Brief Communications

Unusual case of catalysis by palladium clusters

I. P. Stolarov,[a] Zh. V. Dobrokhotova,[a] G. N. Kryukova,[b] N. Yu. Kozitsyna,[a] A. E. Gekhman,[a] M. N. Vargaftik,[a]★ and I. I. Moiseev[a]

[a]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 952 1274. E-mail: mvar@igic.ras.ru

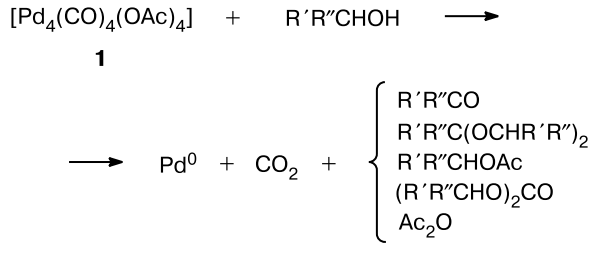
[b]G. K. Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, 5 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383) 234 3056. E-mail: kochub@catalysis.nsk.su

An unusual for Pd catalysts dehydration of α-alkyl- and α,α´-dialkylbenzyl alcohols PhCR´R″OH (R´ = H, Me, Et, Bu; R″ = H, Me) occurs in the presence of the palladium(I) cluster $[Pd_4(CO)_4(OAc)_4]$ (**1**) in an inert atmosphere to form ethers PhCR´R″—O—CR´R″ and water. The catalyst is an intermediate of cluster **1** reduction to Pd black, while neither the starting cluster **1**, nor Pd black, which is the decomposition product, are active in the catalysis of this reaction.

Key words: palladium, clusters, benzyl alcohol, α-alkylbenzyl alcohol, α,α´-dialkylbenzyl alcohol, dibenzyl ethers, catalysis.

Aliphatic alcohols (MeOH, EtOH, Pr^iOH) have previously[1] been shown to be oxidized with the palladium(I) carbonyl acetate cluster $[Pd_4(CO)_4(OAc)_4]$ (**1**) according to the stoichiometric reaction affording Pd black, CO_2, and a set of organic products: aldehydes or ketones, acetals, and esters (Scheme 1).

Scheme 1



R´ = H, Me; R″ = H, Me, Et

In this work, we studied the reaction of cluster **1** with alkylaromatic alcohols.

Results and Discussion

We found that the reaction of cluster **1** with benzyl alcohol and its α-alkyl- and α,α´-dialkyl derivatives PhCR´R″OH (R´ = H, Me, Et, Bu; R″ = H, Me) in an inert atmosphere (argon) involves two types of catalytic

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reactions along with the stoichiometric reduction of cluster **1**: (I) unusual for Pd catalysts alcohol dehydration (in acid-free medium) to form ether (Scheme 2, reaction (1)) or arylalkene (reaction (2)) and (II) alcohol redox disproportionation to form aldehyde (ketone) and alkylarene (reaction (3)).

Scheme 2

$$2\ PhCR'R''OH = PhCR'R''OCR'R''Ph + H_2O, \quad (1)$$

R′ = H, Me, Et, Bu; R″ = Me, Et, Bu,

$$PhCR'R''OH = PhCR{=}CH_2 + H_2O, \quad (2)$$

R′ = Me, R″ = Me,

$$2\ PhCH(R')OH = PhC(O)R' + PhCH_2R' + H_2O, \quad (3)$$

R′ = H, Me, Et, Bu.

The transformations of benzyl alcohol and its α,α′-dialkyl derivatives *via* reactions (1)—(3) occur with a high conversion of the starting alcohol (60—90%) when a suspension of cluster **1** is stirred in a medium of the initial alcohol without additives of any acid under argon at 40—60 °C (Table 1, Fig. 1). Unlike benzyl alcohols, β-phenylethanol does not undergo reactions (1)—(3) under the conditions under study.

The catalytic redox disproportionation of benzyl alcohol to benzaldehyde and toluene (reaction (3)) has previously been observed under anaerobic conditions in the presence of giant palladium clusters Pd-561 and Pd-147 [2—4] and Pd black.[5] However, catalysis by palladium compounds of aromatic alcohol dehydration to form ethers or olefins in a medium containing no strong acid (reactions (1) and (2)) is rather unusual and, as far as we know, is unprecedent.

