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Post-metallocene catalysts for olefin polymerisation

K P Bryliakov

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Abstract. The main types of post-metallocene catalysts for olefin polymerisation based on bis(imino), bis(imino)pyridyl, bis(phenoxyimino), bis(pyrrolylimino) and other complexes of transition metals developed in the last 10 – 15 years and having prospects for practical use are considered. Modern views on the mechanism of action of these catalysts are discussed. The bibliography includes 375 references.

I. Introduction

During the last 30 years the main attention of scientists studying catalytic olefin polymerisation has been attracted to the catalysts based on metallocene complexes of Group 4 elements in combination with activators, namely, Lewis acids [methylaluminoxane (MAO), fluoroarylboron derivatives and some others],[1–11] which have replaced the Ziegler – Natta catalysts. The cationic nature of the active sites (an activator should form a non-coordinating anion) and the correlation between the ligand structure and the structure of polymer are typical of metallocene-based catalytic systems. Such properties of metallocene systems as high catalytic activity, narrow range of molecular masses of the obtained polyolefins, the ability of catalysing co-polymerisation of ethylene with higher α-olefins, the possibility of controlling the catalytic properties by variation of ligand structure, have stimulated their broad industrial production in the 1990s,[12,13] which was even called a 'metallocene revolution'.[11,14] However, at present the scope of industrial applications of metallocene systems is smaller than it was predicted. This is a result of some disadvantages of such systems, namely, significant consumption of expensive activators increasing the cost of products and the oxophilicity of Group 4 metals, which makes them unsuitable for the synthesis of co-polymers with functionalised olefins. Obviously, catalysts of other classes are required in order to increase the variety of polyolefins. This has inspired the search for more effective and inexpensive catalysts. Moreover, in view of the higher resistance of complexes of the so-called 'late' transition metals (Ni, Pd, Co) to heteratomic fragments compared to that of complexes of 'early' transition metals (Ti, Zr, V), one could hope for the development of catalysts that would be active in co-polymerisation of ethylene and olefins with polar functional groups.[14,15]

Thus as early as the first half of the 1990s the interest in the synthesis of a new type of homogeneous one-centred catalysts of polymerisation, *viz*. of a non-metallocene (or, according to the chronology, post-metallocene), catalysts increased. During this period, a significant attention was paid to complexes of Group 4 metals with one cyclopentadienyl ligand and other ligands containing donor heteroatoms. An important event in the development of post-metallocene systems was the synthesis of nickel(II) bis(imine) complexes capable of catalysing ethylene polymerisation.[16] Later, systems based on nickel complexes and not requiring an activator have been found.[17] At the end of the 1990s, iron bis(imino)pyridyl complexes highly active in ethylene polymerisation were discovered.[18,19] In addition, it was found that not only MAO but also trialkylaluminium derivatives may be used as activators.[20–22] This substantially simplified and decreased the cost of a catalytic system.

In recent years, significant interest has arisen in titanium and zirconium bis(phenoxyimine) complexes[23] and titanium bis(pyrrolylimino) complexes.[24] These compounds are able to catalyse the so-called 'living' polymerisation of olefins[25] and produce polymers with narrow molecular mass distribution (the ratio M_w/M_n is around 1.1) and high molecular masses.

In order to convert post-metallocene catalysts to an active form (as for metallocene catalysts), co-catalysts are required. These co-catalysts are Lewis acids, which produce cationic active centres with a high olefin affinity. Immobilisation of active catalytic systems on a solid support is of a great practical importance, as it facilitates the system handling, simplifies the catalyst composition (as the support itself may work as an activator; both a catalyst and an activator may be deposited on the same support), increases the resistance of the system against adverse external effects (*e.g.*, heating and oxidation) and also improves the morphology of the product.

To date, a series of reviews,[14,15,26] books[27,28] and generalising reports[23,24] on the non-metallocene olefin polymerisa-

K P Bryliakov G K Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, prosp. Acad. Lavrentieva 5, 630090 Novosibirsk, Russian Federation. Fax (7-383) 330 80 56, tel. (7-383) 330 68 77, e-mail: bryliako@catalysis.ru

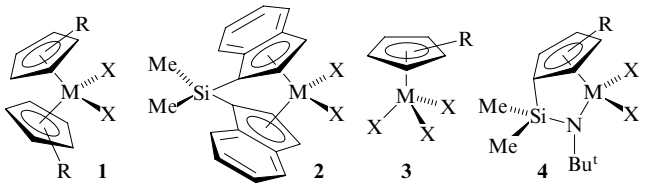
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Uspekhi Khimii **76** (3) 279 – 304 (2007); translated by D S Yufit

tion catalysts have been published. However, these papers were written before 2003 and usually discuss only one particular type of catalytic systems and reflect the contribution of only one research group. The author of the present review has aimed at following the development of studies of post-metallocene catalytic systems of olefin polymerisation during the recent years. The attention is focused on the most scientifically and industrially important systems. To this end, it appeared expedient to abandon the traditional systematisation of the post-metallocene complexes according to the metal position in the Periodic Table [15, 26] and classify them according to the type of ligand, because catalysts based on different metals with several main types of ligands are known. The order of discussion of the ligands in the present review mainly corresponds to the chronology of their appearance in the literature.

It should be noted that some caution is needed when comparing the properties of catalysts reported by different authors, because no universal procedure of catalyst testing exists and the experimental data are affected by particular reaction conditions, such as the reactor configuration, stirring speed, the method of activation, *etc*. Quite often the authors do not report the kinetics of polymerisation (or even the lifetime of a catalyst), but provide, for example, the data about the activity of a catalyst during the first 1–5 min of the reaction, which may create an inadequate idea of the catalytic properties of a complex in the case of its rapid deactivation. A slightly modified scale suggested by Gibson and co-workers [26] is used here for the activity classification: very low, low, medium (moderate) and high, which correspond to the following values <1, 1–10, 10–100, 100–1000 and higher in terms of (kg of polymer) (1 mol of catalyst)$^{-1}$ h^{-1} bar^{-1} units (or in the abbreviated form, kg mol^{-1} h^{-1} bar^{-1}), respectively.

II. Monocyclopentadienyl complexes

Up to the mid-1990s, most papers on the catalytic olefin polymerisation dealt with metallocene (**1**), including *ansa*-metallocene (**2**), and monocyclopentadienyl catalysts, particularly with 'half-titanocenes' (**3**) and the so-called 'constrained geometry' complexes (**4**).[1–11]



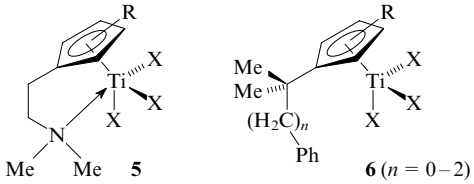
M = Ti, Zr, Hf; X = Cl, Alk; R = Alk.

To date, the processes that take place upon the activation of metallocene complexes with alkylaluminium chlorides,[29–31] methylaluminoxane [32–41] and the trialkylaluminim–tetrakis-(pentafluorophenyl)borate system,[42–45] have been studied in detail. The cationic complexes that are the precursors of active intermediates have been detected and identified by NMR spectroscopy. The genuine intermediates, *i.e*., the complexes in which the central atom is coordinated by the growing polymeric chain, were also detected.[33, 36, 46]

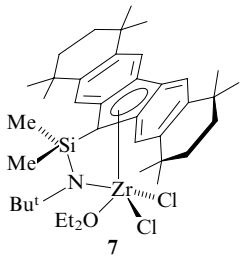
Naturally, the initial attempts of the search for new catalysts were aimed at the synthesis of non-metallocene complexes of Group 4 metals. Monocyclopentadienyl complexes of titanium and zirconium and of some other metals with additional donor atoms are discussed in this Section. Generally, the monocyclopentadienyl complexes are less active in olefin polymerisation than their bis(cyclopentadienyl) analogues, but more active in ethylene co-polymerisation with α-olefins. The incorporation of additional donor atoms into catalysts often adds new important properties, for example, high thermal stability (as in the case of complexes **4** with constrained geometry) and high polymerisation activity.

1. Complexes of Group 4 metals with one cyclopentadienyl ligand and an additional ligand containing a donor atom

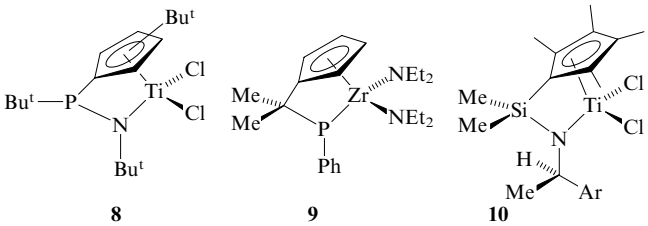
As noted above, titanium(IV) and zirconium(IV) monocyclopentadienyl complexes **3** are less active in olefin polymerisation than their bis(cyclopentadienyl) analogues.[47–49] Complexes **4** and **5** (R = H, X = Cl) with the activity of about 2500 kg mol^{-1} h^{-1} bar^{-1} (Ref. 50) were obtained by introduction of an additional ligand containing a donor atom (for example, N). However, such complexes are highly sensitive to traces of oxygen which deteriorates the process.[51] Another possible modification is introduction of a non-coordinating substituent into the cyclopentadienyl ring (complex **6**).[52] Interestingly, complex **6** (X = Cl, $n = 0$) is able to catalyse highly selective ethylene trimerisation when activated by MAO.[53] The role of pendant phenyl ring in this process is discussed comprehensively in a review.[54]



The monocyclopentadienyl systems in which an additional ligand containing a donor atom is covalently bonded to the metal have also become popular. Such catalysts (*e.g*., complex **4**) are applied in industry due to their high thermal stability and ability to initiate co-polymerisation.[55, 56] The catalytic properties of the complexes may be controlled by introducing substituents (including heteroatoms) into the cyclopentadienyl ring. Thus the application of fluorenyl complex **7** in the co-polymerisation of ethylene with higher α-olefins yields ethylene co-polymers with cycloolefins [57–65] and also with oct-1-ene (the octene content >70 mol %, Ref. 61).

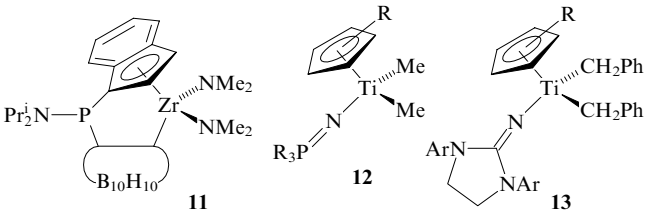


Several attempts at changing the nature of the bridging and the donor atom were described. For instance, linear high-molecular-mass polyethylene (PE) was obtained by using complex **8**,[65] while complex **9** and its titanium analogue catalyse the co-polymerisation of ethylene with octene.[66] The presence of a bulky aromatic substituent in complex **10** facilitates the polymerisation of propylene with a relatively high degree of isotacticity ([*mmmm*] = 56%).[67] Complex **11** containing the C-donor bridge $C_2B_{10}H_{10}$ is able to initiate the ε-caprolactone polymerisation besides being a catalyst of ethylene polymerisation.[68] The activity of complexes with ligands similar to phosphinimide (**12**)[69] and guanidinate (**13**)[70] is >1000 (kg PE) mol^{-1} h^{-1} bar^{-1}.



8 **9** **10**

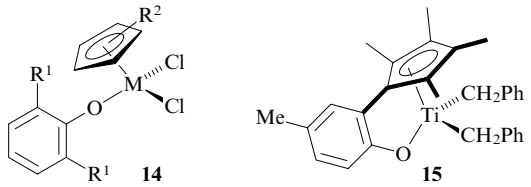
Ar = 1-naphthyl.



11 **12** **13**

Ar = 2,6-$Me_2C_6H_3$.

The aryloxide complexes **14**[71,72] and **15**[73] should be mentioned; in the latter complex, the aryloxy group is linked to the cyclopentadienyl ligand. The complexes of type **14** are highly active in etylene polymerisation [>2000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ for M = Ti and >4000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ for M = Zr], while the activity of complex **15** is somewhat lower. Complexes **14** and **15** are also able to catalyse propylene and styrene polymerisation.

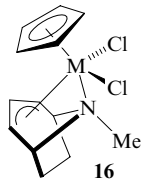


14 **15**

M = Ti, Zr; R^1 = Alk; R^2 = H, Alk.

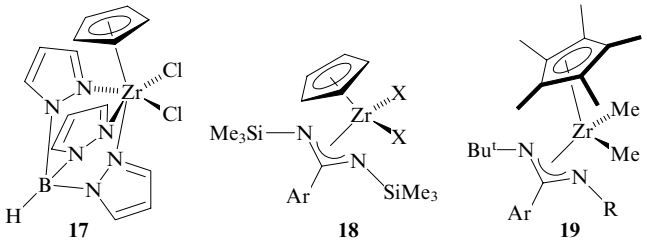
2. Complexes of Group 4 metals with one cyclopentadienyl ligand and an additional ligand containing several donor atoms

Among derivatives of Group 4 metals with one cyclopentadienyl ligand, complexes **16** proposed by Bergman and co-workers[49] should be noted. The zirconium complex with a tropidinyl fragment, isoelectronic to cyclopentadienyl, is highly active in ethylene polymerisation in the presence of MAO (comparable with the activity of Cp_2ZrCl_2, Cp = η^5-C_5H_5); the corresponding titanium complex is less active.[49]



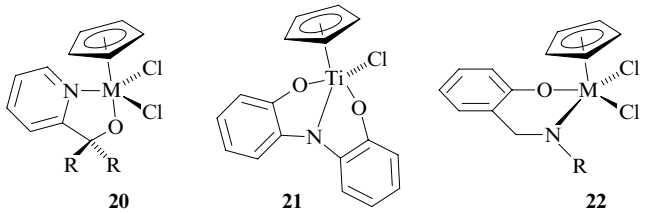
16 M = Zr, Ti.

Nakazawa *et al.*[74] have described complex **17** with a tris(pyrazolyl)borate ligand, which is active in ethylene polymerisation. The complexes $LZrCl_3$ and $LTiCl_3$ with additional bulkier mesityl-substituted tris(pyrazolyl)borate ligands L are slightly more active in ethylene polymerisation; they are able to catalyse the co-polymerisation of ethylene with hex-1-ene.[75,76] In the presence of an activator $B(C_6F_5)_3$, complex **17** yields high-molecular-mass polyethylene [$M_w = (4-6)\times10^5$]. Moderately active catalysts **18** can be activated by both MAO (X is a halogen)[77] and perfluoroarylborate compounds (X = Me).[78] Structurally similar complexes **19** (R = Alk, Ar) are able to catalyse living polymerisation of hex-1-ene with $[PhMe_2NH][B(C_6F_5)_4]$ as an activator.[79]



17 **18** **19**

Among other monocyclopentadienyl complexes of Group 4 metals, compounds **20**–**22**[80–82] with alkoxy and aryloxy ligands deserve attention. They exhibit moderate activity in ethylene polymerisation.



