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Alternating and Non-Alternating Pd-Catalysed Co- and Terpolymerisation of Carbon Monoxide and Alkenes

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The co- and terpolymerisation of carbon monoxide and alkenes are usually catalysed by palladium complexes, and the properties of the produced polyketones can be finely tuned by an appropriate choice of catalyst and olefinic monomer. After a general overview of the topic, selected recent advances in this field are described. The use of palladium systems containing modified diphosphane and/or new phosphorus-based ligands, and the results obtained using a series of modular N and S ligands, including chiral ligands, in CO/styrene co- and terpolymerisations are reported. The use of new P-O ligands in non-alternating CO/ethene copolymerisation is also described.

Introduction

The industrial interest in polyketones obtained by the catalytic copolymerisation of carbon monoxide with one or more alkene monomers has increased relentlessly over the last few decades. These materials represent a class of low-cost thermoplastics whose synthesis, properties and applications are still the object of intense fundamental and applied research. At least two of these CO/olefins polymers are produced industrially, namely Carilon® by Shell[1] and Ketonex® by BP.[2]

Polyketones provide a unique web of chemical and physical properties, which include photo- and biodegradability, good chemical resistance to acids, bases and solvents, impermeability to hydrocarbons and strong rigidity and impact strength.[3,4] These properties can be both modified and improved by changing the number or nature of the comonomers and tuning the structure of the metal catalyst. The diversity of their properties makes polyketones superior to polyolefins, polyamides and polyacetals.[5]

With this review, we wish to present a concise overview of relevant advances in Pd-catalysed CO/olefin co- and ter-

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Carmen Claver (second from left) is Professor of Inorganic Chemistry at the University Rovira i Virgili (URV) in Tarragona, Spain, a position she has held since 1991. She received her PhD in 1978 from the University of Zaragoza, Spain, working in the field of organometallic chemistry and homogeneous catalysis. Her research is aimed at the development of advanced transition metal catalysis and covers the synthesis of ligands and complexes and the characterisation of intermediates, focusing mainly on their application in enantioselective catalysis and polymerisation processes. She has co-authored scientific contributions in this field and has participated in the edition and publication of several books. She has received several scientific awards, and was recognised in 2003 as a Distinguished Researcher by the Catalan Government.

Eduardo J. García Suárez (second from right) was born in 1973 in Gijón, Spain. He completed his undergraduate studies in 2002 at the Universidad de Oviedo. In 2003, he was awarded a Marie Curie training fellowship at the Istituto di Chimica dei Composti Organometallici in Florence, Italy. He is currently working towards his PhD under the supervision of Prof. Carmen Claver and Dr. Claudio Bianchini at the Universitat Rovira i Virgili in Tarragona, Spain.

Aurora Ruiz (right) completed her undergraduate studies in chemistry at the Universitat de Barcelona (UB) and was awarded a PhD from the same university in 1983. She is now Professor of Inorganic Chemistry at the Faculty of Chemistry of the Universitat Rovira i Virgili (URV) in Tarragona. Her current research field is homogeneous catalysis covering aspects of synthesis, characterisation of chiral organometallic complexes and their application in asymmetric catalysis.

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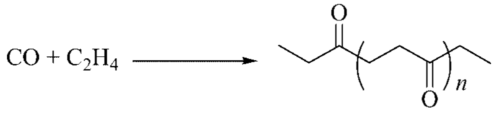
polymerisation. As the first developments have already been reviewed,[6] particular focus will be given to recent advances in this field, including contributions from our research group.

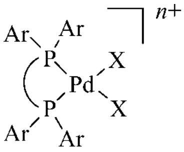
Perfectly Alternating CO/Ethene Copolymerisation

The simplest polyketone is the CO/ethene copolymer (Scheme 1).



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

Perfectly alternating CO/ethene copolymerisation is efficiently carried out in methanol at moderate temperatures (about 80 °C) in the presence of a catalyst system that contains a Pd^{II} salt with a weakly coordinating counterion and a chelating diphosphane as essential components (Figure 1).[6]



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

Figure 1. Usual pre-catalysts for perfectly alternating CO/ethene copolymerisation.

1,3-Bis(diphenylphosphanyl)propane (dppp) was the ligand that opened the way to the efficient synthesis of polyketones.[7] Pressures between 30 and 60 bar of CO/ethene are usually employed. When all the CO has been consumed, the catalyst promotes the dimerisation of ethene into butenes. Polyketones with different combinations of end groups such as diketone, keto-ester and diester groups can be obtained.

The optimal reaction conditions in methanol require the presence of both a strong oxidant ($E^0 \geq 0$) and a protic acid ($pK_a \leq 4$) whose conjugate base must have a low binding affinity to Pd^{II}. 1,4-Benzoquinone (BQ) and p-toluenesulfonic acid (TsOH) are two examples that fulfil these requirements and are the stabilising compounds for the most productive catalytic systems. Productivities as high as 11000 $g\,CP\,(g\,Pd\,h)^{-1}$ (CP = copolymer) can be obtained under these experimental conditions.[6]

The role of the 1,4-benzoquinone is to oxidise the Pd^0 or Pd^I species that are formed in the catalytic process to Pd^{II}, and the main role of the protic acid is to prevent the deactivation of the palladium(II) catalyst into inactive (P-P)Pd^0 by protonating the latter species to reform the catalytically active species [(P-P)PdH]$^+$.

Ligand Systems Used in CO/Ethene Copolymerisation

One of the advantages of catalytic systems bearing phosphorus-based ligands is the structural diversity and the ease of modification of this type of ligand. Drent et al.[6a,7b] were the first to investigate the influence of the structure of the diphosphane ligand on the activity of the Pd^{II} catalyst. This study found a strong dependence of the catalytic activity on the chain length of the carbon backbone between the two phosphorus atoms, with dppp giving the highest productivity.

Since the discovery of the efficiency of the Pd-dppp catalyst by Shell Research in 1984, various dppp-like ligands have been designed and successfully employed to catalyse CO/ethene copolymerisation in combination with Pd^{II} salts. Most ligand variations have involved substitutions in both phenyl groups and/or the carbon backbone, and a considerable increase in the productivity (ca. 50%) was obtained when alkyl groups were introduced in both the 1- and 3-positions of the dppp backbone to yield *meso*-2,4-bis(diphenylphosphanyl)pentane (bdpp). Both electronic and steric factors have been suggested to explain the remarkable activity of these catalysts, and it was proposed that the increased activity of Pd(*meso*-bdpp) could be due to the more facile re-oxidation of the one-electron-reduced species by both 1,4-benzoquinone or H$^+$, which would result in a larger number of active Pd centres in the catalytic mixture.

