Carbonylation of Ethene in Methanol Catalysed by Cationic Phosphine Complexes of Pd(II): from Polyketones to Monocarbonylated Products

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Abstract This review article describes the advances on the carbonylation of ethene in methanol since the discovery of highly active cationic *cis*-chelating diphosphine-Pd(II) catalysts for the production of perfectly alternating high molecular weight polyketones, which led to the recent development of efficient catalysts for the synthesis of monocarbonylated products. After dealing with the activation of the catalyst precursor and with mechanistic aspects of the catalytic cycles, the influence of the operating conditions, the nature of the counter anion, the acidity of the reaction medium and the nature of the ligand on both the rate and the selectivity is delineated. In particular, it is shown that the

catalytic activity can be finely tuned by varying the electronic, bite angle and steric bulk properties of the ligand and that, within a series of related ligands, the selectivity mainly depends on the steric bulk.

Abbreviations

dppp	1,3-bis(Diphenylphosphino)propane
dppe	1,2-bis(Diphenylphosphino)ethane
dppb	1,4-bis(Diphenylphosphino)butane
dapp	1,3-bis[bis(2-Methoxyphenyl)phosphino]propane,1,3-bis(dianylidphosphino) propane
dppm	1,1-bis(Diisobutylphosphino)methane
dibpp	1,3-bis(Diisobutylphosphino)propane
dippe	1,2-bis(Diisobutylphosphino)ethane
dibpe	1,2-bis(Diisopropylphosphino)ethane
dtbpe	1,2-bis(Di-t-butylphosphino)ethane
dtbpp	1,3-bis(Di-t-butylphosphino)propane
dtbpx	1,2-bis(Di-tert-butyl)phosphinomethyl)benzene
dppf	1,1'-bis(Diphenylphosphino)ferrocene
dppo	1,1'-bis(Diphenylphosphino)osmocene
dppomf	1,1'-bis(Diphenylphosphino)octamethylferrocene
dba	Trans,trans-dibenzylidenacetone
HOMs	Methanesulfonic acid
TFA	Trifluoroacetic acid
TFA⁻	Trifluoroacetate anion
HOTf	Trifluoromethanesulfonic acid
HOTs	4-Toluenesulfonic acid
DEK	Diethylketone
MP	Methylpropanoate
BQ	Benzoquinone
NQ	Naphtoquinone
OX	Oxidant

1
Introduction

The discovery in the early 1980s that cationic palladium-phosphine complexes catalyse the copolymerisation of carbon monoxide with ethene or a higher α-olefin to yield perfectly alternating polyketones has since attracted continuous increasing interest [1, 2]. This is because the monomers are produced in large amounts at a low cost and because polyketones represent a new class of thermoplastics of physical-mechanical and chemical properties that have wide applications [3–6]. In addition, easy functionalisation can open the way to a large number of new materials [7]. The copolymerisation has

been extended to other olefins, such as cyclic alkenes, dienes, styrenes, and functionalised α-olefins and also to terpolymerisation. The introduction of a second olefin in the CO-ethene backbone lowers the melting point and makes the terpolymer more easily processable. The development of highly active palladium-diphosphine catalysts has opened the way to the commercialisation of the CO-ethene-propene terpolymer [2, 8–10].

Early disclosing of the results in some articles and reviews is still a basic guideline [1, 6, 11–16]. Perfectly alternating polyketones form because consecutive insertion of two molecules of CO is not allowed for thermodynamic reasons and two consecutive insertions of ethene do not occur for kinetic reasons [11–13]. Cationic palladium-diphosphine catalysts (typically dppp) are far superior, as far as both rate of copolymerisation and molecular weight of the polyketone, to catalysts having the metal coordinated by a monophosphine, such as PPh$_3$. This striking difference was explained as the result that the diphosphine is always cis-chelate, so that the other two coordination sites of the d^8-square planar palladium centre, one occupied by the growing polymer chain and the other by the monomer, are also always cis to each other, which is ideal in favouring the chain growth through migratory insertions of the monomers. Differently, Pd(II) coordinated by a monophosphine can assume both cis and trans geometry, so that chain growth is relatively slow compared to chain termination [14–16]. Since then many articles have been published. Research efforts have been focused towards the deeper understanding of the key factors that rule the catalysis. The subject has been extensively and excellently reviewed up to very recently [17–21]. The last review deals in particular the structure and physicochemical and mechanical properties of copolymers of less common olefins, such as higher olefins and styrenes, dienes, cyclic dienes and functionalised olefins. In addition the stereochemical copolymerisation has also been reviewed [22, 23], as well as theoretically investigated [24].

Several types of bidentate ligands, different from diphosphines, for example bipyridines and phenantrolines, have been proven to give active catalysts, particularly in the CO-styrene copolymerisation [25], but, particularly with ethene, diphosphines give higher performances.

The carbonylation of ethene has a wider interest as it can lead to the production not only of polyketones, but also to many other products ranging from low molecular weight cooligoesters, down to methyl propanoate (MP) and also cooligodiesters, cooligodiketones down to diethyl ketone (DEK). The insertion of the monomers into MeOH is schematized by Eq. 1, n ranging from 1 to even more that 10000:

$$nCO + nCH_2{=}CH_2 + CH_3OH \longrightarrow H{-}(CH_2CH_2CO)_n{-}OCH_3 \qquad (1)$$

Mixtures of low molecular weight products and DEK can find large uses as low volatility "green" solvents [18, 26].

MP is a potential intermediate to methyl methacrylates, an important monomer produced annually on a multimillion tonne scale worldwide [27–29].

Highly active, selective and stable catalysts for the production of MP [30–33] and DEK [33] with sterically demanding basic diphosphine ligands have also been developed. In addition, these type of catalysts selectively convert internal olefins to linear esters for the production of detergents, plasticizers and nylon intermediates [32, 34].

The alkoxycarbonylation of olefins has also been reviewed recently [35].

Hereafter, the factors ruling the activity and selectivity of Pd(II)-phosphine catalysts for the carbonylation of ethene in MeOH are presented. In order to make the exposition clearer some of the concepts already discussed in other reviews will be shortly resumed. It will deal first with copolymerisation because it includes more general aspects, several of which are involved also in the catalysis to monocarbonylated non-polymeric products. The literature search covers all up to 2004.

2
Mechanistic Aspects of the CO–C₂H₄ Copolymerisation
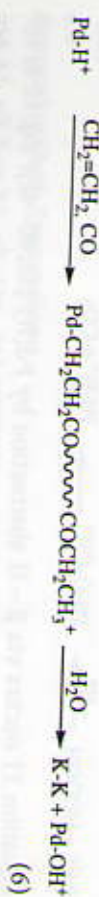
2.1
General Aspects

The most active and selective catalysts for both the copolymerisation process and for the apparently simpler ethene carbonylation to monocarbonylated products MP or DEK are cationic square planar Pd(II) complexes in which the metal centre is cis-coordinated by a bidentate P–P ligand, by a ligand involved in the initial step of the catalysis or in the process of forming the product and with the fourth "vacant" site coordinated by CO or ethene or a keto group of the growing chain or MeOH (or H_2O, always present in the solvent even when not added on purpose) or even by a weakly coordinating anion.

In general, when using an active Pd-diphosphine catalyst, the end groups of the perfectly alternating CO – C_2H_4 polymer chains are couples of EtCO-(keto, K) and -COOMe (ester, E) or K–K or E–E groups [14]. When using a monodentate ligand, such as PPh₃, only K–E cooligomers form, together with MP. In this case it has been proposed that the hydride mechanism only is operative (Eq. 3) [11]. Polymers with K–E end groups form through initial insertion of CO into a Pd–OCH_3 bond, followed by sequential insertions of the monomers and ends by protonolysis by MeOH of a Pd-alkyl bond with reformation of the initiating species; it can also form starting from a Pd–H^+ species and end by methanolysis of a Pd-acyl bond, with regeneration of the starting species. The polymer E–E forms from Pd–OCH_3^+ and

ends through methanolysis of a Pd-acyl bond, with formation of a Pd–H^+ species, different from the starting one. In turn Pd–H^+ can start the process that leads to the polymer K–K, if the termination occurs via protonolysis of a Pd-alkyl bond with formation of Pd–OCH_3^+, different from the species that initiates this cycle (in Eqs. 2–5 and in the following ones, Pd–OCH_3^+, Pd–H^+, Pd^{2+}, etc., are also coordinated by a P–P ligand or two monophosphines). The last two cycles can be interconnected and, when they occur at comparable rates, the E–E and K–K chains should balance and the expected K/E ratio should be 1/1 [14].

$$\text{Pd-OCH}_3^+ \xrightarrow{\text{CO, CH}_2\text{=CH}_2} \text{Pd-COCH}_2\text{CH}_2\text{CO} \sim\sim\sim \text{COOCH}_3^+ \xrightarrow{\text{CH}_3\text{OH}} \text{K-E + Pd-OCH}_3^+ \quad (2)$$

$$\text{Pd-H}^+ \xrightarrow{\text{CH}_2\text{=CH}_2, \text{CO}} \text{Pd-COCH}_2\text{CH}_2 \sim\sim\sim \text{COCH}_2\text{CH}_3^+ \xrightarrow{\text{CH}_3\text{OH}} \text{E-K + Pd-H}^+ \quad (3)$$

$$\text{Pd-OCH}_3^+ \xrightarrow{\text{CO, CH}_2\text{=CH}_2} \text{Pd-COCH}_2\text{CH}_2\text{CO} \sim\sim\sim \text{COCH}_2\text{CH}_3^+ \xrightarrow{\text{CH}_3\text{OH}} \text{E-E + Pd-H}^+ \quad (4)$$

$$\text{Pd-H}^+ \xrightarrow{\text{CH}_2\text{=CH}_2, \text{CO}} \text{Pd-CH}_2\text{CH}_2\text{CO} \sim\sim\sim \text{COCH}_2\text{CH}_3^+ \xrightarrow{\text{CH}_3\text{OH}} \text{K-K + Pd-OCH}_3^+ \quad (5)$$

However, this is not always the case. Excess of K–K has been found to occur during the initial stage of the copolymerisation when the coligomer chain bound to the metal is still soluble and catalysis occurs in the homogeneous phase [36]. This may also occur when protonolysis involves H_2O in place of MeOH, with formation of a Pd–OH^+ species, which regenerates Pd–H^+ by insertion of CO to Pd–$COOH^+$ followed by CO_2 evolution. Thus in each catalytic cycle one molecule of CO is not incorporated into the polymer chain, but is consumed as CO_2:

$$\text{Pd-H}^+ \xrightarrow{\text{CH}_2\text{=CH}_2, \text{CO}} \text{Pd-CH}_2\text{CH}_2\text{CO} \sim\sim\sim \text{COCH}_2\text{CH}_3^+ \xrightarrow{\text{H}_2\text{O}} \text{K-K + Pd-OH}^+ \quad (6)$$

$$\text{Pd-OH}^+ + \text{CO} \longrightarrow \text{Pd-COOH}^+ \longrightarrow \text{Pd-H}^+ + \text{CO}_2 \quad (7)$$

Excess of polymer E–E has been also been found and in some cases only E–E forms, for instance during the initial stage of catalysis by Pd(dapp)²⁺ in the presence of an oxidant, usually benzoquinone or naphtoquinone (BQ, NQ) [37]. The oxidant favours the formation of Pd–OCH_3^+ at the expense of Pd–H^+ [15] and in the copolymerisation process one molecule of oxidant is

consumed in each catalytic cycle:

$$Pd\text{-}H^+ + CH_3OH + OX \longrightarrow Pd\text{-}OCH_3^+ + OXH_2 \qquad (8)$$

$$2CH_3OH + (n+1)CO + nC_2H_4 + OX \longrightarrow CH_3OCO\text{-}(CH_2CH_2CO)_n\text{-}OCH_3 + OXH_2 \qquad (9)$$

The catalyst is not introduced into the reaction medium as the $Pd\text{-}OCH_3^+$ or $Pd\text{-}H^+$ species. These form in situ by reactions of a relatively stable "cationic" catalyst precursor with MeOH or a hydride source. In turn, the precursor can be prepared by adding to a $Pd(AcO)_2$ solution a solution of the P–P ligand (1/1) and then a solution of a strong acid HX, whose conjugate base may be a weakly or a non-coordinating anion, like $CF_3SO_3^-$, BF_4^-, TsO^-, CF_3COO^-, or from preformed $[PdCl_2(P\text{-}P)]$ by metathetical exchange with AgX or salts of metals that have a stronger affinity for Cl^- than palladium [38]; it can also be preformed $[PdX_2(P\text{-}P)]$ or $[PdX_{2-n}L_n(P\text{-}P)]X_n$ (n = 1 or 2, L = easily displaceable ligand such as H_2O or CH_3CN). Alumoxanes have also been used to abstract the acetate or chloride ligands [39].

