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Palladium(II) allyl complexes of chiral diphosphazane ligands: ambident coordination behaviour and stereodynamic studies in solution †

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The chemistry of η^3 -allyl palladium complexes of pyrazolyl substituted diphosphazane ligands, Ph₂P(E)N(R)-PPh(N₂C₃HMe₂-3,5) [E = lone pair, R = CHMe₂ (1); E = lone pair, R = (S)-*CHMePh (2); E = S, R = CHMe₂ (3)] bearing a stereogenic phosphorus centre has been investigated and the complexes, [Pd(η^3 -1,3-R'₂-C₃H₃){ κ^2 -Ph₂P(E)-N(R)PPh(N₂C₃HMe₂-3,5)}](PF₆) [E = lone pair or sulfur; R = CHMe₂ or (S)-*CHMePh; R' = H, Me or Ph; 4–13], have been isolated. Detailed NMR studies reveal that these complexes exist as a mixture of isomers in solution. The structures of four complexes have been determined by X-ray crystallography and only one isomer is observed in the solid state in each case. The allyl complexes formed by ligands 1 and 2 display a P,N-coordination mode except the 1,3-diphenyl allyl complex, [Pd(η^3 -1,3-Ph₂-C₃H₃){ κ^2 -Ph₂PN(CHMe₂)PPh(N₂C₃HMe₂-3,5)}](PF₆) (8), which shows the presence of both P,N- and P,P-coordinated isomers in solution with the former predominating. On the other hand, the complexes bearing the diphosphazane monosulfide ligand 3 display P,S-coordination. Two-dimensional phase sensitive ¹H⁻¹H NOESY and ROESY measurements indicate that several of the above allyl palladium complexes undergo *syn-anti* and/or *cis-trans* position with respect to the phosphorus centre. Preliminary investigations show that the diphosphazanes (1 and (*SR*)-2) function as efficient auxiliary ligands for catalytic allylic allylation reactions but lead to only low levels of enantiomeric excess.

Introduction

The chemistry of palladium(II) allyl complexes is a topic of considerable contemporary interest in view of the various fluxional processes observed in these systems and also from the point of view of the potential applications of these type of complexes in asymmetric synthesis.¹ There has been a growing interest in elucidating the structures and stereodynamic behaviour of η^3 -allyl palladium complexes in solution. Multinuclear and multidimensional NOE based NMR spectroscopy is a valuable tool for this purpose.²

The use of C_2 symmetry as a chiral auxiliary ligand design element is a well-recognised strategy for restricting the number of possible diastereomeric transition states.³ Equally powerful stereochemical restrictions may also be realised with chiral ligands lacking C_2 symmetry through the use of electronic effects such as trans influence.⁴ Chiral bidentate ligands incorporating strong and weak donor heteroatom pairs such as P,N-,⁵ P,S-⁶ or S,N-⁷ have the capacity to influence both the stability and reactivity of the diastereomeric intermediates in the catalytic cycle. In the palladium catalysed allylic alkylation of symmetrically substituted allyl moiety, the regio-selectivity of nucleophilic attack determines the ratio of the enantiomeric products (Scheme 1).⁸ For the mixed-donor ligand systems it is generally accepted that the nucleophilic attack takes place preferentially at the allyl terminus *trans* to the more π -accepting donor centre.9 However, uncertainty still exists concerning the inherent reasons leading to such a site selectivity.¹⁰

As a part of our ongoing research on the organometallic chemistry of diphosphazane ligands,^{11,12} we have recently reported the synthesis and dynamic behaviour of unsymmetrically substituted allyl palladium complexes of the diphospha-

Electronic supplementary information (ESI) available: NMR and crystallographic data, stereodynamic behaviour schemes. See http://www.rsc.org/suppdata/dt/b2/b207447h/



zane ligands, Ph₂PN(R)PPh(N₂C₃HMe₂-3,5) [R = CHMe₂ (1) or R = (S)-*CHMePh(2)] bearing a stereogenic phosphorus centre and the diphosphazane monosulfide ligand Ph₂P(S)-N(CHMe₂)PPh(N₂C₃HMe₂-3,5) (3).¹³ In this paper, we report the synthesis, structural characterisation, and dynamic behaviour of a range of cationic symmetrically substituted allyl palladium complexes of these ligands. The main purpose of this investigation is to make a systematic study of allyl palladium complexes of ligands and to investigate the roles of phosphorus chirality and *trans* influence as control elements in asymmetric catalysis involving these ligands.

Experimental

Materials and instrumentation

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures¹⁴ and distilled under nitrogen prior to use. The chlorobridged palladium allyl dimers, $[Pd(\eta^3-C_3H_5)-(\mu-Cl)]_2$,¹⁵ $[Pd(\eta^3-1,3-Me_2-C_3H_3)(\mu-Cl)]_2$ ¹⁶ and $[Pd(\eta^3-1,3-Ph_2-C_3H_3)(\mu-Cl)]_2$,¹⁷ were prepared as previously described. The diphosphazane ligands **1**, **2** and **3** were prepared by published procedures.^{11b,11e,18} In the case of **2**, the $S_C R_P$ -diastereomer, absolute configuration of which has been determined by X-ray crystallography,¹⁸ is used for the preparation of allyl palladium complexes unless specified otherwise. The NMR spectra were

[†] Organometallic chemistry of diphosphazanes. Part 17.^{11g}

Table 1 Yield, melting point and elemental analysis data for η^3 -allyl palladium complexes 4–13

	Yield (%)	Mp/°C	Elemental analyses ^a		
Compound			C (%)	H (%)	N (%)
4	85	195–97 decomp.	46.9 (47.2)	4.6 (4.6)	5.6 (5.7)
5	90	135–38 decomp.	50.9 (51.1)	4.4 (4.5)	5.2 (5.2)
6	82	198–200 decomp.	48.7 (48.6)	5.0 (4.9)	5.6 (5.5)
7	95	204–206 decomp.	52.1 (52.2)	4.8 (4.8)	5.0 (5.1)
8	87	200–202 decomp.	55.1 (55.3)	4.6 (4.7)	4.8 (4.7)
9	74	184–87 decomp.	58.5 (58.0)	4.7 (4.6)	4.5 (4.4)
10	34	196–98 decomp.	58.7 (58.0)	4.7 (4.6)	4.6 (4.4)
11	89	178–81 decomp.	44.9 (45.3)	4.4 (4.4)	5.7 (5.5)
12	84	155–59 decomp.	46.8 (46.7)	4.8 (4.8)	5.3 (5.3)
13	77	190–93 decomp.	53.5 (53.4)	4.4 (4.6)	4.5 (4.6)

^a Calculated values are in parentheses.

