Intramolecular Exchange in the Cation 1,2-Bis(diphenylphosphino)ethane(2-methylallyl)palladium[1]

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Abstract: The compound 1,2-bis(diphenylphosphino)ethane(2-methylallyl)palladium hexafluorophosphate has been prepared, and the pmr examined. In $CDCl_3$ or *o*-dichlorobenzene the pmr spectrum to temperatures above 145° is characteristic of an allyl group undergoing no motion with respect to the remainder of the molecule. A simplified analysis of the spectrum leads to estimates of the coupling constants of $J(\text{P–P}) = 12$, $J(\text{H}_2\text{–P}_{cis}) = 0$ Hz, $J(\text{H}_2\text{–P}_{trans}) = 5.0$, $J(\text{H}_3\text{–P}_{cis}) = 1.3$, and $J(\text{H}_3\text{–P}_{trans}) = 10.7$ Hz, where H_2 and H_3 refer to allyl protons *syn* and *anti*, respectively, in relation to the 2-methyl group. Addition of pyridine causes H_2–H_3 exchange to occur. Because of the presence of the scalar P–P interaction, it is possible to conclude that the two sides of the allyl group are not exchanging. Thus, it appears that the base promotes π–σ equilibration, but does not bring about rotation of the allyl group.

The intramolecular motions leading to exchange of allyl groups π-bonded to metal systems have been the subject of extensive literature. These motions, as evidenced by temperature-dependent nmr spectra, are generally considered to consist in (a) a π–σ equilibrium,[3,4] in which the π-bonded allyl group becomes momentarily σ-bonded (rotation may then occur about the metal–carbon bond, or about the adjacent carbon–carbon single bond, followed by re-formation of the π-bonded form); (b) rotation of the allyl group in the plane of its equilibrium position relative to the metal,[5–7] *i.e.*, roughly in a plane which is normal to the metal–allyl group bond axis; (c) rotation of the terminal CH_2 groups about the carbon–carbon bond in which the allyl group as a whole retains the π configuration relative to the metal;[8] (d) a flip motion,[9,10] in which the allyl group rotates backward, the central carbon moving away from the metal. The axis of the rotation lies in the plane of the equilibrium position of the allyl group, and passes roughly through the terminal carbon atoms. These motions are, in varying degrees, distinguishable by use of nmr. With a labeling system as shown in Figure 1, the exchanges effected by the four motions described above are listed in Table I.

Table I. Exchanges Effected by Allyl Group Motions

π–σ equilibrium	H_2–H_3 or H_2'–H_3'
Rotation in plane	H_3–H_3' and H_2–H_2'
Rotation about C–C	H_2–H_3 or H_2'–H_3'
Allyl flip	H_2–H_3 and H_2'–H_3'

In cases where the allyl group is bonded symmetrically to a metal, *i.e.*, in which there is a plane of symmetry passing through the central carbon and the metal, certain of these motional alternatives are indistinguishable. When the allyl group is bonded unsymmetrically to the metal, so that H_2 and H_2' and H_3 and H_3' are chemically distinct, both π–σ equilibrium and C–C bond rotation possess different rates for the two sides of the allyl group. An additional possibility for unsymmetrically bonded systems is that exchanges involving the other ligands bonded to the metal might produce an equivalence of the two otherwise distinct sides of the allyl group, without requiring any motion of the allyl group relative to the metal.[11] For example, 2-methylallyltriphenylphosphinepalladium chloride undergoes two exchange reactions on the nmr time scale in the presence of excess triphenylphosphine.[6] From −100 to +40° the phosphine coordinated to the palladium exchanges with free phosphine in solution. At temperatures greater than 40° the *syn* and *anti* protons of the allyl group exchange (*i.e.*, H_2–H_3, H_2'–H_3'). Since both these reactions seem to be first order in both (π-C_4H_7)PdCl(PPh_3) and triphenylphosphine, a five-coordinate intermediate has been proposed. It has been stated that the allyl group can[6] or might[5] rotate in its own plane in an intermediate of this type. Because of ligand exchange, however, the relationship between one particular end of the allyl group and the coordinated phosphine is lost, so that the two ends of the allyl are equivalent ($H_2 \approx H_2'$, $H_3 \approx H_3'$). Therefore rotation of the allyl group, if it exists, is not observable in the spectra.

