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Vinylic, allylic and homoallylic oxidations of alkenes via π- and σ-organopalladium complexes

N.Yu. Kozitsyna, M.N. Vargaftik, I.I. Moiseev *

N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31, Leninski Prospect, GSP-1, Moscow 117907, Russian Federation

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Dedicated to Professor Fausto Calderazzo in recognition of his outstanding contribution to inorganic chemistry.

Abstract

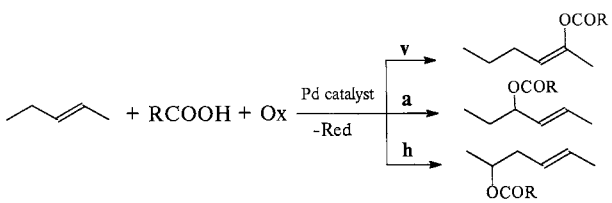
The stoichiometric and catalytic pathways of oxidative esterification of alkenes via intermediate organopalladium complexes are discussed. The oxidation of propylene, hex-1-ene and cyclohexene by Pd^{II} acido complexes containing achiral, racemic and chiral carboxylate ligands was first studied in a series of solvents other than acetic acid. Significant changes in the selectivity of the Pd^{II}-promoted reaction with changes in the solvent nature and ligand chirality were observed. A way to allylic esters based on low-valence Pd nanoclusters provide highly selective oxidation of acyclic alkenes into allylic esters, whereas cycloalkenes undergo mostly redox disproportionation. The role of π-alkene, σ-alkenyl and π-allyl complexes in the mechanism of the alkene oxidative esterification with Pd^{II} complexes and low-valence Pd clusters is discussed.

Keywords: Palladium; π-Complexes; σ-Complexes; Alkenes; Oxidative esterification; Regioselectivity; Solvent effects; Ligand effects; Cluster catalysis; Reaction mechanism

1. Introduction

Organic reactions catalysed by derivatives of Group VIII metals are still poorly understood notwithstanding the progress in this field during the last four decades. In this context, the nature of organopalladium intermediates of the catalytic alkene oxidations is of great interest.

The ability of Pd(II) carboxylates to form alkene π-complexes, whose redox decomposition affords vinylic or allylic esters [1] is used in the synthetic practice [2–5]. Oxidative esterification of alkenes with palladium-based catalysts provides a direct synthetic way to alkenyl esters. In this reaction, alkenes undergo replacement of an H atom by an RCOO group in the vinyl (**v**), allyl (**a**) or homoallyl (**h**) positions of the alkene molecule (see Scheme 1)):



Scheme 1.

In this Scheme Ox = $1/2O_2$, Cu^{II}, *p*-benzoquinone or benzoyl peroxide, Red = H_2O, Cu (I), hydroquinone or benzoic acid, respectively.

Reactions shown in Scheme 1 were first observed as early as in 1960 [5]. During the study of the reactivity of palladium(II) π-complexes toward nucleophilic reagents, we have found [5] that the Kharash complex $(\pi\text{-}C_2H_4{\cdot}PdCl_2)_2$ [6], which is fairly stable in glacial acetic acid, readily decomposes when alkaline acetate is added to its AcOH solution, producing vinyl acetate and Pd^0 according to Eq. (1):

* Corresponding author. Tel.: +7-095-952-1203; fax: +7-095-954-1279.

E-mail address: iimois@ionchran.rinet.ru (I.I. Moiseev)

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$$(\pi\text{-}C_2H_4\cdot PdCl_2)_2 + 4NaOAc = CH_2 = CHOAc + 2Pd^0 + 4NaCl + 2AcOH \quad (1)$$

Alkene–palladium(II) π-complexes were found [7] to be formed by the reaction of Pd(II) chloride with alkenes in an AcOH solution as shown in Eq. (2):

$$2PdCl_2 + 2C_2H_4 = [\pi\text{-}C_2H_4\cdot PdCl_2]_2 \quad (2)$$

The π-complex does not undergo further reactions [7] until an alkaline acetate or another nucleophilic agent are absent from the solution. When NaOAc was added, the π-complex was immediately converted to Pd^0 and vinyl acetate [5] (see Eq. (1)).

Direct reaction between $PdCl_2$ and ethylene in an AcOH solution containing alkaline acetate has been found [5] to produce vinyl acetate (see Eq. (3)) and a small amounts of ethylidene diacetate (Eq. (3a)).

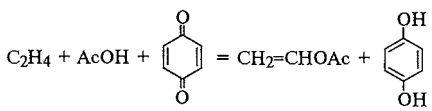
$$PdCl_2 + C_2H_4 + 2NaOAc = CH_2{=}CHOAc + Pd^0 + 2NaCl + HOAc \quad (3)$$

$$PdCl_2 + C_2H_4 + 2NaOAc = CH_3CH(OAc)_2 + Pd^0 + 2NaCl \quad (3a)$$

Palladium (0) formed in reaction (3) was shown to undergo re-oxidation to Pd^{II} by such oxidants (Ox) as *p*-benzoquinone or $O_2 + Cu^{II}$:

$$Pd^0 + Ox + 2Cl^- = PdCl_2 + Red, \quad (4)$$

(Red = hydroquinone or $Cu(I) + H_2O$, respectively), thus resulting in a catalytic cycle, in which ethylene is converted into vinyl acetate and where palladium serves as the catalyst:

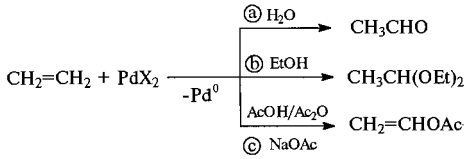


(5)

$$C_2H_4 + AcOH + O_2 = CH_2{=}CHOAc + H_2O \quad (6)$$

Under the conditions of stoichiometric (Eq. (3)) or catalytic (Eqs. (5) or (6)) reactions, propylene is oxidized to isopropenyl acetate as the main reaction product, along with *n*-propenyl and allyl acetates [8–13]. Higher acyclic alkenes C_4–C_{10} are converted to mixtures of alkenyl acetates, and the product distribution between vinylic and allylic esters varies in a wide range depending on the reaction conditions (temperature, time of reaction, concentrations of the oxidant, alkaline acetate and water, etc.) [9–18]. In the case of cyclic alkenes homoallylic esters are also formed [18–24] (Scheme 1, path **h**).

The reactions in Scheme 1 have been studied by many research groups (see, for instance, recent review paper [4]). Nevertheless, some important problems concerning with its regioselectivity and mechanism remain unsolved till now.



Scheme 2.

In this paper, we present a fresh insight into the mechanism of the alkene oxidative esterification based on both previous data and our recent experiments on the solvent and ligand effects in the oxidative esterification of alkenes (propylene, cyclohexene and hex-1-ene) by Pd^{II} complexes with achiral and chiral carboxylate ligands in different solvents other than acetic acid. On the basis of data for reactions mediated by Pd^{II} complexes and Pd nanoclusters, the pathways of formation of vinylic, allylic and homoallylic esters via π- and σ-organopalladium complexes are discussed.

2. Reactions with Pd(II) complexes

Oxidation of alkenes by Pd^{II} in aqueous, alcoholic and acetic acid solutions (see Scheme 2) has been studied extensively [1,4].

The reactions in Scheme 2 can be carried out as Pd-catalysed processes, being supplemented by re-oxidation of the Pd^0 formed (see Eq. (6)). The reaction in aqueous solution (path ≪a≫) is the basis for the commercial production of acetaldehyde from ethylene (Wacker–Hoechst process) [7], and its mechanism have been studied in most detail. The other two reactions, those in alcohol (≪b≫) and AcOH (≪c≫) solutions, are also of practical interest [2–4].

The main mechanistic features of the reactions in Scheme 1 were first found in early works [5,9,19,22]. Essential idea of the mechanism proposed is that the oxidation of an alkene molecule by Pd^{II} complex occurs via three stages:

(I) formation of alkene–Pd^{II} π-complex:

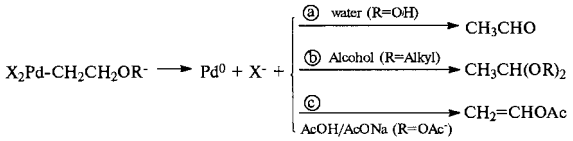
$$PdX_4^{2-} + C_2H_4 \underset{-X^-}{\rightleftharpoons} \pi\text{-}C_2H_4\cdot PdX_3^- \overset{RO^-}{\underset{-X^-}{\rightleftharpoons}} \pi\text{-}C_2H_4\cdot PdX_2OR^- \quad (7)$$

(R = OH, OAlk, OAc)

(II) oxymetallation of the alkene C=C bond via isomerization of the π-complex to σ-organopalladium compound involving inner-sphere [1] or outer-sphere [4] nucleophilic attack:

$$\pi\text{-}C_2H_4\cdot PdX_2OR^- \rightarrow XPd_2\text{–}CH_2CH_2OR^- \quad (8)$$

(III) redox disproportionation of the σ-complex to Pd^0 and the product of alkene oxidation which depends on the solvent as seen in Eq. (9):



(9)

Studies of the reaction kinetics and equilibria of π-complex formation for C_2–C_6 alkenes [25–39] have confirmed the original suggestions.

A rather risky (in early 60s, before R.F. Heck [40]) statement of the involvement of a σ-bonded alkyl–palladium(II) derivative into the oxidation has been confirmed by our experiments [1,41], in which palladium organyls were generated independently via the metathesis of palladium chloride with β-halo-, β-oxy- and β-acetoxyethylmercurials:

$$XHgCH_2CH_2OR + PdCl_2 \rightarrow ClPdCH_2CH_2OR + HgClX \quad (10)$$

(X = Cl, Br, OH; R = H, Et, Ac)

The intermediate σ-organopalladium compounds are unstable toward redox decomposition. The products of their fast transformation are Pd^0 and the oxygen-containing products whose nature depends on a solvent. In an ether or aqueous solution acetaldehyde was formed:

$$ClPd–CH_2CH_2OH \rightarrow Pd^0 + HCl + CH_3CHO \quad (11)$$

In glacial acetic acid containing NaOAc vinyl acetate (and traces of ethylidene diacetate) were obtained:

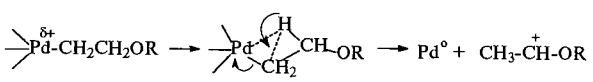
$$ClPd–CH_2CH_2OAc = Pd^0 + HCl + CH_2{=}CHOAc \quad (12)$$

The same products were found in the direct reaction between alkene and $PdCl_2$ in these solvents [1,41].

