Synthesis and Stereochemical Studies of η^3-Allyl Palladium(II) Complexes containing a Chiral Chelating Ligand

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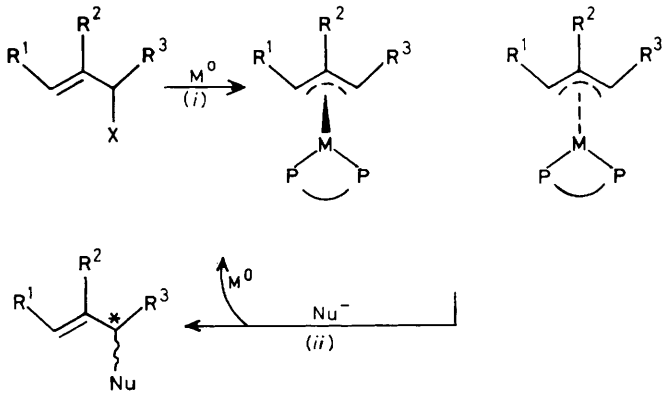
A complex of the type $[Pd(\eta^3\text{-}CH_2CMeCH_2)(P\text{–}P')]^+$ [where P–P′ = the chiral chelating ligand (*S*)-(*N*-diphenylphosphino)(2-diphenylphosphinoxymethyl)pyrrolidine, not having C_{2v} symmetry] has been prepared and its ^1H, ^{13}C, ^{31}P, and two-dimensional H–X (X = ^{13}C or ^{31}P) correlation spectra recorded. On the basis of n.m.r. data the absolute configurations in solution of the major and minor diastereoisomers have been assigned. Proton and ^{13}C n.m.r. data have been discussed in terms of *trans* influence of the chelating ligand P–P′. Correlations between the n.m.r. parameters of the intermediate η^3-allyl diastereoisomers, donor properties of the ligand, and regiochemistry of nucleophilic addition to the allyl termini have been proposed.

Currently one of the most important reactions in organic chemistry is selective C–C bond formation and much effort is addressed to the design of a catalytic system which competes with enzymes in activity and selectivity. η^3-Allyl complexes of the Ni group elements have been found to play a key role in such metal-mediated organic transformations.[1–4] Concentrating on asymmetric allylation promoted by Pd complexes, in spite of the relevant number of studies and applications reported[5] since the observations by Tsuji *et al.*[6] in 1965 the control of asymmetric induction and optical yields are still unsatisfactory. It has been suggested that the optical yield of asymmetric catalytic allylation can be related to the equilibrium concentration of the diastereoisomeric complexes arising from oxidative addition of allylic substrates to Pd^0 chiral chelating phosphine species [step (*i*) in Scheme 1]. The slow step of the catalytic reaction, as well as the stereo-differentiating step, is the *exo* addition of the nucleophile to the co-ordinated allyl fragment [step (*ii*) in Scheme 1].[7]

The alternative approach is based on creation of 'a chiral pocket' with sterically controlled attack of the nucleophile on the η^3-allyl fragments.[8] An electronic effect was also invoked previously in the stoicheiometric reaction with a chiral molybdenum complex.[9] All these studies, although demonstrating the potential of the method, are based on a semi-empirical approach and do not allow a systematic prediction of the outcome of such a reaction. In particular the absolute configuration of the chiral centre of the product cannot be predicted *a priori* because (*a*) it is unknown if the asymmetric induction relies upon thermodynamic or kinetic factors, (*b*) the regioselectivity of the nucleophilic attack is not defined, and (*c*) the stereochemistry and chirality of the allyl binding of the intermediate diastereoisomers cannot usually be assigned other than by *X*-ray analysis together with experiments which correlate the structure in the solid and in solution. In particular, according to the symmetry of the allyl and of the phosphorus chelating ligand the stereochemical complexity illustrated in (**A**)—(**D**) is generated.

Structures (**A**), (**B**) and (**C**), (**D**) refer to a chiral chelating ligand with and without C_{2v} symmetry respectively: (**A**) is achiral; provided that the allylic substituents retain a preferred *syn* disposition, (**B**) and (**C**) give rise to a couple of diastereoisomers and (**D**) exists as four diastereoisomers.

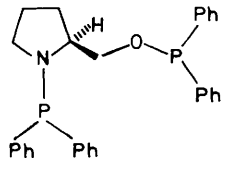
In order to design a more rational approach to asymmetric allylation, a clear definition of all the factors governing the regioselectivity and the stereoselectivity of this process is required. With the aim of offering an insight into the correlation between precursor, intermediate, and product under 'real' conditions we report herein a solution characterization of a $[Pd(\eta^3\text{-allyl})(P\text{–}P')]^+$ complex (allyl = CH_2CMeCH_2, P–P′ = chelating chiral phosphine ligand without C_{2v} symmetry). Moreover the rather unique feature of the chiral chelating ligand, having two electronically very different phosphorus atoms, should give an indication of whether the proposed correlations between donor properties of the ligand, n.m.r. parameters of the intermediate, and regiochemistry of the nucleophilic addition[10,11] apply more generally to this class of compounds.



