

Organometallic chemistry of chiral diphosphazane ligands: Synthesis and structural characterisation

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Abstract. The diphosphazane ligands of the type, $(C_{20}H_{12}O_2)PN(R)P(E)Y_2$ ($R = CHMe_2$ or (S) -*CHMePh; $E =$ lone pair or S ; $Y_2 = O_2C_{20}H_{12}$ or $Y = OC_6H_5$ or OC_6H_4Me-4 or OC_6H_4OMe-4 or $OC_6H_4Bu^t-4$ or C_6H_5) bearing axially chiral 1,1'-binaphthyl-2,2'-dioxy moiety have been synthesised. The structure and absolute configuration of a diastereomeric palladium complex, $[PdCl_2\{h^2-((O_2C_{20}H_{12})PN((S)$ -*CHMePh)PPh $_2\})]$ has been determined by X-ray crystallography. The reactions of $[CpRu(PPh_3)_2Cl]$ with various symmetrical and unsymmetrical diphosphazanes of the type, $X_2PN(R)PY_2$ ($R = CHMe_2$ or (S) -*CHMePh; $X = C_6H_5$ or $X_2 = O_2C_{20}H_{12}$; $Y = Y' = C_6H_5$ or $Y = C_6H_5$, $Y' = OC_6H_4Me-4$ or $OC_6H_3Me_2-3,5$ or $N_2C_3HMe_2-3,5$) yield several diastereomeric neutral or cationic half-sandwich ruthenium complexes which contain a stereogenic metal center. In one case, the absolute configuration of a trichiral ruthenium complex, viz. $[Cp^*Ru\{h^2-Ph_2PN((S)$ -*CHMePh)*PPh $(N_2C_3HMe_2-3,5)\}Cl]$ is established by X-ray diffraction. The reactions of $Ru_3(CO)_{12}$ with the diphosphazanes $(C_{20}H_{12}O_2)PN(R)PY_2$ ($R = CHMe_2$ or Me ; $Y_2 = O_2C_{20}H_{12}$ or $Y = OC_6H_5$ or OC_6H_4Me-4 or OC_6H_4OMe-4 or $OC_6H_4Bu^t-4$ or C_6H_5) yield the tri-ruthenium clusters $[Ru_3(CO)_{10}\{m(O_2C_{20}H_{12})PN(R)PY_2\}]$, in which the diphosphazane ligand bridges two metal centres. Palladium allyl chemistry of some of these chiral ligands has been investigated. The structures of isomeric h^3 -allyl palladium complexes, $[Pd(h^3-1,3-R'_2-C_3H_3)\{h^2-(rac)-(O_2C_{20}H_{12})PN(CHMe_2)PY_2\}](PF_6)$ ($R' = Me$ or Ph ; $Y = C_6H_5$ or OC_6H_5) have been elucidated by high field two-dimensional NMR spectroscopic and X-ray crystallographic studies.

Keywords. Chiral phosphorus ligands; diphosphazanes; half-sandwich ruthenium complexes; chiral tri-ruthenium clusters; h^3 -allyl palladium complexes.

1. Introduction

Diphosphazanes constitute a class of versatile short-bite bidentate P-donor ligands that have given rise to a varied and extensive transition metal organometallic chemistry. The organometallic chemistry of diphosphazane ligands with almost every transition metal in the periodic table is well documented^{1–3}. A very attractive feature of diphosphazane ligands is that 'chirality' can be incorporated at the phosphorus centres as well as at the substituents attached to the nitrogen and the two phosphorus atoms. Furthermore, these ligand systems can be suitably modified thus providing an access to a range of mixed donor ligands. Heterofunctional diphosphazanes bearing P,O-, P,S- or P,N-

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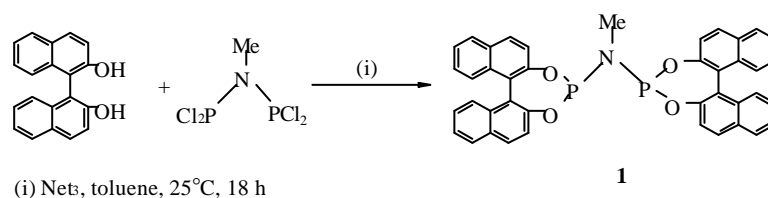
functionalities at one or both the phosphorus centers can be readily prepared. Interest in chiral diphosphazanes and their transition metal complexes has burgeoned recently^{4–6}. As a part of our ongoing investigations on the organometallic chemistry of diphosphazane ligands^{7–11}, herein we present a review of our recent work on the design and synthesis of several chiral diphosphazane ligands and their reactivity with various transition metal precursors. The synthesis and characterization of a new series of half-sandwich cyclopentadienyl ruthenium complexes and tri-ruthenium carbonyl clusters bearing chiral symmetrically and unsymmetrically substituted diphosphazanes are highlighted. In addition, results of highfield two-dimensional NMR studies on η^3 -allyl-palladium complexes of chiral diphosphazanes are reported.