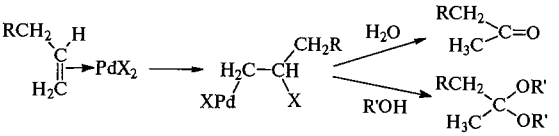
All three reactions in Scheme 2 were rationalized as involving intermediate formation of the key palladium organyls Pd-Ch_2Ch_2OR (where R = H, Et or Ac) groups. Heterolytic cleavage of the Pd–C bond of the intermediate, involving hydride 1,2-shift, possibly assisted by Pd atom interaction, was assumed to give rise to Pd atoms in a reduced oxidation state and a carbocation preceding the product of alkene oxidation (see Scheme 3):

The driving force for the key stage shown in Scheme 3 was assumed to be a tendency of the Pd^{II} atom to be reduced by withdrawing an electron pair from the organic moiety.

At first glance it seems that this general mechanism gives a plausible explanation for all reactions between Pd^{II} and alkenes in different media (e.g., in water,



Scheme 3.



Scheme 4.

alcohols and acetic acid). Meanwhile, some problems are still not solved.

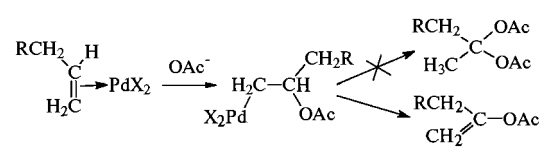
(1.) The oxidation of 1-alkenes higher than ethylene in aqueous and alcohol solutions (paths ≪a≫ and ≪b≫ in Scheme 2) produces ketones and ketals, respectively [1,3]. This means, within the framework of the mechanism under question, that the oxypalladation stage occurs according to the Markovnikov rule: an anion adds to the least hydrogenated C atom, and Pd^{II} electrophilic atom adds to another C atom at the double bond of the alkene molecule (see Scheme 4):

The ketals in Scheme 4 are genetically related to the carbonyl compounds, and by analogy with this, alkylidene diesters could be expected to form in an AcOH solution. The question arises: why unsaturated reaction products, alkenyl esters, are formed instead of alkylidene diesters in an AcOH medium (see Scheme 5)?

(2.) Both reactions, ≪a≫ and ≪b≫ in Scheme 2, are highly regioselective. Contrary to these, the reaction in an AcOH medium (path ≪c≫) is much less selective, and mixtures of vinylic and allylic esters are commonly obtained [3,4,18,22]. The question arises: why is the reaction in the AcOH/NaOAc system much less selective than those in aqueous and alcohol solutions?

(3) Oxidative acetoxylation of cyclic and higher acyclic alkenes in AcOH medium affords, as a rule, allylic and little or no vinylic esters. In addition, homoallylic esters were often found among the reaction products [13,21,23]. Meanwhile, homoallylic oxidations are absent from aqueous and alcoholic solutions [1,7,18]. The question arises: what is the reason for homoallylic oxidation in the AcOH/NaOAc system?

(4) Acetic acid plus OAc^- anion have mostly been employed in studies of reaction (1). In fact, the scope of this reaction was still restricted to oxidative acetoxylation in an AcOH medium. Studies with other solvents and carboxylate ligands are scarce (few reports such as Ref. [42a,b] for the CF_3COO^-/AcOH and AcOH/CH_2Cl_2 systems seem to be rather exceptions). The question arises: is it possible to perform the alkene oxidative esterification in other solvents but acetic acid with other carboxylates but acetate anion?



Scheme 5.

(5) The catalytic cycle of reaction (1) formally involves Pd^{II} and Pd^0 (see Eqs. (3) and (4)). It seemed that the reaction can start from either of these palladium species. Nevertheless, the product distribution of the reaction starting from Pd metal (for example, Pd black or supported Pd/SiO_2 catalyst) is quite different from that starting from Pd^{II} [17,43–47]. The question arises: what is in fact the valence state and chemical nature of the Pd species responsible for the stoichiometric and catalytic oxidative esterification?

In view of these problems, we recently studied the solvent and ligand effects on the regioselectivity of oxidative esterification of propylene, hex-1-ene and cyclohexene by Pd(II) carboxylates using different achiral, racemic and chiral carboxylate ligands. The reaction media were aprotic solvents of different polarities and solvation abilities: chloroform, dichloromethane, 1,1,2-trichloroethane, liquid CO_2 and THF.

2.1. Reactive forms of Pd^{II}

In our experiments palladium(II) was introduced into reaction solutions in the form of neutral salts $Pd_3(RCO_2)_6$ (R = Me, Me_2CHCH_2, (±)-$CF_3CF_2CF_2$-OC*F(CF_3), S(+)-MeC*H(Et) and (+)-$CF_3CF_2CF_2$-OC*F(CF_3)). The molecular structure of the first synthesized Pd(II) salt with chiral (+)-S-2-methylbutyrate anion was established by X-ray diffraction study of the single crystal [48].

According to the X-ray data [48], the molecule of Pd^{II} (+)-S-2-methylbutyrate is a carboxylate-bridged cyclic trimer $Pd_3(\mu^2$-S(+)-MeC*H(Et)COO)$_6$ with the structure (Fig. 1) similar to those of the previously investigated Pd^{II} salts with achiral carboxylate anions (acetate, propionate and pivalate, see for instance [49–52]).

Studies of reaction (1) in low polar organic solvents turned out to be difficult due to a poor solubility of alkaline carboxylates. For this reason, we chose bis(triphenylphosphoranilidene)ammonium $(Ph_3P)_2N^+$, PNP, carboxylates as the source of additional carboxylate anions (see Eqs. (13) and (14)) instead of commonly used sodium or potassium salts. PNP salts, including those with metal complex anions, are well soluble in aprotic low polar media [53–55].

When the PNP salt of the corresponding carboxylate anion, (PNP)OCOR, was added to the reaction solution in a molar ratio of $RCOO^-$:$Pd^{II} \leq 1{:}2.5$, the original trinuclear complex $Pd_3(\mu^2$-OCOR)$_6$ was partly transformed[1] into di- and mononuclear anionic complexes according to Eqs. (13) and (14) [45,56a–c,57], and the most of the additional $RCOO^-$ anions entered the composition of the anionic Pd^{II} complexes formed:

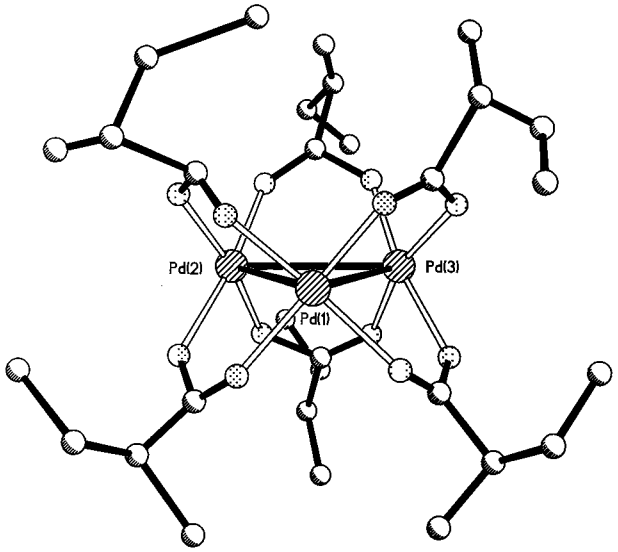


Fig. 1. The structure of the complex Pd_3[S(+)-2-EtC*H(Me)COO]$_6$ from the single crystal X-ray diffraction data [48]. Interatomic distances (Å): Pd(1)…Pd(2) 3.153(4); Pd(2)…Pd(3) 3.125(4); Pd(1)…Pd(3) 3.128(5); six Pd–O distances are within the range of 1.913(37)–2.074(31) Å. Angles in the Pd_3 triangle (°): Pd(2)Pd(1)Pd(3) 59.7(1); Pd(1)Pd(3)Pd(2) 60.6(1); Pd(1)Pd(2)Pd(3) 59.8(1).

$$2[Pd(OAc)_2]_3 + 6OAc^- \rightleftharpoons 3[Pd_2(OAc)_6]^{2-} \quad (13)$$

$$[Pd(OAc)_2]_3 + 6OAc^- \rightleftharpoons 3[Pd(OAc)_4]^{2-} \quad (14)$$

The observed reactions with alkenes are due to the more reactive anionic complexes $[Pd_2(OAc)_6]^{2-}$ and $[Pd(OAc)_4]^{2-}$ because trinuclear Pd^{II} complexes are fairly inert kinetically toward alkene oxidations [45,57].

2.2. Solvent effects

A dramatic increase in the allylic versus vinylic esterification of propylene by the complexes $[Pd_2(OAc)_6]^{2-}$ and $[Pd(OAc)_4]^{2-}$ was found [55,59] when acetic acid was changed for CH_2Cl_2, $CHCl_3$ or $CHCl_2CH_2Cl$. The yield of allyl acetate was at least 99% based on propylene and Pd^{II} consumed, whereas only traces of isopropenyl and *n*-propenyl acetates and acetone were found (Table 1, entries 1–3). The same product composition was found in catalytic runs with the use of nitrosobenzene and benzoyl peroxide as oxidants (Table 1, entries 4, 5). The involvement of Pd^0 was practically ruled out in the presence of these oxidants.

When 5% (vol.) of AcOH was added to the chlorocarbon solvents, noticeable amounts of isopropenyl and *n*-propenyl acetates (and also acetone) appeared in the reaction products (overall yield of 10%, see Table 1, entry 6). The decrease in the reaction selectivity with

[1] Solutions with overall concentrations of 0.05 M of $Pd_3(OCOR)_6$ (calculated for the Pd**II** mononuclear unit) and 0.01 ÷ 0.02 M of (PNP)OCOR − were used in our experiments. Under these conditions, at most 1/3 of original $Pd_3(OCOR)_6$ can be converted into $Pd_2(OCOR)_6^{2-}$ and $Pd(OCOR)_4^{2-}$.

