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Studies of Exchange Equilibria of Palladium(II) Tertiary Phosphine Complexes

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The reactions of tertiary phosphine complexes of Pd(II) with phosphine ligands have been investigated by NMR and conductivity measurements. Depending on the nature of the phosphine ligand either ligand exchange or the formation of cationic complexes can occur. Relative equilibrium constants for these reactions have been obtained. NMR line broadening experiments have enabled the relative rates of ligand exchange between the neutral and cationic complexes and between the cationic complex and free ligand to be obtained. A mechanism for the former process is suggested. The equilibrium constant data suggest that optimum stability for the complexes is achieved with ligands of intermediate donor ability. The significance of this observation is discussed.

Introduction

Tertiary phosphines form an extensive series of complexes with ions of the group VIII transition metals. The chemistry of these compounds has been the subject of numerous investigations and has been reviewed by Booth [1]. One of the factors which has particularly encouraged research in this area in recent years has been the discovery of a number of examples of reactions homogeneously catalyzed by group VIII phosphine complexes. Perhaps the best known is the hydrogenation of olefins using tristriphenylphosphine rhodium chloride [2]. The common feature to such catalytic reactions is that they proceed by a number of steps which are essentially ligand exchange reactions. In some cases there is direct exchange between free and complexed ligands. In other cases the solvent may be involved. In still other cases (*e.g.*, "insertion" reactions) ligands already present may rearrange to give new ligands. In each case though the net result is a change in the ligand environment of the metal. The overall efficiency of the catalytic reaction will depend on the rates and equilibrium constants of these ligand exchange reactions. It is therefore of interest to enquire how the rates and equilibrium constants of ligand exchange reactions depend on the nature of the ligand and on the nature of the metal ion. The present paper presents some data on equilibria involving Pd(II) and different tertiary phosphine ligands.

In order to investigate the dependence of rates and equilibrium constants on ligand properties it is desirable to study a series of complexes with a constant metal ion. Our initial choice was palladium(II) for several reasons. The large majority of Pd(II) complexes are square planar and the involvement of tetrahedral and octahedral geometries found in Ni(II) is unlikely. On the other hand Pd(II) complexes are considerably more labile than the corresponding Pt(II) complexes and the ligand exchange reactions are correspondingly more accessible to study by NMR [3]. They are also much less susceptible to oxidation reactions than are d^8 Rh(I) and Ir(I) complexes. They therefore seemed to offer the best possibilities for studying ligand exchange without complicating side reactions. We shall report in subsequent papers some results with other transition metal ions and also some experiments designed to investigate the complimentary problem of the variation of properties in a system with a constant ligand and variable metal ion.

The intent in the present work was to use NMR as the primary experimental technique. Providing the free and complexed ligand have different chemical shifts relative equilibrium constants can be found for two phosphine ligands competing for coordination sites on a limited number of metal ions. Line broadening studies will give information on the rates of ligand exchange providing they are of a suitable magnitude. It might be anticipated that the equilibrium constants and rates would depend on either the steric properties of the ligand or the electron donating ability of the ligand or a combination of both. Tolman [4] has reported parameters measuring both of these properties for an extended series of phosphine ligands. In the course of this work it became apparent that the formation of ionic complexes was important in many cases and the NMR experiments have therefore been supplemented with conductivity data.

Proton NMR spectra for a number of Pd(II) phosphine complexes have been reported [5, 6]. In most

TABLE I. Methyl Group Chemical Shifts[a] of Phenyl Methyl Phosphine Complexes.

L	X	Neutral[b] *Trans*	Neutral *Cis*	Cation[c] *Trans*	Cation *Cis*
$(CH_3)(C_6H_5)_2P$	Cl	2.03	2.06	1.95	2.48
	Br	–	2.26	1.92	2.78
	I	–	2.61	–	–
$(CH_3)_2(C_6H_5)P$	Cl	1.77	–	1.25	2.07
	Br	–	1.93	1.18	2.21
	I	–	2.22	1.06	2.39

[a] Chemical shifts in ppm to low field of TMS. Solvent $CDCl_3$. 220 M Hz. [b] Neutral complexes PdL_2X_2. *Trans* and *Cis* refer to position with respect to halide ligand. [c] Cationic complexes PdL_3X^+. *Trans* and *Cis* refer to position with respect to halide ligand.

cases the data has been used to obtain structural information. In particular for complexes containing a methyl group attached to the phosphorus the presence or absence of "virtual coupling" has been used to infer whether the complex has *cis* or *trans* geometry. Fackler *et al.* [7] has discussed the effect of ligand exchange on the "virtual coupling" patterns. However this discussion did not take account of the formation of ionic species which modifies the interpretation of the results proposed by Fackler. A recent paper by Cooper and Powell [8] has made use of NMR in a study of the mechanism of *cis–trans* isomerization of some Pd(II) phosphine complexes. It was demonstrated that the isomerisation is catalyzed by added ligand and proceeds via an ionic intermediate.

