https://doi.org/10.1070/RCR5021

Catalytic oligomerization and polymerization of ethylene with complexes of iron triad metals: influence of metal nature and new prospects

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In the last five years the field of catalytic oligomerization and polymerization of olefins using complexes of late transition metals has been the most intensively developing area of post-metallocene catalysis. This review is devoted to detailed analysis of the influence of metal nature on the catalytic properties of systems based on complexes of iron triad metals. Some novel and developing areas of application of such complexes in olefin oligomerization and polymerization (ethylene trimerization, production of olefins with an odd number of carbon atoms and polyethylene waxes, targeted synthesis of heavy fractions of ethylene oligomers) are surveyed. Different approaches to the heterogenization of catalysts on various solid supports are considered.
The bibliography includes 225 references.

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1. Introduction

Catalytic processes of homo- and copolymerization of olefins play a key role in the production of modern polymer materials, such as polyethylene (PE), polypropylene (PP) and various polyolefin copolymers, having diverse physico-mechanical properties (depending on their structure and composition). In particular, the fraction of polyethylene and polypropylene among the plastics produced in 2017 (380 million ton in total) was dominant: 36 and 21%, respectively, and their annual production steadily increases.[1] No less important for modern technologies is ethylene oligomerization, which provides a wide range of linear α-olefins (LAOs). The latter, in turn, are used as comonomers in production of various grades of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), or as intermediates in production of synthetic oils, surfactants, oil additives, *etc*. Most of commercial technologies and laboratory studies of the two aforementioned processes imply the use of catalytic systems based on compounds of first-row transition metals. In recent years coordination compounds of iron triad metals

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Translation: Yu.P.Sin'kov

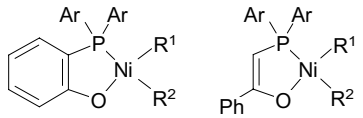
Received 29 March 2021

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(primarily, nickel complexes) have been widely investigated as the main component of these systems.

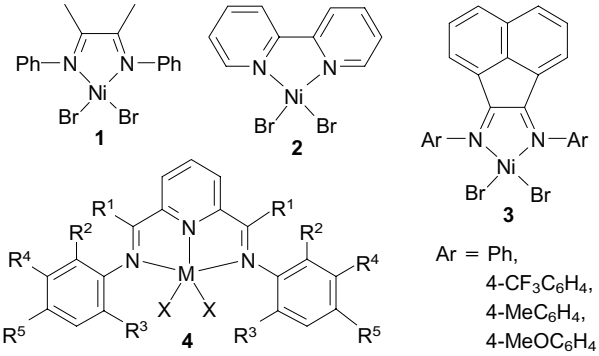
The use of nickel compounds as catalysts for olefin oligomerization begins with the discovery of the 'nickel effect' by Ziegler *et al.*[2] in 1954; its essence is the switching from polymerization of olefins to their dimerization when replacing titanium salts with nickel salts in the ($TiCl_4 - AlR_3$) system. A technology for large-scale production of higher terminal olefins was developed based on the results of these studies: Shell higher olefin process (SHOP).[3,4]

Structures of SHOP-type Ni(II) complexes



R^1 = Alk, Ar
R^2 = PPh_3, Py, *etc.*

Structures 1 – 4



Ar = Ph, 4-$CF_3C_6H_4$, 4-MeC_6H_4, 4-$MeOC_6H_4$

M = Fe, Co; X = Cl, Br; R^1 = H, Me; R^2 = Me, Ph; R^3 = H, Ph; R^4 = H, Me; R^5 = H, Me

In 2017 more than 1.3 million tonnes of α-olefins were produced using this technology all over the world.[5] Furhter development of the studies in the field of SHOP-type catalysts was described in reviews.[6–8]

The growth of research interest in nickel coordination compounds with different chelating ligands is related to the discovery of Ni(II) α-diimine complexes (**1** – **3**) by Brookhart *et al.* After activation with organoaluminium compounds, these complexes showed the ability to polymerize[9] or oligomerize[10,11] ethylene and α-olefins.

Later on Brookhart *et al.* and Gibson *et al.* independently synthesized complexes of Co(II) and Fe(II) **4**, which demonstrated [after activation by methylaluminoxane (MAO) or modified methylaluminoxane (MMAO)] high productivity in both ethylene polymerization[12–14] and oligomerization.[15] These pioneer studies were followed by an active search for new types of coordination compounds of iron triad metals with diverse organic ligands and study of their catalytic properties in the aforementioned reactions.

The steady interest in the complexes of these metals (Fig. 1) is due to the high variability of their catalytic properties. In particular, depending on the organic ligand, activator and reaction conditions, complexes of iron triad metals make it possible to produce many diverse products: from light oligomers (butenes) to linear high-molecular-weight[16] and ultra-high-molecular-weight polyethylene (UHMWPE) with different degrees of branching.[17–21] Nickel-based catalysts make it possible to produce branched elastomers directly from ethylene due to the 'chain-walking' process, which leads to isomerization of the polymer chain.[22–27] In addition, nickel-based catalytic systems can catalyze copolymerization of ethylene and polar monomers,[28–33] resulting in formation of polymers possessing with unique adhesion, compatibility with dyes and other polymers, *etc.*

Ethylene oligomerization using complexes of nickel,[22,34–36] cobalt and iron[16,37–47] also remains an important field of research (see Fig. 1). Most publications on this subject are devoted to the search for more selective catalysts; however, catalytic systems characterized by increased productivity have also been described. The tandem Friedel – Crafts alkylation of toluene with ethylene oligomers obtained in the first stage of the catalytic reaction is also worth mentioning.[39] However, the mechanism of this process has not been completely understood yet.

