1 Introduction

The catalytic polymerisation of olefins by well-defined organometallic catalysts has traditionally been the exclusive field of the early transition metals (groups 3 – 5). Metallocene catalysts (with a ligand set based on two η5-cyclopentadienyl moieties), which often contain a group 4 metal in its highest oxidation state, can achieve tremendous activities. These catalysts can readily be fine-tuned by ligand modifications and continue to be a subject of research, both in academia and in industry.1

Early transition metal catalysts are usually hard Lewis acids which implies formation of strong complexes with hard Lewis bases. Olefins, however, are relatively weakly bound since they are soft Lewis bases, binding through their π-cloud to the metal. The combination of a hard Lewis acidic active site and a soft substrate makes these catalysts extremely sensitive to the presence of polar molecules (containing e.g. O or N) in the reaction medium (either as impurities, or as part of the substrate). Therefore, they are often designated ‘oxophilic’. Polymerisation may be inhibited because the olefin has to compete for the metal centre with Lewis bases in the reaction medium. In the case of a hard Lewis base, coordination may even lead to irreversible poisoning of the catalyst. In addition, early transition metal catalysts contain highly polar Mδ++–Cδ– bonds, which are vulnerable to protonolysis (e.g. by adventitious H2O in the medium). As a consequence, polymerisations with these catalysts often require the use of a large excess of cocatalyst to scavenge impurities from the reaction medium.

An associated disadvantage of the early transition metal catalysts is that they cannot be employed for the copolymerisation of monomers with polar functionalities. The late transition metals (groups 9 – 11) are much less oxophilic and coordination of polar molecules is often readily reversible. The increased heteroatom tolerance allows polymerisations to be run at lower cocatalyst concentrations. The late metals also offer much better chances for copolymerisation of ethene or propene with comonomers containing polar functionalities.2 The reduced oxophilicity of the late transition metals is illustrated by the SHOP (Shell Higher Olefin Process) system for oligomerisation of ethene, which utilises a homogeneous Ni(II) catalyst in an alcoholic solvent.3-11 Heteroatom tolerance also enables the alternating copolymerisation of ethene and carbon monoxide by Pd(II) catalysts.12 Nevertheless, homopolymerisation of simple olefins by late transition metals has been largely unknown for a long time, although polyethylene formation had occasionally been observed with certain SHOP catalysts.6,10,11,13,14 The failure of most Ni catalysts to polymerise ethene to high molecular weight polyethylene is related to the fact that β-H elimination is fast, resulting in the formation of dimers15 or oligomers at most.

1.1 Late transition metals

A major breakthrough was accomplished in 1995 when Brookhart introduced Ni(II) and Pd(II) catalysts based on α-diimine ligands with α-substituted aromatic N-substituents. In the presence of methylalumoxane (MAO), these compounds are active in the polymerisation of ethene and α-olefins.
In principle, the transfer of a $\beta$-H atom from the growing polymer chain to the metal center alone does not necessarily lead to chain termination: simple dissociation of the olefinic polymer resulting from $\beta$-H-elimination is significantly endothermic. If the coordinated olefinic polymer remains coordinated to the metal centre, reinsertion will take place enabling further chain growth (Scheme 1.1). However, the olefinic polymer can be displaced from the metal by associative coordination of a new monomer molecule. Brookhart recognised that chain termination can thus be retarded by blocking associative displacement of the chain through well-positioned steric hindrance applied by the ancillary ligand.

In the Ni and Pd catalysts, the aryl rings of the ligand are forced into an orientation perpendicular to the diimine backbone. The $\alpha$-substituents effectively shield the axial positions of the square coordination plane, thus preventing associative displacement of the coordinated polyolefin chain by the monomer. This retardation of chain transfer with respect to chain growth, enables the formation of high molecular weight polymers. If aryl groups with sterically less demanding $\alpha$-substituents are employed, the catalysts produce oligomers ($\alpha$-olefins).\textsuperscript{16,17} Besides their influence on the ratio of rate of chain transfer to the rate of chain growth, the large aryl substituents also hamper the formation of inactive [(diimine)$_2$M] complexes.\textsuperscript{18,19}

Since Brookhart's original findings, the use of appropriate steric protection on the ancillary ligand to block associative chain displacement has led to many new Ni and Pd polymerisation and oligomerisation catalysts. Many of these contain an $\alpha$-diimine...
as the key ligand structure,\textsuperscript{18,20-26} although other neutral \((N,N)\)-,\textsuperscript{27,28} \((N,O)\)-,\textsuperscript{29} \((P,O)\)-,\textsuperscript{30,31} \((P,P)\)-,\textsuperscript{32-35} and \((P,N)\)-ligands\textsuperscript{36-43} have yielded active systems as well.