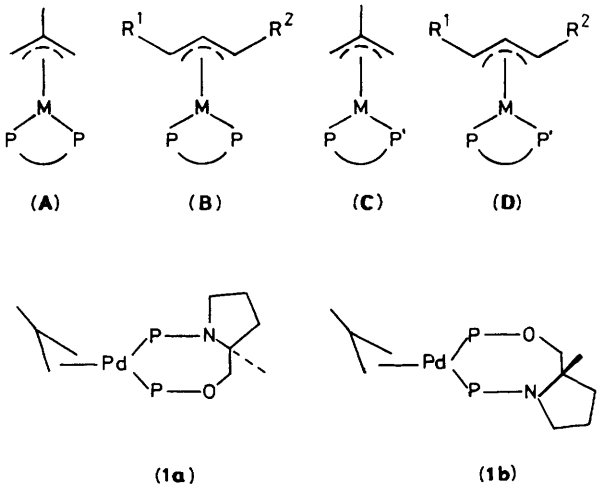
Scheme 1. Catalytic allylation process

Results and Discussion

The structure of the P–P′ ligand chosen for this study, (*S*)-(*N*-diphenylphosphino)(2-diphenylphosphinoxymethyl)-pyrrolidine (dpopyr) is shown below. This ligand has several interesting features: (*a*) it is cheap and readily available in



dpopyr



optically pure form;[12] (*b*) it produces high asymmetric induction in the homogeneous catalytic hydrogenation of dehydroamino acids promoted by Rh complexes;[12-14] (*c*) due to the expected different donor properties of the phosphorus atoms it should be a good probe to determine whether electronic effects exert some role in asymmetric allylation compared with steric ones; (*d*) upon complexation it produces a rather flexible seven-membered ring generating a steric environment which is expected to provide higher asymmetric induction in allylation.[8]

The complex $[Pd(\eta^3\text{-}C_4H_7)(dpopyr\text{-}PP')]X$ (X = PF_6 or BF_4) (**1**) was prepared according to Scheme 2. The reaction is almost quantitative but care must be taken to filter off completely the AgCl before adding the ligand because dpopyr reacts with Ag^+ forming very soluble species which severely interfere in the isolation and purification of complex (**1**). The crude reaction product is a mixture of two diastereoisomers, (**1a**):(**1b**) = 2.5:1. The most abundant isomer (**1a**) was obtained almost pure by slow recrystallization from methanol.

Complex (**1**) is a stable white solid which is slightly less stable in solution, separation of an insoluble black material occurring in a few cases. The compound afforded satisfactory elemental analysis and was fully characterized by n.m.r. and mass spectroscopy.

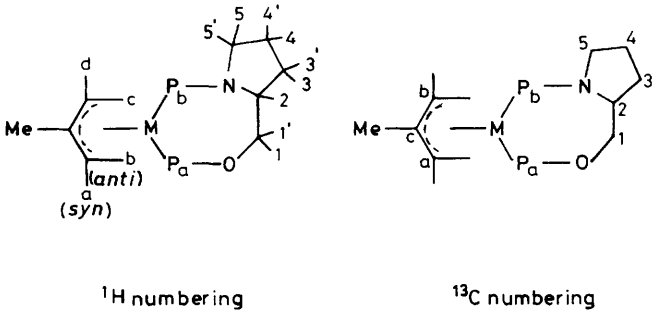
$$[\{Pd(\eta^3\text{-}C_4H_7)Cl\}_2] + AgX \xrightarrow{CH_2Cl_2} [Pd(\eta^3\text{-}C_4H_7)]X + AgCl$$

$$\downarrow \text{dpopyr, } CH_2Cl_2$$

$$[Pd(\eta^3\text{-}C_4H_7)(dpopyr\text{-}PP')]X \quad (1)$$

Scheme 2.

N.M.R. Spectroscopy.—The numbering of the ^1H, ^{13}C, and ^{31}P resonances is given in structures (**E**) and (**F**). Before discussing the results for complex (**1**) it is of interest to illustrate



the n.m.r. characterization of the free ligand for which only the ^{31}P spectrum has been reported[15] (see Tables 1 and 2).

The spectrum of dpopyr in $CDCl_3$ at 298 K is reported in Figure 1. The assignment of the spectrum was complex because of the presence of strongly coupled spin systems and overlapping multiplets even at 400 MHz. By changing the solvent from $CDCl_3$ to C_6H_6 a significant anisotropic shielding effect was observed at high field (the resonance at δ 1.89 was split

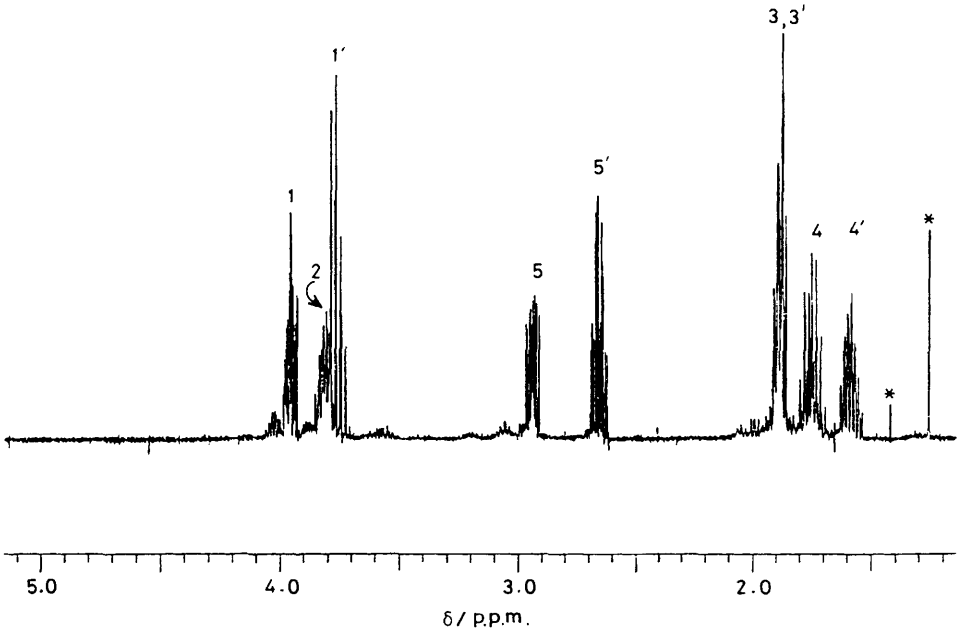


Figure 1. Proton n.m.r. (400.13 MHz, $CDCl_3$, 298 K) spectrum of dpopyr (excluding phenyls); * indicates impurity

