

# Unusual stability of hydrosoluble Pd(II)—diphosphine system

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## Abstract

The hydrolysis and the redox process of the water soluble system dppp-s/Pd<sup>II</sup> has been investigated at room temperature by <sup>31</sup>P NMR spectroscopy, polarography and potentiometry {dppp-s = sodium salt of 1,3-bis(dimetasulfofenylphosphino) propane}. In dilute solution [palladium salt] = 3.3 × 10<sup>-4</sup> mol/l (molar ratio dppp-s/Pd<sup>II</sup>, R = 1), contrary to the TPPTS/Pd<sup>II</sup> system, the complex Pd(dppp-s)<sup>2+</sup> was hydrolyzed without phosphine oxidation, keeping a surprising stability up to pH = 9 or 10. Above pH = 10, the bidentate phosphine is oxidized. The hydrolysis and the reduction reactions are linked to the palladium salt concentration. In more concentrated solutions, the hydrolysis reaction and the phosphine oxidation occurs at lower pH (pH = 4). The hypothesis of the binuclear complex formation {[dppp-s)Pd(H<sub>2</sub>O)][dppp-s)Pd(OH)]<sup>3+</sup> or [(dppp-s)Pd(μ-OH)<sub>2</sub>Pd(dppp-s)]<sup>2+</sup> was proposed.

An excess of phosphine restricts the redox and the hydrolysis reactions (pH < 10; R = 2). In this case, four phosphorus atoms are bounded to Pd<sup>II</sup> (δ = 3.1 ppm) and prevents the complete hydrolysis. The stability of the system dppp-s/Pd<sup>II</sup> is dictated by the pH value, the molar ratio dppp-s/Pd<sup>II</sup> and the dilution.

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## 1. Introduction

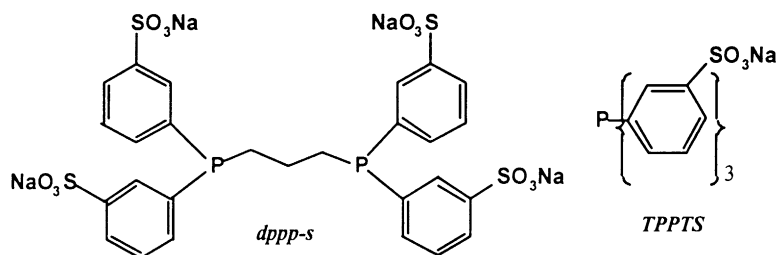
The catalytic dppp/Pd<sup>II</sup> system (dppp: 1,3-bis(diphenylphosphino) propane) is used as catalyst in copolymerization reaction of ethylene and carbon monoxide in ethanol [1]. Recently, this reaction was performed in water using the sodium salt of

hydrosoluble ligand dppp-s<sup>1</sup> (dppp-s: sodium salt of 1,3-bis(dimetasulfofenylphosphino) propane) [2]. The copolymerization of olefins catalyzed by this new stable system was extremely efficient: 4 kg of polymer/(g of palladium h). This copolymerization

<sup>1</sup> In [2], the abbreviations used for the ligand 1,3-bis(diphenylphosphino) propane and 1,3-bis(dimetasulfofenylphosphino) propane were dpppr and dppp-s, respectively. However, both of authors have chosen dppp for the same ligand 1,3-bis(diphenylphosphino) propane. In this text, the abbreviations dppp and dppp-s have been taken in order to avoid the confusion.

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reaction was carried out in acidic solution with low concentration of palladium (0.14 mmol/l), without phosphine oxidation [2]. This result characterizes a great stability of the complex allowing an analytical study in water. Several works were already performed on the hydrolysis of L/Pd<sup>II</sup> amine system in water [3]: L = ethylenediamine, 2,2'-bipyridyl, 1,10-phenanthroline). In these cases, the ligands were not oxidized.



In a similar study, we established in a previous paper the great instability of the TPPTS/Pd<sup>II</sup> system [4] (TPPTS: sodium salt of tri(metasulfophenyl)phosphine). The Pd<sup>II</sup> is a well-known oxidizing agent of arylphosphines. At low pH without complexing anion, TPPTS was oxidized as the following reaction:



where OTPPTS is TPPTS oxide.