Table 1
Solvent effects in the acetoxylation of propylene by Pd^{II} complexes ($[Pd(OAc)_2]_0 = 0.11$ mol l^{-1}, $[(PPN)OAc]_0 = 0.04$ mol l^{-1}, $p(C_3H_6) = 1$ atm, 25°C, time of reaction 3 h)

Number	Solvent	T (°C)	Reaction products (mol/mol Pd)				Allyl:vinyl ratio
			Allyl acetate	Isopropenyl acetate	*n*-Propenyl acetate *cis*+*trans*	Acetone+propanal	
1	$CHCl_3$	25	0.99	0.01	0.01	0.01	>1000
2	CH_2Cl_2	25	0.99	0.01	–	–	>1000
3	$CHCl_2CH_2Cl$	25	0.99	0.01	–	–	>1000
4	CH_2Cl_2+benzoyl peroxide	25	0.99	0.01	–	–	>1000
5	CH_2Cl_2+nitrosobenzene	25	0.99	0.01	–	–	>1000
6	$CHCl_2CH_2Cl$+5%AcOH	25	0.92	0.058	–	0.023	11
7	AcOH+0.9 M NaOAc	25	0.94	0.06 (total vinylic products)			16
8	AcOH+0.9 M NaOAc+1% H_2O	25	0.49	0.51 (total vinylic products)			~1
9	AcOH	25	0.009	0.986	0.005	–	<0.01
10	CO_2 liquid [a]	25	0.62	0.38 (total vinylic products)			1.6
11	CO_2 fluid [b]	42	0.76	0.24 (total vinylic products)			3.1
12	CO_2 fluid+10%AcOH [b]	46	0.72	0.28 (total vinylic products)			2.6

[a] $p(CO_2) = 90$ atm, $p(C_3H_6) = 12$ atm.
[b] $p(CO_2) = 90$ atm, $p(C_3H_6) = 12$ atm.

respect to allyl acetate is in line with our (Table 1, entry 8) and literature [43,57] (Table 1, entry 7) data for reaction (1) in an AcOH solution.

It was found that the oxidation of propylene in liquid CO_2 containing ~1 wt.% H_2O produced a mixture of allylic and vinylic esters in both liquid and superctitical regions. In fact, this reaction medium is a ~0.5 M solution of H_2CO_3 in liquified CO_2. As seen in Table 1 (entries 10–12), the product distribution is close to that in an AcOH medium, and it is little wonder that the addition of AcOH almost did not change the reaction selectivity (Table 1, entry 12).

Our experiments showed that vinylic esters also are entirely absent from the products of the oxidative acetoxylation of hex-1-ene in a $CHCl_3$ solution. Allylic, mainly *cis*- and *trans*-hex-2-en-1-ol acetates, and homoallylic hex-3-en-1-ol acetate were found as the oxidation products (Eq. (15))[2] [58].

$$CH_2{=}CH(CH_2)_3 \xrightarrow[-Pd^0,\ -AcOH]{Pd(OAc)_2,\ CHCl_3} \begin{cases} AcO-CH_2CH{=}CH_2CHCH_2CH_3 & (\sim 70\%) \\ AcO-CH_2CH_2CH{=}CHCH_2CH_3 & (\sim 15\%) \end{cases} \quad (15)$$

These findings differ from those in early studies [13,18], where substantial amounts of vinylic esters have been obtained by the oxidation of 1-alkenes C_3–C_5 by $Pd(OAc)_2$ in AcOH solutions containing alkaline acetates.

[2] Other allylic esters, e.g., hex-2-ene-4-ol acetate, were also found as minor reaction products.

Reaction of cyclohexene with Pd^{II} carboxylates in low polar aprotic solvents is very sensitive toward the presence of oxidants. When oxidative reagents, which can re-oxidize Pd^0 to Pd^{II} (*p*-benzoquinone, nitrosobenzene or benzoyl peroxide) were absent from the reaction solution, the main reaction product was benzene with the yield at least 98% based on cyclohexene consumed. The esters of cyclohexen-2-ol and cyclohexen-3-ol were formed in negligible yields (Table 2, entry 2). In this case cyclohexene undergoes oxidative dehydrogenation (Eq. (16)) and disproportionation (Eq. (17), the Zelinsky reaction). Both reactions are efficiently catalysed by highly dispersed Pd metal that is formed from the very beginning of reaction.

$$C_6H_{10} + 2Pd(OCOR)_2 \xrightarrow{Pd^0} C_6H_6 + 2Pd^0 + 4RCOOH \quad (16)$$

$$3C_6H_{10} \xrightarrow{Pd^0} C_6H_6 + 2C_6H_{12} \quad (17)$$

In the presence of *p*-benzoquinone, benzoyl peroxide or nitrosobenzene reactions (16) and (17) are practically absent, and the esters of cyclohex-2-en-1-ol and cyclohex-3-en-1-ol are the main reaction product in all aprotic solvents (Table 2, entries 3–13). No vinylic esters were found in the reaction products.

Thus, on going from protic (CH_3COOH, H_2CO_3/CO_2) to aprotic ($CHCl_3$, CH_2Cl_2, 1,1,2-trichloroethane, THF) media a sharp variation in the regioselectivity of reaction (1) occurs: the vinylic route of alkene esterification disappears, the main reaction is allylic esterification, and in the case of C_6 alkenes a homoallylic route is present along with the allylic route.

Table 2
Ligand effects in the esterification of cyclohexene by Pd^{II} carboxylates in aprotic solvents at 25°C

Number	Solvent	Carboxylate ligand	Additional oxidant	Reaction products (%)			
				Allyl:cyclohexene-2-ol ester	Homo-allyl:cyclohexene-3-ol ester	Ratio A:H	Other products
1	$CHCl_3$	OAc^-	–	≤1	≤1	~1	$C_6H_6 \geq 98\%$
2	$CHCl_3$	OAc^-	*p*-Benzo-quinone	61.3	38.7	1.6	$C_6H_6 < 1\%$
3	$CHCl_3$	OAc^-	$(PhCO)_2$ O_2	52.9	44.1	1.2	$C_6H_6$3.0%
4	*i*-$C_5H_{11}OMe$	OAc^-	*p*-Benzo-quinone	65.36	34.64	1.9	$C_6H_6 < 1\%$
5	Cyclohexene	$R_fCO_2^-$ (racemic) [a]	*p*-Benzo-quinone	No reaction			
6	$CHCl_3$	$R_fCO_2^-$ (racemic) [a]	–	–	–		C_6H_6 62% C_6H_{12} 59%
7	$CHCl_3$	$R_fCO_2^-$ (racemic) [a]	*p*-Benzo-quinone	70.59	29.41	2.4	$C_6H_6 < 1\%$
8	$CHCl_3$	$R_fCO_2^-$ (chiral)	*p*-Benzo-quinone	85.63	14.37	5.9	$C_6H_6 < 1\%$
9	$CHCl_3$	3-Methylbutyrate (achiral)	*p*-Benzo-quinone	84.3	15.7	5.4	$C_6H_6 < 1\%$
10	$CHCl_3$	2-(±)-Methyl-butyrate	*p*-Benzo-quinone	86.7	13.3	6.5	$C_6H_6 < 1\%$
11	$CHCl_3$	2-(+)-Methyl-butyrate	*p*-Benzo-quinone	98.5	1.53	64.4	$C_6H_6 < 1\%$
12	THF	2-(±)-Methyl-butyrate	*p*-Benzo-quinone	84.02	15.98	5.3	$C_6H_6 < 1\%$
13	THF	2-(+)-Methyl-butyrate	*p*-Benzo-quinone	68.22	31.78	2.2	$C_6H_6 < 1\%$

[a] $RfCO_2^- = CF_3CF_2CF_2OC^*F(CF_3)COO^-$.

2.3. Ligand effects

In order to gain additional information on the nature of these routs, the ligand chirality effects in the oxidative esterification of cyclohexene by Pd^{II} carboxylates were studied.. As seen in Table 2, the oxidation of cyclohexene by Pd^{II} complexes containing different carboxylate ligands in aprotic media affords the corresponding allylic and homoallylic esters, and vinylic oxidation is absent.

The cyclohexene molecule possesses two pairs of enantiotopic centres in the α- and β-positions relative to the double bond. Owing to this, reaction (1) could has afforded optically active cyclohexenyl esters. The ester molecule containing a chiral carboxylate has two chiral centres: one C* atom in the α- or β-position of the cyclohexenyl group and another C* atom in the carboxylate group (Scheme 6).

Stereoisomeric composition of the products of cyclohexene esterification by Pd^{II} complexes with chiral anions $(S(+)\text{-}MeC^*H(Et)CO_2^-$ and $(+)\text{-}CF_3CF_2CF_2\text{-}OC^*F(CF_3)CO_2^-$ in chloroform was investigated by GC/MS. The capillary column with the universal stereoselective phase α-Decs failed to satisfactorily separate the diastereoisomeric cyclohexenol esters [58]. For this reason the mixtures of the esters obtained were preliminarily hydrolyzed by 10% methanolic NaOH with retention of configuration [60]. It was found by GC/MS that the stereoisomeric cyclohexene-2-ols obtained after hydrolysis are present in practically equal concentrations[3]. Therefore, the mechanism of reaction (1) is inadequate to utilize the asymmetric induction of the chiral carboxylate ligands.

Meanwhile, the chirality of carboxylate ligand affects noticeably the regioselectivity of reaction (1). As seen in Table 2 (entries 7,8), the allyl: homoallyl ratio increased more than twofold (from 2.4 to 5.8) on going from the racemic $(\pm)\text{-}R_f^*COO^-$ anion to chiral $(+)\text{-}R_f^*COO^-$ anion when cyclohexene was oxidized by the Pd^{II} complexes in chloroform. Even more pronounced effect was found in the reaction involving 2-methylbutyrate ligand. In this case the allyl: homoallyl ratio increased in more than one order of value, from 6.5 for racemic to 64.4 for chiral S(+) ligand (Table 2, entries 10,11).

This effect almost disappeared when reaction (1) was carried out in the more donor solvent, THF. In this medium the reactions involving 2-methylbutyrate ligand were found to be low sensitive to the ligand chirality (see Table 2, entries 12,13).

2.4. Reaction mechanism

On the basis of the above-mentioned data some mechanistic conclusions can be drawn. A sharp increase

[3] The concentrations of stereoisomeric cyclohexene-3-ols were too low for quantitative analysis by GC/MS.