Table 2 Crystallographic data for complexes 5a, 7a, 8a and 12a

Complex	5a	7a	8a	12a
Empirical formula	C ₃₄ H ₃₆ F ₆ N ₃ P ₃ Pd·0.5CH ₃ COCH ₃	$C_{36}H_{40}F_6N_3P_3Pd$	C41H42F6N3P3Pd	C ₃₁ H ₃₈ F ₆ N ₃ P ₃ PdS
Fw	829.01	828.02	890.09	798.01
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_1/n$	$P2_1/n$
a/Å	9.2253(2)	9.474(4)	10.826(3)	9.836(5)
b/Å	37.0328(9)	19.627(4)	18.176(4)	10.758(2)
c/Å	10.9457(2)	19.837(5)	41.424(10)	33.860(9)
$a/^{\circ}$	90.00	90.00	90.00	90.00
B/°	90.5650(10)	90.00	90.75(2)	97.03(3)
v/°	90.00	90.00	90.00	90.00
V/Å ³	3739.3(1)	3688.5(2)	8150.0(3)	3556.0(2)
Ζ	4	4	8	4
Density (calcd)/Mg m^{-3}	1.473	1.491	1.451	1.491
Abs. coeff./mm $^{-1}$	0.685	0.694	0.634	0.773
No. refl.	15784	3638	15726	8210
Indep. refl.	10038	3638	14315	7757
Flack parameter	-0.03(2)	-0.08(5)	_	_
Final \hat{R} indices: R_1 , wR_2 ($I > 2\sigma_I$)	0.0383, 0.0989	0.0427, 0.1081	0.0609, 0.1604	0.0522, 0.1404
R indices (all data)	0.0441, 0.1091	0.0604, 0.1184	0.0985, 0.1846	0.0950, 0.1660

recorded using Bruker DRX-500 MHz, Bruker AMX-400 MHz and Bruker ACF-200 MHz spectrometers. Chemical shifts downfield from the reference standard were assigned positive values. Optical rotations were measured on a Jasco DIP-370 digital polarimeter. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyser. The ³¹P{¹H} NMR data are presented in Table 5 (see below). The ¹H and ¹³C NMR data for the allyl moiety are listed in Tables ES1 and ES2, respectively, as Electronic Supplementary Information (ESI);[†] the remaining ¹H and ¹³C NMR data are also given in the ESI.

Synthesis

$[Pd(\eta^{3}-C_{3}H_{5})\{\kappa^{2}-Ph_{2}PN(CHMe_{2})PPh(N_{2}C_{3}HMe_{2}-3,5)\}]$ -

(PF₆), 4. A mixture of 0.036 g (0.98 × 10^{-4} mol) of [Pd-(η^3 -C₃H₅)(μ -Cl)]₂, 0.033 g (2.02 × 10^{-4} mol) of NH₄PF₆ and 0.095 g (2.13 × 10^{-4} mol) of 1 was dissolved in 20 cm³ of acetone. The solution was stirred for 2 h at 298 K and the white precipitate formed during the reaction was filtered off. The resulting colourless filtrate was concentrated under reduced pressure to 10 cm³ and the solution was layered by adding 10 cm³ of hexane (bp 40–60 °C) to yield colourless crystals. The other allyl palladium complexes, **5–13** were synthesised by an analogous procedure by varying the allyl palladium chloro dimer and the diphosphazane ligand. The yields, melting points and elemental analyses for these complexes are given in Table 1.

X-Ray crystallography

Crystal data for complex **5a** was collected using Siemen's SMART-CCD diffractometer. The intensity data for complexes **7a**, **8a** and **12a** were collected using an Enraf-Nonius CAD-4

diffractometer. The crystallographic data and details of data collections are summarised in Table 2. The structures were solved by Patterson's heavy atom method using the program SHELXS 86¹⁹ and refined on F^2 values for all unique data by full-matrix least-squares using SHELXS 97.²⁰ The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed at their calculated geometrical positions and allowed to ride on the non-hydrogen atoms to which they are attached. The validity of the absolute structure for **5a** and **7a** was established by the method of Flack.²¹

CCDC reference numbers 190877–190880.

See http://www.rsc.org/suppdata/dt/b2/b207447h/ for crystallographic data in CIF or other electronic format.

General procedure for palladium-catalysed allylic alkylation

The ligand (2.5 mol%) and $[Pd(\eta^3-C_3H_5)(\mu-Cl)]_2$ (1 mol%) were dissolved in 4 cm³ of degassed (by three freeze–thaw cycles) CH₂Cl₂. A solution of (*rac*)-1,3-diphenyl-2-propenyl acetate (I) or (*E*)-1-phenyl-2-propenyl acetate (III) (1 equiv.), in 2 cm³ CH₂Cl₂, was added followed by dimethyl malonate (2 equiv.), N,O-bis(trimethylsilyl)acetamide (2 equiv.), and a catalytic amount of KOAc. The mixture was stirred at 298 K for 24 h and the reaction was monitored by TLC. A saturated aqueous solution of NH₄Cl (10 cm³) was added to the reaction mixture and the organic part was extracted with diethyl ether (10 × 3 cm³). The ether extract was filtered over activated celite, washed with water (3 × 10 cm³) and dried over anhydrous Na₂SO₄. Solvent was removed from the ether extract under reduced pressure and the crude product was purified by column chromatography over silica gel (eluent hexane/ethyl acetate, 9 : 1). The optical rotation was measured for the product, PhCH=CH-CHPh{CH(CO₂Me)₂} (II) and the enantiomeric excess (e.e.) was calculated from the optical rotation value using the literature data.^{6b,22} The enantiomeric excesses obtained were $29 \pm 2\%$ in favour of the '*R*' enantiomer (observed $[a]_D =$ + 6.10, c = 3.2, EtOH) when ligand 1 was used and $28 \pm 2\%$ in favour of the '*S*' enantiomer (observed $[a]_D = -5.96$, c = 3.2, EtOH) when ligand (*SR*)-2 was used as the chiral auxiliary.

Results and discussion

The cationic allyl palladium complexes **4–13** have been prepared from the reactions of the chlorobridged palladium allyl dimers, $[Pd(\eta^{3}-1,3-R'_{2}-C_{3}H_{3})(\mu-Cl)]_{2}$ (R' = H or Me or Ph) with the appropriate ligands in the presence of NH₄PF₆ in acetone (Scheme 2). These complexes have been characterised by elemental analyses and NMR spectral data (see ESI † and Table 5 below). The isomeric composition in each case has been determined from NMR spectroscopy. The salient features of the spectroscopic data and dynamic behaviour are discussed below.



R = CHMe₂, E = lone pair (l.p);
 R = (S)-*CHMePh, E = l.p;
 R = CHMe₂, E = S

 $[Pd(\eta^{3}-1,3-R'_{2}-C_{3}H_{3})(1 \text{ or } 2 \text{ or } 3)](PF_{6})$

NH₄PF₆

4, R' = H, R = CHMe₂, E = l.p; 5, R' = H, R = (S)-*CHMePh, E = l.p; 6, R' = Me, R = CHMe₂, E = l.p; 7, R' = Me, R = (S)-*CHMePh, E = l.p; 8, R' = Ph, R = CHMe₂, E = l.p; 9, R' = Ph, R = (S)-*CHMePh, E = l.p; 10, R' = Ph, R = (S)-*CHMePh, E = l.p; (S_cS_p -diastereomer) 11, R' = H, R = CHMe₂, E = S; 12, R' = Me, R = CHMe₂, E = S; 13, R' = Ph, R = CHMe₂, E = S

Scheme 2

Palladium allyl complexes of $Ph_2PN(R)PPh(N_2C_3HMe_2-3,5)$ [R = CHMe₂(1) or (S)-*CHMePh (2)]

