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Diastereomerism in palladium(II) allyl complexes of P,P-, P,S- and S,S-donor ligands, $Ph_2P(E)N(R)P(E')Ph_2$ [R = $CHMe_2$ or (*S*)-*CHMePh; E = E′ = lone pair or S]: solution behaviour, X-ray crystal structure and catalytic allylic alkylation reactions☆

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Abstract

The reactions of achiral homodonor diphosphazane ligands, $Ph_2P(E)N(CHMe_2)P(E')Ph_2$ [E = E′ = lone pair (**1**) or S (**2**)] with the chloro bridged palladium dimers, $[Pd(\eta^3\text{-}1,3\text{-}R'\text{-}R''\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ (R′, R″ = H, Me or Ph) in the presence of NH_4PF_6 give cationic η^3-allyl palladium complexes, $[Pd(\eta^3\text{-}1,3\text{-}R'\text{-}R''\text{-}C_3H_3)(L\text{-}L')]$. Each of these complexes exists as single species in solution except the 1,3-dimethyl allyl complex, which exists as two isomers (*syn*/*syn*- and *syn*/*anti*-) in solution. Analogous allyl palladium complexes derived from the chiral homodonor diphosphazane ligand, $Ph_2PN((S)\text{-}*CHMePh)PPh_2$ (**3**) exist as a single species when the allyl moiety is symmetrical (R′ = R″ = H or Ph) but a 1:1 mixture of two different face-coordinated diastereomers if the allyl moiety is unsymmetrically substituted (R′ ≠ R″). The 1,3-dimethyl–allyl complex, $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{–}C_3H_3)\{Ph_2PN((S)\text{-}*CHMePh)PPh_2\text{-}k^2P,P\}]PF_6$ (**20**) exists as a mixture of two isomers. The major isomer (**20a**) has the *syn*/*syn*-allylic arrangement while the minor isomer (**20b**) has the *syn*/*anti* configuration. These isomers (**20a** and **20b**) equilibrate in solution via a *syn*–*anti isomerisation* pathway. Achiral and chiral heterodonor monosulphide ligands, $Ph_2P(S)N(R)PPh_2$ [R = $CHMe_2$ (**4**), (*S*)-*CHMePh(**5**)] give rise to allyl palladium complexes which exist as several isomers in solution. The presence of a chiral centre in the ligand **5** enables the observation of two NMR distinguishable face-coordinated diastereomers for its allyl complexes. However, the solid state structure of $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2P(S)N((S)\text{-}*CHMePh)PPh_2\text{-}k^2P,S\}]PF_6$ (**27**) shows the presence of only one diastereomer. Two-dimensional (2D) phase sensitive ^1H–^1H NOESY and ROESY measurements indicate that the monosulphide complexes undergo exchange by the opening of the η^3-allyl group selectively at the *trans* position with respect to the greater π-acceptor phosphorus centre to generate a η^1-bonded intermediate. Preliminary studies on the use of the ligands **1**–**5** for catalytic allylic alkylation reactions of an unsymmetrically substituted substrate, (*E*)-1-phenyl-2-propenyl-acetate are reported.

Keywords: Palladium; Allyl complexes; P ligands; S ligands; Stereodynamics by NMR spectroscopy; Allylic alkylation

1. Introduction

Palladium catalysed nucleophilic substitution reactions of allylic substrates constitute a highly useful and versatile methodology for C–C bond formation [1,2]. Enantioselective allylic substitution reactions have been the subject of considerable interest in recent years [1–3]. A key intermediate in these reactions is a cationic complex, $[Pd(\eta^3\text{-allyl})(\text{auxiliary ligand})]^+$. The exact mechanism by which the catalyst imprints its chirality upon the product remains unclear; however, the nature of the auxiliary ligand such as its electronic and steric properties, shape and depth of the chiral pocket created

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by a chiral auxiliary ligand and ligand bite angle play a significant role in catalysis [3,4]. Several donor atom combinations such as P,P- [5], N,N- [6], P,N- [3], N,S- [7] and P,S- [8] bidentate ligand systems have been successfully tested for the enantioselective allylic alkylation using the 1,3-symmetrically substituted substrates as model systems. The use of a chiral auxiliary ligand can make the η^3-allyl intermediate to exist as diastereomers, which can exhibit a complex dynamic behaviour in solution. The interconversion among the various diastereomers in solution makes the prediction of the outcome of the allylic substitution often difficult. The situation becomes more complicated when both the auxiliary ligands and the allyl moiety are unsymmetrical as this would lead to the formation of various geometrical isomers along with different allylic arrangements. As a part of our ongoing research [9,10] on the organometallic chemistry of diphosphazane ligands [11], we have recently reported our investigations on the palladium allyl chemistry of 3,5-dimethylpyrazolyl substituted diphosphazanes $Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5) (R = $CHMe_2$ or (*S*)-*CHMePh) and the monosulphide $Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2$-3,5) [12]. In this paper, we report the synthesis, characterisation and dynamic behaviour of cationic palladium(II) allyl complexes containing the ligands $Ph_2P(E)N(R)P(E')Ph_2$ [R = $CHMe_2$, E = E′ = lone pair (**1**); R = $CHMe_2$, E = E′ = S (**2**); R = (*S*)-*CHMePh, E = E′ = lone pair (**3**); R = $CHMe_2$, E = S, E′ = lone pair (**4**); R = (*S*)-*CHMePh, E = S, E′ = lone pair (**5**)]. The purpose of this investigation is to identify the source of diastereomerism in palladium allyl complexes of this type of ligands on the basis of a systematic variation of both the allyl moieties and auxiliary ligands and to study the various stereodynamic processes in solution besides investigating the utility of these ligands in palladium catalysed alkylation reactions.

2. Results and discussion

2.1. Synthesis

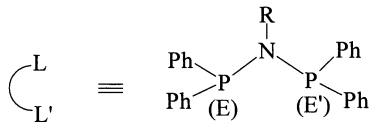
The cationic allyl complexes of general formula, $[Pd(\eta^3\text{-}1,3\text{-}R'\text{-}R''\text{-}C_3H_3)(\mathbf{1}\text{–}\mathbf{5})]PF_6$ (**7**–**31**) are prepared from the reactions of the chlorobridged palladium allyl dimer, $[Pd_2Cl_2(\eta^3\text{-}1,3\text{-}R'\text{-}R''\text{-}C_3H_3)_2]$ (**6**) with the appropriate ligands (**1**–**5**) in the presence of NH_4PF_6 in acetone (Scheme 1). All these complexes have been characterised by NMR spectral data and elemental analyses. The salient features of the spectroscopic data and dynamic behaviour are discussed below.

2.2. Palladium allyl complexes with achiral homodonor ligands, $Ph_2P(E)N(CHMe_2)P(E')Ph_2$ (*1*, *2*)

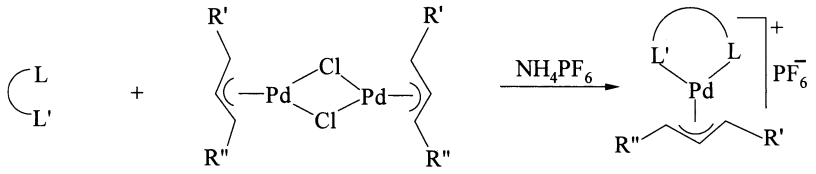
The allyl palladium complexes (**7**–**16**) derived from the achiral homodonor ligands $Ph_2P(E)N(CHMe_2)P(E')Ph_2$ [E = E′ = lone pair (**1**) or E = E′ = S (**2**)] (shown in Scheme 1) exist as a single species in each case except in the case of the 1,3-dimethyl allyl derivative (**10**) of ligand **1** (see Fig. 1). The $^{31}P\{^1H\}$-NMR spectra of the complexes (**7**, **10a**, **11**, **12**, **15** and **16**) bearing symmetrical allyl moieties (R′ = R″) show a singlet. The phosphorus chemical shifts lie downfield as compared to that of the free ligand **1** and the magnitude of coordination shift, $\Delta\delta[\Delta\delta = \delta$ (complex)—δ (free ligand)] is in the range 9–1.6 ppm. On the other hand, the phosphorus chemical shifts for the complexes (**12**–**16**) derived from the disulphide ligand **2** are close to that of the free ligand. The $\Delta\delta$ values lie in the range −0.1 to −2.8 ppm except in the case of the 1-phenyl–allyl complex, **14** for which the $^{31}P\{^1H\}$-NMR spectrum is of the AX type with one of the phosphorus nuclei showing a $\Delta\delta$ of −9.2 ppm. The low $\Delta\delta$ values observed for the allyl palladium complexes of the disulphide ligand **2**, are not surprising as the coordination to the metal centre would not significantly affect the chemical environment of the phosphorus centres which are not directly bonded to palladium.

The allylic proton resonances are assigned on the basis of a ^1H–^1H COSY experiment, which shows three sets of magnetically equivalent allylic protons for the complexes having unsubstituted allyl group (R′ = R″ = H). The two *syn* protons give rise to a signal at a lower field as compared to that for the two *anti* proton resonances (see Table 1). The incorporation of a substituent in the allyl part (R′ ≠ R″) leads to non-equivalence of the phosphorus and the proton nuclei as reflected in the ^{13}C, ^{31}P and ^1H-NMR spectra of the complexes **8**, **9**, **13** and **14**. The substituted allyl moiety can have different arrangements [13] (*syn* or *anti* with respect to the central allyl proton, H_c) as shown in Scheme 2.

