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New palladium nanoclusters. Synthesis, structure, and catalytic properties*

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The reduction of palladium(II) carboxylates $Pd_3(OCOR)_6$ (R = Me, Et, $CHMe_2$, CMe_3) with hydrogen in alcohol solutions containing 1,10-phenanthroline (phen) and subsequent oxidation with oxygen gave new palladium nanoclusters, mainly particles with a nearly spherical metal core and an average size of 18 Å. Based on elemental analysis, NMR, X-ray photoelectron spectroscopy, and EXAFS, nanoclusters were described by the idealized formula $Pd_{147}phen_{32}O_{60}(OCOR)_{30}$. The specimens contained up to ~25% smaller 55-atomic Pd clusters with a ~10 Å metal core. New nanoclusters catalyze hydrogenation of alkynes and alkenes, reduction of nitriles with formic acid, oxidation of aliphatic and benzylic alcohols, oxidative esterification of ethylene and propylene, and disproportionation of benzyl alcohol into toluene and benzaldehyde.

Key words: palladium, nanoclusters, synthesis, catalytic properties.

Previously,[1,2] we obtained giant palladium clusters with the idealized formula $Pd_{561}L_{60}(OAc)_{180}$ (**1**, L is 1,10-phenanthroline (phen); **2**, L is 2,2´-dipyridine (dipy)) by the reduction of palladium(II) acetate $Pd_3(OAc)_6$ with gaseous H_2 in acetic acid in the presence of chelating heteroaromatic ligands L (phen or dipy) and subsequent treatment with oxygen. Clusters **1** and **2** efficiently catalyze diverse liquid-phase reactions of organic compounds (alkenes, alkyarenes, alcohols, *etc.*) under mild conditions (20—60 °C, 1 atm).[3]

The OAc^- ligands are readily replaced by other X^- anions (PF_6^-, O^{2-}, BF_4^-, CF_3COO^-, *etc.*) upon treatment with the corresponding salts or acids.[3—6] This produces no change in the $[Pd_{561}L_{60}]^{180+}$ metal core but a rearrangement of the icosahedral packing mode of metal atoms to a cubooctahedral one.[7]

We found that the reduction of $Pd_3(OAc)_6$ and its analogs in lower aliphatic alcohols can be used to prepare nanoclusters with a much smaller metal core in high yields. This communication describes the synthesis of new palladium nanoclusters by the reduction of palladium(II) carboxylates $Pd_3(OCOR)_6$ (R = Me, Et, Pr^i, Bu^t) with hydrogen followed by treatment with oxygen in alcohol solutions (MeOH, EtOH, or Pr^iOH). The chemical composition, morphology, some structural characteristics, and the catalytic properties of the new clusrers were studied.

Experimental

Solvents and reagents. *n*-Pentane, *n*-hexane, and benzene (all analytically pure grade) were purified by standard procedures.[8] Diethyl ether (OST 84-2006-88) was kept over solid KOH, passed through Al_2O_3, and distilled under argon. Ethanol (rectified, 96%), propionic and trimethylacetic acids (Merck, Germany), and glacial acetic acid (chemically pure grade) were used as received.

Benzyl alcohol (analytically pure grade) and cyclohexene (pure) were purified by fractional distillation under argon. α-Methylbenzyl alcohol was prepared by a known procedure.[9] *o*-Phenanthroline monohydrate $C_{12}H_8N_2 \cdot H_2O$ (analytically pure grade) was recrystallized from benzene to give an anhydrous specimen. To remove nitrate and nitrite impurities, palladium(II) acetate (pure grade, TU 6-09-40-2472-87) was refluxed with freshly prepared Pd black in glacial AcOH until evolution of nitrogen oxides ceased and recrystallized from the same solvent. Palladium(II) propionate, isobutyrate, and pivalate were prepared from the acetate $Pd_3(OAc)_6$ by ligand exchange with the corresponding acids. The giant $Pd_{561}phen_{60}(OAc)_{180}$ cluster was synthesized from $Pd_3(OAc)_6$ and *o*-phenanthroline in AcOH using a previously described procedure.[3] The 10% Pd/C catalyst was prepared by a known procedure.[10]

