

Review

Ethylene oligomerization, homopolymerization and copolymerization by iron and cobalt catalysts with 2,6-(bis-organylimino)pyridyl ligands

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Abstract

In this review are highlighted the key advances that have occurred in the discovery and development of 2,6-bis(imino)pyridyl iron(II) and cobalt(II) catalysts for the transformation of ethylene into linear and branched homopolymers or into α -olefins with either Schulz–Flory or Poisson distribution. Particular attention has been paid to studies of the electronic and geometrical structure of both supporting ligands and metal complexes as well as to the mechanisms of precatalyst activation, chain-propagation and chain-transfer.

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transition metal complexes) are manifold, spanning from the ease of preparation and handling to the use of low-cost metals with negligible environmental impact. Another intriguing feature of bis(organylimino)pyridyl Fe^{II} and Co^{II} precursors (organyl = aryl, alkyl) is provided by the facile tuning of their polymerization activity by simple modifications of the ligand architecture. It has been shown, in fact, that the size, nature and regiochemistry of the substituents in the iminoaryl groups are of crucial importance in controlling the polymerization [33–52] and oligomerization [39,44,46,48,49,52,55–64] of ethylene. Moreover, due to the good compatibility with various early and late metal copolymerization catalysts, 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} dihalides can be used as oligomerization catalysts in tandem catalytic systems for the production of branched PE as well as in reactor blending to give PE with controlled molecular weight distribution [56–58].

The catalysts for α -olefins production have experienced a development similar to that of ethylene polymerization catalysts. Originally linear α -olefins were produced by the Ziegler (Alfen) process which consists of a controlled oligomerization of ethylene in the presence of AlEt₃ at 90–120 °C at a monomer pressure of 100 bar [65–67]. Common industrial catalytic systems for ethylene oligomerization still comprise alkylaluminum compounds or their combinations with early transition metal compounds [e.g., TiCl₄]. However, but well-defined late transition metals such as Ni^{II} and Pd^{II} in conjunction with chelating ligands [65–67], Fe^{II} dihalides modified with 2,6-bis(organylimino)pyridines [68,69] and Co^{II} dihalides modified with iminopyridines constitute a valid, in some cases, better alternative [70–74].

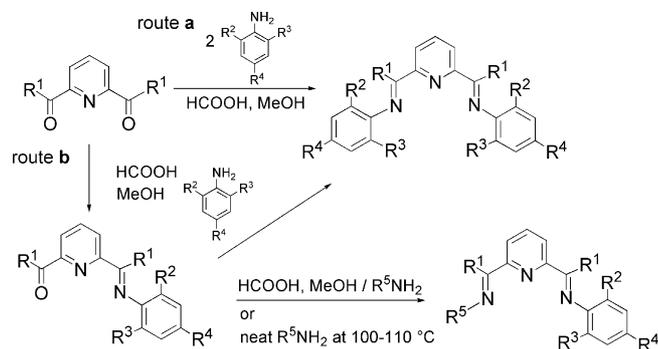
In this article, we have reviewed the activity of 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} dihalides as catalyst precursors for the homopolymerization, oligomerization and copolymerization of ethylene. In an attempt of correlating structure and activity, we have focused much of our attention on the many structural variations that feature these ligands. To the best of our knowledge, review articles covering this specific subject have not appeared elsewhere.

2. Synthesis of 2,6-bis(organylimino)pyridine ligands

Most 2,6-bis(arylimino)pyridyl ligands are commonly prepared by condensing 2,6-bis(acetyl)pyridine with 2 equiv. of the required aniline in the presence of an acid co-catalyst (route a, Scheme 5). The use of 2,6-bis(formyl)pyridine leads to aldimine derivatives [27–32].

The method of reacting 2,6-bis(acetyl)pyridine, first, with 1 equiv. of a substituted aniline and then with 1 equiv. of either a primary amine or a different aniline (route b, Scheme 5) has been developed to prepare (2-arylimino-6-alkylimino)pyridines or 2,6-bis(arylimino)pyridines with different symmetry, respectively [39,49,55,75,76].

Due to hindered aryl ring rotation, variable substitution patterns on the aryl rings can lead to the formation of 2,6-bis(arylimino)pyridyl ligands with C_{2v}, C₂, C_s, or C₁ symmetry (vide infra). Apparently, the ligands resulting from the reactions



Scheme 5. Synthetic procedures to 2,6-bis(organylimino)pyridyl ligands.

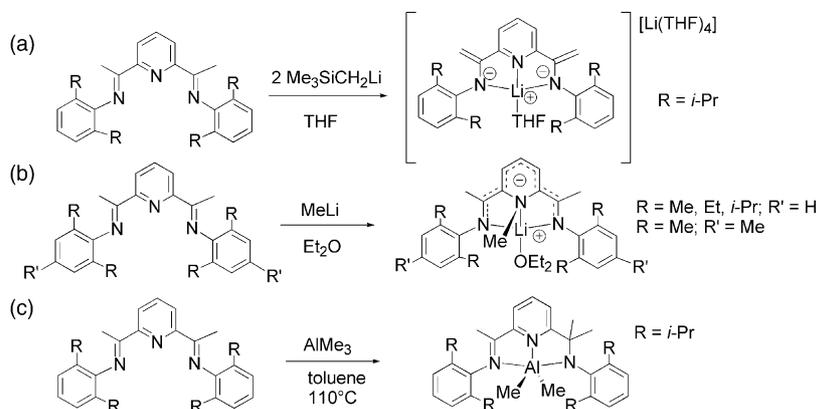
of the keto-imine intermediate with a primary amine or with an aniline different from that used to make the keto-imine intermediate can exhibit exclusively either C_s or C₁ symmetry.

The ligands in Scheme 5 are shown in the U-shaped configuration seen in the metal complexes, with the aryl groups orthogonal to the N–N–N plane. This position is maintained on the timescale of polymerization only when the barrier to aryl ring rotation is sufficiently high, and this happens invariably when the aryl rings are substituted at both *ortho*-positions by alkyl groups and the imine carbons bear an alkyl group (generally a methyl) [75].

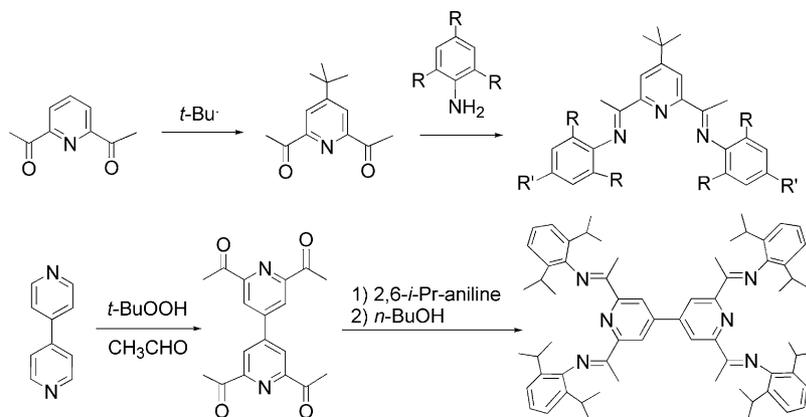
Unlike traditional ligands for olefin polymerization, bis(imino)pyridyl ligands exhibit a rich chemistry on their own, due to many potentially reactive sites, including the nitrogen carbon centers of the imine unit as well as the pyridine ring [77–83]. Deprotonation of the ketimine methyl group by strong non-nucleophilic bases, such as Me₃SiCH₂Li, to give dianions has been reported by Gambarotta [80] (Scheme 6a), while monoanionic species have been isolated by Gibson by nucleophilic attack of MeLi at the nitrogen atom in Et₂O (Scheme 6b) [79]. Notably, the reaction of the monoanionic ligands with FeCl₃, followed by MAO activation, gave ethylene polymerization catalysts which were as active as the corresponding 2,6-bis(imino)pyridyl FeCl₂ derivatives. The recovery of the neutral ligands after catalysis has been taken as an indication for a methyl migration from nitrogen to iron [79]. Selective nucleophilic attack at an imine nitrogen atom to give monoanionic ligands has been also achieved by reaction of the ligands with AlMe₃ in toluene at elevated temperatures (Scheme 6c) [81]. In contrast, nucleophilic attack at the pyridine ring (2 and 3 positions) requires complexation of the 2,6-bis(imino)pyridyl ligand with a vanadium(III) center [83].

Radical attack at the pyridine ring has been used to introduce bulky alkyl groups in the 4 position in an attempt of improving the solubility of the ligands in apolar solvents [83] or to double the 2,6-bis(imino)pyridyl moiety to give N₆ ligands capable of coordinating two metal centers (Scheme 7) [84,85]. Bis-iron and bis-cobalt derivatives have been synthesized, which have shown high activity for ethylene polymerization to high-density polyethylene (HDPE) [84].

Besides deprotonation and nucleophilic attack, 2,6-bis(imino)pyridyl ligands, either free or complexed to metal, exhibit a remarkable tendency to accept negative charge [86–88].



Scheme 6.

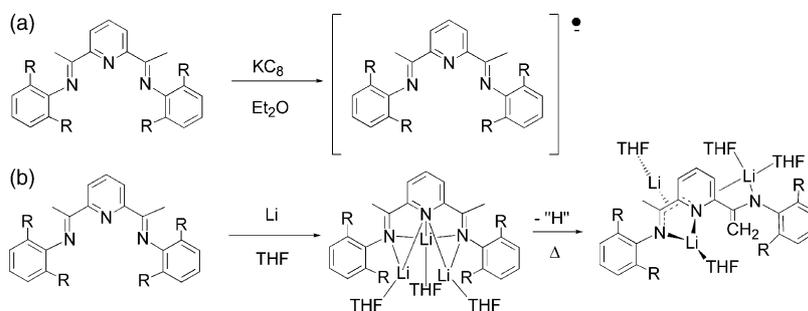


Scheme 7.

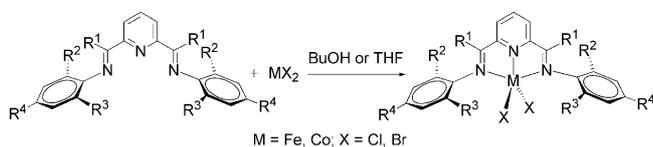
One-electron reduction to give a radical monoanion (EPR signal at room temperature with $g_{\text{eff}} = 2.00$) has been achieved by reaction of 2,6-(2,6-($i\text{-Pr}$) $_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$ with KC_8 in OEt_2 by Gibson and Clentsmith [86] (Scheme 8a). These authors were also able to crystallographically characterize the reduction product as $\text{K}(\text{OEt})_2$ salt. Three-electron reduction of the same ligand has been reported by Gambarotta and coworkers who were also able to isolate both paramagnetic and diamagnetic trianions (Scheme 8b) [87]. The ability of the large π -system, featuring all 2,6-bis(imino)pyridyl ligands, to accommodate negative charge has been proposed to increase the Lewis-acidity of the coordinated metal centers with a positive impact on the polymerization activity [87].

Pyridine N -alkylation by Li, Mg and Zn alkyl reagents has been further investigated by Gibson [89]. The alkylation mechanism has been proposed to involve coordination of the metal alkyl by the ligand, followed by alkyl transfer, favored by reduced steric crowding at the metal center. The loss of aromaticity of the pyridine ring would be compensated by extensive charge delocalization between the imine nitrogens through the ligand backbone.

Finally, it worth stressing that the bis(imino)pyridyl ligands bonded to iron or cobalt are not attacked by MAO or AlMe_3 under the conditions of the polymerization reactions (*vide infra*) and the intact ligands have been recovered quantitatively following hydrolytic work-up after the polymerization [81].



Scheme 8.

Scheme 9. Synthesis of Fe^{II} and Co^{II} dihalides.

3. Synthesis of 2,6-bis(organylimino)pyridine iron(II) and cobalt(II) catalyst precursors

The synthesis of the Fe^{II} and Co^{II} catalyst precursors is straightforward and involves the plain addition of the solid ligands to *n*-BuOH or THF solutions of either anhydrous or hydrated dihalides (Scheme 9) [27–32]. Irrespective of the metal, the dihalides are sparingly soluble in aromatic hydrocarbons, while they dissolve fairly well in polar solvents. The solids are rather air-stable, whereas they decompose in solution unless protected by an inert gas atmosphere.

The IR spectra of all compounds show a red shift of $\nu(\text{C}=\text{N})$ by ca. 50–60 cm⁻¹ as compared to the corresponding free ligand, which reflects the coordination of the imine nitrogen atoms to the metal.

Table 1 summarizes the 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} catalysts for ethylene polymerization, while Table 2 shows the catalysts for ethylene oligomerization.

3.1. Fe^{II} complexes

All Fe^{II} dihalides are dark blue and exhibit high-spin electronic configuration with magnetic moments μ_{eff} ranging from 5.5 to 5.7 BM, consistent with the values expected for Fe^{II} five-coordinate complexes with a quintuplet ground state [27–32,55]. The quintuplet ground state makes the complexes EPR-silent even at 4 K and irrespective of the EPR frequency.

The molecular structure of several Fe^{II} derivatives has been determined by single-crystal X-ray diffraction techniques [27,29,31,32,75]. The coordination geometry at the iron center is quite flexible, varying from trigonal-bipyramidal to square-pyramidal, with various degrees of distortion from the idealized geometries, depending on the substitution pattern of the N-aryl groups. The substitution patterns determines also the crystallographic symmetry that may be C_{2v}, C_s or C₁.

ORTEP drawings of complexes with C_s [31] or C₂ [46] symmetry are given in Fig. 1, while Fig. 2 shows side-

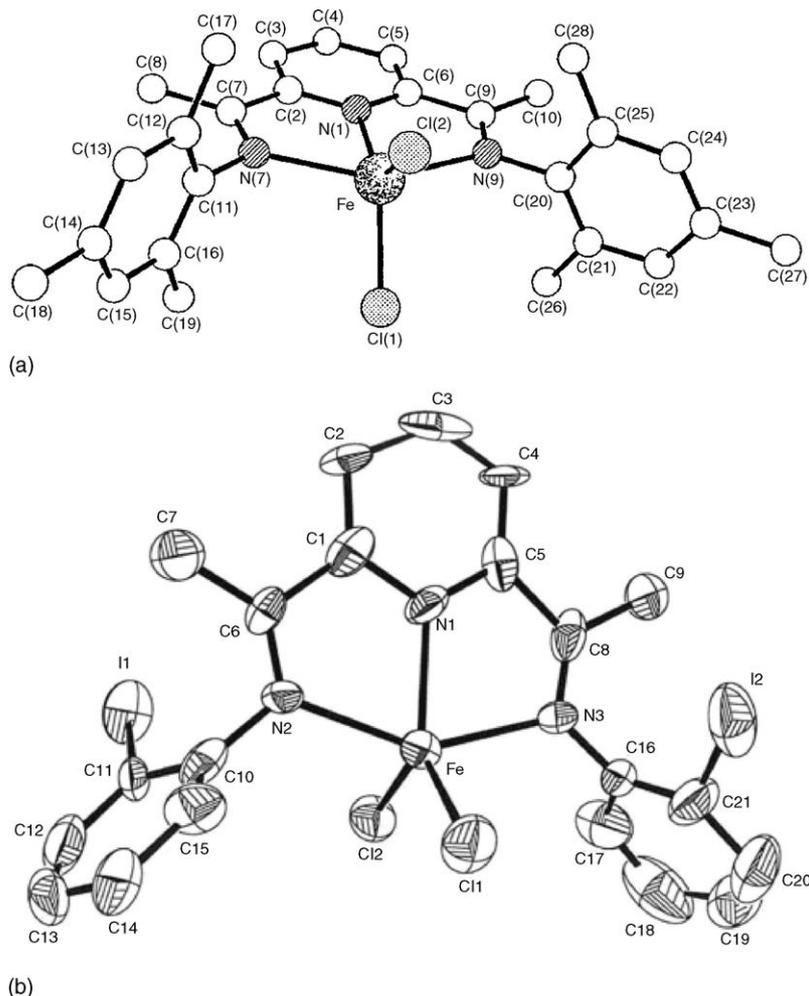


Fig. 1. Molecular structures of FeCl₂L complexes: (a) C_s symmetry, L = 2,6-(2,4,6-Me₃C₆H₂N=CMe)₂C₅H₃N (figure was reproduced from ref. [31], with permission of the copyright holders); (b) C₂ symmetry, L = 2,6-(2-IC₆H₄N=CMe)₂C₅H₃N (figure was reproduced from ref. [46], with permission of the copyright holders).