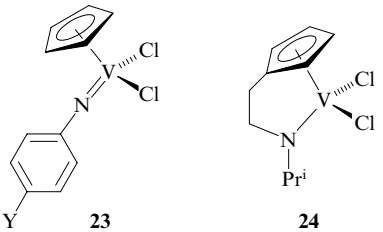
20 **21** **22**

R = Ph, Pr^i.

M = Zr, Ti;
R = cyclo-C_6H_{11}

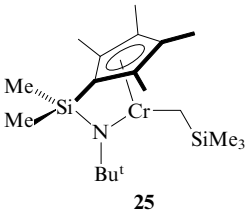
3. Monocyclopentadienyl complexes of other metals with additional ligands containing donor atoms

Group 5 metals in the formal oxidation state +4 and +5 form monocyclopentadienyl complexes that are active in ethylene polymerisation (it should be noted that the metal oxidation state may change during activation of the catalyst[15]). Thus complex **23** (Y = Me)[83] is slightly active [27 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$] when activated by MAO; the fast deactivation of the catalyst is caused by the formation of inactive dinuclear vanadium complexes.[84] Immobilisation of the active centres of complex **23** on polystyrene (Y is polystyrene) increases the lifetime of the active species which results in the production of high-molecular-mass polyethylene ($M_w = 1.9\times10^6$) when activated by diethylaluminium chloride.[85] Among vanadium(IV) derivatives, complex **24**, isostructural to the 'constrained geometry' catalysts based on Group 4 metals should be noted. This complex is less active in ethylene polymerisation than its titanium analogue.[86]

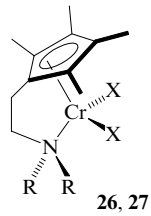


23 **24**

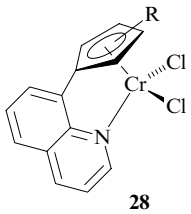
Chromium(III) complex **25** is almost catalytically inactive in ethylene polymerisation[87] and is able to catalyse only oligomerisation or isomerisation of higher α-olefins, while complex **26** is relatively active [8300 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$] when activated by MAO.[88] Structurally similar complex **27** is even more active in these reactions.[89] Compounds **28** are able to catalyse the polymerisation of ethylene[90] and propylene[91] (to give atactic polypropylene).



25



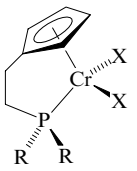
26, **27**



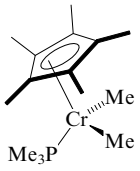
28

X = Cl, Me;
R = Me (**26**),
R – R = $(CH_2)_4$ (**27**).

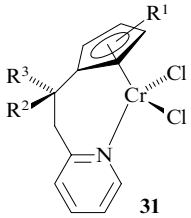
Complexes with phosphine ligands **29**,[92,93] which provide ethylene conversion into oligomers and low-molecular-mass polyethylene upon activation by methylaluminoxane, and complex **30**,[94] which ensures the formation of linear saturated hydrocarbons due to the chain transfer from MAO to aluminium are also known. Complex **31** with an additional pyridyl ligand is active in ethylene polymerisation [up to 1000 (kg PE) mol^{-1} h^{-1} bar^{-1}, Ref. 95]. In general, chromium cyclopentadienyl complexes containing an additional ligand with a donor atom exhibit significant polymerisation activity.[96,97]



29



30

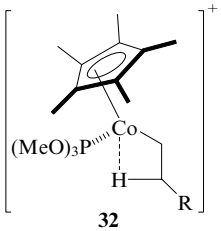


31

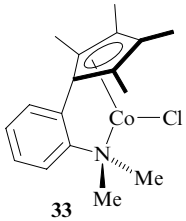
X = Cl, Me, Pr;
R = Et, Pr, cyclo-C_6H_{11}.

R^1 = H, 1,4-benzo;
R^2 = Me, cyclo-C_5H_9, cyclo-C_6H_{11}; R^3 = Me, Et, cyclo-C_5H_9, cyclo-C_6H_{11}.

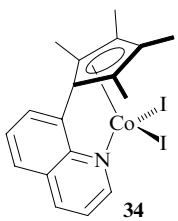
The monocyclopentadienyl complexes of late transition metals should also be noted. Thus complexes **32** show low activity in living ethylene polymerisation (M_w/M_n = 1.1 – 1.2).[98] The polymerisation activity of complexes **33** and **34**[99] is several orders of magnitude lower then the activity of their chromium analogues.[99] Branched polyethylene (up to 10 branches per 1000 carbon atoms) was obtained when complex **35** with a sulfide donor fragment was used,[100] and the application of nickel complex **36** with monoindenyl and phosphine ligands yielded high-molecular-mass polyethylene [the activity of the complex was up to 130 (kg PE) mol^{-1} h^{-1} bar^{-1}].[101]



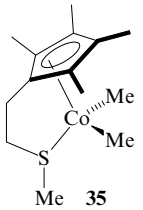
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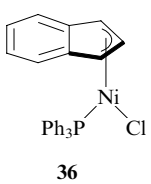
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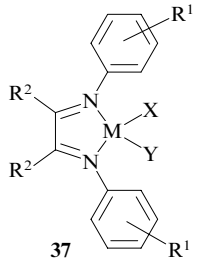
35



36

III. Complexes of late transition metals

The catalysts briefly discussed in Section II are generally not used in industry (except for the constrained geometry catalysts of type **4**). The discovery of nickel and palladium bis(imino) complexes **37** and their analogues by Brookhart and coworkers[16] has become an important event in the search for new catalysts of polymerisation. The complexes with bis(imino) ligands are widely used due to the specific properties of ligands, namely, their ability to effectively stabilise organometallic compounds, relatively high steric hindrance and the possibility of fine tuning of their electronic and steric properties by introduction of substituents into the aryl rings. A number of such complexes were found to be active in polymerisation of ethylene, linear α-olefins, styrene, norbornene, and in co-polymerisation of ethylene with higher olefins and polar co-monomers.



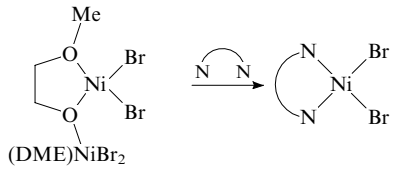
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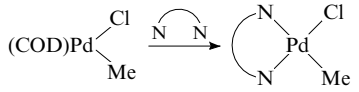
M = Ni, Pd; X, Y = Br, Cl, Me;
R^1 = Alk; R^2 = H, Me, 1,8-$C_{10}H_6$.

The complexes that do not require activation (the transformation into cationic form) were developed. The main types of nickel and palladium bis(imino) and other complexes are discussed below as well as the development of the views on the mechanism of polymer chain growth and the effect of ligand structure on the catalytic properties.

1. Nickel and palladium bis(imino) complexes

The first studies of nickel and palladium bis(imino) complexes were published by Brookhart.[16,102–105] The simplest way of their synthesis is the reaction of a ligand with a metal derivative, for example, (DME)$NiBr_2$, (COD)PdMeCl (DME is 1,2-dimethoxyethane, COD is cycloocta-1,5-diene) and others.[14]

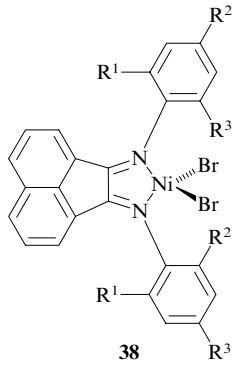




N N is a bis(imino) ligand.

Active centres in these complexes are formed upon alkylation and then activation by transformation into a cationic form. Both boron derivatives {NaBAF, $H(Et_2O)_2BAF$, BAF = $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$} and MAO may be used as activators. Nickel(II) complexes **37** are highly active [up to 11 000 (kg PE) mol^{-1} h^{-1} bar^{-1}] in ethylene polymerisation.[16] β-Elimination of a hydrogen atom with subsequent secondary 2,1-addition (see below) results in the formation of branched polymers with up to 70 and more branches per 1000 carbon atoms. Polyethylene with molecular mass of up to 10^6 may be obtained by varying the temperature and pressure as well as the structure of the ligand. The polymerisation of α-olefins at low temperatures (– 10 °C) follows a living mechanism (the polypropylene obtained had $M_n = 1.6 \times 10^5$ and

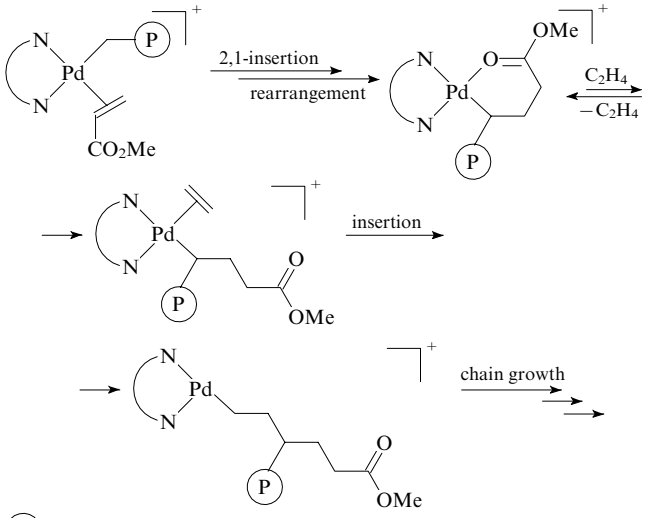
M_w/M_n = 1.13), which allows one to produce di- and tri-block co-polymers.[104, 106] The living polymerisation of a series of α-olefins (from but-1-ene to oct-1-ene) with catalysts **38** (R^1 = H, R^2 = C*HMePh, R^3 = Me) was observed in the temperature range from −30 to −40 °C by Coates and co-workers.[106] Besides, the syndiotactic polypropylene may be obtained at low temperature.[107]



38

R^1 = H, cyclo-C_nH_{2n+1};
R^2, R^3 = H, Alk, Hal.

Palladium(II) complexes **37** are usually less active and produce highly branched amorphous polyethylene with up to 100 branches per 1000 carbon atoms.[16, 108, 109] Palladium complexes are able to catalyse co-polymerisation of ethylene with α-olefins and with functionalised co-monomers (methyl acrylate, methyl vinyl ketone).[102, 103] Thus the incorporation of up to 25% of co-monomer was achieved in co-polymerisation of ethylene with methyl acrylate. The activity of such catalysts in co-polymerisation of ethylene with α-olefins is substantially lower than that in homopolymerisation; the introduction of a co-monomer sharply reduces the polymer molecular mass and narrows its molecular mass distribution. The suggested mechanism of co-polymerisation of ethylene with methyl acrylate includes 2,1-insertion of co-monomer with the formation of an intermediate cyclic adduct followed by the insertion of ethylene molecule.[103]

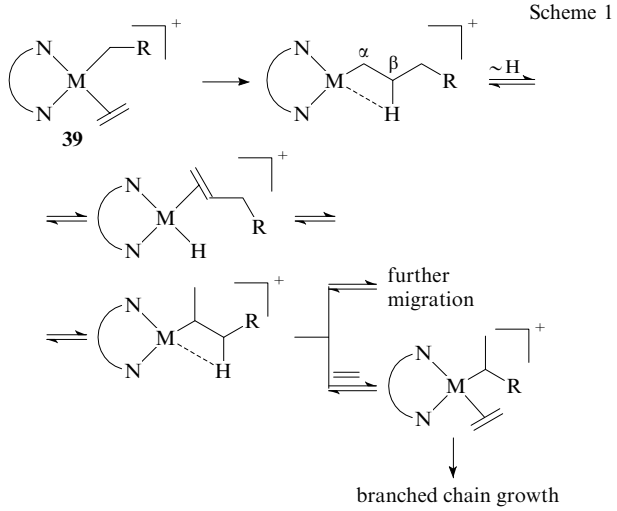


(P) is a growing polymer chain.

Note that palladium bis(imino) complexes are also active in the living polymerisation. For example, polyethylene with polydispersity of 1.05 was obtained by Gottfried and Brookhart in polymerisation of ethylene at 5 °C in the presence of palladium(II) bis(imino) complex **37** (R^1 = 2,6-Pr^i_2; R^2 = X = Me; Y = Cl) activated by NaBAF.[110]

The ability of nickel(II) and palladium(II) bis(imino) complexes to catalyse the formation of branched polymers is unique: the topology of the resulting polymers varies from linear with a small number of branches up to the hyper-branched one (in the latter case, oils are formed). A migratory insertion mechanism of the ethylene polymerisation into branched polyethylene (Scheme 1) was suggested on the basis of low-temperature ^{1}H NMR studies.[16, 111] A key feature of the mechanism is that the main form of the catalyst is alkyl-ethylene complex **39**. Note that for early transition metals such intermediates have never been observed. The limiting step of the reaction is the addition of ethylene to complex **39**; therefore, the rate of the chain growth is of zero order with respect to ethylene. The energy barrier to ethylene insertion is 17–18 kcal mol^{-1} for M = Pd [16, 112] and 13.5–14 kcal mol^{-1} for M = Ni.[112] This explains the difference between the observed activities of the polymerisation catalysts. The β-elimination of a hydrogen atom leading to the formation of alkenyl hydride complex may follow the ethylene insertion. The repeated 2,1-addition of coordinated olefin may take place in the coordination sphere of this complex resulting in branching of the polymer chain.

Scheme 1

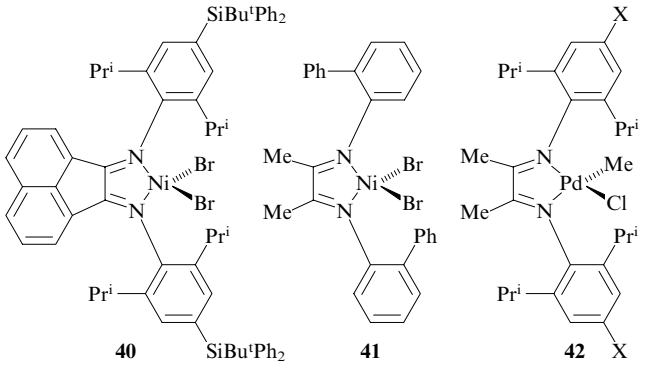


The effect of conditions of the process on the activity of the catalyst and the properties of the polymers formed was studied.[113–121] Various aspects of the mechanism of polymerisation were discussed in a number of theoretical studies (see for example, Refs 122–129).

In all of the previously discussed schemes, MAO, ionic tetrakis(aryl)borate derivatives or alkylaluminium chlorides were used as activators. If $B(C_6F_5)_3$ is used, the activity of the ethylene polymerisation catalyst is significantly lower.[130] Nevertheless, $B(C_6F_5)_3$ was used in co-polymerisation of ethylene with acrylates in the presence of nickel bis(imino) complexes,[131, 132] and the achieved degrees of co-monomer incorporation were higher than those in the presence of palladium complexes.