NMR Studies

The proton NMR spectrum of the complex $[(CH_3)_2C_6H_5P]_2PdCl_2$ obtained at 18 °C in $CDCl_3$ using a 220 MHz instrument shows a complex group of resonances between 7.3 ppm and 7.7 ppm to low field of TMS and a doublet of 11 Hz splitting at τ = 1.77 ppm. The former resonances arise from the aromatic protons and the latter from the methyl groups. The observation of a doublet for the methyl group rather than a "virtually coupled" triplet shows that the compound has *cis* geometry. On adding excess ligand to such a solution the methyl doublet collapses to a single resonance and no addition line due to free ligand is observed. This observation parallels that of Fackler [7] on the same system who inferred that the result indicated fast ligand exchange between $P(CH_3)_2C_6H_5$ and $[(CH_3)_2C_6H_5P]_2PdCl_2$. However when the experiment is repeated at –50 °C somewhat different results are obtained. On addition of free ligand the resonance due to the starting complex diminishes in intensity and two new resonances appear. Neither of the new resonances can be attributed to free ligand. The new lines appear as a doublet of intensity one at 1.95 ppm from TMS and a triplet of intensity two at 2.48 ppm from TMS. We assign this spectrum to the cation $[(CH_3)_2C_6H_5P]_3PdCl^+$. The doublet arises from the phosphine *trans* to the chloride ion and the triplet from the two phosphines *cis* to the chloride ion. This assignment is confirmed by the conductivity data reported below.

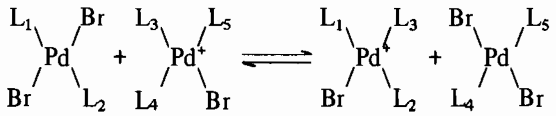
The formation of cationic phosphine complexes of Pd(II) has been reported in the literature. Clark and Dixon [9] prepared tetraphenylborate salts of a number of such cations. Cooper and Powell [10] have obtained NMR spectra of the analogous Pt(II) complexes and in a recent paper presented evidence for the existence of cationic complexes of Pd(II) compounds containing *o*-tolylphosphine ligands as intermediates in the *cis–trans* isomerization reaction [8]. In a ^{31}P NMR study Grim and Keiter [11] noted a colour change from yellow to red on adding phosphine ligand to neutral phosphine complexes of Pd(II) and suggested the formation of either a five coordinated complex or a cationic complex.

The reaction:

$$L_2PdX_2 + L \rightleftharpoons L_3PdX^+X^-$$

has been followed by NMR for the cases where L = $(CH_3)_2C_6H_5P$ and $CH_3(C_6H_5)_2P$ and X = Cl, Br, I. In each case the equilibrium constants for this reaction are large and mixtures of equimolar quantities of complex and free ligand show only the resonances of the cationic complexes. Chemical shift data for the cationic complexes is presented in Table I. Some of the details however vary depending on the nature of L and X.

Consider first the cases where L = $(CH_3)(C_6H_5)_2P$ and X = Cl, Br, I. In each case addition of free ligand to L_2PdX_2 at –50 °C leads to the appearance of the resonances due to the cation and the disappearance of those due to the starting complex. At equimolar concentrations of ligand and complex (L/M = 1) the lines of the starting complex have completely disappeared. With L/M > 1 a free ligand resonance appears. At –50 °C there is slow exchange (on the NMR time scale) between the cation and free ligand. The experiments provide no evidence on the rate of exchange between free ligand and neutral complex since at L/M < 1 no free ligand is present and at L/M > 1 no neutral complex is present. They do however give some information on exchange reactions between the cationic and neutral complexes and between the cationic complex and free ligand. Fig. 1 shows a series of spectra for mixtures at different ratios of L/M for the case where X = Br. The significant observations are that at L/M < 1 the lines from the neutral complex and from the phosphines *cis* to the Br of the cationic complex are broadened while those from the phosphine *trans* to the Br are sharp. At L/M > 1 the free ligand line and that from the phosphine *trans* to the Br are broadened while the line from the phosphine *cis* to the Br is sharp. From the first of these observations we deduce that the exchange process between the neutral and cationic complexes does not affect the environment of the phosphine *trans* to the Br in the cationic complex. This condition can be fulfilled by a reaction in which a bromide of L_2PdBr_2 is exchanged directly with the phosphine *trans* to the Br of L_3PdBr^+, *i.e.*



The effect of this reaction is to exchange the environments of L_1 and L_2 with those of L_4 and L_5 but to leave L_3 always situated *trans* to Br on the cationic complex. A reasonable mechanism would involve bridging of the exchanging Br to give a five coordinated intermediate followed by transfer of the phosphine with retention of configuration.

