 (t, 2 H, J 9 CH$_{Ar}$), 8.09 (m, 2 H, CH$_{Ar}$)
6a	21.5 (s)	0.75/0.83 (2d, 6 H, J 6.6/6.7, CHCH$_3$), 1.81 (s, 3 H, CH$_3$), 2.51 (sept, 1 H, J 6.8, CHCH$_3$), 4.96 (d, 1 H, J 6, CH), 5.07 (d, 1 H, J 6, CH), 5.1 (d, 1 H, J 6, CH), 5.23 (d, 1 H, J 6, CH)	1.78 (s, 6 H, NCH$_3$), 3.17 (m, 1 H, CH), 3.25 (br m, 2 H, CH$_2$), 6.74 (d, 2 H, J 7, CH$_{Ar}$), 6.96 (m, 3 H, CH$_{Ar}$), 7.15–7.25 (m, 6 H, CH$_{Ar}$), 7.69 (t, 2 H, J 9, CH$_{Ar}$), 7.96 (m, 2 H, CH$_{Ar}$)
6b	22.3 (s)	5.26 (s, 6 H, CH)	1.79 (s, 6 H, NCH$_3$), 3.15 (m, 1 H, CH), 3.26 (br m, 2 H, CH$_2$), 6.73 (d, 2 H, J 7, CH$_{Ar}$), 6.95 (m, 3 H, CH$_{Ar}$), 7.14–7.23 (m, 6 H, CH$_{Ar}$), 7.71 (t, 2 H, J 9, CH$_{Ar}$), 7.98 (m, 2 H, CH$_{Ar}$)
6c	23.2 (s)	1.69 (s, 18 H, CH)	1.78 (s, 6 H, NCH$_3$), 3.18 (m, 1 H, CH), 3.25 (br m, 2 H, CH$_2$), 6.76 (d, 2 H, J 7, CH$_{Ar}$), 6.95 (m, 3 H, CH$_{Ar}$), 7.15–7.24 (m, 6 H, CH$_{Ar}$), 7.70 (t, 2 H, J 9, CH$_{Ar}$), 7.98 (m, 2 H, CH$_{Ar}$)
7a	22.6 (s)	0.78/0.88 (2d, 6 H, J 6.9/6.9, CHCH$_3$), 1.79 (s, 3 H, CH$_3$), 2.49 (sept, 1 H, J 6.9, CHCH$_3$), 4.90 (d, 1 H, J 6, CH), 5.08 (d, 1 H, J 6, CH), 5.12 (d, 1 H, J 6, CH), 5.18 (d, 1 H, J 6, CH)	0.61/0.63 (2d, 6 H, J 7/7, CHCH$_3$), 1.54 (m, 1 H, CHCH$_3$), 1.85 (s, 6 H, NCH$_3$), 2.20 (m, 2 H, CH$_2$), 2.72 (m, 1 H, CH), 7.34–7.54 (m, 6 H, CH$_{Ar}$), 7.92–8.11 (m, 4 H, CH$_{Ar}$)
7b	23.1 (s)	5.3 (s, 6 H, CH)	0.61/0.63 (2d, 6 H, J 7/7, CHCH$_3$), 1.55 (m, 1 H, CHCH$_3$), 1.87 (s, 6 H, NCH$_3$), 2.19 (m, 2 H, CH$_2$), 2.75 (m, 1 H, CH), 7.32–7.56 (m, 6 H, CH$_{Ar}$), 7.98–8.14 (m, 4 H, CH$_{Ar}$)
7c	24.3 (s)	1.67 (s, 18 H, CH$_3$)	0.61/0.63 (2d, 6 H, J 7/7, CHCH$_3$), 1.54 (m, 1 H, CHCH$_3$), 1.84 (s, 6 H, NCH$_3$), 2.20 (m, 2 H, CH$_2$), 2.74 (m, 1 H, CH), 7.39–7.44 (m, 6 H, CH$_{Ar}$), 8.02–8.11 (m, 4 H, CH$_{Ar}$)
8a	133.8 (s)	0.87 (m, 6 H, CHCH$_3$), 1.87 (s, 3 H, CH$_3$), 2.39 (m, 1 H, CHCH$_3$), 4.85 (d, 1 H, J 5.5, CH), 5.21 (br s, 2 H, CH), 5.28 (d, 1 H, J 5.5, CH)	1.30 (d, 3 H, J 7.2, CHCH$_3$), 2.04 (s, 6 H, NCH$_3$), 2.89 (m, 3 H, CH, CH$_2$), 3.8 (m, 2 H, CH$_2$) 2.74 (m, 1 H, CH), 6.8 (m, 8 H, CH$_{Ar}$), 7.25–7.80 (m, 12 H, CH$_{Ar}$)

^{a} δ values with J in Hz; solvent = CDCl$_3$. ^{b} H$_3$PO$_4$ as external standard. ^{c} SiMe$_4$ is the standard.

CCDC reference number 186/2086.

See http://www.rsc.org/suppdata/dt/b0/b003514i/ for crystallographic files in .cif format.

Results and discussion

Synthesis

The chiral P,N-ligands **1**–**4** (Chart 1) were prepared starting from the corresponding chiral aminoalcohol, modifying in some cases the procedure reported;[11,12] they represent a series of widely different steric and, for **4**, electronic properties. Differently from **1**–**3**, which form by chelation to a metal centre five-membered ring, the aminophosphinite ligand **4** gives a seven-membered ring; in addition the phosphorus basicity in **4** is lower than in **1**–**3**.

