

Reactions of palladium(I) carbonylacetate cluster with alcohols

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Reactions of a tetranuclear palladium cluster $[\text{Pd}(\text{CO})(\text{OAc})]_4$ with C_1 – C_3 alcohols have been found to proceed simultaneously *via* several routes to form CO_2 and dialkyl carbonates, the products of oxidation of coordinated CO ligands, along with carbonyl compounds which form due to oxidation of the corresponding alcohols. Alkoxy, alkoxyacetyl, and acyl palladium derivatives are shown to be the intermediates of the reactions studied.

Key words: palladium(I), carbonyl complexes, clusters, alcohols.

Synthesis of dialkyl carbonates *via* oxidative carbonylation of alcohols



proceeds in the presence of compounds of copper, palladium, and other transition metals.^{1–6} One can suggest^{6–10} that carbonyl, alkoxy, and carbalkoxy intermediates of the $\text{L}_n\text{M}(\text{CO})$, $\text{L}_n\text{M}-\text{OR}$, $\text{L}_n\text{M}-\text{COOR}$ types participate in the key stages of the process. The participation of Pd^+ complexes in this reaction has been postulated.¹¹

In order to elucidate the possibility of participation of the Pd^+ carbonyl complexes in this reaction, the interaction of cluster $[\text{Pd}(\mu\text{-CO})(\mu\text{-OAc})]_4$ (**1**) with aliphatic alcohols C_1 – C_3 was studied in this work.

Experimental

Cluster **1** was obtained by the reaction of palladium(II) acetate with carbon monoxide in an acetic acid solution according to the procedure described in Ref. 12. Carbon monoxide, argon, methane, ethane, and propane of chemically pure grade were used without additional purification. Methanol of chemically pure grade was freed of water (see the procedure reported previously¹³). Most of water was removed by fractional distillation, then methanol was kept over molecular sieve 4 Å. Ethanol of chemically pure grade was purified by boiling with CaO followed by fractional distillation. Further removal of water from the alcohol was carried out with magnesium (see Ref. 13). Isopropanol of chemically pure grade was freed of water by refluxing over CaO followed by distillation over anhydrous calcium sulfate (see Ref. 12). Samples of the alcohols with the water content of 0.2–0.4 wt.% were used for the experiments.

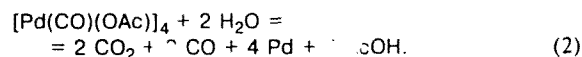
The reactions of cluster **1** with the alcohols were carried out in the thermostated glass vessel equipped with a magnetic stirrer, gas buret, and a connection line for an inert gas. In the reaction vessel 0.2 g (1 mmol) of cluster **1** was placed, purged

with argon, and the alcohol was introduced with a syringe through a rubber seal; then the mixture was stirred for 1–1.5 h. The reaction was monitored volumetrically and by composition (by GLC) of the evolved gas.

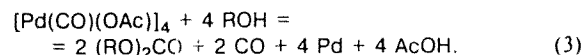
The analysis of the gaseous reaction products was carried out by GLC on a Biochrom-1 chromatograph (molecular sieve 4 Å, column, 2 m; Polysorb 1, column 2 m). The liquid reaction products were analyzed by GC-MS (an Automass 150 GC-MS instrument, Delsi Nermag; capillary columns: PEG 20M, 25 m and SE 30, 50 m) and GLC (chromatographs Varian 3600, columns: PEG 20M, 50 m and Carbowax 20M, 50 m, and LKHM 80, columns: Carbowax 20M on Chromatone, 3 m; 0.5% SKTF 50 + 5% Polyethylene glycol sebacate on Polychrom-1, 2 m; 7% polyphenyl ester on Polychrom-1, 2 m; Polysorb 1, 2 m).