At ratios of L/M greater than 1 the phosphine *trans* to Br in L_3PdBr^+ is still the more labile ligand but in this case direct exchange with free ligand leads to broadening of the *trans* phosphine and free ligand lines. The complex with L = $(CH_3)(C_6H_5)_2P$ and X = Cl can exist in either the *cis* or *trans* isomeric forms. On solution in $CDCl_3$ the proton NMR indicates that both isomers are present. The CH_3 resonance of the *cis* isomer comprises a doublet (J = 11 Hz) at δ = 2.03 ppm from TMS and the *trans* isomer gives an overlapping triplet at δ = 2.06 ppm. On addition of a small amount of free ligand the resonances due to the *trans* isomer disappear and lines attributable to $[(CH_3)(C_6H_5)_2P]_3PdCl^+$ appear. Since this occurs when considerably less $(CH_3)(C_6H_5)_2P$ has been added than the amount of *trans*-$[(CH_3)(C_6H_5)_2P]_2PdCl_2$ originally present it is inferred that the mixture of *cis* and *trans* isomer originally present is not at equilibrium and that the added ligand catalyzes the *trans* → *cis* isomerization. The reaction is so rapid that no trace of the *trans* isomer remains 30 secs after the addition of a catalytic amount of free ligand. This observation is in accord with the studies of Cooper and Powell [10] on the isomerization of *o*-tolylphosphine complexes of Pd(II).

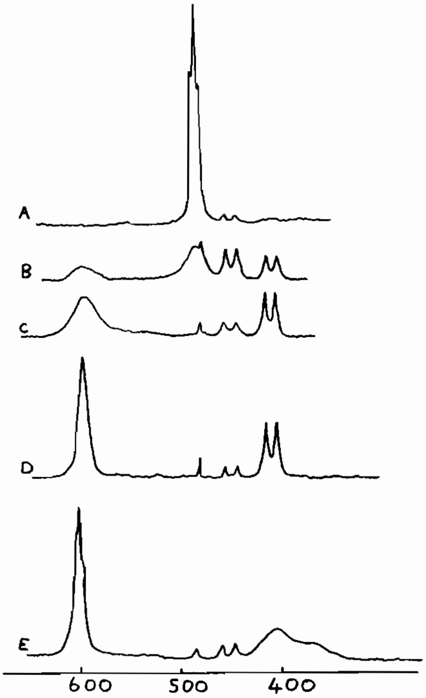


Figure 1. 220 MHz PMR spectra of mixtures of $[(CH_3)(C_6H_5)_2P]_2PdBr_2$ and $(CH_3)(C_6H_5)_2P$. Solvent $CDCl_3$. Temperature −50 °C. A. Free ligand to metal complex ratios L/M = 0. B. L/M = 0.5. C. L/M = 0.9. D. L/M = 1.0. E. L/M = 1.2. Scale gives shifts in Hz to low field of TMS. Assignments. L_2PdBr_2, 497 Hz; L_3PdBr^+ (*trans*), 422 Hz; L_3PdBr^+ (*cis*), 612 Hz; L, 356 Hz.

The results for the complexes with L = $(CH_3)_2(C_6H_5)P$ and X = Cl, Br, I differed somewhat from those described above. For X = Cl and Br at ratios of L/M < 1 there is again quantitative formation of the cation and (at −50 °C) slow exchange between L_2PdX_2 and L_3PdX^+. For X = I there appears to be fast exchange (at −50 °C) between the neutral complex and the cation. Thus initial addition of free ligand causes the L_2PdI_2 resonance to broaden and shift to low field. This complex is present as the *trans* isomer and the line represents an average of the L_2PdI_2 ligands and the mutually *trans* phosphines of L_3PdI^+. Simultaneously a new somewhat broadened resonance appears at δ = 1.06 ppm and gradually moves towards the free ligand position of δ = 1.34 ppm. This must be ascribed to the average of the resonances from the free ligand and the complexed ligand *trans* to the iodine in the L_3PdI^+ complex. This result implies that the reaction forming the cationic complex is not quantitative in this case. At ratios of L/M > 1 only a single averaged resonance was observed for all three cases (X = Cl, Br, I). Thus complexes of $(CH_3)_2(C_6H_5)P$ differ from those of

$(CH_3)(C_6H_5)_2P$ in showing fast exchange at −50 °C between free ligand and cationic complex.

