Role of Homogeneous Catalysis in Oligomerization of Olefins : Focus on Selected Examples Based on Group 4 to Group 10 Transition Metal Complexes

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Abstract Homogeneous olefin oligomerization plays a pivotal role in the field of petrochemistry. Through catalyst, technology, and process developments, market requirements in terms of productivity, selectivity and sustainability have been addressed. Over more than 50 years, intensive research has been devoted to the design of new Group 4 to Group 10 transition metal complexes and to the study of their reactivity towards olefins leading to several breakthroughs of prime importance for academia as well as for industry. Since the early 1960s, IFPEN contributed to bring innovative industrial solutions to different targets from gasoline production to alpha-olefin on purpose processes with over 100 production units built worldwide. Based on nickel, titanium, zirconium or chromium, the catalytic systems for such processes and their next generation are subject to continuous research where the adaptation of the ligand architecture to the nature of the metal and their mode of activation, play a crucial role to control the reaction selectivity and the catalyst lifetime. Interesting relationships between the complex structure and their reactivity have been drawn and will be discussed in selected examples.

Keywords Homogeneous catalysis · Oligomerization · Olefins · Petrochemistry

1 Introduction and Scope

Oligomerization reactions are widely used on an industrial scale to upgrade light olefin streams coming from different hydrocarbon forming processes (steam cracking, FCC, Fischer–Tropsch …) into heavier olefins that find applications in the field of energy or petrochemistry. This reaction is catalytically achieved by means of different technologies such as heterogeneous acid-catalysis which is applied to the production of fuels or by homogeneous catalytic systems mainly applied to provide high added value chemicals [1].

1.1 Ethylene Oligomerization : General Market and Current Commercial Technologies

A few new industrial homogeneous-catalyzed processes have emerged in the past 10 years. An especially growing area of homogeneous catalysis is the oligomerization of short chain alkenes, an important reaction mainly for the synthesis of second generation intermediates (or base materials) for the chemical industry. The oligomerization of ethylene to linear alpha olefins (LAOs, even-carbon numbered olefins ranging from C4 to C30$^+$ carbon atoms) dominates the market for homogeneous-catalyzed oligomerization. The main applications for LAOs are as co-monomers for polyethylene production, for oxo-alcohols used in detergent and plasticizers, and for the production of poly-alpha-olefins for the synthetic lubricant pool. The total world production for LAOs accounted for 3.5 Mt in 2012 for a total capacity of 4.3 Mt/y (with the exception of 1-butene production from refinery streams). The global annual average growth for LAOs is estimated at 3.3 % (2012–2018) but depends largely on the region with a higher growth in developing countries. Globally, co-monomer grade LAO consumption (C4–C8) is the largest and fastest-growing application, particularly for the production of linear low-density polyethylene resins (LLDPE). Controlling the amount of short-chain branching in the

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Table 1 LAOs by ethylene oligomerization processes—technology and market survey [2]

Company (industrial)	Type of catalyst	Typical LAO distribution (wt%)	World capacity (2012, kt/y)	Announced new capacities (> 2012, kt/y)
CPChem	AlEt$_3$ (1 step)	C$_4$–C$_{10}$ = 54 (49)[a] C$_{12}$–C$_{14}$ = 18 (18) C$_{16}$–C$_{20+}$ = 28 (33)	1,053	140
Ineos	AlEt$_3$ (2 steps)	C$_4$–C$_{10}$ = 70–77 C$_{12}$–C$_{14}$ = 21–28 C$_{16}$–C$_{20+}$ = 2	565	375
Shell	Ni/P–O (biphasic)	C$_4$–C$_{10}$ = 54 (32)[a,b] C$_{12}$–C$_{14}$ = 18 (16) C$_{16}$–C$_{20+}$ = 28 (52)	1,251	650
Idemitsu	Zr/L/AlR$_{3-x}$Cl$_x$ (solvent)	Non disclosed	60	330
SABIC/Linde	Zr/L/AlR$_{3-x}$Cl$_x$ (solvent)	C$_4$–C$_{10}$ = 82 (26)[a] C$_{12}$–C$_{20+}$= 18 (74)	250	37

[a] Typical distribution, in brackets possible flexibility

[b] possible distribution of LAOs after oligomerization and before isomerization and metathesis processing

polyethylene polymer through co-monomer addition determines the density of the resin and modifies the processing and mechanical properties of the polymer. As examples, HDPE (high density PE) uses 2–4 % of co-monomer (C4–C6), while LLDPE (linear low density PE) uses 8–10 % of co-monomer (C4–C8). 1-butene is still the most used co-monomer, in the commodity end-use applications of LLDPE (more flexible and resilient PE), and to a lesser extent HDPE. However, 1-hexene and 1-octene are becoming increasingly attractive because of the excellent properties imparted to the co-polymer product, including greater stress-crack resistance and tear resistance. For example, LLDPE with 1-hexene leads to tougher film than with 1-butene incorporation and can be produced in a thinner form (preferred for packaging application PE). The incorporation of 1-octene gives the highest quality products with good surface finish, good transparency and improved resistance to tearing (produced in solution or slurry-based PE processes).

The global LAO supply is still dominated by the three majors, Chevron Phillips Chemical (CPChem), Ineos and Shell, who operate with different catalytic systems, with more or less flexibility (Table 1). These processes are named "*full-range processes*" because they produce a broad distribution of olefins. The oldest processes use aluminum under harsh reaction conditions of temperature and pressure due to the low activity of aluminum. The first commercial production of LAOs started in 1966. The one step process using triethylaluminum catalyst developed by the Gulf Oil Company (now CPChem) produces alpha olefins with a broad Schulz–Flory carbon number distribution. The distribution of olefin chain lengths can be changed (to a certain extent) by altering the reaction conditions. The two-step process (stoichiometric and catalytic steps), known as the Ethyl process (now Ineos) also uses triethylaluminum but leads to a Poisson distribution with a relative narrow distribution of olefins (this method involves recycling of butenes to produce higher olefins) and an increased branching of olefins in higher fraction (C14–C18). It is a less flexible process in term of product distribution. In these two processes, the olefin streams produced are separated by distillation in quite similar ways (in concept). However, an extra demand has appeared for higher quality alpha olefins. This demand is driven by the metallocene polyethylene catalyst and process developments in which short chain LAOs are used as co-monomers. For this purpose, the alpha-olefin quality upgrade can be achieved by adding a distillation column in the full-range processes. Shell developed the Shell Higher Olefin Process in the 1970s (first commercial use in 1977). In the SHOP process, ethylene is oligomerized to a broad Schulz–Flory distribution of olefins. Compared to the other full-range processes, this process is the most complex but it is quite exceptional because the distribution of oligomers may be adjusted through consecutive isomerization and metathesis steps to meet the required linear internal olefin chain lengths (for applications as detergents and plasticizers). Processes catalyzed with zirconium-based complexes emerged later. Idemitsu Kosan Co. Ltd. developed an oligomerization process catalyzed by a system based on a zirconium(IV) complex associated with an chloroalkyl aluminum derivative and a Lewis base. This process was commercialized in 1989. IFP Energies nouvelles (IFPEN) and SABIC-Linde both separately developed processes based on a Ziegler–Natta catalytic system composed of a zirconium precursor, a proprietary ligand and an aluminum co-catalyst. The SABIC-Linde technology was operated at SABIC in 2009.

In Table 1, the additional estimated new capacities for LAOs using these existing technologies are also mentioned. The applications of the additional capacities are mainly for the polyethylene market but other applications, such as poly-alpha-olefins, oil drilling fluids and surfactants can also contribute to the growth in demand for LAOs.

1.2 Main Recent Industrial Developments in the Field

Today, the oligomerization of ethylene ("full-range" processes) is the predominant route to produce LAOs. However, as the demand for short-chain C4 to C10 linear alpha olefins is growing faster than that for LAOs in the $C10^+$ range, significant recent progress has been made to direct product distribution towards shorter alpha olefins (flexibility of the most recent Zr-based processes) or even to produce *selectively* one main alpha-olefin such as 1-butene, 1-hexene or 1-octene. Transition metal homogeneous catalysis again opens the door to the development of new selective oligomerization processes. These selective processes are called "on purpose" technologies. Some of these technologies have recently been commercialized or industrialized (Table 2).

It is now generally accepted that the mechanism for the selective ethylene transformation into 1-hexene and 1-octene goes through a metallacycle formation as illustrated in Scheme 1 (route A). On the other hand, the generalized mechanism for the "full-range process" occurs via a degenerated polymerization route as shown in Scheme 1 (route B). Discussion is still open for 1-butene production.

Today, there is an increased availability of natural gas [3], especially in North America as a result of the shale gas exploration. The large production of shale gas in the US had the effect of reducing US natural gas prices, making ethane supply abundant, increasing the use of lighter feed in crackers, and contributing to the construction of new ethane crackers. Globally, this has contributed to a growing price gap between crude oil and natural gas. This dynamic makes lighter feedstock derived from natural gas (like ethane) more attractive input for cracking operations, compared to heavier feedstock derived from crude oil (like naphtha). The shift toward greater use of these lighter feedstocks has resulted in the production of significantly less C3 and C4 fractions which could generate a shortfall for certain major intermediates. If most 1-butene is today still supplied from refinery sources (extraction from C4 fraction), one can expect that in the future, "on purpose" production via selective dimerization processes will become predominant.

1.3 IFPEN Achievements in Olefin Oligomerization

Since the early 60s [4], IFPEN has been deeply involved in the search of innovative homogeneous transition metal based catalytic systems. In 1977, the first Dimersol industrial plant was put on-stream in the United States producing gasoline by oligomerization of propylene coming from a fluid catalytic cracking C3 fraction. This reaction was catalyzed by a homogeneous Ziegler–Natta nickel-based catalyst. In the 1980s, a new challenging activity was to selectively dimerize ethylene into 1-butene, the most popular key ethylene co-monomer for manufacturing LLDPE and HDPE. An efficient soluble titanium-based complex was designed. The first AlphaButol industrial unit was started up in 1987 in Thailand. The demand and annual growth rates for LAOs, motivated the development of a "full-range" ethylene oligomerization process. Ziegler–Natta type systems based on zirconium complexes were chosen for this purpose leading to the AlphaSelect process. In the mid-1990s, research was initiated at IFPEN in one of the most promising recent areas in liquid phase homogeneous catalysis: the use of non-conventional, non-aqueous ionic liquids for biphasic catalysis. This new technology, trade-named Difasol, was successfully applied to a nickel-catalyzed butene or propylene selective oligomerization/dimerization making possible a better use of the catalyst associated with a more efficient process scheme. The market demand for 1-hexene drove our research, in the 1990s, to the design of a selective trimerization catalyst. An efficient catalytic system based on chromium associated with a low investment cost process was developed and optimized to produce high purity 1-hexene. The first AlphaHexol unit was commercialized in 2011 [5].

