Catalyst design and mechanistic aspects of the alternating copolymerisation of ethene and carbon monoxide by diphosphine-modified palladium catalysis †

Claudio Bianchini,* Andrea Meli and Werner Oberhauser

Istituto di Chimica dei Composti OrganoMetallici, ICCOM-CNR, Via J. Nardi 39, 50132 Firenze, Italy. E-mail: bianchin@fi.cnr.it; Fax: +39 0552478366; Tel: +39 055

This article addresses fundamental mechanistic aspects related to the perfectly alternating copolymerisation of CO and ethene in MeOH through the analysis of both actual reactions catalysed by palladium(II)–diphosphine precursors and stoichiometric reactions with model compounds. Most recent *in situ* studies of CO/ethene copolymerisation, applying high-pressure IR and NMR techniques, have been reviewed and commented.

---

† The illustration of John Dalton (reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry) marks the 200th anniversary of his investigations which led to the determination of atomic weights for hydrogen, nitrogen, carbon, oxygen, phosphorus and sulfur.

Introduction

The alternating copolymerisation of carbon monoxide and olefins assisted by diphosphine-modified palladium(II) catalysts (Scheme 1) is a process of extraordinary interest, yet nowadays at the centre of a paradox.[1] Indeed, in comparison to the growing scientific attention in both the industry and academy

Claudio Bianchini

Claudio Bianchini was born in Florence, Italy, in 1949 and received his "Laurea" in Chemistry from the University of Florence in 1973. Upon graduation, he joined the Chemistry Department as a bourse-holder (1974–1975). He then moved to the Research Centre of the pharmaceutical industry A. Menarini (1976–1977). In 1977, he got a position in the group headed by Prof. L. Sacconi at ISSECC-CNR in Florence. He is currently Director of Research of the Consiglio Nazionale delle Ricerche (CNR) and Head of the Institute of Chemistry of Organometallic Compounds (ICCOM-CNR) in Florence. His research interests are mainly in homogeneous and heterogeneous catalysis. He is a Fellow of the Institute of Advanced Study of the Indiana University since 1991, and is a recipient of the following awards: Federchimica (1991, Milan, Italy), Arthur D. Little Award in Inorganic Chemistry (1998, MIT, USA), Seaborg Memorial Lecture (2001, Berkeley University, USA). He has authored about 350 papers and patents.

Andrea Meli was born in Florence, Italy, in 1948 and received his "Laurea" in Chemistry from the University of Florence in 1974. In 1976, he joined the group headed by Prof. L. Sacconi at ISSECC-CNR in Florence. Currently, he is a first-class researcher at ICCOM-CNR and responsible for the Catalysis department. His current research interests are in the field of homogeneous and heterogeneous catalysis (HDS, HDN, polymerisation and copolymerisation of olefins) and high-pressure NMR spectroscopy. He has authored about 190 papers and patents

Werner Oberhauser was born in Brunico, Italy in 1967 and received his Mag. rer. nat. in Chemistry from the University of Innsbruck in 1994. After taking a Ph.D. in Professor Brueggeller's group in Innsbruck (Austria) in 1997 he spent three years as a Post-doc in Claudio Bianchini's laboratory in Florence, before becoming a researcher of the Institute of Chemistry of Organometallic Compounds (ICCOM-CNR) headed by Claudio Bianchini in 2001. His research interests are mainly focused on the development of homogeneous catalysts and mechanistic investigations of catalytic reactions by means of high-pressure NMR and IR.

Andrea Meli

Werner Oberhauser
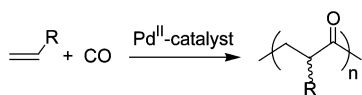
Scheme 1

(more than 200 publications and patents over the last four years),[2] the production of polyketones by CO/olefin copolymerisation is virtually stagnant and the thermoplastics market seems to be uninterested in these materials.

Only research can revitalize the industrial interest in alternating polyketones, improving their chemical–physical properties, discovering new applications and reducing the production cost. This means that increasing research efforts should be devoted to design new catalysts, new processes and new olefinic monomers.

Among the hundreds of papers on CO/olefin copolymerisation reactions appeared over the last ten years, there are at least 10 reviews of excellent quality, covering more or less all the aspects of both the copolymerisation process and the material properties.[2,3]

In an attempt of avoiding a pointless duplication, this perspective article will address only very recent and innovative mechanistic aspects related to the copolymerisation of CO and ethene in MeOH and will also provide some practical instructions to prepare active palladium(II) pre-catalysts for general use in CO/olefin copolymerisation reactions.

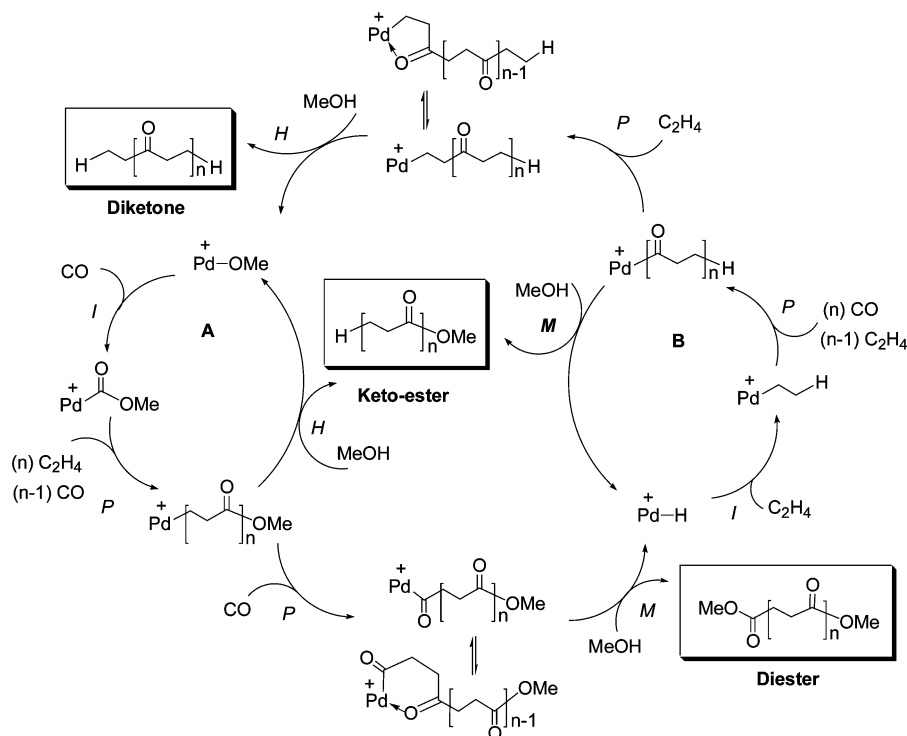## Mechanism of CO/ethene copolymerisation by palladium(II) catalysts with chelating diphosphines

The mechanism reported in Scheme 2 summarizes all the principal steps of the alternating CO/ethene copolymerisation in MeOH by palladium(II) catalysts stabilised by bidentate ligands.[3b] The process comprises two competing cycles, connected by two cross termination steps, the prevalence of either cycle depending on the experimental conditions. Cycle **B** initiates (*I*) with the insertion of ethene into a Pd–H bond that can be generated in a variety of ways (see below). Insertion of CO into the resulting ethyl complex is reversible and faster than ethene insertion, while CO insertion into the Pd–acyl is thermodynamically disfavoured. Since ethene insertion into the

