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Teaching a palladium polymerization catalyst to mono-oxygenate olefins

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Teaching a Palladium Polymerization Catalyst to Mono-Oxygenate Olefins

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Catalyst systems consisting of a palladium(II) diphosphine complex with weakly or non-coordinating counterions are efficient catalysts for the hydrocarbonylation of olefins. With these catalyst systems, the oxo-synthesis can be fully exploited to produce, at will, aldehydes/alcohols by hydroformylation or monoketones by hydro-acylation of olefins. The reactions described here constitute the first examples of selective formation of ketones by hydrocarbonylation of higher olefins and the first examples of Pd catalyzed hydroformylation of olefins. Variation of ligand, anion and/or solvent can be used to steer the reaction selectively towards aldehydes/ alcohols, ketones or oligoketones. Non-coordinating anions and arylphosphine ligands produce primarily (oligo)ketones; increasing ligand basicity shifts selectivity towards monoketones, while increasing ligand basicity and/or increasing anion coordination strength leads to high selectivity for hydroformylation products, aldehydes and alcohols. For the mechanisms of the aldehyde-producing step, we propose protonation of Pd(II)-acyl intermediates, assisted by the coordination of the anion, followed by reductive elimination of the aldehyde and heterolytic dihydrogen cleavage. For selective saturated monoketone formation we propose protonation at the Pd(II)-alkyl stage, now assisted by chelating carbonyl coordination followed by reductive elimination of the ketone and heterolytic dihydrogen cleavage. Unsaturated ketone formation involves β-hydride elimination from the same Pd(II)-alkyl intermediates.

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INTRODUCTION

The term "oxo-synthesis", which denotes the reaction of olefins with mixtures of carbon monoxide and hydrogen to give aldehyde, alcohol and/or ketone products, was originally introduced in the 1940's by Otto Roelen[1,2] He observed that with a cobalt catalyst and ethene as olefinic substrate, a mixture of propionaldehyde and diethyl ketone was formed (Eqs 1).

$$CH_2 = CH_2 + CO + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CHO \quad (1)$$
$$2\ CH_2 = CH_2 + CO + H_2 \rightarrow CH_3\text{-}CH_2\text{-}C(O)\text{-}CH_2\text{-}CH_3$$

Later it appeared that only with ethene significant formation of ketone (and aldehyde) product occurred. With higher olefins selective synthesis of aldehydes and/or alcohols takes place and these reactions have become generally known as hydroformylation of olefins (Eqs 2).

$$R\text{-}CH = CH_2 + CO + H_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CHO$$
$$R\text{-}CH = CH_2 + CO + 2\,H_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH \quad (2)$$

Driven by the need to produce oxygenates from petrochemical hydrocarbons, hydroformylation has become the largest-scale industrial chemical application of homogeneous catalysis by transition-metal complexes, with a present worldwide volume of about 10 million t/a of aldehydes and alcohol products. This development would not have been possible without several advances in homogeneous catalysis by organometallic complexes.

In the 1960's, it was discovered that ligand substitution in the original cobalt carbonyl catalyst $HCo(CO)_4$ could influence the performance significantly[3]. This forms the basis for a process that allows the production of predominantly linear alcohols from internal straight-chain olefins. This process was first commercialized by Shell.

Another major breakthrough in catalyst activity and regio-selectivity was made possible by by the discovery of complexes based on Rh as efficient olefin hydroformylation catalysts[4]. Based on this, workers at Union Carbide, Johnson and Matthey, and Davy Powergas jointly developed a rhodium/phosphine based hydroformylation process to produce *n*-butanal from propene. This process was first commercialized in 1976.

In the last decades numerous hydroformylation catalysts, predominantly based on the metals Co and Rh (and to a much lesser extent Pt) combined with a wide variety of ligands, have become available. How-

ever, none of these catalysts has allowed the full and general exploitation of the originally envisaged scope of oxo-synthesis: the selective production of ketones or aldehydes/alcohols at choice from olefins and syngas has thusfar remained an elusive goal[5]. In this comment we wish to draw attention to cationic Pd catalyst systems which bring just this goal within reach.

Our interest in the palladium-catalysed hydrocarbonylation of olefins was awakened by the discovery of a class of highly efficiencationic palladium catalysts for the alternating copolymerization of olefins with carbon monoxide (eqn.(3))[6].

$$n\ \text{R-CH} = \text{CH}_2 + n\text{CO} \rightarrow \text{+(CHR-CH}_2\text{-CO)}_n \qquad (3)$$

The catalytically active species in polyketone formation is a square-planar cationic palladium(II) complex, general formula $[L_2PdR]^+\ X^-$, where L_2 stands for a bidentate ligand (e.g. phosphine, pyridyl or thioether) and R represents the growing polymer chain. The cationic species is associated with weakly or non-coordinating anions (X^-). The fourth coordination site at palladium may be occupied by an anion, a solvent molecule, a carbonyl group of the chain, a monomer molecule or a chain-transfer molecule, usually alcohol or hydrogen. Competition for the vacant site appears to be an important factor affecting the performance of the catalyst and provides an explanation for the sensitivity for the choice of solvent, counterion and chain-transfer molecule. The mechanism of copolymer chain growth involves two sequential propagation steps: the reversible migratory insertion of CO in a Pd-alkyl bond, followed by the irreversible migratory insertion of the olefin into the resulting Pd-acyl bond of the growing polymer chain. From polymer chain end-group analysis by NMR[6] it has been concluded that initiation in protic (alcohol) solvents may start at a Pd-alkoxide species to generate an ester polymer end-group or at a Pd-hydride species to generate a ketone end-group, while termination may occur from Pd-alkyl by protonolysis to generate a ketone endgroup[7] and Pd-alkoxy or by β-hydride elimination to generate an unsaturated ketone end-group and Pd-hydride, and from Pd-acyl by alcoholysis to generate an ester end-group and Pd-hydride.