The species that initiate the catalysis form in situ according to the reactions:

$$Pd^{2+} + CH_3OH \longrightarrow Pd\text{-}OCH_3^+ + H^+ \qquad (10)$$

$$Pd\text{-}OCH_3^+ \longrightarrow Pd\text{-}H^+ + HCHO \qquad (11)$$

$$Pd^{2+} + H_2O + CO \xrightarrow{-H^+} Pd\text{-}COOH^+ \longrightarrow Pd\text{-}H^+ + CO_2 \qquad (12)$$

$$Pd^{2+} + CH_3OH + C_2H_4 \longrightarrow Pd\text{-}H^+ + CH_2=CHOCH_3 + H^+ \qquad (13)$$

$$Pd^{2+} + H_2O + C_2H_4 \longrightarrow Pd\text{-}H^+ + CH_3CHO + H^+ \qquad (14)$$

$$Pd\text{-}OCH_3^+ \xrightarrow{CO,\ CH_3OH} Pd\text{-}H^+ + (CH_3O)_2CO \qquad (15)$$

$$Pd^{2+} + HCOOH \xrightarrow{-H^+} Pd\text{-}O_2CH^+ \longrightarrow Pd\text{-}H^+ + CO_2 \qquad (16)$$

Equation 11 occurs via β–H abstraction by Pd(II) [33, 40–42]; Eq. 12 is related to the water–gas shift reaction (WGSR) [43–45]; Eq. 13 and Eq. 14 are related to the oxidation of C_2H_4 to acetaldehyde by Pd(II) in the presence of H_2O in the Wacker process [46]. Equation 15 has been shown to occur with octamethylferrocene-phosphine complexes [47]. Formic acid can also be a source of hydride species [48].

Pd–Me$^+$, Pd–COR$^+$ complexes, Pd–Ar$^+$ related to the Pd–H$^+$ catalytic cycle, and Pd–COOCH$_3^+$ complexes, related to the other cycle, can be also used to start the catalysis [11,39,49–60].

In MeOH, Pd–H$^+$ species are unstable and have the tendency to deprotonate with reduction to less active dimeric Pd(I) and Pd(0) complexes, which may lead to degeneration of the catalyst with formation of inactive palladium metal and free ligands, which in turn may give less active bis-chelate complexes $[Pd(P\text{-}P)_2]^{2+}$ [55,61]. Possible deactivation paths have been delineated in [17]. In order to maintain or improve the catalytic activity, the precursor is used together with an oxidant and an excess of acid (usually $BQ/Pd = 100$ – 200 and acid/$Pd = 10$ – 20) [15,47].

Furthermore, even the ligand, necessary to stabilize the catalyst, can reduce Pd(II) to Pd(0) complexes and formation of phosphine oxides [62–64]. In the preparation of $[Pd(AcO)_2(dppp)]$, from $Pd(AcO)_2$ and dppp in MeOH, phosphine oxides have been found to form together with methyl acetate and palladium metal [65]. The reaction can be schematized as follows;

$$Pd(AcO)_2 + H_2O + P\text{-}P \longrightarrow Pd_{metal} + 2AcOH + P{=}O \qquad (17)$$

Equations 12, 14 and 17 require the presence of H_2O. Thus H_2O plays an important role in promoting the catalytic activity, but can also cause deactivation. Catalysis will be more efficient when all the reactions directly involved in the catalytic cycle are faster than the side reactions subtracting active species. Deactivation is related to the requirement of the palladium centre to have a "vacant" coordination site to ensure high catalytic activity. However, palladium tends to achieve the usual coordination number four, for example through dimerisation. Dimerisation/deactivation can be prevented by coordination of labile ligands, like H_2O, which acts also as an efficient hydride source. Also deprotonation leads to dimerisation/deactivation; an acid can prevent it.

Thus, it has been found that H_2O and TsOH have a beneficial effect on the catalytic system $Pd(AcO)_2/dppp/TsOH$, first reported by Drent, as the copolymerisation rate significantly increases (with respect to the use of "anhydrous" MeOH) about five times and passes through a maximum in the presence of ca. 1000 ppm of H_2O and when Pd/TsOH = 1/8 (ca. 12 000 g polymer$(g\ Pd\cdot h)^{-1}$ at 90 °C, 60 bar, CO/ethene = 1/1) [66].

2.2
Alternating Chain Propagation

The process of chain growing involves alternating reversible CO insertions and irreversible ethene insertions [13, 15, 67]. As already mentioned, consecutive insertion of two molecules of ethene does not occur for thermodynamic reasons and consecutive insertion of two molecules of CO does not occur because the insertion of CO is much faster than that of ethene [11–13,67]. It was subsequently proposed that coordination through the oxygen atom of a carbonyl group of the growing chain with formation of β- and γ-chelates
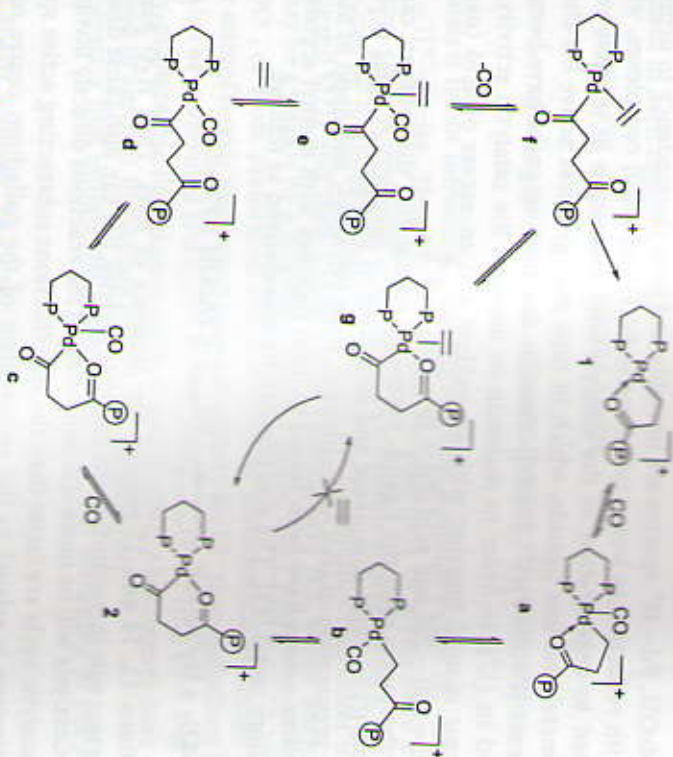
Fig. 1 Proposed alternating chain growing process, with observed intermediates, **1** and **2**, and proposed ones, **a–f**. Adapted from [51]

(Fig. 1) contributes to the perfect alternation. Because of its higher binding affinity, CO inserts into a five-membered β-chelate to give a six-membered γ-chelate. Since a five-membered ring is more stable that a six-membered one, further propagation occurs with the insertion of ethene and formation of the next five-membered ring [15].

By the use of polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS), Drent and colleagues monitored in the microcrystalline state the single insertion steps catalysed by [Pd(CH₃)(OTf)(dppp)] and the presence of β- and γ-chelates **1** and **2**. It was proposed that substitution of the chelating cheto group by ethene is CO-assisted and occurs in two steps, associative substitution of the chelating keto group by CO by ethene (**2 → c → d**) followed by associative substitution of CO by ethene (**d → e → f**), and that the substitution of the chelating keto group by CO is more facile than by ethene for steric reasons. It was also found that the total abundance of **1** and **2** and their ratio remain constant, so that both are resting states of the catalyst [51].

Such chelates have been detected also by variable temperature multinuclear NMR spectroscopy, which showed that basically the above mechanism is also operating in solution [47, 55, 58].

For a series of model alkyl complexes of the type [Pd(R)(CO)(P−P)]+ (R = Me, Et) it has been found that the CO Eqs. 18 and 19 are reversible

and that the energy barriers, in the range of 14–18 kcal/mol, decrease with increasing P−Pd−P angles and steric bulk of the ligands [52, 54–56, 68]. However, a rate-enhancing effect was observed with ligands 1, n-bis(diphenyl)phosphinoalkanes in the order $n = 4 > n = 3 > n = 2$ [69].

For a series of model acyl of the type [Pd(COMe)(C₂H₄)(P−P)]+ it has been found that the insertion of ethene into the Pd-acyl bond with formation of a β-chelate (Eq. 20) is irreversible and that the energy barrier is ca. 12 kcal/mol [52, 55, 56]. From thermodynamic and kinetic data, Schultz et al. calculated that the insertion of ethene into a Pd-alkyl bond (double ethene insertion) could occur every ca. 10^5 CO insertions into the same bond [52], which accounts for the strict alternating chain growing.

In addition, it has been established that the energy barriers of the β-chelate opening by CO (Eq. 21) decrease by increasing the length of the chain bridging the two P atoms and hence with increasing P−Pd−P bite angles, and that there is correlation between the intrinsic catalytic activity and the energy barrier Eq. 21 [55, 56]. It is noteworthy to report that ethene insertion into a β-chelate has never been observed, in spite of the fact that ethene insertion reactions have been studied in the absence of free CO, so that, at least in principle, ethene could insert, since double ethene insertion is known to occur in the absence of CO. Moreover, under actual catalytic conditions, imperfect alternating copolymers with ethene content > 50%, risen from multiple ethene insertions, have been obtained by increasing the ethene/CO ratio using o-alkoxy derivatives of diphenylphosphinobenzene sulfonic acid acting as P−O ligands [70].

On the basis of these studies both in solid and in solution, even under actual catalytic conditions, the importance of the chelates in controlling both the strict alternating chain growing and the chain propagation rate is well ascertained [19, 47, 51, 58].

(18)

(19)

(20)

(21)
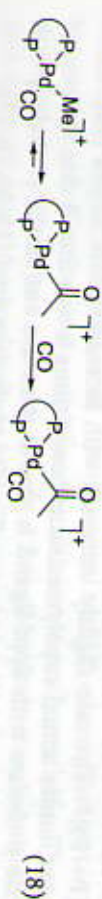
2.3
Chain Transfer (Termination–Initiation)

Ideally, the $Pd-OCH_3^+$ or $Pd-H^+$ species that initiate the catalytic cycle regenerate at the termination step of the chain propagation process. Chain transfer occurs via protonolysis or methanolysis.

2.3.1
Protonolysis

Protonolysis involves the reaction of a β-chelate moiety with methanol and produces a polymer with keto end group and a $Pd-OCH_3^+$ species. The mechanism proposed to explain deuterium enrichment in the 2-position with respect to 1-position involves a pre-equilibrium of the β-chelate with its enolate isomer by a β-H elimination/hydride migration and protonation to the more nucleophilic oxygen atom to give an enol, which rearranges to the ketone [49,71]. This mechanism is operative also in the hydroacylation of ethene to DEK [72]. When protonolysis occurs by H_2O, the binuclear complex $[Pd(\mu\text{-}OH)(P-P)]_2^{2+}$, which may form if excess acid is not used, reacts with CO with regeneration of a $Pd-H^+$ species after CO_2 evolution (Eq. 7) [73]. In turn the hydride may undergo deprotonation with formation of a less active dimer as shown in Fig. 2 [47,55,56]. Efficient catalytic activity is achieved by using the precursor in combination with a quinone and an acid [47].

A lowering of the molecular weight upon increasing acid concentration could be expected, but this is not the case [74]. For several ligands enolate formation was found to be much slower than protonation. It was concluded that enolate formation is the rate-determining step [49].

