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Structure of Complexes Formed by Dissolution of Palladium Diacetate in Methanol and Chloroform. In Situ NMR Study

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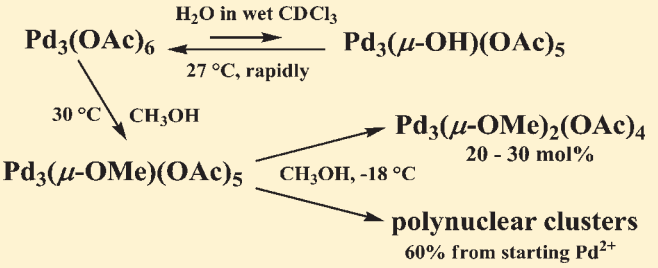
Supporting Information

ABSTRACT: The behavior of palladium diacetate cyclic trimer $[Pd(OAc)_2]_3$ (**1**) upon its dissolution in methanol and wet chloroform was studied by ^1H and ^{13}C NMR including 2D-HSQC and 2D-DOSY techniques. Upon dissolution, trimer **1** reacts with methanol and is completely transformed first into the methoxo complex $Pd_3(\mu\text{-OMe})(OAc)_5$ (**2**), which already at −18 °C undergoes a slow exchange of second bridging acetate ligand between the same palladium atoms to form the symmetric dimethoxo complex $Pd_3(\mu\text{-OMe})_2(OAc)_4$, the maximum relative concentration of which reaches 20−30 mol % of initial loading trimer **1**. Along with the dimethoxo complex, both soluble and insoluble polynuclear palladium clusters are gradually formed at −18 °C, and their total amount reaches up to 60% of the starting Pd^{2+} loading. The increase of temperature to 27 °C results in the reduction of palladium(II) to Pd metal by methanol, which is oxidized and transformed into formaldehyde hemiacetal and methyl formate. Upon dissolution in wet chloroform, trimer **1** is reversibly hydrolyzed to the hydroxo complex $Pd_3(\mu\text{-OH})(OAc)_5$ (**10**) in ratio **1**/**10** ≈ 3/1. The temperature decrease and addition of acetic acid shift the equilibrium in this system toward trimer **1**, and addition of water shifts it in the opposite direction. Addition of methanol to the equilibrium mixture of **1** and **10** results in the fast exchange of bridging acetate in trimer **1** by the μ-OMe group. Substitution of the μ-OH ligand by μ-OMe in **10** occurs in parallel but more slowly. Complex **2** formed in both cases is more stable in chloroform than in methanol.



INTRODUCTION

Palladium diacetate is widely used as a precursor and precatalyst in various catalytic systems for cross-coupling, carbapalladation, allylic substitution, palladium-assisted functionalization of olefins, acetylenes, aromatic compounds, and other powerful synthetic methods.[1] The structure of catalytically active particles formed upon interaction of palladium diacetate with donor ligands substantially depends on the solvent used and reaction conditions. Since many solvents are not inert toward palladium diacetate, finding answers on the question about the form in which it exists in various solvents is very important. A few works were devoted to this problem.[2−10]

There are two distinct crystalline forms of palladium diacetate: a cyclic trimer $[Pd(OAc)_2]_3$ (**1**) with bridging acetate groups,[2a,b] highly soluble in many organic solvents, and a linear polymer (catena-polyform) $[Pd(OAc)_2]_n$, almost insoluble in common solvents.[2c] The data of osmometry, cryoscopy, and spectrophotometry show that the cyclotrimeric structure of **1** is retained in benzene, dichloroethane, dioxane, acetone, ethyl acetate, carbon tetrachloride, chloroform, acetic acid, and acetic anhydride solutions.[3−5] It is assumed that the formation of trimer **1** from *trans*-$[Pd(NO_3)_2(H_2O)_2]$ in acetic acid proceeds through the consecutive and reversible formation of intermediate monomer, dimer, and open-chain trimer.[6]

The data published[7] indicate that the partial cleavage of **1** in glacial acetic acid takes place at the concentrations below 10^{-4} M to form monomeric particles $Pd(OAc)_2$. According to IR spectroscopic data,[8] palladium diacetate exists as an equilibrium mixture of trimer **1** and dimer in chloroform (concentration range from 1×10^{-3} to 0.7 M). The fraction of dimer increases with dilution of the solution. The addition of small amounts of acetic acid shifts the equilibrium toward **1**. The content of dimer is 10% in 0.1 M solution of $Pd(OAc)_2$ in acetic acid−chloroform mixture (1:1 v/v).[8]

The structure of palladium diacetate in methanolic solutions is of special interest. Marson and co-workers[9] showed that ^1H NMR spectra of palladium diacetate in methanol contained many signals of acetate groups in δ region around 2, and their relative intensities depended on concentration of palladium

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acetate and water amount contained in the solvent. In the authors' opinion, this indicates formation of aggregates $[Pd(OAc)_2]_n$ ($n = 1$, 2, 3, etc) and probably even ionic forms $[Pd_n(OAc)_{n-1}]^+ \cdot (OAc)^-$. However, Bakhmutov et al.[10] suggested that the hypothesis about various $[Pd(OAc)_2]_n$ species in solution with n other than 3 seems unnecessary, since upon dissolution of palladium diacetate in thoroughly dried $CDCl_3$ and C_6D_6, the proton spectra exhibit only one singlet signal of trimer **1**. Additional signals appear in spectra only when solvents contain a small amount of water. Their number and relative intensities depend strongly on the solvent used. The authors[10] believe that hydrolysis occurs in wet $CDCl_3$ and C_6D_6, because a water molecule binds to a palladium atom and one of the bridging bidentate acetate groups is displaced to become a monodentate ligand. Bianchini and co-workers[11] believe that palladium diacetate in solutions can exist as a monomer and various aggregates, the structures of which depends on solvent, temperature, and concentration.

Methanol exerts a special effect on composition and properties of systems prepared from palladium diacetate.[5,10,12] For example, it was shown[5] that the rate of oxidative dimerization of styrene in the presence of palladium diacetate followed the same kinetic equation in all solvents studied, except for methanol. No conjugated diene is formed in methanol, but Pd^{II} is rapidly reduced to Pd^0. It was also observed[10] that, in methanol, palladium diacetate behaved in a different manner than in benzene and chloroform. For instance, in contrast to ^1H NMR spectra of palladium diacetate solutions in $CDCl_3$ and C_6D_6, its spectrum in methanol exhibits more than one signal in the acetate region, regardless of solvent drying degree. After several hours keeping at room temperature, a dark water-soluble precipitate is formed from methanol solutions of palladium acetate. Based on this, authors[10] believed that palladium diacetate reacts with methanol but did not provide any data on product structures. While studying the oxidative methoxycarbonylation of phenylacetylene,[12] we found that reaction of palladium diacetate with triphenylphosphine in methanol afforded a different complex instead of the expected compound $Pd(PPh_3)_2(OAc)_2$. Based on NMR data, we proposed an ionic structure $[Pd(PPh_3)_3(OAc)]^+ \cdot (OAc)^-$ for this new complex.

Thus, the data on the behavior of palladium acetate in solutions published to date is abundant but highly controversial, and further research is apparently required to provide better understanding of palladium forms that are involved in formation of catalytically active complexes. In the present work, we have studied in detail the behavior of **1** in methanol and chloroform by ^1H and ^{13}C NMR methods using 2D-HSQC heterocorrelation spectra[13] and 2D-DOSY (diffusion-ordered NMR spectroscopy),[14,15] which allowed to measure self-diffusion coefficients of different components in solution.

RESULTS AND DISCUSSION

Palladium Diacetate in Methanol. Solutions of $[Pd(OAc)_2]_3$ **1** in methanol and methanol-d_4 of varied concentrations were studied at different temperatures (see the Experimental Section, solutions **A**−**D**). First, ^1H NMR spectra were obtained at room temperature (solutions **A** and **B**) and at 0 °C (solution **C**), which showed that, in the initial period, two dominant species could be detected in these solutions (Supporting Information, Figures S1 and S2). Concentration of the first species (exhibiting three singlets in δ range 1.85−1.91 with a ratio of ca. 2:1:2) decreased with time, whereas the signal intensity of the second substance

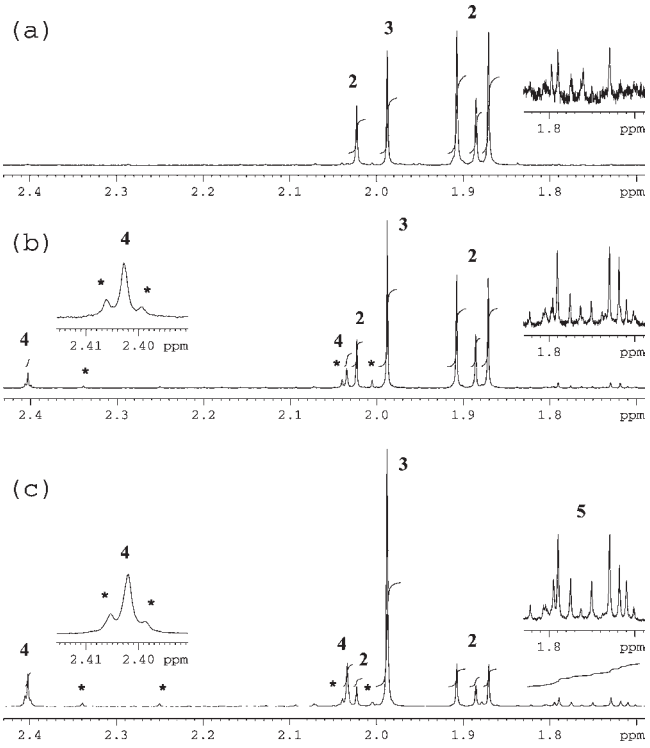

Figure 1. ^1H NMR spectra (−3 °C) of $Pd_3(OAc)_6$ **1** in CH_3OH (solution **D**): (a) within 30 min after dissolution; (b) after 50 h at −3 °C; (c) after 1.5 months of observation at −18 °C. **2**, $Pd_3(\mu\text{-OMe})(OAc)_5$; **3**, acetic acid; **4**, $Pd_3(\mu\text{-OMe})_2(OAc)_4$; **5**, methanol-soluble n-nuclear ($n \geq 3$) palladium complexes, $Pd_n(\mu\text{-OMe})_m(OAc)_p$; *, nonidentified signals.