When the copolymerization catalysts were exposed to olefins and carbon monoxide in aprotic solvents, chain transfer by alcohol is eliminated and only saturated and unsaturated ketone end-groups are formed. With aprotic solvents and the presence of small quantities of H_2, mainly

saturated and some unsaturated ketone end-groups were generally also observed. These polymer chains are apparently formed by initiation at a Pd-hydride exclusively, and termination by both hydrogenolysis and β-H elimination respectively, at the Pd-alkyl stage[6].

The anion can also be important. If, in the ketone-producing aprotic solvent/H_2 system we moved from a non-coordinating anion to a moderately coordinating anion, aldehyde end-groups became also visible. This indicates that polymer chain transfer by H_2 is possible both at the Pd-alkyl *and* the Pd-acyl stage of the growing chain.

This led to the idea that it might be possible, under sufficiently high hydrogen pressure and with an appropriate choice of the catalyst ligand and anion constituents, to speed up hydrogen chain transfer of the copolymerization so much that only low-molecular weight products and ultimately only aldehydes and/or monoketones could be selectively produced, depending on the stage (Pd-alkyl or Pd-acyl) of the growing chain at which hydrogenolysis would occur.

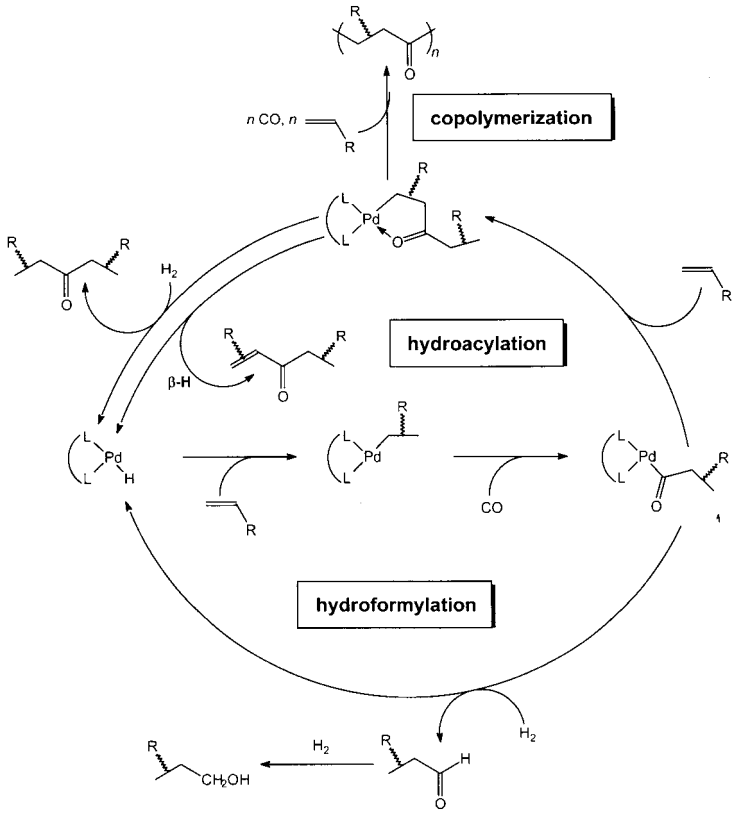
The proposed aldehyde- and ketone formating reactions and their link to olefin-CO co-polymerization have been summarized in Scheme 1. In analogy with the term hydro-*formylation* for the aldehyde forming reactions, ketone forming reactions can best be termed as hydro-*acylation*.

In this paper, we will show that with L_2PdX_2 complexes as catalyst precursors, aldehydes and ketones can indeed be produced from olefinic substrates in general. Moreover, we will show that by a proper choice of the ligand (L_2) and the anion (X^-), hydrocarbonylation of olefins can be tuned to proceed selectively towards either aldehydes (alcohols) or ketones. This class of catalysts, thus provides for the first time a means of control for the selective production of both oxo-type products.

RESULTS

The catalyst precursors (L_2PdX_2) tested in hydrocarbonylation were formed *in situ* by the combination of a suitable bidentate ligand (L_2) with a palladium (II) species, e.g. $Pd(OAc)_2$, and an acidic anion source, containing the weakly or non-coordinating anions (X^-), via a ligand complexation-anion displacement reaction, eqn. 4.[6,8]

$$L_2 + Pd(OAc)_2 + 2HX \rightarrow L_2PdX_2 + 2HOAc \qquad (4)$$



SCHEME 1 Proposed mechanisms of Pd catalyzed hydroformylation, hydro-acylation and olefin-CO copolymerization

We will limit ourselves to describing the effects of variations of the ligand and acid components of the catalysts on the chemo- and regio-selectivity in oxo-synthesis with simple aliphatic olefins (propene and 1-octene) as substrate. Steric and electronic (basicity) properties of the diphosphine ligands $R_2P(CH_2)_nPR_2$ were varied by variation of R and n (no active catalysts could be obtained with monodentate ligands). In the text, we will use abbreviations for both ligands and acids; these abbreviations are explained in Table I.