From these considerations, we report our investigations on the behavior of dppp-s/Pd<sup>II</sup> system as a function of different parameters in solution: pH, molar ratio dppp-s/Pd<sup>II</sup> and palladium concentration at room temperature.

## 2. Experimental

### 2.1. Materials and reagents

We reported a description of the general apparatus in a previous paper [4]. All reagents were used without any further purification. They included PdCl<sub>4</sub>Na<sub>2</sub> (Aldrich), PdSO<sub>4</sub>, Pd(OAc)<sub>2</sub> (Strem Chemicals), HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, NaOH (Laurylab). The dppp-s was prepared by sulfonation of dppp [5]. The content of dppp-s oxide Odppp-s was less than 5% (<sup>31</sup>P NMR,  $\delta \cong +40$  ppm).

### 2.2. General procedure

Metallic salt was weighed in a schlenk tube and deoxygenated by passing argon through it and keeping it under an inert atmosphere. With PdSO<sub>4</sub> salt, a deoxygenated HClO<sub>4</sub> aqueous solution was added (such as C = 0.16 mol/l) to avoid Pd(OH)<sub>2</sub> precipitation. The dppp-s aqueous deoxygenated solution was introduced

into the schlenk tube. The palladium concentration C<sub>0</sub> in the solution was about 3 × 10<sup>-2</sup> mol/l.

For polarographic and potentiometric analysis in dilute solution (C<sub>0</sub> = 3 × 10<sup>-4</sup> mol/l), 0.5 ml of the contents of the schlenk tube was carefully transferred into 50 ml of a 0.1 mol/l NaNO<sub>3</sub> solution previously degassed with argon. The pH value was modified by NaOH addition. In more palladium concentrated solutions, the schlenk tube was directly equipped with a glass electrode under an inert atmosphere.

For <sup>31</sup>P NMR analysis, D<sub>2</sub>O was introduced into a NMR tube (D<sub>2</sub>O/H<sub>2</sub>O = 20%). The <sup>31</sup>P NMR spectra are referenced to H<sub>3</sub>PO<sub>4</sub>.

## 3. Results and discussion

### 3.1. General behavior of dppp-s/Pd<sup>II</sup> system in water

Unlike the TPPTS/Pd<sup>II</sup> system, the dppp-s/Pd<sup>II</sup> system showed a good stability in water (acidic media) regardless of the concentration (0.032 mol/l of palladium salt, R = molar ratio = TPPTS/Pd<sup>II</sup> = 2 and R = dppp-s/Pd<sup>II</sup> = 1). Indeed, 17% of the TPPTS was oxidized with PdCl<sub>4</sub>Na<sub>2</sub> (pH = 4) and 72% with PdSO<sub>4</sub> (pH = 0.9) after 24 h under the same conditions [4]. In the similar mixture using dppp-s, we did not detect the production of dppp-s oxide (Odppp-s) which

Table 1  
 $^{31}\text{P}$  NMR characteristics of the diphosphine/ $\text{Pd}^{\text{II}}$  system ( $R = 1$ , reference  $\text{H}_3\text{PO}_4$ )

	$^{31}\text{P}$ NMR $\delta$ (ppm)
dppp-s/ $\text{PdCl}_4\text{Na}_2$	+15 <sup>a</sup>
dppp-s/ $\text{PdSO}_4$	+18.1 <sup>a</sup>
dppp/ $\text{PdCl}_2$	+11.9 <sup>b</sup> ; +13 <sup>c</sup>
dppp/ $\text{Pd}(\text{OAc})_2$	+11.1 <sup>d</sup>
dppp/ $\text{Pd}(\text{OAc})_2 + p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$	+17.5 <sup>d</sup>
$[\text{dpppPd}(m\text{-OH})_2\text{Pddppp}]\text{X}_2$	+15.2 <sup>e</sup>

<sup>a</sup> Our works in water.

<sup>b</sup> In  $\text{CDCl}_3$  [6].

<sup>c</sup> In THF [7].

<sup>d</sup> In acetone ([8] and see also references therein).

<sup>e</sup> In  $\text{CDCl}_3$ ,  $\text{X}=\text{BF}_4^-$  or  $p\text{-MeC}_6\text{H}_4\text{SO}_3^-$  [9].

is characteristic of the redox reaction ( $\text{pH} = 3.4$  for the dppp-s/ $\text{PdCl}_4\text{Na}_2$  system and  $\text{pH} = 0.9$  for the dppp-s/ $\text{PdSO}_4$  system). Under these experimental conditions, the pH value was stable. These results confirm the good stability encountered in the copolymerization process [2].

