Pd-2(dba)(3) as a Precursor of Soluble Metal Complexes and Nanoparticles: Determination of Palladium Active Species for Catalysis and Synthesis

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$Pd_2(dba)_3$ as a Precursor of Soluble Metal Complexes and Nanoparticles: Determination of Palladium Active Species for Catalysis and Synthesis

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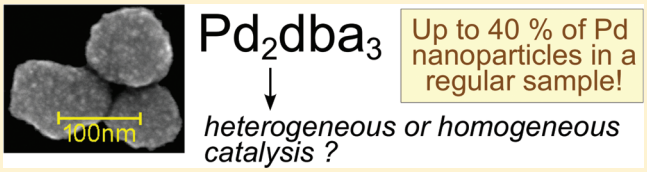
Supporting Information

ABSTRACT: Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) is ubiquitously used as a source of soluble Pd species for catalysis and as a precursor in the synthesis of more complex Pd structures. In spite of the massive usage of this convenient Pd complex, its nature in solution has not been revealed in detail and the applications rely on the assumed state and purity of the compound. In the present study we have developed a convenient NMR procedure to reveal the nature of $Pd_2(dba)_3$ and to determine the purity of the complex. Surprisingly, it was found that commercially available samples of $Pd_2(dba)_3$ may readily contain up to 40% of Pd nanoparticles in a wide range of sizes (10−200 nm). The study has shown that the routinely accepted practice of utilization of $Pd_2(dba)_3$ without analysis of the purity (both commercially available and prepared by common procedures) can introduce significant errors in the estimation of catalyst efficiency and lead to incorrect values of TON, TOF, and reported mol % values in the catalytic procedures. The presence of Pd nanoparticles in the catalyst precursor provides an opportunity for heterogeneous catalytic systems of different nature to be directly accessible from $Pd_2(dba)_3$. In the present study we report a modified procedure for the synthesis of $Pd_2(dba)_3{\cdot}CHCl_3$ with 99% purity.



1. INTRODUCTION

Tris(dibenzylideneacetone)dipalladium(0) is a canonical precursor widely used to generate catalytically active palladium species for diverse applications. Typically, $Pd_2(dba)_3$ is considered as a source of soluble Pd(0) complexes formed upon interaction with suitable ligands and substitution of dba. For example, these include various coupling reactions such as Suzuki,[1] Negishi,[2] Stille,[3] Hiyama,[4] and Kumada−Corriu[5] cross-coupling reactions, Heck reactions,[6] Buchwald−Hartwig aminations,[7] and carbon−heteroatom bond formation.[8] Carbonylative Suzuki cross-coupling reactions in the presence of carbon monoxide were mediated by $Pd_2(dba)_3$ as a ligand-free catalyst as well as carbonylation of metal carbenes.[9] $Pd_2(dba)_3$ has been used as a convenient source of Pd(0) for numerous catalytic cyclizations, leading to the formation of substituted heterocycles,[10] as well as for different alkyne[11] and allene[12] transformations. Some of the catalytic approaches demonstrated outstanding potential in multistep syntheses of biologically important compounds.[13] Another important area is the usage of $Pd_2(dba)_3$ as a starting material for generation of more complex Pd-containing structures, cluster compounds,[14] potential catalysts,[15] and synthesis and study of plausible intermediates of the catalytic cycles.[16,17]

The mechanistic nature of generation of catalytically active species from $Pd_2(dba)_3$ was extensively studied.[18−22] For example, for phosphine ligands it was found that addition of excess phosphine to $Pd_2(dba)_3$ readily yields the complex $Pd(dba)(PR_3)_2$.[18,23] This complex can either lose the remaining dba ligand (slow), furnishing a catalytically active low-ligated $Pd(PR_3)_2$ complex, or participate in oxidative addition, leading directly to catalytic intermediates (fast) (Scheme 1).[18] Structural studies of free dibenzylideneacetone[24] as well as complexes of palladium with dba analogues[19] proved the possibility to tune the reactivity of the complex by varying the electronic structure of dba ligands.[22,25]

The ubiquitous utilization of $Pd_2(dba)_3$ in transition-metal catalysis on one hand has been governed by its simple preparation from readily available Pd(II) salts and on the other hand by its relative stability in air and convenient generation of desired PdL_n species. The synthesis of $Pd(dba)_2$ was first performed by addition of sodium acetate to a warm methanol solution of Na_2PdCl_4 and dba;[26] the same procedure was reported using $PdCl_2$ as a source of palladium.[27,28] Later it was suggested on the basis of IR spectral data that the original complex $Pd(dba)_2$ likely has a structure of a dibenzylideneacetone solvate with the formula $Pd_2(dba)_3{\cdot}dba$.[29,30] It was found that recrystallization of $Pd(dba)_2$ from organic solvents leads to formation of the $Pd_2(dba)_3{\cdot}solv$ solvates (solv = benzene, chloroform, dichloromethane),[27,29] which appeared to be more stable in air. For practical purposes chloroform was found to be the solvent of choice, because it gave the highest yield of the complex after recrystallization.[29]

In the solid state $Pd(dba)_2$ was characterized by means of elemental analysis and IR spectroscopy.[26] IR data suggested that dba molecules are connected to palladium units by C═C