The principle of shielding axial positions has also revived the development of monoanionic ligands for neutral \(\text{Ni(II)}\) catalysts. Neutral catalysts are expected to have a higher heteroatom tolerance than the cationic catalysts. Grubbs introduced a family of catalysts based on sterically hindered salicyaldiminato ligands (Figure 1.2A).\textsuperscript{44,45} In the presence of \(\text{B(C}_6\text{F}_5)_3\) or \(\text{Ni(COD)}_2\) (\(\text{COD} = \text{cis-1,5-cyclooctadiene}\)), these complexes polymerise ethene with high activity. Many related \(\text{Ni}\) polymerisation catalysts with monoanionic \((N,O)\)-ligands have been reported, some of which do not require a cocatalyst at all (Figure 1.2B,C).\textsuperscript{19,46-53}

With respect to the charge and denticity of the ligand, the Grubbs-type catalysts can be compared to the SHOP oligomerisation catalysts. Not surprisingly, SHOP-type \(\text{Ni(II)}\) \((P,O)\)-chelates equipped with well-positioned steric bulk have now been reported to produce polyolefins.\textsuperscript{54,55} Anionic \((N,N)\)-ligands equipped with sterically demanding groups have also been applied in \(\text{Ni}\) polymerisation catalysts.\textsuperscript{56,57}

1.2 Iron-based catalysts

In 1998, the groups of Gibson and Brookhart reported highly active catalysts based on divalent \(\text{Fe}\) and \(\text{Co}\) producing highly linear polyethylene in the presence of MAO cocatalyst.\textsuperscript{58,59} The catalyst precursor complexes contain a pyridine-2,6-diimine (PDI) ligand with sterically demanding aryl groups on the imine nitrogens. In general, the \(\text{Fe}\) derivatives are much more active than the \(\text{Co}\) derivatives. These catalysts again demonstrate the principle of steric protection of the metal centre. Reduction of the steric bulk on the nitrogen aryl substituents, converts the polymerisation catalysts into oligomerisation catalysts.\textsuperscript{60-64} If the steric bulk is reduced too drastically, however, inactive \(([\text{PDI}]_2\text{Fe}]^{2+}\) complexes are formed.\textsuperscript{65}
Several attempts have been made to develop new Fe or Co based catalysts by modification of the basic structure of the PDI ligand. Instead of aryl substituents, NR₂ groups have been introduced in the PDI ligand as steric protection. The corresponding Fe and Co complexes produce oligomers or low molecular weight polyethylene.⁶⁶ Related to these derivatives are pyrrolyl-substituted PDI ligands.⁶⁶,⁶⁷ Replacement of one or both imine donors by amine functionalities strongly decreases the activity of the iron complexes.⁶⁸ Replacement by N-heterocyclic carbene donors results in loss of activity with cobalt.⁶⁹ Bis(iminophosphanyl)pyridine ligands have been employed by Al-Benna et al. to prepare the complexes \([\text{C}_5\text{H}_3\text{N}(\text{R}_2\text{P}=\text{NR}’)\text{MX}_2]\) (M = Fe, Co). In spite of their structural similarity to the PDI ligand, the Fe and Co complexes showed only low (Fe) to moderate (Co) activity in ethene polymerisation in the presence of MAO.⁷⁰ Variation of the central donor by changing the pyridine for thiophene, furan, carbazole, pyrimidine or triazine moieties also leads to significantly less active catalysts.⁶⁷,⁷¹ If the pyridine donor is replaced by the anionic pyrrolato group, the ligand coordinates to Fe(II) in bidentate mode, forming bis(ligand)Fe complexes which are inactive upon activation with MAO.⁷² In general, any modification of the basic PDI ligand structure leads to loss of activity.

Attempts to develop alternative olefin polymerisation catalysts based on Fe have met with very limited success. In the patent literature examples have appeared of Fe(II) precatalysts with tridentate monoanionic ligands (Figure 1.4A–C). Their activities however, are very much lower than those achieved by the Gibson/Brookhart system.⁷³ Phosphinimide Fe(III) complexes (Figure 1.4D) have been found to form modestly active systems with MAO under rather demanding conditions.⁷⁴

It appears that design of new polymerisation catalysts based on Fe or Co is less straightforward than in the case of Ni or Pd. One of the main reasons is that for the former systems there is still uncertainty about the nature active species (see section 1.6). Possibly, the electron configuration on the metal forms a special combination
with the electronic structure of the ligand. It may well be that the known redox-activity of the PDI ligand contributes to the success of the PDI/Fe- or PDI/Co-combination.\textsuperscript{75}

1.3 Activation of precatalysts

As seen from the examples in the preceding sections, active olefin polymerisation catalysts are now available for a range of late as well as early transition metals. In many cases, the actual active catalyst species is not isolated and used as a well-defined organometallic complex, but is generated \textit{in situ} from a catalyst precursor or precatalyst (that itself is not active) and a cocatalyst. In order to discuss the nature and properties of the active catalyst species, the various methods used to generate such active species are briefly reviewed.

