The effects of the solvent and the ligand chirality on the regioselectivity of alkene oxidative esterification by Pd^{II} carboxylates

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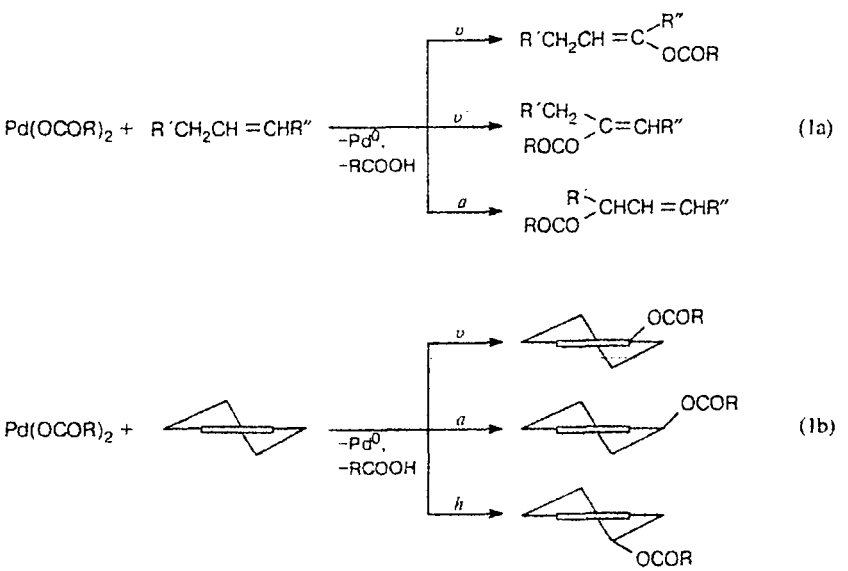
The effects of the solvent and the ligand chirality on the regioselectivity of oxidative esterification of propylene and cyclohexene by Pd^{II} carboxylates were studied using achiral ($MeCO_2^-$, $Me_2CHCH_2CO_2^-$), racemic ((±)-$CF_3CF_2CF_2OC^*F(CF_3)CO_2^-$), and chiral ((*S*)-(+)-$MeC^*H(Et)CO_2^-$, (+)-$CF_3CF_2CF_2OC^*F(CF_3)CO_2^-$) carboxylate ligands. The oxidation of alkenes in aprotic media ($CHCl_3$, CH_2Cl_2, CO_2, THF) affords mainly allylic esters (in the case of cyclohexene also homoallylic esters) and the oxidative esterification at the vinylic position is absent. In weakly solvating media ($CHCl_3$, CH_2Cl_2) the regioselectivity of cyclohexene oxidation (the allyl to homoallyl ratio) increases substantially on going from achiral or racemic acido ligands to chiral acido ligands. In a more donor medium (THF) the ligand chirality effect almost vanishes. The effects of the ligand chirality and the nature of the solvent on the mechanism of alkene oxidation by Pd^{II} complexes are discussed.

Key words: palladium, alkenes, π-complexes, σ-complexes, oxidative esterification, regioselectivity, solvent effects, chiral ligands.

Reactions of alkyl derivatives of group VIII metals, in particular, redox transformations of palladium π-alkene and π-allyl complexes, which are key intermediates in catalytic oxidation of alkenes, are still deficiently understood.

The ability of Pd^{II} carboxylates to form alkene π-complexes whose redox decomposition affords vinylic or allylic esters[1–3] is used in synthetic practice.[4–6] The interaction of alkenes with Pd^{II} carboxylate complexes (Scheme 1, reaction (1a)) results in the replacement of the H atom in vinylic (routes *v*, *v'*) or allylic (route *a*) positions of the alkene molecule by the RCOO group.[3,7–10] In the case of cyclic alkenes (Scheme 1, reaction (1b)) homoallylic esters (route *h*) are formed along with vinylic (*v*) and allylic (*a*) esters.[11,12]

Scheme 1



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Previously,[3,7—16] general mechanistic concepts of the alkene oxidation by Pd^{II} complexes have been formulated. It is suggested that oxidative esterification proceeds either *via* 1,2-carboxypalladation of an η^2-coordinated alkene molecule to form an intermediate σ-organopalladium compound[3,8,13] or *via* an intermediate palladium π-allyl complex.[12] The reaction regioselectivity is determined by the relative contribution of these routes.[7]

Nevertheless, factors controlling the regioselectivity of reaction (1a) are still poorly understood. According to some data,[12,16—18] the ratio of esters that are the products of reaction (1a) changes in a wide range depending on the temperature and the presence of oxidants (*e.g.*, Cu^{II}, *p*-benzoquinone, O_2, peroxides), water, and strong acids and bases. The effects of solvent nature and the carboxylate ligand are still not understood. In the majority of works reactions (1a), (1b) have been studied only in an acetic acid solution and only anion $MeCO_2^-$ has been used as the carboxylic ligand.

In this work, the solvent and ligand effects on the regioselectivity of oxidative esterification of propylene and cyclohexene by palladium(II) carboxylates was studied in aprotic solvents with different donor abilities, $CHCl_3$, CH_2Cl_2, 1,1,2-trichloroethane, liquified CO_2, and THF. Achiral ($MeCO_2^-$, $Me_2CHCH_2CO_2^-$), racemic ((±)-$CF_3CF_2CF_2OC^*F(CF_3)CO_2^-$), and chiral ((*S*)-(+)-$MeC^*H(Et)CO_2^-$ and (+)-$CF_3CF_2CF_2OC^*F(CF_3)CO_2^-$) carboxylate anions were used as the ligands.

