Rearrangements in Allylpalladium Complexes with Hemilabile Chelating Ligands

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In memoriam Professor *Luigi M. Venanzi*

In addition to η^3- to η^1-allyl rearrangement, η^2- to η^1-chelating-ligand rearrangements can affect the dynamic properties in allylpalladium complexes containing hemilabile ligands. These rearrangements have the potential of altering stereochemistry, which can ultimately affect the stereochemistry and regiochemistry of reactions upon the allyl group, *e.g.*, allylic alkylation. Apparent rotation of an η^3-allyl in four-coordinate Pd^{II}-complexes can be the result of ligand exchange or intramolecular processes. NMR Studies indicate that the effects of η^2- to η^1-chelating-ligand stereochemistry and rearrangements may be hidden or subtle, and both intra- and intermolecular processes may be important.

Introduction. – The synthetic utility of transition-metal-catalyzed alkylations involving allyl intermediates has been shown to be effective for the regio- and stereocontrolled formation of C–C bonds over the past thirty years [1][2]. Asymmetric variants have been developed more recently [3]. Early work focused on the use of bisphosphane ligands, such as chiraphos [3], where C_2-symmetric ligands were considered to have special advantages [4]. More recently, however, some of the most impressive enantioselectivities have been obtained with asymmetric P,N ligands, *e.g.*, phosphinoaryloxazolines [5–13]. In general, the complexes show dynamic NMR spectra, which indicate that the complexes are rearranging rapidly. The stereodynamics in these systems can be important in enantioselective allylic alkylations and has been reviewed recently [14], but many of the principles were established previously [3][15–19]. A number of rearrangements are possible that can affect the geometry. In earlier work, there was a tendency to overemphasize the importance of a C_2-symmetric ligand for obtaining high levels of asymmetric induction. However, the excellent levels of enantioselectivity obtained with P,N ligands has demonstrated that asymmetric bidentate ligands can be as effective as, if not superior to, C_2-symmetric ligands [5–13].

With a C_2-symmetric ligand, such as chiraphos [3], a rotation of the allyl group or the ligand will yield an equivalent structure; hence, the presence or absence of a rotation mechanism may be irrelevant. With a non-C_2-symmetric ligand, however, a different isomer will be produced and this has the potential to have significant consequences with regard to the resulting stereochemistry of the allyl product (see *Fig. 1*). Although, regiochemistry has often been determined on the basis of substitution patterns of the termini of the allyl, *Hayashi et al.* have recently shown that the regiochemistry of nucleophilic attack in some cases can be determined by differences in *trans* influence of the phosphine and the other ligand [20].

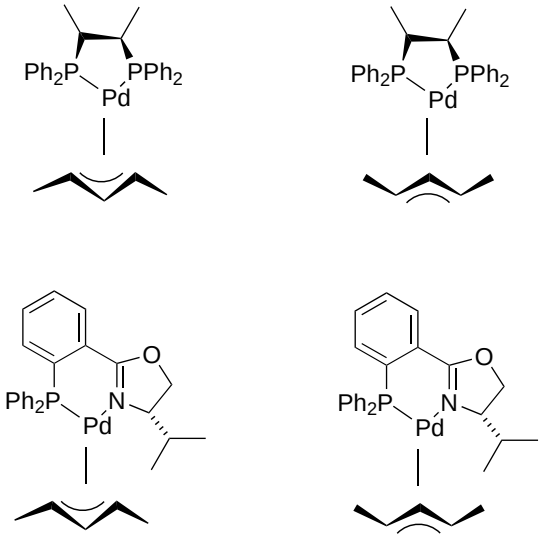

Fig. 1. *Comparison of effects of rotation of an allyl.* Different diastereoisomers result with a P,N ligand.

True rotation of the allyl has been rarely reported in Pd^{II}-complexes, based on square-planar coordination (the allyl group is presumed to occupy two coordination sites) [16]. However, when the coordination number is effectively 5 or 7 and, where fluxionality is common, then rotation of an allyl group has been observed in preference to η^3- to η^1-allyl interconversion (the most commonly observed process for Pd). $[Cp(CO)_2Mo(allyl)]$ is a typical example [21].

Since the non-C_2-symmetric ligands show every promise of surpassing the effectiveness of many C_2-symmetric ligands, and often have the advantage of more straightforward syntheses [5–13][22–24], the potential importance of the mechanistic possibility of a rotation or pseudorotation is essential for understanding the enantioselectivities observed. This led us to investigate some model systems that bear on this question with regard to P,N-ligands. With a P,N-ligand, there is the possibility of hemilability. This has generally been considered an important feature in catalysis with the hemilabile P,O-ligands [25]. This feature, as well as key stereodynamic aspects of the allyl rearrangement must be considered. As part of our continuing interest in allyl-Pd complexes, we prepared (η^3-methallyl {[*o*-(diphenylphosphino)benzylidene]-isopropylamine}palladium tetrafluoroborate and examined the apparent rotation of the allyl group.

