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Alternating copolymerization of carbon monoxide and olefins by single-site metal catalysis

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Contents

Abstract

The alternating copolymerization of carbon monoxide and olefins is a reaction that transition metal complexes, generally containing palladium, catalyze in different phase variation systems. The polyketone products are not only low cost thermal plastics that can be made but also polymeric materials featured by unique chemical and physical properties. These properties can be finely tuned by an appropriate choice of the catalyst and olefinic comonomer. After introducing the topic, the specific metal catalysts for each type of olefinic substrate are described together with the reaction mechanisms involved. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alternating copolymerization; Polyketones; Carbon monoxide; Alkene; Asymmetric; Stereoselective

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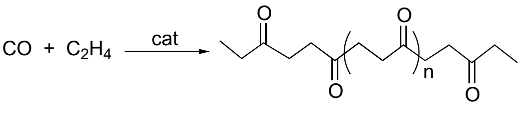
1. Introduction

Polyketones obtained by alternating copolymerization of carbon monoxide with one or more olefinically unsaturated monomer represent a class of low-cost innovative thermoplastics whose synthesis, properties and applications are still the object of intense fundamental and applied research.

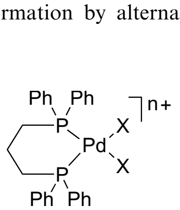
The industrial production of CO/olefins copolymers is a reality and at least two products are already on the market: Carilon® from Shell [1] and Ketonex® from BP [2]. Other companies such as BASF and EniChem have filed an impressive amount of patents covering different types of polyketones and catalytic systems.

Since the discovery of the first copolymerization of CO and ethene in 1941 by Farbenfabriken Bayer [3], the synthetic procedures to polyketones have experienced constant improvement in terms of selectivity, productivity, environmental impact and economy [4]. In a relatively short time, catalytic systems based on nickel, 200 °C, 200 bar CO/ethene have been improved so as to include palladium, <80 °C, <20 bar CO/ethene. Chlorinated hydrocarbons have been replaced by methanol or water and then drastically reduced or completely eliminated as occurs in slurry and gas phase processes, respectively [5]. Moreover, a great variety of functionalized olefins have been found to copolymerize with CO affording alternating copolymers featured by a wealth of performance parameters [4].

Major drawbacks for the commercialization of these thermoplastics are represented by both their imperfect stability, in particular when exposed to high temperatures for extended periods or subjected to repeated cycles of melting and solidification, and the propensity of palladium to plate out during both catalyst preparation and copolymer work up. A wide margin of improvement in both catalyst and material stability as well as catalytic productivity does exist as shown also by the continuous appearance of publications and patents dealing with CO/olefins copolymerization.



Scheme 1. Polyketone formation by alternating CO/ethene copolymerization.



$X = F_3CCO_2^-$, $p\text{-}Me(C_6H_4)SO_3^-$, $n = 0$;
MeCN, $n = 2$

Fig. 1. Efficient catalyst systems for the perfectly alternating CO/ethene copolymerization and the CO/ethene/propene terpolymerization.

Polyketones, the simplest of which is the CO/ethene copolymer (poly-3-oxotrimethylene) (Scheme 1), are featured by a unique web of chemical and physical properties, which include photodegradability, biodegradability, good chemical resistance to acids, bases and solvents, ease of functionalization, impermeability to hydrocarbons, strong rigidity and impact strength, tracking resistance, stability against electrolytic corrosion, etc. [4c,6]. All these properties may be improved and new properties may be envisaged by changing the number and/or nature of the comonomers as well as finely tuning the structure of the metal catalysts. It is now apparent that the diversity of properties makes polyketones superior to polyolefins, polyamides and polyacetals [7].

Current industrial applications of polyketones range from objects to fibers, film coatings, adhesives, membranes, photoresists, packaging materials, etc, but the continuous discovery of new structures forecasts a wealth of new applications, especially in optoelectronic and electronic devices.

Our motivations for this article transcend an updated review of the status of the art of the synthesis of alternating CO/olefin copolymers and, in fact, include kinetic, mechanistic and structural studies which would be helpful for designing catalysts with improved efficiency as well as tailoring polymers with new structures for advanced applications.

2. CO/ethene copolymerization and CO/ethene/propene terpolymerization

2.1. Palladium catalysts stabilized by 1,3-bis(diphenylphosphino)propane and structurally related ligands

The perfectly alternating CO/ethene copolymerization and the CO/ethene/propene terpolymerization are efficiently carried out in methanol at moderate temperature (80–90 °C) in the presence of a catalyst system comprising, as essential components, a Pd(II) salt with weakly coordinating counteranions and a 1,3-bis(diarylphosphino)propane ligand (Fig. 1) [4a,4b,4c].

Indeed, 1,3-bis(diphenylphosphino)propane (dppp) is the ligand that actually opened the way of efficient synthesis of polyketones, hence attracting business interest [8]. CO/ethene pressures as high as 30–60 bar are generally employed, but the perfect alternation is maintained even in the presence of a very low concentration of CO. Only when all CO has been consumed does the catalyst start promoting the dimerization of ethene to butenes. The terpolymerization reactions are generally carried out at similar CO/ethene pressures in the pres-

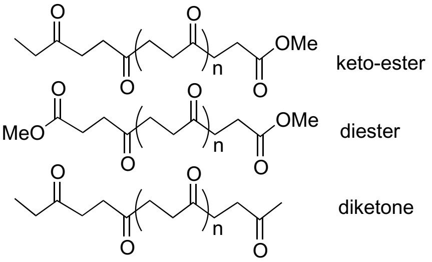


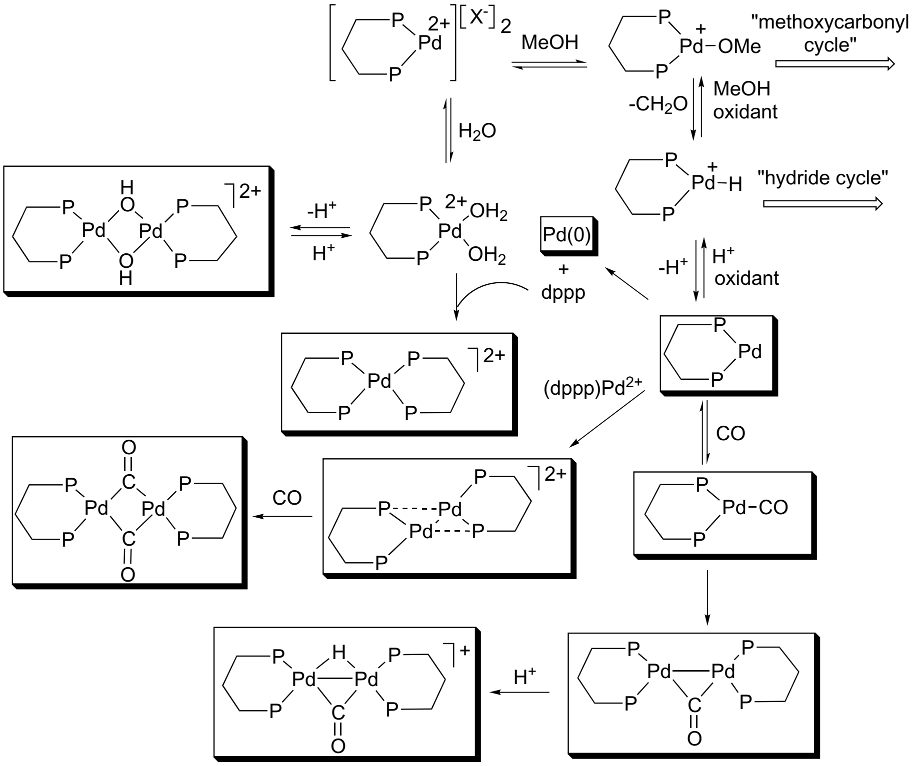
Fig. 2. Polyketone structures obtained by CO/ethene copolymerization in methanol.

ence of variable amounts of propene [9]. In these experimental conditions, the polyketones are featured by three different combinations of end groups: keto-ester, diester and diketone (Fig. 2).

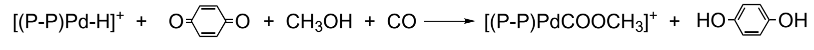
Optimal reaction conditions in methanol require the co-presence in the catalytic mixture of both a strong oxidant with $E° \geq 0$ (vs. SCE) and a protic acid with $pK_a \leq 4$ whose conjugate base must have a low binding affinity for Pd(II). *p*-Toluenesulphonic acid (TsOH) ($pK_a = -2.7$) and 1,4-benzoquinone (BQ, $E° = 0.7$ V) amply fulfill these requirements and indeed constitute the ingredients of most productive catalytic systems. Applying these experimental conditions, productivities as high as 11 kg polyketone (g of Pd)$^{-1}$ h^{-1} can be obtained [4a,4b,4c].

The main role of the protic acid is to create facile access of the monomers to the palladium center by substituting weakly bound ligands such as TsO^- or $CF_3CO_2^-$ (TFA^-) for $CH_3CO_2^-$ (OAc^-). The acid is also important for decreasing catalyst deactivation as it is able to convert inactive (P–P)Pd(0) into catalytically active $[(P–P)PdH]^+$. The most serious drawback of Pd(II)–diphosphine catalysts is actually their facile reduction to Pd(0) species in polyketone synthesis conditions. An electrochemical study in methanol has shown that the standard precursor $(dppp)Pd(OAc)_2$ undergoes a one-electron reduction already at -0.68 V (vs. SCE), followed by rapid degradation of the electrogenerated Pd(I) species (dppp = 1,3-bis(diphenylphosphino)-propane) [10]. On the other hand, the $[(dppp)PdH]^+$ moiety is not stable in methanol and slowly undergoes deprotonation with formation of (dppp)Pd(0) which may either separate Pd metal and free ligand or couple with $[(dppp)Pd]^{2+}$ to form the catalytically inactive binuclear complex $[Pd(dppp)]_2^{2+}$ [11]. Scheme 2 illustrates all the experimentally proven deactivation paths that a dppp–Pd(II) precursor may follow in the chemical environment of the copolymerization reactions. The compounds in the boxes are intrinsically inactive and can be converted to catalytically active Pd–H or Pd–OMe by using a protic acid, preferably in conjunction with an oxidant.

The oxidation of either Pd(0) or Pd(I) to Pd(II) is therefore the main role played by BQ, which is actually



Scheme 2. Possible deactivation paths of dppp–Pd(II) catalysts under CO/ethene copolymerization conditions.



Scheme 3. Role of BQ in the conversion of Pd–H into Pd–C(O)OMe.

employed in excess with respect to palladium. Another important function of the oxidant is to convert Pd–H into Pd–OMe as shown in Scheme 3. Initiation by Pd–OMe implies that copolymer has been obtained with either keto-ester or diester end groups depending on whether termination occurs by protonolysis or methanolysis, respectively (see Section 2.5.1) [8b].

Since the discovery of the effectiveness of Pd–dppp catalysts in 1984 at Shell Research, various dppp-like ligands have been designed and successfully employed to catalyze the CO/ethene copolymerization in combination with palladium(II) salts. Common ligand variations have generally involved substitution(s) at either the phenyl rings or the saturated carbon backbone; excellent results have been obtained also with tetrakisphosphines obtained by linking two dppp units with CH_2 spacers (Fig. 3) [12]. Ligand variations involving the substitution of alkyl groups for aryl groups on the phosphorus donor atoms are not considered in this review as they give rise to Pd(II) catalysts featured by scarce activity and selectivity. In fact, under standard copolymerization conditions, ligands with $P(alkyl)_2$ groups preferentially yield the alkoxycarbonylation of the olefin, most likely due to their reluctance to form *cis*-chelate structures [8b,13,14].

It has been found that the introduction of alkyl substituents in the 2-position of the carbon backbone of dppp does not significantly improve the catalytic performance of the corresponding Pd(II) precursors [10]. Eventually a decrease may occur. In contrast, a considerable increase in productivity, even by 50%, was observed when methyl groups were introduced in both 1-positions of the dppp backbone, particularly with *R*,*S* (*S*,*R*) stereochemistry as in *meso*-2,4-bis(diphenylphosphino)pentane (*meso*-bdpp) (Fig. 3) [10]. Under comparable experimental conditions, $(dppp)Pd(TFA)_2$, (*rac*-bdpp)$Pd(TFA)_2$ and (*meso*-bdpp)$Pd(TFA)_2$ have been reported to catalyze the CO/ethene copolymerization yielding 16, 17 and 24 kg polyketone (g Pd)$^{-1}$ in 3 h, respectively. Both electronic and steric factors have been suggested to account for the remarkable activity of the *meso*-bdpp catalyst. In particular, (*meso*-bdpp)$Pd(TFA)_2$ was found to undergo in methanol a quasireversible one-electron reduction ($E° = -0.77$ V vs. SCE), whereas both $(dppp)Pd(TFA)_2$ and (*rac*-bdpp)$(TFA)_2$ were irreversibly reduced ($E_p = -0.68$ and -0.71 V, respectively). It was therefore proposed that the increased activity of (*meso*-bdpp)$Pd(TFA)_2$ might also be due to the more facile re-oxidation of the one-electron reduced species by either BQ or H^+, which ultimately results in a large number of active Pd centers in the catalytic mixture [10].

The *R*,*S* (*R*,*S*) stereochemistry of the methyl groups makes the six-membered (*meso*-bdpp)Pd ring preferentially adopt a chair conformation with equatorial methyl groups and with one equatorial and one axial phenyl on each phosphorus atom as shown in sketch **A** of Fig. 4. In contrast, the *rac* isomer adopts in solution the well-known δ-skew conformation in which the steric hindrance due to the phenyl rings is diagonally positioned with respect to the PPdP plane (**B**, Fig. 4) [15]. In the absence of carbon substitution as in the dppp metallaring, many ring conformations are possible, but the two skew conformers are energetically equivalent with a preferred spatial disposition of the phenyl rings similar to that of the *rac*-bdpp catalyst. Whether the pseudo-chair conformation with two axial and two equatorial phenyls as in the (*meso*-bdpp)Pd ring disfavors the termination step or favors the propagation step was not established [10]. Recent kinetic and thermodynamic studies in CH_2Cl_2 suggest that a greater rigidity of the ligand backbone as in *meso*-bdpp favors the propagation step by decreasing the stability of the β-chelates $[(P–P)Pd(CH_2CH_2COR)]^+$ [16,17].

Higher activity for *meso*-bdpp as compared to (*S*,*S*) or (*R*,*R*)-bdpp and dppp has recently been observed also by Consiglio in the copolymerization of propene with CO catalyzed by cationic $[(P–P)Pd(solvent)_2]^{2+}$ complexes [18].

In combination with various dppp-like ligands, a non-coordinating counter-anion and BQ, dinitrogen ligands such as 2,2′-bipyridine (bipy), 1,10-phenanthroline

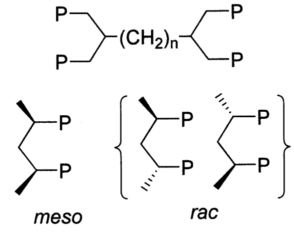


Fig. 3. Dppp-like ligands employed in CO/olefin copolymerization.

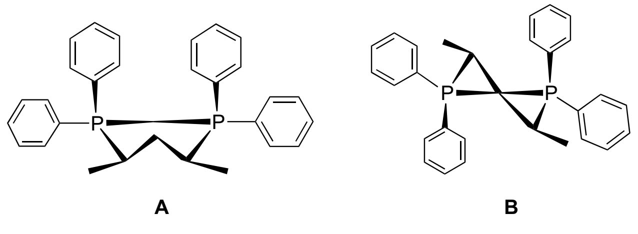


Fig. 4. Preferred conformations adopted by the six-membered chelate rings with *meso*-bdpp (chair, **A**) and *rac*-bdpp (δ-skew, **B**).

(phen) or 1,8-napthyridine (napy) have been reported to form bis-chelated Pd(II) precursors that, under comparable experimental conditions, are more efficient than dppp-Pd(II) systems (Fig. 5) [19,20]. The dinitrogen coligands have been found capable of modulating the proton concentration in the reaction mixtures with consequent beneficial effects on both the catalyst activity and the molecular weight of the polyketone product.

The bipy-containing catalysts display higher productivity as compared to the phen and napy analogs. This evidence has been interpreted in terms of the intrinsic electrochemical activity of bipy that may favor the oxidation of inactive Pd(0) to active Pd(II). The best catalytic systems are those containing bipy and *meso*-bdpp with 26 kg copolymer (g Pd)$^{-1}$ in 3 h versus 13 kg copolymer (g Pd)$^{-1}$ produced by the bipy/dppp combination. Steric factors associated with the chair conformation of the metallaring have been suggested to play a major role in enhancing the activity of the *meso*-bdpp precursors [20].

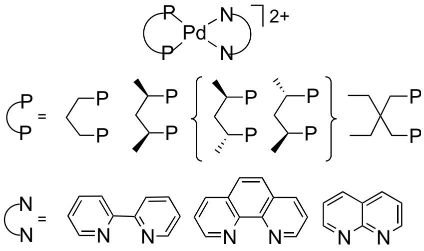


Fig. 5. Bis-chelated Pd(II) precursors formed by both dppp-like and dinitrogen ligands.

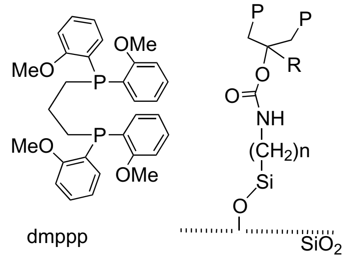


Fig. 6. Diphosphine ligands employed in either fluid or slurry CO/ethene copolymerization.

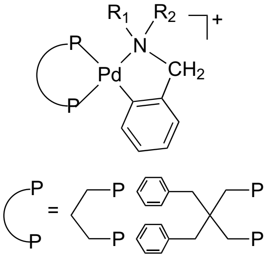


Fig. 7. Cationic palladacycles employed in CO/ethene copolymerization in aprotic solvents.

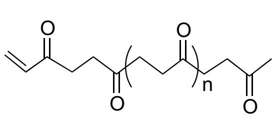


Fig. 8. Keto-vinyl end groups in the polyketones produced in aprotic media.