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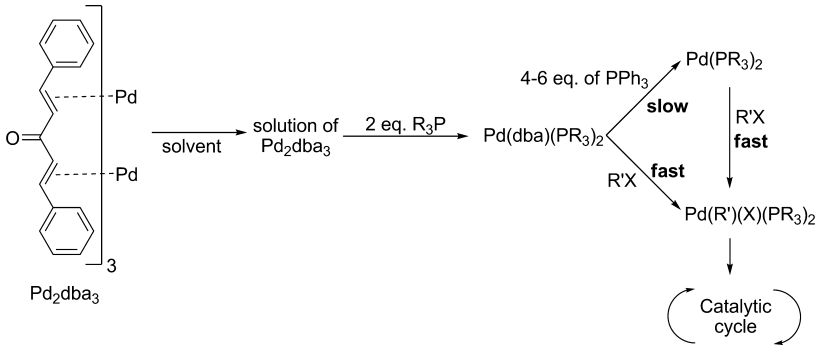
Scheme 1. Possible Pathways of Conversion of $Pd_2(dba)_3$ to Catalytically Active Species in the Presence of Phosphine Ligands



bonds, leaving carbonyl groups uncoordinated.[26] X-ray analysis of the solvate $Pd_2(dba)_3{\cdot}CH_2Cl_2$ carried out afterward confirmed these suggestions and noted a very short Pd–Pd contact of 3.240 Å.[31,32] A very flexible conformational behavior was noted for the coordinated dba molecules. Multiple X-ray studies indicated low symmetry in the solid-state structure of $Pd_2(dba)_3$ due to diverse conformations of dba ligands in the complex.[29,31,33] Particularly, the final structure of the complex was different depending on the solvent chosen for recrystallization: all s-cis,s-trans for $Pd_2(dba)_3{\cdot}CHCl_3$[29] and $Pd_2(dba)_3{\cdot}CH_2Cl_2$[33] and two s-cis,s-trans plus one s-cis, -cis for $Pd_2(dba)_3{\cdot}C_6H_6$.[31,33]

In contrast with solid-state studies, little is known about the structure of the complex in solution. It was reported that the ^{1}H NMR spectrum of $Pd_2(dba)_3$ in solution is heavily crowded in the olefinic region, which impeded its analysis. X-ray structure analysis[31−33] suggests that all olefinic and aromatic protons became nonequivalent after coordination, thus resulting in the appearance of several resonances in the NMR spectrum. The low solubility of the complex and poor signal-to-noise ratio further complicated the NMR studies.[29] Pioneering work in this area was carried out by Kawazura and co-workers to get insight into the ^{1}H NMR spectrum using deuterium labeling,[34] and the conformational behavior of metal-coordinated dba ligands still is a subject of debate.[35]

An attempt to identify catalytically active species in our research has surprisingly revealed a much more complicated nature of $Pd_2(dba)_3$. In addition to soluble palladium species, this catalyst precursor contained significant amounts of palladium nanoparticles (NPs) and the Pd(0):Pd NP ratio was subject to large variations. In the present study we have characterized both types of metal precursors represented in $Pd_2(dba)_3$ for homogeneous and heterogeneous catalysis applications. A fast and efficient procedure has been developed to determine the purity of the complex by ^{1}H NMR. The structure of the complex in solution was established using molecular diffusion measurements with a DOSY NMR approach and signal assignment with 2D COSY and NOESY experiments. Pd NPs spontaneously formed from $Pd_2(dba)_3$ were isolated and characterized by electron microscopy.

2. RESULTS AND DISCUSSION

2.1. Assignment of ^{1}H NMR Spectrum of $Pd_2(dba)_3$ using DOSY NMR Analysis. It is well-known that the ^{1}H NMR spectrum of $Pd_2(dba)_3$ in solution is rather complex and contains more than 50 resonances (see top projection in Figure 1). It exhibits several signals in the olefinic region (4.5–6.8 ppm) and complex crowded multiplets in the aromatic region (6.8–7.5 ppm). Signal assignment in the spectrum of such a sample

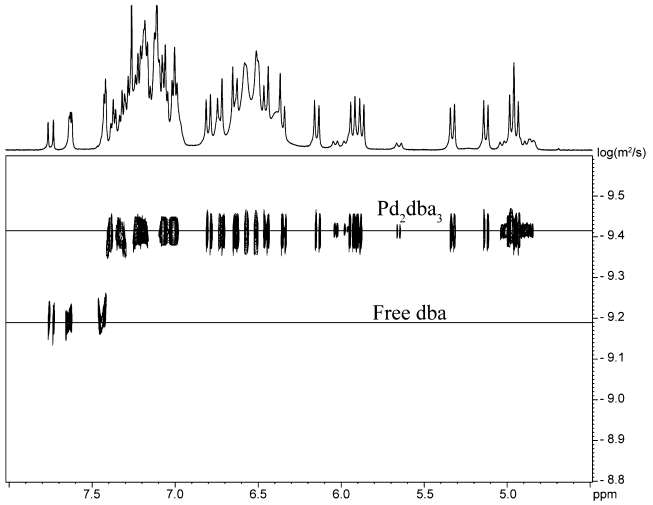


Figure 1. ^{1}H DOSY spectrum of $Pd_2(dba)_3$ in $CDCl_3$ solution at 260 K, 600 MHz.

using conventional techniques would be a difficult and time-consuming task. However, we have found that analysis of the spectrum can be significantly simplified using the DOSY technique.

DOSY is a well-proven NMR approach, with successful applications shown for various chemical systems, including transition-metal complexes.[36,37] The idea of DOSY NMR is to analyze the mixture in liquids according to translational diffusion coefficients. Diffusion coefficients are related to the speed of molecular motions in solution and depend on the size of dissolved compounds. The diffusion coefficient for a molecule represented with a rigid sphere is inversely proportional to the sixth power of hydrodynamic radius of the sphere according to the Stokes–Einstein equation.[36] For transition-metal complexes it was shown that DOSY NMR can distinguish mononuclear and dinuclear Pd species in solution as well as free ligands.[17]

DOSY NMR of $Pd_2(dba)_3$ in $CDCl_3$ allowed discrimination of the ^{1}H spectrum of the mixture into principal components (Figure 1). The DOSY way to represent diffusion data is very useful and demonstrative, because the signals belonging to the compounds of similar size appear aligned with the same diffusion coefficient value. In particular, the signals corresponding to free dba were aligned on a horizontal line at log D = −9.19 ± 0.05.[38] Two other sets of resonances, distinguished by different intensities, were recorded aligned on the same horizontal line of the DOSY spectrum at log D = −9.42 ± 0.13.[39] These signals correspond to the compounds of the same size and according to the diffusion coefficient can be assigned to major and minor isomers of $Pd_2(dba)_3$ in solution.