The *syn*-arrangement in all the mono-substituted allyl complexes of ligands **1** and **2** is established by performing ^1H–^1H NOESY experiments. For example, the allyl–methyl protons show a strong NOE cross-peak to the central allyl proton H_c revealing a *syn*-configuration of the allyl–methyl group with respect to the central allyl proton H_c. The 1,3-dimethyl allyl complex **10** exists as two isomers in solution. The major isomer **10a** is assigned the *syn*/*syn*-arrangement and the minor isomer the *syn*/*anti*-arrangement of the allyl substituents (see Fig. 1). The isomer **10b** is present to an extent < 5%. However, the 1,3-diphenyl analogues of ligand **1** and **2** exist as a single species having the *syn*/*syn*-arrangement of the allyl–phenyl groups which is expected from the



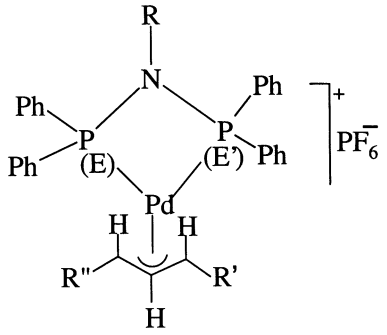
1; R = $CHMe_2$, E = E' = lone pair
2; R = $CHMe_2$, E = E' = S
3; R = (*S*)-*CHMePh, E = E' = lone pair
4; R = $CHMe_2$, E = S, E' = lone pair
5; R = (*S*)-*CHMePh, E = S, E' = lone pair



1-5 **6** **7-31**

R' = R" = H, Me or Ph
R' = H, R" = Me or Ph

Scheme 1.



R = $CHMe_2$ and E = E' = lone pair

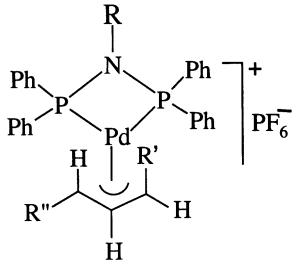
7; R' = R" = H
8; R' = H, R" = Me
9; R' = H, R" = Ph
10a; R' = R" = Me
11; R' = R" = Ph

R = $CHMe_2$ and E = E' = S

12; R' = R" = H
13; R' = H, R" = Me
14; R' = H, R" = Ph
15; R' = R" = Me
16; R' = R" = Ph

R = (*S*)-*CHMePh and E = E' = lone pair

17; R' = R" = H
18a and **18b**; R' =H, R" = Me
19a and **19b**; R' =H, R" = Ph
20a; R' = R" = Me
21; R' = R" = Ph



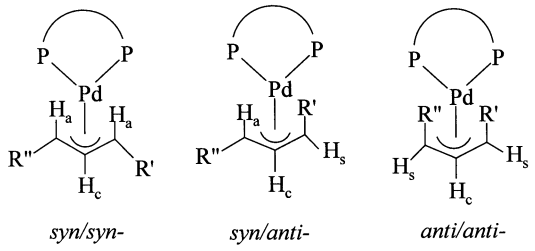
10b; R = $CHMe_2$, R' = R" = Me
20b; R = (*S*)-*CHMePh, R' = R" = Me

Fig. 1. The η^3-allyl palladium complexes [Pd(η^3-1,3-*R′*-*R″*-C_3H_3){$Ph_2P(E)N(CHMe_2)P(E')Ph_2$-$\kappa^2$*P,P* or *S,S*}]$PF_6$ (E = E′ = lone pair or S; **7**–**21**) with homodonor ligands **1**–**3**.

Table 1
Selected ^{1}H-NMR data [a] for complexes **7**–**21** (only allyl protons are listed)

Complex	H_s	H_a	H_s'	H_a'	H_c	CH_3 [b]
7	4.59 m	3.30 m	–	–	5.68 m	–
8	4.34 br	3.10 br t (10.2) [c,d]	–	4.34 [e]	5.69 m	1.76 dt (12.6) [d] (6.4) [c]
9	3.82 m	3.82 [e]	–	5.25 dt (13.0) [c] (5.0) [d]	6.29 m	–
10a	–	–	–	4.12 m	5.68 t (12.4) [c]	1.72 dt (13.2) [d] (6.4) [c]
10b	–	–	5.20 br	4.40 br	5.55 m	1.73 [e] and 0.93 m
11	–	–	–	5.63 dt (12.8) [c] (9.2) [d]	6.59 t (12.8) [c]	–
12	4.23 br	2.79 br	–	–	5.20 m	–
13	3.99 br s	3.66 br s	–	2.63 br s	4.95 m	1.36 br s
14	4.23 br	2.90 br	–	4.49 br	5.64 m	–
15	–	–	–	3.52 br s	4.80 t (11.6) [c]	1.37 br s
16	–	–	–	4.64 br	6.06 t (11.7) [c]	–
17	4.51 br	3.23 m	–	–	5.65 m	–
18a and **18b**	4.31 m	2.97 t (12.4) [c,d]	–	4.22 m	5.57 m	1.67 m
19a and **19b**	4.42 m	3.46 m	–	5.31 dt (12.7) [c] (5.0) [d]	6.21 m	–
20a	–	–	–	4.08 m	5.64 t (11.1) [c]	1.82 m and 1.73 m
20b	–	–	5.11	4.45	5.46	1.78 and 0.89
21	–	–	–	5.48 m	6.58 t (12.8) [c]	–

Abbreviations: br, broad; br s, broad singlet; t, triplet; br t, broad triplet; dt, doublet of triplets; m, multiplet.
[a] The ^{1}H-NMR spectra were recorded in $CDCl_3$ at 25 °C. H_s and H_a are *syn* and *anti* allyl protons, respectively attached to unsubstituted allyl terminus. H_s' and H_a' are *syn* and *anti* allyl protons, respectively at the substituted allyl terminus. Coupling constants in Hz are given in parenthesis.
[b] Allyl CH_3 protons.
[c] ^3J(H,H).
[d] J(P,H).
[e] Overlapped with signal arising from other allyl proton.



Scheme 2.

higher steric demand of the allyl–phenyl group at the *anti* allylic position.

The allylic carbon nuclei are assigned by recourse to a ^{13}C–^{1}H COSY experiment with the help of pre-assigned proton chemical shifts. The central allyl carbon resonance appears as a triplet with a low ^2J(P,C) value (~ 9.0 Hz) for the complexes bearing ligand **1** (see Table 2). The resonances arising from the two terminal allyl carbon nuclei in the allyl complexes **7**, **10** and **11** bearing symmetrical allyl moiety appear as a triplet [^2J(P,C) = ca. 30 Hz] at a relatively higher field compared to those of the central allyl carbon resonances. For the mono-substituted allyl derivatives (**8** and **9**) of ligand **1**, two sets of terminal ^{13}C resonances (doublet of doublets in each case owing to coupling to two different phosphorus nuclei) are observed. As expected, the ^2J(P,C) involving the allyl ^{13}C nuclei in the *trans* position to phosphorus is larger than the ^2J(P,C) involving the ^{13}C nuclei in the *cis* position [14]. The substituted allyl carbon terminus (C_t') gives rise to a signal in the ^{13}C-NMR spectrum at a chemical shift value which is down field compared to the chemical shift value for unsubstituted allyl terminus (C_t). The same trend is observed in the ^{13}C chemical shifts of the allyl carbon nuclei for the complexes (**12**–**16**) formed by the disulphide ligand, $Ph_2P(S)N(CHMe_2)P(S)Ph_2$ (**2**). However, the allyl ^{13}C signals for these complexes are singlets indicating that the ^3J(P,C) coupling is close to zero.

2.3. Palladium allyl complexes with the chiral homodonor ligand, $Ph_2PN((S)$-*$CHMePh)PPh_2$ (**3**)

The various isomers observed for the palladium allyl complexes of the chiral homodonor ligand $Ph_2PN((S)$-*$CHMePh)PPh_2$ (**3**) are shown in Fig. 1. Incorporation of chirality in the ligand backbone does not alter nature of the allyl complexes of **3** as compared to those of its achiral analogue **1** if one considers the symmetrical allyl derivatives ($R' = R''$). Thus, only a single species is observed in the NMR spectra for the allyl complexes **17** and **21** containing a symmetrical allyl group. However, asymmetry in the allyl part ($R' \neq R''$) causes the complexes (**18** and **19**) to exist as a 1:1 mixture of two isomers. The ^{1}H-NMR spectrum does not distinguish the two isomers. However, the ^{13}C-NMR and ^{31}P-NMR spectra (see Table 2) reveal the presence of two isomers. The ^{31}P–^{31}P COSY spectrum of complex **18** reveals four doublets arising from the two isomers. The ^{13}C-NMR spectrum of complexes **18** or **19** exhibits four different

Table 2
The ^{13}C-NMR (the allyl carbon nuclei only are listed) and ^{31}P{^{1}H}-NMR data [a] for η^3-allyl palladium complexes **7**–**21**