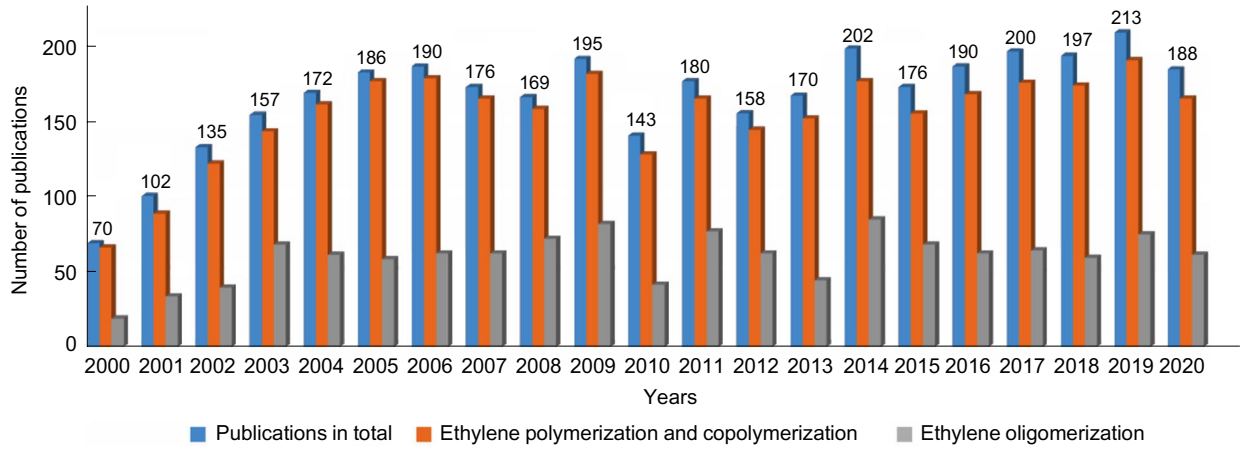


Figure 1. Annual distribution of the number of publications devoted to the catalysts based on iron triad metal complexes used for oligomerization, polymerization and copolymerization of ethylene, according to the Web of Science data. Data on the total number of publications are indicated on the top (the sum of two subcategories exceeds 100%, because polymerization and oligomerization were considered jointly in some papers).

In the last years, the number of scientific publications devoted to complexes of iron triad metals with previously unknown properties (ability of trimerizing ethylene, catalyzing the formation of olefins with an odd number of carbon atoms or ethylene oligomers with a chain length $>C_{20}$) has been constantly increasing. Studies aimed at searching for catalytic systems making it possible to synthesize polyethylene waxes with different microstructures have been actively continued. Much attention has been paid to the use of different carriers suitable for immobilization of complexes and their further application as heterogeneous catalysts for ethylene oligomerization and polymerization.

In this review we consider the coordination compounds of nickel, cobalt and iron, which are capable of catalyzing ethylene oligomerization or polymerization after activation by different organoaluminium compounds (OACs) (MAO, Et_2AlCl, $Et_3Al_2Cl_3$, $AlEt_3$, *etc.*). In the first part of the review, the catalytic properties of Co(II), Fe(II) and Ni(II) complexes with the same structure of the organic ligand and its coordination mode, operating under identical conditions during ethylene oligomerization, are compared. Much attention is also given to the relationship of the structure of a coordination compound and its catalytic properties, which also depend on the used organoaluminium activator and solvent.

In the second part of the review, some promising lines of development of ethylene oligomerization and polymerization catalyzed by iron triad metal complexes with the above-mentioned unique properties are considered.

The catalytic activity of all considered systems was converted to the dimension kg mol(M)$^{-1}$ h^{-1}; when necessary, ethylene pressure is indicated (in atmospheres). However, these data are not always objective, because the duration of catalytic reactions can vary from publication to publication; hence, one cannot take into account the differences in catalyst deactivation rate during the experiment. The duration of short (<10 min) experiments is indicated separately in our review.

2. Mechanistic aspects of ethylene oligomerization and polymerization using complexes of iron triad metals

The Cossee–Arlman mechanism is considered to be the generally accepted mechanism for late transition metal catalyzed ethylene polymerization and oligomerization (Fig. 2 *a*).[48,49] In the general case, activation of a neutral precatalyst by organoaluminium compounds gives rise to an alkyl or hydride cationic complex, that is responsible for polymer chain growth through successive ethylene coordination and insertion steps. However, there are neutral organometallic nickel complexes that exhibit catalytic activity in the abscence of organoaluminium cocatalyst.[33] There are also some examples in the literature, where nickel is present in a complex precatalyst in the anionic form; However, after activation these complexes are able to catalyze ethylene oligomerization[50] or polymerization,[51] thus leaving open the question about the nature of active sites in such systems.