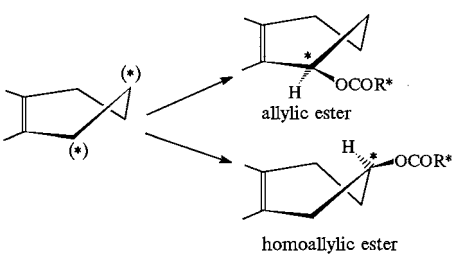
in the selectivity in respect to allylic oxidation of propylene on going from acetic acid to low polar aprotic solvents (Table 1) hardly can be understood within the framework of the conventional mechanism (Scheme 7) with 1,2-oxypalladation in a single stage (≪a≫), which has been forwarded at the early studies of the reaction [1,4,22,57].

According to this mechanism, the oxidation of propylene should afford isopropenyl acetate, when the stage ≪**a**≫ in Scheme 7[4] occurs via the Markovnikov-addition followed by Pd–C bond heterolysis (stage ≪**b**≫ in Scheme 7). In fact, this reaction product has been repeatedly observed in AcOH solutions containing 0.1–0.5 mol l^{-1} additional OAc^- ions [1–4,57]. (Note that in the presence of anions with high elecronegativity such as NO_3^-, 1,2-glycol ester also can be obtained [62]). When 1,2-oxypalladation occurs via anti-Markovnikov-route, *n*-propenyl acetate, the second observable reaction product of propylene oxidation by Pd^{II} in the AcOH/NaOAc system [1–4,57] should be expected as shown in Scheme 8.

Meanwhile, the third reaction product, allyl acetate is commonly formed in the same reaction system, and its formation cannot be realized within the single-step 1,2-oxypalladation mechanism (Scheme 7).

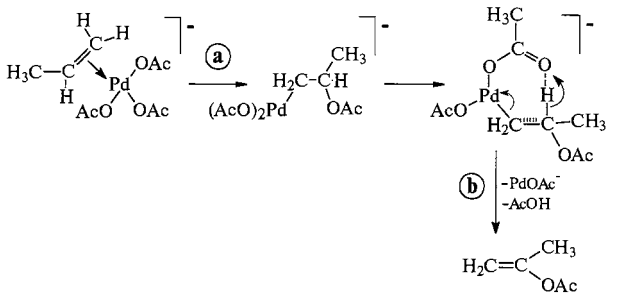
An alternative mechanistic viewpoint suggests the reaction proceeds via an intermediate π-allyl complex [4,9,18,61a,b,63].

At first glance this mechanism looks fairly attractive, especially because the palladium π-allyl complexes are well known since 1959, when the first stable complex $[\pi\text{-}C_3H_5{\cdot}PdCl]_2$ has been synthesized independently by the reactions of $PdCl_2$ with allyl alcohol (Moiseev, Fedorovskaya and Syrkin [65]) and allyl chloride (Smidt and Hafner [66]). The involvement of π-allyl complexes in the mechanism like that shown in Scheme 9 seems to be quite plausible for alkene oxidations in an AcOH solution with high concentration of OAc^- an-



Scheme 6.

[4] The 1,2-oxypalladation stage may occur with the participation of either coordinated OAc^- group as *cis*-attack shown in Scheme 7 or as *trans*-attack by free OAc^- anion from a bulk solution [1,4,18,61]. In both cases the Markovnikov-route is preferable.



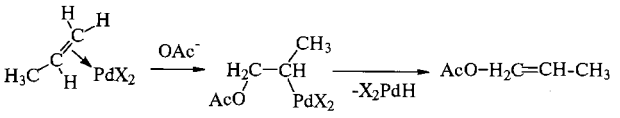
Scheme 7.

ion, which is necessary for the transformation of the palladium η^2-alkene to η^3-allyl complex (stage ≪a≫ in Scheme 9). Recently Grennberg and Bäckvall [67] has provided elegant evidence for the formation of the π-allylpalladium intermediate by the example of reaction between $Pd(OAc)_2$ and 1,2-dideuterocyclohexene in an AcOH solution. However, the way in which the π-allyl complex undergoes redox disproportionation into allyl acetate and Pd^0 (Scheme 9, stage ≪b≫) is still not clear. Direct studies of the reactivity of Pd^{II} π-allyl complexes toward nucleophilic and electrophilic reagents [9,12,18,32,61] showed that such a disproportionation occurs in fact but is often a side reaction accompanied with other transformations of the π-allyl complex not leading to allylic esters.

In our experiments 'free' OAc^- anions were in negligible concentration, ($[OAc^-] \leq 10^{-3}$ mol l^{-1}), being mostly bound into the complexes $[Pd_2(OCOR)_6]^{2-}$ and $[Pd(OAc)_4]^{2-}$. Even minor amounts of OAc^- anions unbound with palladium(II) should exist as tight ionic pairs with bulky PNP cations, being hardly accessible for attacking the η^2-alkene complex in a low polar organic medium ($CHCl_3$, CH_2Cl_2, THF).

In our opinion, an alternative explanation of data obtained may be proposed by the mechanism, whose key stage is an intramolecular electrophilic attack of the Pd^{II} atom on the coordinated alkene molecule not accompanied by the OAc^- attack to form a Pd^{II} σ-complex (see Scheme 10). The electrophilic attack by the Pd^{II} atom to η^2-alkene ligand cannot be assisted with simultaneous attack of the outer-sphere OAc^- anion ('nucleophilic assistance' [1,22,29]) because of the deficiency of 'free' OAc^- anions. Most likely that a palladium σ-complex with a carbenium moiety is formed under these conditions (see Scheme 10, stage ≪a≫).

In the virtual absence of outer-sphere OAc^- anions, the coordinated carbenium group $CH_3CH^+CH_2$–Pd is expected to react intramolecularly, through a proton elimination from the CH_3 group, possibly assisted by an additional Pd…H weak interaction (stage ≪b≫ in Scheme 10).



Scheme 8.

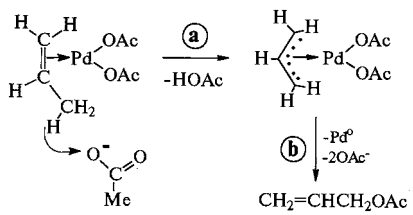
Our results for the oxidative esterification of cyclohexene in low polar aprotic media (Table 2) agree well with the mechanism shown in Scheme 10. Note that homoallyl esters always form along with allylic esters. Within the frameworks of the 'allylic' mechanism, this fact needs the assumption that reaction (1) is accompanied by the positional isomerization of the double bond in the allylic esters first formed. However, such an isomerization is known to be catalysed by Pd metal and low-valence Pd complexes and is efficiently inhibited by *p*-benzoquinone and other oxidants capable of re-oxidizing Pd^0 compounds [1,35–38,68,69]. Our experiments showed that such oxidants in fact terminate the oxidative dehydrogenation and disproportionation of cyclohexene (Eqs. (15) and (16)), which are also catalysed by Pd^0, but have no effect on the formation of homoallylic esters. Moreover, the assumed isomerization could produce vinylic esters, which in fact were absent from all experiments in aprotic media.

All these data seem to support the mechanism (see Scheme 10), which is similar to that in Scheme 10 and includes an inner-sphere attack of the coordinated carboxylate anion $RCOO^-$ to the CH_2 group of the σ-bonded carbenium ligand.

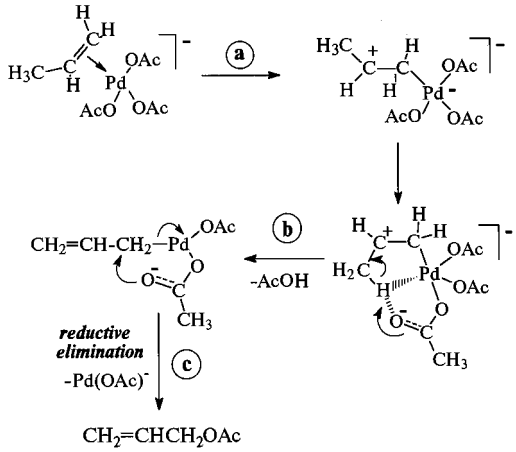
The mechanism in Scheme 11 assumes that the lifetime of the σ-complex **1** is long enough to undergo 1,2-hydride shift and displacement of the carbenium centre to adjacent C atom of the cyclohexane ring before the redox transformation of the original σ-complex **1**. The inner-sphere attack of the OAc^- ligand to the CH_2 group of the original σ-complex results in the formation of allylic ester (path ≪a≫), whereas a similar process involving the isomerized σ-complex **2** affords homoallylic ester (path ≪b≫).

Our data on the regioselectivity of oxidative acetylation of hex-1-ene in a chloroform solution (see above) also well agree with the 'carbenium' mechanism (see Scheme 12).

The data on the oxidation of cyclohexene can be suggested as an example of the stereocontrol of the

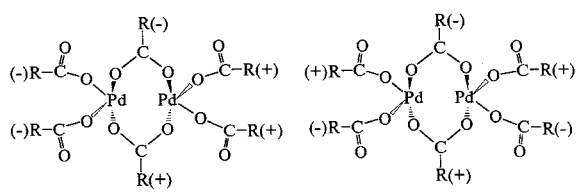


Scheme 9.



Scheme 10.

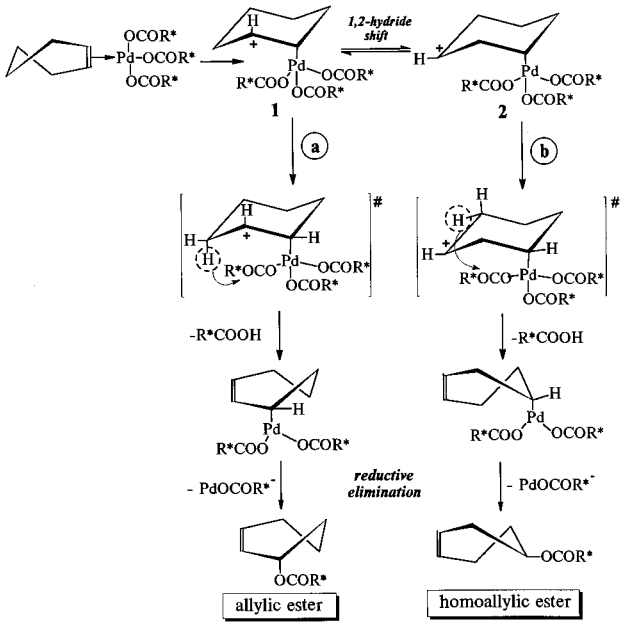
reaction regioselectivity. In the case when the original salts $(PNP)OCOR^*$ and $(PNP)_2Pd_3(OCOR^*)_6$ contain only one stereoisomer of the chiral carboxylate anion (for instance, (+)-S-2-methylbutyrate, see Scheme 12), the acido complexes $[Pd(OCOR^*)_4]^{2-}$ and $[Pd_2(OCOR^*)_6]^{2-}$ that react with alkene are built from the stereochemically identical anions R^*COO^-. Unlike this, in experiments with the racemic anions (±)-R^*COO^-, the alkene is to react with a set of stereochemically different Pd^{II} carboxylate complexes, which contain both (+)-R^*COO^- and (−)-R^*COO^- ligands in various combinations, such as shown, for instance, in structures **3** and **4**.