Complex	^{13}C-NMR (δ)				^{31}P{^{1}H}-NMR (δ)
	C_t	C_t'	C_c	CH_3 [b]	
7	69.0 t (20.6) [c,d]	–	123.9 t (8.5)	–	60.9 s
8	63.8 dd (31.7) [c] (9.7) [d]	89.8 dd (32.6) [c] (10.3) [d]	123.8 t (9.1)	18.6 s	57.8 d (90.3), 61.6 d
9	65.4 dd (33.0) [c] (8.2) [d]	92.3 dd (32.2) [c] (10.6) [d]	118.5 t (9.3)	–	58.3 d (107.1), 63.3 d
10a	–	84.4 t (21.7) [c,d]	125.3 t (9.0)	18.5 s	64.4 s
10b	(–) [e]	(–) [e]	(–) [e]	(–) [e]	65.4 br s, 63.8 br s
11	–	88.3 t (26.6) [c,d]	113.3 t (11.0)	–	62.6 s
12	68.6 s	–	114.9 s	–	67.2 s
13	63.8 s	88.2 s	115.0 s	18.0 s	67.4 br s, 66.2 br s
14	64.3 br s	89.2 br s	109.0 s	–	67.3 br s, 58.3 br s
15	–	82.9 s	116.4 s	(–) [e]	65.2 s
16	–	104.6 s	127.8 s	–	64.7 s
17	69.3 t (23.7) [c,d]	–	124.0 t (9.2)	–	66.l s
18a and **18b**	64.3 dd (34.0) [c] (8.5) [d] and 64.9 dd (33.7) [c] (9.0) [d]	89.9 dd (34.0) [c] (10.7) [d] and 90.7 dd (33.6) [c] (10.0) [d]	124.5 m and 124.5 [f]	19.4 d (4.1) and 19.2 d (4.2)	66.7 d (94.7), 69.5 d and 66.1 d (95.2), 69.4 d
19a and **19b**	66.0 dd (32.9) [c] (8.4) [d] and 65.4 dd (32.8) [c] (7.6) [d]	92.3 dd (31.2) [c] (10.5) [d] and 93.0 dd (31.2) [c] (10.6) [d]	119.0 t (9.8) and 118.5 t (9.1)	–	64.9 d (112.9), 69.8 d and 68.4 d (109.3), 69.4 d
20a	–	84.93 dd (28.6) [c] (15.3) [d] and 83.7 dd (27.5) [c] (16.0) [d]	125.3 t (10.0)	18.7 br s and 18.4 br s	70.9 br s, 70.7 br s
20b	(–) [e]	(–) [e]	(–) [e]	(–) [e]	71.4 br s, 70.2 br s
21	–	89.3 dd (30.7) [c] (10.9) [d] and 88.2 dd (30.8) [c] (11.8) [d]	113.3 t (10.3)	–	68.7 d (123.4), 66.6 d

Abbreviations: s, singlet; br s, broad singlet; d, doublet; dd, doublet of doublets; t, triplet.

[a] The ^{13}C-NMR and ^{31}P{^{1}H}-NMR spectra were recorded in $CDCl_3$ at 25° C. The coupling constants in Hz {^{2}J(C,P) and ^{2}J(P,P)} are given in parenthesis. C_t is the unsubstitutcd terminal allyl carbon. C_t' is the substituted terminal allyl carbon. C_c is central allyl carbon.

[b] Allyl-methyl carbon.

[c] $^{2}J(P,C)_{trans}$.

[d] $^{2}J(P,C)_{cis}$.

[e] The signal could not be observed.

[f] Overlapped with signal arising from other isomer.

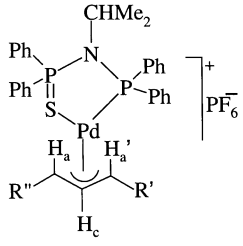
sets of doublet of doublets for the terminal allyl carbon nuclei arising from the two isomers in each case. The chemical shift values for allyl carbon resonances of **17**–**21** are listed in Table 2. Similarity in the chemical shift values of different allylic protons for the two isomers suggests that they posses very closely related structures. Thus each of the complexes **18** and **19** may be regarded as a pair of diastereomers arising from two different allyl face coordination to the palladium centre.

As observed for the 1,3-dimethyl–allyl palladium complex (**10**) of $Ph_2PN(CHMe_2)PPh_2$ (**1**), the 1,3-dimethyl allyl palladium complex (**20**) of the ligand $Ph_2PN((S)$-*$CHMePh)PPh_2$ (**3**) exists as a mixture of two isomers which may be assigned the *syn*/*syn*- and *syn*/*anti*-configurations of the allyl moiety. Of these, the *syn*/*syn*-isomer (**20a**) is the major one. The analogous 1,3-diphenyl allyl complex (**21**) of ligand **3** exists as a single isomer (*syn*/*syn*-) in solution. Unlike the spectra observed for the complexes of the achiral ligands **1** and **2**, the ^{31}P-NMR spectra of the 1,3-disubstituted *syn*/*syn*-allyl isomers (**20a** and **21**) feature an AB spin system. The ^{13}C-NMR spectra show two different terminal allyl carbon resonances. The presence of an asymmetric centre in the ligand backbone destroys the molecular symmetry even in the case of symmetrically substituted allyl complexes of ligand **3**. This feature is also reflected in the ^{1}H-NMR spectrum of the *syn*/*syn*-isomer **20a** revealing two different allyl–methyl groups. The phase sensitive ^{1}H–^{1}H NOESY and ROESY spectra of complex **20** lead us to conclude that there is a dynamic process equilibrating the two isomers (**20a** and **20b**) in solution. The conversion of a *syn*/*syn*-isomer to the *syn*/*anti*-isomer is well-known process (termed as *syn–anti isomerisation*) in palladium allyl chemistry [2a,3a,15]. The *anti* allyl–methyl protons of the *syn*/*anti*-isomer (**20b**) show exchange cross-peaks with allyl–methyl protons of both methyl groups of the *syn*/*syn*-isomer (**20a**). This result can be explained by postulating an η^1-allyl intermediate, which is formed by the opening of the η^3-allyl group at either of the allyl termini. Thus the opening of the allyl moiety is not selective with respect to any one of the allyl termini.

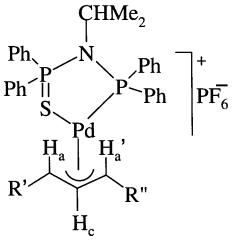
2.4. Palladium allyl complexes of the achiral heterodonor diphosphazane monosulphide ligand, $Ph_2P(S)N(CHMe_2)PPh_2$ (**4**) and dynamic behaviour in solution

The structures of the allyl palladium complexes formed by **4** are formulated as shown in Fig. 2 on the

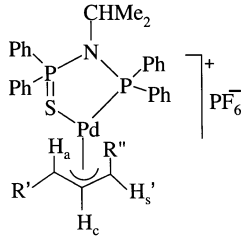
basis of NMR studies. The $^{31}P\{^{1}H\}$-NMR spectra of the complexes **22**–**26** feature an AX spin system; the $-P(S)Ph_2$ and the $-PPh_2$ chemical shifts are assigned the values 75–81 and 91–98 ppm respectively based on the magnitude of $\Delta\delta$. The coordinated phosphorus ($-PPh_2$) chemical shift lies very much downfield as compared to that of the free ligand, **4** and the magnitude of $\Delta\delta$ is 34–44 ppm. On the other hand, the magnitude of $\Delta\delta$ for the non-coordinated phosphorus [$-P(S)Ph_2$] lies in the range 9–14 ppm. The diphosphazane monosulphide ligand $Ph_2P(S)N(CHMe_2)PPh_2$ (**4**) breaks the allylic symmetry in complex **22** having the unsubstituted allyl moiety. The ^{1}H-NMR spectrum of **22** reveals five distinct allylic protons and they are assigned on the basis of a $^{1}H-^{1}H$ COSY experiment. The *syn* allylic proton H_s, *trans* to the coordinated phosphorus centre gives rise to a signal at 4.76 ppm which is downfield to the resonance (3.93 ppm) arising from the *syn* proton H_s', which is *trans* to the sulphur atom. The chemical shifts of the *anti* allylic protons (H_a and H_a') follow the same trend (see Table 3). The allyl carbon resonances in the ^{13}C-NMR spectrum of **22** are assigned on the basis of a $^{13}C-^{1}H$ HSQC experiment with the help of pre-assigned allylic proton chemical shifts. The terminal allylic carbon (C_t) *trans* to the coordinated phosphorus centre gives rise to a doublet at a lower field region as compared to the terminal allyl carbon resonance (C_t') *trans* to the sulphur atom.



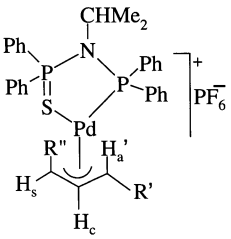
22; R' = H_s', R" = H_s
23a; R' = H_s', R" = Me
24a; R' = H_s', R" = Ph
25a; R' = R" = Me
26; R' = R" = Ph



23b; R' = H_s, R" = Me
24b; R' = H_s, R" = Ph



23c; R' = H_s, R" = Me,
25b; R' = R" = Me



23d; R' = H_s', R" = Me
25c; R' = R" = Me

Fig. 2. The η^3-allyl palladium complexes (**22**–**26**) of achiral unsymmetrical diphosphazane ligand, $Ph_2P(S)N(CHMe_2)PPh_2$ (**4**).