(singlet δ 1.981) increased. An additional fifth signal at δ 2.031 was observed (Supporting Information, Figure S1c) in the proton spectrum of solution **B** (CH_3OH) and not observed in spectra of solutions **A** and **C** (CD_3OD). This allowed us to assign it to an OMe group. After keeping solution **C** for one day at room temperature, the signal with just the same chemical shift at δ 2.027 was observed in the ^1H NMR spectrum, but the three signals of the first substance became barely visible (Supporting Information, Figure S2d). Proton chemical shifts are presented here and further up to three decimal places (see Section 2.3).

Next, to explain the changes in methanol solutions and to establish the structures of substances formed, we have carried out a detailed spectral study of a more concentrated solution **D** (CH_3OH) at low temperature. The spectra were recorded at −3 °C, and between NMR measurements, solution **D** was stored in a freezer at −18 °C to suppress the reactions. This study allowed us to establish that, in the initial period, two main substances are methoxo complex $Pd_3(\mu\text{-OMe})(OAc)_5$ (**2**) and acetic acid (**3**). Trimeric palladium diacetate **1** was absent in methanolic solutions.

The ^1H NMR spectrum of freshly prepared solution **D**, which was immediately placed into spectrometer probehead at −3 °C, showed the same five signals as in solution **B** (Figures 1a, S1c of the Supporting Information). The ^{13}C NMR spectrum contained four pairs of signals belonging to acetate groups and one signal with comparable intensity at δ 59.90 (Supporting Information, Figure S3a). The mutual correspondence of all proton and carbon signals of each acetate group for both substances in solution **D** was determined from 2D-HSQC spectra (Table 1 and Figure S4

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Table 1. Chemical Shifts ^{1}H and ^{13}C of Complexes 1, 2, 4, 10, Acetic Acid 3, Formaldehyde Hemiacetal 7, and Methyl Formate 8 in Methanol and Chloroform Solutions A−E[a]

substance	solution, solvent	temp, °C	fragment	^{1}H, δ, ppm[b]	^{13}C, δ, ppm ($^{1}J_{C-H}$, Hz)[b]
1, $Pd_3(OAc)_6$	**E**, $CDCl_3$[c]	27	OAc	1.986	22.82; 188.43
		−3	OAc	2.007	
2, $Pd_3(\mu\text{-OMe})(OAc)_5$	**A**, CD_3OD	27	OAc	1.862, 6H	22.16; 189.87[d]
			OAc	1.880, 3H	21.58
			OAc	1.902, 6H	22.61; 190.54[d]
	B, CH_3OH + 10% CD_3OD	27	OAc	1.861, 6H	
			OAc	1.879, 3H	
			OAc	1.901, 6H	
			μ-OMe	2.031, 3H	
	D, CH_3OH + 10% CD_3OD[c]	−3	OAc	1.871, 6H[e]	22.10 (130.09); 189.60
			OAc	1.885, 3H[e]	21.57 (129.88); 186.40
			OAc	1.907, 6H[e]	22.55 (129.90); 190.23
			μ-OMe	2.023, 3H	59.90 (143.75)
		27	OAc	1.862, 6H	
			OAc	1.880, 3H	
			OAc	1.901, 6H	
			μ-OMe	2.032, 3H	
	E, $CDCl_3$ + CH_3OH[c]	−3	OAc	1.860, 6H	22.42; 188.22
			OAc	1.912, 3H	21.85; 185.08
			OAc	1.954, 6H	23.09; 189.40
			μ-OMe	2.024, 3H	60.00
		27	OAc	1.844, 6H	
			OAc	1.893, 3H	
			OAc	1.934, 6H	
			μ-OMe	2.021, 3H	
3, acetic acid[f]	**A**, CD_3OD	27	OAc	1.981	20.75; 175.25
	B, CH_3OH + 10% CD_3OD	27	OAc	1.980[g]	
	C, CD_3OD[h]	27	OAc	1.979	20.80; 175.31
	D, CH_3OH + 10% CD_3OD[c]	−3	OAc	1.987	20.77 (128.46); 175.42
	CH_3OH + 10% CD_3OD[i]	−3	OAc	1.991	20.83; 175.72
	E, $CDCl_3$[c]	27	OAc	2.091	20.19; 174.11
			H^+	≈9 bs[j]	
		−3	OAc	2.102	
			H^+	≈11 bs[j]	
	E, $CDCl_3$ + CH_3OH[c]	27	OAc	1.965	
		−3	OAc	1.972	20.85; 174.40
4, $Pd_3(\mu\text{-OMe})_2(OAc)_4$	**C**, CD_3OD[h]	27	OAc	2.027	22.22; 185.75
			μ-OCD_3		≈60 m
	D, CH_3OH + 10% CD_3OD	−3	OAc	2.034, 12H	22.18 (129.68); 185.44
			μ-OCH_3	2.402, 6H	60.73 (142.98)
		27	OAc	2.029, 12H	
			μ-OCH_3	2.403, 6H	
7, HO−CH_2−OCH_3	**C**, CD_3OD[l]	27	OCD_2O	4.617, 2D[k]	90.43
			OD	6.58 bs, 1D[k]	
			OCD_3	[m]	54.18
	D, CH_3OH + 10% CD_3OD	27	OCH_2O	4.645, 2H	91.11
			OH	6.6 bs, 1H	
			OCH_3	[m]	54.98
8, H−C(O)OMe	**C**, CD_3OD[l]	27	OCD_3	3.685, 3D[k]	50.41
			DC═O	8.096, 1D[k]	163.21 t ($^{1}J_{C-D}$ = 34.8)
	D, CH_3OH + 10% CD_3OD	27	OCH_3	3.713 d, 3H[n]	51.08
			HC═O	8.076 q, 1H[n]	163.28 (226.6)

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Table 1. Continued

substance	solution, solvent	temp, °C	fragment	^{1}H, δ, ppm[b]	^{13}C, δ, ppm ($^1J_{C-H}$, Hz)[b]
10, $Pd_3(\mu\text{-OH})(OAc)_5$	**E**, $CDCl_3$[c]	27	OAc	1.882, 6H	22.47; 189.52
			OAc	1.959, 3H	21.91; 185.94
			OAc	2.018, 6H	23.22; 189.88
			μ-OH	−1.0 bs, 0.59H[o]	
		−3	OAc	1.896, 6H	
			OAc	1.976, 3H	
			OAc	2.035, 6H	
			μ-OH	−0.9 bs, 0.87H[o]	
	E, $CDCl_3$ + CH_3OH	−3	OAc	1.831, 6H	
			OAc	1.906, 3H	
			OAc	1.962, 6H	

[a] bs = broad singlet; t = triplet. **A**−**D**, solutions in methanol; **E**, solution in wet $CDCl_3$. For their preparation, see the Experimental Section. [b] For NMR spectra referencing, see the Experimental Section. [c] Signals assignment was carried out by 2D-HSQC {^{1}H−^{13}C} using constants $^1J_{C-H}$ and $^2J_{C-H}$. [d] Assignment was carried out by analogy with solution **D** in CH_3OH. [e] Exactly the same δ value was observed in solution **C** at 0 °C (CD_3OD). [f] Data for acetic acid from ref 16. (1) $CD_3C(O)OD$ (TMS): 18.25; 176.60. (2) $CH_3C(O)OH$ (TMS): 19.10; 177.05; from ref 17: 2.098; 11.417 (^{1}H, 0.04 mL in 0.5 mL $CDCl_3$); 20.80; 178.12 (^{13}C, 0.5 mL in 1.5 mL $CDCl_3$). [g] Exactly the same δ value was observed in solution **D** at 27 °C. [h] Spectra were measured after a day (NMR tube was stored at 27 °C). [i] Spectra of acetic acid solution without palladium diacetate. [j] $\nu_{1/2}$ = 227 Hz (27 °C), 143 Hz (−3 °C). [k] Deuterium chemical shifts in ^{2}D NMR spectrum (92.12 MHz) were measured relative deuterium signal of Me group (δ 3.300) in CD_3OD. [l] Spectra were measured after 10 months of storage of the NMR tube at 27 °C. [m] Signal of OMe group was overlapped by intensive signal of methanol. [n] ^4J = 0.825 Hz. [o] $\nu_{1/2}$ = 123 Hz (27 °C), 73 Hz (−3 °C).

of the Supporting Information). It turned out that carbonyl signals of three acetate groups were observed in δ range 186−191 (these chemical shifts are characteristic for bridging acetate groups of palladium complexes[18]), whereas the signal of one C═O carbonyl group was observed at δ 175.42. Measuring ^{13}C-{$^1H_{sel}$} heteronuclear double resonance spectrum (Supporting Information, Figure S5) with selective proton decoupling at δ 2.023, we established that the carbon signal at δ 59.90 was related to this proton signal. Thus, it was proved that this pair of signals belonged to a OMe group. Based on these data, we assumed that one acetate group was replaced by a bridging μ-OMe group upon dissolution of trimer **1** in methanol.