1.3.1 Activation by alumoxanes

Many transition metal precatalysts can be activated by MAO (MethylAlumOxane) cocatalyst.\textsuperscript{76-78} The composition and structure of MAO are not well-understood, and therefore MAO is often represented by the formula \([\text{AlOMe}]_n\). MAO is obtained by controlled hydrolysis of AlMe\(_3\) and constitutes a complex mixture involving many species and equilibria.\textsuperscript{79} Residual AlMe\(_3\) (either free or associated) present in MAO participates in many of these equilibria and a formulation as \([\text{AlOMe}]_n(\text{AlMe}_3)_x\) is therefore more appropriate. MAO is thought to serve three important purposes in homogeneous catalytic olefin polymerisation. Firstly, when transition-metal halide complexes are used as catalyst precursor, MAO will methylate this precatalyst to generate species with metal-methyl bonds. Secondly, MAO acts as a Lewis acid species in abstracting an alkyl (or halide) anion \(R^-\) from the transition metal, generating a cationic metal-alkyl species with a weakly nucleophilic \([R^-\text{MAO}]^-\) anion as counterion. Thirdly, the excess MAO used in activating the catalyst can conveniently scavenge impurities from the feed/medium, thus protecting the active catalyst species. Nevertheless, there are some disadvantages associated with the use of MAO as activator. It appears that the alkyl abstraction process and the concomitant generation of the weakly nucleophilic anion requires a substantial excess of MAO to be at its most effective (at least several hundreds of equivalents, frequently more). This, combined with the relatively high cost of MAO, makes it less attractive for industrial application. In addition, the poorly defined nature of MAO makes it more difficult to establish the true nature of the active species in MAO activated systems.

1.3.2 Activation by abstraction of halide or alkyl ligands

Due to the disadvantages attached to the use of MAO as activator (described above), alternative activation strategies have been actively pursued (Scheme 1.2). Activators, other than MAO, have been developed which react with catalyst precursors in a stoichiometric ratio to give active catalysts with a well-defined composition and structure. These so-called ‘single-component’ systems provide an opportunity to study the catalytic species in much more detail. The alternative activators however, often require alkylated metal centres in the precatalyst. In most cases, such precatalysts are conveniently obtained by alkylation of dihalide complexes using alkylaluminum, alkyllithium or Grignard reagents.
An alkyl halide precursor can be dehalogenated by treatment with an alkali or silver salt resulting in the precipitation of the alkali or silver halide. The resulting cationic transition metal complex is left with a vacant site and its charge is balanced by the anion provided by the abstracting agent. Alternatively, the vacancy can be created by treatment of a dialkyl metal complex with a Brønsted acid. Protonation eliminates an alkane and generates an alkyl cation with a vacancy. The proton is usually introduced in the form of an oxonium or ammonium salt. The conjugate base of the Brønsted acid (e.g. Et₂O or C₆H₅NMe₂) may coordinate to the metal centre, however this is not necessarily problematic as these are quite weak Lewis bases, in particular with the less electrophilic late transition metals. Nevertheless, it is mandatory that the complementary anion displays very weak nucleophilicity (vide infra).

A third route to cationic single component catalysts involves abstraction of an alkyl anion from a dialkyl precursor by a strong Lewis acid. Reaction of a metal dialkyl complex [LnMR₂] with triphenylcarbenium (trityl) salts provides an electron deficient monoalkyl cation [LnMR]⁺ with concomitant formation of RCPH₃. Tris(pentafluorphenyl)borane, B(C₆F₅)₃ is also frequently used as alkyl abstracting agent. In this case, the cationic species will be accompanied by the borate anion [RB(C₆F₅)₃]⁻ which incorporates the alkyl group formerly attached to the metal centre of the catalyst precursor. A fourth method for dealkylation consists of oxidative cleavage of the M–R bond using e.g. ferrocinium of silver salts.

1.4 Basic demands for catalytic activity

Although active catalytic systems described in section 1.3 are obtained from different precursors in combination with various activators, they are believed to produce the same cationic active species (Scheme 1.2). In all cases, at least one alkyl group remains bound to the cationic transition metal complex. The activity of [(Cp)₂ZrX₂], [(α-dimine)NiX₂] or [(PDI)FeX₂] precatalysts can be rationalised by invoking the electron deficient cations [(Cp)₂Zr(IV)R]⁺, [(α-dimine)Ni(II)R]⁺ and [(PDI)Fe(II)R]⁺, respectively as the catalytically active species. These cationic species [(Ligand)MR]⁺ all have valence electron counts of 14 (or less).
For the early transition metals, it has been shown that the ionic species \([\text{(Cp')}_2\text{ZrR}][\text{XB(C}_6\text{F}_5)_3]\) (R = Me, CH\(_2\)Ph, X = R, C\(_6\)F\(_5\)) are active for olefin polymerisation without the need for an additional cocatalyst.\(^{82-86}\) Brookhart and others have undertaken detailed mechanistic studies to establish the nature and reactivity of the late transition metal α-diimine systems. Single-component catalysts were generated by alkyl abstraction from the alkylated precursors \([\alpha\text{-diimine})\text{MR}_2]\) (M = Ni, Pd). It was found that the electron deficient cations \([\alpha\text{-diimine})\text{MR}]^+\) are indeed responsible for the polymerisation activity.\(^{87-91}\) Many theoretical studies on the α-diimine Ni and Pd catalysts have been based upon these cations as the active species.\(^{92-102}\) For the Fe and Co catalysts, however, the presumed active species \([\text{(PDI)MR}]^+\), has not been isolated thus far (see section 1.6).

One common property of the active species is the presence of a metal carbon σ-bond. This is involved in the migratory insertion process with the alkene substrate, leading to the C–C bond formation. Secondly, their low electron counts (≤ 14 VE) suggest that at least two empty valence orbitals are required for high activity. For insertion to take place, an empty coordination site (vacancy) is needed cis to the metal carbon σ-bond. These three seem to be the minimal criteria for polymerisation activity. For late transition metals, associative displacement of the growing polymer chain has to be prevented (otherwise only dimers or low oligomers are formed). This requires specific steric protection of the active centre. The examples of catalysts that are mentioned in this paragraph all involve cationic active species. Although positively charged metal alkyl catalysts indeed generally show higher activities in olefin polymerisation than isoelectronic neutral species, the cationic nature is not a prerequisite for activity. This is demonstrated by the highly active neutral Ni catalysts discussed in section 1.1.

