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Structure and dynamics of chiral allyl complexes of Pd(II): NMR spectroscopy and enantioselective allylic alkylation[1]

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Contents

Abstract

The idea of NOE 'reporter ligands', be they simple nitrogen chelates or relatively complicated bidentate phosphine compounds, is explored. These NMR experiments lead to a better understanding of subtle (allyl hybridization, phenyl–phenyl stacking) and gross (three-dimensional aspects, shape of the chiral pocket) structural features in the chemistry of chiral palladium–allyl complexes. Combined with X-ray crystallography and MM2* calculations, one can learn how the BINAP, CHIRAPHOS and JOSIPHOS families of chiral ligands use steric effects to transfer chiral information. A relatively rigid chiral pocket seems a necessary, but not sufficient, condition, since an intrusive chiral pocket leads to syn–anti isomers. Two-dimensional exchange NMR has shown unexpected selectivity with respect to allyl isomerization. The η^3-η^1 isomerization can be under either electronic or steric control. The terminal allyl ^{13}C chemical shifts in 1,3-diphenylallyl palladium(II) complexes of various chelate ligands are discussed.

Keywords: Allyl complex of Pd(II); Enantioselective allylic alkylation

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[1] We are delighted to dedicate this manuscript to Professor Kees Vrieze, whose seminal contributions in coorination and organometallic chemistry have been a beacon to us all.

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1. Introduction

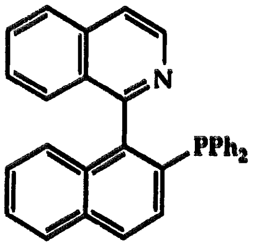
The chemistry of Pd(II) allyl complexes has been and remains an interesting theme. A variety of organic substrates can be allylated in the presence of catalytic amounts of palladium salts [1] and, in some cases, the relatively stable allyl-intermediates can react further, e.g. with CO, to give allylic acids and their derivatives [2]. Moreover, Pd–allyl intermediates are presumed in a number of condensation and oligomerization reactions [3].

In recent years, the Pd-catalyzed enantioselective allylic alkylation [4,5] and amination [6] reactions have preempted much of the limelight. These reactions are often modelled, rather arbitrarily, using the 1,3-diphenyl allyl precursor, as shown in Eq. (1).

$$\mathrm{PhCH(OAc)CH{=}CHPh + CH(CO_2Me)_2^-} \xrightarrow{\text{chiral catalyst}}$$

$$\mathrm{PhC^{*}H\{CH(CO_2Me)_2\}CH{=}CHPh + OAc^-} \qquad (1)$$

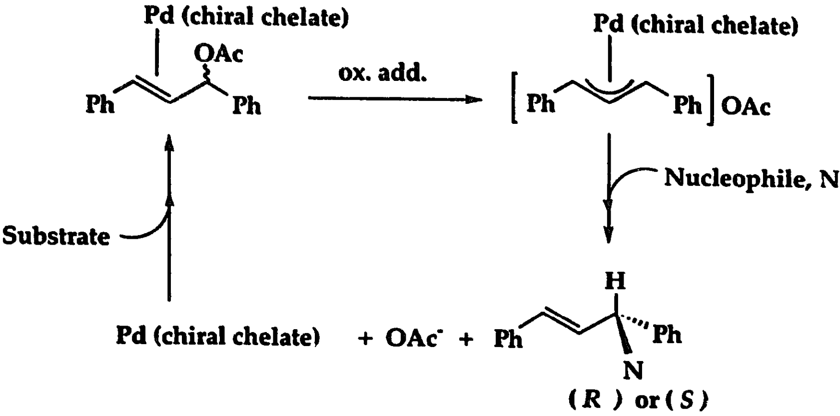
The reaction can be carried out in either THF or CH_2Cl_2 and is relatively slow. The chiral catalyst often consists of a precursor palladium complex containing a chiral chelating ligand; however, the catalyst can be generated in situ, from e.g. $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ or via the Pd(0) benzylidene acetone complex, $Pd_2\{(PhCH{=}CH)_2CO)\}_3 \cdot CHCl_3$, and a suitable number of equivalents of the chiral auxiliary. There seems to be little restriction on the donor atoms of the chelating chiral auxiliary, in that P–P [7], P–S [8,9], P–N [10], P–O [11], N–N [12,13] and N–S [14] combinations have all been successfully used, with enantiomeric excesses greater than 95% no longer unusual. QUINAP [10] is one such ligand.



QUINAP

The mechanism [1,4,10,15–19] of this palladium-mediated allylation reaction is now reasonably well understood. A chiral Pd(0) olefin complex, oxidatively adds the prochiral allylic acetate to afford an isolable η^3-allyl cationic compound of the form $[Pd(\eta^3\text{-}PhCHCHCHPh)(chiral\ chelate)]^+$, which is then attacked, in the rate-determining step, by the carbon or nitrogen nucleophile. If the nucleophile is added as a sodium salt, then sodium acetate is a by-product. If an amine is used, then acetic acid is produced and is usually neutralized by adding a base (Scheme 1).

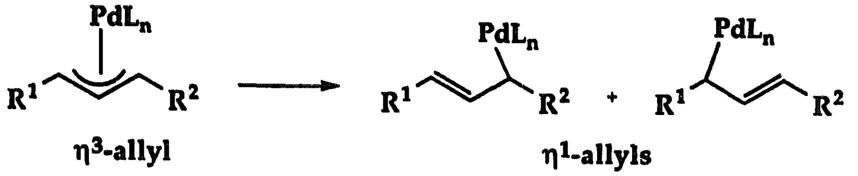
The carbon (or nitrogen) nucleophile attacks from the side remote from the metal and, since the initial oxidative addition proceeds with inversion, the complete reaction is often found to go with retention of configuration at carbon. The complications arising from the possibility that the Pd(0) complex acts as a nucleophile have been



Scheme 1. Mechanistic scheme for the catalytic allylation.

considered [18,19]. These fundamental steps are clear; however, the way in which the auxiliary transfers its chiral information is still somewhat clouded.

Another interesting aspect (and potential problem) in much of this synthetic allyl chemistry concerns possible allyl isomerization reactions. An η^3-π allyl can isomerize to an η^1-σ allyl counterpart:

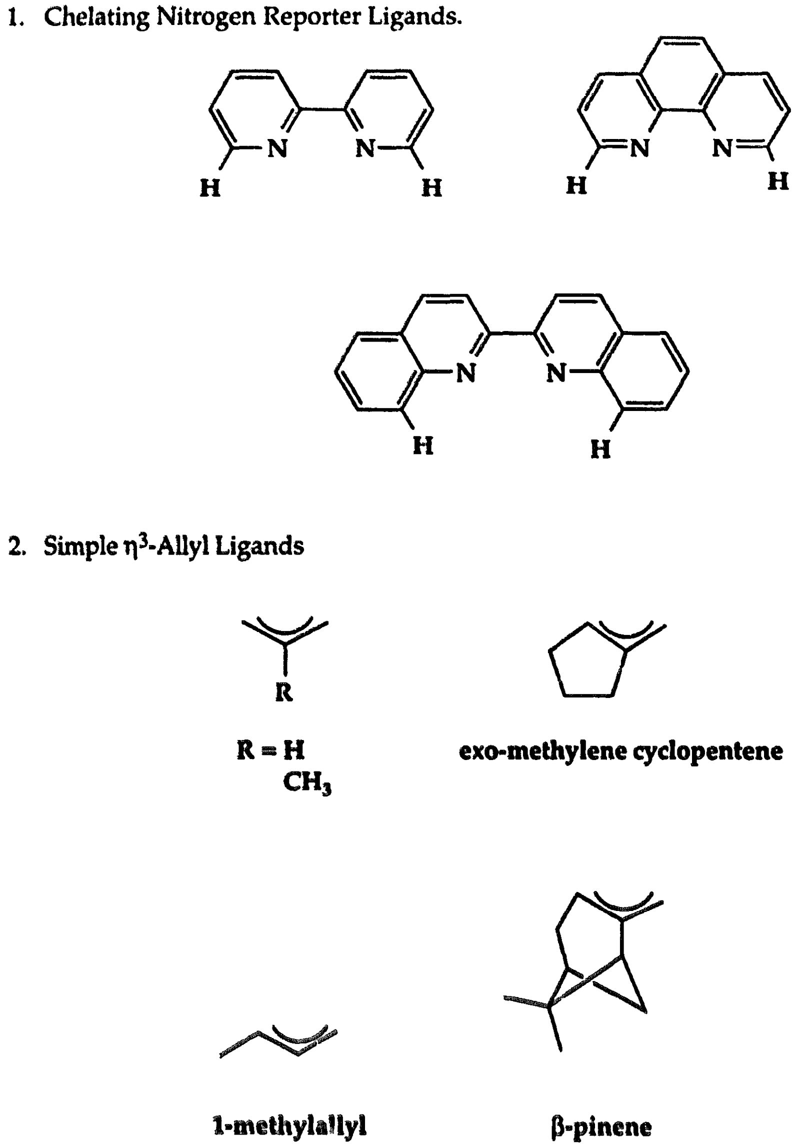


and then react further with a reagent, e.g. with CO, to give mixtures of products. The isomerization mechanism for allyl complexes has been a subject of research for many years with Faller [20] and Vrieze [21] amongst others [22], making seminal contributions. An η^3-η^1-η^3 mechanism is well established for many $Pd(allyl)L_1L_2^+$ cations [20–22] (both with and without L dissociation [23]). Unfortunately, much of this basic research involved achiral complexes of the relatively simple η^3-C_3H_5 and η^3-C_4H_7 allyl anions. Consequently, although much is known, in principle, one cannot readily extrapolate to more complex allyl-containing organic substrates.

2. Solution characteristics of chiral allyl complexes

2.1. Nitrogen chelates and 'reporter' ligands

Structural coordination chemistry is almost synonymous with X-ray diffraction work, and, given the abundant literature [24], Pd–allyl chemistry is no exception. It is possible to take a somewhat modified view of the word 'structure', in that one can often (but not always) assume that the composition and gross features of a chiral allyl complex are known. The more pertinent questions in enantioselective catalysis now address themselves to the subtle interplay between the chelate auxiliary and the coordinated substrate in one or more diastereomers in solution. One approach to



Scheme 2. Some *N,N*-ligands and η^3-allyl ligands.

mapping some of these finer structural features involves NMR 'reporter ligands' [25,26].

This involves incorporating a chelating ligand into an allyl complex such that several of its protons come close enough to different sections of the allyl moiety to afford measurable nuclear Overhauser effects (NOEs). If properly positioned, the protons of the chelate then 'report' via the intra-molecular (but inter-ligand) NOEs. If there are a sufficient number of NOEs one can triangulate the specific allyl ligand protons and thus build-up a 3-D solution picture. Since an observed NOE arises via the $^1H,^1H$ dipole–dipole relaxation, there is a $1/r^6$ dependence, where r is the separation of the two protons in question[2] [28]. Experience shows that, for metal

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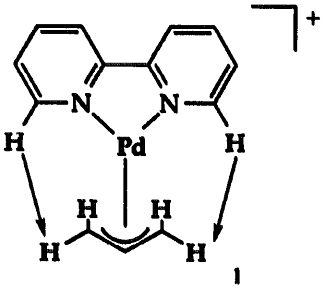
[2] The basic idea has recently been used in rhodium chemistry; see Ref. [27]

complexes with molecular weights in the range ca. 500–1000, one generally observes strong NOEs when the proton spins are ca. 2.5–2.7 Å apart, medium-to strong NOEs when the distances are ca. 2.7–3.0 Å and weak NOEs over 3.0 Å. In fact, measuring and interpreting NOEs can become somewhat complex for higher molecular weights and/or molecules which are tumbling slowly at low temperature; however, this is a general NMR problem and not related to allyl chemistry [28] (On several occasions the molecular weight of the compound under study, and/or slow motions due to low temperatures and higher viscosity of the solvent, resulted in NOE cross-peaks with the same phase as the diagonal. This proved to be the case in two recent studies on chiral ferrocene bis-phosphine complexes of Hg(II) and Ag(I), although not specifically mentioned in these papers; see Ref. [29].)

The cationic complexes [Pd(allyl)(*N,N*)]$^+$ [26,30] **1**–**3**, *N,N* = bipyridine (bipy), **1**, phenanthroline (phenan), **2**, and biquinoline (biquin), **3**, allyl = C_3H_5, C_4H_7, C_6H_9 and $C_{10}H_{15}$, see Scheme 2, proved to be useful test molecules. X-ray diffraction studies, [26,30,31] had shown that, for the bipy and biquin complexes, **1** and **3**, the chelate protons indicated by arrows, can 'intrude' differently into the allyl coordination sphere with the latter coming much closer.