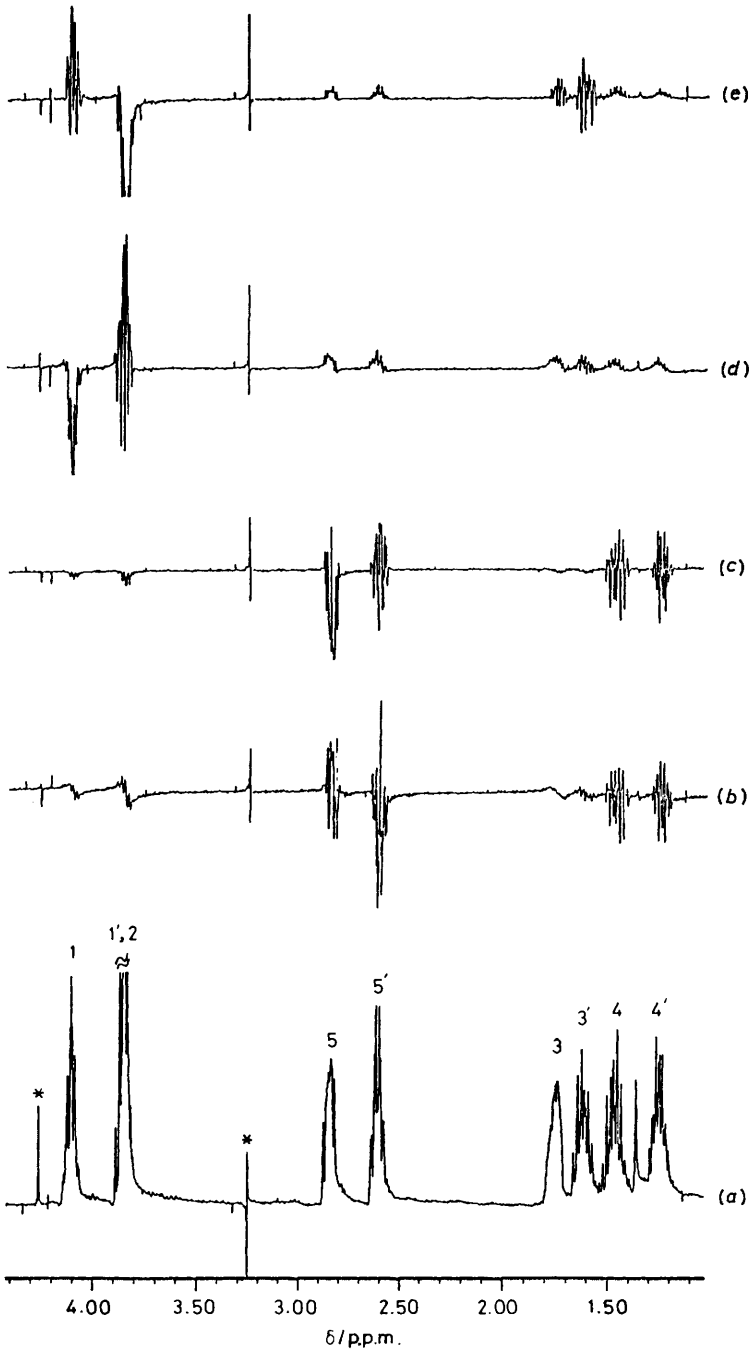


Figure 2. Proton decoupling difference (400.13 MHz, C_6D_6, 298 K) spectra for dpopyr: (*a*) spectrum in the aliphatic region; (*b*) difference spectrum irradiating at δ 2.62; (*c*) irradiating at δ 2.85; (*d*) irradiating at δ 4.10; (*e*) irradiating at δ 3.85; * indicates impurity

into two multiplets which integrated 1 H each), although the two overlapping protons at δ 3.8 remained unresolved. The decoupling difference spectra shown in Figure 2 allowed us to assign all the resonances as indicated in Table 1. However, due to the complexity of the multiplet structures the single H–H couplings and the relative *cis–trans* arrangement of vicinal protons [H^2 *cis* to H^1 or $H^{1'}$, *etc.*] were not determined. The assignment was confirmed by two-dimensional n.m.r. spectroscopy. In Figure 3 the counter plot of a two-dimensional n.m.r. ^{31}P–^1H correlation spectrum through long-range X–H couplings clearly shows the three-bond connectivities P_a–H^1, P_a–$H^{1'}$, and P_b–H^2. [The assignment of the ^{31}P spectrum: δ 113.7 (P_a, bonded to oxygen) and 46.7 (P_b, bonded to nitrogen), was reported in ref. 12.] The poor resolution (6.16 Hz per point) in the ^1H spectrum did not allow resolution of the P–H couplings, and the choice of delays (Δ1, Δ2) in the pulse sequence led to the cancellation of cross-peaks due to the smaller P–H interaction. To complete the measurements we performed a two-dimensional n.m.r. JRES experiment with a resolution of 0.17 Hz per point in the F2 dimension (homodecoupled ^1H spectrum with splitting due to P–H couplings). The spectrum revealed the expected ^3J coupling P_b–H^5 and P_b–$H^{5'}$ and gave the set of coupling values in Table 1. The ^{13}C n.m.r. data are reported in Table 2. Since the ^1H