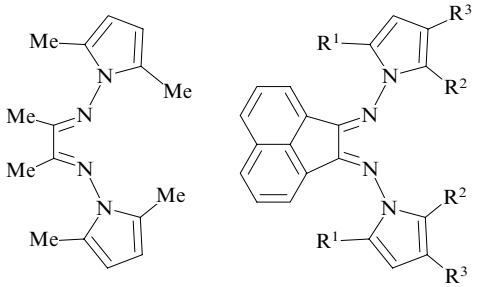
The substituents in the aromatic rings greatly affect the catalytic properties of bis(imino) complexes: the shielding of a vacant coordination position of the central atom due to an increase in the bulk of the *ortho*-substituents decreases the catalytic activity; at the same time, the chain propagation rate decreases and, as a consequence, the molecular mass of the polymer increases. The size of the *ortho*-substituent does not affect the number of short-chain branches very much; however, this number rapidly increases with temperature. Oligomeric products are obtained in the presence of complexes with one *ortho*-substutuent.[14–16, 26, 133] Complexes **37** containing aliphatic substituents in the aromatic rings are able to function at temperatures up to 50 °C, but at higher temperatures, their activities significantly decreases. Ivanchev and co-workers have shown[133–136] that the incorporation of bulky *o*-cycloalkyl substituents into 1,2-bis(arylimino)acenaphtyl complexes **38**

slightly increases the thermal stability of the catalysts. Other nickel and palladium complexes (such as **40**–**42**) [137–139] and different bis(imino) ligands (for example **43**–**45**) [16, 28] are also in use.



40 **41** **42**

X are electron-witdrawing substituents



43 **44**, **45**

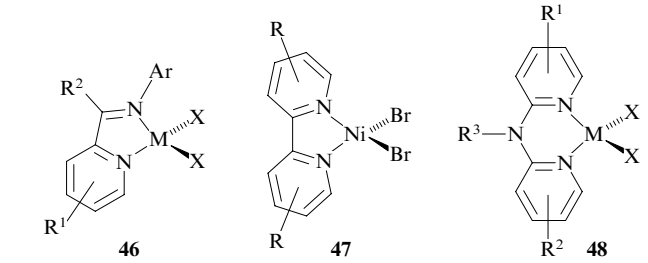
44: $R^1 = R^2 =$ Alk, $R^3 = H$;
45: $R^1 =$ Alk, $R^2 - R^3 =$ 1,4-benzo.

The nickel and palladium bis(imino) complexes are applied in the production of polymers by the so-called in-reactor blending methods. In essence, most of these methods consist of the introduction of a composite catalyst containing a metallocene complex of earlier transition metal in combination with a complex of later transition metal, into the reactor.[135, 140–143] The resulting polymeric product possesses an extended molecular mass distribution, which facilitates its processing.

The bis(imino) complexes are catalytically active in polymerisation of cycloolefins and in co-polymerisation of linear olefins with cycloolefins. Thus complexes **38** catalyse polymerisation of cyclopentene in the presence of ethylaluminium chloride.[144] In co-polymerisation of ethylene with norbornene, nickel bis(imino) complexes are inactive. At the same time, palladium complexes **37** are able to catalyse this process. Depending on the structure of the ligand, the molecular mass of the resulting co-polymers of ethylene with norbornene was up to 8×10^5 (and higher) and the degree of incorporation of norbornene was as high as 90%.[145]

2. Miscellaneous nickel and palladium N,X-donor chelate complexes

A series of complexes with other *N*,*N*-chelate ligands (**46**–**51**) deserve attention. It should be noted that efficient olefin polymerisation requires sterically hindered ligands; otherwise, β-elimination with subsequent dissociation of the coordinated olefin will result in the predominant formation of higher α-olefins.[146] Complexes **46** with various (alkyl, aryl and other, including polar) substituents in the pyridine and benzene rings of the ligand are less active in ethylene polymerisation than bis(imino) complexes and produce polymers with lower molecular masses.[147–153] Complexes **47**–**49** in the presence of various co-catalysts [MAO, modified methylaluminoxane (MMAO), $Al_2Et_3Cl_3$] produce mainly α-alkenes.[144, 146, 154, 155] Ethylene oligomerisation proceeds slowly in the presence of complex **50** without a neutral co-catalyst.[156] Complex **51** is active in the polymerisation and oligomerisation of hex-1-ene.[157] The catalysts with this type of ligand are described in patents; the corresponding references can be found in a review.[14] Various types of post-metallocene catalysts immobilised on polymeric supports have been discussed.[158]

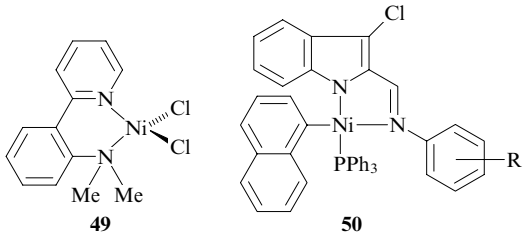


46 **47** **48**

R^1 = Alk, Ar *etc.*;
R^2 = Alk, Ar.

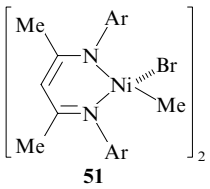
R = Alk.

$R^1 = R^2 = R^3 = H$, Alk; X = Cl, Br



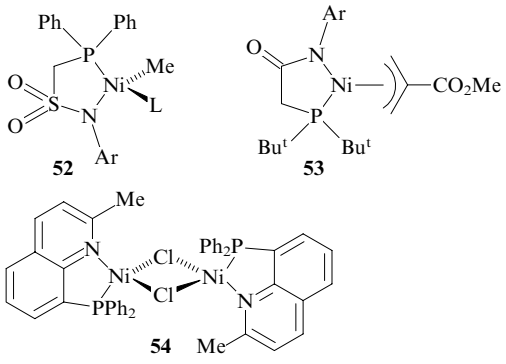
49 **50**

R = H, Alk.



51

Complexes with *N*,*P*-chelating ligands **52**–**54** have been reported.[159–161] Among the variety of catalysts, compounds with bis(imino), *N*,*N*-chelate (see above) and *N*,*O*-chelate ligands, which will be discussed later, turned out to be most active.



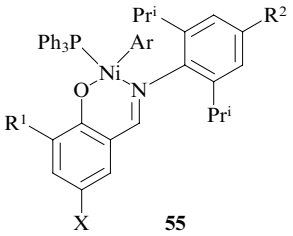
52 **53**

54

3. Nickel salicylaldiminate and other N,O-chelate complexes

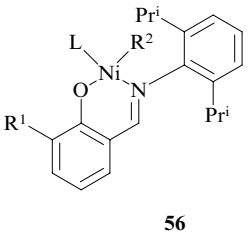
In 1998, Grubbs and co-workers [162] have prepared catalysts based on nickel salicylaldiminate complexes **55** with bulky substituents. Ethylene polymerisation has been performed in the presence of two equivalents of a co-catalyst [$Ni(COD)_2$ or $B(C_6F_5)_3$]. The productivity of the catalyst (13.3–253 kg PE per 1 mol of catalyst in 40 min under ethylene pressure from 7 to 14 atm) and the molecular mass of the polymer ($M_w = 4 \times 10^3 - 3.6 \times 10^4$) strongly depended on the substitu-

ent. The number of branches in the obtained polyethylene samples varied from 5 (for R^1 = Ph, X = H) to 55 per 1000 carbon atoms (for R^1 = Bu^t, X = H). The molecular mass distribution fluctuated from 1.4 to 12.4. Theoretical studies have shown that elimination of the donor group PPh_3 from complex **55** takes place in the initial step of the process.[163] Catalysts **56** (R^1 is anthracenyl, R^2 = Ph) turned out to be more active: their productivity was up to 6400 (kg PE) mol^{-1} h^{-1} under the pressure of 17 atm.[17] Triphenylphosphine as well as acetonitrile may be used as the ligand L.



55

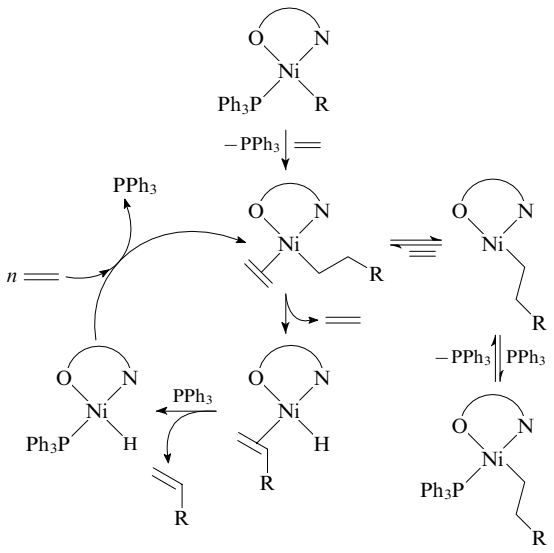
R^1 = H, Alk, Ar, CHO, NO_2;
R^2 = H, Pr^i;
X = H, OMe, NO_2, Cl;



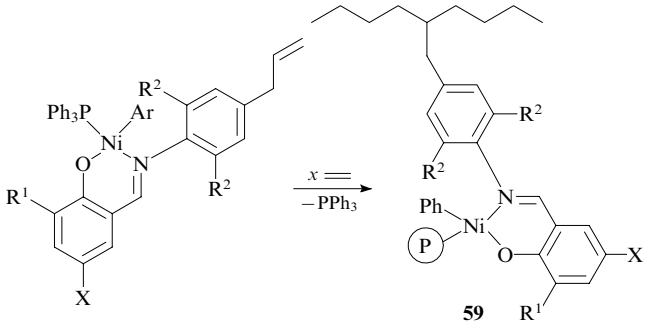
56

R^1 = 9-anthracenyl;
R^2 = Ph, Me;
L = PPh_3, MeCN.

Some of the discussed catalysts are able to function without a co-catalyst (the testing was continued for 1–2 h).[17, 164] The following catalytic cycle of polymerisation with nickel salicylaldiminate complexes has been suggested on the basis of ^{31}P NMR studies.



Data on dinuclear complex **57** which exhibits similar catalytic properties, have been published recently.[165] Catalysts of this type are quite resistant to the effect of polar functional groups; this makes it possible to obtain co-polymers of ethylene with substituted norbornenes and α,ω-functionalised olefins [17, 166, 167] and also to perform polymerisation in polar and protic solvents.[168, 169] However, the co-polymerisation of olefins with vinyl-functionalised co-monomers turned out to be impossible due to the catalyst deactivation.[170] Nevertheless, Li *et al.*[171] have managed to perform homo- and co-polymerisation of ethylene with methyl metacrylate (the incorporation of co-monomer was up to 16.7%) on catalyst **58** and MMAO as a co-catalyst. The co-polymerisation of ethylene with methyl metacrylate on nickel catalysts activated by $Ni(COD)_2$ and then by methylaluminoxane has been discussed.[172] It was shown [173] that complexes containing a vinyl substituent in the aromatic ring are transformed into 'self-immobilised' catalysts **59** during ethylene polymerisation.

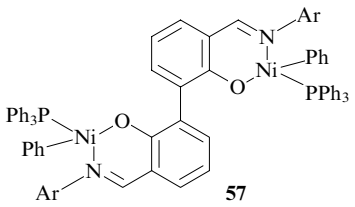


59

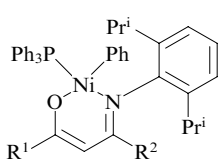
X = H, NO_2, Me; R^1 = H, Bu^t, Ph, NO_2; R^2 = Me, Pr^i.

Hicks and Brookhart [174] have reported nickel anilinotropolone complex **60**, which does not require a co-catalyst in olefin polymerisation. This complex produces polyethylene with molecular mass $M_n = 1 \times 10^5 - 3 \times 10^5$, a rather narrow molecular mass distribution ($M_w/M_n = 1.7-2.0$) and the number of branches ranging from 8 to 100 per 1000 carbon atoms. Later, it was shown that the polymerisation has a migratory mechanism (see Scheme 1), the predominant state of the catalyst being the complex LNiR(C_2H_4) (L is the anilinotropolone ligand, R is the polymeric chain); the activation parameters of separate stages of the process were also evaluated.[175]

The effect of reaction conditions on ethylene polymerisation in the presence of dinitro-substituted nickel catalysts **55** (R^1 = X = NO_2, R^2 = H, Pr^i) and methylaluminoxane has been studied.[176] A linear polyethylene of high molecular mass has been obtained and the activity of the catalyst was as high as 200 (kg PE) mol^{-1} h^{-1} bar^{-1}. A tenfold increase in the activity of the catalytic system was achieved by varying the content of trimethylaluminium in MAO.[177] It was shown [178] that complex **55** (R^1 = cyclo-C_6H_{11}, R^2 = H, X = Me) is able to catalyse ethylene polymerisation and its co-polymerisation with functionalised substrates (*tert*-butyl undec-10-enoates, methyl undec-10-enoates, pent-4-en-1-ol) when activated by $Ni(COD)_2$. A similar catalyst (R^1 = cyclo-C_6H_{11}, R^2 = H, X = Cl) is active in the homo- and co-polymerisation of ethylene with esters of undecenoic acid when $Ni(COD)_2$ or $AlBu^i_3$ are used as co-catalysts.[179] Nickel *N*,*O*-chelates are very convenient as they are applicable to various substrates. For instance, β-ketoiminate complexes **61** are inactive in olefin polymerisation; however they catalyse the norbornene polymerisation when activated by MAO. The activity of such system may reach 1600 (kg polynorbornene) mol^{-1} h^{-1} bar^{-1} with $M_w/M_n = 1.3-2.0$.[180]

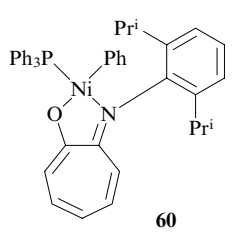


57

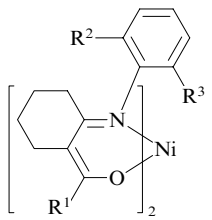


58

R^1 = Ph, CF_3;
R^2 = Me, CF_3.



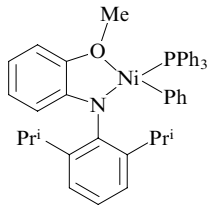
60



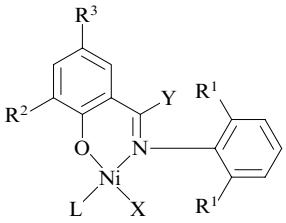
61

R^1 = Me, Ph; R^2, R^3 = Me, Pr^i.

Among other nickel *N,O*-chelates, worthy of note are complexes **62** [160] and **55** (X = Cl, R^1 = CHO, Ar is 1-naphthyl),[181] which are active in ethylene oligomerisation with $B(C_6F_5)_3$ and MAO co-catalysts, respectively. The results of a systematic study of the effect of substituents in various positions of salicylaldiminate ligands (complexes **63**) on the structure of the polymers obtained were reported.[17, 162, 182–184]



62



63

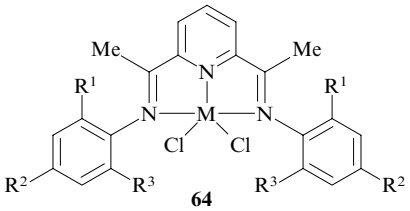
L = X = All; X = Me, Ph;
L = MeCN, ArCN, PPh_3, pyridine, lutidine; R^1 = Me, Pr^i, Br;
R^2 = Bu^t, Ph, 9-anthracenyl, 9-phenanthrenyl, Cl, NO_2; R^3 = H, Cl, NO_2;
Y = H, Me.