Excellent results in terms of both productivity and catalyst stability have been obtained by introducing a methoxy substituent in the *ortho* position of each phenyl group as in 1,3-bis{di(2-methoxyphenyl)-phosphino}propane (dmppp, Fig. 6) or in tetrakisphosphines [21]. A recent study with a water-soluble version of dmppp containing *m*-sodium sulphonatophenyl groups has confirmed that the methoxy substituents can exert both steric and electronic influence on the palladium center [22].

Rather efficient and remarkably stable CO/ethene copolymerization catalysts in aprotic solvents are generated by cationic palladacycles [{*o*-$C_6H_4(CH_2)N(R)_2$-Pd(P–P)}$^+$ containing an amine ligand (P–P = dppp, $(PhCH_2)_2C(CH_2PPh_2)_2$; R = H, CH_3, $CH_2C_6H_5$) (Fig. 7) [23].

The productivities of such catalysts are generally lower than those obtained with the mixed P–P/N–N ligands in methanol. However, a peak of productivity (33 kg (g Pd)$^{-1}$ in 14 h) has been obtained for $R_1 = H$, $R_2 = CH_2Ph$ using PF_6^- as counter-anion and BQ as organic oxidant. It is worth noticing that keto-vinyl end groups generally featured the polyketones produced in aprotic media (Fig. 8).

Effective terpolymerization catalysts in CH_2Cl_2 have also been obtained with (dppp)Pd$(OAc)_2$ in the presence of excess $B(C_6F_5)_3$ [24]. In these conditions, the polyketone product was found to contain fluoroaryl groups from the borane in the chain ends. This evidence, combined with the isolation of catalytically active (dppp)Pd{$(C_6F_5)[B(C_6F_5)_3]y$OH} ($y = 1$, 2), suggested a chain initiation involving migratory insertion of monomers into Pd–C_6F_5 (see also Section 2.5.1).

The alternating copolymerization of CO and ethene has been accomplished in CH_2Cl_2 by the use of either (dppp)Pd$(OAc)_2$ or (dppp)Pd(CO^{t}Bu)Cl in the presence of *tert*-butyl alumoxanes, $[(^tBu)Al(\mu\text{-}O)]_n$ ($n = 6$, 7, 9) or $[(^tBu)_7Al_5(\mu\text{-}O)_3(\mu\text{-}OH)_2]$ as co-catalysts [25]. The effects on the catalytic activity of the alumoxane and palladium concentrations were interpreted in terms of a Pd–alumoxane complex. The function of the alumoxane in the catalyst initiation depends on the palladium precursor: the alumoxane abstracts chloride from (dppp)Pd(CO^{t}Bu)Cl, while with (dppp)Pd$(OAc)_2$ the alumoxane initially alkylates the palladium and then abstracts the remaining acetate anion. Vinyl end groups on low molecular weight oligomers were obtained, which is consistent with a chain transfer mechanism involving β-hydrogen elimination.

In the industrial practice, the CO/ethene/propene copolymerization by Pd(0)–dppp catalysis is actually carried out in slurry or gas-phase systems. In the latter case, the diphosphine ligands are currently immobilized onto solid supports. The simplest heterogenization procedure is straightforwardly provided by the polyketone product itself that contains tethered palladium and is capable of catalyzing the copolymerization in solid–gas conditions, although at a slower rate than comparable homogeneous systems [5a]. Alternatively, the dppp ligand has been appropriately modified so as to be covalently tethered to an inorganic support such as silica (Fig. 6) [5b].

Very efficient solid–liquid heterogeneous dppp-based catalytic systems have been obtained by anchoring to silica palladium from $Pd(O_2CNEt_2)_2(NHEt_2)$, followed by use of the immobilized metal to catalyze the alternating CO/ethene copolymerization in methanol solution containing dppp or a structurally related ligand and an excess of protic acid [26].

Although still confined to fundamental research, the immobilization of Pd(II)–dppp copolymerization catalysts in water is an alternative heterogenization procedure at a good stage of development. As a general protocol, the dppp-like ligand is sulphonated so as to make its Pd(II) complexes soluble in water and therefore applicable to both aqueous catalysis with or without a solid support [27]. The first CO/olefin copolymerization reaction in water was reported in 1994 by Sen et al. who employed the catalyst precursor $[Pd(dppp\text{-}SO_3K)(H_2O)_2](BF_4)_2$ prepared in situ. The productivities in both copolymer and terpolymer were quite low however [28]. A remarkable improvement of the catalytic activity (up to 7 kg copolymer $(g\ Pd \times h)^{-1}$ was obtained a few years later by Sheldon et al. with the use of a sulphonated DPPPr–S ligand of better quality as well as the co-addition of TsOH in the reaction mixture (Fig. 9). The polyketone produced in this way was shown to contain both ketone and acid end groups (the mechanism for this reaction is discussed in Section 2.5.1) [29]. Quite similar productivities have also been obtained with the water soluble catalyst $Pd(Na_2DPPPDS)$(TFA) in the presence of an excess of TsOH and of BQ [30].

Unlike the DPPPr–S catalyst, $Pd(Na_2DPPPDS)$(TFA) exclusively produces copolymer with ketonic end groups due to the occurrence of the water gas shift reaction (Pd–H initiator) and the absence of hydrolysis of Pd–acyl (for the mechanism see Section 2.5.1). The copolymers and terpolymers produced in this way showed molecular weights ranging from 10 to 30 kg mol^{-1} [30].

As in methanol, the regioselective introduction of *o*-methoxy substituents in the phenyl rings of DPPPr–S as in $1,3\text{-}C_3H_6(P(C_6H_4\text{-}m\text{-}SO_3Na)_2)_2$ and the use of isolated Pd–Me and β-palladacycles precursors has been found to generate very efficient catalytic systems with productivities as high as 30 kg polyketone $(g\ Pd \times h)^{-1}$ for very low concentrations of Pd (Scheme 4). High molecular weight copolymers (20–125 kg mol^{-1}) were obtained using either aqueous or supported aqueous phase catalysis [22b].

2.2. Palladium catalysts stabilized by other diphosphine ligands

The influence of the structure of the diphosphine ligands on the activity of the corresponding Pd(II) catalysts was primarily investigated by Drent et al. [8b]. The variation was in the number of carbon atoms separating the diphosphino groups. Six catalyst systems were prepared from $Pd(NCMe)_2(TsO)_2$ and bidentate ligands of the formula $Ph_2P(CH_2)_mPPh_2$ ($m = 1$–6). The results of comparable CO/ethene copolymerization reactions showed that three is the magic number of CH_2 spacers for achieving the most efficient and selective copolymerization catalyst (Table 1).

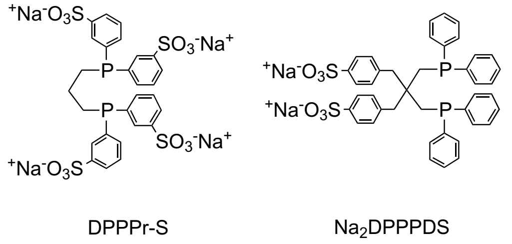
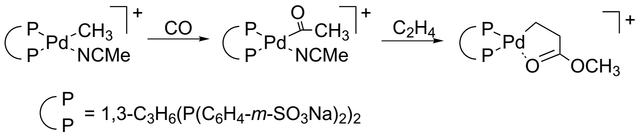


Fig. 9. Sulphonated diphosphine ligands employed in aqueous CO/ethene copolymerization.



Scheme 4. Formation of β-ketoalkyl palladacycles.

Table 1
Effect of ligand on CO/ethene copolymerization[a]

Ligand	$H(CH_2CH_2CO)_n$-OCH_3 (n)[b]	Productivity (g polymer $(g\ Pd \times h)^{-1}$)
$Ph_2P(CH_2)PPh_2$ (dppm)	2	1
$Ph_2P(CH_2)_2PPh_2$ (dppe)	100	1000
$Ph_2P(CH_2)_3PPh_2$ (dppp)	180	6000
$Ph_2P(CH_2)_4PPh_2$ (dppb)	45	2300
$Ph_2P(CH_2)_5PPh_2$ (dpppe)	6	1800
$Ph_2P(CH_2)_6PPh_2$ (dpph)	2	5

[a] Reaction carried out in 150 ml MeOH with $Pd(NCMe)_2(TsO)_2$ (0.1 mmol), $C_2H_4/CO = 1$, temperature = 84 °C, pressure = 45 bar.

[b] Average degree of polymerization determined by end-group analysis from ^{13}C-NMR spectra.

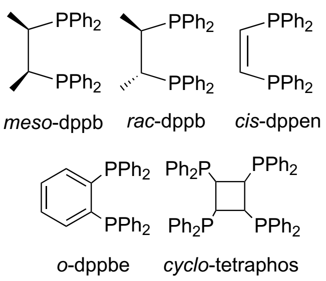


Fig. 10. Sterically rigid diphosphine ligands employed in CO/ethene copolymerization.

Table 2
Alternating CO/ethene copolymerization catalyzed by Pd(P–P)$(O_2CCH_3)_2$[a]

P–P ligand	Productivity (g polymer (g Pd)$^{-1}$)
Dppe	1000
rac-Dppb	8800
meso-Dppb	11 100
cyclo-Tetraphos	9800
cis-Dppen	5500
o-Dppbe	6400

[a] Conditions: precursor (0.01 mmol), MeOH (100 ml), 1,4-benzoquinone (0.8 mmol), TsOH (0.2 mol), initial $p(C_2H_4)$ (300 psi), initial p(CO) (300 psi), temperature 85 °C, time 3 h.

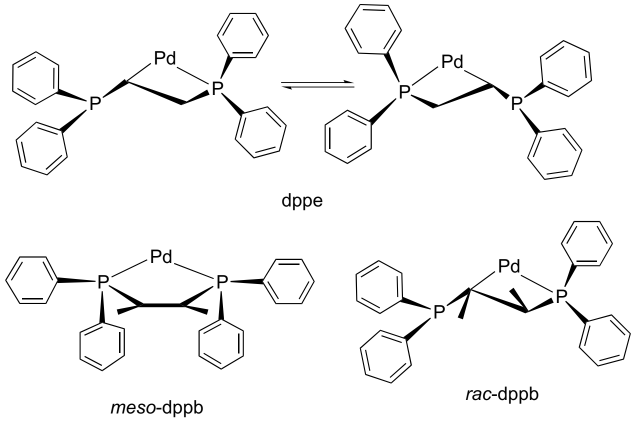


Fig. 11. Preferred conformations in solution of the five-membered metallarings with dppe, *meso*-dppb and *rac*-dppb.

Indeed, the molecular weight of the polyketone produced was found to decrease in the same order of the activity: dppp > dppb > dppe > dpppe. With the latter ligand cooligomers were almost exclusively obtained due to the lower stabilization of the chelating structure.

The different catalytic activity exhibited by the Pd(II) precursors with the $Ph_2P(CH_2)_mPPh_2$ ligands has been the subject of many studies. According to several authors, the Pd(diphosphine) chelate ring is the main factor that effectively controls the catalytic activity. Within this context, three hypotheses have been forwarded to account for the much lower productivity of the dppe-based catalysts as compared to the dppp-based analogs. Drent et al. have suggested that the energy barrier between the square-planar ground state and the five-coordinate transition state is much higher for dppe than for dppp [8b]. Chien et al. have proposed an alternative rationale based on the major ability of the dppe to undergo chelate ring opening [31]. Finally, the formation of a more stable metallacycle involving intramolecular interaction between the β carbonyl group of the propagating polymer and the Pd center has been suggested by Barron et al. to account for the lower activity of the dppe catalyst (see Section 2.5.1) [25].

Other authors have shown that the chelate ring size is not the only parameter controlling the copolymerization activity of Pd(diphosphine) catalysts. In fact, in some cases, the backbone rigidity of the diphosphine ligand and the overall steric crowding at the Pd center seem to be much more important than chelate ring size in determining the catalytic activity. This is certainly the case for the series of ligands, shown in Fig. 10, which have been employed, in conjunction with palladium acetate, to catalyze the copolymerization of CO and ethene.

In comparison with the analogous dppe catalyst, the productivity in polyketone increases remarkably, even by one order of magnitude, when two methyl groups are substituted for hydrogen atoms, especially with *meso* stereochemistry, or when the central carbon atoms of the diphosphine are made part of a cyclobutane ring (Table 2) [32,33].

Since all the ligands shown in Fig. 10 are less flexible than dppe, it was proposed that the skeletal rigidity of the chelating diphosphine (hence the spatial distribution of the phosphorus substituents) and the catalytic productivity are related to each other as is observed also for dppp and its 2,2′-methyl substituted derivatives *meso*- and *rac*-bdpp (vide infra) [10,32].

The preferred conformations of the five-membered chelate rings with dppe, *meso*-2,3-bis(diphenylphosphino)butane (*meso*-dppb) and *rac*-2,3-bis(diphenylphosphino)butane (*rac*-dppb) are illustrated in Fig. 11. The introduction of methyl substituents on the backbone carbon atoms fixes the Pd(*rac*-dppb) and Pd(*meso*-dppb) five-membered rings into single twisted and envelope conformations, respectively, and also forces the phenyl substituents on the phosphorus atoms to adopt different spatial distributions [15a,34].

As the diphosphine ligands maintain the chelating bonding mode all over the catalytic reaction (no change in chemoselectivity is actually observed), it has been suggested that the different conformations of the PPdP chelate ring influence the stability of the β and γ-keto chelate intermediates (see Section 2.5.1), which in their turn control the relative rate of the CO and ethene migratory insertions [4b].

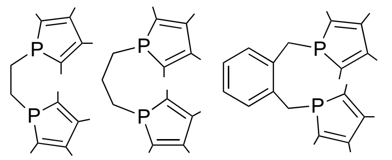


Fig. 12. Bis(phospholyl) ligands employed in CO/ethene copolymerization.

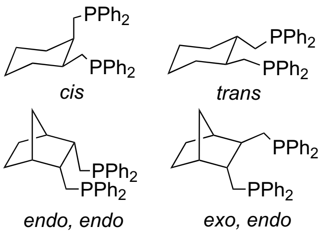


Fig. 13. Stereoisomeric diphosphine ligands employed in CO/ethene copolymerization.

A directly proportional correlation between catalytic activity and backbone rigidity of the diphosphine ligand has also been observed by Doherty for the bis(phospholyl) ligands shown in Fig. 12. Indeed, in comparable reaction conditions (MeOH, TsOH, 1:1 CO/ethene 10 bar, 90 °C, 1 h), the rigid 1,2-bis(2,3,4,5-tetramethylphospholyl)-*o*-xylene ligand is much more active (436 g of polyketone (g Pd)$^{-1}$) than 1,3-bis(2,3,4,5-tetramethylphospholyl)propane (48 g of polyketone (g Pd)$^{-1}$), while 1,2-bis(2,3,4,5-tetramethylphospholyl)ethane does not form any effective catalyst [35a].

To our knowledge, no clear-cut explanation of the role played by the rigidity/flexibility of the diphosphine ligands in determining the copolymerization rate as well as the overall productivity has been given so far. Indeed, too many chemical aspects and reaction steps may be influenced by changes in the ligand backbone: catalyst stability, propagation rate (energy barriers to migratory insertions, kinetic stability of the β- and γ-metallacycles) and chain transfer (metanolysis, protonolysis, β-elimination). Moreover, the solvent of the copolymerization reactions can play a crucial role in controlling the catalytic productivity. For example, $Pd(OAc)_2$(*meso*-dppb) is more active than $Pd(OAc)_2$-(dppe) by one order of magnitude in MeOH, whereas $[Pd(CH_3)(MeCN)($*meso*-dppb$)]PF_6$ and $[Pd(CH_3)(MeCN)(dppe)]PF_6$ are equally active in CH_2Cl_2 [33].

The actual relationship between stereochemistry of the diphosphine ligand and catalytic activity and/or chemoselectivity has recently been highlighted by Knight, Doherty and coworkers [35b]. The four diphosphines shown in Fig. 13 form palladium(II) complexes of the general formula $Pd(OAc)_2(P-P)$ which have been used as catalyst precursors for the CO/ethene copolymerization in MeOH in the presence of methansulphonic acid (10 bar 1:1 CO/ethene, 90 °C).

The catalyst system based on *cis*-1,2-bis(diphenylphosphinomethyl)cyclohexane was found to give a higher productivity in oligomeric polyketones (330 g (g Pd)$^{-1}$; degree of polymerization, $n = 16$) than that based on its *trans*-isomer (73 g (g Pd)$^{-1}$; $n = 20$). In contrast, the catalyst system based on *exo*,*endo*-2,3-bis(diphenylphosphinomethyl)norbornane was highly selective for the production of methyl propanoate (> 90%; polyketone 50 g (g Pd)$^{-1}$; $n = 14$)), and the *endo*,*endo*-isomer gave only polyketone although in very low yield (61 g (g Pd)$^{-1}$; $n = 13$). The chemoselectivity exhibited by the *exo*,*endo*-isomer has been tentatively explained with the occurrence of two distinct catalysts: one containing a chelating diphosphine, the other containing a monodentate phosphine to generate methyl propanoate.

A few other diphosphine ligands have been employed in conjunction with Pd(II) salts to catalyze the copolymerization of CO and ethene. In all cases, however, low productivity and selectivity in alternating polyketone were observed. For example, the substitution of either PPh_2 or PR_2 ($R = Bu^t$, Pr^i, Cy) for the phosphole ring in the *o*-xylyl-based ligands shown in Fig. 12 decreased the selectivity in alternating polyketone with consequent increase in methyl propanoate production [14b].

Low productivity has been reported for the reactions catalyzed by phosphinite-modified palladium catalysts [36], while 1,1′-bis(diphenylphosphino) ferrocene catalysts are scarcely selective producing substantial amounts of cooligomers (Fig. 14) [37].

2.3. Palladium catalysts with miscellaneous ligands

The success of diphosphines in making up efficient CO/ethene copolymerization catalysts immediately stimulated much research aimed at looking into opportunities with different classes of ligands.

