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NMR approach for the identification of dinuclear and mononuclear complexes: The first detection of $[Pd(SPh)_2(PPh_3)_2]$ and $[Pd_2(SPh)_4(PPh_3)_2]$ – The intermediate complexes in the catalytic carbon–sulfur bond formation reaction

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ABSTRACT

In the present study we have analyzed the nature of palladium complexes in the catalytic system for selective carbon–sulfur bond formation *via* the addition of S–S and S–H bonds to alkynes. For the first time the mononuclear and dinuclear palladium complexes were clearly detected by DOSY NMR under the catalytic conditions. It was demonstrated that the concentration of these palladium complexes strongly depends on the amount of phosphine ligand available under reaction conditions.

1. Introduction

Transition metal catalysis has dramatically changed the face of modern organic chemistry and fine organic synthesis. A number of outstanding catalytic systems have been developed in recent years for stereo-, regio-, chemo- and enantio selective transformations of all classes of organic compounds. Amazingly, most of the catalytic systems were discovered by variation and screening of catalysts and ligands (sometimes by chance). Although this approach is still widely utilized, on the moment it became clear that empirical search should be accomplished by rational tuning of the catalytic systems based on mechanistic knowledge. It is the progress in understanding reaction mechanisms that will determine our success in design of new catalytic systems in the nearest future.

Most of the classical mechanisms related to homogeneous catalysis were assumed to involve mononuclear molecular complexes of transition metals. However, recent mechanistic studies have provided increasing number of evidence about involvement of dinuclear and larger metal species in catalysis [1–5]. Generation of dinuclear complexes may take place *via* dissociation of one of the ligands and formation of coordination vacancy, followed by coordination of a lone pair of heteroatom (Scheme 1). Depending on the nature of the system, the reaction may stop on the formation of complex with one bridging ligand (**1**). If the second heteroatom is available for complexation, the complex with two bridging ligands (**2**) is most likely to be obtained.

As representative examples related to catalysis, different dinuclear transition metal complexes are shown on Chart 1 [1–5]. Using Pd catalysts dinuclear complexes with bridged halogens were formed after oxidative addition of organic halides to the metal center (A, Chart 1). The oxidative addition of organic halides is the initial step of several cross-coupling reactions, Heck reaction, etc. and possible involvement and the role of dinuclear complexes have been considered [6]. Coordination of the lone pair of the nitrogen atom may lead to dinuclear complex with the metal atoms connected by the NR_2 groups (B, Chart 1). Formation of such complexes was anticipated in the catalytic hydroamination reactions [7]. Coordination of the oxygen group OR in bridging mode gave rise to dinuclear species (C, Chart 1) important for hydroalkoxylation reactions and Wacker-type chemistry [7].

Dinuclear, trinuclear and polynuclear complexes are of particular importance in the reactions involving metal complexes and

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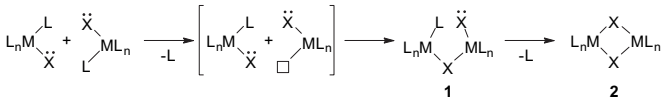


Scheme 1. Formation of dinuclear complexes with one and two bridging ligands.

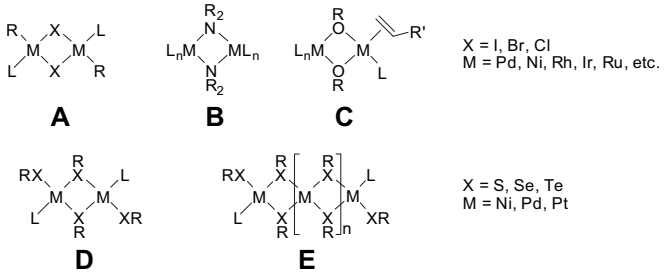


Chart 1. Representative examples of dinuclear and polynuclear metal complexes involved in catalysis [1–9].

chalcogen derivatives (D and E, Chart 1) [8]. Strong binding of chalcogen groups XR to the metal centers can link mononuclear species into a polymeric chain (E, Chart 1). High stability of such polymers was found as the main origin of catalyst poisoning by chalcogen species, for example, by thiols RSH and disulfides RSSR [9]. Splitting of the polymeric metal derivatives by phosphine ligands to smaller size metal complexes was of principal importance for preventing poisoning and maintaining catalytic activity in carbon–sulfur bond formation [8,9].

It should be pointed out that, depending on the nature of reaction, catalyst and reagents involved, dinuclear and polynuclear metal complexes may act as intermediates of the catalytic cycles, represent resting states, or block the catalytic cycle *via* formation of stable unreactive species. In any case the structure and the role of these di(poly)nuclear metal complexes should be clearly revealed in details.

In spite of great mechanistic importance, there are no useful methods available to distinguish mononuclear and dinuclear complexes in solution in the spectral monitoring of catalytic reactions. The NMR signals of peripheral groups are usually not sensitive enough to the nature of the complex. Spectral data taken from the bridging heteroatom could provide more information, but, unfortunately, there are no suitable NMR active nuclei available for high resolution measurements with X = I, Br, Cl, O, S, etc. For other nuclei, like ^{15}N, the measurements are time consuming at natural abundance and are hardly possible under catalytic conditions.

For our study we have chosen metal chalcogen derivatives with phosphine ligands as a suitable model system. Such metal complexes are very well characterized by X-ray analysis in the solid state and by NMR studies in solution [10–12]. The catalytic activity of Pd complexes in carbon-heteroatom bond formation through the addition of X-H and X-X bonds to alkynes (X = S, Se) has been revealed [8,9].