1.5 Cation-anion interactions

For those catalysts which react with an activator to give a cationic species, the conditions of coordinative and electronic unsaturation demand that the interaction between cation and anion is absent or weak. Therefore, the charge of the cation must be counterbalanced by a weakly coordinating anion, since more nucleophilic anions will occupy the free coordination site essential for polymerisation activity. Coordination of the anion is usually a reversible process and the monomer competes with the anion for the active site.

However, since polymerisation reactions are often performed in solvents of low polarity, the active catalyst cannot be considered as an entirely free cation accompanied by a ‘spectator’ anion. Due to the Coulombic attraction, the anion is always in close proximity to the active site. However, adequate steric protection of the metal centre may preclude close association of the ion pair. In fact, the activity of a cationic polymerisation catalyst turns out to be directly dependent on the degree of association between the cationic metal centre and the counterion.\(^{103,104}\) In cases where the steric protection of the metal centre is insufficient, coordination of the anion can even lead to irreversible degradation of the anion by the highly electrophilic cation, which results in deactivation of the catalyst system. Thus, the interactions between cation and anion determine to a large extent the thermal stability\(^{103,105}\) (and consequently on catalyst lifetime) of ionic catalyst systems. Cation-anion interactions can also have a marked influence on chain transfer characteristics and, with some special anions, on the stereoregulation of α-olefin polymerisation.\(^{106,107}\) The well-
known fluorinated tetraaryl borate anions \([B(C_6F_5)_4]^-\) and \([B(3,5-(CF_3)-C_6H_3)_4]^-\) are among the most weakly coordinating anions.\(^{103,108,109}\) The electronegative fluorine atoms dissipate the negative charge on the boron atom, thus reducing the overall nucleophilicity of the anion.

Since single-component cationic systems are well-defined ionic organometallic compounds, these catalysts allow detailed study of cation and anion as well as of their interactions. When \(B(C_6F_5)_3\) is used as abstracting agent, the presence of the \(R\) group in the \([RB(C_6F_5)_3]^-\) anion renders it more coordinating than e.g. \([B(C_6F_5)_4]^-\) and, depending on the nature of the cation, the alkyl moiety may bridge between the boron and the metal centre. In case of a methyl bridge, the methyl hydrogens are bent away from B and oriented toward the metal centre.\(^{82-84,110,111}\) If a benzyl group is abstracted, the boron-bound benzyl is often found to coordinate to the metal by its \(\pi\)-electrons (Figure 1.5B).\(^{84,112,113}\)

Horton \textit{et al.} have correlated the \(^{19}\)F NMR shifts of alkyltris(pentafluorophenyl) anions to their degree of association with cationic \(d^0\) metal cations in the ion pairs \([\text{L}_n\text{MR}]\)[\(RB(C_6F_5)_3\)] (\(R = \text{Me, CH}_2\text{Ph}\)). It was observed that a chemical shift difference between the \textit{meta} and \textit{para} fluorine resonances (\(\Delta\delta(m,p)\)) of 3 – 6 ppm is characteristic for coordination of the alkyl moiety in the anion to the cation, whereas a smaller value (\(\leq 3\) ppm) for \(\Delta\delta(m,p)\) indicates noncoordination.\(^{114}\) \(^{19}\)F NMR spectroscopy can thus be used to differentiate between contact ion pairs and (solvent) separated ion pairs.\(^{115}\) Two dimensional \(^{19}\)F\{\(^1\)H\} HOESY\(^{116}\) (heteronuclear NOESY) NMR spectroscopy has been applied to study the interactions between the tetrafluoroborate anion and the electrophilic \(\alpha\)-diimine complexes \([\beta\text{-diimine}]\text{PtMe}(\eta^2\text{-olefin})]^+\), which are catalytically inactive model systems for the analogous Ni(II) and Pd(II) polymerisation catalysts. The model system confirms that the \(\beta\text{Pr}\) groups on the aryl nitrogen substituents effectively shield the axial positions of the metal centre, as H···F-interactions between the anion and the Pt-methyl and olefinic protons were not observed.\(^{117}\)

Many new boranes and borate anions containing fluorinated aryl groups have been synthesised with the aim of generating ever more weakly coordinating or chemically more inert counterions for cationic olefin polymerisation catalysts.\(^{79,118-122}\) The central atom of the anion is no longer the exclusive realm of the group XIII elements. Recently, the scope of weakly coordinating anions has been widened by investigation
of perfluoraryloxymetalates as counterions, which contain a transition metal as the central atom.\textsuperscript{123}

### 1.6 Active species in iron and cobalt pyridine-2,6-diimine systems

From section 1.4, it becomes clear that the major criteria for homogeneous transition metal catalysts for olefin polymerisation are electronic unsaturation and the presence of a metal carbon bond \textit{cis} to a vacant coordination site. In contrast to the well-documented early transition metal and Ni(II) \(\alpha\)-diimine systems, the nature of active species in the Fe(II) and Co(II) PDI systems is not very well established. Despite intensive research efforts, many questions about the mechanism still remain unanswered, especially those with regard to the nature of the active species.

