

Ethylene oligomerization using iron complexes:
beyond the discovery of bis(imino)pyridine ligandsCite this: *Chem. Commun.*, 2014, 50, 1398Adrien Boudier,^a Pierre-Alain R. Breuil,^{*a} Lionel Magna,^a Hélène Olivier-Bourbigou^{*a} and Pierre Braunstein^b

Since the discovery that bis(imino)pyridine ligands are able to confer high activities in ethylene oligomerization and polymerization to their iron complexes, considerable attention has been focused on catalyst design for these reactions and this research constitutes an ever-growing area in molecular catalysis. The tuning of the ligand structures and properties, and thus of catalysts, generally represents the basis for subsequent work contributing to process development and industrialization. Significant effort is therefore devoted to generate structural diversity in order to access the required catalyst stability and selectivity. This feature article outlines nitrogen-containing ligands that have been developed for the iron-catalyzed oligomerization of ethylene since the seminal discovery of the properties of bis(imino)pyridine ligands.

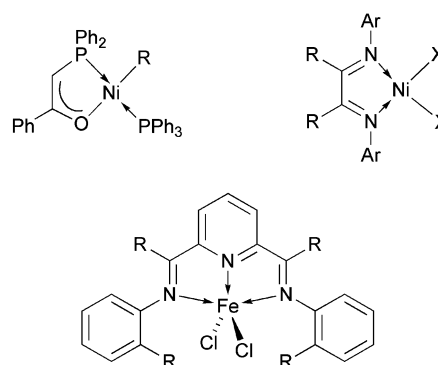
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Introduction

Initial discovery of the so-called “nickel effect” by Ziegler leading to ethylene polymerization¹ and to oligomerization² triggered great efforts to develop new homogeneous late transition metal catalysts enabling the transformation of olefins and led to worldwide processes³ and significant changes in our society. Ligand design plays a pivotal role in the development of more active and selective catalysts for future industrial processes. Monoanionic (P,O) ligands coordinated to nickel complexes and developed by Keim and coworkers and the Shell company proved to be excellent one-component model catalysts for the oligomerization of ethylene⁴ and resulted in the successful Shell Higher Olefin Process (SHOP) (Scheme 1) for the production of linear olefins.⁵ Neutral (P,O) ligands leading to cationic nickel catalysts active in ethylene oligomerization in the presence of MAO (methylaluminoxane) were later reported⁶ and Brookhart *et al.* developed new palladium(II)⁷ and nickel(II)⁸ complexes chelated by α -diimine ligands (Scheme 1) as very active catalysts for α -olefin oligomerization and polymerization. In the 1990s, the groups of Bennett, Brookhart and Gibson reported that tridentate 2,6-bis(imino)pyridine (BIP) ligands yielded the most active ethylene oligomerization catalysts to date, once coordinated to an iron centre and after activation by MAO (Scheme 1), leading to a wide range of linear α olefins (C4–C30).^{9–11} Since then, much work has been devoted to modifications of

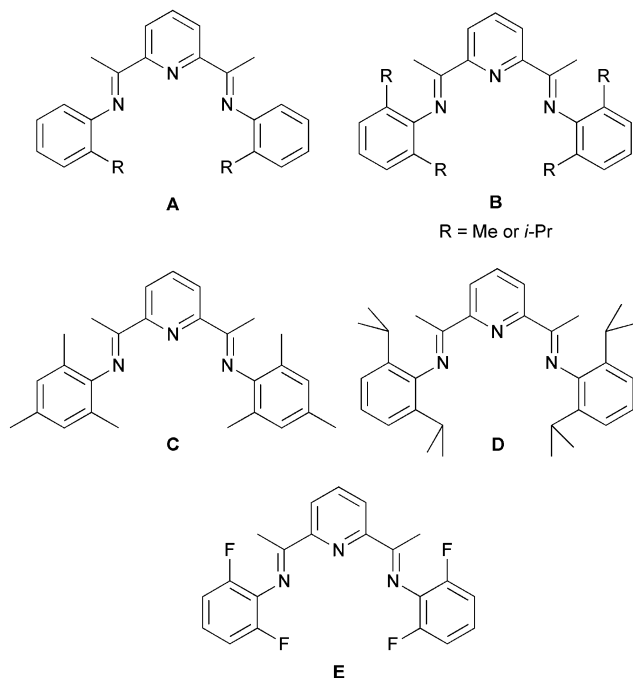


Scheme 1 Examples of homogeneous olefin transformation precatalysts.

these ligands and understanding of the chemistry of their metal derivatives. Bianchini, Gibson and co-workers independently reviewed these results.^{12–14} These iron complexes represent a remarkable new generation of ethylene oligomerization catalysts that have extended our understanding of the influence of electronic and steric properties of the ligands in controlling transition metal-catalyzed olefin polymerization and oligomerization. However, several limitations still need to be addressed for further development of a catalytic system such as the stability of the catalyst, the proper control of the reaction parameters related to the tuning of the selectivity or the limitation of side-products, *i.e.* mainly polyethylene.¹⁵ Circumventing these limitations is of considerable interest for iron-based olefin transformations and would allow the use of an abundant, inexpensive and environmentally friendly metal in additional industrial processes for the production of linear α olefins.

Regarding bis(imino)pyridine-based iron catalysts, the nature of the catalytic reaction, *i.e.*, ethylene oligomerization

^a IFP Energies nouvelles, Rond point de l'échangeur de Solaize, 69360 Solaize, France. E-mail: pierre-alain.breuil@ifpen.fr, helene.olivier-bourbigou@ifpen.fr^b Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, F-67081 Strasbourg Cedex, France



Scheme 2 Various bis(imino)pyridine ligands used for ethylene transformation.

or polymerization, is mainly determined by the bulkiness of the *o*-substituents of the *N*-aryl ring. Indeed, oligomers are obtained with mono *o*-substituted catalysts [FeCl₂(A)] for example (Scheme 2), except for benzyl or trifluoromethyl substituents on the *o*-position or in the case of the *o*-Me group with bulky *p*-substituents. Complexes with *o*-disubstituted rings at the imine nitrogen, such as [FeCl₂(B)], [FeCl₂(C)] and [FeCl₂(D)], catalyze polymerization reactions, except in the case of 2,6-difluoro ligands [FeCl₂(E)] (Scheme 2).¹²