Synthesis of the cluster Pd-147. $Pd_3(OCOBu^t)_6$ (0.772 g, 2.5 mmol) and *o*-phenanthroline (0.2253 g, 1.25 mmol) in 60 mL of 96% EtOH were placed in a 250-mL three-necked flask connected to two 100-mL gas burettes (one filled with H_2 and the other filled with air or O_2), and the mixture was magnetically stirred at ~20 °C. The flask with the suspension was evacuated,

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filled with gaseous H_2, and saturated with hydrogen from a gas burette with intense stirring. The absorption of H_2 was first slow and then it substantially accelerated, and the reaction mixture turned black. After 85—90 mL of H_2 (1.4—1.5 mol per mol of Pd) had been absorbed, stirring was stopped and the flask was evacuated and filled with air or O_2. The solution was poured in 240 mL of Et_2O and the black precipitate was separated by centrifugation at 3000 rpm, washed with ether (3×50 mL, centrifugation), and dried *in vacuo*. The yield of the Pd-147 nanocluster was 0.34 g (64% based on Pd). The Pd-147 clusters containing other ligands (MeCOO, EtCOO, and Pr^iCOO) were prepared in a similar way starting from the corresponding palladium(II) salt.*

Catalytic experiments were carried out under static conditions. A 5-mL two-necked flask provided with a jacket for circulating a thermostating liquid, equipped with a magnetic stirrer and a sampler, and connected to a 100 mL gas burette was used as the reactor. In a typical experiment, the reactor was charged with 3 mL of the solvent, 5—30 mg of the cluster or 15 mg of Pd/C, and 50 mg of a substrate. The experiments were carried out at temperatures of 20 to 70 °C. To monitor the course of the reactions, samples of the reaction solution were taken out at certain intervals with a 1-μL microsyringe and analyzed by GLC. The reaction products were identified by GC/MS analysis.

Methods of analysis. The elemental C,H,N-analysis of the complexes was carried out on a Carlo Erba Strumenzione automated C,H,N-analyzer (Italy). The palladium content in the complexes was determined by gravimetry after calcination at 900 °C.

The GC/MS analysis of the reaction products was carried out on an Automass 150 instrument (Delsi Nermag, France), and GLC analysis was done on a Varian 3600 chromatograph (USA) (OV-1 universal capillary column). NMR spectra were recorded on a Bruker WP-200 spectrometer, and IR spectra were measured on a Specord M80 instrument (Carl Zeiss, Jena) in KBr pellets. The electron micrographs of the nanoclusters were obtained on a Jeol JEM 2010 electron microscope (Japan) in the transmission mode with a magnification of $(0.5—2.0) \cdot 10^6$ using the lowest electron beam current (≤10 μA) to minimize heating of the sample during recording. The samples were prepared by deposition of a solution of the cluster on an amorphous carbon support with a standard copper grid. The palladium K-edge EXAFS spectra were recorded on an EXAFS spectrometer at the Siberian Center for the Synchrotron Radiation (Novosibirsk) in the transmission mode, at an electron energy in the storage ring of 2 GeV, and an average current of 80 mA. The oscillating part of the X-ray photoelectron spectrum was extracted using the VIPER program.[11] The spectra were processed according to the EXCURV92 program.[12] X-Ray photoelectron spectra were recorded on a photoelectron analyzer included in a Riber LAS 3000 instrument set (France).

Results and Discussion

Synthesis of nanoclusters

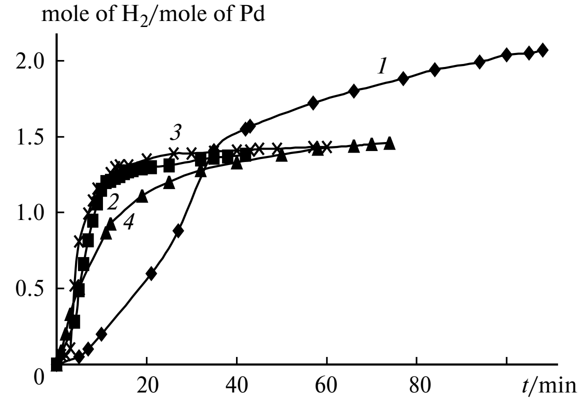

Fig. 1. Curves for H_2 absorption during the reduction of palladium(II) carboxylates $Pd_3(OCOR)_6$ (R = Bu^t (*1*), Me (*2*), Et (*3*), Pr^i (4)) in the presence of 1,10-phenanthroline in EtOH.

