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Half-sandwich cyclopentadienyl ruthenium complexes of achiral and chiral diphosphazanes †

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Reaction of $[CpRu(PPh_3)_2Cl]$ (**1**) {Cp = η^5-(C_5H_5)} with $X_2PN(CHMe_2)PYY'$ {X = Y = Y′ = Ph (L^1); X = Y = Ph, Y′ = OC_6H_4Me-4 (L^4); X = Y = Ph, Y′ = $OC_6H_3Me_2$-3,5 (L^5); X = Y = Ph, Y′ = $N_2C_3HMe_2$ (L^6)} yields the cationic chelate complexes, $[CpRu(\eta^2\text{-}(X_2PN(CHMe_2)PYY'))PPh_3]Cl$. On the other hand, the reaction of **1** with $X_2PN(CHMe_2)$-PYY′ {X_2 = YY′ = $O_2C_6H_4$(L^2)} gives the complex, $[CpRu(\eta^1\text{-}L^2)_2PPh_3]Cl$. Both types of complexes are formed with $X_2PN(CHMe_2)PYY'$ {X = Ph, YY′ = $O_2C_6H_4$ (L^3)}. The reaction of **1** with (*R*),(*S*)-($H_{12}C_{20}O_2$)$PN(CHMe_2)PPh_2$ (L^7) yields both cationic and neutral complexes, $[CpRu\{\eta^2\text{-}(L^7)\}PPh_3]Cl$ and $[CpRu\{\eta^1\text{-}(L^7)\}_2PPh_3]Cl$ and $[CpRu\{\eta^2\text{-}(L^7)\}$-Cl]. The reactions of optically pure diphosphazane, $Ph_2PN(*CHMePh)PPhY$ (Y = Ph (L^8); Y = $N_2C_3HMe_2$-3,5 (L^9)) with **1** give the neutral and cationic ruthenium complexes, $[CpRu\{\eta^2\text{-}(Ph_2PN(R)PPhY)\}Cl]$ and $[CpRu\{\eta^2\text{-}(Ph_2PN(R)$-$PPhY)\}PPh_3]Cl$. "Chiral-at-metal" ruthenium complexes of diphosphazanes have been synthesized with high diastereoselectivity. The absolute configuration of a novel ruthenium complex, $(S_CS_PR_{Ru})$-$[(\eta^5\text{-}C_5H_5)Ru*\{\eta^2\text{-}(Ph_2PN(*CHMePh)$-$P*Ph(N_2C_3HMe_2\text{-}3,5))\}Cl]$ possessing three chiral centers, is established by X-ray crystallography. The reactions of $[CpRu\{\eta^2\text{-}(L^8)\}Cl]$ with mono or diphosphanes in the presence of NH_4PF_6 yield the cationic complexes, $[CpRu\{\eta^2\text{-}(L^8)\}\{\eta^1\text{-}(P)\}]PF_6$ {P = $P(OMe)_3$, PPh_3, $Ph_2P(CH_2)_nPPh_2$ (*n* = 1 or 2)}.

Introduction

The synthesis of half-sandwich optically active "chiral-at-metal" ruthenium complexes has attracted considerable interest in recent years because they can be used as probes to follow the stereochemical course of reactions of organometallic complexes and they have also been investigated as promising catalysts for a variety of organic transformations.[1] Active use of chirality at a metal center in enantioselective catalysis is a challenging area.[2] Several ruthenium complexes with a stereogenic metal center have been synthesised using Schiff-base ligands, chiral bidentate ligands with mixed donor sites or chiral diphosphanes (with chirality at the back-bone of the ligand).[3] However, the synthesis of half-sandwich ruthenium complexes of chiral diphosphazane ligands based on the P–N–P motif has not been attempted.[4,5] In continuation of our work on the organometallic chemistry of diphosphazanes,[4c,4d,5] herein we describe the results of our investigations on the reactions of achiral, unsymmetrically substituted P-stereogenic and optically pure diphosphazanes with $[CpRu(PPh_3)_2Cl]$ (Cp = η^5-C_5H_5) (**1**) (containing a prochiral metal center) to generate "chiral-at-metal" complexes and the isolation and absolute configuration of a novel ruthenium complex bearing three chiral centers, $(S_CS_PR_{Ru})$-$[CpRu*\{\eta^2\text{-}(Ph_2PN(*CHMePh)*PPh(N_2C_3HMe_2$-3,5)}Cl].

Results and discussion

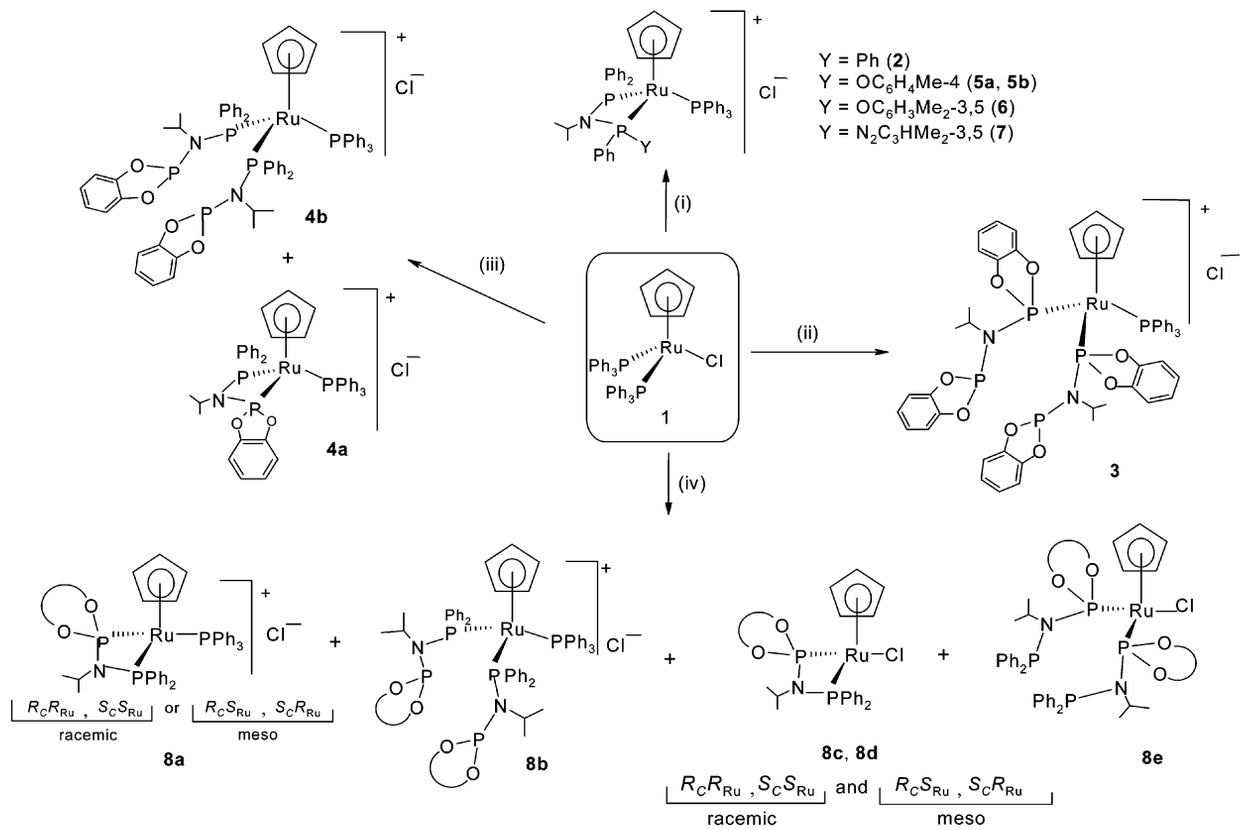
The diphosphazanes used in the present study to synthesise ruthenium complexes are: $X_2PN(CHMe_2)PYY'$ (X = Y = Y′ = Ph (L^1); X_2 = YY′ = $O_2C_6H_4$ (L^2); X = Ph, YY′ = $O_2C_6H_4$ (L^3); X = Y = Ph, Y′ = OC_6H_4Me-4 (L^4); X = Y = Ph, Y′ = $OC_6H_3Me_2$-3,5 (L^5); X = Y = Ph, Y′ = $N_2C_3HMe_2$ (L^6); X = Ph, YY′ = (*R*),(*S*)-$O_2C_{20}H_{12}$ (L^7); (*S*)-$Ph_2PN(*CHMePh)PPh_2$ (L^8) and $Ph_2PN(*CHMePh)*PPh(N_2C_3HMe_2$-3,5) ($L^9$). In the case of L^9, the S_CR_P-diasteromer or a mixture of S_CS_p- and S_CR_P-diasteromers has been used. The absolute configuration of S_CR_P-L^9 has been established previously by X-ray crystallography.[4d]