The ability of complexes of iron triad metals to catalyze oligomerization rather than polymerization of ethylene is determined by the rate of chain termination (Fig. 2 *b*) according to the mechanisms of β-H elimination (1), β-hydride transfer to a monomer (2) or polymer chain transfer to aluminium (3).[52] The latter mechanism is characteristic, in particular, of iron complexes.[53]

The rate of these processes is determined in many respects by the coordination environment of the catalytic site. In particular, when using ligands with bulky groups, the rate of chain termination will be much lower (with a high probability) than the monomer insertion rate, which should lead to the formation of high-molecular-weight polymers. At the same time, in the case of sterically unhindered ligands, the chain termination rate will exceed greatly the ethylene insertion rate, which should result in predominant formation of light oligomers, such as butenes and hexenes. Thus, changing the volume and arrangement

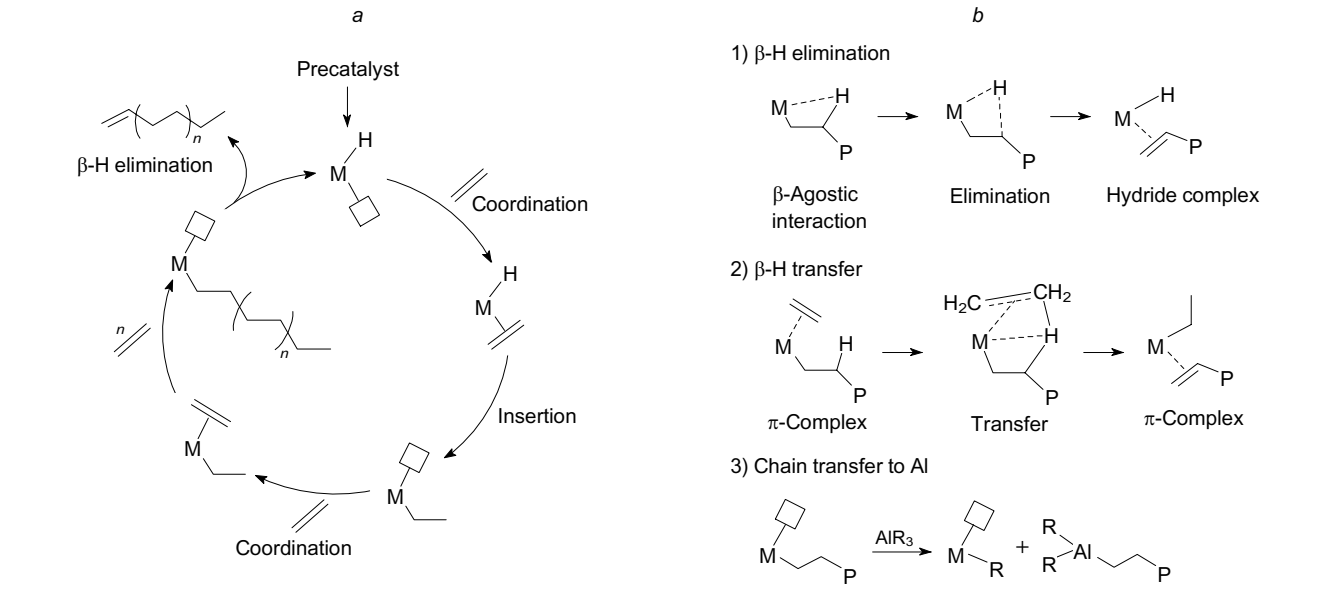


Figure 2. Simplified schemes of (*a*) the Cossee–Arlman coordination/migratory insertion mechanism and (*b*) chain termination mechanisms.

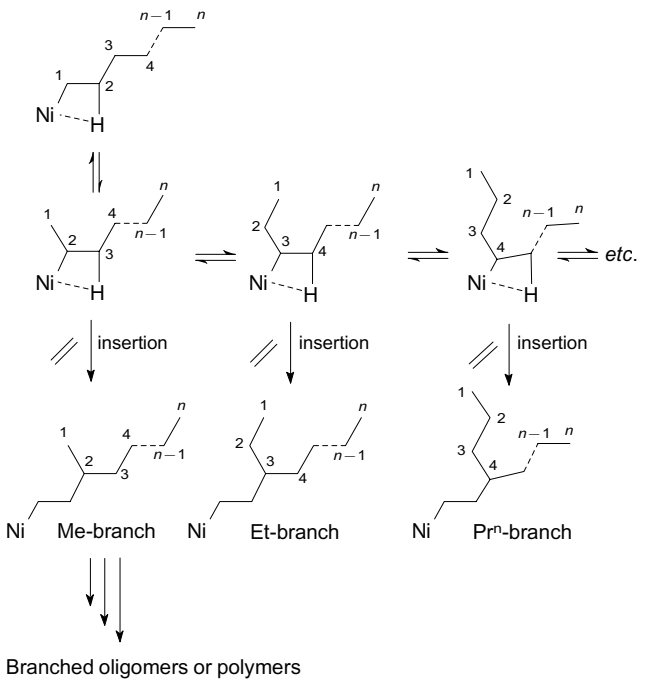


Figure 3. Simplified scheme of the 'chain-walking' process, leading to isomerization of ethylene (oligo)polymerization products.

of substituents near the metal centre, one can control the catalytic reaction selectivity with a rather high accuracy. The branched structure of the polymers and oligomers obtained in the presence of nickel catalysts differs significantly from that of the linear products obtained using cobalt and iron complexes. The formation of branches of different lengths is governed by a 'chain-walking' mechanism (Fig. 3),[9,54] during which the metal can move along the polymer chain before the next event of monomer insertion occurs. The 'chain-walking' process includes two stages: first β-H elimination occurs, which is followed by 2,1-insertion of the newly formed (oligo)polymer at the Ni–H bond. The ratio of the isomerization and insertion reaction rates determines the final product structure.