The ³¹P{¹H} NMR spectra of **4** and **5** in CDCl₃ show two AX spin patterns indicating the presence of two isomers in solution. The relative ratios of the isomers are 3 : 1 and 3.4 : 1 for **4** and **5**, respectively. An analysis of ¹³C NMR spectra of allyl carbons clearly shows P,N-coordination *via* the nitrogen atom of the pyrazole ring instead of the usually observed P,P-coordination.^{11c-e} A doublet is observed for each of the two terminal allyl carbon nuclei. The resonances of the terminal allyl carbon nuclei *trans* to the coordinated phosphorus centre appear in the range *ca*. 75–81 ppm with a ²*J*(P,C) of 28–31 Hz which lies in a region usually observed for *trans* ³¹P–¹³C coupling whereas the signal for the terminal allyl carbon nucleus *trans* to nitrogen resonates in a more shielded region (*ca*. 58–62 ppm) with a ²*J*(P,C) coupling constant of the order of 3–4 Hz which is

typical for a two-bond *cis* coupling of phosphorus and carbon nuclei.²³ The resonances of the central allyl carbon nuclei of all the isomers appear as doublets as would be expected for P,N-coordination. The driving force for the P,N-coordination might be the formation of a stable six-membered ring around palladium rather than a four-membered ring which would result from P,P-coordination. Moreover, electronically the coordination of the σ -donor nitrogen is more favourable than that of the π -acceptor phosphorus as it can synergistically enhance the metal–allyl bonding.²⁴

Detailed 2D NMR studies (1H-1H DQF-COSY, NOESY, ROESY and ¹³C-¹H HSOC) show that the two isomers of 4 and 5 have the endo- (major) and exo- (minor) configurations (Fig. 1).^{2b,25} For the major isomers of 4 and 5, there is a NOE contact between the 3-Me protons of pyrazole and the central allyl proton, H_c and the syn proton H_s. This result indicates that the central allyl hydrogen, H_c points toward 3-Me protons of pyrazole *i.e.* the major isomers (4a and 5a) have the endo-configuration (3-Me protons and H_c are on the same side of the N-Pd-P coordination plane). By contrast, the pyrazole 3-Me protons of the minor isomers of 4 and 5 do not show NOE contact to the central allyl proton H_c but there is a strong NOE contact to the anti allyl proton, H_a. Hence, the minor isomers (4b and 5b) are assigned the exo-configuration (3-Me and H_c are on the opposite sides of the N-Pd-P coordination plane).



Fig. 1 The two isomers of Pd(II)–allyl diphosphazane complexes, $[Pd(\eta^3-C_3H_5)\{\kappa^2-Ph_2PN(R)PPh(N_2C_3HMe_2-3,5)\}](PF_6)$ [R = CHMe₂-(4), (*S*)-*CHMePh(5)] observed in solution. Selective NOE contacts reveal that in the *endo*-isomer, the central allyl proton and pyrazole-3-Me protons are close to each other whereas for the *exo*-isomer, such an NOE contact with the central allyl proton is absent.

The phase sensitive ¹H-¹H 2D NOESY and ROESY spectra of 4 at 298 K clearly reveal syn-anti exchange of the allyl protons trans to nitrogen. Pregosin and coworkers²⁶ have demonstrated that such an exchange can be explained by a selective opening of the η^3 -allyl moiety *trans* to the coordinated phosphorus centre followed by rotation around the sp³-sp² C-C bond and reversal to the η^3 -mode of coordination by the other face of the allyl moiety. Complex 5 does not show any dynamic behaviour at 298 K; presumably the interconversion is slow on the NMR time scale at this temperature. However, at 323 K, the ¹H-¹H 2D NOESY and ROESY spectra of 5 indicate the presence of two simultaneous exchange processes. Close examination of the allyl proton exchange cross-peaks reveals selective syn-anti exchange as well as cis-trans isomerisation. The observed exchange results can be accounted for by considering the sequence of steps shown in Scheme 3. Step (i) is the selective opening of the η^3 -allyl bond to the metal at the carbon *trans* to the coordinated phosphorus centre of 5a to generate the intermediate **D**. This intermediate (**D**) can undergo either a rotation around the sp³-sp² C-C bond to form **5b** [step (ii)] or it can undergo a rotation around the Pd-C bond [step (iii)] thus resulting in 5c. The isomers 5b and 5c are essentially the same and are not distinguishable in the NMR spectrum, as the allyl group is unsubstituted and symmetrical. Thus the isomerisation appears to be subject to electronic control as observed for η^3 -allyl palladium complexes of other heterodonor P,S-,²⁷ P,O-²⁸ and P,N-^{23b,29} bidentate ligand systems.



When a solution of complex 5 in acetone/hexane (1 : 1 v/v) is cooled, crystals of 5a are obtained. The crystallographic data for 5a are summarised in Table 2. Selected bond lengths and bond angles are listed in Table 3. The solid state structure shows the presence of two crystallographically independent molecules 5a(A) and 5a(C) (A and C represent the diastereomeric configuration as explained below) shown in Fig. 2. The 'PdC₂PN' core shows a distorted square-planar geometry with bond distances of Pd-C, Pd-P and Pd-N in the expected range for Pd(II) allyl compounds with P,N-chelate ligands. The P-N-P bond angle is expanded to 121.8(2)° which is normally ca. 100° for P,P-coordinated complexes.¹¹ The relative orientations of the chelating ligand and the allyl moiety are similar in both the molecules. The central allyl carbon and 3-methyl group of the pyrazole ring in 5a(A) lie above the coordination plane defined by N-Pd-P whereas in 5a(C) they are located below this plane. The two molecules are not superimposable; the molecular asymmetry arises because of the presence of chiral centres in the diphosphazane ligand and the position of the η³-coordinated allyl moiety which is obliquely placed with respect to the metal square plane.^{30,31} The configuration at the stereogenic palladium centre in 5a(A) and 5a(C) can be designated as A and C, respectively, following the method adopted by Lanza et al.³⁰ When the molecule is viewed from the central allyl carbon towards palladium, the other two atoms coordinated to the metal viz. P and N (with decreasing CIP priority) follow an anticlockwise direction in 5a(A) whereas these atoms follow a clockwise direction in 5a(C) (see Fig. 2). The sixmembered ring in both the molecules adopts a distorted boat conformation. The difference between the two Pd-C bond distances indicates the greater trans influence of the phosphorus donor compared to nitrogen. The Pd-C bond lengths trans to the coordinated phosphorus centre are 2.213(7) and 2.189(7) Å whereas for the Pd-C bond trans to nitrogen are 2.127(8) and 2.107(7) Å for 5a(A) and 5a(C), respectively (see Table 3).^{10,236,32} This elongation of Pd-terminal allyl carbon bond length trans to the coordinated phosphorus centre as compared to that *trans* to nitrogen is consistent with the proposed mechanism involving selective opening of one of the allyl termini.

To obtain a better understanding of the fluxional process, we have studied 1,3-disubstituted allyl complexes of the ligands 1 and 2 since the unsubstituted allyl moiety is a poor model to understand the stereodynamic process. The various possible allylic arrangements are shown in Scheme 4. For each arrange-

