Allylpalladium Complexes of Mixed-Donor Diphosphazane Ligands Bearing a Stereogenic Phosphorus Centre: Structure and Stereodynamics

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(η^3-Allyl)palladium complexes of general formula [Pd(η^3-R′C_3H_4){η^2-$Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5)}](PF_6) (**3**–**6**) and [Pd(η^3-R′C_3H_4){η^2-$Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2$-3,5)}]($PF_6$) (**7**–**8**), containing pyrazolyl-substituted diphosphazane ligands bearing a stereogenic phosphorus centre, have been synthesised. NMR spectroscopic and X-ray diffraction studies showed that the diphosphazane ligand in [Pd(η^3-R′C_3H_4){η^2-$Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5)}](PF_6) [R′ = Me or Ph; R = $CHMe_2$ (**3** and **5**) or (*S*)-*CHMePh (**4** and **6**)] displayed unprecedented *P,N*-coordination instead of the hitherto observed *P,P*-coordination. These complexes existed in solution as mixtures of *endo,syn,trans*, *exo,syn,trans*, and *endo,syn,cis* diastereomers. In the solid state, only the *endo,syn,trans* isomer was observed for complex **5**. Phase-sensitive 2-D NOESY and ROESY spectra showed that the complexes **3**–**5** underwent *syn,anti* isomerisation; the NMR spectroscopic data were consistent with a mechanism involving the opening of the η^3-allyl group at the *trans* position with respect to the phosphorus centre. The isomerisation thus appeared to be electronically controlled. The complexes [Pd(η^3-MeC_3H_4){η^2-$Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2$-3,5)}]($PF_6$) (**7**) and [Pd($\eta^3$-$PhC_3H_4$){$\eta^2$-$Ph_2P(S)N(CHMe_2)$-$PPh(N_2C_3HMe_2$-3,5)}]($PF_6$) (**8**), bearing the diphosphazane monosulfide $Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2$-3,5) (**1c**), displayed *P,S*-coordination and existed in solution as six and four isomers, respectively. Exchange was observed among four of the six isomers of **7** and among all the four isomers of **8** at 298 K, through the opening of the η^3-allyl moiety, which appeared to be subject to both electronic and steric control.

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Introduction

Palladium-catalysed allylic substitution reactions have emerged as a powerful methodology in organic synthesis;[1] the use of chiral auxiliary ligands can result in the formation of optically active products. Initially, chiral diphosphane ligands were predominantly used, while in recent years, asymmetric mixed-donor ligands have proven to be advantageous. The use of P,N-,[2] P,S-,[3] and S,N-donor[4] ligands in particular has resulted in high enantiomeric excesses in allylic alkylation reactions, which is attributed to the electronic effects of two different donor centres present in these ligand systems. In contrast to most other transition metal catalysed reactions, palladium-catalysed allylic alkylations do not rely solely on a single mechanism as a source of asymmetry.[5] Differentiation of the enantiotopic faces of a π-system is one possible mechanism, but the source of the enantioselectivity is complicated by the problems associated with the regioselectivity of nucleophilic attack, possibility of various configurational isomers, and the existence of several stereodynamic processes.[6] The reaction proceeds through a (π-allyl)palladium intermediate and the configuration of the organic product strongly depends on the nature of this intermediate. There is growing interest in understanding the solution structures and the dynamic solution behaviour of the chiral (η^3-allyl)palladium intermediates, as these may be related to synthetic methods affording optically active products.[7] The situation becomes even more complicated when both the auxiliary ligands and the allyl moiety are asymmetrical; in this case, various geometrical isomers with different allyl face coordination would result, as well as allylic arrangements. As a part of our ongoing investigations into the organometallic chemistry of diphosphazane ligands,[8–9] we have recently begun a program of NMR studies of (π-allyl)palladium complexes of diphosphazane and related ligand systems based on the P−N−P motif. The diphosphazane ligands display versatile transition metal organometallic chemistry[10] and these ligand systems can be suitably modified, thus providing access to a range of mixed-donor ligands. Despite extensive studies of the reactions of diphosphazane ligands with sev-

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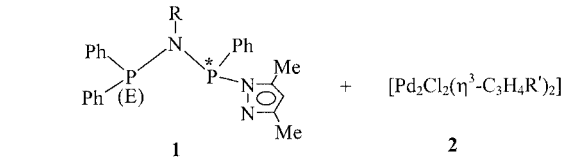
eral transition metal precursors, the allylpalladium chemistry of unsymmetrical diphosphazane ligands has not been explored except for a brief report on allylpalladium complexes of $Ph_2PN(H)P(O)Ph_2$.[10d] Here we report the synthesis, solution characterisation and dynamic behaviour of (η^3-allyl)palladium complexes bearing phosphorus-stereogenic diphosphazane ligands − $Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5) [R = $CHMe_2$ (**1a**) or (*S*)-*CHMePh (**1b**)] − and the diphosphazane monosulfide ligand $Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2$-3,5) (**1c**). In the case of **1b**, the (S_CR_P) diastereomer, the absolute configuration of which has been determined by X-ray crystallography,[8d] was used for the preparation of allylpalladium complexes.

Results and Discussion

Synthesis

The cationic allyl complexes **3**−**8** were prepared by treatment of the chloro-bridged allylpalladium dimer **2** with the appropriate ligands in the presence of NH_4PF_6 in acetone (Scheme 1). These complexes have been characterised by elemental analyses and NMR spectroscopic data (see Exp. Sect.). Several isomers are possible for complexes that contain an unsymmetrically substituted allyl group. In the first place, isomers can arise because of different modes of coordination of the ligands (e.g., *P*,*P* or *P*,*N* for **1a** or **1b**, *P*,*S* or *P*,*N* or *N*,*S* for **1c**). Secondly, geometrical isomers can be formed because the substituent on the allyl moiety can be oriented in a *cis* or *trans* position with respect to one of the phosphorus atoms. Thirdly, several allylic arrangements are also possible since the substituent on the allyl moiety can be positioned *syn* or *anti* with respect to the central allyl proton. Additionally, for each of these isomers, diastereomers can arise owing to the different face coordination (*exo* or *endo*) of the allyl group. The isomeric composition in each case was determined by NMR spectroscopy. The salient features of the spectroscopic data and dynamic behaviour are discussed below.



1a, R = $CHMe_2$, E = lone pair (l.p);
1b, R = (*S*)-*CHMePh, E = l.p; (S_CR_P- diastereomer)
1c, R = $CHMe_2$, E = S

NH_4PF_6

$[Pd(\eta^3\text{-}C_3H_4R')(\mathbf{1})](PF_6)$

3-8

3, R' = Me, R = $CHMe_2$, E = l.p;
4, R' = Me, R = (*S*)-*CHMePh, E = l.p;
5, R' = Ph, R = $CHMe_2$, E = l.p;
6, R' = Ph, R = (*S*)-*CHMePh, E = l.p;
7, R' = Me, R = $CHMe_2$, E = S;
8. R' = Ph, R = $CHMe_2$, E = S

Scheme 1

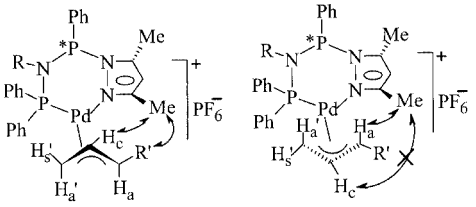
NMR Studies on $[Pd(\eta^3\text{-}R'C_3H_4)\{\eta^2\text{-}Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5)$\}](PF_6)$ (3−6)

The $^{31}P\{^1H\}$ NMR spectra of complexes **3**−**6** in $CDCl_3$ in each case displayed six doublets (see Table 1) in different isomeric ratios, revealing the presence of three isomers. The structures proposed for these isomers are shown in Figure 1. Analysis of the ^{13}C NMR spectra of the allyl carbon nuclei pointed to *P*,*N*-coordination through the nitrogen atom at the 2-position of the pyrazole ring (see Table 2). The resonances of the central allyl carbon atoms of all the isomers appeared as doublets. For *P*,*P*-coordination, one should observe a doublet of doublets pattern in the ^{13}C NMR spectra for each of the palladium-bound allyl carbon nuclei. The signals for terminal allyl carbon nuclei appeared as two doublets and were assigned on the basis of the two-bond phosphorus-carbon coupling and a 2-D ^{13}C-^1H HSQC experiment. The doublets in the ^{13}C NMR spectra in the δ = 94−105 and 78−80 ppm ranges, with $^2J_{P,C}$ values of 28−31 Hz, were assigned to the substituted terminal allyl and unsubstituted terminal allyl carbon atom, respectively, *trans* to the coordinated phosphorus centre. On the other hand, the resonances for the substituted and unsubstituted terminal allyl carbon nuclei *trans* to the nitrogen atom appeared in more shielded regions (δ = 64−77 and