Thus the introduction of bulky substituents in the *ortho*-position of aryl ligand at the nitrogen atom results in the increase in linearity and molecular mass of polyethylene. A linear polyethylene with the highest molecular mass was obtained using catalysts with bulky substituents in the *ortho*-position relative to the phenoxy group. These catalysts also possess the longest lifetimes. More branched polyethylene was obtained when a halogen atom was placed in the *ortho*-position of the aryl substituent or when primary imino group was replaced by a secondary one. The activity of these catalysts remained almost the same; however, the molecular mass of the polymer decreased. Besides, the catalytic activity of nickel salicylaldiminate complexes increased when substituents such as Cl and NO_2, were placed in the *ortho*- and *para*-positions of the phenoxy ring.

Thus, unlike polymerisation catalysts based on Group 4 metals, complexes of the late transition metals are able to catalyse not only homopolymerisation of linear olefins, but also other processes such as oligomerisation, co-polymerisation of olefins with polar co-monomers, living polymerisation, polymerisation in polar media and may produce branched polymers if the mechanism of β-elimination followed by repeated 2,1-insertion takes place. However, unlike Group 4 metal complexes, no obvious correlation between the ligand structure and the microstructure of the obtained polymers has yet been established for the late transition metal complexes.

IV. Complexes with bis(imino)pyridyl and similar ligands

In 1998 the groups of Brookhart [18] and Gibson [19] published independently the first studies dealing with olefin polymerisation catalysts based on iron(II) and cobalt(II) complexes **64** with bis(imino)pyridyl ligands and MAO as a co-catalyst.



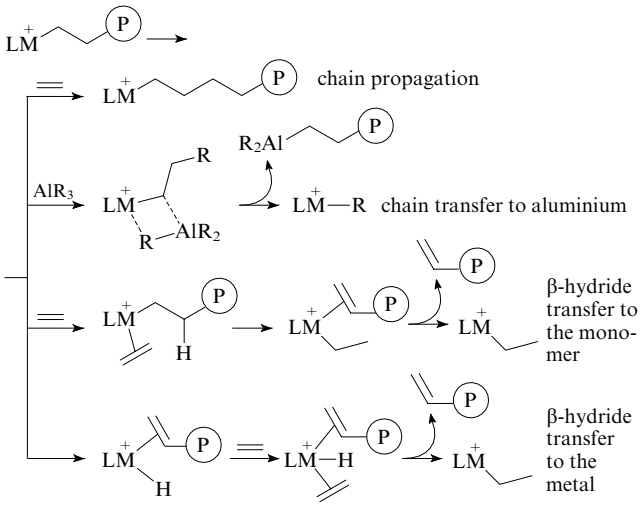
64

M = Fe, Co; R^1, R^2, R^3 = H, Alk.

The extremely high activity of such systems [up to 11 000 (kg PE) mol^{-1} h^{-1} bar^{-1}, which is higher than the activity of Group 4 metal complexes] has attracted attention of scientists and chemical industry professionals. This type of catalysts produce linear polyethylene with wide molecular mass distribution ranging from oligomers to a high-molecular-mass polyethylene. The presence and the bulk of substituents in the phenyl rings at the imine nitrogen atoms strongly affect the activity of the catalyst and the molecular mass of the polymer. Later, it was shown that simpler and cheaper activators, particularly trialkylaluminium, may be used for these catalysts;[20–22, 185, 186] supported catalysts were developed as well as the catalysts based on complexes of other metals (V, Cr) with bis(imino)pyridyl ligands.

1. Iron(II) bis(imino)pyridyl complexes and their analogues

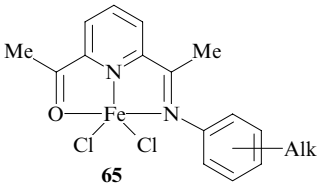
Iron(II) complexes **64** catalyse ethylene polymerisation producing linear polyethylene with M_w up to 6×10^5 (Ref. 187), which usually has a broad molecular mass distribution (M_w/M_n = 2.3–144), including a bimodal distribution.[26, 187] This can be explained by the suggestion that besides β-elimination,[188] chain transfer to aluminium may take place in this type of systems.[187] The following processes are possible in catalytic systems based on iron bis(imino)pyridyl complexes:



R = Me, Bu^i; LM^+ is the active catalyst.

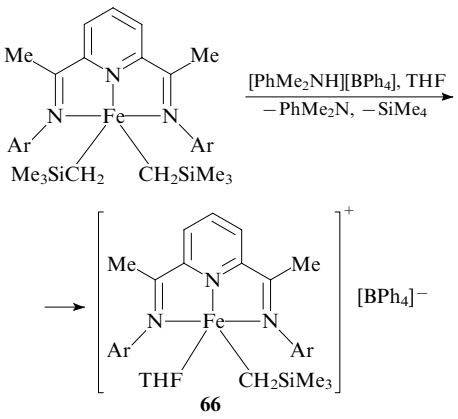
The complexes containing two substituents in the *ortho*-positions of aryl rings at the nitrogen atom (R^1 = R^3 = Alk, R^2 = H) are more active than complexes with one *ortho*-substituent (R^1 = Alk, R^2 = R^3 = H), and the introduction of a *para*-substituent increased the catalyst activity and the molecular mass of the polymer to even a greater extent.[18, 19] Meanwhile, iron bis(imino)pyridyl complexes are able to catalyse the oligomerisation of ethylene to give α-olefins with high selectivity if the aryl rings contain one small substituent in the *ortho*-position (R^1 = Me, R^2 = R^3 = H) or if the ligand is non-symmetric (*i.e.*, two different amines are used in the synthesis of the ligand).[189–191]

Predominant formation of oligomeric products was also observed when only 3- and 4-substituents are present in the aryl fragments at the nitrogen atoms in complexes **64**.[192] It was established [192] that in the presence of acetyliminopyridine complexes **65**, ethylene oligomerisation proceeds with high selectivity (the content of α-alkenes is up to 82%).



65

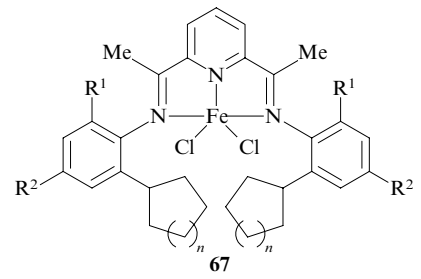
The effect of substituents at the nitrogen atoms on the activity of MAO-activated catalysts has been studied.[193] Single-component catalysts **66** based on the iron(II) complex with bis(imino)pyridyl ligands were proposed by Chirik and co-workers.[194] They were obtained by the reaction of appropriate precursors with activators, $B(C_6F_5)_3$ or $[PhMe_2NH][BPh_4]$.



66

Such systems have attracted considerable interest. A number of papers on their optimisation for practical use have appeared. Thus the thermal stability of iron bis(imino)pyridyl catalysts somewhat increases upon introduction of cycloalkyl substituents in the *ortho*-positions of the aromatic rings (complex **67**).[134, 195–198]

Several research groups have shown that such catalysts may be activated by trialkylaluminium derivatives [$AlMe_3$, $AlBu^i_3$, $Al(n\text{-}C_8H_{17})_3$].[20, 21, 185, 186] It is of interest that, according to Semikolenova and co-workers,[22] the activity of iron complexes in olefin polymerisation in the presence of MAO strongly depends on the content of trimethylaluminium in MAO: the activity is higher at high (28%) or low (1%) contents of Al in the form of $AlMe_3$ than at a content of 10%. This fact



67

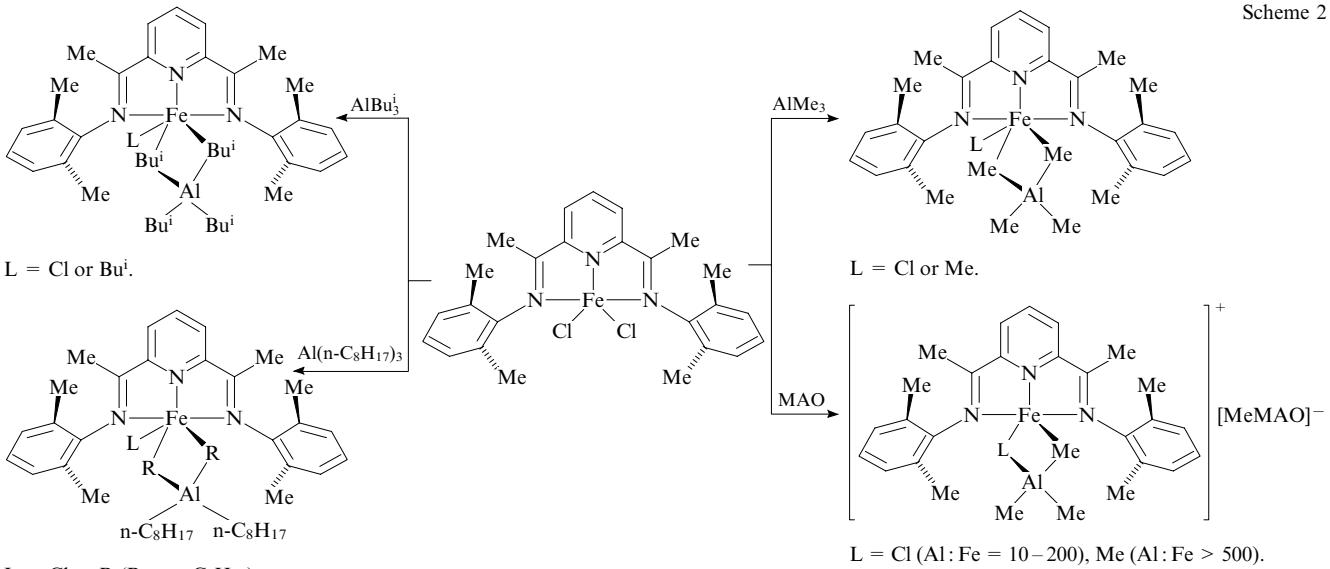
R^1 = Alk, cyclo-Alk; R^2 = Alk; n = 1, 2, 4, 8.

may indicate that different active intermediates operate in systems with trialkylaluminium and MAO. High activity in ethylene polymerisation was observed in the presence of such activators as $AlMe_3$, $AlBu^i_3$ or $Al(n\text{-}C_8H_{17})_3$.[22] The application of trialkylaluminium derivatives for the activation of catalysts **64** results in the formation of polyethylene with a broad molecular mass distribution (M_w/M_n = 4–11), the composition of the activator affects both the molecular mass of the polymer and its polydispersity.[199]

The immobilised homogeneous iron bis(imino)pyridyl catalysts are better suited for industrial application, as immobilisation simplifies their handling, increases their stability and lifetime, and improves the polymer morphology.[22] Thus systems with catalysts supported on silica gel,[22, 200–204] alumina,[202] modified mesoporous material SBA-15 (Ref. 205) or $MgCl_2$ (Refs 200, 206) and encapsulated into cyclodextrin [207] have been reported over the last years. A system containing an iron complex, $MgEtBu^n$ and $Al_2Et_3Cl_3$ which is active in the presence of various trialkylaluminium derivatives was proposed recently.[208] According to the reactor blending approach (tested previously in similar homogeneous systems),[135, 209] Ivanchev *et al.*[203] have proposed catalysts for ethylene polymerisation based on SiO_2-supported iron and nickel complexes **67** and **39**.

Due to the good prospects of bis(imino)pyridyl catalysts, study of active intermediates of polymerisation is of obvious interest. In systems based on such iron complexes ($LFeCl_2$), Talsi and co-workers [21, 210–212] identified, using NMR and EPR methods, the immediate precursors of active species, namely, neutral (when trialkylaluminium derivatives were used as activators) or cationic iron(II) complexes rather than iron(III) complexes as has been suggested earlier.[213]

Scheme 2



L = Cl or Bu^i.

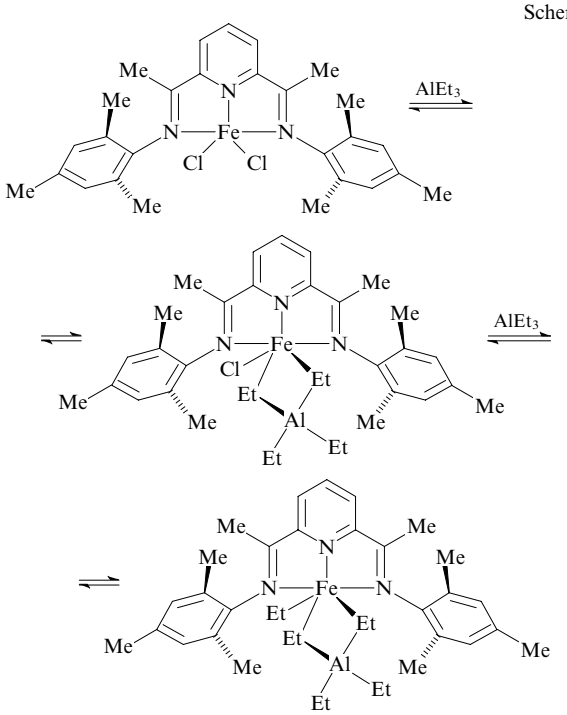
L = Cl or Me.

L = Cl or R (R = $n\text{-}C_8H_{17}$).

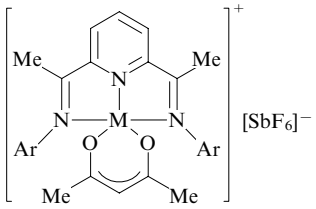
L = Cl (Al : Fe = 10–200), Me (Al : Fe > 500).

