

Unexpected Participation of Nucleophiles in the Reaction of Palladium(II) Acetate with Divalent 3d Metals¹

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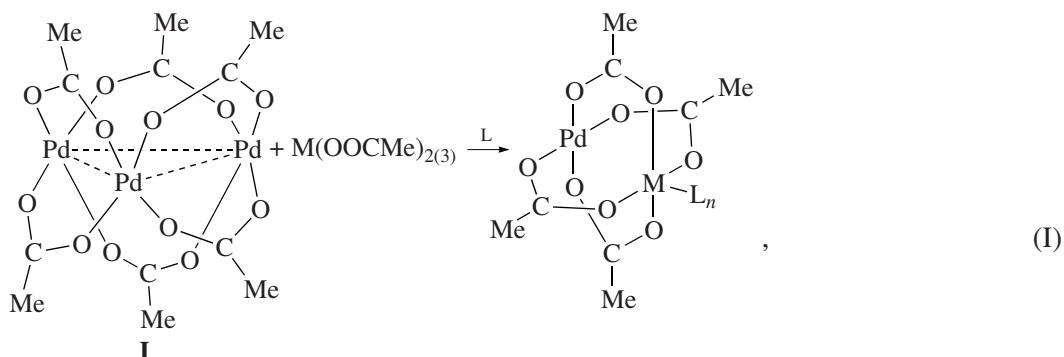
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Abstract—The kinetics of reactions of palladium(II) acetate with cobalt(II), nickel(II), and copper(II) acetates were studied by spectrophotometry. These reactions produce heterobimetallic complexes $Pd^{II}(\mu-OOCMe)_4M^{II}(OH_2)(HOOCMe)_2$, where $M = Co, Ni$, or Cu . These reactions are very slow in carefully dehydrated ($<0.01\% H_2O$) acetic acid, but are considerably enhanced by water or acetonitrile. Our data indicate that the activation of the kinetically inert ring structure of the initial palladium complex $Pd_3(\mu-OOCMe)_6$ by means of the nucleophilic attack of an H_2O or acetonitrile molecule is the key step of the reaction mechanism.

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Heterometallic coordination compounds of palladium(II) are of both fundamental and practical importance as suitable precursors for both heterometallic nanomaterials [1, 2] and catalysts [2–4]. The literature concerning such complexes is scarce. Recently [5–8],

we synthesized and structurally characterized the first heterobimetallic acetate complexes of palladium(II) with divalent 3d transition metals, trivalent 4f rare-earth metals, and 4s–6s divalent alkaline-earth metals with lantern structures:



$M = Co^{II}, Ni^{II}, Mn^{II}, Cu^{II}, Zn^{II}; L_n = OH_2, NCMe, HOOCMe;$

$M = Nd^{III}, Sm^{III}, Eu^{III}; L_n = OOCMe^-, OH_2, THF;$

$M = Ca^{II}, Sr^{II}, Ba^{II}; L_n = (HOOCMe)_4.$

Reductive thermolysis easily converts these complexes to nanosized intermetallic compounds or alloys [9, 10].

Reaction (I) occurs with high yields (up to 95%) when palladium(II) acetate $Pd_3(\mu-OOCMe)_6$ (complex I) is heated with proper metal acetates in glacial acetic acid. Optimizing the synthesis, we unexpectedly discovered that the reaction is very slow in carefully dehydrated acetic acid ($<0.01\% H_2O$) but is considerably enhanced by even minor water or acetonitrile amounts.

This work studies the kinetics of the reaction of $Pd_3(\mu-OOCMe)_6$ with 3d-metal acetates, namely, $Co(OOCMe)_2$ (II), $Ni(OOCMe)_2$ (III), and $Cu(OOCMe)_2$ (IV), in acetic acid containing controlled additives of a nucleophilic agent (water, acetonitrile, or tetrahydrofuran).