The substitution of this type is known[19] for the oxidized trimer of cobalt(III) diacetate, which is transformed in methanol solution into the $[Co_3O(\mu\text{-OMe})(OAc)_5(MeOH)_3]^+$ complex. The chemical shift of protons μ-OMe in this complex is δ 1.33, and five acetate groups are presented in the spectrum as three proton signals with ratio 6H:6H:3H in δ range from 1.9 to 2.4.[19]

The second product of the substitution of the bridging acetate group in trimer **1** by μ-OMe is likely to be acetic acid, but an excessive integral intensity of proton signal at δ 1.987 (Figure 1a) had left some doubt. The additional structure proof for both substances was obtained using the 2D-DOSY technique. (All 2D-DOSY spectra in figures have a relative diffusion scale. For correct values of diffusion coefficients see appropriate section below).

In the 2D-DOSY spectrum of solution **D** (Figure 2), three cross-peaks of acetate groups in the first compound (δ 1.871, 1.885, and 1.907) and the cross-peak of the μ-OMe group (δ 2.023) are arranged at levels corresponding to the diffusion coefficient, log D = −9.12, which confirms that they belong to the same complex, $Pd_3(\mu\text{-OMe})(OAc)_5$, **2**. The cross-peak of the second substance (δ 1.987) is observed at level of log D = −8.83, indicating a faster diffusion and substantially lower molecular mass compared to that of **2**. That is why it can be argued that this substance is not trimer **1**, since the latter must have a diffusion coefficient close to that observed for **2**. The cross-peak at δ 1.987 does not correspond also to monomeric $Pd(OAc)_2$ (molecular

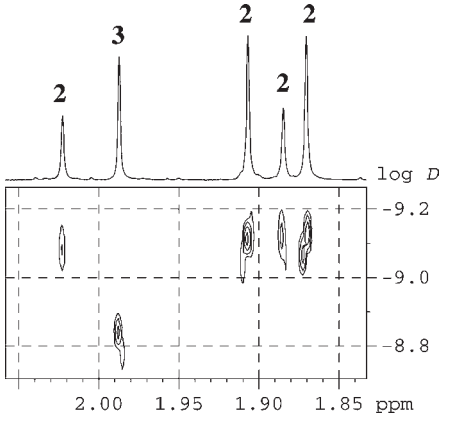

Figure 2. 2D-DOSY spectrum (−3 °C) of $Pd_3(OAc)_6$ **1** in CH_3OH (solution **D**). **2**, $Pd_3(\mu\text{-OMe})(OAc)_5$; **3**, acetic acid; D, relative diffusion coefficient.

mass 224). Since having measured ^{1}H and ^{13}C and 2D-DOSY NMR spectra (−3 °C) of acetic acid in methanol, we have obtained chemical shift values (^{1}H: δ 1.991; ^{13}C: δ 20.83, 175.72), which were very close to those observed in solution **D** for **3** (^{1}H: δ 1.987; ^{13}C: δ 20.77, 175.42), and a value of the diffusion coefficient, log D = −8.82 (Supporting Information, Figure S6), coinciding with that found for **3**.

Therefore, we have proved unambiguously that, upon dissolution in methanol, fast solvolysis of trimer **1** yields methoxo complex **2** and acetic acid **3** via eq 1:

$$\underset{\mathbf{1}}{Pd_3(OAc)_6} + CH_3OH \rightarrow \underset{\mathbf{2}}{Pd_3(\mu\text{-OMe})(OAc)_5} + \underset{\mathbf{3}}{CH_3COOH} \quad (1)$$

According to the ^{1}H NMR spectrum measured after 30 min upon dissolving trimer **1** in methanol, the amount of methoxo complex **2** was 94 mol % of starting trimer **1** (Table 2, entry 1).

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Table 2. Molar Amount *M* of Complexes 2, 4, Sum of 5, 6 and 9, Acetic Acid 3, Formaldehyde Hemiacetal 7, and Methyl Formate 8 Per 1 mol of Initial Trimer 1 (*M*1) in CH_3OH (Solution D),[a] Calculated from ^1H NMR Spectra[b]

				molar amount, *M*					
entry	time of spectral measurement[c]	Σ (27 °C)[d]	Σ (−3 °C), h[e]	*M*2	*M*4	(*M*5 + *M*6)[f] or (*M*5 + *M*6 + *M*9)[g]	*M*3[h]	*M*7[h]	*M*8[h]
1	30 min	1 min	0.5[i]	0.94	0	0.06[f]	1.30		
2	22 h	_ " _	22	0.73	0.04	0.23[f]	1.59		
3	50 h	_ " _	50	0.67	0.08	0.25[f]	1.78		
4	1.5 months	7 min	53	0.31	0.16	0.53[f]	3.00		
5	2.5 months	30 min	83	0.19	0.20	0.61[f]	3.43		
6	3 months[j]	2 h	134	0.16	0.22	0.62[g]	3.50	0.13	
7	3.5 months[j]	5.5 h	136	0.12	0.23	0.65[g]	3.61	0.23	0.02
8	11 months[j]	12 h	140	0.09	0.13	0.78[g]	4.24	1.64	0.46
9	13.5 months[j]	17.5 h	_ " _	0.08	0.10	0.82[g]	4.72	2.22	0.78

[a] **1**, $Pd_3(OAc)_6$; **2**, $Pd_3(\mu\text{-OMe})(OAc)_5$; **4**, $Pd_3(\mu\text{-OMe})_2(OAc)_4$; **5**, methanol-soluble $Pd_n(OMe)_m(OAc)_p$, ($n \geq 3$) complexes (OAc group signals at δ range 1.7−1.85; **6**, insoluble polynuclear palladium complexes fallen out as dark brown precipitate; **9**, Pd metal. [b] *M***1**, molar amount of starting trimer **1** was determined as $^1/_{18}$ of total integral intensity of signals of all acetate groups in the proton spectra and then normalized to 1 mol; *M***2**, molar amount of **2** was determined as $^1/_{15}$ of total integral intensity of three signals from five acetate groups; *M***4**, molar amount of **4** was determined as $^1/_{12}$ of integral intensity of one signal from four acetate groups; *M***3**, molar amount of **3** was determined as $^1/_3$ of integral intensity of corresponding singlet signal. [c] Time, which has passed since the end dissolution of **1** in methanol. Spectra were measured at −3 °C, and solution **D** was stored between measurements at −18 °C. [d] Total time keeping of solution **D** at room temperature, without taking into account of time (≈15 min at 30 °C), which was used for dissolution of weighted sample **1** (12.8 mg) in CH_3OH. [e] Total time during which solution **D** was at −3 °C. [f] (*M***5** + *M***6**), molar amount of initial trimer **1** used for formation of complexes **5** and **6** was determined by the following equation: (*M***5** + *M***6**) = *M***1** − (*M***2** + *M***4**). [g] (*M***5** + *M***6** + *M***9**), molar amount of initial trimer **1** used for formation of **5**, **6**, and **9** was determined by the following equation: (*M***5** + *M***6** + *M***9**) = *M***1** − (*M***2** + *M***4**). [h] *M***3**, *M***7**, and *M***8**, molar quantities of **3**, **7**, and **8** were determined from integral intensities of corresponding signals in the proton spectra. [i] Thermostating of solution and resolution adjustment continued for 30 min. [j] Mirror of Pd metal, **9**, had appeared on walls of the NMR tube, and signals of **7** and **8** were identified in NMR spectra, which were measured at 27 °C.