Results and Discussion

Starting Pd^{II} complexes

Palladium(II) was introduced in solutions in the form of salts $Pd(RCO_2)_2$ (R = Me, Me_2CHCH_2, (±)-$CF_3CF_2CF_2OC^*F(CF_3)$, (*S*)-(+)-$MeC^*H(Et)$, and (+)-$CF_3CF_2CF_2OC^*F(CF_3)$). The structure of Pd^{II} di(*S*)-(+)-2-methylbutyrate was determined by X-ray diffraction single-crystal study (Fig. 1).[19]

According to X-ray data, the molecule of Pd^{II} di-(*S*)-(+)-2-methylbutyrate is a cyclic trimer $Pd_3(\mu^2\text{-}OCOR)_6$ with carboxylate bridges. Its structure is similar to the previously studied Pd^{II} carboxylates with achiral ligands such as acetate, propionate, and pivalate.[20—23]

Pd^{II} reactive forms

Pd^{II} salts are reduced by alkenes very slowly in an AcOH solution. The reaction is substantially accelerated in the presence of alkaline acetates.[1—3] In these conditions, the kinetically inert cyclic trimer $Pd_3(OAc)_6$ is converted to the more reactive di- and mononuclear anionic complexes[24]:

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

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

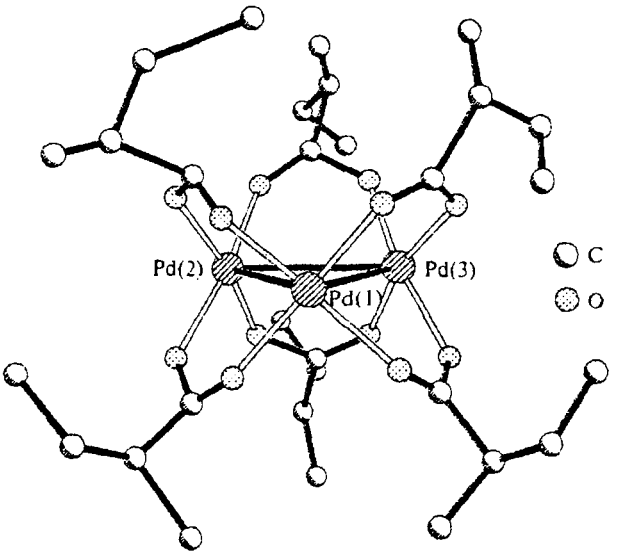


Fig. 1. The structure of $Pd_3[(S)\text{-}(+)\text{-}2\text{-}EtC^*H(Me)COO]_6$ according to X-ray diffraction study.[19]

Our experiments showed that all the Pd^{II} carboxylates are reduced by propylene and cyclohexene extremely slowly in chloroform and THF at 25 °C. The reaction is accelerated on addition of Na or K carboxylates (0.1—0.3 mol per Pd^{II} mol). However, the alkene oxidation occurs slowly, being complicated by heterogeneous processes, because of poor solubility of alkaline carboxylates and Pd^{II} acido complexes in these solvents.

In order to conduct reactions (1a), (1b) in homogeneous conditions, we used bis(triphenylphosphoranilidene)ammonium, $[(Ph_3P)_2N]^+$ (PPN), carboxylates as the source of additional carboxylate anions. Our preliminary experiments[25] showed that PPN acetate and complexes $(PPN)_2[Pd_2(OAc)_6]$ and $(PPN)_2[Pd(OAc)_4]$, which are formed upon addition of (PPN)OAc to the neutral salt $Pd_3(OAc)_6$, are readily soluble in aprotic media, THF, CH_2Cl_2, $CHCl_3$, Cl_2CHCH_2Cl, and liquid CO_2.

The equilibria of reactions (2) and (3) have been studied in solutions of $Pd(OAc)_2$ in acetic acid only.[25] We found by ^1H NMR spectroscopy that at least 90% free acetate anions combine with palladium during 4—5 h on addition of 0.1—0.3 mol PPN acetate per Pd atom to a solution of Pd^{II} acetate in $CDCl_3$. The acetate anions unbound to Pd^{II} practically disappear due to reversible reactions (2) and (3) in 10—12 h. Since the chemical properties of palladium(II) acetate and palladium(II) carboxylates under study are close, we suggested that $Pd_3(OCOR)_6$ molecules and $[Pd_2(OCOR)_6]^{2-}$ and $[Pd(OCOR)_4]^{2-}$ anions are present in comparable concentrations in all the systems under study. A small amount of the AcO^- anions unbound to palladium is probably present in the solution in the form of the PPN salt in the beginning of reaction. Therefore, we cannot rule out that some "free," unbound to palladium $RCOO^-$ anions participate in the reaction with

propylene that virtually ceases during 1—2 h. The reaction with cyclohexene proceeds much slower: the characteristic half-time of the reaction is ~20 h. In this case, the involvement of the outer-sphere $RCOO^-$ anions in the reaction is much less probable.