[Ru(η-arene)(P–N*)Cl$_2$] complexes (P–N* = (S)-phephos, arene = p-cymene, **5a**, benzene, **5b**, or hexamethylbenzene, **5c**; P–N* = (S)-phglyphos, arene = p-cymene, **6a**, benzene, **6b**, or hexamethylbenzene, **6c**; P–N* = (S)-valphos, arene = p-cymene, **7a**, benzene, **7b**, or hexamethylbenzene, **7c**; P–N* = (2S,3R)-chiraldphos, arene = p-cymene, **8a**, benzene, **8b**, or hexamethylbenzene, **8c**) were obtained in high yield upon reaction of the corresponding [Ru(η^6-arene)Cl$_2$]$_2$ with 1 equivalent of the P–N* ligand, in dichloromethane or tetrahydrofuran as solvent, at room temperature. They are orange solids, stable to air in the solid state and to a limited extent in benzene, toluene and dichloromethane solution. On standing in methanol or chlorinated solvents for a long time they afford green solids that do not contain the chiral ligand. They were characterized by microanalysis, IR and ^{1}H and ^{31}P$\{$-^{1}H$\}$ NMR spectroscopy; the crystal structure of compound **5a** was fully established by X-ray analysis.

A view of complex **5a** with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 4. The Ru atom displays a three legged, piano-stool type of co-ordination involving an η^6-co-ordinated p-cymene group (the six Ru–C bond distances are in the range 2.206(4)–2.227(4) Å), two chlorine atoms (Ru–Cl 2.420(1) and 2.425(1) Å) and a P atom from the chiral ligand (Ru–P(1) 2.369(1) Å). The co-ordination geometry can also be described as pseudo-tetrahedral if the centroid of the η^6-ring is taken as a single site. The chiral centre C(2) in the ligand possesses an S configuration.

In accordance with their formulation, compounds **5**–**8** are not conducting in acetone solution. NMR data are reported in Table 1. In the ^{1}H NMR spectra, in CDCl$_3$ solution, the N(CH$_3$)$_2$ group of the co-ordinated ligands **1**–**4** displays a singlet at δ value nearly that of the "free" ligand, indicating that the ligand is monodentate P-bonded. The ^{31}P-$\{^1$H$\}$ NMR spectra, in CDCl$_3$ solution, exhibit a singlet in the range δ 21.1–24.3 for the complexes with the aminophosphine ligands **1**–**3** and at δ 133.8, in the phosphinoxy-region, for the one with ligand **4**. An attempt to induce ring closure of the P–N* ligand in **5a** by reaction with NH$_4$PF$_6$, in dichloromethane solution, afforded $\{$[Ru(η^6-p-MeC$_6$H$_4$Pr^i)]$\{$Ph$_2$PCH$_2$CH(CH$_2$Ph)NHMe$_2\}$Cl$_2]$PF$_6$, **9**, by protonation of the free nitrogen atom. Compound **9** is an orange solid, stable to air in the solid state and in solution. In methanol solution it is a 1:1 electrolyte. The ^{1}H and ^{31}P-$\{^1$H$\}$, in CDCl$_3$ solution, are very similar to those of the starting

Table 2 ^{1}H and ^{31}P-{^{1}H} NMR data for the complexes [Ru(η^6-arene) (P–N*)Cl]Cl^a