Table 1. The $^{31}P\{^1H\}$ NMR spectroscopic data for the complexes **3**−**8**

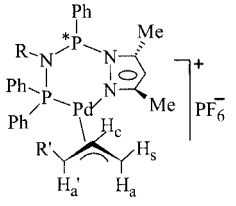
Complex[a]	−PPh($N_2C_3HMe_2$-3,5) (δ_A)	$\Delta\delta_A$	−P(E)Ph_2 (δ_X)	$\Delta\delta_X$
3a	72.7 d (31.1)	0.8	75.0 d	31.1
3b	72.4 d (28.4)	0.5	77.2 d	33.3
3c	71.1 d (29.5)	−0.8	78.9 d	35.0
4a	72.7 d (28.3)	3.9	79.3 d	32.1
4b	73.0 d (28.6)	4.2	78.1 d	30.9
4c	71.1 d (28.7)	2.3	80.0 d	32.8
5a	71.9 d (29.8)	0.0	76.9 d	33.0
5b	71.3 d (28.4)	−0.6	75.2 d	31.3
5c	71.1 d (30.8)	−0.8	78.7 d	34.8
6a	71.9 d (28.3)	3.1	79.1 d	31.9
6b	71.4 d (28.3)	2.6	79.9 d	32.7
6c	72.1 d (29.9)	3.3	77.9 d	30.7
7a	92.4 d (91.8)	21.9	76.0 d	10.7
7b	92.2 d (87.9)	21.7	75.0 d	9.7
7c	94.2 d (100.4)	23.7	79.5 d	14.2
7d	94.7 d (100.5)	24.2	78.7 d	13.4
7e	94.7[b]	24.2	78.4 d	13.1
7f	(−)[c]	(−)	78.3 d	13.0
8a	92.1 d (88.2)	21.6	74.4 d	9.1
8b	91.7 d (83.7)	21.2	73.6 d	8.3
8c	95.7 d (99.2)	25.2	78.8 d	13.5
8d	93.7 d (101.2)	23.2	79.3 d	14.0

[a] The $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ at 298 K except for **3** and **8**, in which cases a 1:1 mixture of $CDCl_3$ and CH_2Cl_2 was used. The ^{31}P-^{31}P coupling constants are given in parentheses [$\Delta\delta$ = δ(complex) − δ(free ligand)]. [b] Overlapped by signals arising from the −PPh($N_2C_3HMe_2$-3,5) phosphorus atom of isomer **7d**. [c] The signal could not be assigned unequivocally.



endo, syn, trans
(**3a**, **4a**, **5a** or **6a**)

exo, syn, trans
(**3b**, **4b**, **5b** or **6b**)



endo, syn, cis
(**3c**, **4c**, **5c** or **6c**)

Figure 1. The three isomers of (allyl)(diphosphazane)Pd^{II} complexes $[Pd(\eta^3\text{-}R'C_3H_4)\{\eta^2\text{-}Ph_2PN(R)PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ [R′ = Me or Ph, R = $CHMe_2$ or (*S*)-*CHMePh] observed in solution; selective NOE contacts (shown by the arrows) revealed that, in the *endo*,*syn*,*trans* isomer, the central allyl proton and pyrazole-3-Me protons were close to each other, whereas in the *exo*,*syn*,*trans* isomer, such an NOE contact with the central allyl proton was absent

Table 2. The ^{13}C NMR spectroscopic data for the allyl carbon nuclei of complexes **3**−**8**

Complex[a]	C_t	C_t'	C_c
3a	105.0 d (29.8)[b]	51.6 d (5.4)[c]	117.2 d (6.2)
3b	94.8 d (28.9)[b]	55.4 br.	120.9 d (5.9)
4a	104.6 d (29.5)[b]	52.1 br.	117.4 d (5.5)
4b	94.6 d (28.6)[b]	55.5 br.	120.7 d (5.3)
4c	78.6 d (28.6)[b]	72.5 br.	117.4[d]
5a	103.7 d (28.5)[b]	54.8 d (3.8)[c]	112.1 d (6.8)
5b	102.5 d (27.8)[b]	54.7 d (3.9)[c]	114.6 d (6.9)
5c	79.2 d (28.1)[b]	76.8 d (4.2)[c]	117.4 d (5.9)
6a	103.0 d (29.2)[b]	53.9 (3.9)[c]	111.4 d (8.2)
6b	104.5 d (27.1)[b]	55.5 d (4.6)[c]	112.5 d (6.1)
6c	78.1 d (27.7)[b]	64.3 d (5.4)[c]	116.6 d (6.6)
7a	96.0 d (30.7)[b]	65.3 s	119.4 br. s
7b	96.9 d (34.8)[b]	65.3[e]	120.2 br. s,
7c	68.6 d (34.9)[b]	91.8 br. s	119.8 br. s
7d	70.5 d (33.3)[b]	89.4 br. s	119.8[f]
8a	96.6 d (32.2)[b]	66.5 br. s	113.7 br. s
8b	97.9 d (30.7)[b]	66.3 br. s	114.2 br. s
8c	68.5 d (33.3)[b]	94.0 br. s	113.2 br. s
8d	70.6 br. d (24.1)[b]	91.4 br. s	113.9 br. s

[a] The ^{13}C NMR spectra were recorded in $CDCl_3$ at 298 K except for **3** and **8**, in which cases a 1:1 mixture of $CDCl_3$ and CH_2Cl_2 was used. The ^{13}C-^{31}P coupling constants are given in parentheses. C_t is the terminal allyl carbon atom *trans* to the coordinated phosphorus centre. C_t' is the terminal allyl carbon atom *cis* to the coordinated phosphorus centre. C_c is the central allyl carbon atom. [b] $^2J_{P,C\ trans}$. [c] $^2J_{P,C\ cis}$. [d] Overlapped with central allyl carbon resonance of **4a**. [e] Overlapped with C_t' resonance of **7a**. [f] Overlapped with central allyl carbon resonance of **7c**.

51−56 ppm, respectively) with $^2J_{P,C}$ coupling constants in the 3−6 Hz range, typical for two-bond coupling of phosphorus and carbon nuclei in a *cis* orientation. It is well documented that in cationic allyl complexes with phosphorus ligands the ^{31}P nucleus shows a larger coupling constant with the terminal allyl carbon atom in the *trans* position than with that in the *cis* position.[11] In all the major isomers (**3a**, **4a**, **5a**, and **6a**) and in the second most abundant isomers (**3b**, **4b**, **5b**, and **6b**), the coordinated phosphorus atom and the substituent on the allyl moiety had a *trans* disposition. The remaining isomers (**3c**, **4c**, **5c**, and **6c**) were assigned structures in which the coordinated phosphorus atom and the substituent on the allyl moiety had a *cis* disposition. The *P*,*N*-coordination was also supported by the ^{31}P chemical shifts (see Table 1).

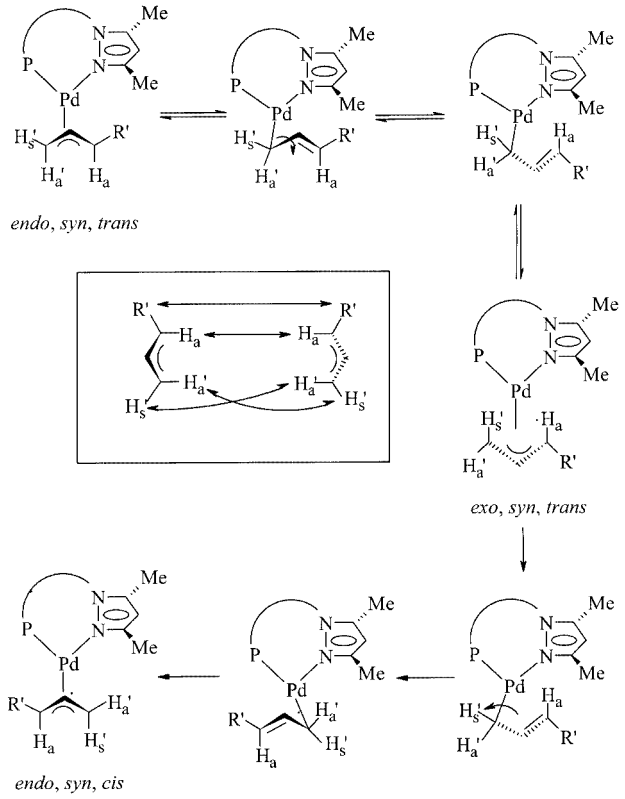
Transition metal complexes of the ligands **1a** and **1b** usually feature *P*,*P*-coordination.[9] The driving force for *P*,*N*-coordination in the (η^3-allyl)palladium complexes **3**−**6** might be the formation of a stable six-membered chelate ring around the palladium centre rather than the four-membered ring that would result from *P*,*P*-coordination. Moreover, coordination of a stronger σ-donor nitrogen atom would electronically stabilise the allyl−palladium bonding much more than coordination with a stronger π-acceptor phosphorus centre, by enhancing the metal-to-allyl back-bonding.[12] Such a pronounced electronic effect is well known[13] and is reflected in the ^{13}C NMR parameters (see Table 2).