Results and Discussion

It was found previously¹⁴ that cluster **1** was decomposed readily by water according to the stoichiometric equation:



We suggested that reaction (2) involves the nucleophilic attack of water on the coordinated CO molecule. In the framework of this concept, the reaction of cluster **1** with alcohols should result in the formation of dialkyl carbonates instead of CO_2 :



Our experiments showed that in the case of $\text{R} = \text{Et}$ and Pr^i , the corresponding dialkyl carbonates formed, but their yields were less than those expected according to Eq. (3) (Table 1). In the reaction with methanol, the corresponding dialkyl carbonate was not found. Dialkyl

Table 1. Products of the interaction of cluster **1** with alcohols

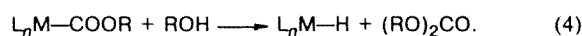
Alcohol	Yield of reaction products/mol. (at. Pd) ⁻¹							
	CO ₂	ROAc	AcOH	Ac ₂ O	(RO) ₂ CO	AcH	Acetals	Acetone
MeOH	0.58	0.15	0.85	—	—	—	—	—
EtOH	0.57	0.60	~0.1	0.55	0.20	0.50	0.70 ^a	—
Pr ⁱ OH	Traces	0.30	0.70	Traces	0.16	0.02	0.06 ^b	0.60

^a MeCH(OEt)₂. ^b Me₂C(OH)OPrⁱ.

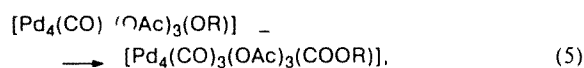
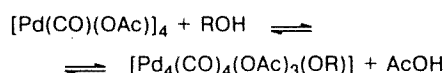
oxalates, which often accompany dialkyl carbonates and even prevail in the products of catalytic reaction (1),¹⁵ were also not observed in any cases.

The data in Table 1 show that the composition of the reaction products of cluster **1** with the alcohols differs substantially from that expected according to Eq. (3). Thus, CO is absent, but CO₂ is present in the gaseous reaction products in all cases; the corresponding alkyl acetate forms along with acetic acid. Diacetyl, acetic anhydride, acetaldehyde, and acetal were observed in the products of the reaction with ethanol; acetaldehyde, acetic anhydride, acetone, and monoisopropyl ketal were found in the case of isopropyl alcohol.

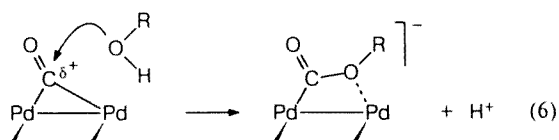
It is believed¹⁶ that the formation of dialkyl carbonates during the oxidative carbonylation of alcohols in the presence of compounds of platinum metals proceeds *via* intermediate formation of the esters of metalcarboxylic acids L_nM—COOR. The attack of an alcohol molecule on this complex results, as a rule, in dialkyl carbonate:



In the case of cluster **1**, a carbalkoxy complex would form either due to ligand exchange followed by the insertion of the CO molecule to the Pd—OR bond:



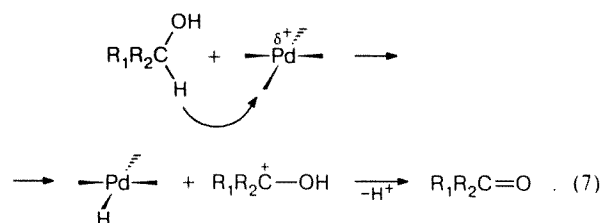
or as a result of the outer-spheric attack of the alcohol molecule on the coordinated carbonyl group, which leads to the reduction of one Pd^{II} atom to Pd⁰ and elimination of a proton.



However, neither of these mechanisms explains, why dialkyl carbonate forms only in the reactions of cluster **1** with ethanol and isopropyl alcohol and is absent in the case of methanol.

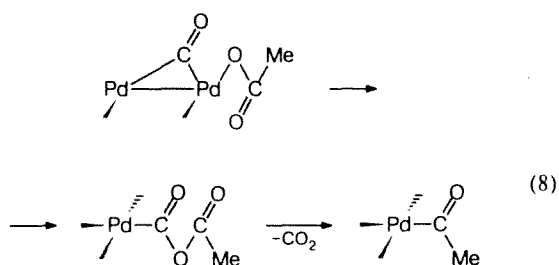
In search for an explanation of this fact, let us consider possible pathways of the formation of the other reaction products, primarily carbonyl compounds. The oxidation of alcohols to carbonyl compounds catalysed by Pd²⁺ is a well-known process.¹⁷ The oxidative potential of Pd^{II} seems to be too low for this process. However, as seen from Table 1, acetaldehyde forms in the reactions of cluster **1** with ethanol, and acetaldehyde and acetone form in its reaction with isopropyl alcohol. The products of addition of the alcohol to the carbonyl compounds primarily formed are also present in both reaction systems. Unlike this, neither acetaldehyde and formaldehyde nor the products of their acetalization form in the reaction of cluster **1** with methanol.