Reactions involving triphenylphosphine ligands have also been studied. The addition of $(CH_3)(C_6H_5)_2P$ or $(CH_3)_2(C_6H_5)P$ to $[(C_6H_5)_3P]_2\ PdX_2$ (X = Cl, Br, I) leads to displacement of triphenylphosphine. It appears that this reaction is quantitative since after the addition of two moles of ligand to one mol of complex only the resonances due to complexed methylphenylphosphine and free triphenylphosphine can be observed. Further addition of ligand leads to the formation of the cations described above. The converse reaction of adding triphenylphosphine leads to some rather unexpected results. For L = $(CH_3)(C_6H_5)_2P$ and X = Cl or Br resonances due to $[(CH_3)(C_6H_5)_2P]_3PdX^+$ are observed in the presence of a large excess of $(C_6H_5)_3P$. The reaction appears to be:

$$3[(CH_3)(C_6H_5)_2P]_2PdX_2 + 2(C_6H_5)_3P \rightleftharpoons$$

$$[(C_6H_5)_3P]_2PdX_2 + 2[(CH_3)(C_6H_5)_2P]_3PdX^+ \quad (1)$$

The occurrence of this reaction may be taken as further evidence for the high stability of the cationic complexes. No reaction is observed for X = I.. The results are rather different for complexes with L = $(CH_3)_2(C_6H_5)P$. In addition to lines due to $[(CH_3)_2(C_6H_5)P]_3PdX^+$ a new somewhat broadened triplet was observed in the region associated with the neutral complexes. We tentatively assign this to the mixed phosphine complex $[(CH_3)_2(C_6H_5)P]\ [(C_6H_5)_3P]\ PdX_2$ which could be formed by the reaction:

$$2[(CH_3)_2(C_6H_5)P]_2PdX_2 + (C_6H_5)_3P \rightleftharpoons$$

$$[(CH_3)_2(C_6H_5)P]_3\ PdX^+ +$$

$$+ \quad [(CH_3)_2(C_6H_5)P]\ [(C_6H_5)_3P]\ PdX_2 \quad (2)$$

This new resonance was not observed for X = I but some broadening of the resonance due to the starting complex was noted. Equilibrium constants for both of the above reactions were obtained by integration of the NMR spectra. This information together with the chemical shift data is presented in Table II.

Experiments similar to those described above have been carried out with the complexes with L = $(C_2H_5)(C_6H_5)_2P$ and L = $(C_2H_5)_2(C_6H_5)P$. It appears that these complexes behave quite similarly but the NMR spectra are more complex and correspondingly more difficult to interpret. We do not therefore report NMR results on these systems.

TABLE II. Equilibrium Constants for Reactions of PdL_2X_2 with $(C_6H_5)_3P$.

L = $(CH_3)(C_6H_5)_2P$		L = $(CH_3)_2(C_6H_5)P$	
X	K^a (l^2/mol^2)	X	K^b (l/mol)
Cl	1.3	Cl	4.9
Br	2.9×10^2	Br	5.6×10
I	small	I	small

[a] For reaction 1 (see text). [b] For reaction 2 (see text). The complexes *trans* $[(CH_3)_2(C_6H_5)P]\ [C_6H_5)_3P]\ PdX_2$ show CH_3 resonances at 1.64 ppm and 1.84 ppm to low field of TMS for X = Cl and X = Br respectively.

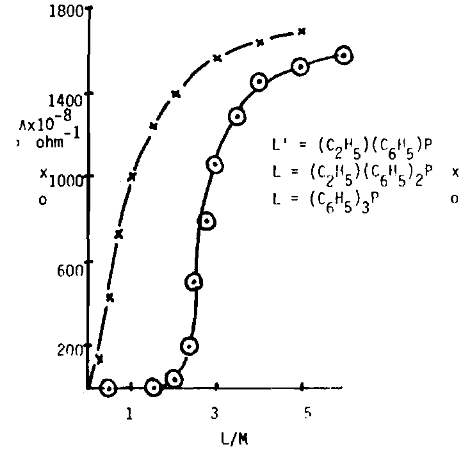


Figure 2. Conductivity of solutions of $[(C_2H_5)(C_6H_5)_2P]_2\ PdI_2$ (X) and $[(C_6H_5)_3P]_2PdI_2$ (○) on addition of $(C_2H_5)(C_6H_5)_2P$. Metal complex concentration 1.5×10^{-3} *M*, solvent nitrobenzene.

Conductivity Studies

Since the reaction of free ligands with these palladium complexes leads to the formation of ionic species it is apparent that the equilibria can be studied by conductometric methods. Conductometric titrations have been carried out in chloroform for the various reactions of the type:

$$L_2PdX_2 + L \rightleftharpoons L_3PdX^+ + X^- \quad (1)$$

Some typical plots are shown in Fig. 2. The conductivities of the iodide complexes were too small for convenient measurement in chloroform and the results for these compounds were therefore obtained in nitrobenzene.