2. Results and discussion

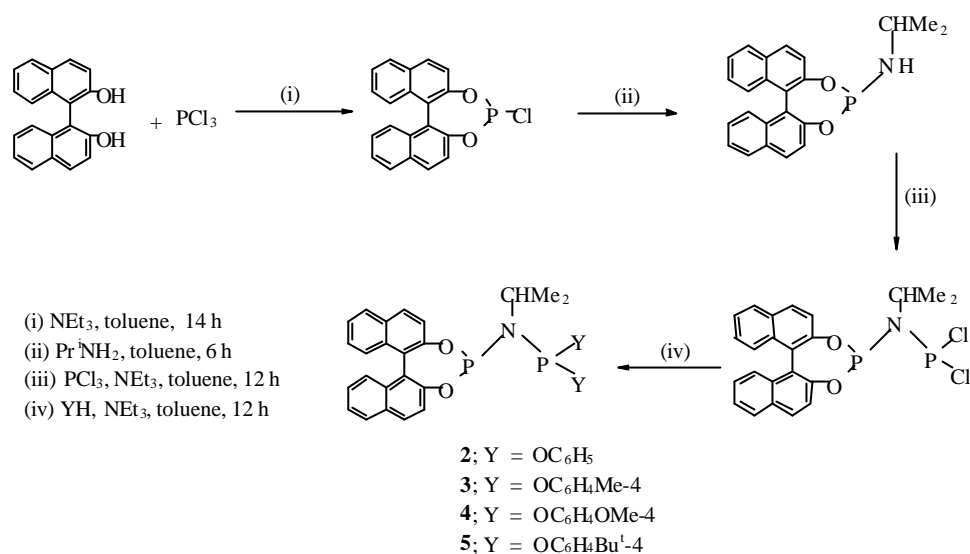
2.1 Synthesis of ligands

Symmetrically substituted diphosphazane (*RR*, *SS*) and (*SR*, *RS*)-($C_{20}H_{12}O_2$)PN(Me)P($O_2C_{20}H_{12}$) (**1**), bearing the axially chiral 1,1'-binaphthyl-2,2'-dioxy moiety, is prepared by the treatment of *bis*(dichlorophosphino)methylamine with two equivalents of racemic-1,1'-binaphthyl-2,2'-diol in the presence of a base such as triethylamine as shown in scheme 1. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture reveals the presence of two diastereomers in 1.4:1 ratio. The diastereomers are assigned as a mixture of the racemic pair (*RR* and *SS*) and the meso pair (*SR* and *RS*). Attempts to separate these diastereomers have so far been unsuccessful. However, the use of optically pure 1,1'-binaphthyl-2,2'-diol (*R* or *S*) has resulted in the synthesis of optically pure symmetrically substituted diphosphazane, (*RR* or *SS*)-($C_{20}H_{12}O_2$)PN(Me)P($O_2C_{20}H_{12}$).

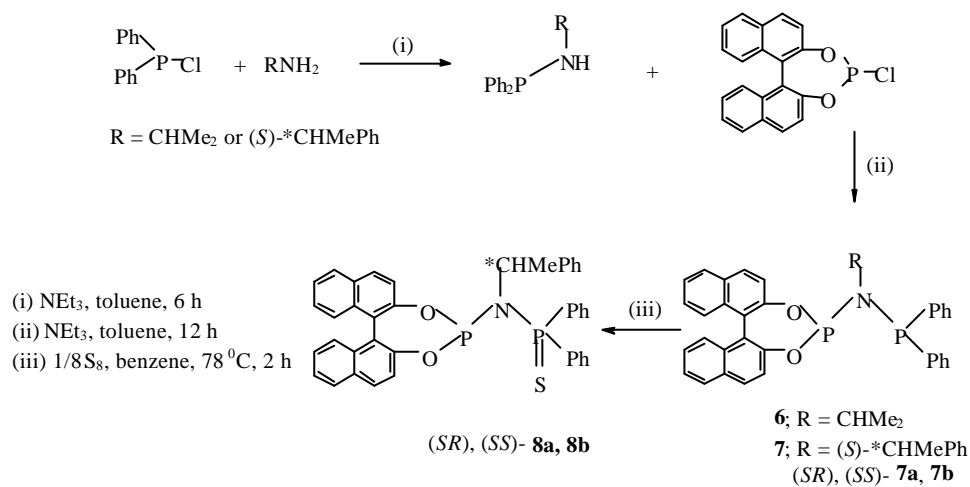
The unsymmetrical diphosphazanes, (*rac*)-($C_{20}H_{12}O_2$)PN(CHMe₂)PY₂ [Y = OC₆H₅ (**2**), OC₆H₄Me-4 (**3**), OC₆H₄OMe-4 (**4**), or OC₆H₄Bu^t-4 (**5**)] are prepared as shown in scheme 2. The reaction of racemic-[1,1'-binaphthyl]-2,2'-phosphorochloridite, (*rac*)-($C_{20}H_{12}O_2$)PCl with three equivalents of Pr^tNH₂ in toluene gives the amino derivative, (*rac*)-($C_{20}H_{12}O_2$)PNH(CHMe₂) which is treated with PCl₃ in the presence of NEt₃ to yield (*rac*)-($C_{20}H_{12}O_2$)PN(CHMe₂)PCl₂. Subsequent derivatization with various phenols gives the unsymmetrically substituted diphosphazane ligands **2–5**. The unsymmetrical diphosphazanes (*rac*)-($C_{20}H_{12}O_2$)PN(R)PPh₂ [R = CHMe₂ (**6**) or (*S*)-*CHMePh (**7**)] have also been prepared by the reaction of the (amino)phosphane, Ph₂PNH(R) with the racemic-[1,1'-binaphthyl]-2,2'-phosphorochloridite, (*rac*)-($C_{20}H_{12}O_2$)PCl in the presence of Et₃N (scheme 3). The ligand **7** exists as a mixture of two diastereomers (*SR* and *SS*) in 1:1 ratio owing to the presence of a stereogenic center on the substituent attached to the nitrogen as revealed by its $^{31}P\{^1H\}$ NMR spectrum. The separation of these diastereomers by fractional crystallization was not successful. Since both the



Scheme 1.



Scheme 2.



Scheme 3.

diastereomers **7a** and **7b** did not show appreciable solubility difference in common organic solvents, attempts were made to separate the diastereomers by converting them to the corresponding monosulfides. A diastereomeric mixture of the diphosphazane monosulfides **8a** and **8b** is obtained by heating the diphosphazanes **7a** and **7b** with elemental sulfur (1:1/8) in boiling benzene (scheme 3). Oxidation to $\text{P}=\text{S}$ unit occurs only at the $-\text{PPh}_2$ end as would be anticipated from the greater nucleophilicity of diphenyl

substituted phosphorus compared to $-\text{P}(\text{O}_2\text{C}_2\text{O}_2\text{H}_{12})$ phosphorus. Attempts to separate these diastereomers (**8a** and **8b**) by fractional crystallization from various solvents have not been successful. The ligands **1–8** are characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and elemental analyses. The unsymmetrically substituted ligands **2–8** show an AX pattern in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

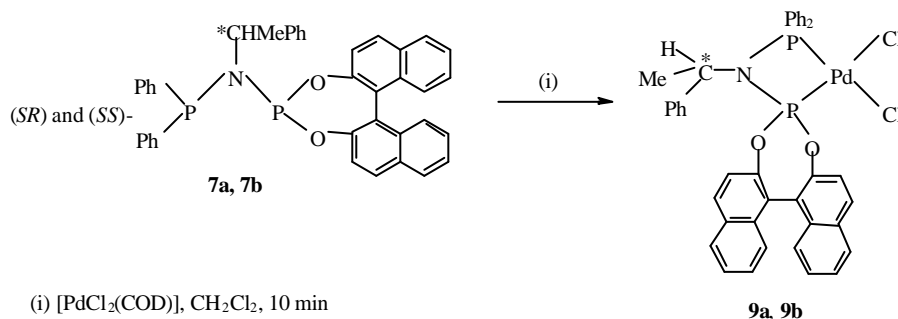
2.2 Synthesis of palladium complexes of (SR) and (SS)- $(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}((S)-^*\text{CHMePh})\text{PPh}_2$ (**7**)