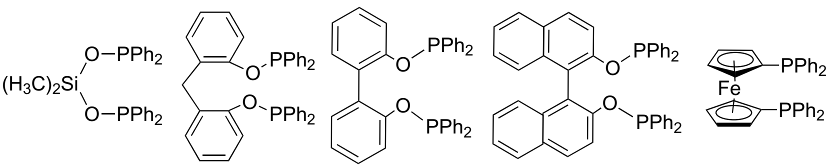


Fig. 14. Miscellaneous diphosphine ligands employed in CO/ethene copolymerization.

Sterically rigid dinitrogen ligands were the first class of ligands considered for the design of new catalysts. Soon, however, it turned out that only bipy, phen and their alkyl-substituted derivatives form efficient alternating copolymerization catalysts in either homogeneous or heterogeneous conditions (Fig. 15) [26,38,39]. In fact, the dinitrogen ligands are generally more useful than diphosphines for mechanistic studies (see Section 2.5.2). The complex $[Pd(phen\text{-}SO_3Na)(H_2O)_2](BF_4)_2$, obtained by reacting $[Pd(MeCN)_4](BF_4)_2$ with the water-soluble phen derivative phen-SO_3Na (Fig. 15), was found to be an active catalyst for the copolymerization of CO and ethene in aqueous solution [28].

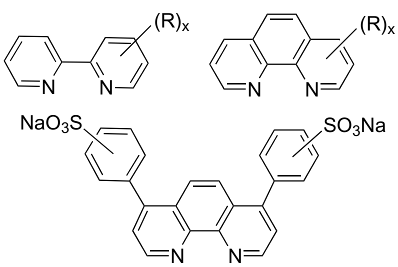


Fig. 15. Sterically rigid dinitrogen ligands employed in CO/ethene copolymerization.

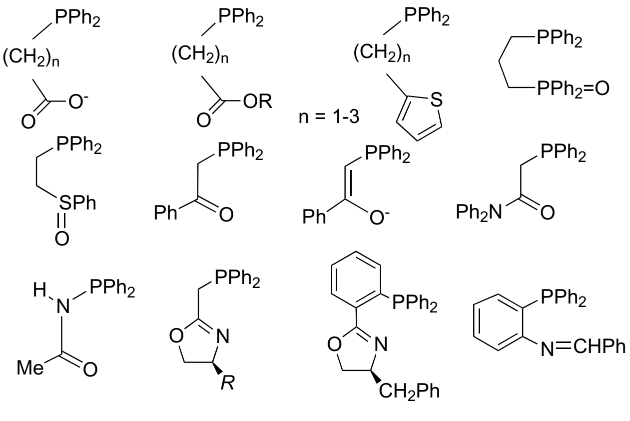


Fig. 16. P–O, P–N, and P–S ligands employed in CO/ethene copolymerization.

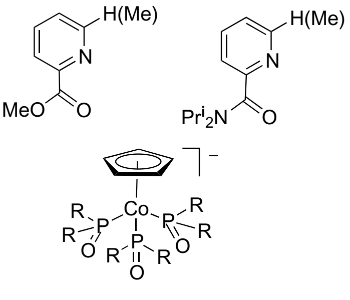


Fig. 17. Miscellaneous ligands employed in CO/ethene copolymerization.

Palladium(II) complexes with either bipy or phen are active, but the activity is generally low in comparison with diphosphine catalysts. The reverse occurs for the copolymerization of α-olefins, such as styrene, for which dinitrogen catalysts are much more efficient than diphosphine catalysts (see Section 3).

Either monochelated $[Pd(N{-}N)(RCOO)_2]$ or bis-chelated $[Pd(N{-}N)(N'{-}N')][X]_2$ precursors with ligand N–N either equal or different to N′–N′ and $X = PF_6^-$, TFA^-, OAc^- have been used to copolymerize CO and ethene. The bis-chelated catalysts are more efficient than the corresponding monochelated derivatives and the best combination of ligand and anion was obtained with phen and PF_6^- [38,40]. Irrespective of the precursor, the catalytically active species was proposed to contain one chelating ligand, while the second molecule is important for increasing both the stability of the catalysts towards the decomposition to palladium metal and improving the molecular weight [19].

After P–P ligands, the heteroditopic phosphine ligands containing oxygen, nitrogen or sulfur functions give rise to the second largest class of Pd(II) CO/ethene copolymerization catalysts. Their catalytic activity is even lower than that of dinitrogen ligands however [41,42].

A survey of the P–O, P–N and P–S ligands that have been employed together with Pd(II) salts to copolymerize ethene and CO is shown in Fig. 16.

In general, the Pd(II) precursors are either cationic species containing methyl, allyl or solvent co-ligands. Neutral catalysts have also been used, but they are generally less efficient than the cationic derivatives [41a]. The reactions are commonly carried out in dichloromethane at 20–90 °C. Irrespective of the combination of the hard and soft donor atom set and of the experimental conditions, the productivity in polyketones is at least two orders of magnitude lower than that obtainable with dppp-like ligands. Moreover, only a few systems are selective for high-molecular weight polyketones. As a general trend, it is observed that the catalysts containing P–O ligands, especially at high ethene/CO ratios, yield alternating cooligomers with the structure $R[C(O)CH_2CH_2]_mH$ ($m \geq 1$; $R = CH_2{=}CH{-}$, $CH_2{=}CHCH_2CH_2{-}$, $CH_3CH{=}CHCH_2{-}$) [41b]. In contrast, P–N ligands can form selective copolymerization catalysts irrespective of the partial pressure of the monomers [41e,41f,41h].

Cationic methylpalladium(II) complexes with the N–O ligands methylpicolinate, methyl 6-methylpicolinate and 6-methyl-*N*,*N*-diisopropylpicolinamide have also been tested as CO/ethene copolymerization catalysts (Fig. 17) [41c]. Like all the other mixed-donor ligands, the (N–O)Pd(II) precursors give rise to very modest copolymerization catalysts, which, however, have been very useful to study some important elementary steps (migratory insertions) relevant to the copolymerization process (see Section 2.5.2).

Selective but scarcely efficient Pd(II) catalysts for high molecular weight polyketone have been obtained with the tripodal anionic ligand $[(C_5H_5)Co\{P(O)(OMe_2\}_3]^-$ shown in Fig. 17 [43].

Immobilization of palladium(II) complexes with ether–phosphine ligands has been achieved by sol–gel procedures, and the resulting polysyloxane-bound catalysts have been employed to promote the CO/ethene copolymerization in solid–gas conditions yielding small amounts of high molecular weight polyketone [44].

2.4. Other metals than palladium with various ligand systems

The alternating copolymerization of CO and olefins is presently dominated by palladium(II)–diphosphine catalysts. In the early stages of development of this reaction, however, other metals were successfully employed. Nickel was actually the metal used to catalyze the first CO/ethene copolymerization already in 1941 by Farbenfabriken Bayer [3]. Later Reppe and Mangini showed that $K_2Ni(CN)_4$ in water produced low melting CO/ethene cooligomers in milder experimental conditions [45]. Further improvements were successively made by Shell [46] and by Klabunde [47] and Keim [41b] who independently reported new nickel catalysts based on bidentate anionic P–O ligands. Klabunde has also shown that Ni(II) systems, like Pd(II) [48], can be active for the synthesis of diblock (polyethene)(*alt*-E-CO)polymers [49]. The most efficient nickel-based systems are still those containing the *o*-methoxy-modified diphosphine 1,2-bis(bis(2-methoxyphenyl)phosphino)ethane [46b,46c]. No clear-cut explanation of the beneficial effect on the productivity caused by the *o*-methoxy substituents has been reported so far. As previously suggested for *o*-methoxy-modified dppp ligands [22], it is very likely that electronic effects play a more major role than steric effects in enhancing the catalytic productivity. Rhodium carbonyls have been tested as copolymerization catalysts, but both the productivities and the molecular weights are much lower than those obtainable with phosphine-modified palladium catalysts [50].

Nowadays, nickel remains the only alternative metal to the more expensive palladium and intense research efforts are still being made to design efficient nickel catalysts. Some recent advances in nickel assisted copolymerization reactions have been reported by Cavell et al. [51] and by Kläui et al. [52]. The first authors have described a family of arylnickel complexes of the general formula [NiR(N–O)L] where N–O is one of the bidentate ligands shown in Fig. 18. These Ni(II) precursors catalyze the copolymerization of ethene and CO in mild conditions, yielding either high molecular weight polymers or lower cooligomers depending on the basicity of the N–O ligand (i.e. the molecular weight of the polyketone decreases with the basicity of the ligand). Besides scarce activity, a major drawback of these Ni(II) catalysts is that the polymerization must be started with ethene alone since CO acts as a catalyst poison [51]. A Ni(II) system that tolerates a CO atmosphere and catalyzes the CO/ethene copolymerization in very mild conditions (60 °C, 50 bar CO/ethene, toluene) is the complex $[Ni(o\text{-tolyl})(PPh_3)(\eta^2\text{-Tp}^{Ph})]$ where Tp^{Ph} is the tris(pyrazolyl)borate ligand shown in Fig. 18. Also in this case, however, a very low productivity in alternating polyketone was obtained [52].

2.5. Mechanism of CO/ethene copolymerization by palladium(II) catalysis with bidentate ligands

2.5.1. P–P ligands

The first exhaustive mechanistic interpretation of the copolymerization of CO and ethene in alcoholic solvents promoted by cationic palladium complexes with diphosphine ligands was reported by Drent et al. in 1991 on the basis of a careful end-group analysis of the polyketone material [8b]. Since then innumerable model and in situ studies have been carried out, applying different experimental and theoretical approaches, which have largely contributed to a better understanding of the initiation, propagation and termination steps as well as the structure, relative stability and exchanges processes of either active intermediates or resting states. Most of these studies have exhaustively been reviewed by Sen in 1993, by Drent and Budzelaar in 1996, and by Sommazzi and Garbassi in 1997 [4a,4b,4c].

As the general mechanistic concepts proposed by Drent are still accepted as being essentially correct, only a brief comment of the catalysis cycle reported in Scheme 5 is given here.

Two competing cycles, connected by two cross termination steps, would be contemporaneously at work for the production of the polyketone in methanol, the prevalence of either cycle depending on the experimental conditions. Cycle B initiates (***I***) with the insertion of

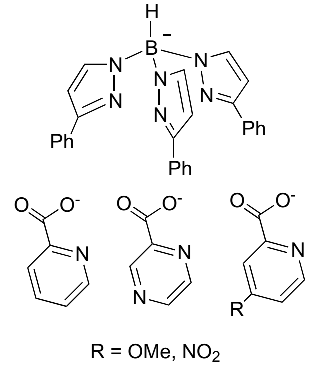
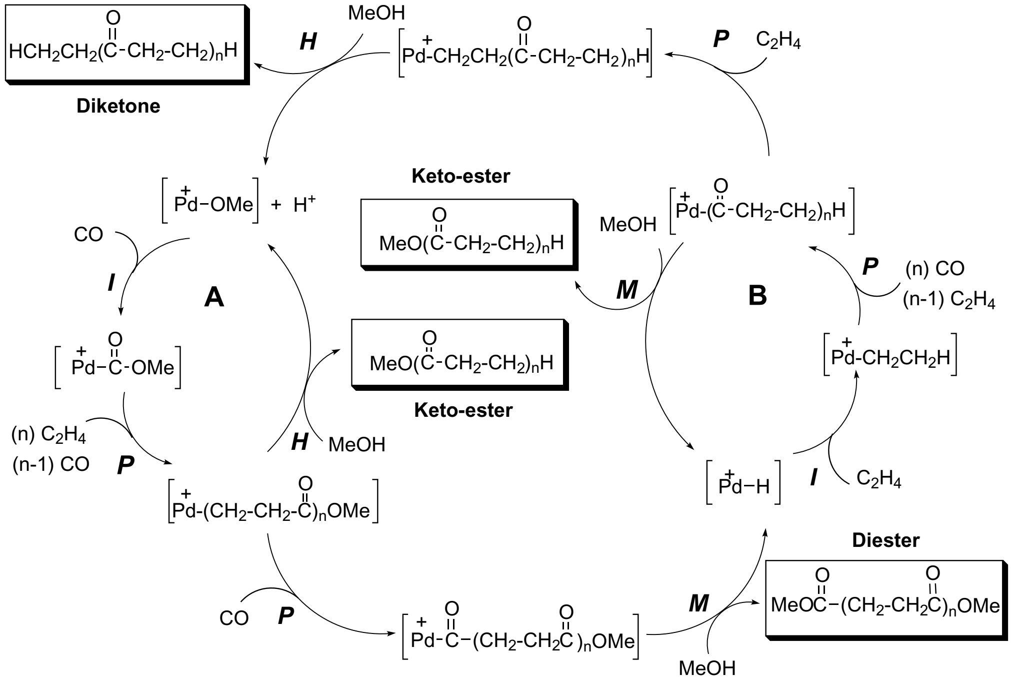


Fig. 18. Ligands employed in CO/ethene copolymerization by Ni(II) catalysis.



Scheme 5. Proposed mechanism of CO/ethene copolymerization by diphosphine palladium(II) catalysis.

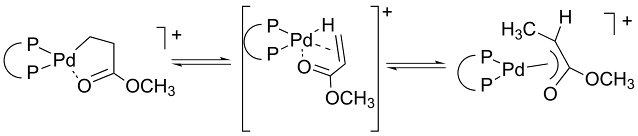
ethene in a Pd–H bond that can be generated in the catalytic mixture by a variety of ways, in particular when the methanol solvent contains traces of water (water gas shift reaction) [53]. Ethene insertion and CO insertion in the resulting ethyl complex are rapid and reversible, whereas the second ethene insertion in the Pd acyl is irreversible so that 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 keto-ester 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 in a Pd–OMe bond to give a Pd carbomethoxy complex. Cycle **B** is also responsible for the production of the copolymer with the diester structure via methanolysis of a Pd–acyl bond.

Catalytic experiments at different temperatures or in the presence of organic oxidants such as 1,4-benzoquinone have shown that the most probable initiator is a palladium hydride and that the main termination mechanism is thus methanolysis; kinetic studies suggest that ethene insertion is the rate-determining step in polyketone formation [4b].

By reacting MeOD with either [(P–P)PdCH_2-$CH_2C(O)CH_3$](OTf) or [(P–P)Pd$CH_2CH_2C(O)OCH_3$](OTf) (P–P = dppp; dppf = diphenylphosphinoferrocene), van Leeuwen et al. have recently demonstrated that the two chain-transfer mechanisms of CO/ethene copolymerization, i.e. protonolysis of Pd–CH_2CH_2-C(O)-chain and methanolysis of Pd–C(O)-chain, occur simultaneously. Most importantly, the former chain-transfer involves termination via isomerization of the chelate β-ketoalkyl ligand into enolate, followed by protonation with methanol and subsequent initiation by CO insertion into Pd–OCH_3 species (Scheme 6) [54].

By using the dissymmetric diphosphine 1-diphenylphosphino-2-*tert*-butyl-3-dicyclohexylphosphino-prop-1-ene, van Leeuwen et al. have demonstrated that the insertion of CO into Pd–CH_3 proceeds via migration of the hydrocarbyl group to the CO ligand [55].

The factors that control the strictly alternating copolymer chain with no detectable errors (e.g. microstructures involving double insertion of ethene) have been the object of detailed studies since the discovery of the effectiveness of Pd(II)–dppp catalysts for the copolymerization of CO and olefins by Drent. Sen was the first to demonstrate that double carbonylation is thermodynamically unfavorable and to suggest that the higher binding affinity of palladium(II) for CO relative to ethene inhibits multiple ethene insertions even in the presence of very



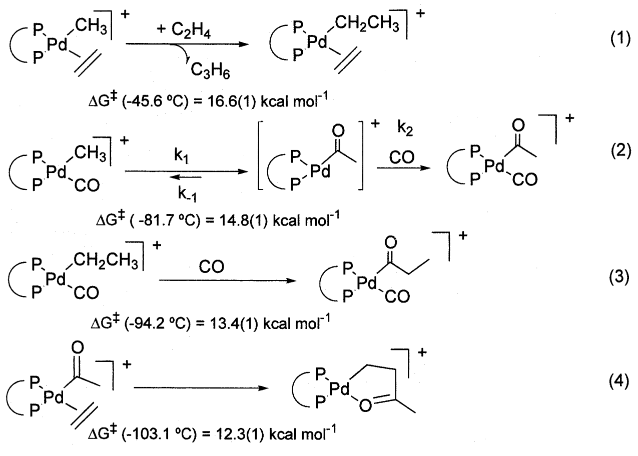
Scheme 6. Mechanism of β-chelate ligand to enolate isomerization.

low concentrations of CO [8b,56]. It follows that, once a palladium alkyl is formed, CO coordination ensures that the next monomer will be a CO molecule to generate the acyl complex.

The flawless nature of the alternating copolymerization has stimulated much research aimed at understanding the intimate chemical reasons governing the process. In particular, several studies of the migratory insertion reactions of carbonyl(alkyl), ethene(alkyl), and ethene(acyl) compounds have been carried out applying either experimental or theoretical approaches [57]. In all cases, Sen's intuition of the existence of a rigid thermodynamic and kinetic control proved to be valid.

An excellent kinetic study of migratory insertion reactions of the ligands that are involved at the (dppp)Pd(II) fragment in either the propagation cycle of CO/ethene copolymerization or ethene dimerization to butenes has been reported by Brookhart et al. [57e]. First-order kinetics have been established for the insertion reactions 1–4 whose free energies of activation have been determined experimentally by ^{1}H-NMR spectroscopy (Scheme 7). For reactions 1 and 2, the $\Delta H^{\ddagger}$ [15.2(7) and 14.8(7) kcal mol^{-1}, respectively] and $\Delta S^{\ddagger}$ [$-6.2(2.9)$ and 0.1(3.5) cal mol^{-1} K^{-1}, respectively] parameters were calculated from Eyring plots.

The thermodynamic parameters associated with the migratory insertion of ethene into the Pd–CH_2CH_3 bond were also determined ($\Delta G^{\ddagger}$ 16.3(1) at -33.7 °C; $\Delta H^{\ddagger}$ 15.9(8) kcal mol^{-1}; $\Delta S^{\ddagger}$ $-1.6(3.7)$ cal mol^{-1} K^{-1}). In contrast to theoretical results reported by Morokuma et al. [57d] and Ziegler et al. [57b,57c] as well as previous studies from the same authors with Pd(II)–phen model compounds [58a], the lowest experimental energy barrier was found for the migratory insertion of the acyl(ethene) complex (reaction 4).



