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Review

Olefin oligomerization, homopolymerization and copolymerization by late transition metals supported by (imino)pyridine ligands

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Contents

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Dedicated to Prof. Fausto Calderazzo on the occasion of his 80th birthday for his incomparable career.

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Late transition metals
Catalysis
Oligomerization
Polymerization

ABSTRACT

In this review, the key advances achieved over more than 10 years on the design and development of (imino)pyridyl transition metal complexes as catalyst precursors for the transformation of ethylene, higher α-olefins and cyclic olefins into either linear/branched homopolymers or oligomers are highlighted. Particular attention has been paid to the relationships between the catalytic activity exhibited by the catalysts and their electronic and geometrical structure.

1. Introduction

Since the independent discovery by Brookhart, Bennett and Gibson that five-coordinate 2,6-bis(arylimino)pyridyl metal dihalides (basically Fe and Co complexes) (Scheme 1a), upon activation with MAO, are effective catalysts for the conversion of ethylene either to high-density polyethylene (HDPE) or to α-olefins with a Schulz–Flory distribution [1], the design of new iminopyridyl-based ligands has been a major research goal in polymerization catalysis.

Among the possible structural variations of the (N3) 2,6-bis(arylimino)pyridyl moiety, bidentate (N2) (imino)pyridines, in conjunction with first and second row late transition metal halides (Co, Ni, Pd, Fe, Cu), have shown excellent and, to a some extent, unique results (Scheme 1b and Table 1). The lower coordination number of (imino)pyridines *vs* 2,6-bis(imino)pyridines

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Table 1
(Imino)pyridyl late transition metal complexes for the catalytic conversion of olefins.

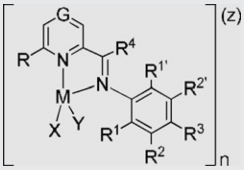
Complex	Entry	M	*n*	R	R^1	$R^{1'}$	R^2	$R^{2'}$	R^3	R^4	G	X	Y	(z)	Reference
	E1	Pd	1	H	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Me	–	[53]
	E2	Pd	1	H	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	CH_3CN	Me	(BAr_4)	[53]
	E3	Pd	2	H	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	–	–	$(BAr_4)_2$	[53]
	E4	Ni	2	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Cl	Cl	–	[59]
	E5	Ni	2	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[12,59]
	E6	Co	2	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[59]
	E7	Co	2	Br	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Cl	–	[3,136]
	E8	Ni	2	H	Me	Me	H	H	H	H	C–H	Br	Br	–	[60]
	E9	Ni	2	Me	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[60]
	E10	Ni	2	H	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Br	Br	–	[60]
	E11	Ni	2	H	*i*-Pr	*i*-Pr	H	H	H	Ph	C–H	Br	Br	-	[60]
	E12	Pd	1	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Cl	Cl	–	[60]
	E13	Pd	1	H	Me	Me	H	H	H	H	C–H	Cl	Cl	–	[60]
	E14	Pd	1	Me	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Cl	Cl	–	[60]
	E15	Pd	1	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	CH_3CN	CH_3CN	$(BF_4)_2$	[60]
	E16	Pd	1	Me	*i*-Pr	*i*-Pr	H	H	H	H	C–H	CH_3CN	CH_3CN	$(BF_4)_2$	[60]
	E17	Ni	1	H	Me	Me	H	H	H	H	C–H	Br	Br	–	[19]
	E18	Ni	1	H	Me	Me	H	H	H	Me	C–H	Br	Br	–	[19]
	E19	Ni	1	H	*i*-Pr	H	H	H	H	H	C–H	Br	Br	–	[19]
	E20	Ni	1	H	*i*-Pr	H	H	H	H	Me	C–H	Br	Br	–	[19]
	E21	Ni	1	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[19]
	E22	Ni	1	H	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Br	Br	–	[19]
	E23	Ni	1	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[2]
	E24	Ni	1	Me	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[2]
	E25	Ni	1	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Et_2O	Me	$(BAr^F{}_4)$	[2]
	E26	Ni	1	H	*i*-Pr	*i*-Pr	H	H	H	H	N	Br	Br	–	[2]
	E27	Ni	1	Me	*i*-Pr	*i*-Pr	H	H	H	H	N	Et_2O	Me	$(BAr^F{}_4)$	[2]
	E28	Fe	2	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Cl	Cl	–	[13]
	E29	Ni	1	H	H	H	H	H	$OSiMe_3$	H	C–H	Br	Br	–	[20]
	E30	Ni	1	H	Me	H	H	Me	$OSiMe_3$	H	C–H	Br	Br	–	[20]
	E31	Ni	1	Me	Me	H	H	Me	$OSiMe_3$	H	C–H	Br	Br	–	[20]
	E32	Ni	2	H	H	H	H	H	OH	H	C–H	1/2 Br	1/2 Br	–	[20]
	E33	Ni	-	H	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Allyl	–	$(BAr^F{}_4)$	[21]
	E34	Fe	1	$COCH_3$	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Cl	–	[31]
	E35	Fe	1	$COCH_3$	H	H	CF_3	H	H	Me	C–H	Cl	Cl	–	[24]
	E36	Fe	1	CO_2Et	Me	Me	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E37	Fe	1	CO_2Et	Et	Et	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E38	Fe	1	CO_2Et	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E39	Fe	1	CO_2Et	F	F	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E40	Fe	1	CO_2Et	Cl	Cl	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E41	Fe	1	CO_2Et	Br	Br	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E42	Co	1	CO_2Et	Me	Me	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E43	Co	1	CO_2Et	Et	Et	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E44	Co	1	CO_2Et	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E45	Co	1	CO_2Et	F	F	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E46	Co	1	CO_2Et	Cl	Cl	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E47	Co	1	CO_2Et	Br	Br	H	H	H	Me	C–H	Cl	Cl	–	[25]
	E48	Ni	1	CO_2Et	Me	Me	H	H	H	Me	C–H	Cl	Cl	–	[32]
	E49	Ni	1	CO_2Et	Et	Et	H	H	H	Me	C–H	Cl	Cl	–	[32]
	E50	Ni	1	CO_2Et	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Cl	–	[32]
	E51	Ni	1	CO_2Et	F	F	H	H	H	Me	C–H	Br	Br	–	[32]
	E52	Ni	1	CO_2Et	Cl	Cl	H	H	H	Me	C–H	Br	Br	–	[32]
	E53	Ni	1	CO_2Et	Br	Br	H	H	H	Me	C–H	Br	Br	–	[32]
	E54	Pd	1	CO_2Et	Me	Me	H	H	H	Me	C–H	Cl	Cl	–	[26]
	E55	Pd	1	CO_2Et	Et	Et	H	H	H	Me	C–H	Cl	Cl	–	[26]
	E56	Pd	1	CO_2Et	*i*-Pr	*i*-Pr	H	H	H	Me	C–H	Cl	Cl	–	[26]
	E57	Pd	1	CO_2Et	Me	Me	H	H	Me	Me	C–H	Cl	Cl	–	[26]
	E58	Pd	1	CO_2Et	F	F	H	H	H	Me	C–H	Br	Br	–	[26]
	E59	Pd	1	CO_2Et	Cl	Cl	H	H	H	Me	C–H	Br	Br	–	[26]
	E60	Pd	1	CO_2Et	Br	Br	H	H	Me	Me	C–H	Br	Br	–	[26]
	E61	Pd	1	$(CH_2)O_2CCH{=}CH_2$	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Cl	Cl	–	[11]
	E62	Co	1	$(CH_2)O_2CCH{=}CH_2$	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Cl	Cl	–	[11]
	E63	Ni	1	$(CH_2)O_2CCH{=}CH_2$	*i*-Pr	*i*-Pr	H	H	H	H	C–H	Br	Br	–	[11]

Table 1 (*Continued*)

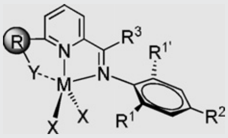
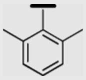
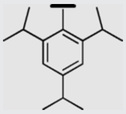
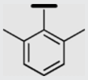
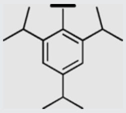
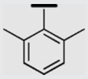
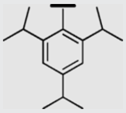
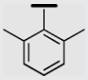
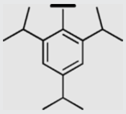
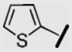
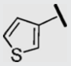
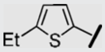
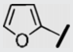
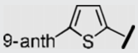
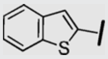
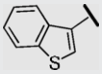
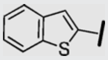
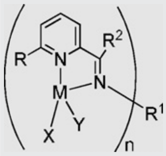
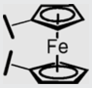
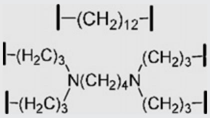
Complex	Entry	M	R–Y	R^1	$R^{1'}$	R^2	R^3	X	Reference
	E64	Co	Ph	*i*-Pr	*i*-Pr	H	Me	Cl	[3–6,8,10,52,111,112]
	E65	Fe	Ph	*i*-Pr	*i*-Pr	H	Me	Cl	[3]
	E66	Ni	Ph	*i*-Pr	*i*-Pr	H	Me	Cl	[3]
	E67	Co	Ph	Me	Me	H	Me	Cl	[8]
	E68	Co	Ph	Me	H	H	Me	Cl	[8]
	E69	Fe		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E70	Fe		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E71	Pd		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E72	Pd		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E73	Ni		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E74	Ni		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E75	Co		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E76	Co		*i*-Pr	*i*-Pr	H	H	Cl	[30]
	E77	Co	2-naph	*i*-Pr	*i*-Pr	H	Me	Cl	[3,5]
	E78	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[3–8,10,86,87]
	E79	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[3,10]
	E80	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[3,5–7,111,112]
	E81	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[3,5,6,8]
	E82	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[7,136]
	E83	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[3–5,7–9,111,112]
	E84	Co		*i*-Pr	*i*-Pr	H	Me	Cl	[3]
	E85	Co		*i*-Pr	*i*-Pr	H	$(CH_2)_3OH$	Cl	[7]

Table 1 (*Continued*)

Complex	Entry	M	*n*	R	R¹	R²	X	Y	Reference
	E86	Pd	1	H	$(CH_2)_2CH_3$	H	Cl	Cl	[16]
	E87	Pd	1	H	$(CH_2)_4CH_3$	H	Cl	Cl	[17]
	E88	Pd	1	H	$(CH_2)_7CH_3$	H	Cl	Cl	[17]
	E89	Pd	1	H	$(CH_2)_{11}CH_3$	H	Cl	Cl	[14,17,44]
	E90	Pd	1	H	$(CH_2)CH{=}CH_2$	H	Cl	Cl	[16]
	E91	Pd	1	H	(C_6H_4)-4-$CH{=}CH_2$	H	Cl	Cl	[16]
	E92	Pd	1	H	Ph	H	Cl	Cl	[16]
	E93	Pd	1	H	(C_6H_4)-4-OH	H	Cl	Cl	[16]
	E94	Fe	1	H	*n*-Propyl	H	Cl	Cl	[13]
	E95	Fe	1	H	*c*-C_6H_{11}	H	Cl	Cl	[13]
	E96	Fe	1	H	*c*-$C_{12}H_{23}$	H	Cl	Cl	[13]
	E97	Fe	1	Me	*n*-Propyl	H	Cl	Cl	[13]
	E98	Fe	1	Me	*c*-$C_{12}H_{23}$	H	Cl	Cl	[13]
	E99	Ni	1	H	1-Naph	H	Br	Br	[19]
	E100	Ni	1	H	1-Naph	Me	Br	Br	[19]
	E101	Ni	1	H		H	Br	Br	[15]
	E102	Ni	1	Me	”	H	Br	Br	[15]
	E103	Pd	1	H	”	H	Cl	Cl	[15]
	E104	Pd	1	H	”	H	Cl	Me	[15]
	E105	Pd	1	Me	”	H	Cl	Me	[15]
	E106	Ni	2	H		H	Br	Br	[15]
	E107	Ni	2	Me	”	H	Br	Br	[15]
	E108	Pd	2	H	”	H	Cl	Cl	[15]
	E109	Pd	2	H	”	H	Cl	Me	[15]
	E110	Pd	2	H		H	Cl	Cl	[14]
	E111	Pd	2	H		H	Cl	Cl	[45]
	E112	Cu	2	H	*n*-Propyl	H	–	–	[58,130,134]
	E113	Cu	2	H	*n*-Propyl	Me	–	–	[130,131]
	E114	Cu	2	H	*n*-Butyl	H	–	–	[130,131]
	E115	Cu	2	H	*i*-Nutyl	H	–	–	[130,131]
	E116	Cu	2	H	1-Methyl-propyl	H	–	–	[130,131]
	E117	Cu	2	H	*n*-Octyl	H	–	–	[130,134]

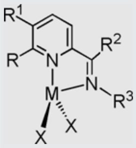
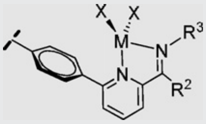
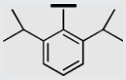
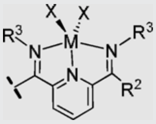
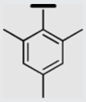
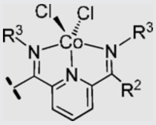
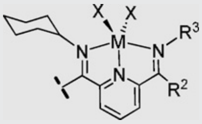
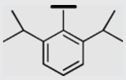
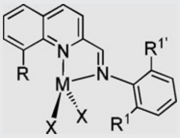
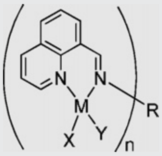
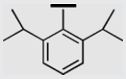
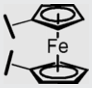
Complex	Entry	M	R	R¹	R²	R³	X	Reference
	E118	Fe		H	Me		Cl	[27]
	E119	Co	”	H	Me	”	Cl	[27]
	E120	Ni	”	H	Me	”	Br	[27]
	E121	Zn	”	H	Me	”	Cl	[27]
	E122	Fe		H	Me		Cl	[28]
	E123	Co	”	H	Me	”	Cl	[28]
	E124	Co	”	H	Me	”	Br	[28]
	E125	Fe		H	Me	”	Cl	[28]

Table 1 (*Continued*)

Complex	Entry	M	R	R^1	R^2	R^3	X	Reference
	E126	Ni	”	H	Me	”	Br	[28]
	E127	Fe	H		Me		Cl	[29]
	E128	Co	H	”	Me	”	Cl	[29]

Complex	Entry	M	R	R^1	R$^{1'}$	X	Reference
	E129	Ni	H	Me	Me	Br	[19]
	E130	Ni	Me	Me	Me	Br	[19]
	E131	Ni	H	*i*-Pr	H	Br	[19]
	E132	Ni	Me	*i*-Pr	H	Br	[19]
	E133	Ni	H	*i*-Pr	*i*-Pr	Br	[2,19]
	E134	Ni	Me	*i*-Pr	*i*-Pr	Br	[19]
	E135	Ni	*i*-Pr	*i*-Pr	*i*-Pr	Br	[19]

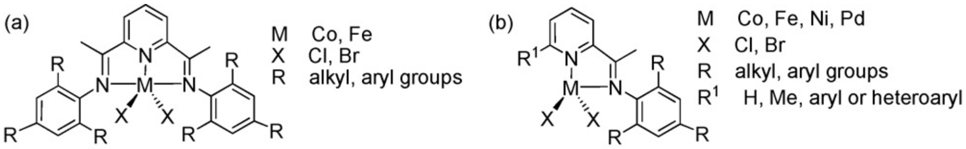
Complex	Entry	M	*n*	R	X	Y	Reference
	E136	Ni	1		Br	Br	[2]
	E137	Ni	1		Br	Br	[15]
	E138	Pd	1	”	Cl	Cl	[15]
	E139	Ni	2		Br	Br	[15]
	E140	Pd	2	”	Cl	Cl	[15]
	E141	Pd	2	”	Cl	Me	[15]

(N2 *vs* N3), combined with the reduced steric protection of the catalyst axial coordination sites, significantly influences both the activity and selectivity, leading to very active catalysts for the conversion of ethylene into low molecular weight polyolefins, low molecular weight oligomers or mixtures thereof [2]. Indeed, several (imino)pyridine Co^{II} complexes exhibit unrivalled activity for the oligomerization of ethylene to short-chain α-olefins (C_4–C_{12}) [3–8].