EXPERIMENTAL

Palladium acetate $Pd_3(OOCMe)_6$ was prepared by oxidizing palladium black with nitric acid in glacial acetic acid as described in [11]; palladium black was

¹ To the 80 birthday of Academician I.I. Moiseev.

prepared by the reduction of PdCl_2 (reagent grade, from Reakhim) with sodium borohydride. Then, palladium acetate was repeatedly boiled in glacial acetic acid in the presence of fresh palladium black portions until NO_2 evolution ceased to free it from nitrito complexes and recrystallized from acetic acid. 3d-Metal acetates ($\text{Co}(\text{OOCMe})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OOCMe})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Cu}(\text{OOCMe})_2 \cdot 2\text{H}_2\text{O}$, all of reagent grade, purchased from Acros) were used as received. Commercially available acetic acid (reagent grade glacial acetic acid from Reakhim), which contained 1.3% (0.72 mol/l) water, was purified before use by freezing and boiling with triacetyl borate followed by fractional distillation. Water concentration in purified acetic acid was $\leq 0.07\%$ (0.04 mol/l) as determined by GLC. The dopants used were bidistilled water, acetonitrile, and tetrahydrofuran. Tetrahydrofuran (reagent grade, from Reakhim) was purified by boiling with sodium benzophenone ketyl in flowing argon using a routine procedure [12] and stored in a refrigerator under argon. Acetonitrile (a high purity grade sample from Merck) was used as received.

Water, acetonitrile, or tetrahydrofuran was added to purified acetic acid gravimetrically and monitored by GLC on an Agilent 5973 chromatograph/mass spectrometer (quartz capillary column HP-50, 70-eV ionization energy). UV-Vis absorption spectra of solutions were recorded on a Cary 50 spectrophotometer in a quartz cell 10 \times 10 mm, where temperature was maintained at (50–80) \pm 0.1°C with a standard Peltier thermostat, while stirring with a built-in magnetic stirrer.

A representative kinetic experiment was carried out as follows. Weighed samples of complex **I** (2.02 mg, 0.3 mmol as palladium atoms) and complex **II**, **III**, or **IV** (0.9 mmol) were each dissolved in acetic acid (5 ml) and kept for 5 min in separate thermostats. Thermostated solutions of complex **I** and complexes **II**–**IV** (1 ml each) were transferred to the spectrophotometer cell, and then the change in absorption intensity was measured over time at the working wavelength ($\lambda = 325$, 334, and 356 nm for the reaction with complex **II**, **III**, and **IV**, respectively) using the Kinetics program of the Cary WinUV package (v. 3.0). Primary rate curves were processed using the OriginPro 7.0 program.

RESULTS AND DISCUSSION

The solution changes color in reaction (I), and electronic spectra offer a convenient means for monitoring this reaction. The concentrations of complexes **I**–**IV** in the kinetic experiments were at a level of 10^{-3} mol/l, and the absorption of the working solutions within 280–700 nm was initially very low. As the reaction progressed, a strong band associated with the heterometallic complex appeared and increased in intensity over time. New bands that appeared after the reaction was over practically coincided in position and intensity with bands observed in the UV spectra of acetic acid solutions of heterometallic complexes $\text{Pd}(\mu\text{-OOCMe})_2\text{M}(\text{OH}_2)(\text{HOOCMe})_2$, where $\text{M} = \text{Co}$ (complex **V**), Ni (complex **VI**), and Cu (complex **VII**), that were prepared by independent synthesis under the same conditions [13]: $\epsilon^{334} = 1337\text{ l}(\text{mol cm})^{-1}$ for complex **V**, $\epsilon^{325} = 1295$ and $\epsilon^{280} = 1345\text{ l}(\text{mol cm})^{-1}$ for complex **VI**, and $\epsilon^{356} = 1163\text{ l}(\text{mol cm})^{-1}$ for complex **VII**.