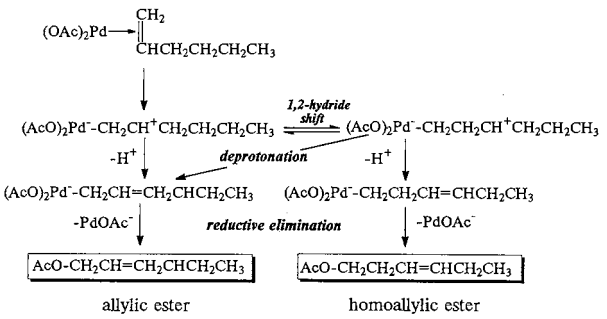
3 **4**

In the stages of π-complex formation, π-σ-isomerization and 1,2-hydride shift, the reactivity of such complexes seem to be not much different. However, this is not the case for the following stage of H^+ abstraction by the coordinated R^*COO ligand, when the gain in the competition between paths ≪a≫ and ≪b≫ should depend on mutual arrangement of the acido ligands controlled by their stereoconfiguration.

The above-mentioned discussion allows one to realize the data for reaction (1) in weakly solvating organic media like chlorocarbons, which only slightly affect the inner-sphere complex transformations. In solvents with higher nucleophilicity like THF, additional factors that depend on the solvation should be taken into consideration. In this case the H^+ ion can be more likely abstracted from the carbenium ion by the solvent molecule, and the competition between allylic and



Scheme 11.



Scheme 12.

homoallylic paths ≪a≫ and ≪b≫ is almost independent of the ligand chirality.

It is noteworthy that the proposed 'carbenium' mechanism of alkene oxidation (Schemes 10 and 11) is in fact closely related to the above-mentioned 'allylic' mechanism by Bäckvall and Grennberg [67] (see Scheme 9). According to numerous NMR observations (see, for instance, [12,31,72]), η^3-allylic complexes readily isomerize to σ-allylic complexes in solutions, and this reaction is normally fast and reversible. Hence, Schemes 10 and 11 can be generalized by supplementing with the reversible π–σ-isomerization stages (Schemes 13 and 14), thus reflecting the totality of data for the allylic pathway of alkene oxidation by Pd^{II}.

Unlike allylic, the homoallyl path of alkene esterification has attracted much less attention. Since the first observations [21,70], the formation of homoallylic esters was mostly treated as an unessential side reaction. The findings [67,71] that addition of strong acids like $MeSO_3H$ favours noticeably the homoallylic oxidation of cyclohexene, seem to agree with the mechanism shown in Scheme 11, because a strong acid should prevent both 1,2-oxypalladation and the transformation of η^2-alkene to η^3-allylic complex, favouring the formation of σ-bonded carbenium ligand.

3. Reactions with Pd nanoclusters

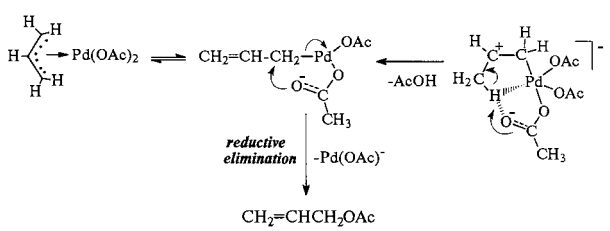
It was believed for a long time that the same mechanism is operative in all of the Pd-catalysed alkene oxidations, including a vapor-phase process [3] in which Pd catalyst is introduced into the reaction system as the Pd metal black or Pd metal supported on an inert carrier [17,73,74], due to the ease of the re-oxidation of Pd^0 to Pd^{II} via reaction (3)–(4).

However, the hypothesis that Pd^{II} is responsible for the alkene oxidation under the conditions of industrial process with heterogeneous Pd catalyst is in contradiction to the data on the selectivity of oxidative acetoxylation of propylene (see above).

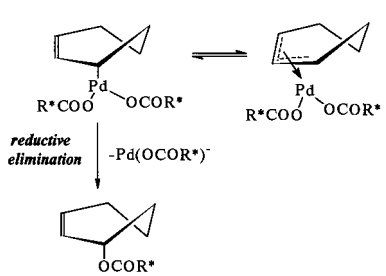
The reaction between Pd^{II} and propylene in AcOH medium produces acetone instead of isopropenyl or allyl acetate due to competitive reaction (18), when water content exceeds ~1%:

$$CH_3CH{=}CH_2 + Pd^{II} \xrightarrow{AcOH + 1\%H_2O} CH_3COCH_3 + Pd^0 \quad (18)$$

Meanwhile, when the Pd metal catalyst and O_2 oxidant are used, the allyl pathway of the propylene acetoxylation predominates in both the liquid- and vapour-phase reactions, and the allylic versus vinylic



Scheme 13.



Scheme 14.

selectivity is only slightly sensitive to a water content up to 10% and the temperature [17,43,73,74]:

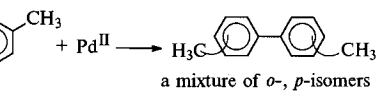
$$CH_3CH{=}CH_2 + AcOH + 1/2O_2 \xrightarrow{[Pd^0]} CH_2{=}CHCH_2OAc + H_2O \quad (19)$$

Unlike this, allylic versus vinylic selectivity of both stoichiometric and catalytic oxidation mediated by Pd^{II} has been found to be highly sensitive to the temperature, the content of acetate salts and water in the acetic acid solvent: allyl to vinyl ratio varied from 0.05 to >10 depending on these variables [43,57,68,75]. Only in aprotic solvents of lower polarity such as CH_2Cl_2, $CHCl_3$, is allyl acetate a prevailing product [55,59].

A similar change in the selectivity was observed in the oxidative acetoxylation of ethylene. When Pd^{II} complexes such as $Pd(OAc)_4^{2-}$, $Pd_2(OAc)_6^{2-}$ were applied as the oxidants or catalysts, even small additives (1–3%) of water to the NaOAc/AcOH solvent resulted in a gain of the 'aqueous' pathway in the competition between the AcO^- and H_2O nucleophiles, producing acetaldehyde instead of vinyl acetate [46,47,75]. Unlike this, heterogeneous Pd metal catalysts provide vinyl acetate from ethylene and AcOH with high selectivity, independently of the concentration of water additives within 0.2–10% [47,75,77] (Eq. (20)).

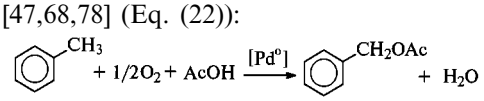
$$CH_2{=}CH_2 + 1/2O_2 + AcOH \xrightarrow{[Pd^0]} CH_2{=}CHOAc + H_2O \quad (20)$$

Differences in the reactivity of Pd^{II} carboxylates and Pd metal toward alkylarenes were also found [68,78]. In an AcOH solution of $Pd(OAc)_2$ or $Pd(OCOCF_3)_2$ in CF_3COOH, toluene is subjected to an electrophilic attack on the aromatic ring forming a mixture of isomeric bis-tolyles, the products of oxidative coupling (Eq. (21)):



(21)

In the presence of high-dispersed palladium metal, toluene is readily oxidized by O_2 in an AcOH solution to afford benzyl acetate, the product of the oxidative acetoxylation at the alkyl group, in the 95% yield [47,68,78] (Eq. (22)):



(22)

All these facts imply that the hydrocarbon activation comes from two different origins: one from Pd^{II} and another from low-valence Pd clusters formed in the Pd^{II}/Pd^0 reaction system. This suggestion was confirmed by experiments with Pd black and palladium nanoclusters [17,68,69,75–78].

Finely dispersed palladium metal (for instance, as-prepared Pd black obtained by reduction of $PdCl_2$ or $Pd_3(OAc)_6$ with HCOONa or $NaBH_4$) is inactive in catalysis of reactions (Eqs. (19) and (20)) in an AcOH solution containing alkaline acetates. However, the Pd black acquired the catalytic activity, if it was prepared by reduction of the Pd^{II} salts in the presence of alkaline acetates [17,43,75]. Better catalyst was obtained when the salt $Pd_3(OAc)_6$ was reduced by H_2 in an AcOH solution containing 1,10-phenanthroline (phen) or 4,4′-dipyridine (dipy) [68].

The phen (dipy)-containing catalysts were isolated from the reaction solutions as X-ray amorphous solids, whose nature were characterized by the TEM, HREM, SAXS, EXAFS, elemental analysis and magnetic susceptibility data [68,69,79,80]. These studies showed that the substance is a colloid-like nanocluster with the chemical composition of $Pd_{570\pm30}L_{63\pm3}(OAc)_{190\pm10}$ (L = phen or dipy). The giant cluster molecule consists of a positively charged metal core of $\sim$25 Å in diameter containing 570 ± 30 dense-packed (f.c.c. or icosahedral packing) Pd atoms. The surface metal atoms are surrounded by coordinated $\sim$63 phen or dipy ligands and $\sim$190 outer-sphere OAc^- anions, and the latter counterbalance the positive charge of the metal core. Average formal charge of Pd atoms in the cluster molecule is equal to 190: $570 = +1/3$. Within the framework of the P. Chini concept of cluster 'magic numbers' [81], the structure of the giant cluster was approximated by idealized formula $Pd_{561}L_{60}(OAc)_{180}$ (**5**).