Table 1
2,6-Bis(arylimino)pyridyl Fe^{II} and Co^{II} catalysts for ethylene polymerization

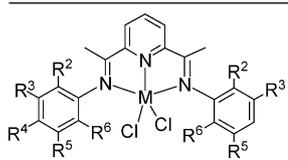
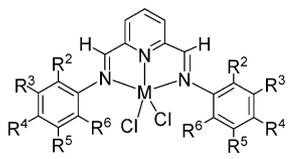
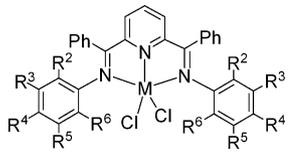
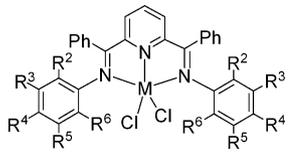
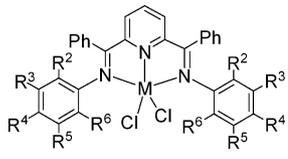
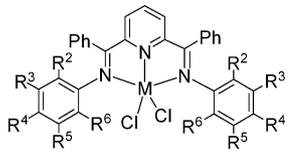
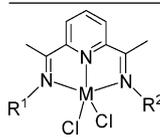
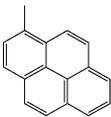
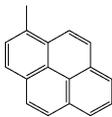
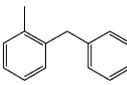
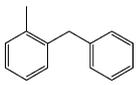
Complex	M	R ²	R ³	R ⁴	R ⁵	R ⁶	References	
	Fe	Me	H	H	H	Me	[27,30,31,38,39,44,45,51,52,75,116–118]	
		Me	H	Me	H	Me	[30,31,52,116]	
		Me	Br	Me	H	Me	[52]	
		Me	H	Br	H	H	Me	[45]
		Me	H	H	H	H	<i>i</i> -Pr	[52,75]
		Et	H	H	H	H	Et	[52]
		<i>i</i> -Pr	H	H	H	H	<i>i</i> -Pr	[27,30,31,33,36,37,39,42,47,50,52,75]
		<i>t</i> -Bu	H	H	H	H	H	[27,31,52,75]
		cycloalkyl	H	H	H	H	cycloalkyl	[36]
		CF ₃	H	H	H	H	H	[48]
		CF ₃	H	F	H	H	H	[48]
		CF ₃	H	H	H	H	F	[48]
		Cl	H	H	H	H	Cl	[46]
		Br	H	H	H	H	Br	[46]
	Co	Me	H	H	H	Me	[27,38,44]	
		Me	H	Me	H	Me	[31,127,130]	
		<i>i</i> -Pr	H	H	H	H	<i>i</i> -Pr	[27,30,31,47,122–124,127,130]
		<i>t</i> -Bu	H	H	H	H	H	[27,31]
		CF ₃	H	H	H	H	F	[48]
		Cl	H	H	H	H	Cl	[46]
Br	H	H	H	H	Br	[46]		
	Fe	Me	H	H	H	Me	[27,31]	
		Me	H	Me	H	Me	[31,86]	
		Me	H	H	H	H	<i>i</i> -Pr	[75]
		Et	H	H	H	H	Et	[31]
		<i>i</i> -Pr	H	H	H	H	<i>i</i> -Pr	[31]
	Co	Me	H	Me	H	Me	[31]	
	Fe	Me	H	Me	H	Me	[40]	
		Me	H	H	H	Me	[40,41]	
		Me	H	Me	H	Me	[40,41]	
		<i>i</i> -Pr	H	H	H	H	<i>i</i> -Pr	[40,41]
	Co	Me	H	Me	H	Me	[40,41]	
Complex	M	R ¹	R ²	References				
	Fe			[34,35]				
				[35]				
				[35]				
				[35]				

Table 1 (Continued)

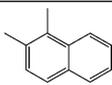
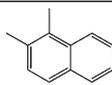
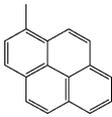
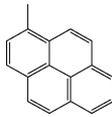
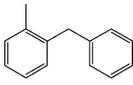
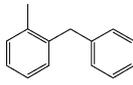
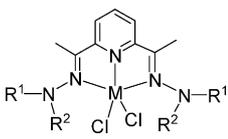
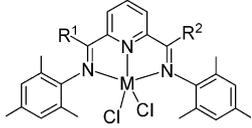
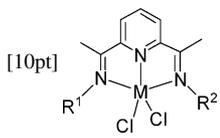
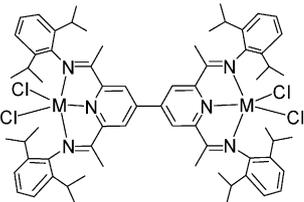
Complex	M	R ¹	R ²	References
				[34]
	Co			[34,35]
				[35]
				[35]
	Fe	Ph Me Me	Ph Ph Me	[51] [51] [51]
				[51]
	Co	Ph Me Me	Ph Ph Me	[51] [51] [51]
	Fe	OMe SMe	OMe SMe	[43] [43]
				[43]
				[43]
[10pt] 	Fe			[75]
				[75]
				[49,75]
				[75]
				[39]
				[39]

Table 1 (Continued)

Complex	M	Reference
	Fe/Co	[84]

on-views, perpendicular to the plane of the three nitrogen atoms, of FeCl_2L ($\text{L} = 2,6-(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) and CoCl_2L ($\text{L} = 2,6-(2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) [31]. The different geometries, square-pyramidal for Co and trigonal-bipyramidal for Fe, are clearly put in evidence by the angles subtended at the metal centers [27,29,31,32,46,75].

UV–vis spectroscopy shows that the preferred structure for the Fe^{II} complexes in solution is trigonal-bipyramidal [49,55,90–95]. In particular, a band in the region $7000\text{--}8400\text{ cm}^{-1}$ has been correlated with a spin-allowed transition in a trigonal-bipyramidal high-spin Fe^{II} environment [96]. The spectra contain also a band at ca. $20,000\text{ cm}^{-1}$ that is

assigned to a metal-to-ligand charge transfer (MLCT). Absorption bands at ca. $14,500\text{ cm}^{-1}$ have been reported by Gibson for C_{2v} -symmetric 2,6-bis(imino)pyridyl Fe^{II} complexes and attributed to MLCT [31]. In general, MLCT bands fall at higher energy than those observed by Gibson, but a lowering in frequency may occur for highly π -conjugated ligand systems, which may be the case for C_{2v} -symmetric 2,6-bis(imino)pyridyl ligands [91]. The reflectance spectra are generally comparable with the solution spectra, which indicates that the primary stereochemistry of the Fe^{II} complexes is the same in both the solid state and solution [55].

The Fe^{II} complexes with 2-(arylimino)-6-(alkylimino)pyridine ligands exhibit either C_1 or C_s symmetry by virtue of the simultaneous presence of substituted aryl groups and either chiral ($\text{CH}(\text{Me})\text{Ph}$ for instance [49,55]) or achiral alkyl groups at the imine nitrogen atoms (Scheme 10). The combined action of the ketimine group and the two *ortho*-alkyl substituents still locks the aryl ring in an orthogonal conformation with respect to the N_3 ligand plane in both solid state and solution, while the alkyl group at the imine nitrogen can rotate about the C–N axis in solution.

The Fe^{II} complexes can be reversibly oxidized at low potential ($E^{0'} = +0.4$ to 0.5 V) to give yellow Fe^{III} derivatives $[\text{FeCl}_2\text{L}]^+$ [49]. Stable C_2 -symmetric 2,6-bis(arylimino)pyridyl $\text{Fe}(\text{III})$ bis-halide complexes have been prepared by Gibson and shown to have the same activity as the Fe^{II} precursors in the oligomerization of ethylene, as a consequence of instantaneous Fe^{III} reduction to Fe^{II} by MAO [31]. It has been also reported the electrochemical reduction of the Fe^{II} complexes to the corresponding Fe^{I} derivatives, which however are not stable in solution where fast decomposition occurs [55].

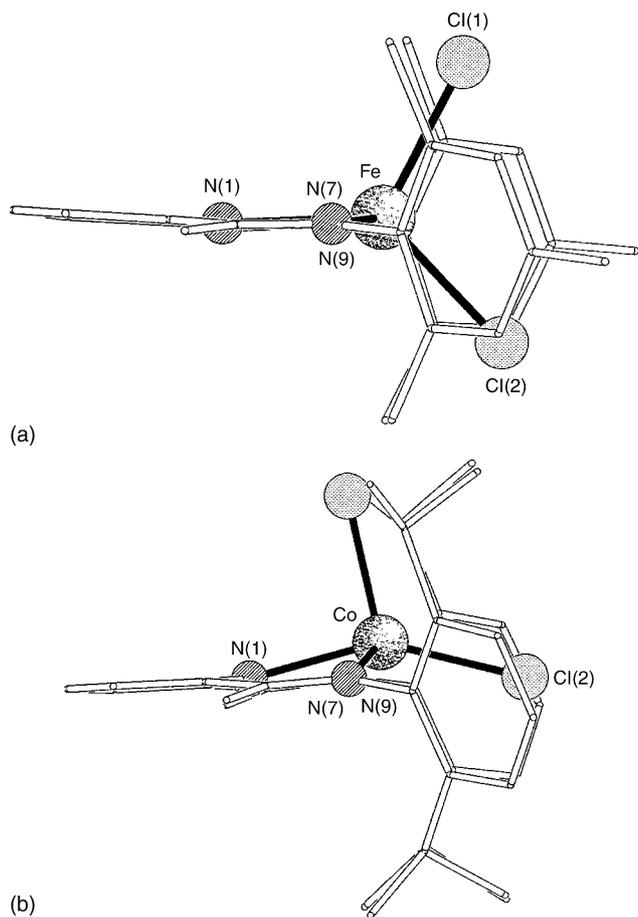
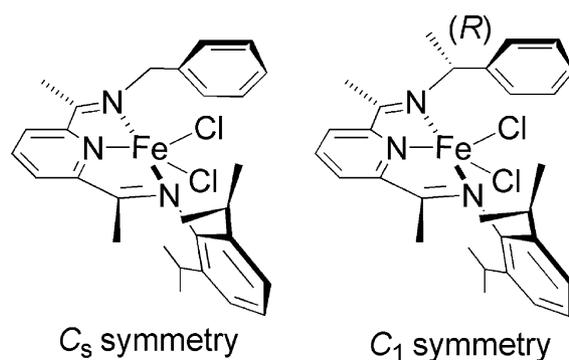


Fig. 2. Side-on-views, perpendicular to the plane of the three nitrogen atoms, of (a) FeCl_2L ($\text{L} = 2,6-(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) and (b) CoCl_2L ($\text{L} = 2,6-(2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) (figure was reproduced from ref. [31], with permission of the copyright holders).



Scheme 10. 2-(Arylimino)-6-(alkylimino)pyridyl Fe^{II} complexes with C_s and C_1 symmetry.

Table 2
2,6-Bis(arylimino)pyridyl Fe^{II} and Co^{II} catalysts for olefin oligomerization

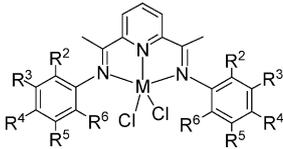
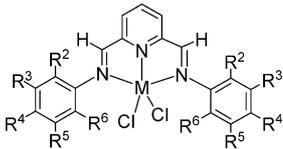
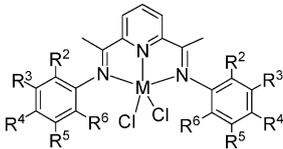
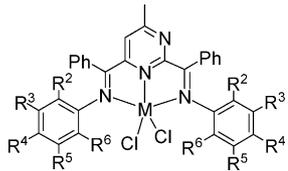
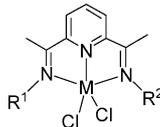
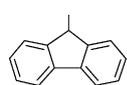
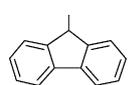
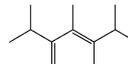
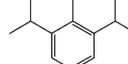
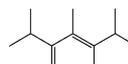
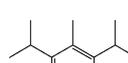
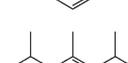
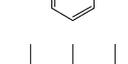
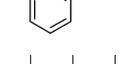
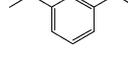
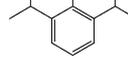
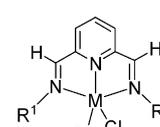
Complex	M	R ²	R ³	R ⁴	R ⁵	R ⁶	References	
	Fe	H	H	H	H	H	[43,46,52,59]	
		H	OMe	H	H	H	[59]	
		H	H	OMe	H	H	[59]	
		H	CF ₃	H	H	H	[59]	
		H	H	CF ₃	H	H	[59]	
		F	H	H	H	H	[46,62,63]	
		F	H	F	H	H	[62,64]	
		F	H	H	F	H	[62]	
		F	H	H	H	F	[62,63]	
		F	H	Me	H	H	[63,64]	
		F	H	H	Me	H	[64]	
		Cl	H	H	H	H	[46,64]	
		Cl	H	F	H	H	[64]	
		Cl	H	Me	H	H	[64]	
		Cl	H	H	Me	H	[64]	
		Br	H	H	H	H	[46]	
		Br	H	Me	H	H	[64]	
		I	H	H	H	H	[46]	
		Me	H	H	H	H	[29,30,32,48,52–54]	
		Me	Me	H	H	H	[32,44,52,60]	
		Me	H	Me	H	H	[32,44,52,53,58,60,63]	
		Me	H	H	Me	H	[44,52]	
		Me	H	H	H	Me	[53]	
	Me	Cl	H	H	H	[52,60]		
	Me	H	Cl	H	H	[52]		
	Me	H	H	Cl	H	[52,60]		
	Me	H	Br	H	H	[52]		
	Me	H	OMe	H	H	[58]		
	Et	H	H	H	H	[29,52,53,56,57]		
	<i>i</i> -Pr	H	H	H	H	[29,52]		
	<i>i</i> -Pr	H	H	Me	H	[52]		
	Fe	Me	H	H	H	H	[32]	
		Ph	H	H	H	H	[32]	
	Co	Me	H	H	H	H	[32]	
	Co	H	H	H	H	H	[54]	
		F	H	F	H	H	[32]	
		F	H	H	H	F	H	[32]
		F	H	H	H	F	F	[32]
		Cl	H	H	H	H	[59]	
		Br	H	H	H	H	[59]	
		I	H	H	H	H	[59]	
		Me	H	H	H	H	[32,48,54]	
		Me	Me	H	H	H	[44]	
		Me	H	Me	H	H	[44,58]	
		Me	H	H	Me	H	[44]	
		Me	H	OMe	H	H	[58]	
		CF ₃	H	H	H	H	[48]	
		CF ₃	H	F	H	H	[48]	
		CF ₃	H	H	H	F	[48]	
		Et	H	H	H	H	[54]	
		<i>i</i> -Pr	H	H	H	H	[54]	