When palladium carboxylates $Pd_3(OCOR)_6$ (ROCO is acetate (R = Me), propionate (R = Et), isobutyrate (R = Pr^i), trimethylacetate (R = Bu^t)) react with gaseous H_2 in alcohol solutions containing 1,10-phenanthroline with an initial Pd^{II} : phen ratio from 1 : 1 to 0.25 : 1, the solution acquires a dark brown color but remains homogeneous, and the amount of absorbed H_2 markedly exceeds 1 mole per mole of Pd (Fig. 1), *i.e.*, the value needed to reduce Pd^{II} to Pd^0 according to the reaction

$$Pd_3(OCOR)_6 + 3\ H_2 = 3\ Pd^0 + 6\ RCOOH. \qquad (1)$$

This implies that the reaction of phenanthroline carboxylate complexes of palladium(II) with H_2 is not limited to the reduction of Pd^{II} to Pd^0 but is accompanied by the formation of hydride complexes of low-valence palladium, similar to the polynuclear hydride complexes $[Pd_4phen(OAc)_2H_x]_n$ ($n \approx 100$), detected previously[13] upon the reduction of $Pd_3(OAc)_6$ with hydrogen in AcOH. The reaction rates and the amounts of absorbed hydrogen are different for different carboxylates (see Fig. 1).

On contact with air or O_2, oxygen absorption (Fig. 2) and oxidation of the hydride complexes take place; during this period, the solution remains homogeneous and the dark-brown, nearly black color virtually does not change. The amount of absorbed oxygen markedly exceeds that necessary for oxidation of all the hydride ligands

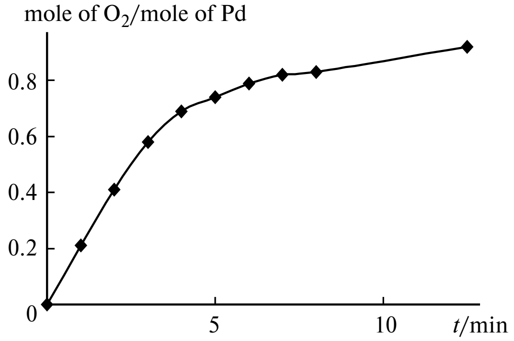

Fig. 2. Curve for O_2 absorption by a $Pd_3(OAc)_6$—phen (2 : 1) solution in EtOH after preliminary treatment with hydrogen.

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* The H_2 absorption during the synthesis should not exceed 1.5 moles per mole of Pd; when 2 moles per mole of Pd are absorbed, the yields of nanoclusters sharply decrease.

Table 1. Elemental analysis data for phenanthroline-containing nanoclusters prepared from $Pd_3(OAc)_6$ and $Pd_3(OCOBu^t)_6$ in EtOH at different ratios of component concentrations ($[phen]_0 : [Pd]_0$)

Starting complex	Experiment					Calculation			
	$[phen]_0 : [Pd]_0$	Found (%)				Calculated (%)			
		Pd	C	N	H	Pd	C	N	H
$Pd_3(OAc)_6$	1	44.16	33.29	6.13	1.27	$Pd_{561}phen_{60}(OAc)_{180}$			
	0.75	50.15	28.73	5.10	0.90	73.59	15.99	2.07	1.26
	0.50	59.20	23.61	4.19	0.51	$Pd_{147}phen_{32}(OAc)_{30}O_{60}$			
	0.25	69.95	17.55	3.73	0.14	64.80	19.34	3.71	1.43
$Pd_3(OCOBu^t)_6$	1.25	40.20	34.56	5.29	2.25	$Pd_{147}phen_{32}(OCOBu^t)_{30}O_{60}$			
	0.75	50.75	27.98	4.58	1.66	61.58	25.23	3.53	2.07
	0.50	56.03	24.67	4.23	1.37				
	0.25	61.67	21.06	3.83	1.05				

(and/or coordinated molecular hydrogen) to give water. According to GLC analysis, some of the oxygen is consumed for palladium-catalyzed oxidation of the solvent (EtOH) to acetaldehyde.