Table 3 Selected bond distances (Å) and angles (°) in 5a, 7a, 8a and 12a

Bond distances/	Å	Bond angles/°	Bond angles/°		
Molecule 5a(A)					
Pd(1)-C(1)	2.127(8)	P(4) - Pd(1) - N(4)	86.2(1)		
Pd(1) - C(2)	2.133(7)	C(1) - Pd(1) - C(3)	67.9(4)		
Pd(1) - C(3)	2.213(7)	C(3) - Pd(1) - P(4)	172.0(3)		
Pd(1) - P(4)	2.297(1)	C(1) - Pd(1) - N(4)	169.5(3)		
Pd(1) - N(4)	2.100(5)	P(2)–N(6)–P(4)	121.8(2)		
Molecule 5a(C)					
Pd(2)-C(38)	2.107(7)	P(3)-Pd(2)-N(1)	86.6(1)		
Pd(2)-C(39)	2.155(8)	C(38) - Pd(2) - C(40)	67.9(4)		
Pd(2) - C(40)	2.189(7)	C(40) - Pd(2) - P(3)	171.0(3)		
Pd(2) - P(3)	2.296(1)	C(38) - Pd(2) - N(1)	169.7(3)		
Pd(2) - N(1)	2.116(5)	P(5)–N(5)–P(3)	121.8(2)		
Complex 7a					
Pd(1)-C(4)	2.12(1)	P(2) - Pd(1) - N(3)	84.2(2)		
Pd(1)-C(3)	2.129(8)	C(4) - Pd(1) - C(2)	66.3(5)		
Pd(1)-C(2)	2.27(1)	C(2) - Pd(1) - P(2)	172.2(4)		
Pd(1) - P(2)	2.304(2)	C(4) - Pd(1) - N(3)	168.8(4)		
Pd(1)-N(3)	2.150(6)	P(1)-N(1)-P(2)	121.6(3)		
Molecule 8a(A)					
Pd(1) - C(3)	2 173(7)	P(1) = Pd(1) = N(3)	84 2(2)		
Pd(1)-C(2)	2.179(7)	C(3) - Pd(1) - C(1)	66.5(3)		
Pd(1)-C(1)	2.224(7)	C(1) - Pd(1) - P(1)	176.4(2)		
Pd(1) - P(1)	2.328(2)	C(3) - Pd(1) - N(3)	165.6(3)		
Pd(1)-N(3)	2.119(6)	P(1)-N(1)-P(2)	122.8(3)		
Molecule 8a(C)					
Pd(2)-C(44)	2.148(7)	P(3)-Pd(2)-N(6)	83.9(2)		
Pd(2)-C(43)	2.178(8)	C(44) - Pd(2) - C(42)	67.1(3)		
Pd(2)-C(42)	2.232(8)	C(42) - Pd(2) - P(3)	174.2(2)		
Pd(2) - P(3)	2.306(2)	C(44) - Pd(2) - N(6)	168.2(3)		
Pd(2)–N(6)	2.128(6)	P(3)–N(4)–P(4)	121.9(4)		
Complex 12a		Complex 12a			
Pd(1)-C(2)	2.171(7)	P(1)-Pd(1)-S(1)	91.7(4)		
Pd(1) - C(3)	2.127(5)	C(2) - Pd(1) - C(4)	67.4(3)		
Pd(1) - C(4)	2.192(6)	C(4) - Pd(1) - P(1)	167.7(2)		
Pd(1) - P(1)	2.262(1)	C(2) - Pd(1) - S(1)	163.6(2)		
Pd(1) - S(1)	2.338(1)	P(1)-N(1)-P(2)	118.3(2)		

ment, there is also the possibility of *exo-* or *endo-*isomers (Scheme 5). Furthermore, there is the possibility of P,P-coordination.



Fig. 2 A view of the molecular structure of 5a, showing the presence of two independent molecules 5a(A) (top) and 5a(C) (bottom) (the hexafluorophosphate anion, the hydrogen atoms and the lattice held Me₂CO are not shown).







The complexes, $[Pd(\eta^3-1,3-Me_2-C_3H_3)(1)](PF_6)$ (6) and $[Pd(\eta^3-1,3-Me_2-C_3H_3)((SR)-2)](PF_6)$ (7) exist as a mixture of four isomers as shown by their ³¹P{¹H} NMR spectra. A detailed analysis of the ¹³C, ¹H and ³¹P{¹H} NMR spectra confirms that all the four isomers are P,N-coordinated species. The isomeric distributions are 43 : 35 : 15 : 7 and 69 : 19 : 9 : 3 for 6 and 7, respectively. Two-dimensional NMR studies have been carried out for complex 7. The assignment of the allyl configuration is based on ¹H spin–spin coupling constants and

intra-allyl NOESY cross-peaks. (Two strong NOE cross-peaks between the central allylic proton with two terminal allyl methyl protons indicate a syn/syn-arrangement while a strong NOE between the central allylic proton and one of the two terminal allyl protons indicates syn/anti- or anti/syn-arrangements.) Appearance of an NOE cross-peak between the central allyl proton and 3-methyl protons of pyrazole moiety would reveal the endo-configuration, whereas the absence of such an NOE involving the central allyl proton would clearly point to the exo-configuration. Additionally, the chemical shift of the central allyl proton for the endo-isomer appears in a deshielded region (ca. 5.5 ppm) compared to that for the exo-isomer (ca. 4 ppm) as observed for complexes 4 and 5. Based on the above considerations, we assign the major species as endo, syn/ syn- (6a and 7a), the second minor species as exo-, syn/syn- (6b and 7b), the third minor species as exo, anti/syn- (6c and 7c) and the fourth minor species as endo, anti/syn- (6d and 7d) isomers (see Fig. 3). The absence of the antilanti-isomer is understandable on the basis of steric grounds but the absence of any syn/ anti-isomer is most probably due to electronic reasons. The anti allyl methyl group is invariably present at the trans position with respect to the nitrogen donor. This is in accord with the proposed mechanism for the exchange processes observed for 4 and 5 (Scheme 3), in which the sp³ carbon is generated at the trans position with respect to the nitrogen donor; in other words, the η^3 -allyl group opens selectively at the *trans* position with respect to the coordinated phosphorus donor to form the 'η¹-coordinated' intermediate.



Fig. 3 The four isomers observed in solution for 1,3-dimethyl allyl palladium complexes, [Pd(η^{3} -1,3-Me₂-C₃H₃{ κ^{2} -Ph₂PN(R)PPh(N₂C₃-HMe₂-3,5)}](PF₆) [R = CHMe₂ (6), (S)-*CHMePh (7)].

Although complex 7 exists as a mixture of four diastereomers in solution, the solid state structure shows that the allyl moiety adopts an endo, syn/syn-configuration (7a) (endo- refers to the relative orientation of the central C-H vector pointing towards the 3-methyl group on the pyrazole ring). The crystallographic data are listed in Table 2. The molecular structure is shown in Fig. 4. The bonding parameters (Table 3) fall in the expected ranges.^{23b,31} A few structural features are worth noting. If one considers the inner coordination sphere as formed by the P and N donor atoms of the diphosphazane ligand and by the terminal allyl carbons C(2) and C(4), the coordination geometry around the metal centre is distorted square planar, with the P(2)-Pd(1)-N(3) and C(4)-Pd(1)-C(2) angles being 84.2(2) and 66.3(5)°, respectively. The two terminal allyl carbon atoms are not coplanar with the coordination plane formed by N(3)-Pd(1)-P(2); the distances of C(2) and C(4) from this plane are



Fig. 4 A view of the molecular structure of complex **7a** (the hydrogen atoms and the hexafluorophosphate anion are not shown).

0.16 and 0.07 Å, respectively. The central allyl carbon atom C(3) is located at a distance of 0.36 Å from the same plane. The 3-Me pyrazole carbon, C(6) lies on the same side of the central allyl carbon with regard to the coordination plane (distance from the coordination plane is 2.23 Å). The terminal Pd–C allyl bond lengths are significantly different from one another; the carbon atom trans to the coordinated phosphorus centre displays the expected longer distance [Pd(1)-C(2) = 2.27(1) Å], as compared to its partner *trans* to nitrogen [Pd(1)-C(4) = 2.12(1)]Å] (Table 3). This is a reflection of the higher *trans* influence^{10,32,33} of the phosphorus donor centre. The six-membered chelate ring adopts a distorted boat conformation as shown by the distance calculation from the mean plane defined by N(1)-N(2)-N(3); both Pd(1) and P(1) lie above the N(1)-N(2)-N(3) plane (the deviations from this plane are 1.17 and 0.74 Å respectively) whereas P(2) atom is almost coplanar with this plane (the deviation is only 0.10 Å below this plane).