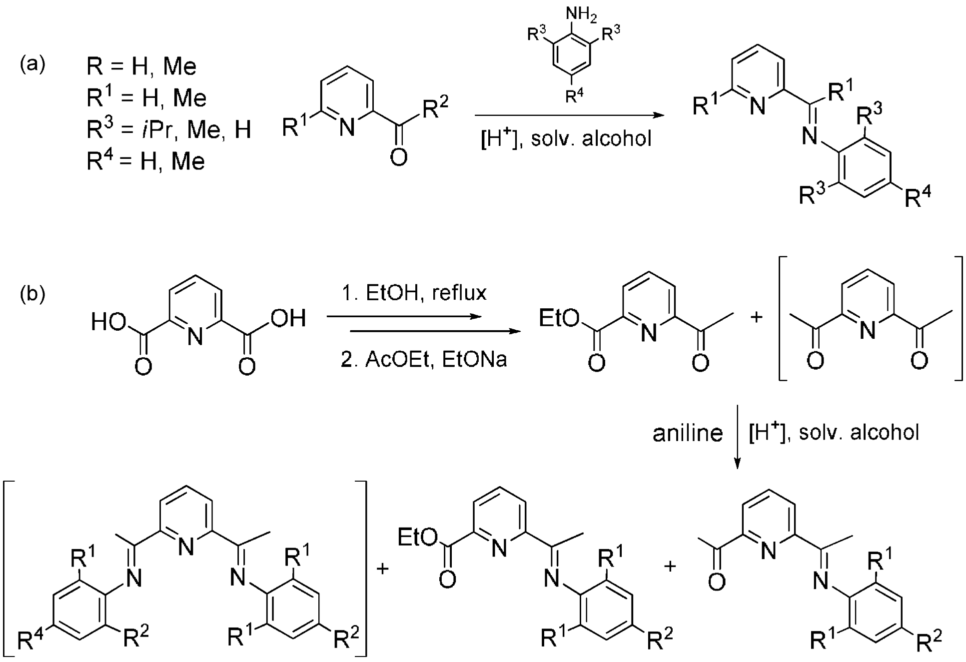
The facile tuning of the polymerization/oligomerization activity of (imino)pyridine metal complexes by simple modifications of their ligand architecture, combined with the ease of preparation and handling, make these systems advantageous over other types of single-site metal catalysts (e.g., metallocenes or constrained-geometry catalysts). Moreover, due to their good compatibility with various early and late metal copolymerization catalysts, (imino)pyridyl metal complexes can be used as oligomerization catalysts in *tandem* catalytic systems for the production in situ of ethylene–olefin copolymers (LLDPEs) as well as in reactor blending to give PEs with controlled molecular weight distribution [9–12].

In this article, we review the synthesis of (imino)pyridyl (N2) metal complexes and their use as catalyst precursors for the homopolymerization, oligomerization and copolymerization of olefins in conjunction with various activators of the MAO family.

In an attempt of correlating structure and catalytic activity, a great deal of attention has been focused on the many structural variations exhibited by these ligands. To the best of our knowledge, review articles covering this specific subject have not appeared elsewhere.



Scheme 1. (a) General structure of the 2,6-bis(imino)pyridyl Fe^{II} or Co^{II} dihalide complexes used by Brookhart and Gibson for ethylene polymerization/oligomerization on activation with MAO. (b) General structure of (imino)pyridyl MII dihalide complexes.



Scheme 2. Synthetic procedures to 2-iminopyridyl and 2-organyl-6-iminopyridyl ligands.

2. Synthesis of 6-organyl-2-iminopyridyl ligands

The vast majority of 2-organylimino-pyridyl ligands are straightforwardly prepared by condensing 2-acetyl or 2-formyl-pyridine systems with an equivalent amount of the proper amine [13–18] or aniline [2,3,5–7,16,19–30], possibly in the presence of an acid co-catalyst (Scheme 2a). The synthesis of 6-organyl-2-iminopyridyl ligands generally requires a more complex procedure and the Schiff-base condensation step just concludes the synthetic path. 2-keto-6-iminopyridyl and 2-alkylcarboxylate-6-iminopyridyl ligands have been synthesized by reacting 2,6-diacetylpyridine [31] and 2-alkylcarboxylate-6-acetylpyridine [25,26,32], respectively, with the proper alkyl substituted aniline. Isolation of the pure 2-organyl-6-iminopyridyl ligands in moderate to good yields, generally requires a careful purification of the reaction mixture from either 2,6-bis(imino)pyridine byproducts or the 2,6-diacetylpyridine precursor (Scheme 2b).

Palladium catalyzed C–C protocols are currently adopted for introducing aryl or heteroaryl substituents on the sixth position of the pyridine ring. Stille coupling [33,34] has been used for preparing 6-heteroaryl-2-iminopyridyl ligands under mild conditions from good to high yields. In general, 2-bromo-6-iminopyridyl systems are reacted with a slight excess of the heteroaryl stannane (Scheme 3a) [3–8]. Conversely, 6-phenyl or 6-naphthyl-containing ligands can be conveniently synthesized by a Suzuki coupling [34,35]. The reaction between 6-bromo-2-acetylpyridine and either phenyl- or naphthyl-boronic acid, followed by the aniline condensation affords the (imino)pyridine ligands in good yield (Scheme 3b) [3–6,8].

The free ligands in Schemes 2 and 3 are shown in their (generally less favorable) s-*cis* configuration (or U-shaped configuration), experimentally observed in their metal complexes (Scheme 1) [36], with the iminoaryl groups lying orthogonal to the $N{=}C{-}C{=}N_{py}$ plane.

Consistent with the important role played by the steric bulk in late transition metal-mediated polymerizations [2,37–40], a range of sterically demanding multidentate binucleating ligands are effective supports for catalytically active binuclear Fe(II), Co(II), Ni(II) and Zn(II) catalysts. To date, however, due to the complexity of the ligand design and synthesis, late metal centers tend to be positioned at the extremities of the manifold ligand, thus limiting any potential cooperative metal-metal interaction. Aimed at forcing two late transition metal centers into close proximity, novel molecular architectures, coupling two iminopyridyl moieties (Scheme 4) [27], or combining and iminopyridyl fragment with a bis(imino)pyridine unit (Scheme 5) [28,29], have been recently proposed as effective scaffolds for the preparation of mono and/or binuclear oligomerization/polymerization catalysts.

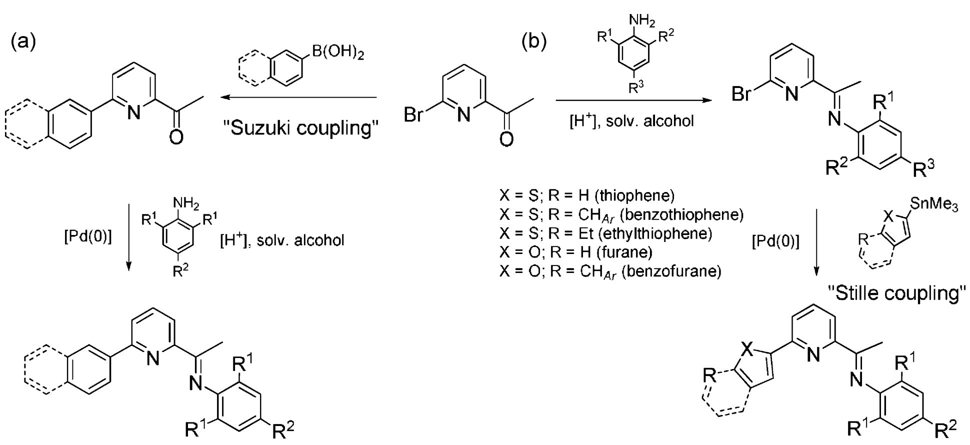
The diketone intermediate $\mathbf{L^1}$ has been prepared by Solan and co-workers in a two step synthesis by pre-reacting 1,3-dibromobenzene with two equivalents of 6-(*n*-butylstannyl) pyridine derivative under standard Stille coupling conditions [33,34], followed by acid deprotection [41]. Acid-catalyzed aniline condensation gave the $\mathbf{N_4}$ bis(imino)pyridine ligand in moderate yield (Scheme 4).

Bis-nickel and bis-cobalt complexes, supported by $\mathbf{N_4}$ ligands have been screened as pre-catalysts for the ethylene oligomerization even though with modest activities [27].

Scheme 5 illustrates the stepwise procedures proposed by Bianchini and Giambastiani to prepare new symmetrical and dissymmetrical $\mathbf{N_5}$ ligands in good yield [28,29]. The symmetrical triketone $\mathbf{L^2}$ has been straightforwardly synthesized by reacting the lithiated form of the bromo(pyridyl)ketal **I** with methylchloroformate, followed by acid cleavage of the *O*,*O*-ketal groups [41]. $\mathbf{L^2}$ was ultimately converted into the desired $^{\mathbf{sym}}\mathbf{N_5}$ ligand by formic acid-catalyzed condensation with the appropriate aniline in MeOH [28].

Shifting the (imino)pyridine fragment with respect to the central imine group required a higher synthetic effort. A description of this procedure is briefly given below. The intermediate **II** was conveniently prepared in a three step synthesis by transformation of 2,5-dibromopyridine into the 5-bromo-2-trimethylsilyl acetylene derivative via a regioselective Sonogashira's protocol, followed by a mercury(II)-catalyzed hydrolysis and protection of the resulting ketone as *O*,*O*-ketal [29,41].

The coupling of the lithium derivative of **I** with the ethyl ester building block **III**, in turn prepared by ethoxycarbonylation of **II**, followed by acid hydrolysis [41], gave the dissymmetrical tris(ketone)



Scheme 3. Synthetic procedures to 6-organyul-iminopyridyl ligands.

bis(pyridine) intermediate **L^3**, which was transformed into the bis(iminopyridyl)-ketone **V** by formic acid-catalyzed condensation with 2,6-diisopropyl aniline in refluxing MeOH. Notably, the central ketone group of **V** remains intact even by treatment with a large excess of 2,6-diisopropyl aniline, irrespective of the solvent and the reaction temperature. Likewise, aniline and other anilines such as 2,6-dimethyl-aniline did not react with **V** even when used as solvents at reflux temperature. In contrast, a selective reaction occurs with neat cyclohexylamine at 100 °C to give the target **$^{diss}N_5$** ligand in good yield.

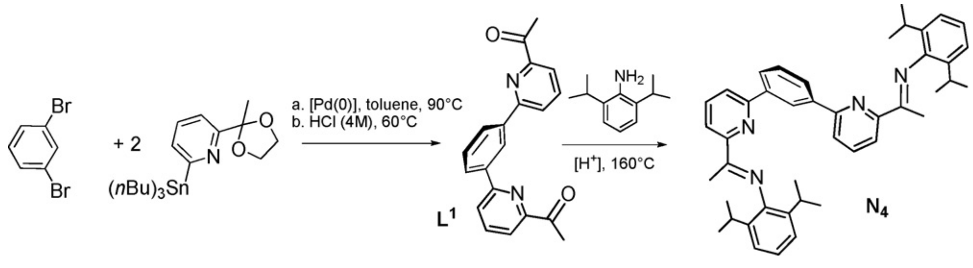
Ferrocenyl-based ligands containing one or two iminopyridyl fragments have been straightforwardly synthesized by Gibson et al. as effective scaffolds for the preparation of mono and binuclear nickel pre-catalysts, respectively (Scheme 6a) [15]. Due to the redox-active properties of the ferrocene unit, these N_2 and N_4-type ligands perturb the electronic properties (and therefore the reactivity) of the transition metal centers to which they are bound [42,43]. Iminopyridyl, bis(imino)pyridyl and tetra(imino)pyridyl ligands featured by long alkyl chain substituents at the imino nitrogens have been prepared by Mapolie et al. [14,44,45], by reacting a solution of pyridine-2-carboxaldehyde with the respective alkyl amine(s) (Scheme 6b).

Unlike traditional ligands for olefin polymerization/oligomerization, (imino)pyridyl ligands can exhibit a rich chemistry on their own, particularly on the nitrogen carbon centers of the imine unit. Deprotonation of the ketimine group on highly conjugated iminopyridyl systems by strong non-nucleophilic bases, such as Me_3SiCH_2Li or MeLi, followed by aqueous quenching, gives vinylaniline derivatives in almost quantitative yields (Scheme 7a) [46]. Nucleophilic attack of MeLi at the imine carbon of unsubstituted iminopyridyl ligands has been reported by Garcia-Herbosa and co-workers (Scheme 7b) [47]. The treatment with an excess of aluminum alkyls (Me_3Al or Et_3Al), followed by hydrolysis, results in the complete reductive alkylation of the imine double bond (Scheme 7c) [48]. Notably, the reaction of aminopyridine or α-diimino ligands with $AlMe_3$ in toluene at elevated temperatures generates highly crystalline aluminum pyridynamido complexes [49] whose molecular structures have been reported by Gibson et al. [50] and more recently by Erker and co-workers [51].