TABLE I Abbreviations used fur ligands and acids

Ligands $R_2P(CH_2)_nPR_2$		
Name	R	n
DPPP	Ph	3
DsBPE	*sec*-Bu	2
DEPP	Et	3
DnBPP	*n*-Bu	3
DsBPP	*sec*-Bu	3
DtBPP	*tert*-Bu	3
Acids		
HOAc	CH_3COOH	acetic acid
TFA	CF_3COOH	trifluoroacetic acid
HOTf	CF_3SO_3H	trifluoromethanesulfonic acid
HOMs	CH_3SO_3H	methanesulfonic acid
HOtBs	$(CH_3)_3CSO_3H$	*t*-butylsulfonic acid
HOTs	p-$CH_3C_6H_4SO_3H$	*p*-toluenesulfonic acid

Chemo-selectivity in palladium catalyzed oxo-synthesis

A series of catalyst systems examined for the chemo-selectivity of hydrocarbonylation of propene and 1-octene is given in Table II. Inspection of the Table shows that variation of the ligand and the acid component of the catalyst system can result in very significant changes in chemo-selectivity. For one substrate (propene) and one acid (HOTs), ligand variation can shift the chemo-selectivity from simultaneous production of aldehydes, monoketones and co-oligomers (with the DPPP ligand), through simultaneous production of aldehydes and monoketones (with the DnBPP ligand) to the selective production of aldehydes (with the ligands DsBPP and DtBPP).

Likewise, for one selected ligand, e.g. DsBPP, acid variation can bring about a remarkable shift in chemo-selectivity from selective aldehydes formation (with TFA) towards selective monoketones formation (with HOTf). With acids containing coordinating anions, such as HCl or HOAc no active catalysts can be generated. The low activity of catalysts containing DtBPP as a ligand is noteworthy.

TABLE II Chemoselectivity in olefin hydrocarbonylation[a]

Ligand	*Acid*	*Olefin*	*T(°C)*	*Rate*[b]	*roducts (%)*[c]	
					Ald/Alc	*MonoKet*
DPPP	TFA	propene	125	200	95/-	4
	HOTs	"	"	500	30/-	50[d]
	HOTf	"	"	100	-/-	70[d]
	TFA	1-octene	"	100	98/-	trace
DnBPP	TFA	propene	125	300	95/-	trace
	HOTs	"	"	1000	15/25	50
	HOTf	"	"	500	-/-	90
	TFA	1-octene	90	60	96/-	trace
	HOTs	"	90	100	80/5	10
	HOTs[c]	"	125	120	3/93	trace
	HOTs[f]	"	"	100	-/-	95
	HOTf	"	"	80	-/-	98
DsBPP	HCl	propene	115	0	–	–
	HOAc	"	115	0	–	–
	TFA	"	125	500	98/-	trace
	HOTs	"	100	800	84/2	7
	HOTf	"	125	800	-/-	95
	TFA	1-octene	115	100	96/2	trace
	HOTs[e]	"	125	150	3/95	trace
	HOTf	"	125	40	-/-	98
DsBPE	TFA	propene	90	100	98/-	trace
	HOTf	"	90	300	-/-	93
DtBPP	TFA	propene	80	<10	–	–
	HOTs	"	80	30	85/10	4
	HOTf	"	80	10	14/11	75

a. Batch experiments, 250 mL Hastelloy C autoclave, 45 mL diglyme, $P_{CO} = P_{H2} = 30$ bar (at room temperature). Propene reactions: 20 mL propene, 0.1 mmol $Pd(OAc)_2$, 0.2 mmol ligand, 0.5 mmol acid. 1-Octene reactions: 20 mL octene, 0.25 mmol $Pd(OAc)_2$, 0.6 mmol ligand, 1 mmol acid. Rates averaged over < 30% olefin conversion.
b. Turnover / hr.
c. Remaining products are diketones and/or keto-aldehydes.
d. Higher oligoketones formed.
e. $P_{CO} = 20$ bar, $P_{H2} = 40$ bar.
f. 45 ml methanol;

The shift in chemo-selectivity for respectively, monoketone and aldehyde/alcohol formation, depends on the olefinic substrate as well as on the reaction conditions.

Thus, the DnBPP/HOTs combination becomes more selective for aldehyde formation with 1-octene as the substrate. The DPPP/TFA combination is clearly selective in aldehyde formation with 1-octene. At a higher H_2/CO ratio (of 2), and with the combination DnBPP/HOTs, ketones formation is completely suppressed and alcohols are formed selectively (93%).

The reaction solvent can also bring about a dramatic effect on the chemo-selectivity. This is demonstrated with the DnBPP/HOTs combination and 1-octene as substrate. Whereas this ligand/acid combination in diglyme as solvent resulted in selective aldehydes/alcohols formation (85%), exclusively ketones were formed in the more polar methanol solvent. The same shift towards ketone formation is observed by changing (in the diglyme solvent) the acid from HOTs to HOTf. Thus, HOTs in methanol behaves similar as HOTf in diglyme.