In an attempt to separate the diastereomers of the title diphosphazane ligand (**7**), a different approach has been attempted and this involves complexation with palladium. The reaction of $[\text{PdCl}_2(\text{COD})]$ with a diastereomeric mixture of (SS) and (SR)- $(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{R})\text{PPh}_2$ ($\text{R} = (S)-^*\text{CHMePh}$) (**7**) at 25°C gives the diastereomeric complexes *cis*-(SS) and (SR)- $[\text{PdCl}_2\{\text{H}^2-(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}((S)-^*\text{CHMePh})\text{PPh}_2\}]$ (**9a** and **9b**) (scheme 4). The formation of both the diastereomers is clearly evident from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture. The separation of the diastereomers **9a** and **9b** can be achieved by selective crystallization from $\text{CH}_2\text{Cl}_2/\text{petrol}$ (1:1).

The (SR)-diastereomer **9a** is isolated in a pure state. The other diastereomer (SS) could not be obtained in a pure state. The (SR)-diastereomer (**9a**) has been characterised by elemental analysis, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and its structure determined by X-ray crystallography. A perspective view of the molecule is shown in figure 1. The absolute configuration of the chiral diphosphazane in the complex can be assigned by applying Cahn, Ingold and Prelog rules. The configuration at the chiral carbon is *S* and based on this, the configuration of the binaphthyl skeleton can be assigned as *R*.

2.3 Reactions of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ with chiral diphosphazanes: Synthesis of chiral half-sandwich ruthenium complexes

The displacement of the two enantiotopic PPh_3 ligands in $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ by a chiral diphosphane would lead to chiral half-sandwich ruthenium complexes¹². The reaction of a racemic unsymmetrical diphosphazane with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ may lead to the formation of two diastereomeric pairs, $\{(RR), (SS)\}$ -racemic pair and $\{(SR), (RS)\}$ -meso pair. The reaction of $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ with the racemic diphosphazane, (*rac*)- $(\text{H}_{12}\text{C}_{20}\text{O}_2)\text{PN}(\text{CHMe}_2)\text{PPh}_2$ in 1:1 molar proportions at 100°C for 5 h in toluene gives the complexes **10a–10e** (scheme 5). Complex **10a** may be either racemic or meso-diastereomer and is



Scheme 4.

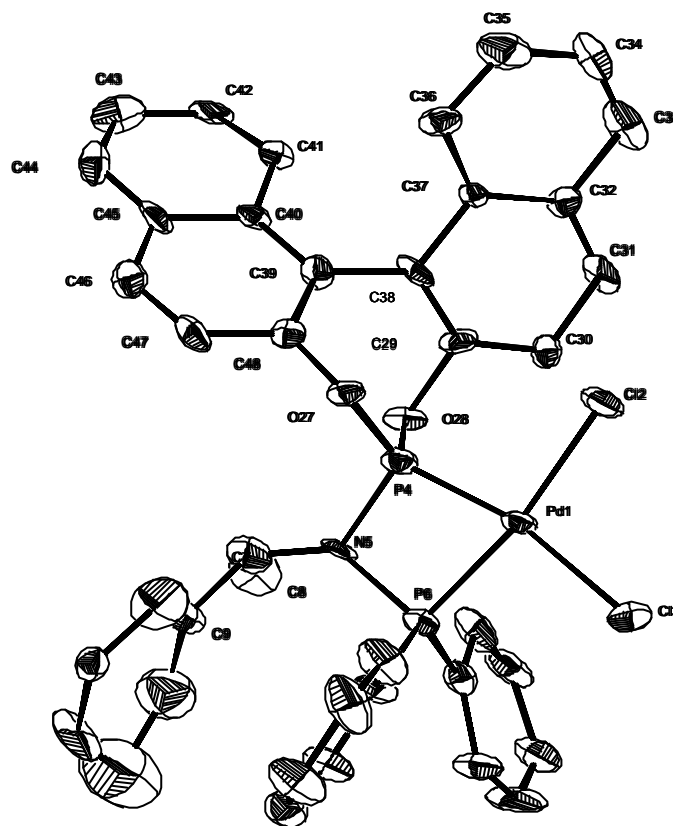
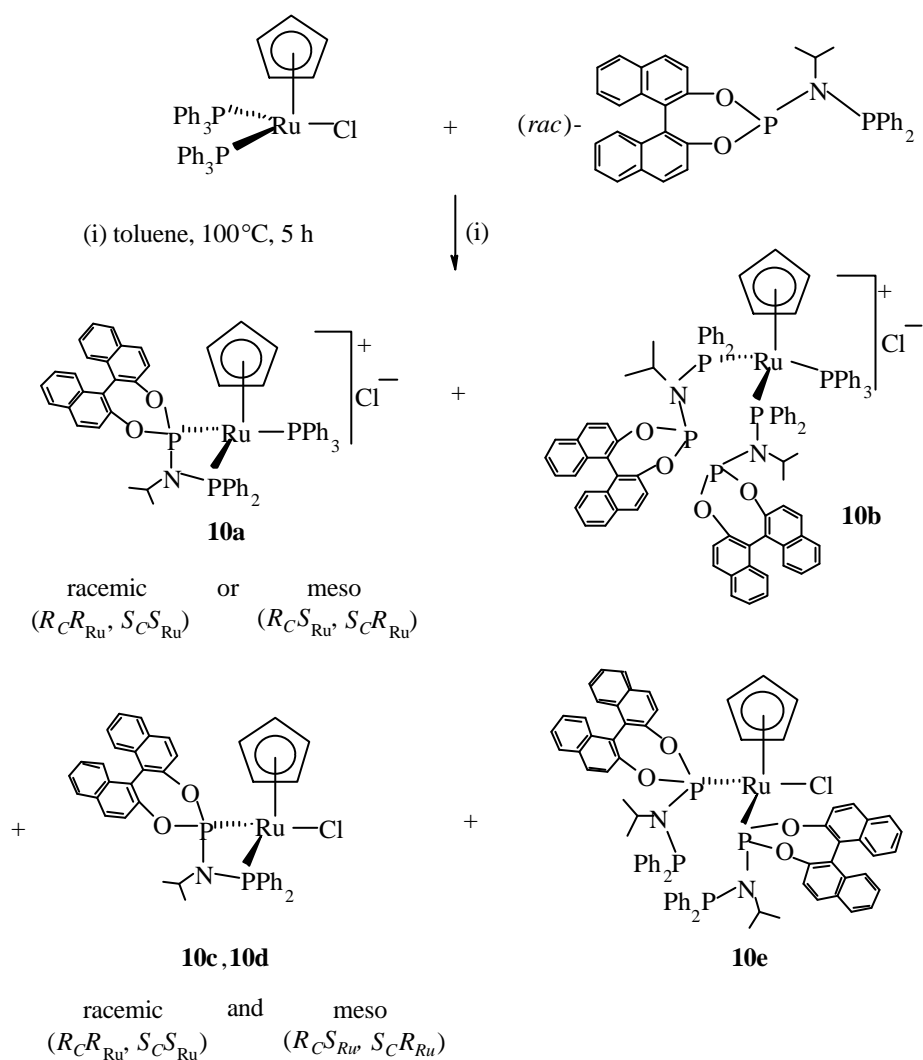