In terms of productivity and catalyst stability, the introduction of *ortho*-methoxy groups at each phenyl unit of the dppp ligand has also been shown to have a beneficial influence (Figure 2).[8]

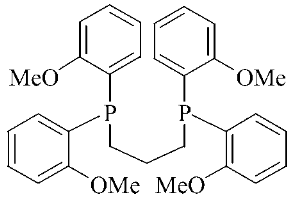


Figure 2. o-MeO-dppp used in CO/ethene copolymerisation.

A water-soluble version of o-MeO-dppp containing m-sodium sulfonatophenyl groups has also been used, which shows that the *ortho*-methoxy moiety can exert both a steric and an electronic influence on the palladium centre.[8b]

Modifications of the ligand backbone of dppe-based ligands have also been investigated and it was found that the backbone rigidity and the overall steric crowding at the Pd centre play a crucial role in determining the catalytic activity.[9] Thus, Pd^{II} catalysts bearing the *cyclo*-tetraphos ligand (Figure 3) are 10-times more efficient than those with dppe.

The beneficial effect of the ligand rigidity for copolymerisation reactions has also been confirmed using bisphospholyl-substituted carbon backbones.[10]

Experimental evidence has also shown that four-membered ring systems with isopropyl-substituted phenyl rings can also exhibit high catalytic activity (Figure 4).[11]

Phosphorus-metallocene based ligands have also been tested recently for the copolymerisation of CO/ethene.[12] Relatively low molecular weight copolymers were obtained and both the catalytic activity and the chemoselectivity of the copolymerisation reaction were shown to depend on the

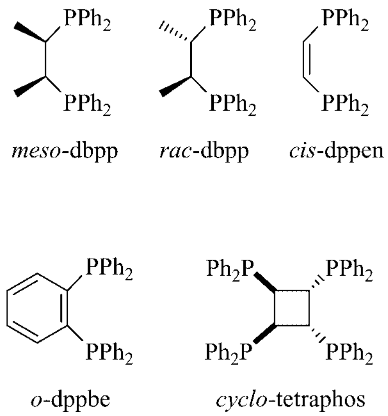
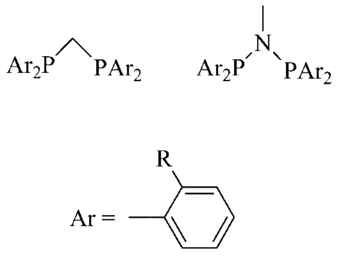


Figure 3. Rigid diphosphane ligands forming five-membered metallacycles.



R = H, OMe, Me, Et or *i*Pr

Figure 4. Ligands that form four-membered metallacycles.

sandwiched metal centre, the substituents on the cyclopentadienido ring and on the substituents bonded to the phosphorus donor atoms.

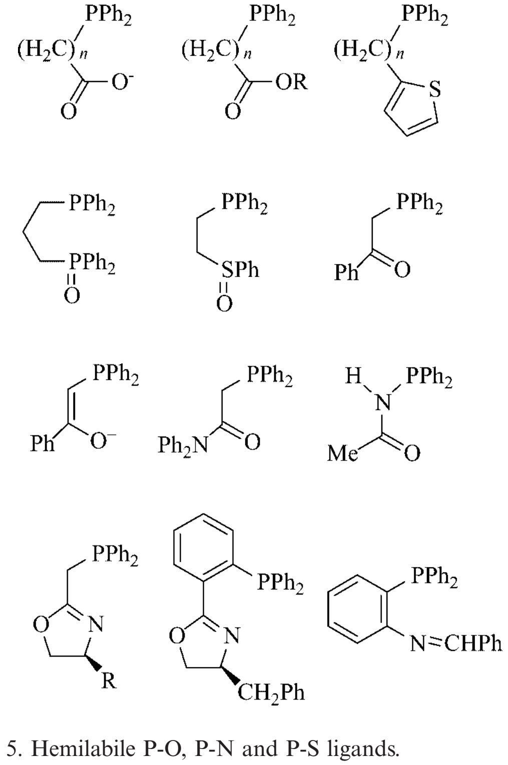


Figure 5. Hemilabile P-O, P-N and P-S ligands.

Another class of ligands used for CO/ethene copolymerisation corresponds to hemilabile phosphane ligands containing oxygen, nitrogen or sulfur donor atoms,[13] although their catalytic activity is lower than that of dinitrogen and diphosphane ligands. Some of the P-O, P-N and P-S ligands that have been studied with the aim of forming efficient catalysts for CO/ethene copolymerisation are presented in Figure 5.

Sterically rigid dinitrogen ligands such as bipyridine (bipy), phenanthroline (phen) and their alkyl-substituted derivatives form efficient catalysts for alternating CO/ethene copolymerisation under both homogeneous and heterogeneous conditions.[14]

CO/Styrene Copolymerisation

Unlike aliphatic olefins, the copolymerisation of styrene and its derivatives with CO requires the use of Pd^{II} catalysts with chelating dinitrogen ligands[3,6a,15,16] – the use of Pd catalysts bearing diphosphane ligands gives only low molecular weight oligomers.[6a,16c,16f,17] It is commonly agreed that termination by β-H elimination is favoured over propagation of the polymer due to the higher electron density on the palladium centre in phosphane-modified catalysts,[6,16–18] and it has also been suggested that the (diphosphane)Pd–styryl intermediates formed in the initial steps of the CO/styrene copolymerisation are so strongly stabilised by π-benzylic coordination that this inhibits CO insertion. Termination by β-H elimination thus becomes favoured and oligoketones are formed instead of polyketones.[17]

Copolymers of the general formula $[CH(Ar)CH_2CO]_n$ show regio- and stereoisomerism due to the presence of truly stereogenic centres in the polymer backbone.[19] Depending on the regioselectivity of the monomer insertion, either primary (1,2-mode) or secondary (2,1-mode), into the polymer chain, three different arrangements are possible during the polymerisation: tail-to-tail, head-to-tail and head-to-head. With dinitrogen ligands styrene insertion into the Pd–acyl bond takes place exclusively in a 2,1-fashion and leads only to head-to-tail units. However, a mechanistic study using a phosphane-phosphite ligand showed that 1,2-insertion of styrene can occur and that in this case β-H elimination occurs from the 2,1-complex rather than the 1,2-complex.[17c]

Syndiotactic and isotactic alternating copolymers present very low and high optical activities, respectively, and control of the regio- and enantioselectivities of styrene insertion, ultimately leading to stereoregular polyketones, can be achieved by a suitable choice of bidentate ligands.

