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VARIABLE PRESSURE AND TEMPERATURE ^{1}H NMR STUDIES ON EXCHANGE MECHANISMS IN π-ALLYLPALLADIUM(II) COMPLEXES

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Summary

High pressure ^{1}H NMR spectroscopy on a mixture of $[Pd(2\text{-methallyl})Cl]_2$ (dimer) and $Pd(2\text{-methallyl})Cl(PPh_3)$ (monomer) in $CDCl_3$ at 22°C gives $\Delta V^\ddagger = 0 \pm 2$ cm^3/mol. At this temperature *syn-anti* exchange of the allyl hydrogens in $Pd(2\text{-methallyl})Cl(PPh_3)$ occurs, catalyzed by the complex $[Pd(2\text{-methallyl})Cl]_2$. To explain this $\Delta V^\ddagger$ value we propose an overall cancelling of opposite volume contributions from the initial partial bridge cleavage of dimer and its subsequent association with monomer. At 56°C $\Delta V^\ddagger$ is 11 ± 2 cm^3/mol. At this temperature, 2-methallyl exchange between $Pd(2\text{-methallyl})Cl(PPh_3)$ and $[Pd(2\text{-methallyl})Cl]_2$ occurs by a process involving dimer cleavage followed by PPh_3 transfer. We propose the bridge cleavage of dimer to Pd(2-methallyl)Cl is the dominant step causing the overall positive $\Delta V^\ddagger$ change.

Introduction

The use of high pressure NMR spectroscopy as a probe of reaction mechanism has been applied to a number of problems in organic and inorganic chemistry [2]. Up to the present, however, little application has been made to organometallic systems, and virtually no research carried out on organometallic compounds which undergo intramolecular exchange processes. Recently we have used this technique to study inversion about the sulfur atom of a complexed thioether ligand [3], and this paper describes our research on intramolecular and intermolecular allyl exchange in a solution containing the π-allyl complexes $[Pd(2\text{-methallyl})Cl]_2$ and $Pd(2\text{-methallyl})Cl(PPh_3)$. Allylmetal complexes offer a useful entry point for the study of exchange processes in organometallic chemistry both because of their significance to homogeneous catalysis [4], and because of their observed tendency to undergo different intramolecular exchange processes in solution [5]. This particular π-methal-

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lylpalladium(II) system was chosen because extensive ambient pressure ^1H NMR studies have already been carried out on these two allylpalladium complexes, and the kinetic data obtained analyzed in detail [6,7]. This previous ambient pressure work has concluded that intramolecular exchange occurs between the *syn* and *anti* allylic hydrogens in the mononuclear complex Pd(2-methallyl)Cl(PPh_3) (hereafter called monomer), and that there is also an exchange occurring which effectively transfers the π-allyl group between this monomer complex and the binuclear species [Pd(2-methallyl)Cl]$_2$ (hereafter called dimer).

Experimental

Synthesis. The complex [Pd(2-methallyl)Cl]$_2$ (dimer) was prepared from palladium(II) chloride and 2-methallyl chloride as described in the literature [8]. The complex Pd(2-methallyl)Cl(PPh_3) (monomer) was prepared by adding PPh_3 (0.60 g; 2.28 mmol) dissolved in a minimum volume of toluene, to a saturated solution of dimer (0.45 g; 1.14 mmol) in toluene at 80°C. Crystals soon began to form and the solution was allowed to cool to room temperature. The solution was chilled in ice and the solid removed by filtration. The monomer complex was recrystallized from ethanol with minimum chloroform present to give light yellow crystals. Yield: 0.71 g (68%).