As exemplified for the series of chalcogen derivatives of Pd and Pt, ^{31}P NMR chemical shifts showed minor changes in the complexes of completely different types, with different metals and bridging groups (Chart 2) [10–12]. The attempts to distinguish a mixture of these complexes by ^{31}P NMR of the phosphine ligands were unsuccessful. Insufficient sensitivity of ^{31}P NMR to the structural changes was noticed with as small as 27.9–30.4 ppm chemical shifts range reported for the palladium complexes and confirmed again with rather small difference of 18.7–21.5 ppm for the platinum analogs (Chart 2). In addition, ^{31}P NMR chemical shifts strongly depended on the solvent. For example, the ^{31}P chemical shift for the common contaminant - triphenylphosphine oxide $Ph_3P{=}O$ - changed from 25.6 ppm in C_6D_6 to 28.6 ppm in $CDCl_3$ and showed a similar difference ($\Delta\delta$ = 3 ppm) compared to those changes observed in the transition metal complexes (Chart 2) [13].

Not surprisingly, nowadays most of the complexes were first isolated in the crystalline form and characterized by X-ray analysis, then the data was extrapolated to solution [14]. This approach limits the scope of the mechanistic study only to the certain types of stable metal complexes available as high quality single crystals. Moreover, this may provide wrong information about reaction mechanism, since very often it is unclear whether polynuclear complex was present in the original solution or it was formed during crystallization and stabilized by interactions in the crystal. Undoubtedly, an appropriate NMR technique is of vital importance to monitor metal complexes directly in solution and to distinguish mononuclear and dinuclear derivatives *in situ*.

2. Results and discussion

In the present study we have carried out diffusion ordered NMR spectroscopy (DOSY) measurements to resolve the presence of mononuclear and dinuclear Pd complexes directly in solution in the catalytic reaction. DOSY is a well-known NMR technique, which has proven the application in various chemical systems including transition metal complexes [15,16]. The idea of DOSY NMR is to differentiate the content of solution according to translational diffusion coefficients. Diffusion coefficients are related to the speed of molecular motions in liquids and depend on the size of dissolved compounds. According to the Stokes–Einstein equation, the diffusion coefficient for a molecule is inversely proportional to the hydrodynamic molecular radius [15]. Particularly, for the studied system we can expect that mononuclear Pd complexes of smaller size and weight should exhibit different diffusion coefficients as compared to dinuclear complexes, which possess larger size and weight.

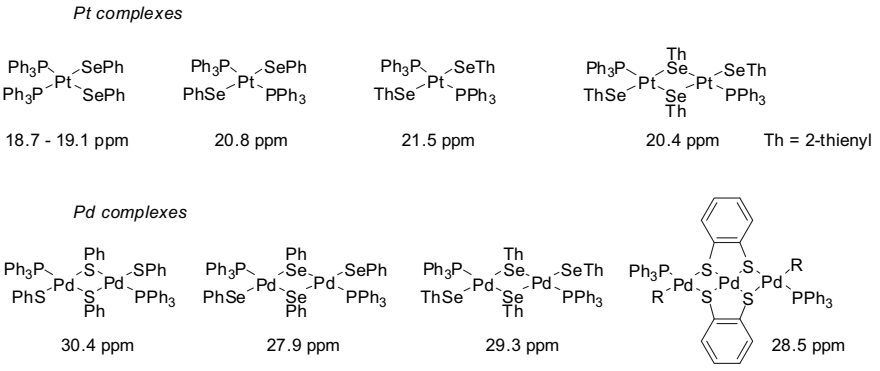
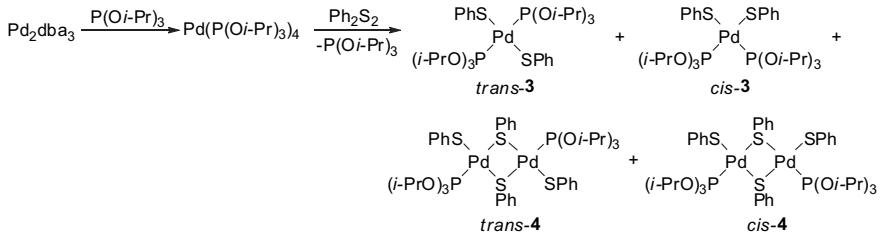


Chart 2. ^{3}P NMR chemical shifts of the PPh_3 ligand coordinated to mononuclear and dinuclear chalcogenide complexes of platinum and palladium [10,11].



Scheme 2. Oxidative addition of Ph_2S_2 in the system Pd/P(O*i*-Pr)$_3$ (dba = dibenzylideneacetone).

First, we have defined the model system to examine reliability of DOSY NMR to distinguish between the mononuclear and dinuclear Pd complexes with sulfur ligands in solution. For this purpose we have studied oxidative addition of diphenyl disulfide to Pd(P(O*i*-Pr)$_3$)$_4$ species generated from Pd_2dba_3 and the P(O*i*-Pr)$_3$ ligand (Scheme 2). The choice of ligand was crucial for the model system. With tri(isopropyl)phosphite both the mononuclear and dinuclear complexes **3** and **4** were isolated and characterized by X-Ray analysis, and ^{1}H and ^{31}P{^{1}H} NMR signals were assigned for *trans*-**3**, *cis*-**3**, *trans*-**4** and *cis*-**4** [17].