The effect of bite angle of P–P ligands on the rate of protonolysis of β-chelates has been investigated with model complexes [Pd(CH$_2$CH$_2$COCH$_3$) (P – P)]$^+$. The rate slightly increases with increasing bite angles [75]. However, under actual copolymerisation conditions it was found that the rate of the β-chelate with dppf ligand is slower than the one of the β-chelate with dppe or dppp, which have a smaller bite angle than dppf [55,56,76,77].
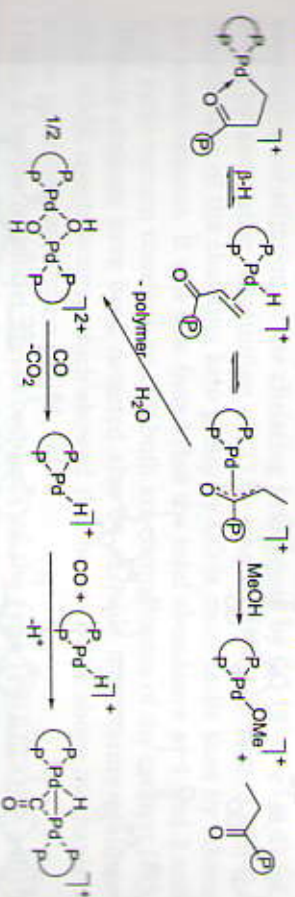

Fig. 2 Termination by protonolysis, with formation of dimeric species

2.3.2
Methanolysis

Methanolysis can occur via inter- or intramolecular nucleophilic attacks by MeOH at the carbon atom of a Pd-acyl moiety and produces an ester end group and a $Pd-H^+$ species. Again, the hydride may deprotonate with formation of less active Pd(0) and dimeric species (Fig. 3) [47,57].

The rate of methanolysis is expected to be dependent on the nature of the alcohol. Indeed, the relative rate of termination versus the rate of chain growing catalysed by a cationic Pd(II) – PPh$_3$ system reported by Sen et al. is in the order of methanol > ethanol > i-propanol > t-butyl alcohol, which is the order of increasing steric bulk [12]. The same order has been observed for the rate of alcoholysis of the Pd-acyl bond of model complexes of the type [Pd(COMe)(P – P)]$^+$ to alkyl acetate [57]. Studies on the methanolysis of complexes of this type, in which the ligand is trans or cis coordinated, led to the conclusions that (1) ester elimination is prevented when the ligand and adopts trans geometry, (2) complexes that have a trans structure but can adopt also a cis structure or complexes that have only a cis geometry do react with methanol to form methyl acetate, (3) methanolysis requires a "vacant" coordination site to coordinate MeOH cis to the acyl ligand and occurs via a migratory elimination or a 1,2-shift of the alkoxy group from palladium to the acyl carbon atom, and (4) the rate of methanolysis increases with increasing steric bulk [57].

That coordination of MeOH to palladium is an essential prerequisite to methanolysis and has been evidenced also by studying the effect of solvent, counter-anion and occupancy of the fourth site on [Pd(dibpp)(COCH$_3$)L]$^{n+}$ ($n = 0$ or 1; L = counter-anion or CH$_3$CN, CO) [78].

However, the complex [Pd(dppomf)(COCH$_3$)]$^+$ undergoes immediate methanolysis at room temperature and even though (1) the dppomf acts as a tridentate η^3-P, P, Fe ligand, with trans P atoms, and (2) ethene does not insert, which is indicative that a coordination site is not easily available. Thus, in this case, methanolysis either occurs via a five-coordinate transition state or it can occur also intermolecularly [47]. This might be also the case for the methoxycarbonylation of ethene catalysed by the osmocene analogue of dppf (Sect. 3.3.2) [79].
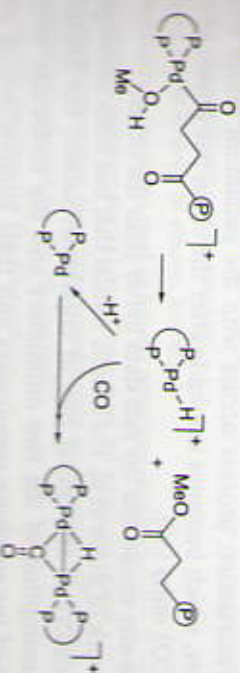

Fig. 3 Termination by methanolysis with formation of Pd(0) and dimeric complexes

2.3.3
Shift From the Hydride Mechanism to the Carbomethoxy Mechanism and Vice Versa

As already mentioned, Pd–H+ generated at the methanolysis step may transform into Pd–OCH3+ by the action of a quinone. Vice versa, Pd–OCH3+ generated in the protonolysis step may undergo β–H elimination with formation of Pd–H+, as it occurs for the hydroacylation of ethene to DEK [33]. Direct shift from the hydride mechanism to the carbomethoxy mechanism has been demonstrated by Iggo et al. [58] (Sect. 3.3.2).

2.4
Kinetic Studies

Of the reports that have appeared [37,72,80–90], only a few deal with more quantitative studies. In [86,89] the copolymerisation kinetics have been studied using the precursor [Pd(TsO)(H2O)(dppp)](TsO) in MeOH over a temperature range of 70–90 °C and total pressure up to 70 bar. The rate increases linearly by increasing catalyst loading, the orders with respect to dissolved CO and ethene are 0.63 and 0.72, respectively; the apparent activation energy is 11.7 kcal/mol.

Table 1 reports different rate equations fitting the data, as functions of the activities of the monomers because their behaviour significantly differs from ideality. They are based on one- or two-"vacant" sites models (Fig. 4). In the one-site model the palladium centre is coordinated by the bidentate ligand, the growing chain, and has the fourth coordination site occupied by one of the monomers (like species b, d or f of Fig. 1). It can be also four-coordinated β- or γ-chelate like 1 or 2, having the fifth site available for the coordination of the monomers, like species a, c or g. In the two-sites model palladium is coordinated by the bidentate ligand, the growing chain, and has the fourth and fifth sites available for coordination of the monomers, like species e. MeOH or the counter-anion can occupy the "vacant" site also, but this has not been taken into account, because their concentration has been considered constant. It is interesting to note that the rate equations are of the type that can be derived from the Hougen-Watson model for solid catalysts. Indeed the copolymerisation process occurs with the palladium centre attached to the polymer, which becomes insoluble after the chain has grown of ca. 13–25 (CH2CH2CO) units [37].

The one-site model fits the rate data better than the other.

In the work of Belov et al. the kinetic model that has been developed quantitatively describes the initial rate of copolymerisation, the kinetic curves of the consumption of the two monomers and the molecular weight characteristics of the resulting copolymers and their composition as function of the total pressure up to 40 bar, ketoesters, diesters, diketones as function of the total pressure up to 40 bar,

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Table 1 Proposed rate equations and mechanism

Kinetic equations	Proposed mechanism
I $\quad r_{pol} = \dfrac{k_r K_{CO} K_{et} AB}{(1+K_{CO}A)(1+K_{et}B)}$	The two sites on Pd atom are non-equivalent; one can coordinate to only CO and the other to only ethene. The rate-determining step is the insertion of one monomer from an intermediate having both monomers simultaneously coordinated
II $\quad r_{pol} = \dfrac{k_r K_{CO} K_{et} AB}{(1+K_{CO}A+K_{et}B)^2}$	The two sites on Pd atoms are equivalent and can be occupied by any of the monomers. The rate-limiting step is the insertion of one monomer from an intermediate in which both sites are occupied
III $\quad r_{pol} = \dfrac{k_r K_{CO} K'_{et} AB}{\{1+K_{CO}A+K_{et}B\}\{1+K'_{CO}A+K'_{et}B\}}$	The two sites on Pd atom are non-equivalent but can be occupied by any of the monomers. The rate-determining step is again the insertion of one monomer from an intermediate in which both sites are occupied by monomers
IV $\quad r_{pol} = \dfrac{k_2 K_1 K_2 AB[Pd]}{k_4 + k_4 K_1 A + k_2 K_2 B}$	CO rapidly occupies the free sites on the Pd atom, and the rate-limiting step is reaction 2. Reactions 3 and 5 are very fast, making steps 2 and 4 practically irreversible
V $\quad r_{pol} = \dfrac{K_3 K'_3 K_6 AB[Pd]}{K_4 A + K_4 K_6 AB + K_3 K_6 B}$	Intermediate 1 coordinates CO only, intermediate 2 can coordinate CO or ethene. The rate-determining step is reaction 3
VI $\quad r_{pol} = \dfrac{k_5 k_4 k_6 AB[Pd]}{k_5 B + k_5 K_4 AB + k_5 K_4 A}$	As in equation V; but here, the rate-determining step is reaction 5
VII $\quad r_{pol} = \dfrac{k_1 k_4 k_6 AB[Pd]}{k_4 + k_4 k_6 AB + k_3 k_6 B + k_4 k_1 A^2}$	As in equation V; but here, CO can occupy both sites
VIII $\quad r_{pol} = K_{obs} A^{\sigma} B^{\beta}$	Empirical power law model

A = liquid phase activity of CO, kmol/m³
B = liquid phase activity of ethene, kmol/m³
k_r = reaction rate constants used in kinetic equations, kmol/(m³s)
K_{CO} = equilibrium constant for CO coordination on Pd atom, m³/kmol
K_{et} = equilibrium constant for ethene coordination on Pd atom, m³/kmol
K_i = equilibrium constant for the ith reaction
k_i = reaction rate constants used in kinetic equations, kmol/m³
K_i = pseudorate constant for the ith reaction
[Pd] = catalyst concentration, kmol/m³

termination $\leftarrow$ MeOH

2

Initiation steps k_3

k_4 k_6 k_5

1

MeOH termination

(a)

$P–Pd \xrightarrow{CO, C_2H_4}_{-CO, -C_2H_4} P–Pd \longrightarrow P–Pd$
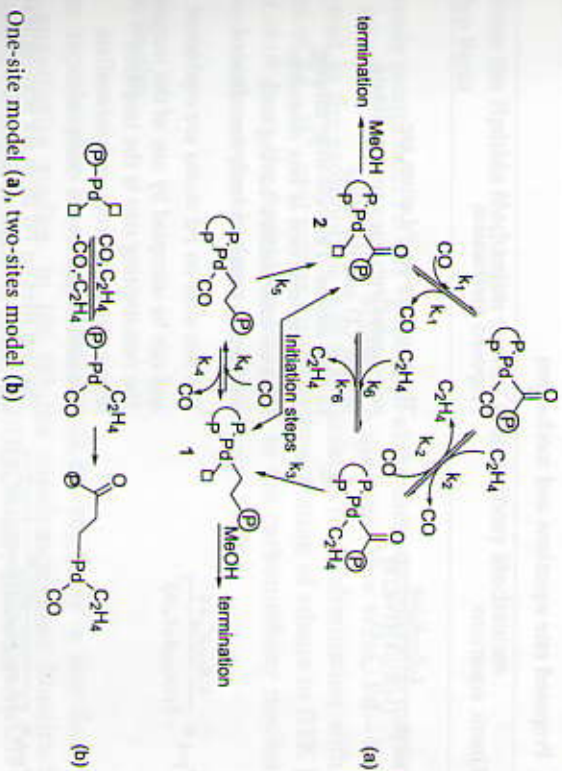
(b)

Fig. 4 One-site model (a), two-sites model (b)

CO/ethene = 1/1, using the catalyst system Pd(AcO)$_2$/dppp/TFA in the ratio 1/1/2 at 90 °C [90].

3 Control of Chain Growth

3.1 General Aspects

The products of the carbonylation of ethene in MeOH range from high molecular weight polyketones, to cooligomers down to low molecular weight oxygenates like dimethyl succinate, diethyl ketone and MP, which can be considered the lowest member of the copolymerisation process. Their abundance in the product mixture depends on the relative rate of the process of chain growing and of chain termination. For any given catalytic system, these are influenced mainly by temperature, pressure, monomers ratio, solvent; the molecular weight of the polyketone depends also on the batch time (Sect. 3.3.1).

The overall energy barrier for chain growing is lower than that for chain termination, thus, if a lower molecular weight product is desired, the copolymerisation should be carried out at higher temperature. In the copolymerisation process, the insertion of ethene is the slow step [13–15], thus upon increasing the pressure of the olefin, as well as the total pressure, it is reasonable to expect an increase in the molecular weight. The nature of the

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solvent also influences the chain growing process. An alcohol is a chain transfer agent, the lower the steric bulk or the nucleophilicity of the alcohol, the faster the chain termination. Thus in t-BuOH or in CF$_3$CH$_2$OH a copolymer of higher molecular weight can be obtained than using MeOH. Also the use of an aprotic solvent may be a better choice when a product of higher molecular weight is desired [1, 11, 55, 56].