The mechanism of activation of iron(II) bis(imino)pyridyl complexes is shown in Scheme 2. In order to explain the observed bimodal molecular mass distribution of the polymerisation products, Wang and co-workers [214] have suggested, on the basis of electron microscopy data, the formation of two types of catalytically active species (Scheme 3) in the activation of iron(II) bis(imino)pyridyl chloride complexes by triethylaluminium. Barabanov *et al.*[215,216] have made an attempt to establish the nature of active centres in such systems. They estimated the concentration of these centres and the rate constant for chain propagation with inhibition of polymerisation by the addition of ^{14}CO. Two types of active centres were found in the system with $AlBu^i_3$. Presumably, the most active (less stable) centres are responsible for the formation of the low-molecular-mass polyethylene fraction. Similar measurements were performed for supported systems and the relative amount of active centres in the supported systems turned out to be significantly lower then that in homogeneous systems.[199,217]

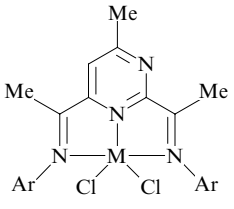
Scheme 3



The diversity of bis(imino)pyridyl complexes is based on the variety of ligand structures. Thus the cationic complex **68** is highly active in ethylene polymerisation when activated by MAO or by the $AlMe_3-B(C_6F_5)_3$ system.[218] The replacement of the pyridine ring by a pyrimidine ring (complex **69**) somewhat decreases the catalyst activity.[219]

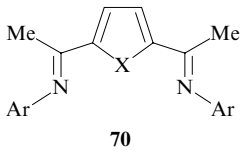


68



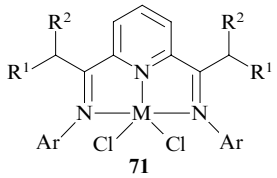
69

The attempts to isolate complexes with ligands containing a five-membered heterocycle (compounds **70**) instead of the pyridine ring were unsuccessful.[219] The replacement of methyl groups in the ketimine fragments by bulkier substituents resulted in the formation of highly active catalysts of ethylene polymerisation **71**.[220]



70

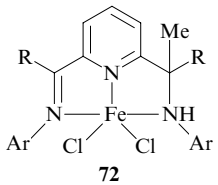
X = N, H, O, S.



71

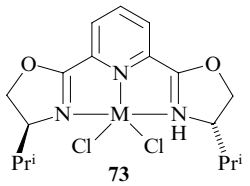
R^1, R^2 = H, Me, CH_2Ph.

However, *N*,*N*′-bis(diphenylmethyl)-2,6-bis(imino)pyridyl complexes do not react with ethylene, while *N*,*N*′-difluorophenyl-2,6-bis(imino)pyridyl complexes are highly active in its oligomerisation.[193,221] Non-symmetric iron bis(imino)pyridyl complexes exhibit high activity in ethylene polymerisation.[193,222] If one (or both) imine fragments are replaced by neutral amino groups (complex **72**), the observed decrease in activity is 1–2 orders of magnitude.[223] Series of studies were performed to elucidate the influence of various substituents at the imine nitrogen atoms in iron and ruthenium bis(oxazoline)pyridine (**73**)[224,225] and bis(hydrazone)pyridine[226,227] complexes on their activities. Several attempts were made to explain the effect of substituents in aromatic rings[228–230] and activators[231,232] on the behaviour of the polymerisation catalysts and also on the structure and molecular mass of the polymers.



72

R = H, Me.



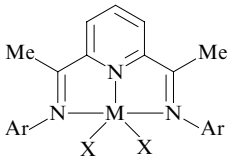
73

M = Fe, Ru.

Iron bis(imino)pyridyl complexes are fairly active in propylene polymerisation.[233,234] Small and Brookhart[233] have reported the activity of up to 950 (kg propylene) $mol^{-1}\ h^{-1}\ bar^{-1}$, the polymerisation proceeding with a high proportion of 2,1-insertion; the content of the [*mm*] diads in the resulting low-molecular-mass propylene ($M_n \approx 6500$) was as high as 67%. These catalysts show low degree of α-olefin insertion, therefore, they are unsuitable for co-polymerisation.[15]

2. Cobalt(II) bis(imino)pyridyl complexes

The catalysts of olefin polymerisation based on cobalt(II) bis(imino)pyridyl complexes **64** (M = Co) were discovered simultaneously with similar iron(II) complexes.[18,19] Very often, the new iron and cobalt bis(imino)pyridyl ligands were studied in parallel.[18,19,187,218,219,226,228–230,235–239] Some papers describe supported iron and cobalt catalysts.[205,239] Interestingly, cobalt complexes with ligands containing bulky polynuclear aromatic substituents at the nitrogen atoms are relatively active in ethylene polymerisation; indeed, the activity of cobalt complex **74** was up to 673 against 950 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ for the similar iron complex when activated by MAO.[240] The activity decreases and the polymer molecular mass increases with an increase in the bulk of the *ortho*-substituents in the phenyl rings at the nitrogen atom. The presence of both *ortho*-substituents is required in order to obtain polyethylene, while in the case of only one substituent, lower oligomers predominate among the products. Generally, the cobalt complexes are an order of magnitude less active than similar iron complexes and produce linear polymers with somewhat narrower molecular mass distribution (M_w/M_n for cobalt complexes rarely exceeds 10, while it is as high as several tens for iron complexes).

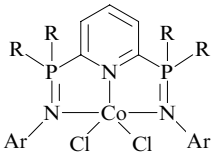


74, **75**

M = Co, Fe;
X = Cl, Ar = 1-$C_{10}H_7$ (**74**);
X = Br, Ar = 2-CF_3-6-FC_6H_3 (**75**).

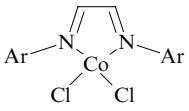
Cobalt bis(imino)pyridyl complexes are rather active in the polymerisation of vinyl ethers in the presence of MAO (iron complexes are significantly less active)[241] and in the co-polymerisation of ethylene with methylcyclopropanes.[242] The cobalt catalysts containing electron-withdrawing substituents are extremely active in selective dimerisation and oligomerisation of α-olefins. Particularly, the selectivity of propylene dimerisation to give hex-1-ene catalysed by complex **75** is 72% and the activity of the catalyst is 19.3 (kg products) (g Co)$^{-1}$ h^{-1} bar^{-1}; this catalyst is also active in ethylene polymerisation, its activity being up to 129 000 (kg PE) mol^{-1} h^{-1} bar^{-1} (however, only for polymerisation time of 2 min).[243] This is a record value for Group 9 metals, complex **75** being the first example of a system where a cobalt complex is more active than its iron analogue. Catalysts **64** (M = Co; R^1 = Me; R^2 = Me, OMe) are highly active in α-olefins formation. Such complexes in combination with [*rac*-ethylene-bis(indenyl)]zirconium(IV) dichloride[244] or with a constrained geometry complex[245] (the reactor blending) are used in ethylene polymerisation to produce linear low-density polyethylene with ethyl, butyl and other long alkyl branches in the side chain.

Of the analogues of cobalt(II) bis(imino)pyridyl complexes, compounds **76** deserve attention: the introduction of phosphinimide fragments results in the formation of moderately active catalysts.[246, 247] In contrast to similar nickel compounds, branched oligomeric products are formed when cobalt bis(imino) complexes **77** are used in ethylene polymerisation in the presence of MAO.[248]



76

R = Ph, cyclo-C_6H_{11};
Ar = 2,6-$Pr^i_2C_6H_3$, 2,4,6-$Me_3C_6H_2$.

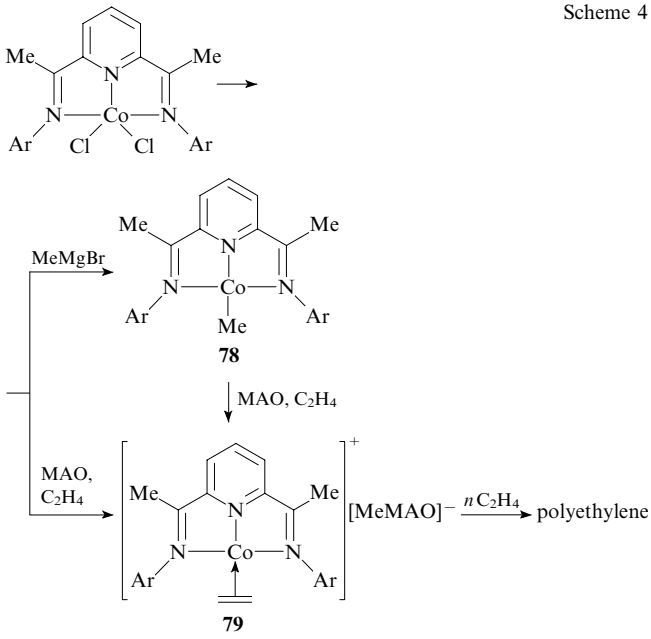


77

Ar = 2,6-$Pr^i_2C_6H_3$.

The structure of the active intermediates in cobalt-based systems has not been determined so definitely as in the case of similar iron(II) complexes. Some authors claim that cobalt(I) derivatives may be the active species.[249, 250] The activation process suggested for systems based on cobalt bis(imino)pyridyl complexes is shown in Scheme 4. Gibson *et al.*[249] have synthesised cobalt(I) complex **78**, a supposed precursor of the active intermediate, and have shown that after MAO activation, the same polymer is formed at the same rate as in the case of the starting cobalt(II) complex. Complex **78** itself is unable to add ethylene, it must be transformed into an active cationic form **79**.[249, 251] According to NMR data, the observed intermediates represent ionic pairs of the types LMeCo(II)Cl–MAO or LMeCo(II)Me–MAO.[22] The activation of cobalt bis(imino)pyridyl complexes by methylaluminoxanes was also studied by electronic spectroscopy.[252]

Scheme 4

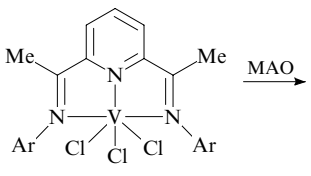


78

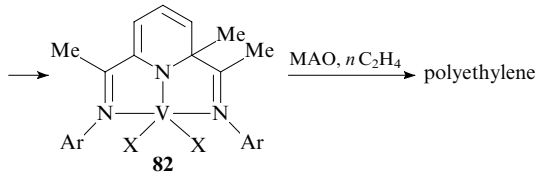
79

3. Vanadium(III) and chromium(III) complexes with bis(imino)pyridyl and other nitrogen-containing chelating ligands

Soon after the discovery of iron(II) and cobalt(II) bis(imino)-pyridyl complexes, similar catalysts based on other metals were developed. Thus Gambarotta and co-workers[253] have observed high activity of vanadium complex **80** in ethylene polymerisation [up to 3300 (kg PE) mol^{-1} h^{-1}] in the presence of MAO. The resulting polymers possessed a bimodal molecular mass distribution and the value of M_w/M_n was as high as 50. Several years later, Schmidt *et al.*[254, 255] have studied systematically the effect of substituents in aromatic rings on the activity of catalysts **81** and the properties of the products. It was found that in contrast to similar iron(II) complexes, oligomeric products are formed predominantly when vanadium complexes are used.[255] Low-molecular-mass polyethylene was formed only if the aromatic rings contained two or more relatively bulky substituents (Et, Pr^i). The introduction of electron-withdrawing substituents into the *ortho*- and *para*-positions of the phenyl ring sometimes increased the activity.[255] Grassi and co-workers[256] have reported low activity of similar complexes in the presence of MAO or $Al_2Et_3Cl_3$ in the processes of homo- and co-polymerisation of butadiene with ethylene. The mechanism of activation of vanadium catalysts is not yet clear. It was found[253] that alkylation of the ligand takes place when the excess of MAO is added to catalyst **80**. It was suggested that it is complex **82** formed (X = Cl) that catalyses ethylene polymerisation. The activation processes of vanadium catalysts were studied by electronic spectroscopy.[257] The results were interpreted by assuming the formation of complex **82** (X = Me) as the precursor of the active intermediate.

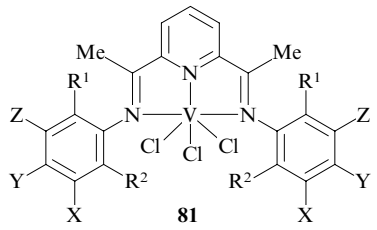


80



82

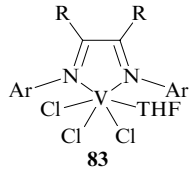
Ar = 2,6-$Pr^i_2C_6H_3$; X = Cl, Me.



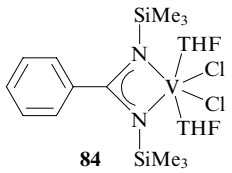
81

R^1, R^2 = H, Alk; X, Y, Z = H, Alk, Cl, Br.

Vanadium(III) bis(imino) complexes **83** have shown low activity in ethylene polymerisation in the presence of MAO and $AlEt_2Cl$.[258] On the contrary, catalyst **84** supported on modified $MgCl_2$ was rather active [up to 3100 (kg PE) mol^{-1} h^{-1} bar^{-1}]; polyethylene formed had high molecular mass and a narrow molecular mass distribution (M_w up to 7×10^5, $M_w/M_n = 2.0-2.3$).[259] Vanadium(III) bis(benzimidazole) complexes **85** are highly active in ethylene polymerisation in the presence of $AlMe_2Cl$ and produce polyethylene with M_w up to 10^6 and $M_w/M_n = 2.4-3.3$.[260]

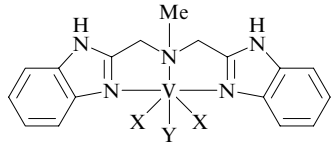


83



84

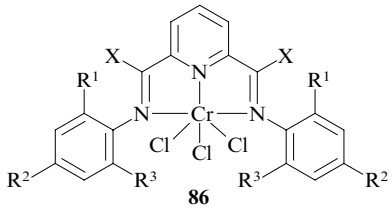
R = H, Me.



85

X = Y = Cl; X = OPr^i, Y = O.

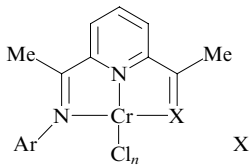
There are very few studies on chromium(III) bis(imino)pyridyl complexes. The first publications on the synthesis of chromium(III) bis(imino)pyridyl complexes **86**[261] and on the study of their catalytic activity in ethylene polymerisation in the presence of MAO, $AlBu^i_3$ and triisobutylaluminoxane[262] appeared in 2002–2004. The resulting polymers usually possess low molecular masses (M_w up to several tens of thousands) and narrow molecular mass distribution [the ratio $M_w/M_n = 1.3-1.9$ is the lowest among bis(imino)pyridyl complexes of various metals] and the activity of the catalysts is very high [for $R^1 = R^2 = R^3$ = Me, the activity was up to 25 000 (kg PE) mol^{-1} h^{-1} bar^{-1} in the presence of MAO and 15 000 (kg PE) mol^{-1} h^{-1} bar^{-1} in the presence of $AlBu^i_3$, polymerisation time 30 min]. A systematic study of the effect of substituents revealed general trends for all bis(imino)pyridyl complexes: the presence of *ortho*-substituents in the aromatic rings is required to achieve high activity and an increase in the bulk of these substituents results in a decrease in the activity and an increase in the molecular masses of the polymers.



86

X = Me, Ph; R^1, R^2, R^3 = H, Alk, AlkO, CF_3.

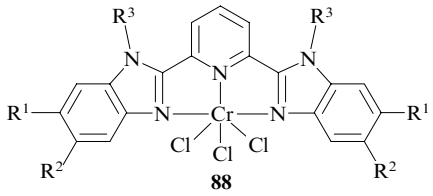
Small *et al.*[263] have studied the catalytic properties of a series of other complexes of the type **87**, including non-asymmetrical ones, mainly in the reaction of ethylene oligomerisation. It was found that at room temperature the monoimine complexes **87** (X = O) are moderately active in ethylene polymerisation ($M_w = 34 \times 10^3 - 103 \times 10^3$) and at higher temperatures (80–100 °C) they behave similarly to the bis(imine) complexes [produce low-molecular-mass PE, the catalyst activity being up to 14 000 (kg PE) mol^{-1} h^{-1} bar^{-1}].