In analogy to the single component systems known for early transition metals and the Ni and Pd \(\alpha\)-diimine systems, an electron deficient, cationic alkyl species \([\text{PDI}M\text{R}]^{+}\) (\(M = \text{Fe, Co}\)) is generally proposed to be responsible for the polymerisation activity. Although experimental evidence for the involvement of such species is lacking, several theoretical studies have been based on this assumption. For the cobalt catalyst, a low spin doublet (\(S = 1\)) ground state is proposed for the 15-valence electron alkyl cation.\textsuperscript{124} For the iron catalyst, \textit{ab initio} calculations by Griffith \textit{et al.} as well as density functional calculations by Deng \textit{et al.}, propose a singlet (\(S = 0\)) ground state for the 14 valence electron alkyl cation.\textsuperscript{125,126} In contrast, Khoroshun \textit{et al.}, using a different functional, conclude that it must have a triplet or quintet ground state.\textsuperscript{127}

The iron catalyst precursors are usually activated with aluminoxane cocatalysts and polymerisation results are strongly dependent on the type or activator.\textsuperscript{128,129} On the basis of NMR data, Bryliakov has proposed dinuclear Fe-Al complexes as the active catalyst, however none of these species has actually been isolated.\textsuperscript{130} In contrast to the early transition metals and to the Ni and Pd catalysts, a single-component catalyst based on the (PDI)M system (\(M = \text{Fe, Co}\)) has not been reported. This is due to the fact that dialkylation of the dihalide precatalysts to obtain \([\text{PDI}M\text{R}_2]\) is not straightforward. This hampers studies directed towards alkyl abstraction, leading to the supposed cationic monoalkyl species. Furthermore, experimental work on the Fe and Co systems is complicated by the paramagnetic nature of the complexes.

For the iron dihalide precursor, dialkylation appears to lead to decomposition with concomitant formation of the dialkyl coupling product, suggesting reductive elimination from an intrinsic dialkyl species \([\text{(PDI)FeR}_2]\).\textsuperscript{131,132} Cationic PDI Fe(II) precatalysts without iron-alkyl bonds have been prepared by halide abstraction from the dihalide complexes using AgSbF\textsubscript{6}. The resulting monohalide species are stabilised by MeCN or THF and have \([\text{BPh}_4]^-\) as the counterion. Halide-free cations are obtained in the presence of acetylacetonate. All these ionic systems form active polymerisation catalysts when activated with MAO or when treated with AlMe\textsubscript{3} (10 equiv.) in combination with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (1 equiv.).\textsuperscript{131} On the basis of EPR and Mössbauer studies, Gibson \textit{et al.} have suggested that the active species obtained from activation with MAO contains iron in the +3 oxidation state.\textsuperscript{133}
In the case of cobalt, attempted dialkylation leads to formal reduction to the diamagnetic cobalt(I) monoalkyl [(PDI)CoR]. The monoalkyl itself is unreactive towards ethene, but in the presence of strong Lewis acids like MAO or Al₂Me₆/B(C₆F₅)₃ it was found to form an active polymerisation catalyst. The ionic dinitrogen adduct [(PDI)Co(N₂)][MeB(C₆F₅)₃] is obtained upon methyl abstraction from the monomethyl Co(I) species [(PDI)CoMe]. ¹H NMR studies show that the ionic species slowly polymerises ethene leaving the ethene adduct [(PDI)Co(C₂H₄)][MeB(C₆F₅)₃] after consumption of the monomer. Note that these precursors do not contain a cobalt-carbon τ-bond and it is still unclear how polymerisation is initiated from the cationic species. Speculation on possible pathways may include reductive coupling of two ethene molecules, C-H activation of ethene or reaction of bound ethene with B(C₆F₅)₃ to form a zwitterionic species, all of which involve the Co(III) oxidation state.¹³⁴⁻¹³⁷ Thus far, it is not clear whether similar redox processes as those found for Co, are also operational in the Fe case. In this context, it is interesting that identical polymerisation activities are found irrespective of the oxidation state of the halide precursor, i.e. [(PDI)FeCl₂] or [(PDI)FeCl₃]. This probably reflects initial reduction of the Fe(III) precursor to Fe(II) by the Al cocatalyst.⁵⁹,¹³⁸

The synthetic inaccessibility of the Fe(II) and Co(II) dialkyl PDI derivatives has thus far prevented isolation of the monoalkyl cations by alkyl abstraction routes. This has prompted the Brookhart group to study the Ru(II) and Rh(III) analogues. For these second row transition metals, the diamagnetic target alkyl cations have been prepared as their ethene adducts [(PDI)RuMe(C₂H₄)]⁺ and [(PDI)RhMe(C₂H₄)]²⁺, respectively. These, however showed little to no polymerisation activity.¹³⁹ Also the Rh(I) monoalkyls [(PDI)RhR] produced no polymer upon activation with MAO.¹⁴⁰

1.7 Electron deficient iron hydrocarbyls

If iron-based homogeneous olefin polymerisation is to be understood in full detail, fundamental knowledge about electron deficient iron alkyls and their reactivity is indispensable. Synthesis methodology and reactivity studies of electronically unsaturated iron alkyls may be extrapolated to existing catalytic systems and can possibly lead to the development of new catalysts.