The phase sensitive $^{1}H-^{1}H$ NOESY and ROESY spectra of complex **22** reveal that the allylic protons H_s' and H_a' *trans* to the sulphur atom exchange with each other while no such exchange is observed among the allylic protons H_a and H_s *trans* to the coordinated phosphorus atom. The exchange result is summarised in Scheme 3. The observation can be rationalised by assuming that *syn–anti isomerisation* occurs by the opening of the η^3-allyl group selectively at the *trans* position with respect to the higher π-acceptor phosphorus centre to give a σ-bonded intermediate. The opening of the η^3-allyl group is thus controlled electronically [16,17]. Because of the greater π-acceptor character of the phosphorus centre compared to that of sulphur, the metal–carbon bond *trans* to phosphorus is weakened and hence it preferentially opens up to give the σ-bonded intermediate as shown in Scheme 3. This type of electronic control over the interconversion process is well known in the case of allyl palladium complexes of P,S-, P,N- and P,O- bidentate heterodonor ligands [14b,17,18]. The *syn–anti isomerisation* process in **22** allows the shifting of the metal coordination from one face of the allyl moiety to the other but the achiral nature of the ligand **4** does not result in the formation of any NMR distinguishable diastereomeric pair.

The incorporation of a substituent on the allyl moiety in complexes **23** and **24** introduces an additional possibility that the substituent can lie at the *trans* or *cis* position with respect to the coordinating phosphorus atom. Thus the 1-methyl–allyl complex **23** exists as a mixture of four isomers as revealed by its ^{31}P- and ^{1}H-NMR spectra. A detailed NMR study (^{13}C, $^{1}H-^{1}H$ DQF COSY, NOESY and ROESY) shows that the allyl–methyl group is *syn* to the central allyl proton and located at the *trans* position with respect to the coordinated phosphorus centre in the major isomer **23a**; in other words, the major isomer has the *syn*, *trans*-orientation of the allyl moiety. The isomer **23b** is assigned the *syn*, *cis*-configuration. The ^{13}C-NMR spectra of these isomers provide support for these assignments (see Table 4). One of the terminal allyl carbon nuclei in isomer **23a** gives rise to a doublet at 96.0 ppm with $^{2}J(P,C) = 31.7$ Hz. This resonance is assigned to the substituted allyl carbon terminus *trans* to the coordinated phosphorus centre. The unsubstituted allyl carbon in **23a** gives rise to a singlet at a relatively higher field (62.7 ppm) which can be assigned to the allyl carbon terminus *trans* to the sulphur atom, On the other hand, **23b** exhibits a singlet at a lower field (86.1 ppm) and a doublet at relatively higher field (70.4 ppm) with a value of $^{2}J(P,C) = 30.9$ Hz. This reverse trend in ^{13}C-NMR spectrum clearly points to the *cis* disposition of the allyl–methyl group with respect to the coordinated phosphorus centre in complex **23b** (see Table 4). The resonances arising from the third and fourth isomers (**23c** and **23d** respectively) could not be

Table 3
Selected ^{1}H-NMR data [a] for complexes **22**–**31** (only allyl protons are listed)

Complex	H_S	H_a	H_s'	H_a'	H_c	CH_3 [b]	CH_3 [c]
22	4.76 br t (6.0) [d,e]	3.41 dd (12.3) [d] (11.4) [c]	3.93 br d (6.0) [d]	2.77 d (12.3) [d]	5.50 m	–	–
23a	–	4.42 m	3.67 br d (5.7) [d]	2.59 br d (11.6) [d]	5.37 m	1.94 dd (10.7) [c] (6.2) [d]	–
23b	4.52 t (75) [d,e]	3.22 t (12.2) [d,e]	–	3.79 m	5.27 m	–	1.17 dd (9.1) [e] (6.2) [d]
23c	4.61 t	3.59 br d	4.75 m	–	5.39 [f]	–	0.40 t
23d	5.73 m	–	3.59 [f]	3.03 br d	5.19 m	1.17 [f]	–
24a	–	5.37 t (12.1) [d,e]	5.37 [f]	4.82 [f]	6.11 m	–	–
24b	4.82 [f]	3.59 t (12.0) [d,e]	–	5.10 d (11.9) [d]	6.05 m	–	–
25a	–	4.23 m	–	3.60	5.20 t (12.0)[d]	1.88 dd (10.0)[e] (6.0)[d]	1.22 dd (8.8)[e] (6.8)[d]
25b	–	4.63 m	4.47 m	–	5.27 [f]	1.91 [f]	0.45 t (6.8) [d,c]
25c	5.45 m	–	–	4.14 m	5.03 br t (6.0) [d]	1.10 [f]	1.15 [f]
26	–	5.60 t (12.2) [d,e]	–	4.95 d (12.1) [d]	6.42 t (12.3) [d]	–	–
27a and **27b**	4.81 m and 4.81 [f]	3.45 m and 3.45 [f]	3.95 br d (6.8) [d] and 3.83 br d (6.8) [d]	2.71 d (13.0) [d] and 2.82 d (12.3) [d]	5.50 m and 5.50 [f]	–	–
28a and **28b**	–	4.44 m and 4.44 [f]	3.73 d (5.8) [d] and 3.62 d (5.9) [d]	2.55 d (12.7) [d]and 2.66 d (12.3) [d]	5.35 m and 5.35 [f]	1.99 m and 1.97 [f]	–
28c and **28d**	4.59 t (7.5) [d,e] and 4.66 t (8.5) [d,e]	3.24 t (12.7) [d,e] and 3.29 t (12.7) [d,e]	–	3.75 [f] and 3.89 m	5.26 m and 5.23 m	–	1.10 dd (9.1) [e] (6.2) [d] and 0.97 dd (9.1) [c] (6.1) [d]
28e and **28f**	3.88 [f] and 3.79 [f]	3.02 br d and 3.14 br	4.73 m and 4.67 [f]	–	5.17 [f] and 5.19 [f]	–	0.43 t and 0.35 t
29a and **29b**	–	5.25 m and 5.25 [f]	3.93 and 3.80 br d	2.94 d (11.8) [d] and 2.86 d (12.1) [d]	6.01 m and 6.01 [f]	–	–
29c and **29d**	4.80 m and 4.75 m	3.52 m and 3.52 [f]	–	4.75 d (11.9) [d] and 4.64 [d] (12.2) [d]	5.87 m and 5.87 [f]	–	–
30a and **30b**	–	4.28 m and 4.28 [f]	–	3.49 m and 3.65 m	5.22 m and 5.20 [f]	1.94 m and 1.94 [f]	1.09 m and 0.91 m
31a and **31b**	–	5.43 m and 5.43 [f]	–	4.75 d (12.0) [d] and 4.89 d (11.9) [d]	6.62 t (12.3) [d] and 6.56 t (12.3) [d]	–	–

Abbreviations: br, broad; s, singlet; d, doublet; br d, broad doublet; dd, doublet of doublets; t, triplet; m, multiplet.

[a] The ^{1}H-NMR spectra were recorded in $CDCl_3$ at 25 °C for all the complexes except for **24** and **31** in which cases a 1:1 mixture of $CDCl_3$ and DMSO-d_6; was used. Coupling constants in Hz are given in parenthesis. H_s and H_a are the *syn* and *anti* allylic protons *trans* to the coordinated phosphorus atom, respectively. H_s' and H_a' are the *syn* and *anti* allylic protons *trans* to the sulphur atom, respectively.

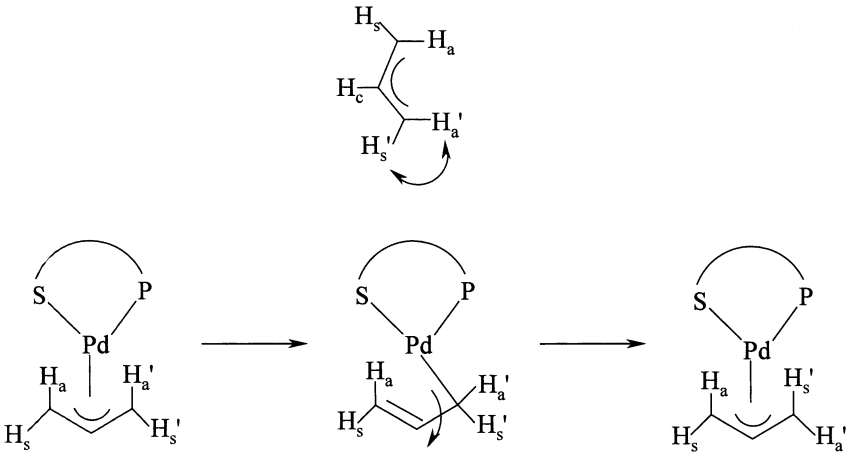
[b] Allyl CH_3 *trans* to the coordinated phosphorus centre.

[c] Allyl CH_3 *trans* to the sulphur atom.

[d] ^{3}J(H,H).

[e] J(P,H).

[f] Overlapped with signal arising from other allyl or ligand proton.