Coefficients in Eq. (1) for reaction (I) in the presence of water

3d metal (M)	$k_{\text{eff}}, \text{l}^2 \text{mol}^{-2} \text{min}^{-1}$	$\beta \times 10^{-3}, \text{l/mol}$
Ni	0.625 ± 0.050	2.8 ± 0.2
Co	1.00 ± 0.05	33.7 ± 2.0
Cu	2.50 ± 0.10	3.74 ± 0.20

$\text{OOCMe})_4\text{M}(\text{OH}_2)(\text{HOOCMe})_2$, where $\text{M} = \text{Co}$ (complex **V**), Ni (complex **VI**), and Cu (complex **VII**), that were prepared by independent synthesis under the same conditions [13]: $\epsilon^{334} = 1337\text{ l}(\text{mol cm})^{-1}$ for complex **V**, $\epsilon^{325} = 1295$ and $\epsilon^{280} = 1345\text{ l}(\text{mol cm})^{-1}$ for complex **VI**, and $\epsilon^{356} = 1163\text{ l}(\text{mol cm})^{-1}$ for complex **VII**.

Accumulation curves for complexes **V**–**VII** plotted on the basis of the above data with account for the extinction coefficients of the reagent and product complexes at the working wavelength are exponential up to ~ 60 –80% conversions for the cobalt complex and $\sim 95\%$ conversions for the nickel and copper complexes. At higher conversions, the product accumulation curves have a more intricate trends (for unclear reasons), and we used initial rates in formal data processing.

Our data show that, in the presence of 0.2–0.5 mol/l water, the rate of reaction (I) increases in proportion to the palladium(II) acetate concentration (Fig. 1a); the reaction rate as a function of concentration of the added metal is a curve with a plateau (Fig. 1b) and is well linearized in the coordinates of the Michaelis–Menten equation (Fig. 1c).

The reaction rate increases linearly with increasing water concentration (within 0.04–2.10 mol/l) or acetonitrile concentration (within 0.01–0.40 mol/l) but is practically independent of tetrahydrofuran concentration up to 0.62 mol/l (Fig. 2).

Thus, in the presence of water at 80°C, the rate equation is

$$w_0 = k_{\text{eff}} \frac{[\text{I}]_0[\text{M}]_0[\text{H}_2\text{O}]_0}{1 + \beta[\text{M}]_0}. \quad (1)$$

The relevant coefficients are indicated in the table.

For discussing the mechanisms of reactions of coordination compounds in solution, one needs to know not only the kinetics and structure of solid complexes but also the state of these complexes in solution. As opposed to a rich literature on aqueous species of palladium(II) complexes, data on anhydrous media, such as acetic acid, are scarce. However, for two participants of reaction (I), namely, cobalt(II) and palladium(II) acetates, such data exist.

After Hendriks et al. [14], for example, cobalt(II) acetate in anhydrous acetic acid mostly occurs as $\text{Co}(\text{OOCMe})_2(\text{HOOCMe})_4$ octahedral complex molecules. When water is added, coordinated acetic acid molecules are consecutively replaced by OH_2 ligands. Unlike this, trinuclear palladium(II) acetate, in which palladium(II) atoms are strongly bound by three pairs