Solution **D** containing **2** and **3** was kept for approximately a day (22 h) at −3 °C, and signals of a new complex (**4**) appeared in the ^1H NMR spectrum at δ 2.402 and 2.034 (ratio ≈1:2), the intensities of which doubled on extending the exposure to 50 h at −3 °C with simultaneous decrease of signal intensities of complex **2** (Figure 1b, Table 2, entries 2 and 3). Further, solution **D** was stored at −18 °C, and ^1H NMR monitoring showed the remaining of a trend in signals of **2** and **4** intensities. After 1.5 months, the signal intensities of **2** and **4** became very close to each other, and the signal of acetic acid **3** increased (Figure 1c, Table 2, entry 4). The color of the solution retained yellow, but on the walls of the NMR tube, a dark brown film was deposited, visually different from the so-called "palladium mirror". A dark precipitate appeared at the bottom of tube. The formation of a similar precipitate was noted by other researchers.[10]

At this stage of transformations in methanolic solution **D** under study, the concentration of **4** increased sufficiently to determine its structure by $^{13}C\{^1H\}$, $^{13}C\{$monoresonance$\}$, $^{13}C\{^1H_{sel}\}$ NMR spectra, and 2D-DOSY experiment. In addition to signals of complex **2** and acetic acid, three new, previously absent signals of complex **4** were identified in the $^{13}C\{^1H\}$ NMR spectrum (Supporting Information, Figures S3b and S7). The signals at δ 60.73 and 22.18 belonged to methyl groups, whereas the signal at δ 185.44 belonged to the C═O carbonyl group. The ratio of signal intensities at δ 60.73 and 22.18 was close to 1:2. The $^{13}C\{^1H_{sel}\}$ heteronuclear double resonance spectra confirmed a correlation of proton (δ 2.402) and carbon (δ 60.73) signals of the OMe group as well as belonging of the proton signal at δ 2.034 and carbon signals at δ 22.18 and 185.44 to one acetate group (Supporting Information, Figure S8).

The value of the diffusion coefficient for **4** (log D = −9.15) obtained from the 2D-DOSY spectrum (Figure 3a) almost coincides with that found for **2** (log D = −9.12), indicating that the molecular masses of these complexes are close. These data show that compound **4** is a symmetric dimethoxo complex $Pd_3(\mu\text{-OMe})_2(OAc)_4$, in which both acetate ligands linking two palladium atoms are substituted by bridging μ-OMe groups. Only in this case, two μ-OMe groups and four μ-OAc groups are equivalent. The molar ratio of **2** and **4** in solution **D** was approximately ≈2:1 at this moment of observation, whereas their total amount was 47 mol % of starting trimer **1** (Table 2, entry 4). The 2D-DOSY spectrum (Figure 3a) also exhibited the cross-peak of acetic acid **3** (δ 1.987, log D = −8.83). The integral intensity of this proton signal (Figure 1c) was 50% relatively of the total integral of acetate groups (3 mols of **3** per mole of **1**).

The data obtained indicate clearly that **1** reacts rapidly with methanol, being transformed into **2**, which further undergoes a slower (with a noticeable rate even at −18 °C) substitution of a second bridging acetate group between the same two palladium atoms to form a more stable symmetric dimethoxo complex **4** via eq 2:

$$\underset{\mathbf{2}}{Pd_3(\mu\text{-OMe})(OAc)_5} + CH_3OH \rightarrow \underset{\mathbf{4}}{Pd_3(\mu\text{-OMe})_2(OAc)_4} + \underset{\mathbf{3}}{CH_3COOH} \quad (2)$$

The further observation of solution **D** stored at −18 °C showed that the concentration of **4** reached a maximum at 23 mol % of starting trimer **1** and then decreased (Table 2).

The signals of acetate groups in δ range 1.7−1.85 were observed in the ^1H NMR spectra of solution **D** in addition to identified signals of complexes **2** and **4** and acetic acid **3**. The total intensity of these signals increased with time and achieved 12% relatively of total integral of all acetate groups (Figure 1c), although intensities of particular signals in this group changed in opposite directions. Many signals with respective intensities

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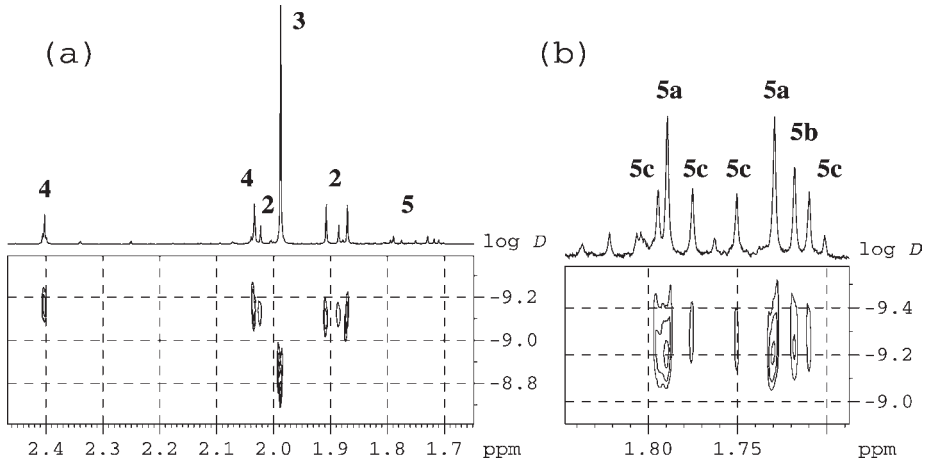

Figure 3. 2D-DOSY spectrum (−3 °C) of $Pd_3(OAc)_6$ **1** in CH_3OH (solution **D**) after 1.5 months of storage at −18 °C: (a) spectrum in δ range 1.65−2.45; (b) amplified fragment in δ range 1.7−1.85. **2**, $Pd_3(\mu\text{-OMe})(OAc)_5$; **3**, acetic acid; **4**, $Pd_3(\mu\text{-OMe})_2(OAc)_4$; **5a**, **5b**, **5c**, methanol-soluble *n*-nuclear ($n \geq 3$) palladium complexes, $Pd_n(\mu\text{-OMe})_m(OAc)_p$; *D*, relative diffusion coefficient.

were detected also in the carbon spectrum in δ ranges 183−189 and 21−23 confirming their assignment to acetate groups (Supporting Information, Figure S9b). The corresponding cross-peaks were observed in the 2D-DOSY spectrum (Figure 3b) at level log *D* from −9.20 to −9.27, that is, above the cross-peak levels of complexes **2** and **4**. Based on these data, we may assume that the signals at δ 1.7−1.85 are assigned to methanol-soluble *n*-nuclear ($n \geq 3$) palladium complexes, $Pd_n(\mu\text{-OMe})_m(OAc)_p$ (**5**). The proton signals of comparable intensity at δ 2−2.8 (Figure 1, marked with an asterisk and Supporting Information, S10) are possibly assigned to OMe groups of these complexes. Multidirectional trends in the change of signal intensities at δ 1.7−1.85 (Figure 1) allow us to distinguish among the three species of complex **5** denoted as **5a**, **5b**, and **5c** (Figure 3b), which contain a different number of nonequivalent acetate groups.

The molar ratio of **2** and **4** in solution **D** became roughly equal to unity (19 mol % **2** and 20 mol % **4**; Table 2, entry 5; Supporting Information, Figure S9b) after 2.5 months at −18 °C. Finely dispersed particles could be seen in the solution, which gradually formed a dark brown precipitate on the bottom of the NMR tube. No palladium mirror was again observed.

The data presented in Table 2 show that the total amount of complexes **2** and **4** in solution **D** decreased, whereas the concentration of acetic acid increased with time. This indicates that a considerable portion of methoxo complex **2**, along with transformation into dimethoxo complex **4** in eq 2, is involved in the formation of other complexes, such as methanol-soluble *n*-nuclear complexes **5** (signals of acetate ligands at δ 1.7−1.85), and insoluble palladium complexes (**6**), which form a dark brown precipitate on the walls and bottom of the NMR tube. After 2.5 months of observation at −18 °C, about 60% of the total amount Pd^{2+} in solution **D** (Table 2, entry 5) appeared in **5** and **6**. Most probably complex **6** can be polynuclear palladium clusters (similar to the giant clusters described in ref 20), but further investigation is required to establish their structure.

Finally, solution **D** containing mainly **5** and **6** (60% Pd^{2+}), as well as **2** and **4** (40% Pd^{2+}) and **3** after three months of research at low temperature, was warmed periodically to 27 °C. As a result, the signals of formaldehyde hemiacetal (**7**) appeared in the proton spectrum after 2 h at 27 °C, while 5.5 h after the signals of methyl formate (**8**) appeared (Table 1, Supporting Information, Figure S10). Their concentration increased with time (Table 2, entries 6−9). The color of solution **D** acquired a greenish tint due to microparticles of reduced Pd metal (**9**), which precipitated as a mirror on the walls of the NMR tube. It should be noted that acetic acid in methanol solution **D** upon prolonged storage at room temperature is expectedly converted into methyl acetate (Supporting Information, Figure S11).