The outer-sphere OAc^- ligands in cluster **5** can be readily replaced by another anions. For instance, complete substitution of OAc^- anions, accompanied by hydrolysis, occurs on treatment of an aqueous solution of **5** with KPF_6, forming the cluster with the idealized formula $Pd_{561}phen_{60}O_{60}(PF_6)_{60}$ (**6**):

$$[Pd_{561}phen_{60}](OAc)_{180} + 60PF_6^- + 60H_2O = [Pd_{561}phen_{60}O_{60}](PF_6)_{60} + 120AcOH + 60OAc^- \quad (23)$$

The composition and structure of cluster **6** and its analogues with other outer-sphere anions has been investigated by the same techniques as those used for cluster **5** [68,80].

Giant clusters **5** and **6** were found to be efficient catalysis for various reactions of organic substrates under mild conditions (293–363 K, 0.1 MPa) [69,79]. For instance, an H atom of alkene molecules can be readily replaced by the OAc group (oxidative acetoxylation) in acetic acid solutions of clusters **5** and **6**:

ethylene is converted to vinyl acetate (Eq. (20)), propylene to allyl acetate (Eq. (19)) and toluene to benzyl acetate (Eq. (22)).

The selectivity of reactions (Eqs. (19) and (20)) with respect to the products of oxidative acetoxylation is at least 95–98%. No decrease in the selectivity was observed even in an AcOH solution containing up to 10% of water. The only side reaction observed with these catalysts is a subsequent oxidation of alkenyl and benzyl esters to form ethylidene, allylidene and benzylidene diacetates, respectively [69].

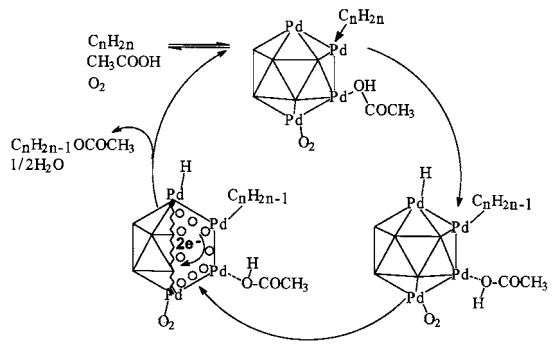
Thus, all the aforesaid is in line with suggestion that giant Pd clusters are the species responsible for the catalysis of alkenes oxidation in these reaction system and in fact, these giant clusters open a new route to the oxidative acetoxylation of alkenes.

Detailed kinetic studies, including the H/D isotope kinetic effects and inhibition kinetics [68,76,78] enabled us to formulate a general mechanism for the Pd nanocluster-catalysed oxidation of alkenes [68,69,82] (Scheme 15).

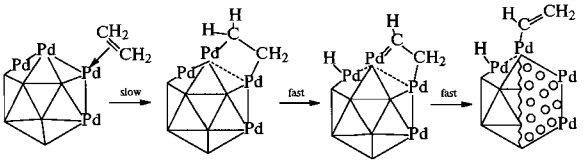
It is noteworthy that oxidative acetoxylation of ethylene by O_2 in the presence of clusters **5** and **6** as well as Pd black (the latter prepared in an AcOH/NaOAc solution) smoothly produced vinyl acetate. Meanwhile, the propylene oxidation in the same reaction systems produced no vinylic esters, and allyl acetate was the sole reaction product at either low or high concentrations of all reacting species, even when benzoyl peroxide or $Pd(OAc)_2$ were used as oxidants instead of O_2 [43,68].

These facts suggested that the rate-determining step is an oxidative addition (with opening the π-bond) of a π-coordinated C_2H_4 molecule to a Pd–Pd group of the cluster to form the σ,σ-coordinated …Pd–CH_2CH_2–Pd… group. Subsequent splitting of the C–H bond with the elimination of a Pd–H fragment in this group is assumed to be a fast step, favored by the Pd=C multiple bond formation in the intermediate **7** [68,69] (see Scheme 16).

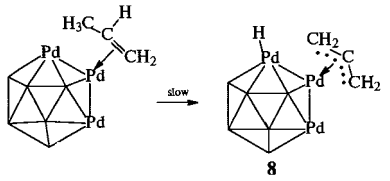
Evidence for the formation of σ,σ-coordinated ethylene and π,σ-coordinated vinyl groups on the palladium (100) surface of palladium crystal has been obtained by HREELS technique [83].



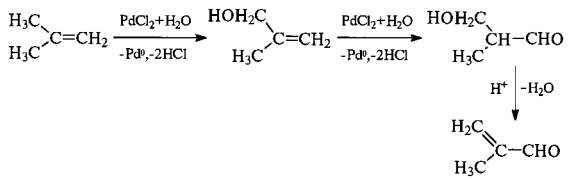
Scheme 15.



Scheme 16.



Scheme 17.



Scheme 18.

In the case of propylene, the energy difference between the carbon–carbon π-bond and the allyl-H bond is much less than that between a carbon–carbon π-bond and the vinyl-H bond in ethylene. Thus, the rate-determining step of the oxidative addition of propylene molecule to the Pd cluster may include the cleavage of the C–H bond in the coordinated propylene molecule to form the surface-coordinated π-allyl and hydride groups (see Scheme 17).

The formation of π-allyl group and coordinated hydride in the intermediate cluster complex **8** appears to favour the allylic route of the reaction in competition with the vinylic one.

Subsequent reactions of the vinyl or allyl groups and H atoms coordinated at the surface of the cluster metal skeleton are assumed to proceed rapidly and exert no influence on the reaction rate. It is unlikely that all three molecules (alkene, O_2, and AcOH) can coordinate to the adjacent palladium atoms at the surface of the cluster core. The alkene molecule is more probably to bound at one site of the cluster surface, while the O_2 molecule is coordinated to another site, not necessarily next to the site where the alkene molecule is located. In this situation, electron transfer from the Pd–alkenyl or Pd–H surface group to the coordinated O_2 molecule can occur though the metal atom chain, the latter acting as an 'electron transfer mediator' [68,69] (see Scheme 15).

Thus, all the aforesaid is in line with suggestion that giant Pd clusters are the species responsible for the catalysis of alkene oxidation in these reaction system and in fact, these giant clusters open a new route to the oxidative acetoxylation of alkenes.

Pd cluster-catalysed oxidation of alkenes drastically differs from the oxidation by Pd^{II} even in several cases that have been observed in aqueous and alcohol solutions. The following two examples are worthy of notice.

(1) 1-Alkenes branched at the double bond (isobutylene, 2-methylbut-1-ene, etc.) cannot be oxidized by Pd^{II} in water via the Markovnikov 1,2-oxypalladation route (Scheme 7). Aldehydes are formed only as trace by-products due to the anti-Markovnikov route [1,18]. Meanwhile, such alkenes are oxidizable by $PdCl_2$ in aqueous solution affording the allylic derivatives [7,63,64] (see Scheme 18)).

No Pd^{II} π-allyl complexes were found in this reactive system, and the reaction mechanism was rather obscure within the common oxidation schemes involving Pd^{II} [18]. On the other hand, the reactions in Scheme 15 are quite explicable in the framework of the cluster-catalysed mechanism (Scheme 16), where low-valence Pd nanocluster functions the catalyst and Pd^{II} is the oxidant.

(2) The oxidation of alkenes by palladium (II) is known to be strongly suppressed by donor ligands, even by such bulky as PPh_3 and phen, due to strong complexation with Pd^{II}, in contrast to the reactions catalysed by giant Pd clusters, whose rates are unaffected by these ligands [1,68]. It is also known that the rates of alkene oxidations by Pd^{II} in aqueous solution are inversely proportional to the H^+ concentration, and the reaction is quenched by addition of 1–2 M mineral acid [1,39]. Quite another phenomena were observed when giant clusters **5** and **6** were employed as catalysts: the oxidation of alkenes did not occur in neutral aqueous solutions. The cluster-catalysed reaction started only after the addition of strong acids (e.g., $HClO_4$, H_2SO_4) [84], and its rate was maximum at the acid concentration, which would be sufficient to stop the reaction of alkenes with Pd^{II}. The products of the alkene oxidations mediated by Pd^{II} and the giant clusters are quite different. At 323 K and 0.1 MPa of 1:1 alkene: O_2 gas mixture ethylene was oxidized in 0.36–1.67 M aqueous solution of H_2SO_4 containing (2.3–4.6) 10^{-4} M of cluster **5** successively to acetaldehyde and acetic acid [84]:

$$C_2H_4 + O_2 \rightarrow CH_3CHO \rightarrow CH_3COOH$$

Note, that acetaldehyde is scarcely oxidized by Pd^{II} to acetic acid under these conditions [1,7,18]. A more pronounced difference was observed for the cluster-catalysed oxidation of propylene: in acidic aqueous solution of cluster **5** propylene was converted successively to allyl alcohol, acrolein, and acrylic acid (Table 3):

$$C_3H_6 + O_2 \rightarrow CH_2{=}CHCH_2OH \rightarrow CH_2{=}CHCHO \rightarrow CH_2{=}CHCOOH$$

Only traces of acetone were found in the reaction products, in contrast to the reaction mediated by Pd^{II} in which acetone was nearly a sole product [1,5,7].

In alcoholic (MeOH, EtOH) solutions acidified with 1.6 M H_2SO_4, allylic oxidation of propylene was also found to occur, affording acrylic esters along with acrolein and acrylic acid (Table 3). In parallel to the main reactions, the oxidation of the alcohols to the corresponding esters (MeOH to HCOOMe and EtOH to CH_3COOEt) took place (see below). In the absence of added acid, the oxidation of alcohols dominated, and the ethylene and propylene remained almost unreacted.

4. Experimental

Solvents (*n*-pentane, benzene, diethyl ether, chloroform, dichloromethane, trichloroethane, acetic acid and THF) of 'reagent grade' were purified by standard methods [85]. Cyclohexene and hex-1-ene of 'reagent grade' were distilled over sodium metal and stored over molecular sieve 4 Å. Propylene of 'special puruty grade' in cylinder was purchased from Moscow Petrol Refining factory. Trade carbon dioxide in cylinder was purified by re-condensation and stored in an 1 l cylinder. *p*-Benzoquinone was purified by vacuum sublimation. Palladium(II) chloride, sodium borohydride and isovaleric acid were of 'chemically pure' grade. (*S*)-(+)-2-methylbutyric and (±)-2-methylbutyric acids, bis(triphenyl-phosphoranilidene)ammonium chloride ('reagent grade', Fluka) were used. Palladium giant clusters with the idealized formula $Pd_{561}phen_{60}(OAc)_{180}$ and $Pd_{561}phen_{60}O_{60}(PF_6)_{60}$ were prepared according to the published procedures [68]. (Heptapropoxy)perfluoropropionic flouroanhydride and (*S*)-(−)-1-phenylethylamine of 'reagent grade' were provided by the Kirovo–Chepetsk Chemical Industries (Russia) and Zeeland Chemicals (USA), respectively.