From the literature and for a  $R$  value equal to 1 (ratio employed in the catalyst of the reaction of ethylene-CO copolymerization), the  $^{31}\text{P}$  NMR data in organic solvent gave a singlet in the +11.9/+17.5 ppm range depending on the palladium salt used (see Table 1). In water, the signal was detected at 18.1 ppm for the dppp-s/ $\text{PdSO}_4$  system and at 15.0 ppm for the dppp-s/ $\text{Pd}(\text{OAc})_2$  and the dppp-s/ $\text{PdCl}_4\text{Na}_2$ . Like in organic solvents<sup>2</sup>, the salt of palladium used in the complex formation induced a shift of several ppm. Consequently, the anion used could be important part in the complex structure. The work on this interesting point is in progress in our laboratory.

The increase of the molar ratio  $R$  lead to the appearance of a new singlet at  $\delta = 3.2$  ppm (characteristic of a new species in solution) and a quantitative decrease of the singlet at 18.1 ppm (for the dppp-s/ $\text{PdSO}_4$  system) or 15.0 ppm (for the dppp-s/ $\text{PdCl}_4\text{Na}_2$  system). Fig. 1 presents the distribution of species in water for the dppp-s/ $\text{PdCl}_4\text{Na}_2$  system as a function of  $R$ . For  $R = 1.0$ , a singlet at only 15.0 ppm was observed. For  $R = 1.80$ , we distinguished two singlets at both

15.0 and 3.2 ppm, with 20 and 80%, respectively (Fig. 1).

At  $R = 2.1$ , the free dppp-s appeared. This behavior is consistent with the presence of a new stable complex  $[\text{PdL}_2]^{2+}$ . A complementary  $^{31}\text{P}$  NMR study at  $-30^\circ\text{C}$  ( $R = 3$ ) in hydro-alcoholic solution emphasized this result. We obtained 33% of free ligand and 67% of phosphine complexed. The oxidized state is with two chelating groups. The complexation reaction can be formulated as follows:



The stability of the  $[\text{PdL}_n]^{2+}$  system is affected by the nature and the concentration of the ligand (TPPTS or dppp-s) and the pH. In this context, a differential pulse polarographic (DPP) was carried out in water at palladium concentration  $C_0 = 3.3 \times 10^{-4}$  mol/l ( $\text{PdSO}_4$  or  $\text{Pd}(\text{OAc})_2$ ) with  $R = 1$  or 1.7. At  $\text{pH} = 7$  and  $R = 1.7$  (Fig. 2), the dppp-s/ $\text{Pd}^{\text{II}}$  system gave a reduction peak at  $-1.1$  V/SCE with a good reproducibility. The pattern of dppp-s/ $\text{Pd}(\text{OAc})_2$  polarogram was unchanged until  $\text{pH} = 9$ . At  $\text{pH} = 10$ , the peak current decreased by only 20%. From this polarographic behavior, an interesting comparison has been established (Fig. 2) with the TPPTS/ $\text{Pd}(\text{OAc})_2$  system already published [4]. Indeed, in the same condition, the polarograms pattern of TPPTS/ $\text{Pd}^{\text{II}}$  system was modified by the hydroxide addition: the reduction peak disappears, characterizing a quantitative reduction in aqueous solution of  $\text{Pd}^{\text{II}}$  at  $\text{pH} = 7$  [4].

As expected, with a concentration close to  $10^{-4}$  mol/l [2], the dppp-s/ $\text{Pd}^{\text{II}}$  system was stable. Particularly, we observe a large pH range of stability (1–9), while a redox reaction occurs from  $\text{pH} = 2$  for the TPPTS/ $\text{Pd}^{\text{II}}$  system [4]. Moreover, no palladium hydroxide precipitation was observed.

