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Assistance of Solvent Molecules to Coordination-Site Exchange of Acetylacetonato(6-chloro-2-pyridyl)(triphenylphosphine)palladium(II)

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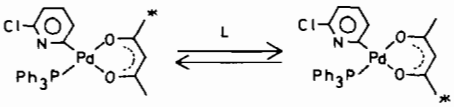
Geometrical isomerization of square-planar complexes has been the subject of extensive investigations [1]. Although some complexes such as *cis*-$PtCl(aryl)(PEt_3)_2$ isomerize spontaneously in polar solvents [2], most of the isomerization reactions proceed in the presence of neutral or ionic free ligands as catalysts [3], and two mechanisms, consecutive displacement and intramolecular rearrangement of five-coordinate intermediates, are well documented [1]. Although the catalytic role of a solvent molecule coordinated to a complex as the fifth ligand has been suggested in some cases [4], no conclusive evidence of solvent catalysis has yet been reported. This communication presents unambiguous evidence for solvent catalysis in the coordination-site exchange of an acetylacetonato-palladium(II) complex.

The reaction of 2,6-dichloropyridine with $Pd(PPh_3)_4$ in toluene at 90 °C gave $PdCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)_2$ in a 95% yield [5], which was transformed in an 89% yield to the perchlorato complex $[PdClO_4(C_5H_3(6\text{-}Cl)N\text{-}C^2)PPh_3]_2$ by the reaction with silver perchlorate in a mixture of dichloromethane and methanol at room temperature. The dinuclear complex reacted with potassium acetylacetonate in the same solvent mixture at room temperature to give the title complex $Pd(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)PPh_3$ (*1*) in an 84% yield.

In conformity with the unsymmetric molecular structure, complex *1* exhibits two methyl signals at 1.70 and 1.92 ppm from Me_4Si in $CDCl_3$ at room temperature. When a base (L) such as pyridine, 2,6-lutidine, triphenylphosphine, and tri-*o*-tolylphosphine is added to the solution, these signals disappear and instead a broad singlet appears at 1.82 ppm. The other proton signals show no change on addition of the base except appearance of peaks due to L. These results indicate that complex *1* is stereochemically rigid in chloroform but undergoes the coordination-site exchange in the presence of L.



(1)

Pyridine or triphenylphosphine was added in various amounts to a dichloromethane solution of *1* and the rate of coordination-site exchange was determined by the line-shape simulation method at several temperatures below 0 °C. The pseudo first order rate constant is proportional to the concentration of L. Table I lists the second order rate constants and activation parameters for reaction 1 catalyzed by pyridine and triphenylphosphine. The small $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ accord with the associative nature of the catalytic reaction. Triphenylphosphine is about one hundred times more effective than pyridine.

Various donor solvents also promote reaction 1, although their catalytic activities are much weaker than those of phosphines and pyridines. Figure 1 shows that the pseudo first order rate constant of reaction 1 at 50 °C increases with proportion of a

TABLE I. Rate Constants and Activation Parameters for Reaction 1 in Dichloromethane.

Temp. (°C)	k^2 ($dm^3\ mol^{-1}\ s^{-1}$)	
	py	PPh_3
0	$(8.05 \pm 0.17) \times 10^2$	
−20	$(2.83 \pm 0.08) \times 10^2$	$(1.58 \pm 0.02) \times 10^4$
−40	$(1.03 \pm 0.03) \times 10^2$	$(8.25 \pm 0.06) \times 10^3$
−58	$(2.33 \pm 0.29) \times 10$	$(3.21 \pm 0.03) \times 10^3$
−80		$(1.03 \pm 0.02) \times 10^3$
$\Delta H^{\ddagger}$ (k J mol^{-1})	25.6 ± 0.8	16.8 ± 0.6
$\Delta S^{\ddagger}$ (J $K^{-1}\ mol^{-1}$)	−94.9 ± 3.0	−96.2 ± 2.4

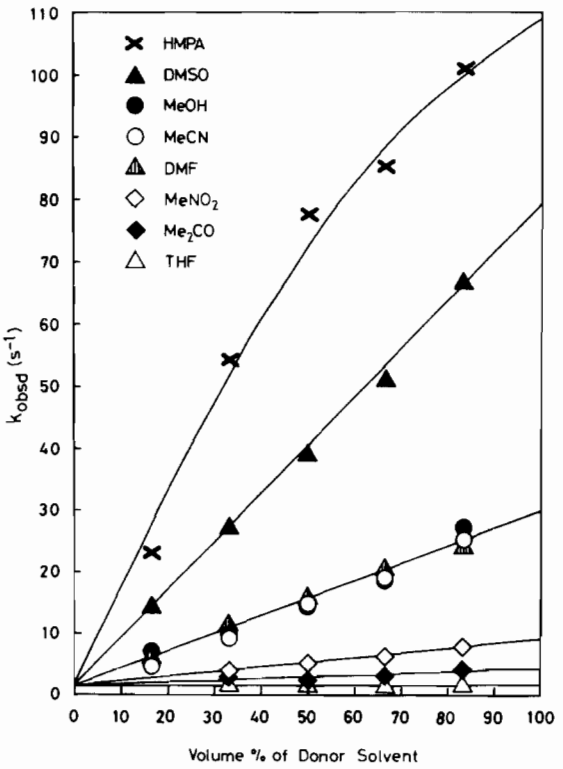
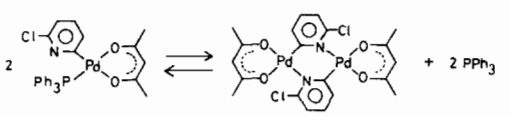