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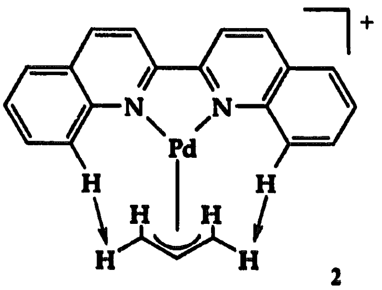
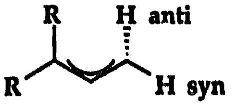


2

In the 2-D NOESY spectra, substantial inter-ligand NOEs were, in fact, observed, and, unexpectedly, some NOE selectivity. Owing to the somewhat less intrusive nature of bipy in **1**, the *N,N*-reporter proton could 'see' the syn protons (substantial NOE observed), but not the anti protons (an example for the $C_{10}H_{15}$ allyl, β-pinene is given in Fig. 1) [26,30]. 1-D NOE studies eventually showed that the NOE to the anti proton was measurable, but relatively small. The observed selectivity was postulated to stem from a specific bending of the anti proton out of the allyl plane, away from the Pd atom



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and thus away from the reporter proton, while the syn proton remains close to the allyl-plane. Theoretical work [32] and diffraction studies [33,34] revealed that this bending of the anti allyl proton is a general phenomenon for allyl complexes and is not specifically related to the presence of palladium.

This modest success using trivial chelating nitrogen ligands prompted a consideration of some structural aspects of the chiral spartein [35–37] and oxazoline [38]

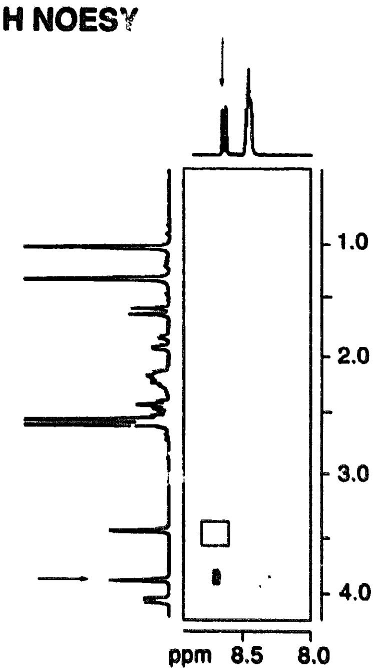
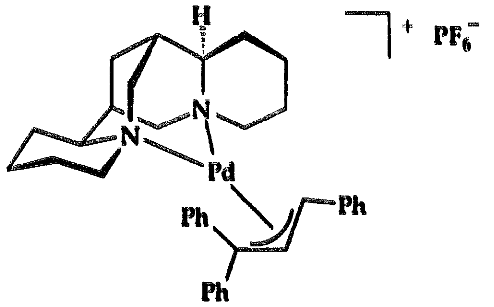


Fig. 1. Section of the ^{1}H 2-D NOESY of cation [Pd(η^3-β-pinene)(bipy)]$^+$, revealing a selective correlation from one *ortho*-bipy proton (horizontal axis with arrow) to the β-pinene *syn*-proton only (vertical axis with arrow). Note that there is no NOE to the *anti*-protons from the *ortho*-bipy proton (the square indicates where the NOE would have been).



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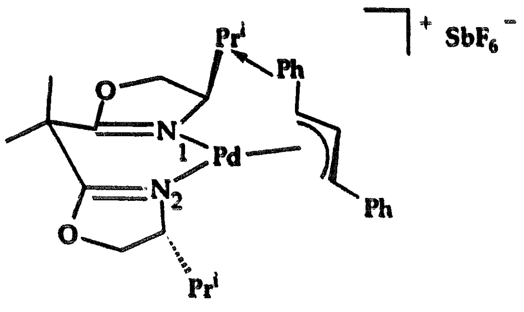
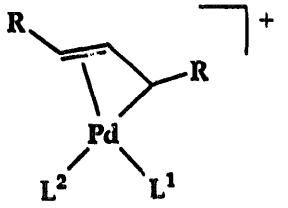


5

chelate complexes, **4** and **5** respectively, both of which contain successful nitrogen auxiliaries in connection with enantioselective allylic alkylation.

Analysis of the 2-D NOESY for **4** revealed short contacts between the *ortho*-phenyl protons of the allyl ligand and a variety of the aliphatic spartein ring protons. Close inspection of these data lead to (a) a 3-D solution picture for **4** and (b) the conclusion that the anti phenyl ring intrudes sufficiently such that there is a much higher activation barrier for rotation about the anti phenyl C(allyl)–C(ipso) bond [36]. This conclusion is supported by a natural abundance $^{13}C,^{13}C$ exchange study (see Fig. 2) [36].

The 2-D NOESY for **5** immediately pin-pointed the important steric interaction between the oxazoline-^{i}Pr and allyl-phenyl groups as indicated by the arrow in **5** (see Fig. 3) [39]. The related benzyl–oxazoline complex has also been studied [38]. These inter-ligand steric interactions represent an important source of chiral differentiation in these oxazoline compounds. An analysis of these, together with ^{13}C and X-ray data, permitted a prediction of the site of attack by the incoming nucleophile (and thus the absolute configuration of the product) [38]. Steric interactions selectively weaken the allyl-bonding to the Pd atom, thus creating an unsymmetrical electronic distribution in the allyl such that the complex develops η^1-alkyl- and η^2-olefin-type characteristics:



The η^2-olefin side is more electrophilic and is thus attacked preferentially by the incoming nucleophile. The structure above is somewhat extreme; however, there are an increasing number of complexes whose ^{13}C spectra reveal one terminal allyl signal at ca. 100–108 ppm, vide infra. This is clearly suggestive of olefinic character and in keeping with literature results for Pd–olefin complexes [40].

It is also noteworthy that, although the solid-state structure for **5** showed the six-membered chelate ring to be puckered, the 2-D NOESY spectrum revealed a facile ring inversion process in solution [38].

2.2. *NOE studies on chiral phosphine complexes*

Because the various *ortho*-phenyl protons of the allyl ligand in **4** and **5** could be used as NOE probes, it was only a small jump to envision the use of *ortho*-phosphine phenyl protons of the chiral chelating phosphine ligands as reporters. In many chelating phosphine chiral auxiliaries, e.g. CHIRAPHOS or BINAP, there are four non-equivalent P-phenyl substituents which make up the chiral pocket:

Assuming that one can assign the *ortho*-protons of rings A–D, 2-D NOESY methods should allow the 3-D solution structures for different allyl compounds to

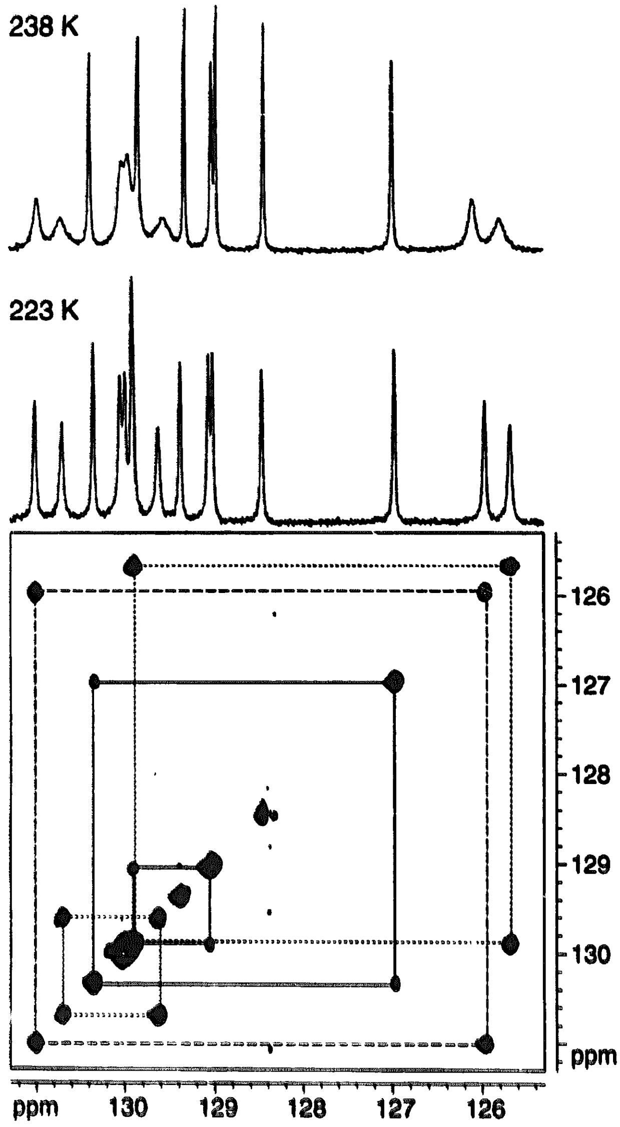
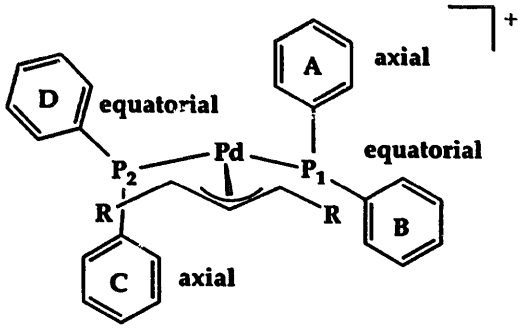


Fig. 2. Contour plot of the aromatic part of the 2-D ^{13}C exchange spectrum (125.9 MHz) recorded in $CDCl_3$ at 223 K showing exchanging *ortho*- and *meta*-carbons of the phenyl groups A^{anti} (full lines), A^{syn} (dashed lines) and C^{syn} (dotted lines). Top traces are conventional ^{13}C NMR spectra measured at 223 K (lower) and 238 K (upper).

be determined. This is an appealing prospect since many chelating phosphine auxiliaries are currently in use.

Naturally, the assignment of these phosphine ligand protons is more complicated and requires both $^{31}P,^{1}H$-correlation and NOE spectroscopy. The former measurement selectively finds the allyl protons trans to the P-atoms (the usual geometric dependence in square-planar complexes [41]), while simultaneously correlating two sets of *ortho*-protons to a single ^{31}P-spin. The latter spectrum differentiates between the two *ortho*-proton sets of one ^{31}P-spin via proximity effects to the allyl ligand. It is often useful to add a $^{13}C,^{1}H$-correlation so that we can assign the allyl-^{13}C spins via the assigned ^{1}H-allyl protons (and sometimes the protons via the ^{13}C signals!).



Structural fragment showing a possible arrangement of the phenyl groups in a chiral (*R*)-BINAP allyl complex.

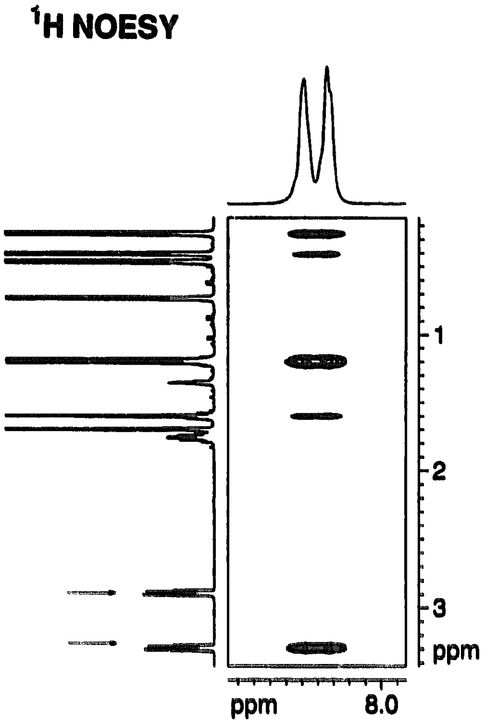
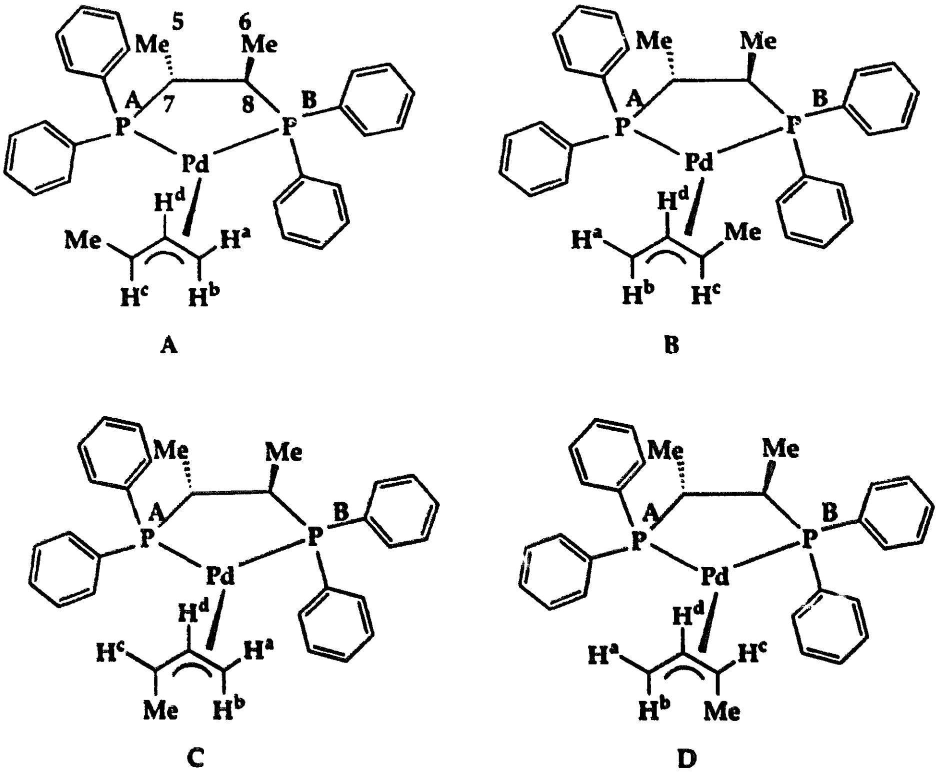


Fig. 3. Section of the ^{1}H 2-D NOESY of cation **5** revealing the selective cross-peaks from the *ortho*-protons of one allyl phenyl group (horizontal) to one of the two ^{i}Pr methine protons (lower left with arrows). There are also two cross-peaks to two of the four ^{i}Pr-methyl groups (500 MHz, CD_2Cl_2).