Pd–acyl is rapid and irreversible, the propagation (*P*) can occur by alternating insertion of CO and ethene. The copolymer produced by this cycle shows either keto-ester or diketone terminal structure depending on the termination path: the ketoester end structure is obtained *via* methanolysis (*M*) of a Pd–acyl bond, while the diketone structure requires the protonolysis (*H*) of a Pd–alkyl intermediate. A copolymer with keto-ester end groups is produced also by protonolysis of a Pd–alkyl bond formed during the propagation in the alternative cycle **A** that starts with the insertion of CO into a Pd–OMe bond to give a Pd carbomethoxy complex. The diester structure is obtained *via* methanolysis of a Pd–acyl arising from cycle **A**.
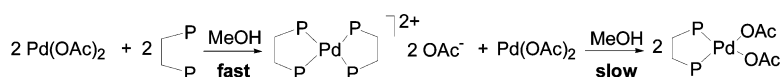
Formation of active palladium(II) sites and initiation

The catalytically active species in the alternating CO/ethene copolymerisation in methanol are generally constituted by square-planar Pd[II] complexes of the general formula [Pd[II]-(Pk)(S)(P–P)]X where P–P is a chelating diphosphine, Pk is the growing polyketone chain, and S may be MeOH, water, a comonomer, or a keto group from the chain. X is a counteranion of weak nucleophilicity in order to avoid competition with the co-monomer for coordination to palladium. These active species are formed by appropriate neutral ([Pd(X)$_2$-(P–P)]) or cationic ([Pd(S)$_2$(P–P)]X$_2$) precursors that can be also prepared *in situ* by reaction of a palladium(II) salt (commonly Pd(OAc)$_2$ or [Pd(NCMe)$_4$](BF$_4$)$_2$) with the phosphine. In either case, a slight excess of strong protic acid (commonly trifluoroacetic acid or *p*-toluenesulfonic acid) must be added to the reaction mixture to neutralise anionic nucleophiles (*e.g.*, acetate ions) that may compete with MeOH in the activation of the precursor and with the co-monomers in the propagation step. A further important role of the protic acid is to convert inactive Pd[0] species, eventually formed during the catalysis (*vide infra*), into active Pd[II]–H.[3]

Recent studies have shown that, depending on the chelating diphosphine, the preparation of the catalyst precursor *in situ* may give much lower productivities as compared to reactions where a preformed Pd[II] complex is used. 1,3-Bis(diphenylphosphino)propane (dppp), that forms very active catalysts, can be equally used in either preformed or *in situ* generated systems. In contrast, dppe, 1,2-bis(diphenylphosphino)benzene (dppbz)


Scheme 2

$$2\ Pd(OAc)_2\ +\ 2\ \left[\begin{array}{c}P\\[-2pt]P\end{array}\right] \xrightarrow[\textbf{fast}]{MeOH} \left[\begin{array}{c}P\quad P\\ Pd\\ P\quad P\end{array}\right]^{2+}\ 2\ OAc^-\ +\ Pd(OAc)_2 \xrightarrow[\textbf{slow}]{MeOH}\ 2\ \left[\begin{array}{c}P\quad OAc\\ Pd\\ P\quad OAc\end{array}\right]$$

<div align="center">Scheme 3</div>

and 1,3-bis[di(*o*-methoxyphenyl) phosphino]propane (bdompp) give much worse results when used *in situ*.[4,5] For example, under comparable experimental conditions, isolated [Pd(OAc)$_2$(dppe)] yielded 3.20 kg of polymer (g Pd)$^{-1}$, while {Pd(OAc)$_2$ + dppe} produced 0.14 kg of polymer (g Pd)$^{-1}$.[5]

A detailed kinetic investigation of the reaction of dppe has shown that this ligand reacts with Pd(OAc)$_2$ in MeOH at room temperature to give the kinetic bis-chelate product [Pd(dppe)$_2$]-(OAc)$_2$, which slowly reacts with the residual Pd(OAc)$_2$ converting to the thermodynamic, and catalytically active, mono-chelate complex [Pd(OAc)$_2$(dppe)] (Scheme 3).[4] This transformation is assisted by the acetate ion, and its rate depends on the concentration of both the bis-chelate and Pd(OAc)$_2$.[4,5b] The initial shortage of active palladium(II) is characteristic of Pd(OAc)$_2$ that exists in MeOH in various forms, from monomers to aggregates, depending on the temperature and concentration.[4]
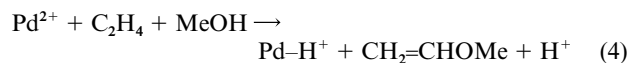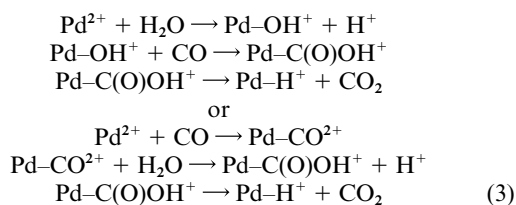
The Pd^{II} precursors need to be activated to generate the Pd–H and Pd–OMe moieties that, upon insertion of C$_2$H$_4$ and CO, respectively, will initiate the copolymer propagation.[1,3]

In the absence of specific reagents, the activation of the promoter starts with the formation of a Pd^{II}–OMe complex [eqn. (1)] that may generate a Pd^{II}–H complex *via* β-H elimination, yielding formaldehyde [eqn. (2)].[6]

$$Pd^{2+} + MeOH \longrightarrow Pd\text{–}OMe^+ + H^+ \qquad (1)$$

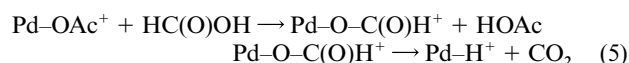$$Pd\text{–}OMe^+ \longrightarrow Pd\text{–}H^+ + HC(O)H \qquad (2)$$
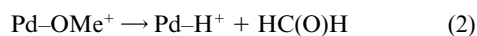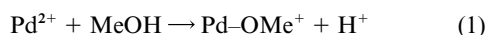
The reactions reported in eqns. (1) and (2) account for why tertiary alcohols are rather inefficient in CO/olefin copolymerisation; indeed, the formation of alkoxypalladium complexes is slower for tertiary alcohols than for primary and secondary ones, while the lack of β hydrogens does not allow for the formation of Pd–H moieties. It is also worth mentioning that some primary alcohols bearing electron-withdrawing substituents, such as CF$_3$CH$_2$OH, are unable to form Pd–H due to their low propensity to oxidation.[7]

Pd–H moieties can also be generated by either the water–gas shift reaction [eqn. (3)] or Wacker-type reaction [eqn. (4)].[3] In the former case, hydrogen atoms are provided by water that may be adventitious or even added,[8] in the latter case, it is ethene that provides hydrogen atoms.