When crystalline 7a is dissolved in CDCl₃ at 298 K, it undergoes slow isomerisation (not detectable by phase sensitive ¹H–¹H NOESY and ROESY spectra at 298 K) to produce 7b, 7c and 7d. The formation of exo, syn/syn-isomer (7b) from the endo, syn/syn-isomer (7a) can be rationalised by considering a rotation around the Pd-C bond (step (i), Scheme 6). Thus complex 7b represents 5c shown in the isomerisation pathway for unsubstituted allyl complexes (see Scheme 3). The exo, anti/synisomer (7c) is the 1,3-dimethyl substituted analogue of 5b which is formed by rotation around sp³-sp² C-C bond (step (ii), Scheme 6). Formation of 7d can be explained by considering a further syn-anti exchange process starting from 7b (step (iii), Scheme 6). This isomerisation pathway is supported by the ¹H-¹H NOESY and ROESY spectra at 323 K for complex 7. The exchange results at 323 K reveal that complex 7a undergoes exchange with complex 7b by *cis-trans* isomerisation and at the same time complex 7b also shows fluxional behaviour with complex 7d by syn-anti isomerisation pathway (on the basis of exchange pattern observed for the allyl methyl groups of the two isomers). There is no observable exchange between 7a and 7c at 323 K.

When we move to the 1,3-diphenyl allyl system containing the more bulky substituents with enhanced electron donating capacity compared to the 1,3-dimethyl allyl system, the complex formed by the diphosphazane ligand 1, *viz*. [Pd(η^3 -1,3-Ph₂-C₃H₃){ κ^2 -Ph₂PN(CHMe₂)PPh(N₂C₃HMe₂-3,5)}](PF₆) (8) exists as a mixture of three isomers in solution in the ratio 75 : 15 : 10 as shown by its ³¹P{¹H} and ¹H NMR spectra. The ¹³C NMR and ¹H–¹H NOESY spectra show that the major component is the P,N-coordinated *endo*, *syn/syn*-isomer (8a) and the other two minor isomers (8b and 8c) are P,P-coordinated diastereomers (shown in Fig. 5). The magnitude of ${}^{2}J(P,P)$ for P,N-coordination (ca. 30 Hz) is much less than that for P.P-coordination (*ca.* 115 Hz). Such a large difference in ${}^{2}J(P,P)$ is probably due to the difference in P-N-P bond angle in the two cases. The assignment of the resonances arising from the two minor isomers (8b and 8c) are based on the chemical shift difference of two methyl groups at 3- and 5-positions of the pyrazole ring. The value of the chemical shift difference $\Delta\delta(CH_3) [\delta(5-CH_3) - \delta(3-CH_3)]$ for the isomer **8b** is 1.10 ppm whereas this difference for the isomer 8c is 0.16 ppm. Such a large difference indicates that in 8b the central allyl carbon and pyrazole ring are on the same side of the P-Pd-P coordination plane and the allyl phenyl group comes close to one of the pyrazole methyl groups. Thus the two methyl groups experience different steric and electronic environments. By contrast, the phenyl groups and the pyrazole methyl groups in 8c are on opposite sides of the coordination plane resulting in lesser extent of interaction of the pyrazole methyl groups with the allylic moiety. The 1,3-diphenyl allyl complexes of the more bulky diphosphazane ligands, (SR)-Ph₂PN((S)-*CH-MePh)PPh(N₂C₃HMe₂-3,5) and (SS)-Ph₂PN((S)-*CHMe-Ph)PPh(N₂C₃HMe₂-3,5) form only the P,N-coordinated isomers 9 and 10 with endo, syn/syn-configuration as revealed by ¹H-¹H NOESY NMR spectra. The formation of only one isomer is not surprising as the synlanti- or antilanti-arrangements are not favourable for allylic moiety containing bulky phenyl groups.



exo, syn/syn-; (8c)

Fig. 5 The isomeric species observed in solution for the 1,3-diphenyl allyl palladium(II) diphosphazane complexes, $[Pd(\eta^3-1,3-Ph_2-C_3H_3)\{\kappa^2-Ph_2PN(R)PPh(N_2C_3HMe_2-3,5)\}](PF_6)$ [R = CHMe₂ (8), (S)-*CHMePh (9, 10)].

The molecular structure of complex 8 reveals that only the endo, syn/syn-isomer (8a) is present in the solid state. The crystal data are given in Table 2 and selected bond angles and bond distances are listed in Table 3. There are two independent molecules in the unit cell, which are not superimposable. An ORTEP plot of the two molecules is shown in Fig. 6. Both the molecules feature P,N-coordination. Furthermore, the central allyl carbon points towards the 3-methyl of the pyrazole ring revealing an endo-configuration with syn/syn-arrangement of the allyl phenyl groups in both the molecules 8a(A) and 8a(C). The two molecules differ in their relative direction of P-Pd-N when the molecule is viewed from the central allyl carbon towards palladium; in 8a(A) it follows an anticlockwise direction whereas in 8a(C) it is in the clockwise direction. The coordination geometry around the palladium metal is distorted square planar, with the allyl ligand markedly displaced from its idealised position. In molecule 8a(A), the two terminal carbon







Fig. 6 A view of the molecular structure of 8a showing the presence of two independent molecules 8a(A) (top) and 8a(C) (bottom) (the hydrogen atoms and the hexafluorophosphate anion are not shown).

atoms are on the same side of the coordination plane formed by N(3)-Pd(1)-P(1) (the distances are 0.01 and 0.12 Å for C(1) and C(3) respectively) and the central allyl carbon atom C(2) resides on the opposite side (the distance is 0.61 Å). On the other hand, in molecule **8a**(C), the terminal allyl carbons are located on opposite sides to the plane formed by N(6)-Pd(2)-P(3) (the distances are 0.06 and 0.115 Å for C(42) and C(44) respectively). The central allyl carbon, C(43) is located at a distance of

0.65 Å from the coordination plane on the same side of C(42), as shown below:



The deviation of the terminal carbon atoms from the coordination plane is less for the carbon atom *trans* to the coordinated phosphorus than the one *trans* to nitrogen. The plane of the allyl ligand is tilted (20.4° in molecule 8a(A) and 20.3° in molecule **8a**(C)) from an axis perpendicular to the N-Pd-P coordination plane. The allyl ligands are rotated markedly around the Pd-allyl bond axis away from the -PPh₂ group to minimise steric interaction with the allyl phenyl groups. A similar rotation of the allyl moiety with respect to its idealised position has also been observed in the related cationic complexes with P,N-chelating ligands, containing the sterically demanding η^3 -1,3-diphenylallyl fragment.^{10,23a,32} As expected, the palladium-terminal allyl carbon bond distance, which is trans to the coordinated phosphorus, is longer than that trans to nitrogen in both the molecules, revealing the greater trans influence of the phosphorus donor centre. The chelated six-membered rings adopt boat conformations.