One complicated assignment problem concerned the CHIRAPHOS butenyl Pd(II) complex $[Pd(\eta^3\text{-}CH_3CHCHCH_2)(S,S\text{-}CHIRAPHOS)]CF_3SO_3$, **6** [42]. Complex **6** exists in four isomeric forms, A–D, two diastereomeric and two geometric, in the ratio 10:10:1.7:1 respectively, see Scheme 3.

The fragments A and B refer to the two different coordinated faces, whereas A and C indicate the syn and anti arrangements of the methyl group with respect to the central allyl proton.

In this mixture, the ^{31}P,^{1}H-correlation pin-points both the allyl protons and the allyl methyl signals (see Fig. 4), whereas the ^{1}H NOE spectroscopy (Fig. 5) allows a differentiation between the coordinated faces in A and B. Specifically, the distinction

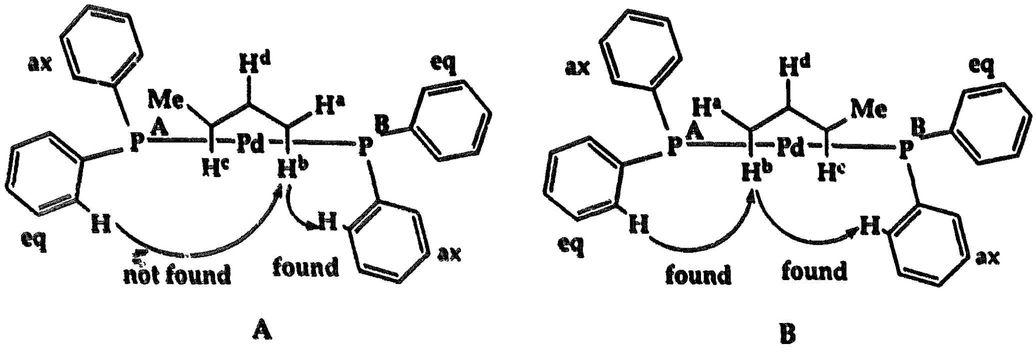


Scheme 3. Four isomers of [Pd(η^3-$CH_3CHCHCH_2$)(*S,S*-CHIRAPHOS)]CF_3SO_3, **6**.

between these two isomers could be made based on the number of strong NOEs to the allyl proton. We show this for H^b below and for H^a, separately, in Fig. 5.

In isomer A there is only one strong interaction, whereas in isomer B two strong NOEs are found. Indeed, this empirical tool (one vs. two NOEs) has proven useful in subsequent work. The syn and anti isomers can be distinguished via intra-allyl NOEs and proton–proton coupling constants. Clearly, a correct structural analysis of such a mixture of diastereomers is important to the understanding of the mechanistic side of the enantioselective allylic alkylation.

Although CHIRAPHOS is an interesting ligand, BINAP [43,44] (and BIPHEMP [45])-type auxiliaries have become quite popular. The (*R*)- and (*S*)-BINAP *β*-pinene allyl complexes [Pd(η^3-$C_{10}H_{15}$){BINAP}]CF_3SO_3 could easily be prepared [40].



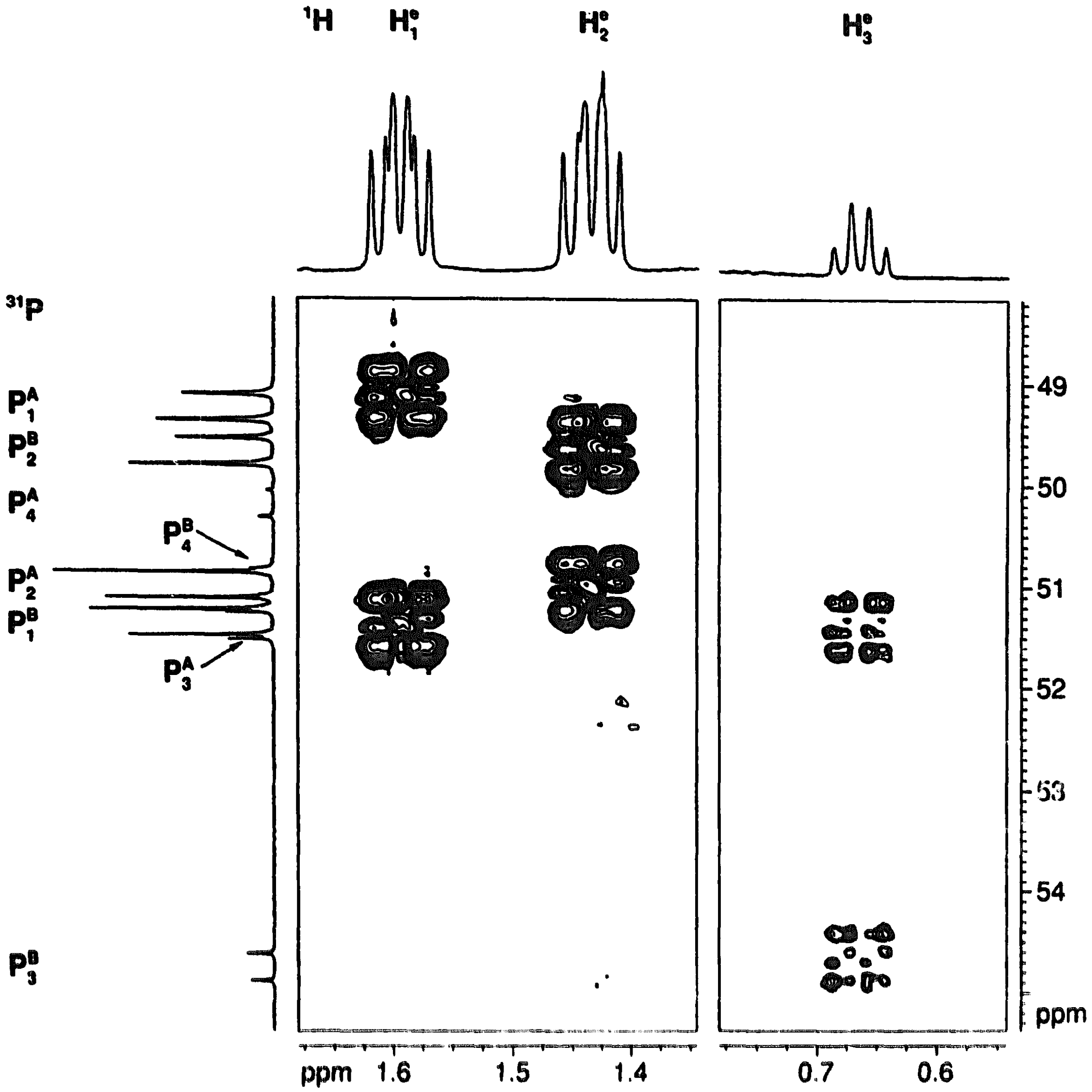


Fig. 4. Section of the ^{31}P,^{1}H correlation showing three of the four allyl methyl groups correlated to their respective phosphorus resonances. Note that (a) the ^{31}P AB spin system for the fourth isomer is visible (P^A4 and P^B4 are noted) and (b) there is no marked cis-trans selectivity in the coupling to the allyl methyl group in that both ^{31}P spins of each isomer couple to this CH_3 group.

This pinene ligand coordinates only one face [26,30], that remote from the $C(CH_3)_2$ moiety (see Scheme 2), thus eliminating the problem of diastereomers; however, as it is an asymmetric moderately-sized allyl, the ^{1}H-spectra are more complex. Nevertheless, the spectra for both the (*R*)- [46] and (*S*)-BINAP [47] analogs as well as the (*S*,*S*)-CHIRAPHOS [48] β-pinene complex could be assigned. A comparison of the BINAP and CHIRAPHOS structures, based on the NOE work together with X-ray crystallography and MM2* calculations [48,49], showed that the phosphorus phenyl groups of the former bidentate ligand intrude more into the sphere of the allyl ligand than do those of the latter ligand. Moreover, the equatorial phenyl groups intrude more into the sphere of the allyl ligand than do the axial phenyl groups.

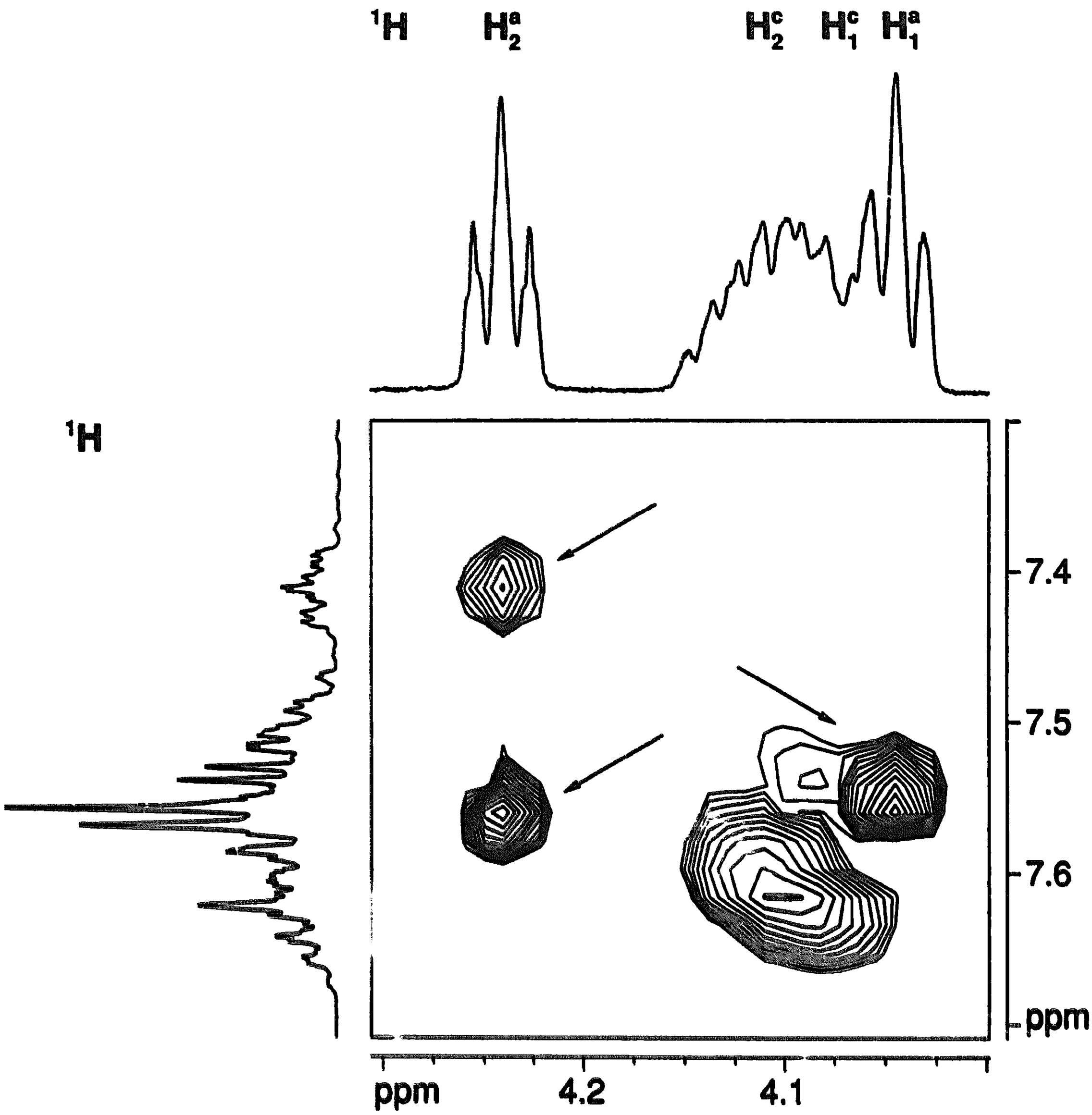
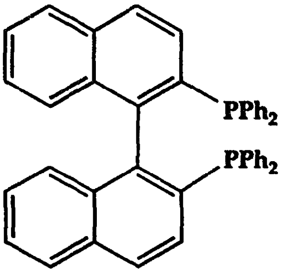
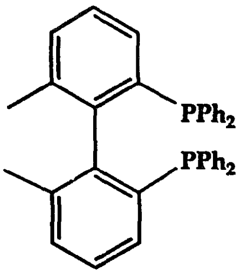


Fig. 5. Section of the ^{1}H 2-D NOESY revealing selective correlations from the H^a allyl protons of the diastereomeric isomers 1 and 2. There are two moderate-to-strong interactions from the *ortho*-PPh_2 protons to H^a2 but only one such interaction to H^a1, thereby helping to distinguish between these two diastereomers.