$$\begin{aligned} Pd^{2+} + H_2O &\longrightarrow Pd\text{–}OH^+ + H^+\\ Pd\text{–}OH^+ + CO &\longrightarrow Pd\text{–}C(O)OH^+\\ Pd\text{–}C(O)OH^+ &\longrightarrow Pd\text{–}H^+ + CO_2\\ &\text{or}\\ Pd^{2+} + CO &\longrightarrow Pd\text{–}CO^{2+}\\ Pd\text{–}CO^{2+} + H_2O &\longrightarrow Pd\text{–}C(O)OH^+ + H^+\\ Pd\text{–}C(O)OH^+ &\longrightarrow Pd\text{–}H^+ + CO_2 \qquad (3) \end{aligned}$$

$$\begin{aligned} Pd^{2+} + C_2H_4 + MeOH &\longrightarrow\\ Pd\text{–}H^+ &+ CH_2{=}CHOMe + H^+ \qquad (4) \end{aligned}$$

Another efficient source of hydrogen atoms for the formation of Pd–H initiators is formic acid [eqn. (5)].[9]

$$\begin{aligned} Pd\text{–}OAc^+ + HC(O)OH &\longrightarrow Pd\text{–}O\text{–}C(O)H^+ + HOAc\\ Pd\text{–}O\text{–}C(O)H^+ &\longrightarrow Pd\text{–}H^+ + CO_2 \qquad (5) \end{aligned}$$

The high reactivity under copolymerisation conditions does not allow for the spectroscopic detection of Pd–H species, however sound experimental evidence has been obtained for their presence using indirect methods such as analysis of the

end groups of the polyketone, isotopic labelling, and the use of model compounds.[3]

To achieve high productivities, commonly expressed as kg of polyketone (g Pd)$^{-1}$, the reactions are carried out in the presence of an excess of either organic (*e.g.*, 1,4-benzoquinone (BQ), 1,4-naphthoquinone) or inorganic (*e.g.*, Cu^{II} salts) oxidants. BQ is the most common oxidant and its presence in the reaction mixture may increase the overall productivity by more than an order of magnitude.[3b] In general, the oxidant does not affect the copolymer molecular weight, rather it favours the formation of ester end groups due to the occurrence of reaction in eqn. (6).

$$\begin{aligned} Pd\text{–}H^+ + BQ + MeOH + CO \longrightarrow\\ Pd\text{–}C(O)OMe^+ + BQH_2 \qquad (6) \end{aligned}$$
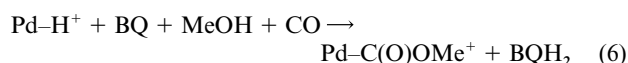
Therefore, the oxidant influences neither the propagation nor the termination. It simply serves to maintain as level as possible the number of active Pd^{II} sites that, as will be shown in following sections, tend to decrease owing to the occurrence of various deactivation pathways.

Chain propagation

The chain propagation comprises two alternating migratory insertion steps involving Pd(alkyl)(CO) and Pd(acyl)(ethene) moieties. The Pd(alkyl)(ethene) misinsertions are virtually absent (*ca.* one double ethene insertion for every *ca.* 10^5 CO insertions into Pd–alkyl).[10] Early studies under actual copolymerisation conditions showed a dependence of the copolymerisation rate on the ethene pressure, and therefore it was concluded that the insertion of ethene is rate-determining.[3b] This is probably true, yet the overall rate-limiting step seems to be mechanistically more complicated than a simple migratory insertion of Pd(acyl)(ethene), and apparently involves a competitive coordination of ethene with other ligands present in the reaction mixture, such as CO, MeOH and keto groups of the propagating chain. Sound experimental evidence in this sense has been provided by Drent and co-workers for a case of heterogeneous CO/ethene copolymerisation with the catalyst precursor [Pd(Me)(OTf)(dppp)].[11] With the use of polarization modulation reflection absorption infrared spectroscopy (PMRAIRS), these authors proved that ethene insertion into the Pd–acyl bond of the γ-keto chelate complex [Pd{C(O)CH$_2$CH$_2$C(O)Me}(dppp)]$^+$, in equilibrium with the β- keto chelate [Pd{CH$_2$CH$_2$C(O)Me}(dppp)]$^+$, does not occur unless some CO is present (Scheme 4). It was proposed that the substitution of the chelating ketone in **a** by ethene proceeds in two consecutive steps: associative substitution of the chelating ketone by CO (**a** → **b** → **c**), followed by associative substitution of CO by ethene (**c** → **d** → **e**). The disruption of the chelate structure of **a** was proposed to be more facile for CO than for ethene for steric reasons (end-on *vs.* side-on approach).

The importance of β- and γ-keto chelates in controlling both the selectivity and the propagation rate of the CO/ethene copolymerisation has been confirmed by several *in situ* and model studies.[5a,12,13]

Under real catalytic conditions (typically, MeOH, 80–85 °C, 30–40 bar 1 : 1 CO/C$_2$H$_4$), the chain transfers by protonolysis of β-keto chelates and methanolysis of γ-keto chelates (see below) are generally too fast to allow for the spectroscopic detection of either chelate. Consistently, in the course of reactions catalysed by very active Pd^{II} systems with dppp or related diphosphines, no catalytically relevant species has ever been seen by high-
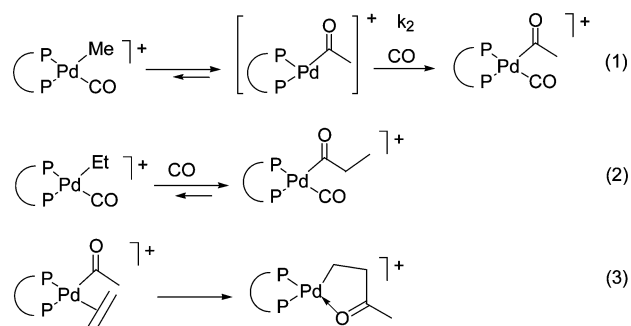
Scheme 4

Scheme 5

40 bar C$_2$H$_4$/CO
MeOH-d_4, RT

R = C$_2$H$_4$D(H), OCD$_3$
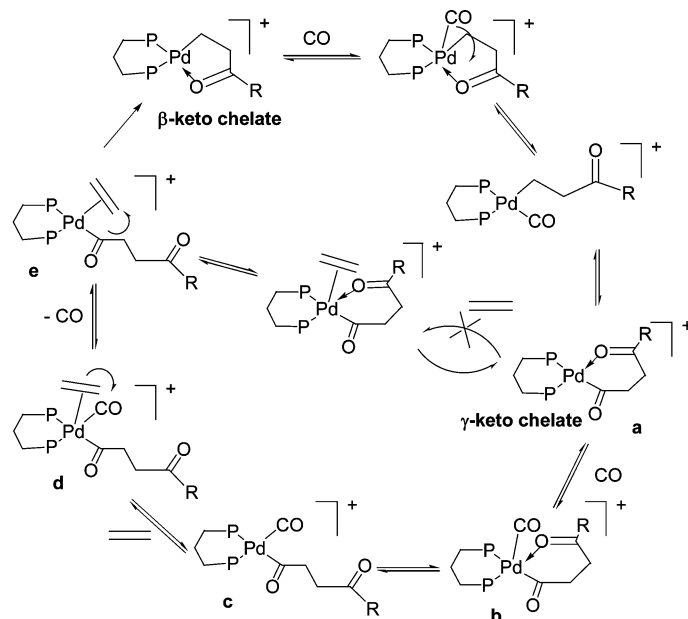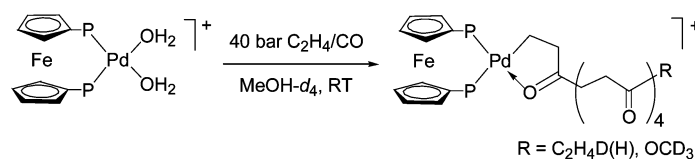
pressure NMR spectroscopy (HPNMR). At room temperature, the HPNMR technique has allowed for the detection of a β-chelate complex in a copolymerisation reaction catalysed by a Pd^{II} precursor containing the diphosphine dppf (Scheme 5).[14] This β-chelate intermediate disappeared already at 50 °C.