Table 1. Proton n.m.r. data for complex (**1**) and dpopyr*

	H_a	H_b	H_c	H_d	CH_3	Phosphine ligand
(**1a**)	3.93	3.48	3.46	3.63	1.40	3.83 (H^1), 3.51 ($H^{1'}$), 4.93 (H^2), 2.30 (H^3), 1.33 ($H^{3'}$)
	[5]			[5]		[24] [4] [12]
						1.84 (H^4), 1.70($H^{4'}$), 3.11 (H^5), 2.73 ($H^{5'}$)
(**1b**)	4.12	2.35	2.97	3.63	2.16	4.59 (H^2)
	[5]	[10]	[12]	[5]		[12]
dpopyr						3.96 (H^1), 3.74 ($H^{1'}$), 3.81 (H^2),1.89(H^3,$H^{3'}$)
						[8,2.5] [2] [7] [2.5,1.5]
						1.76 (H^4), 1.60 ($H^{4'}$), 2.94 (H^5), 2.66 ($H^{5'}$)
						[2] [3.5]

* In $CDCl_3$, 298 K, at 400 MHz; chemical shifts (δ) are in p.p.m. referred to $SiMe_4$. Coupling constants (Hz) to ^{31}P are given below the δ values in square brackets.

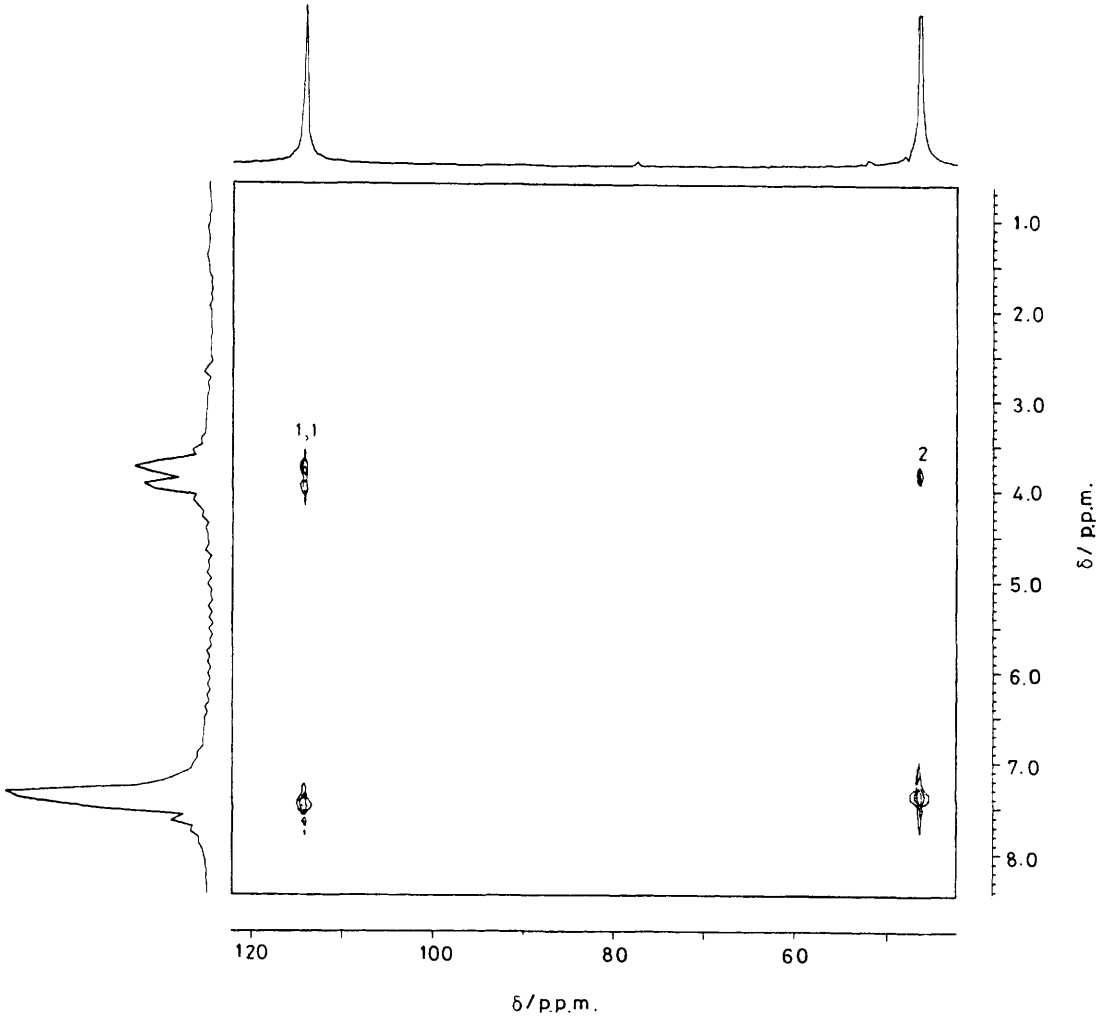


Figure 3. Counter plot of two-dimensional ^{31}P–^1H (200.13 MHz, $CDCl_3$, 298 K) correlation spectrum for dpopyr. Horizontal projection: one-dimensional ^{31}P-{^1H} spectrum; vertical projection: one-dimensional ^1H homodecoupled spectrum

resonances were known, the assignment of the ^{13}C spectrum was straightforward on the basis of selective ^1H decoupling experiments. Moreover using a DEPT sequence (which permits the determination of the multiplicity of each carbon), the CH and CH_2 resonances were unambiguously identified.