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Thus, the overall composition of the mixture shown in Figure 1 was determined as the molar ratio free dba:$Pd_2(dba)_3$ (major isomer):$Pd_2(dba)_3$ (minor isomer) = 1.0:1.4:0.3.

2.2. Determination of the Solution Structure of $Pd_2(dba)_3$. Although DOSY NMR has provided an easy and quick assignment of the mixture, we have carried out additional 2D NMR analysis to determine the spectral patterns of $Pd_2(dba)_3$. Two sequential steps were carried out in the analysis: (i) assignment of 12 major resonances in the olefinic area of the spectrum to 3 individual dba molecules of $Pd_2(dba)_3$ and (ii) determination of relative conformations of the dba skeleton in the dinuclear complex.

The analysis on the first step was performed using a 2D COSY experiment in order to identify HC═CH olefinic fragments in the spectrum (Figure 2). The 2D spectrum allowed us

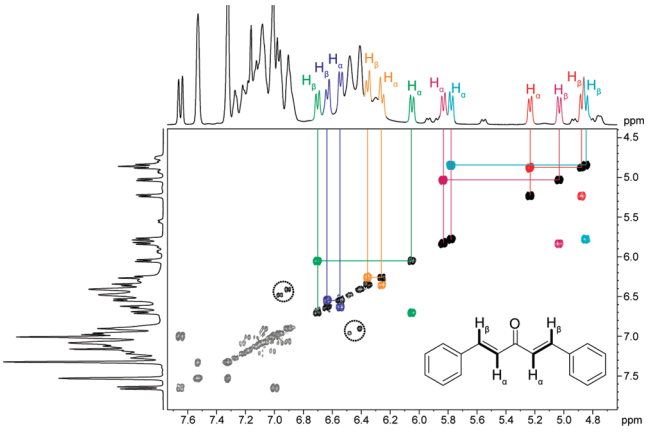


Figure 2. Olefinic part of the 2D COSY spectrum of $Pd_2(dba)_3$ in $CDCl_3$ at 600 MHz. Six pairs of the $H_\alpha C{=}CH_\beta$ systems are shown in different colors, and the cross-peaks corresponding to ^4J values between H_β and ortho protons of aromatic rings are highlighted by circles.

to split 12 separate peaks into 6 groups, each representing a HC═CH fragment of the coordinated dba molecule. The typical values $^3J(H_\alpha{-}H_\beta)$ = 12.8 Hz suggested a preferred *E* geometry of the double bonds. The interconnections between these groups were determined by performing an LR-COSY experiment optimized for observation of long-range (LR) proton−proton coupling constants (Figure 3). Three cross-peaks shown in different colors have arisen due to the $^4J(H_\alpha{}^1{-}H_\alpha{}^2)$ coupling constant, which binds together two parts of the dba molecule across the carbonyl group. These data were further confirmed with $^1H{-}^{13}C$ HMBC NMR spectroscopy. We were able to identify two $H_\alpha{-}C{=}O$ couplings and one $H_\beta{-}C{=}O$ coupling for each of the molecules, which represents another way to bind two HC═CH systems together across the carbonyl group. The interconnections obtained were in total agreement with those from the LR-COSY experiment.

Thus, we have assigned each of the 12 peaks to corresponding olefinic protons in $Pd_2(dba)_3$ molecule. Long-range correlation allowed us to identify each of three molecules individually. In the second step we have determined the relative conformation of dba molecules in the complex. In principle, three different conformations are possible for the dba ligand (Scheme 2). Indeed, for a solution of pure dba it was shown that the molecule in the liquid phase changes between all of the three conformations.[24]

The structural arrangement of the conformers reveals that each form should exhibit a unique H−H through-space interaction (Scheme 2). Consequently, we have employed a 2D

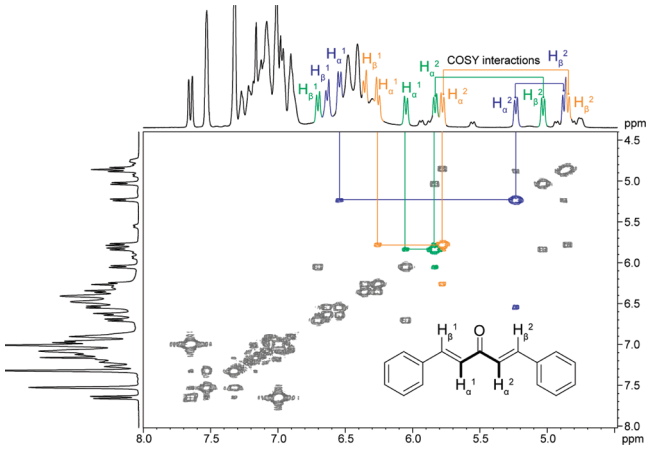
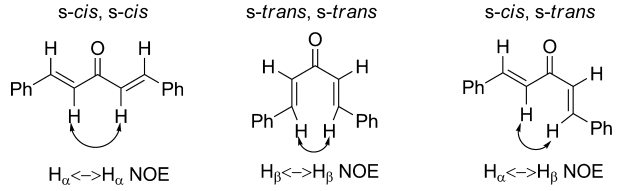


Figure 3. Olefinic part of the LR-COSY correlation of $Pd_2(dba)_3$ in $CDCl_3$ at 600 MHz. The key long-range cross-peaks are marked by colors for three different dba molecules in the complex. Relevant COSY interactions (Figure 2) helpful in binding two HCCH systems together are shown in the top projection.