Under optimized conditions (30 atm and 90 °C) and activated by 1000 equiv. of MMAO (modified methylaluminoxane), an iron precatalyst containing the chelating ligand A oligomerizes ethylene with high activity (1.2×10^8 g (mol h atm)⁻¹) and yields a full range (C₄–C₂₄) distribution of oligomers with an excellent selectivity in α -olefins.¹⁰ The oligomeric products followed a Schulz–Flory distribution ($K = 0.70$). The Schulz–Flory coefficient K (eqn (1)) represents the probability of chain transfer;¹⁶ a high K value means that the catalyst produces high molecular weight oligomers. To the best of our knowledge, this catalyst precursor [FeCl₂(A)] exhibits the highest activity among all iron precatalysts reported in the literature at the time of its publication.

$$K = \frac{k_{\text{prop}}}{(k_{\text{prop}} + k_{\text{ch transfer}})} = \frac{\text{mol}C_{n+2}}{\text{mol}C_n} \quad (1)$$

In this Feature article, we review the recent developments of iron-based catalysts for ethylene oligomerization in which the metal is chelated by tridentate or bidentate, neutral or anionic N-based ligands and wish to highlight the directions in which ligand and catalyst designs have developed since Brookhart's and Gibson's discovery. Bis(imino)pyridine ligands are excluded from this article since several recent

reviews have detailed their development.^{12–14} Recent reviews and articles, which appeared during the preparation of this manuscript, have reported the influence of N-containing ligands, including large bis(imino)pyridine derivatives, on the catalytic properties of iron complexes in ethylene oligomerization and polymerization.¹⁵ We will first examine the recent progress made with tridentate ligands based on pyridine or related heterocycles, on 1,10-phenanthroline, quinoxaline or quinoxazoline ligands. We will then examine other tridentate ligands in which the central donor atom is part of a five-membered ring and then various tridentate systems including those containing a diimine moiety. We will continue with bidentate ligands and finish with anionic ligands, which have emerged much more recently in iron-based catalysts for ethylene oligomerization. For consistency, activities will be expressed in g_{C₂H₄} (mol_{Fe} h atm)⁻¹ and the figures reported correspond to the optimal activity for the given family of ligands. It should be noted that these performances are obtained under a defined set of conditions specific to each research group and are equipment-dependent (reactor size, stirring, ethylene admission...) and experimentation-dependent (solvent, ethylene concentration, nature of the cocatalyst, order of introduction of the catalyst components...). Therefore reference catalyst(s) should definitely be evaluated by the same research group in each catalytic test campaign for an effective benchmark. Extrapolating the catalyst activity to 1 h should be considered very carefully for short reaction times.

Neutral tridentate ligands

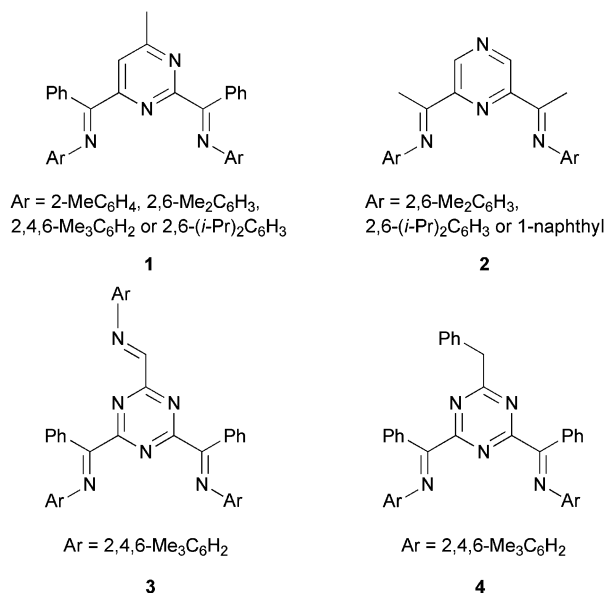
Modifications of the central ring

The properties of the central ring were tuned by introduction of additional N-atoms in the heterocycle.^{17–21} Less basic heterocycles such as pyrimidine in 1 or pyrazine in 2 led to lower activities of the corresponding iron catalysts in ethylene oligomerization or polymerization compared to the bis(imino)pyridine-based catalysts, with values of 10⁵ g (mol h atm)⁻¹ and 10⁸ g (mol h atm)⁻¹, respectively (under 1 to 4 atm and at 25 to 50 °C).^{9,11,17} While with a triazine moiety, as in ligands 3 and 4 (Scheme 3), attempts at coordination to iron failed.¹⁹

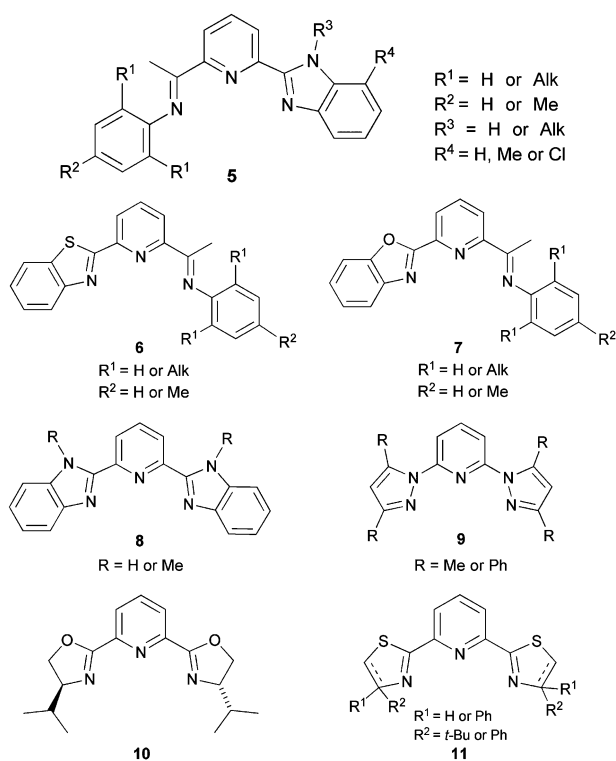
Modifications of the imino groups

Derived from bis(imino)pyridine complex backbones, iron precatalysts chelated by dissymmetrical tridentate ligands 5 bearing benzimidazolyl groups (Scheme 4) were studied by Sun and co-workers and shown to oligomerize ethylene after activation with MAO or MMAO with activities around 10⁴–10⁵ g (mol h atm)⁻¹ and high selectivity for α -olefins with a Schulz–Flory distribution ($K = 0.46$ – 0.62).^{22–27} No clear correlation could be drawn from the variation of the different groups R¹–R⁴ introduced, the highest activity (4.7×10^5 g (mol h atm)⁻¹ at 30 atm and 20 °C) being obtained for R¹ = *i*-Pr, R² = R⁴ = H and R³ = Me.