Data collection. The ^1H NMR measurements were made on a chloroform solution containing dimer (50.9 mg; 0.130 mmol), monomer (141.7 mg; 0.309 mmol) and $CDCl_3$ (1.326 g). The ambient pressure data for this solution showed the resonances and multiplicities found in previous studies [5–7]. The NMR spectra under pressure were obtained on a Bruker WH-90 Fourier transform spectrometer. For the probe arrangement the tank circuit used a 4 mm rf coil double tuned to the ^1H and ^2D frequencies. The lock sample was D_2O in a 4 mm o.d. NMR tube. The sample solution was in a 2 mm o.d Wilmad precision glass capillary. The two solutions in the two tubes were arranged coaxially in the rf coil. The pressurizing fluid was CCl_4. Sample solutions were separated from the pressurizing fluid by a Nylon cap inside the sample tube and a Teflon cap over it. The titanium-alloy bomb containing the doubly tuned rf coil and thermocouple was constructed along the general lines of those used by the Merbach group [9]. Electrical connections were made through a self-sealing arrangement of brass cones, insulated with Torrseal epoxy, and titanium or Berylco plugs. The bomb was placed in a modified Bruker probe head containing the necessary tuning capacitors. A deuterium lock was used for field stabilization, and the experimentally found inhomogeneity was 5 Hz. Spectral quality was concentration limited and multiple pulses were collected to obtain acceptable line shapes. Temperature checks were made both before and after data collection. Spectra were collected as a function of pressure at 22 and 56°C. As a general apparatus and procedure check the tautomerization of *N,N′*-dimethylacetamide was studied. A value of 11 ± 1 cm^3/mol was obtained for $\Delta V^{\ddagger}$, as compared to a literature value of 10.3 cm^3/mol [10].

Spectra at ambient pressure for ^1H were collected on a Nicolet spectrometer operating at 200 MHz and over a temperature range of -40 to $+96$°C.

Fitting of spectra. Since second order effects are negligible the spectra can be calculated using the Bloch equations modified for exchange (eq. 1) [11], where υ is

$$\upsilon = -\tilde{\vec{1}} \cdot \left[(W-K)+(F^0-F)(W-K)^{-1}(F^0-F)\right]^{-1} \cdot \vec{P} \tag{1}$$

the absorption signal, W is the line width matrix, K is the exchange matrix, F^0 is the chemical shift matrix, F is the frequency matrix, $\vec{P}$ the site atom fraction vector, and $\vec{1}$ the unit vector. For the dimer, lines located at δ values of 3.83 (*syn*-dimer), 2.86 (*anti*-dimer), and 2.09 (methyl-dimer), and for the monomer, lines at δ values of 4.52(*syn*-monomer-P), 3.59(*anti*-monomer-P), 2.83(*syn*-monomer-Cl), 2.74(*anti*-monomer-Cl) and 1.95(methyl-monomer), were used in the calculations [6]. The designation P or Cl means the protons were *trans* to the phosphorus or chlorine atoms, respectively. Also a splitting of the *syn*-monomer-P line of 6.8 Hz and the *anti*-monomer-P line of 9.8 Hz was included, but some smaller splitting by protons of the *syn* protons in the monomer was ignored.

The exchange matrix contained pseudo first order rate constants for the *syn*-monomer-P//*anti*-monomer-P exchange (k_A), the *syn*-monomer-Cl//*anti*-monomer-Cl exchange (k_B), the pseudo rotation of the monomer allyl which gives *syn*-monomer-P//*syn*-monomer-Cl and *anti*-monomer-P//*anti*-monomer-Cl exchange (k_C), the monomer//dimer pseudo allyl exchange ($k_E = k_D$*P-methyl-monomer/P-methyl-dimer), and the *syn*-dimer//*anti*-dimer exchange (k_F). The observed instrumental inhomogeneity was used in the line width matrix and the P vector was calculated from the weights of monomer and dimer in the solutions.

The equation for v was programmed into a computer and spectra were printed out for various values of k_A through k_F entered by the operator. Calculated spectra were compared visually with experimental spectra and k's were varied to determine the sensitivity of various features of the spectra to the various k values.