Table 2 (Continued)

Complex	M	R ²	R ³	R ⁴	R ⁵	R ⁶	References
	Fe	Me	H	H	H	H	[40]
	Co	Me	H	H	H	H	[40]
Complex	M	R ¹	R ²	Ref.			
	Fe			[39]			
				[53]			
		Ph		[49]			
				[49]			
		CH ₂ Ph		[49]			
		CH(Me)Ph		[49,55]			
		CH(Me)Naphthyl		[55]			
		cyclohexyl		[55]			
		cyclohexyl		[55]			
		Co	CH(Me)Ph		[55]		
			CH(Me)Naphthyl		[55]		
			cyclohexyl		[55]		
			cyclohexyl		[55]		
			Fe			[32]	

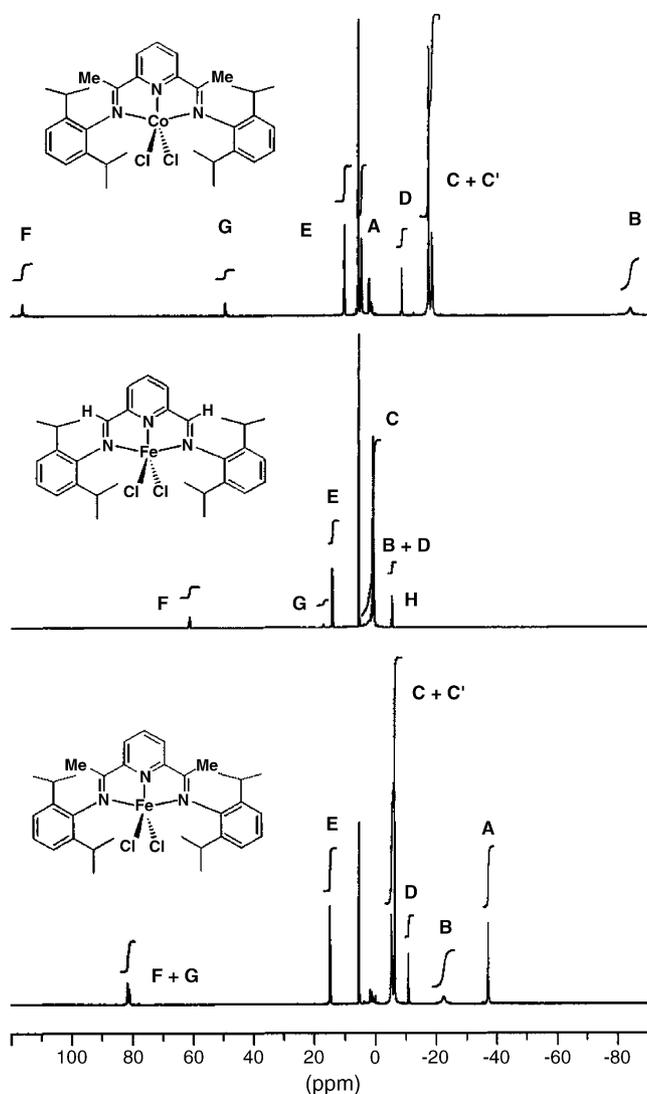


Fig. 3. ^1H NMR spectra (CD_2Cl_2 , 20°C) of 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} dichlorides (figure was reproduced from ref. [31], with permission of the copyright holders).

Despite the paramagnetic nature of the bis-halide precursors, ^1H NMR spectroscopy can provide valuable information on the solution structure of 2,6-bis(arylimino)pyridyl Fe^{II} dihalides, especially to compare the coordination geometry of Fe versus Co as well as estimate the energy barrier to aryl rotation about the $\text{N}-\text{C}_{\text{aryl}}$ axis [31,55]. Fig. 3 compares the ^1H NMR spectra in CD_2Cl_2 at room temperature of the isostructural Fe and Co derivatives MCl_2L ($\text{L} = 2,6-(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CH})_2\text{C}_5\text{H}_3\text{N}$) and of the Fe^{II} aldimine analogue [31]. A key difference between the ketimine and aldimine Fe^{II} complexes is a singlet for the CHMe_2 protons in the spectrum of the latter, which is consistent with free rotation of the aryl groups.

The ^1H NMR spectra (CD_2Cl_2 , 21°C) of the Fe^{II} and Co^{II} complexes MCl_2L ($\text{L} = 2-(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})-6-(c\text{-C}_6\text{H}_{11}\text{N}=\text{CMe})\text{C}_5\text{H}_3\text{N}$) [55] are reported in Fig. 4. The spectra are significantly different from each other, which reflects the structural diversity of the two complexes in solution. In particular, the resonances of four hydrogens from the cyclohexyl

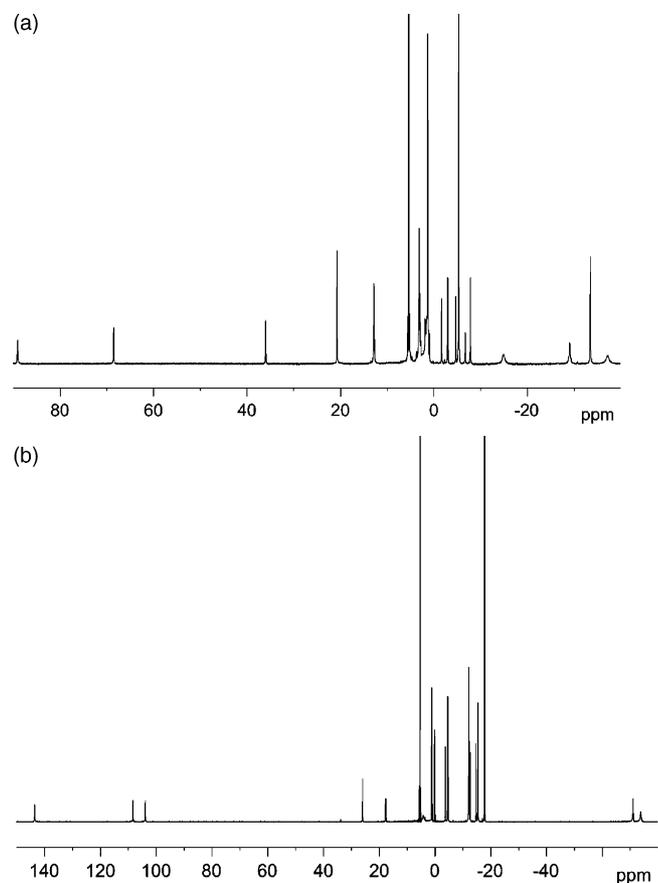


Fig. 4. ^1H NMR spectra (500.13 MHz, 21°C , CD_2Cl_2) of Fe (a) and Co (b) dichloride complexes with the pyridine ligand 2-(2,6-(*i*-Pr) $_2\text{C}_6\text{H}_3\text{N}=\text{CMe}$)-6-(*c*- $\text{C}_6\text{H}_{11}\text{N}=\text{CMe}$) $\text{C}_5\text{H}_3\text{N}$ (figure was reproduced from ref. [55], with permission of the copyright holders).

group are shifted to high-field (ca. -30 and -37 ppm) and show very broad line-widths, which suggests that the cyclohexyl ring is spatially very close to the paramagnetic Fe center on the NMR time-scale. Such remarkable line-width broadening for the cyclohexyl resonances has not been observed for the Co^{II} analogue [55]. The presence of two relatively narrow signals for the *i*-Pr groups confirms the hindered rotation of the aryl group in either system.

3.2. Co^{II} complexes

All 2,6-bis(imino)pyridyl Co^{II} complexes are green crystalline solids with μ_{eff} at room temperature ranging from 4.6 to 4.8 BM, consistent with the values expected for high-spin Co^{II} five-coordinate complexes [90–93]. As shown by the molecular structure of CoCl_2L ($\text{L} = 2,6-(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) [31] (Fig. 2b) as well as by that of the cyclohexyl-2,6-dimethylphenyl derivative [55] reported in Fig. 5, the presence of a rigid chelating terdentate ligand causes important distortions from the idealized geometries. However, in no known case, these are so important to favor spin pairing and give a doublet ground state ($S = 1/2$).

The reflectance and solution UV–vis spectra of the 2,6-bis(imino)pyridyl Co^{II} complexes are similar to each other indi-

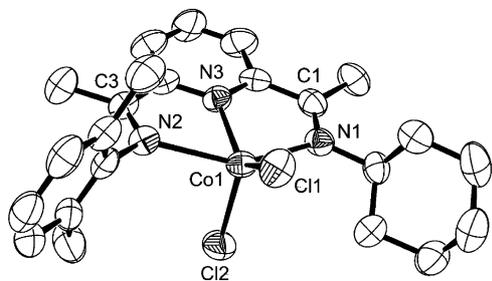


Fig. 5. ORTEP drawing of $[\text{CoCl}_2\{2-(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N}=\text{CMe})\text{-}6\text{-}(c\text{-C}_6\text{H}_{11}\text{N}=\text{CMe})\text{C}_5\text{H}_3\text{N}\}]\cdot\text{H}_2\text{O}$ (hydrogen atoms omitted). Selected distances (Å) and angles ($^\circ$): Co1-N1 2.185(6), Co1-N2 2.348(6), Co1-N3 2.032(6), Co1-Cl1 2.243(2), Co1-Cl2 2.269(2), N3-Co1-N1 76.7(2), N3-Co1-Cl1 131.87(18), N1-Co1-Cl1 99.91(18), N3-Co1-Cl2 107.58(18), N1-Co1-Cl2 99.80(17), Cl1-Co1-Cl2 120.12(9), N3-Co1-N2 73.4(2), N1-Co1-N2 149.3(2), Cl1-Co1-N2 94.88(15), Cl2-Co1-N2 95.72(16) (figure was reproduced from ref. [55], with permission of the copyright holders).

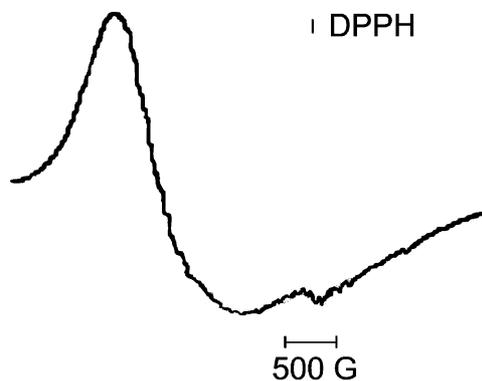


Fig. 6. X-band EPR spectrum of the complex CoCl_2L ($\text{L} = 2-(2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})\text{-}6\text{-}(\text{PhCH}(\text{Me})\text{N}=\text{CMe})\text{C}_5\text{H}_3\text{N}$) in CH_2Cl_2 at 4 K (figure was reproduced from ref. [55], with permission of the copyright holders).

cating that the primary stereochemistry is the same in both the solid state and solution, i.e., intermediate between the square-pyramid and the trigonal-bipyramid. Although the spectra show some changes in band shape and frequency as the substituents at the imine nitrogen atoms are varied, these are not sufficient for them to be due to substantial differences in structure. Such differences are likely due to the different steric bulk of the substituents in the complexes.

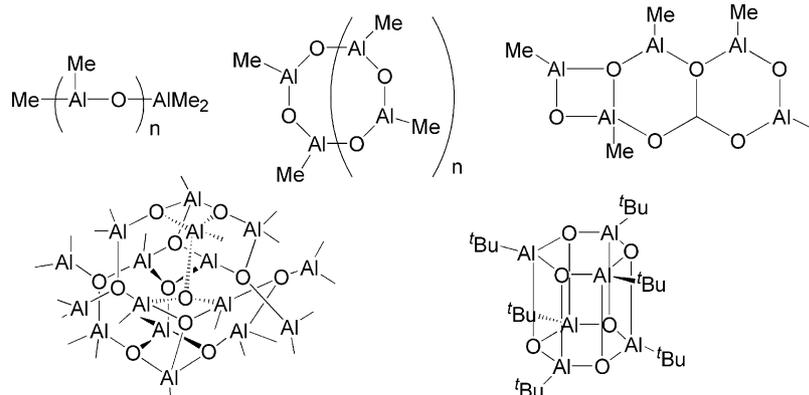
The presence of three unpaired electrons ($S = 3/2$) in each complex molecule makes all Co^{II} compounds EPR silent at room temperature in both the solid state and CH_2Cl_2 solution. A low-temperature X-band EPR study in CH_2Cl_2 has been reported for the derivative containing the 2,6-diisopropylphenyl- N -[(E)-1-(6-[(1*R*)-1phenylethyl]ethanimidoyl)-2-pyridinyl]-ethylidene]aniline ligand [55]. At 4 K the spectrum displays a broad and poorly resolved rhombic structure, which has been interpreted in terms of an $S = 1/2$. Effective spin Hamiltonian occasioned by large zero field splitting (ZFS) effects ($g_1 = 5.06(8) > g_2 = 3.03(8) > g_3 = 1.95(8) \neq g_{\text{elect}}$ ($g = 3.35(8)$; a_1 40(8) G, a_2 80(8) G, a_3 94(8) G; $\langle a \rangle$ 71(8) G) (Fig. 6) [97–103].

Unlike Fe^{II} , the Co^{II} centers in CoCl_2L complexes undergo only irreversible electron-transfer processes, in general a one-electron oxidation and a one-electron reduction [55].

4. Principal activators of 2,6-bis(organylimino)pyridine Fe^{II} and Co^{II} catalyst precursors

At present, MAO and modified methylaluminoxanes (MMAO), commonly with 20–25% $\text{Al}(i\text{-Bu})_3$, are the most widely used activators for 2,6-bis(organylimino)pyridine Fe^{II} and Co^{II} dihalides. For the sake of simplicity, MAO is commonly referred to as linear chain or cyclic rings $[-\text{Al}(\text{Me})-\text{O}-]_n$ containing three-coordinate aluminum centers, yet the true structure of MAO is still a matter of debate [104]. It may be a dynamic mixture of linear-, ring- and cage-complexes, all formed from methyl aluminoxane subunits during the controlled hydrolysis of trimethyl aluminum [105–107]. Some proposed structures for MAO include one-dimensional linear chains and cyclic rings containing three-coordinate Al centers, two-dimensional structures, and three-dimensional clusters (Scheme 11) [108]. A three-dimensional structure has been recently suggested by Sinn on the basis of structural similarities with *tert*-butylaluminoxanes [109] which form isolable cage structures [110].

Other activators for 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} dihalides are Lewis-acids such as ethylaluminum chloride, triethylaluminum, and combinations of triisobutylaluminum/tris(pentafluorophenyl)borane. However, MAO and



Scheme 11. Principal structures proposed for aluminoxanes.

Table 3
Predicted growth in the PE business^a

PE type	Volume, million t	
	1997	2015
LDPE	15.5	12.7
LLDPE	9.2	62.1
HDPE	18.7	64.5
Total PE	43.4	139.3

^a A.M.A. Bennett, CHEMTECH 24 July 1999.