Scheme 2. Possible Conformations of the dba Molecule and the Key NOE Contacts



nuclear Overhauser effect spectroscopy to map the conformations of the dba units in $Pd_2(dba)_3$ (Figure 4). The recorded

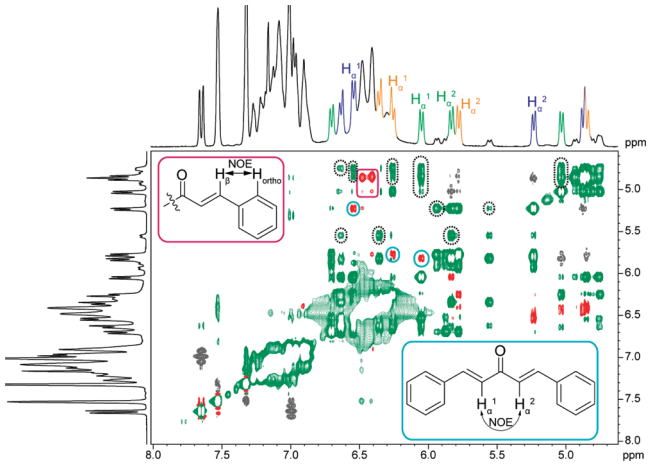


Figure 4. 2D NOESY spectrum of $Pd_2(dba)_3$ in $CDCl_3$ at 600 MHz (0.3 s mixing time). NOE peaks are shown as positive out of phase with diagonal peaks (red), whereas exchange peaks are shown as negative in phase with diagonal peaks (green).

2D NOESY spectrum clearly showed three well-resolved NOE cross-peaks corresponding to H−H interactions in the molecules of dba. On the basis of the proton spectrum assignment, all three peaks (marked with solid blue circles on the spectrum) were found to represent $H_\alpha{}^1{\leftrightarrow}H_\alpha{}^2$ NOE contacts, which indicated that each of the ligands of the complex exists in solution in an s-cis,s-cis conformation.[40] The remaining NOE

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peaks (marked with magenta squares on the spectrum) represent NOE contacts between olefinic H_β and ortho protons of aromatic rings. The rest of the peaks demonstrated chemical exchange between different dba moieties. It is important to emphasize that some of the exchange cross-peaks (rounded with dotted lines on the spectrum) appear between the major olefinic resonances and low-intensity signals, which serves as direct evidence of the fact that the latter indeed correspond to the minor form of the $Pd_2(dba)_3$ complex (major and minor forms of $Pd_2(dba)_3$ as detected above in the DOSY study).

The detailed NMR study carried out with conventional 2D NMR methods totally confirmed the conclusions made by analysis of the diffusion data (section 2.1). The spectral patterns of $Pd_2(dba)_3$ were identified, and both major and minor isomers were located. The rather fluxional nature of the dba ligand in $Pd_2(dba)_3$ should be clearly pointed out, and the structure may depend on the preparation conditions of the palladium complex[41] and experimental conditions for recording NMR spectra. To our knowledge, in agreement with the present NMR findings, the s-cis,s-cis conformation should be thermodynamically more preferred due to minimized steric repulsions in the ligands.

2.3. Characterization of Soluble and Insoluble Components of $Pd_2(dba)_3$. Decomposition of $Pd_2(dba)_3$ in the solid state and in solution leads to release of dba and formation of palladium black: $Pd_2(dba)_3 \rightarrow dba + [Pd]$. Although the initial NMR spectrum of the mixture seemed rather complicated, after carrying out the assignment we can propose a simple and easy-to-use method to determine the purity of $Pd_2(dba)_3$ (Figure 5).

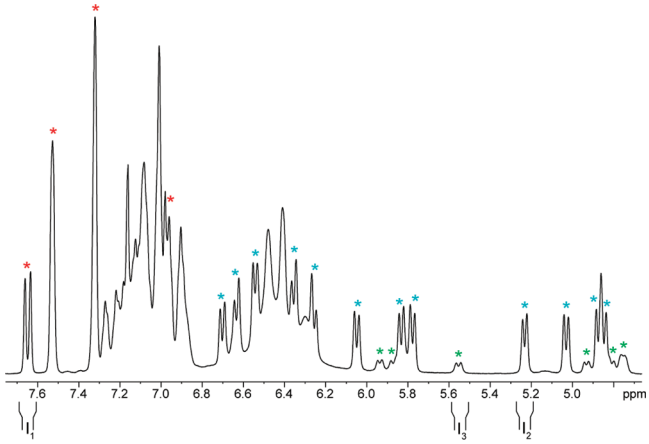

Figure 5. ^1H NMR spectrum of $Pd_2(dba)_3 \cdot CHCl_3$ in $CDCl_3$ at 600 MHz: olefinic signals of major (blue) and minor (green) isomers of $Pd_2(dba)_3$, signals of free dba (red), and the integral regions I_1-I_3 used for analysis of purity.