Ethylene mainly originates from steam cracking. Fluctuating steam cracking traditional ethylene prices as well as consumer orientation toward renewable materials prompted our search for new resources able to bridge the gap between

Table 2 "On purpose" processes for the selective production of 1-butene, 1-hexene, and 1-octene

LAO produced	Process/ company	Catalyst type	Capacity (kt/y)[a]
1-Butene	AlphaButol/Axens	Ti/AlR$_3$	708
1-Hexene	CPChem	Cr proprietary/ AlR$_3$	397
1-Hexene	AlphaHexol/Axens	Cr proprietary/ AlR$_3$	50[b]
1-Hexene	Mitsui	Ti proprietary/ "MAO"	30
1-Octene/1-Hexene	Sasol	Cr proprietary/ "MAO"	100

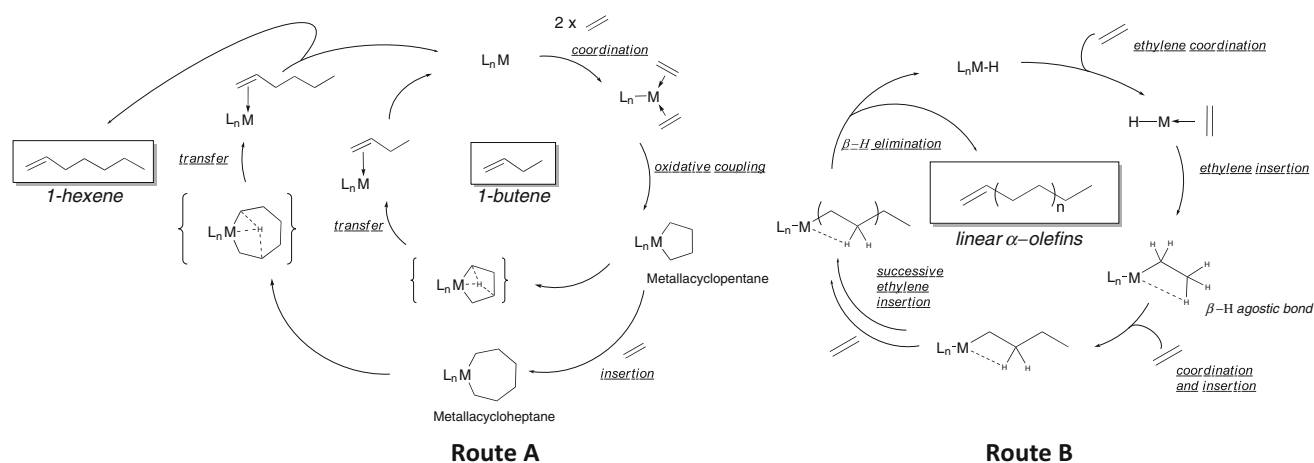Only commercialized processes are cited here

[b] Includes planned capacities

[c] Total capacity for 2 AlphaButol et AlphaHexol units

Scheme 1 Ethylene oligomerization mechanisms—metallacycle pathway (route A), degenerative polymerization (route B)

bio-based and traditional petrochemicals. One of these resources is bio-ethanol. Using bio-ethanol feed based on non-food biomass (also called 2nd generation resources), enables to produce ethically acceptable and renewable plastics with the same properties and recyclability as existing polyethylene grades. A process chain encompassing ethanol to ethylene technology and "on purpose" alpha-olefin processes (e.g. AlphaButol or AlphaHexol) was fitted into develop a complete process portfolio to turn bio-ethanol into 100 % bio-polyethylene containing 100 % bio co-monomers.

1.4 Scope of the Review

Since the early days, important work has been devoted to the design of new transition metal complexes and to the study of their reactivity towards olefins, mainly ethylene. However, during these last years, interest grew in developing a new generation of catalysts with greater selectivity for the desired linear alpha olefins. The architecture of the ligands, which have to be adapted to the nature of the metal, plays a crucial role. Recent years have seen growth in the design of versatile multidentate ligands. Several studies have clearly demonstrated that even minor variations in the steric and electronic properties of these ligands and the geometrical constraints they impose on the metal can lead to great changes in catalytic reactivity such as oligomerization versus polymerization, initial activity (TOF), productivity (TON) as well as catalyst stability and lifetime. Interesting relationships between molecular structures of the complex precursor and their reactivity have in some cases been drawn. However, it should be noted that most of the catalysts used in oligomerization are based on Ziegler–Natta type systems, a multi-component combination of a metal precursor and a suitable activator such as an alkylaluminum derivative. In the open literature, the molecular structures generally depict catalyst precursor,

which must be activated to form the catalytically active species. This pre-catalyst activation is determining and directs the following catalytic steps. There is generally only limited direct information on the nature and the structure of the active species. The introduction of MAO as a suitable activator for transition metals (Group 4 to Group 10) oligomerization was a major breakthrough but it also introduced an important issue with regards to the elucidation of the nature of the active species involved.

Few reviews dealing specifically with olefin oligomerization have been published [6–9]. The aim of this present review is not to give an exhaustive overview of the recent developments in the field of oligomerization. This review highlights some selected examples based on our own achievements in the light of the major industrial developments. The catalytic systems are classified according to their industrial importance, across different families of ligands. In group 10, nickel is the most described and used oligomerization catalyst with a considerable number of publications. It is applied in three different industrial processes currently in operation for different purposes. In this review, we choose to take the nature of the nickel active species as the main theme to exemplify its reactivity and use. Group 6, particularly chromium, has seen particular growth in research activity recently. This part focuses on industrial developments of chromium catalysis and the associated key ligand design. Metals from Group 4, particularly titanium, are illustrated with "cyclopentadienyl/phenoxy" ligand oriented research. The new developments regarding iron are then presented. Finally, tungsten even though not applied in industry in the oligomerization field up to now is discussed. Despite some very recent examples, tantalum [10] as well as vanadium [11] catalysts are not treated here. It is worth underlining that no heterogeneous or supported catalyzed processes emerged for ethylene oligomerization despite the numerous studies published in this field from both academia and industry.

2 Nickel Industrial Developments and Future Challenges

Nickel catalyzed olefin oligomerization has a long history [12]. The discovery of the "nickel effect" by Wilke [13] was the beginning of the major breakthrough by Ziegler who observed that nickel salts could modify the outcome of AlR_3-catalyzed "growth reaction". Since this first discovery in the 1960s, nickel is still playing a central role in late-transition metal catalysis for olefin oligomerization and polymerization, and continues to be one of the most studied metals in this field both by academic and industrial laboratories [14]. The interest has mainly been focused on ligand design. A myriad of multifunctional ligand backbones has been reported including phosphorous, nitrogen and/or oxygen heteroelements. A large number of nickel(II) pre-catalysts were described opening to a very rich coordination chemistry. This article does not cover these developments which have already been reviewed elsewhere [9, 14].

Two main families of active nickel species have so far been recognized, and they are classified according to the nature of the ligand bonding around the nickel metal: *neutral and cationic nickel catalysts* (Fig. 1). Cationic nickel active species (type A) are electronically unsaturated and highly electrophilic. They involve nickel(II), incorporate a donor ligand and present generally a square planar geometry. They are difficult to isolate because of their high reactivity. Cationic π-allyl nickel complexes have nevertheless been isolated by Wilke [15] and can be considered as a model of this kind of active species. It is worth noting that the neutral π-allyl nickel halide complexes are not active towards olefin. However, combined with Lewis acids such as aluminum halides, they are active homogenous catalysts for the dimerization of ethylene and propylene and the polymerization of butadiene. The transfer of the halide from the nickel to the aluminum results in the formation of an electrophilic cationic metal center and formation of a free coordination position on the nickel on which the olefin can coordinate. Neutral nickel catalysts (type B) are less electrophilic than those of the cationic family. They commonly contain anionic type ligands
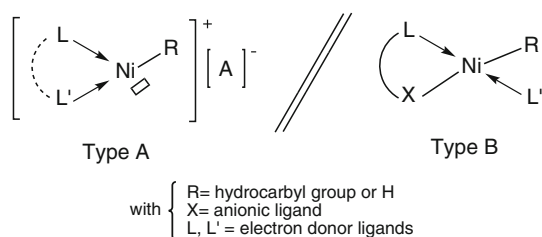
(oxygen or nitrogen based) and a Ni–C or Ni–H active bond in which the olefin will insert to begin the catalytic cycle.

These two kinds of nickel catalysts independently led to the main industrial nickel-catalyzed oligomerization processes: Dimersol/Difasol and Phillips processes (Fig. 1, type A) and SHOP process (Fig. 1, type B). These industrial processes are first briefly described. Then, further developments in the design of ligands will be discussed.

2.1 The Dimersol/Difasol and Phillips Processes : Ni Catalysts of Type A

2.1.1 The Dimersol Process: $Ni(II)/EtAlCl_2$

The industrial Dimersol process [16] was developed by IFPEN to convert light olefins (ethylene, propylene, and/or butenes) into liquid olefin oligomers for the production of high octane sulfur-free gasoline (C6 olefins predominate) and for the production of C8 olefins used for isononylalcohols (INA) for the plasticizer market. Some gasoline Dimersol units are still in operation despite the planned restriction of olefin level in gasoline and the increasing demand of propylene for petrochemistry. The C8 olefins produced from butenes in Dimersol units constitute good quality feeds for oxonation reaction because of their low branching index (production of INA). The INAs produced by this route are of special interest and are competitive alternatives to the 2-ethyl-hexanol (propylene oxonation) the demand of which is decreasing in some regions because of the health issue with DEHP (DiEthylHexylPhthalate) plasticizers.