The line shape analysis program was a non-linear least squares approach analogous to the DNMR programs [12]. The calculated line shapes are plotted using 1 Hz resolution and the experimental and calculated spectra compared visually with respect to half-width and shape. The program is non-iterative but sufficient calculations were done with closely spaced k values to select an optimum value. This procedure led to the conclusion that no *syn-anti* exchange occurred in the dimer, i.e., $k_F = 0$ for all conditions used in our experiments. Also the fitting of the methyl lines at 56°C depended primarily on the value of k_D, and the portion of the spectrum due to the *syn* and *anti* protons of the monomer could be fit with a range of combinations of k_A, k_B and k_C but a "high" value of k_C relative to k_A and k_B was best.

Results and discussion

Transition metal π-allyl complexes undergo exchange processes which result in the interchange of the non-equivalent hydrogen atoms in the π-allyl ligand [6,7,13]. The complexes $[Pd(2\text{-methallyl})Cl]_2$ and $Pd(2\text{-methallyl})Cl(PPh_3)$ undergo all the different intramolecular and intermolecular exchange mechanisms which have been proposed for transition metal allyl complexes. From an analysis of the ambient pressure ^1H NMR spectra it has been found that these complexes undergo intramolecular allyl exchange both by a combination of *syn–anti* (σ–π) interchange, and by a π-allyl group rotation about the palladium which results in *syn–syn* and *anti–anti* interchange [6]. This rotation may be a pseudo-rotation since it can also be accomplished by exchange of ligands *trans* to the methylene groups of the allyl. In a solution containing both dimer and monomer there is also an intermolecular exchange process which causes the apparent transfer of the methyl group in the

2-methallyl ligand between monomer and dimer. These mechanisms have been identified from an analysis of ^{1}H NMR line width data over a temperature range. Activation parameters have been calculated from this line width data. These line width measurements have led to the conclusion that intramolecular π-allyl exchange in both dimer and monomer is slow, but that addition of dimer to monomer catalyzes the *syn–anti* exchange in the monomer species. At higher temperatures coalescence then occurs between the methyl group resonances on the monomer and the dimer, indicating the existence of a slower intermolecular π-allyl exchange [7].

For a solution containing a mixture of dimer and monomer in $CDCl_3$ solvent, we have measured the ^{1}H NMR spectra at both 22 and 56°C with pressures from atmospheric up to 230 MPa. The effects of pressure changes on the spectra at the two different temperatures are shown in Fig. 1 and 2. These temperatures are chosen

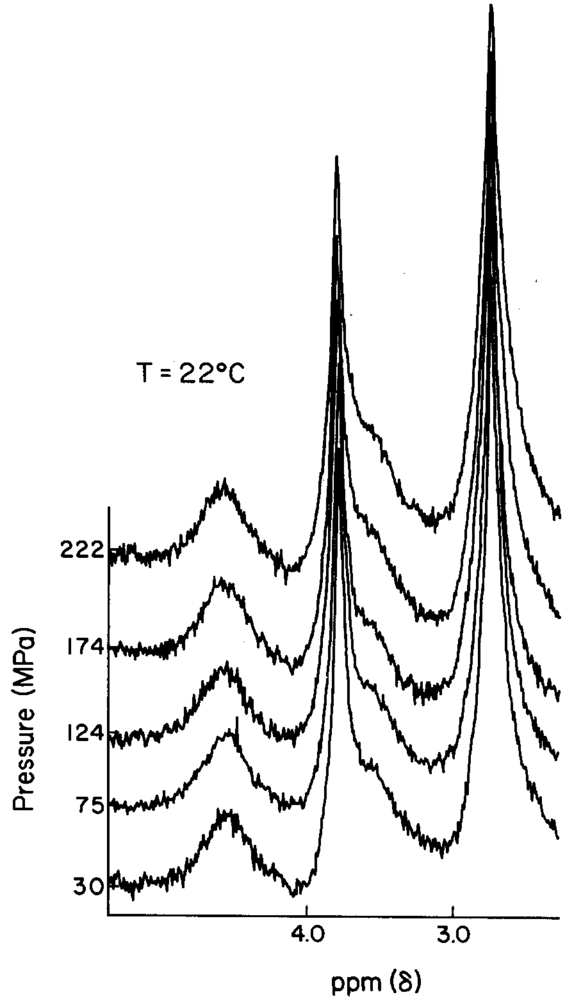


Fig. 1. The effect of changing pressure on the ^{1}H NMR spectrum at 22°C. The resonances are assigned as δ 4.52 (*syn*-monomer-P), 3.83 (*syn*-dimer), 3.59 (*anti*-monomer-P), 2.86 ppm (*anti*-dimer). The line at δ 4.52 ppm shows no measurable change with pressure.