However, when benzothiazolyl- and benzoxazolyl-derived ligands 6 and 7 were used, up to one order of magnitude



Scheme 3 Bis(imino)N-heterocyclic ligands.



Scheme 4 Azole-based derivatives.

improvement (10^6 g (mol h atm)⁻¹ under 10 atm and at 30 °C) was observed for the best activities but selectivities in α -olefins were slightly degraded ($\sim 97\%$).^{23,25} Considering benzothiazolyl ligands **6**, the highest activity was obtained for R¹ = R² = Me (1.1×10^6 g (mol h atm)⁻¹; $\alpha > 97\%$) whereas the most active iron system for ethylene oligomerization of type **7** was found for R¹ = Et and R² = H (1.0×10^6 g (mol h atm)⁻¹ under 10 atm and at 30 °C; $\alpha > 96\%$).

Besides methylaluminoxane cocatalysts, AlEt₂Cl successfully activated the precatalysts [FeCl₂(**5**)], affording short chain oligomers under ethylene, however, with low activities ($< 10^4$ g (mol h atm)⁻¹ under 10 atm and at 20–60 °C). In contrast, iron precursors chelated by ligand **7** yielded inactive systems when AlEt₂Cl or AlEt₃ were used as cocatalysts. Considering the impact of temperature under the same C₂H₄ pressure on catalytic performances, it was established that the higher the temperature, the lower the activity (for ligand **5** with R¹ = *i*-Pr and R² = R³ = R⁴ = H; from 2.6×10^5 g (mol h atm)⁻¹ at 20 °C to 1.0×10^4 g (mol h atm)⁻¹ at 60 °C) and the selectivity in α -olefins.

Iron(III) complexes bearing benzimidazolyl-based ligands **5** were also investigated and found to be less active than iron(II) analogues (2.2×10^4 g (mol h atm)⁻¹ and 9.2×10^4 g (mol h atm)⁻¹, respectively, with R¹ = R³ = Me and R² = R⁴ = H, under 10 atm and at 20 °C).²⁴

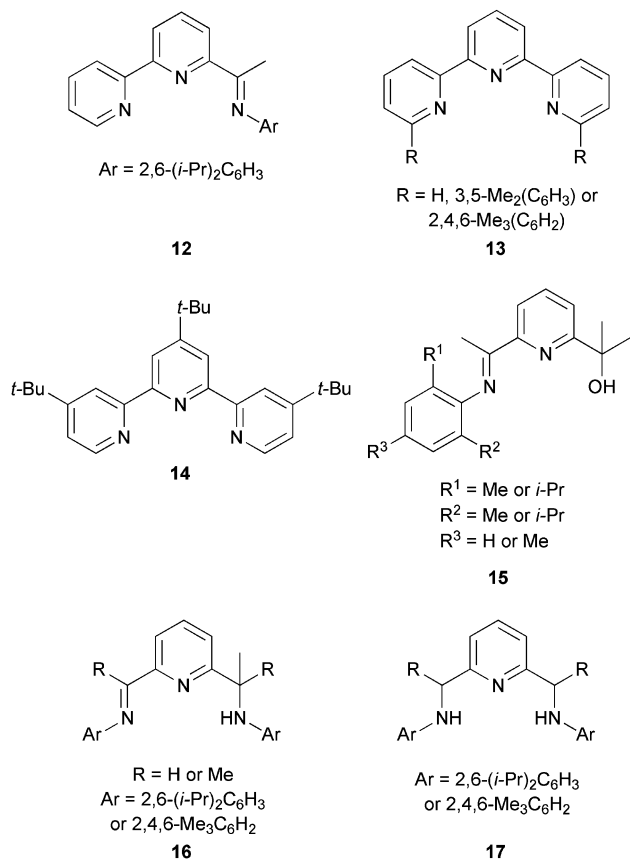
Symmetrical ligands **8** and **9** having benzimidazolyl or pyrazolyl groups were also coordinated to iron but the resulting complexes were poorly active ($< 10^3$ g (mol h atm)⁻¹ at 8 atm and 20 °C) in the presence of MMAO for ethylene oligomerization.²⁸ A symmetrical iron complex containing the bis(oxazoline)pyridine ligand **10** afforded a poorly active catalyst for ethylene transformation with MAO as a cocatalyst.²⁹

Britovsek *et al.*³⁰ reported that bis(thiazolyl)- and bis-(thiazolyl)pyridine ligands **11** afford bis-ligated [Fe(**11**)₂]²⁺[FeCl₄]²⁻ for R¹ = H and R² = Ph or mono-ligated complexes [Fe(**11**)Cl₂] for R¹ = H and R² = *t*-Bu, R¹ = R² = Ph or bis(thiazolyl)pyridine with R¹ = *t*-Bu. Activated by MAO, low polymerization activities were observed.

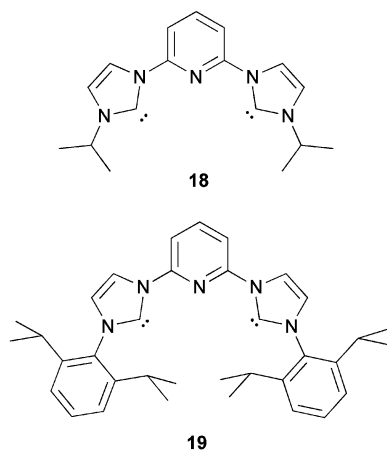
Iron coordination and reactivity of the corresponding complexes towards ethylene were also studied for bi- and terpyridine ligands (Scheme 5).³¹ Iron precursors associated with ligand **12** are active in ethylene oligomerization, producing mainly 1-butene and 1-hexene, with good activity (5.7×10^5 g (mol h atm)⁻¹ at 5 atm and 50 °C). In the presence of FeCl₂, ligand **13** with R = H formed the bis-chelated species [Fe(**13**)₂]²⁺[FeCl₄]²⁻, while for R = 3,5-Me₂C₆H₃ or 2,4,6-Me₃C₆H₂, the complexes [Fe(**13**)Cl₂] were isolated. When tested in ethylene transformation, [Fe(**13**)Cl₂] (for R = H) showed poor activity in the presence of MMAO whereas [Fe(**13**)₂]²⁺[FeCl₄]²⁻/MMAO (for R = 3,5-Me₂C₆H₃ or 2,4,6-Me₃C₆H₂) was inactive. The [Fe(**14**)Cl₃] precatalyst bearing *t*-butyl-substituted terpyridine **14** did not lead to ethylene transformation upon activation with MMAO.