The Dimersol reaction is catalyzed, in the liquid phase, by a homogeneous nickel complex which results from the interaction of a Ni(II) precursor with a chloroethylaluminum compound. The nickel active species is of type A (Fig. 1). The alkylaluminum co-catalyst has a dual role: to alkylate the Ni complex to form the Ni–H bond after β-H elimination and to capture the anionic ligand from the Ni to generate the counter-anion of the cationic Ni complex. The active species is formed inside the oligomerization reactor under olefin atmosphere. The most frequently encountered mechanism for nickel catalyzed oligomerization is the degenerated polymerization mechanism well described by Cossee and Arlman (Scheme 1). The reaction products are mainly composed of dimers due to the high rate of termination step. The reaction is non-(regio) selective and leads to a mixture of the different dimeric isomers. In the case of propylene or butenes conversion, the formed dimers are mainly mono methyl branched internal olefins (methylpentenes and methylheptenes, respectively). Isomerization of the double bond occurs as a side reaction catalyzed by the active Ni–H (insertion of the dimer in Ni–H, followed

Type A   Type B

with { R= hydrocarbyl group or H
       X= anionic ligand
       L, L' = electron donor ligands

Fig. 1 The two main families of Ni active catalysts

by β-H elimination). The heavier product formation mainly originates from consecutive co-dimerization of the monomer with the formed dimers. These consecutive reactions are favored at high monomer conversion.

In this type of nickel catalysis, the main challenges are reaching high conversion and high selectivity for the dimers. The type of reactor technology (CSTR vs. plug flow) has a significant impact on the oligomer by-product formation which results from consecutive reactions [12].

It has to be borne in mind that beside the addition of ligands, process design can impact the formation of these by-products and optimize the dimer yield. This has been one of the drivers of the development of biphasic catalysis.

2.1.2 The Biphasic Difasol Process: Ni(II)/ Chloroaluminate Ionic Liquids

In the early 1990s, biphasic liquid catalysis appeared as a highly attractive approach to solve some of the main issues of homogeneous catalysis such as catalyst recovery and recycling. The cationic nature of the active nickel species and the use of chloroalkylaluminum compounds as activators prompted us to investigate acidic chloroaluminate ionic liquids as a possible medium to perform the reaction. At that time, chloroaluminates were mainly applied as electrolytes [17]. It was the first time that these ionic liquids were used as a combination of solvent and co-catalyst for a chemical reaction [18]. The addition of ethyl aluminum dichloride (EtAlCl$_2$) to the acidic chloroaluminate was found to form anionic mixed alkylchloroaluminate anions that inhibit the formation of higher oligomers due to cationic side reactions [19]. Compared to the homogeneous single-phase reaction, the biphasic process in chloroaluminates, named Difasol, led to a higher selectivity into octenes (>90 wt% of octenes relative to the total products even at 80 % butene conversion). In such systems, consecutive side reactions (octenes + butenes) are minimized as a consequence of the lower solubility of octenes compared to butenes in the ionic liquid. Moreover, the reaction could be performed with diluted feeds (butenes + isobutene or butane) with the same performances. The demonstration of the stability of chloroaluminates and nickel under catalytic conditions was achieved via a continuous long term pilot run. The product separation was efficient and no significant loss of ionic liquid in the product phase could be detected [20]. The Difasol technology [21] extends the field of applications of the Dimersol to the less reactive longer chain olefins such as C5 fractions allowing the production of decenes or nonenes through co-dimerization of C4 and C5 olefins.

The advantages brought by the biphasic approach can be all the more important since costly phosphine ligands are used in excess without recycling. This is the case of the sterically demanding basic tricyclohexyl phosphine involved in the homogeneous Ni-catalyzed propylene dimerization to favor the formation of 2,3-dimethylbutenes (2,3-DMBs, tail-to-tail dimers). 2,3-DMB-1 and 2,3-DMB-2 are key industrial intermediates for fine chemical synthesis (musk fragrance or insecticide) [22, 23]. We switched this reaction into chloroaluminates and operated successfully the reaction in a continuous biphasic way [24]. The main issue was to maintain the phosphine effect with time while optimizing the phosphine consumption. This was achieved by the addition of small amount of a weak organic base which acts as a buffer of chloroaluminate acidity. A new biphasic continuous flow process for the regio-selective dimerization of propylene into 2,3-DMB-1 was developed by IFPEN. Total hexene selectivity was held steady at 75–80 wt% hexenes/total products and 2,3-DMB-1 was held steady at 70–75 wt% relative to the total hexene content [19].

2.1.3 The Phillips Process : Ni(II)/P(n-Bu)$_3$/EtAlCl$_2$

Ni homogeneous Ziegler–Natta systems based on Ni(II) and a chloroalkylaluminum were very early disclosed to catalyze the oligomerization of olefins, such as ethylene. In these early days, there were many patents in this field assigned to different companies [8]. However, nickel catalysts were not highly selective for the formation of dimers (e.g. butenes from ethylene) and resulted in undesirable and wasteful quantities of side products such as higher oligomers. In the late 1960s, Phillips Petroleum company [25] disclosed a process which converts ethylene selectively into 2-butene. A typical catalyst composition consists of bis(tri-n-butylphosphine)nickel dichloride and ethylaluminum dichloride. The Al to Ni molar ratio has an important impact on the reaction selectivity. As described, ethylene dimerization takes place in a circulating loop reactor under mild reaction conditions (P = 10–15 bars and T = 35–45 °C). High velocities are maintained in the reactor to minimize fouling and temperature rise across the reactor.

2.1.4 Toward Alternatives to Monophosphine Ligands

Monophosphines have been largely studied in nickel-catalyzed oligomerization and the well-described phosphine effect has been applied in two main industrial processes for the production of 2,3-DMB and 2-butene. However, one main issue of these systems is the loss of the phosphine effect with time which results from the de-coordination of the ligand from the nickel metal center, particularly when excess Lewis acid aluminum compounds are used as co-catalysts.

To circumvent this issue, different strategies have been developed. One of them uses bidentate neutral ligands (L–L or L–L') which combine interesting properties in catalysis and stabilization of the metal. A large number of ligands such as P–P, P–O, P–N, … have been reported [9]. Nickel usually forms four-coordinated complexes with these ligand systems while a few five coordinated complexes have been reported. If we focus on diphosphines, we can see that they have largely been evaluated in nickel catalyzed oligomerization. However, examples of dissymmetrical diphosphines and their corresponding nickel complexes are scarce, perhaps due to the tedious synthesis required. We recently described a metal-induced rearrangement strategy from iminobisphosphine ligands to symmetrical and non-symmetrical diphosphinoamine nickel complexes (Scheme 2) [26]. Upon activation with MAO, these unprecedented complexes oligomerize ethylene to small chain oligomers (mainly C4–C8) with high productivity, highlighting the prime importance of introducing alkylphosphine moieties in such pre-catalysts.

An interesting approach to generating the active Ni–H cationic species is via oxidative addition of a Brönsted acid to a Ni(0) precursor [27]. This combination promotes ethylene oligomerization in organic solvent but with very low activity. However, the reaction activity can be enhanced by using ionic liquids as solvents. We were nevertheless surprised to observe that in [1-butyl-3-methylimidazolium][NTf$_2$] ionic liquid (NTf$_2$ = bis[(trifluoromethane)sulfonyl]amidure), ethylene was transformed into butenes without any addition of acid. The formation of active nickel complex was explained by an oxidative addition of the imidazolium cation to the Ni(0) to form in situ a [(NHC)Ni–H]$^+$[NTf$_2$]$^-$ species (NHC = N-heterocyclic carbene) [28]. NHC carbene are versatile ligands that share many of the coordination properties with the phosphines with which they are frequently compared. They present stronger sigma-donating properties that can stabilize late transition metal complex. Nickel complexes bearing 1,3-dialkylimidazolin-2-ylidene carbene have been reported for the olefin oligomerization [29, 30] (Fig. 2). Upon combination with chloroalkylaluminum derivatives in toluene, these complexes range from inactive to sparingly active. On the other hand, they are highly active in acidic chloroaluminate ionic liquids. However, disappointingly, they do not present any regio-selectivity with propylene unlike the [NiCl$_2$(PCy$_3$)$_2$] complex in the same conditions.

Moreover, catalyst deactivation occurs rapidly because of the facile reductive elimination of the NHC ligand via the formation of a 1,3-dialkylimidazolium cation bearing an ethyl substituent on the C(2) carbon (Scheme 3) [31].

Guy Bertrand and co-workers have developed a new type of versatile carbene: the cyclic alkyl amino carbene (CAAC) [32]. These ligands are more electron donating and bulkier than classical NHC and phosphine. The synthesis of the corresponding iminium salts is quite simple [33, 34] so that we anticipated that CAAC would be perfect candidates for use as ligands on nickel complexes to form new efficient catalysts in propylene dimerization. The [NiCl$_2$(PCy$_3$)$_2$] complex, partially soluble in toluene, can be used as starting material for "Ni-CAAC" synthesis. For example, the addition of 2 equivalents of CAAC to [NiCl$_2$(PCy$_3$)$_2$] allowed isolation of a new bis(CAAC)nickel(II) complex, soluble in heptane (Scheme 4), the molecular structure of which was determined by single-crystal X-ray analysis (Fig. 3). The carbene ligands are situated *trans* to each other and the geometry is slightly distorted square planar [35].

Starting from the pale green insoluble [NiCl$_2$,2Pyridine] complex, a new mixed complex [NiCl$_2$(CAAC)(Pyr)] could only be isolated in low yield despite many attempts of synthesis optimization (Scheme 5). The X-ray structure of this violet complex shows a distorted tetrahedral geometry [36] (Fig. 4).

The two "Ni-CAAC" complexes were evaluated for propylene dimerization in homogeneous or biphasic systems using acidic chloroaluminate ionic liquids. Upon activation with EtAlCl$_2$, both complexes show some activity but are less active than [NiCl$_2$(PCy$_3$)$_2$] used in similar operating conditions. Moreover, the "Ni-CAAC" complexes do not display any regio-selectivity and form methylpentenes as the major isomers.

