CO/ALKENE COPOLYMERISATION REACTIONS CATALYSED BY CHELATING DIPHOSPHINE, DIIMINE AND HEMILABILE N/O, P/O AND P/N LATE TRANSITION METAL COMPLEXES REVISITED

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The role of late transition metals (especially Ni(II), Pd(II), Pt(II) and Rh(I)) supported by hard and/or soft chelating ligand frameworks (such as diphosphines, diimine and N/O, P/O and P/N groups) in functional complexes towards the catalysed insertion of CO into alkenes is discussed, with an emphasis on the reactive intermediate species involved.

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INTRODUCTION TO ALTERNATIVE COPOLYMERISATION OF OLEFIN/CO

The copolymerisation of olefins and carbon monoxide has attracted great research interest. The resulting polyketones can be easily processed by means of conventional techniques into films, sheets, plates, fibres and shaped articles. These perfectly alternating copolymers are low cost thermoplastic materials with high mechanical strength due to their crystallinity. Their easily modified carbonyl groups make the polyketones excellent starting materials for the preparation of other types of functionalised polymers.

The alternating CO and ethylene copolymerisation process is of both academic and industrial research interest, due to the properties expected from a product with a high density of heteroatom functionalities. It was predicted that the carbonyl group could be derivatised in order to produce new

interesting materials. The presence of the carbonyl functionality in the backbone makes the copolymer biodegradable, environmentally friendly[1-2] and with interesting optical properties.[3] Polyketone - [$CH_2CH_2C(O)$]- is a semi-crystalline (up to 60%) solid with a melting point of 260 °C which can be decreased to about 180-240°C if a second olefin (such as propylene or butene) is introduced. This randomly substitutes the ethylene units, reduces the crystallinity and facilitates the processing of the copolymer. Shell continued research initiated by Reppe[4] leading to the discovery of a class of highly active palladium-based catalysts.[5-7]

Copolymerisation initiated by free radicals[8,9] or γ-rays[10] results in low melting polymers with poor physical properties and high solubility in ordinary organic solvents, due to their irregular carbon monoxide incorporation. Perfectly alternating copolymerisation was achieved using transition metal catalysts in ambient temperatures and significantly lower pressures.

Transition metals initially investigated as catalysts for CO and ethylene copolymerisation include: a) Nickel-based catalysts like $K_2[Ni(CN)_4]$ which produced low melting oligomers, diethyl ketone and propionic acid. Addition of HOTs or HOTf to the mixture and the use of solvents such as $(CF_3)_2CHOH$ lead to the formation of high molecular weight copolymers but in low yield.[11] Klabunde[12-15] and Keim[16-18] studied catalysts containing bidentate anionic ligands based on phosphorus and oxygen donor groups, similar to the systems used in Shell Higher Olefin Process (SHOP). b) Rhodium-based catalysts give alternating copolymers with low molecular weights with low activities probably due to extremely rapid CO insertion at the metal centre followed by the slow insertion of ethylene in the Rh-C bond.[19-20] c) Palladium-based catalysts are the most successful to-date for the production of copolymer, and extensive research followed the initial discovery made at ICI by Gough in 1967.[22] A large variety of ligands have since been investigated, and as a result important aspects of the chemistry of palladium-catalysed polyketone formation are understood. BP chemicals have developed a family of copolymers under the trademark Ketonex[22] and Shell Chemicals have marketed a class of such polymers under the brand name CARILON Polymer.[23]

High catalytic activity and molecular weight polymers have been attained by the use of cationic complexes with bidentate phosphine ligands and weakly coordinating anions. Bidentate ligands often form much more active complexes than monodentate ligands because the required coordination sites are always cis- to one other, which is the most favourable arrangement for insertion reactions.[24,25]

The most commonly used catalyst systems are those based on Pd(II) salts with chelating diphosphine ligands and an oxidant, in a protic solvent or co-solvent which is required to initiate the copolymerisation. The salts can be prepared either separately[26] or in situ with a Brönsted acid of a wealky or non-coordinating anion as cocatalyst.[24,25] Variation of the bidentate phosphine ligand results in significant changes in both the reaction rate and the molecular weight of the copolymer. For a series of diphenylphosphinoalkanes of general formula $Ph_2P(CH_2)_nPPh_2$ the most efficient catalyst is that with n = 3.[27]

In general, the mechanism for the copolymerisation of ethylene with CO has been the centre of experimental and theoretical research. The copolymer forms by alternate migratory insertion of CO into the Pd-alkyl bond and of ethylene into Pd-acyl bond and therefore propagation errors do not occur (Scheme 1.14).[28] The perfect alternation is maintained even with low concentrations of CO and only when all of the CO is consumed does ethylene dimerisation begin to occur.[27] Therefore, the barrier for ethylene insertion into a Pd-alkyl bond is a kinetic barrier. The preference for CO insertion into the Pd-alkyl bond is due to two factors: firstly CO is a better π-acid than ethylene and bonds more strongly to the electron rich Pd(II) centre and secondly there is a lower barrier to insertion of CO into transition metal-alkyl bonds.[29] Insertion of olefins into the subsequent Pd-acyl bond is preferred because the double CO insertion is kinetically and thermodynamically unfavourable.[30-32] The ethylene insertion also acts as the rate determining step.

When copolymerisation takes place in a protic solvent e.g. MeOH, there are essentially two possible initiation mechanisms. One starts with the formation of a Pd-C(O)OMe bond by either CO insertion into a Pd-OMe bond or by direct attack of MeOH at the Pd-CO bond, producing ester end-groups (Scheme 1). Alternatively, a polymer chain can start by insertion of ethylene into a Pd-H bond, followed by CO insertion producing ketone end-groups (Scheme 2). In aprotic solvents e.g. CH_2Cl_2, a monocationic Pd-R (R = H, alkyl, alkoxy, C(O)OR) species is preformed. When [$Pd(Ph_2P(CH_2)_3PPh_2)(MeCN)_2$]$BF_4$ was used for the copolymerisation of ethylene and CO, a long induction period was observed. However, the induction period was reduced to zero when H_2 was added, indicating that the formation of a Pd-H bond was responsible for the initiation of the copolymerisation.[33]
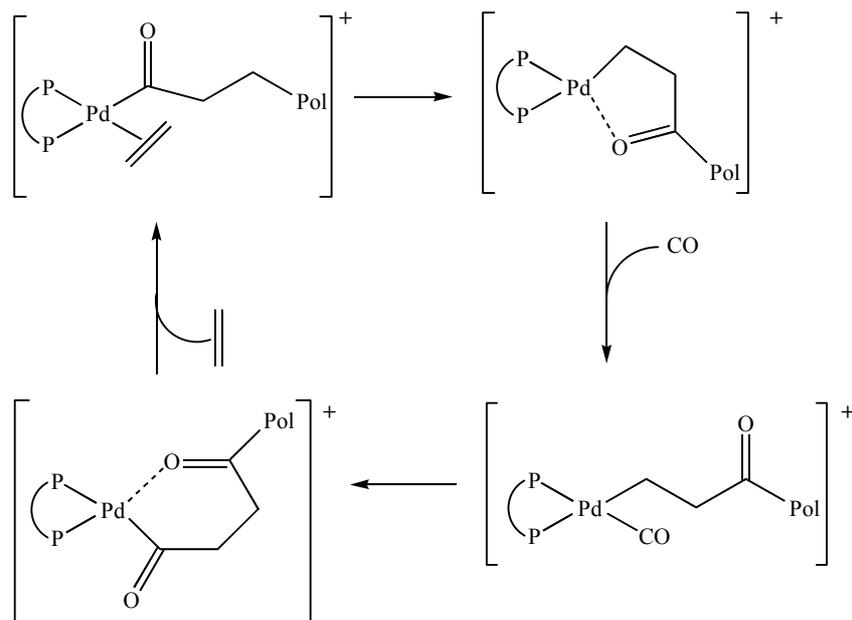
Scheme 1 – Propagation steps of alternate CO/ethylene copolymerization.
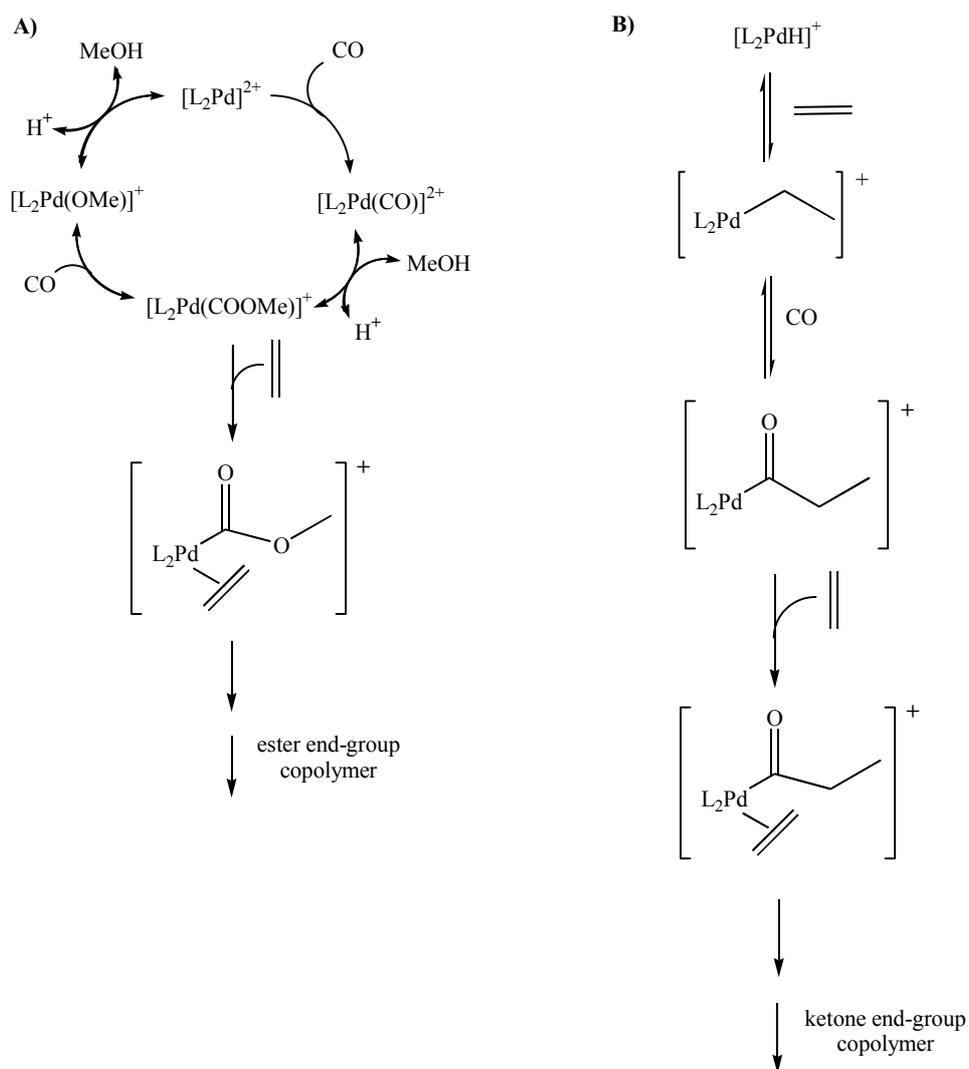
Scheme 2 – Initiation pathways for CO/ethylene copolymerization.