The ^{31}P{^{1}H} NMR spectrum of the studied mixture (Fig. 1A) contained four signals of the complexes *trans*-**3** (δ = 102.7 ppm), *cis*-**3** (δ = 110.5 ppm), *trans*-**4** (δ = 98.8 ppm) and *cis*-**4** (δ = 101.2 ppm). High intensity resonances correspond to thermodynamically more stable *trans*-isomers.

This sample was a subject of DOSY NMR analysis with pulsed field gradient strength varied from 5.5 G/cm to 662.5 G/cm in 128 steps. The experiment was carried out in ^{31}P nuclei detection with the delays $\Delta = 20$ ms and $\delta = 1.6$ ms set in the pulse sequence. The resulting 2D DOSY data showed conventional ^{31}P NMR spectrum in one dimension and the diffusion spectrum was displayed in the second dimension (Fig. 1A and B). The DOSY way to edit diffusion data is very useful since signals belonging to the compounds of similar size appear aligned with the same diffusion coefficient value. Particularly, the signals of both mononuclear complexes were aligned on the same horizontal line of the DOSY spectrum, as well as the signals corresponding to dinuclear complexes were aligned on another horizontal line. The mononuclear (**3**) and dinuclear (**4**) complexes were clearly resolved in the diffusion NMR study. Larger self-diffusion coefficient $5.5 \pm 0.5 \times 10^{-10}$ m^2 s^{-1} was measured for the smaller complexes **3** (MW = 741 Da), while larger complexes **4** (MW = 1066 Da) possessed smaller self-diffusion coefficient $4.5 \pm 0.5 \times 10^{-10}$ m^2 s^{-1}.

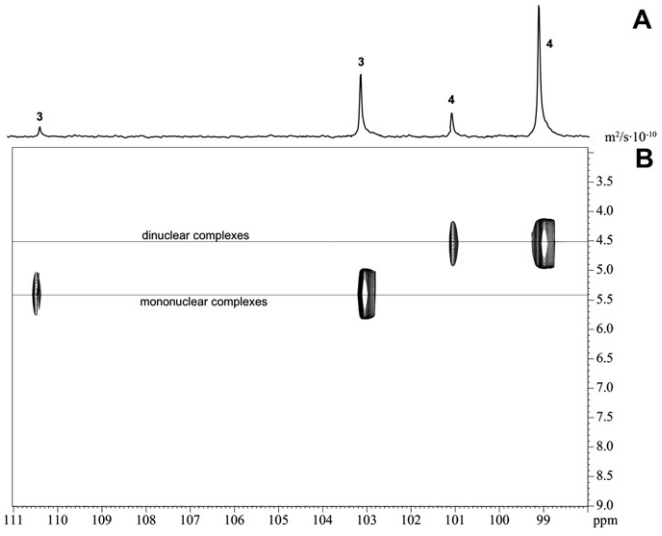


Fig. 1. The ^{31}P{^{1}H} NMR spectrum (A) and DOSY NMR spectrum (B) of the mixture of complexes **3** and **4** (C_6D_6; 400 MHz ^{1}H, 160 MHz ^{31}P) [18].

After this successful application of DOSY NMR to the known model system we have studied the system with PPh_3 ligand, which may contain complexes **5** and **6** (Chart 3). The ^{1}H NMR spectrum can not be used to distinguish the nature of palladium complexes in this mixture, neither ^{31}P{^{1}H} NMR spectrum (Fig. 2A) can provide the required information. In the X-Ray structure analysis the Pd complex **5** has never been obtained and structurally characterized, only corresponding dinuclear species **6** have been isolated [10,11]. The possibility of formation of mononuclear species in the system remained a puzzling mechanistic question, raised in several studies related to catalysis (see reviews [9]).

In the DOSY NMR spectrum we have clearly resolved two patterns of the signals belonging to mononuclear **5** (MW = 849 Da) and dinuclear **6** (MW = 1174 Da) complexes with self-diffusion coefficients $6.1 \pm 0.5 \times 10^{-10}$ m^2 s^{-1} and $4.9 \pm 0.5 \times 10^{-10}$ m^2 s^{-1}, respectively (Fig. 2B). Larger self-diffusion coefficient of $9.1 \pm 0.5 \times 10^{-10}$ m^2 s^{-1} was measured for the O=PPh$_3$ (MW = 278 Da). Although *cis*-**5**, *trans*-**5** and O=PPh$_3$ showed close ^{31}P NMR shifts, they were clearly resolved on the diffusion axis (Fig. 2B) [19].

In the present study for the first time we have revealed the presence of mononuclear [Pd(SPh)$_2$(PPh$_3$)$_2$] complexes, and have determined their ^{31}P NMR chemical shifts δ = 26.2 and 25.5 ppm. In a similar manner as discussed above, *cis*- and *trans*- complexes were observed in each case and we can propose that more intense signals correspond to thermodynamically more stable *trans*-isomers.