When **1** was dissolved in CD_3OD in the presence of air (solution **C**), it was also transformed into **2** and **3**. Further methoxo complex **2** was transformed into dimethoxo complex **4**. Complex **2** disappeared almost completely after a day at room temperature, and the amount of **4** was 30 mol % of starting trimer **1** (Supporting Information, Figure S2d). Since CD_3OD was used in this case, the bridging $(\mu\text{-OMe})_2$ proton signal of **4** was absent, whereas a multiplet of $(OCD_3)_2$ was observed at $\delta \approx 60$ in the carbon spectrum (Supporting Information, Figure S12a). The integral intensity of the proton signal of acetic acid was 56% relatively of the total integral of acetate groups (3.4 mols of **3** per mole of **1**). ^1H NMR spectrum also exhibited the signals of soluble complexes **5** (δ 1.7−1.85) (Supporting Information, Figure S13), whereas ^{13}C and ^2D NMR spectra contained the signals of **7** and **8** with ratio 2:1. After 10 months at room temperature, the total amount of **7** and **8** in solution **C** was approximately 20−25 mols per mole of starting Pd^{2+} (Supporting Information, Figures S12b and S14). This result showed that, upon prolonged storage, methanol was catalytically oxidized by oxygen present in solution **C**. Catalysts of this oxidation could be the clusters containing Pd(I),[21,22] and colloidal palladium formed during the reduction of Pd(II) by methanol.

Palladium Diacetate in Chloroform-d_1. Both regular chloroform and commercially available chloroform-d_1, applied for measurements of NMR spectra, always contain minor amounts of water, a narrow resonance signal of which is usually observed at δ 1.5−1.7. In the proton spectrum of $CDCl_3$ used, we observed this signal at δ 1.52 (width at half-height $\nu_{1/2}$ = 1.6 Hz) with integral intensity of 0.64 relative to the signal of residual $CHCl_3$. After dissolution of a weighed sample of palladium diacetate **1** (solution **E**), the intensity of the water signal almost doubled due to water present in solid palladium diacetate, which is known to be a crystalline hydrate $[Pd_3(OAc)_6]\cdot{}^1/_2\ H_2O$[2a] or solvate[2a,d,10] depending on the preparation procedure. The signal of residual

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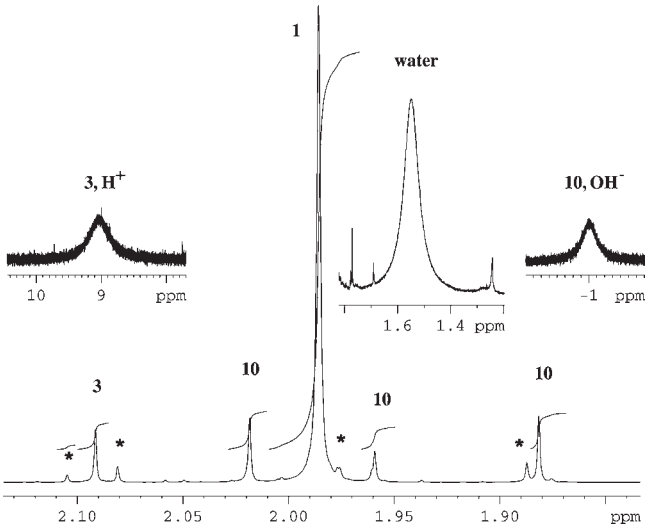

Figure 4. ^{1}H NMR spectrum (27 °C) of $Pd_3(OAc)_6$ **1** in $CDCl_3$ (solution **E**). **10**, $Pd_3(\mu-OH)(OAc)_5$; **3**, acetic acid; *, signals of impurities.

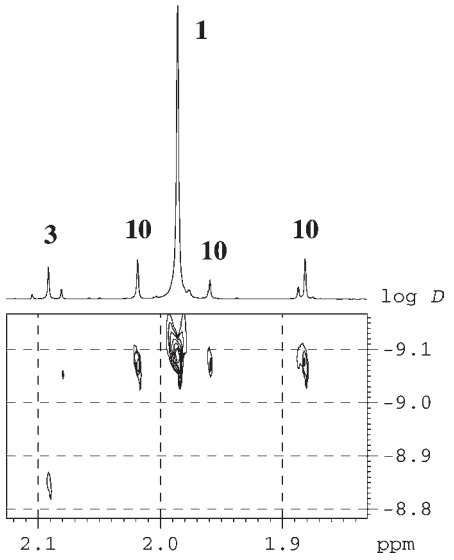

Figure 5. 2D-DOSY spectrum (27 °C) of $Pd_3(OAc)_6$ **1** in $CDCl_3$ (solution **E**). **10**, $Pd_3(\mu-OH)(OAc)_5$; **3**, acetic acid; *D*, relative diffusion coefficient.

water also broadened strongly and underwent a downfield shift (δ 1.55, $\nu_{1/2}$ = 39 Hz).

The ^{1}H NMR spectrum of solution **E** (Figure 4) agreed nicely with the one presented in ref 10.

We observed five main signals and assigned the most intense of them at δ 1.986, according to published data,[10] to trimer **1** (Table 1). The positions (δ 2.091, 2.018, 1.959, and 1.882) and relative intensities (1:2:1:2) of four other signals resembled the signals of acetic acid **3** (δ 2.091) and methoxo complex **2**, which have been described above in solutions **A**−**D** of palladium diacetate in methanol. Based on this, the signals at δ 2.018, 1.959, and 1.882 were ascribed to the corresponding hydroxo complex $Pd_3(\mu-OH)(OAc)_5$ (**10**) via eq 3. According to integration data, the molar ratio of trimer **1** and **10** in solution **E** was approximately 3.3:1.

$$\underset{\mathbf{1}}{Pd_3(OAc)_6} + H_2O \rightarrow \underset{\mathbf{10}}{Pd_3(\mu\text{-}OH)(OAc)_5} + \underset{\mathbf{3}}{CH_3COOH} \quad (3)$$

The resonance signal of the carboxylic proton of acetic acid lied at δ 9. In addition to this signal, the signal of μ-OH with a relative intensity of 0.59H compared to 6H of the signal at δ 1.882 was observed in the high-field region at δ −1 (Figure 4). The proton region from δ −1 to −4 is characteristic of bridging μ-OH groups.[23] The signals of residual water, acetic acid, and the μ-OH group were strongly broadened, indicating that rather fast proton exchange occurs in solution **E**. The ratio of molar concentrations of palladium diacetate and water (including integral intensities of signals H^+ and μ-OH) was $Pd^{2+}/H_2O \approx 5:1$ in solution **E**.

The 2D-DOSY spectrum confirmed conclusions about the structure of complexes in solution **E** (Figure 5). Three cross-peaks of hydroxo complex **10** (log *D* = −9.07) and the cross-peak of trimer **1** (log *D* = −9.09) were observed almost at the same level, as could be expected. The diffusion coefficients of acetic acid **3** and chloroform are close (log *D* = −8.85 and −8.79, respectively, Supporting Information, Figure S15). Since the diffusion coefficients are related to the molecular masses, this confirmed the commonly known fact that carboxylic acids exist in dilute solutions in inert solvents mostly as dimers.

The mutually coupled proton and carbon signals of all acetate groups in solution **E** containing **1**, **3**, and **10** were determined using 2D-HSQC spectra (Table 1, Supporting Information, Figures S16 and S17).

It is known that bridging μ-OH groups can be replaced by μ-OMe.[19,24] We added methanol ($CH_3OH/Pd^{2+} \approx 40:1$) at room temperature to the solution **E** of **1** in chloroform. Immediately upon the signal of trimer **1** disappeared from the ^{1}H NMR spectrum (recorded at −3 °C), the signals of hydroxo complex **10** decreased in intensity, and four signals of methoxo complex **2** appeared instead (Supporting Information, Figure S18a, b). Three exchange-broadened signals at δ −1, 1.55, and 9 also disappeared to give way to a single broadened signal at $\delta \approx 3.9$ (δ 3.1 at 27 °C). This result indicates that fast transformation of trimer **1** into methoxo complex **2** occurs in chloroform solution **E** containing methanol. The substitution of μ-OH by μ-OMe in hydroxo complex **10** proceeds more slowly, and signals of **10** disappeared from the spectrum after roughly a day (solution **E** was stored overnight at −18 °C and ca. 20 min kept at 30 °C; Supporting Information, Figure S18c). The 2D-DOSY spectrum as well as $^{13}C\{^1H\}$, $^{13}C\{^1H_{sel}\}$, and 2D-HSQC spectra (−3 °C, Supporting Information, Figures S19, S20, and S21) confirmed the formation of methoxo complex **2** and the corresponding amount of acetic acid. Note that the stability of methoxo complex **2** in chloroform is much higher than in methanol: the concentration of **2** remained unchanged within 16 h at 27 °C.