Scheme 7. Kinetic study of migratory insertion reactions occurring at the (dppp)Pd(II) fragment.

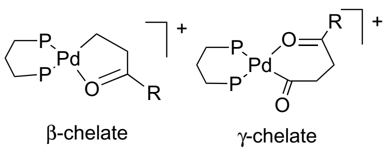


Fig. 19. β- and γ-chelates as catalyst resting states during CO/ethene copolymerization.

On the basis of the relative rates of alkyl to CO and alkyl to ethene migratory insertion reactions, it was estimated that sequential ethene insertions (errors in the alternating copolymer) occur once for every ca. 10^5 insertions of CO into the Pd–alkyl bond [57e].

Using in situ NMR spectroscopy, Brookhart et al. have tried to determine the activation barriers for the migratory insertion steps corresponding to chain growth in CO/ethene copolymerization catalyzed by dppe-derived nickel(II) complexes [58b]. Surprisingly, activation barriers remarkably lower than those of analogous dppe-palladium catalysts were obtained (<10 kcal mol^{-1}), which contrasts with the much lower copolymerization activity of nickel as compared to palladium. The isolation of several four- and five-coordinate intermediates relevant to the alternating copolymerization process led the authors to conclude that nickel is much less active than palladium for the formation of a strongly stabilized catalyst resting state relative to the transition state for the turnover-limiting step [58b].

The discovery of stable Pd(II) β-metallacycles obtained by olefin insertion in Pd–acyl bonds (Fig. 19) has led several authors to conclude that the greater binding affinity of CO to Pd(II) ions as compared to ethene and the thermodynamics preventing double CO insertion are not the only factors accounting for the perfectly alternating structure and the lack of termination by β-elimination [4b,17,59]. It is agreed, in fact, that the internal coordination of the growing polymer chain to the metal center as in the chelate species shown in Fig. 19 contributes to create strict alternation and also inhibits β-elimination paths.

Displacement of the chelate carbonyl by ethene is not an easy process, essentially for steric reasons, and apparently contributes to raise the energy barrier to ethene insertion in Pd–alkyl under polyketone synthesis conditions. Carbon monoxide is smaller and exhibits a greater binding affinity for palladium than ethene. It was suggested, therefore, that β-chelate opening is brought about by CO to generate a six-membered metallacycle in which the chelate carbonyl group is located γ with respect to palladium. As six-membered rings are less stable than five-membered ones, it was then proposed that propagation occurs by displacement of the γ carbonyl group by ethene, followed by formation of the next five-membered ring [4b].

This mechanistic view of the propagation cycle involving Pd–diphosphine catalysts is still largely accepted.

Recently, however, a different mechanism has been proposed by Drent et al. on the basis of gas-phase CO/ethene copolymerization experiments in the presence of solid catalysts as occurs in actual industrial processes [60].

Polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) was employed to follow the reaction of CO, C_2H_4 and CO/C_2H_4 with microcrystalline (dppp)Pd(CH_3)(OTf) deposited onto a gold coated wafer. Single insertion steps were observed by alternately exposing the catalyst precursor to low CO (500–333 mbar) and ethene (333 mbar) pressures (Fig. 20).

The PM-RAIRS study clearly showed that the β- and γ-keto chelate complexes $[(dppp)Pd\{CH_2CH_2C(O)CH_3\}]^+$ and $[(dppp)Pd\{C(O)CH_2CH_2C(O)CH_3\}]^+$ are resting-states in equilibrium under catalytic conditions (666 mbar CO/ethene, room temperature). Most importantly, it was discovered that ethene insertion into the Pd–acyl bond of the γ-keto chelate complex $[(dppp)Pd\{C(O)CH_2CH_2C(O)CH_3\}]^+$ does not occur unless some CO is present, in other words ethene insertion is CO assisted in solid–gas copolymerization. Based on the PM-RAIRS study, the cycle outlined in Scheme 8 was proposed, to account for the catalytic propagation.

In an attempt to rationalize the CO-assisted insertion of ethene into the Pd–acyl bond it was proposed that the substitution of the chelating ketone in **c** by ethene proceeds in two consecutive steps: associative substitution of the chelating ketone by CO (**c** → **d** → **e**), followed by associative substitution of CO by ethene (**e** → **f** → **i**). The disruption of the chelate structure of **c** was proposed to be more facile for CO than for ethene for steric reasons (end-on versus side-on approach).

Pd(II) complexes structurally similar to some intermediate species in the catalytic cycle shown in Scheme 8 have been intercepted and characterized in homogeneous CO/ethene copolymerization reactions catalyzed by Pd–diphosphine complexes, i.e. intermediates **g**, **e** and **i** [54,57a,57e].

The information provided by the model organometallic and theoretical studies has certainly contributed to expand our knowledge of the copolymerization mechanism allowing for improved catalyst design. Nonetheless, one has to be conscious that the environment of highly efficient polyketone catalytic reactions is much more complicated than any model system, and that intermediates are usually too reactive to isolate or even to detect. Recently, however, experimental evidence for intermediate species in actual catalytic conditions has been reported by some groups with the use of high-pressure spectroscopic techniques.

Luo et al. have studied the copolymerization of CO and ethene assisted by Pd(II)/dppp catalysts (MeOH, CF_3COOH, 60 bar 1:1 CO/C_2H_4) via ^1H-NMR, ^{31}P-NMR, IR and EXAFS techniques [61]. Most of the results obtained applying this multiform spectroscopic investigation were in fairly good agreement with the organometallic model studies. A series of Pd–K-edge

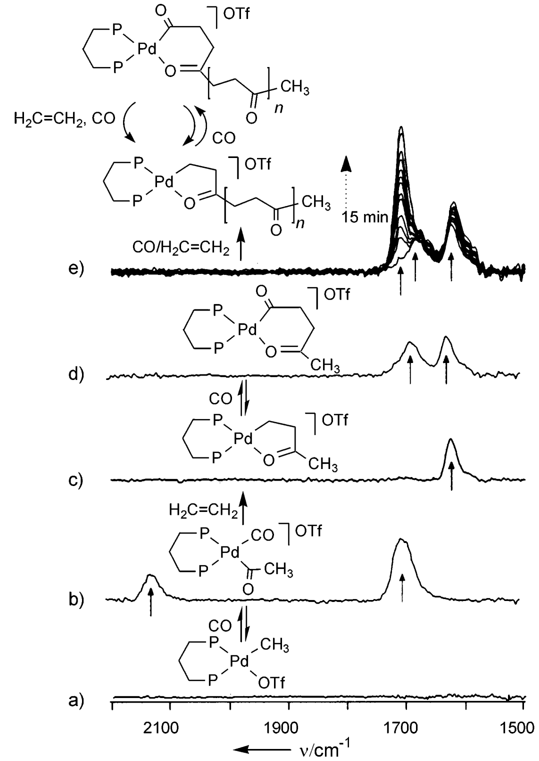
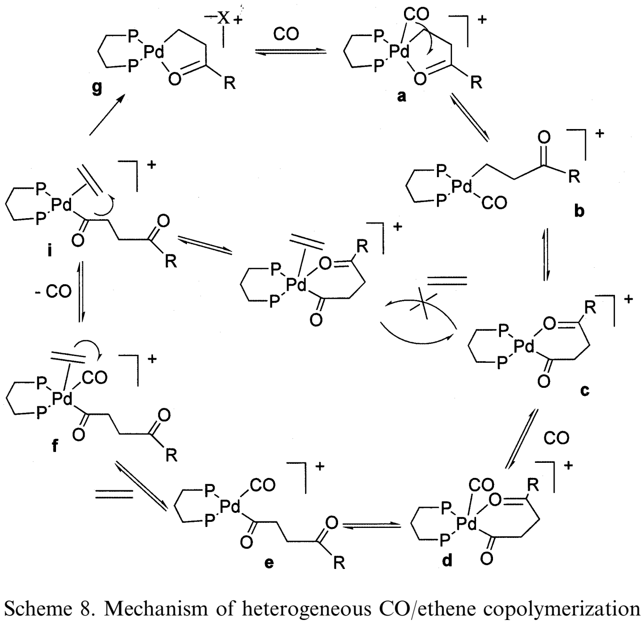


Fig. 20. In situ PM-RAIRS spectra of a microcrystalline sample of $[(dppp)Pd(CH_3)(OTf)]$. (a) At room temperature; (b) under 500 mbar CO; (c) under 2 mbar CO and 333 mbar of ethene; (d) under subsequent exposure to 750 mbar CO; and (e) during subsequent polymerization under 666 mbar of CO/ethene (evolution of the spectrum at 15 min intervals). Taken from Ref. [60].



Scheme 8. Mechanism of heterogeneous CO/ethene copolymerization proposed on the basis of the PM-RAIRS study.

EXAFS experiments showed the presence of five-coordinate Pd(II) species in the course of polyketone formation, while an IR study with 40 bar C_2H_4 and 4 bar CO showed the formation of three intermediates species that were assigned the (ethene)acyl, β-metallacycle and (alkyl)CO structures illustrated in Fig. 21. Increasing the partial pressure of CO was found to increase the concentration of the (alkyl)CO complex at the expense of those of the other two Pd(II) species. ^{1}H-NMR assignments were also made, which however must be considered with extreme caution given the presence of the very many species in the reaction mixture.

^{31}P-NMR spectra in catalytic conditions showed the exclusive presence of a unique phosphorus signal with the chemical shift of the Pd(II) precursor prior to CO/C_2H_4 addition. A similar ^{31}P-NMR picture had previously been reported by Bianchini et al. for CO/ethene copolymerizations catalyzed by a variety of Pd(II)–diphosphine complexes in either methanol or 1,1,1,3,3,3-hexafluoro-2-propan-2-ol-d_2 (HFIP-d_2) where the reactions are truly homogeneous [10,20]. It has been suggested that C_2H_4 initiates the copolymerization reaction which involves the formation of several intermediate species and the occurrence of fast equilibria none of which allows for the NMR detection of any catalytically active species. The single ^{31}P-NMR resonance was therefore assigned to the (dppp)Pd^{2+} moiety which is in rapid exchange with solvent molecules and counteranions and is ready to generate catalytically active palladium hydride by several well-established routes [4b]. It is noteworthy that the reaction of the catalyst precursors with CO alone led to their rapid deactivation due to the formation of both the binuclear complex $[Pd(dppp)_2]^{2+}$ and inactive Pd carbonyl complexes [11b,11c,11d].

A sequence of variable-temperature high-pressure ^{31}P-NMR spectra acquired in the course of a CO/ethene copolymerization reaction catalyzed by $(dppp)Pd(TFA)_2$ in MeOH is presented in Fig. 22.

The only ^{31}P-NMR signal observed all over the catalytic process was a broad singlet at the same chemical shift of the Pd(II) precursor. As the polyketone production was in progress, the intensity of this signal decreased slowly, due to tethering of palladium to the polymer accumulated at the liquid–gas interface [10]. An essentially identical ^{31}P-NMR picture was observed for the aqueous-phase CO/ethene copolymerization catalyzed by the water-soluble complex $Pd(Na_2DPPPDS)$(TFA) in the presence of an excess of TsOH (Scheme 9) [30].

Variable-temperature ^{31}P-NMR spectra recorded during polyketone formation showed that, at least on the NMR timescale, water dominates the coordination chemistry of palladium. At room temperature, neither CO nor ethene formed adducts with palladium and the NMR spectrum was identical to that of the precursor in neat water. The broad featureless resonance in Fig. 23a was ascribed to the formation of several species containing trifluoracetate, p-toluenesulphonate, H_2O, hydroxo and/or μ-hydroxo species, eventually in equilibrium with each other. In contrast, a single sharp signal was reversibly observed at 85 °C when the polymer began to separate as an off-white microcrystalline solid and accumulated at the water–gas interface (Fig. 23b).

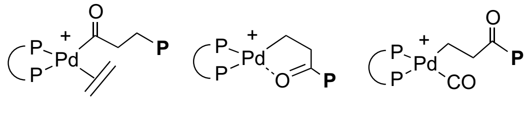


Fig. 21. Palladium(II) species intercepted by NMR or IR spectroscopy during CO/ethene copolymerization.

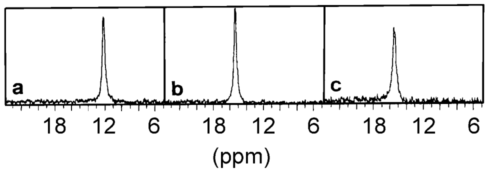
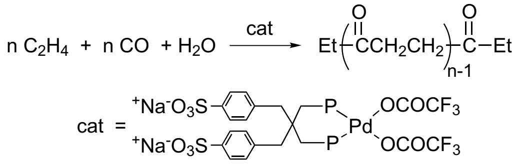


Fig. 22. Selected $^{31}P\{^1H\}$-NMR spectra recorded during a CO/ethene copolymerization assisted by $(dppp)Pd(TFA)_2$ (10 mm sapphire tube, MeOH-d_4, 20–85 °C, 81.01 MHz). (a) Spectrum at room temperature; (b) after addition of TsOH (5 equiv.) and pressurization with 600 psi 1:1 CO/ethene; and (c) at 85 °C during copolymer synthesis.



Scheme 9. Polyketone formation in aqueous CO/ethene copolymerization catalyzed by the water-soluble complex $Pd(Na_2DPPPDS)$-(TFA).

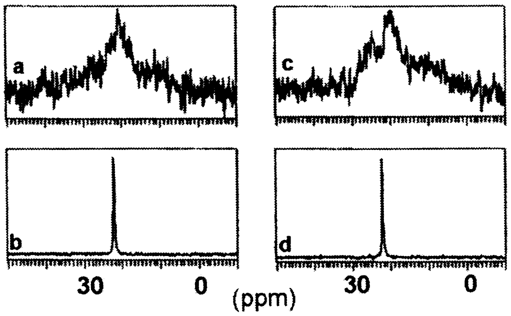
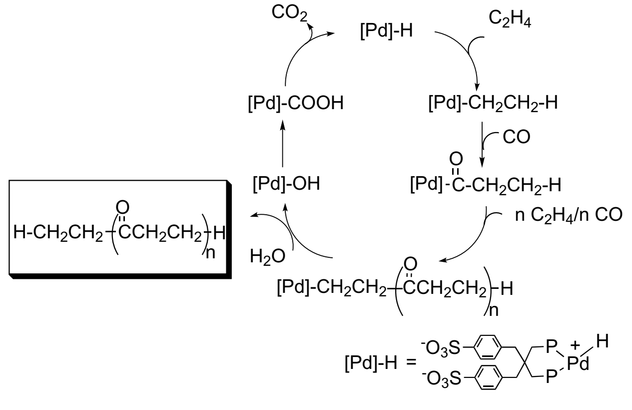


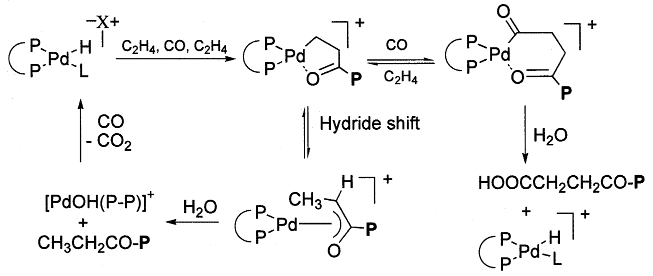
Fig. 23. Selected $^{31}P\{^1H\}$-NMR spectra recorded during a CO/ethene copolymerization assisted by $Pd(Na_2DPPPDS)(TFA)$ in the presence of 20 equiv. of TsOH and a 1:1 CO/C_2H_4 pressure of 600 psi (10 mm sapphire tube, D_2O, 20–85 °C, 81.01 MHz). (a) Spectrum at room temperature; (b) heating to 85 °C; (c) cooling to room temperature; and (d) heating again at 85 °C.

Since the ^{31}P-NMR signals shown in Fig. 23a and b were also observed in an aqueous solution of the catalyst precursor in the presence of an excess of TsOH, it was proposed that, like in MeOH, most of the palladium in solution exists as (DPPPDS)Pd moieties stabilized by coordination of both water and the conjugate base of the protic acid. From this resting state, a very small aliquot of catalytically active palladium is delivered into the catalysis cycle [30].

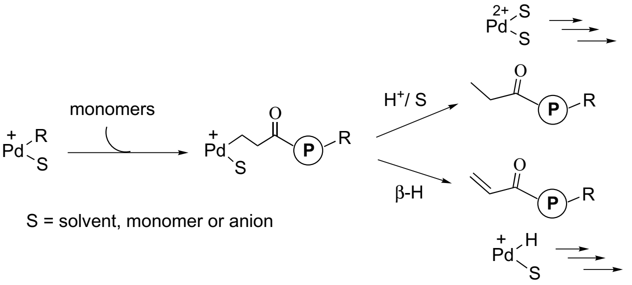
On the basis of the exclusive formation of copolymer bearing ketonic end groups (diketone structure) and the occurrence of the water gas shift reaction, it was proposed the catalysis cycle shown in Scheme 10 for the aqueous reaction promoted by Pd(Na_2DPPPDS)(TFA).



Scheme 10. Proposed mechanism of CO/ethene copolymerization catalyzed by the water-soluble catalyst precursor Pd(Na_2DPPPDS)-(TFA).



Scheme 11. Propagation and chain-transfer mechanisms in the CO/ethene copolymerization catalyzed by water-soluble palladium catalysts modified with sulphonated diphosphine ligands.



Scheme 12. General mechanism of the CO/ethene copolymerization in aprotic media.

The cycle in water contains the usual steps of insertion of ethene into Pd–H to give Pd–ethyl (initiation), CO insertion to give Pd–acyl, $n$$C_2H_4$/$n$CO insertions (propagation), and hydrolysis to give Pd–OH (termination). Either water gas shift or reaction of the protic acid co-reagent with reduced Pd(0) species have been proposed to account for the initial formation of Pd–H moieties [30].