With the characteristic NMR parameters at hands we have studied the catalytic reaction of Ph_2S_2 addition to the triple bond of alkynes, catalyzed by Pd/PPh_3 system (Scheme 3). The reaction is unique due to exceptional stereoselectivity of the transformation (Z/E > 99/1) and high product yields (>90%). It was proposed that [Pd$_n$(SPh)$_{2n}$(PPh$_3$)$_m$] complexes formed after oxidative addition of the S–S bond to zerovalent palladium are the intermediates of the catalytic reaction, however, the nature of these metal species

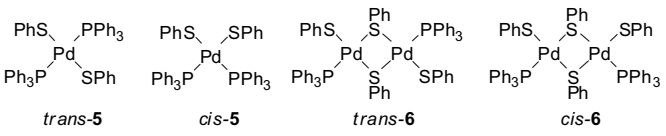


Chart 3. Mononuclear and dinuclear Pd complexes with triphenylphosphine ligand.

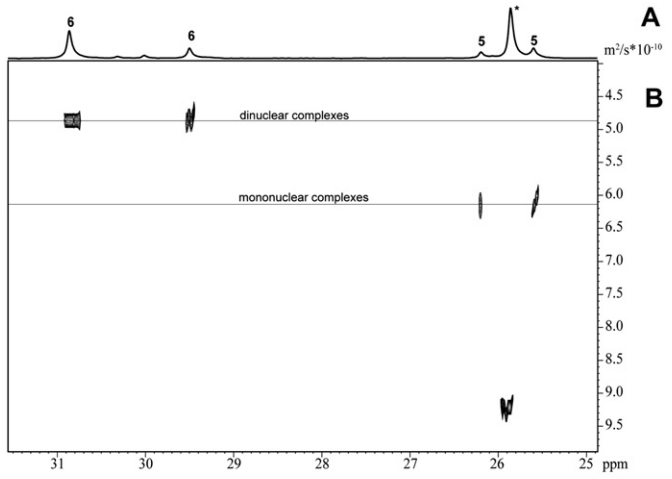
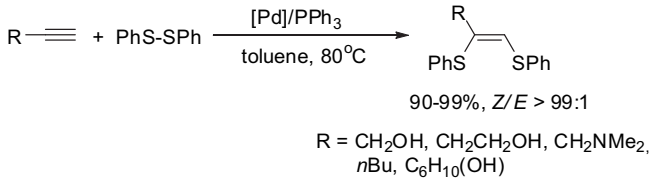


Fig. 2. The $^{31}P\{^{1}H\}$ NMR spectrum (A) and DOSY NMR spectrum (B) of the mixture of complexes **5** and **6** (C_6D_6; 600 MHz ^{1}H, 240 MHz ^{31}P); the signal marked by the asterisk corresponds to triphenylphosphine oxide.



Scheme 3. The catalytic reaction of stereoselective Ph_2S_2 addition to alkynes in the Pd/PPh_3 system [20].

remained unclear [9]. Involvement of the $[Pd_n(ER)_{2n}(PPh_3)_m]$ complexes in the catalytic RE-H bond addition to alkynes in the presence of phosphine ligands was also discussed for E = S and Se [8b,9].

We have measured $^{31}P\{^{1}H\}$ NMR spectrum in the conditions of catalytic reaction and have detected the signals of mononuclear complexes **5** with the chemical shifts δ = 26.2, 25.5 ppm and dinuclear complex **6** with the chemical shifts δ = 29.5, 30.9 ppm.

The performance of the catalytic reactions was evaluated at different Pd: phosphine ligand ratios. The plot reflecting the yield of the reaction after 1 h of heating at 80 °C showed an increase from 10% at 1:1 ratio to 33% at 1:8 ratio, with the further increase of the yield to 46% at 1:32 ratio (Fig. 3). Clearly, an excess of the ligand facilitated product formations and enhanced the performance of the catalytic reaction [8,9]. After 4 h of heating at 80 °C the reaction reached 86%, 63% and 29% yields at 1:4, 1:2 and 1:1 metal:ligand ratios, respectively (>95% conversion for the other ratios). Interesting to point out that at 1:64 ratio the large excess of the ligand decreased the performance of the catalytic system (Fig. 3).

With the NMR spectroscopic study we have analyzed the nature of the catalytic system and have determined the amounts of mononuclear and dinuclear palladium complexes under catalytic conditions (Fig. 4). The amount of dinuclear complexes increased at 1:1–1:12 metal:ligand ratios due to suppression of polymerization of palladium sulfur species. Indeed, the systems with 1:1 and 1:2 ratios were heterogeneous and contained insoluble $[Pd(SPh)_2]_n$ species, the system at 1:4 ratio was nearly homogeneous with minor amount of precipitate, and the systems with 1:8–1:64 ratios were completely homogeneous. The NMR study has shown that splitting of the metal polymers resulted in formation of soluble metal complexes of smaller size, simultaneously, an increase of the reaction yield was observed.

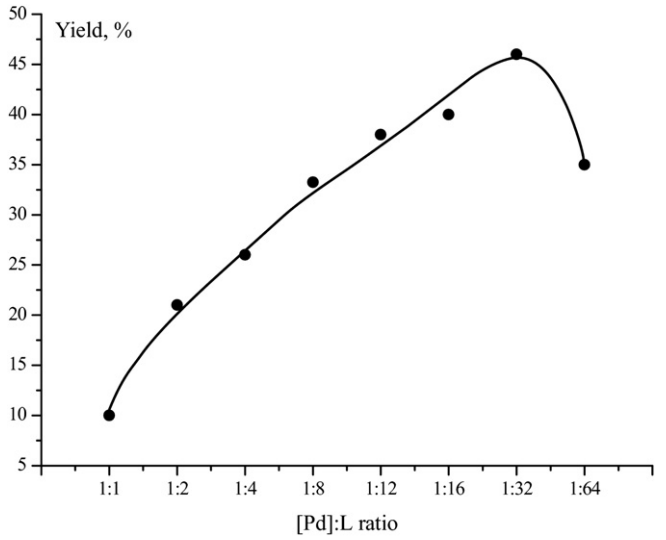


Fig. 3. The plot of reaction yield in the catalytic Ph_2S_2 addition to hexyne-1 at different $Pd:PPh_3$ ratios measured after a short period of time (1 h; 80 °C).