4.1. Analysis methods

Element C,H,N-microanalysis of the complexes was performed on an automatic C,H,N-analysator 'Carlo-Erba Strumentazione', Italy. NMR spectra were recorded on Bruker WP-200 spectrometer, IR spectra were recorded on a spectrometer Specord M80 (Carl

Table 3
Oxidation of propylene in acidic solutions of cluster **5** (50°C, 1 atm of C_3H_6: O_2 (1:1) gas mixture, time of reaction 1 h) [84]

Solvent	C_3H_6:O_2	[**5**] 10^{-4} M	[H_2SO_4] M	Initial rate of propylene consumption 10^{-3} mol (l min)$^{-1}$	Reaction products (%)
H_2O	1:1	2.34	1.67	4.04	CH_2=CHCH$_2$OH (38) CH_2=CHCHO (14) CH_2=CHCOOH (20) MeCOMe (4) Me_2CHOH (11) [a]
MeOH	2:3	1.61	1.61	5.25	CH_2=CHCHO (4) CH_2=CHCOOH (40) CH_2=CHCOOMe (40) MeCOMe (4) HCOOMe (2)

[a] Isopropyl alcohol formed due to the acid-catalysed propylene hydration, independently of the presence of Pd cluster.

Zeiss, Iena) in pellets with KBr. GC/MS analyses of the reaction products were performed on an Automass 150 instrument (Delsi Nermag, France, capillary columns with OV-1Па-Decs deposited phases), GLC analyses were conducted on a chromatograph Varian 3600, USA, (universal capillary column with the OV-1 stationary phase).

4.2. X-Ray diffraction study of palladium S(+)-2-methylbutyrate [48]

Experimental reflection set was recorded on a four-cycle automatic diffractometer Siemens R3/PC (λMo–K_α, $\lambda = 0.71074$ Å, $T = -120$°C). The parameters of elementary cell were measured and refined from 24 equivalent reflections with $2\theta < 26$–28°.

The structure was solved by direct method and refined in full-matrix anisotropic approximation for all non-hydrogen atoms. The H atoms of the EtC*HMe groups were generated geometrically and refined in a rider model It was found that the C atoms of the EtC*HMe groups have rather high temperature factors due to some irregularity of these fragments. For this reason, refinement was performed for the atoms in intermediate positions with the multiplicity of 1. The correction for absorption ($\mu = 13{,}35$ cm^{-1}) was introduced according to the program [86]. Calculations were performed by the program complex SHELXTL PLUS (PC version) [87]. The cell parameters, atomic coordinates, bond lengths and angles are given in Ref. [48].

4.3. (±)-(Heptapropoxy)perfluoropropionic acid

(±)-(Heptapropoxy)perfluoropropionic acid was prepared by hydrolysis of the corresponding fluoroanhydride in water followed by fractionation of the aqueous solution by a modified method [88].

4.4. (+)-(Heptapropoxy)perfluoropropionic acid

(+)-(Heptapropoxy)perfluoropropionic acid was obtained by the separation of diastereoisomeric (*S*)-(−)-1-phenylethylamides according to the known method [89,90].

4.5. Palladium(II) acetate

Palladium(II) acetate was obtained by the oxidation of as-prepared Pd black (obtained from $PdCl_2$ and $NaBH_4$) by concentrated HNO_3 in glacial AcOH by the previously reported method [91] and purified from the traces of nitrates and nitrito complexes by refluxing in glacial AcOH with as-prepared Pd black.

4.6. Palladium(II) (S)-(+)-2-methylbutyrate

A total of 1 g (10 mmol) of (*S*)-(+)-2-methylbutyric acid in 5 ml of benzene was added to a solution of 0.5 g of palladium(II) acetate (2.23 mmol) in 30 ml of benzene and refluxed under mixing during 2 h. The dark precipitate formed after cooling was filtered off, the mother liquid was evaporated on a rotary evaporator until a viscous orange oil was formed. The oil was dissolved in pentane, the excess of the acid was washed off with water (3–4 times by 200 ml), and the oil was dried over $CaCl_2$ and then over a molecular sieve. Excess pentane was evaporated on a rotary evaporator, and the residue was dried in vacuum. Yield 0.52 g (75% based on Pd). According to GC/MS data, the substance obtained as a viscous orange oil contains ~1% of an admixture of (*S*)-(+)-2-methylbutyric acid. The sample was used in experiments on cyclohexene oxidation in the form of solutions in chloroform or THF without additional purification. IR spectrum (Vaseline oil), νCO cm^{-1}:

1637, 1425. ^{1}H-NMR spectrum ($CDCl_3$, δ ppm, J Hz): 0.62 (t, 3H, $^3J = 7.36$); 0.83 (d, 3H, $^3J = 7.01$); 1.41 (m, 2H); 2.2 (m, 1H).

4.7. Palladium(II) (±)-2-methylbutyrate and isovalerate

Palladium(II) (±)-2-methylbutyrate and isovalerate were prepared by the same method. Yields based on Pd are 77–72%, respectively.

4.8. Palladium(II) (+)-(heptafluoropropoxy)-perfluoropropionate

The acid (+)-$CF_3CF_2CF_2OCF(CF_3)CO_2H$ (1.63 g, 4.9 mmol, 10% excess) was added under stirring to a solution of $Pd(OAc)_2$ (0.5 g, 2.23 mmol) in 25 ml of benzene, heated at 60°C for 2 h and filtered. The residue was washed with diethyl ether, and the dark brown solution was evaporated to dryness on a rotary evaporator. The oil obtained was dried over KOH during 3 days and purified by crystallization from THF, precipitating the palladium carboxylate by hexane. Yield 1.02 g (60% based on Pd). Found (%): C, 19.01; Pd, 13.58. $C_{12}F_{22}O_6Pd$. Calc. (%): C, 18.85; Pd, 13.92. ^{19}F-NMR spectrum (acetone d_6, δ ppm, J Hz): −81.0 (t, 3F, CF_3–CF_2–, $^3J = 6.6$); −82.1 (d, 3F, CF_3–CFO–, $^3J = 2.5$); −85.7 (m, 2F, –CF_2–CF_3); −126.2 (m, 1F, CF_3–CFO–); −129.3 (m, 2F, –O–CF_2–CF_2–).

4.9. Palladium(II) (±)-(heptafluoropropoxy)-perfluoropropionate

Palladium(II) (±)-(heptafluoropropoxy)perfluoropropionate was prepared by the same method. Yield 1.1 g (65% based on Pd).

4.10. Bis(triphenylphosphoranilidene)ammonium acetate

Bis(triphenylphosphoranilidene)ammonium acetate was prepared by the modified method [53]. To a solution of $(Ph_3P)_2NCl$ (1 g, 1.75 mmol) in 40 ml of $CHCl_3$ a solution of AgOAc (0.44 g, 2.62 mmol, 20% excess) in 30 ml of $CHCl_3$ was added. The reaction mixture was stirred during 1 h and the AgCl precipitated was filtered off. The solution was evaporated on a rotary evaporator to a volume of 10 ml and added diethyl ether to the beginning if crystallization. The main amount of PNP acetate was first precipitated as a colorless oil, which crystallizes on storing in a fridge for 10–12 h. The substance was purified by recrystallization from $CHCl_3$–diethyl ether. Yield 0.94 g (90% based on $(Ph_3P)_2NCl$). Found (%): C, 76.43; H, 5.61; N, 2.37. $C_{39}H_{33}NO_2P_2$. Calc. (%): C, 76.37; H, 5.57; N, 2.34. ^{1}H-NMR spectrum ($CDCl_3$, δ ppm): 1.95 (s, 3H, OAc^-); 7.3–7.7 (m, 30H, Ph).

4.11. Bis(triphenylphosphoranilidene)ammonium isovalerate

A suspension of ZnO (0.10 g, 1.23 mmol) in isovaleric acid (0.25 g, 2.45 mmol) and water (0.3 ml) was stirred at a room temperature for 24 h till complete dissolution of ink oxide. The solution was added to a saturated at ~50°C aqueous solution of $(Ph_3P)_2NCl$ (0.705 g, 90% with respect to ink isovalerate). The reaction mixture was heated at 60°C for 0.5 h to form a pale rose oil, which was washed with water (3–4 times by 50 ml) and extracted with chloroform. The organic layer was dried with molecular sieve 4Å. After filtration and evaporation of the solution to 1/3 of the volume, diethyl ether was added to the beginning of precipitation, and the product was crystallized in 0.5–1 h. The substance was recrystallized from a chloroform–diethyl ether mixture. Yield 0.47 g (62% based on $(Ph_3P)_2NCl$). Found (%): C, 76.42; H, 6.20; N, 2.15. $C_{41}H_{39}NO_2P_2$. Calc. (%): C, 76.97; H, 6.15; N, 2.19. IR spectrum (KBr), νCO cm^{-1}: 1605, 1425. ^{1}H-NMR spectrum ($CDCl_3$, δ ppm, J Hz): 0.65 (d, 6H, $^3J = 6.2$); 1.25 (m, 1H); 2.02 (m, 2H); 7.68 − 7.4 (m, 41H).

4.12. Bis(triphenylphosphoranilidene)ammonium (+)-(heptafluoropropoxy)perfluoropropionate

A suspension of ZnO (0.125 g, 1.52 mmol) and (+)-$CF_3CF_2CF_2OCF(CF_3)COOH$ (1.02 g, 3.07 mmol) was stirred at a room temperature till complete dissolution of ZnO (~12 h). The reaction mixture was added together with 5 ml of H_2O to a warm (~50°C) solution of $(Ph_3P)_2NCl$ (1.57 g, 1 equiv. with respect to a 90% yield of $Zn(R_FCOO)_2$). The mixture was heated for 0.5 h at 60°C and then was worked up by the same procedure as that for bis-(triphenylphosphoranilidene)ammonium isovalerate (see above). Yield 0.93 g (85% based on $(Ph_3P)_2NCl$). Found (%): C, 58.56; H, 3.5; N, 1.73. $C_{42}H_{30}NF_{11}O_3P_2$. Calc. (%): C, 58.14; H, 3.49; N, 1.61. ^{19}F-NMR spectrum ($CDCl_3$, δ ppm, J Hz): −84.3 (t, 3F, CF_3–CF_2–, $^3J = 7.43$); −84.7 (d, 3F, CF_3–CFO–, $^3J = 3.3$); −86.0 (m, 2F, –CF_2–CF_3); −126.8 (m, 1F, CF_3–CFO–); −132.7 (m, 2F, –O–CF_2–CF_2–).