Upon the addition of nonpolar solvents (Et_2O, 1,4-dioxane), the Pd nanoclusters thus formed precipitate, and the precipitate is separated by centrifugation. The elemental composition of the resulting black amorphous powder changes depending on the initial Pd : phen ratio, the nature of the carboxylate ligand, and the amount of H_2 absorbed at the first stage of the synthesis.

According to elemental analysis data (Table 1), the content of palladium in any of the obtained specimens is substantially lower, while that of organic ligands is much higher than those in the giant Pd-561 clusters obtained previously.

The radial distribution curves of atoms calculated from the EXAFS data show one palladium—light atom interatomic distance (2.01 Å) and only one metal—metal interatomic distance (2.70 Å), which virtually coincides with the Pd—Pd distance in the bulk metal and in the Pd-561 clusters with the close-packed metal core.[4] This provides the conclusion that the specimens obtained are characterized by close packing of palladium atoms whose oxidation state is close to zero.

High-resolution transmission electron microscopy showed that the specimens contain metal particles of nearly spherical shape (Fig. 3). The distribution curves of particles over the metal core sizes have two local maxima at ~10 and ~18 Å (Fig. 4).

On the basis of close packing of metal atoms and the Pd—Pd interatomic distance (2.70 Å), one can estimate the numbers of palladium atoms in the metal core of the cluster particles corresponding to both maxima in the size distribution curve (see Fig. 4). In the case of icosahedral or face-centered cubic packing typical of palladium nanoclusters, these values nearly coincide with those expected for the 12-vertex Chini clusters[14] with "magic" numbers of palladium atoms, 55 and 147.[15,16]

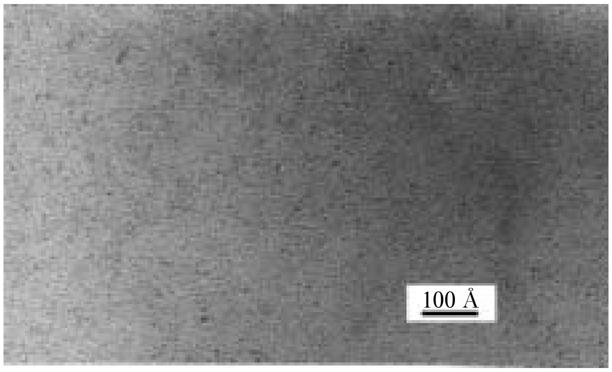


Fig. 3. TEM image of a specimen of the phenanthroline-containing palladium nanocluster prepared from $Pd_3(OCOBu^t)_6$ in an alcohol solution (transmission mode, magnification ×650000).

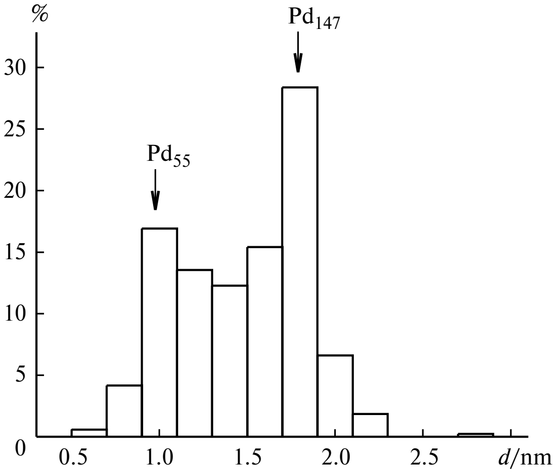


Fig. 4. Diameter distribution (*d*) of metal particles of the phenanthroline-containing palladium nanocluster prepared from $Pd_3(OCOBu^t)_6$ in an alcohol solution according to transmission electron microscopy.