The ^1H NMR spectra of the complexes **3**−**6** showed three sets of four nonequivalent resonances for the allylic protons at 298 K. The magnetic nonequivalence of the allylic protons arises because of the asymmetry in the ligands **1a** and **1b**. The presence of two *anti*-allyl protons in each set of signals indicated a *syn* arrangement of the allyl substituent with respect to the central allyl proton in each isomer. The major isomers of these complexes showed NOE contacts between the 3-Me protons of the pyrazole ring and the central allyl proton H_c. This result indicated that the central allyl hydrogen atom H_c pointed towards the 3-Me group of the pyrazole. Hence, the major isomers (**3a**−**6a**) have the *endo*,*syn*,*trans* arrangement.[7b,14] For the second set of isomers (**3b**−**6b**), the pyrazole 3-Me protons did not show NOE contacts to the central allyl proton H_c but there was an NOE contact to the *anti*-allyl proton H_a. The central allyl proton H_c thus pointed away from the 3-Me group of the pyrazole, and so these isomers (**3b**−**6b**) could be assigned the *exo*,*syn*,*trans* configuration. The central allyl proton resonances for the *endo* isomers **3a**−**6a** appeared at a more deshielded region (δ ≈ 5.7 ppm) than those (δ ≈ 4.5 ppm) for the *exo* isomers **3b**−**6b**. This trend has also been observed for other allylpalladium complexes $[Pd(\eta^3\text{-}1,3\text{-}R'_2C_3H_3)\{\eta^2\text{-}Ph_2PN(R)PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ [R′ = H, Me or Ph; R = $CHMe_2$ or (*S*)-*CHMePh] bearing **1a** and **1b** ligands.[15] On this basis, we assigned the *endo*,*syn*,*cis* configuration (see Figure 1) to the third set of minor isomers (**4c**−**6c**) as the chemical shifts of the H_c protons in each of these isomers were close to those observed for **4a**−**6a**. The *cis* geometries and the *syn*-allylic arrangements for the minor isomers were confirmed by ^{13}C NMR (see Table 2) and 2-D NMR spectroscopy, respectively. The ^{13}C and ^1H NMR signals for isomer **3c** could not be ob-

served because of its low abundance and poor solubility in $CDCl_3$. However, the ^{31}P chemical shift and P-P coupling constant values for **3c** were similar to those of **4c**, and so an *endo*,*syn*,*cis* configuration may tentatively be assigned to **3c**. An important difference was observed between the relative abundances of the isomers of 1-methylallyl and 1-phenylallyl derivatives. For the 1-methylallyl derivatives (**3** and **4**), the *exo*,*syn*,*trans* isomers were present to an extent of 40%, whereas for the 1-phenylallyl derivatives (**5** and **6**), the *exo*,*syn*,*trans* isomers were present to an extent of less than 10%. The low relative abundances of the *exo*,*syn*,*trans* isomers in the case of 1-phenylallyl derivatives is probably related to the steric demand of the larger phenyl group on the allyl moiety.

Dynamic Behaviour of the Complexes 3−6

The dynamic behaviour of the complexes **3**−**6** was examined by ^1H-^1H NOESY and ROESY spectra. No exchange among the isomers of complexes **4**−**6** was observed in $CDCl_3$ at 298 K. For complex **3**, on the other hand, exchange between the isomers **3a** and **3b** was observed at 298 K in [D_6]acetone. The high-temperature (323 K) ^1H-^1H NOESY and ROESY spectra for the complexes **4** and **5** revealed that the major isomers **4a** and **5a** exchanged with the minor isomers **4b** and **5b**, respectively, in a way similar to that observed for the isomers **3a** and **3b** at 298 K. The phase-sensitive ^1H-^1H NOESY spectrum of complex **4** recorded at 323 K is shown in Figure 2 and the exchange results are summarised in Scheme 2. Pregosin and coworkers[16] have shown that this type of exchange can be explained in terms of a selective opening of the η^3-allyl moiety at the *trans* position with respect to the phosphorus centre to generate an η^1-bonded intermediate, followed by a rotation around the sp^3-sp^2 C−C bond and reversion to the η^3-mode of coordination by the other face of the allyl group. This type of electronic control over the interconversion process is especially well known in cases of mixed-donor P,N-, P,S-, and P,O- bidentate ligand systems.[17−19] The minor isomers (**4c** and **5c**) did not show any observable exchange even at 323 K, but their formation can be interpreted, starting from isomers **4b** and **5b**, respectively, in terms of *cis*,*trans* isomerisation by rotation around the Pd−C bond in the corresponding η^1-bonded intermediate.



Scheme 2

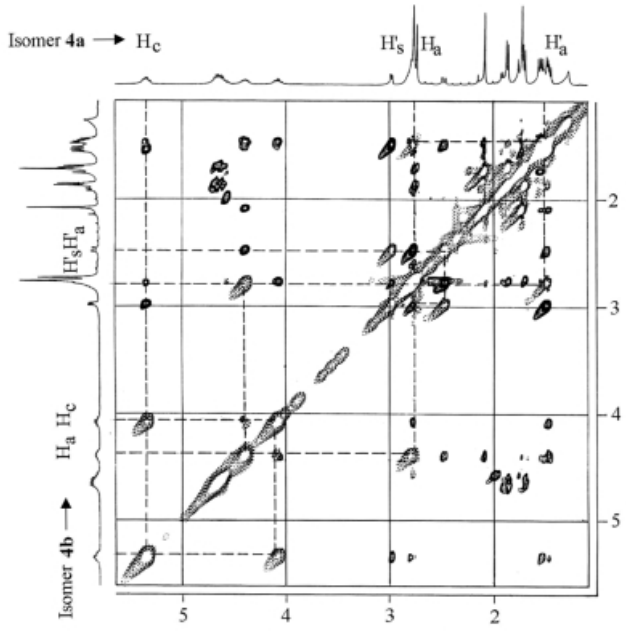


Figure 2. The ^1H-^1H phase-sensitive NOESY spectrum ($CDCl_3$, 400 MHz) of complex **4** at 323 K, showing the exchange cross-peaks in the isomers **4a** and **4b**

Solid-State Structure of Complex 5a

The details of the crystal data are presented in Table 3. The molecular structure is shown in Figure 3. The solid-state structure reveals the presence of only one isomer with *P*,*N*-coordination and a *trans* disposition of the *syn*-allylphenyl group with respect to the coordinated phosphorus centre. The central allyl carbon atom C(2) and the 3-methyl carbon atom C(10) of the pyrazole ring in **5a** lie on the same side of the coordination plane defined by P(2)−Pd(1)−N(3), thus revealing an *endo* arrangement in the solid state (*endo* refers to the relative orientation of the central C−H vector pointing towards the 3-methyl group on the pyrazole ring[7b,14]). The bonding parameters fall in the expected ranges observed for cationic allylpalladium

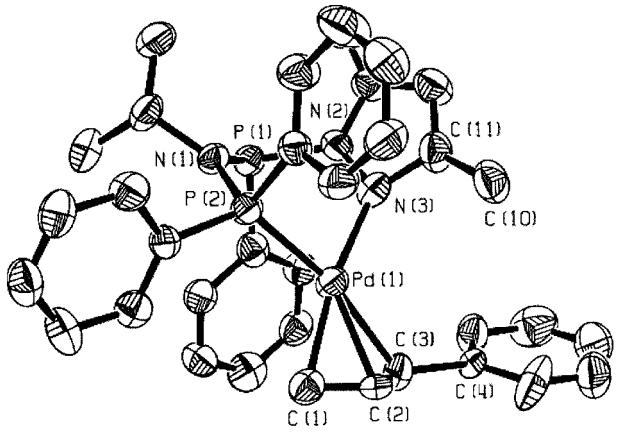


Figure 3. Molecular structure of **5a** in the solid state (the hydrogen atoms and the hexafluorophosphate anion are not shown); selected bond lengths [Å] and angles [°]: Pd(1)−C(1) = 2.075(2), Pd(1)−C(2) = 2.137(2), Pd(1)−C(3) = 2.263(2), Pd(1)−P(2) = 2.293(3), Pd(1)−N(3) = 2.075(1); N(3)−Pd(1)−P(2) = 85.4(3), C(1)−Pd(1)−C(3) = 64.0(8), N(3)−Pd(1)−C(1) = 169.8(5), C(3)−Pd(1)−P(2) = 167.8(6), P(2)−N(1)−P(1) = 122.5(6)