87

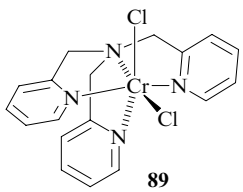
X = O, NAr′; n = 2, 3.

Nakayama *et al.*[264] have studied a number of chromium(III) complexes with halo-substituted bis(imino)pyridyl ligands. The activity of such complexes in the presence of MMAO ranged from moderate to high. Among the analogues of bis(imino)pyridyl complexes, compound **88** has to be noted. This complex produces a mixture of oligomeric products alongside with low-molecular-mass polyethylene.[265] The chromium(II) and chromium(III) complexes with tris(pyridylmethyl)amine (TPA) **89** show low activity in ethylene polymerisation.[266, 267] Complexes **90** containing a donor sulfur atom are moderately active in the presence of MMAO [72–188 (kg PE) mol^{-1} h^{-1} bar^{-1}] and yield relatively high-molecular-mass linear product (M_w up to 3.94×10^5).[268]

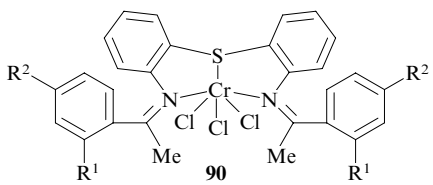


88

R^1, R^2, R^3 = H, Alk.



89



90

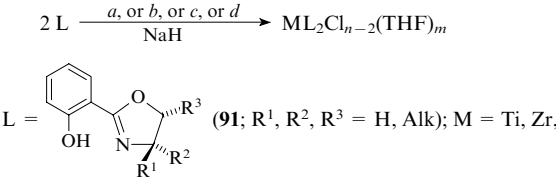
R^1, R^2 = H, Me.

It should be noted that chromium and vanadium bis(imino)pyridyl complexes are not currently used for ethylene polymerisation as extensively as the iron complexes. This is attributable, first, to the fact that they were discovered later than iron and cobalt complexes and, second, to the fact that they are less active and the molecular masses of the obtained polymers are lower. The zirconium(IV), titanium(III), titanium(IV) and manganese(II) bis(imino)pyridyl complexes have also been reported;[269,270] however, due to their low activity, they would hardly find any industrial application.

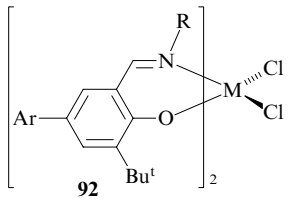
Taking into account the above-mentioned features of bis(imino)pyridyl complexes, one may conclude that the iron(II) and chromium(III) complexes are the most active in ethylene polymerisation; the iron-based catalysts produce polyethylene with a broad molecular mass distribution ($M_w/M_n > 10$), while the chromium derivatives produce polyethylene with a narrow molecular mass distribution ($M_w/M_n < 10$, sometimes even 1.3–1.9). The cobalt(II) and vanadium(III) complexes are less active and the polymers formed usually have $M_w/M_n < 10$ and a lower molecular mass than those obtained with iron- and chromium-based catalysts. The vanadium-based catalysts mainly produce oligomeric products. The product characteristics strongly depend in all cases on the substituents in the aromatic rings at the imino-group nitrogen atoms.

V. Complexes with phenoxyimine, pyrrolylimine and similar ligands

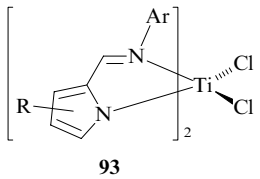
The first catalysts of ethylene polymerisation based upon titanium(III), titanium(IV) and zirconium(IV) complexes with N,O-donor bis(hydroxyphenyloxazoline) ligands **91** were synthesised by Floriani's research group in 1995; however the activities of these catalysts were very low.[271,272]



Later, at the end of the 1990s, the synthesis of new highly active catalysts of olefin polymerisation based on complexes of Group 4 metals with bis(phenoxyimine) ligands **92** was reported.[273,274] The activity of these catalysts was equal to or even higher (depending on the substituents) than the activity of metallocene-based systems. Some complexes were able to catalyse living polymerisation of ethylene, stereospecific polymerisation of propylene and even co-polymerisation of ethylene and α-olefins with polar co-monomers.[23,275] Later, highly effective bis(pyrrolylimine) catalysts **93** have been synthesised.[24]



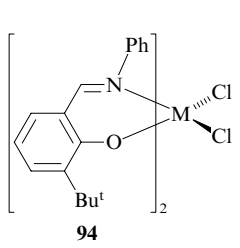
R = Ph, polyfluorophenyl, 2-MeC_6H_4, 2-$Pr^iC_6H_4$; M = Zr, Ti.

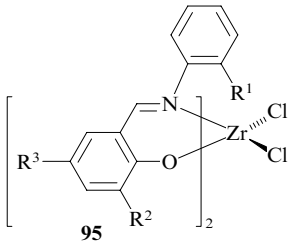


R = Alk.

1. Zirconium complexes with phenoxyimine ligands

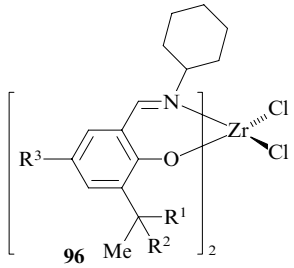
The optimal structure of the ligand for complexes **94** which makes them active catalysts in ethylene polymerisation upon activation with MAO was found even in the first studies of Fujita and co-workers.[276–278] Whereas the titanium and hafnium complexes were highly active [3300 and 6500 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ respectively], the zirconium complex has shown a unique activity of 519 000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ at 25 °C and polymerisation time of 5 min. Zirconium catalyst **94** effectively maintained the activity for at least 30 min at room temperature. In the presence of MAO, the maximum activity was observed at 40 °C [587 000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$]; the polyethylene obtained had $M_w = 10^4$. However, if the $Ph_3CB(C_6F_5)_4 - AlBu^i_3$ combination was used as an activator, the activity drastically decreased [down to 11 000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ at 50 °C] and ultrahigh-molecular-mass polyethylene was obtained.[279] The catalytic properties were strongly affected by the presence of substituents in the aromatic ring and the aniline fragment. Thus, the introduction of alkyl substituents (R^1 = Alk) in the *ortho*-position of the aniline ring (complex **95**) resulted in a decrease in the catalyst activity and in an increase in the polymer molecular mass in the presence of MAO.[280]



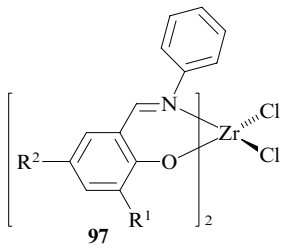


M = Ti, Zr, Hf.

Further development of this catalytic system involved mainly the modification of ligands. The activity was increased by selecting bulky R^2 substituents and the activity of complex **95** (R^1 = H, $R^2 = CMe_2Ph$, R^3 = Me) reached 2.1×10^6 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ (Ref. 279). The replacement of aniline by cyclohexylamine increased the activity of these catalysts even more. In the presence of MAO, complex **96** ($R^1 = R^2$ = Ph, R^3 = OMe) has shown the activity of 9 350 000 (kg PE) $mol^{-1}\ h^{-1}$ under a pressure of 9 bar at 75 °C during 15 min of polymerisation.[23,280,281] Matsui and Fujita[279] have called these highly active catalysts 'FI Catalysts'.



Polyethylene with a relatively narrow molecular mass distribution (M_w/M_n = 1.1–2.5) is obtained in the presence of most zirconium bis(phenoxyimine) complexes. However, polyethylene obtained in the presence of complexes **97** possesses a trimodal distribution (each maximum has $M_w/M_n \approx 2$) and the content of the high-molecular-mass fractions may be controlled by temperature variation.[282] It was suggested that this effect is caused by existence of equilibrium of several coordination isomers of the catalyst.



97

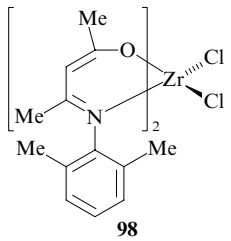
R^1 = Bu^t, R^2 = H;
R^1 = R^2 = CMe_2Ph.

In the presence of MAO and $Ph_3C[B(C_6F_5)_4]-AlBu^i_3$, zirconium systems are able to catalyse propylene polymerisation [277] and also co-polymerisation of ethylene with propylene [279, 280] (with 20% – 30% of propylene content) including co-polymerisation which produces an ultrahigh-molecular-mass co-polymer ($M_w = 10.2 \times 10^6$).[283] The catalytic properties of phenoxyimine catalysts and the structures of the resulting polymers have been surveyed.[284, 285]

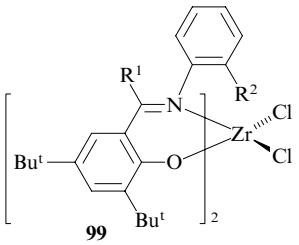
It was found that these catalysts may also be activated by activators other than MAO and $Ph_3C[B(C_6F_5)_4]$, for example, by $AlEt_3$ and a phosphomolybdenum heteropoly compound [286] or even by trialkylaluminium derivative alone.[287] In the latter case, the molecular masses of the products are higher and their molecular mass distribution is broader than those in the case of MAO activation, while the activity of catalysts remains approximately the same. The $MgCl_2-R_mAl(OR)_n$ system was used as an activator and a support for zirconium, titanium and vanadium bis(phenoxyimine) complexes.[288, 289] Also, highly active 'self-immobilised' zirconium and titanium systems containing an allyl substituent in the aniline ring were proposed, the molecular mass distribution (M_w/M_n = 3.5 – 19.2) attained with the 'self-immobilised' catalysts being wider than that for similar homogeneous systems ($M_w/M_n < 3$).[290]

The mechanism of polymerisation with zirconium bis(phenoxyimine) complexes is little studied. Makio and Fujita [291] have attempted to detect active intermediates by ^{1}H NMR spectroscopy, but the results were not highly informative.

Bis(ketimine) complexes **98**, which are moderately active in ethylene polymerisation, should be noted among the analogues of zirconium bis(phenoxyimine) complexes.[292] Highly active bis(phenoxyketimine) complexes **99** were synthesised; the introduction of the R^1 substituents into the imine group results in an increase in the catalyst activity and the molecular mass of polyethylene.[293]



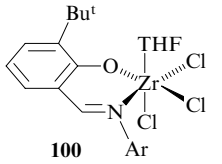
98



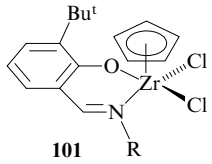
99

R^1 = Me, Et, Ph, 2-MeC_6H_4, 2-FC_6H_4, 2-ClC_6H_4, 2-BrC_6H_4,
R^2 = Alk.

It is remarkable that removal of one phenoxyimine ligand or its replacement by cyclopentadienyl results in a significant decrease in the activity of complexes **100** and **101**.[82, 294] Complexes **102** with tridentate N,O,O-donor ligands are highly active in ethylene polymerisation and co-polymerisation of ethylene with propylene in the presence of MAO [up to 5700 (kg PE) mol^{-1} h^{-1} bar^{-1} at 25 °C for polymerisation time of 5 min] and $Ph_3CB(C_6F_5)_4-AlBu^i_3$ [up to 36 590 (kg PE) mol^{-1} h^{-1} bar^{-1} under similar conditions]. The increase in temperature has resulted in a decrease in the polymer molecular mass and in the narrowing of the molecular mass distribution due to acceleration of chain transfer processes.[295] The catalysts containing phenoxyimine ligands linked by a polymethylene bridge were also highly active.[296] The zirconium complexes containing bis(phenoxyimine) ligands linked by different types of bridges were moderately active in the polymerisation [297 – 299] and oligomerisation of ethylene.[300, 301]

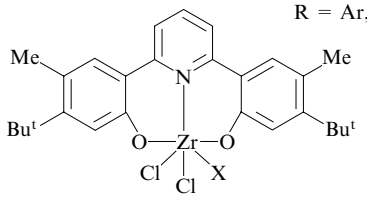


100



101

R = Ar, cyclo-Alk.

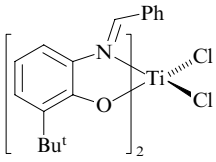


X = THF, OEt_2, *etc.*

102

2. Titanim complexes with phenoxyimine ligands

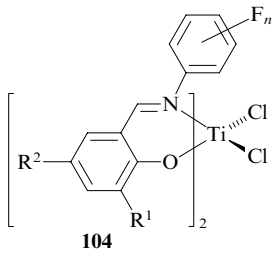
In contrast to zirconium complexes, titanium complexes with bis(phenoxyimine) ligands are not highly active in polymerisation but produce polymers with higher molecular masses. Thus the activity of titanium complexes **94** [276 – 280, 302] in ethylene polymerisation in the presence of MAO was equal to 2280 – 4150 (kg PE) mol^{-1} h^{-1} bar^{-1}; a high-molecular-mass polyethylene ($M_w = 2.9 \times 10^5 - 8.8 \times 10^5$) was obtained at 25 – 75 °C. This complex is less active in the presence of $Ph_3CB(C_6F_5)_4-AlBu^i_3$; however, the resulting polyethylene had an ultrahigh molecular mass ($M_w = 3.9 \times 10^6 - 5.9 \times 10^6$). Note that titanium complex **94** may be reduced by triisobutylaluminium to a phenoxyamine derivative, which is active in polymerisation of higher olefins, particularly, hex-1-ene.[303] Structurally related *N*-benzylidene complex **103** is also highly active in ethylene polymerisation in the presence of MAO or $Ph_3CB(C_6F_5)_4-AlBu^i_3$ yielding high-molecular-mass polyethylene.[304]



103

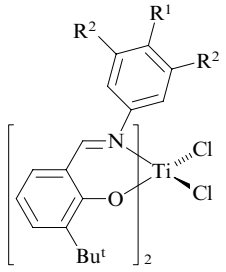
The most interesting properties were found for catalysts with electron-withdrawing substituents in the aniline ring. Thus it was established that complexes **104** (R^1 = Bu^t, R^2 = H) are able to catalyse living polymerisation of ethylene [305] and propylene with high syndioselectivity ([*rr*] of up to 87% – 93%, $M_w/M_n \sim 1.1$) in the presence of MAO.[306, 307] The presence of even one fluorine atom in the *ortho*-position of the aniline fragment is sufficient to trigger the living polymerisation mechanism; the highest activity [up to 36 000 (kg PE) mol^{-1} h^{-1} bar^{-1} at 50 °C] was achieved with a catalyst containing a pentafluorinated phenyl ring, and the polymer molecular mass was also the highest in this case ($M_n = 4.24 \times 10^5$).[23, 308] Complexes containing fluorine atoms only in the *meta*- and/or *para*-positions of the aniline ring are also highly active but do not catalyse living polymerisation (M_w/M_n = 1.78 – 2.18).[23, 305 – 308] It is characteristic that upon introduction of electron-withdrawing substituents into the

salicylaldimine ring, polymerisation in the presence of titanium bis(phenoxyimine) complexes **104** ($R^1 = R^2 = I$; F_n = 2,6-F_2) is no more living and the activity of the catalyst decreases. Complexes **104** are able to catalyse the production of block co-polymers with styrene.[309–311] It should be noted that in all cases, the polymerisation time was very short (from 1 to 5 min).