Results and Discussion. – 2-Methallylpalladium chloride dimer was treated with $AgBF_4$ and 2-(diphenylphosphino-*N*-isopropylbenzylideneamine to produce (η^3-methallyl)[2-(diphenylphosphino)-*N*-isopropylbenzylideneamine]palladium tetrafluoroborate (**1**).

Stereodynamics of **1**. The 298 K ^{1}H-NMR spectra of **1** are consistent with the onset of a $\eta^3-\eta^1-\eta^3$-allyl interconversion. At room temperature the allyl H-atoms in **1**

resonate at δ 4.71 (1 H), 3.73 (1 H), 3.17 (1 H), 2.77 (1 H) ppm, with δ 4.71 and 3.73 showing significant splittings from ^{31}P, and δ 3.17 and 2.77 showing broadening. As couplings *trans* to the P-atom are expected to be greater, and *syn* H-atoms usually resonate downfield of *anti* H-atoms δ 4.71 and 3.73 ppm are assigned to the allyl H-atoms, which are *syn* and *anti*, respectively, as well as *trans* to the P-atom (*Fig. 2*). The

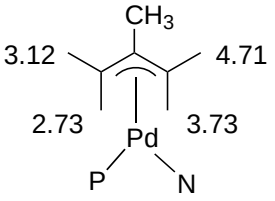

Fig. 2. *The ^{1}H-NMR assignments for* **1**

breadth of the upfield resonances implied a dynamic process; hence, variable temp. studies were performed.

The $\eta^3-\eta^1-\eta^3$-Allyl Interconversion in **1**. At 233 K, the broad resonances became sharp *singlets* at δ 3.11 and 2.73 ppm. The averaged i-Pr Me resonances originally observed as a *doublet* at 1.28 ppm in the room-temperature spectrum separated into two *doublets* at δ 1.28 and 1.17 ppm at 233 K. As the temperature was raised to room temperature (298 K), the allyl and i-Pr Me resonances started to show the same degree of initial broadening and, therefore, indicate that the same dynamic process averages them. The i-Pr Me groups are diastereotopic if the allyl is not rearranging and, therefore, are 'reporters' of the chirality in the system. This shows that, in effect, the chirality is averaging and the enantiomers which gave rise to the diastereotopicity are being racemized.

Previously reported nomenclature of square-planar allyl palladium complexes have failed to unambiguously describe compounds such as **1**. Others [5][14] have described diastereoisomers as *endo* and *exo*, but the defining element which distinguishes them is not always obvious. In **1**, there are two enantiomers considering the Pd(allyl)NP fragment, and there is no reference point to assign a descriptor of *endo* or *exo*; therefore, we have extended *Cahn*, *Ingold*, and *Prelog* (*CIP*) rules to assist in accurately describing the configuration in these systems. Considering the metal as the chiral center, the priority rules were applied where the centroid of the allyl was given the priority of atomic number 18 consistent with other polyhapto ligands [26]. (*Note that the centroid is above the P–Pd–N plane and on the same side as the central allyl C-atom.*) Hence, the enantiomers of compound **1** were designated (*R*)-**1** or (*S*)-**1** owing to the clockwise or anticlockwise assignment of priorities as shown in (*Scheme 1*)[1]).

Stereochemically, one might have considered the relationship of (*R*)-**1** and (*S*)-**1** to be that of a difference of degree of rotation of the allyl in the two enantiomers. If a true

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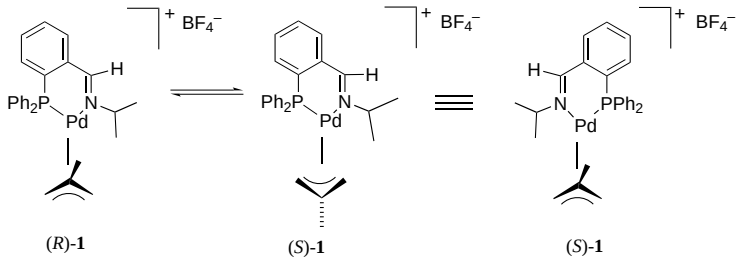
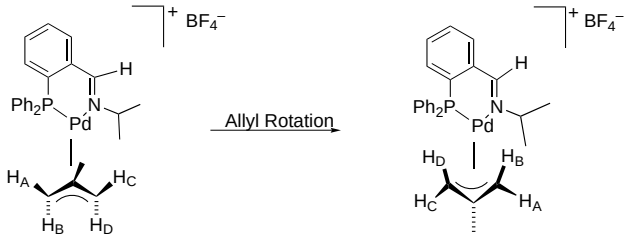
[1]) At this point, we are focusing attention on the chirality of the Pd(allyl)PN moiety. One should note that conformers of the Pd(P,N-ligand) are possible, and that they also are chiral. Different P,N-ligand conformers are not observed in the NMR at the temperatures recorded here. P,N-Ligand conformers, which are exchanging at room temperature, have previously been observed in ferrocene-based derivatives (*vide infra*) [27][28].