Figure 1. A view of the molecular structure of complex **9a**. Hydrogen atoms have been omitted for clarity.

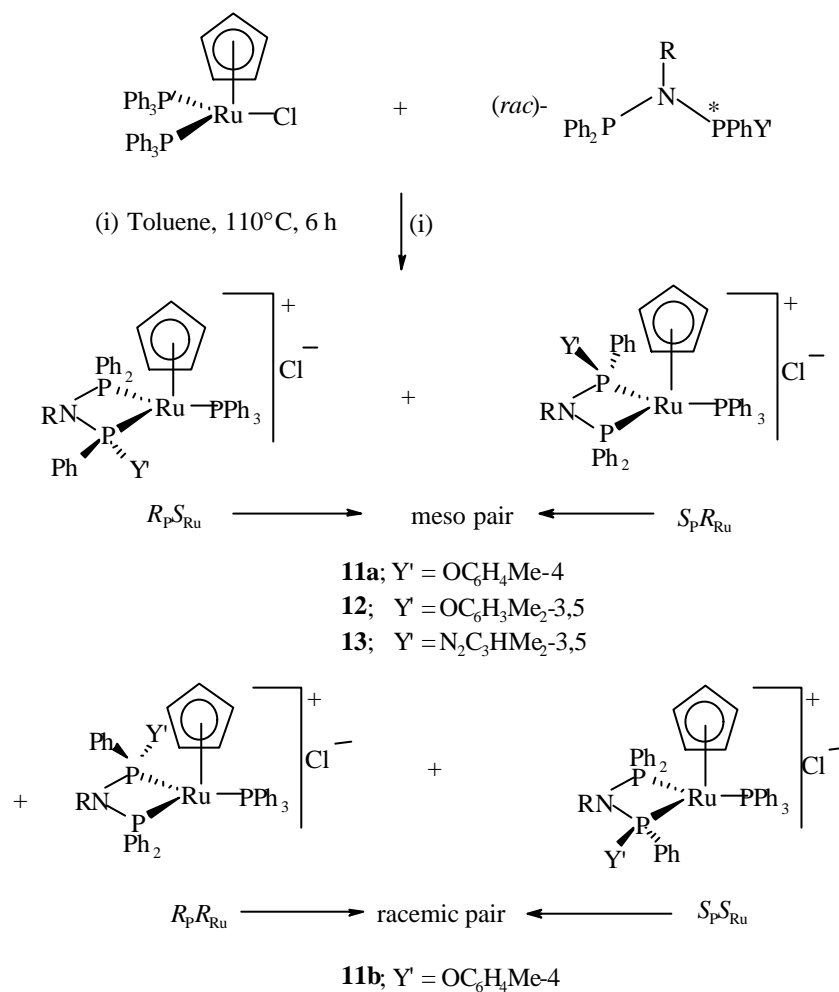
the major product. It is isolated in a pure state and characterized by elemental analysis, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the mother liquor after removing complex **10a** shows the presence of four other complexes (**10b–10e**) (scheme 5). These complexes (**10b–10e**) could not be isolated in a pure state owing to difficulties in their separation and also sensitivity of these complexes towards air and moisture. Nevertheless, the presence of these complexes is confirmed by the $^{31}\text{P}\text{--}^{31}\text{P}$ COSY spectrum of the mixture and their structures assigned on the basis of $^{31}\text{P}\{^1\text{H}\}$ NMR data.

The reactions of racemic unsymmetrical ‘P-stereogenic’ diphosphazanes of the type $\text{X}_2\text{PN}(\text{R})^*\text{PYY}'$ with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ have been investigated (scheme 6). In these reactions, the steric bulk at the chiral phosphorus is varied; substituents R, X and Y are kept constant ($\text{R} = \text{CHMe}_2$, $\text{X} = \text{Y} = \text{Ph}$) while Y' is varied ($\text{Y}' = \text{OC}_6\text{H}_4\text{Me-4}$, $\text{OC}_6\text{H}_3\text{Me}_2\text{-3,5}$ or $\text{N}_2\text{C}_3\text{HMe}_2\text{-3,5}$). The reaction of $\text{Ph}_2\text{PN}(\text{CHMe}_2)^*\text{PPh}(\text{OC}_6\text{H}_4\text{Me-4})$ with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ in 1:1 molar proportion gives two diastereomeric cationic complexes (racemic and meso) $[\text{Cp}^*\text{Ru}\{\text{H}^2\text{-Ph}_2\text{PN}(\text{CHMe}_2)^*\text{PPh}(\text{OC}_6\text{H}_4\text{Me-4})\}\text{PPh}_3]\text{Cl}$ (**11a** and **11b**) in the ratio 1.5:1. The major diastereomer **11a** (meso or racemic) has been isolated in a pure form as a yellow crystalline solid, whereas the minor diastereomer **11b**