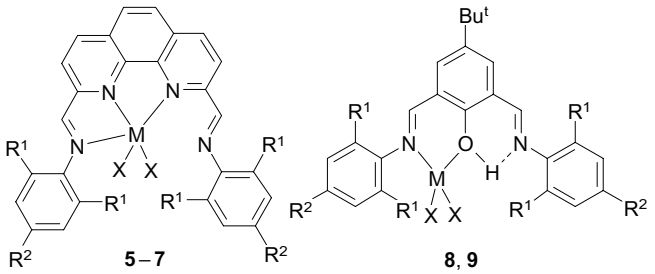
3. Comparison of the efficiency of nickel, cobalt and iron complexes in ethylene oligomerization

Despite the large number of studies devoted to the application of Ni(II), Co(II) and Fe(II) complexes in ethylene oligomerization, the catalytic activities of the three aforementioned metals were directly compared in only a few studies. The results of pairwise investigations of Ni(II) and Pd(II) complexes, as well as Co(II) and Fe(II) complexes, which have most similar catalytic properties, are mainly presented. The coordination compunds of all iron triad metals were considered in reviews;[38,55] however, no comparison of the influence of the metal centre on the catalytic properties of complexes and properties of reaction products was conducted. In this review we compare the catalytic properties of systems based on complexes of iron triad metals only for ethylene oligomerization, because products with a radically different microstructure are formed during ethylene polymerization. After activation, iron and cobalt complexes catalyze the formation of linear polyethylene ranging from low-molecular-weight waxes to UHMWPE,[16,21,56,57] whereas in the case of nickel complexes, due to the high 'chain-walking' rate, branched polyethylenes are mainly formed, which can be used as thermoplastic elastomers.[22–25]

The first comparison of the efficiency of Ni(II), Co(II) and Fe(II) complexes in ethylene oligomerization was performed by Sun and co-workers[58] in 2002. Iron complexes **5a**,**c** did not exhibit any catalytic activity after activation by MAO, and complex **5b** catalyzed the formation of a small amount of polyethylene under the same conditions. Cobalt complexes **6**, after activation by MAO, catalyzed formation of a mixture of polymer and low-molecular-weight oligomers (C_4, C_6), but were less active [700–930 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10–20 atm] in comparison with their nickel analogues **7** [2000–3300 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10–20 atm]. Catalytic systems **7a**–MAO and **7c**–MAO led to the formation of a mixture of polymer and oligomers (C_4–C_{10}), whereas in the presence of **7b**–MAO only ethylene oligomerization occurred. These differences in the catalytic properties of complexes **7** can be explained by the influence of the bulky substituent R^1 (**7a**) or the donor substituent R^2 (**7c**) on the β-H elimination rate. It should be noted that only isobutylene was observed among the oligomers in the butene fraction, while the hexene-1 fraction did not exceed 12%. This fact is indicative of a high isomerization rate during the catalytic process.

After activation by MAO, complexes **9** catalyzed the formation of C_4–C_{16} oligomers, and exhibited activity of up to 210 kg mol(Ni)$^{-1}$ h^{-1} (**9c**, $p_{ethylene}$ = 1 atm).[59] Similar cobalt complexes **8** were barely active [~1 kg mol(Co)$^{-1}$ h^{-1}] under the same conditions. The presence of a bulky group near the metal centre (R^1 = Pr^i) led to the shift of product selectivity from light olefins C_4–C_6 (**9b**, **9c**) to heavier ones C_4–C_{16} (**9a**).

Structures 5–9



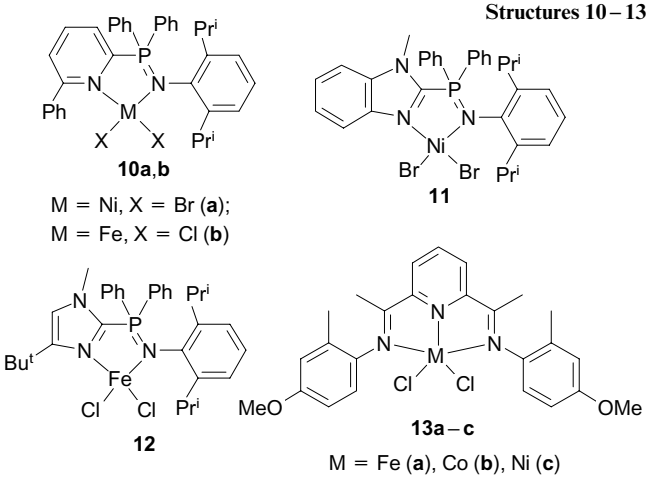
5–7 **8, 9**

5: M = Fe, X = Cl
6: M = Co, X = Cl
7: M = Ni, X = Br

8: M = Co, X = Cl;
9: M = Ni, X = Br;
5–9: R^1 = Pr^i, R^2 = H (**a**);
R^1 = Me, R^2 = H (**b**);
R^1 = Me, R^2 = Me (**c**)