Scheme 3.

seen in the ^{13}C-NMR spectrum owing to their relative low concentrations (< 5%). However, their structures can be deduced on the basis of the ^{1}H–^{1}H COSY and NOESY spectra as the *anti*, *cis*- (**23c**) and *anti*, *trans*- (**23d**) isomers (see Fig. 2). The ^{1}H chemical shifts are listed in Table 3. The most abundant isomers **23a** and **23b** contain the *syn* allyl–methyl group as the ^{1}H–^{1}H COSY spectrum reveals that the central allyl proton of **23a** or **23b** couples strongly to two *anti* allylic protons and weakly to one *syn* allylic proton. The allyl–methyl protons (*trans* to the coordinated phosphorus centre) of **23a** resonate at 1.94 ppm which is relatively at a lower field compared to the allyl–methyl protons (*trans* to the sulphur atom) of isomer **23b**. The allyl–methyl protons of isomer **23b** resonate at 1.17 ppm. This trend in chemical shifts arises from the different electronic effects of the two different donor centres (phosphorus and sulphur) bonded to palladium and supports the assignment of **23a** as the *syn*, *trans*- and **23b** as the *syn*, *cis*- isomer respectively. The relative low abundance (< 5%) of minor isomers **23c** and **23d** and overlap of several allylic proton resonances with those of major isomers (**23a** and **23b**) make their assignment difficult. However, a careful look at the ^{1}H–^{1}H COSY spectrum shows that the allyl–methyl protons at 0.40 ppm couples with a proton at 4.75 ppm in isomer **23c** while in isomer **23d** the allyl–methyl protons at 1.17 ppm couples with a proton at 5.73 ppm. The high field resonances at 0.40 and 4.75 ppm in **23c** are assigned to the *anti* allyl–methyl protons and *syn* proton (H_s') respectively *trans* to sulphur; hence **23c** is the *anti*, *cis*-isomer (the *anti* allyl–methyl group in **23c** is *cis* to the coordinated phosphorus centre; see Fig. 2). On the basis of the trends observed in the chemical shifts of the allyl protons in P,S-coordinated palladium allyl complexes (see above), the resonances at 1.17 and 5.73 ppm are assigned to the *anti* allyl–methyl protons and *syn* proton (H_s) of **23d** respectively (the *anti* allyl–methyl group in **23d** is *trans* to the coordinated phosphorus centre; see Fig. 2).

Unlike the case observed for complex **23**, the 1-phenyl–allyl derivative **24** exists as a mixture of two isomers in the ratio 1.4:1, The major isomer **24a** is assigned the *syn*, *trans* configuration and the minor isomer **24b** the *syn*, *cis*-configuration on the basis of ^{13}C, ^{1}H, ^{31}P(^{1}H}, ^{1}H–^{1}H COSY and NOESY spectra. The ^{1}H–^{1}H COSY and NOESY spectra reveal that the isomers **24a** and **24b** possess the *syn*-allylic arrangement of the phenyl–allyl group. The chemical shifts and coupling constants observed in the ^{13}C-NMR spectrum of **24** (see Table 4) show that the major isomer **24a** contains the allyl–phenyl group at the *trans* position with respect to the coordinated phosphorus and the minor isomer **24b** has a *cis* disposition of the allyl–phenyl group with respect to the coordinated phosphorus centre. The absence of any *anti*-isomer in this case is not surprising because of the higher steric demand of the larger allyl–phenyl group compared to the allyl–methyl group at the *anti*-allylic position. The major component for both the complexes **23** and **24** is the *syn*, *trans*-isomer. The preference for the *syn*, *trans*-isomer can be understood in terms of the higher *trans* influence of the phosphorus centre so that the electron releasing substituent (Me or Ph) preferably occupies the *trans*-position.

The phase sensitive ^{1}H–^{1}H NOESY (shown in Fig. 3) and ROESY spectra of complex **23** reveal two types of stereodynamic processes in solution. The major exchange process is the one between *syn* and *anti* protons of the isomer **23a** at the *trans* position to the sulphur atom and is similar to the selective *syn–anti isomerisation* observed for the unsubstituted allyl complex **22**. The isomer **23a** at the same time exchanges with the *syn*, *cis*-isomer **23b**. The exchange behaviour (shown in Scheme 4) suggests a *cis-trans isomerisation* between **23a** and **23b** via a rotation around the Pd–C(sp^3) bond in the σ-bonded intermediate '**A**'. On the other hand, the isomer **23b** exchanges with the *anti*, *cis*-isomer **23c**, which may he explained by considering a *syn–anti*

Table 4
The ^{13}C-NMR (the allyl carbon nuclei are only listed) and $^{31}P\{^1H\}$-NMR data [a] for the, η^3-allyl palladium complexes (**22**–**31**)

Complex	^{13}C-NMR				$^{31}P\{^1H\}$-NMR	
	C_t	C_t'	C_c	CH_3 [b]	P_A	P_x
22	75.3 dd (32.6) [c] (4.0) [d]	68.2 d (4.5) [d]	121.0 d (7.0)	–	78.7 d (90.3)	93.7 d
23a	96.0 d (31.7) [c]	62.7 br s	119.9 d (6.2)	18.5 br s	76.5 d (72.7)	93.6 d
23b	70.4 d (30.9) [c]	86.1 br s	120.1 d (7.0)	18.2 br s	80.9 d (90.4)	97.4 d
23c	(–) [e]	(–) [e]	(–) [e]	(–) [e]	77.2 d (80.9)	92.7 d
23d	(–) [e]	(–) [e]	(–) [e]	(–) [e]	77.3 d (89.6)	93.3 d
24a	96.1 d (29.4) [c]	63.5 s	114.5 d (6.9)	–	76.5 d (72.6)	93.6 d
24b	71.1 d (32.9) [c]	87.3 d (5.8) [d]	114.2 d (6.7)	–	80.9 d (90.4)	93.4 d
25a	92.0 d (26.8) [c]	80.4 br s	121.0 d (6.5)	18.4 d (4.9) and 18.2 br s	76.4 d (80.9)	94.6 d
25b	(–) [e]	(–) [e]	(–) [e]	(–) [e]	75.9 d (78.1)	93.0 d
25c	(–) [e]	(–) [e]	(–) [e]	(–) [e]	78.3 d (97.9)	93.0 [f]
26	94.0 d (26.0) [c]	83.6 br s	109.1 d (7.0)	–	78.0 d (76.2)	91.7 d
27a and **27b**	75.2 dd (16.0) [c] (3.1) [d] and 75.5 dd (16.0) [c] (3.3) [d]	68.5 d (4.2) [d] and 68.6 d (4.5) [d]	121.0 d (6.5) and 120.8 d (6.4)	–	78.1 d (81.6) and 78.1 [f]	90.0 d and 90.5 d
28a and **28b**	95.6 d (29.7) [c] and 95.3 (30.3) [c]	62.6 s and 62.1 br s	119.5 br s and 119.1 br s	18.4 s and 18.6 s	76.5 d (59.6) and 76.8 d (60.2)	90.4 d 90.1 d
28c and **28d**	69.8 d (32.8) [c] and 70.1 d (32.4) [c]	86.7 br s and 85.7 br s	119.7 br s and 119.6 [f]	17.6 s and 17.5 s	80.2 d (70.3) and 79.7 d (69.1)	92.8 d and (92.4) d
28e and **28f**	(–) [e]	(–) [e]	(–) [e]	(–) [e]	78.9 d (67.4) and 79.0 d (64.1)	89.3 d and 90.0 [f]
29a and **29b**	96.0 d (29.9) [c] and 95.6 d (28.7) [c]	64.8 br s and 64.8 [f]	114.1 d (6.7) and 114.4 d (6.8)	–	74.1 d (71.2) and 74.0 d (70.4)	87.7 d and 87.0 d
29c and **29d**	71.7 d (26.2) [c]and 71.4 d (28.9) [c]	88.7 br s and 88.0 br s	114.7 d (5.4) and 113.7 d (5.9)	–	78.1 d (84.2) and 77.7 d (83.4)	90.4 d and 91.5 d
30a and **30b**	91.7 d (30.6) [c]and 92.0 d (29.3) [c]	80.0 d (6.0) [d] and 80.1 d (4.7) [d]	120.9 d (6.2) and 120.8 d (6.6)	17.9 s,17.7 s and 18.4 br s	75.2 d (82.2) and 75.2 [f]	89.2 d and 88.9 d
30c and **30d**	(–) [e]	(–) [e]	(–) [e]	(–) [e]	77.4 d (77.1) and 77.9 d (81.8)	86.8 d and 85.9 d
30e and **30f**	(–) [e]	(–) [e]	(–) [e]	(–) [e]	73.9 d (86.1) and 74.5 d (88.2)	90.8 d and 90.0 d
31a and **31b**	93.3 d (29.1) [c] and 92.9 d (31.6) [c]	83.9 s and 83.9 [f]	108.9 d (4.2) and 108.6 d (4.6)	–	76.5 d (76.0) and 76.3 d (75.8)	92.5 d and 91.9 d

Abbreviations: s, singlet; br s, broad singlet; d, doublet; dd, doublet of doublets.