MMAO remain the most active and used co-catalysts in ethylene polymerization/oligomerization.

5. Ethylene polymerization by 2,6-bis(arylimino)pyridyl iron and cobalt catalysts

The acronyms HDPE, LDPE (low-density polyethylene) and LLDPE (linear low-density polyethylene) define the three major classes of commercial PE. HDPE is a linear semicrystalline homopolymer produced commercially by ZN or chromium-based coordination polymerization technology. LLDPE is a random copolymer of ethylene and α -olefins (1-butene, 1-hexene or 1-octene) prepared using ZN, chromium or metallocene catalysts. LDPE is a branched ethylene homopolymer generally obtained by high-temperature and high-pressure free-radical processes. Table 3 reports the predicted growth of PE in the next years [111,112].

Upon activation by MAO, 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} dihalides generate robust and highly active catalysts for the polymerization of ethylene to HDPE on condition that the aryl rings bear either alkyl/aryl groups on both *ortho*-positions or a large alkyl group, such as *tert*-butyl, on an *ortho*-position (Scheme 12) (Table 1). As anticipated in a previous section, the presence of *ortho*-substituents locks the aryl groups orthogonal to the N–N–N plane also on the timescale of polymerization, which induces a retarding effect on the chain-transfer rate (see Sections 2 and 7.2). Catalysts modified with aldimine ligands (i.e., R² = H in Scheme 12) still produce HDPE, yet with lower molecular weight as compared to analogous ketimine catalysts [27–32]. The reactions are commonly carried out in toluene at temperatures ranging from –10 to 90 °C. Beyond the latter temperature the catalysts undergo irreversible decomposition.

The iron catalysts exhibit exceptionally high activities with TOFs as high as 10⁷, corresponding to ca. 3 × 10⁵ kg PE

(mol Fe × h)^{–1}, while the cobalt catalysts are much less active, even by two orders of magnitude at comparable conditions. Irrespective of the metal, aldimine-derived catalysts are less active by about an order of magnitude as compared to ketimine analogues.

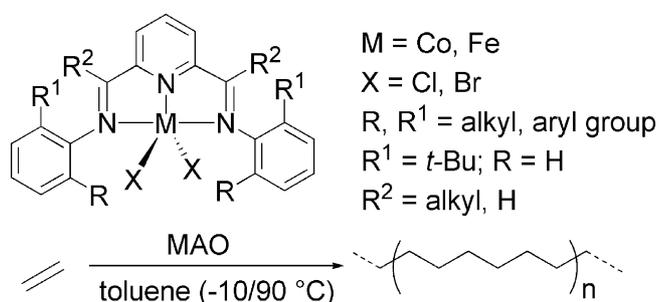
The steric bulk of the aryl *ortho*-substituents in Fe^{II} catalysts affect both the productivity and the polymer molecular weight. In particular, it is observed that decreasing the size of the *ortho*-substituents increases the activity and decreases the molecular weight. A similar trend is not generally valid for Co^{II}-based catalysts as, for example, the *ortho*-diisopropyl-substituted derivative is less productive and gives lower molecular weight polymers than either *ortho*-mono *tert*-butyl- or mesityl-substituted derivatives [32–37].

It is worth commenting that the iron complex bearing the unsubstituted 2,6-(PhN=CMe)₂C₅H₃N ligand has been employed by several authors as precursor in both polymerization and oligomerization reactions. Curiously, the catalyst has been reported as completely inactive [46,52], active for either PE [35] or active for gaseous or liquid linear α -olefins with a Schulz–Flory distribution [59]. From a perusal of the literature, it is clear that this discordance of results is most likely attributable to the purity of the precursor. The latter may contain other complexes due to scarce attention to the synthesis conditions, for example the use of hydrated Fe^{II} and Co^{II} salts that may promote the partial hydrolysis of 2,6-bis(imino)pyridyl ligands to yield keto-imine derivatives. The formation of the ion pair [Fe(ligand)₂]²⁺/[FeCl₄]^{2–}, authenticated by X-ray crystallography for some bis(imino)pyridyl complexes, has been invoked to account for the cases of inactivity [46,62–64].

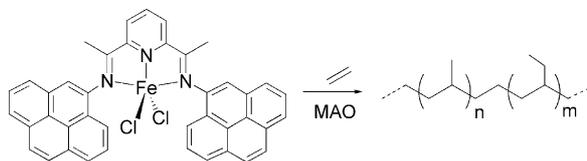
All the HDPEs produced by 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} catalysis appear as semicrystalline off-white solids and exhibit high melting points (133–139 °C) accompanied by remarkably high heats of fusion (ΔH = 220–230 J/g versus 170 J/g for commercial HDPE produced by ZN, Cr or metallocene catalysis). The molecular weights are generally high (M_w in the range 14,000–61,1000) in function of several factors (vide infra). The polydispersity, M_w/M_n , may equally vary in a broad range, from 2.6 to 144 depending on the reaction conditions. Bimodal distributions have been observed for high values of polydispersity.

The absence of branches on the polymer chains indicates that the Fe^{II} and Co^{II} polymerization catalysts neither are able to isomerize the produced alkyl via a chain-walking mechanism as occurs for Ni^{II} and Pd^{II} α -diimines [9–22], nor incorporate significantly early-produced α -olefins into the growing polymer chain (vide infra). In agreement with the scarce propensity of Fe/Co-alkyls to accommodate a *cis*- α -olefin, even the most reactive iron systems do not catalyze propene polymerization to a large extent [75].

Despite the huge amount of work and the many available structural variations, there has been only one report claiming for the formation of a PE with a microstructure containing branches. Abu-Surrah and co-workers have reported that 2,6-bis(imino)pyridyl Fe^{II} and Co^{II} precursors bearing bulky, alkyl-free aromatic terminals such as naphthyl, pyrenyl, 2-benzylphenyl are active for the polymerization of ethylene to



Scheme 12. High-density PE by 2,6-bis(imino)pyridyl Fe^{II} or Co^{II} catalysis.



Scheme 13. Branched PE obtained with 2,6-bis(imino)pyridyl iron(II) complexes bearing alkyl-free large aromatic groups at the imino nitrogen donors.

give either linear or methyl- and ethyl-branched PE (Scheme 13) [35]. The branching mechanism is still obscure, however.

Besides the molecular structure of the catalyst, MAO concentration, ethylene pressure and reaction temperature influence the catalyst productivity as well as the material properties.

Increasing the concentration of MAO increases the productivity of both Fe and Co catalysts, but, exclusively for the Fe-catalyzed reactions, it also leads to a bimodal molecular weight distribution, accompanied by the formation of increasing amounts of low molecular weight material. The enhanced productivity in the presence of a large excess of MAO has been attributed to the generation of a larger number of active sites, whereas the bimodal distribution of the PE has been related to the increased concentration of AlMe_3 in the reaction mixtures. Indeed, the residual AlMe_3 , contained in commercial MAO solutions, can favor termination by chain-transfer to aluminum over termination by β -H transfer (see Section 7.2) in the early stages of the polymerization. For this reason, NMR end group analysis of PE produced by Fe catalysis shows always a larger number of saturated end groups as compared to vinyl end groups. In contrast, in the HDPE produced by Co catalysis, the ratio between the numbers of vinyl and saturated end groups is approximately equal to 1 irrespective of the MAO concentration because cobalt catalysts do not terminate by chain-transfer to aluminum (see Section 7.2).

The productivity increases linearly with the ethylene concentration which is consistent with a first-order rate dependence on monomer as expected for a Cossee–Arlman chain-propagation mechanism (see Section 7.2). On the other hand, since the polymer molecular weight does not vary with the ethylene pressure, also the chain-transfer rate is first order in monomer concentration [27–32].

Both the productivity and the molecular weight decrease with increasing temperature due to the lower solubility of ethylene as well as the enhanced rate of catalyst deactivation at high temperature.

Since the early studies by Brookhart and Gibson, several research groups have been involved in the design of new bis(imino)pyridyl ligands and their use in ethylene polymerization (Table 1). A great deal of work has been focused on structural-activity relationships, involving both metal precursors and activators. As shown in Table 1, a large variety of catalyst precursors have been synthesized where the ligand structure has been varied as systematically as possible, especially as regards (i) variation on the central pyridine donor core [40,41]; (ii) change of the substituents at the imine carbon atoms (Ph, OR, SR) [40,43]; (iii) substitution of alkyl groups on the imino aryl rings with groups of different electronegativity (Cl, Br, CF_3)

[45,46,48,52]; (iv) substitution of alkyl groups on the imino aryl rings with cycloalkyl groups [36]; (v) replacement of the 2,6-alkylphenyl moiety with other bulky systems (arylates, NR_2) [34,35,39,51]; (vi) use of ion-pair precatalysts [47]; (vii) use of precatalysts bearing unsymmetrical ligands [39,49].

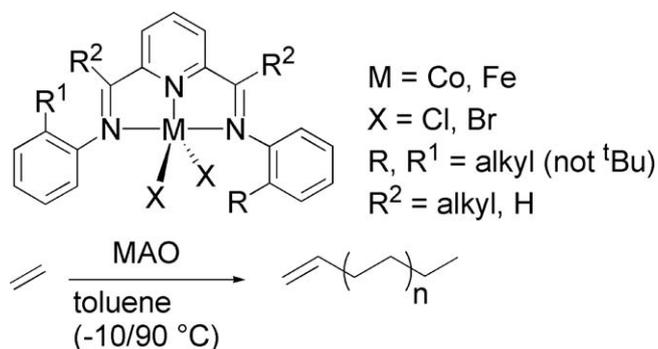
In addition to the mandatory presence of bulky substituents in the *ortho*-positions of the N-aryl groups, the polymerization activity of 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} precursors is apparently affected by other factors, both structural and electronic in nature. However, no clear-cut understanding of their role has been provided in many cases. This is particularly true for the Fe^{II} ion due to its d^6 electronic configuration that may give rise to a variety of low- and high-spin states (see Section 3.1). Just to make an example of the importance of the electronic structure on the catalytic activity, a metal atom net charge correlation (MANCC) analysis of the relation between the net charge on the Fe^{II} center and the catalytic activity of 20 complexes for ethylene polymerization/oligomerization has surprisingly indicated that the activity increases with the net charge in the lower charge area, while it increases with reducing the net charge in the higher area [113].

Besides electronic factors, even very subtle structural factors may have a role in determining the catalytic activity of 2,6-bis(arylimino)pyridyl Fe^{II} complexes as shown, for example, by the increased activity at high temperature of precursors bearing cycloalkyl substituents on the aryl rings versus analogous complexes with alkyl substituents [36]. A quantum mechanical study has proposed that the structure of the *ortho*-substituents (cycloalkyl versus alkyl) in the phenyl rings does not affect the reaction energies for the transformation of the precursors into the active catalysts, rather the cycloalkyl substituents increase the thermal stability of the precursors [36].

6. Ethylene oligomerization by 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} catalysts

α -Olefins are currently produced at a rate of more than 2×10^6 t/year predominantly through the oligomerization of ethylene. These linear oligomers are extensively used for the preparation of detergents, plasticizers and, most importantly, as comonomers in the polymerization of ethylene to give LLDPE. A successful example of late transition metal technology to α -olefin production is the SHOP process that uses Ni^{II} stabilized by chelating monoanionic P,O-ligands [65–69].

It is now apparent that bis(arylimino)pyridyl Fe^{II} and Co^{II} complexes bearing a single *ortho*-substituent on the aryl rings are a valid alternative to known late transition metal catalysts in terms of both activity and selectivity. Indeed, on activation by MAO, bis(arylimino)pyridyl Fe^{II} and Co^{II} complexes form selective catalysts for ethylene oligomerization to α -olefins with Schulz–Flory distribution and TOFs as high as 10^6 mol C_2H_4 (mol catalyst \times h \times bar) $^{-1}$ (Scheme 14) [29,30,32]. The selectivity in linear products is generally very high (>95%), while the α parameter, characteristic of any Schulz–Flory distribution (Eq. (1)), is typically in the range between 0.65 and 0.85 (95% formed by C_4 – C_{40} oligomers). Instead of α , some authors use the notation β to characterize a Schulz–Flory distribution of α -



Scheme 14. α -Olefins with Schulz–Flory distribution produced by generic 2,6-bis(imino)pyridyl Fe^{II} or Co^{II} catalysts.

olefins (Eq. (2))

$$\alpha = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of chain transfer}} = \frac{\text{moles of } C_{n+2}}{\text{moles of } C_n} \quad (1)$$

$$\beta = \frac{\text{rate of chain transfer}}{\text{rate of propagation}} = \frac{1 - \alpha}{\alpha} \quad (2)$$

Lower α values (i.e., minor production of higher α -olefins) can be achieved by either increasing the reaction temperature or decreasing the bulkiness of the alkyl substituents.

Like for polymerization, the oligomerization activity depends on the catalyst structure, and, in particular on the metal, the ketimine/aldimine ligand architecture and the steric hindrance of the *ortho*-substituent. To summarize, the activity decreases in the orders $\text{Fe}/\text{ketimine} > \text{Fe}/\text{aldimine} > \text{Co}/\text{ketimine} > \text{Co}/\text{aldimine}$ and $\text{Me} > \text{Et} > i\text{-Pr}$. Co^{II} catalysts are invariably less active than Fe^{II} ones by one to two orders of magnitude, while the ketimine catalysts are generally three times more active than the aldimine analogues [29,30,32].

At high ethylene conversion, after substantial buildup of α -olefins, Brookhart has found that Fe^{II} catalysts modified with *ortho*-mono-methyl or mono-ethyl substituted ligands produce also small but appreciable amounts of branched α -olefins due to re-incorporation of α -olefins into oligomers made later in the reaction [29]. Independent experiments with ethylene/1-pentene yielding also odd carbon number oligomers confirmed unambiguously the re-incorporation mechanism.

Besides the structure of the supporting 2,6-bis(imino)pyridyl ligand, the oligomerization activity is affected by a number of experimental parameters, which include ethylene pressure, type and concentration of activator, temperature, catalyst concentration, solvent, reaction time and volume of the reactor. A representative example in this sense is provided by *ortho*-methyl-[2,6-bis(imino)pyridyl] Fe^{II} and Co^{II} dihalides that, depending on the choice of the previous parameters, exhibit TOFs ranging, for iron, from 4.6×10^4 to 4.4×10^6 and, for cobalt, from 0.4 to $3.8 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol catalyst} \times \text{h} \times \text{bar})^{-1}$ [29,30,32].

In an attempt of establishing relationships between oligomer distribution and molecular structure of the catalyst, several authors have systematically varied the nature and position of

the substituents on the N-aryl rings. The additional presence of methyl substituents in the *meta*-positions of the aryl rings in *ortho*-methyl substituted Fe^{II} and Co^{II} catalysts increases the activity with little effect on the oligomer distribution [32,44]. Noteworthy, the Fe catalysts show the best activity with 2,3-dimethyl substituted aryl rings [32,44], while the corresponding Co catalysts are most active with methyl substituents in both 2 and 5 positions [44].