Simultaneous presence of water, acetic acid, trimer **1**, and hydroxo complex **10** in reaction mixture, and the pronounced exchange broadening of signals of water, acidic proton, and proton of the μ-OH ligand in **10**, as stated above, indicates that the formation of **10** is an equilibrium process (eq 4).

$$\mathbf{1} + H_2O \rightleftarrows \mathbf{10} + CH_3COOH \quad (4)$$

Experiments on shifting this equilibrium by adding water and acetic acid gave the following results. Upon addition of one water droplet to solution **F** (trimer **1** in chloroform, initial molar ratio

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1/**10** ≈ 3.9:1) at room temperature, the equilibrium was shifted toward hydroxo complex **10** to ratio **1**/**10** ≈ 2:1. The second water droplet changed the equilibrium to ratio **1**/**10** ≈ 1:1 (Supporting Information, Figure S22). The signal intensity of acetic acid also increased proportionally to intensity increase of signals **10**. The signal of μ-OH at δ −0.84 was strongly broadened (width at half-height $\nu_{1/2}$ = 480 Hz), and the broadening of carboxylic proton signal turned out to be so strong that the signal could not be observed. Further addition of water did not change the equilibrium, because the solubility limit of water in chloroform was exceeded. Excessive water formed the upper layer of liquid above chloroform and appeared as fine droplets on the walls of the NMR tube. A broad signal of the "block" water appeared at δ 4.8 in the proton spectrum along with broad signal of monomeric (dissolved in chloroform phase) water at δ 1.66. On the contrary,

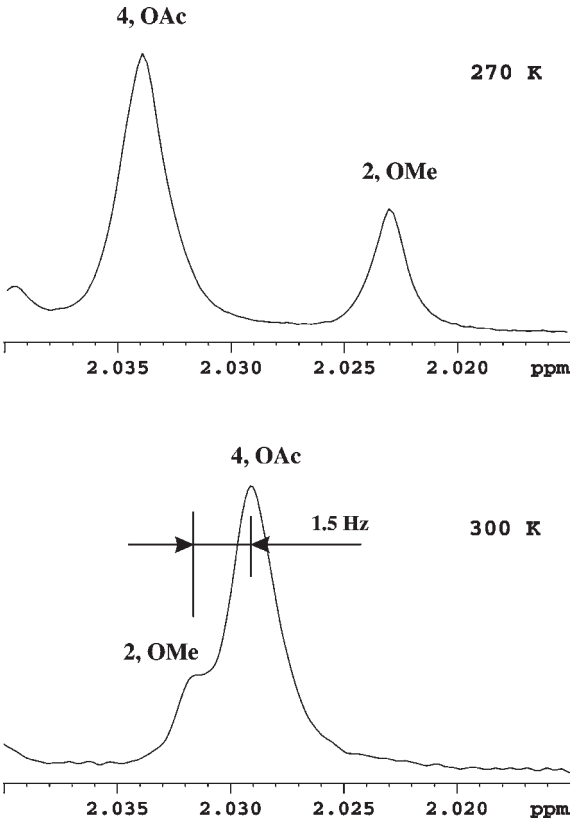

Figure 6. ^{1}H NMR spectra at 27 and −3 °C of $Pd_3(OAc)_6$ **1** in CH_3OH (solution **D**) in δ region 2.015−2.040. **2**, $Pd_3(\mu\text{-OMe})(OAc)_5$; **4**, $Pd_3(\mu\text{-OMe})_2(OAc)_4$.

addition of several droplets of a very dilute solution of acetic acid in chloroform shifted equilibrium (eq 4) toward trimer **1**. The position of equilibrium shifted to the same direction when the temperature decreased to −12 °C, but temperature increase to 27 °C restored the original ratio (Supporting Information, Figures S23, S24 for solution **G**). Equilibrium constant K calculated on the basis of molar concentrations of initial and final species in solution **E** (obtained from ^{1}H NMR spectrum) was estimated approximately 1.62×10^{-1}.

The formation of hydroxo complexes at the presence of small amounts of water in solvent was observed also in benzene solutions of both palladium diacetate **1** and trimeric palladium dipivalate, $Pd_3(Me_3CCOO)_6$, and proven by 2D-DOSY spectra. The detailed spectral data will be reported in a due course elsewhere.

Accuracy of Proton Chemical Shifts Measurements. High accuracy of measurements of proton chemical shifts in mixtures studied was necessary to distinguish the signals of various species with very small chemical shifts differences. For example, chemical shifts values of the OMe group of complex **2** and the OAc group of complex **4** in methanol solution **D** at 27 °C are δ 2.032 and 2.029, respectively (their difference being 1.5 Hz, i.e., 0.0025 ppm). At −3 °C, these signals undergo shifts in the opposite directions, and their positions change (δ 2.034, OAc of **4** and 2.023, OMe of **2**, Figure 6).

Signals of the OAc group of complexes **2** and **10** in chloroform solution **E** after adding of methanol also differ very little. The chemical shift difference at −3 °C is 0.006 ppm for signals at δ 1.912 (**2**) and 1.906 (**10**) and 0.008 ppm for signals at δ 1.954 (**2**) and 1.962 (**10**) (Table 1, Supporting Information, Figure S18b).

To check a real accuracy of proton chemical shifts measurements, we have prepared a new solution of palladium diacetate in CH_3OH (solution **H**, Experimental Section). Fourteen proton spectra of this solution were recorded at room temperature during a day. Chemical shifts to fourth decimal places were measured and presented in Supporting Information (Table S1 and Figures S25 and S26). These data showed that chemical shifts of complexes **2** and **4** have negligible changes over time (less than 0.0015 ppm), and thus, accuracy of chemical shift measurements in solution **H** was not worse than ±0.0008 ppm. On this basis, values of proton chemical shifts are presented to three decimal places.

This high accuracy allowed us to establish an interesting fact: the proton chemical shifts of complexes **1**, **2**, **4**, and **10** are very stable and practically concentration independent in the range of 4−70 mmol/L of Pd^{2+} (methanolic solutions **A**−**D**, **H**) and of 50−80 mmol/L of Pd^{2+} (solutions **E**−**G** in $CDCl_3$). These data are presented in Tables 3 and 4.

Table 3. Chemical Shifts ^{1}H of Complexes $Pd_3(\mu\text{-OMe})(OAc)_5$, 2, and $Pd_3(\mu\text{-OMe})_2(OAc)_4$, 4, in Methanolic Solutions at 27 °C

	signal of **2**, δ, ppm				signal of **4**, δ, ppm			
solution	OAc	OAc	OAc	OMe	OAc	OMe	concentration of Pd^{2+}, mmol/L	molar ratio of **2** and **4**
A, CD_3OD[a]	1.862	1.880	1.902	–	[b]	–	22.3	
B, CH_3OH	1.861	1.879	1.901	2.031	2.029	2.402	20.6	10:1
C, CD_3OD	1.862	1.879	1.901	–	2.027[c]	–	4.46	1:7.7
D, CH_3OH	1.862	1.880	1.901	2.032	2.029	2.403	68.6	1:1.4
H, CH_3OH	1.862	1.880	1.902	2.033	2.030	2.405	55.8	5:1

[a] Spectrum was measured immediately after preparation of solution **A**. [b] Signal not observed. [c] Spectrum was measured after a day (NMR tube was stored at 27 °C).

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Table 4. Chemical Shifts ^{1}H of Complexes $Pd_3(OAc)_6$, 1, and $Pd_3(\mu\text{-}OH)(OAc)_5$, 10, in $CDCl_3$ at 27 °C

		signal of **10**, δ, ppm				
solution	signal OAc of **1**, δ, ppm	OAc	OAc	OAc	concentration of Pd^{2+}, mmol/L	molar ratio of **1** and **10**
E	1.986	1.882	1.959	2.018	61.4	3.3: 1
F	1.983	1.879	1.959	2.016	78.7	3.9: 1
G	1.983	1.880	1.958	2.016	50.2	2.2: 1

Table 5. Diffusion Coefficients, $D \times 10^{-9}$, $m^2\ s^{-1}$, Measured on TBI[a] (G = 55.6 G/cm) and BBO[b] (G = 53.5 G/cm) Probeheads for Complexes 1, 2, 4, 10,[c] and Acetic Acid 3

substance	probehead	temp, °C	solution[d], solvent	concentration, mmol L^{-1}	$D \times 10^{-9}$, $m^2\ s^{-1}$	parameter[e] Δ, δ, D1
1	[a]	27	**E**, $CDCl_3$	15.7	1.74	[f]
2	[a,g]	−3	**D**, CH_3OH	16.7	0.54	[h]
	[a,i]	−3	**D**, CH_3OH	7.1	0.56	[f]
	[a]	−3	**E**, $CDCl_3$ + CH_3OH	15.4	0.68	[j]
	[b]	27	**E**, $CDCl_3$ + CH_3OH	15.4	2.16	[k]
	[b]	−3	**E**, $CDCl_3$ + CH_3OH	15.4	0.62	[l]
4	[a,i]	−3	**D**, CH_3OH	3.7	0.51	[f]
10	[a]	27	**E**, $CDCl_3$	4.7	1.82	[f]
	[a]	−3	**E**, $CDCl_3$ + CH_3OH	2.5	0.68	[j]
3	[a]	27	**E**, $CDCl_3$	4.7	3.06	[f]
	[a]	−3	**D**, CH_3OH	36.4	1.00	[h]
	[a]	−3	**E**, $CDCl_3$ + CH_3OH	22.3	1.06	[j]
	[b]	27	**E**, $CDCl_3$ + CH_3OH	22.3	2.90	[k]
	[b]	−3	**E**, $CDCl_3$ + CH_3OH	22.3	1.01	[l]

[a] Triple broadband inverse (TBI). [b] Broadband multinuclear (BBO) probeheads. [c] **1**, $Pd_3(OAc)_6$; **2**, $Pd_3(\mu\text{-}OMe)(OAc)_5$; **4**, $Pd_3(\mu\text{-}OMe)_2(OAc)_4$; **10**, $Pd_3(\mu\text{-}OH)(OAc)_5$. [d] **D**, solution in methanol; **E**, solution in wet chloroform; for their preparation, see the Experimental Section. [e] Big delta Δ, ms, diffusion time; little delta δ, ms, gradient pulse length; D1, s, relaxation delay. [f] Δ = 40 ms; δ = 2 ms; D1 = 5 s. [g] Diffusion coefficient was measured after 22 h at −3 °C. [h] Δ = 40 ms; δ = 2.1 ms; D1 = 4.5 s. [i] Diffusion coefficient was measured after 1.5 months of observation at −18 °C. [j] Δ = 40 ms; δ = 1.6 ms; D1 = 4 s. [k] Δ = 40 ms; δ = 1.1 ms; D1 = 5 s. [l] Δ = 50 ms; δ = 1.7 ms; D1 = 8 s.