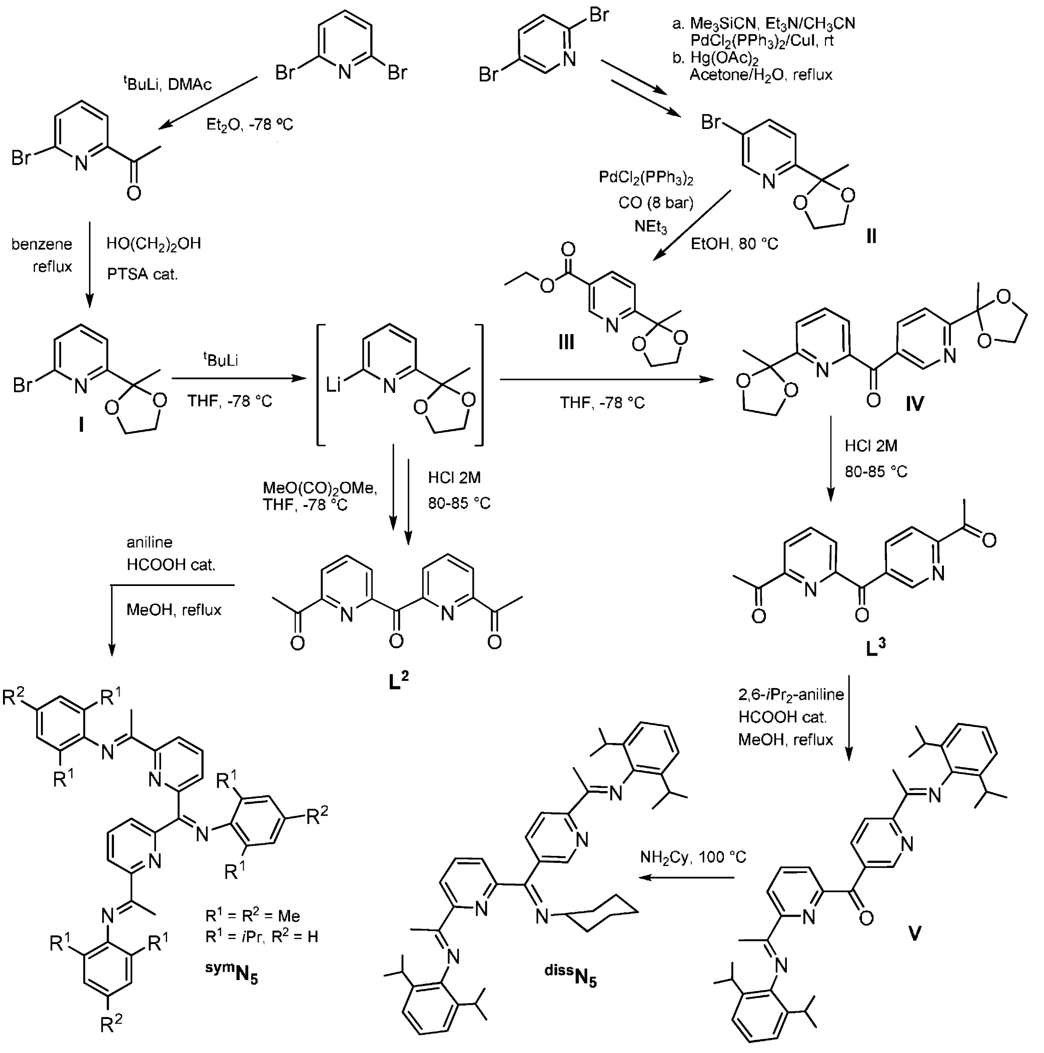
Finally, it worth stressing that the (imino)pyridyl ligands bonded to cobalt or iron are not modified by the activator (most commonly methylalumoxane, MAO or modified methylalumoxane, MMAO), under catalytic conditions and the intact ligands have been recovered quantitatively, following hydrolytic work-up, after the oligomerization/polymerization. For cobalt systems, the dihalide precursors are expected to follow a "traditional" activation pathway, leading to a cationic alkyl propagating species [3,8,52].

3. Synthesis of 6-organyl-2-iminopyridyl late transition metal complexes

The synthesis of late transition metal catalyst precursors (mostly from the first transition row) is a straightforward process, which involves the plain addition of the solid ligands to *n*-BuOH, THF, toluene or CH_2Cl_2 solutions of either anhydrous or hydrated dihalides (Scheme 8) [1,2,9–12,14,15,20,21,25,26,32,33,37,38,47–49,53,54]. Irrespective of the metal, the dihalides are sparingly soluble in aromatic hydrocarbons, while they dissolve fairly well in polar solvents. Improved solubilities in aromatic hydrocarbons are generally exhibited by metal dihalide solvent adducts [13,55–57]. Generally, these compounds are microcrystalline air-stable solids, whereas they decompose in solution either for prolonged times or unless protected by an inert atmosphere. They can be isolated as mononuclear complexes or, depending on both the metal halides and degree of substitution of the pyridine ring, as centrosymmetric dimers [13,20,22,28,53,58–60].



Scheme 4. Synthetic procedure to the bis(iminopyridyl)benzene ligand N_4.



Scheme 5. Synthetic procedures to $^{sym}N_5$ and $^{diss}N_5$ ligands.

The IR spectra of all compounds show a red shift of ν(C=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.

Tables 1–3 summarize the structure and catalytic activities of a series of late transition metal complexes featured by (imino)pyridyl ligands for the catalytic conversion of olefins.

3.1. Co^{II} complexes

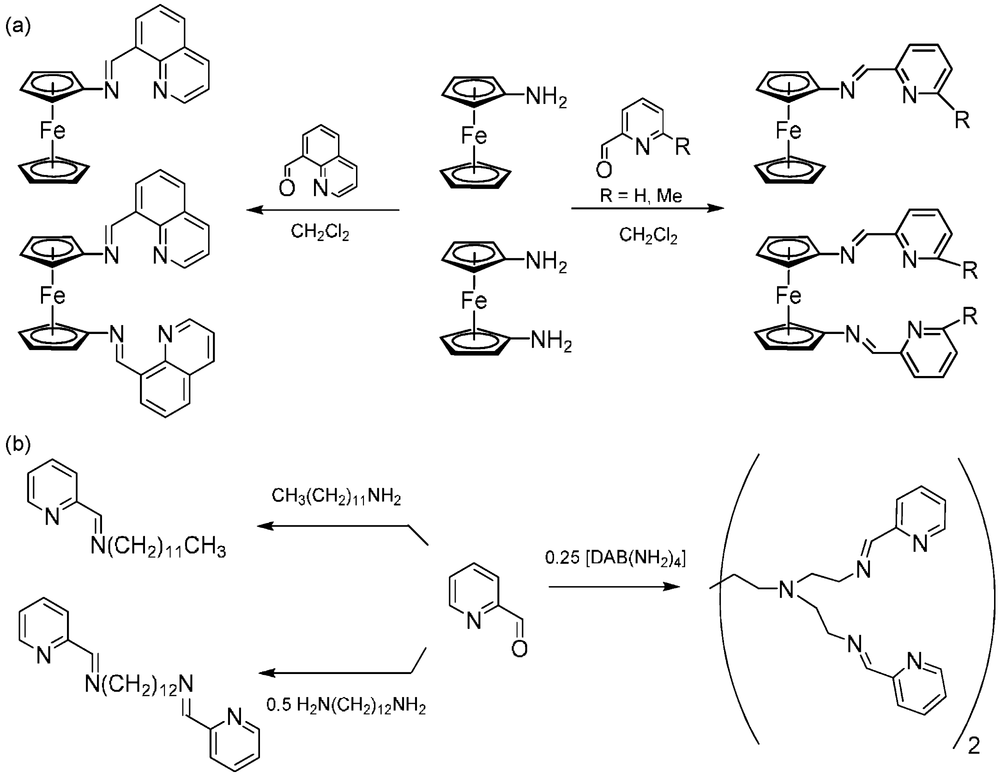
All iminopyridyl Co^{II} complexes are straightforwardly prepared by reacting the ligand with anhydrous Co^{II} dihalide in THF to give green crystalline solids featured by μ_{eff} values at room temperature ranging from 4.6 to 5.1 BM, consistent with a d^7 high-spin Co^{II} configuration [3,6,25,27–29,61,62]. The coordination geometry at the cobalt center is quite flexible, varying from tetrahedral to trigonal-bipyramidal, with various degrees of distortion from the idealized geometries, depending on the substitution pattern of the *N*-aryl groups.

As shown by the molecular structures of $CoCl_2L$ (L = (2,6-(i-Pr)$_2$$C_6H_3N$ = CMe)-2-C_5H_3N) [22,23] and the 6-phenyl(pyridyl) derivative [6] reported in Fig. 1, the presence of a rigid chelating ligand causes important distortions from the idealized geometries. In the former complex, the less sterically hindered ligand results in the formation of a chloro-bridged dimer with a coordination geometry which can be described as distorted trigonal-bipyramidal with two equivalent half molecules in an overall C_2-symmetric framework, while the latter shows a remarkable distortion from a regular tetrahedron. However, in no known case, these are so important to favor spin pairing and give a doublet ground state (S = 1/2). The substitution patterns determines therefore the molecular symmetry in the crystal that may be C_{2v} or C_s.

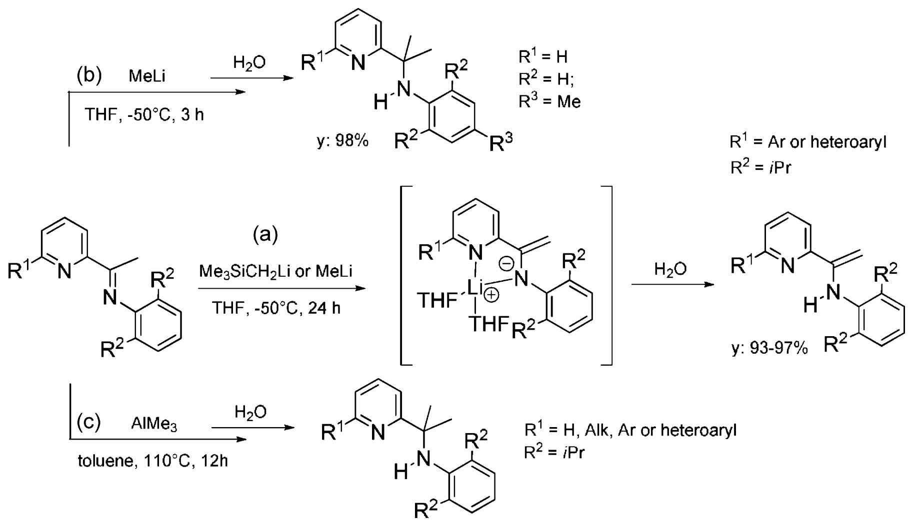
The electronic visible-near-IR spectra of the mononuclear Co^{II} complexes are similar to each other showing, both in solution and in the solid state, three d–d absorption bands in the spectral regions 1800–1640,1430–1330,1050–990 nm, respectively, and three or two higher intensity bands in the region 690–550 nm, consistent with a high-spin tetrahedral coordination of the Co^{II} ion (Fig. 2) [6,61,62].

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 [63,64]. Low-temperature X-band EPR studies have been reported for the solid complexes containing 6-(thiophenyl)pyridyl and 2-bromopyridyl ligands (Fig. 3) [3]. At low temperature, the appearance of a signal typical for an S = 1/2 effective spin Hamiltonian with largely anisotropic g values has been attributed to large zero field splitting (ZFS) effects of the S = 3/2 state [63–69].

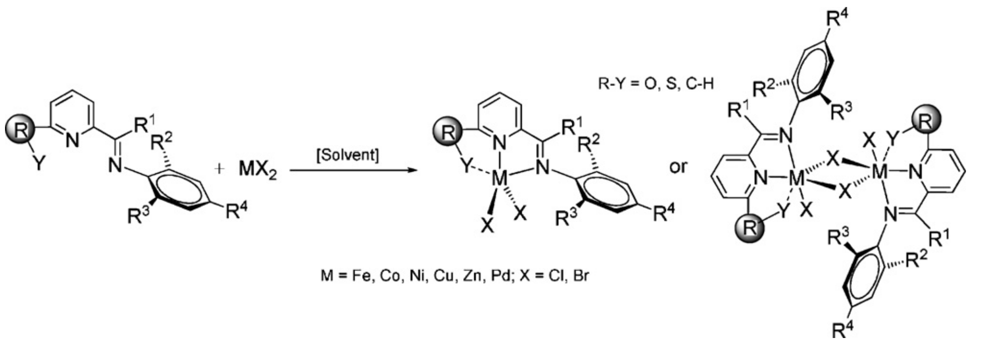
Despite the paramagnetic nature of the bis-halide precursors, ^{1}H NMR spectroscopy can provide valuable information on the solution structure of the iminopyridyl Co^{II} dihalides. Fig. 4 compares the ^{1}H NMR spectra in CD_2Cl_2 at room temperature of the



Scheme 6. Synthetic procedures to $\mathbf{N_2}$ and $\mathbf{N_4}$ ligands.



Scheme 7. Reactivity at the imine unit.



Scheme 8. Synthesis of late transition metal dihalides.

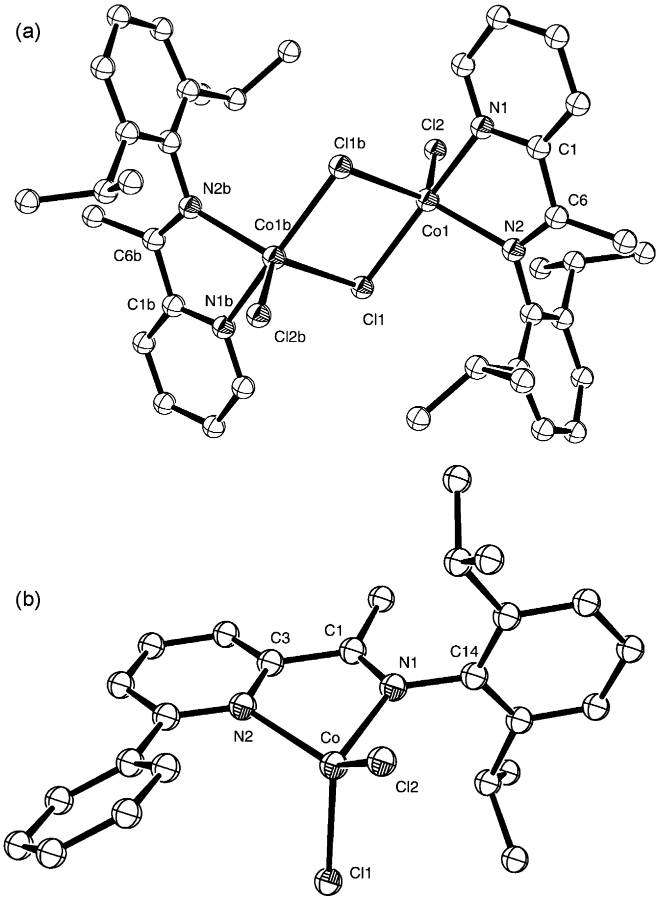


Fig. 1. ORTEP drawing of (a) $[CoCl_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)C_5H_3N\}]_2$ (hydrogen atoms omitted) [22]. Selected distances (Å) and angles (°): C_1–C_6 1.482(2), C_6–N_2 1.290(2), Co_1–N_1 2.093(1), Co_1–N_2 2.123(1), Co_1–Cl_1 2.3419(5), Co_1–Cl_2 2.2878(6), Co_1–Cl_{1b} 2.4589(5), N_1–Co_1–N_2 76.64(5), Cl_1–Co_1–Cl_2 103.42(2), Cl_1–Co_1–Cl_{1b} 86.01(2). ORTEP drawing of (b) $CoCl_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}6\text{-}(C_6H_5)C_5H_3N\}$ (hydrogen atoms omitted) [6]. Selected distances (Å) and angles (°): Co–N_2 2.084(4), Co–N_1 2.049(4), Co–Cl_1 2.206(2), Co–Cl_2 2.205(2), N_1–Co–N_2 80.71, N_2–Co–Cl_2 129.78.

Co derivative $CoCl_2L$ ($L = 2\text{-}(2,6\text{-}iPr_2C_6H_3N = CMe)\text{-}6\text{-}(2\text{-}C_3H_2S\text{-}5\text{-}C_2H_5)C_5H_3N$) with that of its free ligand. All protons resonate at chemical shifts significantly different from those of the corresponding protons in the free ligand $N_2{}^{2ThE}$, which is consistent with the presence of three unpaired electrons in the cobalt complex. Unambiguous signal assignment has been achieved on the basis of the isotropic shifts, essentially attributable to a Fermi contact contribution [70–72].