The ^1H spectrum of complex (**1**), reported in Figure 4, is not readily assigned due to the presence of co-ordinated ligand and CH methallyl absorptions which severely overlap. The presence of the two diastereoisomers (**1a**) and (**1b**) is indicated by the doubling of CH_3 absorptions which appears as two singlets at δ 1.40 and 2.16 respectively. The full assignment of the spectrum required a variety of one-dimensional and two-dimensional n.m.r. measurements. By ^1H two-dimensional n.m.r. JRES we determined the ^1H–^{31}P couplings given in Table 1. Decoupling

Table 2. Carbon-13 and ^{31}P n.m.r. data for complex (**1**) and dpopyr*

					Phosphine ligand		
	C_a	C_b	C_c	CH_3	^{13}C	P_a	P_b
(**1a**)	69.1 [32.2]	74.5 [34.2]	n.o.	23.2 [n.o.]	70.6 (C^1), 61.2 (C^2), 28.1 (C^3), 26.1 (C^4), 48.4 (C^5) [n.o.] [n.o.] [n.o.] [n.o.] [n.o.]	122.2 [57.6]	72.9
(**1b**)	68.7 [32]	75.4 [34]	n.o.	23.8 [n.o.]	70.6 (C^1), 61.2 (C^2), 28.1 (C^3), 25.9 (C^4), 48.1 (C^5) [n.o.] [13.6] [8] [4.5] [6]	124.8 [58]	74.0
dpopyr					73.1 (C^1), 63.6 (C^2), 29.7 (C^3), 25.4 (C^4), 47.2 (C^5) [16.1] [29.1] [6.0] [4.5] [8.1]	113.7	46.7

* In $CDCl_3$, 298 K, at 100.6 MHz (^{13}C) and 81.3 MHz (^{31}P); chemical shifts (δ) are in p.p.m. referred to $SiMe_4$ (^{13}C) and external H_3PO_4 (^{31}P). Coupling constants (Hz) to ^{31}P are given in square brackets; n.o. = not observed.

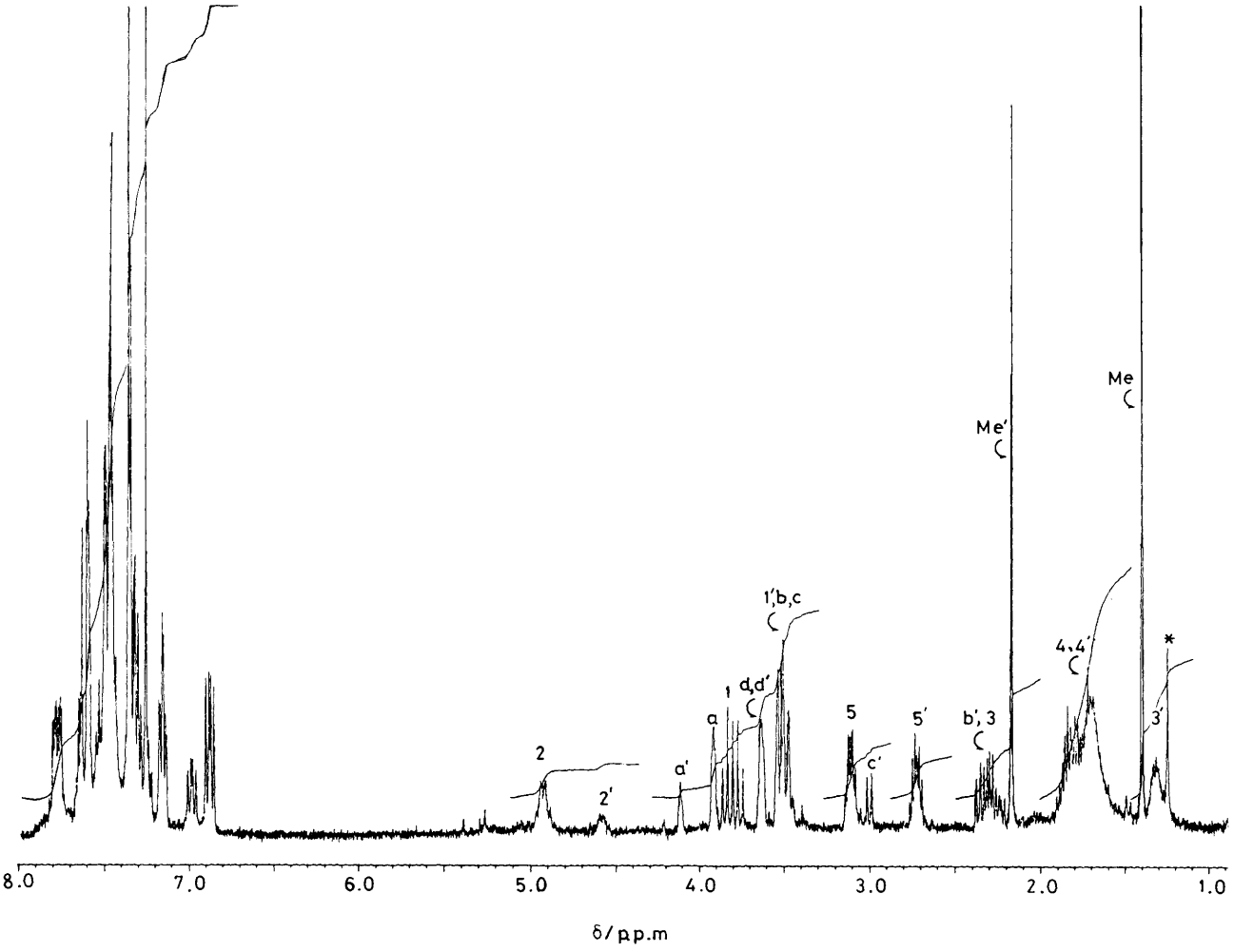


Figure 4. Proton n.m.r. (400.13 MHz, $CDCl_3$, 298 K) spectrum for complex (**1**): 2', Me', a', b', c', and d' refer to signals of minor isomer; * indicates impurity