The Pd–PPh$_3$ system is particularly instructive. In CHCl$_3$, the catalyst, prepared in situ from [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ and PPh$_3$, gives a high molecular weight polyketone. It was proposed that catalysis starts from a Pd–H$^+$ species formed from adventitious H$_2$O and CO. The high molecular weight did not allow the identification of the end groups [11]. Under similar conditions, (rt, 45 bar, CO/ethene = 1/1), but using the complex cis-[Pd(H$_2$O)$_2$(PPh$_3$)$_2$][(TsO)$_2$]2H$_2$O, a copolymer having average n = 27 with only keto end groups forms together with concomitant evolution of CO$_2$ [59]. These findings support the suggestion that catalysis initiates via a Pd–H$^+$ species; termination occurs via protonolysis by H$_2$O, with formation of a Pd–OH$^+$ species which re-enters the catalytic cycle by insertion of CO followed by CO$_2$ evolution (see Sect. 2.3.1 and Eqs. 6 and 7). The use of the aquo complex introduces enough water to lower significantly the molecular weight. The same system in MeOH, at 70 °C, 70 bar, CO/ethene = 1/1, yields low molecular weight products according to Eq. 1, with n = 1–5, together with a minor amount of higher polyketo esters with n > 6. In t-BuOH only polyketo esters with n > 5 are obtained. By lowering the pressure, chain propagation is slower and the only product is the propanoate ester. At higher temperature (100–110 °C) the "cationic" complex [Pd(TsO)$_2$(PPh$_3$)$_2$], in the presence of PPh$_3$ and TsOH (Pd/P/TsOH = 1/6/8), is an efficient catalyst for the production of MP in MeOH [35, 91]. The chloride analogue is expected to give also MP, because the coordinating anion competes for chain propagation. Rather surprisingly, we have found that under similar conditions the main product is a polyketone. Only at a higher temperature and in the presence of relatively large amounts of PPh$_3$ (115 °C, Pd/P/HCl = 1/30/20), the main product is MP [14].

It is noteworthy to report also the results obtained using the Pd(AcO)$_2$ precursor in combination with an excess of PPh$_3$ or with the monosulfonated derivative PPh$_2$.PhSO$_3$H, in acetic acid and in the presence of TsOH (Pd/P/TsOH = 1/8/80–800, 90 °C, 1–50 bar). The reaction switches from monocarbonylation with formation of propionic acid to oligocarbonylation with formation of propionic acid to oligocarbonylation with formation of propanoate esters and to polyketones as the pressure and concentration of TsOH increase. The yield in polyketones also increases upon increasing the acidity [82, 87]. A similar acid effect has been found with the dtbpe-based catalyst in MeOH for the production of DEK in the presence of excess acid, as the selectivity lowers from 99% DEK to ca. 33%, ca. 60% being cooligomers (see Sect. 3.2 and Sect. 4.2).

The effect of the anion and of the ligand deserves a separate consideration.

3.2
Influence of the Counter-Anion

As already mentioned the anion has to be weakly coordinating in order to favour the coordination of the monomers and chain growing. The coordinating capacity depends not only on the nature of the anion, but also on that of the solvent. Polar solvents help the dissociation of the anion from the cationic active catalyst, thus favouring the polymerisation process. This is well illustrated by comparing the activity of the catalysts $[PdX_2(dppp)]$ ($X = TfO, TsO, TFA^-, AcO^-, Cl$). In MeOH the activity is comparable when X is weakly coordinating like TfO, TsO, TFA$^-$ (ca. 7000–6000 g polymer(g Pd·h)$^{-1}$ at 90°, 45 bar, CO/ethene = 1/1). When X = AcO or Cl the catalyst is ineffective [14], but becomes very active when used in $H_2O - AcOH$, ca. 40–50% molar ratio (27 000 g polymer(g Pd·h)$^{-1}$, under the conditions just reported), in spite of the lower solubility of the monomers in this medium [92, 93]. In $H_2O - AcOH$ the copolymerisation process occurs with concomitant evolution of CO_2 and the polyketone presents keto end groups only, suggesting that $Pd - H^+$ initiates the catalysis and that termination occurs via protonolysis by H_2O or H_3O^+ with formation of $Pd - OH^+$ or $Pd - OH_2^{2+}$, which regenerate the starting $Pd - H^+$ species upon interaction with CO followed by evolution of CO_2 (see Eqs. 6 and 7). Thus in $H_2O - AcOH$ the AcO$^-$ or Cl$^-$ do not prevent coordination of the monomers and chain growing, probably because they are dissociated from the metal centre. The high activity may be due to the possibility that the acid and H_2O prevent deprotonation/dimerisation of the active hydride with formation of dimeric species of the type shown in Figs. 2 and 3, thus ensuring a relatively high concentration of the most active species. Moreover, the acid might destabilize the β- or γ-chelates through protonation of the oxygen atom of the coordinating keto group, thus favouring the insertions of the monomers.

It has also been reported that the precursor Pd(AcO)$_2$/dppp in combination with HCOOH, though having relatively high pKa = 3.75, becomes an efficient catalytic system provided the acid is used in relatively large excess (ca. 7500 g polymer/g Pd/h, HCOOH/Pd = 3000/1, under the conditions reported above) [48].

The activity of water-soluble catalysts based on the hydrophilic bidentate phosphines is also significantly influenced by the nature of the anion [94–100]. Thus for example, using the catalyst formed in situ from [Pd(TsO)$_2$(NCMe)$_2$] and the *metha*-sulphonated analogue of dppp under conditions close to the ones reported above, but in water as solvent and with an excess of acid (acid/Pd = 500/1), the productivity is ca. 3900, 3600 or 2250 g polymer(g Pd·h)$^{-1}$, when the acid is TsOH, TFA or AcOH, respectively, under usual conditions [96]. If one considers that the monomers are a little soluble in H_2O, very high productivity and molecular weight are obtained using [Pd(CH$_3$)(NCCH$_3$)(dppp-s)](OTf) (dppp-s =

metha-sulphonated analogue of dppp): 32.2 kg·(gPd·h)$^{-1}$, molecular weight 125 kg/mol, at 90 °C, 60 bar, C_2H_4/CO = 1/1 at very low catalyst concentration, [Pd] ca. 10^{-5} mol/l [99].

For catalysts which promote the formation of low molecular weight products, the anion might make the difference, as in the case of the catalyst with C_2-bridged diphosphine ligand 23 (Fig. 5), which gives a low molecular weight polymer or MP when the counter-anion is MsO$^-$ or propanoate, respectively [101].

However, there is a limit to operating conditions such as temperature, pressure and also the choice of solvent is rather restricted, particularly for commercial exploitations, and also batch time cannot be more that 6–8 hours, because generally the productivity lowers with time, and also the choice of the anion is not limitless. It is the ligand that can make the difference.

3.3
Influence of the Ligand

3.3.1
High Molecular Weight Polyketones

The influence of the nature of the ligand on the catalytic activity was first studied by Drent et al. using Ph$_2$P(CH$_2$)$_n$PPh$_2$ ligands ($n = 1-6$) [15]. The highest productivity, molecular weight and selectivity is obtained when $n = 3$; when $n = 4$ the catalyst is moderately active; when $n = 2$ the productivity is around one order of magnitude lower; when $n = 1$ the catalyst is ineffective. Considering the requirement of *cis*-coordination for fast chain growing in both ground and transition states, it was suggested that the activation energy is lower when the bite angle is close to 90°, which is better satisfied when $n = 3$ [15]. The *ortho*-methoxy substituted analogue with $n = 3$, dappp, used in the commercial production of the CO/ethene/propene terpolymer, gives a particularly high performance for both productivity and molecular weight (see below).

Noteworthy is the activity of the catalyst with the zwitter-ionic ligand 4, in which the P atoms are also separated by 3 atoms [102].

Even though these results might be rationalised in terms of bite angle effects [103], further studies evidenced that other factors have to be considered, like steric hindrance induced by stereochemical rigidity of the ligand [55, 56, 60, 76, 77, 104]. Ligands 2, 3, 5–7, shown in Fig. 5, which have methyl substituents at the chain backbone, give catalysts that are more active than the unsubstituted ones, particularly that with methyl groups at 1- and 3-carbon atoms of the bridging chain in *meso*-position in ligand 2. It was suggested, also on the basis conformational consideration and of kinetic and thermodynamic studies, that a higher rigidity of the ligand backbone in the *meso*-ligand forces the phenyl substituents on the phosphorous atom to adapt
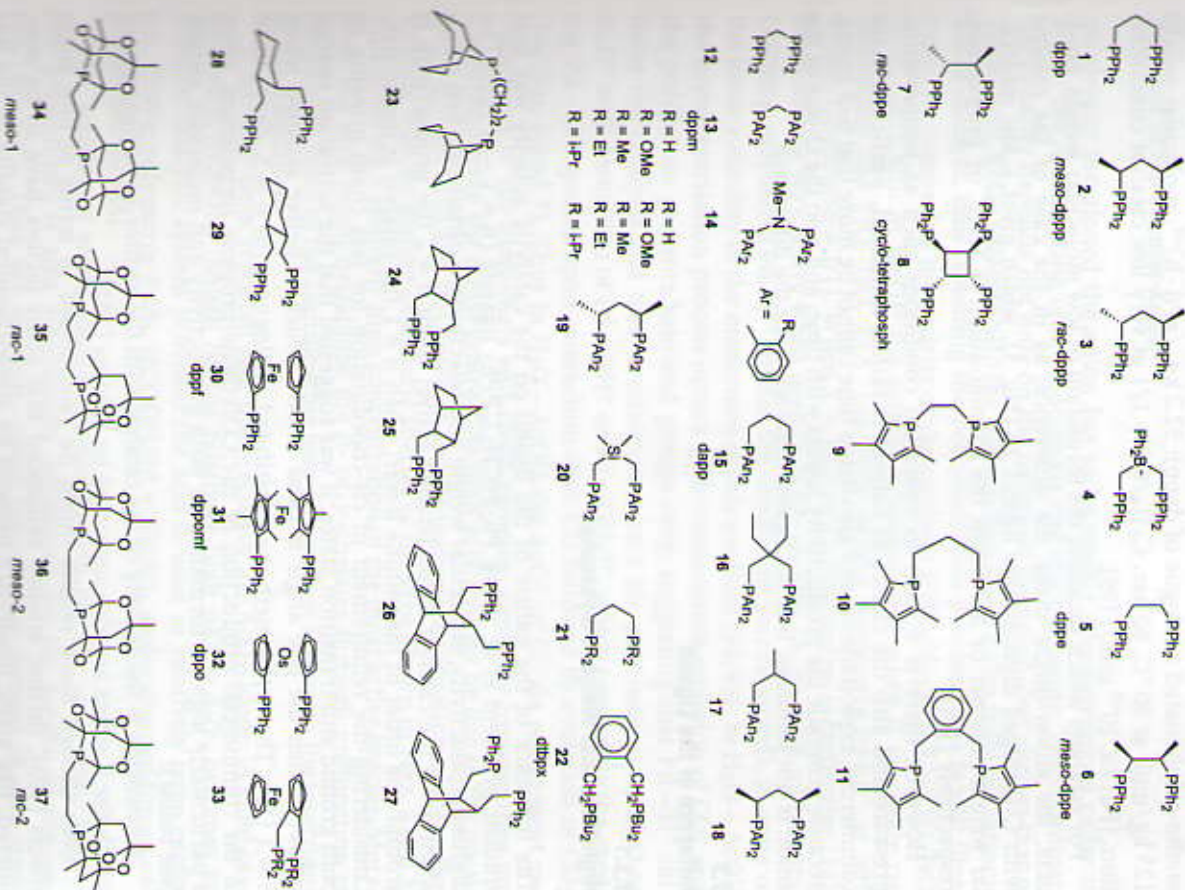
Ligand structures (Fig. 5):

1 dppp; 2 meso-dppp; 3 rac-dppp; 4 dppe; 5 meso-dppe; 6 meso-dppe; 7 rac-dppe; 8 cyclo-tetraphosph; 9; 10; 11; 12 dppm; 13 dppm (R=H); 14 (R=H; R=OMe; R=Me; R=Et; R=iPr); 15 dapp; 16; 17; 18; 19 (R=OMe, R=Me, R=Et, R=iPr); 20; 21; 22 dtbpx; 23; 24; 25; 26; 27; 28; 29; 30 dppf; 31 dppomf; 32 dppo; 33; 34 meso-1; 35 rac-1; 36 meso-2; 37 rac-2

Fig. 5 Ligands in the text (An = Anisyl))

a conformation of higher steric hindrance which causes a higher destabiliza-tion of the β-chelate ring thus favouring the propagation step [55, 56, 60, 76, 77]. The *meso*-effect related to steric rigidity is more general as it has been found also in the bridge substituted dapp ligand (see below). The same has

been found with the ligand "*cyclo*-tetraphos" 8, which gives a catalyst more efficient than the one with dppe by one order of magnitude [60].