Fig. 1. The pseudo first order rate constant of reaction 1 at 50 °C as a function of the content (volume percent) of the deuterated donor solvent in a mixture with $CDCl_3$.

donor solvent in the mixture with chloroform. All data except those for hexamethylphosphoric triamide (HMPA) lie on straight lines, giving a common intercept at $k_0 = 2.0\ s^{-1}$. Extrapolation of these lines to 100% gives rate data (k_1) in neat donor solvents which cannot be determined directly because of insufficient solubilities of complex *1* in these solvents. (The curve for the HMPA–$CDCl_3$ system was also tentatively extrapolated to 100% HMPA.) Tetrahydrofuran is practically ineffective and the rate value 2.0 s^{-1} given by the intercept corresponds to an intrinsic reaction which is not assisted by donor solvents. It is not certain whether the reaction proceeds truly noncatalytically or is promoted by a trace of triphenylphosphine liberated by reaction 2.



(2)

The k_1 values (s^{-1}) decrease in the sequence, HMPA (109.5) > dimethylsulfoxide (DMSO) (78.0) > MeOH (30.3) ~ MeCN (29.8) ~ dimethylformamide (DMF) (29.1) > $MeNO_2$ (8.8) > Me_2CO (4.9)

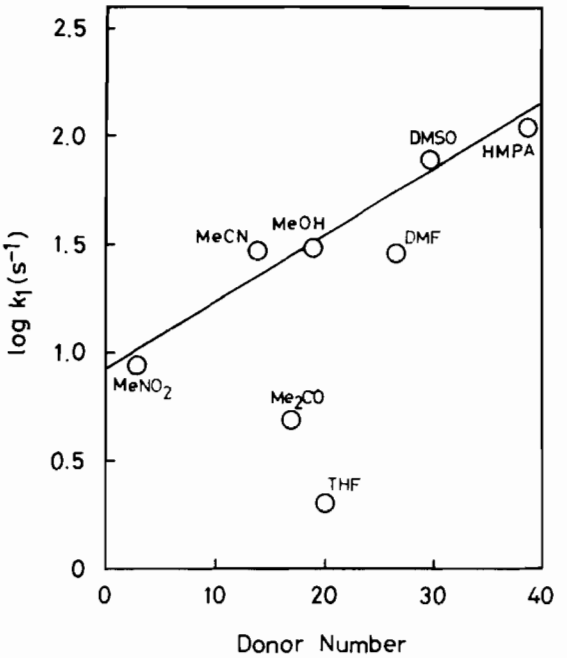
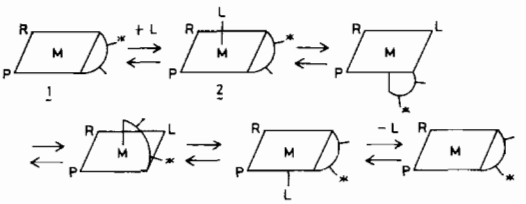


Fig. 2. Relation between the estimated rate constants of reaction 1 at 50 °C in donor solvents and their donor numbers.

and are related to donor numbers [6] of these solvents except a few cases (Fig. 2).

The consecutive-displacement mechanism is not applicable to this reaction, since dissociation of the acetylacetonate ligand to give rise to [Pd(pyridyl)(PPh_3)L_2](acac) is not conceivable. By the analogy with the case of $M(hfac)_2PR_3$ (M = Pd(II) and Pt(II); hfac = hexafluoroacetylacetonate ion) [7] and $[Pt(phen)_2CN]NO_3$ [8], the intramolecular rearrangement of a five-coordinate intermediate as illustrated by eqn. 3 is proposed [9], where R and P denote the pyridyl and phosphine ligands, respectively.



(3)

The linear dependence of k_{obsd} on the fraction of a donor solvent except in the case of HMPA (Fig. 1) indicates that the equilibrium constants (K) for the addition step *1* + L ⇄ *2* are very small for these solvent molecules even in the neat state. Assuming that the intramolecular coordination-site exchange of a five-coordinate intermediate by the polytopal rearrangement (k_{tr}) is rate determining, the observ-

ed first order rate constant should be expressed by eqn. 4.

$$k_{obsd} = \frac{k_{tr}K[L]}{1 + K[L]} \quad (4)$$

The fact that the second order rate law holds for the reactions catalyzed by pyridine and triphenylphosphine indicates that K[L] in the denominator of eqn. 4 is much smaller than one even for these strong ligands in the concentration regions examined ([py] < 5.0 mol dm^{-3} and $[PPh_3] < 0.15$ mol dm^{-3} against $[l] = 0.1$ mol dm^{-3}). Although K and k_{tr} cannot be estimated separately at the present stage of investigation, the nature of the Lewis acid L may influence not only K but also k_{tr}, since k_{obsd} spans over many orders of magnitude.

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