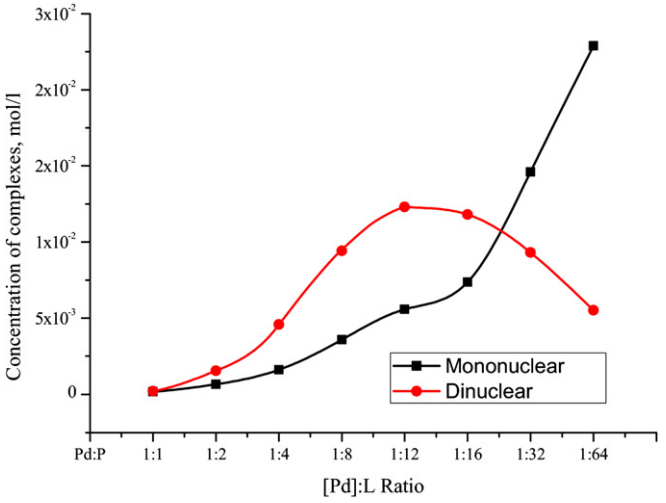
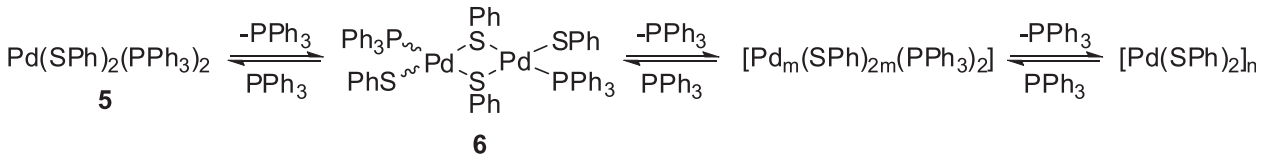


Fig. 4. The plot of amounts of mononuclear (**5**) and dinuclear (**6**) complexes in the catalytic reaction of Ph_2S_2 addition to hexyne-1 at different $Pd:PPh_3$ ratios (measured after 1 h at 80 °C).

Interesting to point out that the curve corresponding to dinuclear complexes showed a maximum at 1:12 ratio, while the amount of mononuclear complexes increased monotonously (Fig. 4). Obviously, at some point (>1:12 ratio) the amount of dinuclear complexes was decreased in favor of formation of mononuclear species. Thus, a series of equilibriums were presented in the studied catalytic system and the overall composition of the mixture depended on the amount of phosphine ligand (Scheme 4).

Comparing the performance of the catalytic reaction (Fig. 3) and the amount of metal species (Fig. 4) at different $Pd:PPh_3$ ratios we may point out that reaction yield did not increase monotonously as the curve for the mononuclear species. The maximum values were observed at different $Pd:PPh_3$ ratios - 1:32 (Fig. 3) and 1:12 (Fig. 4). Thus, the contributions of both types of intermediate metal complexes to the product formation in the studied catalytic reaction should be taken into account. Of course, this is rather preliminary assumption, which should be further rationalized and studied in more details.



5 **6**

Scheme 4. Different palladium species in the studied system.

To conclude, the present study has demonstrated that mononuclear and dinuclear complexes can be clearly distinguished in solution by DOSY NMR. The study of the Pd sulfur complexes with the triphenylphosphine ligand resolved both complexes *in situ* in the reaction mixture. The mechanism of the catalytic reaction should be reconsidered to take into account possible formation of the mononuclear and dinuclear metal complexes and to find out their contribution into the product formation.

3. Experimental part

3.1. General procedures

All experiments were carried out under an argon atmosphere with dry and degassed solvents. All reagents were purchased from commercial sources (Acros, Aldrich), unless otherwise stated, and used as received after purity control with NMR spectroscopy. Tris (dibenzylideneacetone)dipalladium was prepared as reported before [21]. Deuterated solvents were stored over molecular sieves (4 Å, 8–12 mesh). ^{1}H and ^{31}P spectra were acquired on a Bruker Avance II 600 spectrometer equipped with a 5 mm BBO probe. Durations of 90° pulses for ^{1}H and ^{31}P were 10.5 and 19.0 μs, respectively. Chemical shifts are reported in parts per million relative to TMS (^{1}H) or 80% H_3PO_4/H_2O (^{31}P) as internal and external standards, respectively. First, DOSY experiment was carried out with dedicated gradient probe, followed by the measurements of the same samples with routine gradient probe. The results measured on both probes were in total agreement with each other and confirmed reliability of routine hardware for these measurements. The procedure for the measurements with dedicated diffusion probe and routine probe are described below for phosphite and phosphine systems, respectively.