Under 1 atm of ethylene, iron precursors containing ligand **15** polymerize ethylene using MAO as a cocatalyst (10^5 g (mol h atm)⁻¹ at 25 °C).³² Compared to their parent bis(imino)pyridine system, iron complexes bearing **16** and **17** exhibited lower activities (10^5 g (mol h atm)⁻¹ and 10^4 g (mol h atm)⁻¹, respectively, at 10 atm and 35 °C) affording only the polymer.³³

The impact of the chelating bonding mode of the tridentate ligand on the catalysis was investigated by McGuinness and co-workers who developed iron bis(carbene)pyridine complexes and tested them in ethylene transformation (Scheme 6).³⁴ Ligand **18** was obtained by deprotonation of the corresponding



Scheme 5 Ligands based on a central pyridine ring.

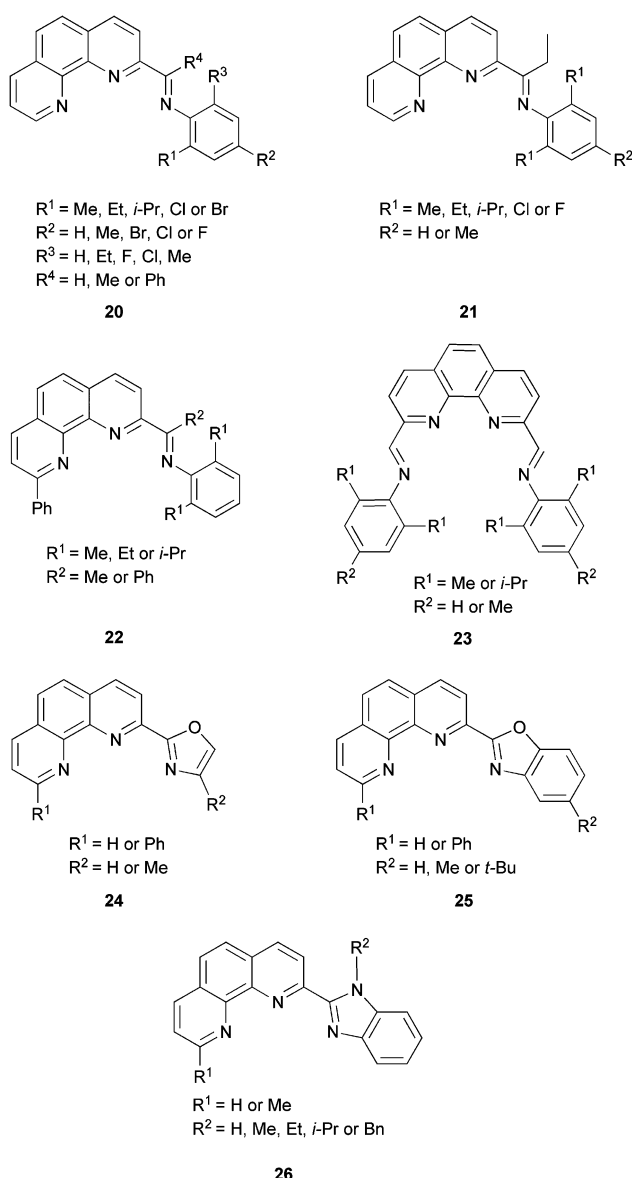


Scheme 6 Bis(carbene)pyridine ligands.

imidazolium bromide using KN(SiMe₃)₂. Treatment of iron dibromide with this bis-carbene ligand in tetrahydrofuran afforded the bis-ligated complex [FeBr₂(**18**)₂]²⁺[FeBr₄]²⁻. With **19**, bearing the bulkier 2,6-*i*-Pr₂ substituent, the mono ligand iron complex [FeBr₂(**19**)] was obtained.^{35–37} Treated by MAO, these iron precursors were totally inactive in the presence of ethylene. From FAB MS analysis of the reaction media and the observation of the methylated ligand, the authors suggested catalyst decomposition *via* reductive elimination.

Toward the development of new generations of ligands

1,10-Phenanthroline ligands. Iron complexes bearing neutral tridentate ligands based on a 1,10-phenanthroline skeleton were widely developed by Sun and co-workers (Scheme 7).^{38–42} Upon activation with MAO, the iron precursors ligated by 2-imino-1,10-phenanthroline **20** promote the oligomerization and polymerization of ethylene following a Schulz–Flory distribution, with the *K* value in the range 0.30–0.62.^{38,39,42} Active catalysts were formed using ligand **20** with R¹ = R³ = Me, R² = Br and R⁴ = Me (4.9 × 10⁶ g (mol h atm)^{−1} under 10 atm and at 40 °C), with a selectivity of α -olefins up to 91%. However, low molecular-weight waxes were formed (1.7 × 10⁶ g (mol h atm)^{−1}).³⁹ The highest wax-free oligomerization activity was obtained for **20** with R¹ = R³ = Cl, R² = H and R⁴ = Me (3.5 × 10⁶ g (mol h atm)^{−1} under 10 atm and at 40 °C) and the oligomer distribution is of



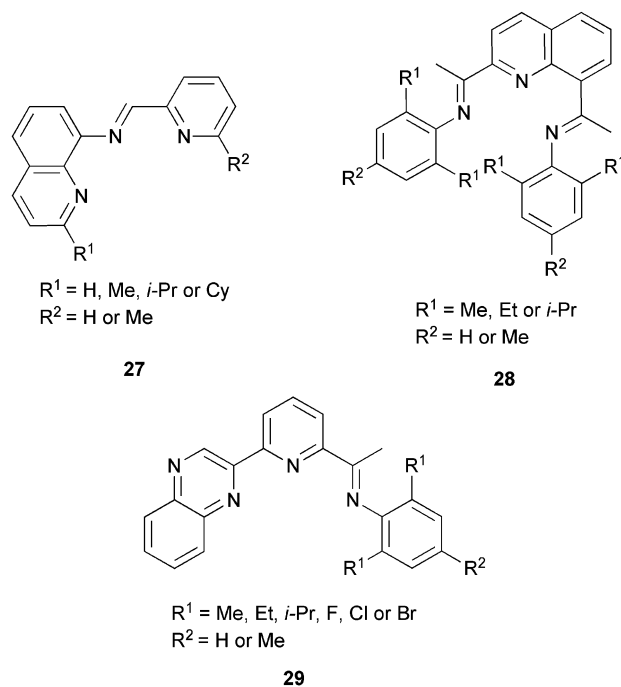
Scheme 7 Ligands based on a 1,10-phenanthroline skeleton.