4.13. Bis(triphenylphosphoranilidene)ammonium (S)-(+)-2-methylbutyrate

A mixture of (S)-(+)-2-methylbutyric acid (0.2 g, 1.96 mmol), NaOH (0.078 g, 1.96 mmol) and water (0.5 ml) was stirred till complete dissolution of

NaOH. To the solution was added a saturated aqueous solution of AgO_3 (0.33 g, 1.95 mmol) acidified with five drops of (*S*)-(+)-2-methylbutyric acid. The Ag[EtC*H(Me)]COO precipitated was filtered off, washed with water, methanol and hexane and dried in a vacuum dessicator over alkali for 24 h. To a solution of $(Ph_3P)_2NCl$ (0.907 g, 1.56 mmol) in chloroform was added a chloroform solution of the silver carboxylate. The AgCl precipitated was filtered off, the mother liquid was evaporated on a rotary evaporator till 1/3 of the initial volume, and added diethyl ether to the beginning of precipitation. After 0.5–1 h, the crystalline precipitate was filtered off and recrystallized from a chloroform–diethyl ether mixture. Yield 0.82 g (81% based on $(Ph_3P)_2NCl$). Found (%): C, 76.63; H, 6.19; N, 2.17. $C_{41}H_{39}NO_2P_2$. Calc. (%): C, 76.97; H, 6.15; N, 2.19. IR spectrum (KBr), νCO cm^{-1}: 1616, 1425. ^{1}H-NMR spectrum ($CDCl_3$, δ ppm, *J* Hz): 0.83 (t, 3H, $^3J = 7.35$); 1.15 (d, 3H, $^3J = 7.1$); 1.75 (m, 2H); 2.35 (m, 1H); 7.68–7.4 (m, 30H).

4.14. Bis(triphenylphosphoranilidene)ammonium (*S*)-(±)-2-methylbutyrate

Bis(triphenylphosphoranilidene)ammonium (*S*)-(±)-2-methylbutyrate was prepared by the same procedure as bis(triphenylphosphoranilidene)ammonium (*S*)-(+)-2-methylbutyrate (see above). Yield 0.80 g (79% based on $(Ph_3P)_2NCl$). Found (%): C, 76.57; H, 6.21; N, 2.22. $C_{41}H_{39}NO_2P_2$. Calculated (%): C, 76.97; H, 6.15; N, 2.19. IR spectrum (KBr), νCO cm^{-1}: 1615, 1425. ^{1}H-NMR spectrum ($CDCl_3$, δ ppm, *J* Hz): 0.85 (t, 3H, $^3J = 7.37$); 1.1 (d, 3H, $^3J = 7.09$); 1.77 (m, 2H); 2.38 (m, 1H); 7.66–7.5 (m, 30H).

4.15. Oxidation of propylene by palladium(II) acetate complexes [55]

4.15.1. Procedure A (liquid solvents)

The reaction was conducted in a small stainless steel autoclave of 7.2 ml free volume. PNP acetate (0.042 mmol), nitrosobenzene or *p*-benzoquinone (0.223 mmol) and $Pd(OAc)_2$ (0.111 mmol) dissolved in 1.5 ml of a solvent (chloroform, dichloromethane, AcOH, etc.) were placed into the autoclave and evacuated (5 Torr) under cooling to 0°C. The reaction vessel was heated to 25°C (water bath) and filled with propylene (6 ml at 25°C and 1 atm (manometric monitoring), ~0.25 mmol). The reaction mixture was stored in a water thermostat for 3 h at 25°C under periodical manual shaking. Then the autoclave valve was open to an evacuated (0.1 Torr) 10 ml round-bottom flask connected with a manometer, the gas pressure was measured and then adjusted to atmospheric with argon. The gaseous and liquid reaction products were analyzed by GLC and GC/MS.

4.15.2. Procedure B (liquefied CO_2 solvent)

The procedure was similar to the previous one, with the difference connected with the use of liquefied CO_2. After loading the solid and liquid reaction components into the autoclave (and additionally 3 glass balls of 3 mm diameter for more efficient mixing), the autoclave was cooled with liquid nitrogen. Propylene (72 ml) and CO_2 (540 ml), both dosed from a gas volumeter at 1 atm and room temperature, were sequentially condensed into the autoclave from a volumeter, the valve was closed, and the reaction mixture was stored in a water thermostat for 3 h at 25°C (liquid CO_2) or 45°C (supercritical (fluid) CO_2) under periodical manual shaking. The total pressure was measured by a pressure gauge at 25°C; the partial pressures and the state of CO_2 (liquid or fluid) at the reaction temperature were calculated from the PVT data [92]. When the reaction ceased, the autoclave was cooled by liquid nitrogen and the valve was open to an evacuated (0.1 Torr) round-bottom 2.5 l flask connected with a manometer. The autoclave was slowly heated to a room temperature, the gas pressure was measured, then adjusted to atmospheric with argon and the reaction products were analyzed as shown above. The results are shown in Table 1.

4.16. Oxidation of cyclohexene and hex-1-ene by palladium(II) carboxylates [59]

PNP carboxylate (0.042 mmol) and *p*-benzoquinone (0.223 mmol) were placed into a two-necked flask. The flask was twice evacuated and filled with argon. Palladium carboxylate (0.111 mmol) dissolved in 1.5–2.0 ml of a solvent and alkene (0.223 mmol) were added in an argon flow. The flask was carefully evacuated with cooling and filled with argon. The reaction mixture was stirred for 10–12 h, and the reaction products were analyzed by GLC and GC/MS. The results are shown in Table 2.

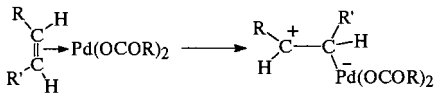
4.17. Oxidation of propylene by O_2 in acidic (aqueous or methanolic) solutions of giant Pd cluster **5** [84]

The reaction was conducted and the products were worked up similarly to the previous procedure using cluster **5** (4 mg, corresponding to 0.027 mmol of Pd) as the catalyst. A propylene–O_2 (1:1) gas mixture was introduced in the reaction flask thermostated at 50°C from a volumetric burette at 1 atm during 1 h. The results are shown in Table 3.

5. Conclusions

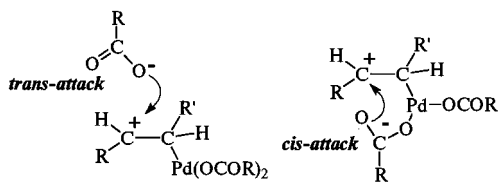
Our results showed that alkene oxidation by Pd^{II} carboxylate complexes in aprotic media most likely does not involve 1,2-oxymetallation of the π-coordinated alkene. Instead of this, two key stages seem to occur in succession:

(1) isomerization of the alkene–Pd^{II} π-complex to a σ-pallado-substituted carbenium ion:



A shift of the Pd atom toward one of the alkene C atoms is separated in time from a nucleophilic attack on the carbenium centre formed at the adjacent C atom;

(2) the attack of a nucleophilic reagent on the C^+ atom of the σ-carbenium complex:



Either inner- or outer-sphere $RCOO^-$ anion may be an attacking group at this stage. Trans-attack by free OAc^- anion could be expected in the AcOH/NaOAc medium. (Noteworthy, a synchronous 1,2-oxypalladation of ethylene in aqueous solution has been found to proceed as a *trans*-attack [93]). When free carboxylate anions are deficient, this stage may occur as a *cis*-attack by the coordinated $RCOO^-$ ligand.

The asynchronism of electrophilic and nucleophilic attacks provides a means for allylic and homoallylic esterification. If the σ-carbenium complex is a fairly long-lived species, it has time to undergo a reversible 1,2-hydride shift (see Schemes 10 and 11) before the nucleophilic attack to occur. The nucleophilic attack might result in either addition of $RCOO^-$ group to the carbenium centre or proton abstraction from the adjacent C atom. The absence of vinylic esters in the products of oxidation of propylene, hex-1-ene and cyclohexene gives evidence that proton abstraction to form the palladium σ-allylic or σ-homoallylic complex followed by the reductive elimination of Pd^0 and $RCOO^-$ anion is in fact the main reaction path, which affords allylic and homoallylic esters.

This mechanistic conception allows one to eliminate the controversy as to whether π-allylic complexes participate in the allylic oxidation by Pd^{II} or not. As seen in Schemes 10 and 11, the reactions under question involve σ-allylic intermediates, which are commonly subjected to fast σ ⇌ π-isomerization. This can explain why π-allylic complexes have been observed by NMR in the reaction solutions during formation of allylic esters (see for example, Ref. [67]). Meanwhile, a role of the σ- and π-allylic species in the mechanism of reductive elimination needs additional studies.

Under the conditions of asynchronous electrophilic and nucleophilic attacks in low-polar solvents, carboxylate anions exhibit lower nucleophilicity toward Pd^{II}-coordinated alkene molecules as compared to those of H_2O and ROH molecules in aqueous and alcohol solutions, correspondingly. Some other explanation should be invoked to account for allylic oxidations in these media.

Palladium chemistry makes available such an alternative way for allylic oxidation. New reaction channel is opened when low-valence palladium clusters are used as the catalysts for alkene oxidation [68,69,82]. This pathway provide advances toward better selectivity and performance under milder conditions.

In many cases a Pd cluster is in fact a precursor of an actual catalyst, but experimental data on the transformations of starting forms of cluster catalysts are still scare. On the other hand, when starting from a mononuclear Pd^{II} complex, palladium cluster or cluster-like material (e.g., giant Pd cluster or colloidal palladium) can form in the course of reaction, being the actual species responsible for the catalytic reaction.

Speculations based on the idea of mechanisms involving the oxidative addition of a substrate to a cluster molecule with the cleavage of the metal–metal bond can be used to rationalize the experimental data available. In catalysis of redox reactions, metal clusters can serve a function of an electron transfer mediator.

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