A correlation between catalytic activity and backbone rigidity has been also established for the diphosphine ligands 9–11. The rigid ligand 9 gives a more active catalyst than ligand 10; ligand 11 gives poor results [104].

That steric bulk plays a role of paramount importance is suggested by the fact that the ineffective dppm-based catalyst becomes highly active in CH_2Cl_2 when the phenyl rings are *ortho*-substituted with bulky alkyl groups (ligands 13). Polymerisation rate, catalyst stability and polymer molecular weight all increase with increasing steric bulk of the aryl *ortho* substituent [105, 106]. The catalyst can be prepared in situ from $Pd(AcO)_2$, and the ligand by acti-vation through the borane method with $B(C_6F_5)_3$ which forms a $Pd–C_6H_5^+$ species that initiates the catalysis [107], which is bulkier than $Pd–COCH_3^+$ and $Pd–H^+$, which usually initiate the catalysis. Rather than acting as a *cis*-coordinating bidentate, the dppm ligand (12) prefers bridging two palladium atoms with mutually *trans* P atoms on each metal [108], which may ex-plain the poor performance for the production of polyketones. Bulky *ortho*-substituted ligand 13 may inhibit dimerisation giving rise to a catalyst in which the ligand acts preferentially as a *cis*-coordinating bidentate on one metal centre. Another possible explanation is that dppm, when acting as a *cis*-coordinating bidentate ligand, leaves too much extra space at the "vacant" site on the metal centre, so that the insertion of the monomers into the species that initiate the catalysis and the subsequent insertions of the chain growing process are not favoured. Upon increasing the steric bulk of the ligand the monomers are "pushed" to give insertions in such a way that fast chain grow-ing can occur. It is note worthy to observe that in MeOH, under the usual conditions, the catalyst is poorly active.

Steric bulk has a similar effect also for the methylamino-bridged diphos-phines ligands 14 in CH_2Cl_2, which give catalysts even of superior perfor-mances [105, 109, 110], again with poor activity in MeOH.

Recently, some important aspects on the development of more efficient catalysts have been disclosed [37]. These studies are hereafter summarized, taking as a base of comparison the dppp-based catalyst.

Electron-donating substituents at the phenyl ring enhance the activity, whereas there is no clear correlation for the molecular weight, which in any case is affected. The productivity and the molecular weight are the highest with the *o*-MeO-substituent (at 90 °C, 50 bar $CO/C_2H_4 = 1/1$, dapp 15: $12.7\ kg\cdot(gPd\cdot h)^{-1}$, LVN = 1.58 dL/g; dppp 1: $7.1\ kg\cdot(gPd\cdot h)^{-1}$, LVN = 1.05 dL/g).

Even though the distinction between the electronic and the steric ef-fects cannot be made so sharp, the close performance with *o*- and *p*-MeO-substituent suggests that the main effect is of electronic nature. However, X-ray structure shows that the oxygen atom of the *o*-MeO groups interact with palladium. In addition, NMR studies reveal an electrostatic interaction

of the o-aryl protons with the filled dz^2-orbital of the metal. It has been suggested that the higher productivity might be due to the lowering of the intramolecular interaction of the β-chelate moiety with palladium.

Variation of the length of the bridging chain $-(CH_2)_n-$ shows that both the productivity and molecular weight decrease in the order $n = 3 > n = 2 > n = 1$, as found for the unsubstituted analogues.

Alkyl substitution in the bridging chain enhances the catalytic activity. The highest productivity is obtained with two ethyl-substituents at the central carbon atom, though the molecular weight is higher with the unsubstituted dapp ligand (at 90 °C, 50 bar, CO/C₂H₄ = 1/1, ligand **16**: 42.7 kg · (gPd · h)⁻¹, LVN ca. 1.20 dL/g, compared to 12.7 kg · (gPd · h)⁻¹, LVN = 1.58 dL/g for ligand **15**). A similar effect of substitution is observed with dppp, though the increase of productivity is smaller (at 90 °C, 50 bar, CO/C₂H₄ = 1/1, ca. 12.4 kg · (gPd · h)⁻¹, LVN = 0.72 dL/g for meso-dppp (ligand **2**) compared to 7.1 kg · (gPd · h)⁻¹, LVN = 0.72 dL/g for **1**).

In addition, the catalyst undergoes a sharp lowering in activity during the first minutes (from about 25 to a constant rate of 8–10 kg · (gPd · h)⁻¹). The deactivation is not due to the formation of less active dimeric species of the type [(dapp)Pd(μ-H)(μ-CO)Pd(dapp)]⁺, [(dapp)Pd(μ-CO)₂Pd(dapp)]²⁺, [Pd(dapp)₂]²⁺ or [(dapp)Pd(μ-CO)-OH)₂Pd(dapp)]²⁺, nor to the formation of bis-chelate [Pd(dapp)₂]²⁺, as it occurs for the dppp system [17]. Initially the growing chain is soluble in MeOH, so that the attached catalyst works in "homogeneous phase", whereas, as the chains grow to 13–25 (CH₂CH₂CO) units, the catalyst precipitates. Moreover, the polymer presents a bimodal molecular weight distribution, one of Flory-Schultz (FS) type, typical for a homogeneous polymerisation, and a Wesslau (W) type distribution, typical for a heterogeneous polymerisation. In addition, it was found that the mo-lecular weight and particle size increase with time and that larger particles contain a larger fraction of chain with W distribution. It was suggested that the heterogeneous catalyst is present in two different environments, in part absorbed on the surface of the particles, producing the copolymer with FS distribution, and in part inside the micropores of the particles, producing the copolymer with W distribution [37].

The kinetics were also studied. The productivity increases regularly with the pressure of C₂H₄, whereas it passes through a maximum at p_{CO} = ca. 15 bar. This trend suggests that CO and C₂H₄ compete for coordination to palladium and that CO impedes coordination of C₂H₄ [37].

3.3.2
From Cooligomers to Low Molecular Weight Products

The general rule earlier proposed by Drent et al., that Pd(II)-diphosphine complexes, better with a bite angle near 90°, capable of maintaining cis-coordination throughout the copolymerisation process, give high molecular

weight polyketones with high productivity, whereas monophosphine ligands are more suitable to give MP [14–16], has been found, by the same proposers, to have important exceptions. For ligands **21** of the type RR'P(CH₂)₃PRR' (R,R' = n-Bu, n-Bu or n-Bu, cyclohexyl or cyclohexyl, cyclohexyl or t-Bu, t-Bu) in which the alkylsubstituents differ only slightly in electron-donating properties, but differ significantly for the steric bulk: R,R' = n-Bu, n-Bu < n-Bu, cyclohexyl < cyclohexyl, cyclohexyl < t-Bu, t-Bu, it was found that productivity and molecular weight decrease when steric bulk increases to the point that with the last ligand the main product is MP (97.4% se-lectivity, TOF = 25000 h⁻¹ at 120 °C, 40 bar, CO/ethene = 2/1) [30, 33]. An even higher performance was obtained by Tooze et al. with ligand **22** dtbpx (99.98% selectivity, TOF = 50000 h⁻¹) under milder conditions, 80 °C, 10 bar, CO/ethene = 1/1, see Sect. 4.1.2) [31, 111]. At first, it was suggested that this diphosphine does not maintain cis-chelation, but opens one coordination arm thus acting as a monophosphine [111].

The same was previously suggested also by Doherty et al., which found that the Pd(II)-diphosphine of type **24** [112] and type **26** [113] produce low molecular weight oligomers of average length 13–20 monomer units and MP and that intermediate products having a low number of monomer units were not present. It was proposed that two different catalytic species are operat-ing, one having the expected identity coordination producing the oligomers, the other with one arm of the diphosphine dissociated and effectively act-ing as a monodentate ligand producing MP. The catalyst with ligand **28** gives only oligomers. The bite angles of ligands **24** and **28** are similar (102°), how-ever, close examination of the structures of the palladium complexes shows that the ligand backbones are oriented in different ways and that the phenyl rings in **24** provide a higher steric bulk [112]. This may be a key factor in determining the chemoselectivity.

As a matter of fact, it was proven, by variable temperature multinuclear NMR studies, that in the dtbpx-based catalyst, which is the most efficient in producing MP, the ligand maintains cis-coordination in all the identified intermediates well above room temperature [42, 114, 115] (see below).

In general, catalysts that promote the cooligomerisation to low molecu-lar weight products promote also the formation of MP. However, apparently slight changes in the bridging chain or in the substituents the P atoms may cause quite different chemoselectivity, as already reported above. Another interesting case is that of dppf- and dppomf-based systems (ligands **30** and **31**) [47, 116]. The first presents a cis-κ²-P,P coordination mode and promotes the formation of several low molecular weight products, from MP to alternat-ing cooligomers, the other exclusively MP. The methyl substituents in dppomf induce significant changes in the coordination mode which changes to κ³-P,P, Fe and in the secondary structure of the complexes (P − Pd − P bond angles 96° in [Pd(H₂O)₂(dpff)]²⁺, 102° in the other), dihedral angles between the (P, Fe, P) and (P, Pd, P) planes, deviations of the phosphorous atoms from

the planes of the Cp rings). The selective production of MP might be due to the higher steric hindrance of dppomf and consequent greater propensity of dppomf versus dppf to give a Fe–Pd bond, thus forcing the P atoms to adopt a trans geometry, and yielding Pd-acyl species that do not react with ethene in MeOH to form β-chelates, which could continue the cooligomerisation process [47].

Quite interestingly, the osmocene analogue of dppf (ligand 32) catalyses the methoxycarbonylation of ethene selectively (TOF = 400 h⁻¹ at 85 °C, 45 bar, CO/ethene = 1/1, Pd/TsOH = 1/40). Multinuclear NMR spectroscopy of complexes [PdX(dppo)](TsO) (X = TsO, Me, COMe) is consistent with the presence of Os–Pd bonds, which has been confirmed by NMR and X-ray studies on [Pd(CH$_3$CN)(dppo)](TsO)$_2$. The coordination geometry around palladium is that of a slightly distorted square planar with trans P atoms, a P–Pd–P angle of 164.9(1)° and a strong bonding Os–Pd interaction distance (2.840(1) A°) [79].

If the ligands dppomf and dppo maintain trans-coordination throughout the catalytic cycle, it will be interesting to establish how the insertions of CO and ethene and methanolysis to MP occur.

An example of how selectivity can subtly depend on the different steric bulk introduced upon varying the length of the backbone, or even when using different diastereoisomers, is the one found for the methoxycarbonylation of ethene or of higher olefins catalysed by in situ generated Pd(II) complexes of meso/rac adamantyl diphosphines (ligands 34–37). Normally C$_3$-bridged diphosphines-based catalysts promote the copolymerisation, but the catalyst derived from C$_3$-bridged meso/rac-1, because of the steric hindrance adamantly moiety, catalyses the methoxycarbonylation of ethene (TOF = 10^4 h⁻¹, selectivity >99% at 90 °C, ethene = 20 bar, CO = 30 bar, Pd(AcO)$_2$/P–P/TfOH = 1/1.5/2.5), whereas the C$_2$-bridged meso/rac-2-based system, inducing less steric hindrance, promotes the formation of polyketones of relatively low molecular weight [32, 117].