Scheme 1. *The Enantiomers of* **1**



rotation occurred, however, the placement of the termini of the allyl would switch, so that the terminus *trans* to the P-atom in (*R*)-**1** would become *cis* to the P-atom in (*S*)-**1**. The initial dynamic process, however is not consistent with a true rotation, which would involve the interchanges of sites shown in *Scheme 2*.

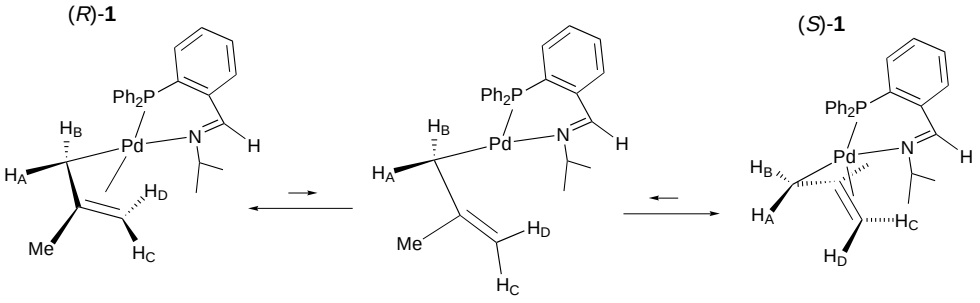
Scheme 2. *Site Exchanges Involved in a True Allyl Rotation*



It is consistent, however, with an η^3- to η^1-allyl interconversion that breaks the bond *trans* to the P-atom and maintains the σ-bond *trans* to the N-atom, as shown in *Scheme 3*.

This $\pi-\sigma-\pi$ or $\eta^3-\kappa C^1-\eta^3$ mechanism retains a given terminus *trans* to a particular donor, while inverting the metal center. *Helmchen* and co-workers [5] found that similar (allyl)(phosphinoaryldihydrooxazole)palladium complexes have terminal Pd–C bond distances that are nonequivalent. The Pd–C bond *trans* to the P-atom is

Scheme 3. *Site Exchanges Occurring during* $\eta^3-\eta^1-\eta^3$ *Racemization of* **1**



significantly longer than the Pd–C bond *trans* to the N donor (2.28 Å and 2.13 Å, resp., in those compounds) [5]. This trend has also been observed with ferrocene-based P,N ligands [27][28]. This weakening of the bond *trans* to the P-atom would suggest that conversion from an η^3- to η^1-allyl would preferentially involve breaking the bond *trans* to the P-atom and maintaining the σ bond *trans* to the N-atom.

Since the shifts (*Fig. 3*) are the same in both (*R*)-**1** and (*S*)-**1**, the interconversion involves the following site exchanges (in *Fig. 4*), which were verified by saturation transfer experiments.

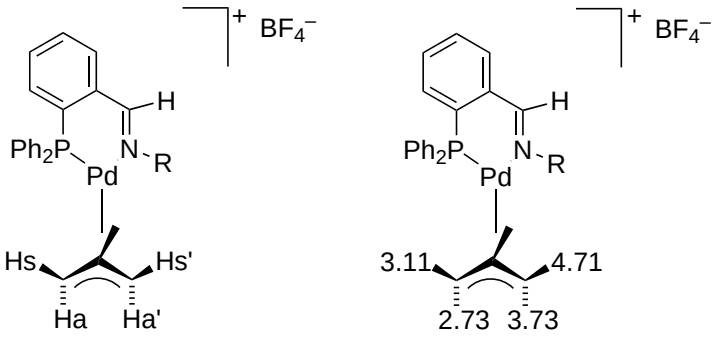


Fig. 3. *NMR Assignments for* syn *and* anti *H-atoms in* **1**

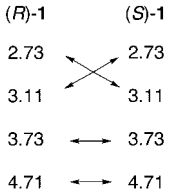
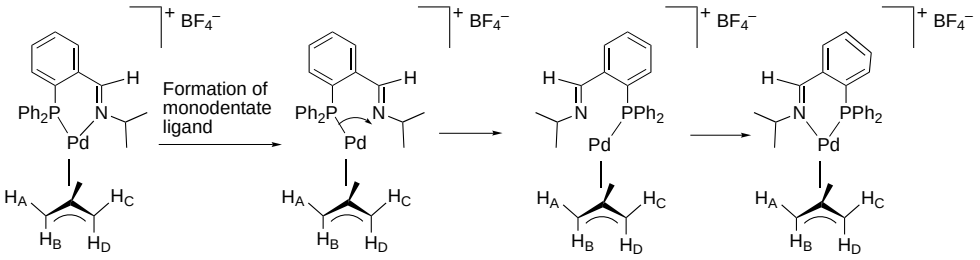