With all catalysts, the rate of hydrocarbonylation with propene was considerably higher than with 1-octene. This is at least partly due to the fact that 1-octene was isomerized to internal octenes in the course of the hydrocarbonylation experiments. In separate experiments with internal olefins as substrate, it was found that these are converted to the same products as the terminal olefins. However, the rate of conversion of internal olefins was about a factor of 8 lower than the initial rate (at < 15% conversion) observed with 1-octene.

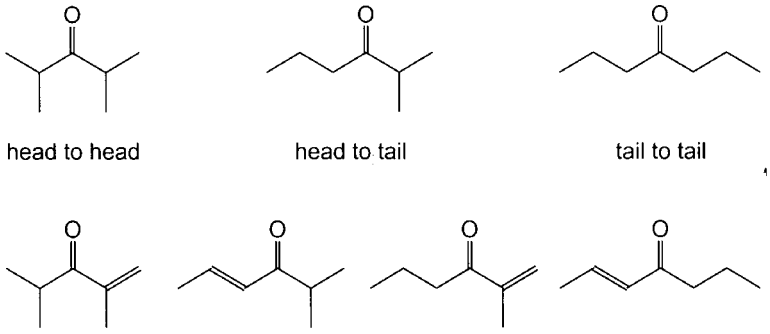
Regio-selectivity in the palladium catalyzed oxo-synthesis

With propene only two aldehydes can be formed: *n*- and *iso*-butyraldehyde. With TFA or HOTs as acid component, hydroformylation linearity increases with the steric bulk of the ligand from 60–65% with DnBPP to 84% with DsBPP. The C_2-bridged ligand DsBPE affords a significantly lower product linearity (76%) than the corresponding C_3-bridged DsBPP ligand (84%).

The acid component also affects regio-selectivity, with stronger acids affording lower product linearity. For example, using the DsBPP ligand, linearity falls from 90% with TFA to 77% with HOTs. The effect of acid strength on product linearity is more pronounced at lower reaction temperatures (e.g at 70 °C).

Similar effects could be noted with 1-octene as substrate. Mainly linear nonanals were formed under aldehyde formation conditions using TFA. With DnBPP as the ligand, n-nonanal comprised 70% of the total amount of aldehydes formed. In addition to the branched isomer α-methyloctanal (20%), the product also contained branched isomers derived from internal octenes (α-ethylheptanal and α-propylhexanal, together 10%). These latter products are a consequence of concomitant isomerization of 1-octene under hydrocarbonylation conditions as noted earlier. As with propene, the acid component also affected aldehyde product linearity. With DsBPP as ligand, it changed from 78% with HOTs to 85% with HOtBs.

The monoketones formed are both saturated- and α,β-unsaturated ketones. With a higher olefin such as propene, a variety of regio-isomeric ketones can be obtained. Three saturated monoketones with, respectively, h(ead) to h(head), h(ead) to t(ail) and t(ail) to t(ail) enchainment of the propyl groups via carbonyl can be formed. Likewise, four unsaturated ketones can be produced with respectively **h to h, h to t** (twice) and **t to t** enchainment of the propyl and the propenyl moiety via carbonyl.



The observed distribution of regio-isomeric ketones, under conditions specified in Table **II**, is dependent on the ligand used. With all ligands mentioned in Table II, the h to t isomer was predominantly formed, but this preference was considerably stronger with alkyl phosphines (up to 92%) than with the arylphosphine DPPP (≈50%). The preference for the **h to t** regio-isomer increased with the steric bulk of the alkylphosphine,

from 82% with DnBPP to 92% with DsBPP. The C_3-bridged diphosphine DsBPP gave a significantly higher preference (92%) for **h to t** enchainment than the C_2-bridged analogue DsBPE (81%). No significant influence of the anion on the isomeric distribution of the ketones could be established.

The proportion of unsaturated ketones depends on the ligand and changes from predominantly unsaturated (≈85%) with DPPP towards mainly saturated with alkylphosphines (≈80–85%). Generally, unsaturation was found to decrease with increasing temperature and increasing hydrogen pressure. The highest degree of unsaturation is consistently found in the **h to h** coupled ketone isomer.

With 1-octene, the **h to t** regio-isomeric ketones (saturated (major) + unsaturated (minor)) are almost exclusively formed under ketone formation conditions with BnDPP and HOTf as catalyst components. Thus, regio-specificity with the bulkier olefin, 1-octene, for **h to t**ketone formation is considerably higher than observed with propene.

DISCUSSION

The variation in chemo-selectivity for propene hydrocarbonylation under the conditions specified in Table II, has been summarized schematically in a graphical representation given in Fig. 1.