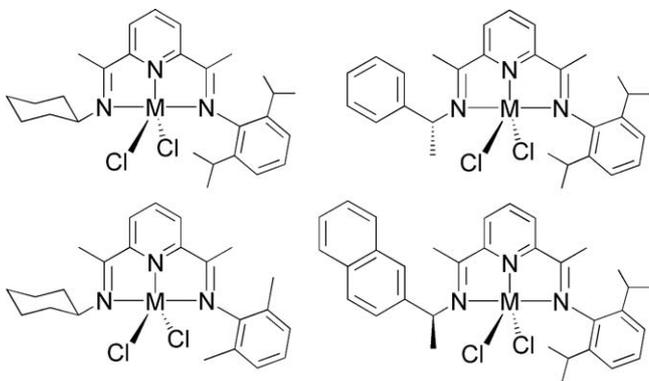
Introduction of chlorine substituents in either *meta*- or *para*-positions of the aryl rings of *ortho*-methyl substituted Fe precursors leads to catalysts capable to oligomerize selectively ethylene to linear α -olefins (>98%) with Schulz–Flory distribution and yields higher than those reported for bis-alkyl substituted catalysts [60]. No explanation has been provided, however, for the simultaneous production of an insoluble polymer.

Unlike the additional presence of methyl in the *meta*-positions, alkyl or alkoxyethyl groups in *para*-positions reduce the catalyst activities [32,44,58].

Even bis(imino)pyridyl Fe^{II} complexes with substituents in only *meta*- or *para*-positions of the imino-aryl rings ($\text{Ar} = m\text{-CF}_3\text{-C}_6\text{H}_4, p\text{-CF}_3\text{-C}_6\text{H}_4, m\text{-OMe-C}_6\text{H}_4, p\text{-OMe-C}_6\text{H}_4$) are able to produce oligomers. However, both the catalytic activity ($1\text{--}7 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol Fe} \times \text{h} \times \text{bar})^{-1}$) and the selectivity for α -olefins (<88%) are relatively low as compared to alkyl-substituted analogues, while the distribution of oligomers obtained is much narrower ($\alpha = 0.30\text{--}0.36$; 95% formed by $\text{C}_4\text{--C}_8$ oligomers) [59].

Electron-withdrawing substituents, such as CF_3 , in *ortho*-position exert a beneficial effect on the activity of bis(imino)pyridyl Co^{II} catalysts affording, on activation by MAO, a much higher activity (3.0×10^5) as compared to that of their alkylated derivatives ($3.8 \times 10^3 \text{ mol C}_2\text{H}_4 (\text{mol Co} \times \text{h} \times \text{bar})^{-1}$) [48]. The CF_3 -substituted catalyst gave a little broader oligomer distribution than that of the non-fluorinated catalyst (α parameter 0.73 versus 0.57). Kinetic studies have shown that the trifluoromethyl catalyst significantly outperforms the non-fluorinated one in terms of both maximum activity and catalyst lifetime [48]. The much higher peak activities and the longer catalyst lifetimes have been interpreted in terms of improved catalyst stability provided by the CF_3 group. Addition of extra fluorine atoms to the ligand framework enhances the turnover rates ($3.7 \times 10^5 \text{ mol C}_2\text{H}_4 (\text{mol Co} \times \text{h} \times \text{bar})^{-1}$). However, no clear explanation has been given for the simultaneous production of approximately 10% low molecular weight PE. An analogous beneficial effect in terms of catalytic activity has been also observed for the corresponding Fe^{II} catalysts [48]. In this case, however, the substitution of CF_3 for CH_3 increases the molecular weight as solid PE instead of liquid oligomers is obtained (vide infra).

Several Fe^{II} and Co^{II} complexes containing *ortho*-halogen (F, Cl, Br, I) in the imino-aryl rings have been employed as catalyst precursors, obtaining interesting results [46,62–64]. For comparative purposes, additional substituents such as F and Me have been also introduced in other positions of the aryl rings [63,64]. All of the Co complexes as well as the Fe complex containing only a single *ortho*-F substituent on each ring are inactive for ethylene oligomerization. The inactivity of the Fe



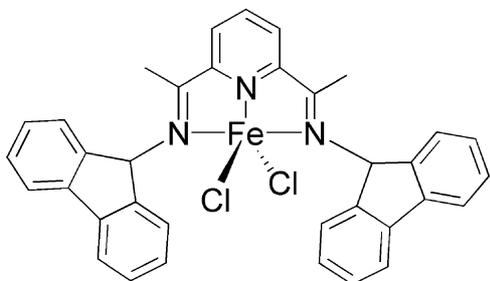
Scheme 15. Oligomerization Fe^{II} and Co^{II} catalyst precursors with C_s and C₁ symmetry.

catalyst has been related to its ion-pair structure [46,62,63]. The activities of the Co catalysts are in the aryl-substitution order *o*-I < *o*-Br < *o*-Cl < bis(*o*-F) and range between 0.3 and 4 × 10⁵ (mol Co × h × bar)⁻¹. It is noteworthy that the F-substituted Fe catalysts produce oligomers with both a high selectivity for α-olefins (>93%) and a narrower distribution (α in the range from 0.33 to 0.44) than that obtained with ligands bearing Cl, Br or I (α = 0.59–0.83) as well as alkyl derivatives (α = 0.65–0.85).

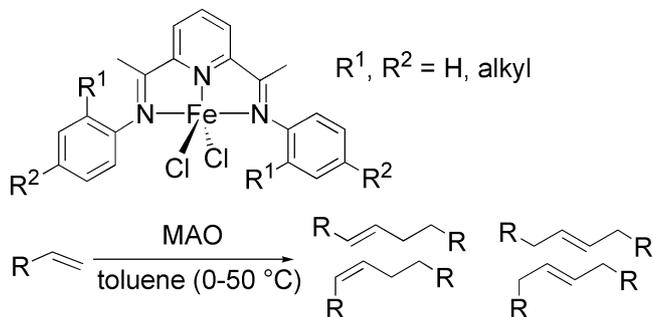
Dissymmetric 2,6-bis(imino)pyridyl ligands containing alkyl/aryl(1) or aryl(2) substituents at the ketimine nitrogen atoms (alkyl = Cy, CH₂Ph; aryl(1) = Ph; aryl(2) = 2,6-Me(C₆H₃), 2,6-*i*-Pr(C₆H₃)) form with CoCl₂ and/or FeCl₂ effective and selective (>93%) catalysts for the oligomerization of ethylene to SF distributions of α-olefins (α = 0.61–0.79) (Scheme 15) [49,55].

The iron catalysts exhibit TOFs as high as 1.2 × 10⁵ (mol Co × h × bar)⁻¹ and are much more active than their cobalt analogues. With appropriate combinations of the substituents (alkyl = CH(Me)Ph, CH(Me)Naph; aryl(1) = 2-Me(C₆H₄); aryl(2) = 2,6-*i*-Pr(C₆H₃)), it has been also possible to achieve the simultaneous production, in the same reactor, of both HDPE and α-olefins (see Section 8) [49].

Finally, a bis(imino)pyridyl Fe^{II} complex bearing fluorenyl terminals at the imino nitrogen atoms (Scheme 16) has been reported to oligomerize selectively ethylene to C₄–C₁₀ olefins [39]. This is the only reported oligo/polymerization catalyst containing non-aromatic substituents at both imine nitrogen atoms. The loss of a hydrogen atom from the N-CH group, on activation



Scheme 16. Fluorenyl-substituted 2,6-bis(imino)pyridyl Fe^{II} complex for ethylene oligomerization.



Scheme 17. Head-to-head dimerization of α-olefins by 2,6-bis(imino)pyridyl Fe^{II} catalysts.

of the precursor by MAO, has been proposed as the key factor for the observed activity.

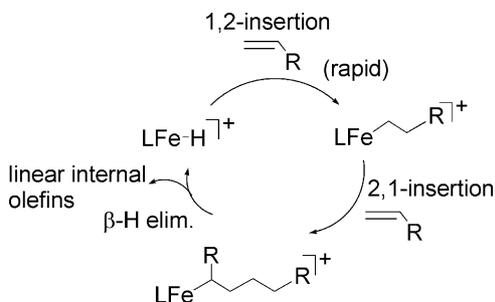
6.1. α-Olefin dimerization to internal olefins

In 2001 Small and Marcucci showed that bis(arylimino)pyridyl Fe^{II} dihalides bearing unencumbered aryl rings (Ar = Ph, 2-Me(C₆H₄), 2-Et(C₆H₄), 2,4-Me(C₆H₃), C₈H₁₁) can form active catalysts for the linear (head-to-head) dimerization of α-olefins (1-butene, 1-hexene, 1-decene, Chevron Phillips' C_{20–24} α-olefin mixture) on activation with either MAO or Lewis-acid/trialkylaluminum combinations (Scheme 17) [53]. The 2,6-dimethyl substituted complex still gave dimers, yet in much lower yield.

The dimers (83–95% selectivity) exhibit ca. 80% linearity depending on the catalysts structure and the reaction conditions. The predominant dimerization mechanism is consistent with an initial olefin 1,2-insertion in a Fe-H species, followed by a 2,1-insertion of the second olefin, resulting in organometallic complexes that undergo chain-transfer to produce linear dimers (Scheme 18).

Common byproducts of these reactions are methyl-branched dimers, which may result from two successive 2,1-insertions, followed by chain termination, and olefin trimers. The undimerized substrate may also contain, even though in low amounts, isomerized olefins due to chain-transfer following an initial 2,1-insertion.

The head-to-head dimerization of α-olefins is not an exclusive prerogative of Fe^{II} catalysts as also bis(imino)pyridyl Co^{II} complexes (Ar = Ph, 2-Me(C₆H₄), 2-Et(C₆H₄), 2-*i*-Pr(C₆H₄)) promote such a dimerization, in particular with 1-butene [54].



Scheme 18. Proposed mechanism for Fe-catalyzed linear dimerization of α-olefins.

The activity of the Co catalysts has been reported to be much lower than that of analogous Fe systems, whereas both the selectivity in dimeric products (97–99%) and the linearity (over 97%) are generally higher. Unlike related Fe systems, the Co complexes prove able also to isomerize 1-butene to give substantial quantities of 2-butene as well as dimerize propene. Linear hexenes, nonenes, and dodecenes have been obtained with the hexenes comprising up to 70% of the product mixture. The hexenes are over 99% linear and may contain over 50% 1-hexene.

Oligomerization of propene, 1-butene, and 1-hexene has been also achieved by using Fe^{II} and Co^{II} systems containing electron-withdrawing CF₃ substituents in *ortho*-aryl positions [48]. Interestingly, the catalysts containing an extra fluorine atom in the other *ortho*-position of the aryl rings, are two orders of magnitude more active than the non-fluorinated analogues. Highly linear dimers predominate in each case, the remainder being formed by trimeric and tetrameric products. The principal product of propene dimerization was 1-hexene (60–73% of total), whereas for 1-butene and 1-hexene internal olefins with *E* configuration were obtained. No isomerization of 1-hexene occurred under analogous reaction conditions. The catalysts have been similarly proposed to operate by a mechanism involving 1,2-insertion, followed by 2,1-insertion (Scheme 18).

7. Proposed mechanisms for activation, initiation, chain-propagation and chain-transfer in ethylene polymerization/oligomerization catalyzed by 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} precursors

Unlike α -diimine Ni^{II} and Pd^{II} precursors, no 2,6-bis(imino)pyridyl Fe^{II} or Co^{II} catalyst with either alkyl or hydride co-ligands polymerizes ethylene in the absence of aluminum activators. This has certainly contributed to overshadow the catalytically active species as the excess of activator makes in situ spectroscopic studies unable to provide useful information. Moreover, the catalyst precursors are not amenable to be studied by NMR spectroscopy due to their paramagnetic nature. Therefore, most of the proposed polymerization mechanisms are still based on either analysis of the polymeric materials (especially, the nature of the end groups, M_n and M_w , and model organometallic and theoretical studies).

7.1. Activation and initiation

7.1.1. Fe^{II} precursors

The activation of 2,6-bis(organylimino)pyridyl Fe^{II} dihalides by MAO is still a matter of debate, especially as regards the metal

oxidation state in the activated species. Early theoretical studies by Gould [114] and Morokuma [115] suggested the initial formation of cationic monoalkyl Fe^{II} species [FeMeL]⁺, likely by methyl abstraction from dialkyl complexes. Later, Mössbauer and EPR studies led Gibson to conclude that the Fe^{II} centers in the precatalysts are oxidized by MAO to Fe^{III} species, which may be either dications [FeMeL]²⁺ or chloride-alkyl compounds [Fe(Cl)MeL]⁺ [86]. Experimental evidence (in situ ¹H NMR and EPR spectroscopy) has been recently provided by Talsi for the reduction of L-Fe^{III} to L-Fe^{II} derivatives by MAO as well as the active participation of Fe^{II} species in the polymerization process [116]. It is now generally agreed that trialkylaluminum reagents, including MAO, bind Fe^{II} centers to give neutral catalytically active species, but the formation of ion pairs of type shown in Scheme 19 cannot be not excluded [117–119].

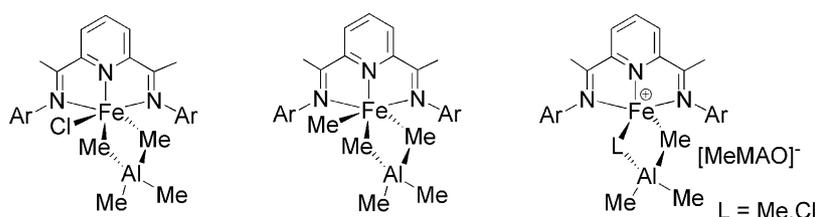
Given for granted that the neutral species shown in Scheme 19 are precursors to catalytically active sites, it is still unclear the mechanism of ethylene coordination, which apparently involves unfastening of a ligating group from the iron coordination sphere to accommodate the incoming monomer. In view of the broad molecular mass distribution of the HDPE obtained with these systems, it is also possible that a set of different active metal centers are formed in catalytic conditions, depending on the activator and its concentration [117–119].

The activation process of FeCl₂L complexes by MAO (L = 2,6-(2,6-(*i*-Pr)₂C₆H₃N=CMe)₂C₅H₃N; 2,6-(2-MeC₆H₄)N=CMe)₂C₅H₃N) has been studied by Schmidt by means of UV–vis spectroscopy [120]. Remarkable spectral changes, associated with the formation of catalytically active species, were observed with time, temperature and MAO concentration. In particular, the absorbances at long wavelengths due to *d* transitions decreased with time, which may indicate a Fe-centered spin transition. As a general trend, both the polymerization (2,6-*i*-Pr substituted ligand) and oligomerization (2-Me substituted ligand) activity decreased with the time elapsed after MAO addition.

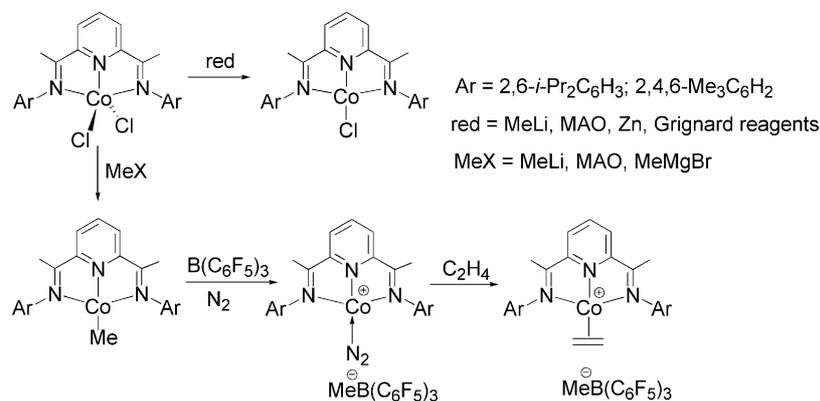
Valuable information on the activation by MAO of FeCl₂L (L = 2,6-(2,6-(*i*-Pr)₂C₆H₃N=CMe)₂C₅H₃N) has been also provided by electrospray ionization tandem mass spectroscopy (ESI-MS). Applying this technique in THF as solvent, Repo has been able to intercept some four-coordinated Fe^{II} species which include the alkyl [FeMeL]⁺, the monochloride [FeClL]⁺, the hydride [FeHL]⁺ and [FeCH₂AlMe₂L]⁺ resulting from α -H-transfer from the Fe^{II} alkyl to AlMe₃ [121].