Preparation of the complexes

Reactions of 1 with achiral diphosphazanes of the type $X_2PN(R)PX_2$ and $X_2PN(R)PY_2$. The reaction of **1** with 1 : 1 molar proportions of L^1 in toluene at 110 °C gives the cationic complex $[CpRu\{\eta^2\text{-}(L^1)\}(PPh_3)]Cl$ (**2**) in 90% yield. An entirely different behavior is exhibited by the diphosphazane L^2, bearing the catecholato moiety at both the phosphorus ends; its reaction with **1** yields the cationic complex, $[CpRu\{\eta^1\text{-}(L^2)\}_2$-$(PPh_3)]Cl$ (**3**) containing one triphenyl-phosphane and two mono-coordinated diphosphazanes (Scheme 1). A similar type of complex is obtained in the reaction of *N*-phenyl biscatecholato derivative with **1** in which the sole product is $[CpRu\{\eta^1$-$(C_6H_4O_2)_2PN(Ph)P(O_2C_6H_4)\}_2PPh_3]Cl$.[6b] The reaction of **1** with the mixed diphosphazane derivative Ph_2-$PN(CHMe_2)$-$P(O_2C_6H_4)$ (L^3) gives a chelate complex $[CpRu\{\eta^2\text{-}(Ph_2PN$-$(CHMe_2)P(O_2C_6H_4)\}(PPh_3)]Cl$ (**4a**) akin to **2** and $[CpRu$-$\{\eta^1\text{-}(Ph_2PN(CHMe_2)P(O_2C_6H_4)\}_2(PPh_3)]Cl$ (**4b**) akin to **3** but in this complex, the PPh_2 phosphorus of the diphosphazane ligand is bonded to ruthenium. Other products are also formed in this reaction as shown by the ^{31}P NMR spectrum of the reaction mixture (see Experimental). Evidently the π-acceptor nature of the phosphorus center has a pronounced effect on the type of products formed. The presence of aryloxy substituents at phosphorus enhances the π-acceptor capability of phosphorus and favours the formation of η^1-coordinated complexes, whereas the presence of aryl substituents favours chelated (η^2-coordinated) complexes.

† Organometallic chemistry of diphosphazanes. Part 15.[5]

Electronic supplementary information (ESI) available: the $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) spectrum of the reaction mixture obtained by the reaction of **1** with (S_CR_P)- and (S_CS_P)-L^9. See http://www.rsc.org/suppdata/dt/b2/b205247d/



(i) $Ph_2PN(CHMe_2)PPhY$, (L^1, L^4, L^5 or L^6), toluene, 110 °C, 5 h
(ii) $(H_4C_6O_2)PN(CHMe_2)P(O_2C_6H_4)$, ($L^2$) toluene, 110 °C, 5 h
(iii) $(H_4C_6O_2)PN(CHMe_2)PPh_2$, ($L^3$), toluene, 110 °C, 5 h
(iv) $Ph_2PN(CHMe_2)P(O_2C_{20}H_{12})$, ($L^7$), toluene, 110 °C, 5 h

= (*R*, *S*)-$C_{20}H_{12}O_2$

Scheme 1 Synthesis of half-sandwich ruthenium complexes of diphosphazanes (**2**–**8**)

Reactions of [CpRu(PPh$_3$)$_2$Cl] with chiral racemic diphosphazanes of the type X$_2$PN(R)PYY′. The reaction of a racemic unsymmetrical diphosphazane such as L^4–L^6 with **1** may lead to the formation of two diastereomeric pairs, {(*RR*), (*SS*)}-racemic diastereomer and {(*SR*), (*RS*)}-meso diastereomer as a result of the generation of a stereogenic center at the metal. The ligand exchange reaction between **1** and the chiral racemic diphosphazanes L^4–L^6 in boiling toluene yields the cationic chelate complexes [CpRu*{η^2-($Ph_2PN(CHMe_2)PPh(Y)$)}-PPh_3]Cl (**5**–**7**) by the replacement of only one PPh_3 ligand. As shown in Scheme 1, chelation of the unsymmetrical diphosphazanes L^4–L^6 produces a chiral center and the phosphorus atom provides a second chiral center; one would therefore expect the formation of two diastereomeric {(*RR*),(*SS*)}-(racemic) and {(*SR*), (*RS*)}-(meso) pairs. In the reaction of L^4 with **1** both the diastereomeric pairs (**5a** : **5b**) are formed in the ratio 2.3 : 1; the major diastereomeric pair **5a** (racemic or meso) has been isolated in a pure form as a yellow crystalline solid, whereas the minor diastereomeric pair **5b** (meso or racemic) is obtained only as an oily liquid. In contrast to the above result, the reactions of L^5 and L^6 with **1** give only one diastereomeric pair of cationic ruthenium diphosphazane complexes, [CpRu-{η^2-(L^5 or L^6)}PPh_3]Cl (L^5 **6** or L^6 **7**) respectively, in good yields. The reaction of **1** with 1 : 1 molar proportions of the racemic diphosphazane L^7, bearing the C_2-chiral binapthylene dioxy moiety, in toluene at 110 °C for 5 h gives the complexes **8a**–**8e** of which the cationic complex, [CpRu{η^2-(L^7)}PPh_3]Cl **8a** is the major product and is isolated in a pure state; it may be either racemic or meso diastereomer. The remaining compounds (**8b**–**8e**) could not be isolated in a pure state but have been identified using ^{31}P NMR spectroscopy (see Fig. 1 for ^{31}P–^{31}P COSY NMR spectrum).