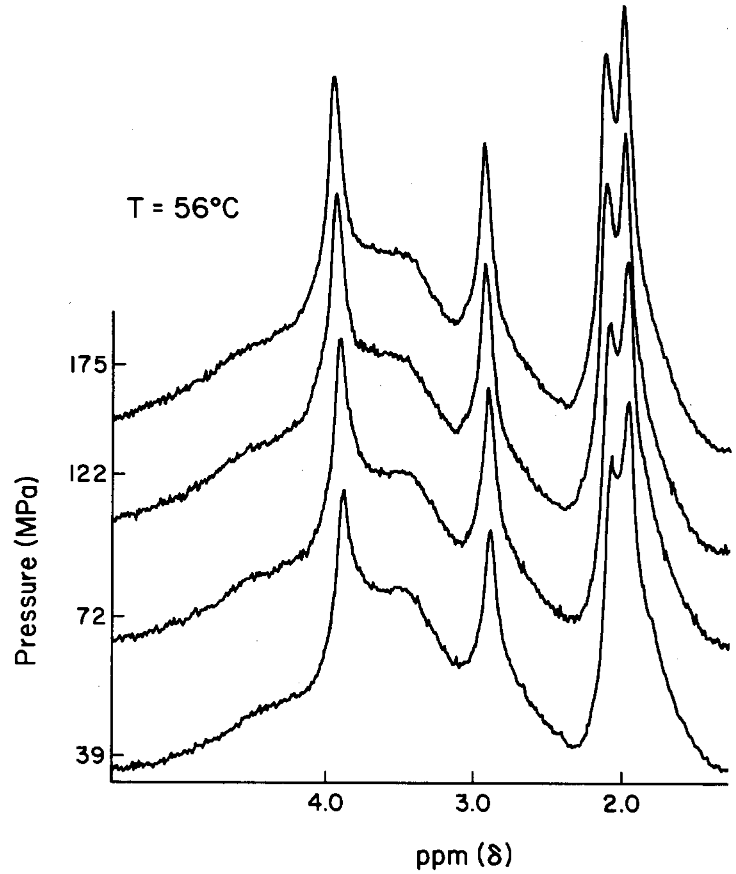


Fig. 2. The effect of changing pressure on the ^{1}H NMR spectrum at 56°C. The resonances are assigned as δ 3.89 (*syn*-dimer), 2.86 (*anti*-dimer), 2.09 (methyl-dimer), 1.95 ppm (methyl-monomer). The methyl lines at δ 2.09 and 1.95 ppm show narrowing as the pressure is increased to 175 MPa.

because they are close to the coalescence temperatures found at ambient pressure for the two separate allyl exchange processes occurring in this mixed solution [7]. With the dimer in solution no significant quantities of triphenylphosphine are present, and consequently the solution does not contain the ionic complex [Pd(2-methallyl)$(PPh_3)_2$]Cl [6e].

At 22 and 56°C we therefore have data available for two separate exchange processes. At 22°C, the monomeric complex is undergoing *syn–anti* exchange of the hydrogens *trans* to the triphenylphosphine at a rate where the pressure effects could make a discernable difference in the line width [7]. These *syn* and *anti* hydrogens are doublets at sub-ambient temperatures (^4J(PH)) centered at δ 4.52 and 3.59 ppm, but at 22°C they are broadened to two single lines. The line at δ 3.59 ppm is poorly resolved from the resonance of the *syn* protons from dimer at δ 3.83 ppm, but the resonance at δ 4.52 ppm is clearly discernible. From Fig. 1 it is apparent that for pressures up to 230 MPa there is little observable change in these resonances. Calculated line shapes indicate that a change in rate of ±20% for the process broadening the line at δ 4.52 ppm would have been observable. We conclude that $\Delta V^{\ddagger} = 0 \pm 2$ cm^3/mol for the *syn–anti* exchange on monomer.