There are two proposed termination mechanisms in protic solvents: protolysis of the Pd-alkyl bond to produce a saturated ketone end-group and palladium methoxide species, or alcoholysis of the Pd-acyl bond to give an ester end-group and palladium hydride species.[24] However, in aprotic solvents, the chain termination mechanism is β-H-elimination resulting in vinyl end groups.[34]

The use of oxidants in the copolymerisation does not affect the chain lengths but does influence the propagation step. It is known that the hydride of active monocationic Pd-H species can "drop out" of the catalytic cycle and can combine with a dicationic species Pd(II) to form an inactive dimer. Oxidants can oxidise these dimers to active Pd(II) species which can then re-enter the cycle (Scheme 3). The effect of oxidants is often negligible when using an aprotic solvent, although Schwarz *et al.* found enhanced copolymerisation activities when using 1,4-benzoquinone in CH_2Cl_2 solvent.[35]

$$[L_2Pd]_2^{2+} + 2H^+ + O\!\!=\!\!\langle\rangle\!\!=\!\!O \longrightarrow 2\,[L_2Pd]^{2+} + HO\!-\!\langle\rangle\!-\!OH$$
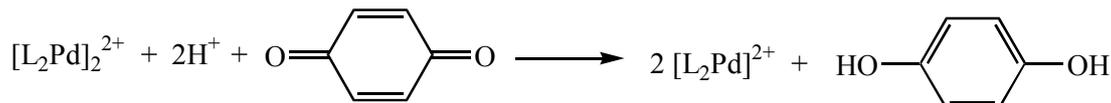
Scheme 3 – The role of the oxidant in the catalytic cycle of copolymerization.

Nickel diphosphine complexes are much less active than the corresponding Pd complexes because they form catalysts with strongly stabilised resting states relative to the transition state for the turnover-limiting step.[36] Rigid diimine ligands, *e.g.* Ar-BIAN, are also active copolymersation catalysts in conjunction with Pd(II) ions but their activity is generally low in comparison with the dppp-based catalysts.[27,37,38] Sections 2-6 below present a more detailed overview of the most common classes of homogeneous catalysts for CO/ethylene copolymersation.

COPOLYMERISATION OF CO AND ALKENES USING CHELATING DIPHOSPHINE COMPLEXES OF Ni (II) AND Pd(II)

Cationic palladium(II) and tertiary phosphine complexes containing weakly coordinated anions have been studied by Drent and co-workers[7] in order to investigate their catalytic properties towards alkoxycarbonylation of ethylene to yield methyl propionate. Replacement of the PPh₃ ligand by bidentate phosphine ligands affects the selectivity of this process and leads to formation of high molecular weight CO/ethylene copolymers at very high rates (ca. 6.39×10^5 g × mol⁻¹× h⁻¹). The fact that production of polyketone with turnover numbers above 10^6 can be achieved (under reaction conditions such as 85°C and 45 bar) and catalysts readily isolated or formed *in situ*, makes this process very attractive economically. By combining the high activity of catalysts incorporating bidentate ligands with the presence of weakly coordinating anions around a cationic Pd(II) centre, access to efficient synthetic processes for perfectly alternating polyketone can be gained.

In general, Pd-diphosphine based systems for this process use the bidentate ligand bis(diphenyl-phosphine)propylene (DPPP) or derivatives thereof, together with weakly coordinating anions, essentially 'non-coordinated' anions or weakly coordinating neutral ligands as co-catalysts. MeOH is frequently used both as a solvent and as an activator and reactions are generally carried out in CH_2Cl_2.

It has been observed that:[7] (i) the chelating ligand enforces *cis* coordination of the monomer and growing polymer chain and facilitates insertion; (ii) the structure of the ligand affects the rate of ethylene/CO copolymerisation and the molecular weight of the product; (iii) alternate insertions of CO and C_2H_4 occur into a preformed Pd-alkyl or Pd-hydride bond.

In a simplified fashion, the mechanism of CO/ethylene copolymerisation catalysis can be depicted as in Scheme 4 (R = H, alkyl).

It is widely accepted that CO insertion into the Pd-alkyl bond is favoured on kinetic grounds over the insertion of C_2H_4, whereas only C_2H_4 can insert into the resulting Pd-acyl bond, as the insertion of a second CO group is thermodynamically disfavoured.[7-39] When MeOH is present in the process, this acts as an activator of the Pd-dication $[Pd(L_2)]^{2+}$ by forming *in situ* a species in which the insertion of CO or ethylene is favourable. In Scheme 1.8, $[Pd(OMe)(L_2)]^+$ can initiate polymerisation by undergoing β-hydride elimination leading to formation of a hydride
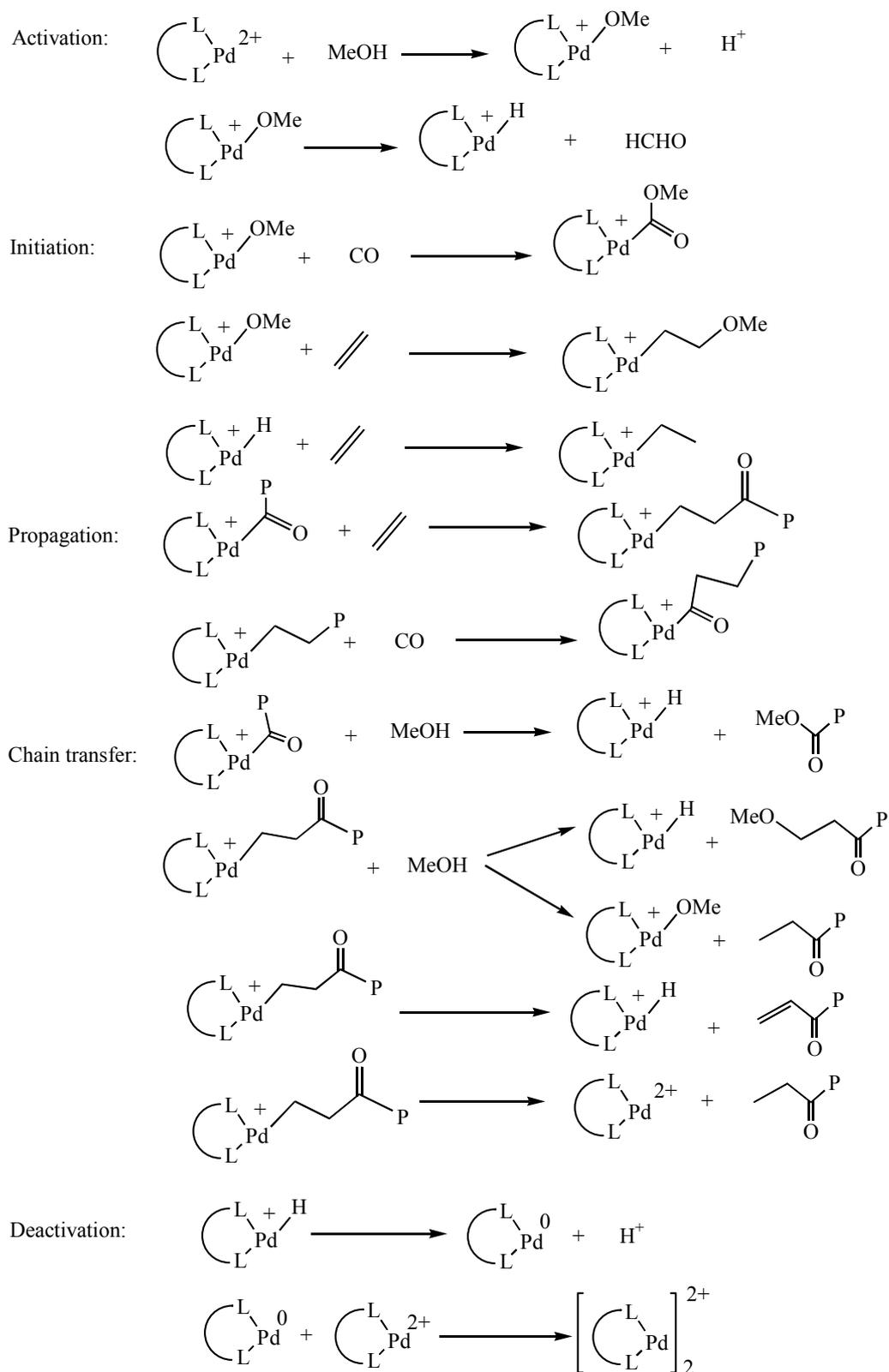
$[L_2PdH]^+$, also an initiating species. The species $[Pd(OMe)(L_2)]^+$ and $[PdH(L_2)]^+$ can initiate the copolymerisation process via insertion of CO or ethylene into Pd-OCH$_3$ or of C$_2$H$_4$ into a Pd-H bond, respectively. The productivity can thus be improved significantly when the concentration of active $[PdH(L_2)]^+$ and $[Pd(OMe)(L_2)]^+$ is enhanced. The copolymerisation reaction can also take place in the presence of a suitable amount of water and HOTs. These processes lead to the formation of a palladium alkoxycarbonyl complex $[Pd(CO)(OMe)(L_2)]^+$. The propagation process consists of alternating insertions of CO (into a Pd-alkyl bond) and of C$_2$H$_4$ (into a Pd-acyl bond). The growing chains are mainly terminated by reaction of MeOH with the various propagating species to produce new initiators in a chain transfer processes. The species $[PdH(L_2)]^+$ is deactivated by decomposition into $[Pd(L_2)]^0$ which can combine with a $[Pd(L_2)]^{2+}$ species to form a Pd(I)-dimer $[Pd(L_2)]_2^{2+}$. In the case when oxidants such as 1,4-benzoquinone are used as co-catalysts, their function is to oxidize this Pd(I)-dimer into $[Pd(L_2)]^{2+}$ which contains two vacant sites at the Pd-centre and can therefore continue the catalysis cycle. A similar role with that of MeOH is believed to be played by p-toluenesulfonic acid, which can act as a co-catalyst when present in the copolymerisation processes using complexes of the type $[L_2Pd(OAc)_2]$ (where L_2 is a bidentate phosphine) to enable the formation of active

species $[L_2Pd(solvent)_2]^{2+}$. Scheme 5 provides an closer insight in the processes described above.