Fig. 4. *Exchange observed at lower temperatures*

Allyl Rotation or Apparent Allyl Rotation. This $\eta^3-\eta^1-\eta^3$ result is not surprising on the basis of previous experience; however, another exchange process also occurs at higher temperatures, which involves onset of initial broadening of δ 3.73 and 4.71 ppm at 0°. This process appears to be intramolecular since saturation of the upfield component of the ^{31}P-coupled *doublet* at δ 4.71 ppm results in greater saturation transfer to the upfield component of the *doublet* at 3.73 ppm. (*If intermolecular P,N-ligand exchange were involved, the lower* doublet *would show equal saturation of both components of the* doublet). This was consistent with being the start of a $\eta^3-\eta^1-\eta^3$ process retaining the σ bond *trans* to the P-atom; however, further experiments showed that exchange between the resonances that are *cis* and *trans* relative to the P-atom was also occurring. This was shown by saturation of the 2.77 ppm resonance (average of 3.11 and 2.73 ppm) and the observation of a decrease in intensities of the resonances at 4.71 and 3.73 ppm at 25°. A similar effect was noted by *Helmchen* and co-workers by EXSY experiments and attributed to a rotation of the allyl [5].

There are several other processes that could exchange termini, however, and can give rise to an *apparent* rotation: exchange through a T-shaped intermediate of either

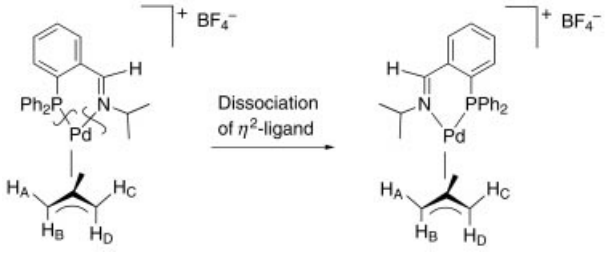
Scheme 4. *Formation of an* η^1*-Ligand and Terminus Exchange* via *a T-Shaped Intermediate*



an η^1-allyl or η^1-(P,N-ligand) intermediate or a complete dissociation of the P,N-ligand (*Scheme 4*).

The third mechanism involves the complete dissociation of the bidentate ligand, followed by a 180° rotation, a switch of termini through a T-shaped intermediate and reformation of the chelate (*Scheme 5*). This mechanism provides site exchanges equivalent to an allyl rotation. *One should note that the NMR spectrum would not be affected by formation of an* η^1*-(P,N-ligand) intermediate followed by reformation of the* η^2*-complex, since no environments would be altered by that process.* We favor the formation of the η^1-(P,N-ligand) as the route to apparent rotation through a T-shaped intermediate rather than η^1-allyl, since a number of cases of η^1-allyl formation have not been accompanied by *cis*/*trans* isomerization. It is not clear whether the Pd–N or the Pd–P bond terminus is breaking; the product and effect on the NMR spectrum is the same for either.

Scheme 5. *Complete Dissociation of the P,N-Ligand*



Intermolecular Exchange and Apparent Allyl Rotation. Further experiments were carried out to elucidate the mechanism of this apparent allyl rotation. Next, excess ligand (0.0067 g) was added to **1** (0.0210 g) at room temperature. The room-temperature NMR immediately showed broadening of the allyl and i-Pr resonances suggestive of increased rates of intermolecular exchange. This suggested the possibility of a second-order reaction in which intermolecular ligand exchange occurred. Since our goal was to understand the effects in the absence of excess ligand, we examined the possibility of intermolecular exchange *via* a crossover experiment.

Compounds **2**, **3** and **4**, as shown in *Fig. 5*, were prepared, and characteristic resonances were noted in the ^{1}H-NMR. Compounds **2**–**4** all showed the $\eta^3-\eta^1-\eta^3$

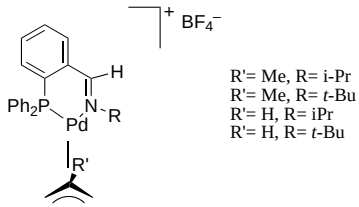
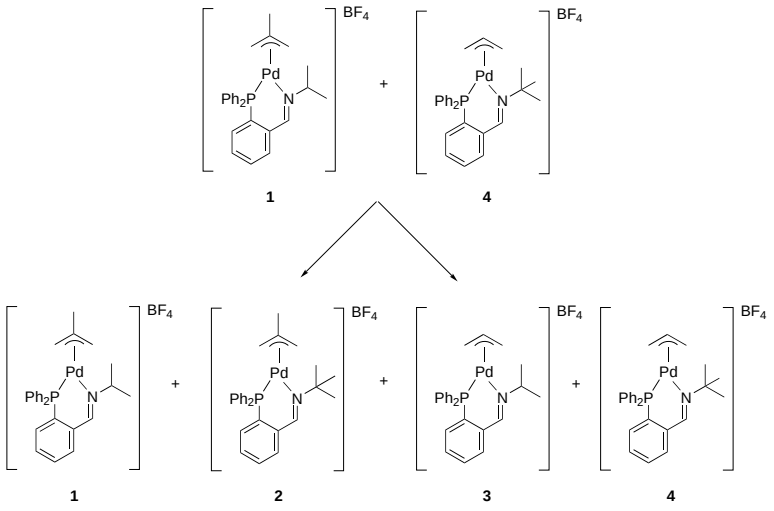