The mechanism proposed by Sheldon et al. for the alternating copolymerization of CO and ethene catalyzed by Pd(II) complexes with various diphosphine ligands sulphonated at the phenyl substituents is quite similar (see Section 2.1) to that shown in Scheme 10 except for the occurrence of a termination step involving hydrolysis of Pd–acyl as demonstrated by the obtainment of some copolymer bearing acid end groups [29a]. On a purely speculative basis, Sheldon has proposed the formation of β and γ metallacycles to account for the two different chain transfer mechanisms (Scheme 11). In particular, hydrolysis of the γ metallacycle would give acid end groups and Pd–H, while the protonation of the enolate, in equilibrium with the β metallacycle via hydride shift, would give keto end groups and Pd–OH [29b].

As for the mechanisms of copolymerization in aprotic media, it is generally agreed that they are quite similar to cycle **B** in Scheme 5, the main differences being a Pd–alkyl initiator and termination occurring by either protonolysis or β-H elimination (Scheme 12) [4a,4b,4c,23].

2.5.2. N–N ligands

The general mechanistic issues established by Sen [56] and Drent [8b] for phosphine-modified Pd catalysts are unanimously considered as essentially valid for dinitrogen ligands as well as any bidentate chelating ligand that gives rise to an effective copolymerization catalyst. Indeed, many dinitrogen ligands form active copolymerization catalysts in conjunction with Pd(II) ions, but the activity is generally low in comparison with dppp-based catalysts. However, dinitrogen ligands have proved to be more amenable than diphosphines for detailed kinetic and thermodynamic studies of the alternating CO/ethene copolymerization; in particular, rigid dinitrogen ligands such as bipy, phen and bis(arylimino)acenaphthene (Ar-BIAN) have been very useful for determining the thermodynamic parameters associated with the migratory insertions occurring in the initiation and propagation steps [17,58a,62]. Detailed mechanistic studies of the CO/ethene copolymerization have been carried out by Brookhart et al. with the use of phen complexes of the general formula [(phen)Pd(R)(L)][3,5-$(CF_3)_2C_6H_3$)] where the R/L combination may be CH_3/CO; CH_3/

C_2H_4; $C(O)CH_3/C_2H_4$; $C(O)CH_3/CO$; $CH_2CH_2C(O)CH_3/C_2H_4$; $CH_2CH_2C(O)CH_3/CO$; $C(O)CH_2CH_2C(O)CH_3/C_2H_4$; or $C(O)CH_2CH_2C(O)CH_3/CO$. A low-temperature NMR study of the intramolecular migratory insertions involving these R/L combinations allowed the authors to determine the barriers for insertion which increase in the order: $\Delta G^{\ddagger}$ (R → CO) ≈ 15 kcal mol^{-1} (−66 °C) < $\Delta G^{\ddagger}$ ($Ac \rightarrow C_2H_4$) ≈ 17 kcal mol^{-1} (ca. −45 °C) < $\Delta G^{\ddagger}$ ($R \rightarrow C_2H_4$) ≈ 19 kcal mol^{-1} (−25 °C). The relative ground state stabilities of several species, including the β- and γ-keto chelate complexes $[(phen)PdCH_2CH_2C(O)CH_3]^+$ and $[(phen)PdC(O)CH_2CH_2C(O)CH_3]^+$ were determined through a combination of competitive and relative equilibria studies. Based on this multiform investigation, a complete mechanistic cycle of chain propagation was proposed, which still remains a milestone in CO/ethene copolymerization (Scheme 13) [58a].

The insertions of CO into $Pd-CH_3$ and of strained alkenes into Pd–COR supported by various dinitrogen ligands have been studied by Vrieze, Elsevier et al. [17]. In analogy to analogous reactions involving diphosphine ligands [10,32], it was found that backbone rigid dinitrogen ligands (e.g. Ar-BIAN) have an activating effect on the insertion of both CO and olefins in Pd–C bonds. According to Vrieze, ligand rigidity would disable dissociation of one ligating nitrogen, and hence stabilize the NPdN metallaring.

2.5.3. Miscellaneous ligands

Unlike P–P and N–N ligands, the copolymerization mechanism assisted by heteroditopic N–O, P–O and P–S ligands is believed to involve intermediates with a dangling or weakly interacting donor atom [41b,41d, 41g,41h,63]. Experimental evidence of the hemilability of the bidentate ligand and the occurrence of *trans–cis* isomerization of the donor atoms was first reported by Cavell et al. using the methyl picolinate complex $[Pd(Me)(PPh_3)(NC_5H_3CO_2Me)]BF_4$ [41a]. Scheme 14 shows the catalytic mechanism proposed by Cavell for the copolymerization of CO and ethene in aprotic media [41c].

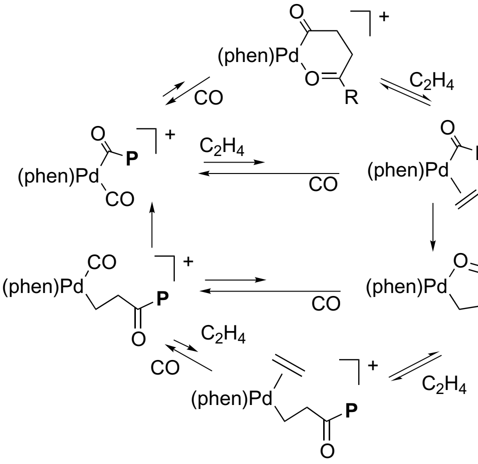
A relevant intermediate in the catalysis cycle is the square-pyramidal palladacycle $[Pd(CH_2CH_2COMe)(NC_5H_4CO_2Me-2)(PPh_3)]BF_4$, which was independently obtained by reaction of ethene with an isolated sample of the acyl intermediate and was shown to contain a weakly interacting carbonyl oxygen in an apical position (Pd–O distance = 2.78(1) Å) [41a]. The propagation occurs by the usual alternating insertion of CO and ethene, while the termination takes place via β-H elimination.

Valuable mechanistic information on the early stages of the chain growth process has also been obtained by Braunstein et al. with the acetamido-derived P–O ligand $Ph_2PNH(CO)Me$. The stepwise reaction of the Pd(II) precursor with CO and ethene allowed the authors to isolate the four intermediates shown in Scheme 15a as well as identify the reversible and irreversible steps. Unlike diphosphine ligands [60], the insertion of ethene into the γ-keto chelate acyl complex was found to be a facile process occurring without the intervention of CO [41g].

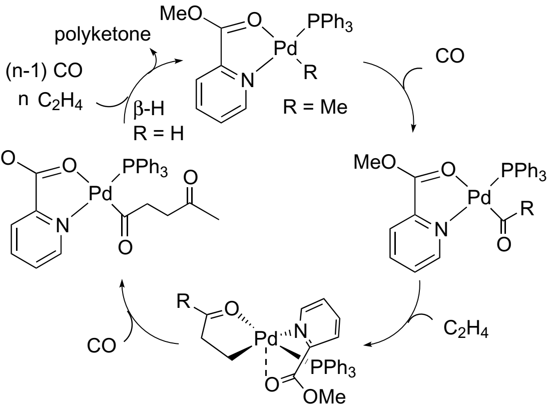
Further mechanistic information on the first steps of the CO/ethene copolymerization was obtained by employing bimetallic templates (Scheme 15b). Although a clear influence of the metal adjacent to the reactive Pd on the rate of the various C–C coupling reactions did not appear, the template complexes allowed the isolation and characterization of key intermediates [41i].

3. Copolymerization and terpolymerization of styrene with CO

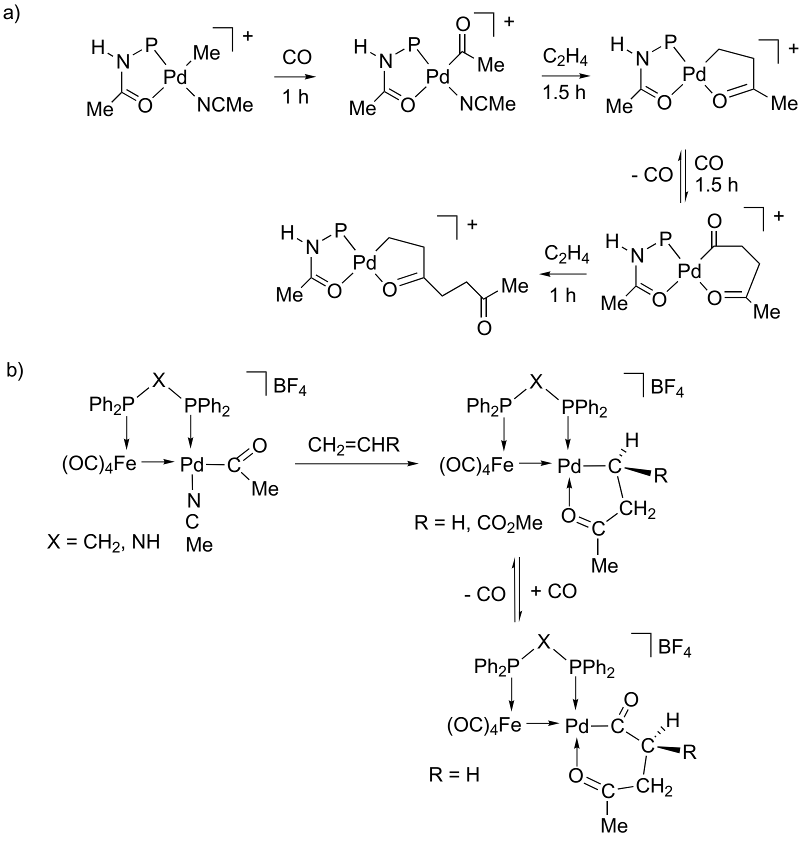
Unlike ethene and aliphatic α-olefins, the copolymerization of styrene and its derivatives with CO requires the use of palladium(II) catalysts with N–N chelating



Scheme 13. Mechanistic cycle of chain propagation of the CO/ethene copolymerization catalyzed by phen-based palladium catalysts.



Scheme 14. Proposed mechanism of the CO/ethene copolymerization catalyzed by N–O palladium(II) precursors in aprotic media.



Scheme 15. Model study of intermediate palladacycles in the CO/ethene copolymerization.

ligands to be effectively accomplished [4b,4c,39,64]. Low molecular weight oligomers are in fact generally obtained with palladium catalysts stabilized by chelating diphosphines [4b,64c,64f,65a,65b].

It is commonly agreed that termination by β-H elimination prevails over propagation to polymer due to the higher electron density on the palladium center in phosphine-modified catalysts as compared to nitrogen-modified catalysts [4b,64–66]. It has also been suggested that the (diphosphine)Pd–styryl intermediates formed in the initial steps of the CO/styrene copolymerization are so strongly stabilized by π-benzylic coordination to inhibit CO insertion. The termination process by β-H elimination thus becomes the favored reaction and oligoketones are formed instead of polyketones [66].

Copolymers of the general formula $[CH(Ar)CH_2CO]_n$ show regio- and stereoisomerisms due to the presence of truly stereogenic centers in the polymer backbone [67]. Depending on the regioselectivity of the monomer insertion, primary (1,2 mode) or secondary (2,1 mode), into the polymer chain, three different arrangements might be possible during the polymerization: tail-to-tail, head-to-tail and head-to-head (Fig. 24). Styrene insertion in Pd–acyl takes place exclusively in the 2,1-fashion however (see Section 3.3).

The occurrence of the same insertion mode during the chain growth leads only to head-to-tail units. Moreover, the sequence of the absolute configuration of the stereogenic centers in the backbone can control the formation of atactic (stereoirregular), syndiotactic (*RSRSRS* sequence) or isotactic (*RRRRRR* or *SSSSSS* sequence) copolymers (Fig. 25). Syndiotactic and isotactic alternating copolymers are characterized by vanishing small and high optical activities, respectively. The control of the regio- and enantioselectivities of

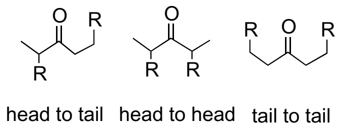


Fig. 24. Regioselectivity of propagation during CO/styrene copolymerization.

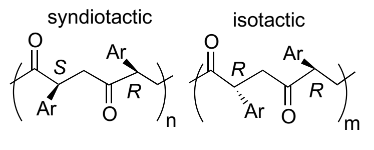


Fig. 25. Syndiotactic and isotactic copolymers in CO/styrene copolymerization.

styrene insertion, ultimately leading to stereoregular polyketones, can be achieved through a suitable choice of the bidentate ligands.

Unfortunately, CO/styrene polyketones are obtained neither in high yield nor with a sufficiently high molecular weight to ensure industrial application [68]. Moreover, these materials are very difficult to process as they often undergo loss of desirable properties when exposed to high temperature for extended periods or subjected to repeated cycles of melting and solidification.

3.1. Palladium catalysts stabilized by achiral N–N ligands

In general, copolymerization promoted by catalytic systems containing achiral ligands produces materials which are featured by both head-to-tail regioselectivity and syndiotactic stereoselectivity (^{1}H- and ^{13}C-NMR and X-ray diffraction). The head-to-tail selectivity ($>$ 90%) is a consequence of the occurrence of consecutive secondary migratory insertions of styrene into palladium–acyl during the chain growth [64b,64c,64f], while the stereoselectivity is due to the chain end-controlled enantioface selection: the enantioface of the incoming styrene, which inserts almost exclusively in the 2,1-mode, is selected by the chiral center of the last-incorporated styrene [4b,4d].

The perfectly alternating copolymerization of CO with styrene and its aryl-substituted derivatives to give syndiotactic polyketones requires the use of catalytic systems that are typically composed of a palladium(II) salt (acetate or trifluoroacetate) and of a chelating dinitrogen ligand such as bipy or phen. The reactions are generally carried out in methanol as solvent and in the presence of strong oxidants such as BQ in excess to palladium and of a suitable Brønsted acid (e.g. TfOH or TsOH) as cocatalyst. Unlike CO/ethene copolymerization, the addition of an oxidant to the catalytic mixture is of mandatory importance for efficiently copolymerizing styrene and CO. In the absence of oxidants, in fact, the polymer production is strongly reduced [4b,4c,39,64]. Also, hydrogen has been found to be a powerful polymerization inhibitor leading to the prevailing formation of aldehydes and/or ketones [11a,64e,69,70].

Irrespective of the catalytic system, the productivities in polyketones are rather low (<500 g (g Pd)$^{-1}$) and the molecular weights are not high enough to obtain materials with useful properties [68].

Recently, a remarkable beneficial effect on the stability of the catalytic systems during the CO/styrene copolymerization has been obtained using 2,2,2-trifluoroethanol (TFE) as solvent [71a]. Indeed, the dicationic bis-chelated Pd(II) complex [Pd(bipy)$_2$](PF$_6$)$_2$ in the presence of a five-fold excess of BQ gives rise to very active catalysts in TFE, which remain active after 48 h of reaction yielding high molecular weight copolymers with a productivity of 360 g (g Pd × h)$^{-1}$. The molecular weights of the polyketones are inversely proportional to the initial concentration of BQ. Even in the absence of oxidant, however, the copolymerization reactions in TFE give polyketones in high yields and with high molecular weights (up to 80 kg mol^{-1}) 71b. The formation of polyketones with these unusually high molecular weights has been attributed to the higher stability of the Pd–acyl intermediates in TFE than in methanol. In particular, the much lower nucleophilicity of TFE as compared to methanol has been suggested to inhibit the chain termination by alcoholysis.

The effect of different counter-anions on the CO/styrene copolymerization catalyzed by monochelated monocationic complexes of the general formula [Pd(η^1,η^2-C$_8$H$_{12}$OMe)(bipy)]Y (Y = BPh$_4$, OTf, BF$_4$, PF$_6$, SbF$_6$, B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$; C$_8$H$_{12}$OMe = cyclooctenylmethoxy group) has been studied in CH$_2$Cl$_2$ under very mild conditions (room temperature and 1 bar CO). The catalytic activity decreases in the order $BPh_4 \ll OTf < BF_4 < PF_6,\quad SbF_6 < B(3,5\text{-}(CF_3)_2C_6H_3)_4$. The influence of the anion has been related to the different strength of the interionic interactions: the productivity decreases as the effectiveness of the interionic interaction increases [72].

Syndiotactic copolymers have been obtained under mild conditions (room temperature, 1 bar CO) by using catalyst precursors containing unsymmetrical chelate ligands with pyrazolyl moieties (Fig. 26). The C_s-symmetry of the ligands does not affect the stereochemistry of the polymer, which is controlled by the chain end. With these systems, rather high molecular weights (20–70 kg mol^{-1}) and polydispersities (1.1–1.3) are obtained. The catalyst precursor reported in Fig. 26b has been found to give the highest activity with a productivity of 11.8 g (g Pd × h)$^{-1}$. The lowest productivity was obtained with the catalyst containing the sterically demanding dimethyl substituted ligand (Fig. 26c) [73].

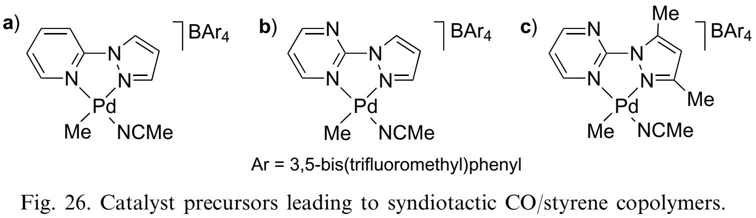


Fig. 26. Catalyst precursors leading to syndiotactic CO/styrene copolymers.

Mild reaction conditions (1 bar CO and 0 °C) were also employed in the syndiotactic copolymerization of styrene and 4-methylstyrene with CO promoted by the complex [(Pr^{i}DAB)Pd(Me)(NCMe)]BAr$_4$ (Pr^{i}DAB = 1,4-diisopropyl-1,4-diaza-buta-1,3-diene) (Fig. 27). This complex was employed as precursor in model studies of the first steps involved in the 4-methylstyrene/CO polymer chain growth [74].

3.2. Palladium catalysts stabilized by chiral bidentate ligands

Chiral catalysts have been found to switch the chain-end control to enantiomorphic site control yielding regioregular optically active highly isotactic polyketones, the enantioface of the incoming styrene being selected by the chiral ligand and not by the chain-end.