Iron is found in oxidation states ranging from –II to +VI.¹⁴¹ However, organoiron compounds have mainly been reported for Fe(II). Even for the very common +III oxidation state, organometallic species are scarce in literature. The rich organometallic chemistry of Fe(II) deals for the larger part with diamagnetic, electronically saturated, 18-valence electron compounds. In most cases the valence shell of iron is completed by strong-field ligands like Cp or CO.¹⁴²

Literature reports on isolable, electronically unsaturated, (i.e. 14 valence electrons or less) iron hydrocarbyls, are rather scarce. As a consequence, reactivity studies involving such complexes are limited as well. Cationic, electron deficient iron hydrocarbyls are completely unknown. Iron hydrocarbyls are usually obtained by treatment of halide precursors with organolithium or Grignard reagents.¹⁴² In general, stable compounds are isolated only if alkyl ligands without β-H atoms are employed.

* Alkylation of the first row Mn(II) dihalide (inactive for polymerisation) has also resulted in reduction yielding inactive formally Mn(I) monoalkyl species.¹⁹⁴
Furthermore, in order to obtain low electron counts, sterically hindered alkyls or aryls are preferred, since these limit coordination numbers.

1.7.1 Homoleptic aryl and alkyl complexes

Homoleptic iron(II) aryl complexes\textsuperscript{143} include the neutral tetramesityldiiron \([\text{FeMes}_2]_2\) (Figure 1.6A) and the structurally similar \([\text{Fe}(2,4,6-i\text{Pr}_3\text{C}_6\text{H}_2)]_2\) (10 valence electrons)\textsuperscript{144-147} in which two of the mesityls bridge the iron centres in the dimer.\textsuperscript{148-151} Only for the extraordinary bulky \(2,4,6-t\text{Bu}_3\text{C}_6\text{H}_2\) (Mes\(^*\)), a mononuclear, two-coordinate complex \([\text{Fe}(\text{Mes}^*)]_2\) is obtained.\textsuperscript{152,153} Anionic, homoleptic aryls are represented by \([\text{Li(OEt}_2])_4[\text{FePh}_4]\) (16 valence electrons, Fe(0))\textsuperscript{154} and the tetrannaphthyl ferrate \([\text{Li(OEt}_2])_2[\text{Fe(naphthyl)}_4]\) (14 valence electrons, Fe(II)).\textsuperscript{155} The only isolated homoleptic iron alkyls are the Fe(IV) complex tetrakis(1-norbornyl)iron\textsuperscript{156} (12 VE) (Figure 1.6B) and the dialkyl \([\text{Fe(C(SiMe}_3)_3}]\) (10 VE).\textsuperscript{157-159} The former complex owes its stability to the fact that the iron is bonded to the bridgehead carbons, which precludes decomposition by \(\beta\)-H elimination, the latter lacks \(\beta\)-hydrogens. Due to steric crowding, these complexes are inert towards Lewis bases.\textsuperscript{156} The dialkyl \([\text{Fe(CH}_2\text{SiMe}_3)_2]\) has been mentioned as the product of the reaction between FeCl\(_2\) and LiCH\(_2\)SiMe\(_3\), but experimental or characterisation data are unavailable.\textsuperscript{160} Similarly, preparation of \([\text{Fe(CH}_2\text{Ph}_2]\) has been claimed, but its isolation is doubtful.\textsuperscript{161} Anionic, homoleptic Fe(II) alkyl complexes are represented by the tetraalkylferrates \([\text{FeR}_4]^{2-}\) which result from exhaustive alkylation of FeCl\(_2\) or FeCl\(_3\) and can be isolated as their dilithium salts.\textsuperscript{162,163} The intermediate FeMe\(_2\) cannot be isolated and decomposes in THF at \(ca.\) \(-10\) °C.\textsuperscript{163} Homoleptic Fe(III) aryl or alkyl complexes are unknown.

![Figure 1.6 Homoleptic iron hydrocarbyls](image)

1.7.2 Diaryl and dialkyl complexes with stabilising ligands

Reaction of the homoleptic diaryls \([\text{FeMes}_2]_2\) or \([\text{Fe}(2,4,6-i\text{Pr}_3\text{C}_6\text{H}_2)]_2\) with Lewis bases gives rise to 3- or 4-coordinated diaryl complexes of the type \([L_n\text{FeMes}_2]\) with valence electron counts of 12 or 14 (\(L = \) phosphane, aminophosphane, phosphite, chelating diphosphane, \((\alpha\text{-disubstituted})\) pyridine, chelating diamine, \(\alpha\)-diimines, nitrile, \(n = 1,2\) depending on the steric demands of \(L\)).\textsuperscript{145,147,149,151,164} A systematic
investigation of the geometries and electronic structures of \([L_2FeMes_2]\) compounds was reported very recently by Chirik and coworkers.\(^{165}\) High-spin, \(S = 2\) tetrahedral complexes are observed with monodentate or chelating amines. Monodentate phosphines and phosphites form planar, \(S = 1\) complexes. With chelating phosphines, both geometries are possible, depending on the substituents on the chelating P atoms. Aryl substituents yield planar structures, while alkyl substituents furnish tetrahedral compounds. Alternatively, stabilised iron diaryls can be obtained by arylation of halide precursor complexes. Thus, Chatt and Shaw prepared the planar, \(S = 1\) bisaryl trans-\([(PEt_2Ph)_2FeAr_2]\) (\(Ar = C_6Cl_6\)) by reaction of the corresponding dichloride with \(C_6Cl_6MgBr\).\(^{165,166}\) The use of \(\sigma\)-disubstituted aryls seems crucial for stabilisation of the planar \(S = 1\) configuration.\(^{165,166}\) The doubly orthometallated complex \([\kappa^4C,C,N,N-\{(C_6H_4CH_2)(CH_3)NCH_2CH_2N(CH_3)(CH_2C_6H_4)\}Fe]\) is stabilised by coordination of the diamine moiety in the bisaryl ligand.\(^{167}\) Similar stabilisation by a Lewis basic side arm is found for the bisaryl complex \([\kappa^2C,N-(C_6H_4P(Ph)_2=NSiMe_3)]_2Fe\].\(^{168}\)