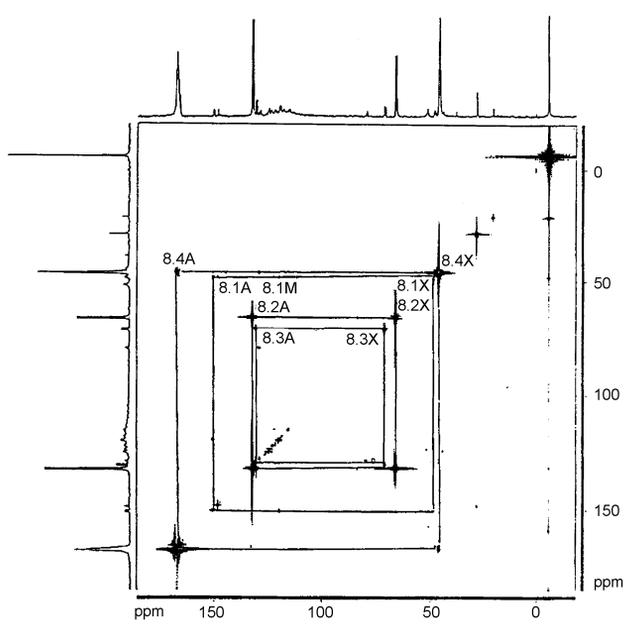
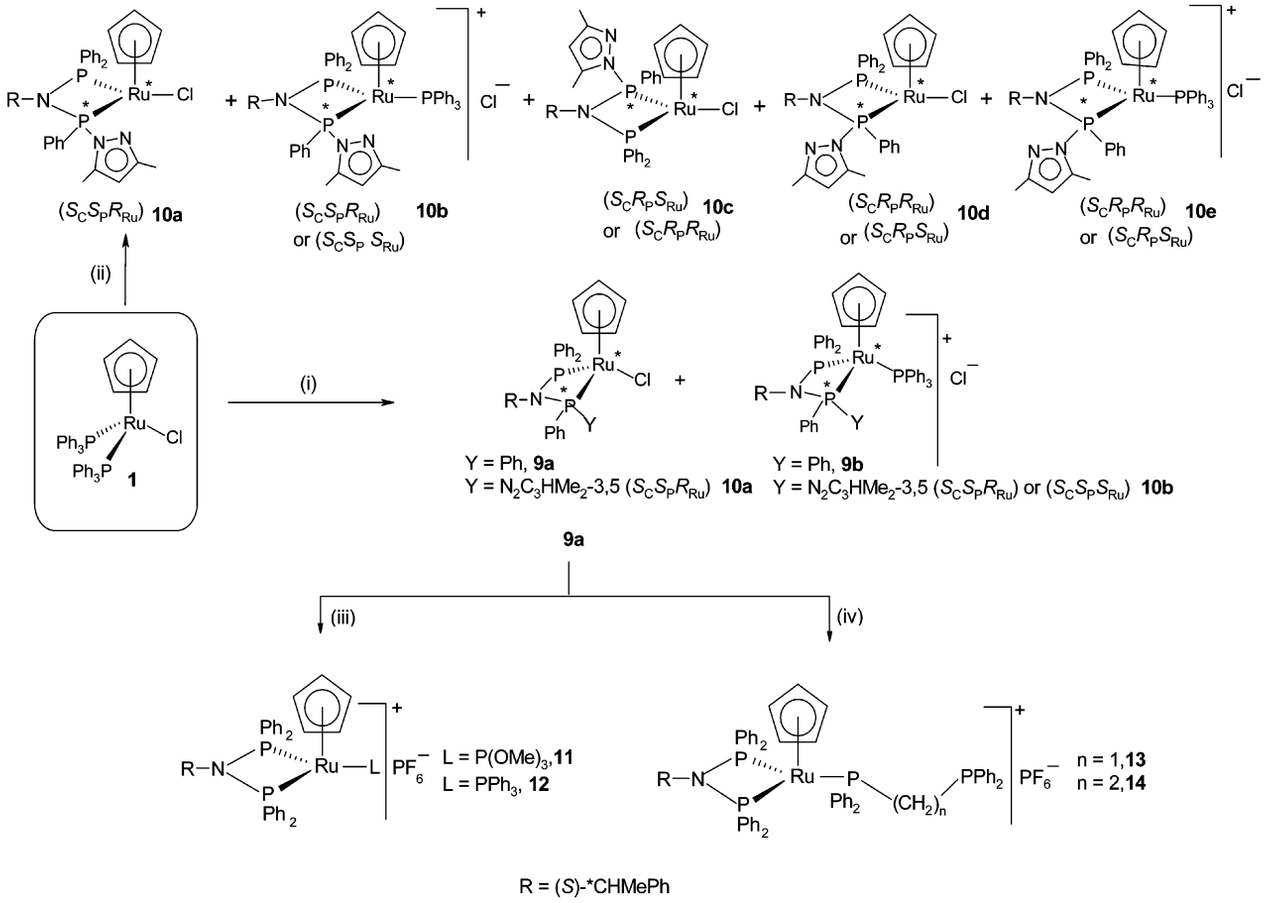


Fig. 1 The ^{31}P–^{31}P COSY (162 MHz, $CDCl_3$) spectrum of the reaction mixture (after separating **8a**) obtained by the reaction of **1** with L^7.

Reactions of [CpRu(PPh$_3$)$_2$Cl] with optically pure diphosphazanes. The reaction of an optically pure diphosphazane L^8 with **1**, in sharp contrast to the *N*-isopropyl derivative L^1, gives the neutral complex [CpRu{η^2-(L^8)}Cl] (**9a**) and the cationic complex [CpRu{η^2-(L^8)}PPh_3]Cl (**9b**) in 70 and 5% yields respectively.



(i) Ph_2PN(*CHMePh)PPhY {L^8 or (S_cR_p)- L^9}, toluene, 110 °C, 5h (ii) {(S_CR_P)- and (S_CS_P)-} - L^9, toluene, 110 °C, 5h
(iii)L, NH_4PF_6, CH_2Cl_2, 6 h (iv) $Ph_2P(CH_2)_nPPh_2$, NH_4PF_6, CH_2Cl_2, 6 h

Scheme 2 Synthesis of half-sandwich ruthenium complexes of diphosphazanes (**9**–**14**).

The results obtained from the reactions of L^4–L^6 suggest that an optically pure P-stereogenic unsymmetrical diphosphazane can be used to synthesise ruthenium complexes with a stereogenic metal center with a high diastereoselectivity. This possibility has been realized in the reaction of the optically pure P-stereogenic unsymmetrical diphosphazane (S_CR_P)-Ph_2PN-(*CHMePh)P*Ph($N_2C_3HMe_2$-3,5) (L^9) with **1**, which yields the neutral chloro complex, ($S_CS_PR_{Ru}$)-[CpRu*{η^2-(Ph_2PN-(*CHMePh)*PPh($N_2C_3HMe_2$-3,5)}Cl] (**10a**) (see below for the X-ray structure) and the cationic complex [CpRu*{η^2-(Ph_2PN-(*CHMePh)*PPh($N_2C_3HMe_2$-3,5)}PPh_3]Cl (**10b**) in 60 and 20% yield respectively. The complex **10a** can be separated from the reaction mixture by selective crystallization. The complex **10b** could not be isolated in a pure form.

The reaction of a diastereomeric mixture of diphosphazanes (S_CR_P)- and (S_CS_P)-Ph_2PN(*CHMePh) P*Ph($N_2C_3HMe_2$-3,5) (L^9) with [CpRu(PPh_3)$_2$Cl] (Scheme 2) gives three diastereomeric neutral chloro complexes [CpRu*{η^2-(Ph_2PN-(*CHMePh)*PPh($N_2C_3HMe_2$-3,5)}Cl] (**10a**, **10c** and **10d**) and two cationic complexes, [CpRu*{η^2-(Ph_2PN(*CHMePh)*PPh-($N_2C_3HMe_2$-3,5)}PPh_3]Cl (**10b** and **10e**). The formation of these complexes is identified only by the ^{31}P NMR spectrum of the reaction mixture (see supplementary material †) and except for **10a**, the other compounds could not be isolated (see below for the ^{31}P NMR data and the assignment of the configurations).