When a crystalline sample of complex 8a is dissolved in CDCl₃, it undergoes slow isomerisation to produce a mixture of complexes 8a-c. The phase sensitive ¹H-¹H NOESY spectrum at 298 K indicates no observable exchange between these isomers which is not surprising as the sterically demanding allyl moiety raises the activation barrier for exchange. When the temperature is raised (323 K), one observes an exchange between the isomers 8b and 8c probably via a cis-trans isomerisation. The formation of 8b and 8c from 8a (the isomer present in the solid state) can be rationalised by considering a pathway as shown in Scheme 7. Alternatively, 8b may be formed first and then it can undergo *cis-trans* isomerisation to form 8c. When the ¹H NMR spectrum is recorded immediately after dissolving the solid 8a in CDCl₃, the three isomers 8a-8c are present in the ratio 91:4:3. This ratio changes to 75:14:11 upon heating the sample at 323 K for 1 h. It may be noted that the relative ratio of 8b and 8c remains the same before and after the



equilibrium is attained although the relative ratios with respect to **8a** vary. This result indicates that the formation of **8b** and **8c** from **8a** involves a common intermediate formed by selective opening of the allyl terminus *trans* to the coordinated phosphorus centre accompanied by a concerted attack of the metal by the non-coordinated phosphorus. Recombination to the η^3 mode before and after a rotation around the Pd–C bond would generate **8b** and **8c**, respectively (Scheme 7).

Palladium allyl complexes of a diphosphazane monosulfide ligand, Ph₂P(S)N(CHMe₂)PPh(N₂C₃HMe₂-3,5) (3)

The unsymmetrically substituted diphosphazane monosulfide ligand, Ph₂P(S)N(CHMe₂)PPh(N₂C₃HMe₂-3,5) (3) consists of three potential donor centres namely, S, P and N at the 2-position of the pyrazole ring. It can form complexes using either P,N- or P,S- or N,S-combinations for binding to the metal resulting in a four-, five- or seven-membered chelate ring, respectively, around the metal. The ³¹P{¹H} NMR spectrum of the complex, $[Pd(\eta^3-C_3H_5)]\kappa^2-Ph_2P(S)N(CHMe_2)PPh(N_2C_3 HMe_2-3,5$](PF₆) (11) in CDCl₃ shows two pairs of doublets in a ratio 4: 1 revealing the presence of two diastereomers. The ¹³C allyl resonances are assigned unequivocally by carrying out a ¹³C-¹H HSQC 2D experiment with the help of pre-assigned allyl 1H resonances by a 1H-1H COSY experiment. Analysis of the ¹³C NMR spectrum shows a doublet pattern with a ${}^{2}J(P,C)$ value of ca. 30 Hz for one of the two terminal allyl carbon resonances in case of isomers 11a and 11b indicating bonding of one phosphorus with the palladium centre. From the ³¹P chemical shifts (Table 5), we can conclude that the pyrazolbearing phosphorus atom and the sulfur atom are coordinated to palladium. The doublet at ca. 91.5 ppm is assigned the coordinated -PPh(N2C3HMe2-3,5) phosphorus nucleus with coordination shift of 26.0 ppm as compared with the free ligand ³¹P chemical shift. The second doublet at *ca*. 77.0 ppm with a coordination shift of 6.5 ppm is assigned the non-coordinated -P(S)Ph₂ phosphorus nucleus. This conclusion is supported by the ¹³C chemical shifts of the allyl carbon nuclei when compared with the chemical shifts of allyl carbon nuclei of P,Ncoordinated complexes 4-10 (see ESI). It may be noted that the chemical shifts of allyl carbon nuclei trans to nitrogen are more shielded (by ~10–20 ppm) than the chemical shifts of the allyl carbon nuclei trans to sulfur when we consider the similar allyl isomers in both the cases. Thus, in contrast to 1 and 2, the ligand 3 does not coordinate through the nitrogen atom of the pyrazole ring. The P,S-coordination is presumably favoured because of the formation of a stable five-membered ring around the palladium centre. The competitive N,S-coordination would lead to the formation of a seven-membered chelate ring around the palladium atom.

Two sets of five non-equivalent η^3 -allyl proton resonances are observed in the ¹H NMR spectrum of **11** at 298 K. Some of the ¹H resonances of the minor isomer **11b** (*e.g.* H_c and H_a) overlap with those arising from the major isomer **(11a)**, but they can be located by 2D NMR ¹H–¹H NOESY measurements. The most interesting NOE interaction is that observed between the 5-CH₃ group of the pyrazole ring and the central allyl proton, H_c and *syn* allyl proton *trans* to the sulfur atom, H_s' for the major isomer **(11a)** revealing an *endo*-configuration (see Fig. 7).



Fig. 7 The two Pd(II)–allyl diastereomers of diphosphazane monosulfide, $[Pd(\eta^3-C_3H_5)\{\kappa^2-Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2-3,5)\}]-(PF_6)$ (11), observed in solution. Selective NOE contacts reveal that in the *endo*-isomer, the central allyl proton and pyrazole-3-Me protons are close to each other whereas for the *exo*-isomer, such an NOE contact with the central allyl proton is absent.

The absence of such an interaction in the minor isomer (11b) indicates that this isomer has an *exo*-configuration.

The ³¹P{¹H} NMR spectrum of the 1,3-dimethyl allyl complex 12 shows three pairs of doublets in the ratio 6 : 4 : 1 indicating the presence of three isomers (12a-c) in solution. The ¹H NMR spectrum shows three different sets of allyl protons each consisting of three resonances. All the proton resonances are unambiguously assigned by recourse to standard ¹H-¹H 2D homo correlation techniques. The ¹³C NMR spectrum is assigned with the help of 2D ¹H-¹³C heteronuclear correlation spectrum. The doublet pattern observed for one of the terminal allylic carbon resonances clearly point to P,S-coordination. The signal arising from the third isomer 12c could not be seen in the ¹³C NMR spectrum owing to its relative low abundance. However, the ³¹P{¹H} and ¹H chemical shifts and ${}^{2}J(P,P)$ coupling constant values for 12c are similar to those of 12a and 12b. Hence, 12c must be structurally close to 12a and 12b. The ¹H-¹H COSY spectrum indicates the presence of two anti allyl protons for isomers 12a and 12b i.e. the methyl groups are in the syn/syn-arrangements (see Fig. 8). This arrangement is supported by the expected NOE interactions between the central allyl proton and two allyl methyl groups for



Fig. 8 The three isomers observed in solution for 1,3-disubstituted allyl palladium complexes, $[Pd(\eta^{3}-1,3-R'_{2}-C_{3}H_{3})\{\kappa^{2}-Ph_{2}P(S)N(CHMe_{2})-PPh(N_{2}C_{3}HMe_{2}-3,5)\}](PF_{6}) [R' = Me (12); R' = Ph (13)].$

the isomers, 12a and 12b. It is difficult to determine the allylic arrangement for 12c from the ¹H-¹H COSY spectrum because the resonances of both the allyl protons appear at the same position (4.75 ppm). However, a careful analysis of the ¹H-¹H NOESY spectrum reveals that 12c is the anti/syn-isomer, because only the methyl proton resonances at 1.99 ppm show an NOE interaction to the central allyl proton, H_c and the other methyl proton resonances at 0.31 ppm do not show any NOE interaction with H_c as would be expected for the anti/syn-isomer in which the anti-allyl methyl group is located trans to the sulfur atom (see Fig. 8). In contrast to the situation for complex 11, the major isomer (12a) observed in solution for complex 12, possesses the exo-configuration. This is revealed by the NOE interaction between the 5-CH₃ protons of the pyrazole ring and the anti allyl proton trans to the sulfur centre, H_a'; the absence of such an interaction with the H_c proton also supports the exoconfiguration for isomer 12a. The isomers 12b and 12c exhibit NOE interaction between the central allyl proton to the respective 5-CH₃ group of the pyrazole ring which is indicative of their endo-configuration.