At 56°C intermolecular methyl group exchange occurs between monomer and dimer. From the ^1H NMR data at 56°C (Fig. 2) over a range of pressures, it is apparent that there are significant changes in the methyl region ($\delta \sim 2$ ppm) for both monomer and dimer when the pressure is varied up to 230 MPa. Increased pressure causes a decrease in the rate of 2-methallyl exchange between the monomer and dimer complexes. Calculated spectra require a decrease in rate by a factor of about 2.5, and this leads to an estimate of $\Delta V^{\ddagger} = 11 \pm 2$ cm^3/mol for this intermolecular exchange.

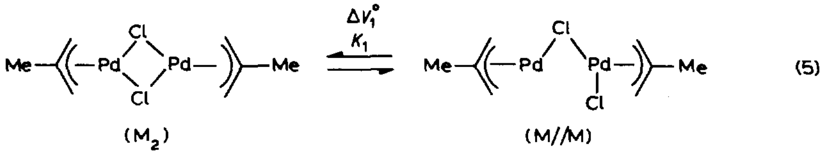
Dimer catalyzed exchange on monomer. The *syn–anti* exchange of the allyl hydrogens of monomer is catalyzed by dimer. This catalytic effect is not specific to [Pd(2-methallyl)Cl]$_2$, but occurs with other dimeric compounds [13]. We need to reconcile a mechanism with our measured $\Delta V^{\ddagger} = 0 \pm 2$ cm^3/mol. Ambient pressure experiments have been interpreted on the basis of the reaction model:

$$M_2 \overset{K_1}{\leftrightharpoons} M//M \qquad (2)$$

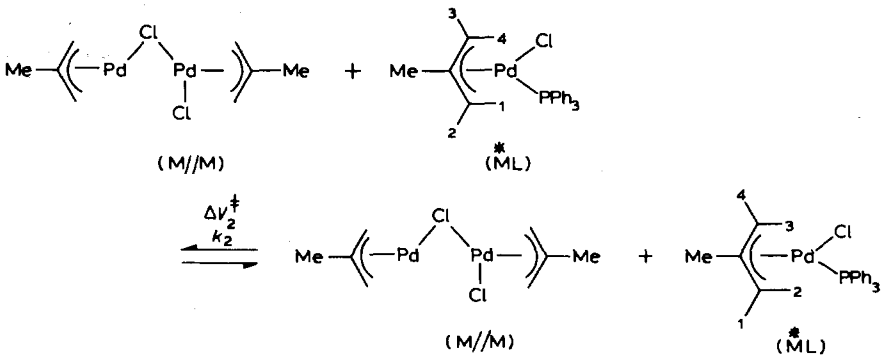
$$M//M + \overset{\star}{ML} \underset{k_2}{\leftrightharpoons} M//M + \overset{\star}{ML} \qquad (3)$$

$$\text{with } 1/\tau_2(ML) = k_2K_1[M_2]. \qquad (4)$$

where M_2 is dimer, $\overset{\star}{ML}$ is monomer, and $1/\tau_2$ is the pseudo first order rate constant. The species M//M which interacts with the monomer to catalyze *syn–anti* exchange [7] has been proposed to be the single-bridged complex formed in eq. 5. Since both k_2 and K_1 (k_1/k_{-1}) are in the previously measured rate law, our explanation must involve reactions 5 and 6 in the slow step. An overall $\Delta V^{\ddagger} = 0$ can



(5)