Copolymerisation catalysts usually contain achiral ligands that lead to the formation of products of head-to-tail regioselectivity and syndiotactic stereoselectivity. The stereoselectivity is a result of chain control, with the enantioface of the incoming styrene being directed by the stereogenic centre of the last incorporated styrene unit, taking into account that styrene inserts exclusively in a 2,1-mode.[16b,16d]

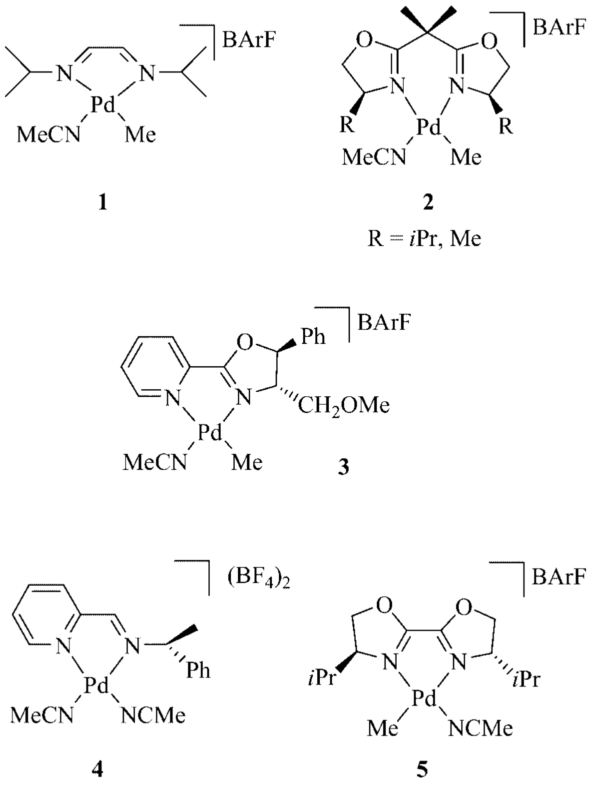
Typical catalysts used for perfectly alternating copolymerisation of CO and styrene for the production of syndiotactic copolymers contain a Pd^{II} salt and a chelating dinitrogen ligand such as bipy or phen. This reaction requires the presence of a Brønsted acid (e.g. TsOH) and a large excess of a strong oxidant such as BQ with respect to Pd. The production of copolymer is strongly decreased in the absence of oxidant, although the molecular weight of the copolymer is inversely proportional to the concentration of BQ.[3,6,15,16] The solvent of choice is usually methanol, although a striking effect has been observed on the stability of the catalytic systems with 2,2,2-trifluoroethanol (TFE) as solvent.[20] This effect was attributed to the higher stability of Pd-acyl intermediates in TFE than in methanol. For instance, the lower nucleophilicity of TFE could inhibit the chain end by alcoholysis. The palladium(II) complex $[Pd(bipy)_2][PF_6]_2$ has been found to still be active in TFE after 48 h of reaction and to yield high molecular weight copolymers with a productivity of $360\,gCP(gPd\,h)^{-1}$, and high yields and high molecular weight copolymers are obtained even in the absence of oxidant.[21]

The influence of various counterions has also been investigated, with the result that the catalytic activity decreases in the order $B[3,5\text{-}(CF_3)_2C_6H_3]_4$ (BArF) > SbF_6/PF_6> BF_4 > OTf >> BPh_4 (OTf = triflate). The strength of the interionic interactions has been shown to have a negative effect on the productivity of the catalysts.[22]

The production of syndiotactic copolymers of 4-methylstyrene and CO has been achieved at 0 °C at 1 atm of CO with the Pd complex **1** (Figure 6), which was also used as a precursor in studies of the first steps of the polymer chain-growth, as catalyst.

It has been demonstrated that when a catalyst bearing ligands that contain one or several stereogenic centres is used, the enantioface discrimination is directed by the ligand and not the chain end control. Brookhart and coworkers, for example, have reported the first enantioselective copolymerisation of CO and styrene using a Pd(bisoxazoline) system (complex **2**, Figure 6). The reaction was performed under 1 atm of CO at room temperature with 4-*tert*-butylstyrene as both solvent and substrate and yielded copolymers with both a highly isotactic microstructure and high optical activity as a result of enantiomorphic site control.[23] The orientation of the incoming styrene was shown to be strongly controlled by the presence of substituents in the 4-positions of the oxazoline ring. However, the use of palladium systems bearing oxazolinyl-pyridine ligands (complex **3**, Figure 6) leads to the production of mainly syndiotactic copolymers, which indicates that chain control predominates.

The production of chiral alternating CO/styrene copolymers has also been reported, although with a lower stereoregularity, with a pyridine-imine system (complex **4**, Figure 6),[24] and Carfagna et al. have reported the production of highly isotactic optically active copolymers of CO and styrene or 4-methylstyrene with a bisoxazoline catalytic system (complex **5**, Figure 6). They obtained only low yields, however, and attributed this to the weak coordinating properties of this ligand which result in a destabilisation of the catalyst under these reaction conditions.[25] Productivities as high as $21\,gCP(gPd\,h)^{-1}$ for average molecular weight copolymers have been obtained at room temperature under a constant CO pressure of 1 bar with palladium complexes bearing chiral diketimines or dialdimines.[26]



1 **2** R = *i*Pr, Me **3** **4** **5**

Figure 6. Some systems used in Pd-catalysed CO/styrene copolymerisation.

Brookhart et al., in a particularly inventive strategy, have achieved the production of stereoblock polyketones by exchanging ligands during the catalytic reaction. Thus, an isotactic segment is produced in a first step using the bisoxazoline system **2** (Figure 6), then addition of bipyridine to the reaction medium results in the elongation of the copolymer in a syndiotactic way.[27]

CO/Olefins Terpolymerisation

Despite the fact that the two polyketones that have been commercialised are terpolymers of CO/ethene/propene,[1,2] terpolymerisation reactions have been much less studied than copolymerisations. Similarly to the copolymerisation catalysts, the terpolymerisation of CO with aliphatic olefins is usually performed using complexes bearing phosphorus-based ligands,[28] and the only reported example of terpolymerisation of CO with two vinylarenes is promoted by Pd(phen) complexes.[13h,29] The terpolymerisation of CO with one aliphatic and one aromatic olefin is somewhat more versatile and various types of ligand systems have been successfully used, such as P-P,[30] P-OP,[31] P-N[13h,32] and N-N[15,16d,22,30,33–35] (Figure 7).