The calculation of absolute equilibrium constants from conductivity data requires a knowledge of the extent of ion pairing and of the transference numbers of the various ions. This information is not readily available. It is however feasible to obtain the relative equilibrium constants of reaction 1 for complexes with the same halide ion. Two assumptions are required:

1. The conductivity due to a given concentration of L_3PdX^+ does not depend on the nature of L.

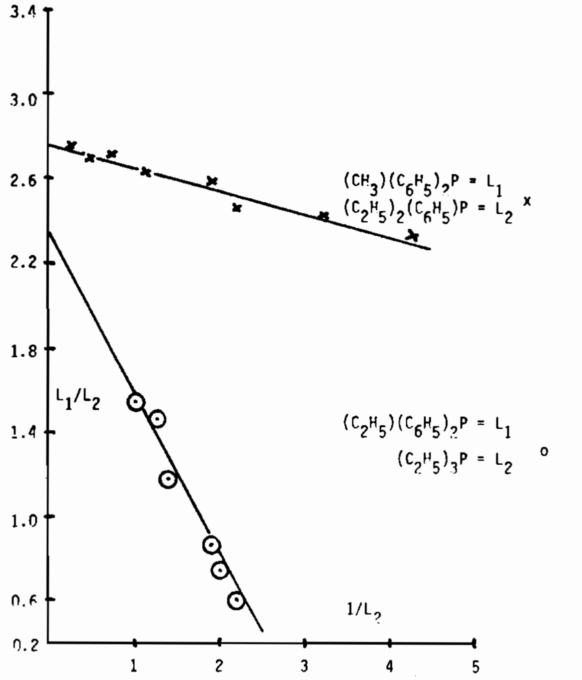


Figure 3. Reaction $L_2PdCl_2 + L \rightarrow L_3PdCl^+ + Cl^-$. Plots of L_1/L_2 *versus* $1/L_2$ for pairs of solutions giving equal conductivities.

2. The extent of ion pairing at a given concentration is independent of the nature of L.

If these assumptions are correct for two conductometric titrations of complexes involving the same halide ion when the measured conductivities are equal the concentrations of charged particles are equal. If then the molar concentration of complex initially present is the same for two titrations and L_1 and L_2 are the concentrations of the two ligands added to reach a given conductivity value it may be shown that:

$$\frac{L_1}{L_2} = \frac{\alpha(K_1 - K_2)}{K_1}\frac{1}{L_2} + \frac{K_2}{K_1}$$

In this equation K_1 and K_2 are the equilibrium constants for reaction 1 involving the ligands L_1 and L_2 and α is the concentration of charged particles. A plot of L_1/L_2 *versus* $1/L_2$ therefore has an intercept of K_2/K_1 and allows the determination of the relative equilibrium constants. A number of typical plots are shown in Fig. 3. We note that this method does not allow comparisons between complexes with different halide ions. Relative equilibrium constants obtained in this way are given in Table III. In this table the equilibrium constants for $L = (CH_3)(C_6H_5)_2P$ have been arbitrarily set at unity. It may be noted that for each halide series the K's vary by approximately an order of magnitude for different alkyl containing phosphines. The NMR results discussed above indicate that the absolute values of these equilibrium constants are large. This conclusion was confirmed by the observation that the conductivities of solutions of $(C_2H_5)_4NX$ (X = Cl, Br) were comparable to the maximum values measured for the palladium complexes.

TABLE III. Relative Equilibrium Constants from Conductivity Measurements, $L_2PdX_2 + L \rightleftharpoons L_3PdX^+ + X^-$.

L	Relative K		
	$X = Cl^a$	$X = Br^a$	$X = I^b$
$(C_6H_5)_3P$	0	0	0
$(CH_3)(C_6H_5)_2P$	1.00	1.00	1.00
$(C_2H_5)(C_6H_5)_2P$	0.91	1.96	7.00
$(CH_3)_2(C_6H_5)P$	1.10	1.20	3.80
$(C_2H_5)_2(C_6H_5)P$	2.36	–	–
$(C_2H_5)_3P$	1.77	0.23	2.80
$(nC_4H_9)_3P$	0.15	0.13	1.93

[a] Conductivities measured in $CHCl_3$. [b] Conductivities measured in $C_6H_5NO_2$.