Fig. 5. *Compounds used for a cross-over experiment*

process at room temperature. Compounds **1** and **4** were mixed and monitored by ^{1}H-NMR. After 5 h at room temperature, compounds **2** and **3** were evident in the spectrum at *ca*. 10% the intensity of **1** and **4**. (This is shown schematically in *Scheme 6*). At equilibrium, all four compounds were present in nearly equal amounts as determined by integration of the imine H-atom resonances. The results of this NMR experiment demonstrate the presence of a slow intermolecular 2-(diphenylphosphino)benzylideneamine exchange. However, the rate of exchange has a half-life on the order of hours in the absence of excess ligand, which is not consistent with either of the intramolecular 2-(diphenylphosphino)-*N*-isopropylbenzylideneamine-dissociation mechanisms because the apparent allyl rotation is nearly occurring on the NMR timescale at room temperature (half-life on the order of 1 s).

Several conclusions can be drawn from the data. In the absence of excess ligand the lowest-energy dynamic process is the $\pi-\sigma-\pi$ mechanism. At -40° the rate of this $\pi-\sigma-\pi$ interconversion has been slowed to reveal a single isomer of **1**. The process that becomes observable in the NMR at 0° is too rapid to be consistent with the rate of the intermolecular crossover experiments. This suggests that there is an intramolecular process that is either: *1*) a true rotation or *2*) an apparent rotation resulting from the

Scheme 6. *Intermolecular Exchange of Ligands upon Mixing* **1** *and* **4**



formation of an η^1-intermediate interconverting *cis*- and *trans*-termini, presumably *via* a T-shaped intermediate (*Scheme 4*). Intermolecular P-ligand exchange has been seen in many cases. Intermolecular exchange of both bidentate and monodentate ligands has also been indicated in analogous cases [17][29][30]. Since one would anticipate differential rates for the breaking of Pd–P and Pd–N bonds in a hemilabile ligand, we believe that a three-coordinate intermediate is the most likely type of intermediate to be involved in the apparent rotation.

Structural Aspects of **1**. Compound **1** crystallizes as a single diastereoisomer, and both enantiomers of it are found in the centrosymmetric crystal. The Pd–C(1) bond *trans* to the P-atom of 2.214(5) Å and the Pd–C(3) bond *trans* to N-atom of 2.105(8) Å can be attributed to the differential *trans* influences of the P- and N-donor. There is higher double bond character in the allyl than in the C-atoms *trans* to the P-atom: C(1)–C(2) = 1.375(7) Å, whereas C(2)–C(3) = 1.430(7) Å.

Conformational Issues with the P,N-Ligand. The crystal structure of **4** shows two interesting features. One is that both the (*R*)- and (*S*)-[Pd(allyl)(P,N-ligand)] are in the crystal even though it is in the chiral space group $P2_12_12_1$. Furthermore, the [Pd(P,N-ligand)] has spontaneously resolved as one conformer (*Fig. 6*). Up to this point in the discussion, we have ignored the conformation of the [Pd(P,N-ligand)]. One should note that the N–Pd–P moiety is prochiral, so that a deviation of the P,N-ligand out of the plane produces a chiral fragment. This is rather pronounced in the crystal as shown in *Fig. 7*. The ligand (P–N–C(8)–C(9)–C(14)) mean plane forms a 134° dihedral angle with the N–Pd–P plane. Thus, the crystal structure, which is disordered among two orientations of the allyl, actually contains two diastereoisomers and is effectively a quasi-racemate owing to the ring chirality being the same in both isomers.

This type of conformational isomerism from the ligand has been observed previously with 2-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine complexes [30][31] (ΔG^* 8.8–10 kcal/mol) and with ferrocene-based P,N-ligands [28][29]. In our system, the interconversion of [Pd(P,N-ligand)] conformers appears to be rapid in solution. Hence, the spectra observed at *ca.* –40° are averages of the two conformers. One notes a slight decoalescence in the i-Pr Me groups between –30° and –40° with an increase

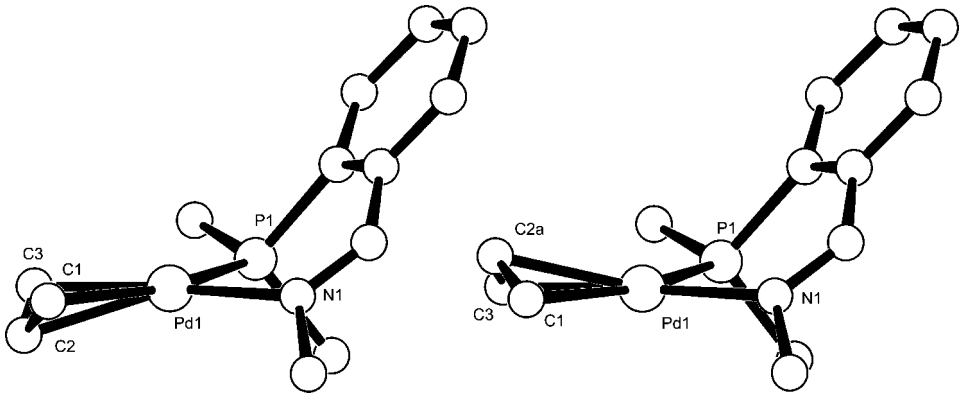


Fig. 6. *The two allyl orientations found in the crystal of* **4**. The methyls of the *t*-butyl group and the C-atoms other than the *ipso* C-atom of the phenyls have been omitted for clarity.