Reactivity of 9a. The neutral ruthenium complex of chiral diphosphazane **9a** reacts with monophosphanes, such as PPh_3 or $P(OMe)_3$ in the presence of NH_4PF_6 in dichloromethane to yield the yellow cationic complexes **11** and **12** respectively in good yields. Analogous reactions of complex **9a** with diphosphanoalkanes (dppm or dppe) yield cationic complexes of the type [CpRu{η^2-(L^8)}{η^1-($Ph_2P(CH_2)_n(PPh_2)$}]Cl (n = 1 (**13**) or n = 2 (**14**)). The diphosphane complexes of **13** and **14** contain an uncoordinated phosphorus center and these "chiral metalloligands" would prove useful synthons for chiral homo- and heterometallic clusters.

NMR spectroscopic data

The structures of ruthenium (II) diphosphazane complexes **2**–**14** have been deduced from ^{1}H and ^{31}P NMR spectroscopic data. The ^{31}P NMR data are given in Table 1. The structure of **10a** has been determined by single crystal diffraction studies (see below). The ^{31}P NMR spectrum of the η^1-coordinated cationic ruthenium complex **3** displays two quartets centred at 171.2 and 141.0 ppm and a triplet at 51.6 ppm. The spectrum is of the A_2X_2M type instead of the expected AA′XX′M pattern. Further investigations are required to ascertain whether any dynamic process is occuring in this system. The resonances centered at 171.2 ppm can be assigned to the coordinated phosphorus centers while the resonances at 141.0 ppm arise from the uncoordinated phosphorus centers as the latter chemical shift is close to that of the free ligand (149.9 ppm). The phosphorus resonance arising from the triphenylphosphane is centered at 51.6 ppm. The ^{31}P{^{1}H} NMR spectra of chelated cationic ruthenium complexes **5**–**7** display an AMX pattern and the chemical shifts lie considerably downfield compared to those of the free ligand. The ^{31}P NMR spectrum of the reaction mixture of **1** with L^4 shows two AMX patterns corresponding to **5a** and **5b**; the diastereomeric composition of **5a** and **5b** (2.3 : 1) was

Table 1 The ^{31}P NMR data of half-sandwich ruthenium complexes of diphosphazanes (**2**–**14**)

Compound	$\delta(P_A)$ (ppm)	$\delta(P_M)$ (ppm)	$\delta(P_X)$ (ppm)	J_{AM}/Hz	J_{AX}/Hz	J_{MX}/Hz
2	80.3[a]	–	45.2[b]	–	35.0	–
3	171.2[c]	141.0[d]	51.6[b]	–	–	–
4a	169.6[c]	121.0[a]	45.0[b]	–	–	–
4b	150.2[d]	123.0[a]	48.6[b]	–	–	–
5a	128.4[e]	89.5[a]	43.6[b]	95.0	40.0	31.0
5b	119.3[e]	77.3[a]	47.2[b]	85.0	49.0	32.4
6	123.1[e]	86.3[a]	43.7[b]	93.0	40.0	30.0
7	130.5[e]	118.4[a]	51.9[b]	61.0	49.0	39.0
8a	129.6[f]	74.3[a]	46.3[b]	86.0	53.5	29.1
8b	150.5[f]	119.7[a]	51.5[b]	–	–	–
8c	132.3[f]	–	67.6[a]	–	104.0	–
8d	130.8[f]	–	71.3[a]	–	103.0	–
8e	167.0[f]	–	45.0[a]	–	–	–
9a	87.7[a]		80.9[a]	–	108.8	–
9b	86.6[a]	82.9[a]	44.2[b]	89.0	34.0	34.0
10a	99.3[e]	–	87.2	–	107.0	–
10b	125.0[e]	118.3[a]	52.4[b]	60.0	46.0	38.0
10c	98.7[e]	–	80.7[a]	–	114.0	–
10d	90.6[e]	–	82.5[a]	–	108.0	–
10e	127.0[e]	116.8[a]	50.0[b]	65.0	42.0	38.0
11[g]	88.2[a]	87.9[a]	147.9[h]	89.0	55.0	55.0
12[g]	87.9[a]	84.2[a]	45.2[b]	89.0	34.0	34.0
13[g i]	87.7[a]	84.4[a]	−23.7[j]	98.5	–	–
14[g i]	87.9[a]	84.9[a]	−13.2[k]	97.9	–	–

[a] PPh_2. [b] PPh_3. [c] $P(O_2C_6H_4)$ coordinated. [d] $P(O_2C_6H_4)$ uncoordinated. [e] PPhY. [f] $P(O_2C_{20}H_{12})$. [g] PF_6 resonates in the range −143.0 to −144.0, septet, $^1J_{PF}$ = 712–715 Hz. [h] $P(OMe)_3$. [i] AMRX system. [j] Uncoordinated PPh_2, PPh_2-coord (P_R) of dppm, resonates at 37.0 (ddd $^2J_{MR}$ = 36.0, $^2J_{AR}$ = 29.0 Hz, $^2J_{RX}$ = 22.5 Hz). [k] Uncoordinated PPh_2, PPh_2-coord (P_R) of dppe resonates at 38.0 (ddd, $^2J_{MR}$ = 36.3, $^2J_{AR}$ = 29.4 Hz, $^2J_{RX}$ = 34.3 Hz).

determined from the relative integrated intensities of the two signals for the Cp (Cp = η^5-C_5H_5) protons at 4.26 (for **5a**) and 4.41 ppm (for **5b**) in their ^1H NMR spectra.

The ^1H NMR spectrum of complex **8a** shows a sharp singlet at 4.60 ppm for C_5H_5 protons. The methyl protons of the isopropyl group show two different resonances (0.73 and 0.67 ppm), as they are diastereotopic. The $^{31}P\{^1H\}$ NMR spectrum of complex **8a** shows an AMX pattern. The $^{31}P\{^1H\}$ NMR spectrum of the mother liquor after removing complex **8a** shows the presence of four other complexes (**8b**–**8e**) (Scheme 1). These complexes could not be isolated in a pure form owing to difficulties in their separation. Nevertheless, the presence of these complexes is confirmed from the ^{31}P–^{31}P COSY spectrum, which is illustrated in Fig. 1. From the spectrum, we can infer that phosphorus nuclei represented by 8.1A (150.5 ppm) shows coupling with phosphorus nuclei marked 8.1M (119.7 ppm) and 8.1X (51.5 ppm); 8.1M and 8.1X are mutually coupled with each other. Based on the chemical shifts, the structure can be assigned as [CpRu*{η^1-(($Ph_2PN(CHMe_2)P(O_2C_{20}H_{12})$)}$_2$ PPh_3]-Cl (**8b**), which is formed in very low yield. The resonances centered at 150.5 ppm can be assigned to uncoordinated $P(O_2C_{20}H_{12})$ phosphorus as the chemical shift lies close to that of the free ligand (148.3 ppm) and the resonances centered at 119.7 ppm is assigned to PPh_2 phosphorus coordinated to ruthenium. The PPh_3 phosphorus resonates at 51.5 ppm. The formation of the neutral chloro complexes **8c** and **8d** (racemic and meso) can also be inferred from the COSY spectrum. The ^{31}P NMR spectra of these complexes would display an AX pattern owing to non-equivalence of the two phosphorous nuclei. The phosphorus nucleus represented by 8.2A (d, 132.3 ppm) shows a cross peak with the phosphorus nucleus represented by 8.2X (d, 67.6 ppm) ($^2J_{AX}$ = 104 Hz); these resonances can be assigned to the neutral complex [CpRu{η^2-(Ph_2PN-$(CHMe_2)P(O_2C_{20}H_{12})$}Cl] **8c** (racemic or meso), which is the major isomer formed. The other diastereomer (minor) [CpRu-{η^2-$(Ph_2PN(CHMe_2)P(O_2C_{20}H_{12})$} Cl] (**8d**) is also identified by the cross peak observed between the phosphorus nucleus marked 8.3A (d, 130.8 ppm) with the phosphorus nucleus represented by 8.3X (d, 71.3 ppm) ($^2J_{AX}$ = 103 Hz). The COSY spectrum also shows a cross peak between the phosphorus nuclei marked 8.4A (m, 167.0 ppm) and 8.4X (m, 45.0 ppm). Based on the chemical shifts, these resonances can be tentatively assigned to the neutral chloro compound, [CpRu-{η^1-(($H_{12}C_{20}O_2$)$PN(CHMe_2)PPh_2$)}$_2$Cl] (**8e**) which contains two monocoordinated diphosphazanes. The coordinated [$P(O_2C_{20}H_{12})$] phosphorus resonates at 167.0 ppm and the uncoordinated PPh_2 phosphorus resonates at 45.0 ppm. The latter chemical shift lies closer to the chemical shift of PPh_2 in the free ligand (28.3 ppm). The $^{31}P\{^1H\}$ NMR data for complexes **8a**–**8e** are listed in Table 1.