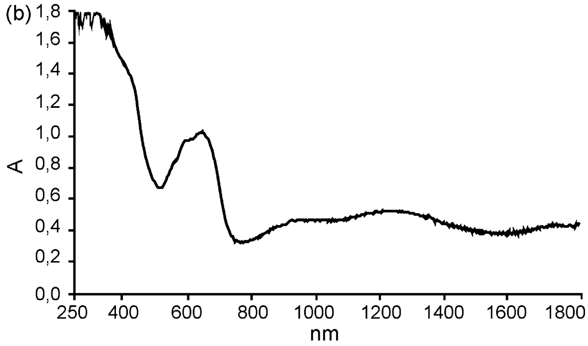


Fig. 2. Diffuse reflectance spectra of $CoCl_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}6\text{-}(C_6H_5)C_5H_3N\}$ (figure was reproduced from ref. [3], with permission of the copyright holders).

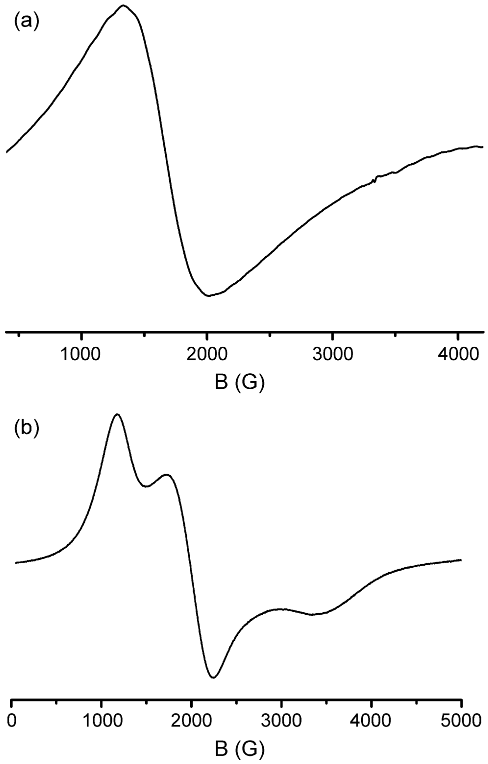


Fig. 3. X-band EPR spectra of the complexes $CoCl_2L$, (a) $L = 2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}6\text{-}(2\text{-}C_3H_3S)C_5H_3N$, (b) $6\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}2Br\text{-}C_5H_3N$ as powders at 10 K (figures were reproduced from ref. [3], with permission of the copyright holders).

3.2. Ni^{II} and Pd^{II} complexes

All Ni^{II} dihalides are generally prepared by reacting the ligand with $NiBr_2(dme)$ or $NiCl_2{\cdot}xH_2O$ in THF or alcohols, respectively, to give from green to orange-yellow solids. Ni^{II}-dialkyl iminopyridinate complexes have been also conveniently prepared in high

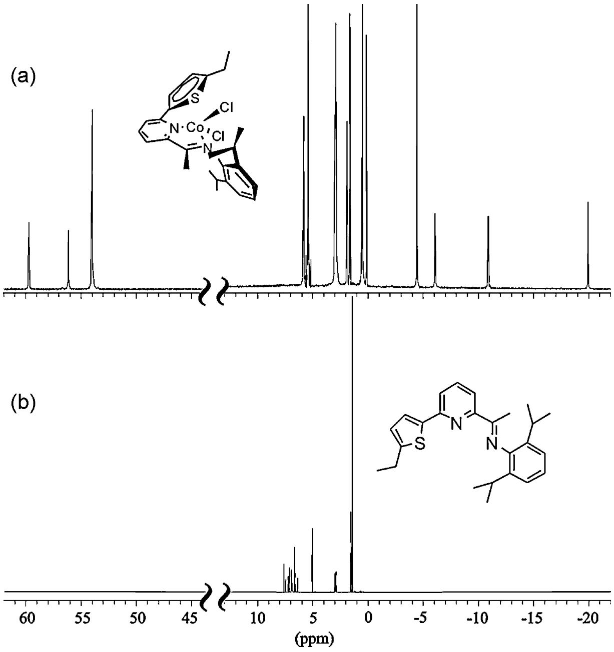


Fig. 4. ^1H NMR spectra (CD_2Cl_2, 22 °C) of (a) $CoCl_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}6\text{-}(2\text{-}C_3H_2S\text{-}5\text{-}C_2H_5)C_5H_3N)\}$ and (b) $2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}6\text{-}(2\text{-}C_3H_2S\text{-}5\text{-}C_2H_5)C_5H_3N)$ (figure was reproduced from ref. [3], with permission of the copyright holders).

yelds by ligand exchange reactions starting from NiR_2Py_2 precursors [73]. The coordination geometry at the nickel center is quite flexible, varying from trigonal-bipyramidal to tetrahedral with various degrees of distortion from the idealized geometries, depending on the substitution pattern of the pyridine ring. The molecular structures of several Ni^{II} derivatives have been determined by single-crystal X-ray diffraction techniques (Fig. 5) [2,20,22,27,28,32,60]. The coordination geometry around the metal center determines also the magnetic properties of the resulting complexes. While tetrahedral [2,15,19,20,27,32] and trigonal-bipyramidal Ni^{II} complexes [22,59,60] have magnetic moments μ_{eff} ranging from 2.8 to 3.4 BM, typical for paramagnetic d^8 high-spin species [74], the square-planar Ni^{II} derivatives [3,61] are diamagnetic [75].

Pd^{II} complexes containing (imino)pyridine ligands are mononuclear, diamagnetic yellow–orange solids with a nearly ideal square-planar coordination geometry [14,15,23,26,30,44,45,53,60,73,76,77] (Fig. 6). Monocationic haloalkyl complexes maintain the coordination geometry of their dihalides precursors with distorted square-planar geometries around the metal center and a favorable *cis* orientation of the alkyl group with respect to the imino function [53,76]. Dicationic derivatives of the type $[(N–N)Pd^{2+}]X^{2-}$ ($X^{2-} = 2BF_4^-$, $2BAr_4^-$ or $2Bar^F{}_4^-$), obtained in a non-coordinating solvent, can accommodate up to two iminopyrydil units with a mutually trans arrangement of the two imino and two pyridyl nitrogens, the palladium atom lying, once again, on a crystallographic symmetry center [53].

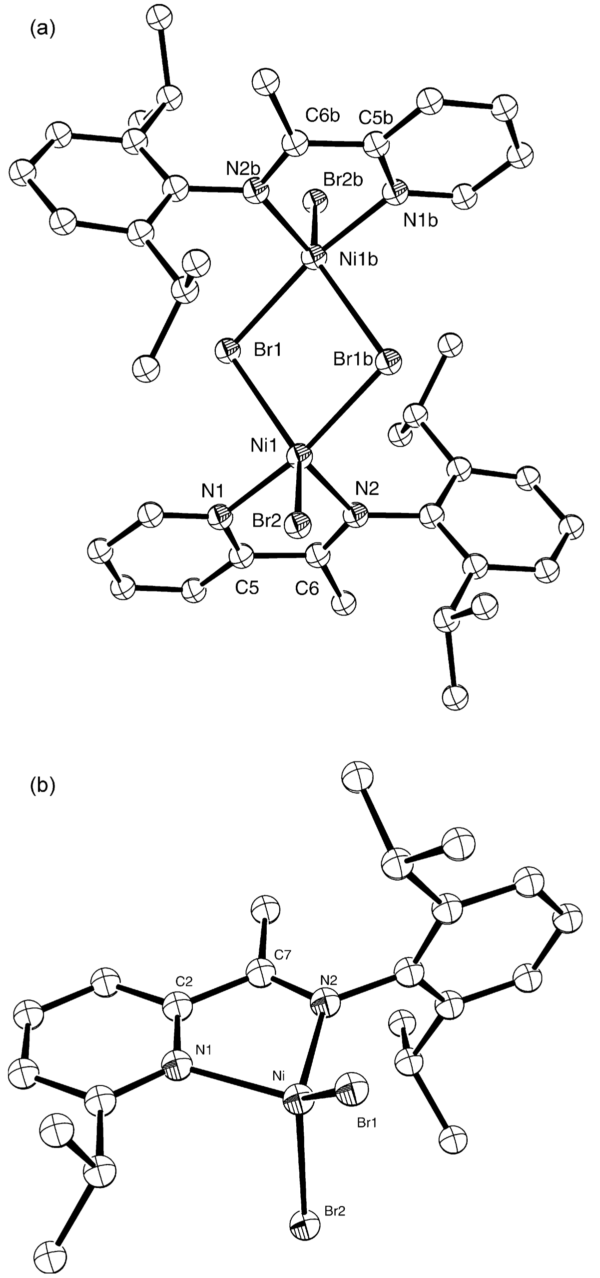


Fig. 5. ORTEP drawing of (a) $[NiBr_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)C_5H_3N\}]_2$ (hydrogen atoms omitted) [60]. Selected distances (Å) and angles (°): $C_5–C_6$ 1.452(8), $Ni_1–N_1$ 2.069(5), $Ni–N_2$ 2.042(5), $Ni–Br_1$ 2.4759(12), $Ni_1–Br_2$ 2.4139(18), $Ni–Br_{1b}$ 2.5479(12), $N_1–Ni_1–N_2$ 79.4(2), $Br_1–Ni_1–Br_2$ 132.06(6), $Br_1–Ni_1–Br_{1b}$ 86.63(4). ORTEP drawing of (b) $NiBr_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)\text{-}6\text{-}(iPr)C_5H_3N\}$ (hydrogen atoms omitted) [22]. Selected distances (Å) and angles (°): $Ni–N_2$ 1.995(2), $Ni–N_1$ 1.994(2), $Ni–Br_1$ 2.3577(5), $Ni–Br_2$ 2.3169(5), $N_1–Co–N_2$ 81.7(1), $Br_1–Ni–Br_2$ 123.64(2).

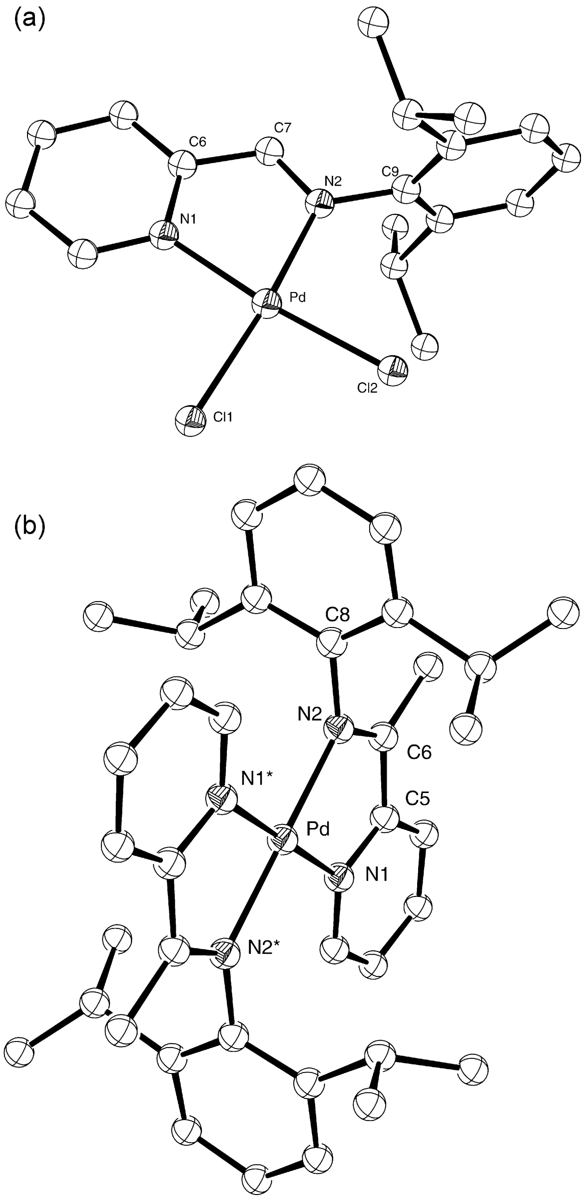


Fig. 6. ORTEP drawing of (a) $PdCl_2\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CH)C_5H_3N\}$ (hydrogen atoms omitted) [23]. Selected distances (Å) and angles (°): $Pd–N_1$ 2.028(3), $Pd–N_2$ 2.022(3), $Pd–Cl_1$ 2.2809(11), $Pd–Cl_2$ 2.2768(10), $C_6–C_7$ 1.457(5), $C_7–N_2$ 1.279(4), $N_1–Pd–N_2$ 80.08(11), $N_1–Pd–Cl_1$ 94.33(9), $N_1–Pd–Cl_2$ 174.51(9). ORTEP drawing of (b) $Pd\{2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CMe)C_5H_3N\}_2$ (hydrogen atoms and $(BAr_4)^{2-}$ omitted) [53]. Selected distances (Å) and angles (°): $Pd–N_1$ 2.054(4), $Pd–N_2$ 2.052(4), $N_1–Pd–N_2$ 78.3(2), $N_1–Pd–N_1{}^* = N_2–Pd–N_2{}^*$ 180.00.

It is worth mentioning that *ortho* metalation, the potential fate of any C–H–metal agostic interaction, is also a feasible reaction opportunity for Pd^{II} complexes with (imino)pyridine ligands, provided there is a suitable organyl fragment on the ligand backbone [78] (Fig. 7).

3.3. Fe^{II} complexes

Fe^{II} complexes supported by (imino)pyridine ligands are straightforwardly prepared by reacting the ligand with the anhydrous iron-dihalide in THF or alcohols to give paramagnetic [74] from red to dark-brown crystalline solids with quite flexible coordination geometries around the metal center [13,22,24,25,27,30,31]. Typical coordination geometries spam from tetrahedral to trigonal-bipyramidal, with various degrees of distortion from the idealized geometries. Similarly to the Co^{II} derivatives (see infra) the use of less bulky iminopyridyl ligands results in the formation of halo-bridged dimers, each metal atom lying within a distorted trigonal-bipyramidal structure [13,22], while more sterically demanding ligands favor pseudo-tetrahedral coordination geometries [22] (Fig. 8).

4. Principal activators of iminopyridyl M^{II} dihalides catalyst precursors

MAO and MMAO, commonly with 20–25% Al(i-Bu)$_3$, are the most widely used activators of iminopyridyl Co^{II}, Fe^{II}, Ni^{II} and Pd^{II} dihalides in olefin oligomerization and polymerization reactions. For the sake of simplicity, MAO is commonly referred to as linear chain or cyclic rings $[-Al(Me)-O-]_n$ containing three-coordinate aluminum centers, yet the true structure of MAO is still a matter of debate [79]. 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 [80–82]. 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 9) [83]. A three-dimensional structure has been recently suggested by Sinn on the basis of structural similarities with *tert*-butylaluminoxanes [84] which form isolable cage structures [85].