Complex	^{31}P-{^{1}H}^{b}	^{1}H^c η^6-arene	P–N*
10a	49.5 (s)	1.28/1.33 (2d, 6 H, J 6.6/6.6, CHCH$_3$), 1.36 (s, 3 H, CH$_3$), 3.58 (sept, 1 H, J 6.7, CHCH$_3$), 5.15 (d, 1 H, J 6, CH), 5.37 (br s, 1 H, CH), 5.99 (d, 1 H, J 6, CH), 6.23 (d, 1 H, J 6, CH)	2.64–2.78 (m, 4 H, CH$_2$), 3.2 (m, 1 H, CH), 3.27 (s, 3 H, NCH$_3$), 3.42 (s, 3 H, NCH$_3$), 7.28–7.65 (m, 15 H, CH$_{Ar}$)
10a′	45.9 (s)	1.36/1.41 (2d, 6 H, J 6.6/6.6, CHCH$_3$), 1.44 (s, 3 H, CH$_3$), 3.62 (sept, 1 H, J 6.7, CHCH$_3$), 5.23 (d, 1 H, J 6, CH), 5.44 (br s, 1 H, CH), 6.06 (d, 1 H, J 6, CH), 6.31 (d, 1 H, J 6, CH)	2.72–2.86 (m, 4 H, CH$_2$), 3.2 (m, 1 H, CH), 3.35 (s, 3 H, NCH$_3$), 3.50 (s, 3 H, NCH$_3$), 7.38–7.72 (m, 15 H, CH$_{Ar}$)
10b	48.7 (s)	5.86 (br s, 6 H, CH)	2.70–2.79 (m, 4 H, CH$_2$), 3.3 (m, 1 H, CH), 3.50 (s, 3 H, NCH$_3$), 3.53 (s, 3 H, NCH$_3$), 7.28–7.75 (m, 15 H, CH$_{Ar}$)
10c	47.2 (s)	2.04 (s, 18 H, CH$_3$)	2.65–2.76 (m, 4 H, CH$_2$), 2.98 (m, 1 H, CH), 3.10 (s, 3 H, NCH$_3$), 3.21 (s, 3 H, NCH$_3$), 7.18–7.55 (m, 15 H, CH$_{Ar}$)
11a	48.1 (s)	1.29/1.32 (2d, 6 H, J 6/6, CHCH$_3$), 1.37 (s, 3 H, CH$_3$), 3.54 (m, 1 H, CHCH$_3$), 5.12 (d, 1 H, J 6, CH), 5.33 (br s, 1 H, CH), 6.09 (d, 1 H, J 6, CH), 6.24 (d, 1 H, J 6, CH)	2.80 (m, 2 H, CH$_2$), 2.99 (s, 3 H, NCH$_3$), 3.15 (s, 3 H, NCH$_3$), 4.52 (m, 1 H, CH), 7.34–7.64 (m, 15 H, CH$_{Ar}$)
11a′	44.3 (s)	1.38/1.40 (2d, 6 H, J 6/6, CHCH$_3$), 1.46 (s, 3 H, CH$_3$), 3.62 (m, 1 H, CHCH$_3$), 5.22 (d, 1 H, J 6, CH), 5.42 (br s, 1 H, CH), 6.18 (d, 1 H, J 6, CH), 6.33 (d, 1 H, J 6, CH)	2.90 (m, 2 H, CH$_2$), 3.09 (s, 3 H, NCH$_3$), 3.25 (s, 3 H, NCH$_3$), 4.60 (m, 1 H, CH), 7.42–7.72 (m, 15 H, CH$_{Ar}$)
11b	48.5 (s)	5.80 (s, 6 H, CH)	2.82 (m, 2 H, CH$_2$), 2.95 (m, 1 H, CH), 3.05 (s, 3 H, NCH$_3$), 4.50 (m, 1 H, CH), 7.35–7.65 (m, 15 H, CH$_{Ar}$)
11c	46.3 (s)	1.96 (s, 18 H, CH)	2.80 (m, 2 H, CH$_2$), 2.91 (m, 1 H, CH), 3.00 (s, 3 H, NCH$_3$), 4.48 (m, 1 H, CH), 7.36–7.65 (m, 15 H, CH$_{Ar}$)
12a	48.4 (s)	1.26/1.32 (2d, 6 H, J 6.9/6.9, CHCH$_3$), 1.29 (s, 3 H, CH$_3$), 3.21 (m, 1 H, CHCH$_3$), 5.09 (d, 1 H, J 6, CH), 5.29 (br s, 1 H, CH), 6.47 (d, 1 H, J 6, CH), 6.88 (d, 1 H, J 6, CH)	0.86/1.08 (2d, 6 H, J 7/7, CHCH$_3$), 2.26 (m, 1 H, CHCH$_3$), 2.60 (m, 1 H, CH), 2.77 (m, 2 H, CH$_2$), 3.32 (s, 3 H, NCH$_3$), 3.44 (s, 3 H, NCH$_3$), 7.34–7.54 (m, 6 H, CH$_{Ar}$), 7.35–7.49 (m, 2 H, CH$_{Ar}$), 7.50–7.61 (m, 8 H, CH$_{Ar}$)
12a′	45.1 (s)	1.35/1.41 (2d, 6 H, J 6.9/6.9, CHCH$_3$), 1.37 (s, 3 H, CH$_3$), 3.29 (m, 1 H, CHCH$_3$), 5.17 (d, 1 H, J 6, CH), 5.39 (br s, 1 H, CH), 6.56 (d, 1 H, J 6, CH), 6.96 (d, 1 H, J 6, CH)	0.95/1.96 (2d, 6 H, J 7/7, CHCH$_3$), 2.35 (m, 1 H, CHCH$_3$), 2.68 (m, 1 H, CH), 2.85 (m, 2 H, CH$_2$), 3.40 (s, 3 H, NCH$_3$), 4.02 (s, 3 H, NCH$_3$), 7.40–7.52 (m, 2 H, CH$_{Ar}$), 7.56–7.68 (m, 8 H, CH$_{Ar}$)
12b	49.1 (s)	5.84 (s, 6 H, CH)	0.83/1.02 (2d, 6 H, J 7/7, CHCH$_3$), 2.24 (m, 1 H, CHCH$_3$), 2.71 (m, 1 H, CH), 2.78 (m, 2 H, CH$_2$), 3.21 (s, 3 H, NCH$_3$), 3.31 (s, 3 H, NCH$_3$), 7.34–7.54 (m, 6 H, CH$_{Ar}$), 7.30–7.45 (m, 2 H, CH$_{Ar}$), 7.52–7.64 (m, 8 H, CH$_{Ar}$)
12c	47.5 (s)	1.94 (s, 18 H, CH$_3$)	0.80/1.05 (2d, 6 H, J 6.0/6.0, CHCH$_3$), 2.2 (m, 1 H, CHCH$_3$), 2.81 (m, 1 H, CH), 2.56 (m, 2 H, CH$_2$), 2.76 (m, 2 H, CH$_2$), 2.81 (m, 1 H, CH), 3.00 (s, 3 H, NCH$_3$), 3.09 (s, 3 H, NCH$_3$), 7.35–7.40 (m, 2 H, CH$_{Ar}$), 7.47–7.59 (m, 8 H, CH$_{Ar}$)
13a	108.0 (s)	0.91 (m, 6 H, CHCH$_3$), 1.91 (s, 3 H, CH$_3$), 2.52 (m, 1 H, CHCH$_3$), 4.96 (d, 1 H, J 5.5, CH), 5.32 (br s, 2 H, CH), 5.39 (d, 1 H, J 6, CH), 6.96 (d, 1 H, J 5.5, CH)	1.35 (d, 3 H, J 7.2, CHCH$_3$), 2.78 (m, 1 H, CH), 2.90 (m, 3 H, CH, CH$_2$), 3.01 (s, 3 H, NCH$_3$) 3.71 (m, 2 H, CH$_2$), 6.9 (m, 8 H, CH$_{Ar}$), 7.27–7.82 (m, 12 H, CH$_{Ar}$)
13a′	109.0 (s)	0.99 (m, 6 H, CHCH$_3$), 1.98 (s, 3 H, CH$_3$), 2.59 (m, 1 H, CHCH$_3$), 5.05 (d, 1 H, J 5.5, CH), 5.40 (br s, 2 H, CH), 5.47 (d, 1 H, J 6, CH), 7.06 (d, 1 H, J 5.5, CH)	1.44 (d, 3 H, J 7.2, CHCH$_3$), 2.86 (m, 1 H, CH), 2.98 (m, 3 H, CH, CH$_2$), 3.10 (s, 3 H, NCH$_3$) 3.80 (m, 2 H, CH$_2$), 7.0 (m, 8 H, CH$_{Ar}$), 7.30–7.88 (m, 12 H, CH$_{Ar}$)