complexes bearing P,N-ligands.[17b,20] The coordination geometry around the metal centre is distorted square-planar, with the N(3)−Pd(1)−P(2) and C(1)−Pd(1)−C(3) bond angles 85.4(3)° and 64.0(8)°, respectively. The two terminal allyl carbon atoms are not exactly coplanar with the coordination plane formed by P(2)−Pd(1)−N(3). The distances of the terminal allyl carbon atoms C(1) and C(3) are 0.120 Å and 0.089 Å, respectively, whereas the central allyl carbon atom C(2) lies at a distance of 0.703 Å from the plane. The terminal Pd−C(allyl) bond lengths are significantly different from one another. The carbon atom *trans* to the phosphorus atom displays the expected longer bond length [Pd(1)−C(3) = 2.263(2) Å], as compared to its partner *trans* to the nitrogen atom [Pd(1)−C(1) = 2.075(2) Å]. This is consonant with the larger *trans* influence of the phosphorus donor.[13] This elongation of the Pd−C(terminal allyl) bond length *trans* to the phosphorus atom relative to that *trans* to the nitrogen atom is consistent with the proposed mechanism (Scheme 2) involving selective opening of one of the allyl termini. The six-membered chelate ring adopts a distorted boat conformation; P(2) is almost coplanar (deviation 0.168 Å) with the plane formed by N(1)−N(2)−N(3), while Pd(1) and P(1) lie on the same side of this plane at 1.063 and 0.778 Å, respectively. The P(1)−N(1)−P(2) bond angle is increased to 122.5(6)°, compared to a value of ca. 100° observed for *P,P*-coordinated complexes.[9]

NMR Studies on Complexes 7 and 8

The $^{31}P\{^{1}H\}$ NMR spectrum of an analytically pure sample of [Pd(η³-1-MeC_3H_4){η²-$Ph_2P(S)N(CHMe_2)PPh$-($N_2C_3HMe_2$-3,5)}](PF_6) (**7**) in $CDCl_3$ showed ten doublets arising from six AX spin systems. The two missing doublets (from the fifth and sixth isomers) overlapped with those arising from the major isomers, as revealed by a ^{31}P-^{31}P COSY spectrum. A 24-line spectrum was consistent with the formation of six isomers. The relative integrated intensities of the doublets indicated that the six isomers were present in the ratio 21:10:9:6:2:1. The allyl ^{13}C resonances for these isomers were assigned by recourse to a ^{13}C-^{1}H HSQC experiment. Analysis of the ^{13}C NMR spectrum showed a doublet pattern with a $^{2}J_{P,C}$ value of ca. 30 Hz for one of the two terminal allyl carbon resonances in the cases of isomers **7a**−**7d**, indicating bonding of one phosphorus atom with the palladium centre. From the ^{31}P chemical shifts (Table 1 and see also below), we were able to conclude that the pyrazolyl-bearing phosphorus atom and the sulfur atom were coordinated to the palladium centre. This conclusion was supported by the ^{13}C chemical shifts of the allyl carbon nuclei, when compared with the chemical shifts of allyl carbon nuclei of *P,N*-coordinated complexes **3**−**6** (see Table 2). It may be noted that the chemical shifts of allyl carbon nuclei *trans* to the nitrogen atom indicated that they were more shielded (by about 10−20 ppm) than the allyl carbon nuclei *trans* to the sulfur atom, if we consider the similar allyl isomers in both cases. Ligand **1c**, in contrast to **1a** and **1b**, thus did not coordinate through the nitrogen atom of the pyrazole ring, *P,S*-coordination presumably being favoured because of the formation of a stable five-membered ring around the palladium centre. The competitive *N,S*-coordination would give rise to the formation of a seven-membered chelate ring around the palladium atom. The fifth and sixth isomers (**7e** and **7f**) could not be detected by ^{13}C NMR, owing to their low relative concentrations (present at less than 5%). However, the similarity of their ^{31}P chemical shifts with those of other isomers (**7a**−**7d**) and the multiplicities of the allyl resonances in the ^{1}H NMR spectrum suggested that these isomers must be structurally closely related to **7a**−**7d**.

The ^{1}H NMR spectrum of complex **7** showed several broad signals; in addition, the chemical shifts of several allylic proton resonances were very close. However, a careful analysis of various 2-D NMR spectra (^{1}H-^{1}H DQF COSY, NOESY, and ROESY) resulted in a correct assignment of the allyl protons. The intra-allyl NOESY spectrum revealed that in the four isomers **7a**−**7d** there was a *syn* arrangement of the allylmethyl group with respect to the central allyl proton (H_c), while in the isomers **7e** and **7f** there was an *anti* arrangement of the allylmethyl group and the central allyl proton. The interligand NOE cross-peaks confirmed the configurations of these isomers. One of the methyl groups of the pyrazole ring came close to the central allyl proton H_c and to the *syn*-proton H_s' in the *endo* isomer, whereas for the *exo* isomer the *anti*-allyl proton H_a' showed NOE contact with this methyl group. The structures assigned to the six isomers on the basis of NMR measurements are shown in Figure 4. The structural assignments for **7a** and **7b** are unequivocal, while there is some uncertainty with regard to the structural assignments for the other isomers (**7c**−**7f**) because of the overlap of the pyrazole methyl proton signals arising from these minor isomers. However, studies on the exchange behaviour of the isomers (see below) lent support to the assignments.

The ^{1}H-^{1}H phase-sensitive NOESY and ROESY spectra at 298 K in $CDCl_3$ showed that isomers **7a**−**7d** were in

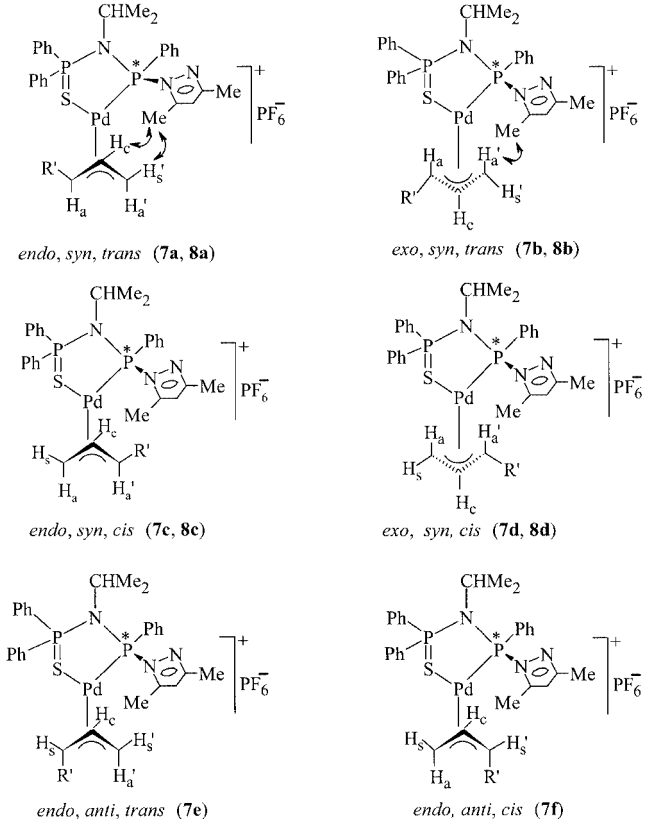


Figure 4. The six isomers for the (methylallyl)palladium complex $[Pd(\eta^3\text{-}MeC_3H_4)\{\eta^2\text{-}Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ (**7**) and the four isomers observed in solution for the (phenylallyl)palladium complex $[Pd(\eta^3\text{-}PhC_3H_4)\{\eta^2\text{-}Ph_2P(S)N(CHMe_2)PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ (**8**)

equilibrium with one another. The exchange followed an η^3-η^1-η^3 pathway, with the opening of the allyl terminus at the position *trans* with respect to the phosphorus centre. The isomer **7a** showed dynamic behaviour with isomer **7b** through a s*yn*,*anti* isomerisation process. Hence, **7b** could be assigned the *exo*,*syn*,*trans* structure, as the starting isomer **7a** had the *endo*,*syn*,*trans* structure. On the other hand, the isomer **7a** transformed into **7d** by a *cis*,*trans* isomerisation process, indicating that **7d** should be the *exo*,*syn*,*cis* isomer. The isomer **7b** showed *cis*,*trans* exchange with the isomer **7c**, and so the isomer **7c** should be *endo*,*syn*,*cis*. Exchange cross-peaks were also observed between isomers **7a** and **7c**, as well as between isomers **7b** and **7d**. The exchange equilibria may be represented schematically as in Scheme 3.