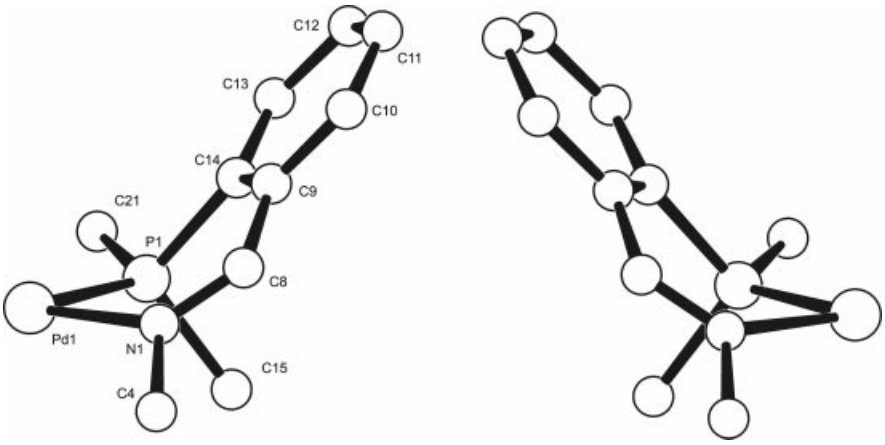


Fig. 7. *The chiral moiety on the left is that observed in the particular enantiomorphic crystal on which the X-ray determination was carried out*. The methyls of the *t*-butyl group and the C-atoms other than the *ipso* C-atom of the phenyls have been omitted for clarity.

in broadening of 1.2 Hz, suggestive of the slowing of conformational interconversion with a barrier < 10 kcal/mol.

As expected, **4**, although disordered with two orientations of the allyl, showed the same trend with the Pd–C bond *trans* to the P-atom of 2.29(1) Å and the Pd–C bond *trans* to the N-atom of 2.15(1) Å. *Helmchen* and co-workers also noted a situation in which two orientations of an allyl were found in the same crystal of a palladium (η^3-allyl) complex of a dihydro(phosphinoaryl)oxazole [5].

Conclusions. – The results presented here indicate that the presence of apparent allyl rotation may arise from several mechanisms. Nevertheless, there are intramolecular paths that can exchange the termini of the allyls relative to other ligands. As the use of P,N-ligands on square-planar allyl-Pd complexes becomes more prevalent, full understanding of the mechanisms of apparent allyl rotation will be needed. This is particularly relevant, since it has potential bearing on the use of P,N-ligands in asymmetric catalysis owing to the electronic influence of the *trans*-ligand, which can direct the attack to one terminus or the other of the allyl.

Experimental Part

General. The 2-(diphenylphosphino)benzaldehyde and $AgBF_4$ were purchased from *Aldrich* and *Strem Chemicals* respectively. All reagents were used as received. Unless otherwise noted, all solvents were dried prior to use: CH_2Cl_2 over P_2O_5, MeCN over CaH_2, THF and Et_2O over Na/benzophenone. The allylpalladium-chloride dimer and methylallylpalladium-chloride dimers were prepared as described in [33].

[2-(Diphenylphosphino)-N-*(1-methylethyl)benzylideneamine] (2-methylallyl)palladium Tetrafluoroborate* (**1**). At r.t., $AgBF_4$ (0.1067 g, 0.55 mmol) was added to (2-methylallyl)palladium-chloride dimer (0.1189 g, 0.302 mmol) in THF (10 ml). The soln. immediately became cloudy and was stirred for an additional 10 min. The soln. was centrifuged, and the supernatant was transferred *via* cannula to a second flask. The AgCl was washed with 2×2 ml of THF, and the extracts were combined with the supernatant. [2-(Diphenylphosphino)-benzylidene]isopropylamine (0.1980 g, 0.59 mmol) in THF (1 ml) was added dropwise at r.t. The soln. was