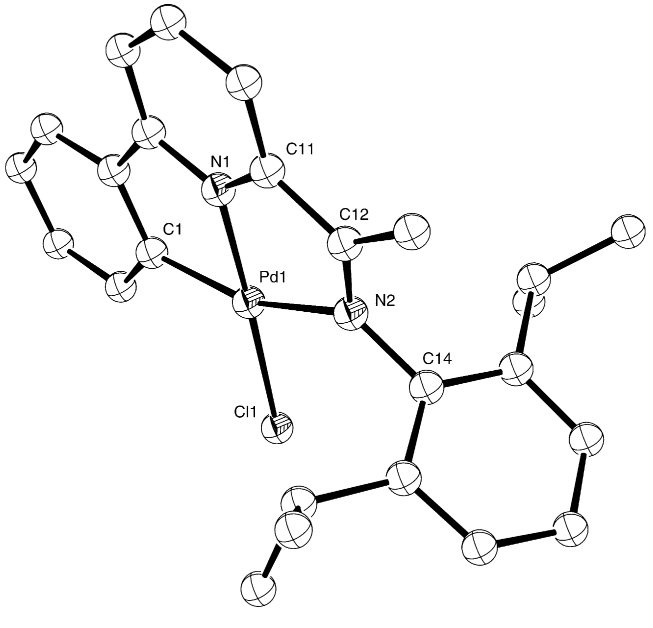


Fig. 7. ORTEP drawing of PdCl{2-(2,6-iPr$_2$C$_6$H$_3$N=CMe)-6-(C$_6$H$_4$)C$_5$H$_3$N} (hydrogen atoms and CH$_2$Cl$_2$·0.5C$_7$H$_8$, omitted) [78]. Selected distances (Å) and angles (°): Pd$_1$–N$_1$ 1.955(5), Pd$_1$–N$_2$ 2.156(6), Pd$_1$–Cl$_1$ 2.295(2), Pd$_1$–C$_1$ 1.970(7), N$_1$–Pd$_1$–N$_2$ 77.7(3), N$_1$–Pd$_1$–C$_1$ 81.6(3), C$_1$–Pd$_1$–Cl$_1$ 97.6(2), N$_1$–Pd$_1$–Cl$_1$ 177.9(2).

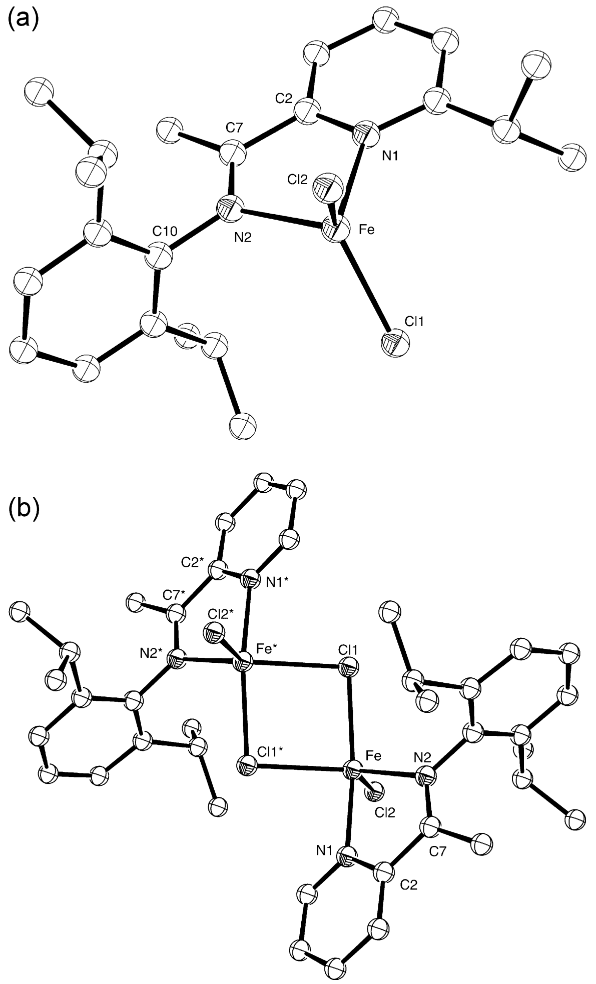


Fig. 8. ORTEP drawing of (a) FeCl$_2${2-(2,6-iPr$_2$C$_6$H$_3$N=CH)-6-(iPr)C$_5$H$_3$N} (hydrogen atoms a THF molecule omitted) [22]. Selected distances (Å) and angles (°): Fe–N$_1$ 2.108(3), Fe–N$_2$ 2.111(3), Fe–Cl$_1$ 2.209(1), Fe–Cl$_2$ 2.223(1), C$_2$–C$_7$ 1.479(5), C$_7$–N$_2$ 1.271(5), N$_1$–Fe–N$_2$ 77.3(1), Cl$_1$–Fe–Cl$_2$ 118.68(5). ORTEP drawing of (b) [FeCl$_2${2-(2,6-iPr$_2$C$_6$H$_3$N=CMe)C$_5$H$_3$N}]$_2$ (hydrogen atoms omitted). Selected distances (Å) and angles (°): Fe–N$_1$ 2.126(7), Fe–N$_2$ 2.201(6), N$_1$–Fe–N$_2$ 74.8(2), Cl$_1$–Fe–Cl$_2$ 105.3(1), Cl$_1$–Fe–Cl$_1$* 84.9(1).

Heterogeneous co-catalysts such as silica gel supported PHT (partially hydrolyzed trimethylaluminum) [19] or physico-chemical supported methylalumoxanes [86,87] (s-MAO or s-MMAO; see also cfr 6.2) have been also proposed as activators for iminopyridyl dihalide complexes. However, MAO and MMAO remain the most active and used co-catalysts in ethylene polymerization/oligomerization.

5. Ethylene polymerization by (imino)pyridyl group 8–10 metal catalysts

In contrast to the high molecular weight polymer formed by either sterically demanding α-diimine or bis(imino)pyridine catalysts, the polymer materials generated by (imino)pyridine systems are essentially low molecular weight, branched polyethylenes. The polymerization studies with (imino)pyridine metal catalysts show that the reduced ligand environment and the subsequently reduced steric protection of the catalyst axial coordination sites, significantly influences both the activity and selectivity (Table 2). The obtainment of low molecular weight polyethylenes is likely due to the fact that (imino)pyridine ligands provide only half of the *ortho*

Table 2
Polymerization activities of the main (imino)pyridyl late transition metal complexes.

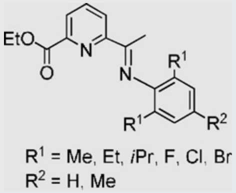
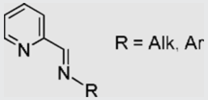
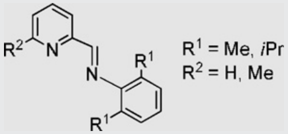
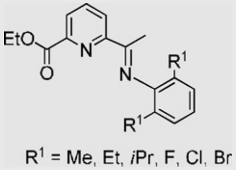
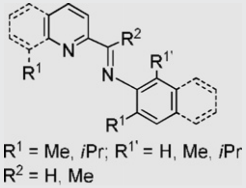
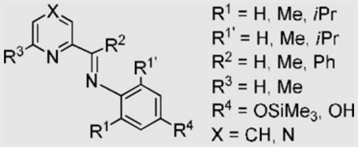
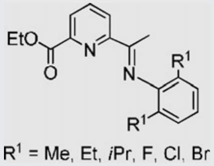
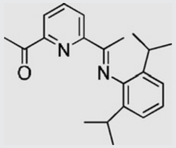
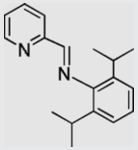
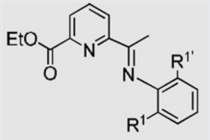
Entries from Table 1	Ligand structure	Metal	Monomer	Activity range (TOFs) kg (polymer) (g(M) × h × bar)$^{-1}$	Activity range (TOFs) mol (monomer converted) (mol (M) ×h × bar)$^{-1}$	Notes
E54–E60		Pd	C_2H_4	$\leq$0.01	Traces to 40	Mixtures with ethylene dimers.
			Norbornene	14.88 ÷ 19.73	56554 to 74988	Norbornene conversions up to 75%.
E86–E93, E110		Pd	C_2H_4	$\leq$1.26	$\leq$4789	–
E12–E16		Pd	Norbornene	$\leq$0.09	$\leq$102	Quantitative norbornene conversions.
E48–E53		Ni	C_2H_4	Inactive to 0.23	Inactive to 489	Prevalently actives for branched low molecular weight olefins with non-Schulz–Flory distribution (C_4–C_8).
E17–E22; E99–E100; E129–E135		Ni	C_2H_4	Inactive to 4.43	Inactive to 9286	High viscous oligomers with low-medium molecular weights.
E4–E5; E8–E11; E23–E27; E29–E32		Ni	C_2H_4	$\leq$26.55	$\leq$55653	Methyl branched low molecular weight polymers/waxes.
E36–E41		Fe	C_2H_4	Inactive to 1.69	Inactive to 3371	Mixtures with linear low molecular weight α-olefins (C_4–C_8).

Table 2 (*Continued*)

Entries from Table 1	Ligand structure	Metal	Monomer	Activity range (TOFs) kg (polymer) $(g(M) \times h \times bar)^{-1}$	Activity range (TOFs) mol (monomer converted) $(mol\ (M) \times h \times bar)^{-1}$	Notes
E34		Fe	C_2H_4	90.61 to 236.55	180720 to 471790	Branched polymers.
E6		Co	C_2H_4	Inactive	Inactive	–
E42–E47	 R^1 = Me, Et, *i*Pr, F, Cl, Br	Co	C_2H_4	Inactive to 0.59	Inactive to 1250	Prevalently actives for linear low molecular weight α-olefins (C_4–C_8).

aryl steric protection (compared to symmetric α-diimine ligands), thus increasing the chain transfer rate [2]. Finally, (imino)pyridine systems, lacking sufficient steric bulk in the *ortho* aryl positions, can be more easily deactivated through the interaction with alkylaluminum reagents [88].

Dinuclear or mononuclear (imino)pyridyl Ni^{II} dihalides of the type showed in Scheme 10 exhibit, upon activation by MAO, from moderate to fairly good activity in the ethylene polymerization (up to 21 kg of PE $(g\ of\ Ni \times h \times bar)^{-1}$), generating branched waxy polyolefin materials, with predominating methyl branches [2,21,59,60]. The extent of branching as well as the polymer molecular weight are function of temperature, ethylene pressure and catalyst structure. Although highly dependent on the polymerization temperature, the molecular weight of the materials produced by these Ni^{II} complexes (M_w in the range 300–45000) remains remarkably lower than that obtained with analogue α-diimine systems under similar conditions [89].

The dominant factor in controlling the molecular weight, besides the reaction conditions, seems to be the reduced axial steric bulk offered by the (imino)pyridine systems which might favor the chain transfer (vide infra). Furthermore, (imino)pyridines containing alkyl or aryl substituents on the 6-position of the pyridine ring, lying on the N_2 plane, show reduced activities, which can ultimately result in a complete catalyst deactivation [19,60]. The effect of the ligand environment can be rationalized looking at the extent of polymer branching. Although polymerization temperature still plays an important role, decreasing the steric bulk on the *ortho* positions of the aryl ring (isopropyl groups *vs* methyl groups) gives more linear polymers. The introduction of a bulky group (H *vs* Me *vs* Ph) at the imino carbon leads, in turn, to an increase of branching as happens with the analogue α-diimine catalysts [90]. The predominant methyl branching (9–70 per 1000 carbon atoms) indicates that the polymerization catalysts are able to isomerize the produced metal-alkyls via a chain-walking mechanism as occurs for Ni^{II} and Pd^{II} α-diimines [90].

Reducing the number of substituents on the *ortho* positions affects both the activity and selectivity of the catalytic system. As a result, complex mixtures of olefins in a Schulz–Flory distribution can be obtained together with hyper-branched low molecular weight PEs with low to moderate TOFs [20]. Although the origin of this dual activity remains still unclear, it is most likely attributable to the dissymmetrical nature of the catalyst precursors [91].

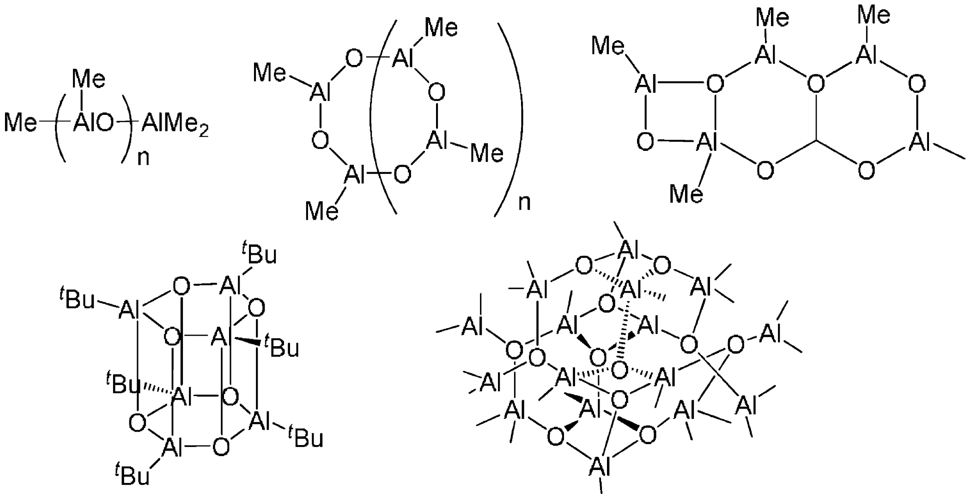
The reactions are commonly carried out in toluene at temperatures ranging from −10 to 40 °C. Beyond the latter temperature the catalysts undergo irreversible decomposition.

A similar trend is not valid for Co^{II}-based (imino)pyridyl catalysts. For example, the dinuclear *ortho* diisopropyl-susbtituted derivative shows only negligible polymerization activity upon treatment by MAO (Scheme 10) [59].

Mononuclear (imino)pyridyl Pd^{II} dihalides complexes, activated with MAO, form active catalysts for the bicycle [2,2,1] hept-2-ene (norbornene, NB) polymerization whereas their dicationic counterparts, prepared from neutral palladium species by treatment with $AgBF_4$, provide poorly active polymerization systems [60].

Mono, binuclear and tetranuclear Pd^{II} complexes with medium-long alkyl chain substituents at the imino nitrogen have been scrutinized for the ethylene polymerization to linear high molecular weight polyolefins with moderate productivities (up to 0.4 kg $(g\ of\ Pd \times h \times bar)^{-1}$) [14,17,44,45]. Activities up to 1.3 kg $(g\ of\ Pd \times h \times bar)^{-1}$ have been obtained, under similar conditions, for systems containing *p*-styryl or *p*-phenol groups at the imino nitrogen [16].