^{a} δ values with J in Hz; solvent = CDCl$_3$. ^{b} H$_3$PO$_4$ as external standard. ^{c} SiMe$_4$ is the standard.

Table 3 Crystal data of compounds **5a** and **11a″**

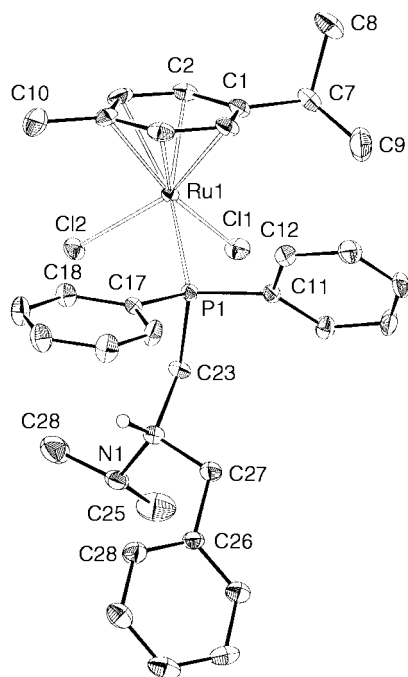|		
Formula	C$_{33}$H$_{40}$Cl$_2$NPRu	C$_{32}$H$_{38}$BClF$_4$NPRu
Formula weight	653.60	690.93
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	17.149(5)	10.886(4)
b/Å	17.903(5)	24.897(5)
c/Å	10.066(4)	11.912(4)
V/Å^3	3090.4(18)	3222.6(17)
Z	4	4
μ/cm^{-1}	7.55	6.64
Reflections collected	4153	19073
Independent reflections	4153	6908 [R_{int} = 0.0421]
Obs. reflections [$I > 2\sigma(I)$]	3167	6467
Data/restraints/parameters	4153/0/354	6908/0/380
Flack index	−0.09(4)	−0.05(2)
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0306, 0.0551	0.0308, 0.0806
(all data)	0.0519, 0.0603	0.0338, 0.0828
Largest difference peak and hole/e Å^{-3}	0.871 and −0.430	0.373 and −0.928

material except for the N(CH$_3$)$_2$ methyl protons resonance which is shifted to lower field (δ 2.9 and 2.95) and the presence of a broad signal at δ 8.35 due to the NH moiety. The ^{31}P-{^{1}H} NMR chemical shift is almost the same as that of **5a** ($\Delta\delta$ 0.9

ppm) indicating that the overall structure of the compound was not changed by protonation of the amine.

Reaction of [Ru(η^6-arene)Cl$_2$]$_2$ with 1 equivalent of the P–N* ligands **1–3**, in methanol, at room temperature, easily afforded

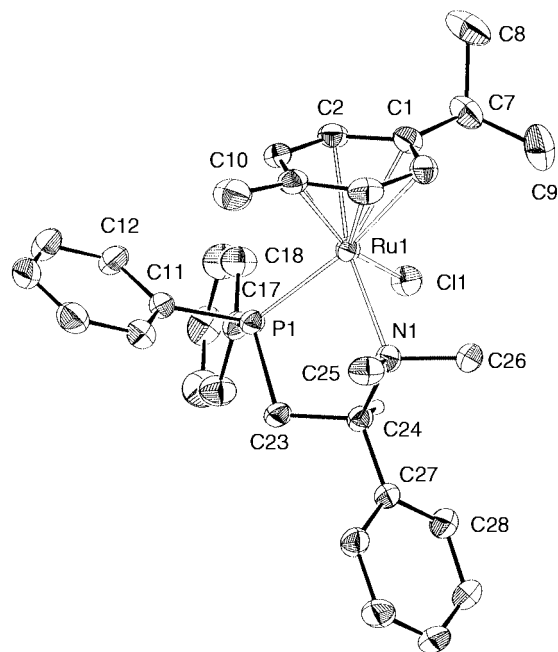**Table 4** Selected bond lengths [Å] and angles (°) for complex **5a**