The ^{31}P NMR spectra of complexes **9a** and **10a** display an AX pattern where as, the complexes **9b** and **10b** display an AMX pattern. The neutral chloro complexes (**10a**, **10c** and **10d**) display an AX pattern and the cationic complexes (**10b** and **10e**) show an AMX pattern. The chloro complex **10a** is formed by the complexation of (*SR*)-diastereomer of the diphosphazane to [CpRu] fragment and the complexes **10c** and **10d** are formed from the complexation of (*SS*)-diastereomer to [CpRu] fragment. The configuration of complexes **10c** and **10d** can be either $S_CR_PR_{Ru}$ or $S_CR_PS_{Ru}$. The absolute configuration at the phosphorus is likely to be '*R*' in the complexes **10c** and **10d** as it is formed from the (*SS*)-diastereomer of the diphosphazane. The cationic complex **10e** is obtained from the complexation of (*SS*)-diastereomer of the diphosphazane. The absolute configuration of cationic complex **10e** may be either $S_CR_PR_{Ru}$ or $S_CR_PS_{Ru}$. Attempts to isolate the complexes other than complex **10a** were unsuccessful.

The "chiral metalloligands" (**13** and **14**) possess four non-equivalent phosphorus nuclei and as a result, an AMRX type $^{31}P\{^1H\}$ spectrum is observed in each case. The spectra show a doublet of doublets for the phosphorus nuclei of the chelated diphosphazane (P_A and P_M). The P_R resonance (coordinated phosphorus of phosphinoalkane) is observed as a doublet of doublet of doublets (ddd); the dangling phosphorus (P_X) resonates as a doublet owing to coupling with the coordinated phosphorus of the diphosphane.

Absolute configuration of 10a

The molecular structure and absolute configuration of the complex **10a** have been confirmed by single crystal X-ray diffraction (Fig. 2). Selected bond lengths and bond angles of

Table 2 Selected bond distances (Å) and bond angles (°) in **10a**

Bond distances		Bond angles	
Ru(1)–Cl(1)	2.420(3)	P(1)–Ru–P(2)	69.3(1)
Ru(1)–P(1)	2.246(4)	Cl(1)–Ru–P(2)	96.8(2)
Ru(1)–P(2)	2.281(3)	Cl(1)–Ru–P(1)	100.2(1)
Ru(1)–C(1)	2.20(2)	Ru–P(1)–N(3)	97.0(4)
Ru(1)–C(2)	2.17(2)	Ru–P(1)–C(24)	130.9(5)
Ru(1)–C(3)	2.17(2)	Ru–P(1)–N(1)	115.6(3)
Ru(1)–C(4)	2.24(2)	N(1)–P(1)–N(3)	106.0(5)
Ru(1)–C(5)	2.21(2)	P(1)–N(1)–C(31)	128.7(1)
P(1)–N(1)	1.75(1)	P(1)–N(1)–N(2)	119.4(8)
P(1)–C(24)	1.81(1)	P(1)–N(3)–P(2)	99.2(5)
P(1)–N(3)	1.67(1)	Ru–P(1)–P(2)	56.0(1)
P(2)–N(3)	1.71(9)	N(1)–P(1)–P(2)	122.5(3)

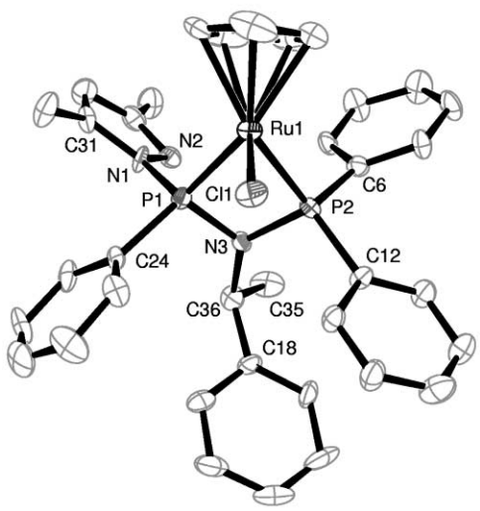


Fig. 2 Crystal structure of **10a**. The hydrogen atoms have been omitted for clarity.

complex **10a** are given in Table 2. The diphosphazane ligand is coordinated to ruthenium in a chelating mode utilizing its two-phosphorus donor sites. The pyrazolyl nitrogen is not involved in coordination to the metal. The ruthenium atom is in an octahedral environment and it is bound to the cyclopentadienyl ring (formally three *fac* positions), to the two phosphorus atoms of the diphosphazane ligand and to a chloride ion. The coordination geometry of the complex is that of a three legged "piano-stool" with a slight distortion because of the small bite angle of the diphosphazane ligand (P1–Ru–P2 angle is 69.3(1)°). The stereogenic carbon center derived from the "chiral-pool" (α-methyl benzylamine) was known to be *S* and this provided an independent check for correctness of the assignment of the absolute configuration. Considering complex **10a** as a pseudo-tetrahedral core with η^5-Cp occupying one coordination site and using modified Cahn–Ingold–Prelog rules[7] with the priority series η^5-Cp > Cl > PPh($N_2C_3HMe_2$-3,5) for ruthenium and Ru > N(*CHMePh) > $N_2C_3HMe_2$ >Ph for phosphorus, the absolute configuration is assigned as $S_CS_PR_{Ru}$. The change of configuration of the chiral phosphorus atom from *R* in the ligand to *S* in the metal complex arises because the ruthenium atom in the complex, which is given the higher preference in assigning the configuration, occupies the position of the lone pair at the chiral phosphorus atom of the ligand. The geometrical arrangement of the substituents around the chiral phosphorus center in the free ligand does not change after complexation.

Conclusions

We have shown here that P-chiral unsymmetrical diphosphazanes can be used to synthesize ruthenium complexes with a stereogenic metal center with a high degree of diastereoselectivity. The diasteromer formation is profoundly affected by varying the steric bulk at the substituent(s) of the chiral P-atom. The substituent at nitrogen also plays an important role; diphosphazanes bearing $CHMe_2$ group at nitrogen favor the formation of the cationic complexes of the type [CpRu{η^2-(X_2PN($CHMe_2$)PYY′)}PPh_3]Cl whereas a diphosphazane bearing *CHMePh group as substituent at the nitrogen favors neutral chloro complexes of the type [CpRu{η^2-(X_2PN(*CHMePh)PYY′)}Cl].