To more fully characterize the motions of the allyl group under various conditions in the π-allyl–palladium systems we have studied the nmr spectra of 1,2-bis(diphenylphosphino)ethane(2-methylallyl)palladium hexafluorophosphate, (diphos)MeAPdPF$_6$. The choice of this compound is based on the expectation that the bidentate phosphine ligand is very tightly bound to the metal, and that ligand exchange will not occur on the nmr time scale. Furthermore, the diphos ligand is particularly valuable in that the scalar couplings of ^{31}P with the protons of the allyl

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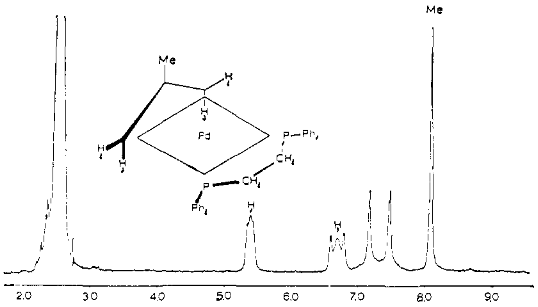

Figure 1. The nmr spectrum of (diphos)MeAPdPF$_6$ in CDCl$_3$ at 44°.

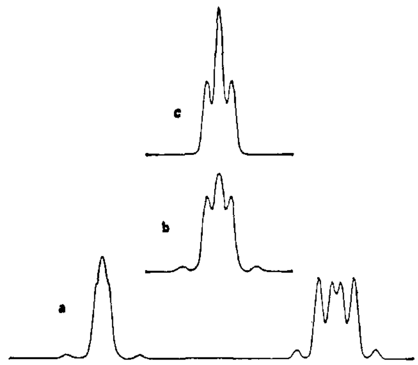

Figure 2. The calculated exchange spectrum for (diphos)-MeAPdPF$_6$: (a) no exchange, (b) H$_2$–H$_3$ exchange with no allyl group rotation, (c) H$_2$–H$_3$ exchange with allyl group rotation.

groups provide a means by which the two ends of the allyl group can be distinguished in the nmr spectrum, even though the allyl group is symmetrically bonded. In addition to observing the proton magnetic resonance spectrum of the compound in a noninteracting solvent, we have examined the effect of added pyridine, which might be expected to coordinate to the palladium, thus promoting certain of the allyl group motions alluded to above, particularly the π–σ equilibrium.

Experimental Section

A. **Preparation of Compounds. 1,2-Bisdiphenylphosphinoethane (diphos).**[12] Lithium foil (6 g) was added to a solution of 100 g of triphenylphosphine in 500 ml of tetrahydrofuran. After 5 hr any remaining lithium was removed, the solution was cooled to 0°, and 30 ml of ethylene dichloride was added in small portions over 1 hr. The solution was stirred for 5 hr. Methanol (750 ml) and sufficient water to precipitate the product were added. The crude product was purified by Soxhlet extraction with petroleum ether (bp 90–110°), yield 50%.

Anal. Calcd for $C_{26}H_{24}P_2$: C, 78.39; H, 6.03. Found: C, 78.57; H, 5.97.

1,2-Bisdiphenylphosphinoethane(2-methylallyl)palladium Hexafluorophosphate. 2-Methylallylpalladium chloride (1 g) and diphos (2.1 g) were dissolved in chloroform. The solution was allowed to stand in the presence of solid potassium hexafluorophosphate until the solution was nearly colorless. The white crystals precipitated from the solution upon addition of hexane. These crystals were recrystallized from chloroform–hexane to remove all traces of color.