Ru(1)–C(1)	2.211(4)	Ru(1)–Cl(2)	2.425(1)
Ru(1)–C(2)	2.227(4)	P(1)–C(23)	1.834(4)
Ru(1)–C(3)	2.212(4)	N(1)–C(24)	1.473(5)
Ru(1)–C(4)	2.206(4)	N(1)–C(25)	1.450(6)
Ru(1)–C(5)	2.157(4)	N(1)–C(26)	1.461(6)
Ru(1)–C(6)	2.183(4)	C(23)–C(24)	1.551(5)
Ru(1)–P(1)	2.369(1)	C(24)–C(27)	1.522(5)
Ru(1)–Cl(1)	2.420(1)	C(27)–C(28)	1.514(5)
P(1)–Ru(1)–Cl(1)	84.46(4)	C(26)–N(1)–C(24)	112.2(4)
P(1)–Ru(1)–Cl(2)	88.15(4)	C(24)–C(23)–P(1)	119.7(3)
Cl(2)–Ru(1)–Cl(1)	88.14(5)	N(1)–C(24)–C(27)	111.4(4)
C(1)–P(1)–Ru(1)	112.42(14)	N(1)–C(24)–C(23)	114.1(3)
C(25)–N(1)–C(26)	112.1(4)	C(27)–C(24)–C(26)	110.5(4)
C(25)–N(1)–C(24)	114.4(4)		

Table 5 Selected bond lengths [Å] and angles (°) for complex **11a″**

Ru(1)–C(1)	2.298(3)	Ru(1)–P(1)	2.319(1)
Ru(1)–C(2)	2.189(3)	P(1)–C(23)	1.828(3)
Ru(1)–C(3)	2.183(3)	N(1)–C(24)	1.511(3)
Ru(1)–C(4)	2.269(3)	N(1)–C(25)	1.502(4)
Ru(1)–C(5)	2.228(3)	N(1)–C(26)	1.491(4)
Ru(1)–C(6)	2.284(3)	C(23)–C(24)	1.521(4)
Ru(1)–N(1)	2.243(2)	C(24)–C(27)	1.520(4)
Ru(1)–Cl(1)	2.383(1)		
P(1)–Ru(1)–Cl(1)	86.68(3)	C(26)–N(1)–Ru(1)	108.8(2)
N(1)–Ru(1)–Cl(1)	85.46(7)	C(25)–N(1)–Ru(1)	110.9(2)
N(1)–Ru(1)–P(1)	81.48(7)	C(24)–N(1)–Ru(1)	109.7(2)
C(23)–P(1)–Ru(1)	104.0(1)	C(24)–C(23)–P(1)	108.3(2)
C(25)–N(1)–C(26)	107.1(3)	N(1)–C(24)–C(27)	116.9(2)
C(25)–N(1)–C(24)	110.9(2)	N(1)–C(24)–C(23)	109.0(2)
C(26)–N(1)–C(24)	109.4(2)	C(27)–C(24)–C(26)	110.5(4)

Fig. 1 An ORTEP[16] view of the structure of complex **5a** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

Fig. 2 An ORTEP view of the structure of the cation of complex **11a″**. Details as in Fig. 1.

the corresponding chelate complexes [Ru(η⁶-arene)(P–N*)Cl]-Cl. Depending on the co-ordinated η⁶-arene, either only one diastereoisomer or a pair of diastereoisomers that differ in the configuration at the ruthenium centre was formed (P–N* = (S)-phephos, arene = p-cymene, **10a** and **10a′**; benzene, **10b**; hexamethylbenzene, **10c**; P–N* = (S)-phglyphos, arene = p-cymene, **11a** and **11a′**; benzene, **11b**; or hexamethylbenzene, **11c**; P–N* = (S)-valphos, arene = p-cymene, **12a** and **12a′**; benzene, **12b**; or hexamethylbenzene, **12c**). Complexes **10–12** were also obtained by adding a small amount of methanol to solutions of [Ru(η⁶-arene)(P–N*)Cl₂] in chloroform. Under these conditions, such as in the kinetic experiments (low methanol concentration), small amounts of the second diastereoisomer were evidenced in solution by ³¹P-{¹H} NMR spectroscopy also when the η⁶-arene is benzene (arene = benzene, P–N* = (S)-phephos, **10b′**; (S)-phglyphos, **11b′**; or (S)-valphos, **12b′**). By monitoring the reactions of [Ru(η⁶-arene)Cl₂]₂ with **1–3** in methanol and the ring-closure reactions of [Ru(η⁶-arene)-(P–N*)Cl₂], in chloroform-methanol solution, by ³¹P-{¹H} NMR spectroscopy, it is evident that one diastereoisomer was predominantly formed (in some cases it is the only diastereoisomer formed) and that their ratio is dependent on the methanol concentration. Using methanol as solvent, [Ru(η⁶-MeC₆H₄Prⁱ)Cl₂]₂ affords **10a** and **10a′**, **11a** and **11a′**, **12a** and **12a′** as a 90:10 diastereomeric mixture while only one

diastereomer was formed in the corresponding reactions when the arene is benzene or hexamethylbenzene. The major diastereoisomer is also the more stable thermodynamically; in fact, slow conversion of the minor diastereoisomer into the major one occurs. At the end only one diastereoisomer was present in the solution; it was easily obtained pure and characterized by microanalysis, conductivity measurements and NMR spectroscopy. In order to assign the absolute configuration at the Ru of the major or unique diastereomer observed in the closure ring process, an X-ray diffraction study of [Ru(η⁶-p-MeC₆H₄Prⁱ)(S-phglyphos)Cl]BF₄, **11a″**, was undertaken. A view of the cation of the complex **11a″** with the atomic numbering scheme is shown in Fig. 2. Selected bond distances and angles are given in Table 5. The structure is strictly related to that of **5a** by substituting a Cl atom with the N atom from S-phglyphos acting as a chelating ligand. The configuration at the Ru atom is R. The six Ru–C bond distances involving the η⁶-co-ordinated p-cymene group are in the range 2.183(3)–2.298(3) Å. The Ru–Cl(1) bond distance, 2.383(1) Å, is only slightly shorter than those found in **5a**, whereas the Ru–P bond distance, much shorter than in **5a**, 2.319(1) Å, may be influenced by the chelation of the ligand. The five-membered chelation ring adopts an envelope conformation with the C(24) atom 0.691(3) Å out of the mean plane through the other four atoms.
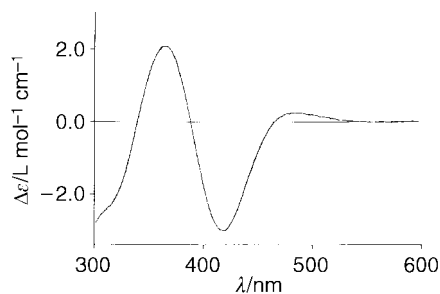
Fig. 3 CD spectrum of complex **10b**, $c = 5 \times 10^{-4}$ M, 20 °C, CH$_2$Cl$_2$. $\Delta\varepsilon$ is in units of dm^3 mol^{-1} cm^{-1}.

