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Kinetics of complex formation between palladium(II) acetate and bis(diphenylphosphino)ferrocene

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ABSTRACT

The kinetics of complex formation between palladium(II) acetate, and 1,1'-bis(diphenylphosphino)ferrocene, dppf, in two different deuterated solvents $CDCl_3$ and $DMSO-d_6$ were investigated using ³¹P NMR spectroscopy. The mole ratio and the ³¹P-chemical shifts in $DMSO-d_6$ solution revealed the formation of an intermediate, which is gradually converted into the more stable [Pd(dppf)OAc)₂] species with a dppf acting as a chelate ligand. In the chloroform solution however, the interaction of metal ion and the ligand resulted directly in the formation of [Pd(dppf)OAc)₂] species with a chelating dppf. The rate constant for the complexation reaction was evaluated from computer fitting of the corresponding integration-time data.

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1. Introduction

Since the time of the synthesis of 1,1'-bis(diphenylphosphino) ferrocene [1], dppf, this ligand is probably the most intensively studied ferrocenyl phosphines compounds to date and a variety of transition-metal complexes stabilized by dppf have been characterized [2–12]. Among them, the Pd-dppf complexes have richer chemistry and have been widely used as catalysts especially for carbon-carbon bond forming reactions [13–27]. It is well known that the bidentate dppf shows a versatile coordination ability adapting its steric bite angle as well as electronic properties to the geometric and electronic requirements of the metal through the appropriate coordination [28–30]. Although the chelating coordination mode is the predominant character of dppf, multinuclear complexes containing bridging dppf are also known [31–60].

While very high efficiency of Pd-dppf catalysts is due to a combination of electronic and steric parameters of these precursors, no comprehensive study on the rate of the formation of dppf complexes has been carried out, albeit to the best of our knowledge. We have recently reported the application of Pd-phosphine catalysts in the Suzuki cross coupling reactions [61]. Our interest in the physicochemical properties of the dppf [62], encouraged us to determine the rate constants for formation of the Pd-dppf complexes and to gain some useful information about the mechanism of complex formation.

2. Experimental

CDCl₃ and DMSO-*d*₆ were commercially available from the Aldrich and used as received. The ligand dppf was prepared as previously described [62]. An authentic sample of Pd(dppf)(OAc)₂ was synthesized by the reaction of equimolar amounts of palladium(II) acetate and dppf according to literature procedure for preparation of Pd(dppf)Cl₂ [63] and characterized by multi-nuclear NMR spectroscopy as well as ICP elemental analysis. *Anal. calc.* for C₃₈H₃₄FeO₄P₂Pd, C, 58.29%, H, 4.92%, Fe, 7.13%, P, 7.91%, Pd, 13.59%. Found C, 58.87, H, 4.65, Fe, 7.52, P, 7.75, Pd, 13.91%. ¹H NMR (200 MHz, CDCl₃): δ 2.15 (s, 6, CH₃ of acetate ions), 4.00–4.45 (m, 8), 7.15–7.90 (m, 20); ³¹P{¹H} NMR (81.014 MHz, CDCl₃): δ 28.05 (s). ³¹P{¹H} NMR (81.014 MHz, DMSO-*d*₆): δ 24.58 (s).

All NMR measurements were made on a Bruker Avance (DPX) 200FT- NMR spectrometer with a field strength of 4.7 T (47 KG) equipped with a temperature controller, (±0.1 °C). At this field, ³¹P resonates at 81.014 MHz. In ³¹P NMR experiments, the standard was %85 H₃PO₄. All chemical shift measurements were carried out at a temperature of 25.0 ± 0.1 °C.

One milliliter of stock solution of the ligand (0.0554 g in 1 mL, 0.1 M) in each solvent was placed in a NMR tube and then, 50 μ L of the stock metal solution of Pd(OAc)₂ dissolved in the same solvent (0.0673 g in 0.3 mL, 1 M, calculated for monomeric form)





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was added. The ³¹P NMR spectrum of the resulting solution was measured at different times.

3. Results and discussion

In the solid state, palladium(II) acetate exists as a trimer and has a maximum at 370–450 nm in its UV–Vis spectrum [64,65]. In contrast, the UV–Vis spectra of this salt in both solvents $CDCl_3$ and DMSO- d_6 do not have such typical signal (Fig. 1). In addition, the trimer–monomer equilibrium strongly depends on the addition of ligand; led to formation of monomeric form of palladium(II) acetate in solution. Therefore, it could be possible to consider it as monomer in kinetic calculations.

NMR spectroscopy has been widely used for the investigation of the kinetics and mechanisms of inorganic reactions. The chemical shifts, line broadening, and the integral of the signals are quantitative factors used for this purposes. In the cases where the changes in the chemical shifts and line broadening are negligible, the integral of the signals could be used as a very sensitive measure of the concentration of a particular species. This tool has been particularly used for consecutive reactions.

The kinetics of the complexation between palladium(II) acetate and dppf were sufficiently slow to lead us monitor all species formed during the complexation.