the Schulz-Flory type ($K = 0.52$).³⁹ For methylketimine complexes ($R^4 = \text{Me}$), the bulkier the aryl group, the higher the oligomerization activity. Fe complexes with 2-iminophenanthrolines have been recently applied to a 500 tonne pilot plant.¹⁵ No activity was detected for iron complexes bearing ligand **20** (with $R^1 = i\text{-Pr}$, $R^2 = R^3 = \text{H}$ and $R^4 = \text{Me}$) when AlEt_2Cl or AlEtCl_2 were used as cocatalysts, while with AlEt_3 ($\text{Al/Fe} = 500$), activities around $10^4 \text{ g (mol h atm)}^{-1}$ were obtained under 1 atm and at 20°C . The iron complexes with 2-ethyl-ketimino-1,10-phenanthroline **21** led to activities for ethylene oligomerization ($2.1 \times 10^6 \text{ g (mol h atm)}^{-1}$ for $R^1 = \text{Me}$ and $R^2 = \text{H}$ under 10 atm and at 50°C) along with polymerization ($0.2 \times 10^6 \text{ g (mol h atm)}^{-1}$) over a period of 30 minutes similar to those with the analogous ligands **20**.⁴¹ Interestingly, the halogenated analogues with $R^1 = \text{F}$ or Cl led to good activities for ethylene oligomerization ($1.0 \times 10^6 \text{ g (mol h atm)}^{-1}$ under 10 atm and at 50°C), traces of low molecular-weight waxes also being formed. Incorporating a phenyl substituent into the phenanthroline moiety as in ligand **22** led to an active iron catalyst in combination with MMAO ($2.7 \times 10^5 \text{ g (mol h atm)}^{-1}$ under 1 atm and at 20°C), yielding mainly 1-butene (selectivity >99% among oligomeric products) with however moderate productivity.⁴³ Symmetric 2,9-bis(imino)-1,10-phenanthroline ligands **23** coordinate iron precursors in a tridentate fashion but the complexes show no activity for ethylene oligomerization in the presence of MAO.⁴⁰ The ligands 2-oxazoline- or benzoxazole-1,10-phenanthroline and 2-(benzimidazol-2-yl)-1,10-phenanthroline **24–26** coordinated to iron led to catalysts of low ($<10^5 \text{ g (mol h atm)}^{-1}$ for **24** and **25**) or moderate activity ($1.2 \times 10^5 \text{ g (mol h atm)}^{-1}$ under 1 or 10 atm and at 20 to 60°C) with short reaction times for **26** with $R^1 = R^2 = \text{H}$.^{44,45} Short chain oligomers were obtained, with up to 95% of butenes and a selectivity in 1-butene up to 92%.

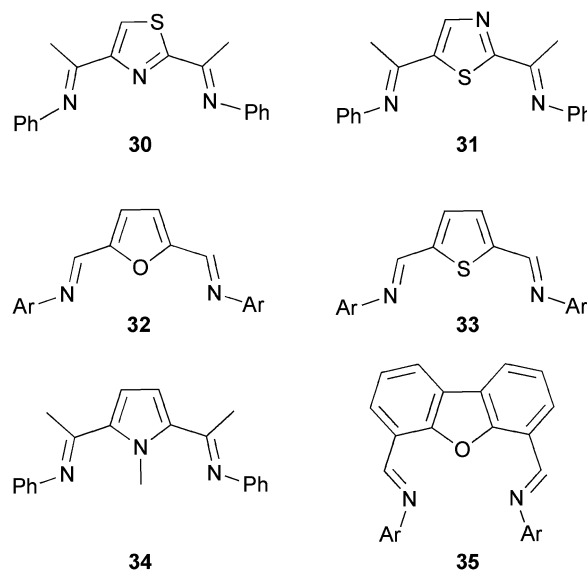
Quinoline and quinoxaline ligands

A one-pot synthesis strategy was employed to prepare iron complexes chelated by ligand **27** starting from aminoquinoline and pyridine carboxaldehyde (Scheme 8).⁴⁶ Upon treatment with MMAO, moderate activities and productivities toward ethylene oligomerization ($<10^5 \text{ g (mol h atm)}^{-1}$ under 30 atm and at 20°C) were obtained, with butenes being the major products (>90%) with a selectivity for 1-butene of 98% ($R^1 = \text{Cy}$ and $R^2 = \text{Me}$).

A series of 2,8-bis(imino)quinoline **28** ligands were synthesized and coordination to iron was only observed for $R^1 = \text{Me}$.⁴⁷ Activated by a substantial excess of MAO (above 2000), iron precatalysts polymerized ethylene at higher temperatures and up to 100°C ($2.5 \times 10^5 \text{ g (mol h atm)}^{-1}$ under 10 atm) while at 40°C , only traces of polymers were detected. Active catalysts were also reported bearing 2-quinoxaliny-6-iminopyridines **29** in the presence of MAO or MMAO.⁴⁸ Under optimized conditions (1 atm and 20°C), activities around 10^5 – $10^6 \text{ g (mol h atm)}^{-1}$ and short chain olefins were reported while at higher pressure, polymer formation accompanied the oligomeric products.



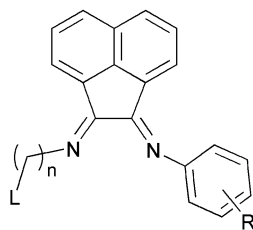
Scheme 8 Quinoline and quinoxaline frameworks.



Scheme 9 Five-membered bis(imino) L-heterocycles.

Five-membered L-heterocyclic ligands

Tenza and co-workers prepared and tested a series of iron precursors bearing tridentate ligands with a five-membered central ring (Scheme 9).²⁸ Catalysts Fe(L)Br_2 prepared from ligands **30** and **31** presented a low productivity ($10^5 \text{ g (mol h atm)}^{-1}$ under 8 atm and at 20°C) in a few minutes with butenes and hexenes as the main products in the presence of MAO or TEA/TA ($\text{AlEt}_3/[\text{Ph}_3\text{C}][\text{Al}(\text{O}t\text{Bu})_4]$). No coordination to iron(II) precursor was observed for ligands **32**, **33**, **34** and **35**.¹⁹



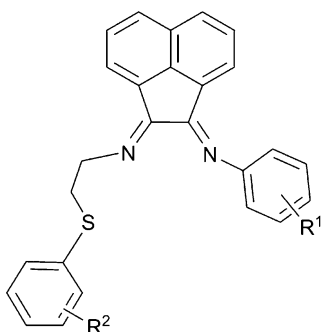
L = SR, PR₂, NR₂, OR, *o*-pyridine, morpholine
 n = 2 or 3
 R = 2,6-Me, 2,6-*i*-Pr, 2,6-*t*-Bu

Scheme 10 Structure of α -diimine N,N,L ligands.