Solvent effect

The reactions of propylene with Pd^{II} acetate complexes in CH_2Cl_2, $CHCl_3$, and Cl_2CHCH_2Cl are highly selective. The yield of allyl acetate based on palladium consumed is at least 99% (see Table 1, entries *1—3*). Only traces of vinyl esters, acetone, and propanal form, likely the products of hydrolysis of vinyl and isopropenyl acetate by the small amount of water (0.02—0.10%) remaining in solvents after drying. The same products were obtained in catalytic runs carried out in the presence of oxidants such as nitrosobenzene and benzoyl peroxide (see Table 1, entries *4*, *5*).

When acetic acid (5 vol.%) was added to chlorocarbon solvents, the yield of *n*-propenyl and isopropenyl acetates and acetone noticeably increased to a total value of 10% (see Table 1, entry *6*), indicating a substantial decrease in the reaction selectivity with respect to allyl acetate. This fact well agrees with our results (see Table 1, entry *8*) and literature data (Refs. 16 and 18, see Table 1, entry *7*) for reaction (1a) in acetic acid, which usually affords both vinylic and allylic esters.

Similar results were obtained for the reaction in liquefied CO_2 (see Table 1, entries *10—12*). Vinyl and allyl acetates form in comparable yields both in liquid and fluid carbon dioxide (*cf.* entries *10* and *11*), and the addition of acetic acid exerts no substantial change in the reaction regioselectivity. The latter fact can be due to a small admixture of water (~1%) in liquefied CO_2, so that the reaction medium was in fact a diluted solution of H_2CO_3 in liquid CO_2. This solvent is expected to be similar in some properties to acetic acid, and the addition of the latter has a slight effect on the reaction selectivity (see Table 1, entry *12*).

It is known that propylene oxidation by *p*-benzoquinone, O_2, or peroxides in solutions of acetic acid containing giant palladium clusters[26] or Pd nanoparticles[27] affords allyl acetate with regioselectivity close to 100%. The reaction proceeds *via* a mechanism in which the cluster metal core functions as an "electron mediator."[26] However, such reactions are very sensitive to the presence of oxidants.[27] Our experiments showed that addition of such oxidants as benzoyl peroxide and nitrosobenzene does not affect either the regioselectivity or rates of propylene oxidative esterification (see Table 1, entries *4*, *5*). This gives evidence that the oxidative esterification of propylene is due to Pd^{II} complexes rather than nanoclusters of the reduced palladium.

Unlike this, the reaction of cyclohexene with Pd^{II} carboxylates is very sensitive to the presence of oxidants. When oxidants capable of re-oxidizing Pd^0 are absent, benzene is formed as the main reaction product in a yield of at least 98% based on Pd^{II} consumed, whereas the esters of cyclohex-2-ene-1-ol and of cyclohex-3-ene-1-ol are formed in minor yields (Table 2, entry *1*). This fact gives evidence for preferential occurrence of the oxidative dehydrogenation and disproportionation of cycloxehene (the Zelinsky reaction)

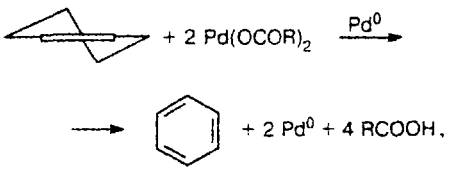


Table 1. Products composition for the oxidative acetoxylation of propylene by palladium(II) acetate complexes in different media ($[Pd^{II}]_0$ = 0.11 mol L^{-1}, $[(PPN)OAc]_0$ = 0.04 mol L^{-1}, $p_{C_3H_6}$ = 1 atm, t = 3 h)

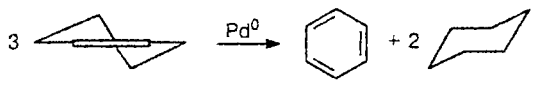
Entry	Solvent	*T*/°C	Products composition (mol/mol Pd)				Allyl/vinyl ratio
			Allyl acetate	Isopropenyl acetate	*n*-Propenyl acetate (*cis*+*trans*)	Acetone + propanal	
1	$CHCl_3$	25	~0.99	0.01	0.01	0.01	>1000
2	CH_2Cl_2	25	~0.99	0.01	—	—	>1000
3	$CHCl_2CH_2Cl$	25	~0.99	0.01	—	—	>1000
4	CH_2Cl_2 + benzoyl 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		Σ_{vinyl} = 0.06[c]		16
8	AcOH + 0.9 *M* NaOAc + 1% H_2O	25	0.49		Σ_{vinyl} = 0.51[c]		~1
9	AcOH	25	0.009	0.986	0.005	—	<0.01
10	CO_2 (liq)[a]	25	0.62		Σ_{vinyl} = 0.38[c]		1.6
11	CO_2 (fluid)[b]	42	0.76		Σ_{vinyl} = 0.24[c]		3.1
12	CO_2 (fluid) + 10% AcOH[b]	46	0.72		Σ_{vinyl} = 0.28[c]		2.6

[a] p_{CO_2} = 90 atm, $p_{C_3H_6}$ = 12 atm. [b] p_{CO_2} = 190 atm, $p_{C_3H_6}$ = 12 atm. [c] The total content of vinylic products.