Along the horizontal axis the acid catalyst components have been ordered for increasing pKa: HOTf (-5.1)< HOTs (-2.7) < TFA (-0.7)[9]. Along the vertical axis the ligand catalyst components have been ordered for increasing basicity: DPPP < DnBPP < DsBPP < DtBPP. Three different regions of chemo-selectivity can be distinguished: co-oligomerization, monoketone formation and aldehyde/alcohol. The regions are separated by fairly discrete boundary regions. For example, the DnBPP/ HOTs combination is located in the boundary region between ketone and aldehyde/alcohol formation (50%/45%), while the combination of DsBPP with the same acid shifts chemo-selectivity to within the region of selective aldehyde/alcohol formation (86%). Likewise, the DPPP/HOTf combination is located in the boundary region between co-oligomerization and monoketone formation, while the combinations of DnBPP and DsBPP with the same acid are located well within the region of selective monoketone formation (90–95 %). The combination of all ligands investigated with TFA is located in the region

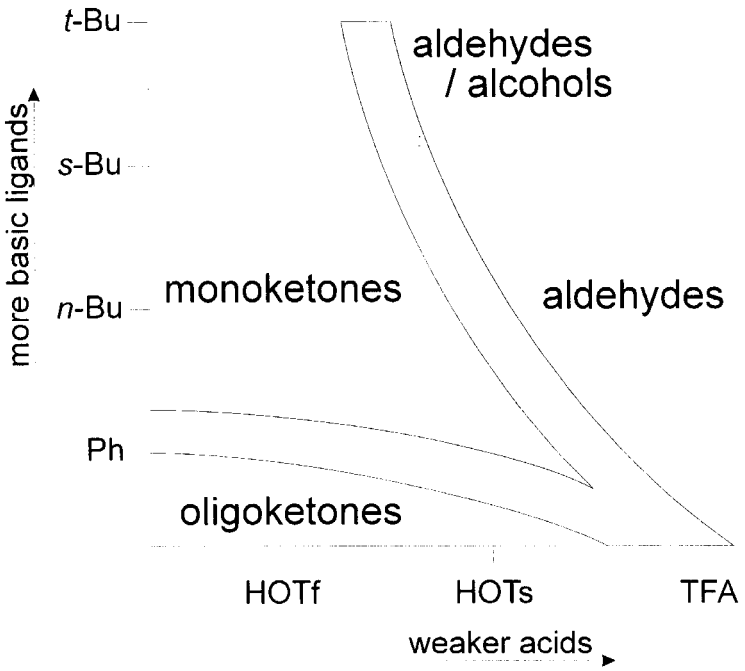


FIGURE 1 Schematic representation of chemoselectivity as a function of ligand and acid properties

of selective aldehyde formation; reduction of the aldehydes to alcohols does not take place to a significant extent, with this acid as catalyst component.

These results clearly illustrate that in cationic palladium catalysts of the type L_2PdX_2, variation of the ligand and anionic component components can be used to control chemo- and regio-selectivity in hydrocarbonylation of olefins.

Elementary steps in hydrocarbonylation

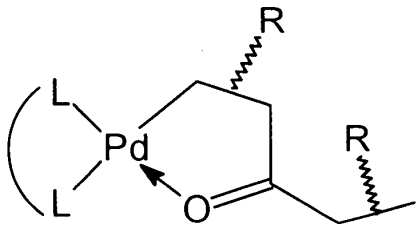
The actual active species in both hydroformylation and hydro-acylation (Scheme **1**) is thought to be a cationic Pd-hydride complex L_2PdH^+,

formed by heterolytic splitting of hydrogen at the electrophilic palladium center of the precursor L_2PdX_2 (eqn. 5).

$$L_2Pd^{2-}X_2^- + H_2 \longleftrightarrow L_2PdH^+X^- + HX \qquad (5)$$

The next step would involve coordination of the olefin to the Pd hydride, followed by migratory insertion of the olefin to generate a Pd-alkyl complex L_2PdR^-. Coordination and subsequent migratory insertion of carbon monoxide then yields the Pd-acyl complex $L_2PdC(O)R^+$. It is at this stage that hydroformylation and hydro-acylation reactions start to diverge.

In hydroformylation, hydrogenolysis of the Pd-acyl bond takes place to give the aldehyde product and regenerate the hydride L_2PdH^+. In hydro-acylation, a second olefin molecule coordinates to the Pd-acyl, and migratory insertion gives an internally coordinated Pd-alkyl complex (structure **1**).



(*1*)

Stable species of this type have been observed spectroscopically in the studies of olefin insertion in L_2Pd-acyl complexes[10]. They are also thought to play a key role as intermediates in the alternating olefin/CO copolymerization. Termination of hydro-acylation can proceed by hydrogenolysis of complex (**1**) to form a saturated ketone and regenerate the hydride L_2PdH^+. Alternatively, complex **1** can undergo β-elimination to give the hydride and an unsaturated ketone. These terminating reactions compete with further insertion steps to give oligo- or poly-ketones. We will now discuss the factors which determine the fate of the crucial Pd-acyl intermediate.

The interplay of ligands and anions in electrophilicity

Inspection of Table II and Figure 1 suggests that the steric properties of the ligand and anions are probably not a very crucial factor for the observed variation in chemo-selectivity. No obvious correlation between chemo-selectivity and ligand size, as manifested by the estimated cone-angle[11] at the phosphorus atoms of the ligand, could be established. Instead, Figure 1 suggests that the electronic properties of both the neutral ligand L_2 and the anion determine the course of hydrocarbonylation. An increasing ligand basicity should lead to a decreasing electrophilicity of the palladium (II) centre. Likewise, weaker acids are generally associated with increasing coordination strength of the anion to the palladium centre and also decrease the electrophilicity of the metal center. Apparently, highly electrophilic complexes are efficient copolymerization or hydroacylation catalysts, whereas less electrophilic complexes give rise to hydroformylation.