Pendant donor α -diimine ligands

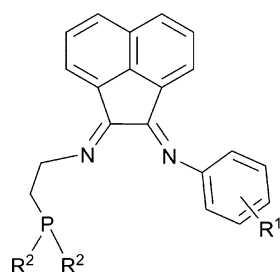
Ligands containing an α -diimine moiety have been widely used for the synthesis of complexes engaged in the transformation of olefins.^{8,49} Small and coworkers developed new iron precatalysts chelated by α -diimine ligands with pendant S, P, N and O donors (Scheme 10).^{50–52}

Independently of the nature of the L donor atom, increasing the length of the spacer resulted in a decrease in activity. A spacer with two carbon atoms between the two donor atoms



R¹ = 2,6-*i*Pr₂, 2,4,6-Me₃, 2,6-Me₂, 2,6-Me₂-4-*t*Bu,
 2,6-Me₂-4-Br
 R² = 4-Cl, 4-*t*Bu, 3,5-Me₂, 4-OMe, 2,6-Me₂, 3,5-Me₂

36

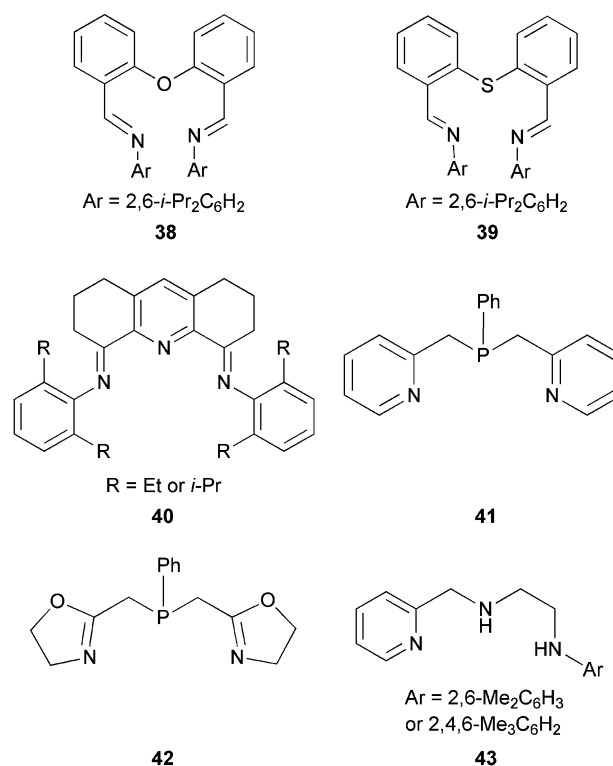


R¹ = 2-*i*Pr-6-Me, 2,6-*i*Pr₂, 2,4,6-Me₃, 2,4-Me₂
 R² = Ph, 3,5-Me₂-Ph, 2-Me-Ph, CyH

37

Scheme 11 N,N,S and N,N,P ligands.

was found to be of optimal length. Evaluated in cyclohexane and activated by MMAO, iron precursors chelated by the sulfur-containing ligand **36** were slightly more active than those bound by the phosphorous-containing ligand **37** (Scheme 11). Both were by far more active than iron precatalysts bearing α -diimine ligands with nitrogen pendant donor groups. The only precatalyst chelated by the N,N,O ligand was inactive. For **36** with L = S-Ph(4-*t*-Bu) and R¹ = 2,4,6-Me₃, the iron complex oligomerized ethylene with an activity up to 1.3×10^6 g (mol h atm)⁻¹ (under 70 atm and at 50 °C) whereas for N,N,P ligands, **37** with L = PPh₂, R¹ = 2,6-*i*-Pr₂ was the best candidate with an activity of 1.0×10^6 g (mol h atm)⁻¹ under similar conditions revealing the potential of α -diimine ligands with a pendant S or P donor group. Generally, α -olefins were obtained with high selectivity (>99%) and no polymer was formed. *Ortho*- and *meta*-substituents on the P and S pendant donors reduced the capacity of the precatalysts to oligomerize ethylene. Considering the phosphorus atom, replacing the phenyl by cyclohexyl substituents led to a decrease in activity (6.9×10^5 g (mol h atm)⁻¹ for R² = Ph and 2.1×10^5 g (mol h atm)⁻¹ for R² = Cy under 70 atm and at 50 °C). The influence of electronic variations was set out with N,N,S ligands. For R¹ = 2,6-Me₂, the complex with a *p*-*t*-Bu substituent on the thioether ring was more active than its analogues functionalized on the *p*-position by chloro or methoxy groups (8.1×10^5 g (mol h atm)⁻¹ for R² = 4-*t*-Bu; 3.1×10^5 g (mol h atm)⁻¹ for R² = 4-Cl and 5.8×10^5 g (mol h atm)⁻¹ for R² = 4-OMe under 70 atm and at 50 °C).



Scheme 12 Other tridentate ligands.