To reduce the deactivation pathway with monodentate carbene, one strategy consists in attaching a donor function to the NHC to form a heterobidentate (L–L') ligand which could undergo hemilabile behavior. Ether-functionalized NHC ligands have recently been studied (Fig. 5) [37]. The corresponding bis-carbene nickel(II) complexes have been isolated and characterized by X-ray analysis. No inter- or intra-interaction between the ether function and the metal was observed. These complexes promote ethylene oligomerization upon activation with EtAlCl$_2$ but they did not lead to remarkable activity.

Scheme 2 Symmetrical and non-symmetrical diphosphinoamine nickel complexes

	R1	R2	R3
	4-BrBz	Ph	Ph
	4-nBuBz	Ph	Ph
	4-BrBz	iPr	iPr
	4-nBuBz	Ph	iPr
	4-nBuBz	Ph	Cy
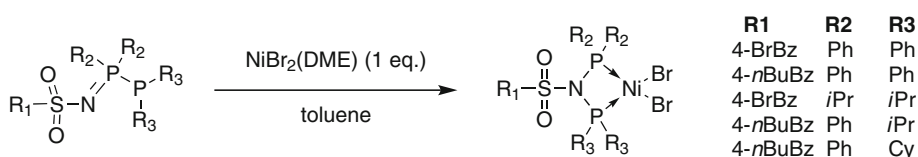
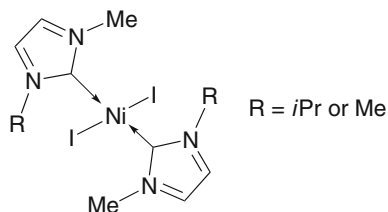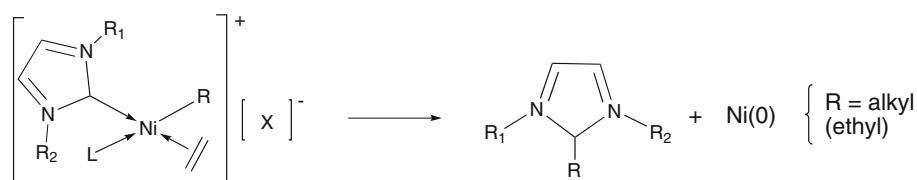**Scheme 3** Deactivation of "Ni-NHC" complexes by reductive elimination

Fig. 2 Examples of non-functionalized "Ni-NHC" complexes evaluated in catalysis

2.1.5 Toward Nitrogen Ligands : Versipol Complexes and Analogues

For a long time, nickel complexes, like other late transition metal complexes, have been considered to be less prone to polymerization and to preferentially lead to olefin oligomerization because of their propensity to generate β-elimination, in contrast to Ti and Cr which were good polymerization catalysts. However, the discovery in the late 1990s that, upon activation with MAO, α-diimine nickel(II) complexes were highly active catalysts for ethylene oligomerization as well as for polymerization (Fig. 6) [38], changes the simple picture of the nickel and triggered a true exploration of the late-transition metal catalysts for olefin polymerization. In oligomerization, the activity of these systems is very high (activity up to 1 370 000 g_{C2H4}/(mol$_{Ni}$.h) upon activation by MMAO, Schulz-Flory distribution of olefins with α-selectivity up to 94 %). Moreover, α-diimine ligands are versatile and easy to synthesize which made these systems very popular. The Schulz-Flory distribution of the olefins can be modulated in a certain limit (K values range from 0.59 to 0.81). The alpha selectivity of the olefins depend on the operating conditions but are generally lower (96 % for the highest) than the quality required for LAO. The isomerization
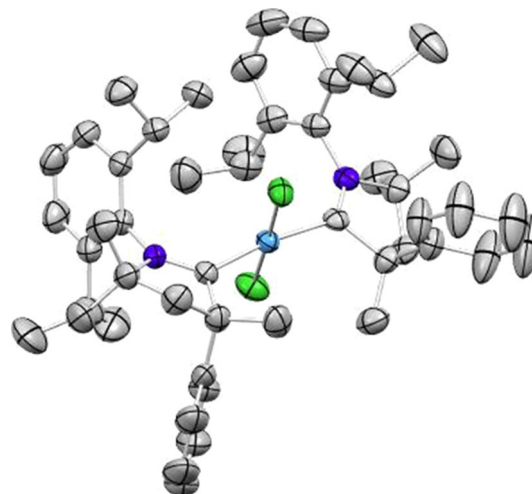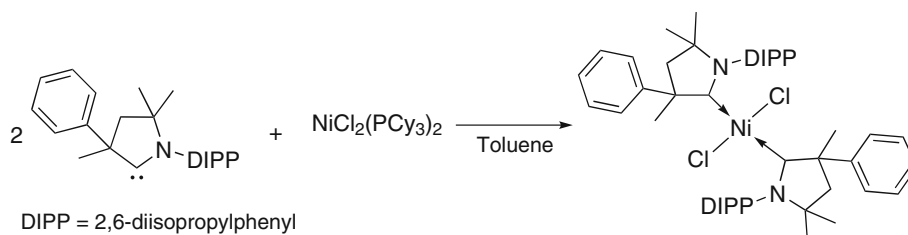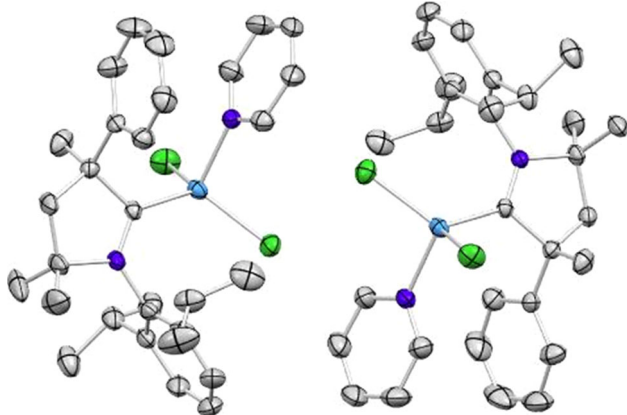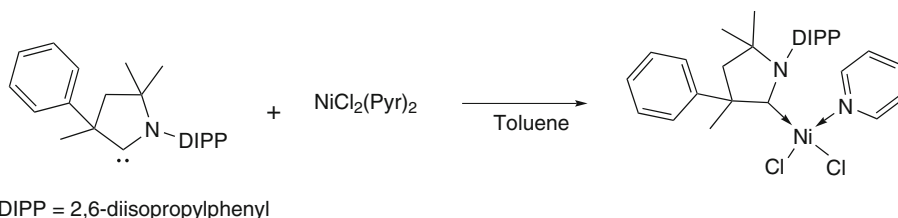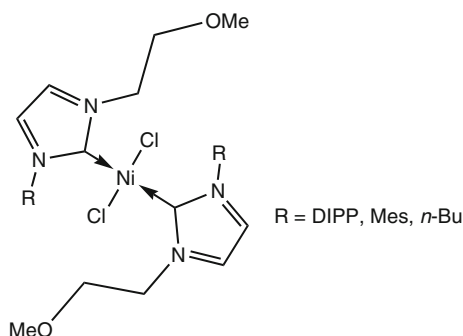

Fig. 3 ORTEP view of [(CAAC)$_2$NiCl$_2$] (CCDC 1030813). H atoms omitted for clarity. Thermal ellipsoids include 50 % of the electron density

ability of cationic Ni hydride cannot be completely avoided.

Other functionalized nitrogen-based ligands (pyrazole, imidazole, oxazole, …) with interesting coordination chemistry have also attracted attention for Ni-catalyzed oligomerization but none of them really differentiate in term of terminal olefin selectivity (>95 % alpha olefin) [14, 39]. Nevertheless, pyridine functionalized ligands remains quite interesting. Reliance reported a few years ago the use of pyridine-oxime derivatives (Fig. 7). Associated to nickel and activated by MAO or Et$_2$AlCl, these ligands were surprisingly found to be particularly active and highly selective for the production of 1-butene (up to 92 % of C4 and 99.5 % 1-butene/C4) [40]. However, no patent or further experimental work was disclosed.
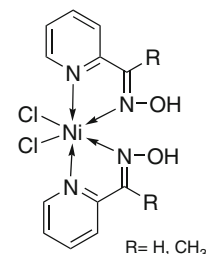
Scheme 4 Synthesis of [(CAAC)$_2$NiCl$_2$]

DIPP = 2,6-diisopropylphenyl

Scheme 5 Synthesis of [(CAAC)(Pyr)NiCl₂]

DIPP = 2,6-diisopropylphenyl

Fig. 4 ORTEP view of [(CAAC)(Pyr)NiCl₂] (CCDC 1030814). H atoms omitted for clarity. Thermal ellipsoids include 50 % of the electron density

Fig. 5 Examples of functionalized "Ni-NHC" complexes

Fig. 6 Example of "Ni-diimine" complexes evaluated in ethylene oligomerization
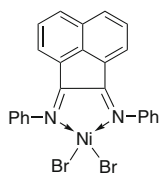
Fig. 7 "Ni-oxime" complexes

R= H, CH₃

phosphorus ylide (typically Ph₃P=C(H)–C(=O)Ph) in presence of Ni(COD)₂ and a coordinating phosphine. They form an isolable model of the SHOP type catalysts. It is worth mentioning that SHOP catalysis is operated in a biphasic system using 1,4-butanediol as the catalyst solvent. This process was the first commercial catalytic process to benefit from two-phase, but non aqueous, liquid/liquid technology. The organometallic SHOP type catalysts have played a predominant role in the development of well-defined catalyst precursors for olefin oligomerization. To rationalize the ligand effects, it was suggested to break the catalyst in two: a chelate part and an organo part [43] (Fig. 8). In toluene, they produce alpha-olefins (under 50 bars of ethylene at 50 °C, activity up to 60,000 g_{C2H4}/(mol$_{Ni}$.h), 99 % of the olefins are linear of which 98 % are terminal) while in hexane polyethylene is formed. These catalysts are also capable of producing polyethylene when combined with a phosphine scavenger, which demonstrates their versatility [44]. Recently, the impact of a number of parameters on the catalytic properties of these complexes has been reported [45].