A small amount of $Pd_2(dba)_3$, typically 3−5 mg,[42] was dissolved in 0.6 mL of $CDCl_3$ followed by recording the ^1H NMR spectrum. The molar ratio can be determined according to the simple equation (1) and the purity of the soluble part of the complex according to the equation (2), where I_1, I_2, and I_3 are the integral intensities of the signals of free dba (2H), the major form of $Pd_2(dba)_3$ (1H), and the minor form of $Pd_2(dba)_3$ (1H), as shown in Figure 5.[43]

$$\text{molar ratio } Pd_2(dba)_3/dba = (I_2 + I_3)/(I_1/2) \quad (1)$$

$$\text{purity of the soluble part of } Pd_2(dba)_3 = ((I_2 + I_3)/(I_2 + I_3 + I_1/2)) \times 100\% \quad (2)$$

An important question is whether the major and minor forms of $Pd_2(dba)_3$ can be involved in generation of active Pd species in solution. To address this question, we have carried out NMR monitoring of the substitution reaction by adding PPh_3 to the solution of $Pd_2(dba)_3$. The spectral study has indicated that the intensities of both major and minor forms of $Pd_2(dba)_3$ were proportionally decreased upon addition of the phosphine ligand. Phosphine complexes of palladium were formed in the solution as a result of the substitution reaction and were identified in ^{31}P NMR spectra as described earlier.[18] Both forms completely disappeared in the presence of an excess of the phosphine ligand and can be considered as a reliable precursors for generation of Pd species in solution.

With the developed procedure in hand, it was of much interest to characterize the purity of $Pd_2(dba)_3$ used in everyday laboratory practice. The measurements carried out for $Pd_2(dba)_3$ received from commercial sources showed large variations in the ratio of the complex and free ligand ranging from 1:0.09 to 1:0.56 (entries 1−3, Table 1). Thus, the purity of the complex may change from 92% (acceptable quality for most cases) to 64% (unacceptable quality).

Table 1. Analysis of Purity of $Pd_2(dba)_3$ Obtained from Different Sources and Stability of the Complex in Solution and in the Solid State[a]

entry	description	$Pd_2(dba)_3$:dba[b]	purity of $Pd_2(dba)_3$, %[b]
1	commercial source 1, as received	1:0.30	77
2	commercial source 2, as received	1:0.09	92
3	commercial source 3, as received	1:0.56	64
4	freshly synthesized[c]	1:0.01	99
5	freshly synthesized, stored for 1 week in the solid state at room temp	1:0.05	95
6	freshly synthesized, stored for 1 month in the solid state at room temp	1:0.05	95
7	freshly synthesized, stored for 6 months in the solid state at room temp	1:0.41	71
8	freshly synthesized, stored for 1 h in solution in air at room temp	1:0.14	88
9	freshly synthesized, stored for 1 day in solution in air at room temp	1:0.39	72
10	freshly synthesized, heated for 1 h at 50 °C in $CDCl_3$ in air	1:0.30	77
11	freshly synthesized, heated for 1 h at 50 °C in $CDCl_3$ under Ar	1:0.28	78

[a]See the Experimental Section for a detailed description of the purity determination. [b]See eqs 1 and 2 for the definitions. [c]Prepared using a modified procedure; see section 4.2 for the synthesis and Figure S1 in the Supporting Information for ^1H NMR.

In the present paper we report a modified synthetic procedure for the preparation of $Pd_2(dba)_3$ with 99% purity of the complex (entry 4, Table 1). The purity of the complex determined by the NMR procedure developed in the present study was independently confirmed by a powder X-ray diffraction study. The content of palladium in the complex was confirmed by microanalysis in the solid state and by ICP-MS after dissolution.

The complex was stable in the solid state for period of about 1 month; however after 6 months of storage at room temperature a noticeable decomposition occurred to 71% purity (entries 5−7; Table 1). A quicker decomposition was observed in solution, with a 1:0.14 ratio after 1 h and a decrease in the content of the complex to 1:0.39 after 1 day at room temperature

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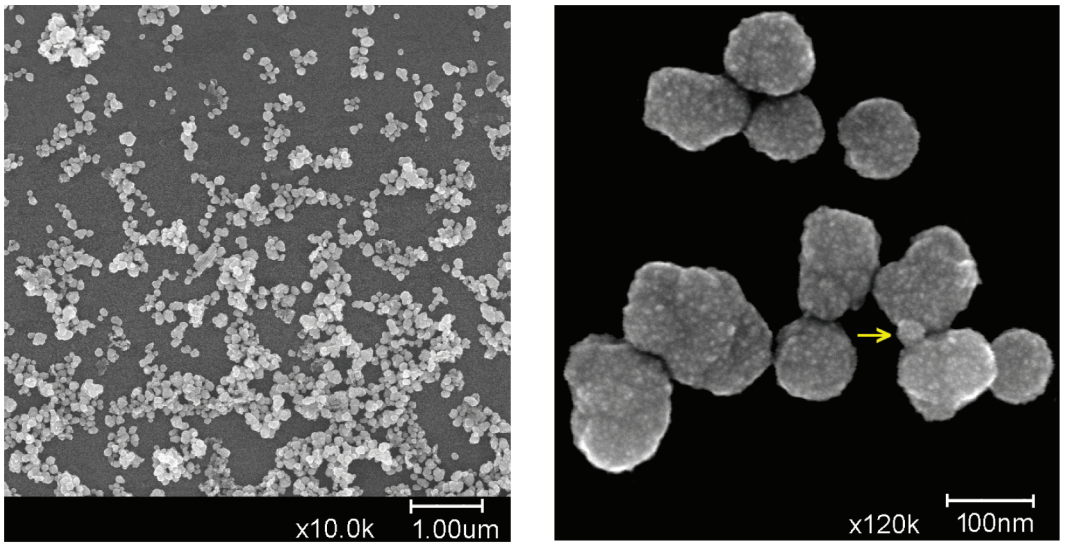

Figure 6. FE-SEM study of the palladium particles formed in the decomposition of $Pd_2(dba)_3$: (a) low magnification image (×10 000; 1 μm scale bar is shown); (b) high magnification image (×120 000; 100 nm scale bar is shown) with a small particle highlighted by an arrow.