Since the mass of a 147-atomic cluster is almost three times as great as that of a 55-atomic species, one can conclude that the obtained samples contain ≥75% of larger

Table 2. X-Ray photoelectron spectroscopy data of palladium nanoclusters

Sample	E_b (Pd $3d_{5/2}$)	
	Pd^0	Pd^{2+}
Pd-foil	335.8	—
$Pd_{561}phen_{60}(OAc)_{180}$	336.5	337.5
$Pd_{561}phen_{60}O_{60}(PF_6)_{60}$	335.8	337.5
Pd_{147}	336.0	337.4—337.8
PdO	—	337.6

(18±5 Å) clusters, while the fraction of smaller (10±3 Å) clusters does not exceed 25%. As in the case of giant Pd-561 clusters,[17] individual components cannot be isolated from a polydisperse specimen of nanoclusters by either fractional precipitation or column chromatography on silica gel.

It follows from the ratio of integral intensities of the proton signals for the phen and Bu^tCOO groups in the ^1H NMR spectrum of new nanoclusters that the number of the Bu^tCOO groups it contains is close to the number of the phen ligands. On the basis of the elemental analysis (see Table 1), electron microscopy (see Figs. 3 and 4), EXAFS, and NMR data, the most representative (~147-atomic) cluster molecules can be roughly described by the idealized formula $Pd_{147}phen_{32}(OCOR)_{30}O_{60}$. Note that a palladium nanocluster with an icosahedral metal core, $Pd_{145}(CO)_x(PEt_3)_{30}$, and with a similar size has recently[18] been prepared and characterized by single-crystal X-ray diffraction.

X-Ray photoelectron spectra (Table 2) showed that the energy of the main maximum, Pd $3d_{5/2}$, is virtually the same for specimens of the giant and new clusters and also for the massive metal (335.8—336 eV) and corresponds to palladium in a zero oxidation state. In addition, the spectra of new clusters also exhibit a small shoulder with the binding energy E_b = 337.4—337.8 eV, which corresponds to Pd atoms in a higher oxidation state close to +2. Since the nanoclusters contain negatively charged $RCOO^-$ (and, probably, O^{2-}) ligands, the metal core has a positive charge, which should be concentrated in a surface layer of the metallic particle.[19] Due to the relatively high positive charge of palladium atoms located in the surface layer of the metal polyhedron, nanoclusters can behave as electrophiles and catalyze reactions that are usually carried out in the presence of Lewis acids.

Catalytic activity of nanoclusters

To estimate the catalytic properties of new nanoclusters, we studied their activity in reactions that are known to proceed efficiently with catalysts based on metallic palladium and giant clusters.

Hydrogenation of alkenes and alkynes. Our experiments showed that the Pd-147 nanoclusters are much more active in the hydrogenation of phenylacetylene and styrene than the giant Pd-561 clusters or the traditional Pd/C catalysts (Table 3). This may be due to the fact that the activity of metallic catalysts increases with an increase in the metal dispersity and with a decrease in the nanoparticle size.

Reduction of nitriles with formic acid. Previously,[20] it has been found that in the presence of giant Pd-561 clusters, MeCN is reduced to Et_3N and NH_3 on treatment with HCOOH under mild conditions. Our experiments showed that the activity of Pd-147 is much lower (see Table 3). Unlike the reaction with Pd-561, that in solutions of Pd-147 starts after an induction period. Apparently, the Pd-147 nanocluster is only the precursor of a catalyst whose nature is still unknown. Heterogeneous catalysts, Pd/C and Pd black, are virtually inactive in this reaction.