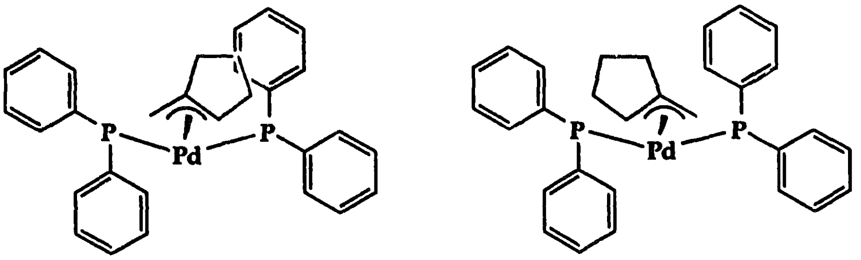
In addition, one finds differences in the structures of the chiral pockets between coordinated BINAP and (*S,S*)-CHIRAPHOS. The former has a phenyl array with more pronounced axial and equatorial character, whereas in the latter, the phenyl rings each occupy one of the four quadrants. Given all of these differences, but particularly the more intrusive nature of the BINAP ligand, one can rationalize the different diastereomeric ratios observed [49] for the two η^3-*exo*-methylenecyclopentene complexes $[Pd(\eta^3\text{-}C_6H_9)((R)\text{-BINAP})]CF_3SO_3$, 7, ca. 8:1 and $[Pd(\eta^3\text{-}C_6H_9)((S,S)\text{-CHIRAPHOS})]CF_3SO_3$, 8, ca. 6:4 (see Scheme 4). The more intrusive equatorial BINAP substituent in the minor isomer of 7 interacts with the



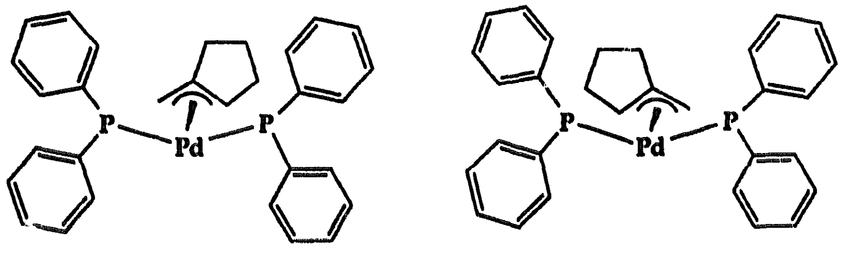
BINAP



BIPHEMP



7 (BINAP), major isomer **7 (BINAP), minor isomer**



8 (CHIRAPHOS), major isomer **8 (CHIRAPHOS), minor isomer**

Scheme 4. Molecular fragments showing the coordination of the η^3-*exo*-methylenecyclopentene allyl in the two pairs of diastereomers from [Pd(η^3-C_6H_9)(*R*-BINAP)]CF_3SO_3, 7, and [Pd(η^3-C_6H_9)(*S*,*S*-CHIRAPHOS)]CF_3SO_3, 8. The observed diastereomeric ratios for [Pd(η^3-C_6H_9)(*R*-BINAP)]CF_3SO_3, 7, and [Pd(η^3-C_6H_9)(*S*,*S*-CHIRAPHOS)]CF_3SO_3, 8, are ca. 8 : 1 and ca. 6 : 4 respectively.

atoms of the five-membered ring thus destabilizing this diastereomer. In the complex of the less intrusive CHIRAPHOS, these steric interactions are not as pronounced.

For several BINAP complexes it was possible to compare the solution structures (obtained with the help of MM2* calculations and NOEs) with those determined via X-ray diffraction; one such comparison [48,49] is shown in Fig. 6.

Recent work by Togni and co-workers [50] has shown that modifications of the ferrocene-based ligand JOSIPHOS, 9 (see Scheme 5) afford excellent chiral auxiliaries.

As 9 is not a C_2-type chelating ligand (indeed has no symmetry element) the β-pinene allyl complex [Pd(η^3-$C_{10}H_{15}$)(9a)]CF_3SO_3, 10, exists as two rotational iso-

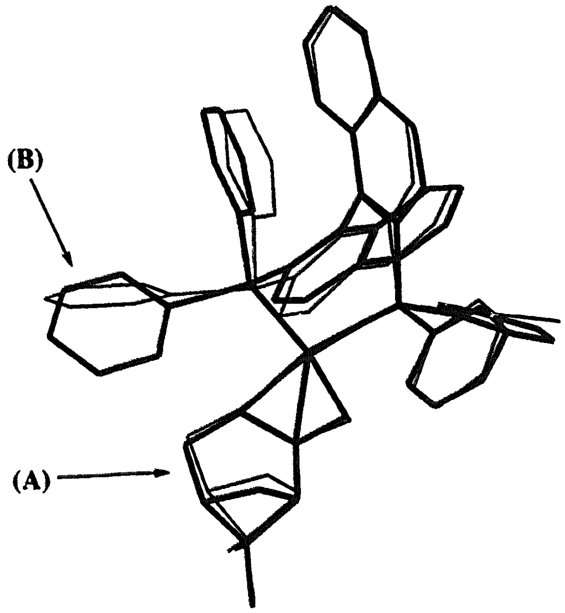
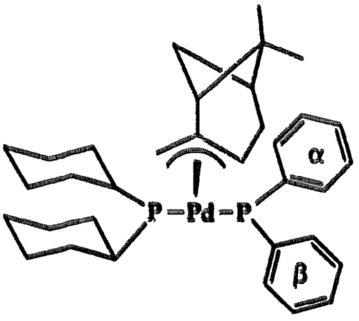
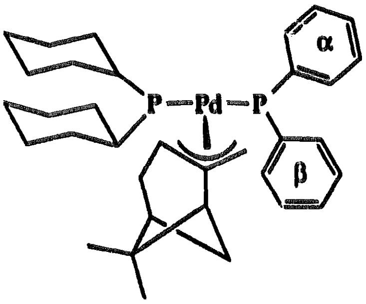


Fig. 6. Comparison of the X-ray structure (bold) for [Pd(η^3-$C_{10}H_{15}$){(S)-BINAP}]CF_3SO_3 with the corresponding calculated structure. Note that the difference at the equatorial phenyl ring of P^A (B) is marked, but that the agreement at the pinene allyl ligand (A) is good.

mers. With respect to a coordination plane defined by the Pd and two P atoms, there are two possible orientations for the η^3-$C_{10}H_{15}$ ligand; fragments of these structures are shown below:



major isomer

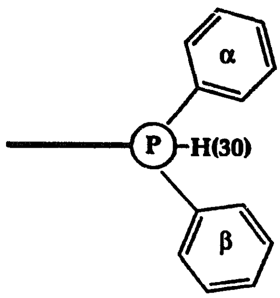


minor isomer

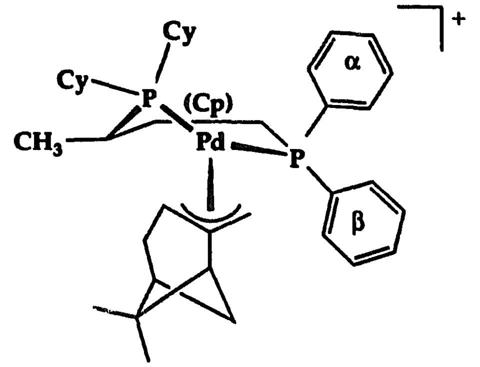
View from behind the allyl towards the Pd. The $C(CH_3)_2$ bridge of allyl is remote from the Pd atom (charges omitted).

The major/minor ratio is ca. 10:1, and we note that the major isomer (exo) has the larger part of the allyl hydrocarbon remote from the two cyclohexyl groups and that the methine allyl carbon is pseudo-trans to the PCy_2 moiety.

The chiral pocket in **10**, as determined via its ^{1}H-NOESY spectrum, differs from that of a BINAP in that the two phenyls do not occupy pseudo-axial and equatorial positions. Based on the strong NOEs from both sets of *ortho*-phenyl protons to one of the upper Cp protons, H(30), the substituted Cp ring approximately bisects the C(α)–P–C(β) angle, i.e.

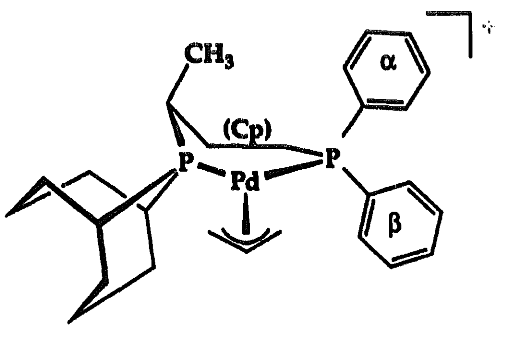


The six-membered *P,P*-chelate ring is in the form of a skew-boat, with the CH_3 of the chiral side-chain lying roughly parallel to the upper Cp-ring as shown:



Fragment of coordinated **9a** in the pinene complex **10**.

This conformation, which also exists in the solid-state structure of $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{9a})]CF_3SO_3$, **11a** [51], places the CH_3 close to an upper Cp ring proton and has the two cyclohexyl groups away from the lower $\eta^5\text{-}C_5H_5$ ring (no NOE between these). This ring conformation can change and for $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{9d})]CF_3SO_3$, **11d**, the conformation is

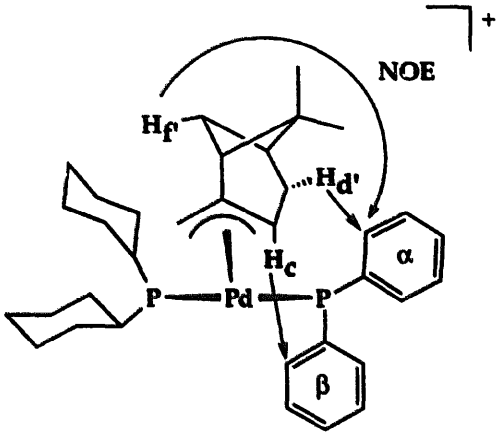


fragment of **11d**

In **11d** the CH_3 group is above the upper Cp plane and close to the α-P-phenyl group (there is an NOE from the methyl to the *ortho*-protons of this ring) [51].

The JOSIPHOS phenyl groups in the β-pinene complex $[Pd(\eta^3\text{-}C_{10}H_{15})(\mathbf{9a})]CF_3SO_3$, **10** [52], intrude more into the coordination sphere of the pinene-allyl than in the analogous complexes $[Pd(\eta^3\text{-}C_{10}H_{15})(S\text{-BINAP})]CF_3SO_3$, and [Pd-

$(\eta^3\text{-}C_{10}H_{15})$(*S,S*-CHIRAPHOS)]$CF_3SO_3$. Under comparable conditions one finds strong NOEs from the JOSIPHOS phenyl groups to the allyl protons H^c, $H^{d'}$ and $H^{f'}$, see Fig. 7.

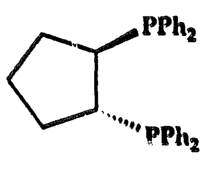


fragment of $[Pd(\eta^3\text{-}C_{10}H_{15})(\mathbf{9a})]\ CF_3SO_3$
showing NOE's

For these same protons in the BINAP and CHIRAPHOS complexes one observes sometimes strong but often moderate-to-weak NOEs to these protons from the corresponding *ortho*-phenyl protons. Clearly, in terms of its ability to intrude into the allyl coordination sphere, JOSIPHOS is a 'big' ligand. The nature of, and the differences between, the chiral pockets of a JOSIPHOS and, for example, a CHIRAPHOS, are important characteristics of these ligands in connection with their effectiveness (or lack thereof) in homogeneous catalysis, in general.

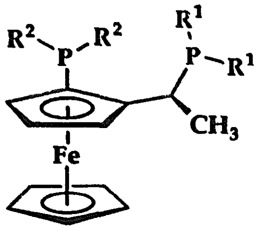
2.3. MM2 and the chiral pocket*

Is size the only important characteristic? NOE results for the ligand DPPCP ({*R*}-1,2-bis-diphenylphosphino-cyclopentane), **12**, based on the cation $[Pd(\eta^3\text{-}PhCHCHCHPh)(\mathbf{12})]^+$, **13**, suggest that this is not an intrusive ligand [53].



12 = (R) - DPPCP

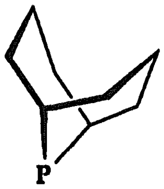
Nevertheless, DPPCP is only slightly less effective in the allylic alkylation, in terms of enantioselectivity, than the relatively large analogous BIPHEMP and BINAP complexes, with ee values for all three in the range 85–90% [53]. In addition, the



9

	R^1	R^2
9a	cyclohexyl	phenyl
9b	phenyl	cyclohexyl
9c	phenyl	phenyl
9d	phobyl	phenyl

These ligands are S (on carbon) and R (on iron)



For the "phobyl" ([3.3.1]-9-phosphabicyclonon-9-yl, C_8H_{14}) complex there are two fused six-membered rings.