The $^{31}P\{^1H\}$ NMR spectrum of complex **8** (see Figure 5) revealed eight doublets arising from four isomers. A detailed NMR investigation (^1H NMR, ^{13}C NMR, ^1H-^1H DQF COSY, NOESY, and ROESY) indicated that all four isomers involved *P*,*S*-coordination with *syn*-allylphenyl arrangement, and that the major isomer had the *endo*,*syn*,-*trans* configuration (**8a**) as shown in Figure 4. In contrast to complex **7**, no *anti* isomer was formed in this case, owing to the presence of a relatively more bulky phenyl group on the allyl moiety. The exchange behaviour for **8a**−**8d** was similar to that observed for **7a**−**7d**; the exchanges are depicted in Scheme 4. The results can be explained in terms of the pathways shown in Scheme 5, the isomers **8a** and **8d** being related by *cis*,*trans* isomerisation and **8a** and **8b** by *syn*,*anti* isomerisation, with both processes occurring by means of a selective opening of the terminal allyl Pd−C bond located *trans* to the better π-acceptor phosphorus centre. Hence, the conversion of **8a** into **8b** or **8d** was electronically controlled.

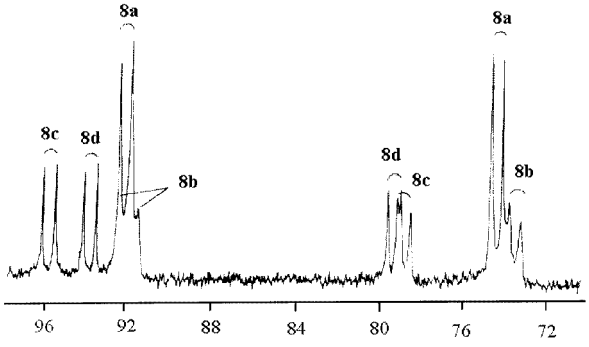
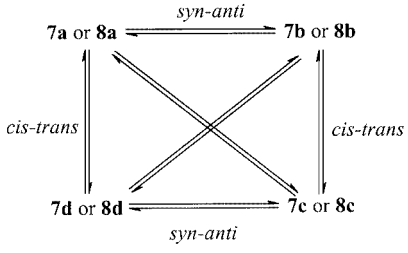
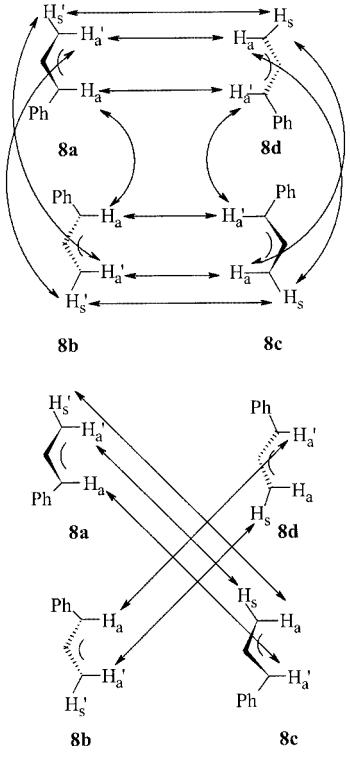


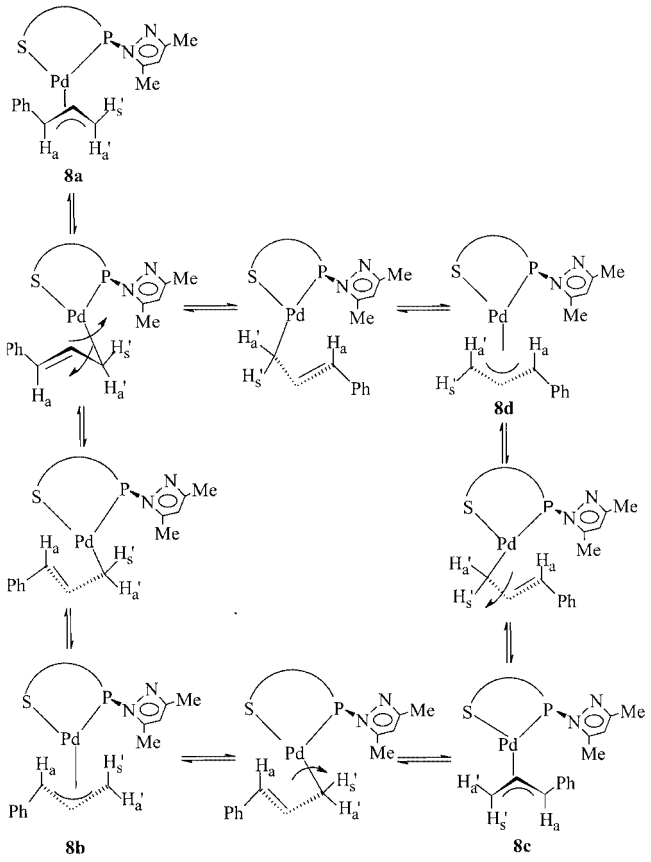
Figure 5. The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 161.9 MHz) of complex **8** at 298 K, showing the presence of four isomers



Scheme 3



Scheme 4



Scheme 5

In contrast, the isomerisation between **8d** and **8c** took place by a selective opening of the η^3-allyl group at the *cis* position with respect to the phosphorus centre, and hence was subject to steric control over the opening of the η^3-allyl moiety. The presence of a bulky allylphenyl group at the position *cis* to the $-PPh(N_2C_3HMe_2$-3,5) group in isomer **8d** exerted a more pronounced steric repulsion than in isomer **8a**, in which the allylphenyl group resided at the position *cis* to the sterically less demanding $-P(S)Ph_2$ group. Hence, the opening of the η^3-allyl moiety to a three-coordinated η^1-bonded intermediate in isomer **8d** relieved the steric strain. This type of steric control over *syn*,*anti* isomerisation has been observed in the case of a cationic allylpalladium complex bearing a P,S-ligand with a bulky allyl moiety.[18] Moreover, the isomer **8a** exchanged with **8c**, and **8b** exchanged with **8d**. Direct exchange between isomers **8a** and **8c** or between **8b** and **8d** should not be permitted, in view of their structural differences. However, NMR measurements clearly indicated exchange between **8a** and **8c** as well as **8b** and **8d**. The exchange information was transmitted via the intermediates **8b** or **8d**, resulting in an equilibrium among all four isomers **8a**−**8d**. The rapid dynamic processes for **7** and **8** were most probably related to the fact that the free nitrogen atom on the pyrazole ring can coordinatively interact with the palladium centre in the η^1-bonded intermediate. Such an interaction would stabilize the η^1-bonded intermediate and could accelerate the dynamic process. It is well known that catalytic amounts of anions such as chloride or fluoride or polar solvents such as DMSO and acetonitrile, which can coordinate to the palladium centre, accelerate the dynamic processes in allylpalladium complexes.[21]

Trends in ^{31}P Chemical Shifts

The ^{31}P resonances were assigned on the basis of the $\Delta\delta$ [$\Delta\delta = \delta$(complex) − δ(free ligand)] and sensitivity of the chemical shifts upon variation of the allyl moiety (see Table 1). The chemical shifts of one of the phosphorus nuclei in each of complexes **3**−**6** lay in the $\delta = 71-73$ ppm range, with $\Delta\delta$ being only 4.2−0.5 ppm. The constancy in the magnitude of chemical shifts on changing the allyl component and the low $\Delta\delta$ value suggested that this chemical shift could be assigned to the noncoordinated phosphorus atom bearing the pyrazole moiety. On the other hand, the chemical shifts of the other phosphorus nuclei showed a greater range of variation ($\delta = 75-80$ ppm). These phosphorus chemical shifts lay very much further downfield from that of the free ligand, and the magnitude of $\Delta\delta$ was in the 30.7−35.0 ppm range. Hence, this chemical shift was assigned to the coordinated $-PPh_2$ phosphorus atom. For the *P*,*S*-coordinated complexes **7** and **8**, the $-P(S)Ph_2$ and the −PPh(pyrazole) chemical shifts were assigned the values $\delta = 73.6-79.5$ and 91.7−95.7 ppm, respectively, based on the magnitude of $\Delta\delta$ and chemical shifts observed for allylpalladium complexes of the ligands $Ph_2P(S)N(CHMe_2)PPh_2$ and $Ph_2P(S)N(CHMe_2)P(S)Ph_2$, and also the chemical shifts of *P*,*P*-coordinated complexes of **1a**.[15]

With regard to P−P couplings, two observations were worthy of note:

(1) The $^2J_{P,P}$ values for *P*,*N*-coordinated complexes of **1a** and **1b** lay in the 29−31 Hz range, whereas $^2J_{P,P}$ values for *P*,*P*-coordinated allyl complexes are observed in the range of ca. 100 Hz.[15]

(2) The $^2J_{P,P}$ values for the *P*,*S*-coordinated complexes of **1c** were in the 80−100 Hz range.