(entries 8 and 9; Table 1). The complex readily decomposed in solution under heating and reached 1:0.30 and 1:0.28 ratios in air and under Ar, respectively (entries 10 and 11; Table 1). The decrease of amount of $Pd_2(dba)_3$ determined by NMR was also confirmed by microanalysis of the content of the solution phase and by ICP-MS.

Decomposition of the complex may take place either due to intrinsic instability or may be initiated by reaction with acid traces and other impurities in the solvent. Of course, it should be pointed out that determined $Pd_2(dba)_3$:dba ratios may be effected by dissociation of the dba ligand from the complex in solution. However, the present data on the 99% purity of the complex (entry 4, Table 1) indicates only a minor contribution (if any) of this process under the studied conditions.

Pd black formed in the decomposition of $Pd_2(dba)_3$ was isolated as an insoluble dark powder. Analysis by ICP-MS confirmed formation of a pure palladium material. The isolated material was studied by field emission scanning electron microscopy (FE-SEM).[44,45] It was found that the isolated material formed in the decomposition of $Pd_2(dba)_3$ consists of metal particles in the broad range of sizes 60−200 nm and contained a minor amount of small nanoparticles of size ca. 10−20 nm (Figure 6). Most of the particles were round or rectangular with round corners. Some of the particles were agglomerated into microstructures, where the boundaries between the individual subunits were kept visible.

3. CONCLUSION

By far, in most reports resulting from the widespread application of $Pd_2(dba)_3$ in modern chemistry, including various catalytic reactions, this palladium complex was obtained from commercial sources and used as received. The present study has clearly shown that this is an unacceptable practice. The content of catalytically active species may significantly vary, thus leading to estimation of incorrect values of mol %, TON, and TOF actually employed in the reaction.

Moreover, the nature of the catalyst precursor strongly depends on the purity of $Pd_2(dba)_3$. The complex may serve not only as a source of soluble Pd(0) species but also as a source of Pd nanoparticles in a wide range of sizes (~10−200 nm). Therefore, a catalytic reaction, assumed to be a homogeneous one, in fact may be catalyzed by Pd nanoparticles under heterogeneous conditions.

Utilization of $Pd_2(dba)_3$ of unknown purity may result in irreproducible procedures; for example, the reaction mediated by a partially decomposed complex (Pd NPs as active species) will not be catalyzed using a pure complex as precursor (soluble Pd species only). The question is of special importance in view of current studies of cross-coupling, Heck, and other catalytic reactions, where the determination of the nature of the catalyst (homogeneous catalysis vs heterogeneous catalysis vs leaching) is a challenging problem.[46] We anticipate more attention to be paid to the quality and nature of metal complexes used as catalyst precursors.

From a certain point of view formation of Pd NPs from $Pd_2(dba)_3$ can be even considered as an extension of the functionality, especially to initiate a heterogeneous catalytic system or to involve both soluble Pd species and Pd NPs in a series of one-pot transformations. For instance, a preliminary heating of $Pd_2(dba)_3$ in solution or in the solid state may be involved to initiate Pd NP formation.

In the present study we report a simple procedure to determine the purity of $Pd_2(dba)_3$ by ^1H NMR. The procedure developed can be used for a quick evaluation of the quality and nature of the catalyst precursor just before use in the catalytic reaction. A modified synthetic procedure is reported for the synthesis of $Pd_2(dba)_3$ with 99% purity.

4. EXPERIMENTAL SECTION

4.1. General Procedures. For better reproducibility the experiments can be carried out under an argon atmosphere with dry and degassed solvents. Deuterated solvents were stored over molecular sieves (4 Å, 8−12 mesh). NMR spectra were acquired on a Bruker Avance II 600 spectrometer equipped with a 5 mm BBI probe. Chemical shifts are reported in parts per million relative to TMS (^1H) as internal standard. Details of DOSY NMR and 2D experiments (COSY, COSY-LR, NOESY, HSQC, HMBC) are described below. For the 2D spectra (except DOSY) the temperature was set at 303 K with a Bruker BVT3000 variable-temperature unit; the air flow was set to 670 L/min. Fresh $CDCl_3$ was

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utilized as a solvent for NMR analysis of the purity of $Pd_2(dba)_3$ to avoid decomposition of the complex.[47]

FE-SEM studies were carried out on a Hitachi SU-8000 field emission scanning electron microscope. The measurements were carried out with accelerating voltage 2−10 kV and a working distance of 2.5−9 mm.

X-ray diffraction patterns were measured with a Bruker D8 Advance difractometer in reflection mode ($\theta/2\theta$ geometry, λ[Cu Kα] = 1.5418 Å, step size 0.02°, 2θ range 4−60°) equipped with a focusing Goebel mirror. To carry out the analysis, known data on $Pd_2(dba)_3$ structures were utilized according to published structures and the Cambridge Structure Database.[29,48] The composition of the pure sample was confirmed using quantitative Rietveld refinement and the DIFFRAC-TOPAS program (Topas 4.2, Bruker-AXS, 2009). Also the XRD pattern in transmission mode was measured using a Bruker D8 Advance diffractometer with Cu Kα_1 radiation (λ[Cu Kα_1] = 1.5406 Å, θ/θ geometry). As in the case of XRD patterns in reflection mode, the reflections from the crystal lattice of metallic Pd were not visible.