A possible explanation for perfect alternation is the stronger coordination of CO to Pd(II) in comparison to ethylene. This ensures that after formation of a Pd-alkyl bond, the next monomer to insert is CO. Although CO coordinates strongly to Pd-acyl species, CO insertion into a Pd-C(O)R bond is thermodynamically unfavourable and an ethylene molecule displacing CO will insert into the Pd-acyl bond. The resting state of the system is a CO-coordinated Pd-acyl species.[40] It was observed that in a copolymerisation reaction with a high ethylene to CO ratio, error-free alternating copolymer is formed until all the CO is consumed, after which the system generates dimers (i.e butenes).[5] The unavoidable competition between olefin and CO for the vacant site could provide an explanation for a lower rate of copolymer formation compared with ethylene dimerisation. This process is described in Scheme 6. The formation of a stable metallacycle reduces the barrier for olefin insertion into the Pd-acyl bond and inhibits the termination step, which can occur by β-hydride elimination from the Pd-alkyl species. [7, 44, 45] The inhibition of β-hydride elimination could offer an explanation for the fact that catalysts of this type can produce high molecular weight polymer in alternating copolymerisation and dimers or oligomers in ethylene homopolymerisation (Scheme 7).

copolymer;
strictly alternating CO : C$_2$H$_4$
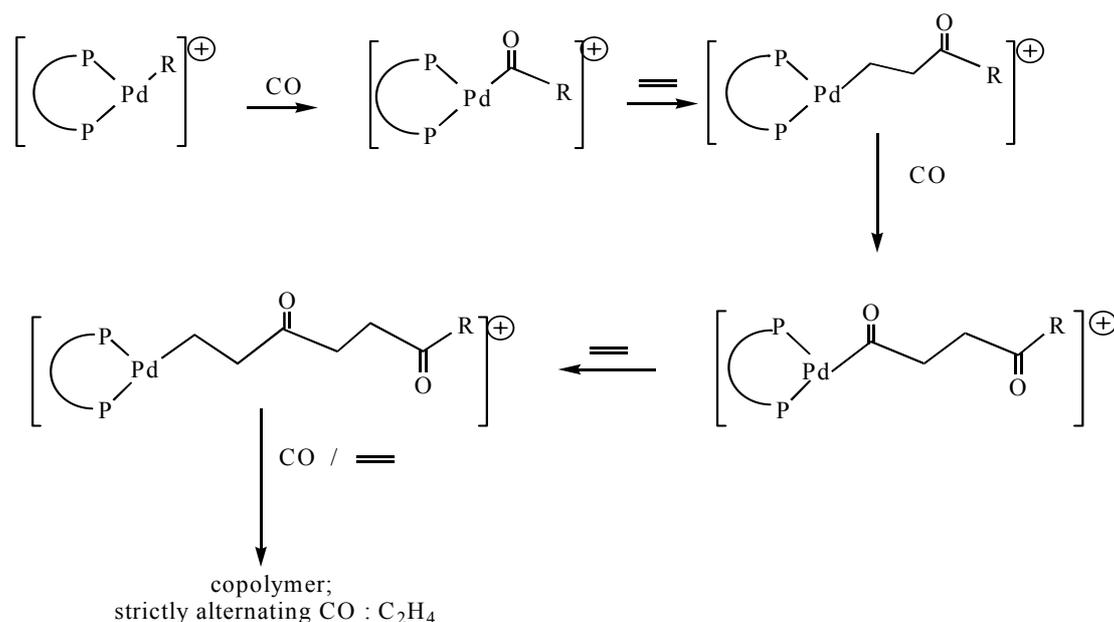
Scheme 4 – CO/ethylene copolymerization, catalysed by Pd(II) chelating-diphosphines.

Activation:

Initiation:

Propagation:

Chain transfer:

Deactivation:

Scheme 5 – The mechanism of alternating ethylene and CO copolymerisation
(L-L = bidentate ligand e.g. diphosphine, P = polymer chain).

Scheme 6 – Competition mechanism in CO / ethylene copolymerisation
using symmetric diphosphine ligands (*P* = polymer chain).

S = solvent, anion or monomer

Scheme 7 – The inhibition mechanism by β-hydride elimination.

Since thermodynamic factors are unfavourable for double CO insertion, a perfect alternation is achieved until a chain termination step occurs. The resulting material is a mixture of polyketones of various chain lengths, with differing terminal groups. When the process is carried out in MeOH,[6-7] these are: i) Polymer I (the most abundant) with ethyl and ester [-C(O)-OMe] terminal groups; ii) Polymer II with ester and ester terminal groups; iii) Polymer II with ethyl and ethyl terminal groups. Mechanistic aspects of the Pd(II)-diphosphines catalysis of CO/ethylene copolymerisation have been studied by end-group analysis and in-situ high-pressure NMR and IR spectroscopies.[41] It has been observed that when alcohols are used as solvents, chain initiation occurs mainly via CO insertion into a Pd-OR bond, whereas in non-alcoholic solvents chain initiation takes places mainly via insertion of ethylene into a Pd-H bond. The presence of weakly coordinating

anions has a large contribution to the stability of the cationic Pd(II) species and facilitates coordination of monomers to the vacant site at a metal centre. Theoretical studies have also been carried out in order to clarify mechanistic aspects of metal-catalysed alternating copolymerisation of olefins with carbon monoxide.[40-42]
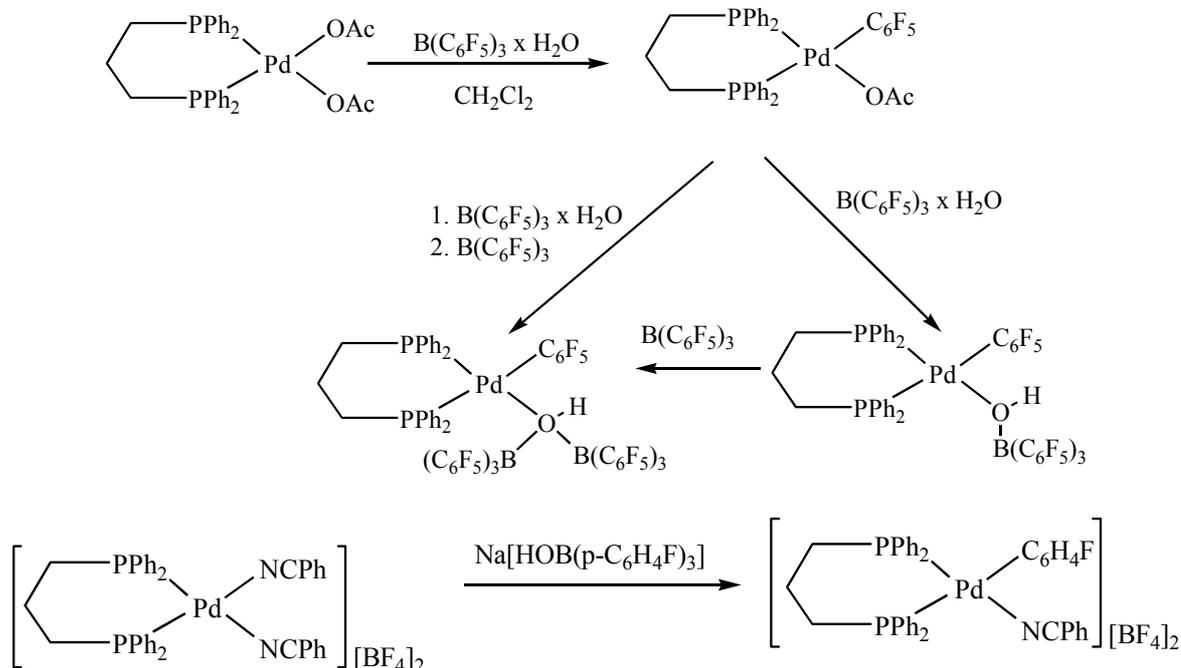
Scheme 8 – Reactions of complexes of the type $[PdX_2(L_2)]$ and $[Pd(solvent)_2(L_2)]^{2+}$ with large weakly coordinating Lewis acids.

A study of the alkene/CO polymerisation with Pd-dppp systems promoted by $B(C_6F_5)_3$ has been reported recently.[43] The reaction *in situ* between $[Pd(OAc)_2(dppp)]$ and $B(C_6F_5)_3$ in CH_2Cl_2 has been shown to generates a highly active catalyst for CO/alkenecopolymerisation. Mechanistic studies have shown that the use of $B(C_6F_5)_3$ as a promoter results in a novel chain initiation process involving an aryl group transfer from the borane to Pd and, as a result, aryl groups from the borane are incorporated into the end – groups of the copolymers. $B(C_6F_5)_3$ is therefore consumed during the polymerisation process. Scheme 8 presents the reactions of Pd-dppp complexes with strong Lewis acids that have been studied in a quest for potential catalysts.

The mechanism described in Scheme 9 is relevant to the general study of polymerisation processes involving fluoroaryl boron as a catalyst component.[44] It has been observed that the polymerisation process is initiated by aryl-transfer from borane to palladium to form a palladium-aryl complex. The migratory insertion of a monomer takes place into the Pd-aryl complex. Analysis of the C_6F_5-polymer end groups showed that the initial insertion is of an ethylene molecule. The main termination process is due to protonolysis whilst some termination occurs via β-elimination and displacement. The catalyst is ready for re-initiation by aryl transfer, and formation of C_6F_5H as a by-product of protonolysis has also been observed.

By comparison with Pd(II)-diphosphine complexes, analogous Ni(II) systems have found little success,[11] despite expectations of lower insertion barriers for CO and olefin copolymerisation processes. SHOP-type Ni(II) catalysts and related Ni-based systems have also shown low activity for CO/ethylene copolymerisation.[12,45]

Initial attempts by Drent[46,47] to use Ni(II) complexes of simple aryl-substituted bidentate phosphorous ligands as CO/ethylene copolymerisation catalysts have shown low activity. To investigate the significant differences between the dppp-Ni system and the highly active dppp-Pd(II) catalysts, mechanistic studies have been carried out by Brookhart *et al.*[48,49] Active species, such as $[NiMe(solvent)(L_2)]^+$ (L_2 = dppp, solvent = Et_2O or H_2O), have been therefore isolated (Scheme 10).[48]

Scheme 9– The mechanism of the CO/ethylene polymerisation process promoted by $B(C_6F_5)_3$ using Pd-dppp systems.

Scheme 10 Synthesis of Ni-based active species for CO/ethylene copolymerisation.

The CO insertion reaction into the Ni-Me bond of species **II** (Scheme 10) was studied by variable temperature NMR spectroscopy and theoretical calculations. In general, insertion barriers found for Ni-complexes are lower[42] than those estimated for Pd-analogues, $[PdMe(CO)(dppp)]^+$.[49-51] Identification of a five-coordinate, carbonyl-acyl intermediate contrasts with the Pd-systems, where the intermediates are four-coordinated. The fact that Ni-dppp based systems are less efficient catalysts than the Pd-dppp systems has been attributed to the presence of a catalyst resting state

which is strongly stabilised relative to the transition state for the turnover limiting step.[48]

3. CHELATING α-DIIMINE COMPLEXES OF PALLADIUM(II) AS COPOLYMERISATION CATALYSTS

Since the discovery by Drent[7] of high-rate catalysts incorporating chelating diphosphine ligands, a wide range of CO/alkene copolymers have been prepared using a variety of catalyst

systems. Brookhart *et al.*[52-54] have shown that Pd(II) supported by a bidentate-diimine ligand can produce high molecular weight copolymers of olefins with alkyl acrylate co-monomers. The copolymerisation reactions are initiated by diethyl ether adducts or by stable chelate complexes, prepared from [PdMeCl(N-N)], alkyl acrylates, and Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (Schemes 11 and 12).
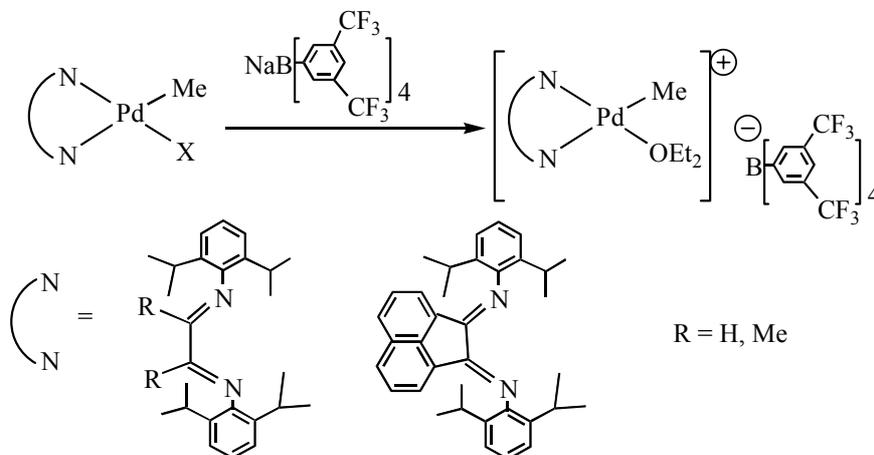
Scheme 11 – Diethyl ether adducts of Pd(II) diimines catalysts.
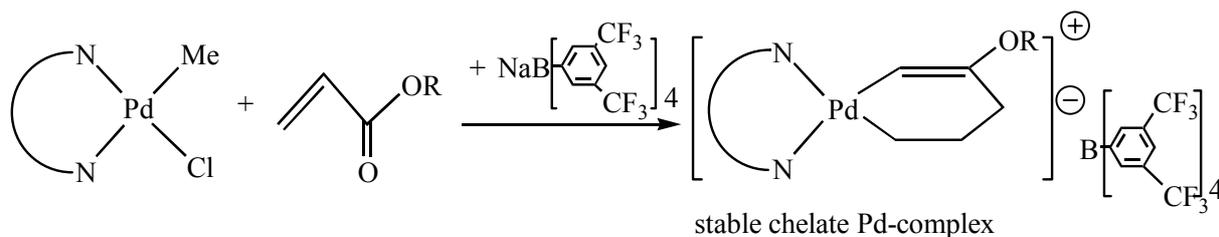
Scheme 12 – Formation of Pd-diimine based initiators for copolymerisation reactions.