Similar conductometric titrations were carried out on solutions of $[(C_6H_5)_3P]_2PdX_2$. The addition of an alkyl containing phosphine lead to no increase in conductivity until two mol of ligand had been added to one mol of complex. The conductivity then increased following a curve identical to that obtained by titration with the corresponding alkyl phosphine complex. Thus the initial reaction is quantitative displacement of the triphenyl phosphine followed by formation of the cation of the alkyl containing phosphine. There was one exception to this behaviour. The addition of $(nC_4H_9)_3P$ to $[(C_6H_5)_2P]_2Pd_2$ leads to no increase in conductivity until an L/M ratio of 2.9 was reached. In this case the displacement of triphenylphosphine by alkylphosphine is obviously not quantitative.

The Rates of Ligand Exchange Reactions

The complexity of the NMR spectra and the small chemical shifts prevented us from obtaining more than qualitative rate data. The following trends have been noted.

Exchange between L_2PdX_2 and L_3PdX^+ is in each case fast on the NMR time scale at room temperature and slow at –50 °C. From coalescence temperatures the following order of decreasing exchange rates was obtained.

$$[(CH_3)_2(C_6H_5)P]_2PdI_2 > [(CH_3)(C_6H_5)_2P]_2PdI_2$$

$$> [(CH_3)_2(C_6H_5)P]_2PdBr_2 > [(CH_3)(C_6H_5)_2P]_2PdBr_2$$

$> [(CH_3)_2(C_6H_5)P]_2PdCl_2 > [(CH_3)(C_6H_5)_2P]_2PdCl_2$

Thus in each case the iodide exchanges most rapidly and the chloride least rapidly. Rates for $(CH_3)_2(C_6H_5)P$ were greater than those for $(CH_3)(C_6H_5)_2P$.

Exchange between the cationic complexes and free ligand can be observed for solutions for which more than an equimolar amount of ligand has been added to the starting palladium complex. In this case the order of decreasing rates is somewhat different:

$$[(CH_3)_2(C_6H_5)P]_3PdCl^+ > [(CH_3)_2(C_6H_5)P]_3PdBr^+$$

$$> [(CH_3)_2(C_6H_5)]\,PdI^+ > [(CH_3)(C_6H_5)_2P]_3PdI^+ >$$

$$> [(CH_3)(C_6H_5)_2P]_3PdBr^+ > [(CH_3)(C_6H_5)_2P]\,PdCl^+$$

We also note that in the series of $(CH_3)(C_6H_5)_2P$ complexes, exchange of the *trans* ligand is clearly faster than exchange of the *cis* ligand. The two series of relative exchange rates are quite different. In the first case it seems that complexes containing better donating ligands exchange most rapidly. In the second case the dependence on halide ions is reversed *i.e.*, Cl > Br > I but the dependence on phosphine remains the same, *i.e.*, $(CH_3)_2(C_6H_5)P > (CH_3)(C_6H_5)_2P$.

Discussion

The results obtained above may be summarized as follows:

1. Phosphines more basic than triphenylphosphine displace this ligand. This reaction is quantitative except for the case of $(nC_4H_9)_3P$, the most basic ligand, for which it is necessary to add approximately three mol of ligand to displace the two mol of $(C_6H_5)_3P$.
2. Complexes other than those of triphenylphosphine form cationic compounds L_3PdX^+ on the addition of excess ligand. The equilibrium constants for this reaction depend on the nature of both the halide ion and phosphine.
3. Two types of ligand exchange reaction have been observed both of which occur at rates suitable for NMR studies. In both cases the relative rates vary with changes in both halide and phosphine ligands. It is desirable to rationalize the data on equilibrium constants and exchange rates in terms of the electronic or steric properties of the ligands.

The relative stability of two metal complexes ML and ML is reflected in the equilibrium constant for the ligand exchange reaction:

$$ML + L' \rightleftharpoons ML' + L$$

The equilibrium constant depends on the change in free energy rather than the change in enthalpy and hence does not directly measure differences in metal–ligand bond strengths. However it seems reasonable that for a series of closely related ligands the entropy change in the ligand exchange reaction should be roughly constant and hence that the equilibrium constant will reflect differences in metal ligand bonding. Similarly the rates of ligand exchange reactions depend on both the enthalpies and the entropies of activation but it has been common practice in the literature to assume that $\Delta S^{\neq}$ remains fairly constant for mechanistically similar reactions. Differences in rates have therefore been rationalized in terms of differences in $\Delta H^{\neq}$.

Tolman [12] has demonstrated that the differences in stabilities of Ni(0) phosphine complexes are largely determined by steric factors. He has presented a set of constants reflecting the steric properties of phosphine ligands. The present results show no correlation between these constants and the measured equilibrium constants. We infer that for Pd(II) phosphine complexes electronic rather than steric factors are dominant.