4.2. Improved Procedure for the Synthesis of $Pd_2(dba)_3$·$CHCl_3$. Below we describe a modified procedure to prepare pure $Pd_2(dba)_3$·$CHCl_3$ from $Pd(OAc)_2$ or $PdCl_2$ (the same yields and purity were obtained with both metal precursors). The standard procedure for the preparation of $Pd_2(dba)_3$·$CHCl_3$ from $PdCl_2$ was reported in the literature.[27,28]

$Pd(OAc)_2$ (100.0 mg, 4.45×10^{-4} mol) was placed into a 25 mL round-bottom flask with a magnetic stirrer. A 365.4 mg (4.45×10^{-3} mol) amount of sodium acetate was added followed by 208.5 mg (8.9×10^{-4} mol) of dibenzylideneacetone and 10 mL of methanol. The reaction mixture was stirred at 40 °C for 3 h. After completion of the reaction a brown solid was formed. The solid was filtered off and washed with 2 × 3 mL of MeOH followed by 3 × 3 mL of water. The residue was completely washed off the filter with $CHCl_3$ (~25 mL),[49] and the solution was evaporated on a rotary evaporator.[50] The solid that formed was redissolved in a minimum amount of chloroform (ca. 5 mL),[49] and 20 mL of acetone was added to the solution. The mixture that was obtained was left overnight in a refrigerator at −18 °C. The crystals of $Pd_2(dba)_3$·$CHCl_3$ were filtered off, washed with 2 × 5 mL of cold acetone (5 °C), and dried under vacuum at 40 °C.[50] The yield of $Pd_2(dba)_3$·$CHCl_3$ was 218.5 mg (95%). A detailed description of the experimental setup and synthetic procedure is given in the Supporting Information.

4.3. Determination of Purity of Synthesized $Pd_2(dba)_3$·$CHCl_3$. $Pd_2(dba)_3$ (3−5 mg) prepared as described above was placed into an NMR tube followed by addition of 0.6 mL of $CDCl_3$ and shaking at room temperature until dissolution. Immediately after sample preparation, the ^{1}H NMR spectrum was recorded (room temperature, 32 scans, 7 s relaxation delay) and processed using standard parameters. Integration of the ^{1}H NMR spectrum of the synthesized complex indicated only a trace amount of free dba and gave 98.6% purity of the complex.

The integral values were I_1 = 0.037, I_2 = 1.000, I_3 = 0.268 (see section 2.3 for a description of integral notations I_1−I_3 and equations), and the obtained ^{1}H NMR spectrum is shown in the Supporting Information (Figure S1).

4.4. Monitoring of the Purity of $Pd_2(dba)_3$·$CHCl_3$. We suggest carrying out the NMR analysis immediately after the synthesis (or receipt) of $Pd_2(dba)_3$·$CHCl_3$ (the procedure is described above in section 4.3 and in the text). The absence of the signals of dba (or trace level) indicates a pure complex. Further NMR monitoring will show an increase in the amount of dba if decomposition of the complex takes place. From the molar ratio of $Pd_2(dba)_3$ and free dba the amount of Pd NPs formed during the decomposition of the complex can be estimated.

If some amount of free dba was detected just after the synthesis (or receipt), it may originate either from partial decomposition of the complex or as a residual amount due to incomplete washing during the preparation of $Pd_2(dba)_3$. In such a case, the analysis of purity should be done in two steps: the ratio between $Pd_2(dba)_3$ and free dba can be determined using the NMR procedure described above (see section 2.3), whereas the overall ratio between the metal and dba can be estimated by elemental analysis. Thus, a complete picture of the $Pd_2(dba)_3$:dba:Pd ratio can be obtained as a starting point, and further NMR monitoring will reflect the changes in the system.

4.5. Repurification of $Pd_2(dba)_3$·$CHCl_3$. In case of partial decomposition or in case an impure complex is received, it can be purified again by a simple procedure (see also section 4.2). The complex was dissolved in an excess of chloroform[49] and insoluble material (Pd black) was removed by filtration or centrifugation. The obtained solution was evaporated on a rotary evaporator.[50] The solid that remained was redissolved in a minimum amount of chloroform,[49] and a 4-fold excess of acetone was added to the solution. The mixture obtained was left overnight in a refrigerator at −18 °C. The crystals of $Pd_2(dba)_3$·$CHCl_3$ were filtered off, washed with cold acetone (5 °C), and dried under vacuum at 40 °C.[50] A more detailed description of the experimental setup is given in the Supporting Information.

4.6. DOSY NMR Analysis of $Pd_2(dba)_3$ in Solution. $Pd_2(dba)_3$ (0.02 g, 0.019×10^{-3} mol) was dissolved in 0.6 mL of $CDCl_3$ in the NMR tube. The 2D DOSY spectrum was acquired using a BBI-Z gradient probe. The sample was not spinning. VTU air was precooled before entering the probe via Bruker BCU05 cooling unit. The temperature was regulated at 260 K. An experiment was performed using a *stebpgp1s* pulse program (stimulated echo with bipolar pulse pairs for eddy current cancellation and one spoil gradient). The durations of gradient pulse (δ) and diffusion time (Δ) were 1.25 and 200 ms, respectively. A sine gradient shape was used. Data acquisition was established in 128 steps with linear gradient evolution from 2.28 to 43.23 G/cm (5−95% of maximum gradient coil current) with 32 scans for each step. 2D DOSY spectra were generated using Bruker Topspin 2.1 software.

4.7. 2D NMR study of $Pd_2(dba)_3$ in Solution. 2D gs-COSY experiments were recorded utilizing the standard *cosygpsw* pulse program. Spectral width in the F2 dimension was set to 5144 Hz with 2048 points acquired in the F2 domain. Acquisition was established in 128 F1 increments, collecting 8 scans for each data point with 8 dummy scans before the start of acquisition. The relaxation delay was set to 2 s. The raw data obtained were zero-filled to a 1024 × 1024 square matrix, and sine multiplications with line broadening factors of 0.3 and 1.00 were applied in F2 and F1 domains, respectively, prior to Fourier transformation.