Spencer *et al.*[60] investigated nickel and iron complexes **10–12** with phosphinimine ligands. After activation by MAO (in toluene) or Et_2AlCl (in chlorobenzene), these complexes catalyzed selective ethylene dimerization. The nickel complexes were much more active [up to 724 kg mol(Ni)$^{-1}$ h^{-1} (**10a**)] than the iron complexes [414 kg mol(Fe)$^{-1}$ h^{-1} (**10b**)] at $p_{ethylene}$ = 20.4 atm. The joint influence of the activator and the solvent for these metals turned out to be opposite: nickel complexes were more active when carrying out the reaction in the presence of Et_2AlCl in chlorobenzene, whereas iron complexes exhibited a higher activity when using MAO in toluene.

Structures 10 – 13



In 2005 Sun and co-workers[61] synthesized Ni(II), Co(II) and Fe(II) complexes **13** with a bis(arylimino)pyridine ligand. After treatment with MAO, the highest activity was observed for iron complex **13a** [1250 kg mol(Fe)$^{-1}$ h^{-1}, $p_{ethylene}$ = 1 atm], leading mainly to the formation of polyethylene and a small amount of C_4-C_{20} oligomers. Cobalt complex **13b** was much less active [398 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 1 atm] and catalyzed the formation of only oligomeric products (C_4-C_{20}); the fraction of C_{8+} olefins was less than 2%. Nickel complex **13c** demonstrated an extremely low catalytic activity [5.13 kg mol(Ni)$^{-1}$ h^{-1}], and the reaction products were isomeric butenes.

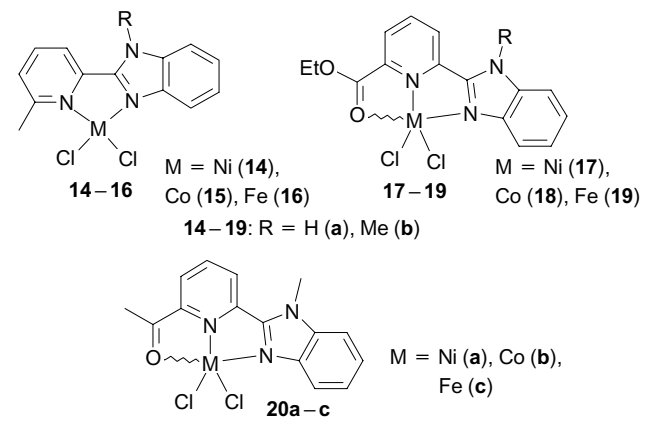
The Ni(II) complexes **14**, **17**, **20a** showed moderate values of catalytic activity after treatment with Et_2AlCl [58 – 630 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 20 atm]. The oligomerization products obtained using complexes with tridentate ligands (**17**, **20a**) showed a significant increase in the hexene fraction: from 4.5 – 11.3% to 25.6 – 68.3%. Note that the activation of complexes by MAO barely decreased (for **14**) and sometimes even increased (for **17**) their catalytic activity. It was found that, in contrast to nickel complexes, cobalt and iron atoms in compounds **18**, **19** and **20b**,**c** do not form the 'normal' donor – acceptor bond with the ligand oxygen atom; nevertheless, a weak interaction between them was observed.[62] After activation by Et_2AlCl, Co(II) complexes **15**, **18** and **20b** were less active [152 – 282 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 20 atm]; they catalyzed mainly the formation of hexenes (18.4 – 62.6%), whose fraction in the mixture was higher for complexes **15** and **20b**. Related Fe(II) complexes **16**, **19**, **20c**, which were activated using mainly MMAO, had the highest activity [156 – 1030 kg mol(Fe)$^{-1}$ h^{-1}, $p_{ethylene}$ = 20 atm];[63] the activity was maximum for complexes **19**. Moreover, complexes **19** catalyzed mainly ethylene dimerization (with a butenes yield of 96.3%). The other systems exhibited formation of a large amount of hexenes (18.6 – 46.1%), whose fraction has increased in the case of avtivation of complex **16** with Et_2AlCl or MAO.