Comparative analysis of ^{1}H NMR spectra in δ range 1.70−1.85 (signals of multinuclear palladium complexes $Pd_n(\mu\text{-}OMe)_m(OAc)_p$, **5**, in methanolic solutions) showed also high stability of chemical shifts of complexes **5a**, **5b**, and **5c** over time (Figures 1, 3, and S10, S13, and S25 of the Supporting Information). We also believe that analogous complexes in other solvents will show the same stable and the characteristic chemical shifts.

Diffusion Coefficient Measurements. We employed 2D-DOSY technique on a qualitative basis to elucidate the structures of unknown complexes formed in methanol and chloroform solutions. To compare 2D-DOSY spectra for different solvents and at different temperatures, we used internal standards, methanol and residual water in $CDCl_3$ (see the Experimental Section). The resulting 2D-DOSY cross-peaks represented the relative diffusion coefficients along the logarithmic vertical scale (Figures 2, 3, 5, and S6, S15, S19, and S27 of the Supporting Information). The correct values of diffusion coefficients (Table 5) were obtained by recalculating of the same 2D DOSY experimental data in accordance with the gradient strength G = 55.6 G/cm (TBI probehead). To ensure reproducibility, the diffusion coefficient measurements were also performed using a BBO probehead (G = 53.5 G/cm) for solution **E** (mixture $CDCl_3$ + CH_3OH) at 27 and −3 °C. Estimated errors of diffusion coefficients ($D \times 10^{-9}$, $m^2\ s^{-1}$) presented in Table 5 did not exceed 8%.

CONCLUSION

The results obtained show that palladium diacetate $Pd_3(OAc)_6$, **1**, readily reacts with methanol and water in the alkoholysis and hydrolysis reactions with retention cyclic trinuclear structure. In methanol, it rapidly and irreversibly substitutes one bridging acetate ligand by a μ-OMe group. In trimeric complex $Pd_3(\mu\text{-}OMe)(OAc)_5$, **2**, formed in such a manner, the substitution of a second bridging acetate proceeds considerably more slowly to form the symmetrical dimethoxo complex $Pd_3(\mu\text{-}OMe)_2(OAc)_4$, maximum amount of which reaches 20−30 mol % of starting **1**. At −18 °C, a major part of **2** is transformed into soluble *n*-nuclear ($n \geq 3$) complexes **5** and insoluble polynuclear complexes **6**. Complexes **5** and **6** (up to 60% based on Pd^{2+}) are slowly formed on prolonged storage at −18 °C, and no noticeable oxidation of methanol occurred at this temperature. The temperature increase to 27 °C activates redox processes resulting in the formation of Pd metal and products of methanol oxidation, formaldehyde hemiacetal and methyl formate. Trimer **1** is quite stable in a chloroform solution in the absence of water or methanol molecules, but it reversibly interacts with water to form hydroxo complex $Pd_3(\mu\text{-}OH)(OAc)_5$, **10**. This labile equilibrium is rapidly established and can be shifted by addition of water and acetic acid or varying temperatures. The exchange of bridging acetate in trimer **1** by μ-OMe to form methoxo complex **2** under the action of methanol on a solution of **1** in chloroform occurs readily, and the exchange of

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the μ-OH ligand in **10** by a μ-OMe under the same conditions, slowly. The stability of methoxo complex **2** in chloroform is considerably higher than in methanol. It is necessary to take into account that methanol is the active reagent and can react along with other organic ligands when $Pd_3(OAc)_6$ is used as a precursor of homogeneous catalytic systems.

EXPERIMENTAL SECTION

General Considerations. The studies were carried out directly in NMR tubes with an outer diameter of 5 mm on Bruker AVANCE 600 spectrometer equipped with BCU05 temperature unit and HR Z-gradient coil in TBI (triple broadband inverse $^1H/^{13}C$/BB) and BBO (multinuclear broadband ^1H/BB) probeheads. ^1H and ^{13}C NMR spectra were measured at 600.13 and 150.90 MHz, respectively. For parameters of ^1H NMR measurements, see the Supporting Information. 2D-DOSY experiments were performed using standard pulse program *ledbpgp2s*, that is, stimulated echo sequence and LED (longitudinal eddy current delay) using bipolar gradient pulse pair and two spoiling gradients.[25] The gradient strength was changed from 2 to 95% with linear type of ramp.[14d] Diffusion time (big delta, Δ = 40−50 ms), sine shaped gradient pulse length (little delta, δ = 1.1−2.1 ms) and relaxation delay (D1 = 4−8 s) were employed.

Preparation of Solutions and NMR Measurements. Palladium diacetate **1** was prepared according to procedure of Dzhemilev.[26] Dried CH_3OH was used for preparation of solutions, commercial CD_3OD was distilled, and $CDCl_3$ (Aldrich) was used as received. Dissolution of weighed sample of palladium diacetate was carried out in 0.8 mL of corresponding solvent in an NMR tube at room temperature (25−30 °C) to complete disappearance of trimer crystals **1**. When using CH_3OH, about 10% CD_3OD was added. After mixing of the solution, the NMR tube was placed into the probehead preliminarily maintained at a certain temperature. The resolution in studied solutions was adjusted using the signal of acetic acid (methanolic solutions) or the residual proton signal in $CDCl_3$. Line width at half-height was $\nu_{1/2}$ = 0.5−1.2 Hz and $\nu_{1/2}$ = 0.5−0.7 Hz, respectively.

Solution ***A***. Palladium diacetate **1** (4 mg, 6.9 mmol) was dissolved in CD_3OD (concentration of Pd^{2+} = 22.3 mmol/L) in an argon-filled NMR tube. ^1H and ^{13}C NMR spectra were measured at 27 °C.

Solution ***B***. Palladium diacetate **1** (3.7 mg, 5.5 mmol) was dissolved in CH_3OH (concentration of Pd^{2+} = 20.6 mmol/L) in an argon-filled NMR tube. Proton spectra were measured at 27 °C.

Solution ***C***. Palladium diacetate **1** (0.8 mg, 1.2 mmol) was dissolved in CD_3OD (concentration of Pd^{2+} = 4.46 mmol/L) in a NMR tube without the prior filling with argon. ^1H and ^{13}C NMR spectra were measured at 0 and 27 °C.

Solution ***D***. Palladium diacetate **1** (12.3 mg, 18.3 mmol) was dissolved in CH_3OH (concentration of Pd^{2+} = 68.6 mmol/L) in an argon-filled NMR tube at 30 °C and intensive stirring during ≈15 min. Immediately after dissolution, the NMR tube with solution **D** was kept at temperature <0 °C. Spectral measurements were performed at −3 °C. Between measurements, the NMR tube was stored in the freezer at −18 °C. After three months of low temperature experiments, solution **D** periodically was kept at room temperature, as shown in Table 2, and proton spectra were measured at 27 °C.

Solution ***E***. Palladium diacetate **1** (11 mg, 16.4 mmol) was dissolved in $CDCl_3$ (concentration of Pd^{2+} = 61.4 mmol/L) in an argon-filled NMR tube. Spectral measurements were performed at 27 and −3 °C. Then, CH_3OH was added to solution **E** (molar ratio CH_3OH/Pd^{2+} ≈ 40:1), and its spectra were measured at −3 °C.

Solution ***F***. Palladium diacetate **1** (14.1 mg, 21.0 mmol) was dissolved in $CDCl_3$ (concentration of Pd^{2+} = 78.7 mmol/L) in an argon-filled NMR tube. Proton spectrum was measured at 27 °C, and then, one drop of water was added to solution **F**. After spectral measurements, the second drop of water was added.

Solution ***G***. Palladium diacetate **1** (9 mg, 13.4 mmol) was dissolved in $CDCl_3$ (concentration of Pd^{2+} = 50.2 mmol/L) in a NMR tube without prior filling with argon. ^1H NMR spectra were measured at 27, −3, −12 °C, and again at 27 °C. Then, several droplets of dilute solution of acetic acid in chloroform were added to solution **G**.

Solution ***H***. Palladium diacetate **1** (10 mg, 14.9 mmol) was dissolved in CH_3OH (concentration of Pd^{2+} = 55.8 mmol/L) in an argon-filled NMR tube at 30 °C and intensive stirring. After full dissolution, proton spectra were measured at 27 °C.