Except for palladium catalysts employed for the NB polymerization [26], Ni^{II} [32], Pd^{II} [26] and Co^{II} dihalide [25] complexes with 2-alcoxycarbonyl-6-(imino)pyridyl ligands generate modest catalysts for the ethylene polymerization, often providing com-



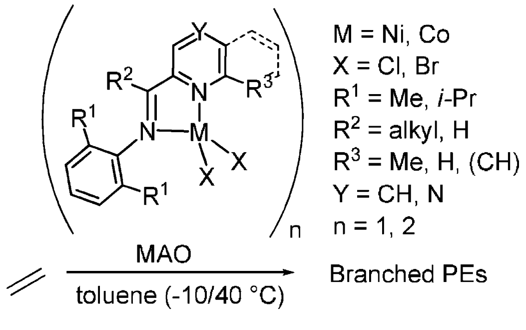
Scheme 9. Principal structures proposed for aluminoxanes.

plex mixtures of olefins and PE. Due to the bonding versatility of the carboxylate substituent in the ligands, the coordination geometry around the metal centers, in solution, is quite unpredictable. As a result, clear structure/selectivity relationships can be hardly outlined. Fe^{II} species stabilized with 2-alcoxycarbonyl-6-(imino)pyridyl ligands exhibit higher activities in the ethylene polymerization with turnover frequencies up to 1.7 kg of PE (g of Fe × h × bar)$^{-1}$, yielding mixtures of linear low molecular weight vinyl end-capped polyolefins with short-chain α-olefins in a Schulz–Flory distribution [25]. Interestingly, activities up to 236 kg of PE (g of Fe × h × bar)$^{-1}$ have been also reported for a Fe^{II} dihalide complex stabilized with an analogue 2-acetyl-6-iminopyridil ligand that gives branched PEs [31,92]. From a perusal of the literature, it is clear that such a difference in catalyst productivity cannot be simply attributed to the substitution of the alcoxycarbonyl group with a keto group. Most likely, this result is due to a poor purification of the precursors. Indeed, the presence of undetectable amount of 2,6-bis(imino)pyridyl ligands [1] may be well responsible of the high polymerization activities.

6. Ethylene oligomerization and polymerization by (imino)pyridyl group 8–10 metal catalysts

α-Olefins are currently produced at a rate of more than 2×10^6 tons/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 linear low-density polyethylenes (LLDPE).

Earlier work by Keim has showed that Ni^{II} complexes stabilized by chelating monoanionic P,O-ligands are effective homogeneous catalysts for the ethylene oligomerization (SHOP process), affording α-olefins in the industrially desirable C_4–C_{20} range [93–97]. Oligomers are produced as a consequence of a highly competitive chain transfer process relative to chain propagation [96]. The chain termination rate is retarded by using sterically demanding bis(arylimino)pyridyl or α-diimine complexes, which block the catalyst axial coordination sites, thus favoring the obtainment of high molecular weight oligomers or polymers. Therefore, asymmetrical (imino)pyridines-type complexes can represent a valid alternative, in terms of both activity and selectivity, to known late transition metal catalysts for the production of light oligomers (Table 3). Pd^{II} imino-pyridine complexes of this series (Scheme 11, type I) have been reported to catalyze the oligomerization of ethylene with productivities of light oligomers (C_4–C_{20}) up to 160 g (g of Pd × h × bar)$^{-1}$ [53]. The selectivity in linear products is quite low and the reaction mixtures mainly contain hyper-branched internal olefins. Ni^{II} complexes modified with aldimine ligands from the same series [20] (Scheme 11, type II) still produce branched olefins, yet as mixtures with insoluble PEs, while the catalyst activities are much lower than those predicted for analogous ketimine Pd catalysts. Carbosilane dendritic compounds containing up to 16 terminal pyridylimine Ni^{II} complexes of this type have been also scrutinized, in combination with methylalumoxane, for the production of mixture of branched oligomers that follow a Schulz–Flory distribution and highly branched low molecular weight PEs (M_w = 2000–177000) [20].

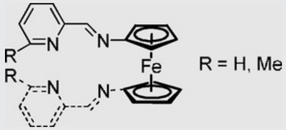
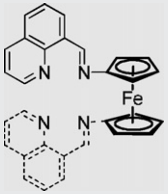
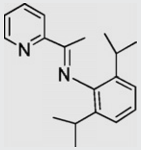
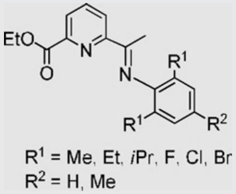
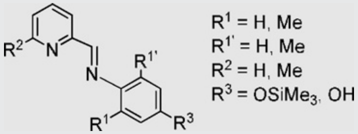
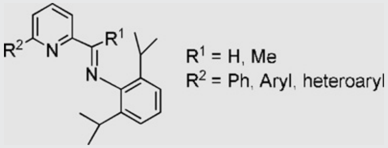
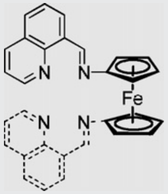


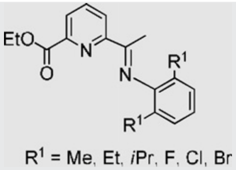
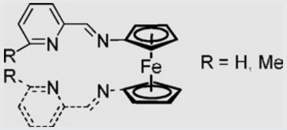
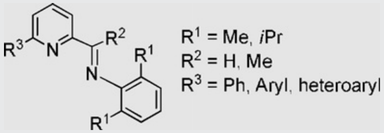
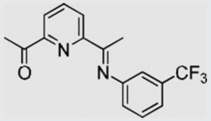
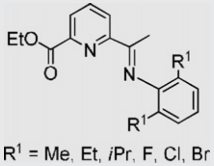
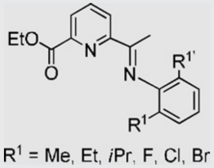
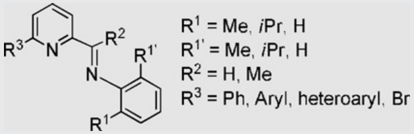
Scheme 10. Branched PE by (imino)pyridyl Ni^{II} and Co^{II} catalysis.

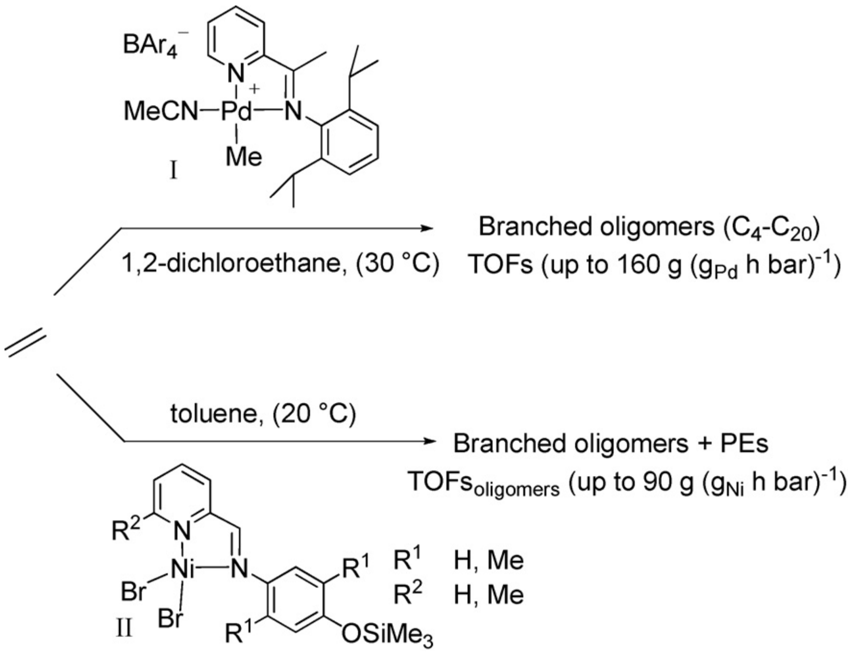
The group of Sun has recently proposed a series of 2-alcoxycarbonyl-6-(imino)pyridyl ligands for the preparation of late transition metal catalyst precursors for the effective ethylene oligomerization/polymerization (Scheme 12). Neutral Pd^{II} dihalides complexes stabilized by these ligands generate, upon activation with MAO, ethylene dimers with oligomerization activities up to 180 g (g of Pd × h × bar)$^{-1}$, yet in mixture with PEs [26]. Productivities up to 5 kg (g of Ni × h × bar)$^{-1}$ of branched light oligomers (C_4–C_8) in a non-Schulz–Flory distribution, always as mixtures with insoluble PEs, have been obtained with the isostructural 2,6-dihalogen(aryl) substituted Ni^{II} dihalide complex under similar reaction conditions [32]. It is worth noting that higher activities (over 13 kg (g of Ni × h × bar)$^{-1}$) and selectivities towards oligomerization products (low-order carbon number oligomers are produced without PEs), have been obtained with the latter Ni^{II} complexes when PPh_3 is used as an auxiliary ligand. Although the role of PPh_3 is not yet clear, the coordination of the auxiliary ligand to the vacant site formed by the action of MAO seems to contribute to the stabiliza-

Table 3

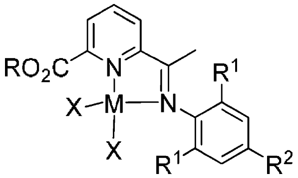
Oligomerization and co-oligomerization activities of the main (imino)pyridyl late transition metal complexes.

Entries from Table 1	Ligand structure	Metal	Monomer	Activity range (TOFs) kg (oligomers) (g(M) × h × bar)$^{-1}$	Activity range (TOFs) mol (monomer converted) (mol (M) × h × bar)$^{-1}$	Notes
E103–E105; E108–E109		Pd	C_2H_4	Inactive	Inactive	–
E138; E140–E141		Pd	C_2H_4	Inactive	Inactive	–
E1–E3		Pd	C_2H_4	≤0.16	≤608	Branched light oligomers (basically C_4–C_{20}). Possible ethylene-alkyl acrylate copolymers (up to 9.3 mol% of the polar monomer incorporated).
E54–E60		Pd	C_2H_4	≤0.18	≤684	Ethylene dimers in mixtures linear PEs.
E29–E32		Ni	C_2H_4	≤0.09	≤186	Oligomers in a Schultz–Flory distribution with α values ranging from 0.45 to 0.70 in mixture with branched PEs.
E66; E73–E74; E120		Ni	C_2H_4	Inactive to 2.66	Inactive to 5576	Light branched oligomers.
E137; E139		Ni	C_2H_4	0.78 to 1.23	1635 to 2557	Dimers + traces of trimers.

E48–E53		Ni	C_2H_4	≤3.63	≤7609	Light branched oligomers with non-Schulz–Flory distribution (C_4–C_8) sometimes in mixture with branched low molecular weight polyolefins.
E101–E102; E106–E107;		Ni	C_2H_4	1.6 to 9.25	3354 to 19390	Dimers + traces of higher oligomers
E65; E69–E70; E118		Fe	C_2H_4	Inactive to 0.04	Inactive to 80	–
E35		Fe	C_2H_4	0.55	1097	Light oligomers.
E36–E41		Fe	C_2H_4	≤1.25	≤2493	Linear low molecular weight α-olefins (basically C_4–C_8) sometimes in mixture with linear PEs.
E42–E47		Co	C_2H_4	0.61 to 22.91	1284 to 48220	Linear low molecular weight α-olefins (basically C_4–C_8) sometimes in mixture with linear PEs.
E7; E64; E67–E68; E75–E84; E119		Co	C_2H_4	6.18 to 88	13000 to 185220	Highly linear low molecular weight α-olefins in a Schultz–Flory distribution (α values ranging from 0.06 to 0.20).
			C_3H_6	0.11 to 1.15	225 to 2415	Basically propylene dimers.
			1-hexene	≤0.3	≤634	Basically hexene dimers.
			Norbornene	0.06 to 32	134 to 67388	Quantitative and highly selective norbornene conversion.
			NB-OH	≤0.06	≤137	High and selective NB-OH conversions
			NB-COOH	≤0.02	≤41	High and selective NB-COOH conversions.



Scheme 11. Oligomerization by (imino)pyridyl Pd^{II} an Ni^{II} catalysis.



M = Pd, Ni, Fe, Co; X = Cl, Br
R = Me, Et
R^1 = Me, Et, *i*Pr, F, Cl, Br
R^2 = H, Me

Scheme 12. Oligomerization by 2-alcoxycarbonyl (imino)pyridyl Pd^{II}, Ni^{II}, Fe^{II} and Co^{II} catalysis.

tion of the electron-deficient transition state for the migratory insertion.

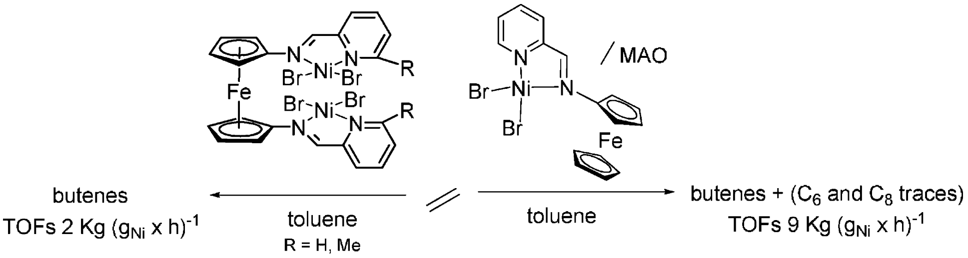
Analogous 2-alcoxycarbonyl iron and cobalt complexes have been reported as active pre-catalysts for the simultaneous ethylene oligomerization and polymerization [25]. While the iron systems show higher activities for the polymerization as compared to the oligomerization, an opposite trend was found for the isostructural cobalt pre-catalysts. Iron complexes provide C_4–C_8 oligomers in a Schultz–Flory distribution with high percentages in 1-olefins (>99%) and TOFs over 1.2 kg (g of Fe × h × bar)$^{-1}$. The isostructural cobalt systems give oligomers in Schultz–Flory distribution (almost exclusively dimers) with high percentages in linear α-olefins (up to 98%) and TOFs over 23 kg (g of Co × h × bar)$^{-1}$.

Activities up to 1.5 kg (g Fe × h × bar)$^{-1}$ for the production of light oligomers in the C_4–C_{18} range with a Schultz–Flory distribution have been obtained with 2-acetyl-6-(imino)pyridyl Fe^{II}-complex bearing a trifluoromethyl-substituted phenyl ring at the imino moiety. The presence of an electron withdrawing group (*m*-CF_3) on the aryl system affects the oligomeric distribution thus making the formation of shorter olefins (maily butenes and hexenes) predominant [24].

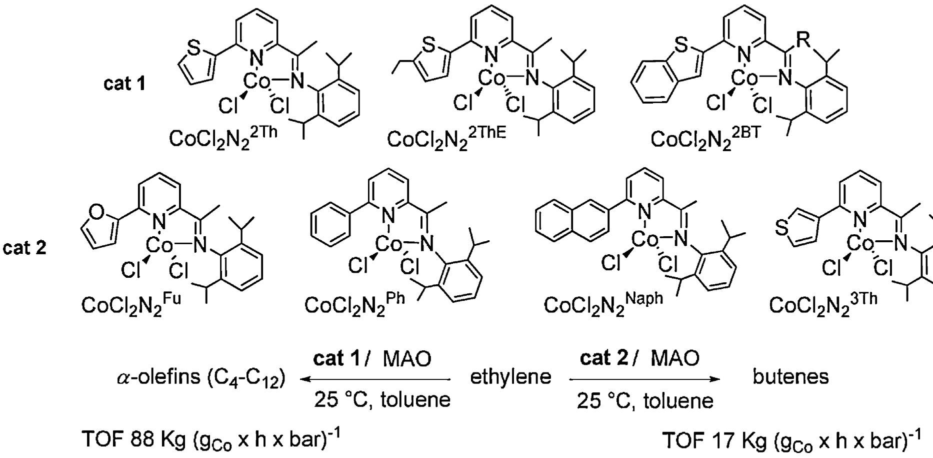
Ethylene dimers with productivities up to 9 kg (g Ni × h × bar)$^{-1}$ are produced with mononuclear Ni^{II} pre-catalysts stabilized by iminopyridyl ligands containing a ferrocenyl substituted imino nitrogen [15]. Compared to other systems containing bulky *ortho*-substituted aryl groups at the arylamine unit that produce branched oligomers and PEs or mixture thereof [2,19,20,59,60], these Ni^{II} catalysts give almost exclusively ethylene dimers. Apparently, the reduced steric protection offered by the ferrocenyl unit favors β-H transfer over chain propagation. Noteworthy, the mononuclear systems showed the best activities with TONs over four times higher than those measured for the binuclear ones (Scheme 13).