Tolman [4] has also studied the donor–acceptor properties of a wide range of phosphines using an infrared technique similar to that suggested by Horrocks and Taylor [13]. He has defined a substituent parameter χ for some 47 phosphine substituents and has found that these parameters are additive and correlate observed carbonyl stretching frequencies with high precision. The χ parameters also correlate well with σ parameters obtained by Kabachnik [14] from measurements of the basicity of phosphines. Tolman's χ values may therefore be taken as a measure of the net donor and acceptor properties of phosphines.

Owing to the formation of cationic complexes the data available on the direct ligand exchange reactions is limited. Of the phosphines examined the χ values indicate that triarylphosphines are the poorest donors followed by diarylalkylphosphines and aryldialkylphosphines in that order. Trialkylphosphines are the best donors. Triphenylphosphine is quantitatively displaced by ligands such as $(CH_3)(C_6H_5)_2P$ or $(CH_3)_2(C_6H_5)P$ but less than quantitatively by $(nC_4H_9)_3P$. It appears therefore that optimum stability of the palladium complex is achieved with a ligand more basic than $(C_6H_5)_3P$ but less basic than $(nC_4H_9)_3P$.

This conclusion is paralleled by the data on the equilibrium constants for the reaction

$$L_2MX_2 + L \rightleftharpoons L_3MX^+ + X^-$$

given in Table III. Fig. 4 shows plots of these relative equilibrium constants *versus* χ. In each case it is clear that the stability of the cationic complex relative

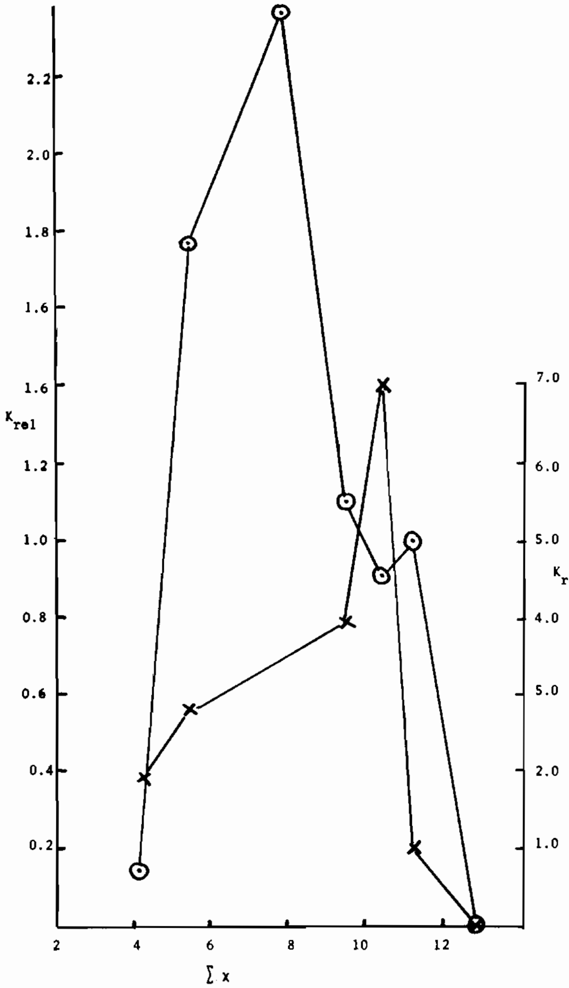


Figure 4. Relative equilibrium constants for the formation of cationic complexes plotted against Σχ. ⊙, X = Cl (left hand scale). x, X = I (right hand scale).

to the neutral complex passes through a maximum with varying χ. The maximum occurs at poorer electron donors on passing from the chlorides to the bromides to the iodides.

Examination of the literature reveals some examples of similar behaviour. Thus Rigo, Guastella and Turco [15] have measured equilibrium constants for the reaction

$$L_2Ni(CN)_2 + L \rightleftharpoons L_3Ni(CN)_2$$

where L represents a variety of phosphines. They do not comment on the variations for different phosphines. In a similar study Boschi, Rigo, Pecile and Turco [16] have obtained equilibrium constants for the reaction:

$$L_2Co(NCS)_2 + L \rightleftharpoons L_3Co(NCS)_2$$

In both cases plots of the equilibrium constants *versus* the χ values for the phosphines exhibit clear maxima as shown in Fig. 4.

A further illustration of the high stabilities of the complexes $[(CH_3)(C_6H_5)_2P]_3PdX^+$ and $[(CH_3)_2(C_6H_5)P]_3PdX^+$ which involve ligands of intermediate donor ability is provided by the observation that the addition of $(C_6H_5)_3P$ to $[(CH_3)(C_6H_5)_2P]_2PdX_2$ or $[(CH_3)_2(C_6H_5)P]_2PdX_2$ leads to the formation of cationic complexes and $[(C_6H_5)_3P]_2PdX_2$. The stability of the cation L_3PdX^+ is such that the concurrent formation of the less stable $[(C_6H_5)_3P]_2PdX_2$ is energetically profitable. It is interesting that the equilibrium constants for these reactions are highest for the bromides, in which the anionic ligand is of intermediate donor ability.