The 1,3-diphenyl allyl complex 13 exists as two isomers 13a and **13b** in solution (in a 1 : 1.3 ratio) as revealed by its ${}^{31}P{}^{1}H{}$ NMR spectrum. NMR studies on these isomers show that they have the syn/syn- allylic arrangement. An NOE interaction between 5-CH₃ group of pyrazole ring and central allyl proton establishes that 13a has the exo-configuration whereas 13b has the endo-configuration (Fig. 8).

From a solution of 12 containing three isomers, the major isomer 12a is isolated as colourless crystals. The structure of 12a has been determined by X-ray diffraction. An ORTEP view of the molecule is shown in Fig. 9. The X-ray structure shows P,S-coordination with a distorted 'PdC₂PS' core. The Pd-C and Pd-S bond distances (Table 3) are in the expected range observed for Pd(II) allyl compounds with P,S-chelate ligands.6b The 5-CH₃ group of the pyrazole and central allyl carbon lie at the opposite side of the coordination plane formed by P(1)-Pd(1)-S(1) revealing the exo, syn/syn-configuration in the solid state.

Variable temperature NMR studies and activation barriers (ΔG^{*})

In order to determine the activation barriers for the exchange process in some of the above complexes, we have carried out variable temperature ¹H NMR studies in DMSO-d₆ at 298-373 K. The coalescence temperatures and the corresponding $\Delta G^{\pm 36}$ values are listed in Table 4. The data show that the change of the substituent on the nitrogen from CHMe₂ to CHMePh of the diphosphazane ligand backbone increases the activation barrier of the isomerisation process as observed for the unsubstituted allyl complexes 4 and 5 (see entries 1 and 2) bearing Ph₂PN(CHMe₂)PPh(N₂C₃HMe₂-3,5) and Ph₂PN((S)*-CHMePh)PPh(N₂C₃HMe₂-3,5) ligands, respectively. The incorporation of Ph or Me substituents at the 1,3-allylic positions increases the free energy of activation for the exchange process as compared to the unsubstituted allyl analogs (see entries 1 and 4, entries 2 and 3). The activation barrier for the allyl isomers bearing P,S-ligand is less as compared to the allyl isomers of P,N-ligand (see entries 3, 5 and 6). The activation barrier for cis-trans isomerisation process is slightly less than that for the syn-anti isomerisation process when the ligand and the allyl moieties are the same (see entries 5 and 6).

Trends in ³¹P chemical shifts

The ³¹P{¹H} resonances are assigned on the basis of the $\Delta\delta$ $[\Delta \delta = \delta(\text{complex}) - \delta(\text{free ligand})]$ and sensitivity of the chemical shifts upon substitution on the allyl moiety (see Table

the selective exchanges observed (see ESI †), the major exchange pathway is found to be the *cis-trans* isomerisation. Apart from this, a second isomerisation is also observed via syn-anti exchange. The syn-anti isomerisation is observed only at the allyl terminus trans to the sulfur atom, suggesting that the opening of the η^3 -allyl ligand to η^1 -bonded intermediate is controlled electronically. Despite the occurrence of these two processes in solution, only two diastereomers are observed as the allyl group is unsubstituted. (Such a result is also observed in the case of P,N-coordinated unsubstituted allyl complex 5.)

The dynamic behaviour of the complexes 12 and 13 has been studied by the phase sensitive ¹H-¹H NOESY and ROESY spectra in CDCl₃ at 298 K. No exchange is observed at 298 K between the isomers 13a and 13b. On the other hand, the crystals of 12a on dissolution in CDCl₃ transform into the other two minor isomers 12b and 12c. The isomer 12c does not show any observable exchange. An analysis of the observed exchange cross-peaks between 12a and 12b shows that the exchange occurs by a cis-trans isomerisation process. A possible mechanism is shown in Scheme 8. The presence of the anti/syn-isomer (12c) indicates that the isomerisation involves initial selective opening of the η^3 -allyl group at the allylic carbon *trans* to the coordinated phosphorus atom to generate an η^1 -bonded intermediate. This type of selective opening can account for the absence of any synlanti-isomer (i.e. the anti allyl methyl group is located trans to the coordinated phosphorus centre) and is well known for P.S-ligands.²⁷ The ¹H-¹H NOESY spectrum (see ESI[†]) shows NOE cross-peaks between the isomers 12a and 12b. These intermolecular NOE interactions arise as a result of a fast exchange process in solution. The rapid dynamic process is most probably related to the possibility that the free nitrogen on the pyrazole ring can interact with the palladium centre in the η^1 -bonded intermediate. This internal coordination of the pyrazole nitrogen stabilises the η^1 -bonded intermediates (**B** and C in Scheme 8) and thereby can accelerate the *cis-trans* isomerisation process. It is well known that catalytic amounts of anions such as chloride or fluoride or polar solvents like DMSO or acetonitrile, which can coordinatively interact with palladium centre in the η^1 -bonded intermediate, can accelerate the dynamic process.^{5e,35} The formation of **12c** can also be rationalised by considering a rotation around $C(sp^3)-C(sp^2)$ bond starting from 12a via the intermediate B (see Scheme 8).

Fig. 9 A view of the molecular structure of 12a showing the exo, syn/ syn-configuration (the hydrogen atoms and the hexafluorophosphate anion are not shown).

Stereodynamic behaviour of allyl complexes 11-13 in solution

The phase sensitive 2D ¹H-¹H NOESY and ROESY spectra of complex 11 in CDCl₃ at 298 K shed light on the intimate nature of the dynamic processes occurring in solution. From



Table 4	Variable temperature ¹ H NMR of	ata ^a and calculated free energy of activation for	or η³-allyl pallad	ium complexes of	diphosphazane	ligands
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Entry	Interchanging isomers	$\Delta v/{ m Hz}$	Coalescence temperature/K	$\Delta G^{\neq}/\mathrm{kJ} \mathrm{mol}^{-1b}$	The protons for which coalescence observed		
(1)	4a and 4b	66.0	313	63.7	-N(CHMe ₂) methyl protons		
(2)	5a and 5b	11.6	318	69.4	-N(*CHMePh) methyl protons		
(3)	7a and 7b	30.8	363	76.7	Allyl methyl protons <i>trans</i> to the coordinated phosphorus centre		
(4)	8b and 8c	17.8	368	79.5	-N(CHMe ₂) methyl protons		
(5)	12a and 12b	44.4	318	65.9	-N(CHMe ₂) methyl protons		
(6)	12a and 12c	25.4	324	68.7	-N(CHMe ₂) methyl protons		

^{*a*} DMSO-d₆ was used as solvent. ^{*b*} Calculated according to the Shanan-Atidi and Bar-Eli method.³⁶ The estimated error in the calculated free energies of activation is $\pm 1 \text{ kJ mol}^{-1}$. $\Delta v =$ frequency separation in the slow exchange limit.