Experimental

Reactions were carried out under an atmosphere of argon by using conventional Schlenk techniques. Solvents were purified according to standard procedures. The starting materials [CpRu(PPh_3)$_2$Cl],[8] $Ph_2PN(CHMe_2)PPh_2$,[9] ($H_4C_6O_2$)PN($CHMe_2$)P($O_2C_6H_4$),[10] ($H_4C_6O_2$)PN($CHMe_2$)PPh_2,[10] Ph_2PN(*CHMePh)PPh_2,[4d] Ph_2P(*CHMePh)P*Ph($N_2C_3HMe_2$-3,5),[4d] and $Ph_2PN(CHMe_2)PPhY$ (Y = OC_6H_4Me-4, $OC_6H_3Me_2$-3,5, $N_2C_3HMe_2$-3,5)[11] were prepared as reported in the literature. The C, H, N analyses were performed on a Heraeus CHN-O rapid elemental analyzer. Nuclear magnetic resonance spectra were recorded using a Bruker ACF-200 or a Bruker AMX-400 spectrometer with $(CH_3)_4Si$ as an internal standard for ^{1}H NMR measurements and 85% H_3PO_4 as an external standard for $^{31}P\{^1H\}$ NMR measurements. Chemical shifts downfield from the standard were assigned positive values. Where necessary, the spectra were simulated using WINDAISY program supplied by Bruker. The X-ray diffraction data were collected using an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation) with a graphite monochromator.

Preparations

Synthesis of 2. A mixture of **1** (0.100 g, 1.37×10^{-4} mol) and L^1 (0.058 g, 1.37×10^{-4} mol) was dissolved in 20 mL of toluene. The reaction mixture was heated under reflux for 5 h and cooled to room temperature. A pale yellow solid was deposited during the course of the reaction. The solid was filtered off and washed with petrol. Recrystallisation of the crude product from CH_2Cl_2/petrol (1 : 3) mixture yielded **2** as a crystalline solid. Yield: 0.110 g (90%), mp 193–195 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.54–6.96 (m, aryl protons), 4.38 (s, C_5H_5), 4.10 (m, CH–Pr^i), 0.93 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). C, H, N analyses for $C_{50}ClH_{47}NP_3Ru$, found (calculated) (%): 67.10 (67.37), 5.17 (5.31), 1.60 (1.57).

Synthesis of 3. A mixture of **1** (0.100 g, 1.37×10^{-4} mol) and L^2 (0.046 g, 1.37×10^{-4} mol) was dissolved in 20 mL of toluene. The reaction mixture was heated under reflux for 5 h and cooled to room temperature. Concentration of the reaction mixture to ~10 mL followed by addition of petrol (10 mL) resulted in the precipitation of a pale yellow solid. The solid was recrystallised from toluene/petrol (1 : 1) mixture to obtain a pure product. Yield: 0.125 g (80%), mp 182–183 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.51–6.64 (m, aryl protons), 4.84 (s, C_5H_5), 2.90 (m, CH–Pr^i), 0.87 (d, $^3J_{HH}$ = 7.1 Hz, CH_3–Pr^i), 0.68 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). C, H, N analyses for $C_{53}ClH_{50}N_2O_8P_5Ru$, found (calculated) (%): 56.95 (56.11), 4.83 (4.44), 1.50 (2.47).

The reaction of 1 with L^3. A mixture of [CpRu(PPh_3)$_2$Cl] (0.1 g, 1.37×10^{-4} mol) and ($C_6H_4O_2$)PN($CHMe_2$)PPh_2 (0.053 g, 1.37×10^{-4} mol) was dissolved in 20 mL of toluene. The reaction mixture was heated under reflux for 3 h and cooled to room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated the formation of several products, of which **4a** and **4b** could be readily identified. Concentration of the reaction mixture to ~10 mL followed by addition of petrol (10 mL) precipitated a pale yellow solid. The solid was filtered

and recrystallized from CH_2Cl_2/petrol (1 : 3). It was identified as **4a**, admixed with **4b**. Efforts to isolate pure **4a** and **4b** were unsuccessful.

[CpRu{η²-(C₆H₄O₂)PN(CHMe₂)PPh₂)}(PPh₃)]Cl ***(4a)***. Yield: 0.046 (40%), mp 203 °C (decomp.). ^{1}H NMR ($CDCl_3$, ppm): 7.83–6.75 (m, aryl protons), 4.76 (s, C_5H_5), 2.86 (m, CH–Pr^i), 0.71 (d, $^3J_{HH}$ = 6.8 Hz, CH_3–Pr^i), 0.78 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). ^{31}P NMR ($CDCl_3$, ppm): 169.6 (t, P($O_2C_6H_4$)), 120 (br, PPh_2), 45.0 (t, PPh_3).

[CpRu{η¹-{Ph₂PN(CHMe₂)P(O₂C₆H₄)}₂(PPh₃)]Cl ***(4b)***. ^{31}P NMR ($CDCl_3$, ppm) (AA′XX′Y) 150.2 (dd, AA′, P($O_2C_6H_4$) uncoordinated), 123.0 (dd, XX′, PPh_2 coordinated), 48.6 (dd, PPh_3).

Synthesis of 5–7. A mixture of **1** (0.100 g, 1.37×10^{-4} mol) and L[4]–L[6] (0.063 g for Y = OC_6H_4Me-4, 0.065 g for Y = $OC_6H_3Me_2$-3,5, 0.061 g for Y = $N_2C_3HMe_2$-3,5, 1.37×10^{-4} mol) was dissolved in 30 mL of toluene and the solution was heated under reflux for 5 h. Concentration of the reaction mixture to ~10 mL followed by addition of 10 mL of petrol led to the precipitation of a pale yellow solid. The solid was recrystallized from toluene/petrol (1 : 2) to obtain the pure complexes.

[CpRu{η²-(Ph₂PN(CHMe₂)PPh(OC₆H₄Me-4))}(PPh₃)]Cl* ***5a***. Yield: 0.076 g (60%), mp 208 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.62–6.87 (m, aryl protons), 4.26 (s, C_5H_5), 3.80 (m, CH–Pr^i), 2.35 (s, Me–C_6H_4Me-4), 1.36 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i), 0.88 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). C, H, N analyses for $C_{51}ClH_{49}NOP_3Ru$, found (calculated) (%): 65.58 (66.48), 5.43 (5.38), 1.49 (1.52).

[CpRu{η²-(Ph₂PN(CHMe₂)PPh(OC₆H₃Me₂-3,5))}(PPh₃)]Cl* ***6***. Yield: 0.096 g (75%), mp 197 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.82–6.64 (m, aryl protons), 4.24 (s, C_5H_5), 3.80 (m, CH–Pr^i), 2.74 (s, Me–$OC_6H_3Me_2$-3,5), 2.42 (s, Me–$OC_6H_3Me_2$-3,5), 1.39(d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i), 0.88(d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). C, H, N analyses for $C_{52}ClH_{51}NOP_3Ru$, found (calculated) (%): 66.63 (66.76), 5.36 (5.49), 1.44 (1.49).