7.1.2. Co^{II} precursors

It has been independently demonstrated by Gibson and Gal that the CoX₂L precursors are converted into diamagnetic



Scheme 19. Structure of the active Fe^{II} species involved in ethylene polymerization by 2,6-bis(arylimino)pyridylFeCl₂/MAO catalysis.

Scheme 20. Synthetic procedures to 2,6-bis(arylimino)pyridyl Co^I complexes.

square-planar complexes CoXL by MAO (1 equiv.) as well as by other alkylating or reducing agents (Scheme 20) [122,123]. On further addition of activator, the CoXL complexes are transformed into methyl derivatives CoMeL. Unequivocal evidence of the reaction paths summarized in Scheme 20 has been obtained by means of various reducing and alkylating agents [122–124].

Most authors describe the square-planar halide or alkyl complexes as containing Co^I centers. However, on the basis of anomalous ¹H NMR chemical shifts in the spectra of CoMeX and CoMeL as well as DFT calculations, Budzelaar has proposed that the singlet ground state may be due to a square-planar, low-spin Co^{II} center antiferromagnetically coupled to a ligand radical anion, i.e., the reduction of high-spin CoX₂L to low-spin CoXL would occur at the ligand rather than at the metal [125]. Whatever the cobalt oxidation state, the square-planar methyl complexes are not catalysts for ethylene polymerization. Indeed, for ethylene activation is required the presence of a strong Lewis-acid (MAO or B(C₆F₅)₃, for instance): abstraction of the methyl ligand by the latter allows for the coordination of ethylene to give a π-adduct that produces HDPE upon treatment with excess ethylene. However, both isolated ethylene adducts and other cationic [CoL]⁺Y⁻ precatalysts (Y = acac, chloride, MeCN, B(C₆F₅)₄) are far less active than comparable systems generated in situ by reaction of CoX₂L precursors with an excess of activator [47,122,123]. This observation has stimulated much research aimed at understanding the manner in which polymer-

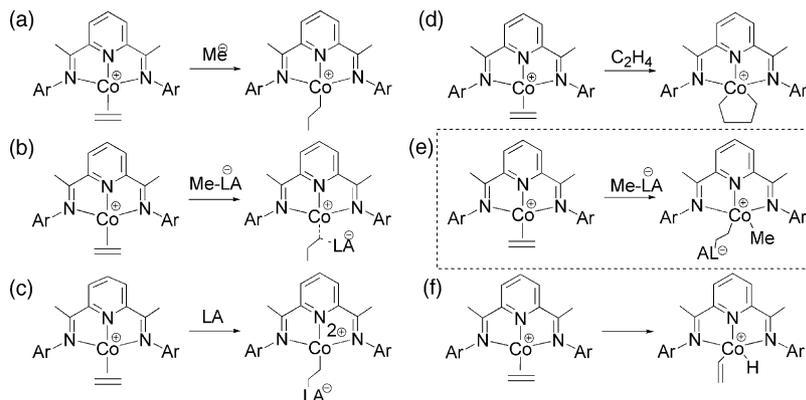
ization is initiated from the Co^IL cations. To this purpose, the π-ethylene adducts have served as excellent model compounds as shown in Scheme 21 that reports the initiation mechanisms investigated.

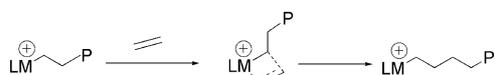
Based on a number of independent reactions with isolated compounds as well as deuterium labeling studies [126], Gibson has unequivocally demonstrated that the initiation of polymerization from Co^I cationic species involves incorporation of methyl groups from non-coordinating [Me-MAO]⁻ anions. The incorporation occurs at the saturated ends of the polyethylene chains, consistent with an activation mechanism that involves nucleophilic attack by an abstracted methyl group on the cationic π-ethylene species (path e, dashed box in Scheme 21).

The small amount of HDPE obtained by using isolated cationic precursors with no need of activator (hence of nucleophilic attack by abstracted methyl) is apparently produced via different mechanisms [122,123,126] that Gibson limits to paths d and f as their occurrence does not contrast with any experimental observable [127].

7.2. Propagation and chain-transfer

Once the metal binds a methyl group and a free coordination site is available for ethylene, the propagation is believed to proceed via the Cossee–Arman mechanism, which involves sequential steps of monomer coordination, followed by ethylene migratory insertion via four-centered transition states

Scheme 21. Possible mechanisms for the initiation of polymerization from π-ethylene Co^I precursors (LA represents a Lewis-acid).



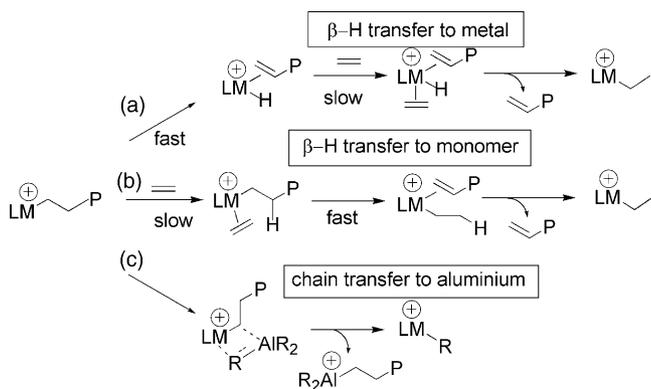
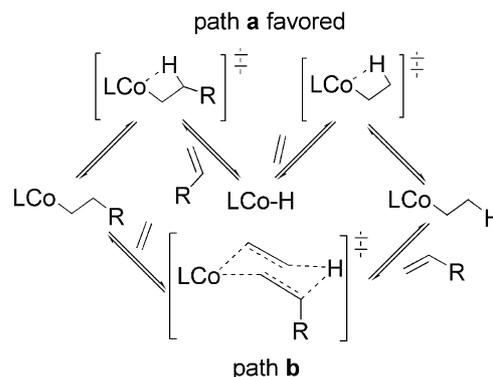
Scheme 22. Cossee–Arlman mechanism of chain-propagation.

(Scheme 22) [128,129]. Propagation continues until chain-transfer occurs. At this point, a macromolecule is freed and, provided a catalytically active site is re-generated, a new chain starts to form.

Consistent with the occurrence of a Cossee–Arlman mechanism, the propagation rate of ethylene polymerization/oligomerization by 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} catalysts activated by MAO is first-order in monomer concentration (i.e., pressure). Moreover, since the polymer molecular weight does not vary with the ethylene pressure, also the overall rate of chain-transfer is first order in monomer concentration [29,31]. These findings have contributed to limit the number of the possible β -H transfers to paths a and b where termination occurs by kinetically indistinguishable H-transfers to metal and monomer, respectively (Scheme 23).

A bimodal molecular weight distribution for increasing MAO concentrations has been uniquely observed for Fe^{II} catalysts, which is consistent with chain-transfer to aluminum (path c in Scheme 23). In a similar way, the occurrence of alkene isomerization during ethylene oligomerization by Co^{II} catalysts, and not by Fe^{II} catalysts, has suggested that β -H transfer to metal is more important for Co than for Fe [29,31]. This has been confirmed by an experimental and theoretical study of β -H transfer between Co^{I} alkyl complexes and ethylene or 1-alkenes. The prevailing occurrence of the dissociative mechanism (path a) has been suggested by the small entropy of activation as well as the independence of the reaction rate on ethylene pressure (Scheme 24) [130].

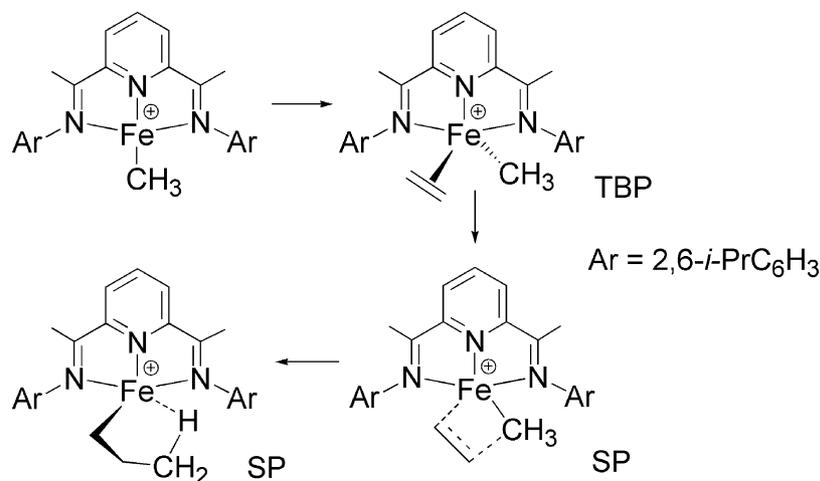
Several theoretical studies of the mechanisms of propagation and chain-transfer in ethylene polymerization have been carried out. The first theoretical study was reported by Gould and Gibson soon after the discovery of the polymerization activity of 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} dihalides [114]. Ab initio calculations provided information on the coordination geometries of key Fe^{II} cations involved in the propagation: distorted square-planar for $[\text{LFe-Me}]^+$, distorted trigonal-

Scheme 23. Proposed mechanisms for chain-transfer in ethylene polymerization by 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} catalysts.Scheme 24. Pathways for β -hydrogen transfer in 2,6-bis(imino)pyridyl Co^{II} -alkyl complexes.

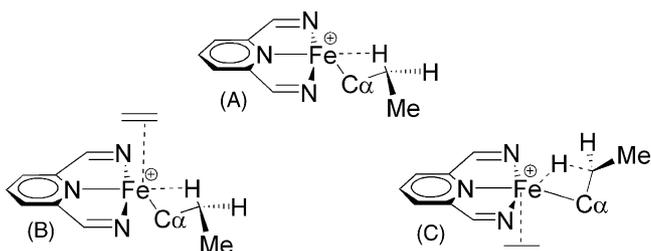
bipyramidal (TBP) for $[\text{LFe}(\text{C}_2\text{H}_4)\text{Me}]^+$, distorted square-pyramidal (SP) for the four-centered transition state, distorted square-pyramidal with γ -agostic interaction for the insertion product $[\text{LFeCH}_2\text{CH}_2\text{CH}_3]^+$ (Scheme 25).

The theoretical study by Gould and Gibson has been later substantiated experimentally by Chirik who reported the synthesis and reactivity of the square-planar cationic Fe^{II} alkyl $[\text{Fe}(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3)(2,6-(2,6-i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ [131]. The latter complex catalyzes, with no need of activator, ethylene polymerization, yielding HDPE with good productivity ($218 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$), only slightly lower than that obtained with the corresponding dichloride/MAO system under comparable conditions ($942 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$).

Detailed theoretical studies on the Fe^{II} catalysts have been reported by Morokuma [115] and Ziegler [132]. These authors investigated the behavior of both generic model compounds and real systems, with a special emphasis on the different metal spin states during propagation and β -H transfer paths. Both authors concluded that quintet and triplet states are preferred over singlet in the real systems. Morokuma confirmed the experimental observable according to which the inclusion of two bulky *ortho*-substituents on the N-aryl groups (as in the real Fe^{II} polymerization catalyst, vide infra) results in steric destabilization of the axial positions, which makes chain-transfer no longer competitive with chain-propagation. The latter would take place on triplet and quintet potential energy surfaces [115]. Based on QM/MM calculations on the real system bearing 2,6-*i*-Pr substituents, Ziegler found that the agostic conformation of the propagating alkyl **A** in Scheme 26 is more stable than any other alkyl conformer, with or without agostic interactions [29,31]. Complex **A** was proposed to be the catalyst resting state. The addition of ethylene at the vacant axial site *trans* to C_α was hindered by the N-aryl groups, resulting in a substantial barrier to ethylene addition. However, since the resulting π -ethylene adduct **B** can lead to chain termination via β -H-transfer, the steric destabilization of this species would have a beneficial effect on the polymerization. In contrast, the formation of **C** via backside attack of ethylene at **A** is less sensitive to the steric hindrance exerted by the aryl groups, and hence is favored over generation of **B**.



Scheme 25. Propagation mechanism proposed by Gould and Gibson.

Scheme 26. Favored conformations of propagating Fe^{II}-alkyl complexes in ethylene polymerization.

The formation of **C** does not require much energy: it suffers from the electronic penalty associated with bringing C_α into an equatorial position, which, however, is alleviated by a spin-state change from the quintuplet to the triplet potential energy surface. Once formed **C** can undergo monomer insertion into the growing polymer chain with only a negligible barrier. In this picture, termination via β-H transfer is not as favourable as insertion. In conclusion, Ziegler's study indicates that the rates of chain-propagation and chain-transfer in ethylene polymerization by Fe^{II} catalysis are determined by the formation of **B** and **C** and not by the subsequent insertion or termination steps, respectively.

The theoretical studies of ethylene polymerization/oligomerization by 2,6-bis(diarylimino)pyridyl Co^{II} complexes are less numerous and less important than those reported for analogous Fe^{II} catalysts [130,133]. The energetics for chain-propagation and chain-transfer have been primarily investigated by Ziegler who was unable to precisely determine the favored chain-transfer mechanism, whereas he contributed to rationalize steric effects affecting propagation and chain-transfer in real catalytic systems [133].