Calibration of the Spectra. Proton chemical shifts for solutions **A** and **C** (in CD_3OD) were measured relative to the residual proton signal of isotopomer CHD_2OD (quintet at δ 3.300). Chemical shifts of protons for solutions **B**, **D**, and **H** (a mixture of 90% CH_3OH + 10% CD_3OD) were measured relative to the middle of ^{13}C satellites of the Me signal in CH_3OH (δ 3.346 from TMS). Proton chemical shifts for solutions **E**, **F**, and **G** (in $CDCl_3$ and mixture $CDCl_3$ + CH_3OH) were measured relative to residual $CHCl_3$ (δ 7.250). ^{13}C chemical shifts were measured relative CD_3OD (δ 49.00) and $CDCl_3$ (δ 77.00). The 2D-DOSY spectra of methanolic solutions were calibrated along the logarithmic diffusion axis using the methanol signal, to which one value of the diffusion coefficient, log D = −8.7, was ascribed in all spectra (including those at different temperatures) for convenience of comparison. The log D value for methanol was determined in the 2D-DOSY spectrum (Supporting Information, Figure S27) of a mixture of four components: sucrose, isopropyl alcohol, methanol, and water (with an addition of D_2O).[14,15] The self-diffusion coefficient, log D = −8.6, was ascribed to the cross-peak of water in 2D-DOSY spectra of chloroform solutions containing dissolved water (Supporting Information, Figure S15).

Calibration of the Pulsed Field Gradient Strength. Calibration of gradient strength was performed[14d,27] on a signal of H_2O at 25 and 30 °C using standard Wilmad coaxial insert (cat. no. WGS-5BL, i.d. = 1.26 mm, o.d. = 2.02 mm, 60 μL). The following actual values were obtained: G = 55.6 G/cm for TBI and G = 53.5 G/cm for BBO probeheads.

ASSOCIATED CONTENT

Supporting Information. ^1H NMR spectra of solutions **A**−**H**; ^{13}C NMR spectra of solutions **C**−**E**; 2D-HSQC spectra of solutions **D** and **E**; 2D-DOSY spectra; accuracy of proton chemical shifts measurements; and parameters of ^1H NMR measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2002. (b) Malleron, J.-L.; Fiad, J.-C.; Legros, J.-Y. *Handbook of Palladium Catalyzed Organic Reactions*; Academy Press: San Diego, CA, 1997; p 304. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147–1169.

(2) (a) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658–659. (b) Lyalina, N. N.; Dargina, S. V.; Sobolev, A. N.; Buslaeva, T. M.; Romm, I. P. *Koord. Khim.* **1993**, *19*, 57–63. (c) Kirik, S. D.; Mulagaleev, R. F.; Blokhin, A. I. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2004**, *C60*, m449–m450. (d) Cotton, F. A.; Han, S. *Rev. Chim. Miner.* **1985**, *22*, 277–284.

(3) (a) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem Soc.* **1965**, 3632–3640. (b) Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1974**, *52*, 1241–1247.

(4) Romm, I. P.; Buslaeva, T. M.; Lyalina, N. N.; Shifrina, R. R.; Sinitsyn, N. M. *Koord. Khim.* **1992**, *18*, 165–170.

(5) Zagorodnikov, V. P.; Ryabov, A. D.; Yatsimirskii, A. K. *Kinet. Katal.* **1981**, *22*, 132–138.

(6) Mulagaleev, R. F.; Kirik, S. D.; Golovnev, N. N. *J. Sib. Fed. Univ. Chem.* **2008**, *3*, 249–259.

(7) Yatsimirskii, A. K.; Ryabov, A. D. *Zh. Neorg. Khim.* **1977**, *22*, 1863–1867.

(8) Stoyanov, E. S. *J. Struct. Chem.* **2000**, *41*, 440–446.

(9) Marson, A.; van Oort, A. B.; Mul, W. P. *Eur. J. Inorg. Chem.* **2002**, 3028–3031.

(10) Bakhmutov, V. I.; Berry, J. F.; Cotton, F. A.; Ibragimov, S.; Murillo, C. A. *Dalton Trans.* **2005**, 1989–1992.

(11) Bianchini, C.; Meli, A.; Oberhauser, W. *Organometallics* **2003**, *22*, 4281–4285.

(12) Khabibulin, V. R.; Kulik, A. V.; Oshanina, I. V.; Bruk, L. G.; Temkin, O. N.; Nosova, V. M.; Ustynyuk, Yu. A.; Bel'skii, V. K.; Stash, A. I.; Lysenko, K. A.; Antipin, M. Yu. *Kinet. Catal.* **2007**, *48*, 228–244.

(13) (a) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301–315. (b) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565–569.

(14) (a) Johnson, C. S., Jr. *Prog. NMR Spectrosc.* **1999**, *34*, 203−256, and references therein. (b) Pregosin, P. S. *Prog. NMR Spectrosc.* **2006**, *49*, 261−288, and references therein. (c) Berger, S.; Braun, S. *200 and More NMR Experiments*; Wiley-VCH Verlag, GmbH&Co. KgaA: Weinheim, Germany, 2004; p 515. (d) Kerssebaum, R. DOSY and Diffusion by NMR. In *Users Guide for XWinNMR 3.5, Version 1.0*; Bruker BioSpin GmbH: Rheinstetten, Germany, 2002.

(15) (a) Gostan, T.; Brun, E.; Tramesel, D.; Prigent, Y.; Delsuc, M.-A.; Guigas, B. *Bruker Rep.* **2004**, *154/155*, 18. (b) Holz, M.; Sacco A. *Almanac, Bruker BioSpin* **2008**, 80.

(16) Breitmaier, E.; Haas, G.; Voelter, W. *Atlas of Carbon-13 NMR Data*; Hyden & Son Ltd. GmbH: Münsterstrasse, 22, West Germany, 1979; Vol. 1, compound 323−325.

(17) Saito, T.; Hayamizu, K.; Yanagisawa, M.; Yamamoto, O. *NMR in Spectral Database for Organic Compounds, SDBS*; National Institute of Advanced Industrial Science and Technology (AIST): Tokyo, Japan; (www.aist.go.jp, http://riodb01.ibase.aist.go.jp/sdbs/).

(18) (a) Vicente, J.; Lagunas, M. C.; Bleuel, E.; Ramirez de Arellano, M. C. *J. Organomet. Chem.* **2002**, *648*, 62–71. (b) Van den Beuken, E. K.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *Organometallics* **1998**, *17*, 636–644. (c) Vicente, J.; Saura-Llamas, I.; Cuadrado, J.; Ramirez de Arellano, M. C. *Organometallics* **2003**, *22*, 5513–5317. (d) Bauer, W.; Prem, M.; Polborn, K.; Sünkel, K.; Steglich, W.; Beck, W. *Eur. J. Inorg. Chem.* **1998**, 485–493.

(19) Babushkin, D. E.; Talsi, E. P. *J. Mol. Catal. A: Chem.* **1998**, *130*, 131–137.

(20) Kozitsyna, N. Yu.; Moiseev, I. I. *Usp. Khim.* **1995**, *64*, 51–65.

(21) (a) Potekhin, V. V.; Matsura, V. A. *Izv. Akad. Nauk SSSR. Ser. Khim.* **2006**, 627–632. (b) Potekhin, V. V.; Solov'eva, S. N.; Potekhin, V. M. *Izv. Akad. Nauk SSSR. Ser. Khim.* **2003**, 2525–2530.

(22) Ebitani, K.; Choi, K.-Min.; Mizugaki, T.; Kaneda, K. *Langmuir* **2002**, *18*, 1849–1885.

(23) (a) Driver, M. S.; Hartwig, J. F. *Organometallics* **1997**, *16*, 5706–5715. (b) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890–1901. (c) Ruiz, J.; Rodriguez, V.; Lopez, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1997**, 4271–4276. (d) Ruiz, J.; Rodriguez, V.; Vicente, C.; Lopez, G. *Transition Met. Chem.* **1997**, *22*, 502–506. (e) Sanchez, G.; Sanmartin, A.; Garcia, J.; Lopez, G. *Transition Met. Chem.* **1997**, *22*, 545–548. (f) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450–5458.

(24) (a) Summer, C. E., Jr.; Steinmetz, G. R. *Inorg. Chem.* **1989**, *28*, 4290–4294. (b) Summer, C. E., Jr. *Inorg. Chem.* **1988**, *27*, 1320–1327. (c) Summer, C. E., Jr.; Steinmetz, G. R. *J. Am. Chem. Soc.* **1985**, *107*, 6124–6126.

(25) Wu, D.; Chen, A.; Johnson, C. S., Jr. *J. Magn. Reson., Ser. A* **1995**, *115*, 260–264.

(26) *Metallocomplex Catalysis in Organic Synthesis. Acyclic Compounds*; Dzhemilev, U. M., Popod'ko, N. P., Kozlova, E. V., Eds.; Khimiya: Moscow, Russia, 1999; p 100.

(27) (a) Brand, T.; Cabrita, E. J.; Berger, S. *Prog. NMR Spectrosc.* **2005**, *46*, 159–196. (b) Connell, M. A.; Bowyer, P. J.; Bone, P. A.; Davis, A. L.; Swanson, A. G.; Nilsson, M.; Morris, G. A. *J. Magn. Reson.* **2009**, *198*, 121–131.