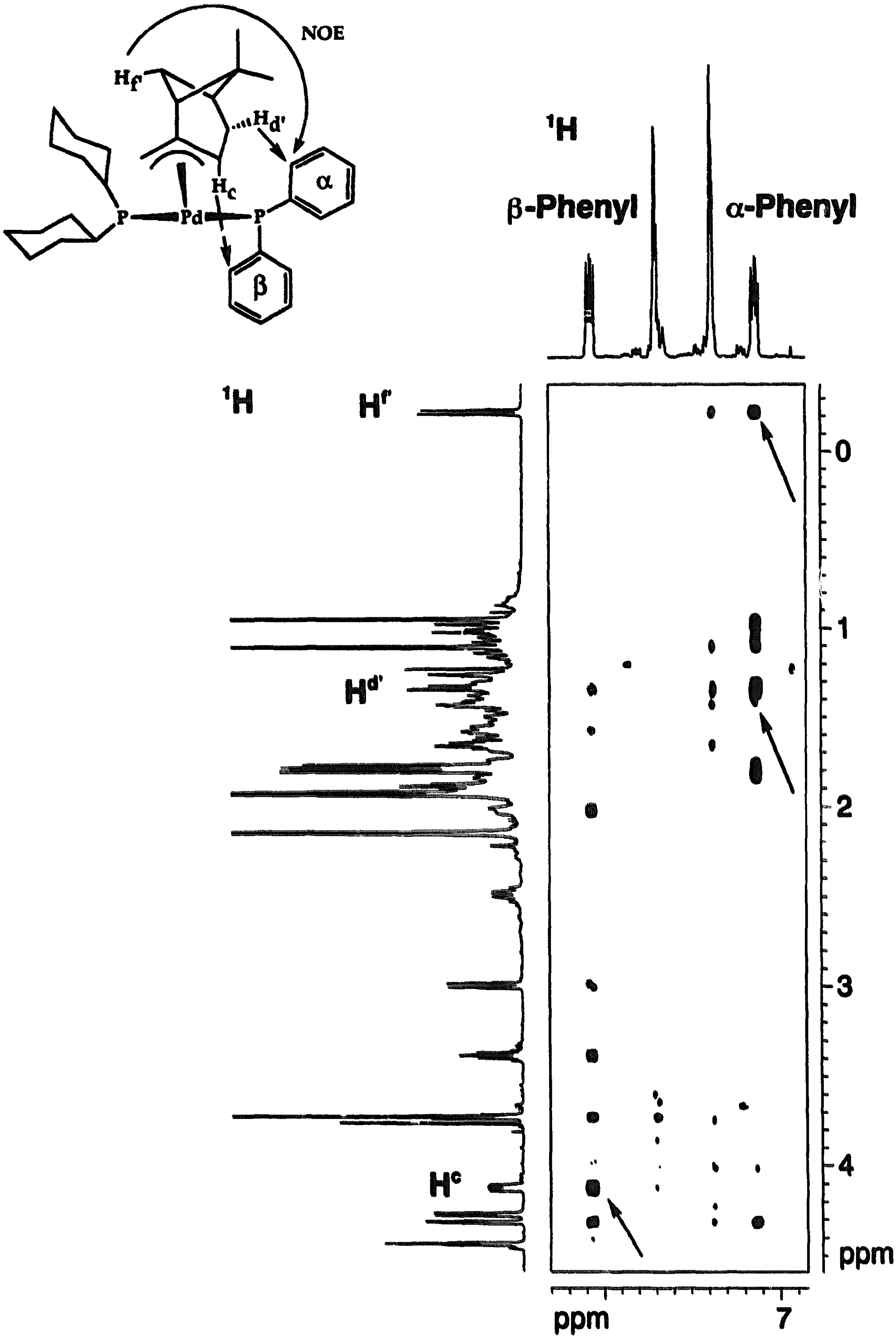
Scheme 5. Some JOSIPHOS-type ligands.

ligand DPPCP has been used successfully in the enantioselective cross-coupling reaction with nickel [54]. Perhaps size is not everything.

Because the larger BINAP and smaller DPPCP complexes were almost equally effective, the chiral pocket was investigated using MM2* [55]. The starting point was a series of structures found via the Cambridge Crystallographic Structure Data Base (CCSDB) whose reference codes are as follows:

The CCSDB search was restricted to five- and seven-membered chelating phosphine rings of metal complexes. The numbers of structures found for each of the four structural types defined as R55, R5, R75 and R7 (R = ring; the second number indicates the second fused ring) were:

Arbitrarily, the four dihedral angles, P–M–P–C(ipso) were taken as a description of one aspect of the chiral pocket, and these 16 experimental angles are shown in Table 1.


NOE
Hf'
Hd'
Hc
α
β
P
Pd
P
¹H
β-Phenyl
α-Phenyl
¹H
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Hd'
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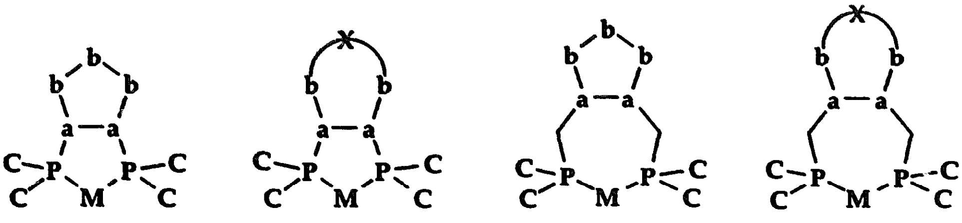
2
3
4
ppm
ppm
7

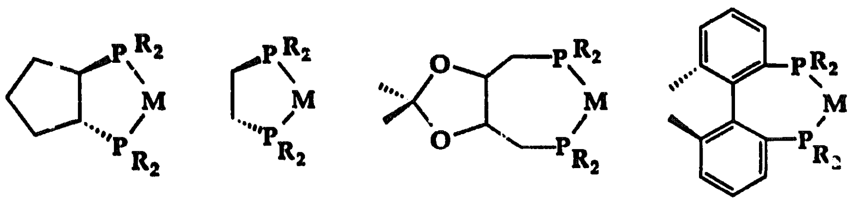


9 **10** **18** **20**

Numbers = structures found; M = any transition element; a = carbon; b = C, N, O atoms.

Histograms of these dihedral angles for two of the four queries, R7 and R75, are shown in Fig. 8. It is sufficient to note from the figure and Table 1, that there is a large spread of angles for the R75 family, and a much smaller distribution for R5 and R55, with R55 narrower than R5 (histograms not shown). The distribution for the R7 family is dimodal (pseudo-axial and pseudo-equatorial phenyl groups), with well-separated modes and a narrow distribution about each mode. This reflects the presence of a preferred conformation in the solid-state.

All the ring conformations for the complexes $PdCl_2$(chelate) were now calculated [53] using an extension to the MM2* force-field found in MacroModel 4.5, where the chelate has been restricted to the four types



(these four are somewhat related to the types R55, R5, R75 and R7 respectively). As previous MM2* calculations for allyl complexes of Pd(II) were satisfactory [46–49], the allyl was omitted in these new calculations in order to concentrate on the chiral auxiliary. To validate the force-field the conformations were calculated with the help of a Monte Carlo (MC) scheme. Table 1 also shows the mean values for the calculated dihedral angles, P–M–P–C(ipso). There is good general agreement between the angles found in the CCSDB search and the MC calculations. Note that both the mean values and the relative sizes of the standard deviations are reproduced. This suggests that the calculations are finding legitimate angular distributions. It is again clear that the R7 family has a more restricted set of angles, thus indicating a more rigid chiral pocket. From both sources, the CCSDB and the calculations, one finds that BIPHEMP (BINAP) and the DPPCP angles are relatively limited, but quite different, so that a coordinated substrate can expect well-defined, relatively rigid, but different chiral pockets in both cases. This may be related to the catalytic observations, i.e. both BIPHEMP and DPPCP function reasonably well.

Fig. 7. Section of the ^1H 2-D NOESY for $[Pd(\eta^3\text{-}C_{10}H_{15})(9a)]CF_3SO_3$ indicating the selective NOEs from the *ortho*- α and β ring protons of the PPh_2 moiety to various aliphatic protons of the $C_{10}H_{15}$ allyl ligand. Specifically note the three arrows which indicate the cross-peaks arising from (top-to-bottom) $H^{f'}$, $H^{d'}$ and the methine allyl proton H^c.

Table 1
Mean values for the four torsional angles P–M–P–C_{ipso}

R55	Experiment	135(5)	98(5)	124(5)	107(4)
	MC Calc.	133(9)	100(9)	122(8)	110(7)
R5	Experiment	143(8)	94(9)	129(6)	108(7)
	MC Calc.	140(11)	95(9)	127(5)	110(6)
R75	Experiment	173(6)	63(10)	135(14)	105(14)
	MC Calc.	167(15)	71(18)	143(16)	94(25)
R7	Experiment	164(7)	76(7)	151(9)	91(9)
	MC Calc.	173(9)	71(9)	156(13)	88(9)

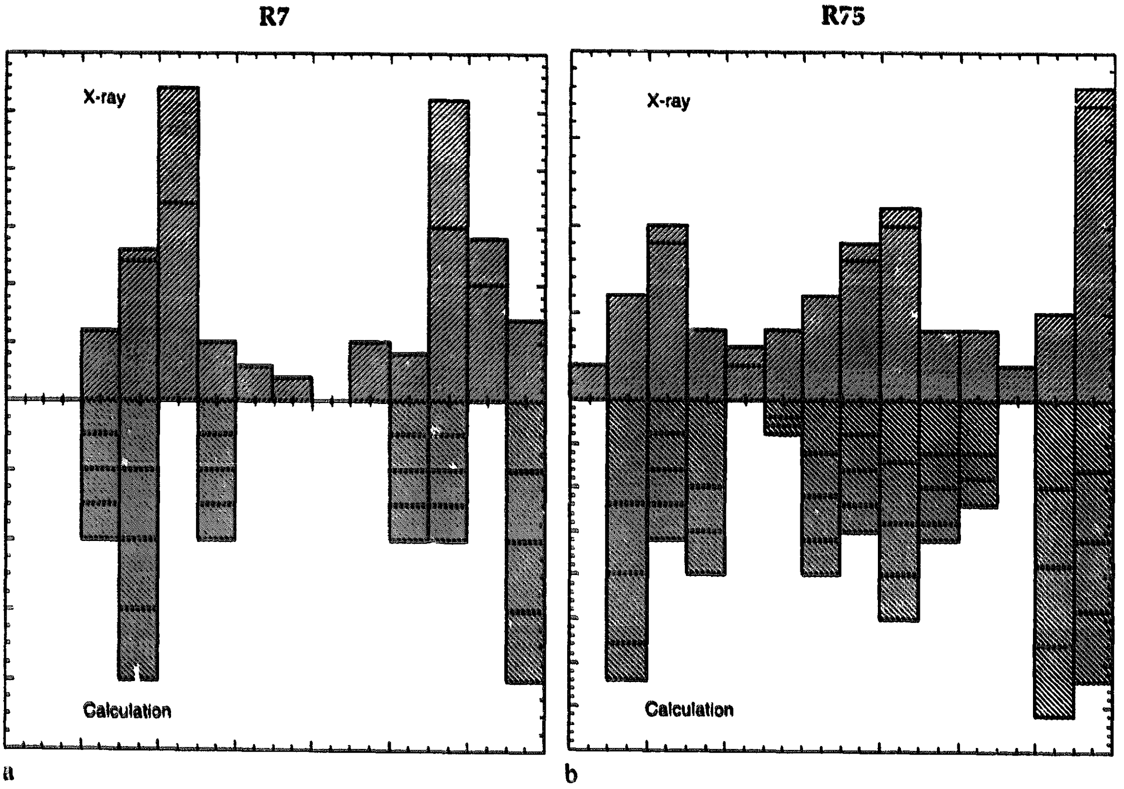


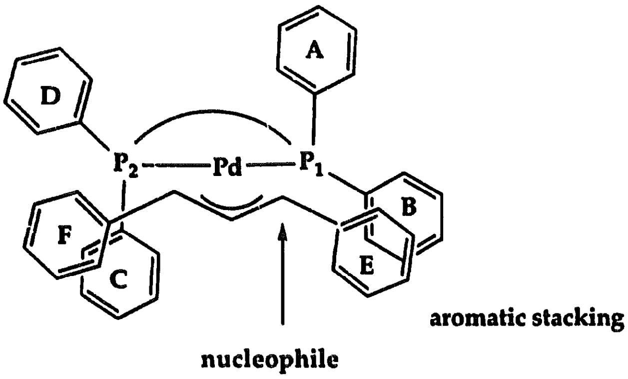
Fig. 8. Histograms showing comparisons for the P–M–P–C angles observed (X-ray) and calculated (MM2*), for the R7 and R75 classes of chelate.