### 3.2. $^{31}\text{P}$ NMR analysis of dppp-s/ $\text{Pd}^0$ system in water

The interest on bidentate Pd complexes increased since the discovery of the efficient copolymerization of olefins + CO by those complexes [1]. At  $25^\circ\text{C}$ ,  $\text{Pd}^0(\text{dppp})_2$  was characterized in the THF at  $\delta = +3.7$  ppm by Portnoy and Milstein [10] while Broadwood-Strong et al. recorded a singlet at 4.0 ppm [7]. In water, no reference has been published. From

<sup>2</sup> In this case, this general remark takes not into account of the solvent parameters (dielectric constant, acidity, etc.).

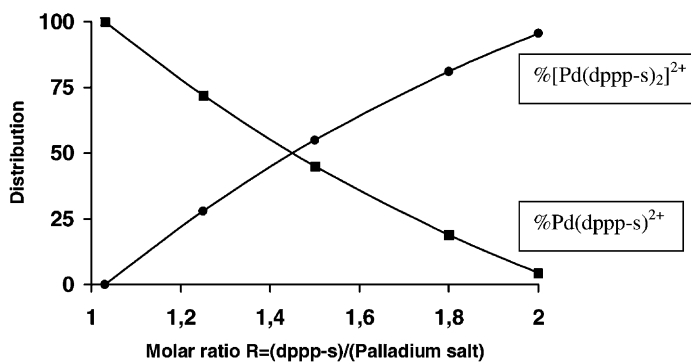


Fig. 1. Relative distribution of Pd(dppp-s)<sup>2+</sup> and [Pd(dppp-s)<sub>2</sub>]<sup>2+</sup> in water from dppp-s/PdCl<sub>4</sub>Na<sub>2</sub> system measured by <sup>31</sup>P NMR spectroscopy versus the molar ratio  $R = \text{dppp-s}/\text{PdCl}_4\text{Na}_2$ .

these considerations, a preliminary analytical study was realized on the water soluble system. The Pd<sup>0</sup> system was prepared starting from the dppp-s/PdSO<sub>4</sub> system ( $R = 1, 1.7$  or  $3$ ) and NaBH<sub>4</sub> or Zn. The reduction of Pd<sup>II</sup> induced a color change: the yellow solution turned to rusty brown. <sup>31</sup>P NMR exhibited a new singlet at 10.1 ppm due to the formation of the dppp-s/Pd<sup>0</sup> system. At  $R = 1$ , this system was not stable. Palladium metal appeared during the reduction, but the singlet at 10.1 ppm was observed. At  $R = 1.7$  or  $3$ , we identified two singlets at +10.1 and -16.1 ppm, according to a mixture of Pd<sup>0</sup> complex and free ligand, respectively. The analysis of peak area showed a ratio of phosphorus atoms/Pd<sup>0</sup> in the complex equal to 3 (at  $R = 1.5$ , we observe only a singlet at 10.1 ppm due to Pd<sup>0</sup> complex). These results

allows to suggest a configuration of the Pd<sup>0</sup> complex where three phosphorus atoms are bounded to Pd<sup>0</sup>. The free phosphorus atoms exchange in a very fast process with the phosphorus atoms linked to the Pd<sup>0</sup>.

The aqueous dppp-s/Pd<sup>II</sup> system ( $10^{-2}$  mol/l,  $R = 3$ ) led, with a complete conversion, to the dppp-s/Pd<sup>0</sup> system in basic medium,  $\text{pH} > 10$  (<sup>31</sup>P NMR gave two singlets: 10.1 and 40 ppm corresponding to the dppp-s/Pd<sup>0</sup> system and to the dppp-s oxide formation, respectively).

### 3.3. Potentiometric titrations

The polarographic analysis of the dppp-s/Pd<sup>II</sup> system at  $3.3 \times 10^{-4}$  mol/l has showed a good stability in aqueous solution (see Section 3.2). In this context,