Exposure of these complexes to ethylene or propylene in the presence of alkyl acrylates such as methylacrylate, tert-butylacrylate or methyl vinyl ketone results in the formation of high molecular weight random copolymers.[55] Similar to the corresponding ethylene homopolymers, the copolymers are amorphous, highly branched materials with the ester groups predominantly located at the ends of branches (Scheme 13). The productivities are lower than those of the homopolymerisation of ethylene by one or two orders of magnitude and decrease linearly with the concentration of acrylate. Productivities are also dependent upon the nature of the diimine backbone substituents, however, variation of the diimine backbone substituents does not significantly affect the degree of acrylate incorporation in the copolymer.[55]
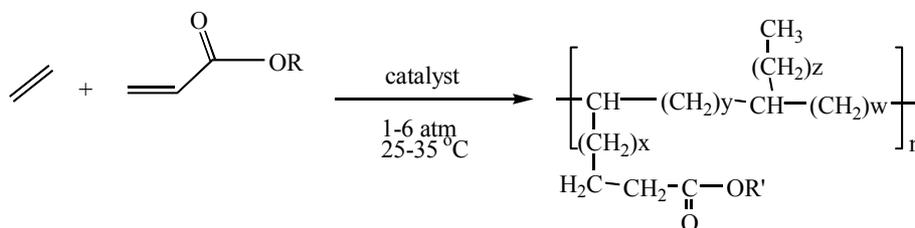
Scheme 13 – Formation of high molar mass random copolymers.

Brookhart *et al.*[52,53] proposed a mechanism for the copolymerisation of ethylene and methylacrylate, based on NMR studies and the structure of the copolymer. In the mechanism presented in Scheme 14, the coordination and insertion of ethylene is the turnover limiting step. Increasing the ethylene pressure increases the ethylene and methylacrylate turnovers.
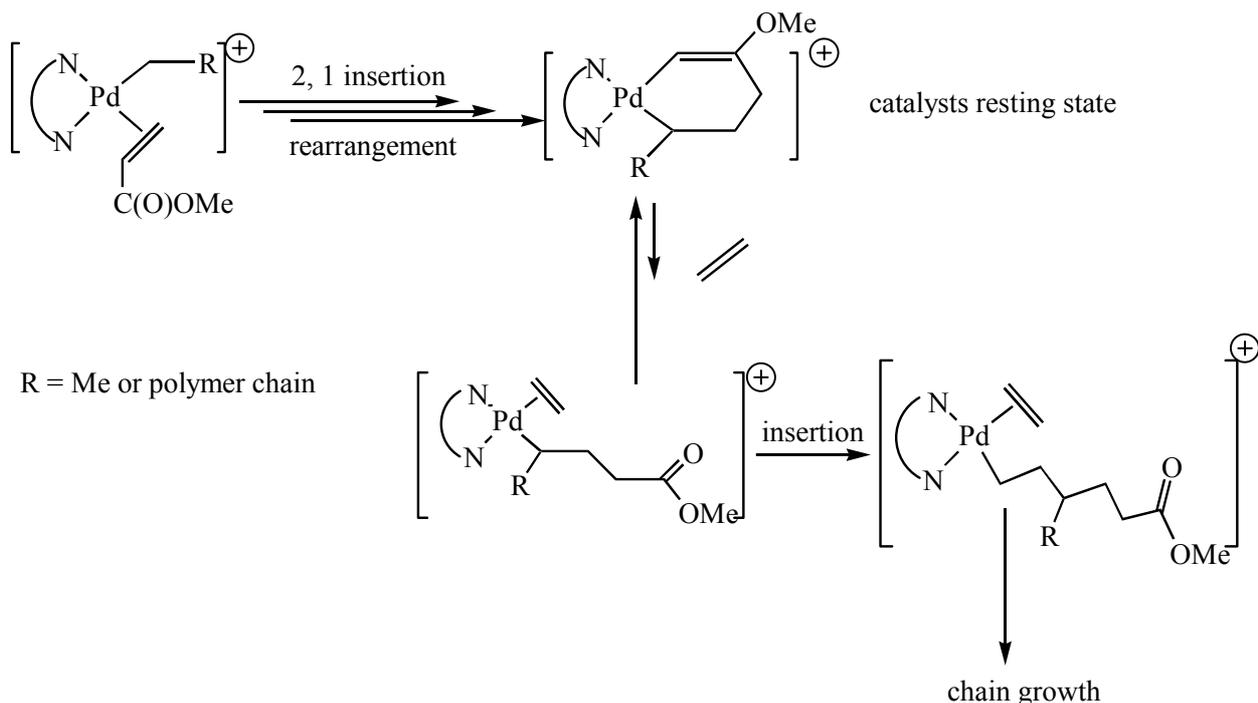
Scheme 14 A mechanism for the copolymerisation of ethylene and methylacrylate.

Both Pd complexes with Shiff-base type diimines and those with simpler 2,2'-bipy promote the copolymerisation of substituted olefins such as styrene with CO.[55] Recently, a Pd(II) bidentate diimine complex, using the ligand 1,4-diisopropyl-1,4-diaza-1,3-butadiene, has been investigated in the context of the regio- and stereo-chemical control in syndiotactic CO/styrene copolymerisation reactions.[55] This system generates copolymers of styrene or p-methylstyrene and CO with alternating head-to-tail syndiotactic structure and a stereochemical purity of 92 % (Scheme 15).

Studies revealed higher activity of 2,2'-bipy-coordinated complexes with respect to those

supported by bis(oxazoline)-type ligands.[55] Recent work was concerned with the ring-opening copolymerisation with CO of more complex olefins under mild conditions (1 atm) promoted by [PdMeCl]-based complexes supported by 2,2'-bipy or Brookhart-type bulky diimines using NaBARF (BARF = [B{3,5-$(CF_3)_2(C_6H_3)$}$_4$]. The resulting copolymers are alternating enone and –CH_2-CH(functionality)- groups, where the functionality may be an additional (bulky) alkyl chain or aryl group (Scheme 16). The stereochemistry of the polymerisation and nature of polymer form is heavily dependent on the type of catalyst used.[55]
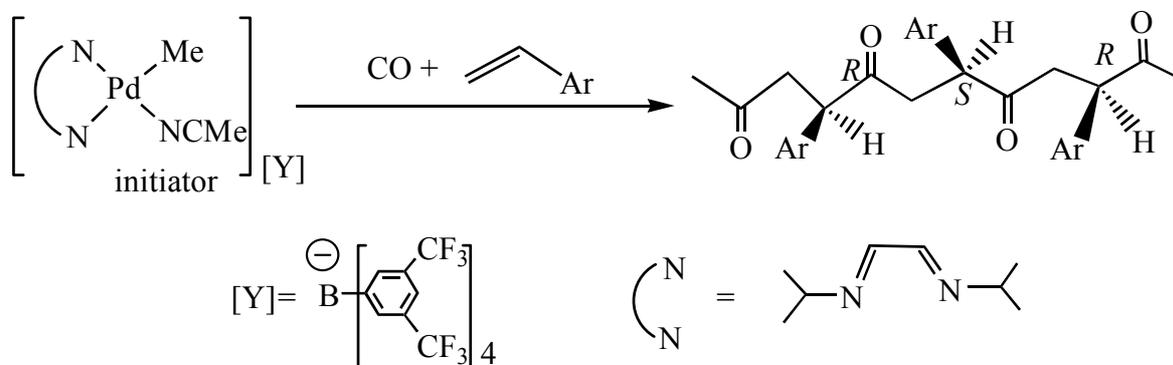
Ar = p-methylstyrene or styrene

Scheme 15 – The copolymerisation of aryl-substituted alkenes and CO using a Pd-diimine catalyst.
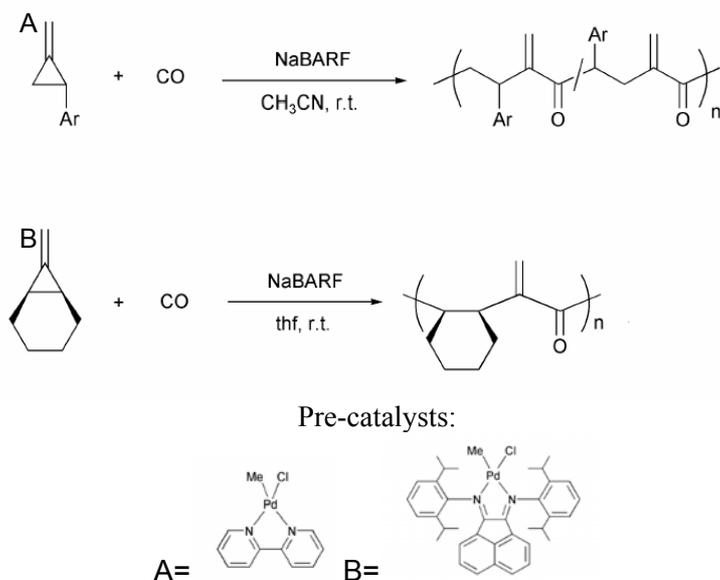
Scheme 16 – Formation of functional CO/higher olefin copolymers (CO ca 1 atm)
catalysed by N/N-supported Pd(II) systems.

COPOLYMERISATION OF CO AND OLEFINS USING CHELATING AND HEMILABILE N/O AND P/O COMPLEXES OF LATE TRANSITION METALS

Studies performed by Klabunde and co-workers[12,14,15] have shown that Ni catalysts incorporating P,O-chelated ligands can produce high molecular weight copolymers of ethylene and polar monomers (Functionalised Linear Low Density Polyethylene). Chemical reactions can be carried out on these polymers, and one of the most important applications is the chemical dyeing of amine-functionalised polymers. Recent studies by Braunstein *et al*[56] have focused on new monocationic Pd(II) complexes, containing either functional P/O ligands such as $Ph_2PCH_2C(O)Ph$ or $Ph_2PCH_2C(O)NPh_2$ or an anionic chelating phosphino-enolate (Scheme 17).