Bands at 1638 and 1616 cm^{-1} that we attribute to γ- and β-chelates, respectively, have been observed at 85 °C by means of high-pressure IR spectroscopy (HPIR) in the course of a CO/ethene copolymerisation catalysed by [Pd(OTs)$_2$(dppp)] in a solution of 2-ethylhexanol. These data, however, must be considered with caution due to lack of details on both the instrument employed and the experimental conditions.[15]

The formation of β- and γ-chelates, by ethene insertion into Pd–acyl and CO insertion into Pd–alkyl, respectively, has been proved in several stoichiometric reactions involving Pd^{II} complexes with P–P, P–O, N–O and P–Fe chelating ligands.[12–15]

Besides the isolation and characterisation of the keto chelates, the model studies in aprotic solvents with Pd^{II} complexes representative of catalytic intermediates (generally NMR experiments in CD$_2$Cl$_2$) have provided valuable information on the energy barriers associated with migratory insertion reactions occurring in the propagation step. Irrespective of the chelating diphosphine (P–P = dppp, dppe, *meso*-2,3-bis(diphenylphosphino)butane (*meso*-2,3-dppb), *rac*-2,3-bis(diphenylphosphino)butane (*rac*-2,3-dppb), *meso*-2,4- bis-(diphenylphosphino)pentane (*meso*-bdpp), *rac*-2,4- bis(di-phenylphosphino)pentane (*rac*-bdpp)), the migratory insertion reactions of [Pd(R)(CO)(P–P)]$^+$ complexes (R = Me, Et) are reversible and follow first-order kinetics (Scheme 6, reactions 1 and 2).[5a,10,13,16,17] The free energies of activation for these three reactions have been calculated from the half-life times ($t_{1/2}$) obtained by ^{31}P{^{1}H} NMR spectroscopy. Indeed, in all the cases investigated, the rate of conversion of the methyl carbonyl complexes has been found to be independent of the CO pressure. Therefore, the Δ$G^‡$ values associated with the migratory insertion of the methyl carbonyl complexes could

Scheme 6

be straightforwardly calculated from the $t_{1/2}$ values using the equation $\Delta G^‡ = RT(\ln k_r - \ln kT/h)$ with $k_r = \ln 2/t_{1/2}$.[10]

The Δ$G^‡$ data for the migratory insertion reactions of methyl carbonyl Pd^{II} complexes with chelating diphosphines span from 14 to 18 kcal mol^{-1}.[5a,10,13,16,17] Trends have been established according to which the energy barriers for the migratory insertions decrease with increasing P–Pd–P angles and steric bulk of the diphosphine ligands.[17]

First-order kinetics have been also observed for the irreversible migratory insertion of [Pd(COMe)(C$_2$H$_4$)(P–P)] yielding β-chelate complexes (Scheme 6, reaction 3). A Δ$G^‡$ value of 12.3(1) kcal mol^{-1} (at –103.1 °C) has been determined by Brookhart and co-workers for the conversion of the dppp complex [Pd(COMe)(C$_2$H$_4$)(dppp)]SbF$_6$ to the corresponding β-chelate. Similar energy barriers (≤12 kcal mol^{-1}) have been estimated for all the migratory insertions of [Pd(COMe)-(C$_2$H$_4$)(P–P)]$^+$ complexes investigated.[5a,10,13]

Displacement of the chelate carbonyl from palladium by ethene has never been observed, which accounts for the virtual absence of double ethene insertions. Carbon monoxide is smaller and also exhibits a greater binding affinity for

palladium than ethene. Therefore, β-chelate opening is actually brought about by CO to generate a six-membered metallacycle (γ-keto chelate). With the only exception of the solid–gas experiment reported by Drent and co-workers[11] and illustrated in Scheme 4, no γ-keto chelate complex has been ever intercepted under actual copolymerisation conditions, which may be due to the lower stability of six-membered metallarings as compared to five-membered ones.

β-Keto chelates of catalytically active systems generally react with CO yielding acyl(carbonyl) complexes even at very low temperature (Scheme 7). For the systems investigated, the activation barriers for the conversion of the β-chelates $[Pd\{CH_2CH_2C(O)Me\}(P–P)]^+$ to the corresponding acyl-(carbonyl) complexes could not be calculated straightforwardly from the $t_{1/2}$ values as the reaction rates were found to be dependent on the CO pressure in the range investigated (commonly 15–25 bar).[5a,13] However, the rates of conversion of the β-chelates to the acyl(carbonyl) complexes were evaluated as half-life times obtained from the decay (and increase) of the phosphorus NMR resonances at appropriate temperatures. The $t_{1/2}$ values and the experimental temperature at which the acyl(carbonyl) species begin to form have been used to estimate the energy barrier to β-chelate opening by CO. The results obtained indicate that these energy barriers decrease in the ligand order: dppe (15 min at 20 °C) > *rac*-dppb (480 min at −40 °C) > *meso*-dppb (97 min at −40 °C) > *meso*-bdpp (200 min. at −70 °C) > dppp (84 min at −70 °C) > *rac*-bdpp (13 min at −70 °C). According to this trend, the energy barriers for β-chelate opening decrease by increasing the number of carbon spacers between the P atoms of the ligand, hence with increasing P–Pd–P bond angle. The rigidity of the ligand backbone appears to have much more effect in the dppe-like series, than in the dppp-like series.
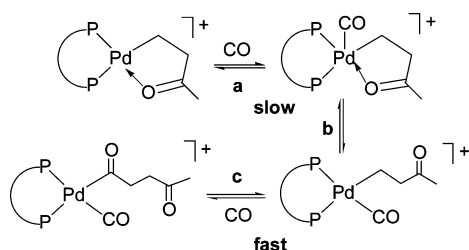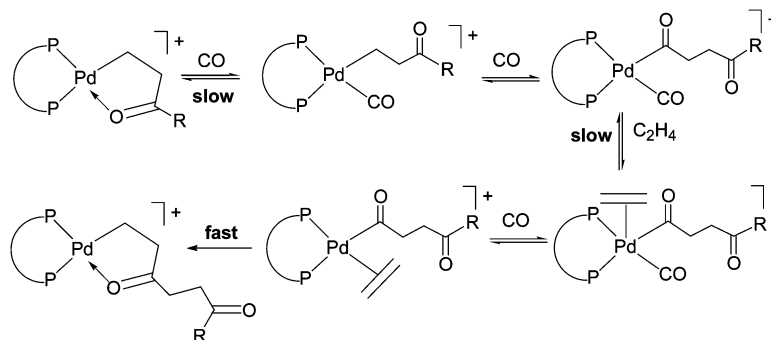

Scheme 7

On the basis of the CO dependence of the transformation of the β-chelates into the acyl(carbonyl) compounds, it has been proposed that the rate-limiting step in the overall conversion of the β-chelates to acyl(carbonyl) complexes is related to the opening of the metallacycle by CO (steps **a** and **b** in Scheme 7) rather than to the following migratory insertion of the alkyl carbonyl complex that is independent of the CO pressure (step **c**).