Since we were interested in the short chain olefins, we have attempted to modify the electronic density at the nickel center in order to facilitate β-elimination during the growing chain. The strategy was to create an intramolecular hydrogen bonding between the enolate oxygen atom and an *ortho*-substituent on the aromatic ring of the P,O chelate, with the aim of generating an electron withdrawing effect (Fig. 9) [46, 47]. We demonstrated that intramolecular hydrogen bonding allows a fine tuning of the selectivity of the complexes. In comparison to the typical SHOP model complex, the alpha-olefin distribution significantly shifts towards the lower C4–C8 olefins of which 95–99 % are linear α-olefins, while the activity remains unchanged.

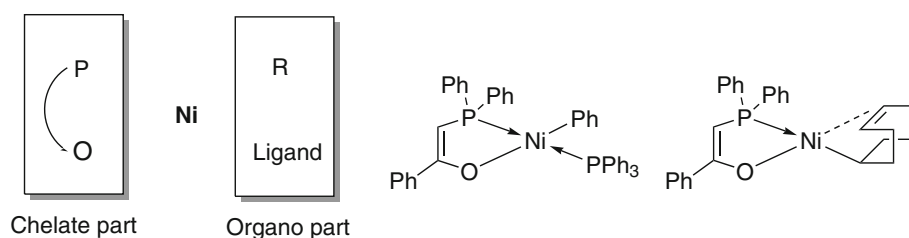## 2.2 The SHOP Process: Ni Catalysts of Type B

Organometallic nickel complexes combining soft phosphorous and hard anionic oxygen atom in a chelate P–O ligand were described and first isolated by Keim in 1978 [41, 42]. These catalysts are synthesized by mixing a

Suitable organometallic model for SHOP catalyst (type B)

Chelate part Organo part

2.2.1 Toward Alternative Anionic Ligands

During the subsequent two decades, there was no significant progress in the design of different types of anionic ligands and corresponding neutral nickel catalysts. But at the beginning of the current century, the discovery of the versatile salicylaldiminato catalysts [48] opened the way to investigations of neutral nickel complexes (type B). However, the studies have focused on the ethylene polymerization with the aim to control the microstructure of the polymer.

3 Chromium Catalysts for Selective Ethylene Tri- and Teramerization

The ability of chromium complexes to oligomerize selectively ethylene was discovered at Union carbide and reported in 1967 [49]. Manyik, Walker, and Wilson observed the predominance of 1-hexene in the liquid fraction during ethylene polymerization with chromium tris(2-ethylhexanoate) activated with partially hydrolyzed triisobutylaluminum, suggesting the presence of several active species and eventually mechanisms. This breakthrough triggered the search for selective trimerization and later tetramerization catalysts leading to industrial successes.

Although the first evidence for selectivity in 1-hexene with chromium-based catalysts was brought with a partially hydrolyzed alkylaluminum as activator, in other words, an aluminoxane, the first industrially relevant catalytic systems commercialized were developed with well-

defined alkylaluminum and/or chloroalkylaluminum compounds. While Chevron Phillips Chemical Company LP (CPChem) reported the use of pyrrolide ligand in 1991 [50], IFPEN developed a catalytic composition based on an aryloxide ligand in 1998 (Fig. 10) [51]. For both proprietary anionic ligands, their association to a chromium(III) precursor lead to selectivities in 1-hexene above 99 % in the C6 fraction, affording a polymer grade co-monomer. CPChem implemented this technology through two joint ventures with Qatar Chemical Company Ltd. in Mesaieed (Qatar) and Saudi Polymers Company in Al Jubail (Saudi Arabia), producing 47,000 t/y and 100,000 t/y, respectively [52]. In 2014, CPChem also announced the start-up of a 1-hexene production unit of 250,000 t/y in Baytown, Texas (USA) [53]. In the meantime, Axens licensed in 2011, a production unit in Primorsk region (Russia) based on the 1-hexene IFPEN catalytic system [54]. In 2009, SABIC, Linde and the Rostock University disclosed a catalytic system formed by a chromium(III) precursor, R_2P-N(R)-P(R)-NHR as ligand and triethylaluminum as activator for the selective ethylene trimerization to 1-hexene (Fig. 10) [55]. The evaluation of such catalytic composition on the pilot plant scale should be ongoing [56].

Although multiple coordination modes and reactivities toward the alkylaluminum and the chromium precursor used are possible, these three catalytic systems are believed to proceed via the well-known metallacyclic mechanism to afford such selectivities in 1-hexene. A closer look at the side products formed agrees with such a hypothesis; indeed, mainly decenes are produced, while octenes are kept to a minimum. It is suggested that decenes are formed by co-trimerization of 1-hexene with two molecules of ethylene through a chromacycloheptane [57]. Detailed

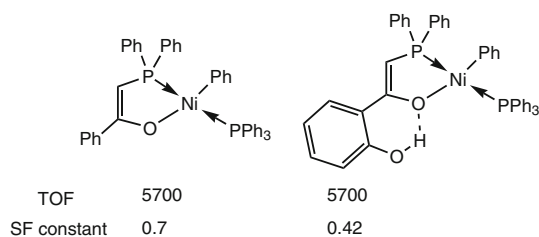|		
TOF	5700	5700
SF constant	0.7	0.42

Fig. 9 Fine tuning of P–O ligand with the occurrence of H-bonding. SF constant obtained in toluene, 0.10 mmol catalyst, 60–95 °C, 60 bar ethylene, 90–300 min
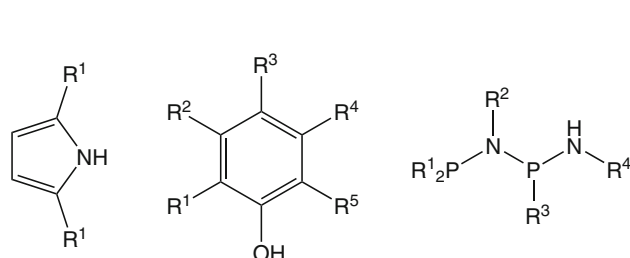

Fig. 10 Ligand precursors for the selective ethylene trimerization processes
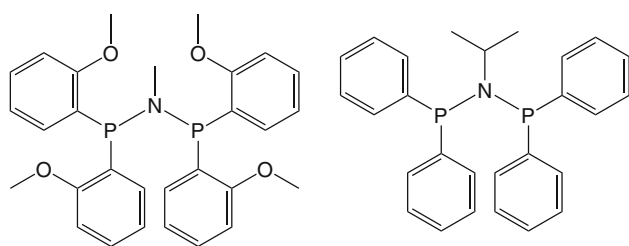
Fig. 11 Diphosphinoamine ligands for tri- and tetramerization of ethylene

studies of these systems and other examples of anionic monodentate or multidentate ligands in association with alkylaluminum have been described in the literature [6, 58].

In 2002, BP Chemicals published a report of a highly active trimerization catalytic system comprising a chromium source and a neutral functionalized diphosphino-amine ligand ($>10^6$ $g_{C2H4}/(g_{Cr}.h)$, Fig. 11) when associated to methylaluminoxane [59, 60]. A few years later, Sasol researchers showed that with a non-functionalized diphosphinoamine ligand, exceptionally high selectivities for 1-octene along with high activities could be obtained (67,4 wt% of 1-octene compared to all products formed, $2.7.10^5$ $g_{C2H4}/(g_{Cr}.h)$) [61, 62]. To satisfy the growing need for 1-octene, Sasol rapidly announced the construction in 2010 of a tetramerization unit producing 100,000 t/y of 1-octene and 1-hexene in Lake Charles, Louisiana (US) [63]. The start-up of the unit was planned for late 2013; no further information, however, is available. Numerous diphosphinoamine and several other diphosphine ligands have also been reported in the literature for selective tetramerization [6, 58].

## 4 Titanium for Selective Ethylene Di- and Trimerization

Very early, titanium-based homogeneous catalysts opened the door to selective ethylene dimerization to 1-butene [64, 65]. In the mid-1980s, IFPEN and SABIC jointly developed the first commercially viable process for this reaction, the AlphaButol process [66]. Today, 30 AlphaButol units have been licensed for an aggregate 1-butene production capacity of 708 kt/y, nearly 25 % of the world's 1-butene consumption as a co-monomer in polyethylene [67]. The catalytic system is based on a proprietary titanium(IV) precursor and an alkylaluminum co-catalyst which are both injected in the reactor to generate the active species [1, 4]. Careful choice of this catalyst composition and reaction conditions lead to selectivity for 1-butene up to 93 % (purity of 1-butene higher than 99.5 %). This field was later the subject of interest for researchers in industry and

academia. Nevertheless, if we except the initial statement of Chauvin et al. [68], few attempts to investigate the reaction mechanism induced by "Ti(OR)$_4$/AlR$_3$" system were undertaken [69]. In his first proposal, Chauvin and co-workers identified titanacyclopentanes as possible intermediates for this reaction. Substituted titanacyclopentanes were then generated by reacting 1,4-dilithiobutanes with [Ti(OBu)$_4$] precursor. The nature of the hydrocarbons formed by thermal decomposition of these compounds and their comparison with the C6 by-products formed under real dimerization experiments, suggested successive formation in the catalytic cycle of metallacycle intermediates. Recently, several experimental [70] and theoretical studies [71] conducted by McGuinness and co-workers suggest that metallacycles are not likely responsible for the selective formation of dimers. According to these studies, a conventional Cossee–Arlman mechanism with very fast β-H elimination could be the preferential route to explain the primary product 1-butene and the secondary reaction products. Despite its apparent simplicity, the mechanism used by the "Ti(OR)$_4$/AlR$_3$" system remains under discussion.