One essential requirement of the anions should be their easy displacement by reactants from the coordination sites around palladium. Too strong coordination, e.g. with halogen or weak carboxylic acids, leads to inactive catalysts (Table II). Even when the anions can be displaced by the reactants, as evidenced by the observed catalytic activity, their basicity still affects chemo-selectivity. It is thought that more basic anions stay in closer proximity to the palladium(II) centre than less basic anions during the elementary steps of the catalytic cycle. For example, they could remain at or near a fifth or temporarily at the fourth coordination site around the Pd centre. Cation-anion interaction, just like acidity, will depend on the reaction solvent. Thus, it can be understood that the OTs^- anion, as far as chemo-selectivity is concerned, behaves as a non-coordinating anion in a polar solvent, i.e. very similar to the non-coordinating OTf anion in a less polar solvent under the same conditions (see Table II, experiments with DnBPP/1-octene). Cation-anion dissociation in methanol is facilitated by solvation, whereas in diglyme such ion-pairs stay in closer proximity.

Hydroformylation vs. hydro-acylation

Apparently, selective hydroformylation does not require a strong electrophilic palladium centre. This can be achieved by using a very basic ligand (DsBPP, DtBPP) and/or a not too poorly coordinating anion (e.g.,

TFA$^-$). Selective hydro-acylation requires a more strongly electrophilic palladium centre, such as achievable with basic ligands (DnBPP through DtBPP) in combination with a non-coordinating anion (OTf). The even more electrophilic palladium centre obtained with OTf and the less basic DPPP ligand leads to oligo- or polyketones.

Since the catalytic cycles for hydroformylation and hydroacylation diverge at the Pd-acyl stage, the electrophilicity of the Pd center apparently determines the ratio of hydrogenolysis (to give aldehydes) and olefin insertion (to give ketones). A more electrophilic metal centre appears to favour olefin insertion over hydrogenolysis. The substrate molecules (CO, olefin) can easily displace the weakly coordinating anion in $L_2Pd(acyl)(X)$. Carbon monoxide insertion in the Pd-acyl bond will not occur for thermodynamic reasons. However, once the olefin enters the coordination sphere, both a low barrier of insertion into the Pd-acyl bond and a strong thermodynamic driving force for olefin insertion are expected. The insertion product is stabilized by internal coordination of the β-carbonyl group to the metal centre (structure **1**)[6]. Since part of this stabilization will already be "felt" in the transition state, the insertion barrier should be lower than for a "normal" olefin insertion. A more electrophilic metal centre should therefore favour olefin insertion over hydrogenolysis.

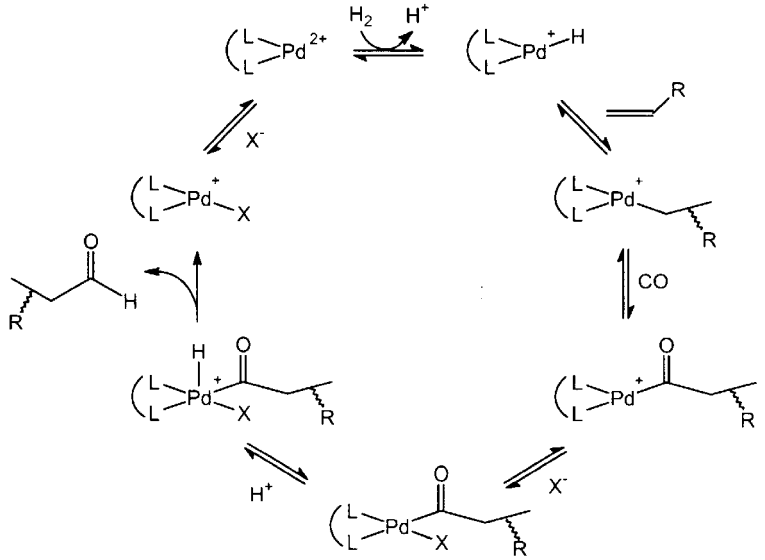
It could also be that the coordinating anions giving rise to hydroformylation, play an *active* role in the hydrogenolysis reaction. The mechanism of the Pd-acyl hydrogenolysis is not known and will certainly require more study. As a working hypothesis we assume an oxidative pathway starting with protonation at the d_z^2 – orbital of the Pd(II) centre.

This would produce a $L_2Pd(IV)(hydride)(acyl)$ complex, which would eliminate aldehyde to regenerate $L_2Pd(II)X_2$ and which then reacts with H_2 to regenerate a $L_2Pd(II)H^+$ and acid (HX) via eqn. 5 (Scheme 2).

The (temporary) coordination of the anion at the fourth coordination site may be essential by boosting the nucleophilicity of the d_z^2 orbital and thus making it accessible for protonation to generate the Pd(IV) intermediate. Non-coordinating anions like OTf are not basic enough to fulfil this role, and also do not stay close to the Pd centre.

Thus, the ligand/anion combination affects the catalysis in a number of ways:

By changing the electrophilicity of the metal center. More electrophilic catalysts tend to give higher hydroformylation rates, but at



SCHEME 2 Proposed heterolytic hydrogen splitting pathway

very high electrophilicity hydroacylation becomes the preferred reaction.