Anal. Calcd for $C_{30}H_{31}PdP_3F_6$: C, 50.92; H, 4.38. Found: C, 50.95; H, 4.36.

B. **Nuclear Magnetic Resonance Spectra.** Measurements of nuclear magnetic resonance spectra were made on Varian Associates Model A-60A, A-56/60, or HA-100 spectrometers. Temperatures were measured on a dummy sample using an iron–constantan thermocouple with ice as reference junction. Comparison of results with those obtained using an ethylene glycol sample showed agreement to within about 2°.

Results and Discussion

The pmr spectrum of (diphos)MeAPdPF$_6$ in CDCl$_3$ at 44° is shown in Figure 1. The spectrum is unchanged on heating to 140°. The doublet just upfield from the H$_3$ "triplet" is due to the CH$_2$ protons of the diphos ligand. The spectrum corresponds to an AA′KK′M$_2$M$_2$′T$_3$XX′ type, in which the H$_2$ = A, H$_3$ = K, ligand CH$_2$ = M, 2-methyl = T$_3$, and X = phosphorus. If it is assumed that all proton–proton coupling constants are zero, as is very nearly the case in all the systems reported,[5,6,9] the experimental spectra can be described in terms of the simpler systems, AA′XX′, KK′XX′, M$_2$M$_2$′XX′, and T$_3$XX′. From the observation that the 2-methyl absorption is a singlet, J(XT) = 0.

The AA′XX′ type of system has been thoroughly investigated, and explicit expressions for the transition energies and intensities have been derived.[13] Calculated spectra were synthesized assuming a Gaussian line shape function.

The spectrum is characterized by four parameters, J(AX′), J(AX), J(AA′), and J(XX′). The separation of the two strong outer lines is equal to [J(AX′) + J(AX)], Figure 1. Since the approximation J(AA′) = 0.0 is made, the AA′XX′ system can be described by the two unknowns, J(XX′) = J(PP′) and by the ratio = J(AX)/J(AX′) which in our case is $J(\text{H–P}_{cis})/J(\text{H–P}_{trans})$.

$$J(\mathrm{AA'}) = 0.0$$

$$J(\mathrm{AX'}) = [J(\mathrm{AX}) + J(\mathrm{AX'})]/(1.0 + \text{ratio})$$

$$J(\mathrm{AX}) = [J(\mathrm{AX}) + J(\mathrm{AX'})] - J(\mathrm{AX'})$$

$$J(\mathrm{XX'}) = J(\mathrm{PP'})$$

Of course the value of J(PP′) will be constant so the larger system AA′KK′XX′ can be described by three parameters: ratio for the AX system, ratio for the KX system, and J(XX′).

A computer program which systematically varies these parameters, and seeks a minimum error in the sums of calculated and observed absorption intensities over the multiplets, was employed. In addition, a noniterative program was employed to calculate the expected fast exchange spectra for various exchange mechanisms, and to demonstrate the sensitivity of the calculated spectra to changes in the coupling constants.

Two sets of coupling constants were found to correspond to minima in the error curve; they are

	J(P–H$_2$)		J(P–H$_3$)		J(PP′)
	trans	*cis*	*trans*	*cis*	
Set 1	4.99	0.0	10.68	1.31	12.01
Set 2	3.89	1.10	8.09	3.90	2.16

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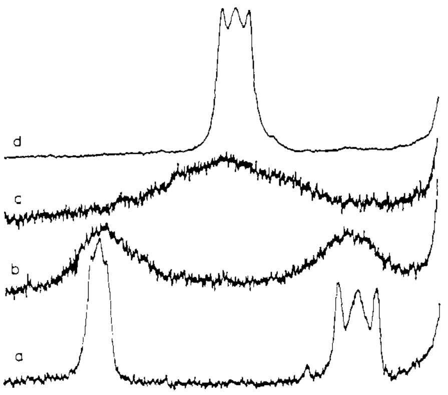

Figure 3. The nmr spectra of (diphos)MeAPdPF$_6$ at 44°: (a) in chloroform, (b) in CDCl$_3$ with 0.41 *M* pyridine, (c) in CDCl$_3$ with 2.93 *M* pyridine, (d) in neat pyridine at 80°.