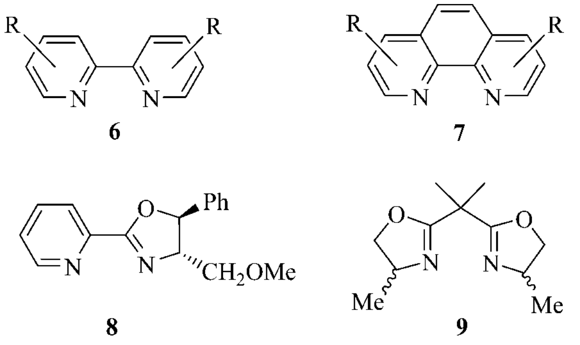


Figure 7. N-N ligands used for the Pd-catalysed terpolymerisation of CO with one aliphatic and one aromatic olefin.

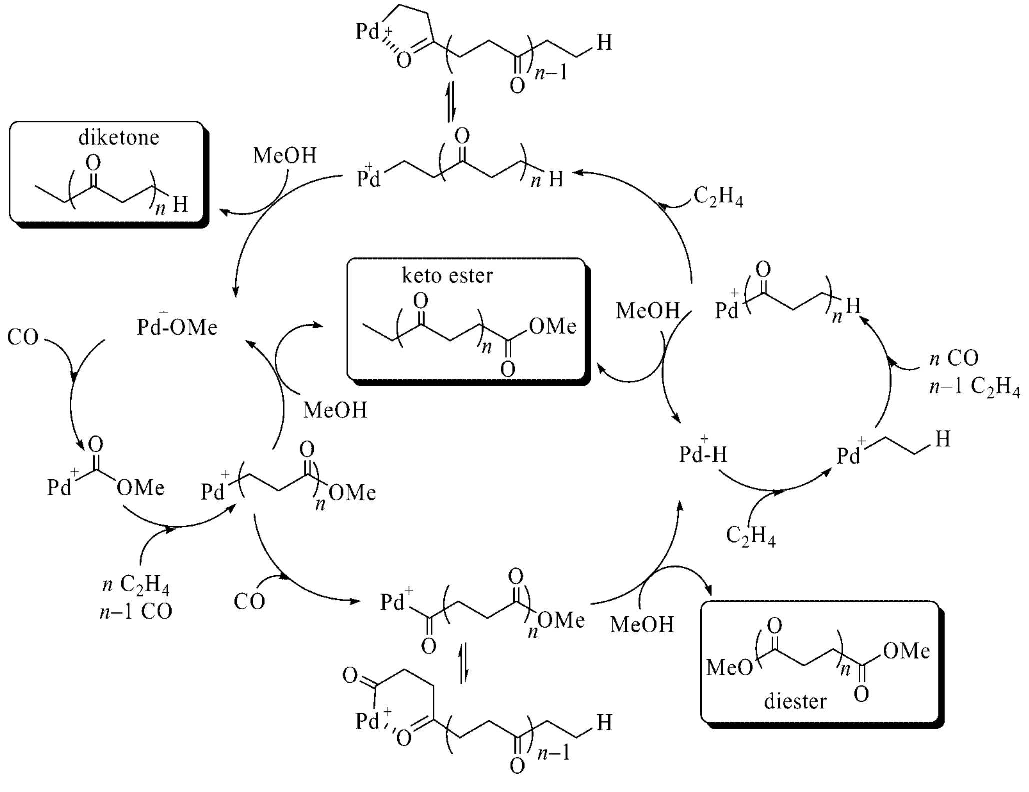
The propagation step of this reaction is based on alternating migratory insertion of CO into a Pd–alkyl bond and of one of the olefins into a Pd–acyl bond. Depending on the characteristics of both the olefins and the catalyst, the resulting terpolymers can have a distinct composition and thus distinct properties.

The dinitrogen systems used for this reaction are essentially derived from planar bipy and phen systems (**6** and **7** in Figure 7), although Brookhart and Consiglio have reported that the use of chiral ligands (**8** and **9**, Figure 7) in this reaction produces optically active terpolymers.

Mechanism

The first detailed mechanistic study of the Pd-catalysed perfectly alternating CO/ethene copolymerisation was reported by Drent et al. in 1991, and since then a large number of studies from both an experimental and theoretical viewpoint have been reported and have contributed to a better understanding of each step of the catalytic reaction. These studies have also helped to identify, and obtain information about, the active species and resting states in the reaction. Most of these studies have been reviewed before therefore only a brief description of the catalytic cycle will be given here.[6,3,36]

As shown in Scheme 2, two competing cycles that are connected by cross terminating steps and whose prevalence depends on the reaction conditions participate in the production of polyketones. One cycle initiates with a Pd–H species and is favoured by traces of water in the solvent (methanol) via the Water Gas Shift reaction.[37] Rapid insertion of ethene gives an alkyl species that reacts reversibly with CO to yield an acyl complex, which then irreversibly inserts a second ethene molecule. The propagation thus occurs through alternating CO and ethene insertions. Keto esters and diketones can be produced from this cycle, depending on the termination path: the methanolysis of an acyl species yields a keto ester whereas protonolysis of an alkyl complex yields a diketone. The second cycle initiates with a Pd-methoxy species that reacts with CO to form a methoxycarbonyl-Pd complex. Keto esters are also produced during this cycle, together with copolymers with a diester structure that are produced by methanolysis of a acyl-Pd. The palladium hydride species is the most probable initiator in the presence of organic oxidants, and methanolysis is therefore the main termination mechanism. Kinetic studies have shown that ethene insertion is the rate-limiting step of the reaction.[6]



Scheme 2. Proposed mechanism for CO/ethene copolymerisation by diphosphanepalladium catalysts.