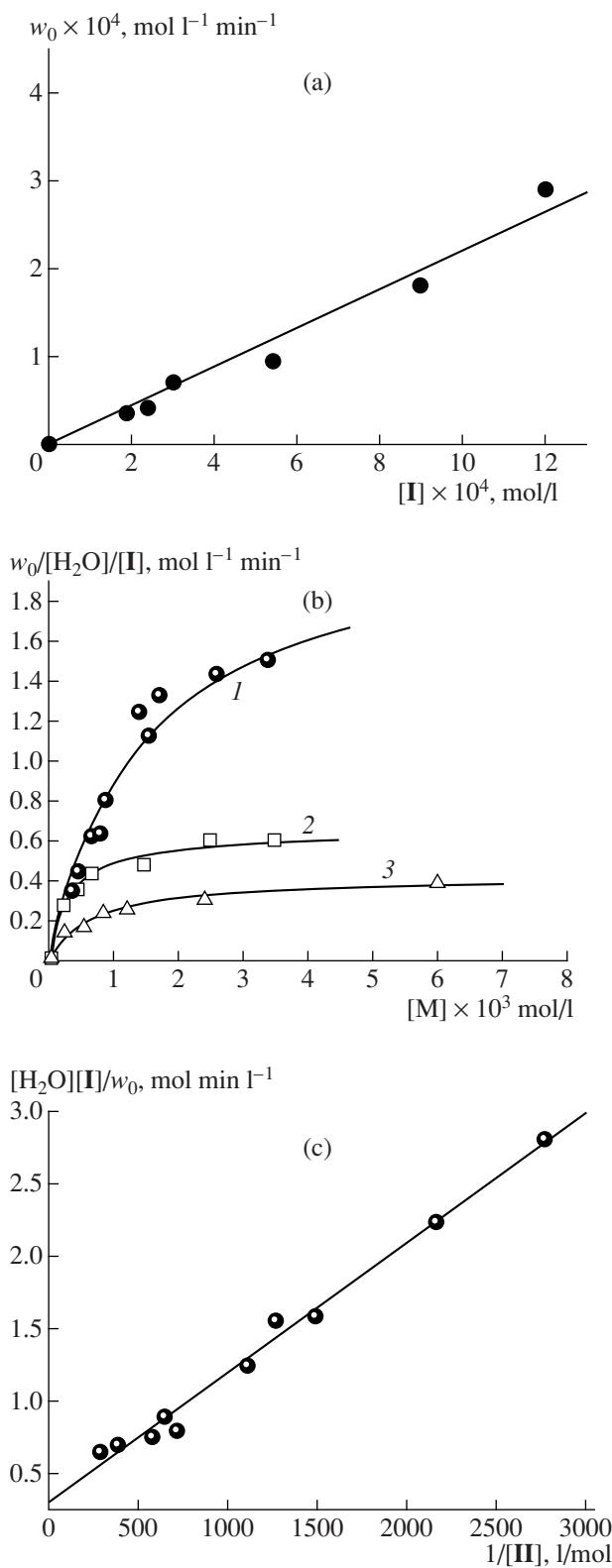


Fig. 1. Panel (a): the reaction rate of palladium(II) acetate **I** with cobalt acetate **II** vs. concentration of complex **II**. Panel (b): the same vs. concentration of 3d-metal acetate (1) **II**, (2) **IV**, and (3) **III**. Panel (c): the rate of reaction **I** + **II** vs. concentration of complex **II** in the coordinates of the Michaelis-Menten equation. Acetic acid contains 0.29 mol/l H₂O. T = 80°C.