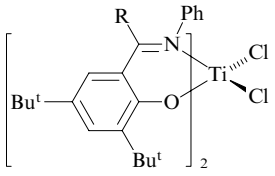
104

Titanium fluorinated phenoxyimine complexes were used for the production of ethylene–propylene block co-polymers.[312] Trifluoromethyl groups (complex **105**) can also be used as substituents that increase the activity; the higher the number of electron-withdrawing groups the higher the catalyst activity and the polymer molecular mass.[313] Coates and co-workers[314] have found that titanium complexes **106** with phenoxyketimine ligands without electron-withdrawing substituents in the aniline ring may be used as catalysts of living polymerisation of ethylene. Complexes **107** produce polyethylene with a relatively broad molecular mass distribution (M_w/M_n = 4–5).[315]



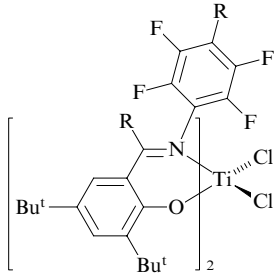
105

$R^1 = CF_3$, $R^2 = H$;
$R^1 = H$, $R^2 = CF_3$.



106

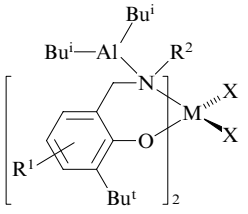
R = H, Me, Et, Ph.



107

R = H, CF_3.

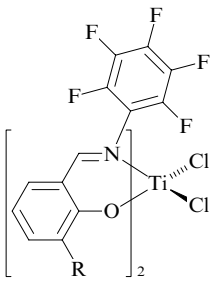
A number of interesting properties were found for fluorinated phenoxyimine catalysts **104** in living polymerisation of propylene.[306,307] Particularly, the syndiotactic polypropylene with a high melting point (up to 149–156 °C) was obtained in the presence of MAO.[316] It is quite remarkable that chain propagation occurs according to the 2,1-insertion mechanism.[317,318] If the $Ph_3CB(C_6F_5)_4$–$AlBu^i_3$ system is used as a co-catalyst, a high-molecular-mass atactic polypropylene is produced; the zirconium and hafnium analogues of complex **104** in combination with this co-catalyst form isotactic polypropylene.[319] This was attributed to the reduction of the imine bond leading to compounds **108**, which possess different catalytic properties.[320] Particularly, these compounds are less active than phenoxyimines and their activity in the polymerisation of higher olefins increases in the series hex-1-ene < oct-1-ene < dec-1-ene < 4-methylpent-1-ene.



108

R^1 = Alk; R^2 = X = Bu^i.

Bis(phenoxyimine) complexes may be used as catalysts of ethylene co-polymerisation with higher olefins. Co-polymerisation of ehtylene with propylene, hex-1-ene and norbornene catalysed by titanium bis(phenoxyimine) complexes **94** has been studied.[321] Complexes **109** may catalyse the production of block co-polymers with hex-1-ene, oct-1-ene, dec-1-ene with narrow molecular mass distributions (M_w/M_n = 1.1–1.3) and co-monomer contents of up to 30%.[322] The homopolymerisation of higher α-olefins (C_6–C_{10}) in the presence of titanium bis(phenoxyimine) complexes and $Ph_3CB(C_6F_5)_4$–$AlBu^i_3$ have been discussed by Fujita and co-workers;[323] atactic polyolefins with high molecular mass were obtained (M_w = 8.5×10^5–1.5×10^6).

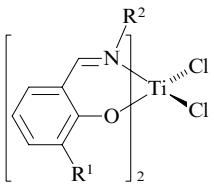


109

R = H, Me, Bu^t, Pr^i, cyclo-C_6H_{11}.

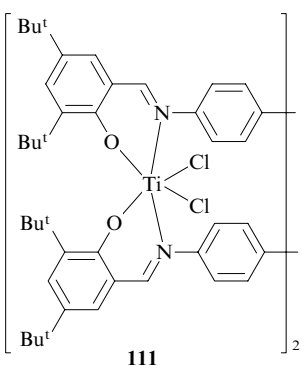
The search for other co-catalysts has brought some results. Particularly, polyethylene[324] and syndiotactic polypropylene[325] were obtained with fluorinated catalysts activated by isobutylaluminium 2-ethylhexyloxide [$Bu^i_mAl(OR)_n$] with $MgCl_2$. Similar co-catalyst systems were used for activation of titanium, zirconium and vanadium phenoxyimine complexes.[288] The first papers on the solid-phase phenoxyimine systems have appeared. For example, Klapper and co-workers[326] supported titanium bis(phenoxyimine) complex on latex particles and obtained ultrahigh-molecular-mass ($M_w > 6 \times 10^6$) polyethylene with M_w/M_n = 3.

The structure of phenoxyimine ligands was varied in a number of studies. Complexes **110** with bulky substituents in the aniline ring had a low activity.[327] Bravaya and co-workers[328] synthesised dinuclear titanium complex **111**, which was highly active in ethylene polymerisation in the



110

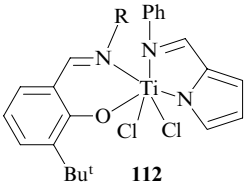
R^1 = H, R^2 = Ph,
2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$,
2,6-$F_2C_6H_3$, 1-$C_{10}H_7$;
R^1 = F, R^2 = 2,6-$F_2C_6H_3$.



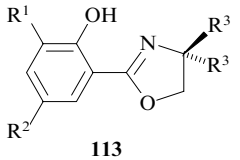
111

presence of MAO and produced high-molecular-mass polyethylene ($M_n = 2.5 \times 10^6$).

Bochmann and co-workers [82] have synthesised titanium monocyclopentadienyl monophenoxyimine and phenoxyamine complexes similar to zirconium complexes **101**; these compounds were active in the polymerisation of 1-alkenes in the presence of MAO. The monosalycylaldimine compounds, for example, the titanium analogues of complexes **100**, exhibit relatively low activities [up to 440 (kg PE) mol^{-1} h^{-1} bar^{-1}].[294, 329] The hybrid salicylaldiminato pyrrolyliminate catalysts **112** are highly active [up to 85 000 (kg PE) mol^{-1} h^{-1} bar^{-1}, polymerisation time 2 min, 20 °C]; however, they are unable to activate living polymerisation.[330] Recently, it has been found that the titanium and zirconuium complexes L_2MCl_2 with salicyloxazoline ligands **113** bearing substituents R^1, R^2, R^3 = H, Me, Pr^i, Bu^t are highly active catalysts of ethylene polymerisation [up to 280 000 (kg PE) mol^{-1} h^{-1} bar^{-1}, polymerisation time 1 min, 22 °C].[331]



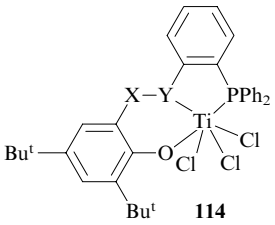
112



113

R = Ph, C_6F_5.

Tang and co-workers [332] have shown that titanium complexes **114** with tridentate N,O,P-donor ligands are active in ethylene polymerisation in the presence of MMAO and are also able to catalyse co-polymerisation of ethylene with propylene, hexene and norbornene.

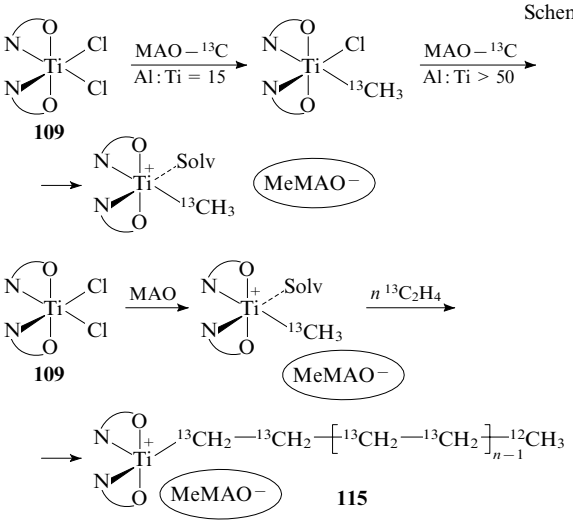


114

X–Y = CH=N, CH_2–NH.

It should be noted that zirconium phenoxyimine and other related complexes particularly, titanium complexes are usually rapidly deactivated; therefore, most of the authors use only the initial parts of polymerisation curves (1–5 min) in the calculation of catalytic activities.

Scheme 5



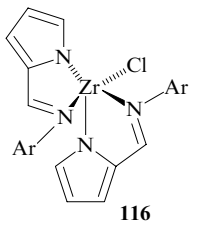
109

115

In the case of titanium phenoxyimine catalysts, active intermediates have been studied in more detail than their zirconium analogues. Thus Fujita and co-workers [289] have identified a series of titanium(IV) complexes in the catalytic system **109** (R = Bu^t) with MAO by ^1H NMR spectroscopy. Later, Talsi and co-workers [333] have used ^1H, ^{13}C and ^{19}F NMR to detect and identify a series of cationic intermediates, including species **115**, in the catalytic systems comprising compound **109** (R = Bu^t) and MAO (Scheme 5) and also with $AlMe_3$–$Ph_3CB(C_6F_5)_4$. It was established that reduction of the metal to titanium(III) and the transfer of the phenoxyimine ligand to aluminium, resulting in the formation of $LAlMe_2$, are the main routes of deactivation of the active species.

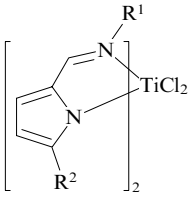
3. Group 4 metal complexes with pyrrolylimine ligands

The first complexes of Group 4 metals with pyrrolylimine ligands were synthesised and tested in polymerisation by Fujita and co-workers [24, 334, 335] and Bochmann and co-workers.[336] Zirconium complex **116** was moderately active in ethylene polymerisation in the presence of MAO [63.8 (kg PE) mol^{-1} h^{-1} bar^{-1}], while titanium complexes **117** proved to be much more active [up to 33 200 (kg PE) mol^{-1} h^{-1} bar^{-1} in the presence of MAO, R^1 = cyclo-C_8H_{15}] to produce linear high-molecular-mass polyethylene ($M_w = 3.1 \times 10^6$). When $Ph_3CB(C_6F_5)_4$–Bu^i_3Al was used as a co-catalyst, the activity decreased severalfold and M_w increased (up to 4.9×10^6), as in the case of phenoxyimine catalysts (see above). Later, it was shown [337] that complex **117** (R^1 = cyclo-C_6H_{11}) is able to catalyse living polymerisation of ethylene with norbornene, the co-monomer content being up to 44%–48%, and the product formed has M_n up to 8×10^5 and $M_w/M_n = 1.1$–1.2. Fujita and co-workers [24] have generally termed the bis(pyrrolylimine) catalysts as 'PI Catalysts'.



116

Ar = 2,6-$Pr^i_2C_6H_3$.



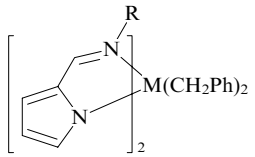
117, **118**

117: R^2 = H: R^1 = Et, Ph, n-C_6H_{13}, cyclo-C_6H_{11}, cyclo-C_8H_{15};
118: R^1 = Ph: R^2 = H, Me, Bu^t, $SiMe_3$.

Titanium bis(pyrrolylimine) complexes are more active than their zirconium analogues and, hence, it is studies of titanium complexes that are the most advanced. Attaining high activity of such complexes does not require necessarily the presence of a bulky substituent in the vicinity of the active centre. Indeed, the complex with R^2 = H is the most active in the series of catalysts **118**.[24] Probably, the higher content of propylene (up to 20%–30% against 4.5% for phenoxyimine systems) and hex-1-ene (up to 1.9% against 0.4% for phenoxyimine systems) obtained upon co-polymerisation of ethylene with these co-monomers may be explained by greater steric accessibility of the central atom in pyrrolylimine complexes.[24, 321] A similar picture was also observed in co-polymerisation of ethylene with norbornene.[24] Details of studies on living co-polymerisation of ethylene with norbornene have been reported.[24, 337] Analysis of the co-polymer structure has revealed that alternating norbornene–ethylene units predominate. Interestingly, the homopolymerisation of ethylene is not living polymerisation (the obtained polymer has M_w/M_n = 2.1) and norbornene is not polymerised at all.[338] For the first time, the authors have managed to obtain block co-polymers of ethylene with norbornene that contained polyethylene and alternating ethylene–norbornene segments.[338, 339] The cal-

culations for ethylene insertion into the metal–carbon bond, which take place in the polymerisation on bis(pyrrolylimine) catalysts, were performed in a theoretical study.[340]

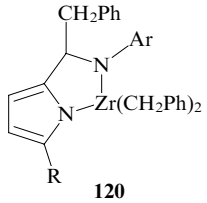
Apart from the titanium bis(pyrrolylimine) complexes, similar hafnium and zirconium complexes have been studied. In contrast to complexes **117**,[336] compounds **119** are extremely active in ethylene polymerisation when activated by MAO or $B(C_6F_5)_3-AlBu^i_3$ [up to 22 900 (kg PE) mol^{-1} h^{-1} bar^{-1}] and zirconium complexes are approximately an order of magnitude more active than the hafnium ones.[341, 342]



119

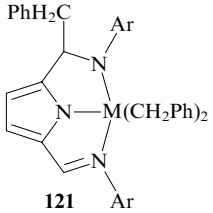
R = Alk, cyclo-Alk, Ar;
M = Zr, Hf.

A study of titanium complexes **112** with one pyrrolylimine and one phenoxyimine ligands has shown that they are able to catalyse co-polymerisation of ethylene not only with norbornene, but also with hex-1-ene or cyclopentene (in the latter case, the co-monomer content reached 37 mol %).[329, 343] Mashima and co-workers[344–346] have synthesised and studied a series of complexes **120** and **121**, which are active in polymerisation of ethylene in the presence of MAO or MMAO. However, their activity is lower than those of titanium bis(pyrrolylimine) complexes.



120

Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$.



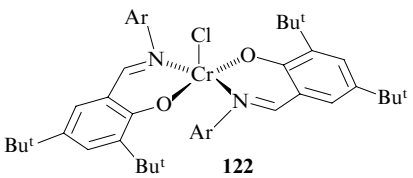
121

M = Zr, Hf; Ar = 2-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$.