Coordinating anions block a coordination site and thus result in lower rates for any reaction.

More basic anions assist hydrogenolysis and favour aldehyde formation.

Finally, we comment on the terminating hydrogenolysis of the Pd-alkyl bond to yield the monoketone hydro-acylation products. The chelate formation in structure **1** could affect the subsequent fate of the Pd-alkyl intermediate in a number of ways. On one hand, chelate formation could prevent or slow down termination by β-hydride elimination (to yield unsaturated ketones) if it would require loss of Pd-O coordination. For β-hydride elimination to occur, the H atom has to approach the palladium ion. On the other hand, hydrogenolysis might proceed via protonation of the Pd (II) centre by attack of the d_z^2 orbital as suggested in Scheme 2, in which case the Pd-O coordination would assist protona-

tion by boosting the nucleophilicity of the Pd(II) centre, similar to the coordination of an anion proposed in the case of Pd-acyl hydrogenolysis. Elimination of the saturated ketone would then regenerate the $L_2Pd(II)X_2$ which then reacts with hydrogen to regenerate [Pd(II)-H]X and acid (HX) via eqn. 5. This would then explain the high selectivity to mono-ketones. The notion that chelating Pd-alkyl moieties of the structure 1 type can undergo rapid hydrogenolysis is supported by observations made with acrylic substrates, such as methyl acrylate, acrylic acid or acryl-amide. With these substrates, unlike with aliphatic olefins, hydrogenation of the substrate itself strongly competes with hydrocarbonylation. The insertion of these olefins in Pd-hydride immediately affords a five-membered chelate ring similar to structure 1, but now involving the ester, acid or amide carbonyl group.

In the extreme case of high electrophilicity of the Pd centre, with aromatic diphosphine DPPP as ligand and OTf as anion (Table II and Figure 1), both the proposed protonation of Pd(II) and termination β-H elimination will become more difficult, and significant amounts of oligo-ketones are obtained. However, the monoketone products in this case are mainly unsaturated, thus indicating that termination by β-elimination is efficiently competing with hydrogenolysis, and both are competing with CO and olefin coordination and subsequent migratory insertion.

Regio-selectivity

In this section, we will briefly comment on the effects of the ligand and anion on the mode of olefin insertion at the palladium center, both in hydroformylation and hydro-acylation reactions.

In hydroformylation of simple aliphatic olefins the regio-selectivity of olefin insertion can directly be related to the linearity of the product. Obviously, linear hydroformylation products can only be obtained via 1,2 (*n*) insertion of olefins in Pd-hydride intermediates, whereas branched products are only accessible via 2,1 (*iso*) insertion. The observation of higher product linearity with bulkier ligands indicates that the mode of olefin insertion is primarily determined by the space available at the palladium centre. It is thought that both olefin insertion in Pd-hydride and CO insertion in Pd-alkyl are reversible and that subsequent aldehyde formation is irreversibly trapped by hydrogenolysis.

Thus, formation/trapping of *n*-acyl intermediates is favoured over that of the sterically more demanding *iso*-acyl intermediates. A higher preference for linear product observed with more coordinating anions could indicate that the anion-assisted hydrogenolysis reaction disciminates between Pd-*n*-acyl and Pd-*iso*-acyl species with the the more strongly coordinating anions favouring n-acyl hydrogenolysis.

In hydro-acylation of aliphatic olefins and with alkyl diphosphines as ligand there appears to be a strong preference for the **h to t** coupling of the olefinic fragments and this preference becomes larger with the steric bulk of the ligand and olefin. Bulkier ligands and higher olefins strongly increase this preference, due to increased steric congestion at the palladium centre. The surprisingly low preference for **h-to-t** coupling observed with the aryl diphosphine DPPP is remarkable because it is larger than the smallest alkyldiphosphine used in the examples. This suggests that not only steric but also electronic factores are important. The **h to t** coupling could in principle be achieved both by two consecutive 1,2 and/or two consecutive 2,1 insertions of the olefin in the Pd hydride and Pd-acyl bond. From the structure of the unsaturated isomers, -e.g. with propene almost exclusively of the iso-propenyl-type- it can be concluded that there is a very clear preference for double 1,2 insertions with alkyldiphosphines. It is thought that, as with hydroformylation, both olefin insertion in the Pd-hydride and CO insertion in the Pd-alkyl bond are reversible. The acyl intermediate can thus be trapped either by irreversible hydrogenolysis to yield the hydroformylation products or by irreversible olefin insertion to give the intermediate (**1**) and eventually ketone. A more detailed analysis[6b] has shown that the proportion of ketones derived from *n*-acyl intermediates is consistently and substantially higher than the proportion of *n*-aldehydes derived from the same mixture of *n* + *iso*-acyl intermediates. Apparently, the olefin insertion reaction is considerably more sensitive to the steric difference between the Pd-*n*- and *iso*-acyl intermediates and therefore has a higher preference for trapping the n-acyl selectively. This preference becomes stronger with bulkier ligands and larger olefins.