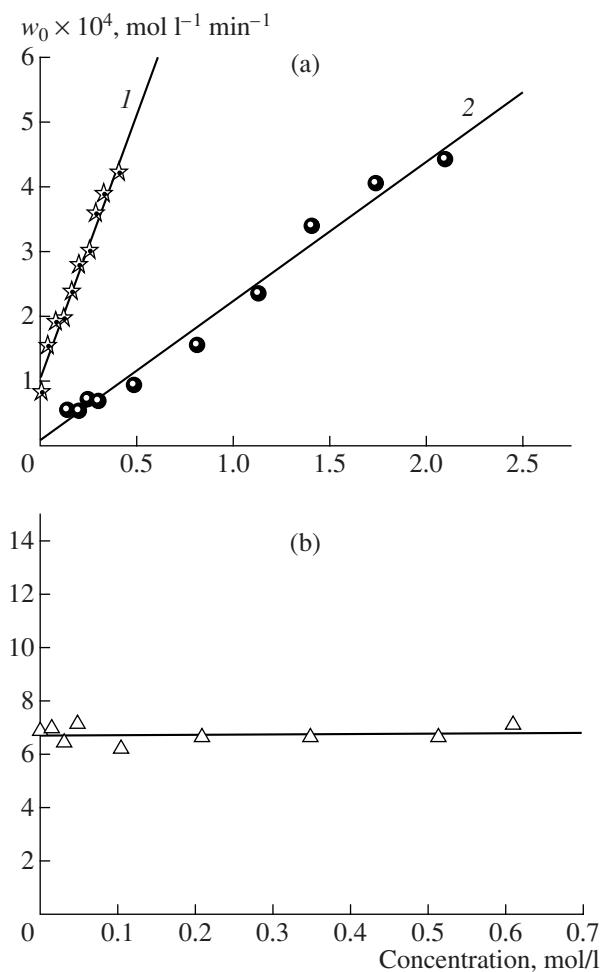


Fig. 2. Reaction rate of palladium(II) acetate **I** with cobalt acetate **II** (a) vs. (1) acetonitrile and (2) water concentration at 80°C and (b) vs. tetrahydrofuran concentration at 60°C. $[I]_0 = 3 \times 10^{-4}$ mol/l, $[II]_0 = 9 \times 10^{-4}$ mol/l.

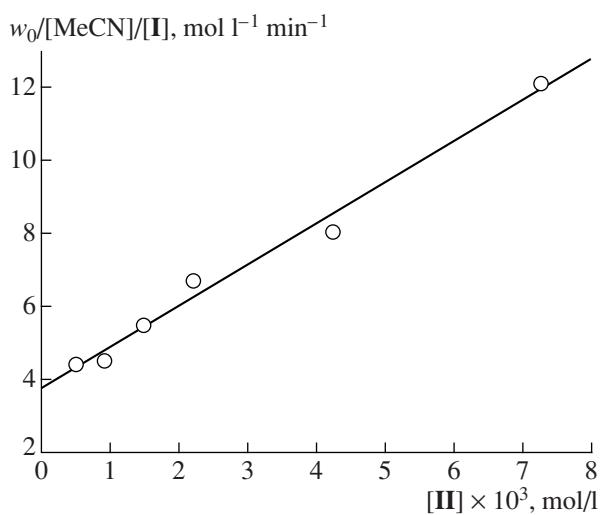
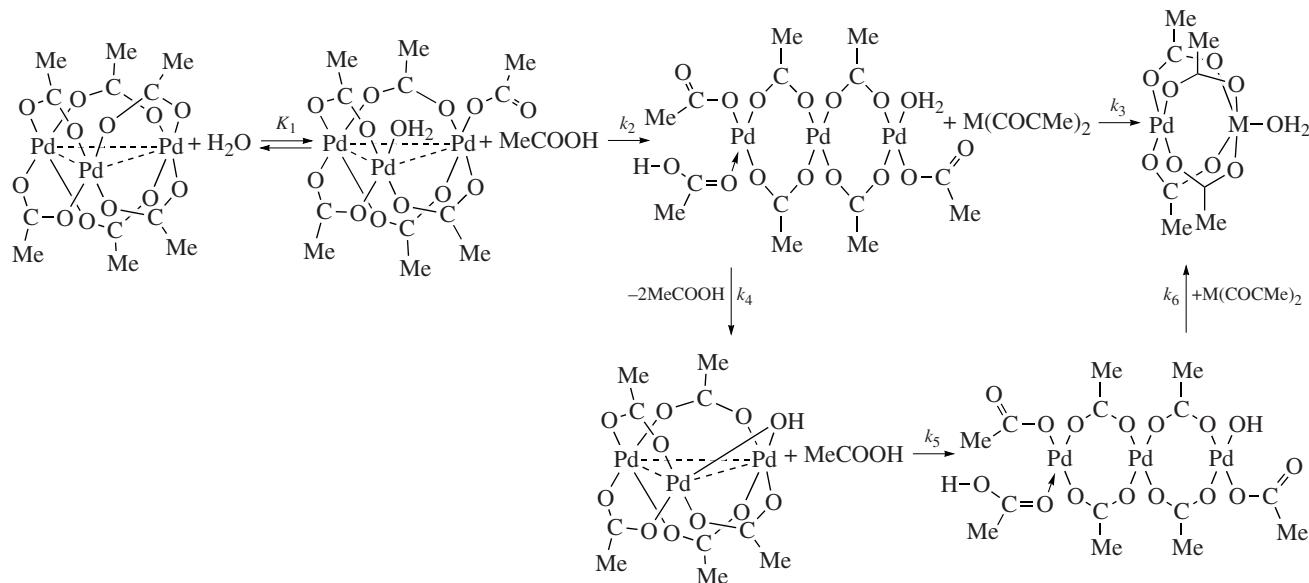