Titanium complexes also appeared in the 2000s as good catalysts for the selective trimerization of ethylene to 1-hexene [6, 58]. The first remarkable example was described in 2001 by Hessen and co-workers [72] with a system based on a cyclopentadienyl ligand bearing an aromatic group (Fig. 12, I). At 30 °C and 10 bar of ethylene, [(η^5Cp-CMe$_2$-C$_6$H$_5$)TiCl$_3$] upon activation with MAO was described as very active ($\approx 6.10^6$ gH$_1^=$/molTi/h) and selective for 1-hexene production (86 % of C6 with more than 99 % of 1-hexene). The thermal stability of the catalyst remains modest as increasing the reaction temperature to 80 °C decreases the overall catalyst productivity and selectivity. The same authors carried out systematic studies of structure performance relationships [73]. They demonstrated the delicate interplay of the steric and electronic properties of the ligands in generating catalysts of high activity and high selectivity for 1-hexene (examples II, III and IV, Fig. 12). Although none of these Cp-Ti(IV) complexes was operated at an industrial scale (to the best of our knowledge), their discovery represents a real breakthrough in the field of selective oligomerization using Ti complexes.

Detailed theoretical studies were also conducted in order to shed light on the mechanism [74–76]. It was predicted that after activation of the catalyst precursor [(η^5Cp–CMe$_2$–C$_6$H$_5$)TiCl$_3$] with MAO to generate a cationic Ti(II) species, a Ti(II)/Ti(IV) metallacycle mechanism would operate. Mechanistic investigations also pointed out the critical role of the arene side arm of the Cp ligand. This part of the ligand has the capacity to modify its coordination mode to the titanium center from η^1, η^3 to η^6 [77]. DFT studies tried to rationalize the selectivity for 1-hexene taking into account the capacity of the R-group grafted on

Fig. 12 Examples of "Cp-Ti(IV)" complexes for selective ethylene trimerization
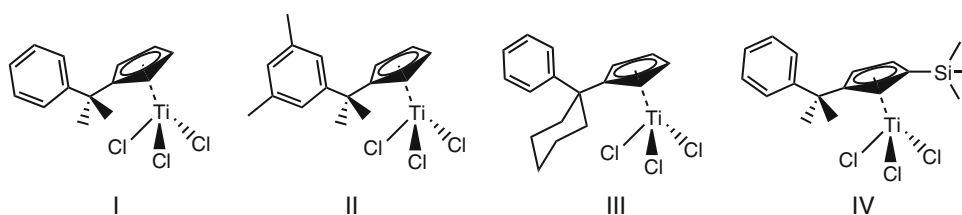
the Cp ring to dissociate from the metal center [78]. Assuming that, whatever the nature of the R-group, the catalyst enters the metallacyclic mechanistic pathway, the authors have presented the dissociation energy of the arene group as a descriptor to explain 1-hexene selectivity. A model is proposed that predicts the formation of 1-hexene when the dissociation energy is larger than 15 kcal/mol. In the case of smaller dissociation energies, multiple insertion reactions are likely to occur producing polyethylene as the major product.

Shortly after the discovery of the [(η^5Cp–CMe$_2$–C$_6$H$_5$)TiCl$_3$]/MAO system, substitution of the arene group by chelating heteroatoms was proposed. In 2003, Huang et al. replaced the pendant arene with a thienyl group (Fig. 13, V) [79]. Selectivity for 1-hexene appeared at a very high level (84 %) with nevertheless apparent poor activity compared with the arene analogue. Substitution of the sulfur by a more coordinating ether group (Fig. 13, VI) renders the system quite inactive [80]. The same group has recently proposed a new evolution of this catalyst by introducing an indenyl group instead of cyclopentadienyl [81]. This evolution is assumed by the authors to improve the activity compared with the corresponding cyclopentadienyl complex (Fig. 13, VII).

Viewing these first examples, hemilability of the ligand [82] appeared as a key parameter to promote selective ethylene oligomerization rather than polymerization. Owing to the expected reversible coordination of the pendant group, such ligands could stabilize highly reactive electrophilic metal centers until the substrate coordinates and replaces the pendant group. Introduced as alternatives to cyclopentadienyl ligands for the development of post metallocenes Group 4 complexes [83], aryloxy-based ligands have also raised a great deal of interest in that field, partly due to their versatile coordination mode and their potential to bring five electrons to the metal center (Fig. 14) [84, 85].

In 2009, Magna and co-workers at IFPEN described several functionalized aryloxy-Ti(IV) complexes of general formula [(ArO-L)Ti(O^{i}Pr)$_3$] as precursors for selective ethylene oligomerization [86]. Depending on the structure of the aryloxy, mononuclear as well as binuclear complexes were obtained (Fig. 15). The hemilabile behavior of the aryloxy ligand in IX (Fig. 15) resulting from reversible coordination of the –NMe$_2$ arm was demonstrated by variable-temperature ^{1}H NMR spectroscopy. Upon activation with MAO these catalysts led to poor activity with respect to ethylene with a selectivity oriented towards polymers (>95 %) [87]. However, when activated with AlEt$_3$ (3 eq./Ti) at 20 bar and 60 °C, these complexes exhibited interesting activity (up to 2,100 g/g Ti/h) for the selective dimerization of ethylene to 1-butene (92 % butenes; 99$^+$ % 1-butene). Noticeable differences in catalyst activity were observed when the hemilabile part was modified. This work was extended later to functionalized bis(aryloxy)-Ti(IV) complexes of general formula [(ArO-L)$_2$Ti(O^{i}Pr)$_2$] with the same catalytic tendencies [88]. In parallel with this study, investigations on functionalized imido Ti(IV) complexes were also undertaken [89]. Upon activation with MAO, all the catalysts evaluated appeared selective for ethylene polymerization.

In the field of selective ethylene trimerization using titanium catalyst, another very recent breakthrough is the work published by Fujita and Mitsui [90, 91]. For many years, Fujita and co-workers performed ligand oriented

Fig. 13 Functionalized "Cp-Ti(IV)" complexes

Fig. 14 Coordination modes of aryloxy type ligands

Fig. 15 Examples of [(ArO-L)$_n$Ti(O^{i}Pr)$_{4-n}$] for selective ethylene dimerization

research with the use of phenoxy-imines type ligand in Group 4 polymerization (named FI systems) [92]. In the course of their investigations, they fo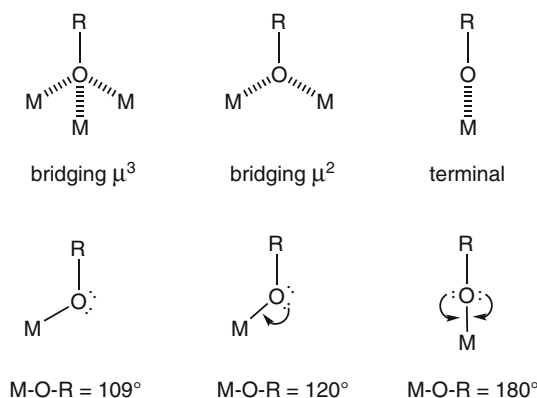und that very specific phenol imine ligand (Fig. 16) can convert ethylene into 1-hexene with high selectivity and quite high productivity. To the best of our knowledge, this system has been implemented at the industrial scale at Ishihara (Japan) [2]. From this study, and the results published in the corresponding patent [93], it emerged that the nature of the bridging spacer linked to the hemilabile ether group is crucial for determining the selectivity for 1-hexene. Variation of 1-hexene selectivity from selected examples extracted from [93] is presented in Fig. 16.

The authors proposed that the reaction mechanism goes through a metallacycle formation from a cationic Ti(II) intermediate [90]. Interestingly, catalyst productivity shows a second-order dependence on ethylene pressure, suggesting that the rate-determining step is the formation of the Ti(IV) metallacyclopentane intermediate. Along the same line, Bercaw et al. recently reported the synthesis and characterization of the cationic [FI-TiMe$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ complex generated from the most selective Fujita pre-catalyst. This complex also proved to be an effective pre-catalyst for the ethylene trimerization reaction [94, 95].

More recently, McGuinness et al. published titanium catalysts, obtained by combination of phenoxy-imine moiety from the FI catalysts and the arene group characteristic of Hessen catalysts [96]. A series of Ti(IV)-catalysts were prepared and tested for the ethylene oligomerization and polymerization reactions (Fig. 17). Predominantly these catalysts formed polyethylene with small amount of 1-hexene in some cases.

In another publication McGuinness et al. reported the investigations of analogues of Fujita titanium catalysts towards ethylene oligomerization reaction [97]. From all the catalysts considered in this study (Fig. 18), complex bearing a thioether as donor group gave the best results in term of selectivity for 1-hexene, however polyethylene was still the main product of the reaction.

5 Zirconium Catalysts for Unselective Ethylene Oligomerization

Along with Group 4 complexes, zirconium-based systems appeared very early as efficient catalysts for olefin polymerization [83]. Cyclopentadienyl-based complexes, once activated with MAO, are among the most active and selective zirconium catalysts for both ethylene and propylene polymerization. In comparison, examples of zirconium catalysts for ethylene oligomerization remain scarce. Processes operating with this metal were nevertheless industrially developed to produce mainly C4 to C12 olefins in order to maximize the amount of α-olefins in the co-monomer range. Processes developed by SABIC-Linde (AlphaSablin [56]), Idemitsu [2] or IFPEN/Axens (AlphaSelect [1, 4]) are by far the most widely described. These processes operate in the liquid phase using proprietary soluble Zr-based catalytic systems activated in situ by an alkylaluminum co-catalyst, affording ethylene oligomers with a Schulz–Flory type distribution. The propensity of zirconium to modulate product distribution makes processes based on this metal versatile and useful to access specific α-olefins distributions (Table 1).

The role of the non-MAO aluminum co-catalyst was described as a key parameter to control the product distributions. A detailed study of this parameter was published in 2002 by Shiraki and co-workers [98]. He describes particularly the role of organic additives on the performances of the three components "ZrCl$_4$-TEA-EASC" oligomerization catalyst. The effect of organic additives was discussed on the basis of their ionization potential (IP) and electron density (ED). As demonstrated, additives with small IP (tetrahydrothiophene) improve the purity of the α-olefins. Heterocompounds additives presenting large electron density (tetrahydrofurane) have detrimental effect on the polymer amount produced.