In the copolymerisation reactions in CH_2Cl_2, no direct correlation was observed between the intrinsic catalytic activity of $[PdMe(S)(P–P)]^+$ precursors (estimated by the initial rates of copolymerisation) and the energy barriers for the migratory insertions of $[Pd(Me)(CO)(P–P)]^+$ and $[Pd(COMe)-(C_2H_4)]^+$.[5a,13] It was therefore concluded that neither migratory insertion is rate-limiting. In contrast, a good correlation was found between the intrinsic catalytic activity and the energy required to open the β-chelates by CO according to Scheme 7.

Incorporation of all of the experimental evidence reported so far does not contradict with the early assumption that ethene insertion is kinetically relevant in the propagation of alternating CO/ethene copolymerisation,[1a] yet suggests that the rate limiting step is more complicated than a single insertion step. This step seems to be the overall opening of a β-chelate by CO, followed by ethene insertion to give the next β-chelate (Scheme 8).

In conclusion, all the studies of the CO/ethene propagation agree to indicate the keto chelates (especially the β ones) as the species that control the strict alternation of the monomers and the intrinsic copolymerisation rate. Therefore, an optimum catalyst for CO/ethene copolymerisation (but this concept can be extended to other olefins) should form keto chelates (to prevent ethene misinsertions) that can be readily opened by CO. Pd^{II} catalysts with diphosphines bearing *o*-methoxyphenyl groups on the phosphorus atoms apparently fulfil these requirements. Indeed, the Pd^{II} catalysts employed in the manufacture of polyketone on a commercial scale by Shell (Carilon®)[3h] are based on 1,3-bis[di(*o*-methoxyphenyl)phosphino]propane (bdompp).[18] Catalysts of the formula [Pd-(bdompp)(Y)_2] (Y = CF_3CO_2, OTs) are by far more active than those containing any other dppp or dppp-modified ligand, and also give higher molecular weight polyketone.[18] Even dppe that forms mediocre Pd^{II} catalysts, generates an active system (comparable to dppp) when *o*-methoxy groups are introduced into the phenyl rings.[19] The beneficial effect of the *o*-methoxy groups seems to be both steric and electronic in nature.[18,20] It is agreed that the *o*-methoxy groups do not influence the phosphine basicity, rather they may interact with the metal centre in hemilabile manner, so as to stabilize complexes that would be coordinatively unsaturated.[21] However, no clear-cut explanation at the molecular level for the *o*-methoxy effect has been forthcoming. Recent studies in our laboratory show that *o*-methoxy groups in the diphosphine ligands destabilise the β-keto chelate metallaring favouring its opening by CO. Evidence has been obtained for the dppe and 1,2-bis-[di(*o*-methoxyphenyl)phosphino]ethane (*o*-MeO-dppe) ligands (Scheme 9).[22]

Were the destabilisation of the β-chelates by *o*-methoxy substituents confirmed for dppp and other chelating diphosphines, then a rationale for the *o*-methoxy effect would be that the methoxy oxygens compete with the keto oxygens for coordination to the palladium centre. In this eventuality, a destabilisation of the β-keto chelates would occur with consequent increase of the propagation rate.
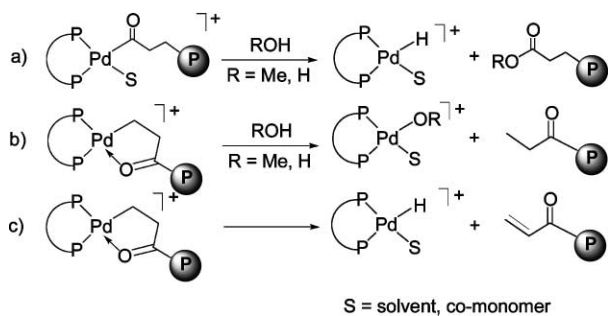

Scheme 8
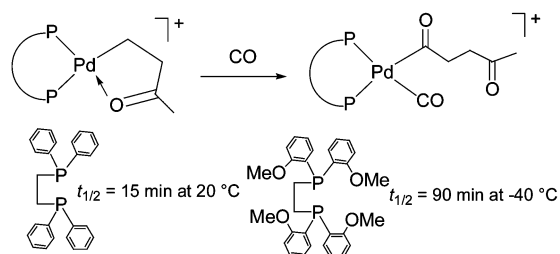
Scheme 9

Chain transfer

The CO/ethene copolymerisation is not a living process; even in the presence of excess co-monomers, the copolymerisation terminates. In order to have high-molecular weight polyketone, the propagation rate must be higher than the chain transfer rate; when the two rates are similar oligomers are formed, while for a net prevalence of chain transfer, only methyl propanoate will be produced. NMR analyses of the polyketone end groups and of the oligomeric fractions obtained by appropriate Pd[II] catalysts show unequivocally that two transfer mechanisms, occurring simultaneously, are at work under typical experimental conditions in MeOH: (a) methanolysis of Pd–acyl and b) protonolysis of Pd–alkyl (Scheme 10).[3b] The unavoidable presence of water in MeOH originates two similar terminations, obviously generating different end groups (–COOH) and metal re-initiator (Pd–OH).[23–25] Termination by β-H transfer (c) is typical for catalyst working in aprotic solvents and has never been observed in MeOH.

S = solvent, co-monomer

Scheme 10

Depending on the chain-transfer mechanism, the termination metal product may contain Pd–OR, Pd–OH and Pd–H moieties, yet all of them can re-initiate the catalysis cycle inserting CO or ethene.

In principle, the rate of chain transfer should not affect the overall productivity, rather it influences the molecular weight of the polyketone product. In practice, this does not happen as the Pd–H initiators are inherently unstable in MeOH, and may undergo deactivation via several pathways (vide infra).

Therefore, when the frequency of formation of the initiators increases by effect of fast chain transfer, the productivities decrease due to a decrease in the number of active palladium sites.