Complexes **21** – **23** with (benzimidazolyl)iminopyridine ligands, which are derivatives of compounds **20**, turned out to be much more active at $p_{ethylene}$ = 30 atm.[62,63] In particular, after activation by Et_2AlCl, Ni(II) complexes **21** efficiently catalyzed the dimerization of ethylene (93.1 – 95.1%); their catalytic activity increased in the series **21a** < **21b** < **21c** < **21d** < **21e** and reached 10200 kg mol(Ni)$^{-1}$ h^{-1} at 20°C. Complexes of Co(II) **22** with similar ligands exhibited an opposite dependence of activity [56 – 354 kg mol(Co)$^{-1}$ h^{-1}] on the structure after activation by MAO. With a decrease in activity, the hexene fraction has increased in the mixture of oligomers (up to 24.2%). Use of iron(II) complexes **23** (upon activation by MAO or MMAO) led to the formation of ethylene oligomers (C_4-C_{28}) in a mixture with a small amount of low-molecular-weight polyethylene (wax). In this case, the catalytic properties were determined both by the structure of the complex and the type of activator in use. In particular, for activation by MMAO, the activity decreased with an increase in the volume of the substituent R, although it was much lower [2122 – 3870 kg mol(Fe)$^{-1}$ h^{-1}] for halogen-substituted complexes than for alkyl-substituted ones [1400 – 7920 kg mol(Fe)$^{-1}$ h^{-1}]. In contrast, an inverse dependence was observed when using MAO: the catalytic activity rose with an increase in the volume of the substituent R [6660 – 14310 kg mol(Fe)$^{-1}$ h^{-1} for **23a** – **c**], whereas for the systems with halogen-substituted complexes, as in the previous case, it was much lower [321 – 1161 kg mol(Fe)$^{-1}$ h^{-1} for **23d**,**e**]. Possibly, this difference in the catalytic activities is due to the presence of isobutyl groups in MMAO, which, along with bulky ligand substituents, slow down the ethylene insertion.

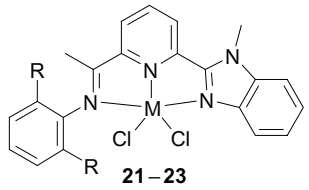
It is known that the introduction of triphenylphosphine (PPh_3) into catalytic systems based on nickel complexes makes it possible to increase significantly their activity.[3,62,64 – 76] However, the study of the formation of such systems did not yet make it possible to establish unambiguously the action mechanism of this additive.[50,64,66,77 – 79] It is suggested that triphenylphosphine plays the role of a labile ligand, which stabilizes the transition state and may facilitate ionization of the complex, leading to the formation of a charged catalytic centre. At the same time, the presence of PPh_3 in systems with iron complexes significantly reduced the catalytic activity (from 7920 to 660 kg mol(Fe)$^{-1}$ h^{-1}), whereas in the case of nickel complexes with a similar ligand the activity increased [from 9180 to 56 400 kg mol(Ni)$^{-1}$ h^{-1}].[62,63] The opposite influence of the PPh_3 additive on nickel and iron complexes can be explained by the higher strength of the Fe – P bond, which prevents the PPh_3 decoordination during catalysis.

Complexes **24** – **26**[73] with a *N*-isopropyl substituent in the benzimidazole moiety, similar to compounds **21** – **23**, were tested at $p_{ethylene}$ = 10 atm; they showed a similar dependence of the catalytic activity on the complex struc-

Structures 14 – 20

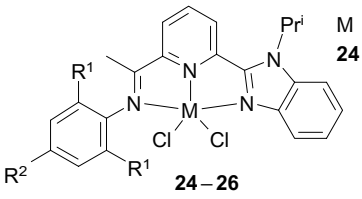


Structures 21 – 36



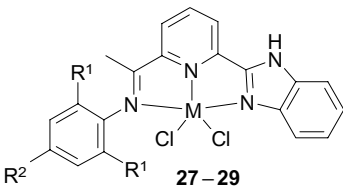
21 – 23

M = Ni (**21**), Co (**22**), Fe (**23**);
21 – 23: R = Me (**a**), Et (**b**), Pr^i (**c**), Cl (**d**), Br (**e**)



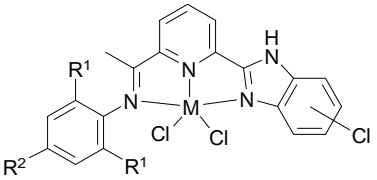
24 – 26

M = Ni (**24**), Co (**25**), Fe (**26**);
24 – 25: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = Cl, R^2 = H (**d**);
R^1 = Me, R^2 = Me (**e**);
R^1 = Me, R^2 = Br (**f**)



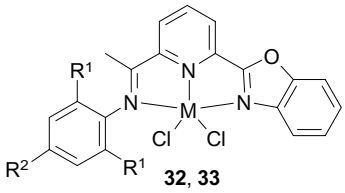
27 – 29

M = Ni (**27**), Co (**28**), Fe (**29**);
27 – 29: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = Me, R^2 = Me (**d**);
R^1 = Cl, R^2 = H (**e**);
R^1 = Br, R^2 = H (**f**)



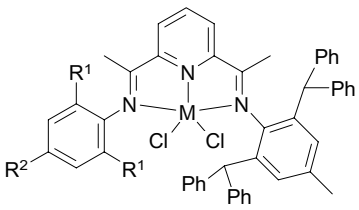
30, **31**

M = Ni (**30**), Fe (**31**);
30, **31**: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = Me, R^2 = Me (**d**);
R^1 = Et, R^2 = Me (**e**);
R^1 = Cl, R^2 = H (**f**)



32, **33**

M = Ni (**32**), Co (**33**);
32, **33**: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**)
R^1 = Pr^i, R^2 = H (**c**);
R^1 = Me, R^2 = Me (**d**);
R^1 = Me, R^2 = Br (**e**);
R^1 = Cl, R^2 = H (**f**);
R^1 = Br, R^2 = H (**g**)