(meso or racemic) is obtained only as an oily liquid. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the mixture confirms the presence of two diastereomers; it shows two AMX patterns corresponding to two diastereomeric complexes **11a** and **11b**. The reactions of diphosphazanes bearing a slightly more bulky substituent on the chiral phosphorus atom, $\text{Ph}_2\text{PN}(\text{CHMe}_2)^*\text{PPh}(\text{OC}_6\text{H}_3\text{Me}_2\text{-}3,5)$ or $\text{Ph}_2\text{PN}(\text{CHMe}_2)^*\text{PPh}(\text{N}_2\text{C}_3\text{HMe}_2\text{-}3,5)$ with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ give only a single pair of cationic ruthenium diphosphazane complexes, $[\text{Cp}^*\text{Ru}\{\text{H}^2\text{-Ph}_2\text{PN}(\text{CHMe}_2)^*\text{PPh}(\text{OC}_6\text{H}_3\text{Me}_2\text{-}3,5)\}\text{PPh}_3]\text{Cl}$ (**12**) or $[\text{Cp}^*\text{Ru}\{\text{H}^2\text{-Ph}_2\text{PN}(\text{CHMe}_2)^*\text{PPh}(\text{N}_2\text{C}_3\text{HMe}_2\text{-}3,5)\}\text{PPh}_3]\text{Cl}$ (**13**) respectively in good yields. In these cases, only one AMX pattern is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixtures. The reactivity difference observed among the above diphosphazane ligands can be attributed to the differing steric bulk of the substituent on the stereogenic



Scheme 5.

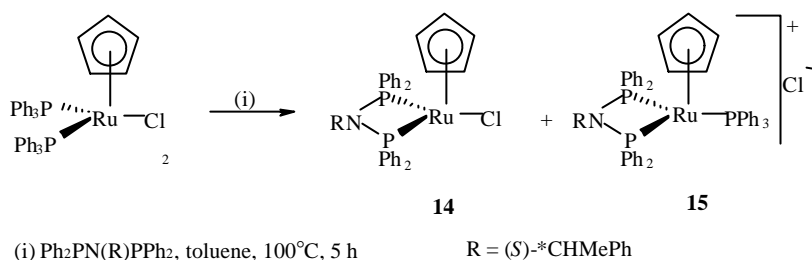


Scheme 6.

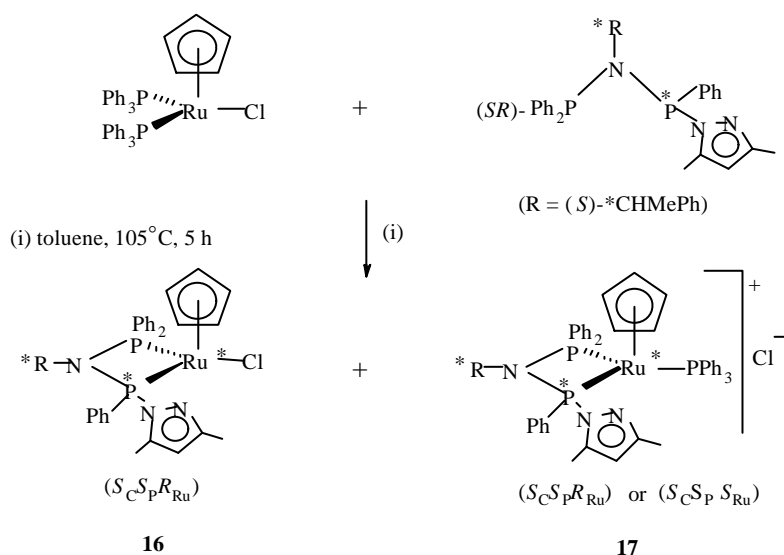
phosphorus atom as the substituents on the nitrogen and the other phosphorus atom are not altered.

The reaction of a chiral symmetrical diphosphazane of the type $\text{Ph}_2\text{PN}((S)\text{-*CHMePh})\text{PPh}_2$ (in which chirality resides at the substituent attached to nitrogen atom) with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ would give an optically active transition metal complex with the chirality at the back bone. The reaction of $\text{Ph}_2\text{PN}((S)\text{-*CHMePh})\text{PPh}_2$ with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ in toluene at 100°C gives the neutral complex $[\text{CpRu}\{\text{H}^2\text{-Ph}_2\text{PN}(\text{R})\text{PPh}_2\}\text{Cl}]$ (**14**) and the cationic complex $[\text{CpRu}\{\text{H}^2\text{-Ph}_2\text{PN}(\text{R})\text{PPh}_2\}\text{PPh}_3]\text{Cl}$ (**15**) in 80 and 5% yields respectively (scheme 7). The complexes **14** and **15** have been characterized by elemental analyses, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the neutral complex **14** shows an AX pattern. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the cationic complex **15** displays an AMX pattern.

The reaction of an optically pure unsymmetrical diphosphazane of the type $X_2PN(*R)*PYY'$ with $[CpRu(PPh_3)_2Cl]$ would give diastereomeric half-sandwich ruthenium complexes with chirality at the metal. By this reaction, complexes containing three stereogenic centers can be synthesized (chirality at the metal is generated). The reaction of the optically pure diphosphazane, $(SR)\text{-Ph}_2PN((S)\text{-*CHMePh})\text{*PPh(N}_2\text{C}_3\text{HMe}_2\text{-3,5)}$ ⁶ with $[CpRu(PPh_3)_2Cl]$ in toluene at 100°C gives the neutral chloro complex, $[Cp^*Ru\{\mathbf{H}^2\text{-Ph}_2PN((S)\text{-*CHMePh})\text{*PPh(N}_2\text{C}_3\text{HMe}_2\text{-3,5)}\}Cl]$ (**16**) and the cationic complex, $[Cp^*Ru\{\mathbf{H}^2\text{-Ph}_2PN((S)\text{-*CHMePh})\text{*PPh(N}_2\text{C}_3\text{HMe}_2\text{-3,5)}\}PPh_3]Cl$ (**17**) (scheme 8). The complex **16** has been isolated in a pure state from the reaction mixture by selective crystallization from toluene. The complex **17** could not be isolated in a pure form. The molecular structure and the absolute configuration of complex **16** are established by single crystal X-ray diffraction. The configuration of complex **16** is assigned as $S_C S_P R_{Ru}$ (S -at carbon, S -at phosphorus and R -at ruthenium) following the Cahn, Ingold, Prelog rules. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **16** displays an AX pattern. The formation of the cationic complex **17** is inferred from the $^{31}\text{P}\{^1\text{H}\}$ NMR



Scheme 7.