Table 2. Products composition for oxidative esterification of cyclohexene by Pd^{II} carboxylate complexes in different solvents at 25 °C

Entry	Solvent	Carboxylate ligand	Reoxidant for Pd^0	Yields of the reaction products (%)			
				Cyclohex-ene-2-ol allylic (**A**) ester	Cyclohex-ene-3-ol homoallylic (**H**) ester	**A** : **H** ratio	Other products
1	$CHCl_3$	Acetate	No oxidant	≤1	≤1	~1	~98 (C_6H_6)
2	$CHCl_3$	Acetate	*p*-Benzoquinone	61.3	38.7	1.6	<1 (C_6H_6)
3	$CHCl_3$	Acetate	$(PhCO)_2O_2$	52.9	44.1	1.2	3.0 (C_6H_6)
4	*i*-$C_5H_{11}OMe$	Acetate	*p*-Benzoquinone	65.36	34.64	1.9	<1 (C_6H_6)
5	Cyclohexene	$R_FCO_2^-$ (racemate)[a]	*p*-Benzoquinone		No reaction		
6	$CHCl_3$	$R_FCO_2^-$ (racemate)	No oxidant	—	—		61.3 (C_6H_6), 58.7 (C_6H_{12})
7	$CHCl_3$	$R_FCO_2^-$ (racemate)	*p*-Benzoquinone	70.59	29.41	2.4	<1 (C_6H_6)
8	$CHCl_3$	$R_FCO_2^-$ (chiral)	*p*-Benzoquinone	85.63	14.37	5.9	<1 (C_6H_6)
9	$CHCl_3$	3-Methylbutyrate (achiral)	*p*-Benzoquinone	84.3	15.7	5.4	<1 (C_6H_6)
10	$CHCl_3$	2-(±)-Methylbutyrate	*p*-Benzoquinone	86.7	13.3	6.5	<1 (C_6H_6)
11	$CHCl_3$	2-(+)-Methylbutyrate	*p*-Benzoquinone	98.5	1.53	64.4	<1 (C_6H_6)
12	THF	2-(±)-Methylbutyrate	*p*-Benzoquinone	84.02	15.98	5.3	<1 (C_6H_6)
13	THF	2-(+)-Methylbutyrate	*p*-Benzoquinone	68.22	31.78	2.2	<1 (C_6H_6)

[a] $R_FCO_2^- = CF_3CF_2CF_2OC^*F(CF_3)COO^-$.



which are efficiently catalyzed by palladium metal formed in the very beginning of the reaction.

In the presence of oxidants preventing the formation of Pd^0 such as *p*-benzoquinone, benzoyl peroxide, or nitrosobenzene, these reactions are absent and the interaction of Pd^{II} carboxylates with cyclohexene in all solvents but acetic acid affords the esters of cyclohex-2-ene-1-ol and of cyclohex-3-ene-1-ol as main reaction products (see Table 2, entries *3—13*). The esters of cyclohex-1-ene-1-ol are formed in acetic acid only, and they are absent when the reaction is conducted in aprotic media (see Table 2, entries *3—13*).

Thus, the regioselectivity of reactions (1a) and (1b) sharply changes on going from protic (AcOH, H_2CO_3/CO_2) to aprotic media ($CHCl_3$, CH_2Cl_2, 1,1,2-trichloroethane, THF): the vinylic route of alkene oxidation is entirely extinct, and an additional route affording homoallylic esters appears in the case of cyclohexene. Additional information on the nature of these reaction routes was obtained in the study of the effects of acido ligand chirality on cyclohexene oxidative esterification.

Effects of ligand chirality

In the α- or β-positions of the cyclohexene molecule enantiotopic centers are present. Therefore, reaction (1b) could result in the formation of optically active esters. When a chiral carboxylic group is introduced, the ester molecule formed should contain two asymmetric carbon atoms, one atom in the α- or β-position of the cyclohexenyl moiety and another atom in the carboxylic group, to form diastereoisomers.

In order to determine the stereoisomeric composition of the esters, the products of cyclohexene oxidation by Pd^{II} complexes with the chiral anions (*S*)-(+)-$MeC^*H(Et)CO_2^-$ and (+)-$CF_3CF_2CF_2OC^*F(CF_3)CO_2^-$ in chloroform were investigated by GC/MS. It was found that a capillary column with the universal optically active stationary phase α-Decs does not efficiently separate the diastereoisomeric cyclohexenol esters. For this reason, the obtained mixture of esters was hydrolyzed by methanolic NaOH, which reaction is known to occur without inversion of the optical configuration.[28] GC/MS analysis of the isomeric alcohols formed upon hydrolysis showed that the optical isomers are present in the reaction mixture in virtually equal concentrations. This fact suggests that the mechanism of reaction (1b) does not provide the stereoselective synthesis of cyclohexenol esters.

Meanwhile, the nature of the carboxylate ligand affects substantially the regioselectivity of reaction (1b). As seen in Table 2, on going from the racemic perfluorocarboxylate anion (±)-$R_F^*COO^-$ to the optically active anion (+)-$R_F^*COO^-$ results in more than two-fold increase in the allyl : homoallyl ratio when cyclohexene is oxidized by the Pd^{II} complexes with perfluorocarboxylate anions (see Table 2, entries *7*, *8*). The more pronounced effect was observed in the reaction

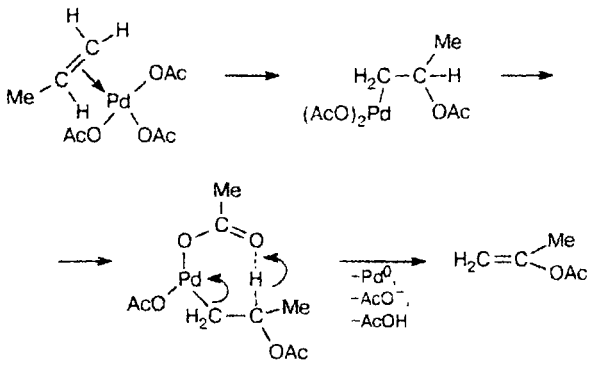
involving the 2-methylbutyrate anion: the allyl : homoallyl ratio was increased at least by an order of magnitude (see Table 2, entries *10*, *11*).