CONCLUSIONS

The cationic palladium complexes, L_2PdX_2, previously shown to be excellent catalysts for the alternating copolymerization of olefins with

carbon monoxide[6], owe their catalytic properties to the electrophilic nature of the palladium(II) centre. The metal has a square-planar environment made up of the cis-chelating neutral ligand (L_2) and anionic ligands (X^-). Cis-chelation by the neutral ligand is considered essential for placing the intermediate palladium-hydride- and palladium-carbon bonds *cis* to the fourth coordination site available to a substrate molecule. This is an ideal situation for the migratory insertion of the substrate molecules to generate intermediate Pd-alkyl- and Pd-acyl species.

The electrophilic palladium centre not only can bind and activate nucleophilic molecules, such as olefins, carbon monoxide and alcohols, but also hydrogen. The possibility of interrupting the chain-growth of CO/olefin co-polymerization by an efficient chain-transfer with hydrogen either at the Pd-alkyl or the Pd-acyl stage, forms the basis of the results on olefin hydrocarbonylation (oxo-synthesis) described in this paper. With these palladium catalysts, the oxo-synthesis can, thus, be fully exploited to produce, at will, aldehydes/alcohols by hydroformylation or ketones by hydro-acylation.

The reactions described in this paper constitute the first examples of selective formation of ketones by hydrocarbonylation of higher olefins and the first examples of Pd catalyzed hydroformylation[8], which have formed the basis for the development of highly efficient palladium catalysts for the hydroformylation of internal olefins to alcohols[12]. We believe that the electrophilicity of the palladium centre is a key parameter for chemo-selectivity control of the catalysis towards either reaction. Both the neutral ligand and the anions can be used to adjust the electrophilicity and the steric environment of the palladium center with high precision. Apart from this, it seems likely that the anions associated with the cationic palladium center play an important role of their own. Apparently anion basicity determines the efficiency of hydrogenolysis at the Pd-acyl stage.

EXPERIMENTAL

Analytical equipment

Product analysis of reaction mixtures was routinely performed by gas-liquid chromatographic (GLC) analysis on a Perkin-Elmer 8500

equipped with two capillary columns, Chrompack 50 m CP-sil-5 and 50 m FFAP. Structural analysis was performed with GLC-mass spectroscopic (GC/MS) analysis on a Finnagin-9610 gas chromatograph fitted with the CP-sil-5 column and coupled to a Finnigan-4000 triple-stage mass-spectrometer using electron impact ionization. This technique was applied to identify reaction products by comparison with authentic samples.

^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer. ^{1}H and ^{13}P NMR spectra were recorded on a Bruker WM 250 spectrometer.

Materials

Palladium acetate, diglyme, THF, the Brønstedt acids, p-toluenesulfonic acid, methanesulfonic acid, trifluoroacetic acid and trifluoromethanesulfonic acid, 1-octene(p.a.), styrene(p.a.), methyl acrylate, acrylic acid and acryl amide were all obtained from Merck and were used as supplied. t-Butylsulfonic acid was prepared in house by oxidation of t-Butylthiol with hydrogen peroxide. Of the phosphine ligands, DPPP was obtained from Strem, whereas DnBPP, DsBPP, DsBPE, DEPP and DtBPP were all synthesized by standard preparation techniques[13], involving the reaction between the respective di-alkylphosphine and 1,3 dibromopropane or 1,2 dibromoethane to give the double HBr salt of the respective di-phosphine. Neutralisation with sodium hydroxide, and subsequent destillation afforded the di-phosphine. Purity of the applied phosphines was always higher than 95% as observed with ^{1}H and ^{31}P NMR. Phosphine-monoxide was observed as the main impurity. The enantiomeric composition of DsBPP and DsBPE was statistical. The air-sensitive phosphines were all stored and handled in a Glove box under nitrogen. Propene of polymer grade quality was used and was obtained from in house sources. Commercial quality carbon monoxide (98 %) and hydrogen (>99 %) were obtained from Air Products.

Batch autoclave procedure

All hydrocarbonylation experiments were carried out in a 300 ml magnetically stirred, electrically heated Hastelloy™ C autoclave. A typical experimental procedure was as follows:

In a nitrogen glove box, the catalyst components as specified in Table II, palladium acetate, and ligand were dissolved in 10 ml diglyme con-

tained in a small closable bottle. The components were allowed to react until no solid palladium acetate was visible. The solution was transferred in the closed bottle from the glove box and introduced in the autoclave under a flowing nitrogen blanket prefilled with 40 ml degassed diglyme and containing the acid catalyst component. The autoclave was subsequently closed and evacuated. Liquid propene (20 ml) was pumped in the autoclave from a high pressure ISCO pump. Subsequently, the autoclave was first pressurized with 30 bar of CO and then with 30 bar of hydrogen. In about 10–15 minutes the autoclave was heated to the desired temperature and kept at this temperature by a Thermo-Electric 100 temperature control unit. The pressure was continuously recorded by using a Transamerica Instruments pressure transducer, series 2000. Activity data during the experiment were calculated from the pressure decrease in time and from GLC analysis of the reaction product at the end of a reaction period of 5 hours. After that time, the autoclave was allowed to cool, depressurized and opened. Selectivity data were obtained from a standard analysis of the final reaction product by GLC. Product identification occurred by GC/MS analysis. The rate data in the tables are "initial" rates, averaged over a period corresponding to < 30 % conversion.

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