Liu et al. delineated the initiation, propagation and termination steps of the carbomethoxy of the hydride cycles for the catalyst [Pd(CH$_3$CN)$_2$(dibpp)] (TfO)$_2$, which promotes both the formation of cooligomers and MP [58]. To generate a Pd–CH$_3$$^+$ species of the carbomethoxy cycle, a base was added, but normally catalytic carbonylation is carried out in the presence of an excess of acid. However, protonolysis, by MeOH in the presence of CO, of a Pd-alkyl intermediate of the hydride cycle, provided an entry to the carbomethoxy cycle (through the shift from the hydride cycle to the carbomethoxy one), without the necessity of using a base. The methyl complex 1' was used to start the hydride cycle, because the hydride could not be prepared separately [58]. All the species indicated were detected, including β- and γ-chelates. The cycles are closely related to the one shown to occur in the solid state [51].
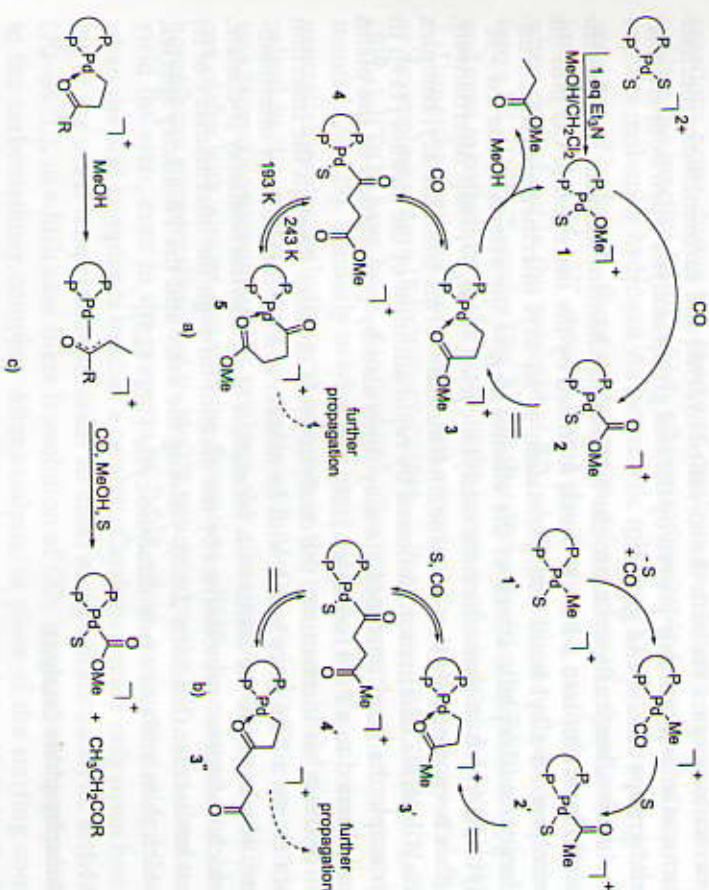
Fig. 6 The carbomethoxy cycle (a), the hydride cycle (b) and the shift of the hydride mechanism to the other (c) (S = CH$_3$CN). Adapted from [58]

It is interesting to point out that with this catalyst formation of MP occurs also through the carbomethoxy cycle, whereas it will be shown that most catalysts that are highly selective to MP operate through the hydride mechanism (see Fig. 6).

4
Selective Synthesis of Monocarbonylated Products

4.1
Synthesis of Methyl Propanoate

From what is reported above, it is evident that the CO-ethene copolymerisation and the methoxycarbonylation of ethene are closely related. In principle the mechanisms discussed for the copolymerisation process are valid also for the case when termination occurs after the insertion of just one molecule of each monomer into the species that initiate the catalysis, Pd–OCH$_3$$^+$ or Pd–H$^+$. These species can form as schematized by Eqs. 10–16. The copoly-

merisation occurs via both the so-called hydride and carbomethoxy mechanisms, as unambiguously proven by the end group analysis when both are ester end groups or keto end groups.

In the alkoxycarbonylation, the hydride mechanism initiates through the olefin insertion into a Pd–H bond, followed by the insertion of CO into the resulting Pd-alkyl bond with formation of an acyl intermediate, which undergoes nucleophilic attack of the alkanol to give the ester and the Pd–H+ species, which initiates the next catalytic cycle [35, 40, 57, 118]. Alternatively, it has been proposed that a ketene intermediate forms from the acyl complex via β-hydride elimination, followed by rapid addition of the alcohol [119]. In principle the alkyl intermediate may form also by protonation of the olefin coordinated to a Pd(0) complex [120, 121].

In the other mechanism, the catalytic cycle initiates through the insertion of CO into a Pd-alkoxy bond, with formation of a Pd-carboalkoxy intermediate, which inserts the olefin with formation of an alkylcarboalkoxy β-chelate, which undergoes protonolysis by the alkanol through the intermediacy of its enolate isomer (see Sect. 2.3.1), yielding the ester and the Pd-alkoxy species, which then initiates a new catalytic cycle [122–125].

4.1.1
Monophosphine Catalysts

The hydride mechanism is the most likely to be operative. In favour of this mechanism there is the fact that after running the alkoxycarbonylation of an olefin catalysed by the precursor trans-[PdCl$_2$(PPh$_3$)$_2$], the acyl complex trans-[Pd(COR)Cl(PPh$_3$)$_2$] is isolated [126, 127]. The acyl complex reacts with an alcohol to give the expected ester in an almost stoichiometric amount and catalyses the alkoxycarbonylation of a different olefin to give the expected ester and a stoichiometric amount of the ester derived from the acyl ligand. This proves that the acyl complex is sufficiently stable to be isolated while being reactive enough to enter the catalytic cycle. Together with the acyl complex, a carboalkoxy complex also forms. However, the latter complex fails to give an ester in reaction with an olefin in the alkanol.

Moreover, catalysis is enhanced when carried out in the presence of HCl, which does not favour the formation of the carboalkoxy complex because of Eq. 22. In addition, no catalysis is observed when carried out in the presence of a base such as NEt$_3$, which favours the formation of the carboalkoxy complex; in this case there is formation of inactive Pd(0) complexes [127].

$$Pd^0 + ROH + CO \rightleftharpoons Pd\text{-}COOR^+ + H^+ \qquad (22)$$

In a subsequent study, it was found that a hydride source like H$_2$O, an acid (TsOH) or molecular hydrogen have an enhancing effect on the catalytic activity of the "cationic" precursor [Pd(TsO)$_2$(PPh$_3$)$_2$]. Water, in combination with CO, generates the hydride [91] and reforms it if Pd–H$^+$ consuming side

reactions occur during the course of catalysis (see below). The acid can re-oxidise the inactive Pd(0), which otherwise inevitably forms; palladium can activate molecular hydrogen via heterolytic splitting [33, 72]. Moreover, in the presence of hydrogen, there is concomitant formation of ethane, which can form only via a Pd–H$^+$ species. It was also found that catalysis is inhibited when carried out in the presence of BQ, which transforms a hydride species into a Pd–OCH$_3^+$ species (Eq. 8) and that decomposition to Pd(0) complexes and even to palladium metal occur in the presence of a base such as NEt$_3$ [91].

Using the "cationic" precursor just reported, the carbomethoxy and the acyl complexes trans-[Pd(COEt)(TsO)(PPh$_3$)$_2$] and trans-[Pd(COMe)(H$_2$O)(PPh$_3$)$_2$](TsO) have been also isolated after methoxycarbonylation experiments [128, 129]. Similarly to what has been suggested for the corresponding neutral chlorides, only the acyl complex is the one most likely involved in the catalytic cycle. It reacts with MeOH giving MP in an almost stoichiometric amount and it catalyses the alkoxycarbonylation of a different olefin with almost quantitative formation of MP. In contrast, the carbomethoxy complex dissolved in MeOH, saturated with C$_2$H$_4$, at rt, does not yield the ester, even in the presence of TsOH, which has a promoting effect when the acyl complex is used as a catalyst. Catalysis occurs only upon heating at the usual temperature in order to observe significant catalytic activity (70–80 °C), in which case there is evolution of CO$_2$ in an amount equivalent to the carbomethoxy complex. After catalysis, in place of the starting complex, the acyl complex is recovered. It has been proposed that H$_2$O displaces MeOH from the carbomethoxy complex, with formation of a Pd–COOH$^+$ species, which upon evolution of CO$_2$ gives the hydride that starts the catalytic cycle which undergoes through an acyl type intermediate. This might explain the promoting effect of H$_2$O, which would bring the less active Pd–COOMe$^+$ species, which might form during the catalysis, back to the catalytic cycle (see Fig. 7).

In addition, it has been observed that, even when starting from the acyl complex, CO$_2$ forms during the catalysis. In principle, this should not occur because at any catalytic cycle, the regenerated hydride should continue the catalysis. Thus some Pd–H$^+$ consuming side reactions occur before the hydride is trapped by C$_2$H$_4$. As a matter of fact, when the acyl complex is used as precursor in the presence of an excess of acid, it is recovered as [Pd(TsO)$_2$(PPh$_3$)$_2$]. This is brought back to the catalytic cycle through a reaction related to the WGSR. This is another way through which H$_2$O might contribute to enhance the catalytic activity. The acid partially consumes the phosphine (see below), but it may prevent the formation of [Pd(μ-OH)(PPh$_3$)$_2$Pd]$^{2+}$ or may stabilize the hydride preventing its deprotonation to [(PPh$_3$)$_2$Pd(μ–H)(μ–CO)Pd(PPh$_3$)$_2$]$^+$ [130] or to inactive Pd(0) complexes, and, when these form, they can be reactivated by the acid. In addition the acid, through protonation at the O atom of the acetyl ligand, may enhance its electrophilicity and hence the methanolysis step [57].
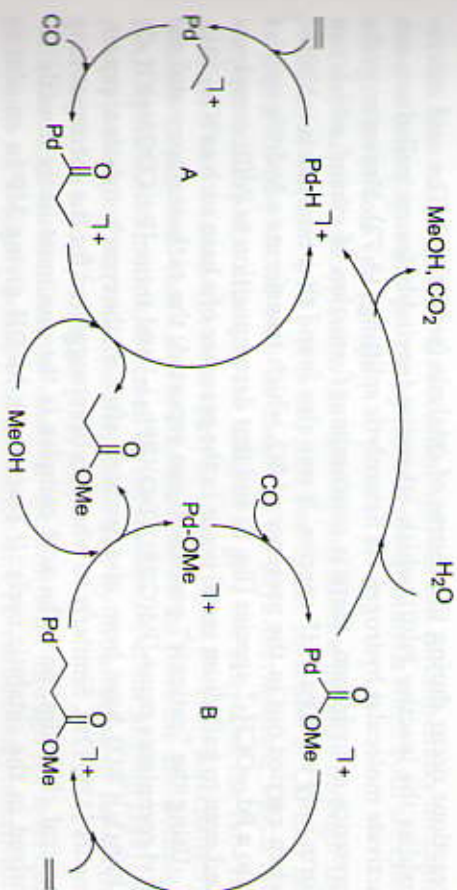
MeOH, CO$_2$ H$_2$O

Pd–H $^{7+}$

A

CO

Pd–OMe $^{7+}$

B

MeOH

CO

Fig. 7 The hydride (**A**) and the carbomethoxy (**B**) cycles, with shift from the latter to the first through the action of H$_2$O

The isolation of acyl and carboalkoxy complexes proves that the insertion of CO into both a Pd-alkyl and into a Pd–OR species occurs easily. Quite interestingly, it has been found that CO inserts only into the Pd–OCH$_3$ bond of the complex [Pd(CH$_3$)(OCH$_3$)(P–P)] and that after insertion methyl acetate eliminates with the formation of [Pd(CO)$_2$(P–P)] [131].

Although the isolation and reactivity of acyl complexes strongly support the hydride mechanism, the other mechanism cannot be excluded. For example H$_2$O, the acid or molecular hydrogen, which can act as a hydride source, can promote the Pd–C splitting of the Pd-alkylcarboalkoxy intermediate in the alkoxy cycle as well. More convincing for the hydride route is the fact that the acid, which does not promote the formation of a Pd–OCH$_3^+$ species, has a promoting effect on the catalysis and can activate a Pd(0) complex, otherwise inactive, whilst a base, which not only promotes the formation of this species, but also deprotonates a Pd–H$^+$ species to Pd(0), suppresses the catalysis.

Phosphine degradation side reactions with formation of phosphonium cations such as MePPh$_3^+$, EtPPh$_3^+$ and EtCOCH$_2$CH$_2$PPh$_3^+$, isolated as TsO$^-$ salts, provide further evidences for the hydride path. The last two have been shown to form by metal mediated pathways and are products of the hydride route. It has been proposed that the 3-oxopentyltriphenylphosphonium cation forms via interruption of the palladium catalysed chain growth of CO-ethene oligomers arising from further insertion of ethene into the Pd-acyl intermediate [132].

It is worthy to note that these monophophine systems must be used in the presence of a free ligand, with a Pd/P ratio even up to 1/20, because the

acid partially consumes the phosphine and drives its dissociation from Pd(II), eventually with the degradation to Pd metal.

4.1.2
Diphosphine Catalysts

As already mentioned, for a long time it was generally accepted that monophosphine catalysts were more suitable to promote the formation of MP selectively. Luckly, it has been found that some diphosphines give catalysts that are highly active and selective to MP. The case of dtbpx deserve further presentation, because it gives the most active, selective and stable catalyst reported up to now (Sect. 3.3.2) and because it has been studied more in detail.