Two competing chain-transfer mechanisms have been proposed for the alternating copolymerisation of CO and ethene. One involves termination by an unexpected isomerisation into the enolate followed by protonation with methanol and subsequent initiation by insertion of CO into the methoxypalladium species, and the second one involves termination by methanolysis of the acylpalladium species and subsequent initiation by insertion of ethene into the palladium–hydride bond.[38]

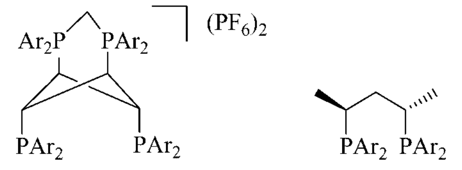
The main features of the catalytic cycle for CO/styrene copolymerisation are similar to those of CO/ethene copolymerisation. The propagation step, in particular, is identical, with alternating insertions of CO into Pd–alkyl bonds and of styrene into Pd–acyl bonds. However, the initiation and termination steps are distinct and depend on the nature of the olefinic substrate.[6] The termination pathway that prevails in methanol involves fast β-hydrogen elimination from alkyl species and thus yields a Pd–H complex at the end of the cycle.

We will now focus on selected recent advances in this field. We describe the use of palladium systems containing modified diphosphane and/or new phosphorus ligands, and the results obtained using a series of modular N and S ligands, including chiral ligands, in CO/styrene co- and terpolymerisation. The use of new P-O ligands in non-alternating CO/ethene copolymerisation is also described.

Ligand Tuning: Modified Diphosphane and Related P-P Ligands

As mentioned in the introduction, Pd^{II} catalysts based on diphosphane ligands have been shown to be the most suitable catalyst systems for the alternating copolymerisation of carbon monoxide and ethene.[6a] Many attempts have been carried out to improve this catalytic system by modifying the diphosphane moiety.[8b] The introduction of methoxy groups in the *ortho* positions in the phenyl rings attached to the phosphorus atoms, for example, has been shown to have a beneficial effect on the copolymerisation in terms of productivity and average molecular weight of the resulting polyketones.[39,40]

Two new chelating diphosphanes ligands have been synthesised and tested in the alternating copolymerisation reaction of carbon monoxide and ethene (Figure 8).[41] The aim of this study was to compare the diphosphane ligand **10** with the neutral and less rigid C_3-bridged diphosphane ligand **11** in the copolymerisation reaction. Ligand **10** is the first example of a diphosphonium ligand for the copolymerisation of carbon monoxide and ethene. The square-planar complexes $[PdCl_2(P-P)]$ and $[Pd(OAc)_2(P-P)]$ (P-P = **10**, **11**) were used as catalyst precursors for the CO/ethene copolymerisation reaction and showed high activity and remarkable control of the molecular weight of the alternating polyketone products.



(o-MeO-PCP)$(PF_6)_2$

10

rac-*o*-MeO-bdpp

11

Ar = 2-methoxyphenyl

Figure 8. New chelating ligands used in CO/ethene copolymerisation.

$[PdX_2(P-P)]$ (P-P = **10**, **11**) complexes (X = Cl or OAc) were then used to generate very active Pd species in water/AcOH mixtures or in MeOH in the presence of *p*-TsOH. The dichloride complexes were tested in mixtures of water and AcOH under standard experimental conditions (40 bar, CO:ethene = 1:1, 85 °C). Perfectly alternating polyketones were obtained in all cases, with only ketone end-groups.

The mechanism of CO/ethene copolymerisation catalysed by $[PdCl_2(P-P)]$ complexes in acidic aqueous media is well known, and the chain transfer and propagation steps have been studied in some detail.[6,42] It is usually accepted that neutral Pd^{II}–H complexes are generated from the dichloride precursors by the a Water Gas Shift (WGS) reaction.[43]

$[Pd(OAc)_2(P-P)]$ complexes were found to be good precursors for the copolymerisation reaction in MeOH in the presence of 2 and 20 equivalents of *p*-TsOH. The acid was used both as a scavenger of the acetate ion and as oxidising agent to form Pd^{II} species from Pd^0.[6,42] With both catalyst precursors, the copolymer product contained keto and ester end-groups in a 1:1 ratio. Both catalysts gave polymers with larger M_n (number-average molecular weights) values than the polymers obtained in water/AcOH. It was therefore concluded that the chain-transfer step is slower in MeOH than in water/AcOH. In contrast with the trend usually observed for CO/ethene copolymerisation in MeOH catalysed by Pd^{II}–diphosphane complexes,[6,40b] an inverse dependence of the productivity on the acid concentration was found for the reactions catalysed by $[Pd(OAc)_2(\mathbf{11})]$.

The polyketones obtained with the diphosphonium-diphosphane catalysts showed M_n values up to five times lower than those obtained with the less rigid C_3 diphosphane catalysts. These results can be explained by a faster chain-transfer due to the electronic and steric properties of the diphosphonium-diphosphane ligand.

In order to gain an understanding on the beneficial effect of the *ortho*-methoxy group on the alternating copolymerisation of carbon monoxide and ethene,[42,44] neutral and dicationic palladium(II) complexes bearing *o*-MeO-dppe, *o*-MeO-dppp and their analogous precursors with dppe and dppp were synthesised. The catalytic activities were compared in various reaction media (MeOH, CH_2Cl_2, TFE, toluene and H_2O/AcOH). In addition, in situ and in operando HP-NMR experiments were performed in order to provide valuable information on catalysis resting states and intermediates. Independently of the reaction media, higher catalyst productivities and polyketone molecular weights were achieved using the modified ligands, except in TFE, in which both productivities and molecular weights were lower. This unexpected behaviour in TFE was suggested to be due to the formation of an effective web of hydrogen-bonding interactions between solvent molecules and the *o*-methoxy oxygen atoms of either *o*-MeO-dppp or *o*-MeO-dppe. A slower diffusion of the monomers would take place as a result of the increased congestion at the metal centre, thus lowering the propagation rate. Although this hypothesis was not supported by experimental evidence, such interactions have previously been reported for related palladium systems.[45] The differences observed in productivity between modified and unmodified ligands for the different reaction media can be attributed to both steric and electronic factors related to the *o*-methoxy groups, which would induce a lower tendency to form inactive bis-chelates and dimers, reduced phosphane oxidation,[46] an increased basicity of the metal centre,[40b] and a reduced stability of catalyst resting states such as β-keto alkyl chelates.[42]

Modular N-N′ Ligands for the Copolymerisation of CO and Styrene

As discussed above, the Pd-catalysed copolymerisation of CO and vinyl arenes has been reported to be more efficient with nitrogen donor ligands than with phosphorus-based ligands.[3,6a,15,16] In contrast with CO/ethene copolymerisation, a stereogenic centre is created in each -($COCHRCH_2$)- unit, therefore the use of a chiral ligand is of interest. The alternating CO/4-*tert*-butylstyrene (TBS) copolymerisation reaction has been investigated in our research group using various systems containing chelating asymmetric dinitrogen ligands (Figure 9).