(6)

be due to zero volume change in both steps (5 and 6), or it can result from cancellation of two consecutive $\Delta V^{\ddagger}$ changes having opposite sign. The possibility of $\Delta V^{\ddagger} = 0$ for both steps is improbable because reaction 6 is a bimolecular associative step. We expect ΔV_1^0 to be positive in eq. 5 since a bond is being broken, and $\Delta V_2^{\ddagger}$

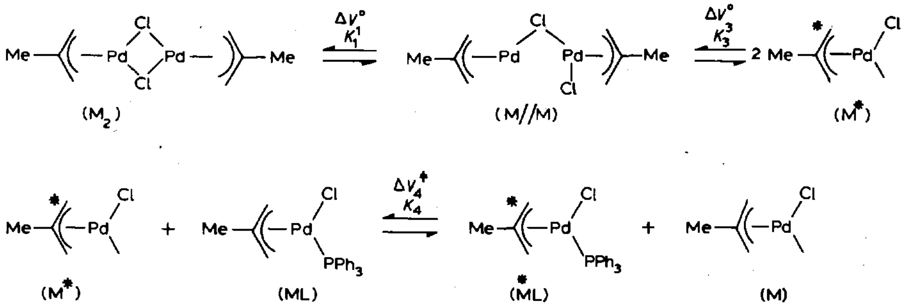
to be negative in eq. 6 since an association occurs. We believe therefore that our observed $\Delta V^\ddagger = 0$ is due to cancellation of volume changes, although we cannot completely ignore the possibility that solvation may keep volume changes small in each step [14]. The dipole moment of $CHCl_3$ is quite large, the dielectric constant low, and with a molar volume of ca. 80 cm^3/mol solvent effects may be important.

Exchange on dimer. At 56°C there is 2-methallyl group exchange between monomer and dimer. The process involves PPh_3 transfer between palladiums since all previous studies on allyl exchange mechanisms show no allyl group dissociation. We find $\Delta V^\ddagger$ is 11 ± 2 cm^3/mol for this exchange. The rate expression for 2-methallyl exchange between monomer and dimer at ambient pressure is given by $1/\tau_{MeML} = k_4(K_1K_3)^{1/2}(M_2)^{1/2}$ [7]. These authors fit this rate law to a reaction scheme involving complete dissociation of dimer M_2 to $M^\star$ (eq. 7), followed by interchange between $M^\star$ and ML (eq. 8) resulting in L (PPh_3) exchange, and therefore π-allyl interchange (Scheme 1).

$$M_2 \overset{K_1}{\rightleftharpoons} M//M \overset{K_3}{\rightleftharpoons} 2M^\star \qquad (7)$$

$$M^\star + ML \overset{k_4}{\rightleftharpoons} \overset{\star}{M}L + M \qquad (8)$$

SCHEME 1



The overall $\Delta V^\ddagger$ of $+11$ cm^3/mol for the 2-methallyl exchange is for $(\Delta V_1^0 + \Delta V_3^0)/2 + \Delta V_4^\ddagger$. We expect ΔV_3^0 to be large and positive, ΔV_1^0 to be small but positive, and $\Delta V_4^\ddagger$ to be small and negative. We believe that ΔV_3^0 is dominant in determining the sign of $\Delta V^\ddagger$, and accounts for the measured 11 cm^3/mol [15].

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14 We estimate $\Delta S^{\ddagger} = \Delta S_1^0 + \Delta S_2^{\ddagger}$ to be about +12 cal/mol K from the data in ref. 7. This value can be rationalized by assuming rotational entropy is gained on forming M//M and little is lost by forming $M//M..\overset{\star}{M}L$. If the allyl group goes to the σ configuration in $M//M..\overset{\star}{M}L$, $\Delta S_2^{\ddagger}$ might be slightly positive also.

15 Using data from ref. 7 gives +9 cal/mol K for $(\Delta S_1^0 + \Delta S_3^0)/2 + \Delta S_4^{\ddagger}$. The gain in entropy from complete dissociation may be partially lost by forming an activated complex (M′...ML) of more restricted geometry than that required for the *syn-anti* exchange.