$Y = PF_6^-, BF_4^-$
R = Ph, R' = Ph
R = Ph, R' = Cy
R = NPh$_2$, R' = Ph
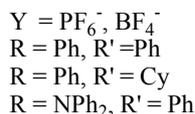
Scheme 17 – Examples of mono- and di-cationic Pd(II) complexes containing neutral and anionic functional P/O ligands.

The anionic functional P/O ligands possess both strong and weak donor groups and also show stereo-electronic control of the coordination sphere of the metal centre.[57,58] They behave formally as neutral four-electron donors and generate complexes with remarkable stability, thus allowing the isolation of reactive intermediates. The phosphino-enolates $[Ph_2PCH=C(O)R]^-$ (R = OEt, Ph, NPh$_2$) are strongly chelating and at the same time render the corresponding complexes active in SHOP-type processes.[59-62] The P-O based Pd(II) catalysts showed lower activity towards CO/ethylene

copolymerisation than the cationic Pd(II) catalysts of diphosphines or diimines.[63,64]

A series of cationic methyl-palladium(II) complexes containing bidentate N-O ligands of the general formula [PdMe(L)(N-O)][BF$_4$] (L = PPh$_3$, PCy$_3$) have been prepared and characterised.[65] Complexes shown in Scheme 18 were found to be active for the copolymerisation of CO and ethylene.

R = H, Me
R' = OMe, N^{i}Pr$_2$
L = PPh$_3$, PCy$_3$
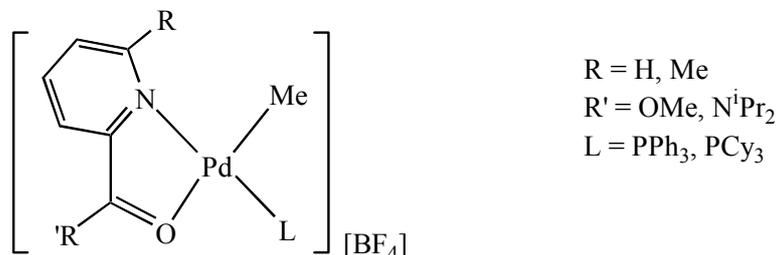
Scheme 18 – Cationic methylpalladium(II) complexes with bidentate [N/O]⁻ ligands.
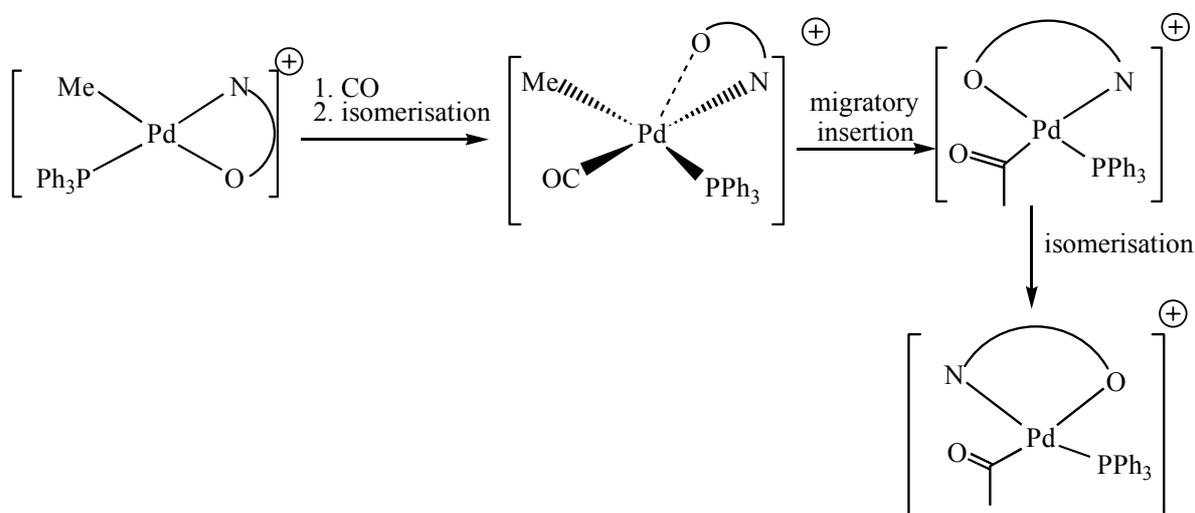
Scheme 19 – CO insertion into the Pd-Me bond of [PdMe(N-O)(PPh$_3$)]⁺.

Pathways for CO and ethylene insertions (Schemes 19 and 20) were proposed.[65] The overall mechanism for the stepwise insertion of CO and ethylene, has been suggested on the basis of spectroscopic studies and *ab initio* calculation (Scheme 21). These studies have been performed on the model cationic complex [PdMe(HN=CHCHO)(PH$_3$)]⁺.

Ab initio calculations indicated that the lowest energy pathway for the carbonylation of the model complex occurs via a five-coordinate square pyramidal intermediate with *trans-cis* isomerisation (of P or N) preceding the CO insertion step.[65] A similar low energy pathway involving *trans-cis* isomerisation of the P and N ligands was also noted for the insertion of ethylene into the resulting Pd-COMe bond.[65] Calculations also indicated that although the 'P *cis* N' isomer is the initial product of the CO migratory insertion step, the 'P t*rans* N' acyl isomer is thermodynamically preferred. Also, it was shown that more strongly coordinating

phosphines such as PCy$_3$ deactivate complexes of this type by preventing the necessary isomerisation of the complex during reaction with CO and ethylene. A low energy pathway for isomerisation, which proceeds via a weakening or elongation of the Pd-P bond, was identified. If a stronger tertiary phosphine donor is present, this elongation is prevented and the energy barrier for isomerisation becomes to great for the migratory insertion to take place.[65]

Neutral complexes of the general type [NiRL(N/O)] (Scheme 22) were found to catalyse the CO/ethylene copolymerisation,[45] as well as the ethylene homopolymerisation. In this series, the complex with R' = NO$_2$ is the most active towards ethylene homopolymerisation, with activity up to 225 g PE x g Ni^{-1} x h^{-1}. This system can selectively copolymerise CO and ethylene to yield high molecular weight perfectly alternating polyketone. In this process, trace amounts of dimers and trimers of ethylene have been isolated, although no

higher ethylene oligomers or oligomeric keto-products were observed. The catalytic activity towards CO and ethylene copolymerisation of the [N/O]⁻ complexes shown in Scheme 21 is low with respect to their homopolymerisation activity. The presence of the phosphine ligand (i.e PPh₃) has been shown to suppress the carbonylation, and therefore reduce the copolymerisation activity of these complexes. These ligands can irreversibly block the coordination sites and therefore prevents the coordination of the substrate.
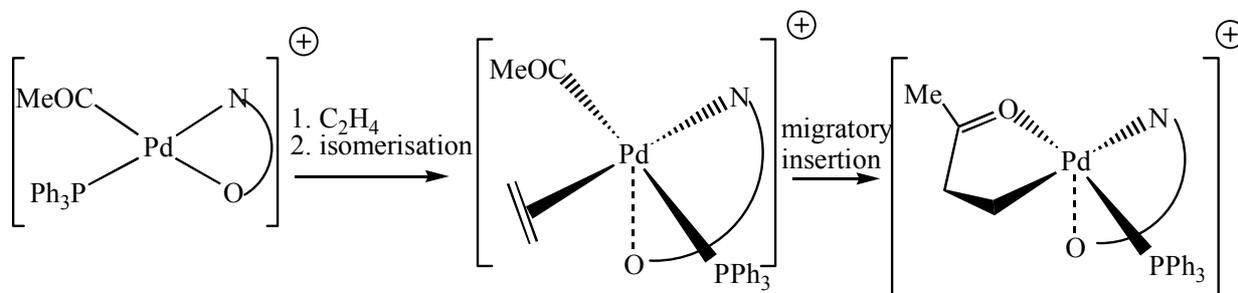
Scheme 20 – Ethylene insertion into the Pd-C(O)Me bond of [Pd(COMe)(N-O)(PPh₃)]⁺.
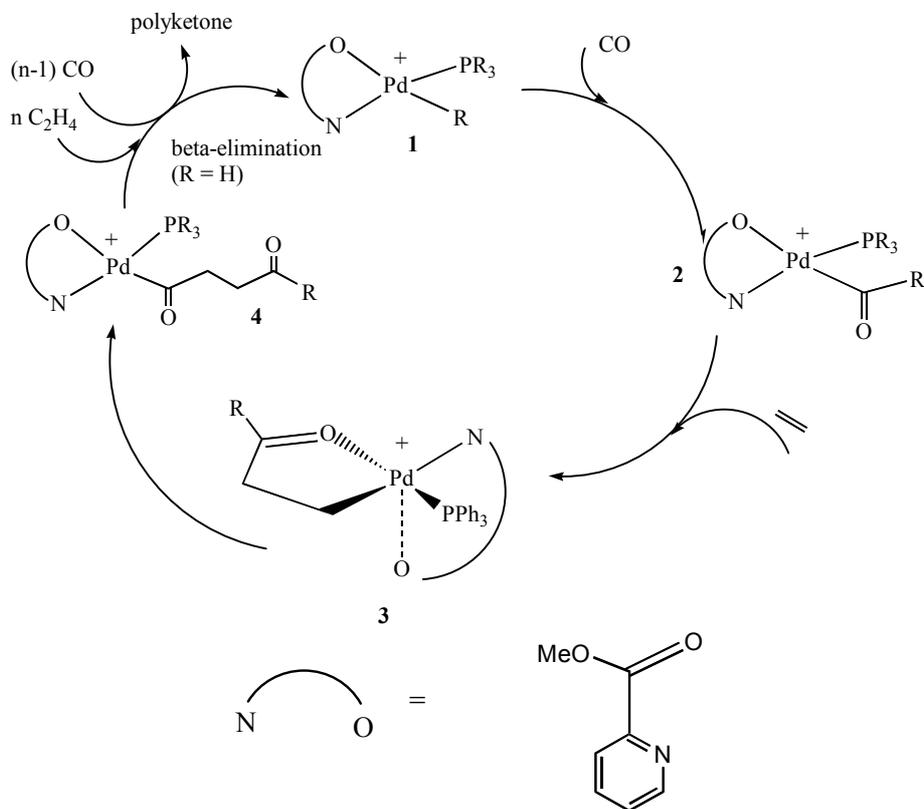
Scheme 21 – Catalytic cycle and intermediates in the CO/ethylene copolymerisation reaction using the catalyst [PdMe(N-O)(PPh₃)]⁺.

R' = H, NO₂, MeO
R = o-tolyl
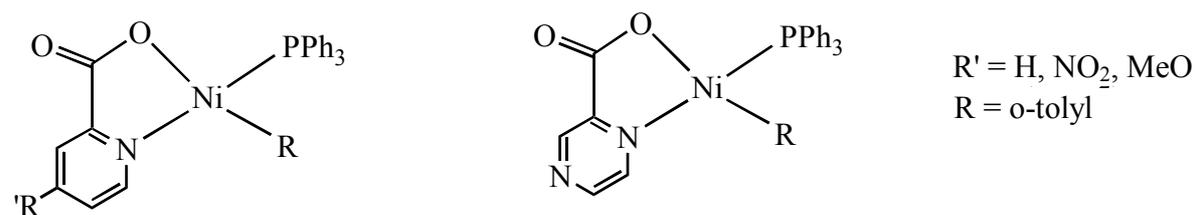
Scheme 22 – Derivatives of the general type [NiR(N-O)L], active towards ethylene homopolymerisation as well as CO and ethylene copolymerisation.