Fig. 3. Reaction rate of palladium(II) acetate **I** with cobalt acetate **II** vs. concentration of complex **II** in acetic acid containing 0.21 mol/l MeCN and 0.03 mol/l H₂O at 80°C. $[I]_0 = 3 \times 10^{-4}$ mol/l.

of acetate bridges, retains its structure in most organic solvents; thus, it has a low reactivity and needs to be activated to enter reaction (I). Bakhmutov et al. [15] have recently discovered such a process by NMR; they demonstrated that, in organic solvents (such as chloroform and benzene) containing even minor water amounts, at least one acetate bridge in a $\text{Pd}_3(\mu\text{-OOCMe})_6$ molecule is subject to hydrolytic dissociation. One of the six bridging acetate groups becomes a

monodentate ligand, and an H_2O molecule occupies the newly appeared coordination vacancy.

If such a hydrolytic dissociation occurs in the reaction system under study, it will enhance the opening of the three-membered ring and subsequent chemical transformations of palladium(II) acetate. If so, our determined rate laws (the first orders of the reaction in complex **I** and H_2O and the Michaelis dependence of the reaction rate on the 3d-metal concentration) are reasonably explained in terms of the kinetic scheme below.



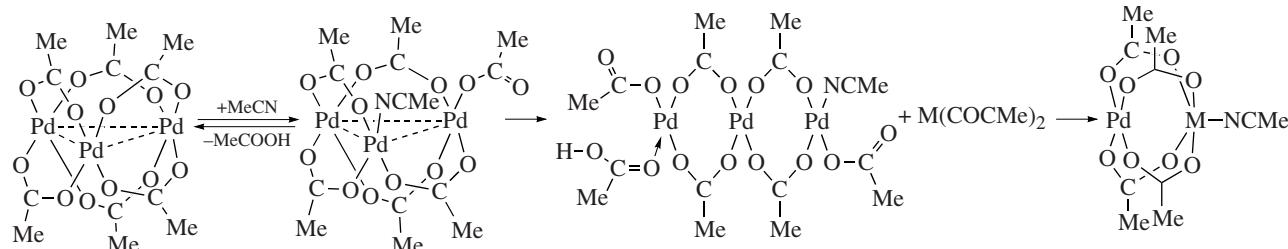
Scheme 1.

For this scheme, the coefficients of Eq. (1) have the following meaning: $k_{\text{eff}} = K_1 \frac{k_2 k_3}{k_4}$ and $\beta = \frac{k_3}{k_4}$.

Presumably, other nucleophilic reagents can also enhance the reaction of complex **I** with 3d-metal acetates. Acetonitrile considerably increases the rate of reaction (I) (Fig. 2a). Acetonitrile is a sufficiently strong nucleophile and, likely, also capable of breaking

the carboxylate bridge in molecule **I**. Our experiments demonstrated that, where even minor amounts of acetonitrile are present, the reaction rate is no longer the Michaelis function of 3d-metal acetate concentration; rather, it becomes linear (Fig. 3).

In this case, both the rate equation (first orders in both reagents and acetonitrile) and the reaction mechanism are simpler (Scheme 2).



Scheme 2.

The MeCN axial ligand at the 3d metal being readily exchangeable for H_2O in the presence of even minor water amounts, the composition of the

resulting complex is dictated by the solvent composition during the release and crystallization of the reaction product.

Unexpectedly, tetrahydrofuran, unlike acetonitrile, virtually does not influence the rate of reaction (I) (Fig. 2b). This fact can be explained as follows: the nucleophilic attack of a tetrahydrofuran molecule on complex **I** is inefficient because of the far larger molecular size of this reagent compared to H₂O or MeCN and the associated steric hindrances.

ACKNOWLEDGMENTS

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