When reaction (1b) was carried out in the more donor solvent, THF, which possesses a higher solvating ability as compared to chloroform, the chirality affect vanished and even somewhat changed its direction. For instance, the allyl/homoallyl ratio was somewhat decreased on going from the racemic to optically active carboxylate anion in reactions involving 2-methylbutyrates (see Table 2, entries *12*, *13*).

Reaction mechanism

The data obtained allow one to make some mechanistic suggestions on the mechanism of the oxidative esterification of alkenes by palladium(II) carboxylate complexes. A sharp increase in the yield of allylic derivatives on going from acetic acid to aprotic media (see Table 1) hardly can be realized within the framework of the conventional mechanism.[3,8] According to this mechanism, a primary intermediate π-alkene complex isomerizes to a σ-organopalladium compound, which subsequently undergoes redox decomposition according to Scheme 2.

Scheme 2

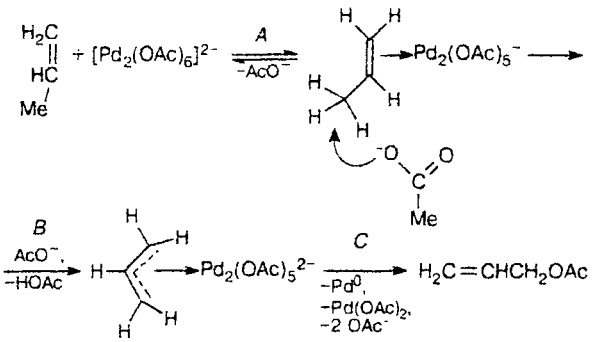


This scheme suggests that isopropenyl acetate should be the main product of propylene oxidation. This ester was in fact observed[1—4,7,8] when propylene was oxidized in acetic acid containing excess acetate anions with the concentration of 0.1—0.5 mol L^{-1}. When highly electronegative ions (for instance, NO_3^-) were present in the solution, glycol ester was also formed.[29]

The observed allylic pathway of the reaction of alkenes with Pd^{II} carboxylate complexes in aprotic media (see Tables 1 and 2) might be explained by intermediate formation of a pallladium η³-allyl complex, for example, according to Scheme 3.

Such a mechanistic concept has been discussed repeatedly in the literature (see, for instance, Refs. 12 and 30). However, the mechanism of redox disproportionation of the π-allyl complex to allyl acetate and Pd^0 is still not clear (Scheme 3, stage *C*). Direct studies of the reactivity of Pd^{II} π-allyl complexes toward electrophilic and nucleophilic reagents[3,7] showed that when such a reaction occurs, it is rather a side rather than the main reaction pathway.

Scheme 3



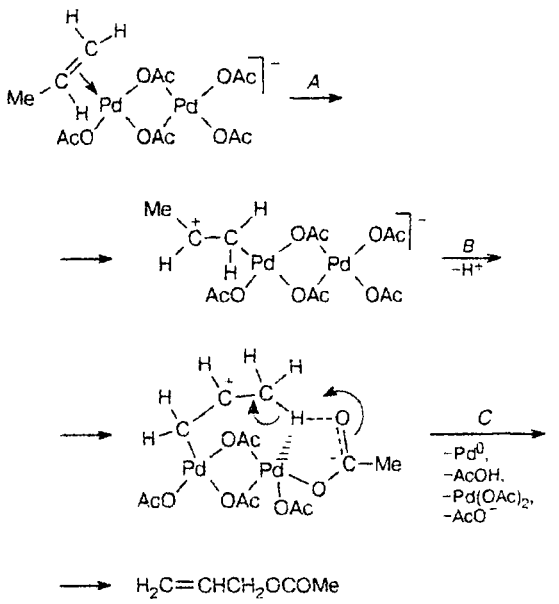
Nevertheless, this mechanism cannot be ruled out in the case of high concentration of a base, AcO^- anions, which are necessary for the conversion of the η^2-alkene complex to the η^3-allyl complex (Scheme 3, stage *B*). Meanwhile, in the conditions of our experiments the main portion of AcO^- anions was bound in the form of inner-sphere ligands in the complexes $[Pd_2(OCOR)_6]^{2-}$ and $[Pd(OAc)_4]^{2-}$, and the concentration of free AcO^- anions was very small ($\leq 10^{-3}$ mol L^{-1}). In aprotic low polar media ($CHCl_3$, CH_2Cl_2, THF), these anions are likely bound into ionic associates with the PPN^+ cations and are not easily accessible for the π-allyl complex. In these conditions, it is doubtful that the η^3-complex forms so rapidly as the reaction is completed in 1—2 h.