[a] The ^{13}C and $^{31}P\{^1H\}$-NMR were recorded in $CDCl_3$ at 25 °C except for **24** and **31** in which cases a 1:1 mixture of $CDCl_3$ and DMSO-d_6 was used. The coupling constants {^2J(C,P) and ^2J(P,P)} in Hz are given in parenthesis. C_t is terminal allyl carbon *trans* to the coordinated phosphorus center. C_t' is terminal allyl carbon *cis* to the coordinated phosphorus center. C_c is central allyl carbon. P_A is $-Ph_2P(S)$ phosphorus and P_X is $-PPh_2$ phosphorus.

[b] Allyl-methyl carbon.

[c] $^2J(P,C)_{trans}$.

[d] $^2J(P,C)_{cis}$.

[e] The signal could not be observed.

[f] Overlapped with signal arising from other isomer.

isomerisation. The isomer **23d** does not show exchange with any of the other isomers (**23a**–**23c**).

The 1,3-dimethyl allyl complex **25** exists as a mixture of three isomers in the ratio 9:1.5:1. The major isomer **25a** is assigned the *syn*/*syn*-allylic arrangement while the minor isomers **25b** and **25c** are assigned the *anti*/*syn*-allylic arrangements (the *anti* allylmethyl group is *trans* to the sulphur atom) and *syn*/*anti*-isomer (the *anti* allyl–methyl group is *trans* to the coordinated phosphorus centre) respectively. These isomeric configurations are shown in Fig. 2. The 1,3-diphenyl allyl complex (**26**) bearing the larger phenyl groups exists as a single species with the *syn*/*syn*-allylic arrangement.

2.5. Palladium allyl complexes of chiral heterodonor diphosphazane monosulphide ligand, $Ph_2P(S)N((S)$-*$CHMePh)PPh_2$ (**5**): the effect of chirality

The structures assigned to the allyl palladium complexes (**27**–**31**) formed by the chiral diphosphazane monosulphide $Ph_2P(S)N((S)$-*$CHMePh)PPh_2$ (**5**) on the basis of NMR spectral data are shown in Fig. 4. The NMR spectra become more complicated as there is an additional possibility of face-coordinated diastereomeric pairs that can exist in the case of a chiral heterodonor ligand **5**. Thus the number of isomers observed in the NMR spectra is doubled for ligand **5**

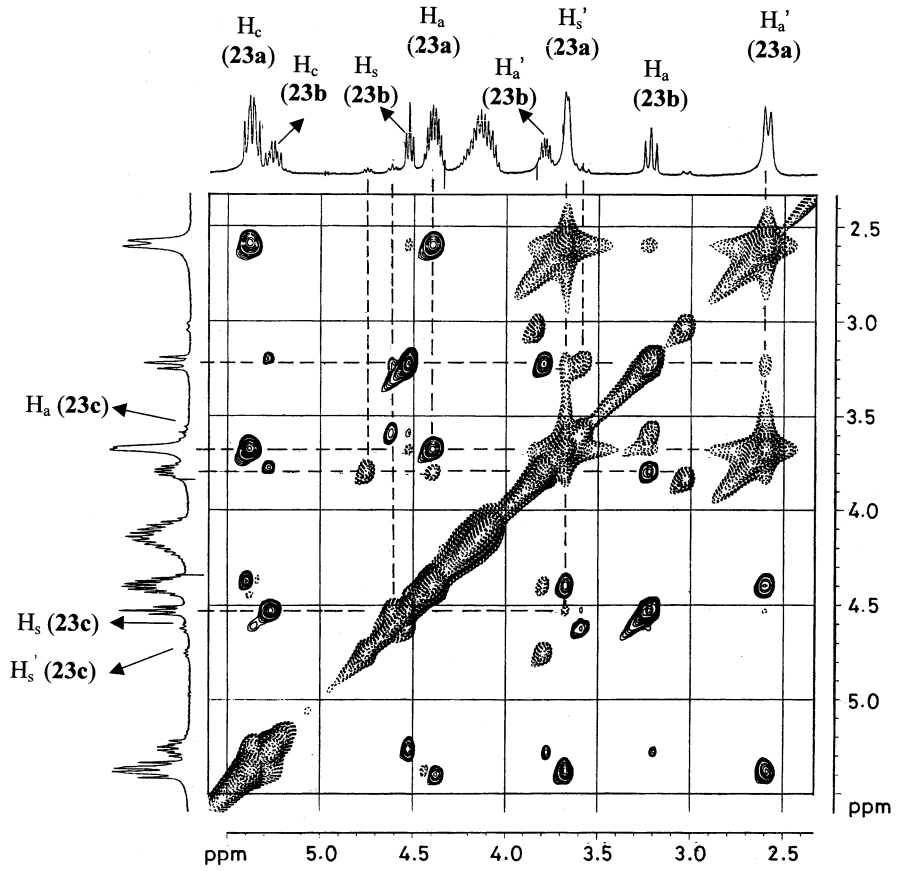
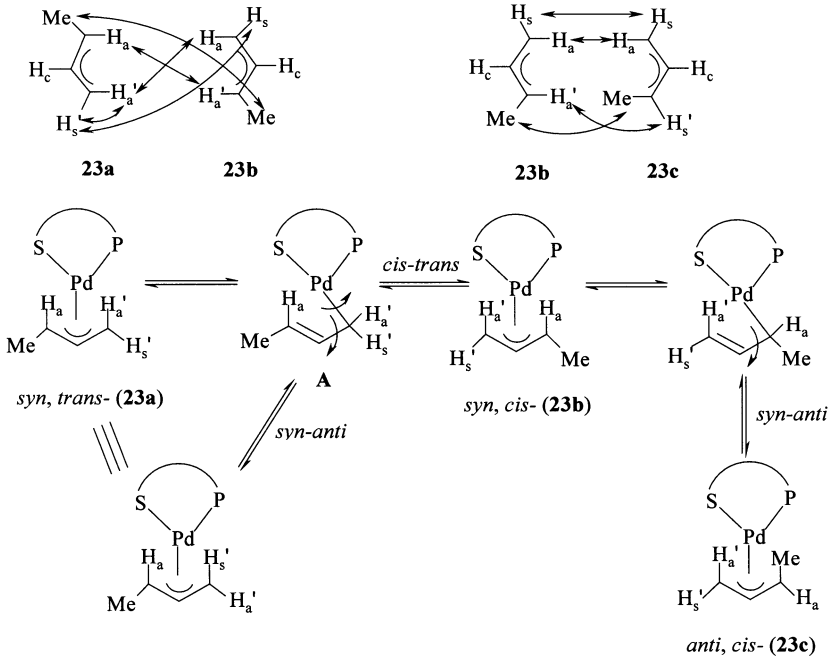


Fig. 3. The phase sensitive $^{1}H-^{1}H$ NOESY (400 MHz, $CDCl_3$, 25 °C) spectrum of [Pd(η^3-1-Me-C_3H_4){$Ph_2P(S)N(CHMe_2)PPh_2$-κ^2P,S}]PF_6 (**23**) revealing various exchange cross-peaks between the allyl isomers **23a**–**23c**.



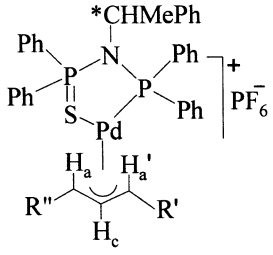
Scheme 4.

as compared to the complexes containing ligand **4**. For example, the unsubstituted-allyl complex **27** exists as a 1:1 mixture of two isomers **27a** and **27b** as shown by its ^{31}P- and ^{13}C-NMR spectra (see Table 4). The phase sensitive ^{1}H–^{1}H NOESY and ROESY spectra show that the two isomers undergo exchange with each other in a similar way as that observed for complex **22**. The two isomers (**27a** and **27b**) thus can be assigned as a pair of diastereomers that are formed by different allyl face coordination to the palladium centre. The introduction of one chiral centre in the ligand backbone thus converts the enantiomeric pair (observed for complex **22** bearing the achiral ligand **4**) into a NMR distinguishable diastereomeric pair. Such a result has been previously reported by Lanza et al. [19] for the palladium allyl complexes of chiral N,N- and S,S-donor dithioxamide ligands. The mono-substituted allyl derivatives **28** and **29** exist in solution as six and four isomers respectively. A detailed NMR study on the 1-methyl–allyl complex **28** reveals that the two major isomers **28a** and **28b** constitute a diastereomeric pair having *syn*, *trans*-geometry. The isomers **28c** and **28d** constitute another pair of diastereomers having *syn*, *cis*-geometry. The isomers **28e** and **28f** constitute the third diastereomeric pair with *anti*, *cis*-allylic configuration (see Fig. 4). The ^{13}C-NMR resonances (see Table 4) for the four isomers (**28a**–**28d**) are assigned on the basis of a ^{13}C–^{1}H HSQC experiment. The structures of the two minor isomers **28e** and **28f** are deduced on the basis of their ^{1}H-(Table 3) and ^{31}P-NMR spectra (Table 4).