The performance of the Ni(II) complexes as CO/ethylene copolymerisation catalysts is strongly dependent on the basicity of the chelate ligand. Reduction of the [N/O]$^-$ ligand basicity facilitates the rate of migratory insertion compared with the rate of β-H elimination and favors production of polymers over oligomers.[45]
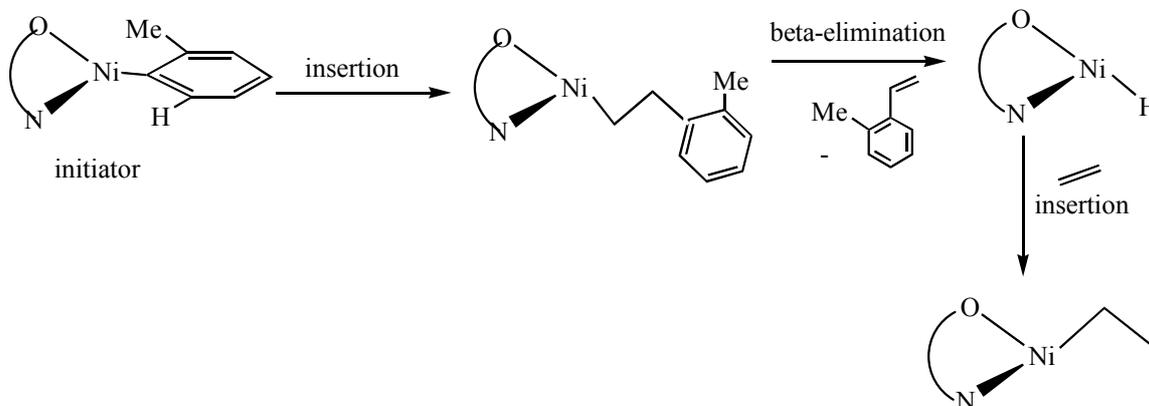

Scheme 23 – The initiation reaction in CO/ethylene copolymerisation using (N/O)-Ni based catalysts.

The pathway proposed for the CO/ethylene copolymerisations with Ni-complexes of non-substituted N-O ligands involves a five-coordinate intermediate, formed via an associative mechanism for the insertion of the coordinated olefin. An alternative mechanism could be via a dissociative route, in which insertion occurs from a four-coordinate intermediate following ligand displacement. Although chelate hemilability cannot be ruled out, NMR studies suggest the dissociation of the monodentate ligand *i.e.* phosphine. It is believed that the initiation reaction in the case of CO/ethylene copolymerisation is achieved in the presence of ethylene only (Scheme 23). NMR experiments have shown that initial presence of CO only leads to rapid decomposition of the complexes. Following the generation of the active Ni-H or Ni-alkyl catalyst, addition of CO initiates chain growth. Copolymerisation proceeds with sequential insertion of CO into the M-alkyl bond and of ethylene into the M-acyl bond analogous to the Pd(II) systems.

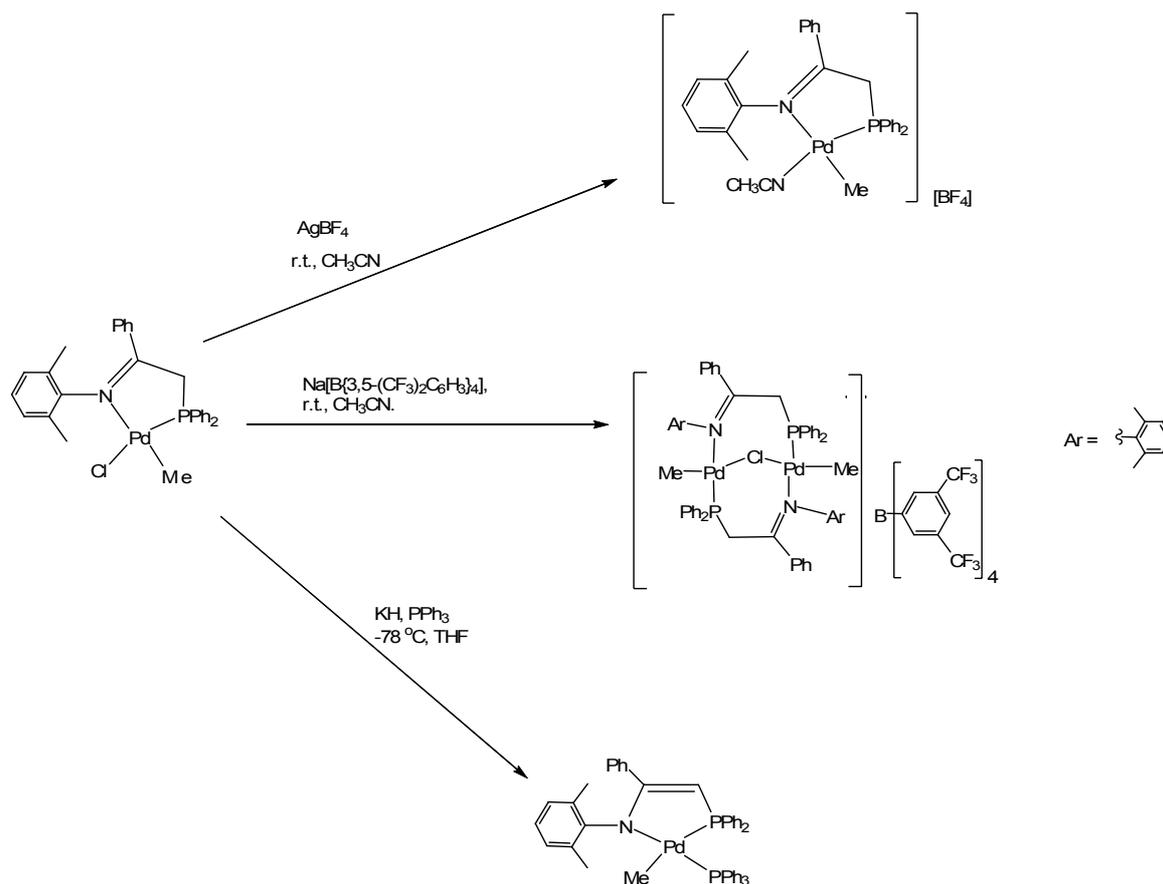## COPOLYMERISATION OF CO AND OLEFINS USING CHELATING AND HEMILABILE P/N COMPLEXES AND RELATED SYSTEMS

Recently, the synthesis and study of new families of iminophosphine ligands was reported.[66-69] These are relevant in terms of their reactivity towards Group 9 and 10 transition metal precursors in order to synthesise new pre-catalysts for a number of carbon-carbon coupling reactions, including CO/ethylene copolymerisation and the Heck coupling of olefins with aryl-halides. Iminophosphine ligands [Ph$_2$PCH$_2$C(Ph)=NAr] (Ar = Ph, 2,6-Me$_2$C$_6$H$_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$) incorporate a flexible backbone. The solution E/Z isomerisation for Ar = 2,6-Me$_2$C$_6$H$_3$ was studied by NMR spectroscopy. Neutral ligands of the type [Ph$_2$PCH$_2$C(Ph)=N(2,6-R$_2$C$_6$H$_3$)] where R = Me (**HL1**) and ^{i}Pr (**HL2**), reacted with various palladium, nickel and platinum precursors to yield the corresponding chelating *cis*-dihalide complexes.[66]
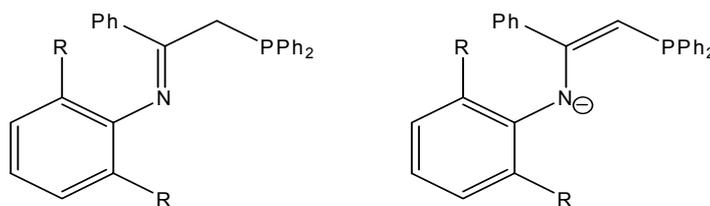
Scheme 24 – Schematic representations of iminophosphine ligands HL1 (R = Me), HL2 (R = iP$_r$) and corresponding anionic forms L.

The ability of these ligands to coordinate in a chelating bidentate fashion was observed using spectroscopic methods and X-ray crystallography. The dimeric palladium complexes [Pd$_2$Br$_2$(L$_1$)$_2$] and [Pd$_2$Br$_2$(L$_2$)$_2$], which incorporate the anionic amidophosphine ligands [Ph$_2$PCH=C(Ph)N(2,6-Me$_2$C$_6$H$_3$)]$^-$ (**L$_1$**) and [Ph$_2$PCH=C(Ph)N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$^-$ (**L$_2$$^-$**), have also been synthesised and characterised. The reaction of [Pd$_2$Br$_2$(L$_1$)$_2$] with AgBF$_4$ and MeOH, a template reaction combining halide-abstraction and ligand protonation, leads to the formation of an unusual dicationic dimer [Pd$_2$(HL$_1$)$_2$][BF$_4$]$_2$. This complex, relevant to the termination step of the CO/ethylene copolymerisation mechanism, was structurally characterised. An insight into the bonding within this complex has been obtained using DFT calculations.[66]

Scheme 25 – Reactivity of the mono-methyl system [PdMeCl(HL$_1$)].