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5). The chemical shift of one of the phosphorus nuclei for all the palladium allyl complexes except for the P,P-coordinated complexes (8b and 8c) lies in the range 70–74 ppm with $\Delta\delta$ being only 0.5-6 ppm. The constancy in the magnitude of chemical shifts on changing the allyl part and the low $\Delta\delta$ value suggest that this chemical shift can be assigned to the noncoordinated phosphorus. On the other hand, the chemical shift of the other phosphorus nucleus shows a greater range of variation (75-83 ppm). This phosphorus chemical shift lies very much downfield as compared to that of the free ligand and the magnitude of $\Delta \delta$ is in the range 31–36 ppm. Hence this chemical shift is assigned to the -PPh₂ phosphorus. For the P,P-coordinated complexes (8b and 8c), the -PPh₂ and the -PPh(N₂C₃HMe₂-3,5) chemical shifts are assigned the values 62-63 and 69-73 ppm, respectively, based on the observed chemical shifts for 1,3-diphenyl palladium allyl complex of the ligand Ph₂PN(CHMe₂)PPh₂ which features P,P-coordination.³⁷ For the P,S-coordinated complexes (11-13), the -P(S)Ph₂ and the -PPh(N₂C₃HMe₂-3,5) chemical shifts are assigned the values 73-77 and 91-93 ppm, respectively, based on the the magnitude of $\Delta\delta$ and chemical shifts observed for palladium allyl complexes of the ligands, Ph2P(S)N(CHMe2)PPh2 and $Ph_2P(S)N(CHMe_2)P(S)Ph_2$.³⁷ The ²J(P,P) values for P,Ncoordinated complexes of 1 and 2 lie in the range 28-30 Hz whereas ${}^{2}J(P,P)$ values for P,P-coordinated allyl complexes (8b and 8c) are observed in the range of ~110 Hz. The ${}^{2}J(P,P)$ values for the P,S-coordinated complexes of 3 are in the range 87-97 Hz.

Catalytic studies

We tested the catalytic activity of the two diphosphazane ligands (1 and (*SR*)-2) in allylic alkylation reaction of the model substrate, (*rac*)-1,3-diphenyl-2-propenyl acetate (I) (Scheme 9) using dimethyl malonate as the nucleophile.³⁴ Catalytic precursors are generated *in situ* from $[Pd(\eta^3-C_3H_5)-(\mu-Cl)]_2$ (1 mol%) and the appropriate ligands (2.5 mol%). The reaction is found to be complete within 24 h as shown by the ¹H NMR spectrum of the reaction mixture. However, only low levels of enantiomeric excess (<30%) is observed in these reactions (see Experimental).

The palladium catalysed allylic alkylation with (*E*)-3-phenyl-2-propenyl acetate (III) is investigated to study the regioselectivity of these systems (Scheme 10). The use of an unsymmetrical substrate, such as III in allylic alkylation would afford a mixture of linear and branched regio-isomers IV and V depending on the nucleophilic attack at one or the other terminal allyl carbon centres. The ¹H NMR spectrum of the reaction mixture shows complete conversion of the substrate in 24 h at 298 K and the ratio of linear and branched isomer is *ca.* 70 : 30 indicating that nucleophilic addition is more favoured at the unsubstituted terminal carbon.

Conclusions

The diphosphazane ligands 1-3 bearing a stereogenic phosphorus centre exhibit diverse palladium allyl chemistry

	Complex	$-PPh(N_2C_3HMe_2-3,5) (\delta_A)^b$	$\Delta \delta_{ m A}$	$-\mathbf{P}(\mathbf{E})\mathbf{Ph}_{2}\left(\delta_{\mathbf{x}}\right)^{b}$	$\Delta \delta_{\mathrm{x}}$			
	4 a	72.5 d (30.0)	0.6	75.6 d	31.7			
	4b	72.5°	0.6	75.3 d	31.4			
	5a	72.7 d (28.4)	3.9	77.7 d	30.4			
	5b	73.0 d (29.0)	4.2	78.4 d	31.1			
	6a	71.6 d (28.3)	-0.3	79.5 d	35.6			
	6b	71.3 d (30.2)	-0.6	76.9 d	33.0			
	6c	71.8 d (29.1)	-0.1	75.4 d	31.5			

70.1 d (27.5)

72.7 d (28.9)

73.7 d (27.8)

73.8 d (28.2)

73.0 d (29.4)

70.9 d (30.3)

73.1 d (114.3)

69.0 d (109.1)

70.8 d (28.8)

72.5 d (28.7)

91.1 d (95.3)

92.0 d (92.4)

92.8 d (91.9)

93.0 d (96.8)

93.3 d (91.2)

91.4 d (92.3)

93.1 d (87.2)

Table 5 The ${}^{31}P{}^{1}H$ NMR data^a for the η^{3} -allyl palladium complexes 4–13

6d 7a

7b

7c 7d

8a

8b

8c

9

10

11a

11b

12a

12b

12c

139

13b

^{*a*} The ³¹P{¹H} NMR spectra were recorded in CDCl₃ at 298 K except for **6** in which case a 1 : 1 mixture of CDCl₃ and CH₂Cl₂ was used. The ³¹P-³¹P coupling constants are given in parentheses. $\Delta \delta = \delta$ (complex) – δ (free ligand). ^{*b*} d: doublet. ^{*c*} Overlapped by a signal arising from the –PPh-(N₂C₃HMe₂-3,5) phosphorus of isomer **4a**.

1.8

3.9

4.9

5.0

4.2

1.0

1.2

-2.9

2.0

6.3

20.6

21.5

22.3

22.5

22.8

20.9

22.6

78.3 d

82 3 d

81.2 d

78.3 d

83.4 d

80.2 d

62.4 d

63.1 d

813d

81.8 d

77.1 d

76.6 d

74.4 d

75.8 d

75.5 d

740d

73.5 d

34.4

35.0

33 9

31.0

36.1

36.3

18.5

19.2

34.0

32.9

11.8

11.3

9.1

10.5

10.2

8.7

8.2



including various fluxional processes in solution. The ligands 1 and 2 prefer P,N-coordination rather than the usually observed P,P-coordination as the former mode of coordination electronically stabilises the palladium allyl bonding besides leading to the formation of a stable six-membered chelate ring. The usual P,P-coordination is observed only in the case of 1,3diphenyl allyl system (complex 8) probably because of the higher electron releasing ability of two phenyl groups thus obviating the necessity of having the σ -donor pyrazole nitrogen to stabilise the metal allyl bonding. On the other hand, the diphosphazane monosulfide ligand, Ph2P(S)N(CHMe2)PPh- $(N_2C_3HMe_2-3,5)$ (3) displays P,S-coordination. The P,Scoordination is preferred owing to the formation of a stable five-membered ring around the palladium centre. Thus the choice of a particular coordination mode (P,N- or P,P- or P,S-) for the ligands 1-3 is the result of combined effect of chelate ring size around the palladium centre as well as electronic nature of the allyl moiety.

The allyl palladium complexes formed by these ligands (1-3) exist as several isomers in solution. However, the solid state structures reveal the presence of only one isomer. In the solid state, the P,N-coordinated complexes (5a, 7a and 8a) show the *endo* configuration for the allyl moity whereas the solid state

structure of P,S-coordinated complex (12a) reveals *exo*-configuration. The isomer observed in the solid state undergoes slow isomerisation to produce a mixture of several isomers in solution. The exchange pathway involves two well-known processes, namely *cis*-*trans* isomerisation and *syn*-*anti* exchange through a common σ -bonded intermediate. The σ -bonded intermediate is generated by the opening of the η^3 -allyl moiety at the *trans* position with respect to the greater π -acceptor phosphorus centre and is thus subject to electronic control. The activation barriers for exchange processes among various allyl isomers bearing the P,S-ligand is less than that observed for the allyl isomers formed by the P,N-ligands.

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