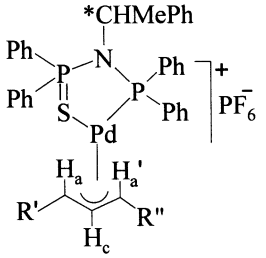
The 1,3-dimethyl complex **30** exists as three diastereomeric pairs as shown by its ^{31}P-NMR spectrum. The major diastereomeric pair **30a** and **30b** (present to an extent of 90%) possesses the *syn*/*syn*-allylic arrangement. The other two diastereomeric pairs are *syn*/*anti*-(**30c** and **30d**; the *anti* allyl–methyl group is *trans* to the coordinated phosphorus atom) and *anti*/*syn*-isomers (**30e** and **30f**; the *anti* allyl–methyl group is *trans* to the sulphur atom). The 1,3-diphenyl allyl complex **31** exists as two face-coordinated diastereomers in 1:1 ratio having the *syn*/*syn*-allylic arrangement.

3. Solid state structure of the complex [Pd(η^3-C_3H_5){$Ph_2P(S)N((S)$-*CHMePh)PPh_2-k^2P,S}]PF_6 (27)

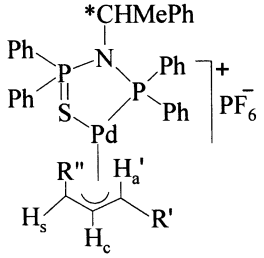
A crystallographic study has been carried out for the complex **27**. The solid state structure consists of only one diastereomer shown in Fig. 5, The coordination geometry around the metal is distorted square planar; the P(2)–Pd(1)–S(1) and C(1)–Pd(1)–C(3) angles are 94.6(8)° and 67.5(5)°, respectively. The Pd–C and Pd–S bond distances are in the expected range observed for



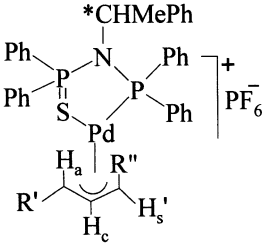
27a and **27b**; R' = H_s', R" = H_s
28a and **28b**; R' = H_s', R" = Me
29a and **29b**; R' = H_s', R" = Ph
30a and **30b**; R' = R" = Me
31a and **31b**; R' = R" = Ph



28c and **28d**; R' = H_s, R" = Me
29c and **29d**; R' = H_s, R" = Ph



30c and **30d**; R' = R" = Me



28e and **28f**; R' = H_s, R" = Me
30e and **30f**; R' = R" = Me

Fig. 4. The η^3-allyl palladium complexes (**27**–**31**) of chiral unsymmetrical diphosphazane ligand, $Ph_2P(S)N((S)$-*CHMePh)PPh_2 (**5**).

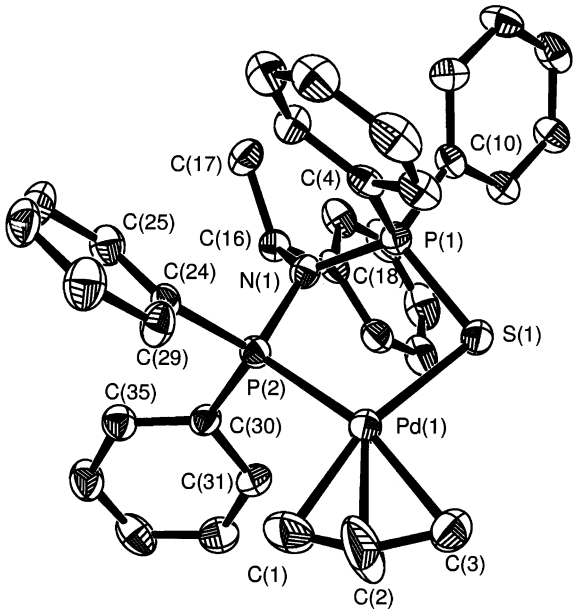
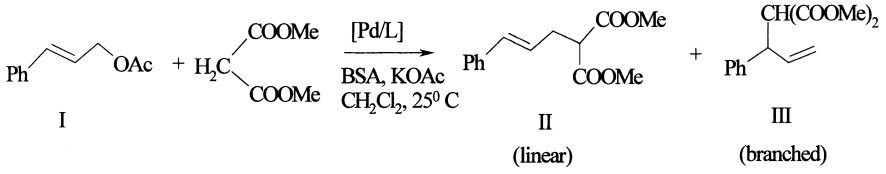


Fig. 5. The molecular structure of $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2P(S)N((S)\text{-}*CHMePh)PPh_2\text{-}\kappa^2P,S\}]PF_6$ (**27**) (The hydrogen atoms and hexafluorophosphate anion are not shown.). Selected bond distances (Å) and angles (°) are; Pd(1)–C(1) = 2.060(1); Pd(1)–C(2) = 2.082(2); Pd(1)–C(3) = 2.192(1); Pd(1)–P(2) = 2.285(2); Pd(1)–S(1) = 2.375(2); P(1)–S(1) = 1.992(3); P(1)–N(1) = 1.685(7); P(2)–N(1) = 1.741(8); P(2)–Pd(1)–S(1) = 94.6(8); C(1)–Pd(1)–C(3) = 67.5(5); C(3)–Pd(1)–P(2) = 165.5(3); C(1)–Pd(1)–S(1) = 165.6(4); P(l)–N(1)–P(2) = 110.2(4).

Pd(II) allyl compounds of other P,S-chelate ligands [8b]. The P–N–P angle is 110.2(4)° which is smaller than that observed [124.3(2)°] for the free ligand **5** [20]. The P–N distances do not change significantly as compared to those for the free ligand whereas the P–S distance increases by 0.04 Å. The two terminal allyl carbon atoms are not coplanar with the coordination plane formed by S(1), Pd(1) and P(2) atoms; the distances of C(1) and C(3) from this plane are 0.23 and 0.17 Å respectively. The terminal Pd–C allyl bond lengths are significantly different from one another; the carbon atom *trans* to phosphorus displays the expected longer distance [Pd(1)–C(3) = 2.192(1) Å], as compared to its partner *trans* to sulphur [Pd(1)–C(1) = 2.060(1) Å]. This is a reflection of the higher *trans* influence [8b,16] of the phosphorus donor centre. This elongation of Pd-terminal allyl carbon bond length *trans* to phosphorus as compared to that *trans* to sulphur is consistent with the proposed mechanism (Scheme 3) involving selective opening of the allyl terminus, which is *trans* to phosphorus. The five-membered chelate ring adopts a non-planar conformation as shown by the distance calculations from the mean plane defined by S(1), Pd(1) and P(2) atoms; N(1) is almost coplanar with this plane (the deviation is only 0.03 Å with respect to this plane) whereas P(1) lies at a distance of 0.81 Å from the S(1)–Pd(l)–P(2) plane. Two phenyl groups on P(2) arc not symmetrically placed with respect to the coordination plane formed by S(1), Pd(1) and P(2) atoms. The dihedral angle between S(1)–Pd(1)–P(2) and C(25)–C(24)–C(29) is 52.7° revealing a pseudo-equatorial arrangement of this phenyl group with respect to the S(1)–Pd(1)–P(2) plane. On the other hand, the dihedral angle between the planes formed by S(1)–Pd(1)–P(2) and C(35)–C(30)–C(31) is 73.9°; hence this phenyl group may be considered as having a pseudo-axial arrangement.

4. Catalytic studies

The palladium catalysed allylic alkylation with (*E*)-1-phenyl-2-propenyl acetate (I) is investigated to study the regio-selectivity in these systems (Scheme 5) using dimethyl malonate as the nucleophile [21]. Catalytic precursors are generated in situ from $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}C)]_2$ (1 mol%) and the appropriate ligands (2.5 mol%). The use of an unsymmetrical substrate such as (I) in allylic alkylation would afford a mixture of linear and branched regioisomer (II) and (III), respectively depending on the nucleophilic attack at one or the other terminal allyl carbon centres (Scheme 5). The ^{1}H-NMR spectrum of the reaction mixture shows complete conversion of the substrate in 24 h at 25 °C and the ratio of linear and branched isomer is shown in Table 5 for various diphosphazane ligands. The results indicate that the nucleophilic substitution takes place predominantly at the unsubstituted terminus of the substrate. The steric effect of the substituent seems to play an important role in determining the regio-selectivity of the nucleophilic attack.



L = diphosphazane ligands (**1-5**)
BSA = N,O-bis(trimethylsilyl)acetamide

Scheme 5.

Table 5
Results of allylic alkylation reactions of an unsymmetrically substituted substrate (*E*)-1-phenyl-2-propenyl acetate using diphosphazane ligands **1**–**5**

Entry	Diphosphazane ligand (L)	Linear product (II) (%) [a]	Branched product (III) (%) [a]
(1)	$Ph_2PN(CHMe_2)PPh_2$(**1**)	96	4
(2)	$Ph_2P(S)N(CHMe_2)P(S)Ph_2$ (**2**)	96	4
(3)	$Ph_2PN((S)$-*CHMePh)PPh_2 (**3**)	97	3
(4)	$Ph_2P(S)N(CHMe_2)PPh_2$(**4**)	95	5
(5)	$Ph_2P(S)N((S)$-*CHMePh)PPh_2 (**5**)	96	4

[a] The relative percentages of the alkylated products are determined from the ^{1}H-NMR spectrum of the reaction mixture.