When the termination processes (a) and (b) occur at comparable rates, the copolymers have diester- (EE), keto-ester- (KE) and diketone- (KK) end groups in a 1 : 2 : 1 ratio, respectively.[1] The analysis of the end groups very often shows a ester to

ketone ratio of 1 : 1; deviations from this ratio are generally observed in reactions performed in the presence of organic oxidants as they convert Pd–H into Pd–OMe (see above).[3b]

The relative occurrence of protonolysis and methanolysis depends on many factors. When the growing copolymer chain reaches a length of about 13–20 –CH$_2$CH$_2$–C(O)– units, and the copolymerisation process assumes heterogeneous character, chain termination can equally proceed via protonolysis and methanolysis.[26] In contrast, protonolysis predominates over methanolysis in homogeneous phase.[26] Protic acids, commonly used to maintain a high number of active Pd[II] sites during the catalysis,[3b] can also influence the methanolysis rate. Evidence in this sense has been provided for [Pd(COMe)(CO)(dppp)]$^+$ whose methanolysis rate increases in the presence of protic acids that interact with the acyl oxygen.[27]

Chain transfer by methanolysis (hydrolysis)

The chain transfer by methanolysis involves the attack of a MeOH molecule on a propagating Pd–acyl to give a free chain, bearing at least an ester-end group, and a Pd–hydride species, which re-initiates the chain growth by insertion of ethene (Scheme 10(a)). Obviously, the use of other alcohols as reaction media can dramatically affect the termination rate as well as the molecular weight of the polyketone.[28] As a general trend, the alcoholysis rate decreases (MeOH > EtOH > ^{i}PrOH > ^{t}BuOH ≈ 2,2,2-trifluoroethanol) by either increasing the steric bulk of the alcohol or decreasing its nucleophilicity. Parallel to the decrease of the chain transfer rate, the molecular weight of the copolymer increases. An effective role of water as hydrolysis agent in MeOH medium appears very unlikely as HOOC-terminated polyketone or oligoketone have never been observed.

Remaining to the exclusive use of MeOH, it has been found that the chain-transfer rate depends on the nature of the chelating diphosphine and, eventually, on the concentration of the added protic acid. Studies on model acetyl palladium complexes have shown that the methanolysis rate increases remarkably with the steric bulk of the diphosphine ligands.[29]

The two most probable mechanisms for the methanolysis chain transfer are the nucleophilic attack by MeOH at the Pd–acyl carbon atom in either intermolecular or intramolecular fashion.

Intermolecular nucleophilic attack by MeOH at the Pd–acyl carbon atom. This type of mechanism (Scheme 11) is similar to that established for the alcoholysis of acyl chlorides.[30]

Recent studies by van Leeuwen and co-workers suggest that an intermolecular attack by MeOH on [Pd(acyl)(P–P)]$^+$ complexes is highly unprobable.[31] Their reasoning is based on the assumption that an intermolecular mechanism of the type shown in Scheme 11 does not require the presence of a *cis*-chelating diphosphine, and therefore should work also for the acyl complex [Pd(COMe)(SPANphos)](Y) containing a truly *trans*-diphosphine ligand. Since the SPANphos acyl complex is indefinitely stable in MeOH, it was concluded that a *cis*-configuration of the phosphorus atoms in Pd[II] acyls is required for methanolysis. In this eventuality, a free coordination site, *cis* to the acyl group would be available for intramolecular methanolysis.
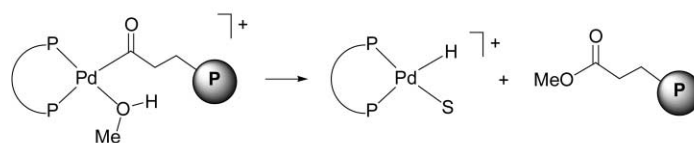
The occurrence of intermolecular methanolysis cannot be excluded, however. Indeed, experimental evidence pointing to intermolecular methanolysis, or at least not excluding this

Scheme 11

SPANphos
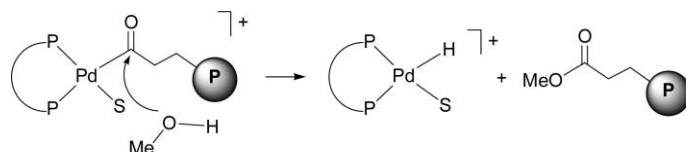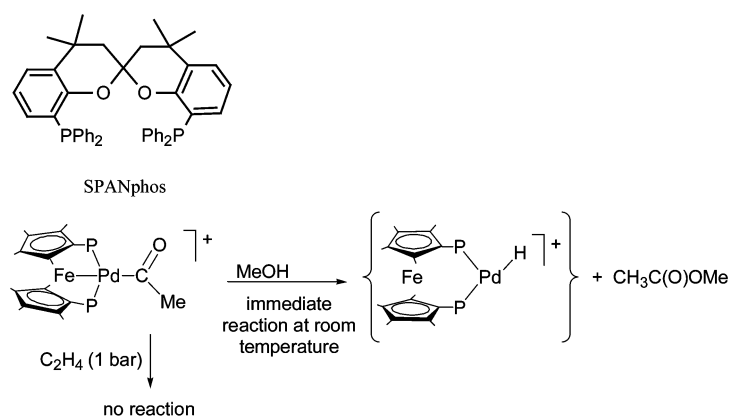
Scheme 12

Scheme 13

termination path, has been obtained by a comparison of the reactivity of the Pd^{II} acyl complexes [Pd(COMe)(dppf)]OTs and [Pd(COMe)(dppomf)]OTs with either MeOH or C$_2$H$_4$.[14] The two acyl complexes differ from each other in the bonding mode of the diphosphine ligands: dppf behaves as a *cis* chelating ligand, while 1,1′-bis(diphenylphosphino)octamethyl-ferrocene (dppomf) behaves as a tridentate ligand with *trans* P atoms. As shown in Scheme 12, both acyl complexes undergo fast methanolysis in CH$_2$Cl$_2$, yet the dppomf does not insert ethene. Since ethene insertion does requires a vacant co-ordination site, it was concluded that methanolysis is either intermolecular or occurring *via* a five-coordinate transition state.

Intramolecular nucleophilic attack by MeOH at the Pd–acyl carbon atom. The chain transfer by intramolecular meth-anolysis is illustrated in Scheme 13.

A *cis*-coordinating ligand is required to bind and activate MeOH so that a methoxy group is transferred to the polyketone chain and a hydride remains on palladium. Two mechanisms are possible for this reaction: (i) nucleophilic attack by the oxygen at the acyl carbonyl with concerted formation of Pd–H; (ii) formation of a Pd(acyl)(methoxy) complex and H$^+$, followed by reductive elimination and subsequent proton attack to a Pd^0 centre.[32] A mechanism of the latter type has been reported for the synthesis of aryloxy esters from Ni^{II} and Pd^{II} acyl(aryloxy) complexes.[32] No experimental evidence favouring either mechanism in CO/ethene copolymerisation has been provided so far.

Chain transfer by protonolysis

The chain transfer by protonolysis represents the predominant termination step in homogeneous CO/ethene copolymerisation, and involves the reaction between a propagating Pd–alkyl species and MeOH or adventitious water (Scheme 10(b)). As a result, the propagation is terminated with formation of a polymeric chain with a ketone-end group and Pd–OMe (or Pd–OH) species. These can re-enter the catalytic cycle by CO insertion.