Catalysis undergoes via the hydride pathway [111, 114, 115, ?, 115]. The active Pd(II)-hydride catalyst [PdH(MeOH)(dtbpx)](TfO) can be easily prepared by mixing [Pd(dtbpx)(dba)] with 2–5 equivalents of TfOH, in MeOH and in the presence of an oxidant, BQ or O$_2$. The formation of the hydride occurs through a multistep process. Protonation of the starting complex [Pd(dtbpx) (dbaH)](TfO), which is readily oxidised by BQ or O$_2$ to give [Pd(dtbpx)((η^2-TfO)](TfO), from which the coordinated anion is displaced by the solvent. In the last step hydride formation occurs via irreversible β-hydride elimination from coordinated MeOH (or another primary or secondary alcohol). The hydride can also be obtained by dissolving [Pd(dtbpx)(TfO)$_2$] in a primary or secondary alcohol.

The hydride is stable in MeOH, deprotonation does not occur, probably because the basicity of the ligand makes the palladium centre more nucleophilic, nor partial deprotonation to (μ-H) dimeric species occurs, probably because of the high steric bulk of the ligand. Though the hydride is very reactive, its formation is quantitative and selective, so that its concentration is the highest possible, which is ideal for catalysis. The Pd(II)/PPh$_3$/TsOH catalytic precursor in MeOH is only partially transformed into an active Pd(II)-hydride, as several other species are present in solution, such as [Pd(μ-OH)(PPh$_3$)$_2$]$^{2+}$ and [Pd$_2$(μ-H)(μ-CO)(PPh$_3$)$_4$]$^+$ [130].

The hydride reacts immediately with ethene to give the expected ethyl complex selectively and quantitatively, which again is ideal for the catalytic activity. The hydride is very unstable when CO is bubbled into MeOH solution, even at low temperature [115]; at room temperature it reacts immediately with ethene giving a cationic ethyl complex. In the presence of both CO and ethene, like under catalytic conditions, decomposition does not occur because the hydride reacts much faster with ethene than with CO. Once the ethyl intermediate is formed, fast insertion of CO occurs with formation of an acyl intermediate, which in turn reacts with MeOH yielding MP with quantitative regeneration of the starting hydride to continue the catalytic cycle [114, 115]. The formation of the ethyl and of the acyl intermediates involves facile equi-

libria shifted toward them, whereas the methanolysis of the acyl complex is irreversible and is probably the rate-determining step (see Fig. 8) [115].

A detailed VT multinuclear NMR study has allowed the solution structure and dynamic properties of all the intermediates to be established. The hydride [PdH(MeOH)(dtbpx)]+ is static, the two P atoms remain coordinated and do not become equivalent through solvent exchange until well above room temperature. The ethyl complex presents a strong β-agostic C–H interaction, which is remarkably stable and it is not displaced even in strongly coordinating solvents such as EtCN. C_α and C_β of the ethyl group become equivalent via a stereospecific interchange involving [PdH(η^2-C₂H₄)(dtbpx)]+ without making the two P atoms equivalent; at higher temperature (ca. 80 °C) the two P atoms become equivalent, maintaining cis-coordination, probably via a T-shaped intermediate [115].

The β-agostic ethyl complex is similar to a transition state intermediate in the step of the ethene insertion into the Pd–H bond. This might be also relevant to the high catalytic activity of this catalyst.

For the acyl complex [Pd(COEt)(dtbpx)(solvent)]+ (solvent = THF, EtCN) there is no β-agostic C–H interaction and the two P atoms become equivalent even below room temperature via movement of the intact acyl group. The MeOH analogue is too unstable to be characterised, it gives MP and the product forming step is too fast to follow quantitatively. The product forming step is too fast to follow by NMR, even at low temperature, thus it is not possible under catalytic conditions (80 °C, 10 bar, CO/C₂H₄ = 1/1) to distinguish between alternative pathways such as whether it proceeds by reductive elimination from the [Pd(dtbpx)(COEt)(MeOH)]+ complex to give MP and Pd(0) species with release of a proton, which subsequently adds to Pd(0) to give the starting

(a)

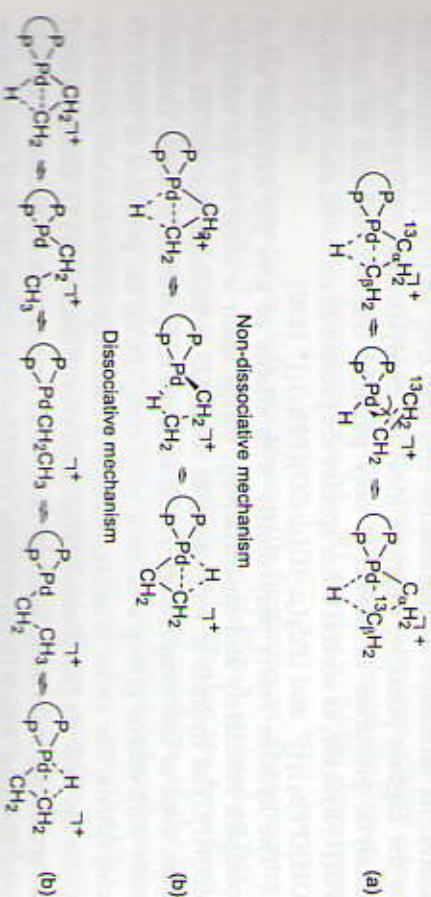Non-dissociative mechanism

(b)

Dissociative mechanism

(b)

Fig. 8 Proposed mechanisms for scrambling the two carbons of the ethyl ligand (a); for making equivalent the two P atoms (b). Adapted from [115]

hydride, or whether reductive elimination and protonation proceed concertedly [115].

Another peculiarity of the acyl complex is that it prefers solvent coordination, even when the solvent has weakly coordinating ability such as THF, rather than CO coordination, even in the presence of free CO. This also can contribute to the high activity observed for these systems, as MeOH has not to compete with CO for coordination before the product-forming step. It is noteworthy that the carbonylation of the closely related complex [Pd(Me)(Et₂O)(dippe)]+ in Et₂O or [Pd(OTf)(CH₃)(dibpp)] results in the complex [Pd(COMe)(CO)(dippe)]+ containing coordinated CO instead of solvent [133].

Further evidence for the hydride mechanism that exclude the other path have been provided by carrying out the catalysis in CH₃OD under conditions of chemical control of the rate of reaction or of CO g/l mass-transfer control [134]. In the first case a mixture of monodeuterated products CH₂DCH₂CO₂Me and CH₃CHDCO₂Me in approximately 1/1 ratio formed, together with low levels of undeuterated MP and of CH₂DCHDCO₂Me, with no H incorporated into the CH₃OD. This can be explained if a hydride mechanism operates with rapid reversible migration of the hydride to coordinated ethene and coordination of CO occurring at a much higher rate than exchange of Pd–H with MeOD. It also suggests that coordination of ethene is essentially irreversible since otherwise significant amounts of undeuterated MP would be formed from loss of C₂H₃D from intermediate 1 in Fig. 9, followed by coordination-insertion of ethene into the Pd–H bond. Under conditions of CO starvation multiple labeled products would arise from Pd–H exchange with MeOD in intermediate 1.

The formation of monodeuterated MP can be explained also by a carbomethoxy mechanism if, after migratory insertion of ethene into the Pd–COOMe bond, β-H abstraction occurs in intermediate 2 to give 3 (see Fig. 10). Deuteration of 2 and 4 by MeOD would then lead to the two products observed. Again, the termination, relative to Pd–H/CH₃OD exchange, has to be rapid, otherwise multiple deuterated products would form. Under conditions of CO starvation these products would arise from the reversible exchange between intermediates 2, 3, and 4, through exchange of Pd–H with MeOD in 3. However, this mechanism cannot explain the formation of large amounts of undeuterated MP, which form in the early stages of the reaction since the termination step must always transfer a D atom from the CH₃OD to end up on one of the ethyl carbon atoms of MP. It was concluded that the methoxycarbonylation of ethene occurs by a hydride mechanism in which the rate-determining step comes after the insertion of ethene into the Pd–H bond and that the carbomethoxy path is not operating.

That the carbomethoxy is unlikely to be operative is suggested also by the fact that in an attempt to synthesize a carboalkoxy derivative, [PdCl₂(dtbpx)] was allowed to react with EtOH in the presence of NEt₃, or with Na(OCH₃), in
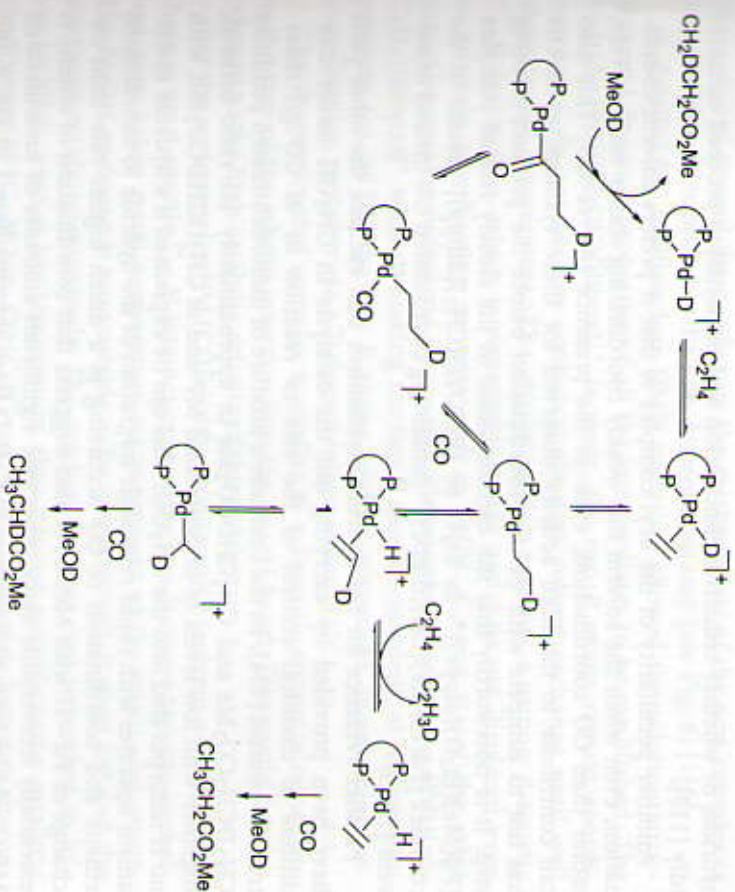
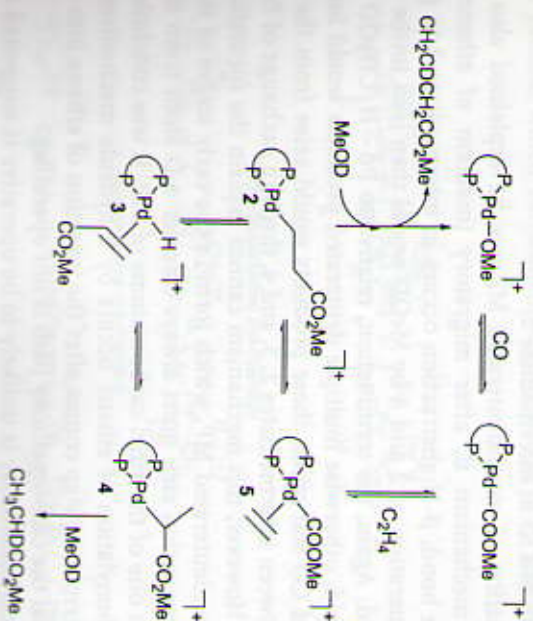**Fig. 9** Proposed hydride mechanism for the formation of d^{0-5} – MP. Adapted from [134]

Fig. 10 Proposed carbomethoxy mechanism for the formation of monodeuterated CH_3CHDCO_2Me and CH_3CHDCO_2Me. Adapted from [134]

both cases in the presence of CO. In place of the anticipated carboalkoxy complex [Pd(COOR)Cl(dtbpx)] [135, 136], the Pd(0) complex [Pd(CO)(dtbpx)] was obtained [136]. Attempts to convert the carbonyl complex to the hydride [PdH(dtbpx)(MeOH)]⁺ by treatment with CF₃SO₃H failed [137], probably because of the instability of the hydride in the presence of CO [115].

In MeOH the hydride reacts with higher α-olefins, propene, 1-hexene and 1-hexadecene with formation of only the linear insertion product, probably for steric reasons. In all the insertion products, the alkyl ligand presents the β-agostic interaction. At room temperature, the insertion of ethene is quantitative whereas with propene an appreciable amount of the hydride is present, with 1-hexene the hydride prevails, with 1-hexadecene only the hydride is present. The fact that the position of the insertion equilibrium strongly depends on the chain length of the alkyl substituent is probably connected with the high steric hindrance of the ligand [115].

$$[PdH(dtbpx)(MeOH)]^+ \overset{CH_2=CHR}{\rightleftharpoons} [Pd(CH_2CH_2R)(dtbpx)(MeOH)]^+ \quad (23)$$

$R = H, (CH_2)_nCH_3 \quad (n = 3 \text{ or } 13)$.