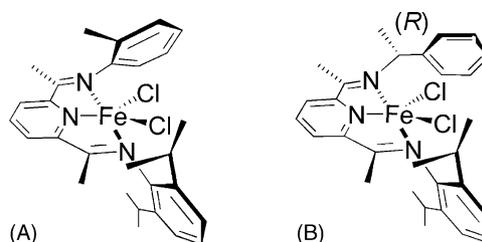
8. Simultaneous oligomerization/polymerization of ethylene by C₁-symmetric 2,6-bis(organylimino)pyridyl Fe^{II} precursors

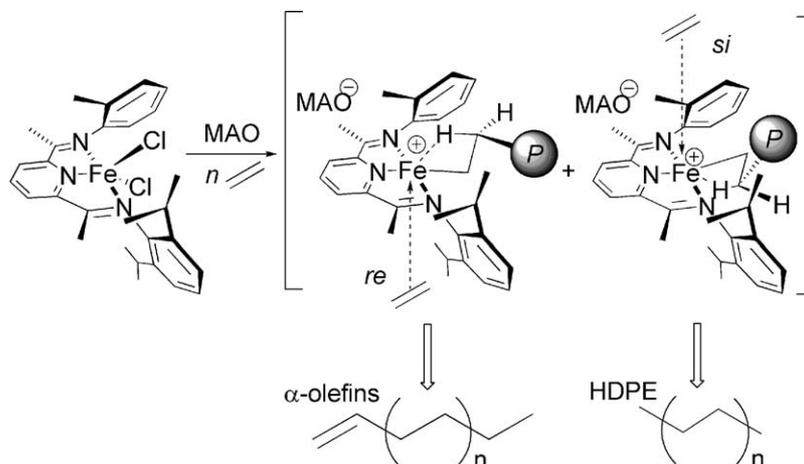
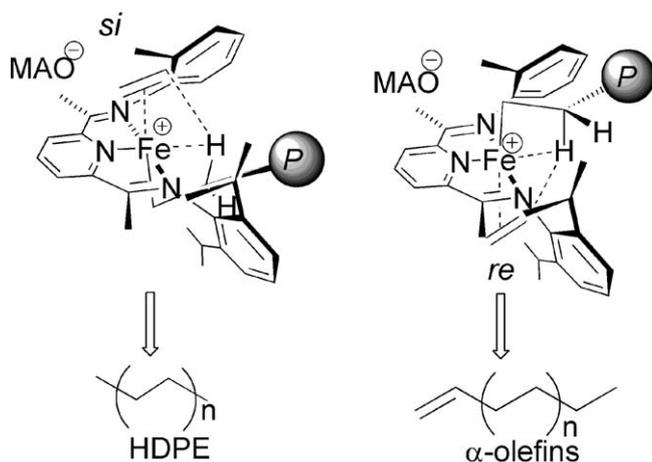
As unequivocally demonstrated in previous sections, the number, nature and position of the substituents on the aryl rings play a crucial role in driving the catalytic activity of 2,6-

bis(organylimino)pyridyl Fe^{II} precursors selectively towards either polymerization or oligomerization. However, it is also possible to achieve the simultaneous production, in the same reactor, of both HDPE and α-olefins using a single C₁-symmetric [2,6-bis(arylimino)pyridyl]iron catalyst [49] Scheme 27 shows drawings of the Fe^{II} dichloride precursors **A** and **B**. The C₁ symmetry of the tolyl-2,6-*i*-PrC₆H₃ derivative **A** is occasioned by hindered rotation of the aryl groups, while **B** is optically pure due to the presence of a stereogenic, stereohomogeneous carbon center [55].

On reaction with MAO, **A** generates two atropisomeric propagating β-agostic alkyl species due to hindered rotation of the tolyl group and the presence of four different donor atoms coordinated to iron (Scheme 28). Therefore, an incoming ethylene molecule will have two different faces (*re* and *si*) available at the metal for coordination and propagation [130]. The insertion through the *si* face is sterically comparable to that of [2,6-bis(arylimino)pyridyl]iron catalysts bearing two *ortho*-substituents on each aryl ring [27,31], for which the propagation rate largely prevails over the chain-transfer rate, leading to PE production. In contrast, the insertion through the *re* face is sterically comparable to that in [2,6-bis(arylimino)pyridyl]iron alkyl species bearing an unsubstituted phenyl ring at one imine nitrogen atom, which are known to produce only α-olefins.

The formation of two atropisomeric alkyl species with *si* and *re* faces for ethylene coordination has been also rationalized in terms of chain-transfer rate. Given for granted that termination by β-H transfer to monomer is important in ethylene polymerization/oligomerization by 2,6-bis(arylimino)pyridyl Fe^{II} catalysts

Scheme 27. Structures of the C₁-symmetric Fe^{II} precursors.

Scheme 28. Ethylene coordination to atropoisomeric propagating β -agostic Fe^{II} alkyls.Scheme 29. Steric effects affecting chain-transfer to monomer in atropoisomeric β -agostic Fe^{II} alkyls.

[27,31], then it is apparent that ethylene coordination (*back attack* at the Fe-alkyl) [115,132] is more disfavored at the *si* face than at the *re* face, resulting in a slower chain-transfer (Scheme 29). Therefore, the selective HDPE production might be obtained by monomer coordination at the *si* face, while α -olefins might be selectively produced by monomer coordination at the *re* face [49].

A similar interpretation has been proposed to explain the production of mixtures of HDPE and α -olefins with the C_1 -symmetric, optically pure precursor **B**. On activation of **B** by MAO, two diastereoisomeric propagating Fe^{II} alkyls are again formed which, as chemically distinct species, may have different

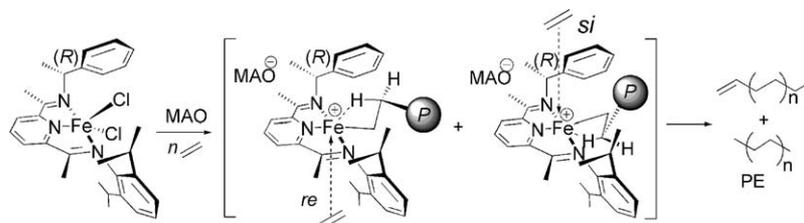
kinetics of propagation and termination and therefore give different products by reaction with the same substrate (Scheme 30).

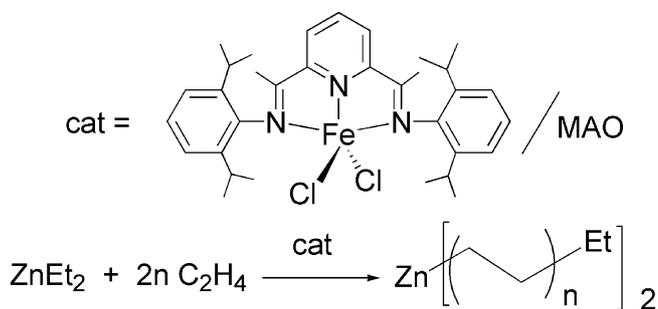
9. 2,6-Bis(arylimino)pyridyl Fe^{II} catalysts for the production of α -olefins with a Poisson distribution

The ability of 2,6-bis(arylimino)pyridyl Fe^{II} alkyls to terminate propagation by chain-transfer to aluminum has been exploited by Gibson to produce α -olefins with a Poisson distribution via iron-catalyzed polyethylene chain growth on zinc and related metals [61,134]. To this purpose was initially used the polymerization catalyst precursor FeCl_2L ($\text{L} = 2,6\text{-}(2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) in combination with MAO and ZnEt_2 (>500 equiv.) (Scheme 31).

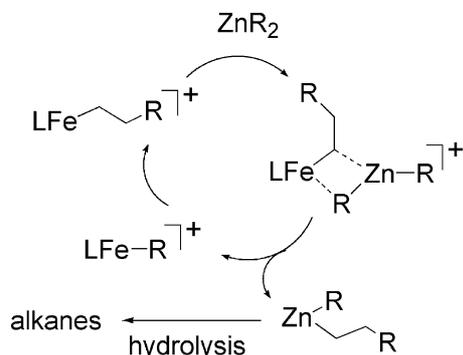
Later, other 2,6-bis(arylimino)pyridyl Fe^{II} and Co^{II} dihalides, differing from each other by the number and regiochemistry of aryl substituents, were employed to catalyze the production of a Poisson distribution of α -olefins from ethylene stock [134].

In all these systems, chain-transfer to Zn constitutes the sole transfer mechanism and the exchange of the growing polymer chain between the Fe and Zn centers is very fast and reversible. The reaction illustrated in Scheme 31 (toluene, 5 mmol catalyst, 100 equiv. MAO, 500 equiv. ZnEt_2 , 1 bar C_2H_4 , 30 min, rt) yielded a $\text{Zn}(\text{polymer})_2$ product with an activity of $1400 \text{ g}(\text{mmol} \times \text{h} \times \text{bar})^{-1}$ and, after hydrolysis, a Poisson distribution of linear alkanes [61]. The proposed reaction mechanism is shown in Scheme 32. Remarkably, the polyethylene produced was featured by a narrow molecular weight distribution (1.1) consistent with two alkyl chain per Zn center.

Scheme 30. Ethylene coordination to diastereomeric propagating β -agostic Fe^{II} alkyls.



Scheme 31. Chain growth on Zn catalyzed by a 2,6-bis(arylimino)pyridyl Fe^{II} complex.



Scheme 32. Proposed mechanism for Fe-catalyzed polyethylene chain growth on Zn.

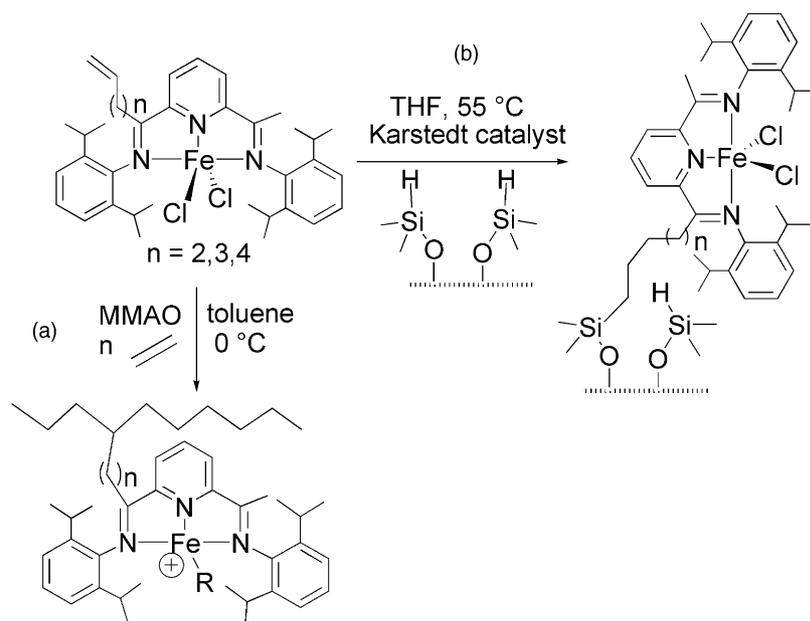
Besides ZnEt₂, other metal alkyls were investigated (AlR₃, GaR₃, *n*-BuLi, (*n*-Bu)₂Mg, BEt₃), yet none of them proved to be as active as the Zn compound, which was attributed to the low steric hindrance around the Zn center, its monomeric nature in solution and the relatively weak Zn–C bond which also matches the Fe–C bond strength [61].

10. Heterogenized 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} catalysts

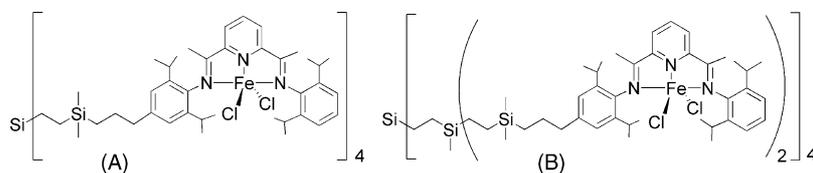
Despite BP-Amoco have recently announced a joint agreement aimed at commercializing HDPE prepared with Fe^{II} catalysts [135], the industrial application of the 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} precursors in continuous flow processes (gas phase or slurries) is still problematic due to extensive reactor fouling and the high exothermicity of the polymerization process. In order to overcome reactor fouling as well as increase the catalyst lifetime, the heterogenization of the homogeneous catalysts is considered a viable and effective technique. To this purpose, Herrmann has reported two immobilization procedures for 2,6-bis(imino)pyridyl FeCl₂ based on the functionalization of one imine carbon by different alkenyl groups [136]. Once functionalized, the ligands are used to bind FeCl₂ and then either self-immobilized by reaction with MMAO/C₂H₄ (Scheme 33a) or covalently tethered to silica *via* hydrosilylation (Scheme 33b). The immobilized catalysts were successfully employed to polymerize ethylene to give linear PEs with properties comparable to those obtained with homogeneous catalysts. The silica-tethered catalysts were more efficient than the self-immobilized ones, but less active than homogeneous counterparts. Remarkably, the silica-immobilized catalysts are thermally stable and do not give reactor fouling due to the different morphology of the polymer produced.

Polyethylene–clay nanocomposites have been prepared by *in situ* polymerization of ethylene with FeCl₂L (L = 2,6-(2,6-(*i*-Pr)₂C₆H₃N=CMe)₂C₅H₃N) supported on a modified montmorillonite pretreated with MAO [137]. A significant degree of exfoliation of the resulting materials was observed by wide-angle X-ray scattering.

Diffuse reflectance infrared spectroscopy (DRIFTS) has been employed to study the precursor FeCl₂L (L = 2,6-(2,6-



Scheme 33. Heterogenization procedures for 2,6-bis(imino)pyridyl Fe(II) complexes.



Scheme 34. The two peripherally bound iron metallodendrimers.

$\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$) supported on either silica or alumina [138]. The Fe^{II} complex retains its structure on heterogenization and is strongly anchored to the support by bonding interaction with surface functional groups. Effective ethylene polymerization activity was obtained by activation with $\text{Al}(i\text{-Bu})_3$.

Bis(imino)pyridyl ligand derivatives and their anchoring on dendrimers have been described by Li [139] and Moss [140]. The former author has reported the synthesis of two types of poly(bis(imino)pyridyl) Fe^{II} dendrimers by Pt-catalyzed hydrosilylation of bis(imino)pyridyl ligands, bearing an allyl group, with Si-H terminating carbosilane dendrimers. The polynuclear precatalysts were straightforwardly obtained by reaction with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ under standard conditions. On activation by MMAO, the two peripherally bound metallodendrimers **A** and **B** (Scheme 34) showed higher activity for ethylene polymerization than the corresponding unsupported complexes, especially at low Al/Fe molar ratio, and also produced higher molecular weight HDPE.

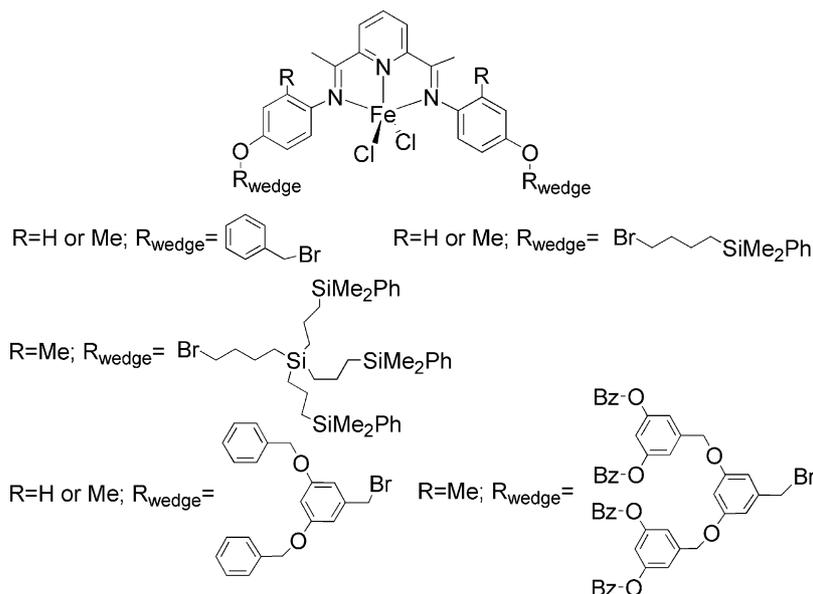
The bis(imino)pyridyl Fe^{II} complexes containing dendritic wedges reported by Moss [140] have been prepared by reacting, under typical Williamson conditions, a number of dendritic wedges containing one alkylbromide functional group with two differently *ortho*-substituted bis(*para*-hydroxyphenylimino)pyridines, followed by complexation of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Scheme 35).