Thus, the titanium bis(pyrrolylimine) complexes are quite attractive as catalysts: they are more active in ethylene polymerisation than the metellocene systems, they are able to catalyse living co-polymerisation of ethylene with norbornene yielding the products with high norbornene content, and are suitable for production of block co-polymers of ethylene and norbornene.

4. Phenoxyimine and pyrrolylimine complexes of other metals and their analogues

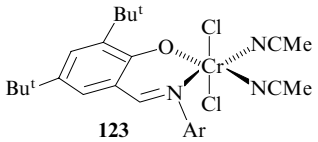
Titanium and zirconium compounds are catalytically the most active in ethylene polymerisation among metal phenoxyimine and pyrrolylimine complexes known so far. Similar complexes of other metals are also able to catalyse this process. Thus the activity of chromium bischelate complex **122** was up to 96 (kg PE) mol^{-1} h^{-1} bar^{-1} with $AlEt_2Cl$ as an activator.[347]



122

Ar = 2,6-$Pr^i_2C_6H_3$.

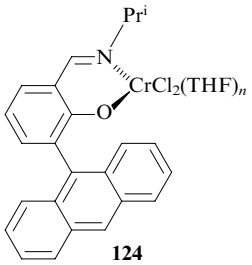
Monochelate phenoxyimine complex **123** is more active [130 (kg PE) mol^{-1} h^{-1} bar^{-1}],[348] and $AlEt_2Cl$ is also more efficient as an activator than MAO.



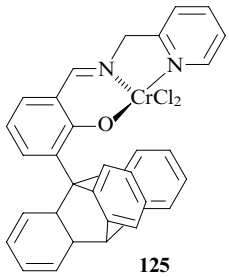
123

Ar = 2,6-$Pr^i_2C_6H_3$.

Monochelate complex **124** containing a bulky anthracenyl substituent is better activated by methylaluminoxane yielding ultrahigh-molecular-mass polyethylene.[349] Complex **125** (and a number of similar complexes) with the tridentate O,N,N-donor ligand was found during screening of a wide variety of ligands. Such complexes are highly active in ethylene polymerisation [6970 (kg PE) mol^{-1} h^{-1} bar^{-1}] producing linear low-molecular-mass polyethylene.[349, 350]

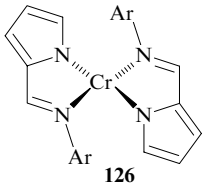


124



125

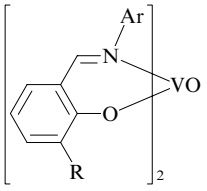
Chromium pyrrolylimine complexes are less active than similar titanium complexes. The activity of catalyst **126** combined with $AlEt_2Cl$ is up to 70 (kg PE) mol^{-1} h^{-1} bar^{-1} (Ref. 351). Subsequently, it was shown[352] that $AlMe_2Cl$ may be used for activation of complex **126**; this results in an increase in the polymer molecular mass and in narrowing of the molecular mass distribution. Complex **126** shows no noticeable activity in the presence of MAO.[352]



126

Ar = 2,6-$Pr^i_2C_6H_3$.

Among other catalysts, vanadium bis(phenoxyimine) complexes should be noted; in particular, compounds **127** (R = H, Ar = Ph) in combination with a heterogeneous activator, $MgCl_2-Et_mAl(OEH)_{3-m}$ (OEH is 2-ethylhexyloxy), is highly active in ethylene polymerisation at high temperature [65 000 (kg PE) mol^{-1} h^{-1} bar^{-1} at 75 °C] and also in the co-polymerisation of ethylene with propylene (M_w = 697 000, propylene content 21.3 mol %). It should be noted that compounds **127** are the first vanadium-based highly active ther-



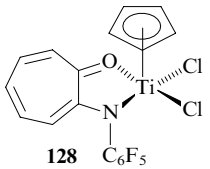
127

mally stable single-centred catalysts of polymerisation.[285, 353] Redshaw *et al.*[354] have used $AlMe_2Cl$ for activation of complexes **127** [R = $CH(2\text{-}OHC_6H_4)_2$, Ar = 2,6-$Pr^i_2C_6H_3$]. The activities were somewhat lower [up to 24 900 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ at 75 °C]; ethyl trichloroacetate, which increases the catalyst thermal stability and service life, was added as a re-activator.

Aluminium(III) mono(phenoxyimine) complexes, which showed low activity in the polymerisation of ethylene and propylene in the presence of $AlEt_3$ or $AlMe_3$ and $B(C_6F_5)_3$, should also be noted.[355–357]

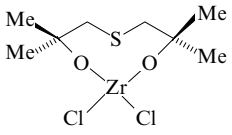
VI. Miscellaneous complexes

We discussed the key complexes used as catalysts of olefin polymerisation and synthesised in the late 1990s and in the early 2000s. However, a number of other complexes, which have been synthesised recently and may turn out to be perspective in the future, should be noted. Thus titanium(IV) complexes **128** containing aminotropolone ligands were synthesised. These complexes combined with MAO are able to to catalyse polymerisation of ethylene and propylene and their activities are comparable with those of metallocene catalysts.[174, 358, 359]

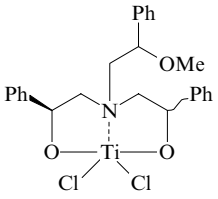


128 C_6F_5

Carpentier and co-workers[360] have synthesised and characterised a series of titanium and zirconium complexes with dialkoxy ligands containing a sulfur bridge. In the presence of MAO, some of these complexes were highly active in ethylene polymerisation [for example, the activity of complex **129** was 7190 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$]. Titanium complex **130** effectively catalyses polymerisation of hex-1-ene in the presence of MAO, the resulting polymer having a narrow molecular mass distribution ($M_w/M_n = 1.07-1.11$). This implies that polymerisation follows a living mechanism; the isotacticity of the *mmmm*-pentad was 80%–85% (for the C_2-form of the catalyst).[361]

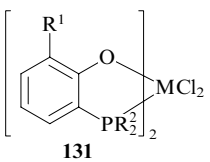


129



130 (C_2- and *meso*-forms)

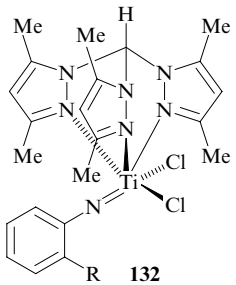
Gibson and co-workers[362] have described Group 4 metal complexes **131** with P,O-donor ligands that are active in olefin polymerisation. The activity of the catalyst with M = Zr, R^1 = Bu^t, R^2 = Ph in ethylene polymerisation during 1 h at 20 °C was equal to 26 700 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$. This is a very high value for non-metallocene systems.



131

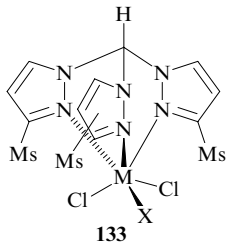
R^1 = H, Bu^t, Ph;
R^2 = Pr^i, Ph;
M = Ti, Zr, Hf.

Titanium complexes **132** with the tris(pyrazolyl)methane ligand show varying activities depending on the substituent at the nitrogen atom. The complexes with R = CF_3, Bu^t were



132

R = CF_3, Bu^t.

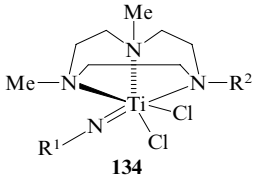


133

M = Ti, X = Cl;
M = V: X = NBu^t, $NC_6H_3Pr^i_2$-2,6;
Ms = 2,4,6-$Me_3C_6H_2$.

extremely active under nearly industrial conditions (100 °C, 7 bar, 10 min), their activities being 133 700 and 152 500 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ (Ref. 363). Titanium and vanadium complexes **133** catalyse ethylene polymerisation in the presence of MAO or the $AlBu^i_3$–MAO system, their activity exceeding 10^4 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$. High-molecular-mass polyethylene ($M_w = 1.2-1.6 \times 10^6$) may be obtained with the vanadium complex (X = NBu^t).[364]

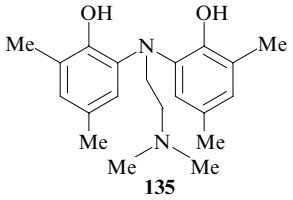
The synthesis and the catalytic activity in ethylene polymerisation for several tens of imidotitanium complexes **134** containing triazacyclic ligands have been reported[365] (only triazacyclononane complexes are shown but triazacyclohexane complexes were also studied). The activities of some complexes reached 4000–10 000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ at 100 °C for a polymerisation time of 10 min.



134

R^1 = Alk, cyclo-Alk, Ar;
R^2 = Me, polystyrene.

A series of complexes containing vanadium in various oxidation states ranging from +2 to +5 with O,N,N,O-donor ligands **135** have recently been reported. In the presence of $AlEtCl_2$, these complexes are moderately active in ethylene polymerisation and in co-polymerisation of ethylene with hex-1-ene and norbornene (the content of norbornene is up to 29 mol%).[366]

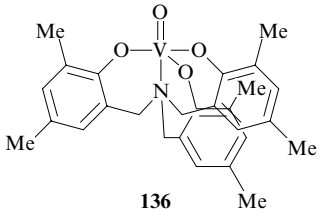


135

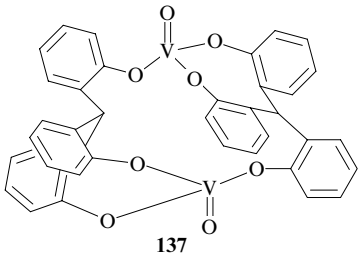
Catalysts **136**–**138** based on mono- and dinuclear vanadium complexes synthesised and studied by Redshaw and co-workers[355, 367] may be of considerable interest. Complex **136** is highly active in ethylene polymerisation in the presence of $AlMe_2Cl$ and ethyltrichloroacetate as the reactivator [up to 96 500 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ at 80 °C, polymerisation time 15 min, Al : V = 2500]; a decrease in the temperature to 25 °C results in a 3.5-fold decrease in activity; however, the molecular mass increases by more than an order of magnitude ($M_w = 5.18 \times 10^6$).[354]

The activity of dinuclear complex **137** was similar under similar conditions.[354] The activity of complex **138** (R^1 = Bu^t, R^2 = Me) was formally a record [up to 640 000 (kg PE) $mol^{-1}\ h^{-1}\ bar^{-1}$ at 80 °C], but only in the presence of a huge excess of $AlMe_2Cl$ (Al : V = 150 000) and polymerisation

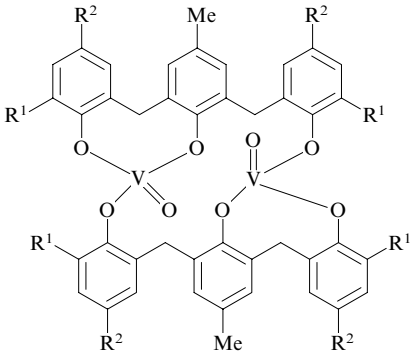
time of 1 min. The melting point of the product obtained under these conditions was 135 °C, which is typical of linear ultra-high-molecular-mass polyethylene.[367] Among other new complexes, vanadium complexes with tris(pyrazolyl)borate ligands supported on SiO_2 should be noted. These systems are highly active [up to 1900 (kg PE) mol^{-1} h^{-1} bar^{-1}] in the presence of MAO, $AlMe_3$, $AlPr^i_3$ (Ref. 368).



136



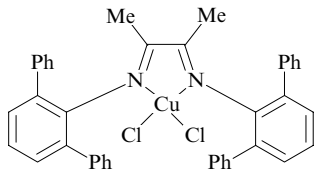
137



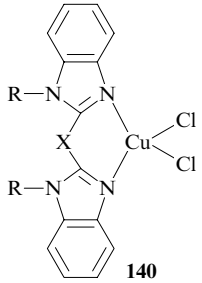
138

R^1 = Bu^t, R^2 = Me; R^1 = R^2 = Bu^t.

No copper complex-based catalysts of olefin polymerisation are discussed in this review because the activity of even the most active ones (complexes **139**[369] and **140**[370]) does not exceed 300 (kg PE) mol^{-1} h^{-1} bar^{-1}. However, copper bis(benzimidazole) complexes **140** are able to catalyse co-polymerisation of ethylene with acrylic acid esters in the presence of MAO.[370, 371] Recently, studies of copper complexes with other *N,O*-[372] and *N,N*-chelating[373] ligands were reported. The state-of-the-art of the studies into olefin polymerisation catalysts based on rare earth metal complexes, including non-metallocene ones, has been reviewed.[374]



139



140

R = Alk; X = CH_2, CHOH, 2,2′-biphenyl.

VII. Conclusion

At the boundary of the century, a great number of new non-metallocene catalytic systems for olefin polymerisation have emerged. Among these systems, the transition metal bis(imine) and bis(imino)pyridyl, bis(phenoxyimine) and bis(pyrrolylimine) complexes stand out. These systems have overcome their metallocenic predecessors in the activity and variety of the obtained polymer products. New classes of ligands have appeared that allow one to control the catalytic properties of the active centres over a broad range by variation and modification of the ligands' structure. In contrast to metallocene systems, which use expensive Lewis acids (methylaluminoxane, perfluoroarylboron derivatives) as activators, much cheaper activators such as trialkylaluminium, alkoxyalkylaluminium derivatives on $MgCl_2$, *etc*., may be used for activation of post-metallocene systems. At present, the main target of the studies of these systems is maximum control over the parameters (molecular mass, composition, structure) of the resulting products. Undoubtedly, very soon we can expect new achievements in this field, as big research groups have started a systematic search for new catalytic systems by employing the 'high-throughput screening' methodology.[15, 350] The experimental and theoretical studies of the structures of active intermediates and the mechanisms of catalytic polymerisation are also in progress.

In an early review on the new catalytic systems, Gibson has mentioned that overcoming of the stereotype that the search for new catalysts should be limited by a narrow class of metals, which have already proved themselves in the formation of active polymerisation centres, and that the development of new systems will be restricted only by imagination of a scientist, would form the distinctive features of the 'post-metallocene age' of olefin polymerisation catalysts.[26] Some research groups proceeded, from the very beginning, from the assumption that the ligand structure is the most important factor because the olefin affinity is pronounced for all transition metals.[24] According to this ligand-oriented approach, high polymerisation activity requires a suitable ligand with balanced electron-releasing and -withdrawing properties. Indeed, up to now, among all complexes of the first raw transition metals, the highly active catalytic systems for olefin polymerisation are practically unknown only for manganese complexes. However, this situation is already changing: manganese(I) hydrotris(pyrazolyl)borate complexes are reported.[375]

At the same time, it should be noted that the development of studies of post-metallocene systems has not resulted so far in a broad commercial application of these systems. On the one hand, some time is required for bringing new processes to large-scale industrial production. On the other hand, the industry demands, first of all, active systems stable at higher temperatures (preferably supported). At present, most of the post-metallocene catalytic systems do not meet these criteria. Therefore, it is obvious that the traditional processes based upon Ziegler–Natta and metallocene catalysts will not be quickly replaced and mainly those post-metallocene systems that produce valuable polyolefin-based materials with new properties will be used by industry in the future.

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