difference ^1H spectra revealed the coupling network of the protons of the co-ordinated ligand [*i.e.* the resonance at δ 4.93 (H^2) exhibits couplings to resonances at δ 3.83, 3.51, 2.30, and 1.33 which were assigned to H^1, $H^{1'}$, H^3, and $H^{3'}$; the resonance at δ 3.11 (H^5) exhibits couplings to resonances at δ 2.73, 1.84, and 1.70 which were assigned to $H^{5'}$, H^4, and $H^{4'}$ respectively]. Nuclear Overhauser enhancement (n.O.e.) ^1H measurements confirmed the assignments, showing significant enhancement between geminal protons: H^5, $H^{5'}$; H^4, $H^{4'}$, *etc.* Using the same techniques we identified the resonances of the allyl protons on the basis of the usual ^1H spectra found for co-ordinated methallyl fragments, *i.e.* (*a*) the *syn* protons exhibit reciprocal ^4J couplings[16,17] and n.O.e. on the relative *anti* protons; (*b*) the *anti* protons show $^3J(HX)$ couplings (where X = n.m.r.-active atom) larger than for *syn* protons;[18,19] (*c*) the central CH_3 group exhibits n.O.e. on the related *syn* protons. However a few

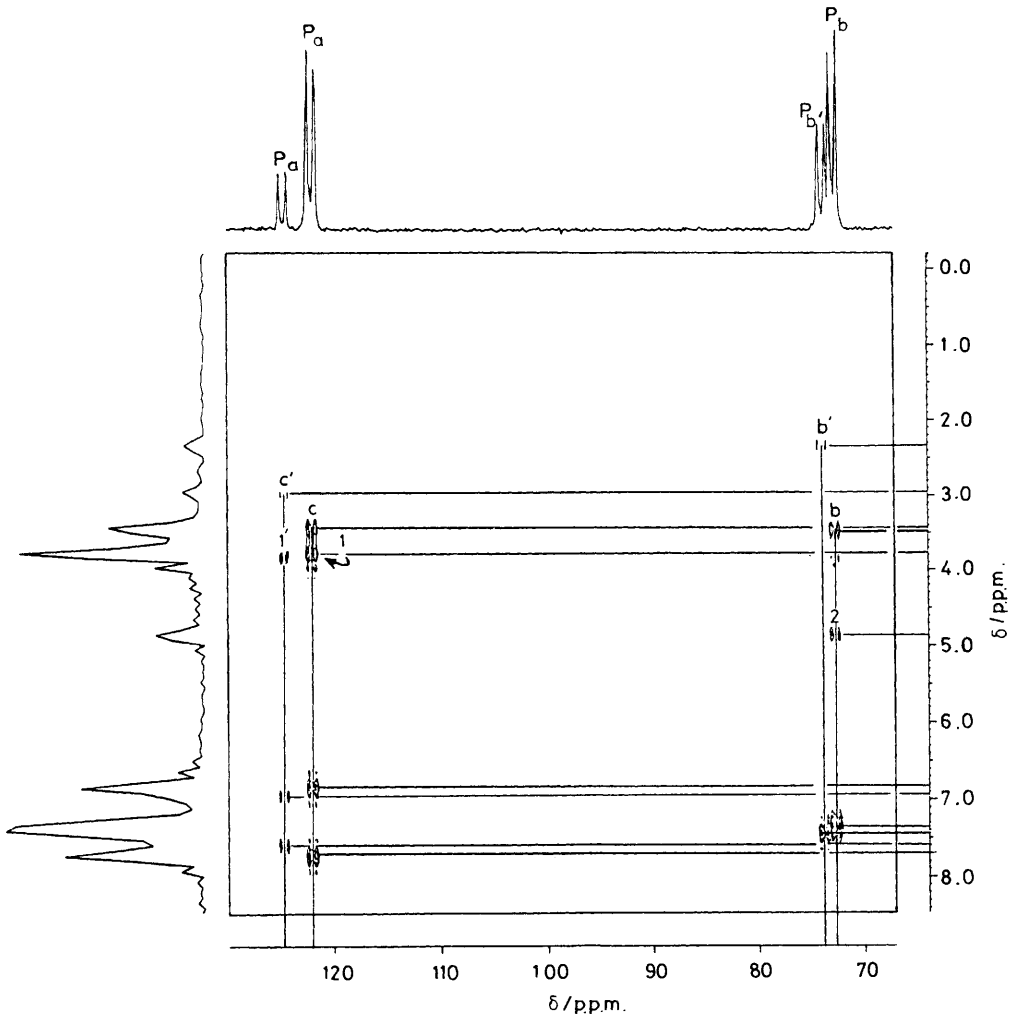


Figure 5. Counter plot of two-dimensional ^{31}P–^{1}H (200.13 MHz, $CDCl_3$, 298 K) correlation spectrum for complex (**1**). Horizontal projection: one-dimensional ^{31}P-{^{1}H} spectrum; vertical projection: one-dimensional ^{1}H homodecoupled spectrum. $P_{a'}$, $P_{b'}$, c', b', and 1' refer to signals of minor isomer

ambiguities still remain for the absorptions of the allylic protons of the major isomer at *ca.* δ 3.5. The combination of ^{13}C, ^{31}P, and relative two-dimensional X–H correlation measurements allowed us to overcome this difficulty.

The ^{31}P spectrum of complex (**1**) consists of a pair of doublets for each diastereoisomer (**1a**) and (**1b**): δ 124.8 and 74.0 (P_a and P_b of the minor isomer), 122.2 and 72.9 (P_a and P_b of major isomer).[20] Using the two-dimensional P–H correlation technique (Figure 5), we resolved the ambiguity at the ^{1}H *anti* absorptions and defined their relative arrangement (*cis* or *trans*, with respect to P_a and P_b). By this method only protons which exhibit large ^{3}J(PH) couplings appear in a two-dimensional spectrum (*i.e. o*-H of the phenyls, H^1 and H^2 of the ligand, and the *anti* allyl protons). It is known that co-ordinated allyl atoms couple with relatively large *J* values to *trans* n.m.r.-active species, in this case ^{31}P.[21,22] Thus we assigned the ^{1}H resonances at δ 2.35 and 3.48 to $H_{b'}$ and H_b and resonances at δ 2.97 and 3.46 to $H_{c'}$ and H_c respectively. Interestingly ^{1}H resonances due to the two phenyls bonded to P_b are found at *ca.* δ 7.4 whereas those of the phenyls bonded to P_a are split into two groups at *ca.* δ 6.9 and 7.7, indicating in the second case a rather different environment for the two rings.