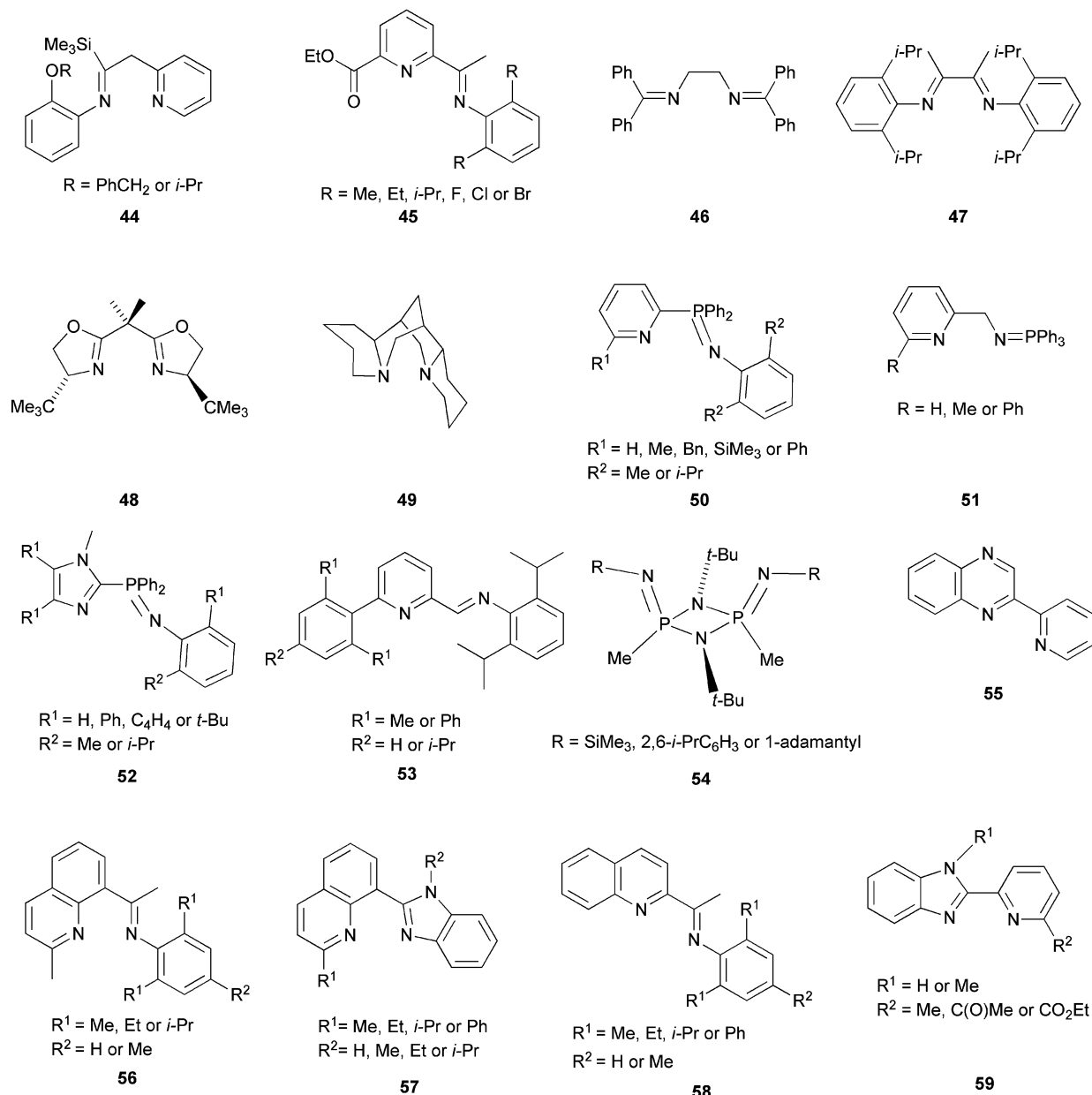
Other tridentate ligands

Like in the cases of bis(imino)furan **32** and bis(imino)-thiophene **33**, ligands **38** and **39** could not be coordinated to iron (Scheme 12).¹⁹ In the presence of MAO, polymerization of ethylene was observed with a complex bearing ligand **40**.⁵³ Tridentate ligands **41** and **42** led to inactive iron precursors towards ethylene transformation upon activation with either AlEt₃ or MAO.⁵⁴ Reaction of ligands **43** with FeCl₂ in *n*BuOH at elevated temperature gave a mononuclear complex for Ar = 2,6-Me₂C₆H₃ while a binuclear complex was obtained for Ar = 2,4,6-Me₃C₆H₂. In both cases, neutral N,NH,NH ligands were coordinated to the metal centre. Upon activation with MAO in a high ratio (Al/Fe = 400), these iron precursors oligomerized

ethylene with poor activities ($<10^3$ g (mol h atm)⁻¹ under 1 atm and at 25 °C).^{55,56}

Neutral bidentate ligands

Wang *et al.* have synthesized iron complexes bearing N,N ligands **44** for ethylene oligomerization (Scheme 13). When MAO was used as a cocatalyst, iron complexes exhibited low activity toward ethylene oligomerization while good activities were obtained with 1500 equiv. of MMAO (5.5×10^5 g (mol h atm)⁻¹ under 1 atm and at 20 °C).⁵⁷ Sun and co-workers prepared a series of 2-(ethylcarboxylato)-6-iminopyridyl complexes from ligands **45**.⁵⁸ Ferrous complexes were characterized by FT-IR spectroscopy.



Scheme 13 Bidentate ligands involved in the transformation of ethylene.

The slight shift of 10–20 cm^{−1} in the $\nu(\text{C}=\text{O})$ stretching vibrations suggested the presence of a weak interaction between the iron and the carbonyl oxygen of the ester group. However, all complexes were chelated by bidentate ligands except for R = Et. In this case, the solid state structure exhibits a Fe–O dative bond of 2.3769 Å. Upon activation with MAO (Al/Fe = 1000) in dichloromethane, all ferrous complexes were moderately active for ethylene oligomerization and polymerization ($\sim 10^4$ g (mol h atm)^{−1} under 10 atm and at 20 °C). Olefins were obtained in good to high linear α -selectivities (93% for R = Br to 99% for R = Me).

Bouwkamp *et al.* have coordinated the diimine ligand (Ph₂C=N)₂C₂H₄ **46** to an iron(II) centre.⁵⁹ Treatment of ferrous chloride complexes with MAO in toluene under ethylene pressure (5 atm) did not lead to any ethylene uptake, while α -diimine iron(II) complexes bearing ligands **47** developed by Chirik polymerized ethylene with low activities.⁶⁰ The activity of the four-coordinated iron precatalysts was significantly diminished in comparison to the Brookhart–Gibson five coordinated iron(II) dichloride complexes. The origin of this effect is most likely electronic rather than steric.⁶¹ Ligands **48** and **49** also yielded poorly active systems under similar conditions to those for ligand **47**.