stirred for 1.5 h, and then the solvent was removed under reduced pressure. The yellow residue was dissolved in CH_2Cl_2 and then precipitated by vapor diffusion of hexane at 0° overnight. The product (0.1704 g, 0.29 mmol, 49.2%) was isolated as pale yellow crystals by filtration. ^{1}H-NMR ($CDCl_3$, 500 MHz, δ in ppm, J in Hz): 8.608 (d, J = 2.6, 1 H); 7.954 (dd, J = 7.2, 4.4, 1 H); 7.702 ('*app.*' t, J = 7.7, 1 H); 7.576–7.496 (m, 7 H); 7.30–7.16 (m, 4 H); 7.034 (dd, J = 10.2, 7.7, 1 H); 4.685 (d, J = 4.8, 1 H); 3.98 (*sept.*, J = 6.1, 1 H); 3.67 (d, J = 9.9, 1 H); 3.17 (br. s, 1 H); 2.28 (br. s, 1 H); 2.01 (s, 3 H); 1.220 (br. d, J = 5.7, 6 H). The broad resonances at 3.17 and 2.78 ppm sharpened to 2s at 3.11 and 2.73 ppm, and the br. d at 1.22 ppm resolved into 2d at 1.284 (d, J = 6.1, 3 H) and 1.173 (d, J = 6.1, 3 H) at −40°. ^{31}P-NMR ($CDCl_3$, 120 MHz, r.t.): 28.14. Anal. calc. for $C_{26}H_{29}BF_4NPPd$: C 53.87, H 5.04; found: C 54.02, H 5.05.

X-Ray Crystal-Structure Determination of **1**. Cell constants corresponded to a monoclinic cell with dimensions: a = 10.5088(6) Å, b = 15.663(2) Å, c = 16.452(2) Å, V = 2564.2(4) Å^3. For Z = 4 and F.W. = 579.70, the calculated density is 1.50 g/cm^3. The systematic absences of: $h0l$: $l = 2n+1$ and $0k0$: $k = 2n+1$, uniquely determine the space group to be $P2_1/c$ (#14). The data were collected at a temp. of $-90° \pm 1°$ on a *Nonius Kappa CCD*. A total of 8622 reflections were measured. The linear absorption coefficient, μ, for MoK$_\alpha$ radiation is 9.2 cm^{-1} and the data were corrected for absorption using SORTAV [34]. The data were also corrected for *Lorentz* and polarization effects. The structure was solved by direct methods (SIR92) [35]. The non-H-atoms were refined anisotropically. The H-atoms were included in calculated positions for those on the P,N-ligand, but those on the allyl were refined. The final cycle of full-matrix least-squares refinement was based on 3152 observed reflections ($I > 3.00\sigma(I)$) and 335 variable parameters and converged with unweighted and weighted agreement factors (on F) of: R = 0.038 and wR = 0.042.

[N-(1,1-Dimethylethyl)-2-(diphenylphosphino)benzylideneamino](2-methylallyl)palladium Tetrafluoroborate (**2**). At r.t., $AgBF_4$ (0.045 g, 0.23 mmol) was added to (2-methylallyl)palladium-chloride dimer (0.0685 g, 0.17 mmol) in THF (10 ml). According to a similar procedure as the preparation of **1**, *N*-(*tert*-butyl)-2-[(diphenylphosphino)benzylideneamine (0.1137 g, 0.33 mmol) in THF (1 ml) was added dropwise to the soln. of the cation at r.t. The product was isolated as pale yellow crystals by filtration from a CH_2Cl_2/hexane soln. (0.468 g, 0.08 mmol, 68.2%). ^{1}H-NMR ($CDCl_3$, 500 MHz, r.t., δ in ppm, J in Hz): 8.554 (d, J = 3.5, 1 H); 8.04 (dd, J = 4.4, 7.0, 1 H); 7.73 ('app.' t, J = 7.7, 1 H); 7.60–7.57 (m, 3 H); 7.52–7.47 (m, 4 H); 7.24–6.91 (m, 4 H); 6.92 (dd, J = 10.5, 7.6, 1 H); 4.69 (br. d, J = 4.7, 1 H); 3.64 (d, J = 9.4, 1 H); 3.02 (br. s, 2 H); 2.05 (s, 3 H); 1.19 (s, 9 H). At −30° the br. resonance at 3.02 ppm sharpens to 2s each with an integration of 1 H at 3.22 and 2.82 ppm. ^{31}P-NMR ($CDCl_3$, 120 MHz, r.t.): 30.31. Anal. calc. for $C_{27}H_{31}BF_4NPPd$: C 54.62, H 5.26; found: C 54.74, H 5.32.

(Allyl)[2-(diphenylphosphino)-N-*(1-methylethyl)benzylideneamine]palladium Tetrafluoroborate* (**3**). At r.t., $AgBF_4$ (0.052 g, 0.27 mmol) was added to allylpalladium-chloride dimer (0.057 g, 0.16 mmol) in THF (10 ml). According to a similar procedure as the preparation of **1**, 2-(diphenylphosphino)-*N*-isopropylbenzylideneamine (0.1208 g, 0.36 mmol) in THF (1 ml) was added dropwise to the soln. of the cation at r.t. The product was isolated as pale yellow crystals by filtration from CH_2Cl_2/hexane (0.0864 g, 0.15 mmol, 49%). ^{1}H-NMR ($CDCl_3$, 500 MHz, r.t., δ in ppm, J in Hz): 8.594 (d, J = 2.2, 1 H); 7.94 (dd, J = 7.1, 4.2, 1 H); 7.70 ('app.' t, J = 7.5, 1 H); 7.59–7.56 (m, 3 H); 7.54–7.49 (m, 5 H); 7.26–7.21 (m, 3 H); 7.03 (dd, J = 7.5, 10.4, 1 H); 5.86–5.77 (m, 1 H); 4.93 (dd, J *ca.* 7.0, *ca.* 7.0, 1 H); 4.02 (*sept.*, J = 6.0, 1 H); 3.80 (dd, J = 13.9, 9.8, 1 H); 3.134 (br. s, 2 H); 1.254 (d, J = 6.0, 6 H). ^{31}P-NMR ($CDCl_3$, 120 MHz, r.t.): 27.19. Anal. calc. for $C_{25}H_{27}BF_4NPPd$: C 53.08, H 4.81; found: C 53.12, H 4.90.