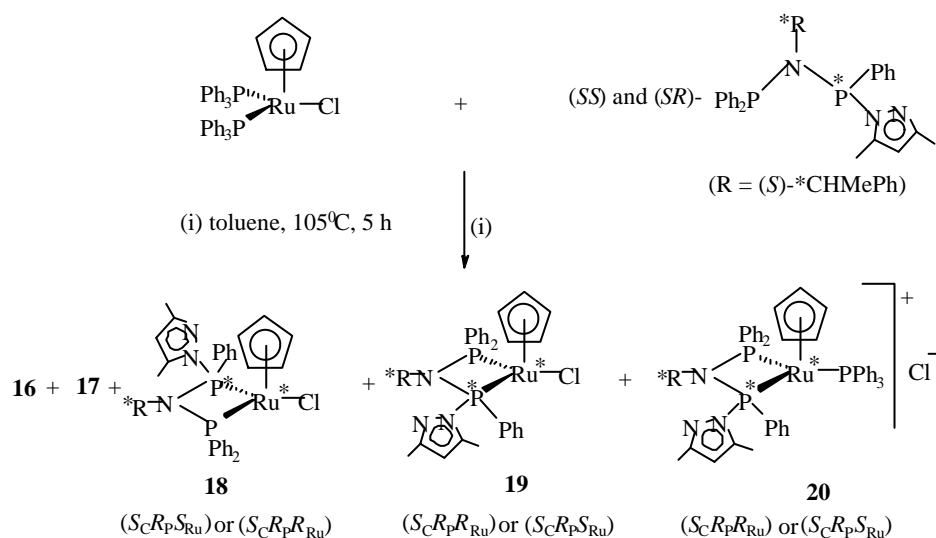
Scheme 8.

spectrum of the reaction mixture; an AMX pattern is observed for **17**. The absolute configuration of the cationic complex **17** can be either $S_C S_P R_{Ru}$ or $S_C S_P S_{Ru}$.

The reaction of a diastereomeric mixture of diphosphazanes (*SR*) and (*SS*)- $\text{Ph}_2\text{PN}((S)\text{-*CHMePh})\text{*PPh}(\text{N}_2\text{C}_3\text{HMe}_2\text{-3,5})^6$ with $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ (scheme 9) gives three diastereomeric neutral chloro complexes $[\text{Cp*Ru}\{\mathbf{H}^1\text{-Ph}_2\text{PN}((S)\text{-*CHMePh})\text{*PPh}(\text{N}_2\text{C}_3\text{HMe}_2\text{-3,5})\}\text{Cl}]$ (**16**, **18** and **19**) and two cationic complexes, $[\text{Cp*Ru}\{\mathbf{H}^2\text{-Ph}_2\text{PN}((S)\text{-*CHMePh})\text{*PPh}(\text{N}_2\text{C}_3\text{HMe}_2\text{-3,5})\}\text{PPh}_3]\text{Cl}$ (**17** and **20**). The formation of these complexes is identified only by $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The neutral chloro complexes (**16**, **18** and **19**) display an AX pattern and the cationic complexes (**17** and **20**) show an AMX pattern. The chloro complex **16** is formed by the complexation of (*SR*)-diastereomer of the diphosphazane to $[\text{CpRu}]$ fragment and the complexes **18** and **19** are formed from the complexation of (*SS*)-diastereomer to $[\text{CpRu}]$ fragment. The configuration of complexes **18** and **19** can be either $S_C R_P R_{Ru}$ or $S_C R_P S_{Ru}$. The absolute configuration at the phosphorus is likely to be '*R*' in the complexes **18** and **19** as it is formed from the (*SS*)-diastereomer of the diphosphazane. The cationic complex **20** is also obtained from the complexation of (*SS*)-diastereomer of the diphosphazane and its absolute configuration would be either $S_C R_P R_{Ru}$ or $S_C R_P S_{Ru}$.

2.4 Ruthenium carbonyl clusters of diphosphazane ligands

There has been a great deal of interest in recent years on the synthesis of transition metal carbonyl clusters¹³, as they are valuable building blocks for cluster growth reactions. In particular, clusters bearing phosphanes as auxiliary ligands have been explored extensively in view of their rich chemistry and applications in catalysis. Studies in relation to the ruthenium cluster chemistry of chiral diphosphazanes are limited. The reactions of $\text{Ru}_3(\text{CO})_{12}$ with several diphosphazanes of the type $\text{X}_2\text{PN}(\text{R})\text{PY}_2$ ($\text{R} = \text{Et}$, $\text{X} = \text{Y} = \text{Ph}$ or OMe or OPr^i or OPh ; $\text{R} = \text{Me}$, $\text{X} = \text{Y} = \text{Et}$) have been investigated by



Scheme 9.

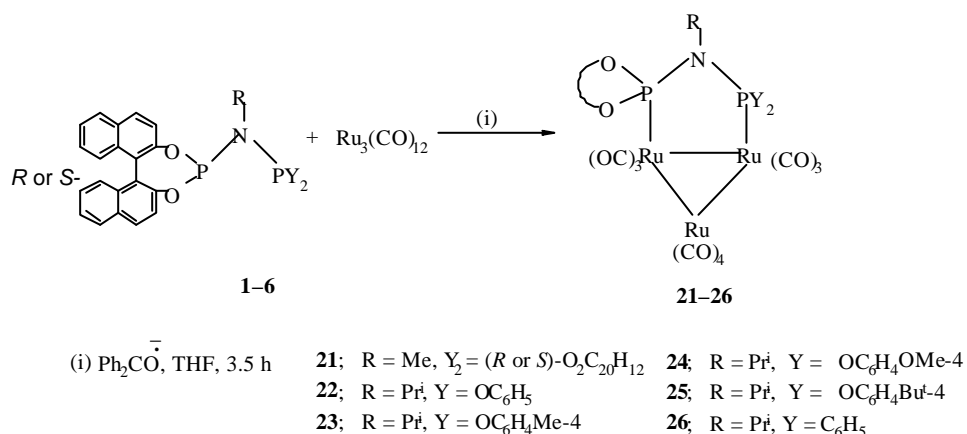
Haines and coworkers and others^{1,14,15}. Several di-nuclear, tri-nuclear and tetra-nuclear clusters have been isolated and structurally characterized. The main objective of the present study is to synthesize chiral ruthenium clusters derived from chiral diphosphazanes.