Table 1. Products of transformation of benzyl alcohols in the presence of cluster **1**

Substrate	Products	Yield (%)*
$PhCH_2OH$	$PhCH_2OCH_2Ph$	5
	PhCHO	50
	$PhCH_3$	45
PhCH(Me)OH	PhCH(Me)OCH(Me)Ph	~90
	PhCOMe	~5
	$PhCH{=}CH_2$	1
$PhC(Me)_2OH$	$PhC(Me)_2OC(Me)_2Ph$	25
	$PhC(Me){=}CH_2$	75
$PhCH_2CH_2OH$	**	—
PhCH(Et)OH	PhCH(Et)OCH(Et)Ph	~90
	PhCOEt	5
	$PhCH_2Et$	1
PhCH(Bu)OH	PhCH(Bu)OCH(Bu)Ph	~90
	PhCOBu	5
	$PhCH_2Bu$	1

Note. Suspension of cluster **1** (0.1 mol L^{-1}) in the substrate (2 h, 60 °C), and the 60—90% substrate conversion.
* Of the sum of organic reaction products.
** No reaction.

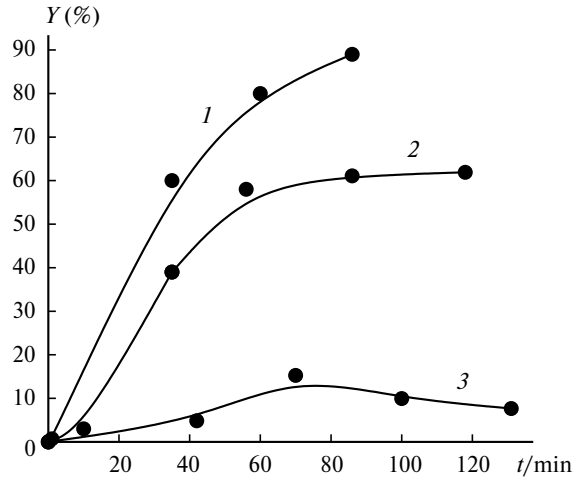


Fig. 1. Curves of di-α-methyl benzyl ether accumulation (*Y*) during the Pd-catalyzed dehydration of α-methylbenzyl alcohol at different temperatures: 60 (*1*), 45 (*2*), and 30 °C (*3*). The solvent is α-methylbenzyl alcohol, and the catalyst precursor is cluster **1** (0.01 *M*).

Remarkably, neither the starting cluster **1** itself, nor Pd black, the final product of its reduction catalyze reactions (1) and (2). After a sample of as-prepared cluster **1** was added to α-methylbenzyl alcohol, its light yellow color changes rapidly to black; however, neither a consumption of the starting alcohol, nor a formation of the products of its transformation were observed within the first 5—10 min at 45 °C. At a higher temperature (60 °C) the induction period shortens to 3—5 min, and at 35 °C the accumulation of the reaction product becomes noticeable only after ~20 min; however, after ~1 h the catalyst completely loses its activity (see Fig. 1).

It is of interest that acetic acid, which can be formed in small amounts as a result of cluster **1** decomposition, exhibits no catalytic effect in reactions (1) and (2) when the cluster is absent. Nevertheless, the addition of AcOH (~0.1 mol L^{-1}) to the catalyst, which had lost its activity, again induces catalysis of the reactions in question but with a lower rate.

Virtually the same catalytic properties but without an induction period exhibit strongly darkened, almost black samples of cluster **1** after short (15—20 min) heating in dry argon to 100—110 °C or after storage in air (20 °C, natural humidity 70—80%) for 1—3 days. Palladium black formed after complete decomposition of cluster **1** is cata-