2D COSY-LR experiments were recorded utilizing the standard *cosylrqf* pulse program. Spectral width in the F2 dimension was set to 5100 Hz with 2048 points acquired in the F2 domain. Acquisition was established in 128 F1 increments, collecting 64 scans for each data point with 4 dummy scans before the start of acquisition. The relaxation delay was set to 2 s. The delay for the evolution of the long-range couplings was 150 ms. The raw data obtained were zero filled to 1024 × 1024 square matrix, and sine multiplications with line broadening factors of 0.3 and 1.00 were applied in F2 and F1 domains, respectively, prior to Fourier transformation.

2D gs-NOESY experiments were recorded utilizing the standard *noesygpph* pulse program. Spectral width in the F2 dimension was set to 5100 Hz with 2048 points acquired in the F2 domain. Acquisition was established in 256 F1 increments, collecting 2 scans for each data point with 16 dummy scans before the start of acquisition. The relaxation delay was set to 2 s. The mixing time was 0.3 s. The raw data obtained were zero filled to a 1024 × 1024 square matrix, and quadratic sine multiplications with line broadening factors of 0.5 and 1.20 were applied in F2 and F1 domains, respectively, prior to Fourier transformation.

2D gs-HSQC experiments were recorded utilizing the standard *hsqcetgp* pulse program. Spectral widths were 5100 and 45 300 Hz for F2 and F1 dimensions, respectively, with 1024 points acquired in the F2 domain. Acquisition was established in 512 F1 increments, collecting 32 scans for each data point with 32 dummy scans before the start of acquisition. The relaxation delay was set to 2 s. The refocusing delay was optimized for direct coupling: J(C−H) = 145 Hz. The raw data obtained were zero filled to a 1024 × 1024 square matrix, and quadratic sine multiplications with line broadening factors of 0.3 and 1.00 were applied in F2 and F1 domains, respectively, prior to Fourier transformation.

2D gs-HMBC experiments were recorded utilizing the standard *hmbcgpndqf* pulse program. Spectral widths were 5100 and 45 300 Hz for F2 and F1 dimensions, respectively, with 4096 points acquired in the F2 domain. Acquisition was established in 512 F1 increments, collecting 32 scans for each data point with 32 dummy scans before the start of acquisition. The relaxation delay was set to 2 s. The refocusing delay was optimized for long-range coupling: J(C−H)= 8 Hz. The raw data obtained were zero filled to a 1024 × 1024 square matrix, and sine multiplications with line broadening factors of 0.3 and 0.5 were applied in F2 and F1 domains, respectively, prior to Fourier transformation.

■ ASSOCIATED CONTENT

Supporting Information

Figures and text giving the ^{1}H NMR spectrum of freshly prepared pure $Pd_2(dba)_3$ and a detailed description of the experimental setup and synthetic procedure for the synthesis of $Pd_2(dba)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(38) The diffusion coefficient for free dba in $CDCl_3$ was independently confirmed using an authentic sample prepared separately.
(39) In the linear scale the diffusion coefficients of $(6.3 \pm 0.6) \times 10^{-10}$ and $(3.9 \pm 0.1) \times 10^{-10}$ m^2 s^{-1} were calculated for the free dba and $Pd_2(dba)_3$, respectively (Figure 1).
(40) Three sets of resonances were measured for the dba units coordinated to Pd, indicating the ligands are not completely equivalent. The result is in agreement with an X-ray structure determination in the solid state.
(41) See refs 29, 31, and 33 and discussion in the Introduction.
(42) We suggest not to exceed the amount of $Pd_2(dba)_3$ sample for a reliable determination. The solubility of $Pd_2(dba)_3$ is limited, while free dba is much more soluble. Thus, using an excess of the analyzed sample may lead to an incorrect $Pd_2(dba)_3$: dba ratio.
(43) The signals convenient for integration were selected (other signals may be also used in the analysis). Note that depending on conditions the minor isomer may or may not be detectable in the NMR spectrum. If more than two isomers of $Pd_2(dba)_3$ are present, the integral intensities of all of the corresponding signals should be taken into account.
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(46) (a) Phan, N. T. S.; van der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609. (b) Molnár, Á. *Chem. Rev.* **2011**, *111*, 2251. (c) Molnár, Á. *Curr. Org. Synth.* **2011**, *8*, 172. (d) Favier, I.; Madec, D.; Teuma, E.; Gómez, M. *Curr. Org. Chem.* **2011**, *15*, 3127. (e) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884. (f) Reetz, M. T.; de Vries, J. G. *Chem. Commun.* **2004**, 1559. (g) Durand, J.; Teuma, E.; Gómez, M. *Eur. J. Inorg. Chem.* **2008**, 3577. (h) Ananikov, V. P.; Beletskaya, I. P. *Organometallics* **2012**, DOI 10.1021/om201120n.
(47) According to our experience freshly received commercial 99.8% pure $CDCl_3$ gave reproducible and accurate measurements. For longer storage $CDCl_3$ should be kept over a silver foil (see Acros Catalog No. 351420250, for example). Acidic impurities in chloroform may cause decomposition of $Pd_2(dba)_3$ in solution and formation of Pd black.
(48) (a) Selvakumar, K.; Valentini, M.; Wörle, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207. (b) See also entries DBZACP01, BOFZIG, and PDDBAM in the Cambridge Structure Database.
(49) It is important to note that the acidity of chloroform can critically lower the yield and purity of $Pd_2(dba)_3$. Only freshly purified chloroform (washed with water, dried over $CaCl_2$, distilled over P_2O_5) should be used to avoid decomposition of $Pd_2(dba)_3$.
(50) The temperature should not be raised above 40 °C while evaporating the solvent and drying; otherwise $Pd_2(dba)_3$ decomposition to Pd black/PdNPs may occur.