The ^{13}C spectrum of complex (**1**) was assigned on the basis of selective ^{1}H decoupling and JMOD ^{13}C measurements. The two-dimensional C–H correlation spectrum (Figure 6) was used to differentiate between the four pairs of geminal allyl protons. Thus the initial assignment of the *anti* protons permits the identification of the four CH_2 carbons which then lead directly to their respective *syn* protons. [The ^{1}H resonance at δ 4.12, not revealed in the two-dimensional C–H correlation spectrum, was unambiguously assigned to proton $H_{a'}$ on the basis of the two-dimensional ^{1}H NOESY spectrum which shows cross-peaks between the two pairs of geminal allyl protons at δ 2.35 ($H_{b'}$), 4.12 ($H_{a'}$), 3.01 ($H_{c'}$), and 3.63 ($H_{d'}$).] Moreover we determined the *cis* or *trans* arrangement of the allyl CH_2 group with respect to P_a and P_b. Thus we assigned the ^{13}C resonances at δ 69.06 and 68.7 to C_a and $C_{a'}$ (*cis* to –PO–) and resonances at δ 74.47 and 75.4 to C_b and $C_{b'}$ (*cis* to –PN–).

The analysis of the data of Table 1 reveals several interesting features: (*a*) protons H^2, H^3, $H^{3'}$ of the co-ordinated ligand show significant shifts relative to free dpopyr; (*b*) the ^{1}H allylic resonances of the major and minor isomers are markedly different, the latter being closer to that usually found in co-ordinated methylallyl species. In particular we notice in the major isomer an unusual high-field shift of the CH_3 resonance (δ 1.40) and low-field shifts of the *anti* protons (H_b, H_c) which bring the four CH absorptions in the region δ 4—3.5. These results are explained on the basis of an anisotropic shielding

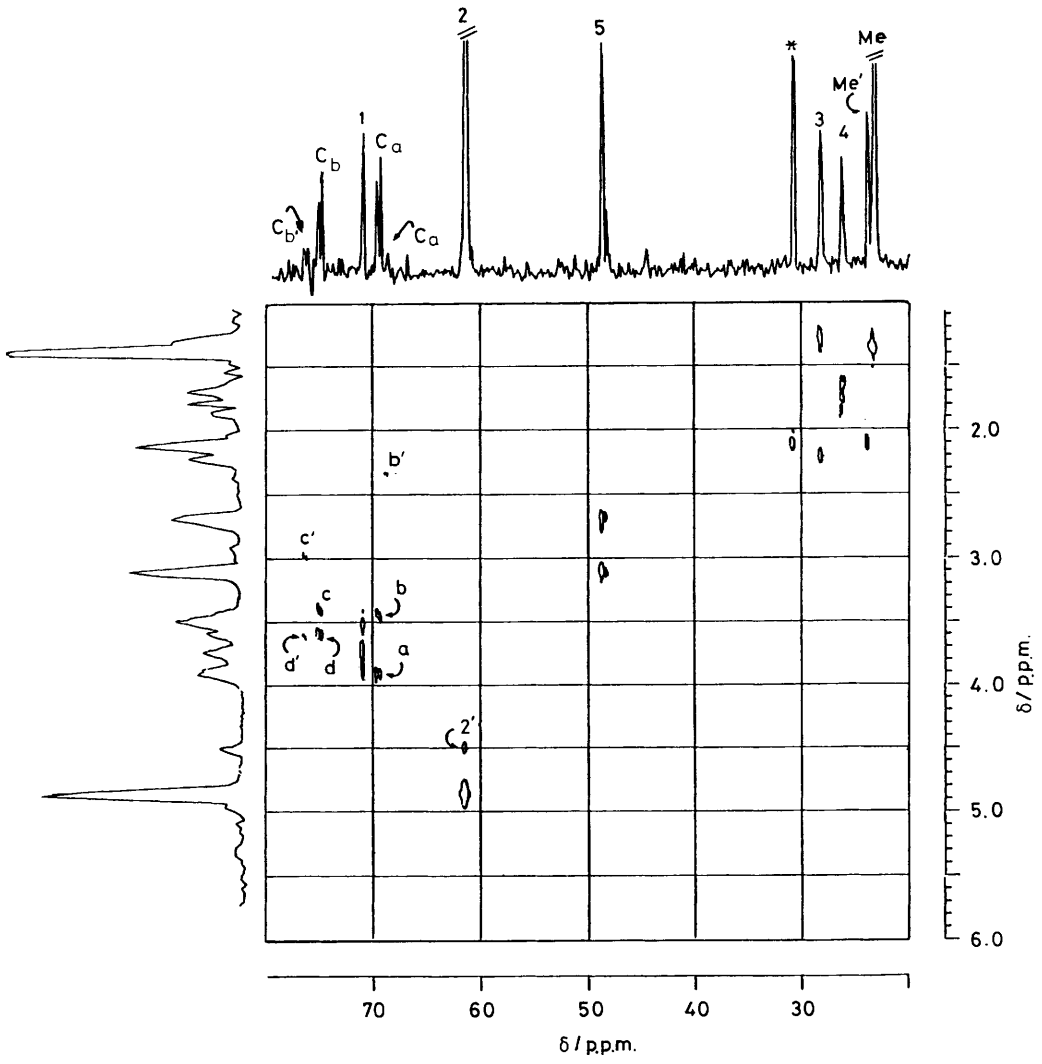


Figure 6. Counter plot in the aliphatic region of two-dimensional ^{13}C–^{1}H (400.13 MHz, $CDCl_3$, 298 K) correlation spectrum for complex (**1**). Horizontal projection: one-dimensional ^{13}C-{^{1}H} spectrum; vertical projection: one-dimensional ^{1}H homodecoupled spectrum. Signals of minor isomer are marked with primes; * indicates impurity