5. Summary and conclusions

The diphosphazane ligands of the type $Ph_2P(E)N(R)P(E')Ph_2$ (**1**–**5**) exhibit diverse palladium allyl chemistry including various fluxional processes in solution. The symmetrical ligands $Ph_2PN(CHMe_2)PPh_2$ (**1**) and $Ph_2P(S)N(CHMe_2)P(S)Ph_2$ (**2**) effectively form only one allyl palladium complex in solution because the achiral nature of these ligands does not permit the differentiation of the two enantiomers arising from the coordination of the two faces of the allyl moiety to the metal by means of NMR spectroscopy. However, the presence of *syn*/*anti*-isomer in the case of complex, $(Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)\{Ph_2PN(CHMe_2)PPh_2\text{-}k^2P,P\}]PF_6$ (**10**) does indicate that these allyl palladium complexes (**7**–**16**) are fluxional in solution. Incorporation of a chiral centre in the ligand backbone introduces the possibility that the palladium allyl complexes can exist as a pair of different face-coordinated diastereomers. Diastereomerism is observed for the allyl complexes bearing the homodonor chiral ligand, $Ph_2PN((S)$-*CHMePh)PPh_2 (**3**) only when the allyl moiety is unsymmetrical. NMR studies on the fluxional behaviour of the complex $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{–}C_3H_3)\{Ph_2PN((S)$-*CHMePh)$PPh_2\text{-}k^2P,P\}]PF_6$ (**20**) show that the opening of the,η^3-allyl group to form a σ-bonded intermediate is not selective as the ligand $Ph_2PN((S)$-*CHMePh)PPh_2 consists of identical donating atoms. Allyl palladium complexes of the achiral heterodonor P,S-ligand, $Ph_2P(S)N(CHMe_2)PPh_2$ (**4**) exhibit geometrical isomerism when the allyl moiety is unsymmetrically substituted ($R' \neq R''$). The incorporation of a chiral centre in the P,S-ligand increases the number of possible isomers as the allyl face-coordination can lead to

Table 6
Yield, melting point and elemental analysis data for η^3-ally palladium complexes **7**–**31**

Compound	Yield (%)	M.p. (°C) [a]	Elemental analysis [b]		
			C	H	N (%)
7	79	181–183	50.9(50.0)	4.9(4.4)	1.7(1.9)
8	68	185–188	51.2(50.8)	4.9(4.6)	1.8(1.9)
9	83	178–180	53.9(54.3)	4.7(4.5)	1.6(1.8)
10	81	188–190	51.4(51.4)	4.4(4.8)	1.9(1.9)
11	83	I82–184	57.8(57.8)	4.8(4.6)	1.6(1.6)
12	89	165–167	46.8(46.0)	4.2(4.1)	1.8(1.8)
13	87	150–152	45.6(46.7)	4.6(4.3)	1.5(1.8)
15	81	174–176	48.1(47.3)	4.5(4.4)	1.7(1.7)
16	85	181–184	54.0(53.9)	4.5(4.3)	1.3(1.5)
17	69	145–147	54.2(53.8)	4.6(4.4)	1.6(1.8)
18	68	174–176	52.7(54.3)	4.5(4.5)	1.7(1.8)
19	61	178–180	56.7(57.4)	4.4(4.4)	1.5(1.6)
21	67	168–170	62.1(60.4)	4.7(4.5)	1.4(1.5)
22	77	170–172	48.5(47.9)	4.5(4.3)	1.9(1.9)
23	90	194–196	48.5(48.6)	4.4(4.4)	1.8(1.8)
24	76	193–195	52.3(52.2)	4.1(4.4)	1.7(1.7)
25	85	191–194	49.3(49.3)	4.6(4.6)	1.9(1.8)
26	91	214–216	54.3(55.8)	4.5(4.4)	1.7(1.6)
27	78	158–160	51.2(51.6)	4.2(4.2)	1.6(1.7)
28	79	175–178	52.0(52.2)	4.3(4.4)	1.6(1.7)
31	78	219–221	58.1(58.4)	4.5(4.4)	1.1(1.5)

The complexes **14**, **20**, **29** and **30** could not be isolated in pure form.
[a] With decomposition.
[b] Calculated values are in parentheses.

different diastereomers. Unlike the case observed for the chiral homodonor ligand $Ph_2PN((S)$-*CHMePh)PPh_2 (**3**), the complexes of the heterodonor chiral ligand $Ph_2P(S)N((S)$-*CHMePh)PPh_2 (**5**) show diastereomerism even when the allyl group is symmetrical and unsubstituted. The stereodynamic behaviour of the allyl complexes bearing the P,S-ligands is subject to electronic control; the σ-bonded intermediate involved in the exchange process is formed selectively at the *trans* position with respect to the sulphur centre.

6. Experimental

6.1. General comments

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 procedures [22] and distilled under nitrogen. The chlorobridged palladium allyl dimers $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, $[Pd(\eta^3\text{-}1\text{-}Me\text{–}C_3H_4)(\mu\text{-}Cl)]_2$, $[Pd(\eta^3\text{-}1\text{-}Ph\text{–}C_3H_4)(\mu\text{-}C1)]_2$, $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{–}C_3H_3)(\mu\text{-}Cl)]_2$ and $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{–}C_3H_3)(\mu\text{-}Cl)]_2$ were prepared as previously described [23]. The diphosphazane ligands $Ph_2PN(CHMe_2)PPh_2$ [24], $Ph_2PN((S)$-*CHMePh)PPh_2 [9e], $Ph_2P(S)N(CHMe_2)PPh_2$ [9d] and $Ph_2P(S)N((S)$-*CHMePh)PPh_2 [9a] were prepared by published procedures. The disulphide ligand, $Ph_2P(S)N(CHMe_2)P(S)Ph_2$ was prepared by the reaction of $Ph_2PN(CHMe_2)PPh_2$ with sulphur in boiling benzene [25]. The NMR spectra were recorded at 298 K using Bruker DRX-500 MHz, Bruker AMX-400 MHz, JEOL-300 MHz and Bruker ACF-200 MHz spectrometers. Chemical shifts downfield from the reference standard were assigned positive values. Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyser. The ^1H, ^{13}C- and ^{31}P-NMR data for complexes **7**–**31** are given in Tables 1–4.

6.2. Synthesis of palladium allyl complexes $[Pd(\eta^3\text{-}C_3H_5)\{Ph_2PN(CHMe_2)PPh_2\text{-}k^2P,P\}]PF_6$ (7)

A mixture of 0.036 g (0.98×10^{-4} mol) of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, 0.033 g ($2.02 \times 10^{-4}$ mol) of NH_4PF_6 and 0.090 g (2.10×10^{-4} mol) of **1** was dissolved in 20 cm^3 of acetone. The solution was stirred for 2 h at 25 °C and the white precipitate formed during the reaction was filtered off. The resulting colourless filtrate was concentrated under reduced pressure to 1.0 cm^3 and the solution was layered by adding 10 cm^3 of hexane (B.p 40–60 °C) to yield light yellow micro-crystals of the title compound. The other allyl palladium complexes, **8**–**31** 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 6.

Table 7
Crystal data and structure refinement for complex **27**

Identification code	**27**
Empirical formula	$C_{35}H_{34}F_6NP_3PdS$
Formula weight	814.00
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	9.4449(9)
b (Å)	15.9292(15)
c (Å)	12.5389(12)
β (°)	109.537(2)
V (Å^3)	1777.9(3)
Z	2
D_{calc} (mg m^{-3})	1.521
Absorption coefficient (mm^{-1})	0.773
$F(0\,0\,0)$	824
Crystal size (mm^3)	$0.12 \times 0.08 \times 0.04$
Theta range for data collection	1.72–23.29°
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 16$, $-13 \le l \le 12$
Reflections collected	8121
Independent reflections	4685 [$R_{int} = 0.0298$]
Completeness to $\theta = 23.29°$	99.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4685/1/419
Goodness-of-Fit on F^2	1.123
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0528$, w$R_2 = 0.1236$
R indices (all data)	$R_1 = 0.0683$, w$R_2 = 0.1362$
Absolute structure parameter	−0.03(5)
Extinction coefficient	0.0029(7)
Largest difference peak and hole (e Å^{-3})	1.142 and −0.544

6.3. X-ray structure determination

Crystal data for complex **27** was collected using Siemen's SMART-CCD diffractometer. The crystallographic data and details of data collection are summarised in Table 7. The structure was solved by Direct method using the program SIR-97 [26] and refined on F^2 values for all unique data by full-matrix least-squares using SHELXTL [27]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed at their calculated geometrical positions and refined isotropically. The validity of the absolute structure was established by the method of Flack [28].

6.4. General procedure for palladium-catalysed allylic alkylation

The ligand (2.5 mol%) and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (1 mol%) were dissolved in 4 cm^3 of degassed (by three freeze–thaw cycles) CH_2Cl_2. A solution of (*E*)-1-phenyl-

2-propenyl acetate (**I**) (one equivalents) in 2 cm^3 CH_2Cl_2 was added followed by dimethyl malonate (two equivalents), bis(trimethyl silyl) acetamide(BSA) (two equivalents) and a catalytic amount of KOAc. The mixture was stirred at 25 °C for 24 h and the reaction was monitored by TLC. The ratio of the linear (II) and branched (III) isomers was determined by ^{1}H-NMR spectrum of the reaction mixture.

7. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 188163 for complex **27**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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