By means of deuterium incorporation experiments, van Leeuwen and co-workers have fully elucidated the mechanism of termination by protonolysis, showing that the β-keto alkyl chelates are in equilibrium with their enolate form (A) by a β-H elimination/hydride migration process (Scheme 14). Chain
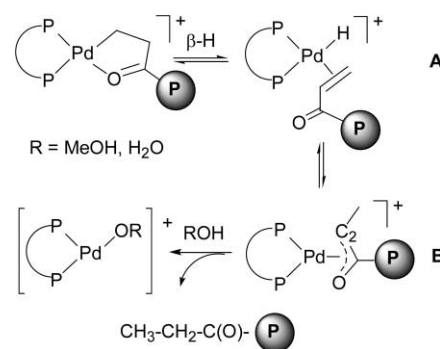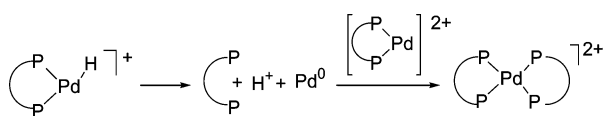

Scheme 14

termination occurs *via* regioselective protonation of the C$_2$ carbon atom of the enolate by either MeOH or H$_2$O. The enolate formation has been reported to be rate determining in the chain transfer.[12c]

The effect of the bite angle of the chelating diphosphines on the protonolysis rate of β-keto alkyl chelates has been recently investigated. Studies by Zuideveld and van Leeuwen with model compounds showed a slight increase of the protonolysis rate with increasing bite angles of the diphosphine ligand.[27] Under actual copolymerisation conditions, a β-chelate with dppf[14] and not with dppe or dppp[5a,13,33] was intercepted by HPNMR, which apparently contrasts with the model studies, as dppf has a wider bite angle than dppe and dppp. This evidence suggests that other parameters in the catalytic system may affect the protonolysis rate.
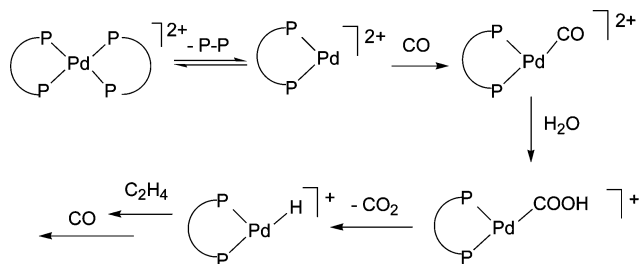
Catalyst deactivation paths

Under actual copolymerisation conditions, the propagation rate decreases with time, and no catalytic activity is generally observed after 8–10 h. As demonstrated by Drent and co-workers, the CO/ethene copolymerisation reaction, initially truly homogeneous, becomes partially heterogeneous by effect of the formation of insoluble Pd–Pk moieties.[26] Besides this phase change, the rate slows down also because the number of catalytically active Pd^{II} sites decreases steadily during the reaction in consequence of several unfavourable events.
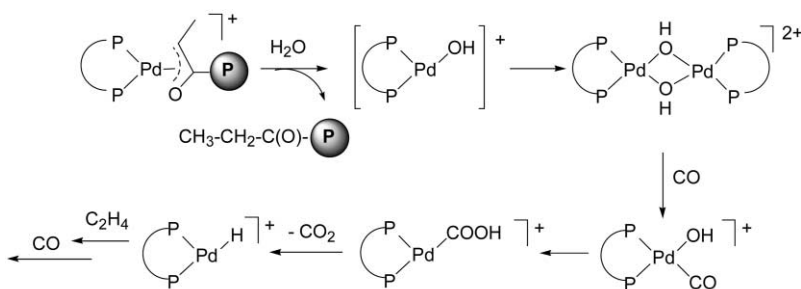
As already commented, the [PdH(P–P)]$^+$ moieties, generated by activation of the precursors and by methanolysis chain-transfer, are inherently unstable in MeOH where they slowly

Scheme 15

Scheme 16

Scheme 17

exclude that intramolecular phosphine oxidation may have a role in the degradation of Pd[II]-based catalysts. On the other hand, it has been shown that the methoxy substituents in bdompp, which forms the most active Pd[II] copolymerisation catalysts, prevent ligand oxidation in Ni[II] complexes, while both dppp and dppe are easily oxidized.[20]

Concluding remarks

The alternating CO/ethene copolymerisation by diphosphine modified Pd[II] catalysis is a fascinating process that transforms two relatively abundant and cheap monomers into a thermoplastic material of high added value. In a few years, a great deal of progress has been achieved in catalyst design, leading to productivities as high as 50 kg of copolymer (g Pd × h)$^{-1}$ with only ppm quantities of residual palladium. Nevertheless, a large margin of improvement is still possible, in terms of both

degrade with formation of inactive Pd[0] and free ligand. The latter can react with active Pd[II] forming bis-chelate complexes (Scheme 15).

Not all bis-chelate complexes represent a dead-end for the CO/ethene copolymerisation, rather some of them may be defined as robust resting states. Indeed, the bis-chelates containing diphosphine ligands with an ethylenic backbone (*i.e.*, dppe) are actually inactive,[5a] but those with dppp-like ligands exhibit an appreciable activity by virtue of their capability to react with CO/water as shown in Scheme 16. Just the contribution of the bis-chelates has been recently invoked to account for the different productivity exhibited by dppp, *meso*-bdpp and *rac*-bdpp precursors [Pd(Me)(NCMe)(P–P)]$^+$ and [Pd(CF$_3$COO)$_2$(P–P)]$^+$ in CH$_2$Cl$_2$ and MeOH, respectively.[13,33] It is also worth mentioning that, unlike dppp, the *o*-methoxysubstituted ligand bdompp does not form bis-chelate complexes [M(P–P)$_2$]$^{2+}$ with Pd[II]. Studies with Ni[II] show that bdompp is too bulky to allow the formation of square-planar bis-chelates. Just the absence of bis-chelates has been claimed as the factor that accounts for the higher hydrogenation activity of Ni[II]–bdompp catalysts as compared to analogous dppe and dppp systems.[4,20,34]

Not less important than the bis-chelates in decreasing the copolymerisation activity are the μ-hydroxo complexes that can be formed upon chain transfer by protonolysis with adventitious water (Scheme 17).[13] The μ-hydroxo complexes can re-enter the copolymerisation cycle through a complex stepwise process involving disruption of the binuclear structure by CO to give Pd–H *via* Pd–C(O)OH.[23–25] The contribution of the μ-hydroxo complexes to the overall productivity in polyketone is generally higher than that of the bis-chelates, and depends on the diphosphine ligand. As a general trend, the stability to carbonylation of the μ-hydroxo complexes decrease with the steric rigidity of the ligand backbone.[13]

Catalyst degradation by intramolecular phosphine oxidation of the Amatore type as occurs in many Pd[II]–diphosphine catalysed reactions,[5b,35] has never been reported to take place appreciably in actual CO/ethene copolymerisation conditions, most likely due to the presence of protic acids. This does not

productivity and material performance. The productivity in alternating polyketone can be improved by developing new and more robust catalysts. Indeed, as shown in this perspective article, small structural variations in the catalyst structure may have a large impact on propagation, chain transfer, and catalyst deactivation. The latter, involving either Pd[II] reduction or Pd[II] aggregation, seem to constitute the real limit to productivities as high as those of polyethene and polyolefins obtainable by insertion polymerisation. Besides tuning the molecular weight and the end groups of the polyketones, new catalysts will also improve the material performance by either combining other co-monomers with ethene (*e.g.*, terpolymerisation with propene as in Carilon®)[3h] or replacing ethene with α-olefins bearing functionalised groups.[3f]