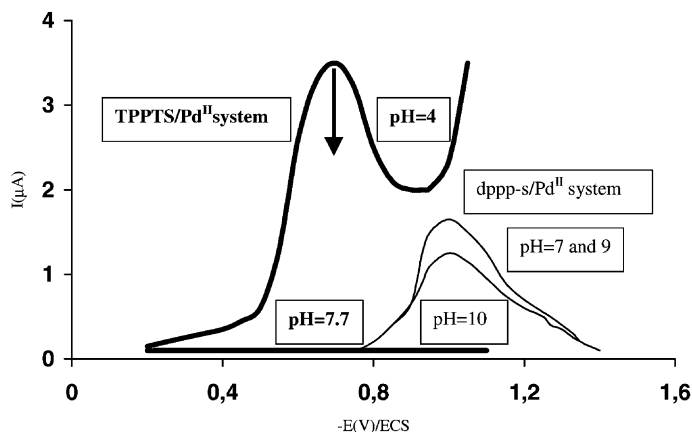


Fig. 2. DPP of L/Pd(OAc)<sub>2</sub> system (L = TPPTS or dppp-s,  $R = \text{concentration ratio L/Pd(OAc)}_2$ ) in water at different pH values;  $R = 3.4$  for L = TPPTS,  $R = 1.7$  for L = dppp-s;  $10^{-3}$  mol/l  $< C_0 < 10^{-4}$  mol/l. Arrow indicates polarogram evolution over the time.

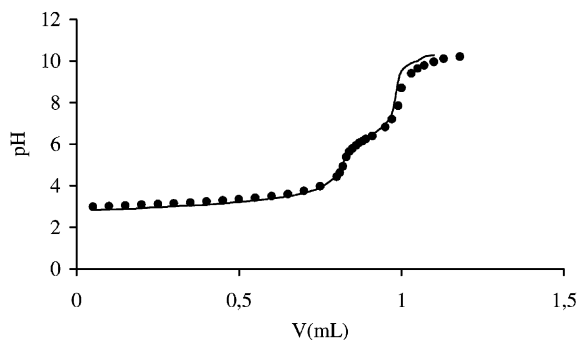
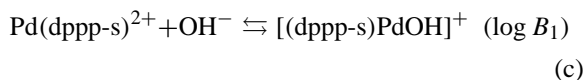


Fig. 3. Potentiometry of 50 ml of an aqueous solution by NaOH 0.098 mol/l. Aqueous solution:  $\text{HClO}_4$   $1.6 \times 10^{-3}$  mol/l +  $\text{dpps}/\text{PdSO}_4$   $3.3 \times 10^{-4}$  mol/l ( $R = 1$ ): (—) simulation of the titration (reaction (c)) with  $\log B_1 = 7.6$ ; (●) experimental curve.

the acid–base properties of this metallic complex have been studied by pHmetric titration for the same concentration. For this titration, the complex was prepared by addition of 1 equivalent of  $\text{Pd}^{\text{II}}$  ( $\text{PdSO}_4 \cdot 2\text{H}_2\text{O}$ ) and 1.07 equivalent of  $\text{dpps-s}$  in acid solution ( $\text{HClO}_4$ ). The pH measured by glass electrode remained stable. The pH evolution was recorded during the addition of a solution of sodium hydroxide. For each quantity of NaOH added, the pH (for  $\text{pH} < 9$ ) was quickly stabilized.

The classical titration of strong and weak acid mixtures ( $\text{HClO}_4$  and  $\text{Pd}(\text{dpps-s})^{2+}$  titrations) were recorded. From this discussion at this concentration, an typical acid–base reaction could be formulated as follows:



$$B_1 = \text{formation constant} = \frac{[(\text{dpps-s})\text{PdOH}]^+}{[\text{Pd}(\text{dpps-s})^{2+}][\text{OH}^-]}$$

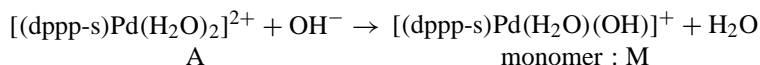
From this reaction only, the fitted curve was calculated for several formation constants  $B_1$  (Fig. 3). The theoretical data for this titration are consistent with the

experimental data for  $\log B_1 = 7.6$ . This result demonstrates the formation of soluble hydroxide complex (see further). The value calculated for  $\log B_1$  reaction (c) was close to  $[(\text{en})\text{Pd}(\text{H}_2\text{O})(\text{OH})]^+$  constant formation (en: ethylenediamine,  $\log B = 7.32$ ) [3]. With  $\text{PdCl}_4\text{Na}_2$   $3.3 \times 10^{-4}$  mol/l, the same value of  $\log B_1$  was obtained. The equilibrium between  $\text{Pd}(\text{dpps-s})^{2+}$  and  $\text{Cl}^-$  is not strong enough to disturb the hydrolysis reaction at this palladium concentration.