[CpRu{η²-(Ph₂PN(CHMe₂)PPh(N₂C₃HMe₂-3,5))}(PPh₃)]Cl* ***7***. Yield: 0.094 g (75%), mp 182 °C. ^{1}H NMR ($CDCl_3$, ppm): 7.50–6.4 (m, aryl protons), 4.32 (s, C_5H_5), 3.70 (m, CH–Pr^i), 2.80 (s, Me–$N_2C_3HMe_2$-3,5), 2.42 (s, Me–$N_2C_3HMe_2$-3,5), 1.12 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i), 0.94 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). C, H, N analyses for $C_{49}ClH_{49}N_3P_3Ru$, found (calculated) (%): 62.84 (64.77), 5.91 (5.43), 5.12 (4.62).

Synthesis of 8. A mixture of [CpRu(PPh_3)$_2$Cl] (0.100 g, 1.37×10^{-4} mol) and (*S*),(*R*)-$Ph_2PN(CHMe_2)P(O_2C_{20}H_{12})$ (L[7]) (0.076 g, 1.37×10^{-4} mol) was dissolved in 30 mL of toluene. The reaction mixture was heated under reflux for 5 h and cooled to room temperature. The ^{31}P NMR spectrum of the reaction mixture indicated that the product was a mixture of complexes **8a**–**8e**. Concentration of the reaction mixture to 10 mL followed by addition of petrol resulted in the precipitation of a pale yellow powder. The solid was filtered and recrystallised from CH_2Cl_2/toluene (1 : 3) mixture to obtain yellow crystals of **8a**. The ^{31}P–^{31}P COSY spectrum of the filtrate confirmed the presence of complexes **8b**–**8e**.

[CpRu{η²-(L[7])}(PPh₃)]Cl ***8a***. Yield: 0.080 g (60%), mp 208–212 °C. ^{1}H NMR ($CDCl_3$, ppm): 8.15–7.11 (m, aryl protons), 4.60 (s, C_5H_5), 3.20 (m, CH–Pr^i), 0.73 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i), 0.67 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–Pr^i). C, H, N analyses for $C_{58}ClH_{49}N0_2P_3Ru$, found (calculated) (%): 69.32 (68.19), 4.64 (4.83), 1.42 (1.37).

Synthesis of 9. A mixture of **1** (0.100 g, 1.37×10^{-4} mol) and L[7] (0.065 g, 1.37×10^{-4} mol) was dissolved in 30 mL of toluene. The reaction mixture was heated under reflux for 5 h and cooled to room temperature. The resultant solution was concentrated *in vacuo* to 15 mL and cooled to 0 °C for 2 h to obtain a pale yellow crystalline solid (**9b**). The solid was filtered. Concentration of the filtrate to 5 mL and addition of 5 mL of petrol gave complex **9a** as cherry red crystals.

*[CpRu{η²-((S)-Ph₂PN(*CHMePh)PPh₂)}Cl]* ***9a***. Yield: 0.067 g (70%), mp 185–187 °C. ^{1}H NMR ($CDCl_3$, ppm): 8.11–6.75 (m, aryl protons), 4.45 (m, CH–*CHMePh), 4.04 (s, C_5H_5), 0.68 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{37}ClH_{34}NP_2Ru$, found (calculated) (%): 64.05 (64.29), 5.23 (4.95), 1.92 (2.02).

*[CpRu{η²-((S)-Ph₂PN(*CHMePh)PPh₂)}(PPh₃)]Cl* ***9b***. Yield: 0.006 g (5%), mp 142 °C (melts with decomposition). ^{1}H NMR ($CDCl_3$, ppm): 7.57–6.62 (m, aryl protons), 4.34 (s, C_5H_5), 4.83 (m, CH–*CHMePh), 1.14 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{55}ClH_{49}NP_3Ru$, found (calculated) (%): 65.05 (65.29), 5.20 (5.18), 1.52 (1.47).

Synthesis of 10. A mixture of **1** (0.100 g, 1.37×10^{-4} mol) and L[9] (0.069 g, 1.37×10^{-4} mol) was dissolved in 30 mL of toluene. The reaction mixture was heated under reflux for 5 h and cooled to room temperature. The ^{31}P NMR spectrum indicated that the product was a mixture of complexes **10a** and **10b**. Concentration of the reaction mixture to 10 mL followed by slow addition of petrol gave complex **10a** as dark red crystals. The complex **10b** could not be isolated in a pure form.

*(S_C S_P R_Ru)-[CpRu{η²-(Ph₂PN(*CHMePh)*PPh(N₂C₃HMe₂-3,5))}Cl]* ***10a***. Yield: 0.067 g (60%), mp 205 °C (melts with decomposition). ^{1}H NMR ($CDCl_3$, ppm): 8.11–6.01 (m, aryl protons), 5.40 (m, CH–*CHMePh), 4.23 (s, C_5H_5), 2.45 (s, Me–$N_2C_3HMe_2$-3,5), 2.04 (s, Me–$N_2C_3HMe_2$-3,5), 1.57 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{36}ClH_{36}N_3P_2Ru$, found (calculated) (%): 61.15 (60.97), 5.30 (5.12), 6.01 (5.92).

The reaction of 1 with (*SS*)- and (*SR*)-L[9]. Reaction of [CpRu(PPh_3)$_2$Cl] (0.100 g, 1.37×10^{-4} mol) with a diastereomeric mixture of the diphosphazane, (*SS*)- and (*SR*)-Ph_2PN(*CHMePh)P*Ph($N_2C_3HMe_2$-3,5) (~0.07 g, ~1.400×10^{-4} mol) in boiling toluene for 5 h gave a mixture of compounds **10a**–**10e** as shown by ^{31}P NMR spectrum of the reaction mixture. Attempts to separate the complexes in a pure form were unsuccessful.

Synthesis of 11 and 12. A solution of **9a** (0.051 g, 7.23×10^{-5} mol) in 20 mL of CH_2Cl_2 was added drop-wise to a solution of PX_3 (0.019 g for PPh_3, 0.008 g for $P(OMe)_3$, 7.23×10^{-5} mol) and NH_4PF_6 (0.012 g, 7.23×10^{-5}mol) in CH_2Cl_2. The reaction mixture was stirred for 12 h and the solvent was removed *in vacuo* to obtain a crude yellow solid. The residue was washed twice with hot petrol to remove the monophosphane and crystallized from CH_2Cl_2/petrol (1 : 3) to obtain a pale-yellow crystalline solid.

*[CpRu{η²-((S)-Ph₂PN(*CHMePh)PPh₂)}(PPh₃)]PF₆* ***11***. Yield: 0.054 g (70%), mp 192 °C (melts with decomposition). ^{1}H NMR ($CDCl_3$, ppm): 7.78–6.70 (m, aryl protons), 4.34 (s, C_5H_5), 4.90 (m, CH–*CHMePh), 1.14 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{55}F_6H_{49}NP_4Ru$, found (calculated) (%): 62.24 (62.15), 4.62 (4.65), 1.33 (1.32).

*[CpRu{η²-((S)-Ph₂PN(*CHMePh)PPh₂)}{P(OMe)₃}]PF₆* ***12***. Yield: 0.047 g (70%), mp 130 °C (melts with decomposition). ^{1}H NMR ($CDCl_3$, ppm): 7.90–6.70 (m, aryl protons), 4.82 (s, C_5H_5), 4.32 (m, CH–*CHMePh), 3.2 (d, Me–P($OMe)_3$, $^3J_{PH}$ = 22 Hz) 1.10 (d, $^3J_{HH}$ = 7.0 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{40}F_6H_{43}NP_5Ru$, found (calculated) (%): 51.20 (51.95), 4.10 (4.69), 2.20 (1.51).