34 – 36

M = Ni (**34**), Co (**35**), Fe (**36**);
34 – 36: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = Me, R^2 = Me (**d**);
R^1 = Et, R^2 = Me (**e**)

ture, which decreases with an increase in the volume of the substituent R^1. However, the introduction of a donor methyl group into the *para* position (R^2) of the phenyl ring (**24e**, **25e**, **26e**) significantly increased the activity and shifted (in the case of iron complex **26e**) the reaction direction towards polymer formation. The activity of catalytic systems with ligands of this type decreased in the series **24** – Et_2AlCl [308 – 1200 kg mol(Ni)$^{-1}$ h^{-1}, C_4-C_6] > **26** – MAO(MMAO) [141 – 824 kg mol(Fe)$^{-1}$ h^{-1}, C_4-C_{20} and waxes] ≫ **25** – Et_2AlCl [56 – 178 kg mol(Co)$^{-1}$ h^{-1}, C_4-C_6], but the fraction of α-olefins in the mixtures of oligomers for cobalt and iron complexes was more than 98%. Addition of PPh_3 to the system **24e** – Et_2AlCl increased the catalytic activity to 5200 kg mol(Ni)$^{-1}$ h^{-1}.

The catalytic activity of complexes **27 – 29** with (NH-benzimidazolyl)iminopyridine ligands, *vice versa*, decreased after the introduction of a methyl group into the *para* position of the phenyl ring (R^2).[80, 81] With an increase in the volume of the alkyl substituent R^1 the activity decreased for nickel (**27**) and cobalt (**28**) complexes but increased for the systems with iron compounds **29**. The use of electron-withdrawing halogen substituents reduced the activity of all compounds, except for the Ni(II) complexes [3030 kg mol(Ni)$^{-1}$ h^{-1} (**27e**), 2790 kg mol(Ni)$^{-1}$ h^{-1} (**27f**), $p_{ethylene}$ = 10 atm], which, in contrast, demonstrated maximum activity. Addition of PPh_3 to the system **27e** – Et_2AlCl increased the catalytic activity to 9310 kg mol(Ni)$^{-1}$ h^{-1}. The activity of iron complexes **29** turned out to be comparable with that of nickel compounds **27** [160 – 4110 kg mol(Fe)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm], while cobalt complexes **28** in the presented series were the least active [36 – 151 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm]. The fraction of α-olefins was maximum for the catalytic systems with iron complexes (98 – 99%) and decreased only with an increase in the process temperature (> 40 °C).

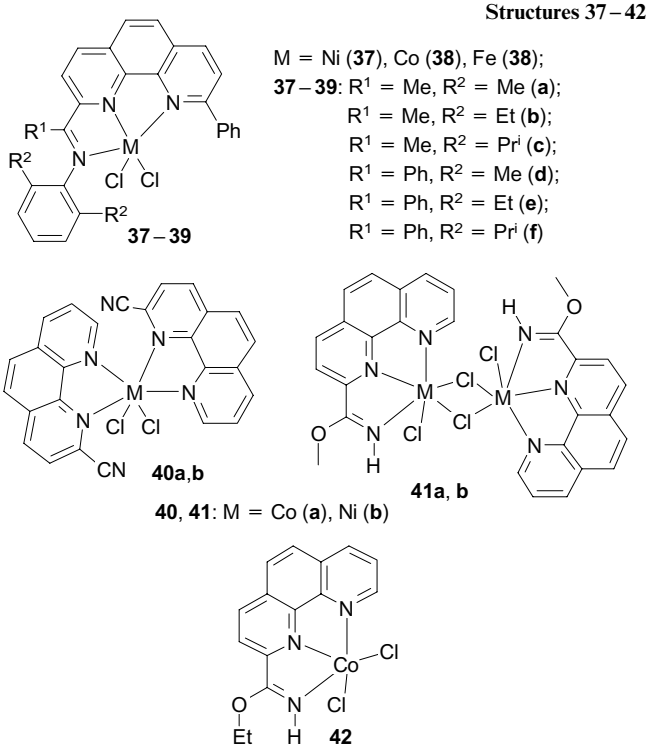
Chlorine-substituted Ni(II) and Fe(II) complexes **30**, **31**[82, 83] were less active in comparison with unsubstituted analogues **27** and **29** [540 – 2590 kg mol(Ni)$^{-1}$ h^{-1} (**30** – Et_2AlCl), 560 – 3030 kg mol(Fe)$^{-1}$ h^{-1} (**31** – MAO), $p_{ethylene}$ = 30 atm]. At the same time, the general composition of the oligomer mixture and the dependence of catalytic properties on the complex structure, remained unchanged for **30**, **31** compared to **27** and **29**. The replacement of the activator (Et_2AlCl with $Et_3Al_2Cl_3$) for nickel complexes **30** led to a rise in the hexene fraction in the oligomer mixture (to 22.3%), while the fraction of α-olefins exceeded 99%.