Conclusions

Diphosphazane ligands of the type $Ph_2P(E)N(R)PPh(N_2C_3HMe_2$-3,5) (**1**), bearing a stereogenic phosphorus centre, exhibited diverse allylpalladium chemistry including various fluxional processes in solution. The preferred mode of coordination with the ligands $Ph_2PN(R)PPh(N_2C_3HMe_2$-3,5) [R = $CHMe_2$ (**1a**) or (*S*)-*CHMePh (**1b**)] was through the phosphorus and nitrogen atoms rather than the usually observed *P*,*P*-coordination. The former mode of coordination should electronically stabilise the allyl−palladium bonding, besides giving rise to the formation of a six-membered chelate ring. On the other hand, the monosulfide ligand $Ph_2P(S)N(R)PPh(N_2C_3HMe_2$-3,5) (**1c**) displayed *P*,*S*-coordination and also gave rise to a larger number of diastereomers with different allylic arrangements than observed in the *P*,*N*-coordinated ligands (**1a** and **1b**), which were more selective towards stabilisation of particu-

lar allyl diastereomers. In addition, in the case of *P,N*-coordinated complexes, there was a drastic decrease in the relative abundances of the *exo*,*syn*,*trans* isomers of 1-phenylallyl derivatives (below 10%) compared to those (40%) of the *exo*,*syn*,*trans* isomers of 1-methylallyl derivatives. Such a trend was not observed for the *P,S*-coordinated complexes. As far as the dynamic behaviour is concerned, the activation barriers for exchange processes among various allyl isomers bearing the P,S-ligand were less than those observed for the allyl isomers formed by P,N-ligands. The exchange pathway involved an η^1-allyl species generated by the opening of the η^3-allyl moiety at the position *trans* with respect to phosphorus atom in the case of *P,N*-coordinated complexes, and so was subject to electronic control. In the case of *P,S*-coordinated complexes, on the other hand, exchange among the allyl diastereomers occurred through the opening of the η^3-allyl moiety at either end (both *trans* with respect to the phosphorus atom as well as the sulfur atom). One possible reason for this difference is that the *trans* influences exerted by the two donor atoms − namely, phosphorus and sulfur − of the P,S-ligand (**1c**) would be reasonably similar to each other, whereas the *trans* influence of the phosphorus atom of the P,N-ligand (**1a** or **1b**) would be much larger than that of the nitrogen atom, as evident from the ^{13}C chemical shift values of the allyl termini.

Experimental Section

General Remarks: Reactions and manipulations were carried out under purified nitrogen by standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures[22] and distilled under nitrogen. The chloro-bridged allyl dimers $[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$ and $[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)(\mu\text{-}Cl)]_2$ were prepared as previously described.[23] Diphosphazane ligands **1a**, the (S_CR_P) diastereomer of **1b** and diphosphazane monosulfide **1c** were prepared according to literature procedures.[8d,9c] The NMR spectra were recorded with Bruker DRX 500 MHz and Bruker AMX 400 MHz spectrometers. Chemical shifts downfield from the reference standard were assigned positive values. Elemental analyses were carried out with a Perkin−Elmer 2400 CHN analyser. The $^{31}P\{^1H\}$ and ^{13}C NMR spectroscopic data are given in Tables 1 and 2, respectively. The remaining NMR spectroscopic data are given below.

Synthesis of Palladium Complexes

$[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)\{\eta^2\text{-}Ph_2PN(CHMe_2)PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ (3): A mixture of $[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$ (0.039 g, $0.99\cdot10^{-4}$ mol), NH_4PF_6 (0.033 g, $2.02\cdot10^{-4}$ mol), and **1a** (0.095 g, $2.13\cdot10^{-4}$ mol) was dissolved in 20 mL 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 to 10 mL under reduced pressure, and the solution was layered by addition of 5 mL of hexane (b.p. 40−60 °C) to yield colourless microcrystals. Yield: 0.140 g (93%). $C_{30}H_{36}F_6N_3P_3Pd$ (751.9): calcd. C 47.93, H 4.79, N 5.59; found C 47.56, H 4.88, N 5.53. m.p.191−194 °C (dec.). Major *endo*,*syn*,*trans* isomer (**3a**): ^1H NMR (400 MHz, CD_3COCD_3): δ = 1.41 (d, $^3J_{H,H}$ = 6.5 Hz, CH_3 $CHMe_2$), 1.66 (d, $^3J_{H,H}$ = 6.6 Hz, CH_3 $CHMe_2$), 1.74 (merged with allyl-CH_3 signal of isomer **3b**, H_a'), 1.79 (dd, $^4J_{H,P}$ = 11.6, $^3J_{H,H}$ = 6.4 Hz, allyl-CH_3), 2.20 (merged with solvent signal, 3-CH_3 $N_2C_3HMe_2$-3,5), 2.86 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 3.11 (m, H_a), 3.30 (d, $^3J_{H,H}$ = 6.6 Hz, H_s'), 4.12 (m, CH $CHMe_2$), 5.76 (m, H_c), 6.61 (br. s, CH $N_2C_3HMe_2$-3,5), 7.16−8.48 (m, aryl protons) ppm. ^{13}C NMR [100.6 MHz, $CDCl_3$ and CH_2Cl_2 (1:1)]: δ = 13.1 (d, $^3J_{C,P}$ = 5.6 Hz, CH_3 $N_2C_3HMe_2$-3,5), 14.8 (s, CH_3 $N_2C_3HMe_2$-3,5), 18.7 (br. s, allyl-CH_3), 25.3 (s, CH_3 $CHMe_2$), 25.5 (d, $^3J_{C,P}$ = 9.0 Hz, CH_3 $CHMe_2$), 52.8 (dd, $^2J_{C,P}$ = 28.05 and 6.5 Hz, CH $CHMe_2$), 110.1 (s, CH $N_2C_3HMe_2$-3,5), 129.5−157.2 (aryl carbon atoms) ppm. *exo*,*syn*,*trans* isomer (**3b**): ^1H NMR (400 MHz, CD_3COCD_3): δ = 1.12 (d, $^3J_{H,H}$ = 6.4 Hz, CH_3 $CHMe_2$), 1.39 (d, $^3J_{H,H}$ = 6.6 Hz, CH_3 $CHMe_2$), 1.69 (dd, $^4J_{H,P}$ = 11.7, $^3J_{H,H}$ = 6.8 Hz, allyl-CH_3), 2.69 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 2.73 (d, $^3J_{H,H}$ = 6.7 Hz, H_s'), 2.88 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 2.92 (d, $^3J_{H,H}$ = 12.1 Hz, H_a'), 4.25 (m, H_c), 4.91 (m, H_a), 6.81 (br. s, CH $N_2C_3HMe_2$-3,5) ppm. ^{13}C NMR [100.6 MHz, $CDCl_3$ and CH_2Cl_2 (1:1)]: δ = 13.3 (d, $^3J_{C,P}$ = 6.5, CH_3 $N_2C_3HMe_2$-3,5), 14.6 (s, CH_3 $N_2C_3HMe_2$-3,5), 17.7 (br. s, allyl-CH_3), 24.6 (d, $^2J_{C,P}$ = 16.6 Hz, CH_3 $CHMe_2$), 24.3 (d, $^2J_{C,P}$ = 19.4 Hz, Me $CHMe_2$), 110.0 (s, CH $N_2C_3HMe_2$-3,5) ppm.

The following complexes were synthesised in a way similar to that used for the preparation of complex **3**.