Potentiometry titration<sup>3</sup> curves of  $\text{dpps-s}/\text{PdSO}_4$  system ( $R = 1$ ) at three concentrations are shown in Fig. 4. The hydrolytic reaction occurs at lower pH when the concentration increases ( $0 < x < 0.4$ ;  $x = [\text{mol of NaOH added}]/[\text{mol of PdL}^{2+}]$ ). This similar phenomenon was already encountered with other palladium amine complexes [3]. Such variations could be ascribed to several hydroxo complexes: the hydrolytic reaction gave more than one hydroxo species or/and the formation of one (or more) oligomeric *m*-hydroxo species [3].

The addition in the equilibrium model of the dimerization reaction leading to  $[(\text{dpps-s})\text{Pd}(\mu\text{-OH})_2\text{Pd}(\text{dpps-s})]^{2+}$  was insufficiency to explain this phenomenon: the simulation curves are not in good agreement with the corresponding experimental one. Consequently, another pathway must be envisaged. Even though the dimer type  $[\text{LPdOH}]_2^{2+}$ ,  $L = \text{dpps}$  is known [3,9], we propose the binuclear species formation  $\{[(\text{dpps-s})\text{Pd}(\text{H}_2\text{O})][(\text{dpps-s})\text{Pd}(\text{OH})]\}^{3+}$ . The hydrolysis reactions could be rewritten from  $(\text{dpps-s})\text{Pd}^{2+}$  diaqua species and monomeric  $(\text{dpps-s})\text{PdOH}^+$ :

Reaction (c),  $B_1$ :



<sup>3</sup> For the concentration  $3.3 \times 10^{-3}$  and  $3.3 \times 10^{-2}$  mol/l, several experimental difficulties appeared during the pH measurements. The pH stabilization took longer after a small addition of sodium hydroxide. Moreover, this phenomenon occurred at lower pH values than when the initial complex concentration increased. The pH evolution at a static titration point decreased slowly. From these results, it can be suggested that a small amount of  $\text{Pd}^{\text{II}}$  complex was reduced to  $\text{Pd}^0$  during the pH titration. The rate of the redox process could be linked to the complex concentration and/or the solution pH. Despite this behavior, we recorded the titration curves.

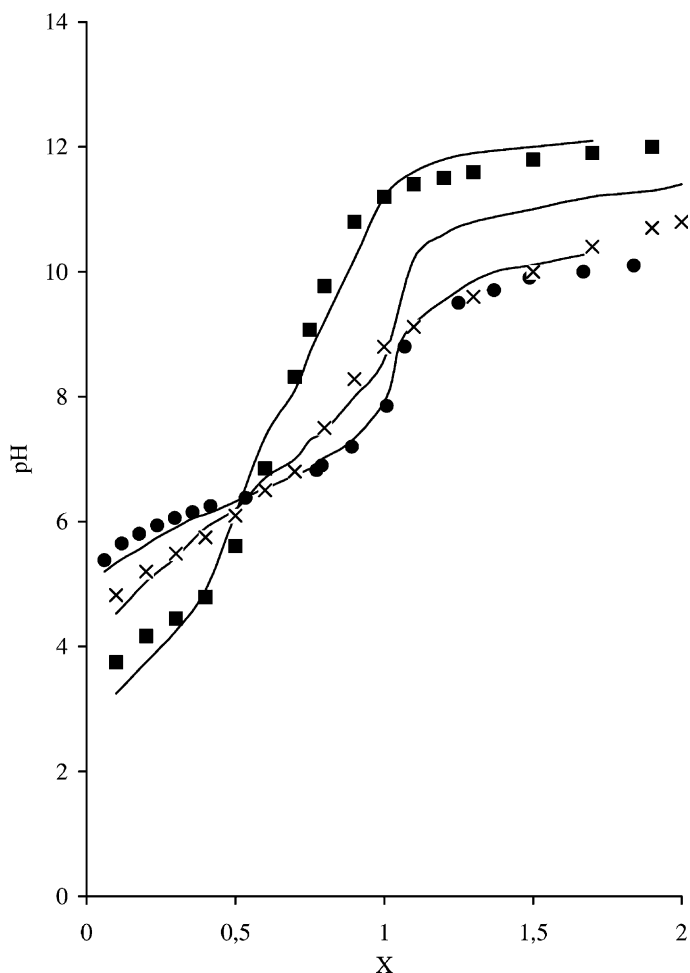
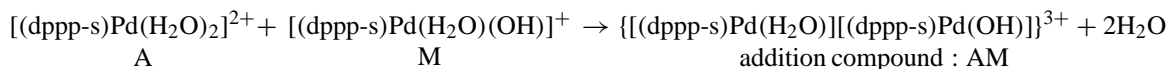