It seems more reasonable that the reaction occurs *via* a mechanism whose key stage is the isomerization of the π-alkene complex to a σ-organopalladium compound through an intramolecular electrophilic attack of a Pd atom on the coordinated alkene molecule. Since free AcO^- anions are deficient, the Pd^{II} electrophilic attack cannot be accompanied by a simultaneous nucleophilic attack of an AcO^- anion (nucleophilic assistance[3]) and is likely to result in the formation of a palladium σ-complex with the carbenium group according to Scheme 4.

In deficiency of the outer-sphere AcO^- anions, the $MeCH^+CH_2$—Pd carbenium group can be stabilized by removing a proton from the Me group (see Scheme 4, stage *B*). This stage occurs as an inner-sphere reaction, involving the coordinated AcO^- ligand and, probably, an additional weak Pd...H interaction. Such a mechanism seems the more probable when the binuclear $[Pd_2(OAc)_6]^{2-}$ complex is involved.

The above-mentioned mechanistic scheme well agrees with our results for the oxidative esterification of

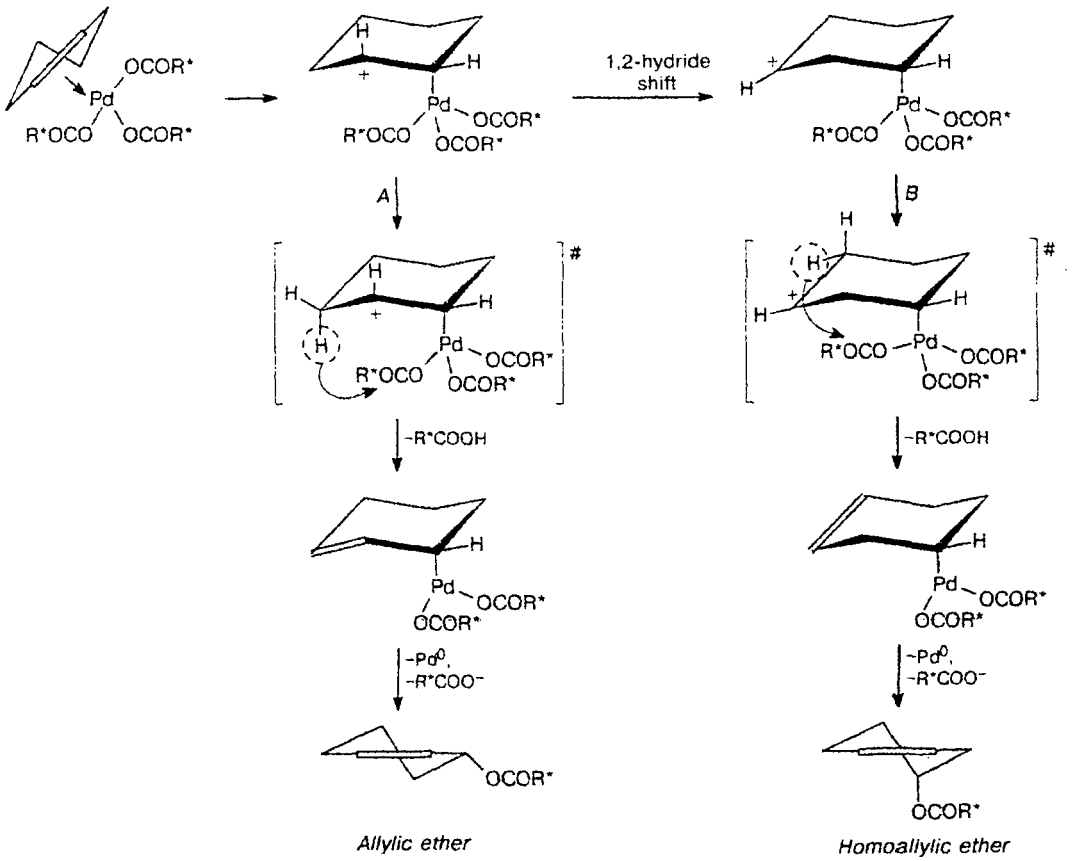
Scheme 4



cyclohexene (Table 2). In this case intermediate formation of a π-allylic complex is also doubtful. In aprotic media ($CHCl_3$, CH_2Cl_2, THF) the reaction of Pd^{II} carboxylates with cyclohexene occurs much slower than that with propylene, and its half-time is longer than 12 h. The main portion of the reaction products is formed during this time, which is enough to achieve equilibrium between the Pd^{II} carboxylate complexes by reactions of type (2) and (3). After equilibration, the concentration of outer-sphere AcO^- anions in the solution becomes negligible and the conversion of the π-alkene complex to the π-allylic complex is improbable.

Cyclohexene-3-ol carboxylates are the products of the oxidative esterification to the homoallylic position of the cyclohexene molecule. The formation of these compounds may be realized within the framework of the "π-allylic" mechanism (Scheme 3) only by double bond displacement in the primary intermediate, allylic ester. However, such an isomerization is suppressed by *p*-benzoquinone and other oxidants (see Table 2).[3] In addition, the double bond displacement could also afford vinylic esters, which are entirely absent from the products of reaction (1b).

Scheme 5*

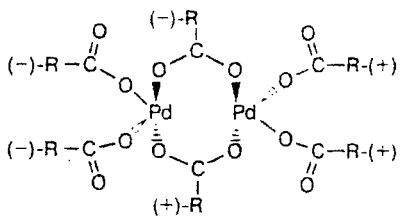


* Reactions involving mononuclear palladium complex are shown for simplicity.