On activation by MAO, these dendrimer-supported precatalysts generate active systems for ethylene oligomerization with

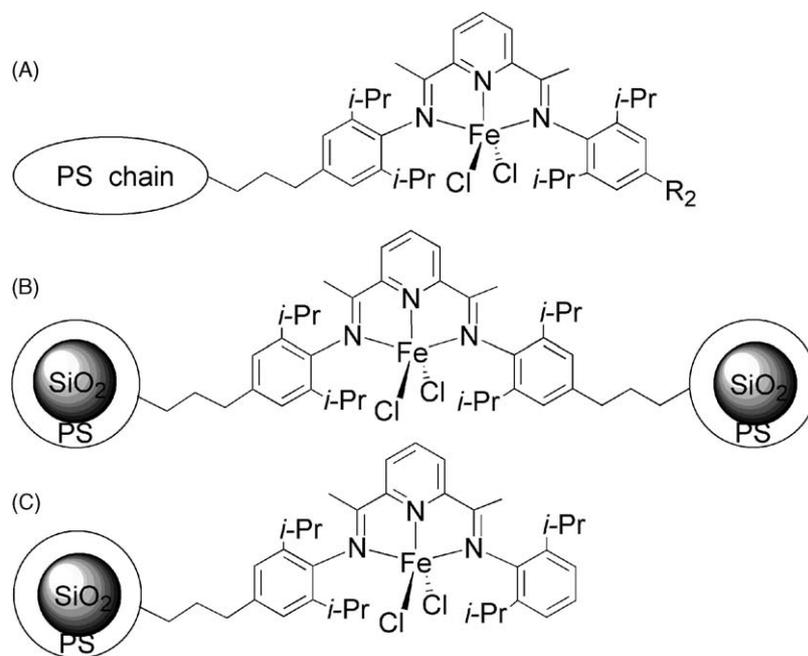
TOF as high as 1.2×10^4 and α values ranging from 0.68 to 0.75. Noteworthy, the activity of these complexes is higher than that displayed by the dendrimer-free complex and is also independent of small variations of the size of the dendritic wedge.

Covalent immobilization of bis(imino)pyridyl Co^{II} and Fe^{II} dichlorides onto silica gel has proved to be a versatile technique for the preparation of heterogeneous ethylene polymerization catalysts [141]. Silica gel-anchoring was successfully achieved by refluxing a properly hydrosilyl ligand derivative in toluene in the presence of a suspension of silica gel, followed by reaction with Fe^{II} and Co^{II} dichlorides. The main features that distinguishes the supported catalysts from the homogeneous counterparts is a lower activity (up to two orders of magnitude) and a higher molecular weight of the HDPE produced.

An original immobilization approach for bis(imino)pyridyl Fe^{II} complexes has been reported by Jin in 2002 [142]. Polystyrene incorporated pre-catalysts **A** and SiO_2 -supported shell-core polystyrene incorporated pre-catalysts **B** and **C** were prepared by radical co-polymerization of styrene with bis(imino)pyridyl Fe^{II} dichlorides bearing allyl functional groups in the presence of AIBN as radical initiator (Scheme 36). On activation by MMAO, these catalysts exhibit high activity, especially the shell-core iron catalysts that also produce high molecular weight HDPE. Interestingly, the SiO_2 -supported shell-core polystyrene incorporated catalysts exhibit a better control of the polymer morphology as compared to the solely polystyrene incorporated derivatives.



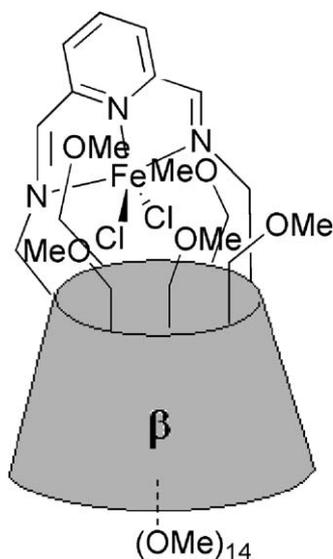
Scheme 35. Iron bis(imino)pyridyl complexes containing dendritic wedges.



Scheme 36. **A**: polystyrene-incorporated catalysts; **B** and **C**: shell-core polystyrene-incorporated catalysts.

Methylated α - and β -cyclodextrins rigidly capped with a 2,6-bis(imino)pyridyl fragment have been synthesized and the corresponding cyclodextrin-encapsulated Fe^{II} compounds have been tested as catalyst precursors for ethylene polymerization on activation by MAO (Scheme 37) [143].

The β -cyclodextrin-based precatalyst is the most active which has been related to the fact that the β -cyclodextrin cavity provides a steric protection of the active site comparable to that of an *ortho*-disubstituted 2,6-bis(imino)pyridyl ligand. As a matter of fact, the HDPE produced exhibits molecular weight, melting temperature and crystallinity which are comparable to those of the polymer obtained with the analogous molecular catalyst.



Scheme 37. Cyclodextrin-encapsulated iron catalyst.

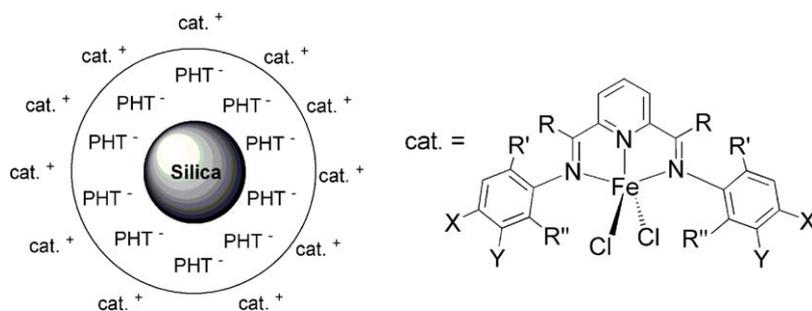
As an alternative to ligand or metal complex immobilization on support materials, Alt and co-workers have employed a highly efficient heterogenization system that involves immobilization of the activator [144]. A partially-hydrolyzed trimethylaluminum (PTH) on calcinated silica gel was used as activator for a number of differently substituted C_5 -symmetric bis(imino)pyridyl Fe^{II} precatalysts (Scheme 38). Depending on the Al/Fe molar ratio, polymerization activities as high as 4.4×10^6 were observed.

Using a similar heterogenization technique, a bis(imino)pyridyl Fe^{II} complex supported on mesoporous and MAO-pretreated molecular sieve MCM-41 has been reported to produce HDPE with higher molecular weight, melting temperature, onset temperature of decomposition as well as a more compact morphology as compared to the polymer obtained with the corresponding homogeneous catalyst [145]. A slightly lower activity was observed for the MCM-41-supported catalyst.

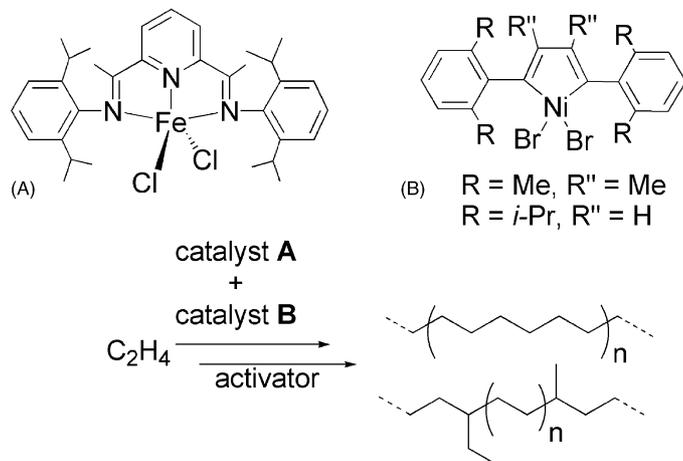
11. 2,6-bis(organylimino)pyridyl Fe^{II} and Co^{II} catalysts in reactor blending and tandem copolymerization reactions

A method for controlling the molecular weight (MW) and the molecular weight distribution (MWD) of polyolefins involves combining two or more types of catalysts in a single reactor to produce polymers with different MW and MWD. This method, known as multi-component polymerization or reactor blending, has achieved considerable industrial attention as it is capable of producing easily polymers with good properties by using just a single polymerization process [146–152].

Mecking has reported the reactor blending of different combinations of late metal polymerization catalysts to obtain blends of linear and branched polyethylenes using ethylene



Scheme 38. PHT-supported catalyst.



Scheme 39. Mixtures of different PEs by reactor blending.

as the sole monomer (Scheme 39) [153]. Notably, the 2,6-bis(arylimino)pyridyl Fe^{II} complex **A** was employed to produce strictly linear PE, while α -diimine nickel complexes gave PE with methyl and long-chain branching.

Tandem copolymerization catalysis, using two or more different single-site catalysts in the same reactor, is a relatively recent technique for the production of branched PE from ethylene stock [151]. A tandem system involves combining in the same reactor a selective α -olefin oligomerization catalyst with a catalyst capable of copolymerizing the produced α -olefins with ethylene. Mandatory conditions for a successful tandem process are: The catalysts must be chemically compatible under the polymerization conditions, which means no or controlled interference between the active sites; The catalysts must show

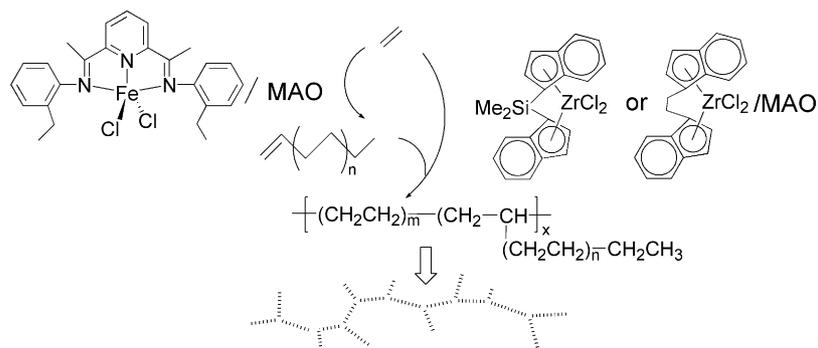
comparable tolerance to the activators; The single catalysts must show comparable activity towards the corresponding substrate in order to maintain an appropriate concentration of all substrates all over the process.

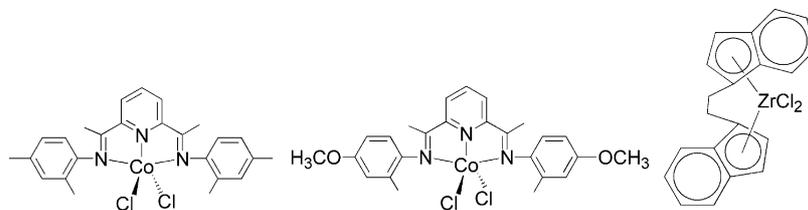
A great variety of combinations of late and early metal catalyst precursors, in different experimental conditions, have been successfully employed in tandem processes to prepare LLDPE and even ULDPE (ultra low-density polyethylene).

A tandem protocol involving the Brookhart catalyst $\text{FeCl}_2\text{L}/\text{MAO}$ ($\text{L} = 2,6-(2\text{-EtC}_6\text{H}_4\text{N}=\text{CMe}_2)_2\text{C}_5\text{H}_3\text{N}$) and the copolymerization catalyst $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}$ or $\text{EtIndZrCl}_2/\text{MAO}$ has been reported by Bazan (Scheme 40) [57].

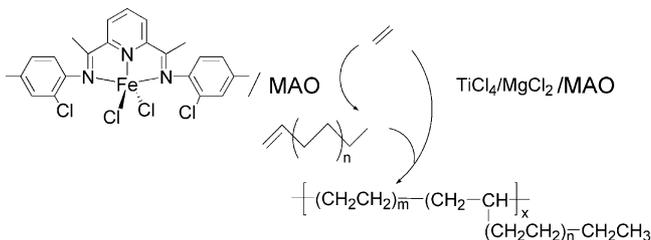
An inefficient control of the polymer structure was observed due to the fact that the Fe^{II} catalyst produces a Schulz–Flory distribution of α -olefins, which are less reactive with increasing molecular weight. Higher activity but less branching was obtained with EtIndZrCl_2 , which gave a more homogeneous LLDPE. It has been proposed that $\text{EtIndZrCl}_2/\text{MAO}$ polymerizes ethylene faster than $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}$ and competes with the iron catalyst for ethylene. By doing so, less α -olefins are produced and a more effective incorporation can be achieved.

LLDPE with ethyl, butyl and longer branches ($n \geq 6$) has been obtained by a tandem system activated by MAO and comprising a zirconocene as copolymerization catalyst and a 2,6-bis(arylimino) Co^{II} dihalide as oligomerization catalyst (Scheme 41) [58]. The olefin incorporation was not particularly high and the lowest melting temperature T_m of the copolymer was around 100°C . The highest productivity was observed for a Co:Zr ratio of 4, consistent with an effective comonomer effect [152].

Scheme 40. Tandem catalysis for LDPE production with a 2,6-bis(arylimino)pyridyl Fe^{II} oligomerization catalysts.



Scheme 41. Oligomerization Co^{II} catalysts and copolymerization zirconocene catalyst employed to produce LLDPE in a tandem process on activation with MAO.



Scheme 42. Tandem catalysis for LDPE production with a 2,6-bis(arylimino)pyridyl Fe^{II} oligomerization catalyst and ZN copolymerization catalyst.

LLDPE with short and long branches has been also obtained by heterogeneous tandem catalysis based on the activation by MAO of a 2,6-bis(arylimino)pyridyl Fe^{II} complex and $\text{TiCl}_4/\text{MgCl}_2$ (Scheme 42) [154]. The LLDPE obtained at low Fe/Ti molar ratio showed more distinct morphology than that obtained at high Fe/Ti ratio, due to the increased solubility of branched PE in toluene.

12. Conclusions

The discovery that iron(II) and cobalt(II) dihalides modified with 2,6-bis(imino)pyridyl ligands are very active catalysts for the polymerization and oligomerization of ethylene, on activation by MAO, has represented one of the major breakthroughs in catalysis over the last years. Like metallocenes, a substantial contribution to the success of these catalysts has been provided by the availability of MAO and related activators. Indeed, 2,6-bis(imino)pyridyl Fe^{II} and Co^{II} dihalides constituted a well-known class of metal complexes already prior to their application in polymerization catalysis [91,155–157]. On the other hand, the specific success of these polymerization catalysts is also attributable to the molecular and electronic structure of 2,6-bis(imino)pyridines. Very few ligands can be actually compared to 2,6-bis(imino)pyridines in terms of stability under polymerization conditions as well as ease of chemical and structural modification. Just the latter property, combined with the excellent chemical compatibility with other catalysts systems, is responsible for the large and increasing number of applications of 2,6-bis(imino)pyridyl Fe^{II} and Co^{II} in C–C bond forming processes involving ethylene and other olefins.

In this article we have reviewed all relevant processes that have been reported to convert ethylene into linear and branched homopolymers as well as α -olefins with either Schulz–Flory or Poisson distribution. Examples of selective dimerization of α -olefins to internal olefins have been analyzed as this reaction may occur under ethylene oligomerization conditions.

Other olefins such as propene or butadiene have not been considered, yet relevant data may be found in the literature [75,80,158,159].

To the best of our knowledge, no report has appeared in the relevant literature dealing with the polymerization or copolymerization of polar monomers or cyclic olefins by 2,6-bis(imino)pyridyl Fe^{II} and Co^{II} catalysis. However, the good functional group tolerance of late transition metals and the ease of chemical modification of 2,6-bis(imino)pyridines do not exclude that new ligand structures and activators may lead to the obtainment of effective catalysts for polar monomers and cyclic olefins polymerization/copolymerization [160]. Likewise, it is predictable that 2,6-bis(imino)pyridyl Fe^{II} and Co^{II} dihalides will have application in the synthesis of nanocomposites and hybrid materials where catalysts stability is mandatory for a successful outcome.

Acknowledgments

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