2.4. Phenyl–phenyl stacking

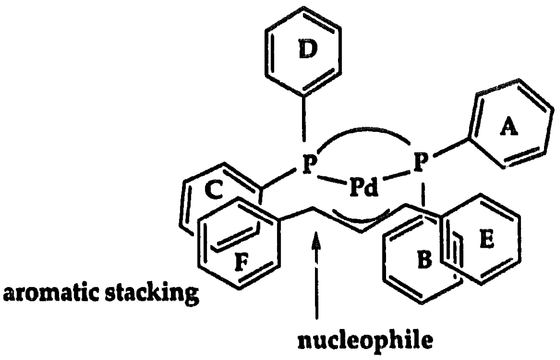
Apart from shape and rigidity of the chiral pocket, what other subtle structural effects can influence the ee and/or the site of attack? In the NOESY spectrum of the 1,3-diphenylallyl cation $[\mathrm{Pd}(\eta^3\text{-PhCHCHCHPh})(\{R\}\text{-DPPCP})]^+$ [53], **13**, there are normal, strong intra-allyl NOEs from the terminal allyl protons to their respective allyl *ortho*-phenyl protons in rings E and F. There is also a strong inter-ligand 'ring–ring' NOE from the *ortho*-protons of the pseudo-axial ring C to the *ortho*-

protons of the allyl phenyl ring F. However, there is an unexpected feature in that one finds little or no NOE between the rings B and E. We believe that the rings B and E stack (see Scheme 6) and presumably move synchronously. Perhaps the allyl phenyl ring F finds more space between the C and D rings and can thus move more freely, but this may not be possible for the B and E phenyls.

For the analogous 1,3-diphenyallyl [Pd(η^3-PhCHCHCHPh)({*S*}-MeO-BIPHEMP)]$^+$ [53], **14**, two isomers exist in solution in the ratio 4.3:1.0 (for the methyl BIPHEMP analog this ratio is 3.8:1.0, and we shall return to these isomers in Section 2.5). For the major isomer of **14a**, there is only a very small NOE between the C and F phenyl rings (see Scheme 6) again suggesting ring stacking. Potentially important is the observation that, as with **13**, the site of attack in the catalytic allylic alkylation of **14** (based on the absolute configuration of the observed organic product) corresponds to the terminal allyl carbon closest to the stacking. Further,



Fragment of the DPPCP complex 13 showing the stacking of rings B and E plus the site of nucleophilic attack (based on the observed product).



Fragment of the major isomer of the MeO-BIPHEMP complex 14a, showing the stack of rings C and F plus the site of the nucleophilic attack (five-membered chelate ring, charge and anion omitted for clarity).

Scheme 6. Stacking of 1,3-diphenylallyl ligands.

recent ^{13}C evidence [53] suggests that the stacking is associated with a relative weakening of the Pd–C (terminal allyl carbon) bond.

This phenyl–phenyl stacking has also been observed [51] in both the solid and solution states in some JOSIPHOS complexes and, consequently, may be an important, but subtle, structural feature. Obviously its relevance is specific for the 1,3-diphenyl allyl ligand when the auxiliary has P-phenyl substituents. Currently, this phenyl ring-stacking is best considered as the compromise that the complex makes in order to accommodate the two proximate phenyl groups. Moreover, its existence implies that 'testing' new chiral auxiliaries using a 1,3-diphenylallyl substrate does not necessarily reflect on the general utility of the new auxiliary, but rather how well it 'tunes' to the particular allyl intermediate.

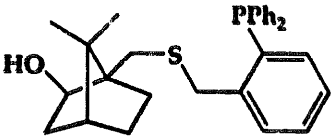
2.5. 2-D exchange NMR dynamics of the η^3-C_3H_5 and η^3-PhCHCHCHPh ligands

Scheme 7 shows a generalized η^3-η^1-η^3 mechanism for the inter-conversion of allyl rotational isomers via exchange of the allyl face, together with a mechanism for exchange of syn and anti substituents.

In route 1 an initial η^3-η^1-isomerization could give a three-coordinate 'T' [56] (or solvated four-coordinate) complex. Isomerization of one T-shaped isomer to another, rotation around the Pd–C bond and then reformation of the η^3-isomer leads to a new rotational isomer. In route 2 the η^1-isomer can rotate around the sp^2–sp^3 C–C bond and then reform the η^3-isomer. This leads to face change together with syn–anti isomerization.

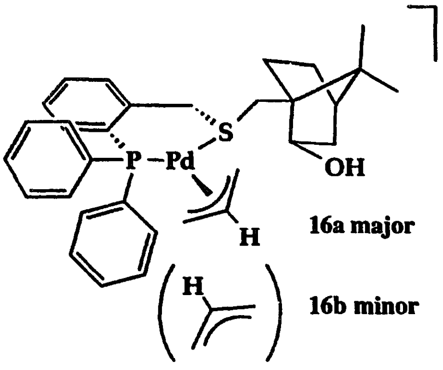
One can also envision variations on these themes in which one of the ligand donors dissociates first and then the allyl isomerizes; this has been shown by Gogoll et al. [57] to be plausible in some chelating pyrimidine complexes and by Faller et al. [23] in a chiral amine complex. Presumably, for a homogeneous catalyst based on a chiral auxiliary, dissociation of one donor would destroy the chiral pocket sufficiently such that the enantioselectivity would be insufficient.

Although many studies have dealt with the mechanisms of allyl isomerization, there is little on chiral chelating complexes. The existing literature concentrates primarily on the simple C_3H_5 and 2-methylallyl compounds. It has become clear that these small allyl ligands are poor models relative to the larger 1,3-diphenylallyl analogs and the allyl chemistry of the *P,S-exo*-norborneol ligand, **15**, is illustrative in this respect.



15

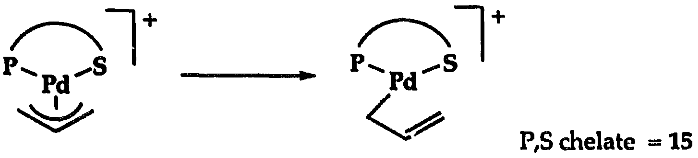
The two cationic allyl complexes $[Pd(C_3H_5)(15)]^+$, **16**, and $[Pd(PhCHCHCHPh)(15)]^+$, **17**, were readily available and a solid-state structure of the former was determined [58]. Both **16** and **17** exist as mixtures of isomers in solution. Complex **16** exists in the two forms shown:



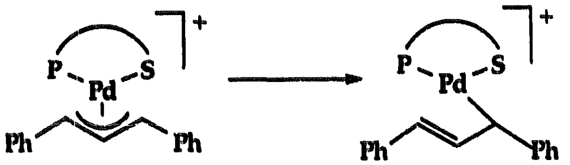
Two rotational isomers of 16

and **17** in four forms (both rotational and syn-anti isomers, see Scheme 8).

The allyl isomerization equilibria for **16** and **17** could be followed by ^1H 2-D exchange spectroscopy [58], since these interconversions are relatively slow, normally [59] ca. 0.1–1.0 s^{-1}. For **16** the exchange is selective and the allyl opens trans to the stronger P-donor, i.e. there is electronic control.



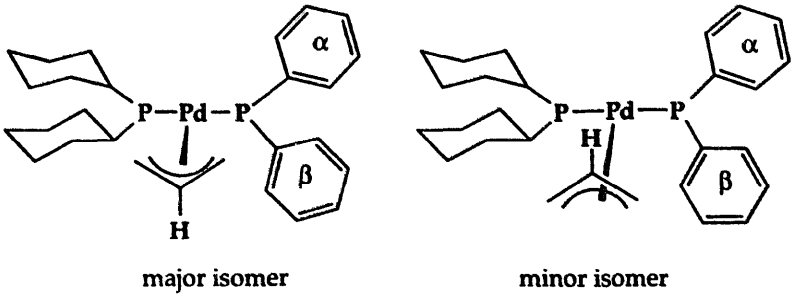
As shown below, and in more detail in the bottom half of Scheme 8, for **17** the 1,3-diphenylallylallyl opens trans to the thioether, i.e. there is steric control [58].



η^3-η^1 for 17

Perhaps the η^3-η^1 process trans to the P-donor is fast, but reversible for **17**, so that we only have isomerization when the allyl opens away from the larger PPh_2 moiety. In any case, the 1,3-diphenylallyl ligand is simply too big to be comfortable cis to the PPh_2 fragment. These results for compounds **16** and **17** show that the C_3H_5 anion is a poor model for the PhCHCHCHPh anion. Fig. 9 shows an additional advantage of 2-D exchange spectroscopy. The two syn–anti minor isomers are in such low abundance that one would not have thought them to be chemically pertinent without the observed strong exchange cross-peaks indicating an equilibrium.

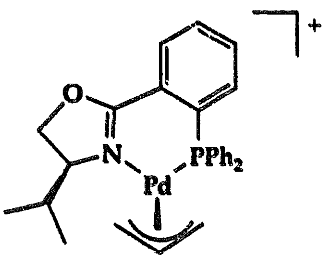
Based on the results for **16** and **17** one might tend to think that the isomerization of the smaller C_3H_5 allyl is always electronically controlled, whereas that for the 1,3-diphenylallyl compound is dominated by steric effects. For the two rotational isomers of the JOSIPHOS complex $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{9a})]^+$, **11a**, abbreviated below, a selective η^3-η^1-η^3 isomerization involving opening of the Pd–C bond cis to the PCy_2 and trans to the PPh_2 moiety was observed [52].

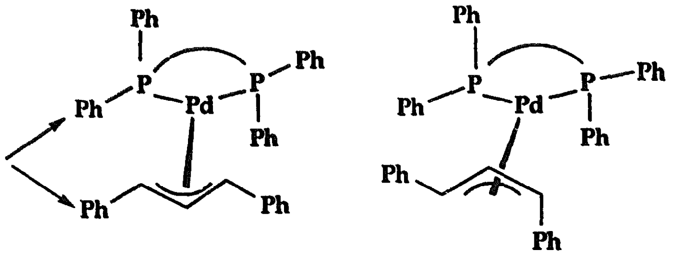


Abbreviated rotational isomers of $[Pd(\eta^3-C_3H_5)(9a)]^+$ (see Scheme 5 for JOSIPHOS).

This is an interesting observation in that the trans influence of the PPh_2 aryl phosphine moiety is generally smaller than that for the alkyl phosphine PCy_2 donor. As the bulk of the PCy_2 group may play a role, the allyl isomerization for the four $\eta^3-C_3H_5$ palladium complexes $[Pd(\eta^3-C_3H_5)(JOSIPHOS)]^+$, **11a–d**, (see Scheme 5), with the JOSIPHOS ligands **9a–9d**, were studied. These complexes which differ in R^1 and R^2, and thus have different electronic and steric effects, include ligands **9a** and **9b** in which the R^1 and R^2 substituents have been 'exchanged'. The results are summarized in Scheme 9 and Fig. 10 shows a section of the corresponding ^1H 2-D spectrum for $[Pd(\eta^3-C_3H_5)(\mathbf{9b})]CF_3SO_3$, **11b**. The lower left corner of Fig. 10 shows exchange between two central protons, H^2. The remainder of the spectrum shows the specific, well-resolved exchange cross-peaks (filled circles) for the eight protons, H^1 and H^3, four from each isomer. The open circle cross-peaks arise from NOE. Analysis of these results shows that there is selective formation of an η^1-allyl cis to the PPh_2-moiety, away from the PCy_2 fragment. Consequently, for $[Pd(\eta^3-C_3H_5)(\mathbf{9b})]^+$, **11b**, as for $[Pd(\eta^3-C_3H_5)(\mathbf{9a})]^+$, **11a**, the Pd–C (terminal) bond which is cis to the PCy_2 fragment opens, i.e. steric control. For the cations $[Pd(\eta^3-C_3H_5)(\mathbf{9c})]^+$, **11c**, with four Ph-substituents, and $[Pd(\eta^3-C_3H_5)(\mathbf{9d})]^+$, **11d**, with 'phobyl' and Ph substituents, we observe no η^3-η^1-η^3 isomerization at ambient temperature. The result for **11d** is pertinent in that, although the cyclic phobyl group is expected to be a donor comparable with other tertiary phosphines with aliphatic substituents, it is a pinned-back fragment, and thus smaller. The absence of isomerization in the phobyl derivative, **11d**, suggests that steric and not electronic effects, are responsible for the selective η^3-η^1-η^3 isomerization in these small C_3H_5 allyl complexes.

In an elegant study on allyl isomerization in a *P,N*-ligand, Sprinz et al. [8] have observed exclusive opening of the allyl terminus trans to the P-donor in the chiral C_3H_5 phosphinoaryloxazoline Pd-complex shown:

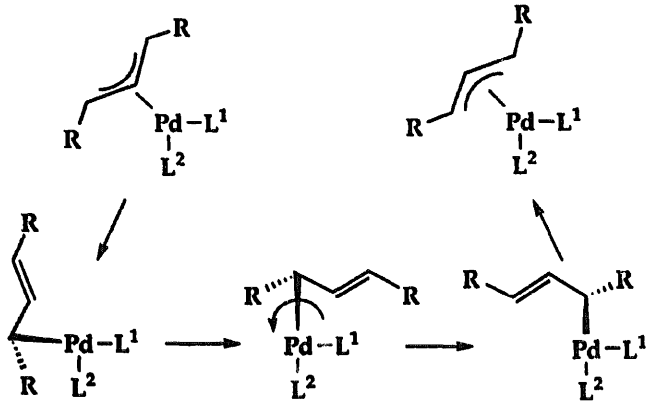




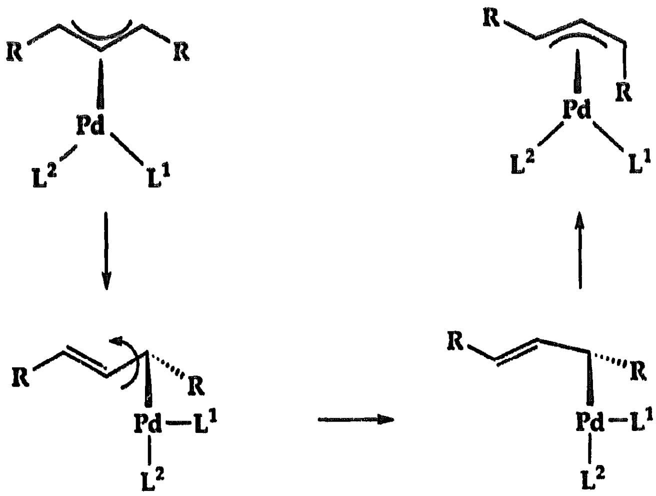
14a **14b**

Abbreviated forms of the syn–syn and syn–anti isomers of complex **14**.