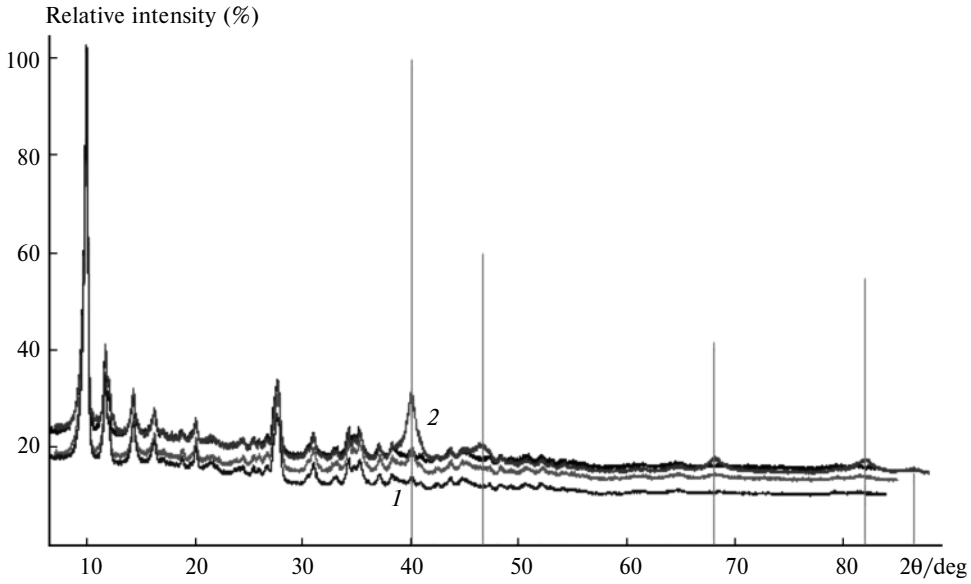


Fig. 2. Diffraction patterns of the samples of cluster **1**: *1*, initial sample; and *2*, after heating to 200 °C under argon. Vertical lines show reflexes characteristic of an fcc lattice of metallic palladium.

lytically inactive in reactions (1) and (2) but catalyzes redox disproportion of benzyl alcohol (reaction (3)).

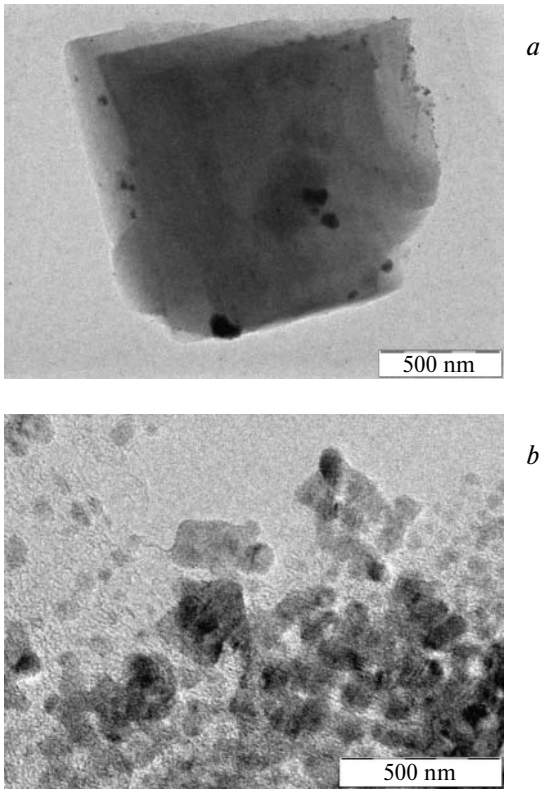
The DTA—TGA data showed that the weight loss of cluster **1** accompanied by a considerable endotherm begins at 110—120 °C, and the endotherm maximum lies at 175 °C.

The X-ray diffraction data (Fig. 2) indicate that after two-step heating to 110 and 140 °C (*i.e.*, until the weight loss was completed) the diffraction patterns of the samples differ slightly from that of the starting cluster **1**, whereas the detected phase of metallic palladium appears only after heating to 200 °C. This sample does not catalyze reactions (1) and (2) but is active in redox disproportionation of benzyl alcohol (reaction (3)).

The IR spectra of cluster **1** after its occurring in the reaction mixture (30 min at 60 °C) indicate a complete disappearance of the ν_{CO} bands (1940 and 1970 cm^{-1}), while the ν_{COO} bands are considerably shifted (1418→1448 and 1550→1630 cm^{-1}) and substantially decreased in intensity.