Fig. 4. Alkalimetric titrations of dppp-s/PdSO<sub>4</sub> system (molar ratio  $R = 1$ ) with NaOH. PdSO<sub>4</sub> concentration: (■)  $3.3 \times 10^{-2}$  mol/l; (x)  $3.3 \times 10^{-3}$  mol/l; (●)  $3.3 \times 10^{-4}$  mol/l; (—) simulation curves.  $X$  = molar ratio NaOH/PdSO<sub>4</sub>.

$$B_1 = \text{formation constant} = \frac{M}{A[\text{OH}^-]} = 10^{7.6}$$

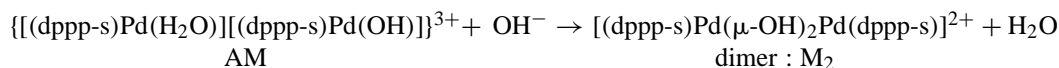
$$B_3 = \text{formation constant} = \frac{M_2}{[\text{AM}][\text{OH}^-]} = 10^{5.5}$$

Reaction (d),  $B_2$ :



$$B_2 = \text{formation constant} = \frac{[\text{AM}]}{[\text{A}][\text{M}]} = 10^{3.4}$$

Reaction (e),  $B_3$ :



The formation constants values of the reactions (c)–(e) (see Fig. 4) allow the best simulation of the titrations curves. We have represented on the Table 2

Table 2  
Distribution of A, M, AM and M<sub>2</sub> at different pH values during the titration<sup>a</sup>

pH	%A	%M	%AM	%M <sub>2</sub>	%Hy
<i>C</i> ( $3.3 \times 10^{-4}$ mol/l)					
4.54	97.63	1.29	1.07	<0.01	1.82
4.95	93.70	3.52	2.78	<0.01	4.91
<i>C</i> ( $3.3 \times 10^{-3}$ mol/l)					
4.54	90.63	1.30	8.07	<0.01	4.33
4.95	81.22	3.04	15.73	<0.01	10.90
<i>C</i> ( $3.3 \times 10^{-2}$ mol/l)					
4.54	48.14	0.72	51.14	<0.01	26.29
4.95	35.39	1.76	62.90	<0.01	33.22

<sup>a</sup> *C*: palladium salt concentration; %Hy = %M + %AM/2.

the distribution of the species A, M, AM and M<sub>2</sub> in the beginning of the titration ( $4.4 < \text{pH} < 5$ ) for the concentrations studied previously. The hydrolysis content (%Hy) was defined by  $\%M + \%AM/2$  (M<sub>2</sub> con-

tent <0.01% was not into account here). For example, with  $C = 3.3 \cdot 10^{-4}$  mol/l and at  $\text{pH} = 4.54$ , the %Hy value for the dppp-s/Pd(SO<sub>4</sub>) system was 1.82% only. At the same pH with  $C = 3.3 \cdot 10^{-2}$  mol/l, the %Hy was 26.22% showing the concentration effect on this system on the titration curves. The formation of the binuclear complex AM explains this phenomenon.

In the case of the TPPTS/Pd<sup>II</sup> system, no hydroxide species was detected because the hydrolysis and redox reaction took place simultaneously. With the dppp-s/Pd<sup>II</sup> system, the NaOH base was consumed before the reduction.

In these titrations, the *R* parameter played also an important role. Several titrations presented in Fig. 5 were performed for different *R* value. For *R* = 1, the complex was hydrolyzed. Until *R* = 1.7, hydrolysis reaction was not quantitative. For *R* = 3, the hydrolysis reaction did not occur at  $\text{pH} < 11$ .