6.1. Olefin oligomerization and co-oligomerization by 6-aryl-2-(imino)pyridyl complexes

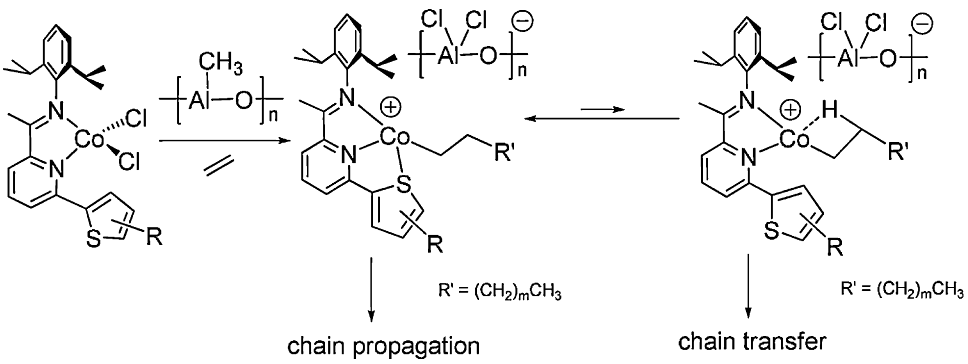
Co^{II} complexes with (imino)pyridine ligands bearing aryl or heteroaryl substituents on the 6-position of the pyridine ring represent a particularly attractive class of catalyst precursors for the highly efficient and selective oligomerization and co-oligomerization of ethylene, propene and norbornene. Bianchini and co-workers have demonstrated that tetrahedral dichloride Co^{II} complexes of the type shown in Scheme 14 are effective catalyst precursors for the Schulz–Flory oligomerization of ethylene [3,5,6]. On activation



Scheme 13. Ethylene dimerization by (ferrocenylimino)pyridyl Ni^{II} catalysis.



Scheme 14. Ethylene oligomerization by tetrahedral Co^{II} 6-aryl substituted imino-pyridine complexes.



Scheme 15. Fastening–unfastening of the sulfur atom in the thien-2-yl activated species.

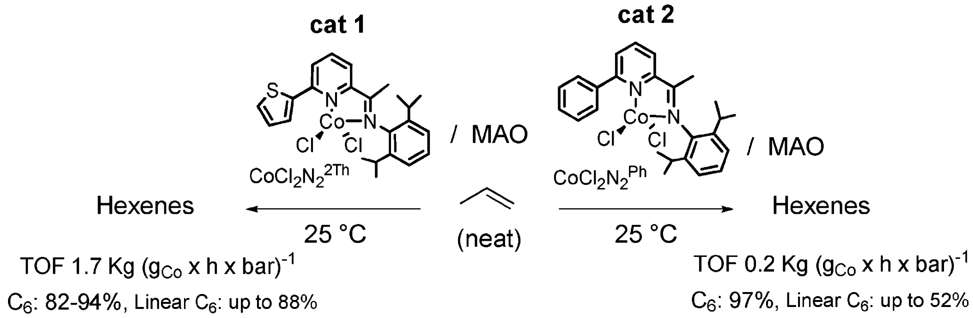
with methylalumoxane (MAO), these Co^{II} complexes promote the conversion of ethylene into short-chain α-olefins with turnover frequencies (TOFs) as high as 88 kg (g of Co × h × bar)$^{-1}$ and selectivity in 1-olefins up to 95%.

Under conditions analogous to those of the $N_2{}^{2Th}$, $N_2{}^{2ThE}$, and $N_2{}^{2BT}$ catalysts (Scheme 14, cat 1), Co^{II} precursors bearing groups of comparable steric size in the pyridine 6-position, yet with no pendant thienyl group (furanyl, phenyl, naphthyl or 3-thiophenyl) are five times less active and also selective for ethylene dimerization (Scheme 14, cat 2) [3,5,6].

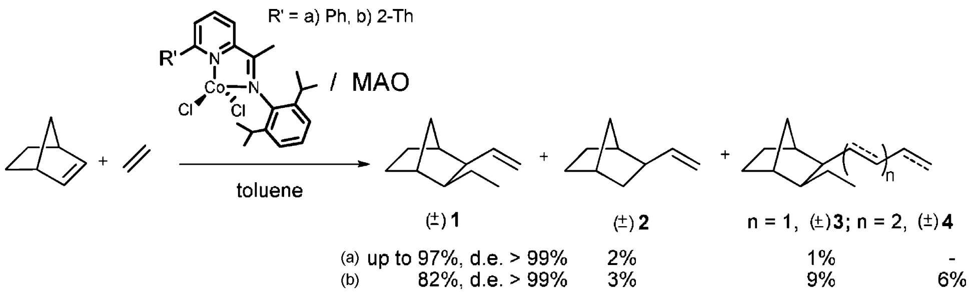
Apparently, the superior activity of the thiophenyl-substituted catalysts is not determined by steric reasons (Scheme 14, $CoCl_2N_2{}^{2Th}$ *vs* $CoCl_2N_2{}^{3Th}$), but by the presence of the sulfur atom in the 2-thienyl group [3]. In situ EPR experiments and DFT calculations on the MAO-activated species have made the authors confident of a decisive role exerted by the 6-organyl group and, in particular, by the position of the sulfur atom in the thienyl ring in steering the ethylene oligomerization activity. Indeed, the fastening–unfastening of the sulfur atom to the cobalt center of the propagating alkyl species would, on one hand, stabilize the electron-deficient transition state for migratory insertion retard, on the other hand, the chain transfer by destabilizing the transition state to the α-olefin elimination (Scheme 15).

In contrast, Co^{II} complexes bearing heteroaryl groups of comparable steric size on the 6-position of the pyridine ring, but featured by a greater σ-ligating character (as 2-pyridyl groups) result completely inactive for olefin oligomerization [3].

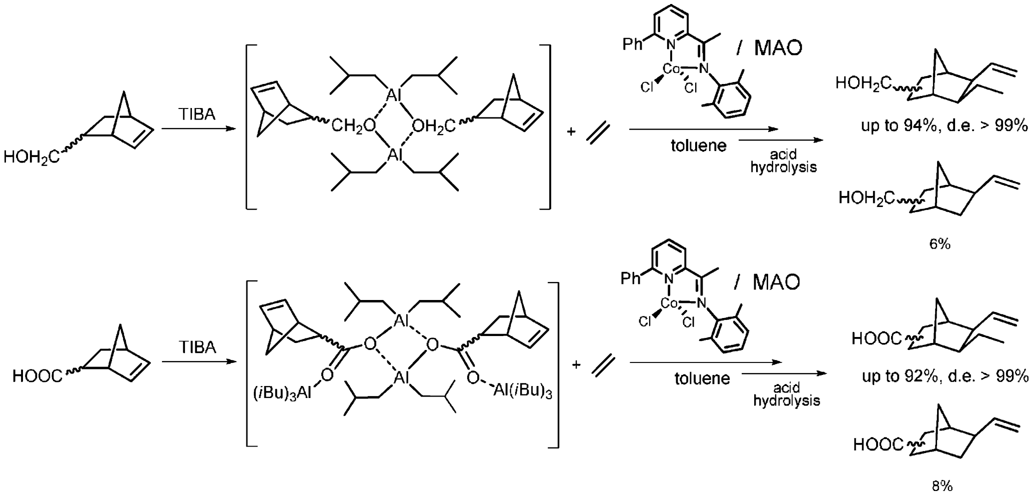
Both classes of catalyst precursors (cat 1 and cat 2) shown in Scheme 14 generate active species for the regioselective dimerization of propylene to hexenes (Scheme 16) [4]. From the results of the ethylene oligomerization it has been revealed that the nature of the substituent in the 6-position of the pyridine ring influences both the selectivity and catalytic activity. The presence of a thien-2-yl group apparently promotes the selective formation of linear



Scheme 16. Propylene dimerization by tetrahedral Co^{II} 6-aryl substituted imino-pyridine complexes.



Scheme 17. Ethylene–norbornene hetero-trimerization protocol catalyzed by Co^{II} imino-pyridine complexes.



Scheme 18. Ethylene–norbornene hetero-trimerization protocol catalyzed by Co^{II} imino-pyridine complexes on NBs containing polar functional groups.

dimers, while the phenyl derivative gives a high level of methyl branched pentenes with only 52% of linear dimers.

Neither the tetrahedral high-spin d^6 Fe^{II} catalysts ($FeCl_2N_2^{Ph}$ and $FeCl_2N_2^{2Th}$) nor the square-planar diamagnetic d^8 Ni^{II} derivatives ($NiCl_2N_2^{Ph}$ and $NiCl_2N_2^{2Th}$) catalyze the oligomerization/polymerization of ethylene on treatment with MAO under the typical experimental conditions used for the cobalt systems [3].

Co^{II} systems for the highly selective dimerization of ethylene and propylene (Scheme 14, cat 2) catalyze the enchainment of one norbornene molecule (NB) with two ethylene molecules to give exo-2,exo-3 ethyl-vinyl norbornane with high activity (up to 107 kg (g Co × h × bar)$^{-1}$ and complete diastereoselectivity (Scheme 17) [8,52].

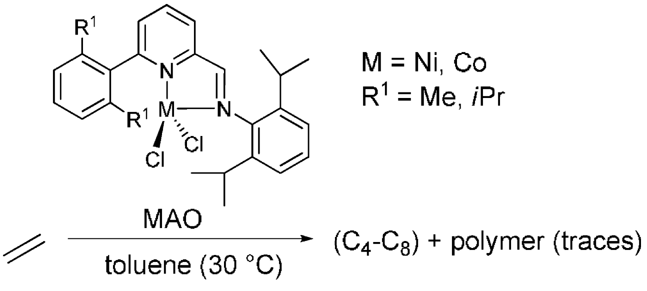
Complexes containing a thien-2-yl moiety (Scheme 14, cat 1) generate more efficient systems for the NB conversion into the ethyl-vinylated derivatives (over two times more active), although they are significantly less selective for the 2ethylene-1NB hetero-trimerization due to the greater ability of the 6-thienyl complexes to oligomerize ethylene to α-olefins higher than 1-butene [8].

The 2-ethylene-1NB hetero-trimerization reaction has been also accomplished with NBs bearing polar substituents such as norbornenemethanol and norbornenecarboxylic acid with activities up to 0.2 kg (g of Co × h × bar)$^{-1}$ and complete diastereoselectivities. To this purpose, a less sterically demanding complex ($CoCl_2N_2^{Ph/Me2}$) is used as catalyst precursor (Scheme 18) [8].

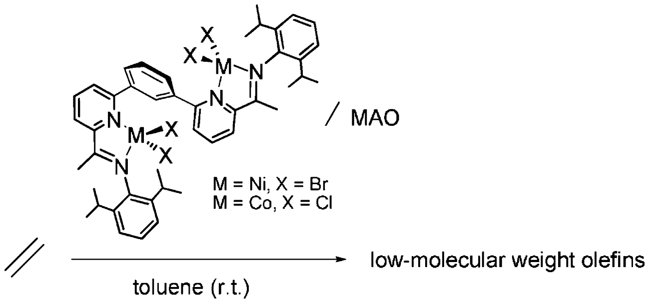
Since hydroxyl and carboxylic acid groups react with MAO and may compete with the monomer for coordination to the cobalt center, these NBs are protected by treatment with aluminum alkyls such as TIBA [98–101]. In this way, the catalyst deactivation is much slower even when a high concentration of the polar comonomer is used.

(Imino)pyridines Co^{II} and Ni^{II} complexes bearing sterically demanding groups on the 6-position of the pyridine ring have been recently described by Kempe and co-workers as efficient catalyst precursors for the ethylene oligomerization to short-chain α-olefins (mainly butenes) with activities up to 8 kg (g of Co × h × bar)$^{-1}$ (Scheme 19) [30].

Compared to similar Co^{II} systems (Scheme 14, cat 2), the introduction of bulky groups on the 6-position of the pyridine ring does not influence the nature of the products formed, yet small amounts of polymeric materials are formed depending on the co-catalyst used. Activation with triethylaluminum (Et_3Al), instead of methylaluminoxane (MAO), leads to reduced activity but suppresses the formation of polymeric byproducts, increasing, at the same time, the selectivity towards ethylene dimers (over 95%). While Fe^{II} complexes turned out virtually inactive towards ethylene oligomerization/polymerization, Pd^{II} counterparts provided only polymeric materials with activities comparable to those reported for less sterically hindered congeners [14,17,44,45].



Scheme 19. Ethylene oligomerization by sterically demanding (imino)pyridyl Ni^{II} an Co^{II} complexes.



Scheme 20. Ethylene oligomerization by binuclear Ni^{II} an Co^{II} complexes.

Binuclear Co^{II} and Ni^{II} (imino)pyridyl systems featured by a novel sterically demanding bis(iminopyridyl) ligand framework (Scheme 20) have been prepared by Solan and co-workers with the intent of forcing two late metal centers into close proximity [27]. In this way, cooperative metal–metal interactions might be favored. Both complexes, once activated with MAO, show fairly low activities (up to 0.7 kg (g of M × h × bar)$^{-1}$ for the ethylene oligomerization. The Co systems forms mainly mixtures of linear α-olefins and internal isomers, while the Ni systems additionally promote the formation of methyl branched structures. The exact nature of the cooperative effects between the two active centers, if any, remains still unclear.

6.2. *(Imino)pyridine Ni^{II} and Co^{II} complexes as efficient tools for the synthesis of branched polyethylenes via tandem catalysis*

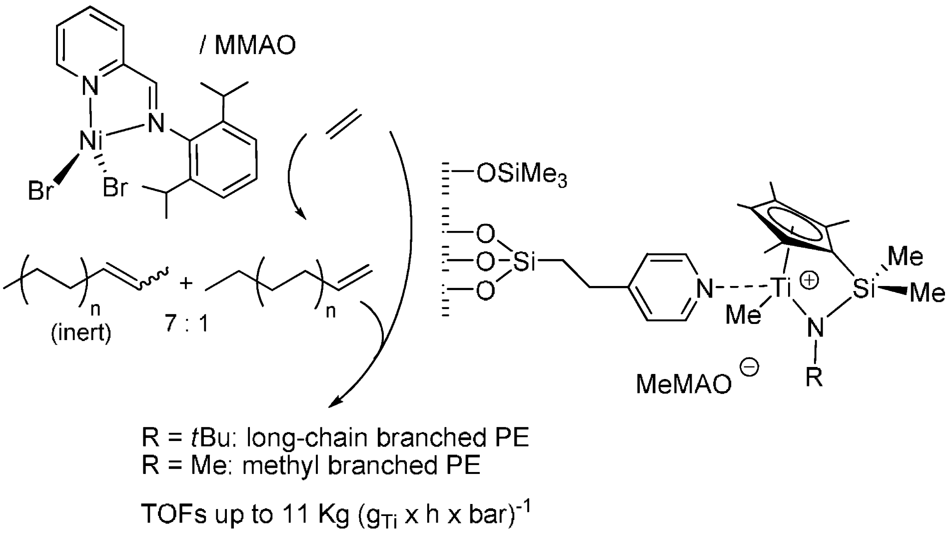
Polyethylene with short-chain branches, known as linear low-density polyethylene (LLDPE) is commonly produced on industrial scale by the copolymerization of ethylene with α-olefin comonomers such as 1-butene, 1-hexene and 1-octene in the presence of a Ziegler–Natta or homogeneous single-site catalysts [102–104]. The discovery of half-sandwich group 4 metal catalyst, known as constrained-geometry catalysts (CGCs), has offered the possibility of efficiently incorporating α-olefin macromonomers, separately synthesized or directly formed in situ, into the polyethylene backbone to give polyethylenes with more or less long-chain branches [105–107].