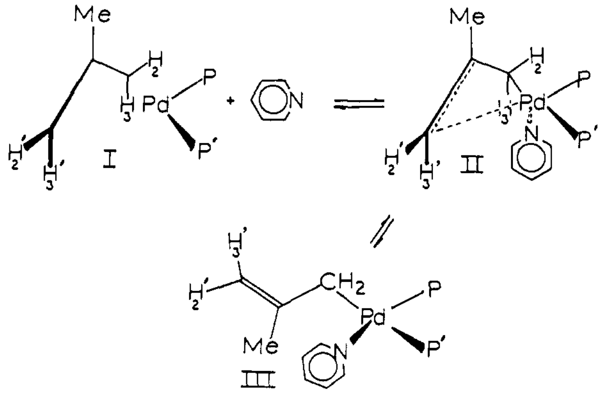

Figure 4. Illustration of the mechanism for π–σ exchange in the presence of pyridine.

The first set of coupling constants was used in all subsequent calculations since its value of J(PP′) is in most reasonable accord with other known *cis* P–P couplings.[14,15] Figure 2a shows the results of these calculations. It should be emphasized that the conclusions described below with respect to the exchange mechanism are not affected by the choice of assignment.

Comparison of Figure 2a with the experimental spectrum, Figure 1, shows that the fit is quite good. The major source of discrepancy is that the central peak of the calculated multiplets, particularly of the H$_2$ "triplet," is too high. This is very probably due to the assumption of zero values for J(H$_2$–H$_2$′) and J(H$_2$–H$_3$). Although a better fit to the spectrum might be obtained by inserting small, nonzero values for these constants, there is little point in doing so, since the quality of the fit is quite sufficient to establish the values for the important P–P′ and H–P coupling constants. Extensive efforts were made to locate the low intensity lines outside the major multiplets, but they could not be discerned. The positions and intensities of these lines are very sensitive to the parameters and it is not surprising that they are not seen.

It is of particular interest that the observed spectrum is invariant with temperature in *o*-dichlorobenzene to about 145°. At 160°, there is some evidence of collapse of the multiplets, but decomposition is also fairly rapid at this temperature. This observation establishes that in the absence of base *the allyl group does not undergo any motion leading to exchange on the nmr time scale in the temperature interval studied, to above 145°.* In particular, rotation of the allyl group, which could not be ruled out by any previous data, *e.g.*, observation of allylpalladium chloride dimer,[5,9] is excluded.

Upon addition of pyridine, H$_2$ and H$_3$ protons exchange. In Figure 3 are shown (a) the spectrum of (diphos)MeAPdPF$_6$ in chloroform, (b) upon addition of 0.41 *M* pyridine at 44°, (c) 2.9 *M* pyridine at 44°, and (d) in neat pyridine at 80°. The H$_2$ line width was measured as a function of added pyridine concentration at 44° in the slow exchange region. Although the H$_2$ resonance is a multiplet and not a single line, the increase in half-intensity width due to exchange should be approximately proportional to $1/\tau_e$, the inverse exchange time for transfer of a proton from the H$_2$ site. The increase in width is proportional to the concentration of added pyridine, showing that the exchange rate is first order in pyridine. Variation of complex concentration at fixed pyridine concentration did not lead to a change in line shape. From these results it may be assumed that the exchange reaction is first order each in complex and pyridine. The exchange presumably occurs as a result of the bimolecular interaction of pyridine and the complex, involving a five-coordinate intermediate or transition state.