3.2. Sample preparation and DOSY analysis of the Pd/P(Oi-Pr)$_3$ system (**3** and **4**)

Pd_2dba_3 (20.0 mg, 0.019 mmol), Ph_2S_2 (8.4 mg, 0.038 mmol), P(O*i*-Pr)$_3$ (4.0 mg, 0.019 mmol) and 0.6 mL of C_6D_6 were added sequentially into an NMR tube. After shaking for 15–20 min a brown suspension was formed. ^{31}P NMR spectrum of the resulting suspension showed formation of mono- and dinuclear complexes **3** and **4** identified according to the published data. Sample was filtered through celite into a Shigemi tube, total sample height was 1 cm.

The 2D DOSY spectrum was acquired on a Bruker Avance 400 spectrometer using Diff60 gradient probe with ^{31}P selective insert. Sample was not spinning and the temperature was regulated at 303 K, VTU air flow was set to 670 l/h. An experiment was performed using a basic diffse (gradient spin-echo) pulse program. Durations of the gradient pulse (δ) and diffusion time (Δ) were 1.6 and 20 ms, respectively. Sine gradient shape was applied. Data acquisition was established in 128 steps with linear gradient evolution from 5.5 to 662.5 G/cm with 88 scans for each step. 2D DOSY spectra were generated using Bruker Topspin 2.1 software.

3.3. Sample preparation and DOSY analysis of Pd/PPh$_3$ system (**5** and **6**)

Pd_2dba_3 (30.0 mg, 0.029 mmol), Ph_2S_2 (12.7 mg, 0.058 mmol), PPh_3 (7.6 mg, 0.029 mmol) and 0.6 mL of C_6D_6 were added sequentially into an NMR tube. After shaking for 15–20 min a brown suspension was formed. ^{31}P NMR spectrum of the resulting suspension showed formation of palladium complexes. Sample was filtered through celite into a Shigemi tube, total sample height was 1 cm.

The 2D DOSY spectrum was acquired on a Bruker Avance II 600 spectrometer equipped with a GAB gradient amplifier using a 5-mm BBO Bruker gradient probe. Temperature was stabilized at 303 K, VTU air flow was set to 670 l/h. An experiment was performed using a standard stegp1s pulse program (stimulated gradient spin-echo with one spoil gradient). Durations of gradient pulse (δ) and diffusion time (Δ) were 6 and 100 ms, respectively. Sine gradient shape was applied. Gradient strength was calibrated relative to self-diffusion coefficient of HDO ($1.9\cdot10^{-9}$ m^2/s) for 1% H_2O in D_2O sample at 298 K and was 6.50 G/cm A for BBO probe. Data acquisition was established in 256 steps with linear gradient evolution from 0.91 to 43.23 G/cm (2–95% of maximum gradient coil current) with 32 scans per step. 2D DOSY spectra were generated using Bruker Topspin 2.1 software.

3.4. Catalytic addition of diphenyl disulfide to 1-heptyne with various PPh$_3$:Pd ratios

Pd_2dba_3 (15.5 mg, 0.015 mmol) was placed into an NMR tube. A corresponding amount of PPh_3 (3.9 mg; 7.9 mg; 15.7 mg; 31.5 mg; 47.2 mg; 62.9 mg 125.9 mg and 251.8 mg for the experiments with 1:1; 2:1; 4:1; 8:1; 12:1; 16:1; 32:1 and 64:1 PPh_3:[Pd] ratios, respectively) followed by Ph_2S_2 (109.2 mg, 0.5 mmol) and 1-heptyne (48.1 mg, 0.5 mmol) were added. Reagents were dissolved in 0.6 mL of C_6D_6 and the sample was heated at 80 °C. ^{1}H and ^{31}P NMR spectra were recorded after 1 h, 4 h, and 8 h of heating. In certain cases a strong overlap of mononuclear complexes signals and signal of triphenylphosphine oxide was observed. In such cases, the peaks were resolved by addition of a small amount of $CDCl_3$ (ca. 0.2 mL) to the sample. The addition of $CDCl_3$ induced downfield shift of PPh_3O resonance, while the signals of palladium complexes did not change noticeably (known chemical shifts of triphenylphosphine oxide in C_6D_6 and $CDCl_3$ are 25.6 and 28.6 ppm, respectively).

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References

[1] Di- and polynuclear Rh complexes in catalysis: (a) T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, J. Am. Chem. Soc. 124 (2002) 5052;
(b) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani, T. Hayashi, J. Am. Chem. Soc. 126 (2004) 13584;

(c) R. Shintani, A. Tsurusaki, K. Okamoto, T. Hayashi, Angew. Chem. Int. Ed. 44 (2005) 3909;
(d) A. Angelini, M. Aresta, A. Dibenedetto, C. Pastore, E. Quaranta, M.R. Chierotti, R. Gobetto, I. Pápai, C. Graiff, A. Tiripicchio, Dalton Trans. (2009) 7924;
(e) C. Zhu, N. Yukimura, M. Yamane, Organometallics 29 (2010) 2098;
(f) C. Ganesamoorthy, M.S. Balakrishna, J.T. Mague, Dalton Trans. (2009) 1984;
(g) A.J. Blacker, S.B. Duckett, J. Grace, R.N. Perutz, A.C. Whitwood, Organometallics 28 (2009) 1435;
(h) R. Mariz, A. Briceno, R. Dorta, R. Dorta, Organometallics 27 (2008) 6605.
(i) Some selected recent representative examples are cited here and below in Refs. [2–5], for the other metals.

[2] Dinuclear Ir complexes in catalysis: (a) T. Yamagata, H. Tadaoka, M. Nagata, T. Hirao, Y. Kataoka, V. Ratovelomanana-Vidal, J.P. Genet, K. Mashima, Organometallics 25 (2006) 2505;
(b) M.A. Salomon, A.-K. Jungton, T. Braun, Dalton Trans. (2009) 7669.