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 polyethylene (PE) from ethylene stock [108–110]. By this way 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 ultra low-density polyethylene (ULDPE).

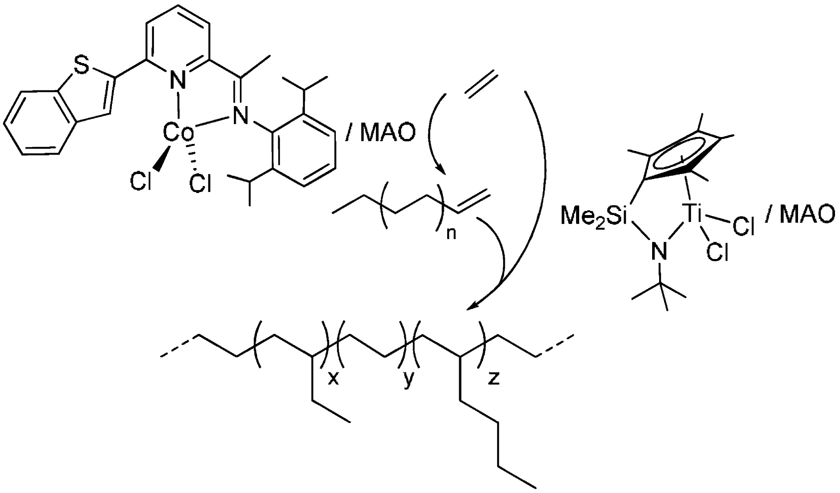
Dibromo(imino-pyridine) Ni^{II} pre-catalyst in combination with silica-supported linked cyclopentadienyl-amido Ti^{IV} complexes, activated with MMAO, have been recently proposed by Okuda and co-workers as a tandem copolymerization approach to the preparation of moderately branched polyethylenes (up to 21 br/1000 C) with controlled microstructures (Scheme 21) [12]. In spite of a relatively high activity of the oligomerization catalyst to give branched 1- and 2-olefins in about 1:7 ratio (non-Schulz–Flory distribution was observed), only the former were incorporated in the growing polymer chain.

Highly selective and efficient Co^{II} iminopyridyl-based oligomerization catalysts for the production of linear α-olefins in a Schulz–Flory distribution (see cfr 6.1), in combination with the CGC, $TiCl_2[(\eta^5\text{-}C_5Me_4)SiMe_2(tBuN)]$, generate, upon activation with MAO, a new class of homogeneous tandem systems for the effective conversion of ethylene into a variety of materials, spanning from LLDPE to rubbery PE with an excellent control on both number and type of branches in the polyethylene microstructures [9,111,112]. By an appropriate choice of catalysts and experimental conditions, polyethylene with C_2–C_8 branches (over 250 br/1000 C), with Tg as low as −60 °C, have been produced for the first time by tandem copolymerization catalysis with productivities as high as 32 kg (g of Ti × h × bar)$^{-1}$ (Scheme 22) [9]. The DSC analysis of the copolymers showed melting points between 111 and 105 °C for the semicrystalline materials containing macromolecules with lower branching. The glass transition temperatures varied between −60 and −54 °C. Unlike α-olefin incorporation and branching, the molecular weight of the copolymers decreases by increasing the oligomerization molar fraction (χ_{Co}), from 570 kg mol^{-1} for the homopolymer obtained with Ti complex alone down to 147 kg mol^{-1} for the copolymer prepared in the presence of a Co molar fraction (χ_{Co}) of 0.5.

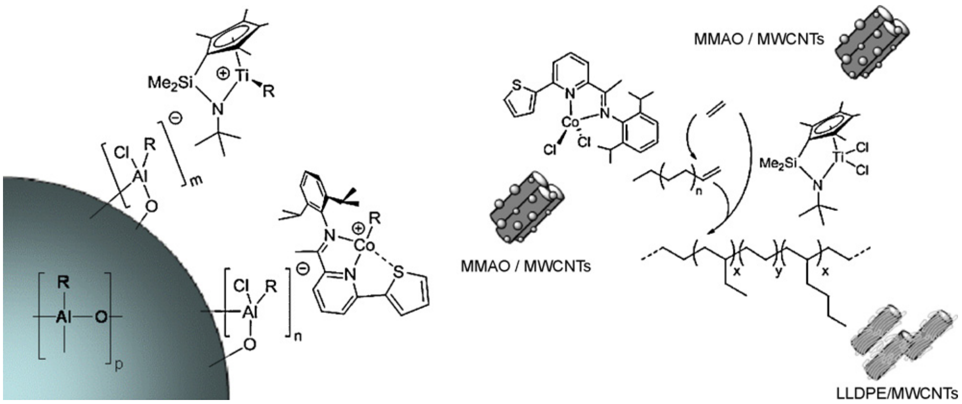
LLDPEs with exclusively ethyl branches (up to 56 C_2 br/1000 C), and higher turnover frequencies (over 139 kg (g of Zr × h × bar)$^{-1}$) have been also prepared by means of a *tandem* protocol involving the same Co^{II} oligomerization catalysts in combination with the more efficient and selective copolymerization system, Cp_2ZrCl_2 [10]. All the LLDPEs produced by the Co^{II}/Zr^{IV} tandem catalysis are semicrystalline off-white solids and exhibit melting points



Scheme 21. Ni^{II}/Ti^{IV} tandem copolymerization catalysis.



Scheme 22. Co^{II}/Ti^{IV} tandem copolymerization catalysis.



Scheme 23. Left: Active species generated at the CNT surface, right: In situ tandem copolymerization catalysis.

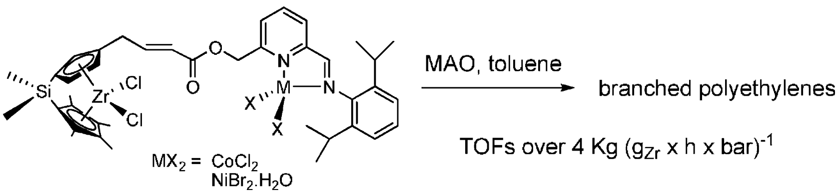
between 87 to 121 °C accompanied by moderately high heats of fusion ($\Delta H = 82–107$ J/g *vs* 170 J/g for commercial HDPE produced by Ziegle–Natta, Cr or metallocene catalysis). The molecular weights are generally low (M_w in the range 64–143 kg mol^{-1}) and decrease when increasing the molar fraction of the oligomerization catalyst while the polydispersity, M_w/M_n, is in the range from 2.1 to 3.7.

Textured surface coating of multi-walled carbon nanotubes (MWCNTs) with LLDPEs has been successfully achieved by Giambastiani and co-workers combining the *tandem* copolymerization protocols with the polymerization filling technique (PFT) [86,87]. This method can be conveniently described as a four-step process which involves (i) the physico-chemical anchoring of the co-catalyst, MMAO, onto the CNT surface, (ii) the addition of the oligomerization and copolymerization pre-catalysts and their subsequent activation at the surface of the nanofillers (Scheme 23, left), (iii) the surface-initiated *tandem* copolymerization of ethylene and α-olefins and, (iv) the growth and precipitation of LLDPE onto the CNTs leading to their coating (Scheme 23, right).

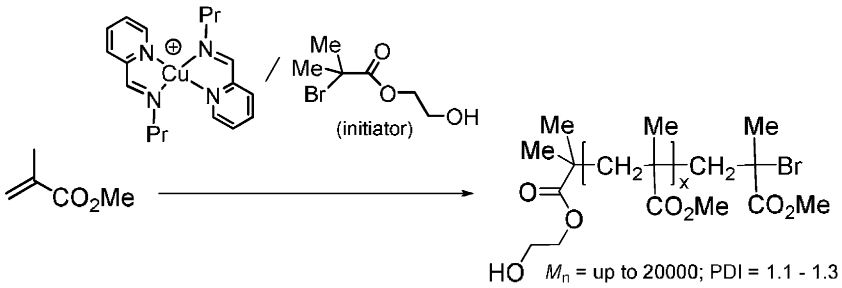
This protocol, which is actually a variation of the PFT originally developed for Ziegler–Natta polymerization [113,114] and more recently applied in metallocene catalysis in conjunction with a large variety of micro and nanofillers [115–118], allows for the complete deaggregation of the native MWCNT bundles and provides an effective way to control the branching in the PEs produced at the nanotube surface (from 3.5 br to 34.5 br/1000 C).

TEM micrographs of the composite materials prepared by this technique show an interesting dependence of the PE-coating morphology on the experimental parameters of the *tandem* system [87].

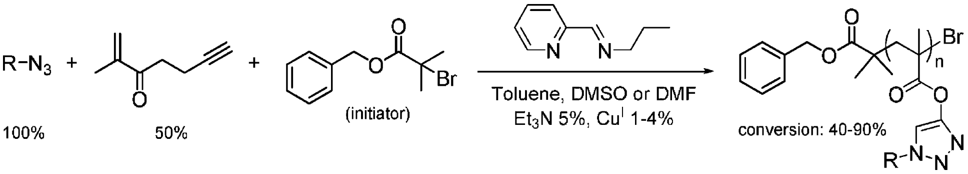
Osakada and co-workers have recently developed an efficient and clean method to prepare new heterobinuclear early-late transition metal catalysts where the late and early metals are in close proximity to each other (Scheme 24) [11,119]. The target was to increase the catalytic efficiency of the "intramolecular" *tan-*



Scheme 24. Tandem copolymerization catalysis initiated by binuclear complexes.



Scheme 25. Cu^I iminopyridyl complexes for the synthesis of α-hydroxy terminally functionalized PMMA from ATRP.



Scheme 26. Cu^I iminopyridyl catalyzed Huisgens/LRP reaction.

dem system [120–123] as well as achieve better control on the PE microstructure and morphology by varying the nature of the oligomerization site (late transition metal). The selectivity and productivity of the heterobinuclear early-late precursors have been compared to those provided by mixtures of independent mononuclear complexes thus showing the existence of a synergistic effect between the two metal centers.

6.3. Cu^I and Fe^{II} (imino)pyridine complexes for atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP) appears to be one of the most universal and widely applicable examples of free radical pseudo-living polymerization of vinyl monomers (styrenic, methacrylic, acrylic) to give a variety of polymeric materials with controlled M_n and narrow molecular weight distributions [124–127].

A number of transition metal complexes have been utilized to catalyze this process, but Cu^I halides stabilized by bidentate nitrogen containing ligands seems to be the most effective and widely studied systems. Of these, pyridyl-2-aldimine ligands are the most promising, because of their capability of stabilizing metals in their low oxidation state [128] as well as producing soluble Cu^I species for homogeneous processes.

Pyridyl-2-(*N*-propyl-aldimine) Cu^I complexes, in conjunction with ethyl 2-bromoisobutyrate as initiator, have been introduced by Haddleton and co-workers for the efficient ATR polymerization of methyl methacrylate (MMA) in both homogeneous [129,130] or heterogeneous phase (silica or polystyrene supported catalysts) [18]. Catalysts containing *n*-alkyl substituents at the imine group are more efficient than those containing branched alkyl groups, the latter resulting in a loss of control of the polymerization process manifested by a slowing of the reaction rate and a broadening of the polydispersity index (PDI) [131]. The same complexes have also demonstrated how α-hydroxy functional PMMAs can be conveniently produced by the Cu^I catalyst precursors using an alkoxy containing alkyl bromide system as initiator with no apparent effect on the control of the molecular weights (M_n) and polydispersities (Scheme 25) [58].

As a further extension of the previous study, Mantovani and Haddleton have also shown how Cu^I-catalyzed azide-alkyne cycloaddition (Huisgens type reaction) and living radical polymerizations (LRP) can share the same CuBr-(imino)pyridine catalytic system in a spectacular and sequential one-pot process for the synthesis of functional molecular materials (Scheme 26) [132,133].

A variety of pyridyl-2-(*N*-alkyl-aldimine) Cu^I complexes with increasing lengths of the ligand alkyl chains and solubility have been investigated for the ATR polymerization of styrene by Amass et al. [134]. Increasing both the length of the ligand alkyl chain (from propyl to octyl) and the solvent polarity increases the catalyst solubility narrowing the molecular weight distribution of the polymerization products, while the polymerization rate is decreased.

Relatively fast and well controlled ATR polymerizations of styrene and MMA promoted by mononuclear or binuclear Fe^{II} iminopyridyl complexes has been recently proposed by Gibson et al. [13]. Relatively bulky substituents at the imino group generally stabilize binuclear species in both solution and solid state and, as a consequence, are relatively slow ATRP catalysts. Mononuclear Fe^{II} pre-catalysts obtained with bulky imine substituents, along with methyl groups on the 6-position of the pyridine ring, generate relatively fast catalysts for the well controlled polymerization of styrene and MMA.

7. Conclusions

In this article, we have reviewed the state-of-the art of (imino)pyridyl metal complexes and, specifically, their use as catalyst precursors for the homopolymerization, oligomerization and copolymerization of ethylene and other linear or cyclic olefins, including monomers containing polar functional groups. Like for 2,6-bis(imino)pyridyl metal complexes and metallocenes, a substantial contribution to the success of (imino)pyridyl metal catalysts in polymerization reactions is due to the availability of MAO. Indeed, without MAO and related activators, no appreciable activity in insertion polymerization would be exhibited by any (imino)pyridyl metal complex and only atom transfer radical polymerization reactions would be catalyzed by these systems.

The success of (imino)pyridyl metal catalysts for the polymerization/oligomerization of olefins is largely attributable to their molecular and electronic structure. Indeed, the facile tuning of the (imino)pyridine framework by simple modification of the ligand architecture and insertion of various substituents, together with the ease of preparation, storage and handling, make these late transition metal catalysts advantageous over other types of single-site catalysts for the conversion of olefins into different types of macromolecules.

The reduced steric protection of the axial coordination sites of the coordinated metal center is an apparent drawback which favors the chain transfer rate over the propagation rate, yet this feature has been exploited to generate (imino)pyridyl cobalt catalysts with unrivalled activity and selectivity in the oligomerization and co-oligomerization of ethylene. Moreover, due to their good compatibility with various early and late metal copolymerization catalysts, (imino)pyridyl metal complexes can be used as oligomerization catalysts in tandem catalytic processes for the production of branched PE, nanocomposites and nanohybrids with unique structures.

Acknowledgments

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The crystal structures were retrieved from the Cambridge Structural Database [135] (CSD version 5.30 November 2008) of Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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