The benzophenone-ketyl radical initiated reaction of $\text{Ru}_3(\text{CO})_{12}$ with various diphosphazanes **1–6** in THF results in the substitution of two carbon monoxide ligands by a diphosphazane ligand as shown in scheme 10. The tri-ruthenium clusters **21–26** are characterized by NMR, IR spectroscopy and elemental analyses. The IR spectra of the clusters **21–26** show the CO stretching frequencies in the region 2085–1983 cm^{-1} which is indicative of terminal CO groups. The solid state structure of the cluster (*rac*)- $[\text{Ru}_3(\text{CO})_{10}\{\text{m}(\text{rac})\text{-(C}_{20}\text{H}_{12}\text{O}_2\text{)PN(CHMe}_2\text{)P(OPh)}_2\}]$ (**22**) has been determined by X-ray diffraction. A bridging mode of coordination of the P–N–P ligand is observed. The ruthenium atoms form a near equilateral triangle with bond angles close to 60°. The P–N–P bond angle is 117.5°. Each of the two phosphorus atoms of the diphosphazane lie on either side of the equatorial plane formed by the three ruthenium centers. The Ru–Ru bond lengths (2.79–2.85 Å) and Ru–C bond lengths (1.91–1.94 Å) are in the range observed for similar type of complexes.

2.5 \mathbf{H}^3 -Allyl palladium complexes of diphosphazanes

The chemistry of \mathbf{H}^3 -allyl palladium(II) complexes is a topic of considerable contemporary interest in view of the various dynamic processes observed in these systems and also from its potential applications in asymmetric synthesis^{16,17}. We have initiated a research program on the chemistry of \mathbf{H}^3 -allyl palladium complexes of diphosphazane ligands and as a part of this program, several \mathbf{H}^3 -allyl palladium complexes have been prepared and their structures and dynamic behavior in solution investigated.

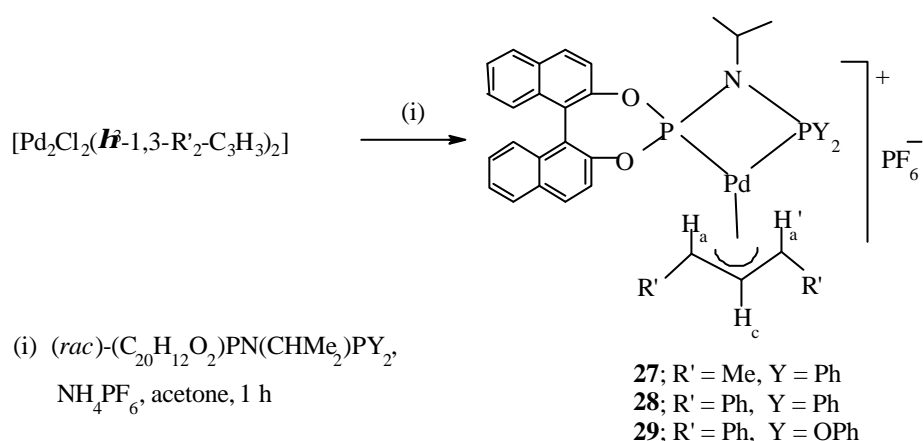
Cationic \mathbf{H}^3 -allyl palladium complexes **27–29** have been synthesized in a straight forward manner by the treatment of the chlorodimer, $[\text{Pd}_2\text{Cl}_2(\mathbf{H}^3\text{-1,3-R}'_2\text{-C}_3\text{H}_3)_2]$ ($\text{R}' = \text{Me}$ or Ph) with the appropriate unsymmetrically substituted diphosphazane ligand (*rac*)-(C₂₀H₁₂O₂)PN(CHMe₂)PY₂ [$\text{Y} = \text{OPh}$ (**2**) or $\text{Y} = \text{Ph}$ (**6**)] in the presence of NH_4PF_6 as shown in scheme 11. The $^{31}\text{P}\{\text{H}\}$ NMR spectra of these complexes reveal the



Scheme 10.

presence of two isomers in solution; two AX spectra are observed in each case. The ^{13}C NMR spectra of these complexes (**27–29**) also indicate the presence of two isomers showing two sets of allyl ^{13}C resonances. The central allyl carbon resonance for the two isomers of **27–29** appears as two separate signals at 113.0–121.8 ppm. The terminal allyl carbon resonances appear as doublet of doublets owing to coupling with the two different phosphorus nuclei present in the molecule. The terminal allyl carbon resonance *trans* to $-\text{P}(\text{O}_2\text{C}_{20}\text{H}_{12})$ gives rise a signal at 89.8–96.4 ppm for these isomers. The other terminal allyl carbon at the *trans* position with respect to the $-\text{PY}_2$ (Y = Ph or OPh) group resonates at 84.0–90.6 ppm.

The 1,3-disubstituted allyl complexes can exist in different allylic arrangements of the two substituents (Me or Ph) with respect to the central allyl proton H_c . The two substituents are *syn* with respect to the central allyl proton H_c in the *syn/syn*-isomer whereas one of the substituents takes the *anti* position with respect to the central allyl proton H_c in the *syn/anti*-isomer. It is also possible that isomers can arise from the different face coordination of the allyl moiety with the palladium centre thus forming different diastereomers in solution. We performed detailed two-dimensional NMR studies ($^1\text{H}-^1\text{H}$ DQF COSY, $^1\text{H}-^1\text{H}$ NOESY and $^1\text{H}-^1\text{H}$ ROESY) to ascertain the allylic arrangement in these isomers and their structures in solution. The COSY experiment clearly shows that the minor isomer **27b** contains two *anti* allylic protons at 3.93 ppm (H'_a) and 4.09 ppm (H_a) which are strongly coupled with the central allyl proton indicating that the two allyl methyl groups are situated in a *syn* position with respect to the central allyl proton H_c . For the major isomer **27a**, the resonances of the allylic protons H_a and H'_a overlap with each other at 4.51 ppm thus making their structural assignment difficult from the COSY spectrum. However, the $^1\text{H}-^1\text{H}$ NOESY spectrum unequivocally establishes a *syn/syn*-arrangement of two allyl methyl groups in the major isomer **27a**. The $^1\text{H}-^1\text{H}$ NOESY spectrum shows two strong cross-peaks arising from the central allyl proton H_c to both the allyl-methyl protons in the isomer **27a** and **27b** supporting their *syn/syn*-allylic arrangements. The spectrum also shows an NOE contact between the H'_a and *o*-phenyl proton(s) on the $-\text{PPh}_2$ group for the major isomer **27a** but no such NOE contact is observed for the minor isomer **27b** (illustrated in figure 2).