Synthesis of 13 and 14. These complexes were prepared by the same procedure as described above for the complexes **11** and **12**.

*[CpRu{η²-((S)-Ph₂PN(*CHMePh)PPh₂)}{η¹-(Ph₂P(CH₂)PPh₂)}]PF₆* ***13***. Yield: 0.064 g (60%), mp 179 °C (melts with

Table 3 Details of the X–ray data collection and refinement for compound **10a**

Empirical formula	$C_{36}H_{36}ClN_3P_2Ru$
M	709.14
Crystal color, habit	Red, prism
Crystal dimensions/mm	0.15 × 0.1 × 0.1
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	13.131(2)
b/Å	14.297(2)
c/Å	17.2878(2)
U/Å^3	3245.5(7)
Temperature/K	293(2)
Z	4
μ/mm	0.694
Measured reflections	3198
Independent observed reflections (R_{int})	3198 [R(int) = 0.0000]
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0634, $wR2$ = 0.0712
R indices (all data)	$R1$ = 0.1787, $wR2$ = 0.0950

decomposition). ^{1}H NMR ($CDCl_3$, ppm): 7.90–6.20 (m, aryl protons), 4.75 (s, C_5H_5), 4.34 (m, CH–*CHMePh), 2.19 (d, CH_2-dppm), 1.92 (d, CH_2-dppm), 0.34 (d, $^3J_{HH}$ = 7.2 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{62}F_6H_{56}NP_5Ru$, found (calculated) (%): 63.11 (62.84), 4.81 (4.76), 1.17 (1.18).

*[CpRu{η^2-((S)-Ph_2PN(*CHMePh)PPh_2)}{η^1-(Ph_2-P(CH_2)$_2PPh_2$)}]PF_6* ***14***. Yield: 0.054 g (75%), mp 168 °C (melts with decomposition). ^{1}H NMR ($CDCl_3$, ppm): 7.90–6.50 (m, aryl protons), 4.69 (s, C_5H_5), 4.50 (m, CH–*CHMePh), 1.48 (d, CH_2-dppe), 1.22 (d, CH_2-dppe), 0.46 (d, $^3J_{HH}$ = 7.2 Hz, CH_3–*CHMePh). C, H, N analyses for $C_{63}F_6H_{58}NP_5Ru$, found (calculated) (%): 63.50 (63.10), 4.90 (4.87), 1.14 (1.17).

X-Ray crystallography

Pertinent crystallographic data for **10a** are summarized in Table 3. A suitable crystal for X-ray analysis was glued to a glass fiber and coated with paraffin oil to protect it from atmospheric air and moisture during data collection. Cell constants were obtained by least-squares refinement of the setting angles of 25 reflections in the range $15 < 2\theta < 30°$. The intensity data collection was monitored for any variations by three repeatedly measured control reflections. Lorentz, polarization and absorption (DIFABS) corrections were applied to the intensity data. The structure was solved by Patterson method using SHELXS-86; least square refinements were performed by the full-matrix method with SHELXL-97.[12] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

CCDC reference number 186808.

See http://www.rsc.org/suppdata/dt/b2/b205247d/ for crystallographic data in CIF or other electronic format.

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References

1 (*a*) E. P. Kundig, C. M. Saudan and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1220; (*b*) C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao and W. Weissensteiner, *J. Chem. Soc., Dalton Trans.*, 2001, 2989; (*c*) V. Ritleng, P. Bertani, M. Pfeffer, C. Sirlin and J. Hirschinger, *Inorg. Chem.*, 2001, **40**, 5117; (*d*) W. Baratta, W. A. Hermann, R. M. Kratzer and P. Rigo, *Organometallics*, 2000, **19**, 3664; (*e*) W. Baratta, A. D. Zotto and P. Rigo, *Organometallics*, 1999, **18**, 5091; (*f*) H. Brunner, C. Valerio and M. Zabel, *New J. Chem.*, 2000, **24**, 275.

2 (*a*) H. Brunner, *Angew. Chem., Int. Ed.*, 1999, **38**, 1194; (*b*) G. Consiglio and F. Morandini, *Chem. Rev.*, 1987, **87**, 761; (*c*) H. Brunner, *Adv. Organomet. Chem.*, 1980, **18**, 151.

3 (*a*) M. Ito, M. Hirakawa, K. Mukarta and T. Ikariya, *Organometallics*, 2001, **20**, 379; (*b*) J. W. Faller, B. P. Patel, M. A. Albrizzio and M. Curtis, *Organometallics*, 1999, **18**, 3096; (*c*) H. Brunner and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, **9**, 3231; (*d*) H. Brunner, B. Nuber and M. Prommesberger, *Tetrahedron: Asymmetry*, 1998, **9**, 3223; (*e*) H. Brunner, R. Oeschey and B. Nuber, *Organometallics*, 1996, **15**, 3616; (*f*) H. Brunner, R. Oeschey and B. Nuber, *J. Chem. Soc., Dalton Trans.*, 1996, 1499; (*g*) J. W. Faller and K. J. Chase, *Organometallics*, 1995, **14**, 1592.

4 For references on chiral diphosphazanes and their transition metal complexes, see: (*a*) Y. Gimbert, F. Robert, A. Durif, M. T. Averbuch, N. Kann and A. E. Greene, *J. Org. Chem.*, 1999, **64**, 3492; (*b*) A. Badia, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1998, **554**, 105; (*c*) R. P. K. Babu, S. S. Krishnamurthy and M. Nethaji, *Organometallics*, 1995, **14**, 2047; (*d*) R. P. K. Babu, S. S. Krishnamurthy and M. Nethaji, *Tetrahedron: Asymmetry*, 1995, **6**, 427.

5 Part 14. M. Ganesan, S. S. Krishnamurthy and M. Nethaji, *J. Organomet. Chem.*, 1998, **570**, 247.

6 For ruthenium complexes of diphosphazanes, see: (*a*) M. S. Balakrishna, R. Panda, D. C. Smith, Jr., A. Klaman and S. P. Nolan, *J. Organomet. Chem.*, 2000, **599**, 159; (*b*) M. S. Balakrishna, K. Ramaswamy and R. M. Abhyankar, *J. Organomet. Chem.*, 1998, **560**, 131; (*c*) J. Ellermann, C. Schelle, F. A. Knoch, M. Moll and D. Pohl, *Monatsh. Chem.*, 1996, **127**, 783; (*d*) J. Ellermann, C. Schelle, M. Moll, F. A. Knoch and W. Z. Bauer, *Z. Anorg. Allg. Chem.*, 1995, **621**, 789.

7 (*a*) T. E. Sloan, *Top. Stereochem.*, 1981, **12**, 1; (*b*) K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, 1975, **97**, 6598.

8 M. I. Bruce, I. Hameister, A. G. Swincer and R. C. Wallis, *Inorg. Synth.*, 1982, **21**, 78.

9 R. J. Cross, T. H. Green and R. J. Keat, *J. Chem. Soc., Dalton Trans.*, 1976, 1424.

10 R. P. K. Babu, S. S. Krishnamurthy and M. Nethaji, *Heteroat. Chem.*, 1991, **2**, 477.

11 R. P. K. Babu, K. Aparna, S. S. Krishnamurthy and M. Nethaji, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1995, **103**, 39.

12 G. M. Sheldrick, SHELXL97, Program for the refinement of crystal structures, University of Göttingen, Germany, 1997.