Up to now, attempts to selectively oligomerize ethylene to 1-butene, 1-hexene or 1-octene with zirconium catalysts have been quite unsuccessful [7]. Shortly after the discovery of Cp-based titanium catalysts for selective trimerization of ethylene to 1-hexene [72], theoretical calculations were
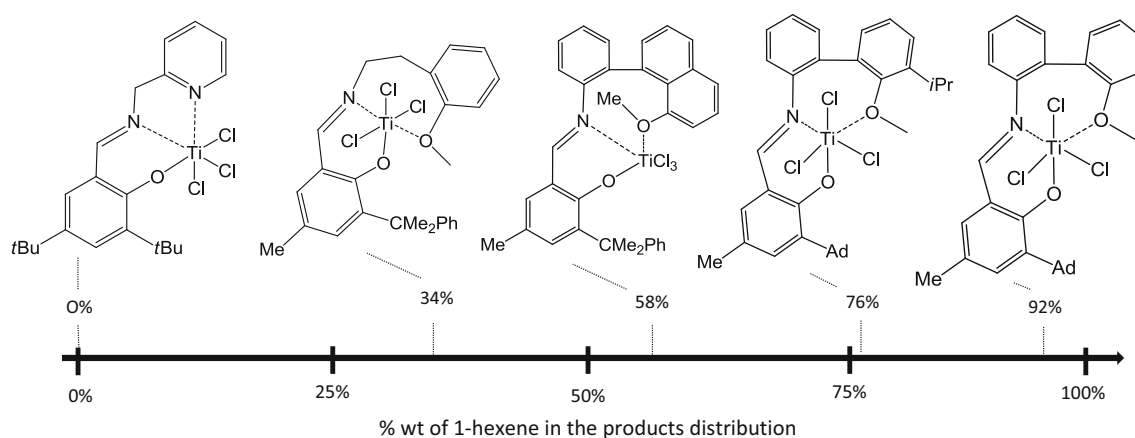
Fig. 16 From polymerization to selective ethylene trimerization with tridentate FI-type catalysts
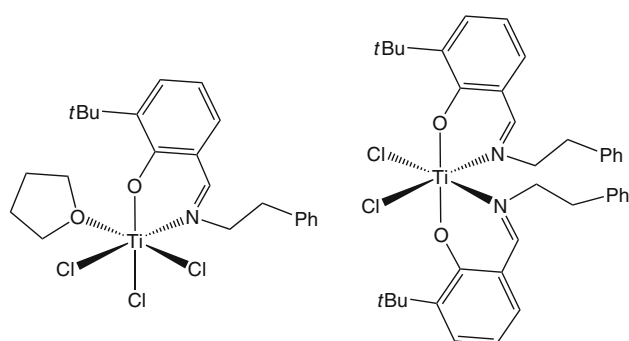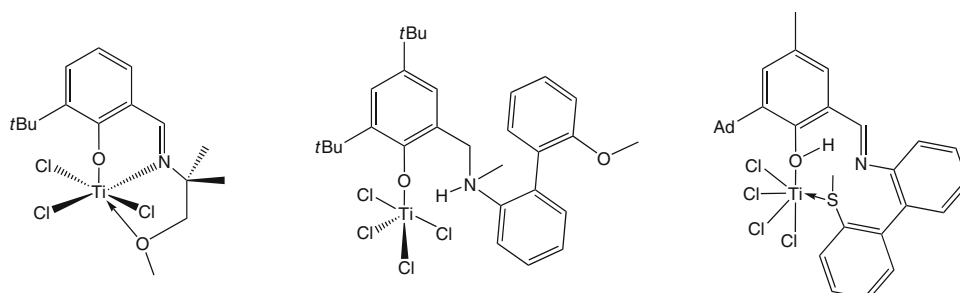

Fig. 17 Examples of functionalized aryloxy-imine Ti(IV) complexes

performed to evaluate the potential of zirconium and hafnium analogs to selectively produce 1-hexene and/or 1-octene [99–101]. Calculations predict 1-hexene as the major product for zirconium catalysts. Experimental investigations performed later by McGuinness et al. did not confirm these predictions as all the zirconium-based catalysts evaluated produced only polyethylene [102].

6 Iron Based Catalysts for Unselective Ethylene Oligomerization

The ability of iron catalysts to form carbon–carbon bonds from unsaturated compounds was initially reported by Hata

in the 1960s, focusing on dienes such as butadiene and isoprene [103–105]. Mainly monodentate donor ligands such as PPh_3 have been investigated in Ziegler–Natta type systems comprising an iron(III) precursor with an alkyl-aluminum as $AlEt_3$. Bipyridine [106] followed by diimine ligands [107, 108] were then described by Misono and tom Dieck, respectively, for the cyclodimerization of butadiene to cyclooctadiene and vinylcyclooohexene. It is suggested that all these homogeneous systems lead to iron(0) active species as co-catalysts with reductive properties that are mainly used as $AlEt_3$, or Grignard reagents.

Until the late 1990s, the reactivity of iron towards mono-olefins was not reported to the best of our knowledge. The breakthrough independently reported by the groups of Brookhart [109] and Gibson [110] triggered an "iron age" for the transformation of olefins, especially the oligomerization and polymerization of ethylene. This surprising reactivity arose from the fine association of a tridentate bis(imino)pyridine ligand with an iron(II) pre-catalyst activated by a methylaluminoxane, leading to exceptional activities along with an excellent alpha selectivity for the olefins produced (Fig. 19). Moreover, the easy tuning of the ligand structure led to a broad range of products from low molecular weight linear alpha olefins to high molecular weight linear polyethylenes. The technology was commercialized under the trademark of Versipol by DuPont which offers the technology for licensing [111]

Fig. 18 Fujita's analogues for ethylene trimerization and polymerization

for high density polyethylene production and a range of olefin oligomers (Schulz–Flory distribution). However, no commercial unit has been announced yet. It seems that operating this kind of highly active catalytic system is still challenging and involves the development of novel approaches to resolve the technical challenges [112]. Detailed recent reviews cover all the complex modifications that have been studied [113, 114], but also bring to the foreground several limitations of the iron-catalyzed ethylene oligomerization. While the most active systems are based on iron(II) precursors bearing a tridentate neutral ligand and activated by a methylaluminoxane, they present by-product and stability issues, particularly regarding thermal stability. Considering the different iron(II) pre-catalysts reported in the literature, the donor-functionalized diimine- and phenantroline-based complexes appear among the most promising systems when activated by (modified) methylaluminoxane, leading to wax- or polymer-free distributions of oligomers (Fig. 19) [115, 116].

In comparison, bidentate *N,N* neutral ligands such as pyridine-imine [117] and quinoline-imine [118] on iron(II) precursors have also been investigated [113] and generally led to low active or inactive catalysts towards ethylene in presence of MAO (Fig. 20).

IFPEN was interested in the development of mono-anionic tridentate ligand and obtained *N,NH,N* ligands based on a 1,2-dihydro-1,10-phenanthroline scaffold from condensation of 2-acetylpyridine with 8-aminoquinoline derivatives [119]. In presence of a base such as BuLi, these ligands were coordinated on an iron(III) precursor leading to a pseudo-square pyramidal coordination geometry (Fig. 21) [120]. While little to no activity was observed in presence of MAO at 40 °C and 30 bar of ethylene, at
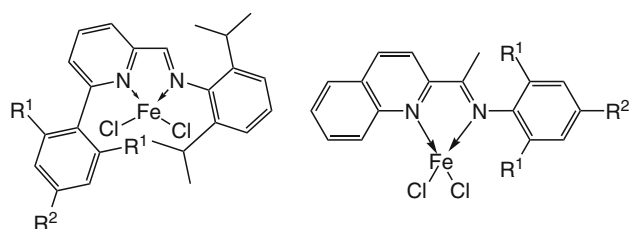
80 °C, a steady ethylene uptake was noticed over 2 h. Ethylene was transformed to short-chain oligomers with up to 63 wt% of butenes compared to all products formed. Polymer production (12 wt%/all products) was also observed accompanying the product distribution that may suggest multiple active species. The iron(III) complex coordinated by the tridentate ligand under its neutral form and the corresponding iron(II) complexes appeared to be inactive under ethylene in presence of MAO, highlighting the synergistic combination of the anionic ligand with the oxidation state of the iron precursor.

Starting from the iron(II) precursor bearing the *N,NH,N* ligand, we investigated an oxidative path to access iron(III) pre-catalysts. In solution in acetonitrile and with bubbling O_2, the pink solution containing the iron(II) complex progressively turned to a dark purple mixture [121]. The characterization by IR of the complex formed showed the absence of proton. By analogy, we performed the same oxidation reaction on an iron(II) 1,3-bis(2′-pyridylimino)isoindoline complex and the μ-oxo-bridged diiron(III) complex could be isolated and characterized by XRD (Scheme 6). Such species has already been described although the synthesis was performed with an equimolar amount of the ligand and $FeCl_3 \cdot 6H_2O$ [122].

The proposed μ-oxo-bridged diiron(III) bearing a 1,2-dihydro-1,10-phenanthroline (Fig. 22) obtained by oxidation could transform ethylene upon MAO activation at 80 °C and 30 bar, affording a C_4 to C_{12} distribution of oligomers along with polymer (11 wt%) [123].