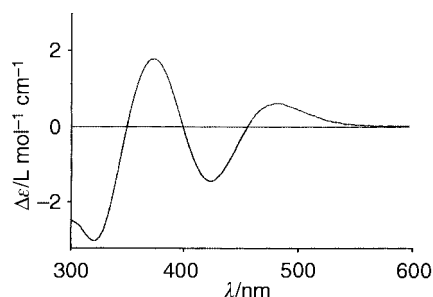**Fig. 4** CD spectrum of complex **11a″**. Details as in Fig. 3.

Scheme 1 Arene = p-cymene, C$_6$H$_6$ or C$_6$Me$_6$; R = PhCH$_2$, Ph or (CH$_3$)$_2$CH.

The crystallographic determination of the absolute configuration of complex **11a″** allowed us to assign the configuration $R_{Ru}S_C$ to the related complexes **10a**–**10c**, **11a**–**11c** and **12a**–**12c**. Consequently, diastereomers **10a′**, **11a′** and **12a′** have the $S_{Ru}S_C$ configuration.
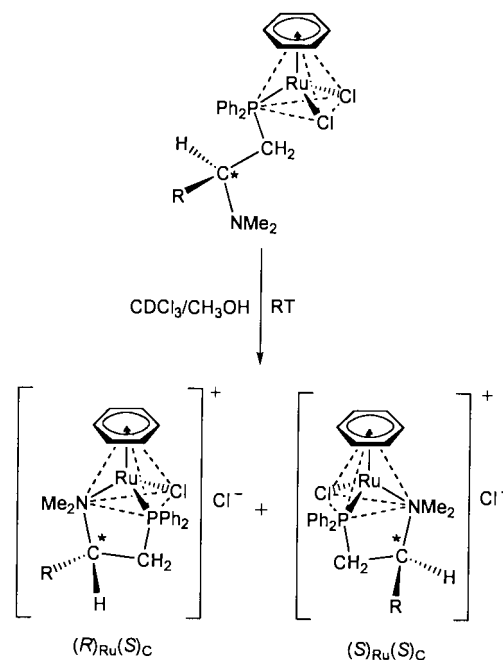
In Figs. 3 and 4 are reported, as example, the CD spectra, in CH$_2$Cl$_2$, of the diastereoisomers **10b** and **11a″**. The CD spectra of the other major diastereomers are very similar, supporting the conclusion that their absolute configurations in solution are the same. Compounds **10**–**13** are orange solids, stable in the air; in methanol solution they are 1:1 electrolytes. In Table 2 are reported their ^{1}H and ^{31}P-$\{^1$H$\}$ NMR data, in CDCl$_3$ solution. The pairs of diastereomers show, in their ^{31}P-$\{^1$H$\}$ NMR spectra, resonances at different δ values; $R_{Ru}S_C$ diastereomers containing the ligands **1**–**3** exhibit a singlet at lower field (in the range δ 48.0–49.5) than $S_{Ru}S_C$ diastereomers (about δ 45.5).

The reaction of [Ru(η^6-p-MeC$_6$H$_4$Pr^i)Cl$_2$]$_2$ with ligand **4**, in the molar ratio 1:2, in methanol, afforded the ionic diastereomers [Ru(η^6-p-MeC$_6$H$_4$Pr^i)(2S,3R-chiraldphos)Cl]Cl, **13a** and **13a′**, in the molar ratio 60:40; their ^{31}P-$\{^1$H$\}$ NMR spectra, in CDCl$_3$, show resonances at δ 108.03 and 109.01. In this case, conversion of one diastereomer into the other in methanol or ethanol does not occur.

Steric hindrance due to ring substituents is a determining factor for asymmetric induction. Kumada and co-workers,[12] using β-aminoalkylphosphines such as **1**–**3** in the catalytic cross-coupling of a racemic Grignard reagent and vinyl bromide, found higher stereoselectivity when bulky substituents were present on the chiral carbon atom in α position to nitrogen. In some cases high diastereomeric excesses have been explained through specific intramolecular interactions that stabilize one diastereomer in comparison to the other.[17] For example, the C–H · · · π interactions such as the β-phenyl effect can account for the relatively high configurational stability at the metal atom of one diastereomer with respect to the other.[18] The stereoselectivity of the reactions seems not to be affected strongly by the substituents on the chiral carbon atom of **1**–**3** but is affected to a major extent by the nature of the co-ordinated arene. In fact, only when the arene is p-cymene both diastereomers were obtained.