*(Allyl)[*N-*(1,1-dimethylethyl)-2-(diphenylphosphino)benzylideneamine]palladium Tetrafluoroborate* (**4**). At r.t., $AgBF_4$ (0.1257 g, 0.65 mmol) was added to allylpalladium-chloride dimer (0.1222 g, 0.34 mmol) in THF (10 ml). According to a similar procedure as the preparation of **1**, *N*-(*tert*-butyl)-2-(diphenylphosphanido)benzylideneamine (0.2067 g, 0.60 mmol) in THF (1 ml) was added dropwise to the soln. of the cation at r.t. The product was isolated as pale yellow crystals by filtration from CH_2Cl_2/hexane (0.2390 g, 0.41 mmol, 68.9%). ^{1}H-NMR ($CDCl_3$, 500 MHz, r.t., δ in ppm, J in Hz): 8.509 (d, J = 3.3, 1 H); 7.99 (dd, J = 7.7, 1 H); 7.72 (app. t, J = 7.7, 1 H); 7.61–7.58 (m, 3 H); 7.58–7.48 (m, 4 H); 7.28 (dd, J = 7.6, 12.8, 4 H); 6.984 (dd, J = 7.7, 10.5, 1 H); 5.80–5.72 (m, 1 H); 4.96 (dd, J = 6.8, 6.8, 1 H); 3.79 (dd, J = 14.8, 9.9, 1 H); 3.48 (br. d, J = 6.7, 1 H); 2.93 (br. d, J = 11.9, 1 H); 1.24 (s, 9 H). ^{31}P-NMR ($CDCl_3$, 120 MHz, r.t.): 29.91. Anal. calc. for $C_{26}H_{29}BF_4NPPd$: C 53.87, H 5.04; found: C 53.65, H 5.05.

X-Ray Crystal-Structure Determination of **4**. A pale yellow prismatic crystal of $C_{26}H_{29}BF_4NPPd \cdot CH_2Cl_2$ having approximate dimensions of $0.12 \times 0.25 \times 0.48$ mm was mounted on a glass fiber. As this structure was disordered and in an orthorhombic space group, the data do not provide accurate metric parameters; however, the structure provides some interesting conformational details. Cell constants corresponded to an orthorhombic cell with dimensions: a = 10.221(2) Å, b = 15.710(6) Å, c = 18.098(7) Å, and V = 2906(1) Å^3. For Z = 4 and

F.W. = 664.63, the calculated density is 1.52 g/cm^3. The systematic absences of: $h00$: $h = 2n+1$, $0k0$: $k = 2n+1$, $00l$: $l = 2n+1$, uniquely determine the space group to be: $P2_12_12_1$ (#19). The correct enantiomers were selected on the basis of the *Flack* parameter (0.0468) and on the comparison of the final residuals (the R and wR values of the opposite hand were 0.045 and 0.047, resp.).

The data were collected at a temp. of $-90° \pm 1°$ on a serial diffractometer (*Nonius CAD4*). A total of 3339 reflections was collected. The linear absorption coefficient, μ, for MoK_α radiation is 9.2 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for *Lorentz* and polarization effects. The structure was solved by the *Patterson* method and expanded by means of *Fourier* techniques. The non-H-atoms were refined anisotropically. The BF_4-group F-atoms were disordered about a three-fold axis. One F-atom was included at full occupancy and the other three F-atoms were included in two positions, each at 50% occupancy. Disorder was also observed in the central allyl C-atom (C(2) and C(2a) = C(28)). This C-atom was refined in two positions with the occupancy of one position constrained to equal to one minus the occupancy of the other position (to yield a total occupancy of 1.0 and an occupancy of C(2) of 0.603). H-atoms, except for those of the allyl, were included in calculated positions but not refined. The final cycle of full-matrix least-squares refinement was based on 1910 observed reflections ($I > 3.00\sigma(I)$) and 366 variable parameters and converged with unweighted and weighted agreement factors (on F) of: $R = 0.044$; $wR = 0.046$. The standard deviation of an observation of unit weight was 1.78.

Crystallographic data for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-164435 for **4** and No. CCDC-164436 for **1**. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

Mrs. *Susan DeGala* collected the X-ray data for **4** and carried out the initial solution of the structure. We thank the *National Science Foundation* and the *Petroleum Research Fund* administered by the *American Chemical Society* for support.

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