The electronic microphotographs of the catalytically active cluster samples show that immediately after the induction period the microcrystal surface of the starting cluster **1** begins to cover with fine metallic particles (Fig. 3, *a*). Thirty min after the beginning of the catalytic reaction, only formless structures and fine nanoparticles of metallic palladium are seen instead of microcrystals of cluster **1** (Fig. 3, *b*).

The data obtained are insufficient to draw a certain conclusion about the chemical nature of a palladium compound responsible for catalysis of reactions (1) and (2). Nevertheless, it is clear that this is neither the starting cluster **1** nor metallic palladium. It can be assumed that the catalyst of the reaction is a low-stability palladium compound formed due to the removal of the bridging CO



a

b

Fig. 3. Electron microphotographs of cluster **1** drawn from the reaction mixture: *a*, 5 min after the beginning of the reaction at 60 °C (immediately after the end of the induction period); and *b*, 30 min after the beginning of the reaction at 60 °C.

ligands from cluster **1**, while the OAc^- ligands are probably retained

$$\underset{\mathbf{1}}{[Pd_4(CO)_4(OAc)_4]} \xrightarrow{-4\ CO} [Pd_n(OAc)_n].$$

By analogy to the kinetic scheme of positional butene isomerization in the presence of the chloropalladium(I) complex $[Pd_2Cl_4]^{2-}$, which proceeds *via* the nonradical chain mechanism,[6,7] this reaction can be considered as a step of generation of the catalytically active complex (catalytic chain initiation). Products of the catalytic reaction appear and the catalytically active complex is generated in the stages of catalytic chain propagation

$$\left\{\begin{array}{l} [Pd_n(OAc)_n] + PhCR'R''OH \xrightarrow{-AcOH} \\ \longrightarrow PhCR'R''^{-}O[Pd_n(OAc_{n-1})] \\ PhCR'R''^{-}O[Pd_n(OAc_{n-1})] + HOCR'R''Ph \xrightarrow{+AcOH} \\ \longrightarrow PhCR'R''—O—CR'R''Ph + [Pd_n(OAc)_n] + H_2O \end{array}\right.$$

The decomposition of the catalytically active complex $[Pd_n(OAc)_n]$ terminates the chain and deactivates the catalyst.

$$[Pd_n(OAc)_n] \xrightarrow{-n\ AcOH} \text{Pd-black}$$

Experimental

Benzyl, β-phenylethyl, and α-methyl-, α-ethyl-, α-butyl-, and α,α′-dimethylbenzyl alcohols (all reagent grade, Aldrich) were distilled *in vacuo* (1 Torr) before use. Palladium(I) carbonyl acetate was synthesized by carbonylation of palladium(II) acetate with carbon monoxide in acetic acid using a known procedure.[8]

α-Methylbenzyl alcohol (2 mL) and cluster **1** (20 mg) were magnetically stirred in a 5-mL glass flask, whose temperature was maintained constant. Experiments were carried out at temperatures from 40 to 60 °C. Reaction products were identified by GC-MS on an Automass-150 GC-MS spectrometer (Delsi Nermag, France). Concentrations were determined by GLC on a Shimadzu GC-17A chromatograph.

Elemental analyses of catalyst samples were carried out on an automated C,H,N-analyzer (Carlo Erba Strumentazione, Italy). The palladium content was determined by the gravimetric method after calcination at 900 °C. IR spectra were recorded on a Specord M-80 spectrophotometer (Carl Zeiss, Jena) in KBr pellets or Nujol. X-ray diffraction analyses of catalyst samples were carried out using an FR-552 monochromator chamber ($CuK_{\alpha 1}$ radiation, germanium as internal standard). DTA—TGA analyses were carried out on DSC-20 and TG-50 modules of a TA-3000 thermoanalyzer (Mettler) in dry argon with a rate of 5 deg min^{-1}. Electron microphotographs of nanoclusters were obtained on a JEM 2010 electron microscope (JEOL, Japan) in a transmission mode (amplification $(0.1—2.0)\cdot 10^6$, beam current 2—10 μA). Samples were prepared by mechanical powder sputtering or supporting of a catalyst suspension in MeCN on an amorphous carbon support with a standard copper grid.

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