3.2.1. N–N ligands

The first example of enantioselective copolymerization of a styrene monomer with CO has been obtained by Brookhart with cationic palladium catalysts modified with enantiomerically pure C_2-symmetric bisoxazoline ligands (Fig. 28a) [75].

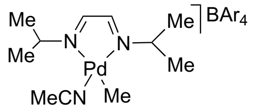
In a typical reaction, *p-tert*-butylstyrene (TBS) reacts with carbon monoxide (1 bar) in solvent free systems at room temperature yielding copolymers (2.5 g (g Pd × h)$^{-1}$, $M_n = 26$ kg mol^{-1}, $M_w/M_n = 1.4$) featured by both highly isotactic microstructure and high optical activity. The presence of substituents in the four positions of the oxazoline rings strongly controls the orientation of the incoming styrene around the metal center during the propagation process. Surprisingly, palladium catalysts modified with pyridine–oxazoline ligands (Fig. 28b) give polymers that are largely syndiotactic [75].

Chiral alternating styrene/CO copolymers, although with a lower stereoregularity, have also been produced with catalysts stabilized by enantiomerically pure 2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine (Fig. 29) [76].

Brookhart has produced a stereoblock polyketone applying an innovative strategy that involves ancillary ligand exchange during a living palladium-catalyzed polymerization [77]. The alternating copolymerization of TBS with CO was achieved using a combination of chiral and achiral ligands. An isotactic segment was first produced using the methyl chiral bisoxazoline ligand (Fig. 28a). Addition of bipy into the reaction mixture resulted in the displacement of the bisoxazoline from the palladium catalyst and thus in the elongation of the polyketone in a syndiotactic manner (Fig. 30). The efficient displacement of the bisoxazoline by bipy enabled the stereoblock copolymer formation.

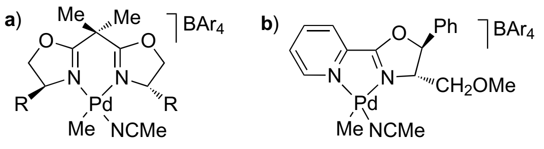
Cationic bioxazoline Pd(II) complexes have also been used for the enantioselective synthesis of highly isotactic optically active copolymers of CO with styrene or 4-methylstyrene (Fig. 31) [78].

The reactions, carried out in either styrene or 4-methylstyrene as solvent under 1–4 bar of CO at room temperature, gave the corresponding copolymers with productivity of 0.3 g (g Pd × h)$^{-1}$ and 2.5 g (g Pd × h)$^{-1}$, respectively. These low yields have been attributed to the weak coordination ability of the bioxazoline and bisoxazoline ligands that ultimately



Ar = 3,5-bis(trifluoromethyl)phenyl

Fig. 27. Catalyst precursor for syndiotactic CO/styrene copolymerization.



R = CHMe$_2$, Me

Fig. 28. Chiral dinitrogen catalyst for enantioselective CO/styrene copolymerization.

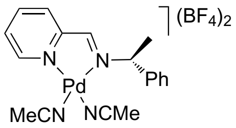
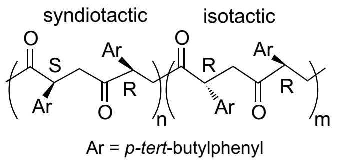
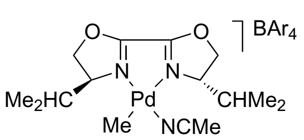


Fig. 29. Chiral dinitrogen catalyst for enantioselective CO/styrene copolymerization.



Ar = *p-tert*-butylphenyl

Fig. 30. Stereoblock polyketone obtained from CO/TBS copolymerization.



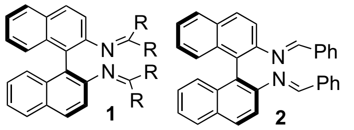
Ar = 3,5-bis(trifluoromethyl)phenyl

Fig. 31. Bioxazoline complex employed to produce highly isotactic optically active CO/styrene(4-methylstyrene) copolymers.

leads to unstable catalyst systems in copolymerization conditions.

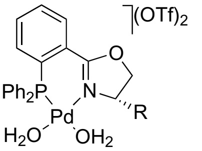
Palladium complexes modified with chiral diketimine or dialdimine ligands (Fig. 32) of the formula [(N–N)PdMe(solvent)]Bar$_4$ have been tested as catalyst precursors in the alternating copolymerization of TBS with CO in CH_2Cl_2. The reactions were carried out under a constant pressure of CO (1 bar) at room temperature [79].

The TBS/CO copolymers obtained with these catalysts show average molecular weights (M_n, kg mol^{-1}) in the range from 40 to 50 ($M_w/M_n = 1.2$ by GPC) and isotacticity $> 97\%$ (^{13}C-NMR, integration of the signals of the methylene carbon atoms C_3). Interestingly, the catalysts derived from the diketimine **1b** and the dialdimine **2** are inactive, while those prepared from the diketimines **1a**, **1c**, and **1d** give polyketones with productivities of 4, 3, and 8 g (g Pd × h)$^{-1}$, respectively. Following an optimized procedure, productivities as high as 21 g (g Pd × h)$^{-1}$ were obtained that are comparable to those reported for very efficient chiral ligands. Interestingly, the observed activity trend (**1a** > **1b** > **2**) was in line with that deduced from a theoretical AMS model study, in which the accessible molecular surface at the active site in a homologous series of transition metal catalysts was calculated and correlated with the catalyst activity [80].



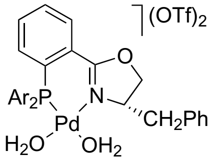
a, R = Ph
b, R + R = 2,2'-$(C_6H_4)_2$
c, R = *p*-$MeOC_6H_4$
d, R = *p*-ClC_6H_4

Fig. 32. Chiral diketimine and dialdimine ligands employed in CO/TBS copolymerization.



R = Ph, CH_2Ph, *t*-Bu
R = H

Fig. 33. Chiral P–N catalysts employed in enantioselective CO/styrene copolymerization.



Ar = Ph, *p*-$MeOC_6H_4$, *o*-$MeOC_6H_4$, *o*-MeC_6H_4

Fig. 34. Phosphine–imine precursors employed in CO/styrene copolymerization.

3.2.2. P–N ligands

The enantioselective copolymerization of styrene and CO has been effectively achieved with palladium catalysts stabilized by chiral hybrid phosphine–dihydrooxazole ligands (Fig. 33) [42a].

Under optimized reaction conditions (MeOH, 50 °C, 320 bar of CO, ca. 20 equiv. of BQ), the benzyl-substituted catalyst system gave the best productivity [10.7 g (g Pd × h)$^{-1}$]. It is noteworthy that, under 5 bar of CO, only trace amounts of copolymer were obtained. The materials isolated are isotactic and exhibit molecular masses up to 20 kg mol^{-1} (end groups in the ^{1}H-NMR spectra). The optical activity is comparable to those reported for the copolymers obtained with the bioxazoline derived catalysts. Negative rotation was assigned to the prevailing (*R*)-configuration [78].

Interestingly, due to the substantial loss of stereoregularity during the chain growth, an atactic copolymer was obtained with the achiral catalyst containing the unsubstituted oxazole ring (Fig. 33, R = H).

Recently Consiglio et al. have reported that the nature of the phosphorus substituents in phosphine–imine hybrid ligands strongly affects the stereoregularity of the styrene/CO polyketone product (Fig. 34) [42b]. The regularity was found to decrease in the order phenyl > *p*-anisyl > *o*-anisyl > *o*-tolyl. The *o*-tolyl derivative showed quite a low regioregularity. Steric factors have been claimed to be more important than electronic factors in controlling the regioselectivity. It has been suggested, in fact, that the site-selective coordination of styrene is controlled by the interaction of the growing chain with the aryl substituents on the phosphorus donor atoms.

The enantioselective terpolymerization of ethene, styrene and CO has been achieved by using the benzyl-substituted catalyst precursor shown in Fig. 33 [81a]. When a comparable concentration of the two olefins was used, the terpolymers contained more ethene than styrene, which is in contrast with the fact that the catalyst is separately more active for styrene than for ethene by a factor of about 3.5.

Similar results have been reported for the terpolymerization of ethene, styrene and CO catalyzed by a palladium system containing a phosphanyl–dihydrooxazole ligand (Fig. 35) [81b,81c]. The rate at which the terpolymer was produced is close to that observed for the copolymerization of ethene.

On the basis of the results of a modeling NMR study, the easier enchainment of ethene as compared to styrene has been attributed to the faster insertion rate of ethene into the Pd–acyl bond. In contrast, the

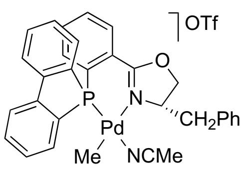


Fig. 35. Phosphanyl–dihydrooxazole precursor employed in the terpolymerization of CO/styrene/ethene.

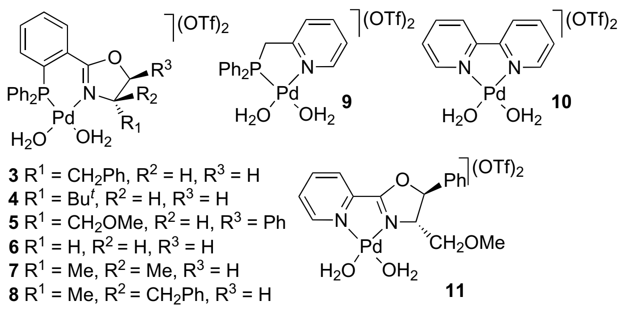


Fig. 36. P–N and N–N palladium(II) catalysts employed in CO/styrene copolymerization.

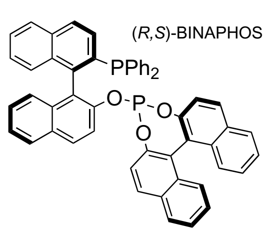


Fig. 37. (*R*,*S*)-BINAPHOS ligand employed in CO/TBS copolymerization.

slower CO/ethene copolymerization rate has been attributed to a higher energy barrier to CO insertion into a palladium–primary carbon atom bond (Pd–C_2H_4R) as compared to insertion into a palladium–secondary carbon bond (Pd–C(Ph)H–CH_2R).

In order to gain further insight into the factors responsible for the stereoregulation during the CO/styrene copolymerization process, the performances of several P–N-modified catalysts have been compared to those of catalysts containing N–N ligands (Fig. 36) [82]. The cationic palladium(II) complexes **5** and **11**, modified by C_1-symmetric chelate ligands containing the 3-phenyl-4-methoxymethyl-4,4-dihydrooxazole chiral moiety, have been found to catalyze the copolymerization of styrene with CO yielding highly isotactic or prevailingly syndiotactic microstructures, respectively. It is noteworthy that precursor **11** is structurally related to the pyridine–dihydrooxazole catalyst (Fig. 28b) which gives a prevailing syndiotactic TBS/CO copolymer. The tacticity selectivity observed for **11** was attributed to a pronounced site selective coordination that makes the chain-end control more efficient than the enantiomorphic site control.

Unlike chiral and achiral P–N precursors, the productivities of the N–N precursors **10** and **11** was found to decrease with the CO pressure, which is in agreement with the negative reaction order with respect to CO found for ethene copolymerization promoted by bipy and phen precursors [58a].

3.2.3. *P–P ligands*

The asymmetric copolymerization of TBS with CO has been achieved with the palladium catalyst [((*R*,*S*)-BINAPHOS)Pd(Me)(NCMe)]BAr_4 (Ar = 3,5-bis(trifluoromethyl)phenyl) containing the unsymmetrical chiral bidentate phosphine–phosphite (*R*,*S*)-BINAPHOS [(*R*)-2-(diphenylphosphino)-1,1′-binaphthalen-2′-yl (*S*)-1,1′-binaphthalene-2,2′-diyl phosphite] (Fig. 37).

In CH_2Cl_2 at room temperature was obtained a material featured by almost complete isotacticity, low molecular weight (M_n 4 kg mol^{-1}; $M_w/M_n = 1.3$) and low stereoregularity [65a,65b]. Isotactic materials were also obtained with styrene and its *para*-substituted derivatives (R = Me or Cl) [83]. The best productivity (70 g of copolymer per g of Pd in 24 h), even higher than that obtained with TBS, was achieved with 4-methylstyrene. It is noteworthy that no catalytic activity was observed in the presence of electron-withdrawing groups such as NO_2 and CF_3, while only a radically formed, atactic homopolymer was produced with the electron donating OMe substituent.

The catalyst system modified with the BINAPHOS ligand has been found to be active also in the enantioselective terpolymerization of propene and TBS with CO [84]; the olefins were incorporated in a head-to-tail and isotactic fashion. Propene was more easily incorporated in the polymer chain than TBS, although the latter was more reactive towards the insertion into an acylpalladium species. This contradiction is analogous to that found for the terpolymerization of ethene, styrene and CO with the phosphine–imine catalysts reported in Figs. 33–35. The ethene contents in the terpolymer was higher than that of styrene, although the copolymerization of styrene and CO was much faster than that of ethene and CO [81].

3.3. *Mechanism of CO/styrene copolymerization*

The general features of the reaction mechanism discussed for the ethene copolymerization in Section 2.5 are also substantially valid for the styrene/CO copolymerization. In particular, the propagation steps are identical in both copolymerization reactions and consist of subsequent alternated migratory insertions of alkyl to CO and of acyl to olefin. Moreover, the propagating species in the two alternating copolymerizations consists of a cationic Pd(II) complex stabilized by a suitable bidentate ligand (generally, a diphosphine for ethene and a chelating dinitrogen ligand for styrene) containing the coordinated monomer and the growing chain in a reactive *cis*-arrangement forced by the *cis*-coordination of the chelating ligand. In contrast, the initiation and termination steps are different and strongly depend on the nature of the olefin [4].

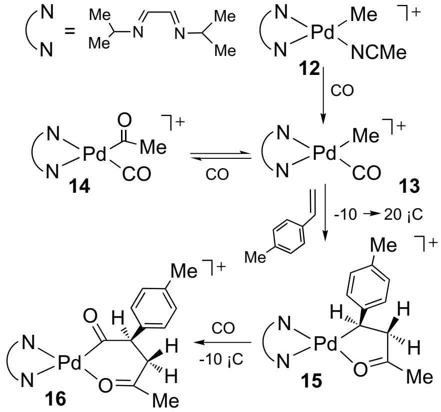
Unlike CO/ethene copolymerization, the mayor pathway to chain termination in CO/styrene alternating copolymerization in methanol consists of a fast β-hydrogen elimination from the last inserted styrene unit. Generally, this pathway prevails over the termination path by methanolysis that, however, may become important at very high concentrations of BQ. Thus, irrespective of the termination step, only Pd(II)–H species are produced at the end of the cycle. These species do not reinitiate, as for ethene, the copolymerization (styrene insertion in the Pd–H bond followed by the insertion of CO into the formed Pd–styryl bond) but are converted by the oxidant to Pd–C(O)OMe initiators via Pd–OMe intermediates. It is generally agreed that a large excess of BQ with respect to palladium is mandatory for an effective copolymerization reaction. BQ is necessary to oxidize intermediate Pd(0) complexes that may form in the reducing environment of the reaction to active Pd(II) species preventing their decomposition into palladium metal or other catalytically inactive species. In particular, it has been demonstrated that the reaction of Pd(II)–H with MeOH and CO to give Pd(II)–C(O)OMe can occur through a series of equilibria involving the initial formation of an unstable Pd(0) complex species that is then oxidized by BQ. Intermediate Pd(0) complexes containing an η^4-BQ ligand have been detected along proton-assisted oxidation paths of Pd(0) to Pd(II) [4].

Recently, the conformations of the first intermediates in the syndiotactic copolymerization of styrene derivatives with CO have been determined by NMR spectroscopy using the complex [(Pr^{i}DAB)Pd(Me)(NCMe)]BAr$_4$ (**12**) as precursor (Fig. 27) [74]. The five-membered metallacycle **15** forms by insertion of 4-methylstyrene into the Pd–acyl bond of a species derived from **13** by α-methyl migration. Reaction of **15** with CO gives the six-membered metallacycle **16** that represents the second step of the copolymerization reaction (Scheme 16).

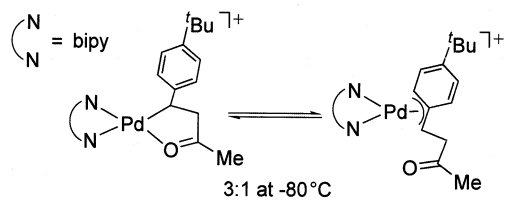
It is worth noticing that previous model studies of the insertion of styrene into palladium–acyl complexes described intermediates analogous to **15** as either η^3-π-benzyl species [85] or mixtures of chelate and benzyl structures if fast exchange [64d] (Scheme 17).

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry was employed to carry out the end group analysis of the copolymer obtained in the styrene/CO copolymerization promoted by the highly active bis-chelated complex [Pd(bipy)$_2$](PF$_6$)$_2$ in TFE [86]. Analysis of the polymeric chains found in the material produced in the absence of BQ (Fig. 38) showed that the termination by β-H elimination is accompanied by three different initiators: palladium alkyls from Pd–H formed by reaction of the precursor with CO and water (a and b) and palladium carboalkoxy species formed by reaction of the precursor with the fluorinated alcohol and CO (c). The suppression of the chain-transfer by alcoholysis was proposed to be responsible for the enhanced stability of the palladium acyl intermediates and thus for the high molecular weight of the copolymers.