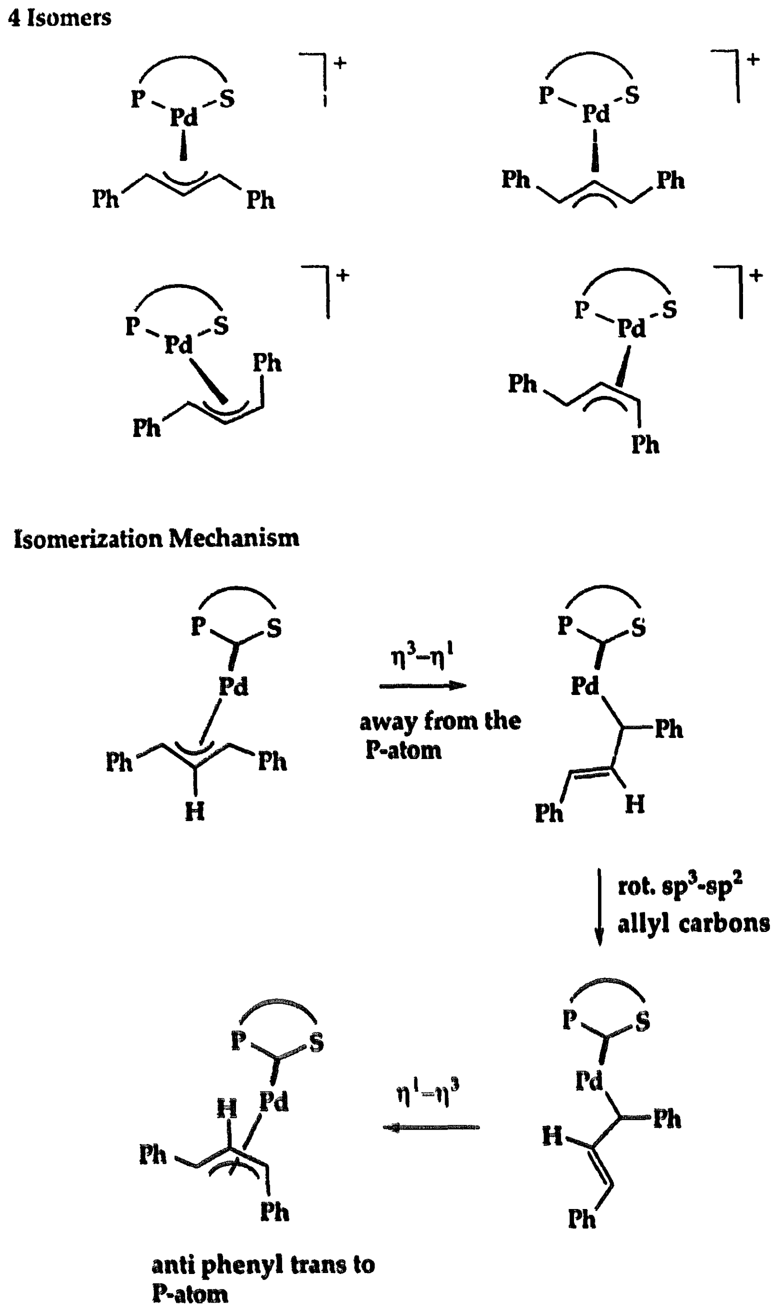
Route 1. Allyl Face Change



Route 2. Allyl Face Change and syn/anti Isomerization



Scheme 7. η^3-η^1-η^3 mechanisms.



Scheme 8. Details for the diphenylallyl *exo*-norborneol *P,S* complex **17**.

This is presumably another example of electronic control of the isomerization. Obviously, it will be difficult to generalize.

2.6. *syn–anti Isomers;* ^{13}C *NMR*

As mentioned above, the MeO–BIPHEMP complex **14** exists in two isomeric forms. The presence of exchange cross-peaks in the phase-sensitive ^1H-NOESY

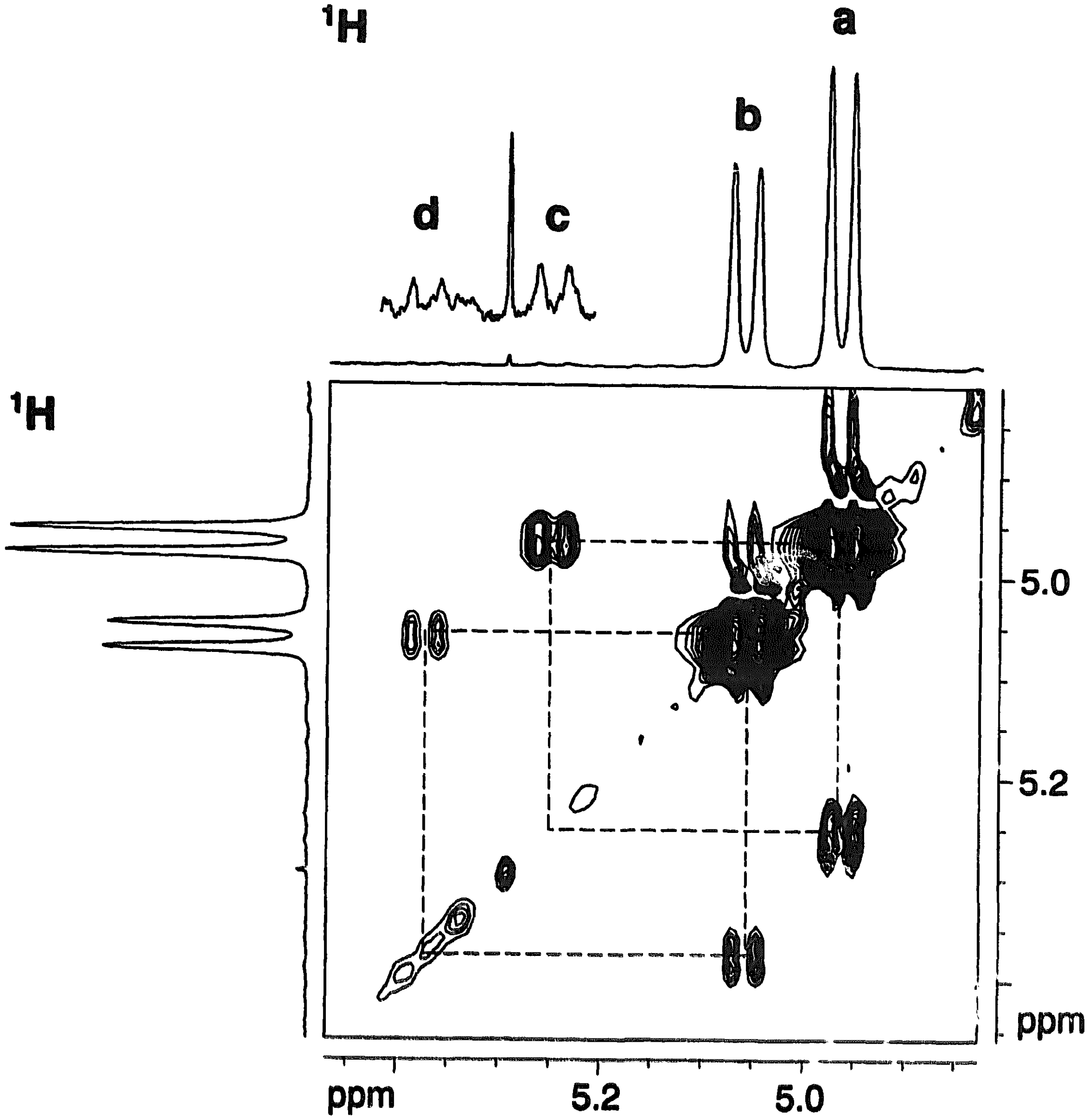


Fig. 9. Section of the ¹H 2-D NOESY ($CDCl_3$, 296 K) of **17** showing the various exchange peaks. The protons a and b are trans to sulfur. Note the almost invisible signals (d and c) with which the two major isomers exchange.

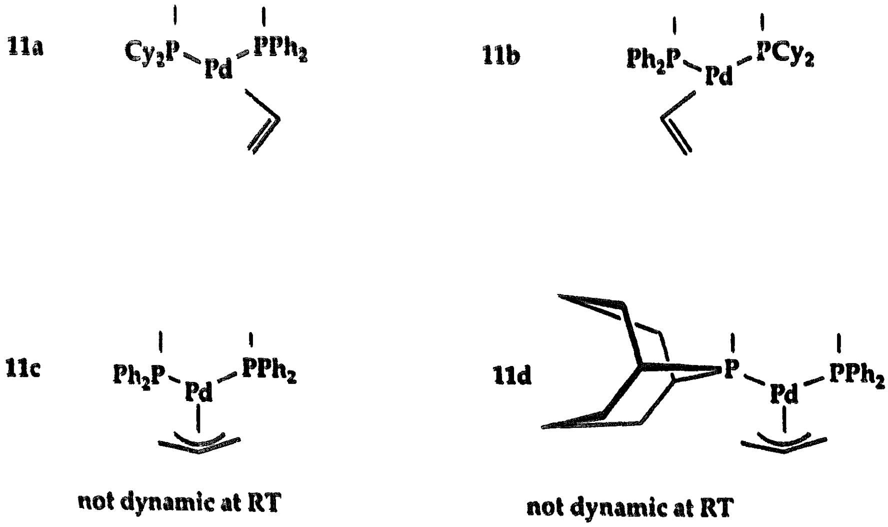
shows that these are in equilibrium, and Fig. 11 demonstrates this for the methoxy methyl signals. Again, the exchange is selective both in the allyl and methoxy regions, with one allyl proton of the major isomer in exchange with just one allyl proton in the minor isomer. The minor syn–anti isomer can exist in two forms which differ with respect to the placement of the anti phenyl group relative to the BIPHEMP phenyl groups. The exchange and NOE data clearly point to **14b** as the correct structure. Remember that complex **14a** stacks the phenyl groups indicated with the arrows.

It is tempting to think that the repulsive interaction between the stacked rings leads to an η^1-isomer in which this strain is relieved. Subsequent rotation around the sp^2–sp^3 C–C bond and reformation of the η^3-complex would give **14b**.

Recent studies [53] have also shown the existence of syn–anti isomers in palladium 1,3-diphenylallyl complexes with BINAP- and JOSIPHOS-containing complexes; also, other relatively large intrusive (nitrogen) ligands have been found by Åkermark and Hansson [60]. Since the syn–anti isomer is no longer uncommon, if not usually prevalent, one should note that the observed relative populations of these syn–syn and syn–anti isomers frequently do not always correlate with the observed enantiomeric excesses for these chiral auxiliaries. Perhaps one allylic terminus is attacked in one isomer and the other in the second isomer. Alternatively (and more likely), the rates at which these diastereomeric isomers react with the carbon (or nitrogen) nucleophile are different. In any case, the recognition of these isomers may be important.

Although not directly related to either the structure or the dynamics of allyl complexes, the subject of terminal allyl ^{13}C chemical shifts [61] for the 1,3-diphenylallyl palladium compounds deserve a comment. Table 2 contains these values for a series of $[Pd(\eta^3\text{-PhCHCHCHPh})(chelate)]^+$ cations.

In all cases where the chelate is chiral (there are also achiral *P,P*- and *N,N*-ligands included for comparison) the two terminal allyl carbons have different chemical shifts. These differences can be quite substantial, e.g. 18.5 ppm for the major isomer of the MeO–BIPHEMP complex, **14a**. Moreover, some of these terminal allyl chemical shifts are greater than $\delta = 100$, suggesting some olefin-like character. It is likely that the different steric interactions between the individual chelate P-Ph rings (or for **5**, the oxazoline ring substituents) and the 1,3-diphenylallyl ligand, lead to these ^{13}C NMR changes. For an auxiliary with two strongly differing donor atoms, e.g. a *P,N*-ligand, there is the well-known trans-influence, an electronic effect, which will result in ca. 30–40 ppm differences between the two allyl carbon termini.



Scheme 9. Summary of the allyl dynamics for **11** (fragmental structures shown, charges omitted). η^3-η^1-η^3 proceeds in both (a) and (b) such that the bond cis to the PCy_2 opens. No observable η^3-η^1-η^3 isomerization at ambient temperature for (c) and (d).