Electron deficient Fe(II) dialkyls have been stabilised by chelating diphosphane ligands with sterically demanding substituents. The complexes \([(\text{dippe})FeR_2]\) (\(\text{dippe} = 1,2\)-bis(diisopropylphosphino)ethane) were obtained by treatment of the corresponding dibromides with dialkyl magnesium reagents (\(\text{dippe} = 1,2\)-bis(diisopropylphosphino)ethane).\(^{169}\) With smaller alkyls (e.g. Et or \(t\)Bu), decomposition in benzene or toluene takes place above 0 °C, producing \([(\text{dippe})Fe(\eta^6\text{-arene})]\) which is assumed to result from solvent trapping by intrinsic decomposition products.\(^{170}\) Nitrogen donor ligands have also been reported to stabilise 14 VE iron alkyls. The complex \([(\text{TMEDA})FeCH_2Ph)]_2\) (\(\text{TMEDA} = N,N\text{-tetramethylethlenediamine}\)) was only observed by \(^1H\) NMR spectroscopy.\(^{171,172}\) Alkyl ligands bearing a pyridine donor have successfully been employed in the tetrahedral complexes \([\text{Fe}(\text{R}_2C(2\text{-py}))_2]\) (Figure 1.7B) and \([(\text{TMEDA})\text{Fe}(\text{R}_2C(2\text{-py}))]]\) (14 VE).\(^{173-175}\) Chirik recently reported a series of Fe(II) dialkyls supported by diimine or diamine ligands (Figure 1.7C–E).\(^{176}\) Alkyl ligands with considerable sterical demands like benzyl, (trimethylsilyl)methyl or neopentyl are required. Attempts to introduce smaller alkyls, e.g. methyl, ethyl or benzyl, resulted in reduction to Fe(0) and dissociation of the ancillary ligand.
The only Fe(III) dialkyl complex was reported very recently. The dimethyl complex is stabilised by a monoanionic 1,8-bis(iminocarbazolide) ligand (Figure 1.8).177

1.7.3 Monoalkyl complexes with stabilising ligands

Iron(II) monoalkyls with 14 valence electrons have been prepared using substituted derivatives of hydrotris(pyrazolyl)hydroborate.178 In spite of its formal electron deficiency, the ethyl complex \([\text{Tp}^\text{Pr}]\text{FeEt}\) (Figure 1.9A) is resistant to \(\beta\)-H elimination.179-182 A monoanionic mixed P,N-donor ligand was used by Fryzuk to stabilise the 14 valence electron iron monoalkyls \([\{\text{N(SiMe}_2\text{CH}_2\text{PPh}_2)\}_{2}\text{FeR}\} (R = \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{C}_6\text{H}_4\text{Me})\).183 Gibson has reported a 14 VE methyl Fe(II) complex supported by a monoanionic 1,8-bis(iminocarbazolide) ligand (Figure 1.9B).177 As a part of our own research strategy (section 1.8), we have employed the \(\beta\)-diketiminate ligand to synthesise Fe monoalkyls with a formal electron count of 12VE (Figure 1.9C). In the course of this research the group of Holland has also intensively studied this family of Fe(II) monoalkyls with a wide variety of hydrocarbyls.184-187 A more detailed discussion can be found in Chapter 4.
Fe(III) monoalkyls and monoaryls with 15 VE have been isolated with dianionic tetradeutate ligands that enforce square pyramidal geometry, e.g. porphyrin or salen (N,N'-ethylenebis(salicylaldiminato)). The iron-carbon bonds in these complexes however, are of limited stability due to rapid homolysis.

![Figure 1.9](image)

### 1.8 Research objectives and strategy

Active species in homogeneously catalysed olefin polymerisation are generally cationic, electron deficient (i.e. formal electron count ≤ 14) transition metal alkyls, but for the (PDI)Fe-system the nature of the active species is still unclear. Therefore, fundamental research directed at synthesis and characterisation of new, electron deficient iron alkyls can be valuable for the design of new Fe-based polymerisation catalysts. Such compounds are still relatively rare in literature and consequently, the generation of cationic iron derivatives through alkyl abstractions has remained an unexplored field of research. Alkyl abstraction studies may yield useful information on interactions of highly electrophilic cations with substrates, solvents and anions. This information can provide further insight into mechanisms of propagation, inhibition and deactivation of Fe-based catalysts. Thus far, only one type of iron catalyst, based on the PDI ligand framework, has proved to be highly active for olefin polymerisation and it is not clear why Fe(II) and the PDI ligand form an apparently uniquely effective combination. This forms an incentive to develop new ligands for use with Fe as polymerisation catalysts.