Scheme 11.

On the basis of this observation, the two isomers are formulated as shown in figure 3. The isomers arise because of the different allyl face coordination to the palladium centre.

The 1,3-diphenyl-allyl complexes **28** and **29** exist as a mixture of two isomers in the ratio 8:1 as revealed by their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The ^1H - ^1H COSY spectrum suggests *syn/syn*-allylic arrangement in both the isomers of **28** and **29**. The structures of these isomers in solution are determined by a careful analysis of the ^1H - ^1H NOESY spectrum

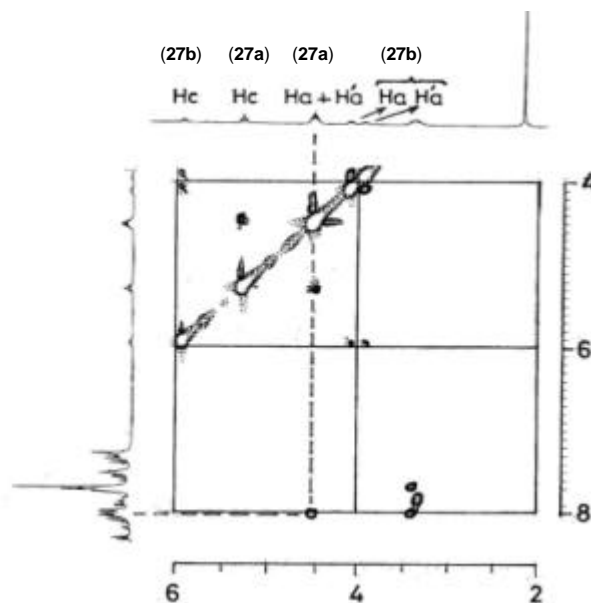


Figure 2. The ^1H - ^1H NOESY (400 MHz, CDCl_3) spectrum of $[\text{Pd}(\eta^3\text{-}1,3\text{-Me}_2\text{-C}_3\text{H}_3)\{\eta^2\text{-}(rac)\text{-}(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{CHMe}_2)\text{PPh}_2\}](\text{PF}_6)$ (**27**); only part of the spectrum illustrated showing the selective NOE cross-peak between the H_c proton and *ortho*-phenyl proton(s) of the -PPh_2 group in **27a**.

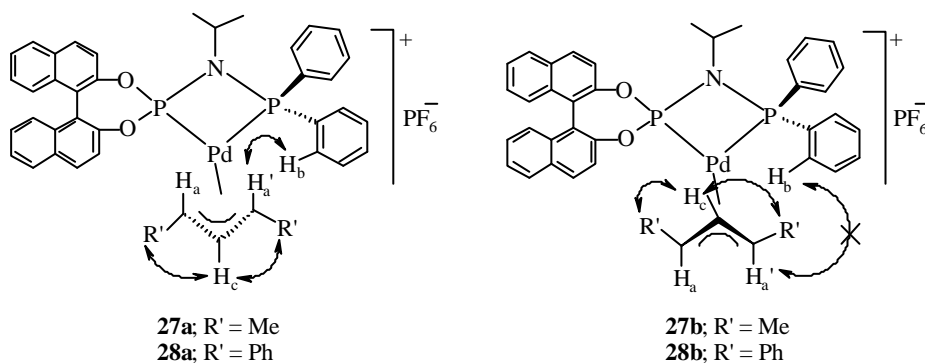


Figure 3. The two isomers of 1,3-disubstituted-allyl palladium complex, $[\text{Pd}(\eta^3\text{-}1,3\text{-R}'_2\text{-C}_3\text{H}_3)\{\eta^2\text{-}(rac)\text{-}(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{CHMe}_2)\text{PPh}_2\}](\text{PF}_6)$ [$\text{R}' = \text{Me}$ (**27**) or Ph (**28**)] observed in solution.

as described above for the structural elucidation of the two isomers of **27**. The ^1H - ^1H NOESY spectrum displays a selective cross-peak between the *anti* allyl proton H'_a and *o*-phenyl proton(s) of the $-\text{PPh}_2$ group for the major isomer **28a**; for the minor isomer, **28b** no such NOE contact between H'_c and *o*-phenyl proton(s) of the $-\text{PPh}_2$ group is observed. The two isomers arise because of the different allyl face coordination to the palladium centre. A crystallographic study has been carried for the complex **28**. The solid state structure consists of only the major isomer **28a**¹⁸. The geometry around palladium is distorted square-planar. The P(1)-Pd(1)-P(2) bond angle is 70.4 which deviates very much from the ideal value.

3. Summary and outlook

Simple and elegant methodologies have been developed for the synthesis of chiral and unsymmetrical diphosphazane ligands based on the P-N-P motif and bearing 1,1'-binaphthyl-2,2'-dioxy moiety. The reactivity of these ligands towards late-transition metal complexes has been investigated and several chiral transition metal complexes have been isolated and structurally characterized. Various approaches for induction of chirality at a ruthenium metal center using chiral and unsymmetrically substituted diphosphazanes of the type, $\text{X}_2\text{PN}(\text{R})\text{PYY}'$ have been delineated and the absolute configuration of a novel trichiral metal complex viz. $[\text{Cp}^*\text{Ru}(\text{H}^2\text{-Ph}_2\text{PN}((\text{S})\text{-CHMePh})\text{*PPh}(\text{N}_2\text{C}_3\text{HMe}_2\text{-3,5})\text{Cl})]$ has been established by X-ray crystallography. The utility of the chiral ligands to prepare tri-ruthenium carbonyl clusters has been demonstrated. These ligand systems also provide a convenient entry to H^3 -allyl palladium chemistry. The structures and dynamics of H^3 -allyl palladium complexes can be systematically probed by two-dimensional NMR techniques. The use of the chiral phosphorus ligands and their transition metal complexes in enantioselective catalysis is a topic of considerable contemporary interest and studies in this direction using chiral diphosphazane ligands will be rewarding.

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