In order to confirm these last potentiometric observations, <sup>31</sup>P NMR analysis were carried out at different

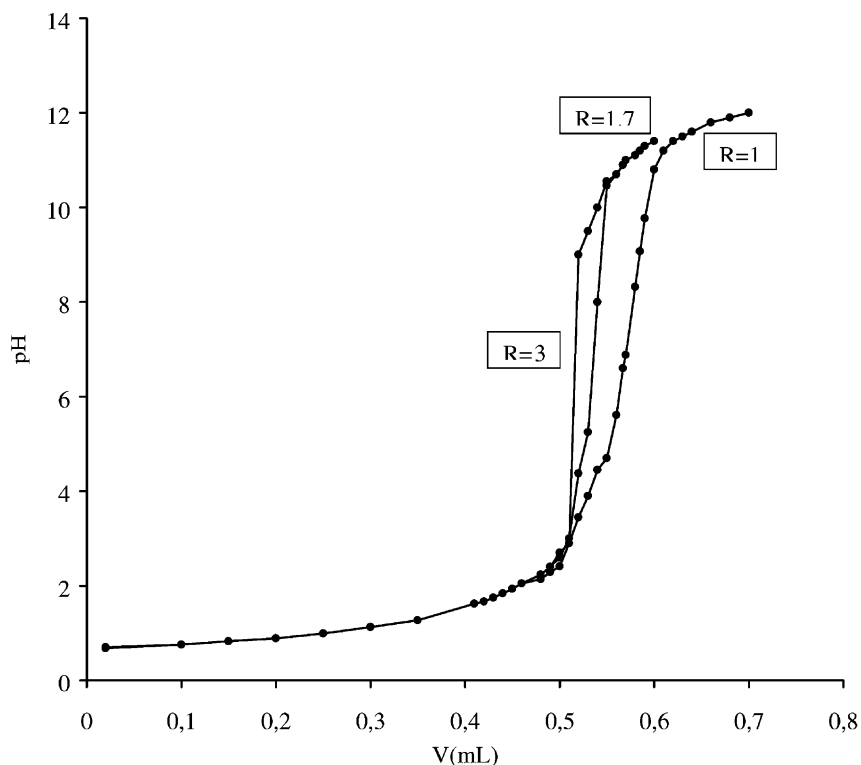
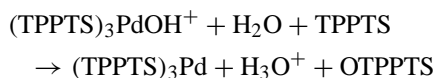


Fig. 5. Titration curve at 0.033 mol/l of dppp-s/PdSO<sub>4</sub> system for different *R* value (*R* = molar ratio dppp-s/palladium salt) in presence of HClO<sub>4</sub>. [NaOH] = 0.983 mol/l.

pH values. The complex was prepared at pH = 1 in presence of HClO<sub>4</sub> as in the potentiometric experiments from PdSO<sub>4</sub> salt. The concentration of the dppp-s/Pd<sup>II</sup> system was 4.10<sup>-3</sup> mol/l (1.5 < R < 1.7). At pH = 4.4, after the addition of NaOH, a new singlet was obtained at 16.4 ppm while the singlet at 18.1 ppm decreased (18.1 ppm: Pd(dppp-s)<sup>2+</sup> complex). In basic solution (pH = 9), the NMR spectrum exhibited a singlet at 16.4 ppm, probably the hydrolytic species. At this pH, no Pd(dppp-s)<sup>2+</sup> signal was detected. Going back to acid solution (pH < 2) led to the initial NMR spectrum. The signal at 16.4 ppm disappeared in favor of the singlet at 18.1 ppm. The pH–NMR analysis allowed an assignment of the singlet at 16.4 ppm to an hydroxide compound, which appeared stable. Moreover, this hydrolysis reaction was reversible in the experiment time.

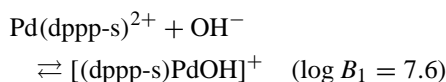
#### 4. Conclusion

With the TPPTS/Pd<sup>II</sup> system, it was known that the hydrolysis and redox process occurred in acid media. The neutralization of the acidity accelerates the disproportionation of an hydroxo complex into OTPPTS and Pd<sup>0</sup> by a simultaneous proton elimination:



In contrast, the bidentate palladium complex Pd(dppp-s)<sup>2+</sup> is less sensitive to hydrolysis and redox process. In dilute solution (3.3.10<sup>-4</sup> mol/l), the hydrolysis reaction is observed at pH between 4 and

9 without phosphine oxidation:



In more concentrated solutions, the presence of binuclear complexes strongly modified the system behavior: the hydrolysis and the redox process occur at lower pH.

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