Initial investigation of reaction rates was carried out using different metal to ligand mole ratio. It was observed that the concentration of the product as a measure of the rate of reaction, increases with increasing the concentration of palladium(II) acetate linearly. This evidence led us to conclude that the reaction is first-order with respect to the palladium source (Fig. 2).

The best intensity changes in the ³¹P NMR lines were observed at 0.5 metals to ligand mole ratio. In addition, many reports have been published in where, the catalytic reactions were carried out using this mole ratio [66]. Therefore, the kinetic studies were investigated using this mole ratio.

3.1. Investigation of the species involved in the CDCl₃ solution

In CDCl₃ solution, 1,1'-bis(diphenylphosphino)ferrocene, dppf, has two chemically and magnetically equivalent phosphorus atoms, which appear as a singlet at -18.90 ppm, with respectto an internal standard solution of H₃PO₄ (Fig. 3). During the complexation at 25 °C, the intensity of this signal is gradually decreased and simultaneously, a signal at 28.05 ppm downfield-shifted from the ligand appears which corresponds to [Pd(dppf)(OAc)₂] [67].



Fig. 1. Spectra of Pd(II) acetate $(4.5 \times 10^{-4} \text{ M}, \text{ calculated for the monomeric form)}$ at 25 °C in CDCl₃ (a) and DMSO-*d*₆ (b).



Fig. 2. The product formation as a measure of the rate of reaction vs. the metal to ligand mole ratio. All concentrations were determined by the integration of their ³¹P NMR signals at the same times.

The ICP elemental analysis confirms the formation of [Pd(OAc)₂(dppf)] (Scheme 1).

Therefore, the reaction may be considered as a simple secondorder reaction either reversible Eq. (1) or irreversible reactions Eq. (2)

$$[Pd] + dppf \stackrel{k_1}{\underset{k_1}{\longrightarrow}} [Pd(dppf)]$$
(1)

$$[Pd] + dppf \xrightarrow{k_1} [Pd(dppf)]$$
⁽²⁾

where [Pd] represents the starting palladium(II) acetate.

3.2. Kinetic studies in chloroform solution

The concentration of the free dppf and its Pd complex are determined by the integration of their ³¹P NMR signals. The stack diagram for the ³¹P NMR spectra is shown in Fig. 4.

At the first stage, calculations were carried out using the second-order reversible Eq. (1). The resulted rate constants show that the forward rate constant is much greater than the backward rate constant (Table 1). In addition, careful monitoring of the ³¹P NMR spectra rules out any dissociation of dppf and reaction reversibility. Therefore, the overall reaction may be considered as irreversible Eq. (2) which involves the following rate law Eq. (3):

$$\frac{1}{\left[dppf\right]_{0} - \left[Pd\right]_{0}} Ln \frac{\left[Pd\right]_{0} \left[dppf\right]_{t}}{\left[dppf\right]_{0} \left[Pd\right]_{t}} = k_{1}t$$
(3)

with subscripts t and 0 representing time t and 0, respectively. A plot of the left term of Eq. (3) versus time should be a straight line with a positive slope equal to k (Fig. 5). The overall rate constant of the reaction is listed in Table 1.

It is reported that even if one reagent (here [Pd]) be maintained in only a two-fold excess over another reagent (here [dppf]), the error in the computed second-order rate constant is $\leq 2\%$ for 60% conversion and as the reaction proceeds toward the end of the reaction, pseudo first-order conditions certain hold [68,69]. Similar re-computation of our kinetics data for pseudo first-order irreversible reaction was carried out and the resulted rate constant confirmed this hypothesis (Table 1, entry 3). Other re-computations of the kinetic data for other kinetic models such as third-order resulted poor regressions.

3.3. Investigation of the species involved in the DMSO-d₆ solution

In the DMSO-d₆ solution, the free ligand appears at -19.27 ppm. This signal is gradually decreased during the complexation and a



Fig. 3. ³¹P NMR spectrum of reaction mixture of Pd(II) acetate/dppf in CDCl₃ at 25 °C.



Scheme 1. Structure of [Pd(dppf)(OAc)₂] complex.



Fig. 4. The change in the ${}^{31}P$ NMR spectra vs. time in CDCl₃ at 25 °C.

signal appears at 29.70 ppm, which may be due to the formation of a M_2L_2 di-palladium intermediate (Fig. 6) [70–72]. The observation of this intermediate is probably due to the coordinating ability of DMSO, which probably makes the coordination of dppf slower and allows the formation of the intermediate.

The relative intensities of both signals are decreased on going to continue the reaction and an additional signal appears at 24.58 ppm corresponding to the ML species involved chelating dppf [67]. The ICP elemental analysis confirms the formation of $[Pd(OAc)_2(dppf)]$. The pattern of relative intensity changes indicates that the ML is produced possibly from two paths; directly from the starting reactants via a consecutive reaction as a main path [73,74] together with a simple second-order reaction Eq. (4)



Fig. 5. Second-order irreversible plot for reaction of Pd(II) acetate:dppf in CDCl_3 at 25 °C.