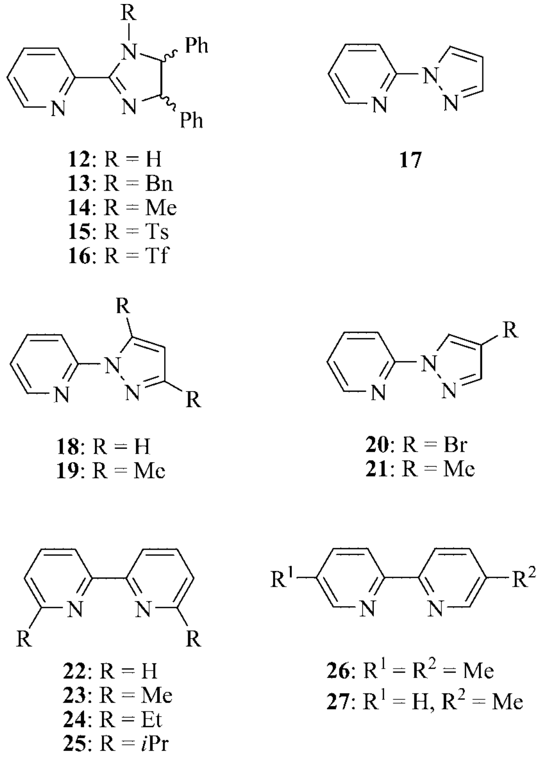


Figure 9. N-N′ ligands used in our group for CO/TBS copolymerisation.

When modular imidazolyl-pyridine ligands **12**–**16** were used, the stereochemistry of the corresponding palladium complexes [PdMe(NCMe)(N-N′)][BArF] was found to be influenced by the electronic properties of the R substituents of the imidazole moieties.[47,48] Indeed, in the case of ligands **12**–**14** the imidazole unit was always found to be *cis* to the methyl group bonded to Pd whereas in the case of ligands **15** and **16**, which contain electron-withdrawing substituents, a mixture of *cis* and *trans* isomers was obtained. This correlation between the relative stability of the *cis* and *trans* isomers of these cationic complexes and the nature of the R substituents was also confirmed by density functional theory calculations.[48] In terms of catalysis, productivities between about 2 and 30 $g\,CP\,(g\,Pd\,h)^{-1}$ were achieved, with molecular weights of between 17000 and about 80000 under mild conditions (P_{CO} = 1 bar, room temp., TBS/Pd = 620). The nature of the substituents was found to influence both the productivity of the catalyst and the stereoregularity of the polymer but had no effect on the molecular weight of the polyketones. The catalysts bearing the less basic imidazole moieties **15** and **16** were found to be the most active, probably because they favour the coordination of the styrene substrate. They were also shown to favour the production of *u* diads, giving highly syndiotactic copolymers. The microstructure of the polyketones obtained with the (*R*,*S*)-4′,5′-imidazolines was found to depend on the electronic properties of the ligands, whereas only syndiotactic polyketones were obtained when the (*R*,*R*) diastereoisomers were used. This result indicates that chain-end control is more effective than enantiosite control. A comparison of the structures of the complexes containing (*R*,*R*)- and (*R*,*S*)-4′,5′ imidazoline moieties showed that the presence of the (*R*,*R*) diastereoisomers leads to a lower degree of distortion that stabilises the complexes during catalysis, although no direct trend with the productivity of the catalyst could be determined.

When the imidazole moiety was replaced by a pyrazole unit (ligand **17**), the productivity of the catalyst and the molecular weight of the polyketone produced were both found to be moderate under the same conditions (ca. 20 $g\,CP\,(g\,Pd\,h)^{-1}$ and 30000, respectively).[49]

In the case of pyrimidine-pyrazole ligands, the coordination to the palladium centre to give [PdMe(NCMe)-(N-N′)]$^+$ complexes was found to be directed by the steric bulk of the pyrazole moiety.[49,50] Indeed, when ligand **18** was used, the pyrazole moiety was found to be in a *cis* position to the PdMe group. However, when methyl substituents were introduced in positions 3 and 5 of the pyrazole unit (ligand **19**), the pyrimidine moiety was found to be *cis* to the methyl group. The corresponding polyketones were obtained in high yield with a molecular weight of up to 82000 and polydispersities ranging between 1.3 and 1.7, which are close to the best values reported for planar C_s-symmetric dinitrogen ligands with styrene derivatives. The high yield is due to the stability of the active species when the reaction is carried out in TFE. Similarly, the enhanced growth of the polymeric chain, as a result of competition between the propagation and the termination steps, is due to the greatly enhanced stability of the acyl- and/or alkylpalladium intermediate in TFE with respect to CH_2Cl_2 or chlorobenzene, which causes a remarkable increase in the catalyst lifetime. Optimisation of the amount of trifluoroethanol required for the copolymerisation reaction was performed with bipyridyl ligands and was shown to have a direct effect on the productivity of the catalyst.[51] This effect is shown in Figure 10 using $[Pd(bipy)_2][BArF]_2$ as catalyst precursor.

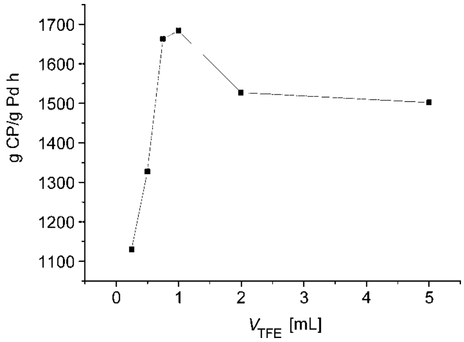


Figure 10. Optimisation of the amount of trifluoroethanol required for CO/TBS copolymerisation (T = 60 °C, V_{TBS} = 10 mL, nPd = 5.1×10^{-4} mmol; nBQ = 5.1×10^{-3} mmol).