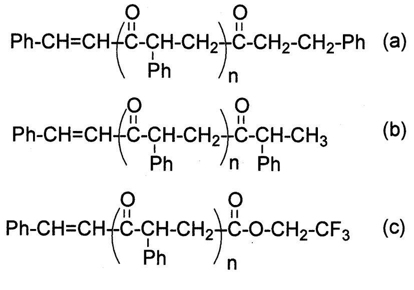
Useful information on the regioselectivity of styrene insertion to acyl–Pd bond in Pd–(*R*,*S*)-BINAPHOS complexes was obtained by ^{31}P-NMR spectroscopy. In particular, the polyketone-substituted complex [((*R*,*S*)-BINAPHOS)Pd{$CH_3(CH_2CHCH_3CO)_{14}$}]BAr$_4$ was



Scheme 16. Conformation of the first intermediates in the syndiotactic copolymerization of 4-methylstyrene with CO using the complex [(Pr^{i}DAB)Pd(Me)(NCMe)]BAr$_4$ as catalyst precursor



Scheme 17. Equilibrium between β-chelate and η^3-π-benzyl structures.



$$\mathrm{Ph\text{-}CH{=}CH}\left(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\right)_n\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{CH_2\text{-}CH_2\text{-}Ph} \quad \text{(a)}$$

$$\mathrm{Ph\text{-}CH{=}CH}\left(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\right)_n\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\mathrm{CH_3} \quad \text{(b)}$$

$$\mathrm{Ph\text{-}CH{=}CH}\left(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\right)_n\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{O\text{-}CH_2\text{-}CF_3} \quad \text{(c)}$$

Fig. 38. Different end-groups obtained in the CO/styrene copolymerization catalyzed by [Pd(bipy)$_2$](PF$_6$)$_2$ in TFE.

employed to mimic the real copolymerization conditions. Styrene insertion occurred only in 1,2 fashion for chain propagation, which is in sharp contrast to the predominant 2,1-insertion mode observed with dinitrogen ligands. Theoretical studies suggested that 1,2-insertion is derived from the steric demand of (*R*,*S*)-BINAPHOS rather than the electronic one [65c].

4. CO/propene copolymerization

4.1. Palladium catalysts stabilized by diphosphine ligands

Optimal catalyst systems for the alternating copolymerization of propene and carbon monoxide are of the type $[L_2PdX_2]^{n+}$ in which X represents a weakly or noncoordinating anionic ligand or a neutral ligand and L_2 is a chelating bidentate phosphine. Brønsted or Lewis acids and/or oxidants are generally added to the catalytic mixtures in order to increase the activity of the catalyst. The reactions are generally carried out in solvent mixtures containing at least one alcoholic component (THF/MeOH, NO_2Me/MeOH, ^{t}BuOH/MeOH/toluene, CH_2Cl_2/MeOH) [4].

Depending on the reaction conditions, the copolymer product can be isolated in the form of either polyketone as poly(1-oxo-2-methyltrimethylene) (Fig. 39, A) or polyspiroketal as poly[spiro-2,5-(3-methyltetrahydrofuran)] (Fig. 39, B). The latter can be transformed into the thermodynamically more stable polyketone form either thermally or by dissolution in HFIP [4b,4c,87,88].

The control of the regioselectivity and stereoselectivity of the olefin insertion into the palladium–acyl intermediates during the propagation, as already highlighted for styrene, is exceedingly important also for the production of stereoregular alternating propene/CO copolymers. Unlike styrene, 1,2 olefin insertion is the preferred mode for propene [4b,4c,4d].

The catalytic systems based on the chelating diphosphine ligand dppp which enables high performances in the copolymerization of ethene with CO, produce only regioirregular copolymers (both 1,2 and 2,1 olefin insertion is operative during the chain growth) with no steric order at low rates [89].

The regularity of the polymer has been improved by using palladium(II) catalytic systems modified with either sterically demanding basic diphosphines derived from dppp (Fig. 40) [64f,87b,90,91] or chiral symmetric and dissymmetric diphosphines (Figs. 37 and 41) [64f,65,76,87,88,91–93].

The dppp-derived ligands favor the regioregular enchainment of propene units in head-to-tail mode, while the chiral ligands bring about enantiofacial selectivity thus influencing the stereochemistry of the copolymer.

For a series of ligands based on the dppp skeleton, both the chirality of the catalytic system and the basicity of the ligand have been found to play an important role in the production of stereo- and regioregular polymers [4d,87b,91]. The electronic factors are important also in controlling the regioregularity of the copolymerization process in catalyst systems based on achiral ligands.

Unlike the atropoisomeric chiral ligand (*S*)-BICHEP that gives completely regioregular and highly stereoselective copolymers, its completely aromatic analogs (Fig. 42a) give only regioirregular materials. Completely regioregular atactic copolymers have been obtained with the ligand (*all S*)-(R_a)-(6,6′-dimethoxy-

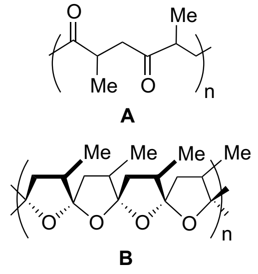


Fig. 39. Poly(1-oxo-2-methyltrimethylene) and poly[spiro-2,5-(3-methyltetrahydrofuran)] structures of CO/propene polyketones.

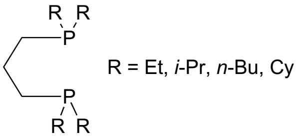


Fig. 40. Dppp-like diphosphine ligands employed in CO/propene copolymerization.

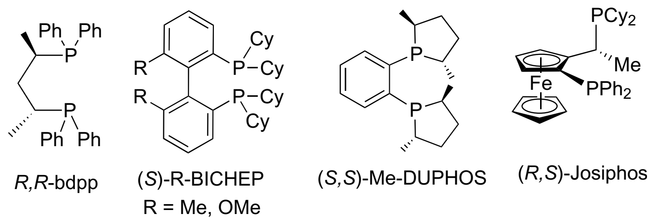


Fig. 41. Chiral diphosphine ligands employed in CO/propene copolymerization.

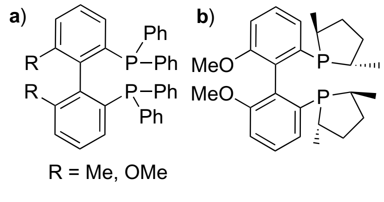


Fig. 42. Chiral diphosphine ligands employed in the stereoselective CO/propene copolymerization.

biphenyl-2,2′-diyl)bis(2,5-dimethylphospholane) (Fig. 42b) [94] while completely regular and isotactic copolymers have been produced with the chiral diphosphines Me-DUPHOS (Fig. 41) [76,88] and (*R*,*S*)-BINAPHOS (Fig. 37) [65].

The nature of the phosphorus substituents in the (*R*,*S*)-BINAPHOS framework has been found to dramatically affect the stereoregularity of the polymeric material [95]. In particular, atactic materials were obtained with the ethyl substituted (*R*,*S*)-Et$_2$-BINAPHOS ligand. Moreover, (*R*,*S*)-H$_8$-BINAPHOS was found to be even more active (propene conversion 29%, $M_n = 27$ kg mol^{-1}) than the (*R*,*S*)-BINAPHOS parent ligand (propene conversion 15%, $M_n = 16$ kg mol^{-1}). Catalysts modified with the achiral phosphine–phosphites **17** and **18** resulted in either no reaction or production of stereoirregular polyketones. In conclusion, the production of completely isotactic copolymers requires a fine steric and electronic tuning of the unsymmetric (*R*,*S*)-BINAPHOS ligand (Fig. 43).

Among the palladium catalysts studied so far, the best ones in terms of activity are those containing ligands based on the diphosphine Josiphos (Figs. 41 and 44) [96]. In a typical experiment, an in situ catalyst system prepared by mixing palladium acetate with the ligand and a two-fold excess of BF$_3$·Et$_2$O in CH$_2$Cl$_2$/MeOH was heated to 50 °C under CO (75 bar) in the presence of propene. The copolymer products showed a very high regioregularity ($>$ 99% head-to-tail enchainments) and stereoregularity ($>$ 96% of isotactic diads). The use of structurally related (ferrocenyl)diphosphine ligands indicated that the combination of two electronically non-equivalent donor groups (i.e. Pcy$_2$ and PPh$_2$) is probably the reason for the good catalytic activity. Moreover, increasing the electronic differentiation of the two phosphorus donor groups by introducing functional groups on the phosphorus phenyl substituents was found to cause drastic changes in the catalytic activity (Fig. 44) [96b]. The highest productivity was obtained with the ligand containing two electron-withdrawing trifluoromethyl groups (1.8 kg (g Pd × h)$^{-1}$, $M_n = 14$ kg mol^{-1}), while the lowest productivity (50 (g Pd × h)$^{-1}$) was given by the ligand containing two electron-donating methoxy groups. Increasing the π-acidity of the arylphosphine increased the reaction rate, probably due to reduced electron density at palladium. The role played by steric effects was highlighted by the introduction of a trifluoromethyl group in *ortho* position, which led to the exclusive production of low-molecular weight oligomers in low yield.

Largely regioregular and highly isotactic copolymers have been recently obtained with achiral cationic catalysts modified with 1,2-bis-(diphenylphosphinomethyl)-benzene derived ligands (Fig. 45) [97]. It was found that appropriate phenyl substituents strongly influence the regioselectivity and the enantioface discrimination of the copolymerization of propene with CO by varying the electronic properties of the phosphorus donor atoms. Due to the achiral nature of the catalyst the enantioface discrimination during the copolymerization process would be chain-end controlled. The results of this study raise doubts about the accessibility of syndiotactic products from the copolymerization of aliphatic 1-olefins with diphosphine-modified palladium catalysts.

4.2. Mechanism of CO/propene copolymerization

The mechanism of the CO/propene copolymerization by palladium catalysis closely resembles that proposed for ethene and styrene. The chain growth can be de-

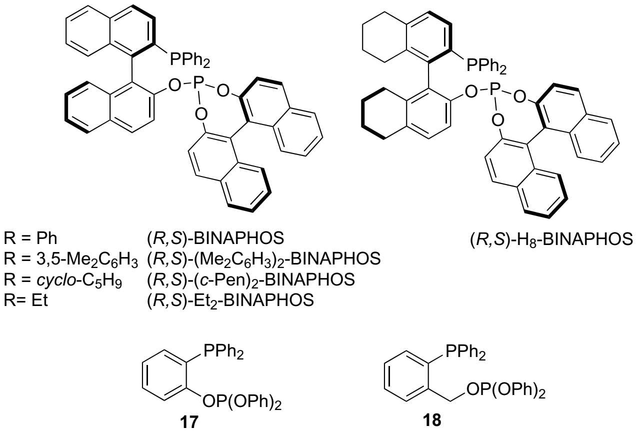


Fig. 43. Phosphine–phosphite ligands employed in the CO/propene copolymerization.

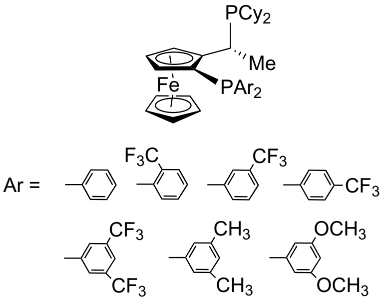


Fig. 44. Steric and electronic effects control the activity and the stereochemistry of Josiphos-based palladium(II) catalysts for CO/propene copolymerization.

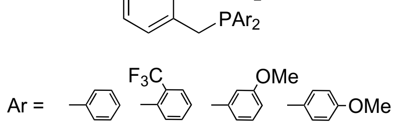
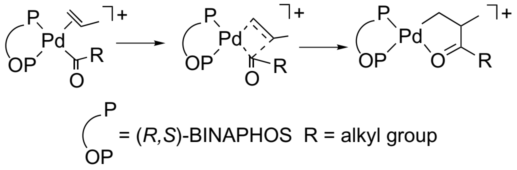


Fig. 45. 1,2-Bis(diphenylphosphinomethyl)benzene ligands employed in CO/propene copolymerization.



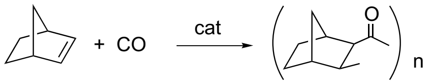
Scheme 18. 1,2 Insertion of propene in the asymmetric copolymerization with CO catalyzed by the complex [((*R*,*S*)-BINAPHOS)Pd(Me)(NCMe)]BAr$_4$.

scribed with a two-step mechanism involving the alternating insertions of carbon monoxide into palladium alkyl and olefin into palladium–acyl [4b]. Cationic palladium–carbene species have also been proposed to be active during the propagation in order to account for the formation of polymers with spiroketal repeating units [87a]. However, the interchange between 1,4-keto and spiroketal units in isotactic alternating α-olefin/CO copolymers has been found to also occur in the absence of metal catalysts [88].

Important mechanistic aspects of the asymmetric copolymerization of propene with CO have been obtained from the reactions catalyzed by the complex [((*R*,*S*)-BINAPHOS)Pd(Me)(NCMe)]BAr$_4$ (**19**) containing the unsymmetrical *cis*-bidentate phosphine–phosphite ligand BINAPHOS [65b]. Propene insertion into an acyl–palladium bond has been proposed to take place via propene coordination to palladium at a site *trans* to the phosphine donor group. Propene inserts in a 1,2 mode due to the steric repulsion between one of the phosphine phenyl groups and the methyl group of propene (Scheme 18).

A plausible mechanism has been proposed on the basis of observed intermediates in stepwise NMR experiments under ambient pressure starting from either **19** or a similar Pt complex (Scheme 19).

Carbon monoxide insertion into the Pd–Me bond in **19** gave the acylpalladium **21** which under propene yielded a 4:1 mixture of the alkyl palladium complexes **23a** and **23b**. Subsequent exposures of the mixture to CO and propene produced second- and third-generation complexes analogous to **21** and **23** containing –[CH$_2$CH(Me)C(O)]Me or –[CH$_2$CH(Me)C(O)]$_2$Me groups, respectively. The alkyl species **19** and **23** were found to be the predominant species under low pressure conditions. In contrast, in analogous NMR experiments carried out under high pressure of comonomers, both acylpalladium and alkylpalladium species analogous to **21** and **23**, respectively, were found to constitute the two major resting states of the catalysis [98].

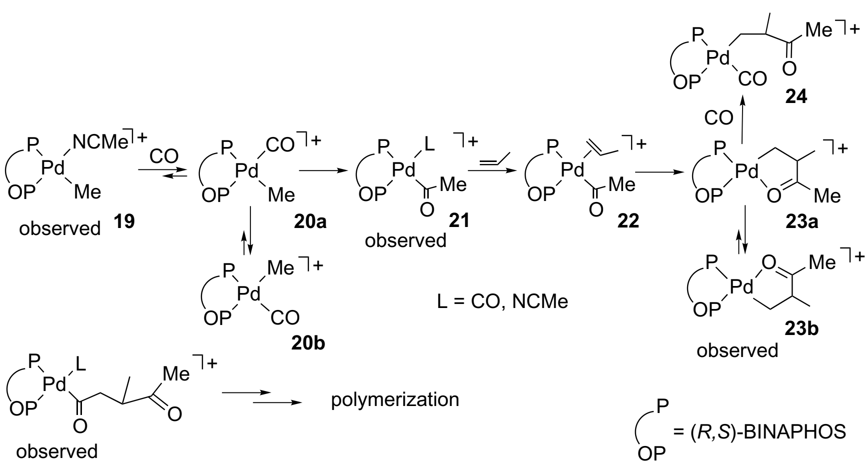


Scheme 20. Synthesis of norbornene copolymers by palladium(II) catalysis.

5. Copolymerization of CO and strained olefins

Strained olefins are attractive substrates for the copolymerization with CO as the resulting copolymers and cooligomers are featured by unique structural and chemical properties [99,100]. Moreover, strained olefins have revealed themselves as useful substrates to study the mechanism of insertion of the olefin into metal–acyl bond during the chain growth process (see below).

The Pd-catalyzed copolymerization of CO and strained olefins such as norbornene and norbornadiene dates back to the late 1960s when PdCl$_2$ was found to be an active catalyst for this reaction [101]. Later, Sen and Lai described the synthesis of norbornadiene copolymers of relatively high molecular weight (3380) and of norbornene cooligomers by catalysis with the phosphine-modified Pd complex [Pd(MeCN)(PPh$_3$)$_3$](BF$_4$)$_2$ (Scheme 20) [102].



Scheme 19. Proposed mechanism of the CO/styrene copolymerization catalyzed by palladium catalysts modified with (*R*,*S*)-BINAPHOS.

A similar Pd(II) catalyst containing two PPh_3 ligands, namely $[Pd(MeCN)_2(PPh_3)_2](BF_4)_2$, has recently been employed by Inoue et al. for the copolymerization of CO and norbornene [103]. Unlike the precursor with three phosphines, 2:2 cooligomers with enol–lactone structure and 3:3 cooligomers with ketal–lactone structure were obtained (Scheme 21). Cooligomers with enol–lactone and ketal–lactone structures were produced with other strained olefins such as bicyclo[2.2.2]oct-2-ene, dicyclopentadiene and dibenzobicyclo[2.2.2]octatriene.

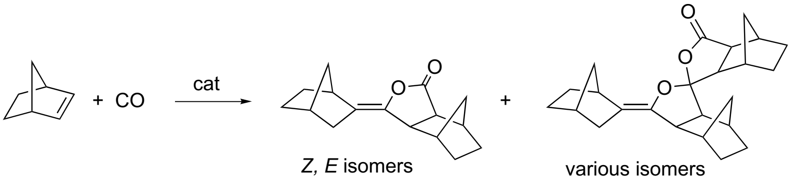
Carbon monoxide/norbornene copolymers terminated by a γ-lactone with an exocyclic double bond have been prepared by Chiusoli et al. by Pd(0) catalysis in the presence of alkyl bromides. The substitution of CF_3COOH for alkyl bromide gave 2:2 cooligomers with *cis*, *exo* stereochemistry [104].

Carbon monoxide and the electron-poor bicyclic olefins diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate or diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate have been copolymerized in a living fashion by Safir and Novak using neutral Pd(II) initiators containing a σ,π-norbornenyl ligand and either PPh_3 or pyridine (Scheme 22) [105].