Kinetics of the chiral P,N*-ligand ring closure

In order to gain some insight into the ring-closure process we have conducted a kinetic study of the chelation process (Scheme 1) in CHCl$_3$ solution containing variable amounts of methanol. The conversion of the [Ru(η^6-arene)(P–N*)Cl$_2$] complexes into the corresponding ionic diastereoisomers proceeds to completion in all the reactions. The kinetics of the reaction were followed by measuring changes in the intensity of the ^{31}P-$\{^1$H$\}$ NMR resonance of the starting material with time. The conversion of [Ru(η^6-p-MeC$_6$H$_4$Pr^i)(S-phephos)Cl$_2$] into the corresponding ionic diastereoisomers was also followed by conductivity measurements to confirm that the slow process can be ascribed to a step affording ionic species. In a separate experiment by UV/VIS spectroscopy we observed that an isosbestic point at 348 nm was maintained when only one diastereoisomer was formed. Kinetic runs were carried out at three different concentrations of methanol (which is the nucleophile) and the rate constants calculated as the means of three kinetic runs. The kinetics were studied under pseudo-first-order conditions and in all cases the methanol concentration was at least 20 times that of the complex. The kinetics follow a first-order course and the k_{obs} values are linearly correlated [eqn. (1)]

$$k_{obs} = k[CH_3OH] \qquad (1)$$

to the nucleophile (methanol) concentration (Table 6) with no significant intercepts (Fig. 5).

The pseudo-first-order rate constants in Table 6 can be related to a bimolecular solvolysis and ascribed to the replacement of Cl$^-$ from the complexes [Ru(η^6-arene)(P–N*)Cl$_2$] by a molecule of methanol. In accordance a decrease of k_{obs} occurred when the reaction was performed in the presence of an excess of added chloride ion. In Table 7 are listed the rate constants for the chelation process of complex **5a**, on changing the alcohol. As expected the rate of chelation is strongly dependent on the nature of the alcohol, showing a significant decrease on going from methanol to Bu^{t}OH. Romeo and co-workers[19] found the same sequence for solvolytic processes of platinum(II) complexes. The electrophilicity and nucleophilicity of the solvent determine the rate of Ru–Cl bond breaking. The solvent electrophilicity is important in determining the removal of Cl$^-$, while solvent nucleophilicity is important in blocking of the vacant co-ordination site. In protic solvents, electrophilic solvation of Cl$^-$ through hydrogen bond formation is the factor determining the differences in the rates observed. This was sup-

Table 6 Pseudo-first-order rate constants k_{obs} and second-order rate constants k_2 for the chelation process of [Ru(η^6-arene) (**1–3**)Cl$_2$] complexes[a]

Complex	[CH$_3$OH][b]	$10^4 k_{obs}$[c]	k_2[d]	Complex	[CH$_3$OH][b]	$10^4 k_{obs}$[c]	k_2[d]
5a	3.2	0.47		**6c**	1.32	2.63	
	7.26	1.03			3.1	6.43	
	11.3	1.63	$(1.43 \pm 0.03) \times 10^{-5}$		5.00	10.55	$(1.99 \pm 0.07) \times 10^{-4}$
5b	1.46	0.236		**7a**	3.2	0.476	
	7.26	1.02			7.26	1.1	
	11.3	1.57			11.3	1.68	$(1.48 \pm 0.02) \times 10^{-5}$
	16.9	2.48	$(1.45 \pm 0.05) \times 10^{-5}$	**7b**	1.46	0.253	
5c	1.46	2.80			7.26	1.09	
	3.2	6.74			11.3	1.57	
	5.29	10.95	$(2.12 \pm 0.07) \times 10^{-4}$		16.9	2.52	$(1.46 \pm 0.06) \times 10^{-5}$
6a	3.2	0.49		**7c**	1.46	2.83	
	7.26	1.09			3.2	6.77	
	11.3	1.71	$(1.50 \pm 0.02) \times 10^{-5}$		5.29	10.96	$(2.12 \pm 0.07) \times 10^{-4}$
6b	1.30	0.207					
	6.97	0.978					
	11.2	1.62					
	16.9	2.49	$(1.48 \pm 0.02) \times 10^{-5}$				

[a] At 298 K. [b] In mol dm^{-3}. [c] s^{-1}. [d] In dm^3 mol^{-1} s^{-1}.

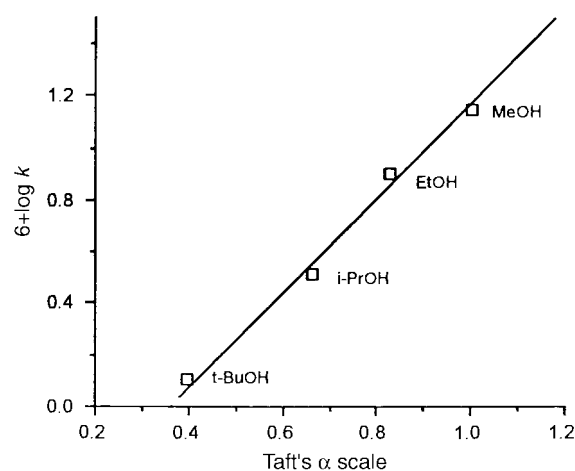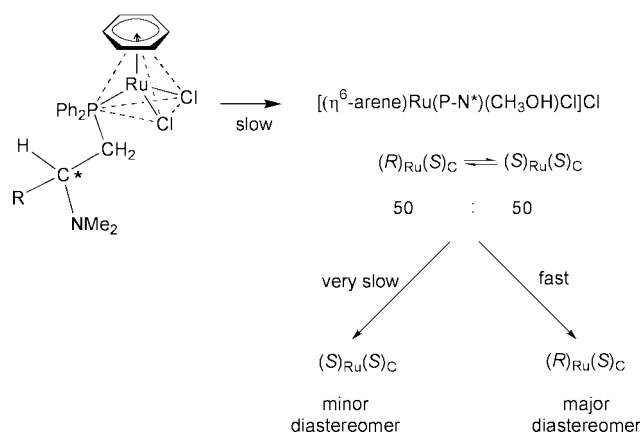**Table 7** Effect of changing the nature of the solvent on the k_2 of the chelation process of complex **5a**[a]