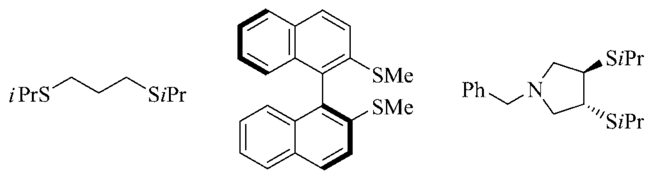
The cationic palladium systems [PdMe(NCMe)(N-N′)]-[BArF] containing imidazolyl-pyridine ligands *cis*-**12**, *cis*-**13**, *cis*- and *trans*-**15** and pyrazolyl-pyridines **18**, **20** and **21** have also been used for the terpolymerisation of CO/TBS/ethene.[50,52] It was found that the choice of the olefin preferentially inserted into the terpolymer is strictly related to the nature of the nitrogen ligand present in the catalyst and not only to the kind of ligand. Thus, a slight modification in the chelating N ligands coordinated to palladium terpolymerisation catalysts leads to unexpected results in the composition of the terpolymers. For example, the catalysts containing imidazolyl-pyridines **12**, **13** and **15** readily insert ethylene, even at low pressures, and terpolymers with a perfectly controlled composition are obtained if the ethylene/styrene ratio is varied. However, complexes with ligands **18**, **20** and **21** show less versatility towards ethylene pressure and give terpolymers with similar amounts of both olefins. Differences are also encountered in activity/stability: while catalysts bearing ligands *trans*-**15**, **18** and **21** are highly active, those with ligands **12**, **13** and *cis*-**15** decompose quickly. Upon comparing the planar ligands **18** and **21** with the bulkier chiral ones **12**, **13** and **15**, it seems that the chiral imidazolyl-pyridines interfere more with the coordination/insertion of the olefin, which is the rate-determining step of the reaction. This would explain why the systems containing planar ligands **18** and **21** are more active than the system containing *trans*-**15**. The similarity between ligands *cis*-**15** and *trans*-**15**, which only differ in the configuration of one asymmetric carbon atom, and their disparate productivities show that it is more probable that a steric rather than an electronic, effect is responsible for these results. In fact, X-ray analysis of the complex $[Pd(Cl)_2($*trans*-**15**$)]$ shows that this ligand presents a unique distortion in the imidazoline plane, which may account for the high reactivity observed with this ligand. Comparison with the CO/TBS results shows that the size of the polymer chain is lower when the chain contains ethylene, which favours β-H elimination. Circular dichroism (CD) analysis of the terpolymer obtained with the enantiomerically pure ligand **15** shows that it is optically active. Since this ligand is not able to induce chirality in the CO/TBS copolymerisation (syndiotactic copolymers were obtained), it is clear that the presence of ethylene in the growing polymer chain decreases the probability of chain-end control exerted by the last inserted styrene unit and makes enantiomorphic site control possible.

The effect of the counterion on the copolymerisation reaction has also been studied.[51] Comparison between the known $[Pd(bipy)_2][PF_6]_2$ system and its BArF analogue showed that the use of the latter system increases the catalyst activity considerably. Important differences were also observed in the X-ray structures of the two complexes. However, the introduction of substituents in the 6-position of the dipyridyl ligands **23**–**25** was found to completely inhibit the catalytic reaction when $[Pd(bipy^R)_2][BArF]_2$ complexes were used as catalyst precursors. Catalyst precursors with mixed ligands such as $[Pd(bipy^R)(bipy)][BArF]_2$ gave copolymers of higher molecular weight than with $[Pd(bipy)_2][BArF]_2$, although the catalyst activity was greatly reduced. However, the introduction of one or two methyl substituents in the 5-position of the pyridyl rings (ligands **26** and **27**) was found to have a positive effect on the productivity of the catalysts, although no effect was observed on the molecular weight and tacticity of the polymers produced.

Modular S-S Ligands in CO/Styrene Copolymerisation

Sulfur-containing ligands have rarely been used in copolymerisation reactions although bis(alkyl)thioether systems have been shown to be active in the copolymerisation of CO/styrene, even though a loss of stereocontrol occurred.[6a,53] We have reported the synthesis and use of thioether ligands in various catalytic processes and we therefore thought that these ligands could provide interesting results in the Pd-catalysed copolymerisation of CO and 4-*tert*-butylstyrene. In 2002, we reported the use of the thioether ligands **28**–**30** for this reaction (Figure 11).[54]

The palladium complexes [PdMe(NCMe)(**28**–**30**)][BArF] were synthesised and used as catalyst precursors. The catalytic results obtained were similar to those reported using chiral P-OP, N-N, and P-N ligands in terms of activity and molecular weights.[23,55,56] However, it should be noted that these results were obtained under mild conditions (1 atm



28 **29** **30**

Figure 11. Thioether ligands used in copolymerisation reactions.

CO and room temperature). Nevertheless, the activities and molecular weights of the polymers obtained were much lower than those achieved with planar N–N ligands such as bipyridine. The rather high polydispersity values and the non-linear relationship between time and molecular weights indicated that these systems are not living.[16d] Although the productivity of the catalyst bearing ligand **28** was found to increase when the CO pressure was increased from 1 to 5 atm, these systems were found to decompose with time under these reaction conditions and long reaction times resulted in a decrease of the catalyst productivities. These systems were, however, stabilised by large excesses of olefinic substrates under 1 atm of CO. Furthermore, although it was suggested that the atactic nature of the copolymers produced using thioether ligands is due to the flexibility of the donor atom structure,[6a] the system bearing ligand **30** yielded polymers with prevailing isotacticity, which therefore indicates that control of the stereoregularity can be achieved using this type of ligand.

P-O Ligands in Non-Alternating CO/Ethene Copolymerisation

In previous sections we have dealt with the palladium-catalysed perfectly alternating copolymerisation of ethene and carbon monoxide and its mechanism. It is well known that the double insertion of carbon monoxide in this reaction does not occur for thermodynamic reasons, whereas the double insertion of ethene is kinetically disfavoured. The formation of a stable five-membered cationic palladium metallacycle (see **A**, Figure 12) by an electrostatic interaction between the oxygen of the carbonyl and the cationic palladium centre, known as "back-biting", kinetically favours the insertion of carbon monoxide over ethene insertion.[17b,57] In over two decades of research in the area of late transition metal catalysed polymerisation of carbon monoxide and ethene, no extra insertions of ethene or carbon monoxide have ever been reported; even high ethene/carbon monoxide ratios produce exclusively error-free polyketone until all the carbon monoxide has been consumed.[7b,58] Nevertheless, the double insertion of ethene should be possible, as the same cationic palladium species that is used for the copolymerisation is known to efficiently dimerise ethene into butenes.[59]