Oxidative dehydrogenation of cyclohexene. Under anaerobic conditions, metallic palladium and Pd/C efficiently catalyze the redox disproportionation of cyclohexene and cyclohexa-1,3-diene to give cyclohexane and benzene:[21]

$$3\,C_6H_{10} \longrightarrow 2\,C_6H_{12} + C_6H_6,$$

$$3\,C_6H_8 \longrightarrow C_6H_{12} + 2\,C_6H_6.$$

The giant Pd-561 cluster exhibits a very low activity, the yield of benzene being somewhat higher than the yield of cyclohexane. In our experiments with Pd-147, disproportionation of cyclohexene did not take place under anaerobic conditions. The reaction products were found to contain no cyclohexane and only a small amount of benzene, not exceeding the amount of palladium introduced in the solution. Apparently, the reaction represents stoichiometric oxidation of cyclohexene with the palladium atoms of the Pd-147 cluster whose formal oxidation state is close to +1. According to calculations,[19] the positive charge of the cluster metal core is mainly concentrated in its outer layer (in the idealized structure, it contains 92 of the 147 atoms), so that the formal charge of these atoms is about +1.5.

Redox disproportionation of benzyl alcohol. Recently, it has been found that giant Pd-561 clusters [22,23] and colloidal palladium[24] catalyze a rather unusual reaction, redox disproportionation of benzyl alcohol to give toluene, benzaldehyde, and water:

$$2\,PhCH_2OH \longrightarrow PhMe + PhCHO + H_2O.$$

Our experiments showed that the Pd-147 nanoclusters efficiently catalyze this reaction at 60 °C under argon (see Table 3). We found that similar redox disproportionation readily occurs also in the case of α-alkylbenzyl alcohols to give the corresponding ketones and alkylbenzenes.

$$2\,ArCH(R)OH \longrightarrow ArCH_2R + ArC(O)R + H_2O,$$

R = H, Me, Et

Table 3. Catalytic activity of palladium nanoclusters

Reaction	Catalyst	T/°C	$w_0{}^a$/mol (mol Pd h)$^{-1}$
Hydrogenation of alkenes and alkynes			
$PhCH=CH_2 + H_2 \rightarrow PhCH_2Me$	Pd-147	20	242
	Pd-561	20	155
	Pd/C	20	25
$PhC\equiv CH + 2\ H_2 \rightarrow PhCH_2Me$	Pd-147	20	360
	Pd-561	20	180
	Pd/C	20	55
Reduction of nitriles with formic acid			
$3\ MeCN + 6\ HCOOH \rightarrow Et_3N + 6\ CO_2 + 2\ NH_3$	Pd-147	20	1.3
	Pd-561	20	4.7
Redox disproportionation of benzyl alcohol [b]			
$2\ PhCH_2OH \rightarrow PhCHO + PhCH_3 + H_2O$	Pd-147	60	24
	Pd-561	60	21
	Pd/C	60	128
Oxidation of alcohols [c]			
$Pr^iOH + O_2 \rightarrow Me_2CO + H_2O$	Pd-147	70	4
	Pd-561	70	8
Oxidative esterification of alkenes [d]			
$C_2H_4 + 1/2\ O_2 + AcOH \rightarrow CH_2=CHOAc + H_2O$	Pd-147	60	0.33
	Pd-561	60	1.10
$C_3H_6 + 1/2\ O_2 + AcOH \rightarrow C_3H_5OAc + H_2O$	Pd-147	60	2.77
	Pd-561	60	2.30

[a] The rate of accumulation of the reaction products.

[b] The solvent was $PhCH_2OH$, argon atmosphere.

[c] The solvent was Pr^iOH, 1 atm of O_2.

[d] The solvent was AcOH, 0.33 atm of O_2.

However, an α-phenyl-substituted benzyl alcohol, benzhydrol, does not enter into this reaction, which may be due to steric reasons.

In solutions of the Pd-561 and Pd-147 clusters in benzyl alcohols, disproportionation occurs without an induction period; however, in the initial period, an amount of carbonyl compound excessive with respect to the reaction stoichiometry is produced. This can be explained by assuming that redox disproportionation is accompanied by parallel oxidation of benzyl alcohols due to the reduction of Pd^{+1} atoms in the cluster to Pd^0, similarly to that observed in the reaction involving cyclohexene (see above).