Solvent	k_2[b]
Methanol	$(1.43 \pm 0.03) \times 10^{-5}$
Ethanol	$(8.1 \pm 0.2) \times 10^{-6}$
2-Propanol	$(3.3 \pm 0.3(\times 10^{-6}$
2-Methyl-2-propanol	$(1.2 \pm 0.4) \times 10^{-6}$

[a] At 298 K. [b] In dm^3 mol^{-1} s^{-1}.
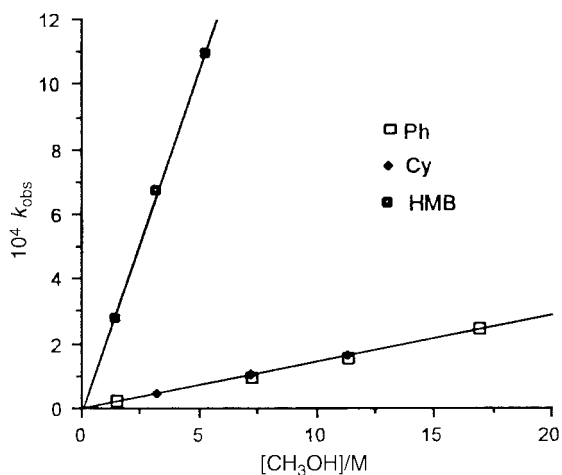
Fig. 5 Plots of k_{obs} vs. [CH$_3$OH] for the chelation process of complexes **5a**, **5b** and **5c**. $T = 298$ K; HMB = C$_6$Me$_6$.

Fig. 6 Correlation plot of the second-order rate constants k_2 for the chelation process of [Ru(η^6-p-MeC$_6$H$_4$Pr^i)(S-phephos)Cl$_2$] with the hydrogen-bonding donor properties of the solvents.

Scheme 2 Arene = p-cymene, C$_6$H$_6$ or C$_6$Me$_6$; R = PhCH$_2$, Ph or (CH$_3$)$_2$CH.

ported by the correlation of the logarithms of the rate constant with Taft's a scale for the solvents (Fig. 6) for the ring-closure process in [Ru(η^6-p-MeC$_6$H$_4$Pr^i)(S-phephos)Cl$_2$]. Taft's a scale values[20] measure the electrophilicity of the solvent, that is its ability to hydrogen bond with the anion.

The kinetic results lead us to propose the mechanism illustrated in Scheme 2. The rate-determining step of the process is solvolysis of the starting complex in methanol. This involves formation of a cationic areneruthenium(II) solvento intermediate via interaction of the co-ordinated halide with methanol. This species is chiral at the metal centre and can assume the configurations $R_{Ru}S_C$ and $S_{Ru}S_C$ depending on the trajectory of the chloride substitution. Very likely these diastereomeric solvento-species are in equilibrium and in equimolar ratio since the stereogenic carbon atom on the monodentate P-donor ligand is remote from the co-ordination sphere of the metal.

The subsequent reaction step is fast closure of the chelate ring by co-ordination of the nitrogen atom to the ruthenium(II) centre. This reaction step determines the stereoselectivity of the process, occurring fast only for the formation of one diastereomer. We are not able fully to establish the factors determining the very different rate (and therefore the different activation energy)[8a] of the ring closure in the intermediate diastereomeric solvento-species. Nevertheless the favoured diastereomer kinetically is also the more thermodynamically

stable as previously pointed out. It is noteworthy that there are not many clear examples of kinetic control of asymmetric induction in the formation of optically active organometallic compounds containing stereogenic metal centres.[8a]

The low $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values of 75.66 kJ mol^{-1} and -48.07 J K^{-1} mol^{-1} respectively, associated with the solvolysis for the ring-closure process on the [Ru(η^6-p-MeC$_6$-H$_4$Pr^i)(S-phephos)Cl$_2$] substrate at three different temperatures are consistent with an associative mode of activation of the chloride.

The correlation of Fig. 6 supports the direct interaction of the solvent with co-ordinated chloride and rules out a mechanism involving direct attack of the solvent at the metal centre followed by departure of the chloride. Besides, such a mechanism is unlikely because the starting substrate is an 18-electron species requiring a η^6–η^4 change in the co-ordination of the arene. Consiglio and Morandini[2a] proposed a mechanism involving formation of a five-co-ordinated square pyramid as intermediate in the reaction of [Ru(η^5-C$_5\eta_5$)LL′R] with electrophiles E$^+$Y$^-$.

Of note is that the nature of the arene affects the rate of solvolysis. As expected, electron-donating substituents on the aromatic ring enhance the rate of solvolysis. For the hexamethylbenzene complex the rate constants are significantly higher than for benzene and p-cymene complexes (Fig. 5). The different basicity associated with the co-ordinated p-cymene and benzene is not enough to discriminate the solvolysis rates of related complexes. In accordance with the proposed mechanism, the nature of the aminophoshine does not significantly influence the rate of ring closure.

Acknowledgements

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