One way of viewing the relative stabilities of metal complexes is in terms of the charge on the metal atom. It is well recognized that the actual charge on the metal atom in a complex is very different from the formal charge. The ligands either donate or accept charge from the metal. Furthermore the type of ligands needed to obtain a stable complex varies with the formal oxidation state of the metal. In general low oxidation states are stabilized by good acceptor ligands and higher oxidation states by good donor ligands. The implication is that the charge on the metal ion should be neither too high nor too low and that maximum stability will be achieved with ligands whose donor and acceptor properties are best suited to provide this optimum metal charge. In the present case it appears that palladium halides require a rather better donor than $(C_6H_5)_3P$ and a rather worse donor than $(nC_4H_9)_3P$ to achieve optimum stability. The results for the formation of cationic complexes may be rationalized by assuming that at the high χ end of the scale (poor donors) the donor properties of the ligands are insufficient to compensate for the increased positive charge on the metal. At the low end of the χ scale (good donors) too much charge is donated to the metal for optimum stability. In a catalytic sequence of ligand exchange reactions none of the intermediates should be of optimum stability otherwise it will become a product of the reaction. It therefore seems to be desirable that empirical data relating the stability of complexes to the ligand donor–acceptor abilities of the type presented above be accumulated if predictive ability in homogeneous catalysis is to be attained.

The factors determining ligand exchange rates are clearly more complex than those determining equilibria. We assume that for these Pd(II) complexes an associative mechanism of ligand exchange is operative. In this case the rate of ligand exchange should be determined by the equilibrium concentration of five coordinated intermediates. The work of Rigo *et al.* [15, 16] referred to above indicates that there will be an optimum ligand donor–acceptor ability for formation of the five coordinated intermediate. For the exchange between L_2PdX_2 and L_3PdX^+ it appears that the rate is enhanced by better

TABLE IV. Properties of Complexes L_2PdX_2.

Complex	Mp, C		Raman	
	Found	Lit.	νPd–P	νPd–X
$[(CH_3)_2(C_6H_5)P]_2PdCl_2$	191–193	192–193	510	299
Br_2	181–184	180–182	506	109
I_2	155–158	159–160		
cis$[(CH_3)(C_6H_5)_2PdCl_2$	197–199	201–203	516, 450	303
Br_2	215–216		509	194
I_2				
$[(C_2H_5)_2(C_6H_5)P]_2PdCl_2$	135–137	139–140	507	298
$[(C_2H_5)(C_6H_5)_2P]_2PdCl_2$	212–214	211–213	506	296
Br_2	200–203		502	187
I_2	168–171			
$[(C_2H_5)_3P]_2PdCl_2$	141–143	138–139	641	305
Br_2	128–131		637	197
I_2	132–134			
$[(nC_4H_9)_3P]_2PdCl_2$	66	65–66	650	257
Br_2	74–76	73	657	194
I_2	63–65	64–65		
$[(C_6H_5)_3P]_2PdCl_2$	d 252	250–270	535	315
Br_2	d 250	250–270	535	155
I_2	d 245	250–270		

donor properties for both the halide and the phosphine. For the exchange between L_3PdX^+ and L the phosphine dependence is the same but the halide dependence is reversed. The significant difference may be that in the former case the reaction is initiated by attack of a complexed halide to form a bridged intermediate, which would require a good donor halide, whereas in the latter case the attack is by a phosphine ligand and this may be favoured by a good electron withdrawing halide which will enhance the positive charge on the metal.

Experimental

Complex Preparation

The complexes were prepared by addition of a stoichiometric amount of the appropriate phosphine (Strem Chemicals, Ltd.) in alcohol to an aqueous solution of K_2PdCl_4 for the chloride complexes or an aqueous solution of $Pd(NO_3)_2$ with added excess KX (X = Br, I) for the bromide and iodide complexes. The resulting precipitate was filtered, dried and recrystallized from chloroform–hexane. The complexes were characterized by their Raman spectra and melting points (Table IV).

The NMR spectra were recorded in $CDCl_3$ using a Varian 220 MHz NMR spectrometer.

The conductivity measurements were carried out using an Industrial Instruments Inc., Model RC1682 conductivity bridge equipped with 0.1 ohm^{-1} cm cell using spectrograde chloroform (J. T. Baker) or spectrograde nitrobenzene (Fisher Chemicals, Ltd.).

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