It is of particular interest to know whether the exchange process involves only H$_2$–H$_3$ and H$_2$′–H$_3$′ exchange, or whether there is in addition an H$_2$–H$_2$′ and H$_3$–H$_3$′ exchange. Because of the particular character of the spin system involved here it is possible to answer this question.

Figure 2b shows the calculated spectrum for exchange of H$_2$ and H$_3$ in the absence of rotation. J(H$_2$–P$_{cis}$) and J(H$_3$–P$_{cis}$) are averaged, J(H$_2$–P$_{trans}$) and J(H$_3$–P$_{trans}$) are averaged. Figure 2c is the spectrum for H$_2$–H$_3$ exchange accompanied by allyl group rotation. J(H$_2$–P$_{cis}$), J(H$_3$–P$_{cis}$), J(H$_2$–P$_{trans}$), and J(H$_3$–P$_{trans}$) are *all* averaged. Since all P–H coupling constants are equal this spectrum is an A$_4$X$_2$ type. The magnetic nonequivalance of the phosphorus atoms has been removed by rotation; the spectrum is first order and can be predicted by the usual first order rules. This spectrum is not affected by the value of J(P–P). The spectrum is also independent of the calculated values of the *cis/trans* coupling constant ratios. J(AX) for the A$_4$X$_2$ is the average of all the phosphorus–hydrogen coupling constants given above. As noted earlier the sums [J(AX′) + J(AX)] and [J(KX′) + J(KX)] are directly obtained from the spectrum, Figure 1. Therefore spectrum 2c is not dependent on any of the previous calculations.

The experimental spectrum for the fast exchange limit, Figure 3d, is closest to the spectrum calculated for H$_2$–H$_3$ exchange with no rotation, Figure 2b. The experimental spectrum is not intermediate between 2b and 2c; the central peak is lower and broader than in either case. *It can therefore be concluded that rapid rotation of the allyl group does not occur.*

It has been established that in certain cases, involving allyl groups π-bonded to metals with a coordination

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number of six, rotation of the allyl group can occur.[16,17] On the other hand, we have shown that in the four-coordinate palladium compound, even at high temperatures, rotation does not occur. The absence of rotation in the exchange catalyzed by pyridine is therefore of significance in characterizing the potential energy surface for the exchange process. The allyl flip motion (d), which is ruled out along with all the other possible motions in the absence of base, is not likely to possess a lower activation barrier in the presence of base. In the transition state for the flip, the palladium is still formally four-coordinate, and it is difficult to see how base might facilitate this pathway. Similarly, rotation about the C–C bond can be disregarded. It is almost certainly the case therefore that the H_2–H_3 and H_2'–H_3' exchanges observed in the presence of pyridine are due to a π–σ equilibrium occasioned by attack of the base at palladium. There must therefore be a four-coordinate intermediate involving coordinated pyridine and σ-bonded allyl group (III, Figure 4). The fact that there is no exchange of the two sides of the allyl group, however, implies that there is not a five-coordinate intermediate in which the allyl group might rotate. It would appear, therefore, that the transition state for the exchange process involves concerted displacement of one side of the allyl group and coordination of pyridine (II, Figure 4).

The lifetime of the four-coordinate, σ-allyl-bonded intermediate is not revealed in these results, but it is presumably quite short, since exchanges of ligands in the four-coordinate species are rapid on the nmr time scale at lower temperatures than are dealt with here.[4,6,11] The probability of a change in the orientation of either ^1H or ^{31}P spins during the lifetime of the intermediate is therefore extremely small.

If there is no rotation in the presence of exchange in this system, at a temperature of 80°, as shown in Figure 3d, it seems unlikely that five-coordinate intermediates in which allyl groups might rotate are operative in *any* exchange systems reported thus far. Unfortunately, efforts to extend the experiment by employing a base of significantly different characteristics, triphenylphosphine, resulted in degradation of the complex, rendering meaningful observations impossible.

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