[3] Di- and polynuclear Pd complexes in catalysis: (a) M.A. Fernández-Rodríguez, Q. Shen, J.F. Hartwig, Chem. Eur. J. 12 (2006) 7782;
(b) A. Sachse, M. John, F. Meyer, Angew. Chem. Int. Ed. 49 (2010) 1986;
(c) N. Tsukada, M. Wada, N. Takahashi, Y. Inoue, J. Organomet. Chem. 694 (2009) 1333;
(d) H. Türkmen, T. Pape, F.E. Hahn, B. Çetinkaya, Eur. J. Inorg. Chem. 2009 (2009) 285.

[4] Di- and trinuclear Ru complexes in catalysis: (a) Y. Nakajima, H. Kameo, H. Suzuki, Angew. Chem. Int. Ed. 45 (2006) 950;
(b) T. Kawashima, T. Takao, H. Suzuki, Angew. Chem. Int. Ed. 45 (2006) 485;
(c) Y. Nishibayashi, A. Shinoda, Y. Miyake, H. Matsuzawa, M. Sato, Angew. Chem. Int. Ed. 45 (2006) 4835;
(d) K. Kanao, Y. Tanabe, Y. Miyake, Y. Nishibayashi, Organometallics 29 (2010) 2381;
(e) Y. Miyake, S. Endo, Y. Nomaguchi, M. Yuki, Y. Nishibayashi, Organometallics 27 (2008) 4017;
(f) Y. Miyake, S. Endo, M. Yuki, Y. Tanabe, Y. Nishibayashi, Organometallics 27 (2008) 6039.

[5] Dinuclear Ni complexes in catalysis: (a) D.M. Spasyuk, D. Zargarian, Inorg. Chem. 49 (2010) 6203;
(b) Y. Xu, S. Matsunaga, M. Shibasaki, Org. Lett. 12 (2010) 3246;
(c) A. Velian, S. Lin, A.J.M. Miller, M.W. Day, T. Agapie, J. Am. Chem. Soc. 132 (2010) 6296;
(d) T. Chattopadhyay, M. Mukherjee, A. Mondal, P. Maiti, A. Banerjee, K.S. Banu, S. Bhattacharya, B. Roy, D.J. Chattopadhyay, T.K. Mondal, et al., Inorg. Chem. 49 (2010) 3121;
(e) N.E. Shepherd, H. Tanabe, Y. Xu, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 132 (2010) 3666.

[6] (a) C. Amatore, A.A. Bahsoun, A. Jutand, G. Meyer, A.N. Ntepe, L. Ricard, J. Am. Chem. Soc. 125 (2003) 4212;
(b) K. Sonogashira, J. Organomet. Chem. 653 (2002) 46;
(c) F. Paul, J. Patt, J.F. Hartwig, J. Am. Chem. Soc. 116 (1994) 5969;
(d) C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc. 113 (1991) 8375;
(e) An excellent detailed mechanistic study: A.G. Sergeev, A. Spannenberg, M. Beller, J. Am. Chem. Soc. 130 (2008) 15549;
(f) A.G. Sergeev, A. Zapf, A. Spannenberg, M. Beller, Organometallics 27 (2008) 297.

[7] Selected representative examples: (a) Selected representative examples: A. Dzudza, T. Marks Chem. Eur. J. 16 (2010) 3403;
(b) M.S. Hadfield, A.-L. Lee, Org. Lett. 12 (2010) 484;
(c) T. Hirai, A. Hamasaki, A. Nakamura, M. Tokunaga, Org. Lett. 11 (2009) 5510;
(d) C. Liu, C.F. Bender, X. Han, R.A. Widenhoefer, Chem. Commun. (2007) 3607;
(e) Y. Zhang, M.S. Sigman, Org. Lett. 8 (2006) 5557;
(f) C. Bruneau, P.H. Dixneuf, Angew. Chem. Int. Ed. 45 (2006) 2176;
(g) N.T. Patil, L.M. Lutete, H. Wu, N.K. Pahadi, I.D. Gridnev, Y. Yamamoto, J. Org. Chem. 71 (2006) 4270;
(h) K. Alex, A. Tillack, N. Schwarz, M. Beller, ChemSusChem 1 (2008) 333;
(i) S. Hong, T.J. Marks, Acc. Chem. Res. 37 (2004) 673;
(j) A. Tillack, V. Khedkar, M. Beller, Tetrahedron Lett. 45 (2004) 8875;
(k) J. Hartwig, Pure Appl. Chem. 76 (2004) 507;
(l) F. Pohlki, S. Doye, Chem. Soc. Rev. 32 (2003) 104;
(m) L. Fadini, A. Togni, Chem. Commun. (2003) 30;
(n) L. Ackermann, R.G. Bergman, Org. Lett. 4 (2002) 1475.

[8] (a) V.P. Ananikov, K.A. Gayduk, I.P. Beletskaya, V.N. Khrustalev, M.Yu. Antipin, Eur. J. Inorg. Chem. (2009) 1149;
(b) V.P. Ananikov, D. Malyshev, I. Beletskaya, G. Aleksandrov, I. Eremenko, Adv. Synth. Catal. 347 (2005) 1993;
(c) D.A. Malyshev, N.M. Scott, N. Marion, E.D. Stevens, V.P. Ananikov, I.P. Beletskaya, S.P. Nolan, Organometallics 25 (2006) 4462.