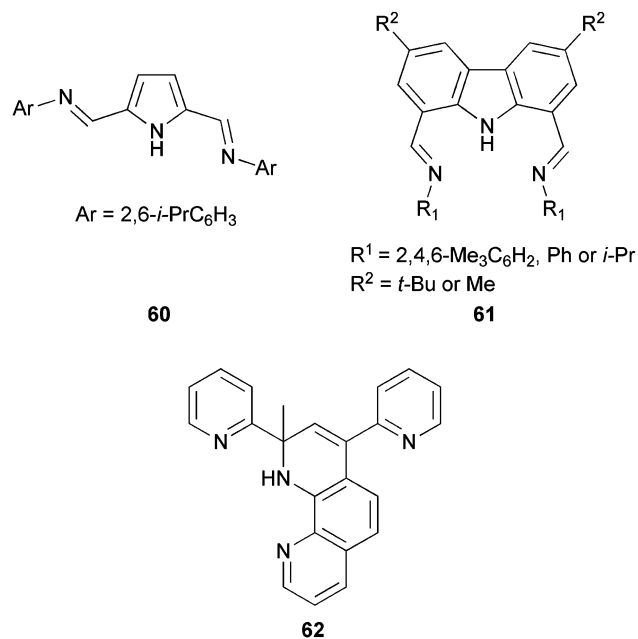
Stephan and co-workers reported on the use of pyridine- and imidazole-phosphinimine ligands **50**, **51** and **52** in the synthesis of bidentate iron(II) complexes.⁶¹ When tested in oligomerization catalysis, these complexes exhibited very low activities (<10³ g (mol h atm)^{−1} under 20 atm and at 35 °C). The same behaviour was observed with ligands **53** developed by Kempe *et al.*⁶² New bidentate bis(imino)cyclodisphosphazane ligands **54** led to inactive systems when associated with an iron centre.⁶³

Sun and co-workers have developed a range of bidentate ligands based on quinoxaline **55**⁶⁴ and quinoline ligands (**56–58**).^{65–67} The iron complex containing 2-(2-pyridyl)quinoxaline ligands gave only marginal activity. According to the authors, this result may be attributed to an improper electronic environment around the iron centres. Upon activation with MMAO, systems involving ligands **56** or **58** exhibited moderate activities toward ethylene dimerization (10⁴ g (mol h atm)^{−1} under 10 to 30 atm and at 20 to 100 °C) while bidentate iron(II) dichloride complexes bearing substituted 8-(benzimidazol-2-yl)quinolines **57** were described for ethylene polymerization ($\sim 10^4$ g (mol h atm)^{−1}). A series of 2-(benzimidazolyl)pyridine derivatives **59** was prepared, starting from *o*-phenylenediamine and 2,6-dimethylpyridine.²⁶ Treatment of these ligands with iron or cobalt dichloride yielded the desired *N,N*-bidentate complexes. Upon activation with MAO, MMAO or AlEt₂Cl, these iron and cobalt complexes gave moderate ethylene oligomerization activities ($\sim 10^4$ g (mol h atm)^{−1} under 10 to 30 atm and at 20 to 80 °C).

Anionic ligands

Very few examples of anionic ligands have been used in the design of new efficient iron precatalysts for the transformation of ethylene (Scheme 14).

The 2,5-bis(imino)pyrrole **60** was synthesized by condensation of pyrrole-2,5-dicarboxaldehyde with 2,6-di-*iso*-propylaniline in



Scheme 14 Anionic ligand precursors.

methanol.²⁰ After deprotonation by *n*-BuLi in Et₂O, the corresponding lithium salt of **60** was then chelated to an iron centre. Two equivalents of the deprotonated ligand were chelated to iron, yielding [Fe(**60**)₂] in which **60** acted exclusively as a mono-anionic bidentate ligand and not as a tridentate one. Upon activation with MAO, no ethylene uptake was observed with bis-ligand complex [Fe(**60**)₂]. Britovsek and Gibson developed iron complexes based on bis(imino)carbazole ligands **61**.^{19,21} Deprotonation of these ligands was achieved in THF solution using either *n*-BuLi at room temperature or NaH at 65 °C. Only mesityl ligands were isolated as lithium salts and characterized by NMR spectroscopy while the other deprotonated ligands were used *in situ*. For R¹ = 2,4,6-Me₃C₆H₂, Ph and *i*-Pr and R² = Me and *t*-Bu, iron(III) complexes were obtained by reaction of the lithium salt ligand with FeCl₃. Only one iron(II) complex was synthesized from a deprotonated ligand (R¹ = Me and R² = Ph). All iron complexes led to inactive catalysts for ethylene transformation upon activation with MAO. According to the authors, this absence of activity was most likely a consequence of steric crowding around the metal centre. Matsui and Matsunaga independently reported the use of ligands **61** in combination with iron(II)⁶⁸ or iron(III)⁶⁹ precursors for the polymerization of ethylene, but these afforded inactive or poorly active systems.

We reported an iron(III) complex formed by the addition of the anionic *N,N,N* ligand **62** to an iron(III) precursor.⁷⁰ This ligand⁷¹ was deprotonated with *n*-BuLi and reacted *in situ* with an equimolar amount of FeCl₃ in THF. Under optimized conditions (20 μmol catalyst, 80 °C, 30 atm), this precatalyst formed a stable active species for the selective oligomerization of ethylene over 2 h (10⁴ g (mol h atm)^{−1}) using a reasonable amount of MAO (Al/Fe = 200). Short chain oligomers (C₄–C₆) were obtained with up to 66 wt% of butenes with a selectivity of 98% in 1-butene. Increasing the MAO concentration to reach a

ratio Al/Fe = 500 led to a similar activity and a slight increase in polymer formation. When additional TMA was used, in a ratio MAO/TMA/Fe = 200/20/1, the activity decreased slightly and up to 66% of butenes were produced with a fraction of 1-butene >98 wt%. Ligand **62** was chelated to FeCl₂ in both anionic and neutral forms but no activity was observed toward ethylene transformation. The same trend was observed when the neutral ligand **62** was associated with FeCl₃. We established the synergistic influence of the anionic character of the ligand and the +III oxidation state of the iron precursor on the catalytic activity.

Conclusion

Since the discovery of the bis(imino)pyridine systems, a wide range of iron complexes has been developed for the catalytic oligomerization of ethylene. Most of the systems are composed of iron(II) complexes chelated by neutral N,N,N tridentate ligands. The framework of the ligands was composed of benzimidazole, phenanthroline, pyridine, quinoline or quinoxaline rings. Diversity was introduced by the use of tridentate N,N,L (L = N,S,P and O) ligands. The highest activities were observed by Small and coworkers for diimine ligands functionalized with a pendant L group (L = S or P). In general, iron complexes oligomerize ethylene with activities in the range of 10⁴–10⁶ g (mol h atm)^{−1} and high selectivities towards linear alpha olefins. Some examples of neutral bidentate ligands were reported but activities remained lower in comparison with tridentate analogues. In spite of many efforts, none of the ligands mentioned here yielded systems able to transform ethylene with similar or higher activities than bis(imino)pyridine iron complexes (10⁸ g (mol h atm)^{−1}). However, the catalytic behaviour and the product distribution could be tuned through this large diversity of catalytic systems, leading to stable catalysts over time or temperature, or selective for short chain oligomers. Being an abundant, readily available and environmentally friendly metal, iron constitutes an attractive source for catalysis and efforts should be pursued in ligand design to meet process requirements and the demands of the market.

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