Reactivity and catalytic studies on the mono-methyl system [PdMeCl(HL$_1$)] have also been also described. (Scheme 25).[66] Surprisingly, the halide abstracting reactions between [PdMeCl(HL$_1$)] and Na[B{3,5-(CF$_3$)$_2$(C$_6$H$_3$)}$_4$] or B(C$_6$F$_3$)$_3$ led to the formation of the head-to-tail A-frame-type cation [Pd$_2$(µ-Cl)Me$_2$(HL$_1$)$_2$]$^+$, whereas the use of AgBF$_4$ generated the complex [PdMe(CH$_3$CN)(HL$_1$)][BF$_4$]. The first structurally characterised example of a SHOP-type Pd-Me iminophosphine complex, [PdMe(PPh$_3$)(L$_1$)] (L$_1$$^-$ = [Ph$_2$PCH=C(Ph)N(2,6-Me$_2$C$_6$H$_3$)]$^-$), was also described and showed moderate activity in the catalytic oligomerisation of ethylene. The X-ray structures of [M(Me)$_2$(HL$_1$)] (M = Pd, Pt) and [PdMeCl(HL$_1$)] were determined,, as well that of [Pd(η^3-allyl)(HL$_1$)][BF$_4$]. It was demonstrated that the compound [PdMeCl(HL$_1$)] is an effective pre-catalyst for the Heck coupling of 4-bromoacetophenone and n-butyl acrylate, and also that [PdMeCl(HL$_1$)] and [Pd(η^3-allyl)(HL$_1$)][BF$_4$] act as catalyst precursors for CO/ethylene copolymerisation processes showing only moderate activity. The molecular structures of some of the more representative square-planar Pd-based organometallic pre-catalysts (supported on neutral or anionic P/N ligands) are shown in Figures 1 (a-c) and Figure 2.
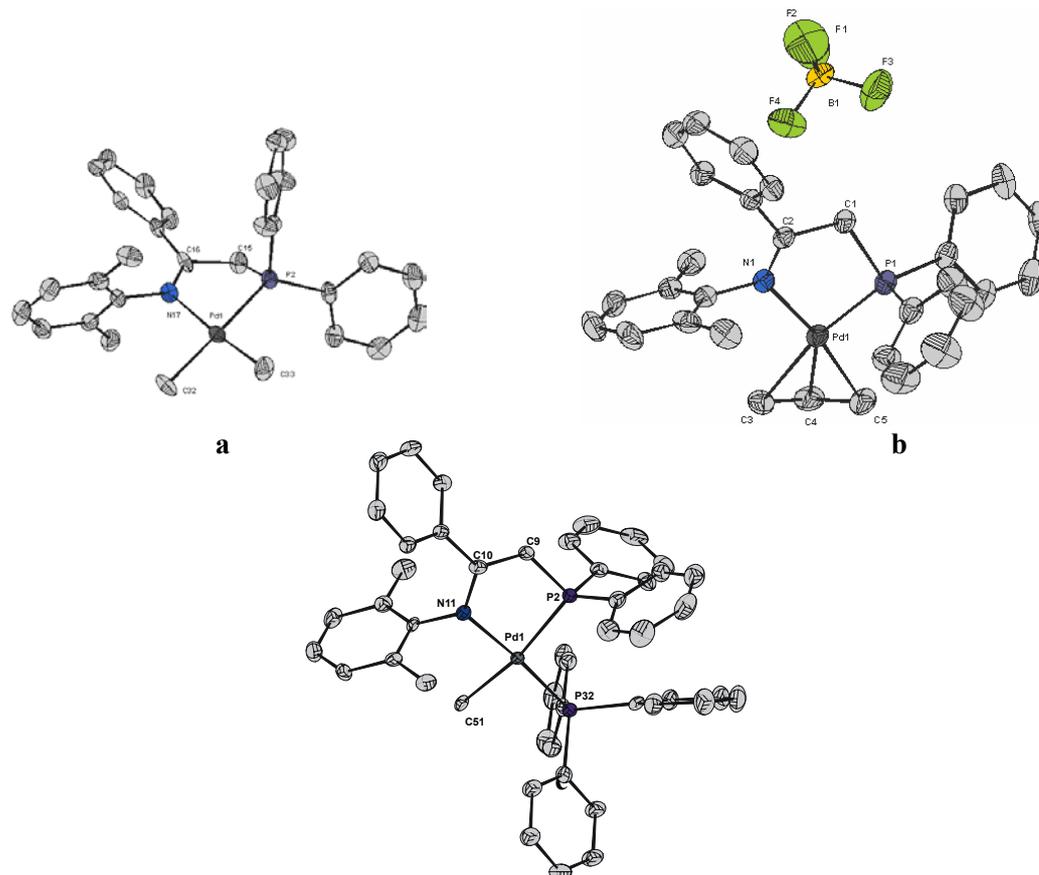
Fig. 1 – Molecular structures of novel Pd-based pre-catalysts with moderate activity in the CO/ethylene copolymerisation processes.
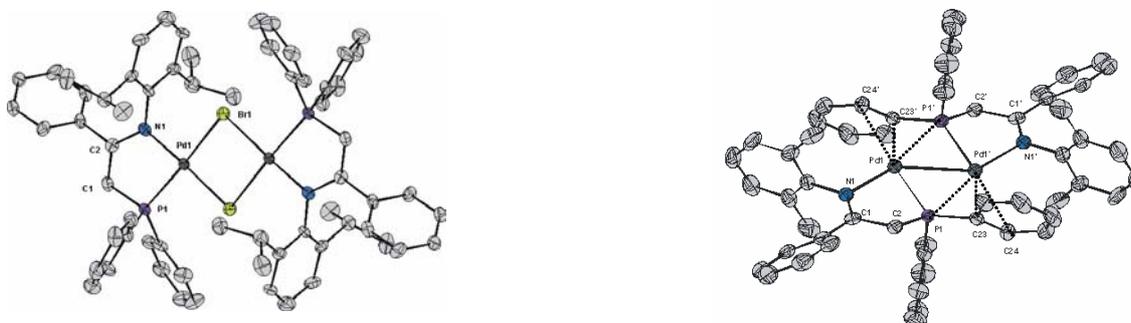

Fig. 2 – Molecular structures of dimeric palladium complexes with relevance in the CO/ethylene copolymersation mechanistic studies.

Our work, as well as others' was in the context of the continued interest in hetero-bifunctional hybrid ligands with two distinct donor sites, each having the ability to interact to a different extent to the metal centre. [66-69] The asymmetry offered by this type of ligands is believed to be the key in tuning the electronic and steric properties of the metallic core, thus offering a flexible coordination environment. Dyer et al reported recently the one-pot synthesis of square planar Pd(II) systems supported by bis(dialkylaminophosphanyl)imines $^iPrN=C[CH_2P(NiPr_2)_2]_2$ and studies on the catalytic activities are in progress.[68] Other related systems were prepared and investigated structurally, such as N-phosphino-amidines and guanidines, where the interesting feature of the ligand backbone is the presence of a P-N bond. This was believed to play a role in mediating the flexibility of the supporting ligand, thus rendering the overall complex relevant to the catalysis of C-C bond formation such as olefin oligomerisation and polymerisation, or transformations such as asymmetric hydrogenation and hydrosilylation etc.[68] Other chelating ligands incorporating P-N bonds within the ligand framework were N-pyrrolylphosphino-N'-aryl-aldimine ligands, which were used to support

Pd(II) and Rh(I) centres. The resulting complexes showed virtually no activity against CO/ethylene

copolymerisation, but were moderately active in ethylene oligomerisation processes (Scheme 26).[68]
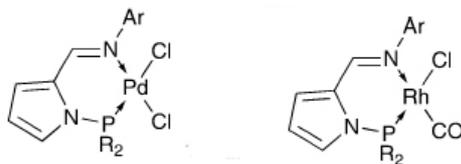
Scheme 26 – Late TM pre-catalysts supported by P/N ligands featuring P-N bonds.[68]

Chiral oxazoline/arsine ligands were synthesised aiming towards a direct comparison with iminophosphines (Scheme 27). Their coordination chemistry is analogous to that of P/N or P/O species discussed above and the catalytic species

used in CO/styrene copolymersation tests was the corresponding BF_4^- salt. However, the productivity was again surprisingly low, ranging between ca. 1-12 g polymer x g Pd^{-1} x h^{-1}.[67]
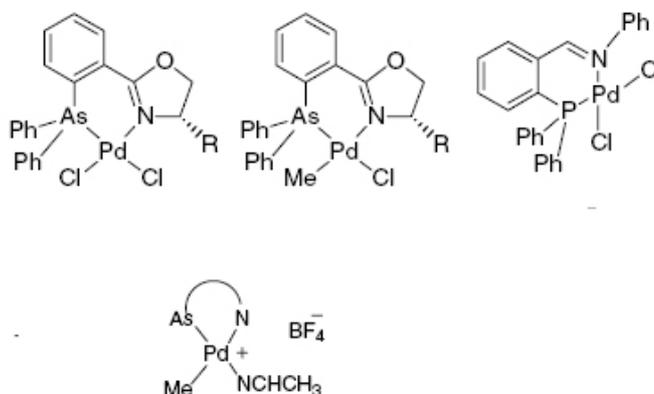
Scheme 27 – Pd(II) pre-catalysts and corresponding catalytic species supported by As/oxazolines.[67]

Similar synthetic methods were used in the synthesis of Pd(II) catalysts supported by flat, aromatic N/N ligands, such as pyrazolyl-pyrimidine-based ligands. Again, large, non-coordinating anion such as $Na[B\{3,5-(CF_3)_2(C_6H_3)\}_4]$ was used to stabilise the vacant site at the pre-catalyst $[Pd(Me)(NCMe)(ligand)]$ $[B\{3,5-(CF_3)_2(C_6H_3)\}_4]$. These catalysed the copolymerisation and terpolymerisation of CO with a range of olefins (including styrene and ethylene). The activity was rather moderate (up to 125 g Polyketone x g Pd^{-1} x h^{-1}) but it was suggested that this may be increased when non-conventional solvent such as 2,2,2,-trifluoroethanol was used.[69]

CO/ETHYLENE COPOLYMERISATION CATALYSED BY Pd (II) COMPLEXES *VS.* OLEFIN POLYMERISATION CATALYSED BY EARLY TRANSITION METAL COMPLEXES: A COMPARISON

A comparison of the Pd-catalysed homogenous CO/olefin copolymerisation and the homogenous

olefin polymerisation catalysed by early transition metal complexes is presented in Table 1 below.[7] In both cases, the presence of weakly coordinating anions make the metal centres highly electrophilic. Monomer activation takes places *via* an electrophilic attack by the metal centre. In both cases, the ligand coordination number is 4. In the case of early transition metals (Ti(IV), Zr(IV) and Hf(IV), all four-valent) two anionic ligands are required to be strongly coordinated (*e.g.* Cp) and the other two are weakly coordinating anions. Late transition metals (in this case Pd(II)) require two neutral and two weakly coordinated anionic ligands.

In both cases, at the active centres the growing polymer chain and the vacant site for binding a monomer must be located *cis* to one another. In d^0 metallocene complexes the *cis* arrangement is induced by the pseudotetrahedral coordination environment of the metal. In the square-planar d^8-palladium complexes *cis* coordination is enforced by the use of neutral bidentate ligands.

The major difference between the two types of catalysts is that the olefin polymerisation metallo-

cene catalysts are much more electrophilic than the Pd(II) complexes commonly used for CO/olefin copolymerisation. For polyketone formation, the electrophilicity needs to be balanced, so that the olefin can compete with CO for insertion. If the metal is too electrophilic, CO will coordinate irreversibly to the metal centre and will poison the polymerisation process.

Table 1

Comparison of typical Pd-catalysed CO/olefin copolymerisation and traditional early transition metal catalysed olefin polymerisation (Cp = cyclopentadienyl or cyclopentadienyl derivatives; L-L = chelating diphosphine or diimine; P = growing polymer or copolymer chain; □ = vacant site)

Products:	Polyolefins	Polyketones
Metal ion:	Mainly Ti(IV), Zr(IV), Hf(IV)	Mainly Pd(II) Ni(II) Rh(I)
Ligand:	2 Cp⁻, 2X⁻	2L, 2X⁻
Anion:	'non-coordinating'	weakly- or 'non'-coordinating
Coordination geometry:	tetrahedral	square planar
Active centre:	(Cp)(Cp)M(P)(□)	(L)(L)M(P)(□)
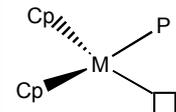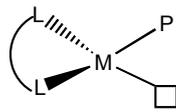
The moderate electrophilicity of Pd(II) catalysts makes them more tolerant to various heteroatom functionalities in the olefin substrate which leads to formation of functionalized polymers. Therefore, polyketone catalysis can have a wider applicability than early transition metal polyolefin catalysis, where the catalyst is generally intolerant of functional groups. Traditionally, late transition metals have been thought to have a crucial disadvantage when acting as catalysts for olefin polymerisation to form high molecular weight polymers. It was believed that the relative rate of β-hydride elimination to chain propagation is generally greater than that of early transition metal catalyst systems. However, examples of highly active olefin polymerisation catalysts have recently been discovered. In the case of the bidentate-chelating diimine Group 10 catalysts, the rate of associative displacement of the growing polymer chain by the free olefin, and of chain transfer, is retarded by the steric bulk of the ligands. This increases the chain propagation rates with respect to the chain transfer rates and as a result high molecular weight polymers are produced.[55, 70]

Modification of SHOP-type Ni catalysts that generate olefin dimers or oligomers, can provide olefin polymerisation catalysts. It is believed that removing the monodentate PPh₃ ligand from the catalysts or replacing it with a weakly coordinated ligand such as pyridine results in an increase of the barrier to β-hydride elimination, and decreases the barrier to coordination of the incoming olefin. This facilitates formation of a σ-alkyl π-olefin (P/O)Ni complex which is believed to play a key role in chain propagation.