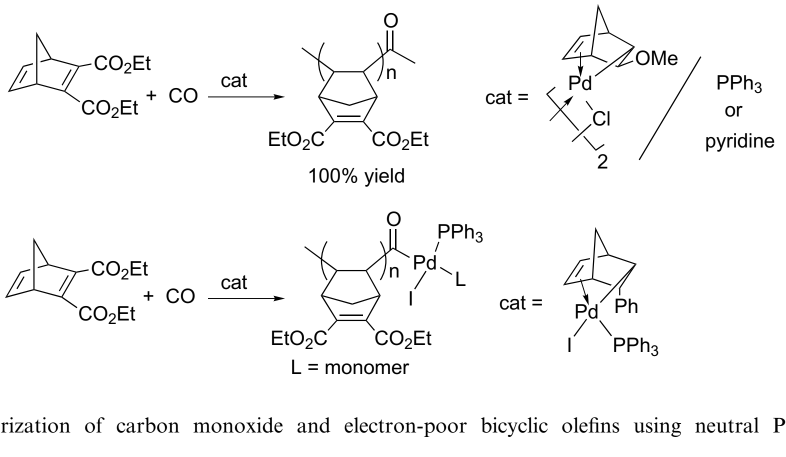
The Pd end group was removed by treatment of the copolymer with a halide scavenger, followed by methanolysis. Interestingly, the copolymerization of CO and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate gave a cross-conjugated poly(ketovinylene) via a retro Diels–Alder reaction that eliminates furan-3,4-dicarboxylate. Moreover, since the copolymers can retain the Pd as end group, they were used to re-initiate copolymerization leading to chain extension or diblock copolymer formation (Scheme 23).

The ability of Pd(II) stabilized by triphenylphosphine to catalyze the copolymerization of CO and strained olefins has been exploited by Liaw for the synthesis of 1,3-dicyclopentadiene–CO copolymers with 1,2- and 1,4-ketone ring structures. The catalytic systems were conveniently prepared in situ from $[Pd(CH_3CN)_4](BF_4)_2$ and variable amounts of PPh_3. Copolymers with 1,2-structure were selectively obtained in $CHCl_3$ [106].

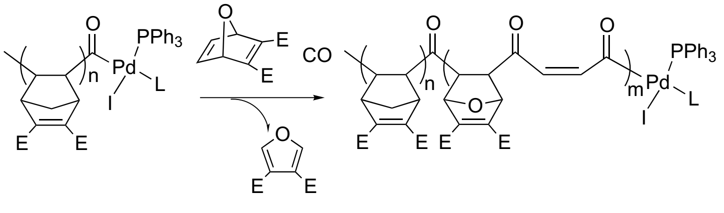
Drent was the first to use chelating dinitrogen ligands such as bipy to prepare active Pd(II) catalysts for the



Scheme 21. Cooligomers with enol–lactone and ketal–lactone structures.



Scheme 22. Living copolymerization of carbon monoxide and electron-poor bicyclic olefins using neutral Pd(II) initiators containing a σ,π-norbornenyl ligand.



Scheme 23. A cross-conjugated poly(ketovinylene) via a retro Diels–Alder reaction that eliminates furan-3,4-dicarboxylate.

alternating copolymerization of CO and a strained olefin [64a]. The reactions with 1,3-dicyclopentadiene were carried out in methanol in the presence of 1,4-benzoquinone as organic oxidant and yielded a polyketone product with a polyspiroketal backbone structure (Scheme 24).

The chelating P–N ligand *o*-(diphenylphosphino))-*N*-*p*-fluorobenzaldimine has been reported to form catalysts of the formula [Pd(P–N)(CH_3)(CH_3CN)]BF_4 which yield high molecular weight CO–norbornene copolymers ($M_n = 2.5$ kg mol^{-1} with $M_w/M_n = 1.26$) in aprotic solvents [41e].

Similar copolymers with $M_w = 4.6$ kg mol^{-1} ($M_n =$ 3.7 kg mol^{-1}) have been obtained in chloroform with the catalyst [Pd(pyimypy)$_2$](PF_6)$_2$ containing the hemilabile terdentate carbene 1,3-bis(2-pyridyl)imidazol-2-ylidene (pyimypy) [107].

As previously mentioned, many model studies aimed at elucidating the elementary steps of CO/olefin copolymerizations mediated by metal systems have successfully been carried out with the use of strained olefins in aprotic media. Indeed, the products resulting from the insertion of strained olefins such as norbornene and norbornadiene do not contain β-hydrogens that are accessible to the metal center. This makes the inserted product quite stable.

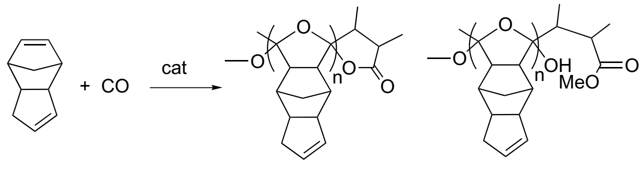
The formation of β-keto metallacycles on the way to polyketone chain growth was actually shown by the isolation of such products from the reactions of palladium complexes with strained olefins. Sen et al. reported the synthesis and X-ray structure of [Pd(PPh_3)$_2$-(C_7H_{10}COMe)]BF_4 by reaction of [Pd(PPh_3)$_2$(CH_3-CN)(COMe)]BF_4 with norbornene [108]. Analogously, a β-keto palladacycle was isolated from the reaction of *cis*-[Pd(dppe)(COMe)(MeCN)]BF_4 with cyclopentene or cycloheptene [59]. These discoveries opened the way to detailed studies of insertion of strained olefins into Pd–acyl bonds.

Elsevier, Vrieze et al. have studied the sequential insertions of CO and norbornene, norbornadiene or dicylopentadiene into Pd–alkyl and Pd–acyl bonds supported by the rigid backbone dinitrogen ligands such as Ar-BIAN (Scheme 25) [17,109]. The Pd complexes isolated after olefin insertion were found to have a similar structure arising from *cis* addition of PdC(O)R to the *exo* face of the olefin.

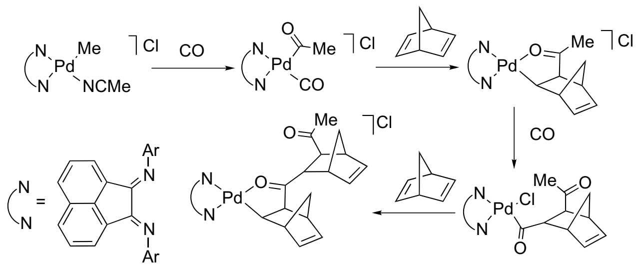
Further studies of the insertion of CO and various norbornenes into Pd–alkyl and Pd–acyl bonds, respectively, have been reported by Boersma, van Koten et al. for palladium(II) complexes stabilized by bipy [110]. These authors confirmed that the *cis*, *exo* insertion of the olefin is both stereo- and chemoselective and showed the first example of reversible olefin insertion in an isolated Pd(II) complex as well as the first isolated CO/olefin cooligomer connected to a Pd(II) center (Scheme 26).

The insertion reactions of chiral strained olefins into Pd–acyl bonds have also been studied by Braunstein et al. with the use of heterodinuclear Fe–Pd complexes containing either dppm or bis(diphenylphosphino)amine (dppa) bridging ligands [111]. Like analogous reactions with dinitrogen ligands [17,110], the insertions were found to occur with high stereo- and regioselectivity, thus indicating that the growth of polyketones containing a chiral center is a feasible goal.

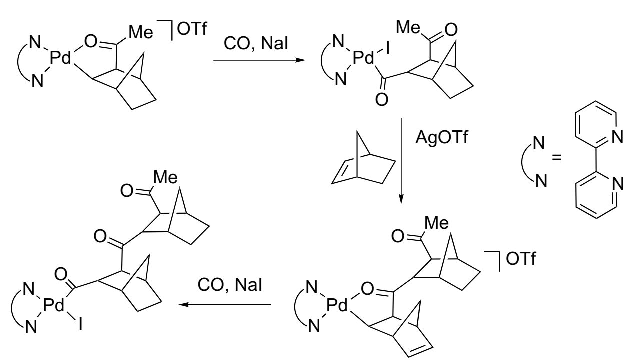
The insertion of norbornene into Pd–acyl has been exploited by Kacker and Sen to demonstrate the lack of chain termination in the alternating copolymerization of CO and ethene in the presence of *trans*-Pd(PPh_3)$_2$Cl-(COC_6H_4Me-*p*) in aprotic media. Interestingly, a



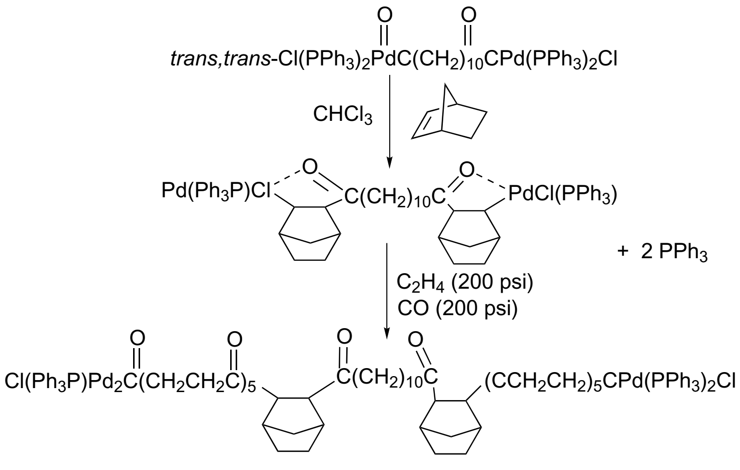
Scheme 24. Polyspiroketal product by alternating copolymerization of CO and strained olefins.



Scheme 25. Sequential insertions of CO and norbornene into Pd–alkyl and Pd–acyl supported by the rigid backbone dinitrogen ligands Ar-BIAN.



Scheme 26. The first isolated CO/olefin cooligomer connected to a Pd(II) center.



Scheme 27. Symmetrical graft triblock polymer obtained by sequential insertion of norbornene into Pd–acyl bonds.

$$[Pd(Me\text{-}DUPHOS)(MeCN)_2]^{2+} + HCO_2H \xrightarrow[\text{- MeCN}]{} [PdH(Me\text{-}DUPHOS)(MeCN)]^{+} + CO_2 + H^{+}$$

Scheme 28. The role of formic acid in generating Pd–H species.

symmetrical graft triblock polymer has been obtained by sequential insertion of norbornene into Pd–acyl bonds as illustrated in Scheme 27 [48].

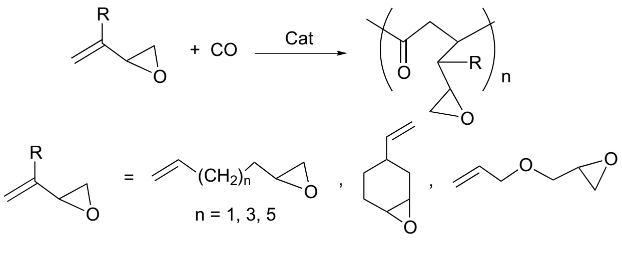
6. Copolymerization of CO and miscellaneous olefinically unsaturated hydrocarbons

The copolymerization of CO with other olefins than those considered so far in this review has received less attention. Sen has reported the copolymerization of functionalized (–COOH or –OH) olefins with CO using [Pd{(*R*,*R*)-Me-DUPHOS)}$(MeCN)_2(BF_4)_2$ (Me-DUPHOS = 1,2 - bis(2,5 - dimethylphospholano) - benzene) [112]. The latter catalyst has recently been employed by Lee and Halper to copolymerize vinyl epoxides with CO in nitromethane or chloroform at 40 °C and 1000 psi CO. Optimum conditions for the copolymerization require the use of 1,4-naphtoquinone as organic oxidant and of formic acid as promoter. The role of formic acid is to generate Pd–H through the reaction shown in Scheme 28 [113].

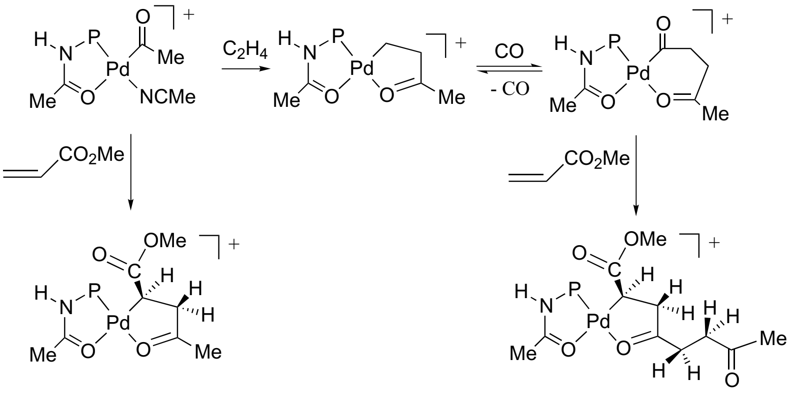
For relatively short reaction times (24 h) soluble copolymers with the poly(1,4-ketone) structure and molecular weights ranging from 10 to 30 kg mol^{-1} were obtained (Scheme 29), while the prevailing formation of insoluble solids with poly(spiroketal-1,4-ketone) structure occurred for longer times.

Catalysts capable of effectively producing copolymers of CO with α-olefins functionalized with polar groups have never been reported. In contrast, the insertion reactions of polar monomers such as alkyl acrylates and vinyl acetate into Pd–acyl bonds have been investigated by several authors and valuable mechanistic information on this important elementary step of the chain growth process has been obtained [41e,41g,59]. Within this context, of particular relevance are recent studies by Braunstein dealing with the stereochemistry of insertion of methyl acrylate into Pd–acyl bonds derived from the reaction of CO into Pd–Me or Pd–CH_2CH_2COMe. The insertion of CO in the latter Pd–alkyl bond has shed light on the mechanism and stereochemistry of alternating copolymer blocks incorporating a polar olefin besides ethene and CO (Scheme 30) [41g].

Although allenes cannot be classified as olefins, it is worth reporting here that the copolymerization of CO and allenes can effectively be achieved by palladium catalysts stabilized by either α-diimine or phosphine ligands [114,115]. Detailed fundamental studies of the insertion of allenes into Pd–acyl bonds supported by dinitrogen ligands have also been reported [116]. Kacker and Sen have described the synthesis of a terpolymer consisting of alternating copolymer blocks incorporating three different types of monomers:



Scheme 29. Copolymerization of CO with vinyl epoxides.



Scheme 30. Mechanism and stereochemistry of alternating CO/ethene copolymer blocks incorporating a polar olefin.

ethene, allene and CO [115]. This intriguing reaction promoted by the neutral complex $Pd(PPh_3)_2MeCl$ is illustrated in Scheme 31.

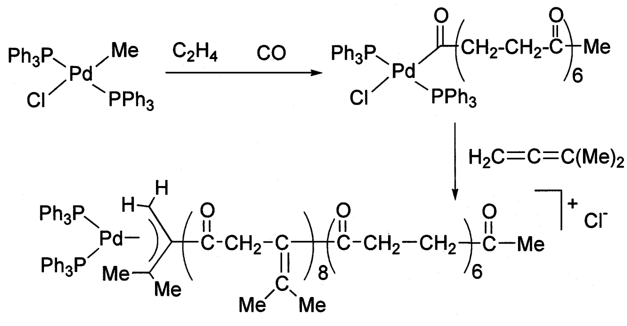
A palladium complex containing a ter-oligomer of CO, allene and norbornadiene has been isolated with the rigid backbone dinitrogen ligand *p*-An-BIAN. The reaction sequence leading to the formation of such a ter-oligomer is shown in Scheme 32 [116a].

Examples of copolymerization of CO with acetylene or 1-alkynes have been reported [117]. These reactions are not commented on in detail as they are beyond the scope of this review. However, it is worth reporting here that the catalysts for the copolymerization of CO and alkynes are very similar to those currently employed for the olefins [117b], and that the synthesis of terpolymers of CO, ethene and acetylene would be highly desirable for the presence of conjugated double bonds and their possible functionalization.

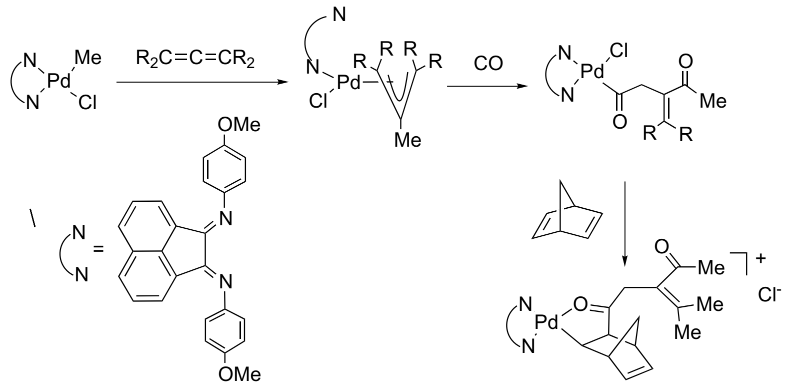
7. Summary and outlook

After reading this review article, who might doubt the remarkable academic and industrial importance of the alternating copolymerization of olefins with CO? It is shown here that almost all fundamental organometallic reactions are involved in the metal-catalyzed synthesis of polyketones: M–H, M–C, C–C and C–H bond making and breaking; migratory insertions of monomers into M–H, M–alkyl, and M–acyl bonds; metal activation of O–H bonds from water and alcohols to give either M–H or M–OR. As well, it is shown that the productivity and selectivity of any copolymerization catalyst is strictly controlled by a complex web of chemical, electrochemical, stereochemical and kinetic properties. Finally, it is reported that the alternating CO/olefin copolymerization can be achieved in different phase variation systems, spanning from true homogeneous processes in organic or aqueous solvents, to heterogeneous processes in slurry or microcrystalline systems. Carrying out reactions in such different environments requires a deep knowledge of the chemistry in interphases and the use of a large variety of extra and in situ spectroscopic techniques.

From the industrial perspective, alternating CO/olefin copolymers are not only the lowest cost bulk plastic that can be made but also materials featured by unique chemical and physical properties as well as an environmentally friendly nature that, taken altogether, make polyketones superior to many polyolefins, polyamides and polyacetals [4c,6,7]. Many properties of polyketones may be improved and new properties may be envisaged by changing the number and/or the nature of the comonomers as well as finely tuning the structure of the metal catalysts. However, a wide margin of improvement in the stability and performance parameters of the material as well as in the activity and cost of catalysts does exist and is sufficient to justify the increasing research efforts aimed at designing new catalytic systems for the alternating copolymerization of CO and olefins.



Scheme 31. Synthesis of alternating copolymer blocks incorporating ethene, allene and CO.



Scheme 32. Reaction sequence leading to the formation of a palladium complex containing a ter-oligomer of CO, allene and norbornadiene.

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