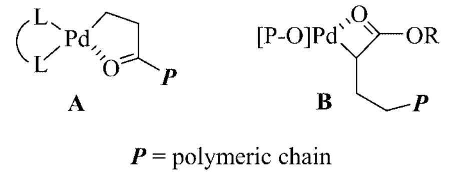
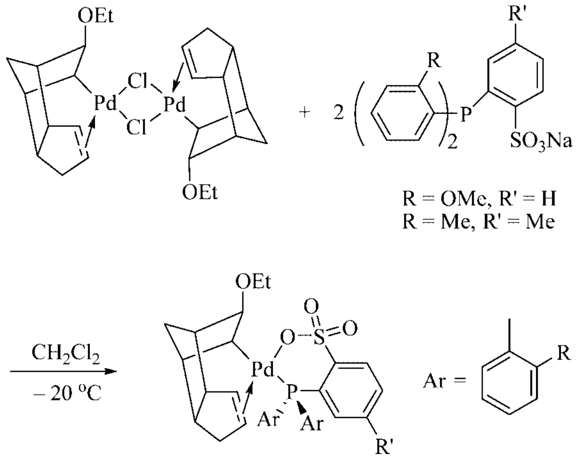


Figure 12. Chelates formed during the copolymerisation reaction.

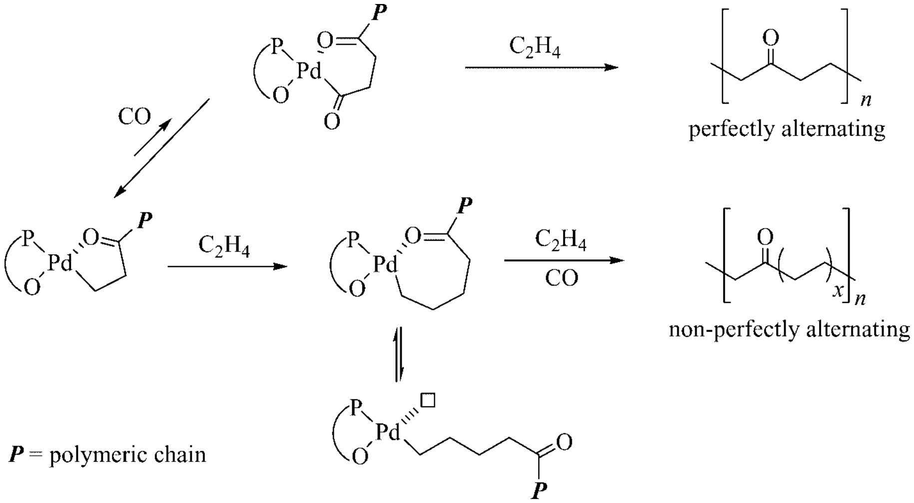
The development of novel late transition metal catalysts for the synthesis of new copolymers containing a non-polar backbone and a controlled amount of a polar monomer is of considerable interest to both academia and industry.[59] However, the design of metal catalysts for such copolymerisation reactions is not a trivial task and, despite the many attempts that have been made in this area so far, only a very few new materials have been obtained.[60] The production of non-perfectly alternating carbon monoxide and ethene copolymers is one of the main aims in polyketone research in order to obtain new materials with desirable properties and which can be further functionalised.

In 2002, Drent et al. reported the first example of a palladium-catalysed non-perfectly alternating copolymerisation of carbon monoxide and ethene. The Pd-containing catalyst precursors bearing alkoxy-arylphosphane ligands containing sulfonic acid groups were formed in situ by mixing palladium acetate and the ligand in a near stoichiometric ratio. Double, triple and quadruple insertions of ethene into the growing polyketone chain were observed. The production of extra insertions of ethene was attributed to the destabilisation of the neutral chelate (**B**; Figure 12) to the extent that ethene effectively competes with carbon monoxide for the next insertion.[61]

More recently, Rieger et al. have reported the first examples of neutral Pd^{II} complexes bearing sulfonated phosphane ligands (Scheme 3). Higher activities as well as higher insertion of extra amounts of ethene (up to 30%) into the copolymer chain were achieved[62] when compared to the previously reported in situ copolymerisation reactions.[61]



Scheme 3. Pd^{II} complexes bearing sulfonated phosphane ligands.



Scheme 4. Mechanism for non-perfectly alternating CO/ethene copolymerisation (□ = vacant site).

The mechanism of the perfectly alternating copolymerisation of carbon monoxide and ethene by Pd^{II} catalysts based on diphosphane ligands has been extensively studied and is now well known.[6] However, only a few studies on the mechanism of the non-alternating copolymerisation of carbon monoxide and ethene have been published.[61–63] Rieger et al. have proposed that this new polymerisation proceeds via two intertwined pathways (Scheme 4), where the same active species may switch between the production of alternating and non-alternating blocks in the same polymer chain.[62] Multiple ethene insertions are suggested to be facilitated by a stereoelectronic destabilisation of the neutral chelate to an extent that enables ethene to effectively compete with carbon monoxide for the next insertion, as previously proposed by Drent et al.[61]

Based on this report, it was assumed that the neutral nature of the CO-inserted 6-membered chelate could lead to a decarbonylation reaction yielding the five-membered ring complex that could then react with ethene to form a seven-membered chelate, which is proposed to open more easily and therefore facilitates the incorporation of further ethylene units. Furthermore, increasing the pressure of ethene and employing high CO/ethene gas blend ratios (1:20) statistically provides a higher probability of ethene insertion over carbon monoxide insertion.

Ziegler and co-workers have reported work based on Drent's ligands that explains the formation of a non-perfectly alternating copolymer based on the decarbonylation of the acylpalladium complexes formed during the catalytic process.[63] This is possible if the acylpalladium complex with sulfonated phosphane ligands does not form a Pd–O chelate bond between the metal and a carbonyl group on the polyketone chain, thus favouring the decarbonylation.

Conclusions

Although co- and terpolymerisation of carbon monoxide and olefins has been the subject of numerous investigations, the demand from industry for new types of material makes this area still challenging and offers new possibilities.

The modification of diphosphane ligands by introducing methoxy groups yields more efficient systems, although the presence of TFE decreases the productivity of the catalysts. Chiral N-N′ and S-S ligands can be used in CO/styrene copolymerisation systems to control the stereochemistry of the catalysts and the stereoregularity of the resulting copolymers. Finally, non-alternating CO/ethene copolymerisation, which can provide new materials with interesting properties, is now possible with Pd/P-O systems. Research in this area is still at a very early stage, however, and therefore represents a new challenge in the field of CO/ethene copolymerisation.

Acknowledgments

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