effect from the phenyl rings of the ligand on the other parts of the molecule. Accordingly, on irradiating at δ 6.9 (which is one resonance of the phenyl group *cis* to P_a) n.O.e. was observed at δ 3.93 (H_a) and 1.4 (either $H^{3'}$ or CH_3). (The signals at δ 1.4 exhibited a further n.O.e. with the phenyl resonance at δ 7.4.) This evidence of steric interactions between the allyl group and the phosphine ligand supports the notion that the ligand has the potential to create a chiral environment and sterically control the nucleophilic attack. Additionally, the relative orientation of the allyl in the two isomers with respect to dpopyr, *i.e.* the absolute configuration of (**1a**) and (**1b**), can be deduced. From the comparison of the CH allyl resonances of the major and minor isomers we observe that the δ values at the *syn* and *anti* protons *cis* to P_a are most affected (H_a and $H_{b'}$ are shifted to high field relative to the corresponding $H_{a'}$ and H_b of $\Delta\delta = 0.19$ and 1.71 respectively). This fact indicates that the *syn* proton H_a, in the former case, and the *anti* proton $H_{b'}$, in the latter, are quite perpendicular to one phenyl ring being bonded to P_a. Thus inspecting the Dreiding models of the two possible structures of complex (**1**) and assuming the ligand in the most favourable conformation, these findings suggest that the major and minor isomers have structures (**1a**) and (**1b**) respectively.

trans *Influence of the Ligand.*—The analysis of ^{3}J(XP) (where X = allylic carbon or proton) allow an evaluation of the relative *trans* influence of the two phosphorus atoms P_a and P_b. Either ^{1}H or ^{13}C measurements show smaller J values for the allylic CH_2 group *trans* to P_b relative to those of CH_2 *trans* to P_a. As a strong *trans* influence of the ligand has been associated with a decrease in *trans* spin–spin coupling constant [23] our data indicate that –PN– is a better σ donor than –PO–. Conversely in both isomers the ^{13}C resonance of C_b shifts downfield relative to that of C_a. In a series of [Pd(η^3-allyl)(LL′)] complexes,[10,11] this has been associated with a variation of relative charge at the η^3-allyl termini induced by the different acceptor capabilities of the ligands L and L′. In particular a relative positive charge has been attributed to the allyl carbon shifted to lower field and opposite to a better acceptor ligand. Our results suggest that –PO– is a stronger π acceptor than –PN–. Thus an asymmetric electron distribution is expected on the co-ordinated allyl in that C_a–C_c has a more pronounced double bond character than C_b–C_c with a residual positive charge on the C_b atom. Consequently nucleophilic attack should occur on the allylic carbon *trans* to –PO–. In principle the stereodifferentiation in asymmetric C–C bond formation promoted by these Pd

complexes should be based on steric interactions as well as electronic properties of the ligand. In order to study whether steric and electronic effects are additive or subtractive, asymmetric allylation experiments are in progress on analogous complexes with prochiral allyls.

Experimental

General Procedures.—The complex was prepared under an atmosphere of dinitrogen, in solvents dried and degassed prior to use. Elemental analyses were performed at the Dipartimento di Chimica Industriale ed Organica, Università de Milano. Mass spectra were recorded on a VG-7070 EQ mass spectrometer and the quoted M^+ is the peak in the parent multiplet which arises from the most abundant Pd isomers. Proton, ^{13}C, and ^{31}P n.m.r. spectra were measured using Bruker AC-200, Bruker WH-400, and Varian XL-200 spectrometers; JMOD, DEPT, and two-dimensional spectra were measured using standard pulse sequences[24] and microprograms from the Bruker manual.

The complex $[\{Pd(\eta^2\text{-}C_4H_7)Cl\}_2]$[25] and ligand dpopyr[15] were prepared according to reported methods.[25]

Preparation of $[Pd(\eta^3\text{-}C_4H_7)(dpopyr\text{-}PP')]BF_4$ (**1**).—Silver tetrafluoroborate (58.5 mg, 0.3 mmol) in tetrahydrofuran (2 cm^3) was added at room temperature to a stirred solution of $[\{Pd(\eta^3\text{-}C_4H_7)Cl\}_2]$ (65 mg, 0.33 mmol) in CH_2Cl_2 (5 cm^3). Immediately the solution changed from yellow to very pale yellow and a white precipitate of AgCl was formed. The precipitate was filtered off through a Celite plug (2 cm) and the ligand dpopyr (140.7 mg, 0.3 mmol) in CH_2Cl_2 (2 cm^3) was added to the solution cooled at −78 °C. On allowing the solution to reach room temperature, the colour was changed to pale brown. The solvent was removed *in vacuo* and complex (**1**) was obtained as a grey solid (183 mg, 85% yield). Recrystallization from CH_3OH gave (**1**) as white needles (91.5 mg, 50% yield based on crude product) (Found: C, 54.8; H, 4.90; N, 1.95%; M^+, 629. Calc. for $C_{33}H_{36}BF_4NOP_2Pd$: C, 55.2; H, 5.00; N, 1.95%; M^+, 630).

The analogous PF_6^- salt was prepared similarly and was fully characterized by n.m.r. spectroscopy.

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