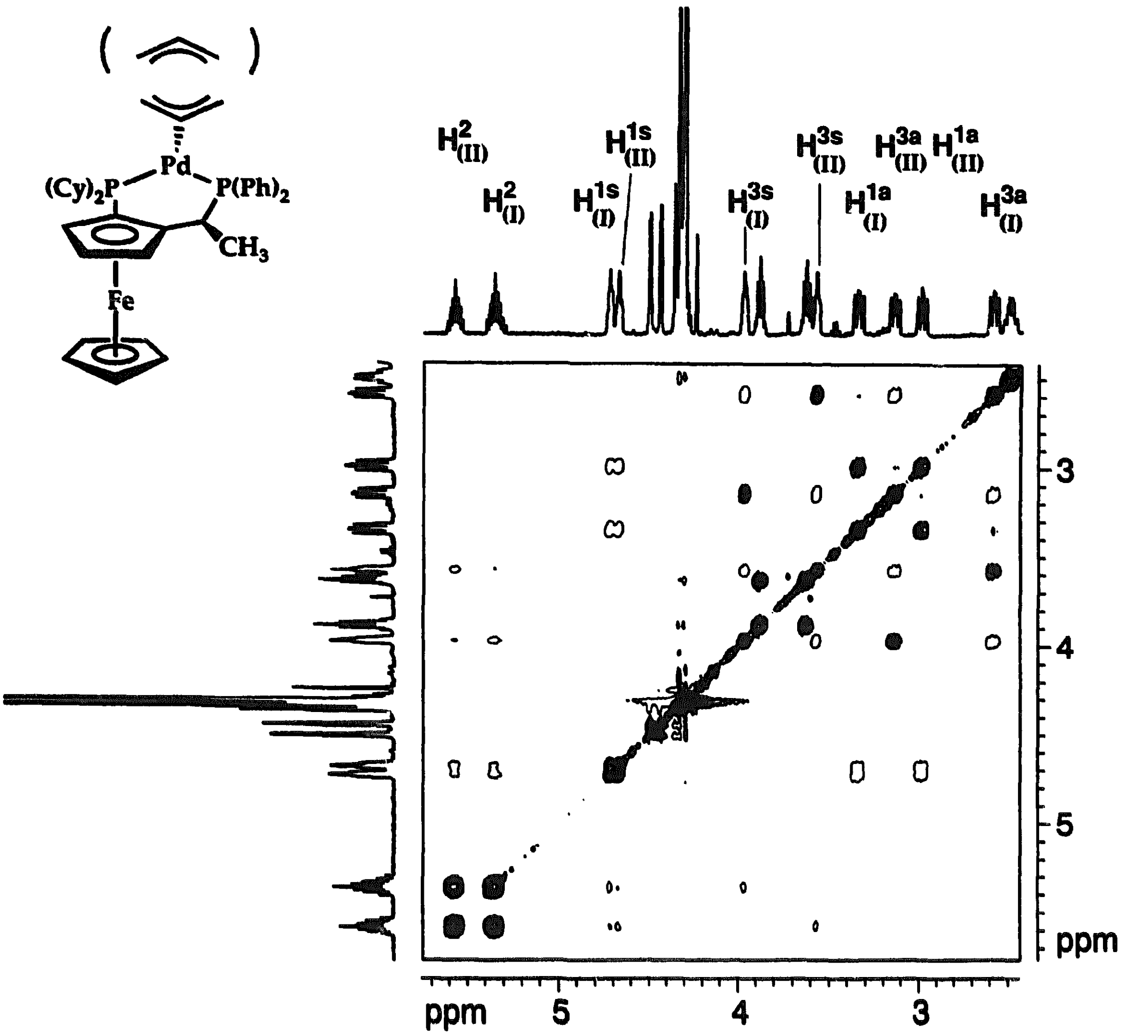


Fig. 10. Section of the phase-sensitive ^1H 2-D NOESY spectrum for the C_3H_5 allyl complex **11b**. The 'filled-in' cross-peaks arise from exchange, whereas the 'open' cross-peaks arise from NOEs. The four signals in the lower-left corner demonstrate exchange between the rotational isomers. The major rotational isomer (I) has the C(2)–H bond pointing away (exo) from the Fe atom ($CDCl_3$, 500 MHz).

There has been some literature discussion [38] on the use of these ^{13}C chemical shifts to predict the site of attack of the incoming nucleophile in catalytic alkylation. The subject is open, and there is at least one other equally attractive proposal, not related to ^{13}C data, involving steric effects in the excited state complex [10,38]; however, we note that where large ^{13}C-differences are observed, there seems to be some correlation in that, based on the absolute configuration of the observed organic product, it is indeed, the high frequency (more olefin-like) carbon-site that is attacked.

3. Summary

The idea of 'reporter ligands', be they simple nitrogen chelates or relatively complicated chiral bidentate phosphine compounds, seems to have potential. The use of

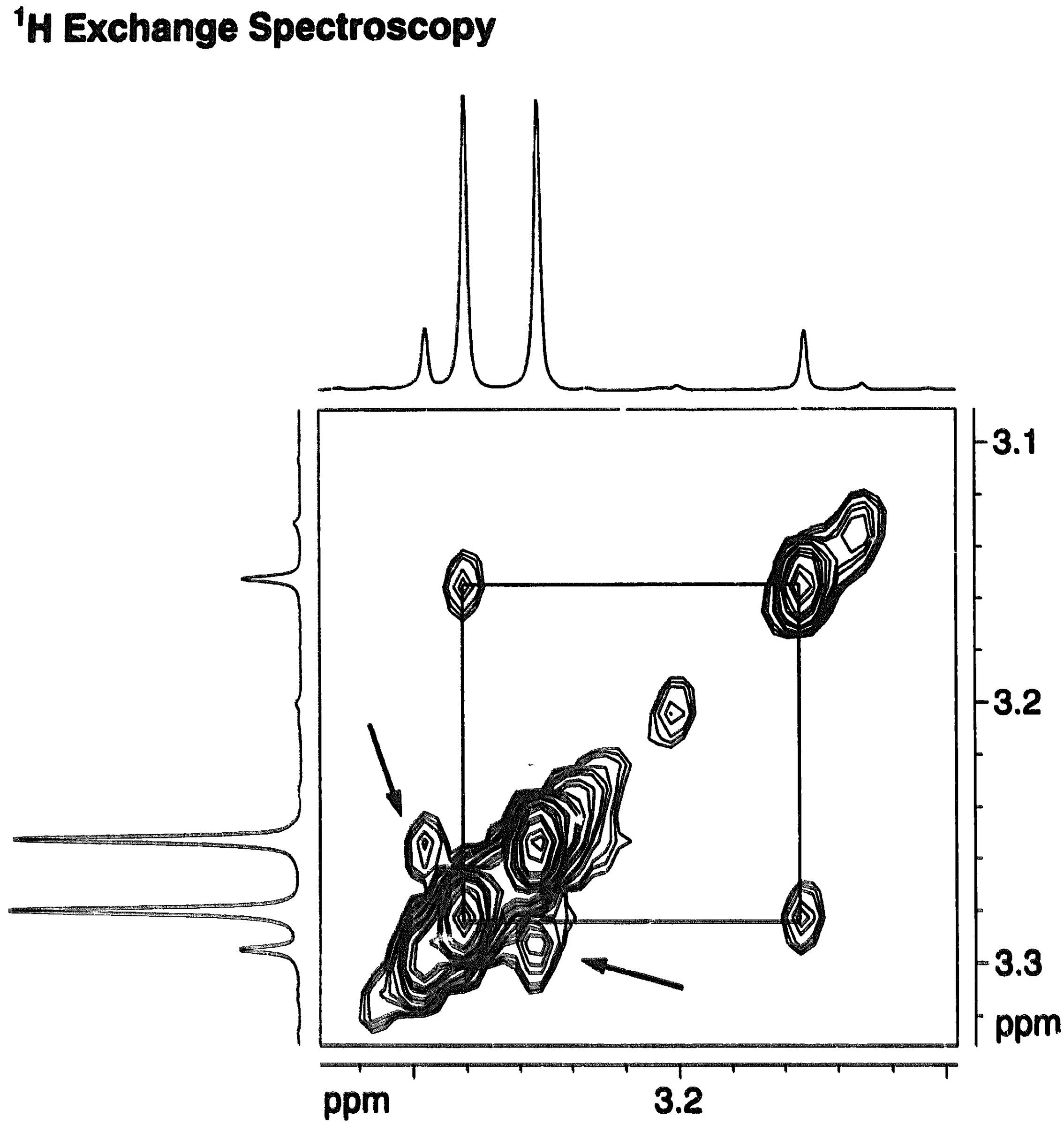


Fig. 11. Section of the phase-sensitive ^{1}H-NOESY for **14** revealing exchange cross-peaks between the BIPHEMP methoxy groups of the two isomers. The appropriate cross-peaks for the two exchanges are indicated by the square and by the arrows. One methoxy of the major isomer exchanges selectively with one methoxy of the minor isomer ($CDCl_3$, 500 MHz).

such ligands as NOE probes can lead to a better understanding of both subtle (allyl hybridization, phenyl–phenyl stacking) and gross (3-D aspects, shape of the chiral pocket) structural features in the chemistry of palladium–allyl complexes. Complexes with commercially available auxiliaries, such as CHIRAPHOS or BINAP, are suitable, as are novel research chelates, e.g. the JOSIPHOS family. Combined with X-ray crystallography and MM2* calculations, one can slowly develop a feeling for the various ways in which these different chiral ligands use steric effects to transfer chiral information. A relatively rigid chiral pocket seems a necessary, but not sufficient

Table 2
^{13}C NMR data[a] for the 1,3-diphenylallyl complexes

Chelate	Central allyl ^{13}C	Terminal allyl ^{13}C	
(*R*)-BIPHEMP	110.1 [7.0] major	103.1 [22.0, 6.0]	85.7 [30.0, 7.0]
	107.7 [7.0] minor	99.5 [25.0, 6.0]	91.2 [30.0, 7.0]
(*S*)-MeO-BIPHEMP	109.4 [7.5] major	103.3 [21.5, 5.5]	84.8 [30.0, 7.0]
	ca. 107 minor	98.2	90.7
(*S*)-BINAP[b]	111.3 [7.0]	104.6 [5.0]	87.2
(*S,S*)-DIOP	112.1 (s,br)	95.5 [22.0]	92.9 [27.0]
(*S,S*)-CHIRAPHOS	112.5 [7.5]	90.1 [24.2, 8.1]	88.1 [25.5, 9.6]
(+)-DPPCP	112.4 [7.5]	91.2 [21.5, 7.5]	89.0 [23.5, 8.5]
DIPHOS	113.6 [7.4]	91.7 [16.0]	91.7 [16.0]
(*R*)-(*S*)-JOSIPHOS[c]	110.9 [6.5] major	96.4 [19.8, 3.1]	82.0 [29.0, 3.0]
	112.6 (s,br) minor	90.2 [6.1]	89.6 (s, br)
(*S*)-(*R*)-PHOBIPHOS[d]	110.8	100.7	80.8
17 (syn-syn major)	112.4	97.5 (tr, P atom)	83.4(tr, S atom)
17 (syn-syn minor)	111.0	98.2	84.0
TMEDA[b]	108.9	78.9 (s)	78.9
BIPY[b]	108.5	78.9 (s)	78.9
BIQUINOLINE[b]	112.1	83.2 (s)	83.2
AMPY[b]	108.4	78.5 (s,br)	78.5 (s,br)
5[e]	108.1	74.2	81.8
(*S*)-PhIMPHOS[f]	111.9 (s,br)	105.9 [21.0]	66.9
	111.9 (s,br)	103.9 [21.0]	68.9
(*R*)-CyIMPHOS[f]	111.9 (s,br)	104.5 [23.0]	67.9 (br)
	111.9 (s,br)		[5.9]
(*S*)-NapIMPHOS[f]	112.88 [7.0]	103.0 [15.0]	70.0 [6.8]
	111.57 [7.0]	103.2 [14.0]	69.7 [6.8]
(+)-MePHOS[a]	111.25 [6.0]	95.9 [24.0]	71.4 [11.2]
	110.2 [6.0]	97.4 [23.0]	69.3 [10.8]

[a] From Ref. [53]; $CDCl_3$, 296 K, 125.8 MHz, P,C *J*-values in brackets. PF_6 salts, unless otherwise indicated; DIPHOS = $Ph_2PCH_2CH_2PPh_2$. AMPY = 2-pyridylmethylamine. The last four entries represent chiral P,N ligands. MePHOS is $Ph_2PCH(Ph)CH(Me)NMe_2$. [b] BF_4 salts. [c] Trans to P. [d] 100.7, trans to P; see Ref. [51]. [e] See Ref. [38]. [f] These three compounds contain chiral Schiffs' bases (P,N-ligands) derived from *o*-diphenylphosphinobenzaldehyde, using $NH_2CH(Me)R$, R = Ph, Cy and Naphthyl respectively.

condition, since an intrusive chiral pocket leads to syn–anti isomers which may result in a reduced ee. ^1H 2-D exchange NMR has shown some unexpected selectivity with respect to allyl isomerization, thereby helping to identify different diastereomeric forms of catalyst precursors in solution. The η^3-η^1 isomerization can be under either electronic or steric control. Quite probably, the various syn–syn and syn–anti diastereoemeric complexes can react at different rates so that their presence may or may not be a problem. The terminal allyl ^{13}C chemical shifts in these palladium(II) complexes could conceivably provide an indirect probe with respect to which allyl carbon will be attacked, but this presumes an 'early' (ground-state-like) transition state which, as yet, has not been proven.

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