These facts suggest that a hydride transfer of the H atom from the α-CH group of the alcohol to the electrophilic Pd atom plays an important role in the mechanism of the reactions of cluster **1** with alcohols:

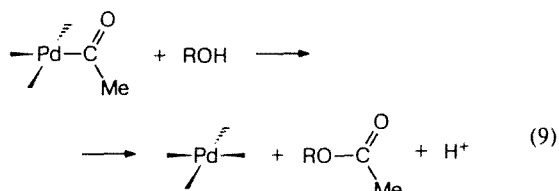


Isopropyl alcohol is the best donor of hydride ion among the alcohols studied; its reaction with cluster **1** afforded the corresponding carbonyl compounds (acetone and its hemiketal) in the highest yield. Acetaldehyde and acetal in some lesser total yield were found in the reaction products of cluster **1** with ethanol, which is a less efficient donor of hydride ion. Unlike both higher alcohols, methanol, the weakest donor of hydride ion practically does not enter the reaction (7). Therefore, in the case of methanol, one can expect the absence of transformations involving hydride complexes of palladium, which could form due to reaction (7).

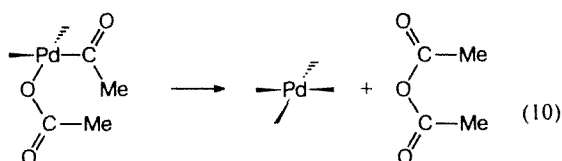
One more fact is worthy of notice, *i.e.*, the formation of acetaldehyde in the reaction of **1** with isopropyl alcohol (see Table 1). In this case, the acetate ligand of cluster **1** is a probable origin of acetaldehyde. Previously,¹² we found that the acetate group could enter the composition of cluster **1** to be transformed into the acetyl ligand MeCO coordinated with the Pd atom due to an intramolecular redox reaction involving the insertion of the CO molecule to the Pd—OCOME bond followed by the elimination of CO₂:



The products obtained, ethyl acetate and isopropyl acetate, seem to form from the MeCO—Pd moiety as a result of the attack by the alcohol molecule:

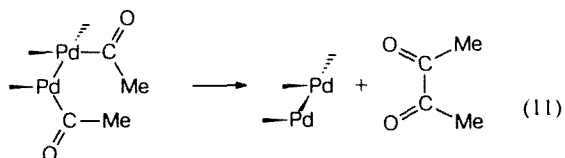


Intramolecular attack of another acetate ligand of cluster **1**, which was not involved in reaction (8), can result in the formation of acetic anhydride.



Acetic acid forms during reaction (9) with the participation of the water molecule (R = H) present in the samples of the alcohols used.*

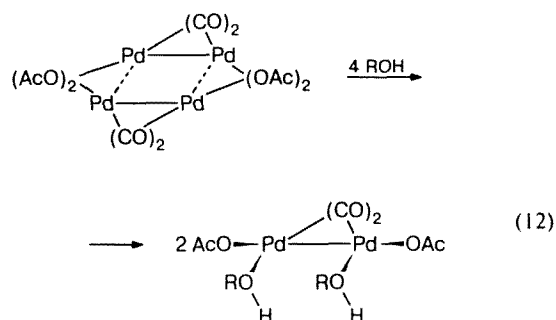
A diacetyl molecule could also form in the coordination sphere of the cluster as a result of the recombination of two acetyl groups.



* Although the alcohols were purified of water, they contained 0.2–0.4% water according to the GLC analysis (see Experimental).

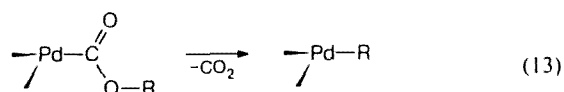
In the framework of this scheme, the formation of acetaldehyde can be explained by the inner-spheric reaction of the acetyl group with a hydride ligand which arises due to the reaction of cluster **1** with the ethanol or isopropyl alcohol molecules according to Eq. (7). Methanol is inefficient as the origin of hydride ions, therefore palladium hydride complexes are absent, and the reaction of cluster **1** with methanol does not afford acetaldehyde. The formation of methyl acetate gives evidence for the participation of the Pd—COMe moiety in the reactions proceeding in this system.