Oxidation of aliphatic alcohols. The giant Pd-561 cluster efficiently catalyzes partial oxidation of alcohols with oxygen under mild conditions:[3]

$$MeOH + O_2 \longrightarrow HCOOMe + CO_2,$$

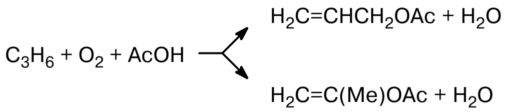
$$EtOH + O_2 \longrightarrow MeCHO + MeCH(OEt)_2 + AcOEt,$$

$$Pr^iOH + O_2 \longrightarrow Me_2CO + Me_2C(OPr^i)_2.$$

The oxidation of Pr^iOH in solutions of the Pd-147 cluster at 50 °C starts after a long (~1 h) induction period. In the transient section of the kinetic curve, the Pd-147 cluster is much more active than Pd-561, but the steady-state rates of the catalytic reaction are equal in both cases. Palladium supported on the BAU carbon or Al_2O_3 exhibits no catalytic activity under these conditions.

Oxidative acetoxylation of ethene and propene. Our experiments showed that in solutions of the Pd-147 nanoclusters in AcOH, diglyme, or MeCN (in the last two solvents, 10% AcOH additive was used), ethene and propene undergo oxidative esterification at 20—60 °C and at 1 atm of O_2 to give the corresponding alkenyl esters; however, the reaction rate is ~3 times lower in solutions of the Pd-147 clusters than in the presence of Pd-561 (Table 4).

$$C_2H_4 + O_2 + AcOH \longrightarrow H_2C=CHOAc + H_2O$$



$$C_3H_6 + O_2 + AcOH \longrightarrow H_2C=CHCH_2OAc + H_2O$$

$$C_3H_6 + O_2 + AcOH \longrightarrow H_2C=C(Me)OAc + H_2O$$

Apart from allyl acetate, the transformation of propene gives isopropenyl acetate, whose yield changes depending on the partial pressure of O_2. As P_{O_2} increases from 0.09 to 0.33 atm, the selectivity of the reaction with respect to allyl acetate decreases from 94 to 53—60% in a solution of the Pd-147 cluster and from 98 to 77% in solutions of Pd-561. Another reaction product is isopropenyl acetate. This change in the reaction selectivity can be explained by the destruction of nanoclusters under the action of O_2 to give Pd^{II} complexes, which oxidize propene to isopropenyl acetate:[25,26]

$$C_3H_6 + PdOAc_2 \longrightarrow H_2C=CH(Me)OAc + AcOH + Pd^0.$$

Table 4. Competitive oxidative esterification of ethene and propene with acetic acid (MeCN + 10% AcOH as the solvent, 0.33 atm of O_2, 60 °C)

Substrate	Catalyst	w_0*/mol (at Pd h)$^{-1}$		
		Vinyl acetate	Isopropenyl acetate	Allyl acetate
Propene	Pd-147	—	0.84	0.82
Propene	Pd-561	—	0.22	2.95
Ethene—propene (1 : 1)	Pd-147	0.30	0.02	0.50
Ethene—propene (1 : 1)	Pd-561	0.29	0.02	1.72

* The rate of accumulation of the reaction products.

The oxidation of ethene with oxygen in solutions of the Pd-147 cluster is slower than that of propene by almost an order of magnitude (see Table 4). However, in the presence of ethene, both the rate and the regioselectivity of propene oxidation sharply change. The introduction of an equimolar amount of ethene terminates almost completely the formation of isopropenyl acetate, but does not affect the oxidation of propene into allyl acetate.

The competitive oxidation of propene and ethene gives allyl acetate (91%) and vinyl acetate (9%) as the major products. This result can by no means be attributed to the formation of Pd^{II} complexes due to the O_2-induced cluster destruction. Our experiments showed that isopropyl acetate is almost the only product of the stoichiometric reaction of Pd^{II} acetate with an equimolar mixture of C_2H_4 and C_3H_6. Therefore, it can be concluded that inhibition of the vinylic oxidation of propene by ethene is due to the fact that oxidative replacements of the H atoms at the vinyl and allyl positions of the olefin molecules occur on different active sites of the cluster and follow different mechanisms.

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