The nature of the active species formed by MAO activation of iron complexes remains a central scientific question. In a recent report, we disclosed the use of a well-defined aluminum-based co-catalyst $[PhOAlMe_2]_2$ for the iron-catalyzed ethylene oligomerization (Fig. 23) [124]. Considering that the cationic alkyl iron(II) species is formed in the activation process, we highlighted in this experimental and theoretical study the mechanisms favoring or inhibiting ethylene oligomerization. A weak interaction in the ion pair is preferred as observed for the well-defined co-catalyst and a representative MAO model leading to active catalyst, whereas trivalent aluminum sites as in $AlMe_3$ may favor the adduct formation leading to catalyst inactivity. Recently, we extended this approach to
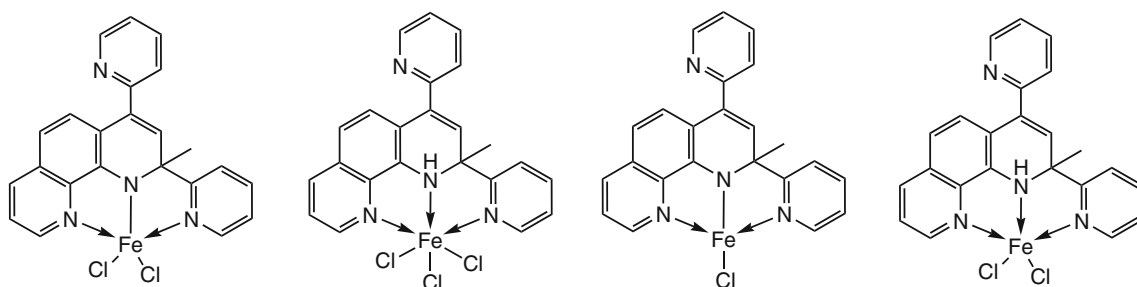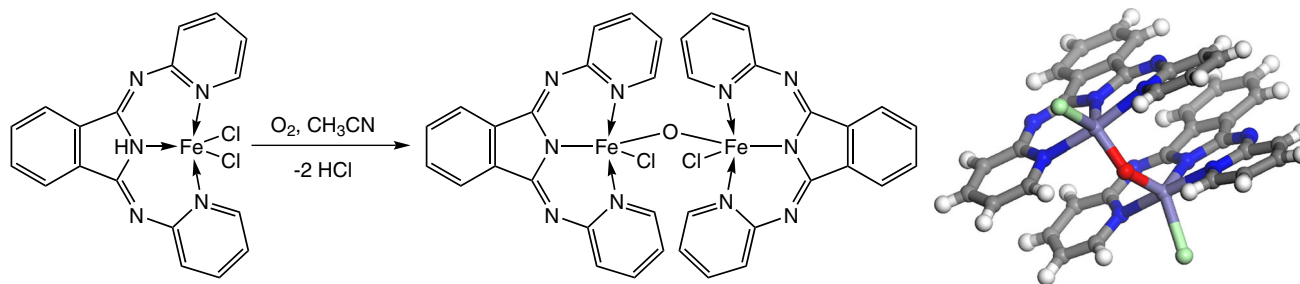
Fig. 20 Bidentate *N,N* ligands coordinated on iron(II) precursor

Fig. 21 Anionic and neutral *N,N,N* ligands on iron(III) and iron(II) precursors

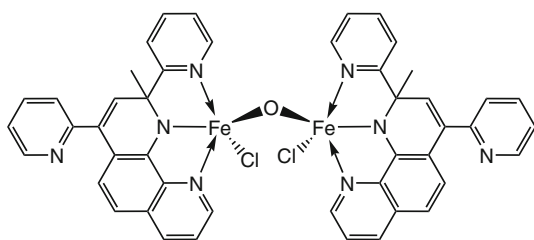**Scheme 6** Synthesis of μ-oxo-bridged diiron(III) complex

Fig. 22 Proposed μ-oxo-bridged diiron(III) complex

diol and bis(phenol) compounds. We observed that in association with AlMe₃, they form well-defined tri-aluminum complexes as described by Ziemkowska (Fig. 23) [125, 126]. In presence of iron(II) or iron(III) complexes, active catalysts are generated affording Schulz–Flory distribution of oligomers comparable to the ones observed with MAO.

7 Tungten Based Catalysts for Selective Ethylene Dimerization

Tungsten-based catalysts were first described in the 1960s as active for the metathesis of olefins [127]. Interestingly, Menapace and coworkers from Goodyear showed in 1975 that for WCl_6 in presence of aniline a reaction switch from metathesis to dimerization of 2-pentene is observed depending on the Al/W ratio [128]. Applied to ethylene, excellent selectivities in 1-butene (>98 % compared to all

products formed) were afforded by refluxing WCl_6 in the presence of 2 equivalents of aniline in chlorobenzene and further activated by Et_2AlCl (Al/W = 80) at 34 bar and 40 °C [129]. More sterically hindered 2,6-dimethylaniline introduced in conditions similar to those described above led to significant enhancement of the activity with up to $2.8.10^4$ $g_{C2H4}/(g_W.h)$ while maintaining the 1-butene selectivity to 98 % [130]. In the meantime, Goodyear filled several patents related to propylene dimerization describing catalyst additives. Prior to the introduction of the aniline compound, the tungsten precursor is mixed with an carboxylic acid [131], a phenol [132] or a diketone [133] molecule leading to active catalysts in association with ethylaluminum sesquichloride (EASC) for example, however no peculiar selectivity is observed.

With such an approach, uncertainties remain regarding the nature of the catalyst precursor, uncertainties which hamper comprehension and formulation of hypotheses regarding the activation step and the catalytic mechanism in operation. Starting from $WOCl_4$, IFPEN synthesized and isolated the mono-imido complex $[(2,6-Me_2C_6H_3)-N = WCl_4]$ (Fig. 24) [134]. Moderate activities were observed over more than 4 h (up to $3.4.10^3$ $g_{C2H4}/(g_W.h)$) affording good selectivity for ethylene dimerization at 40 °C and at 60 bar when activated by Et_2AlCl or $EtAlCl_2$ at a Al/W molar ratio of 40. Two catalytic mechanisms may be considered for high selectivity in 1-butene. They may be initiated whether by the formation of metal alkyl species leading to a Cossee–Arlman type mechanism or by

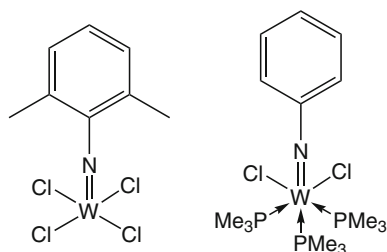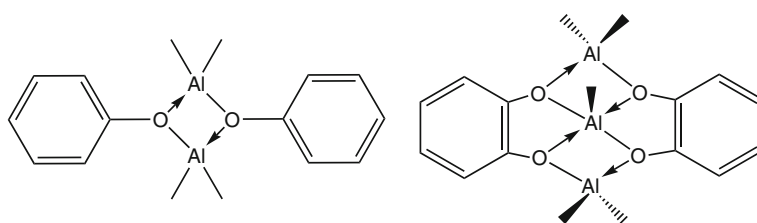**Fig. 23** Well-defined co-catalysts for the iron-catalyzed oligo

Fig. 24 Well-defined tungsten precursors for ethylene dimerization

Fig. 25 Bimetallic bis(imido)complex

the reduction of the tungsten precursor followed by the concerted coupling of two molecules of ethylene. Thus IFPEN prepared and isolated the low oxidation state imido complex, stabilized by PMe_3, $[PhN = WCl_2(PMe_3)_3]$ (Fig. 24), inactive in presence of ethylene alone but that led to ethylene dimerization in presence of 4.5 equivalents of $AlCl_3$, suggesting that the metallacyclic mechanism may be in play.

This hypothesis was supported by a DFT study from Tobisch who described a mono-imido tungsten complex as an effective catalyst when chelated by a Lewis acid [135]. The bis(imido) tungsten compound associated to a Lewis acid was also investigated and may be considered as an efficient system for olefin dimerization [136]. This study as well highlighted that one imido may be released leading to the active mono-imido tungsten catalyst. To confirm or disprove the bis(imido) tungsten complex activity, Hanton, Dyer et al. reported, a few years later, the synthesis of well-defined bimetallic complexes $[PhN=WMe_2(=N(Ph) AlMe(X)(\mu$-Cl)$)]$ (with X = Cl or Me, Fig. 25) [137]. However, these complexes proved to be inactive in presence of ethylene. The in situ generated catalyst, although ill-defined, remains the most efficient system to promote olefin dimerization. A detailed catalytic study from Sasol led to selectivity above 99 % for dimerization of 1-pentene to 1-nonene depending on the catalyst components and their stoichiometry [138]. Having a closer look to the products formed, the authors proposed that the Cossee–Arlman mechanism is effective, supported by a C_2H_4/C_2D_4 co-dimerization experiment leading to full isotopic scrambling. It should however be noted that a second order dependence on the substrate is also described that still raises questions about which mechanism is really operative
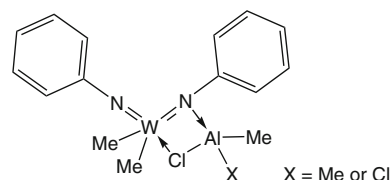
here. Although a series of patents was published in 2007 by Sasol [139], relative to olefin dimerization for methyl branched compounds production, no press release or announcement for a process commercialization was published.

8 Conclusion

Since its discovery 60 years ago, the transition metal homogeneous catalyzed oligomerization of light olefins has remained a topic of prime importance in academia and industry. The oligomerization of ethylene to linear alpha olefins is one of the main growing area of homogeneous catalysis owing to the increasing market demand for LAO, most notably as co-monomers for PE. It is one of the applied catalysis areas that has seen the emergence of the main scientific breakthroughs and developments of novel industrial processes such as for the first time ethylene tetramerization. One of the outstanding features of oligomerization is that many transition metals, representative of Group 4 to Group 10, have shown their ability to be effective catalysts. Despite an abundant literature, only some of them display exceptional activity and selectivity, highlighting that selective ethylene dimerization, trimerization and tetramerization are far from trivial and well-understood reactions. This opens avenues for cutting edge research by the broad scientific community. Moreover, the demand for the selective formation of short chain alpha olefins poses challenges at the interface of different science: coordination, organometallic chemistry, catalysis, modeling and process design.

From the early days, IFPEN has recognized the potential of oligomerization and followed it from basic research to developments. Armed with this experience and in the light of industrial achievement, we attempted in this report to show, with selected examples, the specificity and deficiency of

each metal and the corresponding catalytic systems. For example, the same metal can react via different mechanisms and drive the transformation to polymerization or oligomerization depending on operating conditions or co-catalyst applied. The challenge remains to attain greater control of the selectivity and to design "on purpose processes". The right combination of metal–ligand-activator remains the key of the discovery even if the development of new ligands has been essential. There is no single rule for ligand design and subtle changes can switch the reaction outcome. One may anticipate that in coming years, studies on the fundamental and applied aspects will allow the discovery of new oligomerization catalysts with improved efficiency and sustainability.

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