It is noteworthy that the decomposition of cluster **1** by alcohols proceeds faster and under milder conditions (20 °C, 0.5 h) than intramolecular redox reaction (8), which was observed previously upon the thermolysis of cluster **1** in the solid phase or in boiling toluene (110 °C, 2–3 h).¹¹ It cannot be ruled out that tetranuclear cluster **1** dissociates under the action of an alcohol molecule, for example, to two dinuclear fragments; then bridging ligands OAc⁻ and CO become terminal and the alcohol molecules occupy the free vacancies in the coordination sphere of the Pd atoms.



It can be assumed that reactions of the type of (7)–(11)^d types with the participation of similar dinuclear complexes proceed much more easily than in the case of initial cluster **1**.

The assumption of intermediate formation of a palladium hydride complex in the reactions considered is confirmed by the fact that a small amount of ethane was found in the reaction products of cluster **1** with ethanol and propane was found in the reaction with isopropanol. The intermediate ethoxycarbonyl complex formed in reaction (5) or (6) seems to be capable of eliminating the CO₂ molecule, transforming into the corresponding alkyl derivative whose reaction with the hydride complex results in the formation of alkane.



In line with this scheme, alkane is not formed in the system containing methanol, in which the hydride complex is absent.

The data obtained here call into question the possibility of the intermediate participation of the Pd^{II} complexes in the oxidative carbonylation of alcohols. The findings observed in this work revealed new routes of transformation of palladium complexes in their reaction with alcohols.

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References

1. Yu. B. Yan and B. K. Nefedov, *Sintezy na osnove oksidov ugleroda* [Synthesis Based on Carbon Oxides], Khimiya, Moscow, 1987, 263 (in Russian).
2. *Catalysis in C₁ Chemistry*, Eds. W. Keim and D. Reidel, Dordrecht, 1983.
3. G. E. Morris, D. Oakley, D. A. Pippard, and D. J. H. Smith, *J. Chem. Soc., Chem. Commun.*, 1987, 410.
4. G. E. Morris, D. Oakley, and D. A. Pippard, *J. Chem. Soc., Chem. Commun.*, 1987, 411.
5. D. M. Fenton and R. J. Steinwand, *J. Org. Chem.*, 1972, 37, 2034.
6. D. Delledonne, F. Rivetti, and U. Romano, *J. Organometal. Chem.*, 1995, 488, 15.
7. O. N. Temkin, O. L. Kaliya, L. N. Zhir-Lebed', V. A. Golodov, L. G. Bruk, and N. G. Mekhryakova, *Akad. Nauk Kaz. SSR, Trudy IOKE. Gomogennoe okislénie* [Proceedings of IOKE. Homogeneous Oxidation], Nauka, Alma-Ata, 1978, 17, 3 (in Russian).
8. D. M. Fenton and R. J. Steinwand, *J. Org. Chem.*, 1974, 39, 701.
9. F. Rivetti and U. Romano, *J. Organometal. Chem.*, 1978, 154, 323.
10. L. N. Zhir-Lebed', L. G. Kuz'mina, Yu. T. Struchkov, and O. N. Temkin, *Koord. Khim.*, 1978, 4, 1046 [*Sov. J. Coord. Chem.*, 1978, 4 (Engl. Transl.)].
11. O. N. Temkin and L. G. Bruk, *Usp. Khim.*, 1983, 52, 206 [*Russ. Chem. Rev.*, 1983, 52 (Engl. Transl.)].
12. T. A. Stromnova, N. Yu. Tikhonova, L. K. Shubochkin, and I. I. Moiseev, *Koord. Khim.*, 1993, 19, 450 [*Russ. J. Coord. Chem.*, 1993, 19 (Engl. Transl.)].
13. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., *Organic Solvents. Physical Properties and Methods of Purification*, Interscience Publ., New York, 1955.
14. T. A. Stromnova, M. N. Vargaftik, and I. I. Moiseev, *J. Organometal. Chem.*, 1983, 252, 113.
15. Jap. Pat. 7984514; *Chem. Abstr.*, 1979, 91, 157294a.
16. I. S. Kolomnikov and M. Kh. Grigoryan, *Usp. Khim.*, 1978, 47, 603 [*Russ. Chem. Rev.*, 1978, 47 (Engl. Transl.)].
17. I. I. Moiseev, Ya. K. Syrkin, and A. V. Nikiforova, *Zh. Obshch. Khim.*, 1963, 33, 3239 [*J. Gen. Chem. USSR*, 1963, 33 (Engl. Transl.)].

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