 Table 1

 Rate and stability constants of reaction of Pd(II) acetate:dppf in CDCl3 at 25 °C.

Entry 7	Type of reaction	$k_1 ({ m s}^{-1}{ m M}^{-1})$	$k_{-1}(\mathrm{s}^{-1})\times 10^4$	$K_{\rm e}({\rm M}^{-1})$
1	Reversible second-order	0.52 ± 0.03	$5.2 \times \pm 0.2$	1000 ± 90
2	Irreversible second-order	0.50 ± 0.02		
3	Pseudo first-order	0.53 ± 0.03		



Fig. 6. ³¹P NMR spectrum of Pd(II) acetate/dppf in DMSO-*d*₆ and at 25 °C.

$$\begin{cases} Pd + dppf \stackrel{k_1}{\to} \frac{1}{2} [Pd_2(\mu - dppf)_2] \stackrel{k_2}{\to} [Pd(dppf)] \\ Pd + dppf \stackrel{k_3}{\to} [Pd(dppf)] \end{cases}$$
(4)

3.4. Kinetic studies in DMSO-d₆ solution

The concentration of the free dppf and its Pd complexes are determined by the integration of their characteristic ³¹P NMR signals. Distribution of all species versus time is shown in Fig. 7. It should be noticed that the concentration of the free ligand could not exponentially decay to zero since it is used in two-fold excess.

Initial calculation based on Eq. (5) was carried out by simultaneously solving of three equations for the change of concentration



Fig. 7. Distribution diagram for involving species in the reaction of Pd(II) acetate and dppf in DMSO- d_6 at 25 °C. The solid lines are the best trendlines obtained by Excel program.

Table 2

Rate constants of the reaction of Pd(II) acetate:dppf (1:2) in DMSO-d₆ at 25 °C.

Entry	Type of reaction	$k_{ m obs} \ ({ m s}^{-1}~{ m M}^{-1}) imes 10^2$	$\begin{matrix} k_2 \\ (s^{-1}) \times 10 \end{matrix}$
	Parallel consecutive and irreversible reactions	1.0 ± 0.1	1.0 ± 0.1

of the ligand, [L]; the intermediate, $[M_2L_2]$; and the final chelating complex; [ML], with time Eq. (5)

$$\begin{cases} [L] = [L_0]e^{-k_{obs}t} \\ [M_2L_2] = \frac{k_{obs}[L]}{k_2 - k_{obs}} \{e^{-k_{obs}t} - e^{-k_2t}\} \\ [ML] = [L] \Big\{ 1 - \frac{1}{k_2 - k_{obs}} (k_2 e^{-k_{obs}t} - k_{obs} e^{-k_2t} \Big\} \end{cases}$$
(5)

The corresponding rate constants are calculated by Excel-fitting of the experimental points (Fig. 7) and are given in Table 2.

As Eq. (5) shows, determination of individual amounts of k_1 and k_3 is impossible and a summation of them as k_{obs} could be obtained in this way. An approximate value for these rate constants could be easily calculated by considering two extremes of Eq. (5)

$$\begin{cases} a)k_1 >> k_3 \Rightarrow k_{obs} \approx k_1 \\ b)k_1 << k_3 \Rightarrow k_{obs} \approx k_3 \end{cases}$$

The first extreme was arisen if the consecutive reaction is the major contributor of the overall rate constant while the second extreme could be obtained if the second-order path is the major contributor.

The relative magnitude of the k_{obs} [Pd] (s⁻¹) and k_2 (s⁻¹) rate constants shows that the consecutive reaction is the major contributor of the overall reaction rate. Therefore, the first extreme is more logic.

Interestingly, the intermediate was observed only in metal to ligand mole ratios near 0.5. This may be because both rate of formation (k_1) and consumption (k_2) of the intermediate depend on the concentrations of metal and ligand as a same way (steady state approximation).

4. Conclusion

In comparison, the complex formation is faster in CDCl₃ than DMSO, which may be due to the coordinating ability of DMSO. This coordination probably makes the coordination of dppf slower and allows the formation of the intermediate. It also decreases the electrophilicity of metal as well as the steric crowding at the metal

center [75]. The better solubility of the reactants in CDCl₃ also plays an important role. The difference in the reaction rates make such kinetic studies very important in the catalytic reactions in where, a mixture of metal and ligand are used as catalyst. For example, it is reported that using methanol as solvent, no methoxycarbonylation of 2-bromoaniline was observed. Changing to a solvent mixture of toluene-methanol increased remarkable the conversion [76]. This feature is of greater importance particularly whenever the complex formation between metal and ligand is the rate determining step and/or one of previous catalytic cycle.

Another noteworthy of such kinetics studies outcome on comparing the rate of catalytic reactions using a ML catalyst with *in situ* prepared catalyst by addition of metal and ligand. The similarity between the rates of both reactions may be an excellent evidence for the presence of a similar mechanism.

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