The phosphorus donor can be replaced by a substituted imine moiety to form neutral N/O ligands,

in a quest for higher activity catalysts for olefin polymerisation. Moderately branched to linear polyethylenes are obtained with such catalysts. With the view of tuning the steric and electronic properties of the ligand in order to isolate active single-site catalysts for olefin polymerisation, the investigations were extended to N/O Schiff-base chelates bearing a pendant donor arm.[71] It has been envisaged that this might contribute to the stability of cationic alkyl in the initiation process. Homogenous olefin polymerisation catalysts containing monoanionic [N/O]⁻ and transition metals such as Ti,[72,73] Zr,[74,75] Cr [76] as well as Ni [77] have been isolated. Table 2 presents some representative late transition metal catalysts for olefin polymerisation.

The synthesis of alternating olefin/CO copolymers constitutes an example of transition metal-carbonylation with potentially almost perfect control over selectivity. The cationic Pd(II) catalysts are able to activate nucleophilic substrate molecules due to the electrophilic nature of the palladium-d⁸ centre. The *cis* arrangement of the neutral chelate ligand around the metal centre in a square-planar configuration ensures that the chain-end of the polymer and the incoming monomers will also maintain a *cis* configuration, which is essential for chain propagation. The coordination mode of the olefin at the vacant coordination site is determined by the electronic and steric properties of the ligand and polymer chain-end. The interaction between the polar polymer chain-end and the electrophilic metal centre influences the formation of the alternating copolymer, and plays an important role in the regio- and stereo-selectivity of the insertion of higher olefins into Pd-acyl systems.[6,7] Recent reports on highly active late transition metal catalysts for alternating olefin/carbon monoxide copolymerisation are presented in Table 3.

Table 2

Significant examples of late transition metal complexes active in ethylene polymerisation processes.[78]
(Activity = mol substrate x (mol metal)$^{-1}$x h^{-1})

Catalyst type	Metal	Example	Activity	Polymer Mw	Poly-ethylene branching structure	Functional group tolerance
Neutral P-O complexes (SHOP)	Ni(II)		6×10^3	α-olefin oligomers	Linear	Two phase process in butanediol
Neutral P-O complexes optimised for poly-merisation	Ni(II)		1.8×10^5	10^6	Linear	Stable in various polar organic media. Co-polymerisation of special fnctionalised monomers
Cationic bulky-diimine complexes	Ni(II) Pd(II)		4×10^6 (Ni) 4×10^3 (Pd)	$> 8 \times 10^5$	Ni(II): Highly branched to linear: Me, Et, Pr, Bu and longer Pd(II): Hyper-branched structures	Co-polymerisation of simple polar monomers such as acrylates (Pd). Stable in presence of esters, acetone or water (Pd).
Cationic tridentate bulky diimino-pyridine complexes	Fe(II) Co(II)		10^7 (Fe)	6×10^5	Highly linear	
Neutral N-O complexes with bulky substituents at imine	Ni(II)		2.3×10^5	5×10^5	Moderately branched to linear; mostly Me also Et, Pr, Bu	Stable to added amounts of polar organic solvents and water. Co-polymerisation of functionalised norbornenes.

The field of copolymerisation catalysis for the isolation of new materials with high selectivity is advancing rapidly. The quest for new, highly active and selective catalysts and reaction conditions continues. Recently, the alternating copolymerisation of carbon monoxide and ethylene in CH_3COOH and H_2O mixtures (at 90°C, 4.5 MPa of 1/1 CO/ethylene) and catalysed by [PdCl$_2$(dppf)] [dppf=1,1'-bis(diphenylphosphino) ferrocene] yields alternating polyketone (PK) copolymer selectively with a productivity of ca. 15500 g PK x (g Pd h)$^{-1}$, whereby the limiting viscosity number of the polyketone (LVN) can be tuned with varying the concentration of the acid used.[82] The authors found that the nature of the polymer can also be altered by varying the reaction conditions which directly influence the chain growing and the termination processes, *i.e.* under higher pressure of CO the LVN increases at the expense of the overall productivity, which decreases slightly.

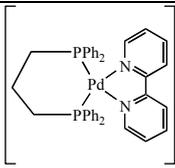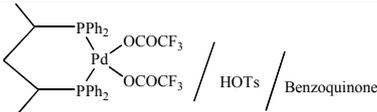To rationalise the selectivity of CO/ethylene copolymerisation process over the ester formation and support of the experimental observations, detailed DFT level computational studies were performed for palladium diphosphine ligands with a variety of bite angles and steric bulks. These studies showed that bulk of bidentate phosphine ligands strongly favours ester formation over polymerization processes at the CO/ethylene

reaction. Possible methanolysis pathways were considered and the direct correlation between the decreases of the barrier for the ester formation and the increase in the bite angle of the diphosphine ligand. The intermediates involved are zero-valent palladium complexes, which are stabilized by wide-bite-angle ligands. As the reductive elimination is the rate-determining step, these studies also confirmed that wide bite angles lead to low molecular- weight products since the reductive elimination in C-X bond formation is faster than that in the case of reactions catalysed by small-bite-angle diphosphines). These studies confirm the origin of the chemoselectivity of palladium catalysts containing bidentate phosphine ligands toward either methoxycarbonylation of ethylenene or the copolymerization of ethylene and carbon monoxide, function of the nature of the bite angle and steric bulk of the supporting ligand (Scheme 28)[83].

Table 3

Examples of Pd(II)-based complexes, active in copolymerisation processes.

Catalyst systems	Alternating CO/olefin copolymerisation			References
	Mw (g/mol)	[η] (dL/g)	Productivity (g/mol x h x bar)	
		0.64-1.1	$7.88\text{-}20.9 \times 10^3$	79
	$1\text{-}2 \times 10^4$	0.5-0.8	$1.06\text{-}2.06 \times 10^4$	80
DPPP/Pd(MeCN)$_2$(O$_3$STol)$_2$	1.01×10^4		14.2×10^3	6
Pd(OAc)$_2$/DPPP/HOTs	1.4×10^3		$12.8\text{-}20.4 \times 10^3$	81
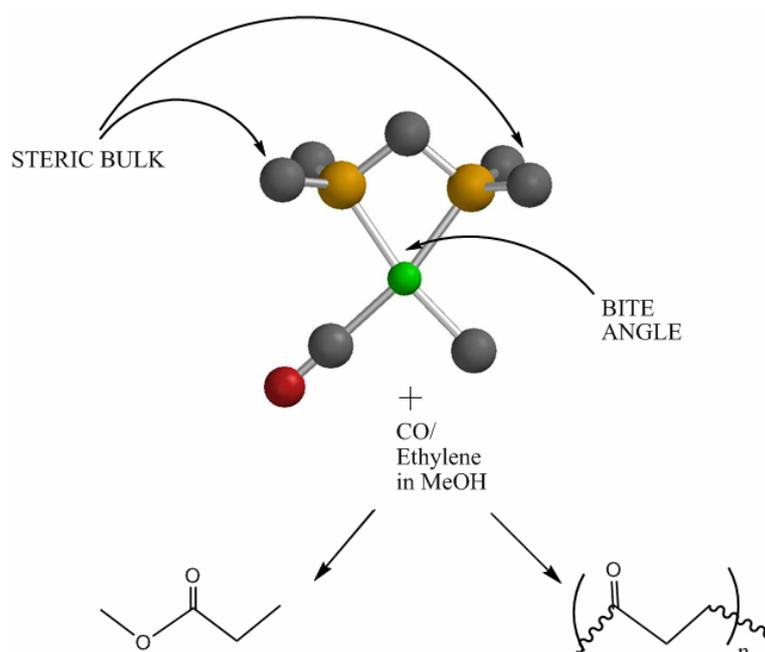
Scheme 28 – Selectivity of CO/ethylene copolymerisation process over
the ester formation can be controlled by tuning the bite angle and ligand bulk.

In addition to the detailed investigations on metal-catalyzed alternating copolymerisation reactions of ethylene and carbon monoxide, which have been the focus of many research groups in the last two decades, new approaches to optimize the nature of the polymer produced in this process are adopted. New investigations were triggered by the fact that alternating polyketone is difficult to process because of relatively low solubility in common solvents and a very high melting point (assigned to the dipolar interactions between carbonyl groups available in 50 mol % in polyketone). Recent reports focused on tuning the CO content in the copolymer and synthesis of non-alternating copolymers where the distribution of CO groups is random.[84, 85] New Palladium(II) complexes, supported by anionic P/O derived from o-[bis(o-alkoxyphenyl)phosphino]benzenesulfonic acid] have been designed and shown to generate non-alternating ethene/CO copolymers where the CO incorporation was kept well below 50%. These family of palladium catalysts (generated *in situ* or available as single-site species) are able to generate high molecular weight random copolymers with Mw ca. 370000 and polydispersity (Mw/Mn) = 2, albeit the melting points remain rather high, at 220-230 °C. The synthesis of polyethylene-block-poly(ethylene-alt-carbon monoxide) has thus been reported, and the chain growth monitored *via* sequential insertions of carbon monoxide and ethylene into palladium-carbon bonds for mechanistic studies. In general, obtaining alkene/carbon monoxide copolymers with low carbon monoxide content *via* the living copolymerization of ethylene with carbon monoxide remains challenging, although they promise improvement in the processing of the resulting materials, with respect to perfectly alternating polyketone.[86]

CONCLUSIONS

Transition metal complexes of ligands containing P, N and/or O donor atoms continue to be of interest since with Group 10 metals such ligands may exhibit hemilabile character, especially when they are heteroditopic. Such behaviour has been exploited in homogeneous catalysis and in the activation of small molecules, as the formation and stabilisation of intermediate species is often facilitated.[58,87] To date, the P/P-based ligand systems remain amongst the most active. Ni complexes of P/O ligands have been investigated as promising

catalysts for the oligomerisation of olefins as in the Shell higher olefin process (SHOP).[12,88] Group 10 transition metals with diimine-based donor ligands have been found to be active catalysts for polymerisation of ethene and propene giving rise to a new generation of polymers,[70] but also showed moderate activity towards CO/ethylene copolymerization processes. Although a variety of N/P ligand systems have been studied, only a small number of bidentate $N(sp^2)$-$P(sp^3)$ ligands, mainly oxazoline and imidazolyl based, and transition metal complexes thereof have been described. The synthesis and reactivity of new N/P ligands and their coordination to late transition metals continues to attract interest owing to the possibility of tailoring the steric and electronic properties of the different donor groups. Recently, oxazoline based N/P ligands displaying both soft and hard character, when coordinated to Pd(II) centres, have shown some activity in the copolymerisation of carbon monoxide and olefins, a reaction typically confined to bidentate phosphine and imine systems.[89] Research interests in our research group were mainly concerned with the synthesis and reactivity of a novel family of iminophosphines with flexible backbones, and the preparation of the corresponding Ni(II), Pd(II), Pt(II) and Rh(I) complexes. Considerations on the ligand steric influence on the catalytic activity, when the ligand subsitutents are placed at the more remote site with respect to the active center, continues to be explored in addition to the electronic aspects above, as part of the complete ligand design.[90] Studies of structure-activity relationships relevant towards ethylene polymerisation, copolymerisation of CO and ethylene reactions continue to be undertaken with the view of gaining deeper understanding of the mechanistic details for these industrially relevant processes.

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