As the iron(II) pyridine-2,6-diimine system has so far not proved to be very suitable for studying organoiron derivatives, it is not the ligand of choice for this research. However, some of its properties will be conserved in the ligands to be used in this research. The ligands must provide adequate steric protection to the Fe centre. This limits the number of ligands around Fe(II), thus ensuring complexes with low electron counts. For the same reason, ligands should donate no more than 6 electrons to the metal. One approach is to change the ligand system from a meridional N₃ system to a facial one while keeping the number and type of donor atoms unaffected. One intrinsic difficulty with neutral ligands is the stability of iron dialkyls which in general
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suffer from reductive elimination. Therefore, monoanionic ligands form an attractive alternative since they will lead to neutral, monoalkyl Fe(II) species.

Characterisation of the iron halides and hydrocarbyls can be complicated due to the expected paramagnetism of these compounds. NMR spectroscopy may not always reveal structural information, although it can still be useful to provide ‘fingerprints’ of the compounds. X-ray diffraction will therefore be an important complementary characterisation method. The targeted Fe(II) alkyls will be screened for insertion chemistry with olefins. Although no reports have appeared to date on neutral Fe(II) monoalkyls with high catalytic activity olefin polymerisation, it cannot be excluded a priori that highly electrophilic Fe(II) monoalkyls may be active.

In order to further increase the electrophilicity of the iron centre, generation of cationic species will be investigated using perfluoroarylborane and -borate alkyl abstracting agents. In the case of Fe(II) monoalkyls, alkyl abstraction will lead to cations without an Fe–C bond required for olefin insertion, and therefore catalytic activity may not be expected. However, the lack of a reactive Fe–C bond also permits study of interactions of the cations with alkenes, solvents, Lewis bases and associated anions without interference of reactions involving the Fe–C bond. $^{19}$F NMR spectroscopy can be a valuable tool to investigate these interactions.

1.9 Outline

The four subsequent chapters (2 – 5) deal with the synthesis and characterisation of electron deficient iron alkyls supported by anionic and neutral nitrogen donor ligands.

Chapter 2 starts with an overview of the rich coordination chemistry of the amidinate ligand as well as its applications and synthesis. The sterically demanding benzamidinate ligand [PhC(NAr)$_2$]$^-$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) is chosen for stabilisation of electron deficient iron alkyls. Complexation to Fe(II) is described as well as the role of added Lewis bases in attempts to obtain monoalkyl derivatives.

Chapter 3 describes the Fe(II) coordination chemistry of two functionalised benzamidinate ligands [RNC(Ph)NCMe$_2$CH$_2$CH$_2$NM$_2$]$^-$ (R = Ar, SiMe$_3$). These ligands have an N,N,dimethylaminoethyl substituent on one of the nitrogen atoms, making the ligand a potential tridentate donor. The preparation and characterisation of dinuclear chloro complexes and their reactivity towards alkylating agents will be discussed.

In Chapter 4, the chelate ring of the monoanionic bidentate ligand is expanded by 2 carbon atoms by the use of β-diketiminates, [HC(C(Me)NAr)$_2$]$^-$, which are expected to bind more strongly to Fe(II) than the amidinates. First, this type of ligand is briefly introduced by discussing its synthesis, coordination chemistry and applications. Synthesis and characterisation of Fe(II) monoalkyls and some exploratory reactivity studies will be reported.

In Chapter 5, an approach is chosen that differs from that of the previous three chapters. Here, a neutral tridentate nitrogen donor ligand is introduced. The pyridyl-substituted β-diketimine ligand [HC(2-py)(C(Me)NAr)$_2$]$_2$, contains the same number and type of donor atoms as the PDI ligand used by Brookhart and Gibson. In contrast to the PDI ligand, this ligand can only coordinate facially to a metal centre. Ligand synthesis is reported, as well as its introduction onto Fe(II) and alkylation of the iron complex.
In Chapter 6, the reactivity of the Fe(II) alkyls isolated in Chapters 2 – 4 towards several borane and borate alkyl abstraction reagents is investigated. The fluoroaryl-substituted borate anions make $^{19}$F NMR spectroscopy a valuable tool to probe the association of the generated ion pairs. Very weak interactions can be revealed due to the paramagnetism of the $d^6$ Fe(II) cations, which induces large shifts and significant line broadening in the $^{19}$F NMR spectra.

The work described in the chapters 2 and 3 revealed that amidinates are kinetically quite labile ligands. This resulted in ligand redistribution reactions, yielding Fe(II) bis(amidinate) complexes that apparently are thermodynamically favoured. Due to this stability, bis(amidinate) complexes offer good perspectives for an in-depth study of the coordination chemistry of sterically hindered amidinates. In Chapter 7, a series of bis(amidinate) complexes of the 3d metals with sterically demanding benzamidinate ligands is described. Structural parameters, spectroscopic and magnetic properties of the bis(amidinate) complexes are compared to assess the effect of metal and ligand variation. Some exploratory reactivity studies are included as well.
1.10 References

Chapter 1

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