[9] (a) I.P. Beletskaya, V.P. Ananikov, Eur. J. Org. Chem. (2007) 3431;
(b) I.P. Beletskaya, V.P. Ananikov, Pure Appl. Chem. 79 (2007) 1041;
(c) A. Ogawa, J. Organomet. Chem. 611 (2000) 463–474.

[10] (a) M.S. Hannu, R. Oilunkaniemi, R.S. Laitinen, M. Ahlgén, Inorg. Chem. Commun. 3 (2000) 397;
(b) R. Oilunkaniemi, R.S. Laitinen, M. Ahlgén, J. Organomet. Chem. 587 (1999) 200;
(c) R. Oilunkaniemi, R.S. Laitinen, M. Ahlgén, J. Organomet. Chem. 623 (2001) 168;
(d) D. Shimizu, N. Takeda, N. Tokitoh, Chem. Commun. (2006) 177;
(e) V.P. Ananikov, I.P. Beletskaya, G.G. Aleksandrov, I.L. Eremenko, Organometallics 22 (2003) 1414;
(f) V.P. Ananikov, I.P. Beletskaya, Org. Biomol. Chem. 2 (2004) 284.

[11] (a) R. Zanella, R. Ros, M. Graziani, Inorg. Chem. 12 (1973) 2736;
(b) I. Nakanishi, S. Tanaka, K. Matsumoto, S. Ooi, Acta Crystallogr. C C50 (1994) 58.

[12] (a) L.B. Kumbhare, A.P. Wadawale, V.K. Jain, S. Kolay, M. Nethaji, J. Organomet. Chem. 694 (2009) 3892;
(b) N. Ghavale, S. Dey, A. Wadawale, V.K. Jain, Organometallics 27 (2008) 3297;
(c) N.D. Ghavale, S. Dey, V.K. Jain, M. Nethaji, Inorg. Chim. Acta 361 (2008) 2462;
(d) V.K. Jain, L. Jain, Coord. Chem. Rev. 249 (2005) 3075;
(e) S. Dey, V.K. Jain, B. Varghese, J. Organomet. Chem. 623 (2001) 48;
(f) A. Singhal, V.K. Jain, B. Varghese, E.R.T. Tiekink, Inorg. Chim. Acta 285 (1999) 190;
(g) V.K. Jain, S. Kannan, E.R.T. Tiekink, J. Chem. Res. Miniprint (1994) 0501.

[13] Surprising inability of 31P NMR to distinguish structurally different Ir complexes was also reported: C.-F. Fu, Y.-H. Chang, Y.-H. Liu, S.-M. Peng, C.J. Elsevier, J.-T. Chen, S.-T. Liu Dalton Trans. (2009) 6991.

[14] Electrospray ionization mass spectrometry (ESI-MS) can be also of help for identification of metal complexes in solution; for the known advantages and limitations see the reviews: (a) Electrospray ionization mass spectrometry (ESI-MS) can be also of help for identification of metal complexes in solution; for the known advantages and limitations see the reviews: M.N. Eberlin Eur. J. Mass Spectrom. 13 (2007) 19;
(b) L.S. Santos, Eur. J. Org. Chem. (2008) 235;
(c) V.B. Di Marco, G.G. Bombi, Mass Spectrom. Rev. 25 (2006) 347;
(d) P. Kebarle, U.H. Verkerk, Mass Spectrom. Rev. 28 (2009) 898;
(e) P.A. Belyakov, V.I. Kadentsev, A.O. Chizhov, N.G. Kolotyrkina, A.S. Shashkov, V.P. Ananikov, Mendeleev Commun. 20 (2010) 125.

[15] (a) C.S. Johnson Jr., Prog. Nucl. Magn. Reson. Spectrosc. 34 (1999) 203;
(b) H. Weingartner, M. Holz, Annu. Rep. Prog. Chem. Sect. C 98 (2002) 121;
(c) P.S. Pregosin, P.G.A. Kumar, I. Fernández, Chem. Rev. 105 (2005) 2977;
(d) P.S. Pregosin, Prog. Nucl. Magn. Reson. Spectrosc. 49 (2006) 261;
(e) A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, Chem. Soc. Rev. 37 (2008) 479;
(f) Y. Cohen, L. Avram, L. Frish, Angew. Chem. Int. Ed. 44 (2005) 520.

[16] S.V. Kharlamov, Sh.K. Latypov, Russ. Chem. Rev. 79 (2010) 635.

[17] V.P. Ananikov, M.A. Kabeshov, I.P. Beletskaya, V.N. Khrustalev, M.Yu. Antipin, Organometallics 24 (2005) 1275.

[18] For the O=P(Oi-Pr)$_3$ (MW = 208 Da) the ^{31}P NMR chemical shift of 139.8 ppm and self-diffusion coefficient of $10.3 \pm 0.5 \times 10^{-10}$ m^2 s^{-1} were observed (corresponding signal is omitted on the 2D spectrum).

[19] Uncoordinated ligand or ligand oxide may serve as an internal reference in DOSY experiment, if a sharp peak on diffusion axis was obtained.

[20] For the experimental conditions of catalytic reactions see Refs. [9a,10e,f].

[21] R.F. Heck, Palladium Reagents in Organic Syntheses. Academic Press, London-N.Y.-Toronto, 1985.