The totality of results can be explained by Scheme 5, which is similar to Scheme 3 for propylene oxidation. Both schemes suggest inner-sphere attack of the carboxylate anion $RCOO^-$ on the CH_2 group of the σ-bound carbenium ligand.

Since the cyclohexenyl σ-complex decomposes rather slowly, its carbenium group may have enough time to undergo 1,2-hydride shift to move the carbenium center to an adjacent C atom of the cyclohexane ring. The inner-sphere attack of an AcO^- ligand on the CH_2 group of the original σ-complex gives rise to allylic ester (route *A*), and a similar process involving the σ-complex that has undergone the hydride shift affords homoallylic ester (route *B*).

The data on cyclohexene oxidation can be suggested as an example of stereo control of the reaction regioselectivity. In the case when the starting salts (PPN)OCOR* and $Pd_3(OCOR^*)_6$ contained only one stereoisomer of the chiral carboxylate anion (for instance, (+)-(*S*)-2-methylbutyrate, see Fig. 1), the acido complexes $[Pd(OCOR^*)_4]^{2-}$ and $[Pd_2(OCOR^*)_6]^{2-}$ that react with cyclohexene consisted of stereochemically identical R^*COO^- anions. In experiments involving racemic (±)-R^*COO^- anions, alkene reacted with stereochemically different complexes that contained both (+)-R^*COO^- and (−)-R^*COO^- ligands in various combinations such as in the binuclear complexes **1** or **2**.



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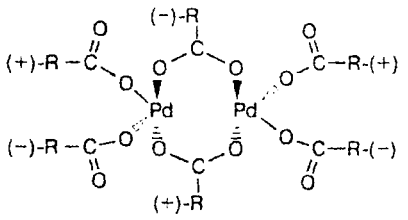

2

Depending on the stereoconfiguration of the Pd complex, alkene oxidation proceeds preferentially through either route *A* or *B* to form allylic or homoallylic ester, respectively. This mechanistic approach allows one to understand the observed difference in the regioselectivity of reaction (1b) in weakly solvating media ($CHCl_3$, CH_2Cl_2) that participate very slightly in inner-sphere complex transformations. In solvents with higher donor ability such as THF, which possesses enhanced solvating ability, an outer-sphere attack by the solvent molecule becomes more efficient in the competition with the inner-sphere attack by the R^*COO^- anion. In such a case the reaction may proceed through proton abstraction by the solvent molecule *via* a mechanism similar to that in Scheme 4 for propylene oxidation. The reaction pathway becomes much less dependent on the stereochemistry of the Pd^{II} complex, diminishing the effect of ligand chirality or even inverting the effect in some cases.

Experimental

Solvents (*n*-pentane, benzene, diethyl ether, chloroform, and THF) of "reagent grade" were purified by standard methods.[31] *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 and bis(triphenylphosphoranilidene)ammonium chloride ("reagent grade," Fluka) were used. 2-(Heptafluoropropoxy)perfluoropropionyl fluoride ("chemically pure grade") was provided by Kirovo-Chepetsk Chemical Industries and (*S*)-(−)-1-phenylethylamine ("reagent grade") was provided by Zeeland Chemicals, USA.

Analysis methods. C,H,N-microanalysis of the complexes was performed on an automatic C,H,N-analyzer Carlo Erba Strumentazione, Italy. NMR spectra were recorded on a Bruker WP-200 spectrometer; IR spectra were recorded on a Specord M80 spectrometer (Carl Zeiss, Jena) 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-1 and α-Decs); GLC analyses were conducted on a Varian 3600 chromatograph (USA) with universal capillary column with OV-1 stationary phase.

2-(Heptafluoropropoxy)perfluoropropionic acid, (±)-$CF_3(CF_2)_2OCF(CF_3)COOH$, was prepared by hydrolysis of the corresponding fluoride in water followed by fractionation of the aqueous solution by a modified method.[32]

(+)-2-(Heptafluoropropoxy)perfluoropropionic acid, (+)-$CF_3(CF_2)_2OCF(CF_3)COOH$, was obtained by the separation of diastereoisomeric (*S*)-(−)-1-phenylethylamides according to a known method.[33,34]

Palladium(II) acetate was obtained by the oxidation of as-prepared Pd black (prepared from $PdCl_2$ and $NaBH_4$) by concentrated HNO_3 in glacial AcOH by the previously reported method[35] and purified from the traces of nitrates and nitrito complexes by refluxing in glacial AcOH with Pd black.

Palladium(II) (*S*)-(+)-2-methylbutyrate. 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 substance was used in experiments on cyclohexene oxidation in the form of solutions in chloroform or THF without additional purification.

IR (Vaseline oil), $\nu CO/cm^{-1}$: 1637, 1425. ^1H NMR ($CDCl_3$), δ: 0.62 (t, 3 H, ^3J = 7.36 Hz); 0.83 (d, 3 H, ^3J = 7.01 Hz); 1.41 (m, 2 H); 2.2 (m, 1 H).