$[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)\{\eta^2\text{-}(SR)\text{-}Ph_2PN[(S)\text{-}*CHMePh]PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ (4): Starting materials: $[Pd(\eta^3\text{-}1\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$ (0.039 g, $0.99\cdot10^{-4}$ mol), NH_4PF_6 (0.033 g, $2.02\cdot10^{-4}$ mol), and **1b** (0.105 g, $2.07\cdot10^{-4}$ mol). Colourless crystals of **4** were grown from acetone solution by layering with hexane (b.p. 40−60 °C). Yield: 0.130 g (80%); m.p. 140−142 °C dec. $C_{35}H_{38}F_6N_3P_3Pd$ (814.0): calcd. C 51.66, H 4.67, N 5.16; found C 51.37, H 4.59, N 5.11. Major, *endo*,*syn*,*trans* isomer (**4a**): ^1H NMR (500 MHz, $CDCl_3$): δ = 1.46 (merged with allyl-CH_3 signal of isomer **4b**, H_a'), 1.54 (dd, $^4J_{H,P}$ = 11.2, $^3J_{H,H}$ = 6.4 Hz, allyl-CH_3), 1.72 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 1.87 [d, $^3J_{H,H}$ = 6.9 Hz, CH_3 (*S*)-*CHMePh], 2.76 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 signal, H_a), 2.77 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 3.01 (d, $^3J_{H,H}$ = 6.5 Hz, H_s'), 4.65 [m, CH (*S*)-*CHMePh], 5.35 (m, H_c), 6.22 (d, $^4J_{H,P}$ = 1.7 Hz, CH $N_2C_3HMe_2$-3,5), 6.52−7.81 (m, aryl protons) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.7 (s, CH_3 $N_2C_3HMe_2$-3,5), 14.6 (s, CH_3 $N_2C_3HMe_2$-3,5), 18.9 (br. s, allyl-CH_3), 25.1 [d, $^3J_{C,P}$ = 22.2 Hz, CH_3 (*S*)-*CHMePh], 60.3 [m, CH (*S*)-*CHMePh], 110.5 (s, CH $N_2C_3HMe_2$-3,5), 126.3−157.2 (aryl carbon atoms). *exo*,*syn*,-*trans* isomer (**4b**): ^1H NMR (500 MHz, $CDCl_3$): δ = 1.45 (merged with H_a' of isomer **4a**, allyl-CH_3), 1.45 (dd, $^4J_{H,P}$ = 10.7, $^3J_{H,H}$ = 6.0 Hz, allyl-CH_3), 1.70 [d, $^3J_{H,H}$ = 7.3 Hz, CH_3 (*S*)-*CHMePh], 2.08 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 2.46 (d, $^3J_{H,H}$ = 11.9 Hz, H_a'), 2.75 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 2.77 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 signal, H_s'), 4.05 (m, H_c), 4.40 (m, H_a), 6.34 (d, $^4J_{H,P}$ = 2.3 Hz, CH $N_2C_3HMe_2$-3,5) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.8 (s, CH_3 $N_2C_3HMe_2$-3,5), 14.9 (s, CH_3 $N_2C_3HMe_2$-3,5), 17.9 (br. s, allyl-CH_3), 24.8 [d, $^3J_{C,P}$ = 21.1 Hz, CH_3 (*S*)-*CHMePh], 110.6 (s, CH $N_2C_3HMe_2$-3,5) ppm. *endo*,*syn*,*cis* isomer (**4c**): ^1H NMR (500 MHz, $CDCl_3$): δ = 0.97 (t, $^3J_{H,H}$ = $^4J_{H,P}$ = 6.5 Hz, allyl-CH_3), 1.75 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 1.92 [d, $^3J_{H,H}$ = 7.1 Hz, CH_3 (*S*)-*CHMePh], 2.06 (merged with 3-CH_3 $N_2C_3HMe_2$-3,5 signal of isomer **4b**, H_a), 2.59 (m, H_a'), 2.74 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 signal of isomer **4a**, 5-CH_3 $N_2C_3HMe_2$-3,5), 4.65 [merged with CH (*S*)-*CHMePh signal, H_s], 5.35 (merged with H_c signal of isomer **4a**, H_c) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 17.4 (s, allyl-CH_3) ppm.

$[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)\{\eta^2\text{-}Ph_2PN(CHMe_2)PPh(N_2C_3HMe_2\text{-}3,5)\}](PF_6)$ (5): Starting materials: $[Pd(\eta^3\text{-}1\text{-}PhC_3H_4)(\mu\text{-}Cl)]_2$ (0.052 g, $1.00\cdot10^{-4}$ mol), NH_4PF_6 (0.033 g, $2.02\cdot10^{-4}$ mol), and **1a** (0.095 g, $2.13\cdot10^{-4}$ mol). Yellow crystals of **5** were obtained by layering with hexane (b.p. 40−60 °C). Yield: 0.135 g (83%); m.p. 193−196 °C (dec.). $C_{35}H_{38}F_6N_3P_3Pd$ (814.0): calcd. C 51.66, H 4.67, N 5.16;

found C 51.48, H 4.88, N 5.17. *endo*,*syn*,*trans* isomer (**5a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 1.13 (d, $^3J_{H,H}$ = 6.5 Hz, CH_3 $CHMe_2$); 1.20 (d, $^3J_{H,H}$ = 6.4 Hz, CH_3 $CHMe_2$), 1.74 (d, $^3J_{H,H}$ = 11.6 Hz, H_a'), 2.60 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 3.17 (dd, $^3J_{H,H}$ = 6.8, $^3J_{H,P}$ = 1.7 Hz, H_s'), 3.73 (m, CH $CHMe_2$), 3.97 (dd, $^3J_{H,H}$ = 13.5, $^3J_{H,P}$ = 11.3 Hz, H_a), 6.01 (d, $^4J_{H,P}$ = 2.1 Hz, CH $N_2C_3HMe_2$-3,5), 6.12 (m, H_c), 6.85−7.71 (m, aryl protons) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.3 (s, CH_3 $N_2C_3HMe_2$-3,5), 13.8 (d, $^3J_{C,P}$ = 17.8 Hz, CH_3 $N_2C_3HMe_2$-3,5), 24.9 (d, $^3J_{C,P}$ = 17.8 Hz, CH_3 $CHMe_2$), 26.1 (d, $^3J_{C,P}$ = 9.1 Hz, CH_3 $CHMe_2$), 53.4 (dd, $^2J_{C,P}$ = 27.9 and 6.1 Hz, CH $CHMe_2$), 110.1 (s, CH $N_2C_3HMe_2$-3,5), 127.7−158.7 (aryl carbon atoms). *exo*,*syn*,*trans* isomer (**5b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3-Me $N_2C_3HMe_2$-3,5), 2.52 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 2.59 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 signal of isomer **5a**, H_s'), 2.61 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 signal of isomer **5a**, H_a'), 4.88 (m, H_c), 5.50 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 12.5 Hz, H_a), 6.17 (merged with H_c signal of isomer **5a**, CH $N_2C_3HMe_2$-3,5). *endo*,*syn*,*cis* isomer (**5c**) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 2.37 (dd, $^3J_{H,H}$ = 12.5, $^3J_{H,P}$ = 10.0 Hz, H_a), 2.62 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 3.29 (d, $^3J_{H,H}$ = 12.0 Hz, H_a'), 4.80 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 7.5 Hz, H_s), 5.91 (m, H_c), 6.29 (br., CH $N_2C_3HMe_2$-3,5) ppm.

[Pd(η^3-1-PhC_3H_4){η^2-(*SR*)-Ph_2PN[(*S*)-*CHMePh]PPh-($N_2C_3HMe_2$-3,5)}](PF_6) (6): Starting materials: [Pd(η^3-1-PhC_3H_4)(μ-Cl)]$_2$ (0.052 g, 1.00·10^{-4} mol), NH_4PF_6 (0.033 g, 2.02·10^{-4} mol), and **1b** (0.105 g, 2.07·10^{-4} mol). Isolation of the title compound in a pure form was unsuccessful. *endo*,*syn*,*trans* isomer (**6a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 1.74 (d, $^3J_{H,H}$ = 12.9 Hz, H_a'), 1.84 [d, $^3J_{H,H}$ = 6.9 Hz, CH_3 (*S*)-*CHMePh], 2.73 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 3.22 (d, $^3J_{H,H}$ = 6.9 Hz, H_s'), 3.92 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 12.3 Hz, H_a), 4.63 [m, CH (*S*)-*CHMePh], 5.96 (d, $^4J_{H,P}$ = 2.1 Hz, CH $N_2C_3HMe_2$-3,5), 6.08 (m, H_c), 6.65−7.68 (m, aryl protons) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.5 (s, CH_3 $N_2C_3HMe_2$-3,5), 13.5 (d, $^3J_{C,P}$ = 18.2 Hz, CH_3 $N_2C_3HMe_2$-3,5), 24.8 [d, $^3J_{C,P}$ = 22.9 Hz, CH_3 (*S*)-*CHMePh], 60.2 [dd, $^2J_{C,P}$ = 24.1 and 6.3 Hz, CH (*S*)-*CHMePh], 110.2 (s, CH $N_2C_3HMe_2$-3,5), 126.6−158.3 (aryl carbon atoms). *exo*,*syn*,*trans* isomer (**6b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 2.52 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 2.71 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 of isomer **6a**, H_a'), 2.82 (br., H_s'), 4.81 (m, H_c), 5.41 (dd, $^3J_{H,H}$ = 13.6, $^3J_{H,P}$ = 11.2 Hz, H_a), 5.99 (br. s, CH $N_2C_3HMe_2$-3,5). *endo*,*syn*,*cis* isomer (**6c**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (br. t, H_a), 3.20 (merged with H_s' of isomer **6a**, H_a'), 4.75 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 7.2 Hz, H_s), 5.83 (m, H_c) ppm.