References

1 (*a*) E. Drent, *Eur. Pat.*, 1984, **121**, 965; (*b*) E. Drent, J. A. M. van Broekhoven and M. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.
2 G. P. Belov, *Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1605.
3 (*a*) A. Sen, *Acc. Chem. Res.*, 1993, **26**, 303; (*b*) E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663; (*c*) E. Drent, J. A. M. van Broekhoven and P. H. M. Budzelaar, in *Applied Homogeneous Catalysis with Organometallics Compounds*, ed. B. Cornils and W. A. Hermann, Wiley-VCH, Weinheim, Germany, 1996, pp. 333–351; (*d*) A. Sommazzi and F. Garbassi, *Progr. Polym. Sci.*, 1997, **22**, 1547; (*e*) K. Nozaki and T. Hijama, *J. Organomet. Chem.*, 1999, **576**, 248; (*f*) C. Bianchini and A. Meli, *Coord. Chem. Rev.*, 2002, **225**, 35; (*g*) E. Drent, J. A. M. van Broekhoven and P. H. M. Budzelaar, in *Applied Homogeneous Catalysis with Organometallics Compounds*, ed. B. Cornils and W. A. Hermann, Wiley-VCH, Weinheim, Germany, 2001, pp. 344–361; (*h*) C. E. Ash, *J. Mater. Educ.*, 1994, **16**, 1; (*i*) R. A. M. Robertson and D. J. C. Cole-Hamilton, *Coord. Chem. Rev.*, 2002, **225**, 67.
4 A. Marson, A. B. van Oort and W. P. Mul, *Eur. J. Inorg. Chem.*, 2002, 3028.
5 (*a*) C. Bianchini, H. M. Lee, A. Meli, W. Oberhauser, M. Peruzzini and F. Vizza, *Organometallics*, 2002, **21**, 16; (*b*) C. Bianchini, A. Meli, W. Oberhauser, *Organometallics*, submitted for publication.
6 H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163.

7 W. Clegg, G. R. Eastman, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *J. Chem. Soc., Dalton Trans.*, 2002, 3300.

8 A. Vavasori and L. Toniolo, *J. Mol. Catal. A: Chemical*, 1996, **110**, 13.

9 (*a*) A. Vavasori, G. Cavinato and L. Toniolo, *J. Mol. Catal. A: Chemical*, 2003, **191**, 209; (*b*) J. T. Lee and H. Alper, *Chem. Commun.*, 2000, 2189.

10 S. Shultz, J. Ledford, J. M. DeSimone and M. Brookhart, *J. Am. Chem. Soc.*, 2000, **122**, 6351.

11 W. P. Mul, H. Oosterbeck, G. A. Betel, G.-J. Kramer and E. Drent, *Angew. Chem., Int. Ed.*, 2000, **39**, 1848.

12 (*a*) C. Rix, M. Brookhart and P. S. White, *J. Am. Chem. Soc.*, 1996, **118**, 4746; (*b*) M. J. Green, G. J. P. Britovsek, K. J. Cavell, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 1563; (*c*) M. A. Zuideveld, P. C. J. Kamer, P. W. N. M. van Leeuwen, P. A. A. Klusener, H. A. Stil and C. F. Roobeek, *J. Am. Chem. Soc.*, 1998, **120**, 7977; (*d*) A. Aeby and G. Consiglio, *J. Chem. Soc., Dalton Trans.*, 1999, 655; (*e*) P. Braunstein, C. Frison and X. Morise, *Angew. Chem., Int. Ed.*, 2000, **39**, 2867; (*f*) P. Braunstein, J. Durand, M. Knorr and C. Strohmann, *Chem. Commun.*, 2001, 211.

13 C. Bianchini, A. Meli, G. Müller, W. Oberhauser and E. Passaglia, *Organometallics*, 2002, **21**, 4965.

14 C. Bianchini, A. Meli, W. Oberhauser, P. W. N. M. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev and A. M. Kal'sin, *Organometallics*, in press.

15 H.-K. Luo, Y. Kou, X.-W. Wang and and D.-G. Li, *J. Mol. Catal. A: Chemical*, 2000, **151**, 91.

16 I. Toth and C. J. Elsevier, *J. Am. Chem. Soc.*, 1993, **115**, 10388.

17 J. Ledford, C. S. Shultz, D. P. Gates, P. S. White, J. M. DeSimone and M. Brookhart, *Organometallics*, 2001, **20**, 5266.

18 Encyclopedia of Polymer Science and Technology 3rd, Wiley-Interscience, E. Drent, W. P. Mul and A. A. Smaardijk, *Polyketones*, 2002.

19 E. Drent and M. C. T. De Kock, *US. Pat.*, 5 688 909, 1997.

20 M. Angulo, E. Bouwman, S. M. Lok, M. Lutz, W. P. Mul and A. L. Spek, *Eur. J. Inorg. Chem.*, 2001, 1465.

21 K. R. Dumbar and J.-S. Sun, *J. Chem. Soc., Chem. Commun.*, 1994, 2387.

22 C. Bianchini, A. Meli and W. Oberhauser, manuscript in preparation.

23 (*a*) G. Verspui, G. Papadogianakis and R. A. Sheldon, *Chem. Commun.*, 1998, 401; (*b*) G. Verspui, F. Schanssema and R. A. Sheldon, *Angew. Chem., Int. Ed.*, 2000, **39**, 804.

24 Z. Jiang and A. Sen, *Macromolecules*, 1994, **27**, 7215.

25 C. Bianchini, H. M. Lee, A. Meli, S. Moneti, V. Patinec, G. Petrucci and F. Vizza, *Macromolecules*, 1999, **32**, 3859.

26 W. P. Mul, E. Drent, P. J. Jansens, A. H. Kramer and M. H. W. Sonnemans, *J. Am. Chem. Soc.*, 2001, **123**, 5350.

27 M. A. Zuideveld, Solvolysis of Palladium–Carbon Bonds in Palladium(II) complexes containing Diphosphine Ligands, Ph.D. thesis, University of Amsterdam, 2001.

28 (*a*) T.-W. Lai and A. Sen, *Organometallics*, 1984, **3**, 866; (*b*) B. Milani, A. Anzilutti, L. Vicentini, A. Sessanta o Santi, E. Zangrando, S. Geremia and G. Mestroni, *Organometallics*, 1997, **16**, 5064.

29 Z. Freixa and P. W. N. M. van Leeuwen, *Dalton Trans.*, 2003, 1890.

30 S. D. Ross, *J. Am. Chem. Soc.*, 1970, **92**, 5998.

31 P. W. N. M. van Leeuwen, personal communication.

32 S. Komiya, Y. Akai, K. Tanaka, T. Yamamoto and A. Yamamoto, *Organometallics*, 1985, **4**, 1130.

33 (*a*) C. Bianchini, H. M. Lee, A. Meli, S. Moneti, F. Vizza, M. Fontani and P. Zanello, *Macromolecules*, 1999, **32**, 4183; (*b*) C. Bianchini, H. M. Lee, P. Barbaro, A. Meli, S. Moneti and F. Vizza, *New. J. Chem.*, 1999, **23**, 929.

34 M. Angulo and E. Bouwman, *J. Mol. Catal. A: Chemical*, 2001, **175**, 65.

35 (*a*) C. Amatore, E. Carré, A. Jutand and M. A. M'Barki, *Organometalllics*, 1995, **14**, 1818; (*b*) C. Amatore, A. Jutand and A. Thuilliez, *Organometalllics*, 2001, **20**, 3241.