It is noteworthy that the ethyl complex does not react even with the least hindered olefin to give higher alkyl complexes or ethene oligomerisation products; nor the acyl intermediate inserts another molecule of ethene to give intermediates that could lead to a cooligomerisation process, but it reacts immediately with MeOH to give the MP and the hydride back to the next catalytic cycle. It is worthwhile to note that the i-Pr, Cy or Ph analogues yield MP with only 20–30% selectivity and that the main product is a mixture of oligomers [111]. Not only, aryl substitution with electron-donating (MeO) and electron-withdrawing (NO₂) groups at the aryl ring of dtbpx have little effect on the rate and selectivity of the methoxycarbonylation of ethene [111]. Thus this unique chemistry of the dtbpx-based catalyst is most likely due to the highly restrictive steric demand of the ligand, which controls the insertion of only one molecule of monomer and then allows the methanolysis step. The relatively large bite angle of the ligand found by X-ray analysis of [Pd(COEt)Cl(dtbpx)] (103.08(3)°) [115] enhances the steric bulk.

In spite of this, the hydride catalyses the isomerisation of higher α-olefins to an equilibrium mixture of all the possible internal isomers and catalyses also the methoxycarbonylation of α-olefins and of internal olefins to the linear esters with 99% regioselectivity.

Preliminary mechanistic studies on the methoxycarbonylation of 1-octene showed that two pathways to methyl nonanoate occur, one involving the direct carbonylation of 1-octene to the linear ester, the other the allene isomerisation in competition with the first one. Subsequently, the linear product forms by tandem isomerisation of the internal alkenes, with the terminal alkyl intermediate being trapped by migration to CO at a higher rate than any branched alkyl species. This has been confirmed by the analysis of products

obtained from reactions carried out in CH_3OD, which can be explained by a hydride mechanism [34, 138].

Recently, it has been reported that Pd(II) complexes with ferrocenyldiphosphines 33, are also efficient catalysts for the selective methoxycarbonylation of ethene with activity comparable to that of the dtbpx-based system (initial $TOF = 30000 h^{-1}$, $TON = 60000$, at 100 °C, 10 bar) [139, 140].

4.2
Selective Synthesis of Diethyl Ketone

Because of its nature, DEK must form via a hydride mechanism. Up to the formation of a Pd-acyl intermediate, the paths leading to MP or DEK are similar. DEK forms if the insertion of a second molecule of ethene into the Pd-acyl bond is followed by protonolysis of the Pd–C bond of the resulting Pd-alkylacyl intermediate.

The first effective catalyst for this reaction has been reported by Zudin et al. [141]. The catalytic system was made in situ from $Pd(AcO)_2$, PPh_3 and aqueous CF_3COOH. In the absence of ethene, this catalyst promotes the formation of the WGSR. In the presence of ethene, the evolution of H_2 is inhibited and the reaction takes a different path, as DEK forms together with an equimolecular amount of CO_2. The source of hydrogen is H_2O [141]. The reaction can be depicted as follows:

$$2C_2H_4 + 2CO + H_2O \rightarrow DEK + CO_2 \qquad (24)$$

A significant increase of the catalytic activity occurs when the reaction is carried out in the presence of molecular hydrogen ($TOF = 35 h^{-1}$ at 70 °C, 1 bar, $C_2H_4/CO/H_2 = 2//1/1$, Pd/P = 1/10). In this case CO_2 forms only in trace amounts [72]. The same active hydride $[PdHL_3]X$ is operative in both cases. In the absence of H_2 the hydride forms via a reaction closely related to the WGSR, in the other case it forms via heterolytic activation of H_2 by Pd(II). Deuterium studies using H_2/D^+ and D_2/D^+ systems elucidated the nature of the product forming steps, which occurs via keto-enol isomerisation of the alkylacyl β-chelate intermediate, followed by protonolysis [72], as shown to occur also for the analogous termination steps of the CO-ethene copolymerisation process.

More recently, Pugh and Drent found that $Pd(AcO)_2)/dtbpe/TfOH$ (Pd/ P = P/TfOH = 1/1.2/2.5) is very active to catalyse the formation of DEK in MeOH and in the absence of H_2O ($TOF = 4500 h^{-1}$ at 120 °C, 40 bar, CO/ethene = 1/1, 90% selectivity, 7.3% $CH_3CH_2COCH_2CH_2COOMe$, 1.5% MP), at variance with an analogous system based on the C_3-bridged analogue dtbpp (97.4% to DEK, $TOF = 25000 h^{-1}$) [33]. The source of hydrogen is MeOH [33]:

$$2C_2H_4 + CO + MeOH \longrightarrow DEK + HCHO \qquad (25)$$

When the reaction is carried out in the presence of hydrogen and excess acid (20 bar of H_2, Pd/TfOH = 1/50) the selectivity and TOF jump up to 98% and $90000 h^{-1}$. The mechanism proposed is shown in Fig. 11. After formation of the acyl intermediate 3, the insertion of a second molecule of ethene is faster than methanolysis. Protonolysis by MeOH of the β-chelate gives the product and a Pd–OCH_3 species, which undergoes β-H elimination with regeneration of the active Pd–H^+ species 1. Direct hydrogenolysis of 4 or of the Pd–OCH_3 bond may explain the promoting effect of H_2.

Differently from the dtbpp or the dtbpx systems, in the case of the dtbpe after the formation of intermediate 3, insertion of a second molecule of ethene wins over termination by methanolysis to MP as, possibly, a consequence of the larger space at the "vacant" side because of the smaller bite angle of the C_2-bridged diphosphine.

Quite interestingly, excess acid changes the selectivity, as a significant amount of copolymer is produced (DEK 33%, oligomers/copolymers ca. 60%). Protonation at the oxygen atom of the β-chelate may open the five-membered (and the subsequent six-membered ring of a γ-chelate) and makes easier the insertion reactions to copolymers. A similar acid effect has been found using the monosulfonatedmonophosphine PPh_2PhSO_3H for the carbonylation to ethene in H_2O (Sect. 3.1) [82, 87].
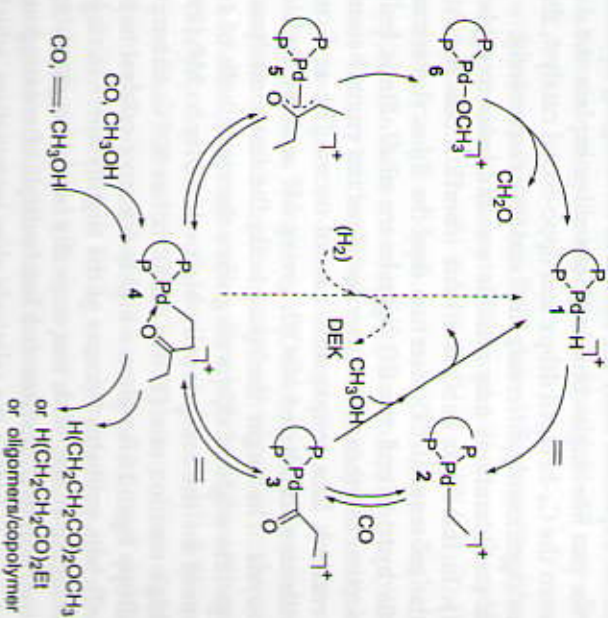

Fig. 11 Proposed mechanism for the formation of DEK. Adapted from [33]

5 Conclusions and Outlook

The most active Pd(II) catalysts for the carbonylation of ethene to high molecular weight polyketones, cooligomers or monocarbonylated products are cationic complexes of bidentate phosphines. Cis-coordination is ideal for promoting the insertion reactions and also methanolysis. Copolymerisation can occur through both the hydride and the carbomethoxy mechanism, whereas the formation of MP is likely to occur via the first mechanism only. The operating conditions, the nature of the counter-anion, the acidity and the nature of the solvent can influence both the rate of reaction and selectivity. But it is the ligand that can make the most significant difference.

After the promising results obtained with the C_3-bridged dppp ligand, which has a bite angle of 90°, believed to be optimal to make lower the activation energy of the copolymerisation process, systematic investigations on steric and electronic influence of modified dppp ligands led to the development of the dapp-type ligands, suitable for commercial exploitation, and also to the discovery of the dtbpp-based catalysts, highly active and selective for the production of MP.

The sharp change in selectivity from high molecular weight polyketones to MP occurring when the phenyl groups in dppp are replaced by bulkier t-Bu groups cannot be explained only on the basis of bridging chain length and bite angles. Nor can bite angle considerations alone explain the different selectivity between the C_4-bridged dtbpx and dppb-based catalyst, though their bite angles are significantly different, 104° and 98°, respectively.

Steric bulk considerations may provide a sound basis to explain the different activity. In the dtbpx catalyst ethene insertion into the Pd–H bond is fast as is the subsequent CO insertion into the Pd-acyl intermediate, because both the hydride and the CO ligands are small. Steric bulk impedes one more insertion of ethene, CO insertion does not occur because of thermodynamic reasons, thus propagation cannot occur. The acyl complex can react only with cis-coordinated MeOH, giving MP and the hydride back to the catalytic cycle. The larger the steric bulk, the faster the methanolysis. The relatively large bite angle of dtbpx magnifies the steric bulk of t-Bu group, this may account for the exceptionally high selectivity to MP (99.98%) and also for the high reaction rate (TOF = 50 000 h^{-1} at 80°C, 10 bar, CO/ethene = 1/1). The dtbpp ligand also gives a highly selective catalyst to MP, though slightly less efficient, probably because of the slightly lower steric bulk due to the shorter bridging chain. With less sterically hindering dppp type ligands, fast ethene insertion to β-chelates and fast multiple alternating insertions of CO and ethene occur before the relatively slow termination, which produces a high molecular weight polyketone.

By replacing the t-Bu groups with the smaller s-Bu in the C_3-bridged diphosphine, the selectivity changes from MP to DEK. Keeping the same sub-

stituents at the P atoms, the steric bulk can be varied by varying the length of the bridging chain. From dtbpp to less bulk dtbpe the selectivity changes from MP to DEK. After formation of the Pd–COEt intermediate, the less sterically hindering s-Bu-substituted diphosphine and the C_2-bridged dtbpe ligand allow the insertion of a second molecule of ethene with formation of an alkylacyl β-chelate intermediate, which undergoes protonolysis by MeOH to monocarbonylated DEK. When the catalysts are used in combination of an excess of acid, there is significant formation of oligomers/copolymers. It might be possible that protonation of the oxygen atom of the chelate destabilizes it and/or increases the electrophilicity of the chelate moiety, thus favouring further insertions.

Though mainly of electronic nature, the higher steric bulk of the dapp ligand, compared to dppp, may also contribute to enhance the performance of dapp. Also the increase of the steric constrains introduced by alkyl substitution in the bridging chain of both ligands may be involved in the increased productivity. The higher steric bulk and constraints may destabilize the β-chelates thus favouring the insertion of ethene, the low step of the copolymerisation process.

Steric bulk may play a role of paramount importance in making the catalysts based on the dppm type ligands 13 and 14 with bulky substituents at the ortho-position of the phenyl rings highly active for the copolymerisation to high molecular polyketones, whereas dppm itself is ineffective. The different selectivities observed using ligands 30 and 31 and 34–37 may also be related to steric bulk.

Ligands with intermediate steric bulk give cooligomers together with lower molecular weight products down to DEK and MP. Monophosphine catalysts also give these products. The P–Pd–P angle in cis-$[Pd(H_2O)_2(PPh_3)_2]^{2+}$ is 97°, close to the bite angle of dppb, but two PPh$_3$ have a higher steric bulk, which may explain the different selectivity shown by the two systems. In addition, the lower activity of the PPh$_3$-based catalyst system may be related to the fact that it undergoes cis-trans isomerisation and that it can undergo insertion and termination reactions only when in the cis geometry.

Though important results have already been obtained in the carbonylation of olefins, the field still remains open. Development of more active, efficient and stable catalysts based also on less expensive metals will make the carbonylation processes more attractive. Carbonylation of less common olefins, including functionalised ones, has to be explored in more depth. Other important targets are the efficient living copolymerisation, the multiple olefin insertion producing non-alternating copolymers and the selective synthesis of unsaturated products like acrylates and methacrylates.

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