[Pd(η^3-1-MeC_3H_4){η^2-Ph_2P(S)N($CHMe_2$)PPh($N_2C_3HMe_2$-3,5)}]PF_6 (7): Starting materials: [Pd(η^3-1-MeC_3H_4)(μ-Cl)]$_2$ (0.039 g, 0.99·10^{-4} mol), NH_4PF_6 (0.033 g, 2.02·10^{-4} mol), and **1c** (0.100 g, 2.09·10^{-4} mol). Colourless crystals of **7** were obtained by layering with hexane (b.p. 40−60 °C). Yield: 0.133 g (85%); m.p. 178−180 °C (dec.). $C_{30}H_{36}F_6N_3P_3PdS$ (784.0): calcd. C 45.97, H 4.59, N 5.36; found C 45.95, H 4.41, N 5.24. *endo*,*syn*,*trans* isomer (**7a**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.41 (d, $^3J_{H,H}$ = 6.9 Hz, CH_3 $CHMe_2$), 1.10 (d, $^3J_{H,H}$ = 6.1 Hz, CH_3 $CHMe_2$), 1.95 (merged with 5-CH_3 $N_2C_3HMe_2$-3,5 signal, allyl-CH_3), 2.40 (merged with 3-CH_3 $N_2C_3HMe_2$-3,5 signal, H_a'), 3.97 (d, $^3J_{H,H}$ = 6.1 Hz, H_s'), 4.60 (merged with CH $CHMe_2$ signal, H_a), 5.40 (m, H_c), 6.16 (br. s, CH $N_2C_3HMe_2$-3,5), 7.19−7.96 (m, aryl protons) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.2 (s, CH_3 $N_2C_3HMe_2$-3,5), 13.6 (s, CH_3 $N_2C_3HMe_2$-3,5), 18.3 (br. s, allyl-CH_3), 22.9 (d, $^3J_{C,P}$ = 20.4 Hz, CH_3 $CHMe_2$), 23.1 (d, $^3J_{C,P}$ = 15.2 Hz, CH_3 $CHMe_2$), 57.8 (br. s, CH $CHMe_2$), 110.7 (s, CH $N_2C_3HMe_2$-3,5), 128.2−155.6 (aryl carbon atoms). *exo*,*syn*,*trans* isomer (**7b**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.15 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 1.96 (merged with allyl-CH_3 signal of isomer **7a**, allyl-CH_3), 2.91 (d, $^3J_{H,H}$ = 12.0 Hz, H_a'), 3.52 (d, $^3J_{H,H}$ = 6.4 Hz, H_s'), 4.46 (br. t, $^3J_{H,H}$ = 7.6 Hz, H_a), 5.49 (m, H_c) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.3 (merged with allyl-CH_3 signal of isomer **7a**, allyl-CH_3). *endo*,*syn*,*cis* isomer (**7c**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (dd, $^4J_{H,P}$ = 9.5, $^3J_{H,H}$ = 6.5 Hz, allyl-CH_3), 2.02 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 3.37 (m, H_a), 3.65 (m, H_a'), 4.46 (merged with H_a signal of isomer **7b**, H_s), 5.42 (merged with H_c signal of isomer **7a**, H_c) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.2 (br. s, allyl-CH_3). *exo*,*syn*,*cis* isomer (**7d**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (br. t, $^3J_{H,H}$ = $^4J_{H,P}$ = 6.6 Hz, allyl-CH_3), 2.10 (s, CH_3 $N_2C_3HMe_2$-3,5), 3.37 (merged with H_a signal of isomer **7c**, H_a), 4.02 (br. s, H_a'), 4.63 (merged with CH $CHMe_2$ signal, H_s), 5.38 (merged with H_c signal of isomer **7a**, H_c) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.5 (br. s, allyl-CH_3). *endo*,*anti*,*trans* isomer (**7e**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.76 (br. d, allyl-CH_3), 2.80 (d, H_a'), 3.73 (br. s, H_s), 4.15 (br. d, H_s'), 5.30 (m, H_c). *endo*,*anti*,*cis* isomer (**7f**): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.27 (t, allyl-CH_3), 3.72 (merged with H_s signal of isomer **7e**, H_a), 4.66 (merged with CH $CHMe_2$ signal, H_s), 5.05 (m, H_s'), 5.29 (merged with H_c signal of isomer **7e**, H_c).

[Pd(η^3-1-PhC_3H_4){η^2-Ph_2P(S)N($CHMe_2$)PPh($N_2C_3HMe_2$-3,5)}]-(PF_6) (8): Starting materials: [Pd(η^3-1-PhC_3H_4)(μ-Cl)]$_2$ (0.052 g, 1.00·10^{-4} mol), NH_4PF_6 (0.033 g, 2.02·10^{-4} mol), and **1c** (0.100 g, 2.09·10^{-4} mol). Yellow crystals were obtained by layering with hexane (b.p. 40−60 °C). Yield: 0.142 g (84%); m.p. 171−174 °C (dec.). $C_{35}H_{38}F_6N_3P_3PdS$ (846.1): calcd. C 49.70, H 4.49, N 4.97; found C 49.62, H 4.55, N 4.65. *endo*,*syn*,*trans* isomer (**8a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (br. s, CH_3 $CHMe_2$), 1.19 (br. s, CH_3 $CHMe_2$), 2.05 (s, 5-CH_3 $N_2C_3HMe_2$-3,5), 2.37 (s, 3-CH_3 $N_2C_3HMe_2$-3,5), 2.79 (br. s, H_a'), 4.23 (br. s, H_s'), 4.61 (br., CH $CHMe_2$), 5.63 (br., H_a), 6.04 (br., H_c), 6.28 (br. s, CH $N_2C_3HMe_2$-3,5), 6.52−7.98 (m, aryl protons) ppm. ^{13}C NMR [100.6 MHz, $CDCl_3$ and CH_2Cl_2 (1:1)]: δ = 13.5 (s, CH_3 $N_2C_3HMe_2$-3,5), 13.9 (br., CH_3 $N_2C_3HMe_2$-3,5), 23.0 (s, CH_3 $CHMe_2$), 58.0 (br., CH $CHMe_2$), 110.8 (s, CH $N_2C_3HMe_2$-3,5), 126.0−155.7 (aryl carbon atoms). *exo*,*syn*,*trans* isomer (**8b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23 (br. s, H_a'), 3.77 (br., H_s'), 5.49 (br. H_a), 6.11 (br., H_c). *endo*,*syn*,*cis* isomer (**8c**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70 (br., H_a), 4.68 (br. t, H_s), 4.73 (br. d, H_a'), 6.18 (br., H_c). *exo*,*syn*,*cis* isomer (**8d**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (br., H_a), 4.79 (br., H_s), 5.00 (br. d, H_a'), 6.00 (m, H_c) ppm.

X-ray Crystallography: Crystal data for complex **5a** were collected by using a Siemens SMART CCD diffractometer. The crystallographic data and details on data collection are summarised in Table 3. The structure was solved by direct methods, using the program SIR-97[24] and refined on F^2 values for all unique data by full-matrix, least squares by using SHELXTL.[25] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed at their calculated geometrical positions and refined isotropically. CCDC-172846 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 3. Crystal data and structure refinement for complex **5a**

Empirical formula	$C_{35}H_{38}F_6P_3N_3Pd$
Formula mass	813.99
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 9.8783(8) Å b = 18.1125(14) Å; c = 10.2360(8) Å β = 97.223(2)°
Volume	1816.9(2) Å^3
Z	2
Density (calculated)	1.488 Mg/m^3
Absorption coefficient	0.703 mm^{-1}
F(000)	828
Crystal size	0.12 × 0.06 × 0.06 mm
θ range for data collection	2.01−23.28°.
Index ranges	$-10 \le h \le 10$, $-20 \le k \le 20$, $-11 \le l \le 9$
Reflections collected	8238
Independent reflections	4817 [R(int) = 0.0275]
Completeness to θ = 23.28°	99.7%
Refinement method	full-matrix, least squares on F^2
Data/restraints/parameters	4817/1/435
Goodness-of-fit on F^2	1.140
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0740, $wR2$ = 0.1785
R indices (all data)	$R1$ = 0.1058, $wR2$ = 0.2102
Absolute structure parameter	0.00(7)
Extinction coefficient	0.0055(13)
Largest diff. peak and hole	2.298 and −0.676 e·Å^{-3}

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