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

Palladium(II) (+)-2-(heptafluoropropoxy)perfluoropropionate, $Pd[(+)\text{-}CF_3CF_2CF_2OCF(CF_3)COO]_2$. (+)-$CF_3CF_2CF_2OCF(CF_3)CO_2H$ (1.63 g, 4.9 mmol, 10% excess) was added under mixing 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 by 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. $C_{12}F_{22}O_6Pd$. Calculated (%): C, 18.85; Pd, 13.92. ^{19}F NMR (acetone-d_6), δ: −81.0 (t, 3 F, $C\underline{F}_3$—CF_2—, ^3J = 6.6 Hz); −82.1 (d, 3 F, $C\underline{F}_3$—CFO—, ^3J = 2.5 Hz); −85.7 (m, 2 F, —$C\underline{F}_2$—CF_3); −126.2 (m, 1 F, CF_3—$C\underline{F}$O—); −129.3 (m, 2 F, —O—$C\underline{F}_2$—CF_2—).

Palladium(II) (±)-2-(heptafluoropropoxy)perfluoropropionate was prepared by the same method. Yield 1.1 g (65% based on Pd).

Bis(triphenylphosphoranilidene)ammonium acetate, $[(Ph_3P)_2N]OAc$, was prepared by the modified method.[36] To a solution of $(Ph_3P)_2NCl$ (1 g, 1.75 mmol) in 40 mL of $CHCl_3$ was added a solution of AgOAc (0.44 g, 2.62 mmol, 20% excess) in 30 mL of $CHCl_3$. The reaction mixture was stirred during 1 h and then the AgCl precipitated was filtered off. The solution was evaporated on a rotary evaporator to a volume of 10 mL and diethyl ether was added to the beginning of crystallization. The main amount of PPN acetate was first precipitated as a colorless oil, which crystallizes on storing in a fridge for 1—12 h. The substance was purified by recrystallization from a $CHCl_3$—diethyl ether solvent. Yield 0.94 g (90% based on $(Ph_3P)_2NCl$). Found (%): C, 76.43; H, 5.61; N, 2.37. $C_{39}H_{33}NO_2P_2$. Calculated (%): C, 76.37; H, 5.57; N, 2.34. ^1H NMR ($CDCl_3$), δ: 1.95 (s, 3 H, AcO^-); 7.3—7.7 (m, 30 H, Ph).

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 room temperature for ~24 h till complete dissolution of zinc oxide. The solution was added to a saturated at ~50 °C aqueous solution of $(Ph_3P)_2NCl$ (0.705 g, 90% with respect to zinc 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 4A. 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. $C_{41}H_{39}NO_2P_2$. Calculated (%): C, 76.97; H, 6.15; N, 2.19. IR (KBr), $\nu CO/cm^{-1}$: 1605, 1425. ^1H NMR ($CDCl_3$), δ: 0.65 (d, 6 H, ^3J = 6.2 Hz); 1.25 (m, 1 H); 2.02 (m, 2 H); 7.68—7.4 (m, 41 H).

Bis(triphenylphosphoranilidene)ammonium (+)-2-(heptafluoropropoxy)perfluoropropionate, $[(Ph_3P)_2N]^+[CF_3CF_2CF_2O\text{—}CF(CF_3)COO]^-$. 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 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 g-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. $C_{42}H_{30}NF_{11}O_3P_2$. Calculated (%): C, 58.14; H, 3.49; N, 1.61. ^{19}F NMR ($CDCl_3$), δ: −84.3 (t, 3 F, $C\underline{F}_3$—CF_2—, ^3J = 7.43 Hz); −84.7 (d, 3 F, $C\underline{F}_3$—CFO—, ^3J = 3.3 Hz); −86.0 (m, 2 F, —$C\underline{F}_2$—CF_3); −126.8 (m, 1 F, CF_3—$C\underline{F}$O—); −132.7 (m, 2 F, —O—$C\underline{F}_2$—CF_2—).

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 magnetically stirred till complete dissolution of NaOH. To the solution was added a saturated aqueous solution of $AgNO_3$ (0.33 g, 1.95 mmol) acidified with five drops of (*S*)-(+)-2-methylbutyric acid. The precipitate of Ag[EtC*H(Me)]COO was filtered off, washed successively 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 diethyl ether added 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. $C_{41}H_{39}NO_2P_2$. Calculated (%): C, 76.97; H, 6.15; N, 2.19. IR (KBr), $\nu CO/cm^{-1}$: 1616, 1425. ^1H NMR ($CDCl_3$), δ: 0.83 (t, 3 H, ^3J = 7.35 Hz); 1.15 (d, 3 H, ^3J = 7.1 Hz); 1.75 (m, 2 H); 2.35 (m, 1 H); 7.68—7.4 (m, 30 H).

Bis(triphenylphosphoranilidene)ammonium (*S*)-(±)-2-methylbutyrate was prepared by the same procedure as that for 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 (KBr), $\nu CO/cm^{-1}$: 1615, 1425. ^1H NMR ($CDCl_3$), δ: 0.85 (t, 3 H, ^3J = 7.37 Hz); 1.1 (d, 3 H, ^3J = 7.09 Hz); 1.77 (m, 2 H); 2.38 (m, 1 H); 7.66—7.5 (m, 30 H).

The oxidation of cyclohexene by palladium(II) carboxylates (general procedure). PPN 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 cyclohexene (0.223 mmol) were added in an argon flow. The flask was carefully evacuated with cooling and then filled with argon. The reaction mixture was stirred for 10—12 h, and the reaction products were analyzed by GLC and GC/MS.

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