Complexes of Ni(II) **32** and Co(II) **33**,[84, 85] after activation by MAO (Co) or Et_2AlCl (Ni), dimerized ethylene with a high selectivity; however, the activity of nickel complexes, as was noted above, exceeded significantly that of their cobalt analogues: 359 – 1450 kg mol(Ni)$^{-1}$ h^{-1} *vs* 50 – 752 kg mol(Co)$^{-1}$ h^{-1} at $p_{ethylene}$ = 10 atm. This difference in the activity was also determined by the difference in the temperature of experiments: 50°C for nickel complexes and 20 °C for cobalt complexes, because ethylene polymerization dominated for the latter case even at 40 °C. It should also be noted that the substitution of *ortho* positions (R^1) of the phenyl ring by halogen atoms increased the catalytic activity in comparison with R^1 = Me.

Complexes of Ni(II) with asymmetric bis(imino)pyridine ligands, activated by $Et_3Al_2Cl_3$, catalyzed ethylene oligomerization with the formation of a mixture of butenes and hexenes.[86] An increase in the volume of the substituent R^1, as well as the introduction of a methyl group into the position R^2, significantly reduced the catalytic activity of compounds **34** [from 170 to 28 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm]. Complexes of Co(II) **35**[87] and Fe(II) **36**[88] of similar structure conducted ethylene polymerization after activation by MAO or MMAO.

Oligomerization of ethylene using complexes **37** was performed immediately in the presence of PPh_3 and

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Et_2AlCl.[72] The catalytic activity ranged from 3680 kg mol(Ni)$^{-1}$ h^{-1} (**37a**) to 6150 kg mol(Ni)$^{-1}$ h^{-1} (**37b**) and the butene fraction in the mixture exceeded 98%. When using MAO, oligomers were formed in only trace amounts. Complexes of Co(II) **38** and Fe(II) **39** were efficiently activated by MAO and then oligomerized ethylene with the formation of linear olefins. The catalytic activities of cobalt **38** and iron **39** complexes were 2800 – 7330 kg mol(Co)$^{-1}$ h^{-1} and 5 – 2690 kg mol(Fe)$^{-1}$ h^{-1} (all experiments were performed at $p_{ethylene}$ = 10 atm), respectively. It should be noted that the catalytic activity of iron complexes depended on the volume of the substituent R^1 and decreased significantly in the series **39a** ≫ **39b** ≫ **39c** and **39d** ≫ **39e** ≫ **39f**. In contrast, such dependence was not observed for the Co(II) and Ni(II) compounds. Systems with Co complexes **38** catalyzed the formation of oligomers with a wide distribution (C_4-C_{22}) over chain lengths, whereas the reaction products for similar systems with Ni and Fe were only butenes and a small amount of hexenes.

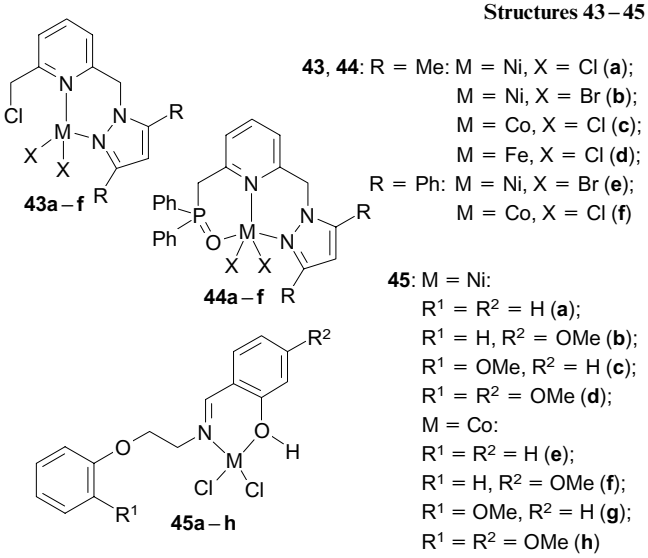
Catalytic systems based on complexes **40** – **42**[89] oligomerized ethylene with a high selectivity for butenes (C_4 > 82%). Among them, the systems with nickel complexes (**40b**, **41b**), activated with Et_2AlCl, turned out to be much more active [up to 323 kg mol(Ni)$^{-1}$ h^{-1} (**40b**), $p_{ethylene}$ = 1 atm] compared to systems activated by MAO or MMAO. However, the 1-butene fraction was found to be less than 19.1%, which can be explained by the higher isomerization rate of reaction intermediates. The optimal activator for cobalt compounds **40a** and **42** was MMAO, whereas the system with complex **41a** demonstrated maximum activity [53.4 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 1 atm] after activation by Et_2AlCl. The fraction of hexenes in the reaction products was 13%, whereas the use of MAO and MMAO as activators led only to the formation of butenes.

Complexes **43** and **44**, obtained by Ojwach and coworkers,[90,91] showed similar catalytic properties for all three metals and were mainly determined by the selected solvent and activator. For example, in the case of activation by $EtAlCl_2$ in toluene, all catalytic systems quantitatively (**43**) or almost quantitatively (**44b**) alkylated toluene. Under these conditions, ethyltoluenes dominated among the reaction products in the case of cobalt (**43c**,**f**) and iron (**43d**) complexes, whereas butyltoluenes were dominant for nickel complexes (**43a**,**b**,**e**, **24b**). For complexes **43**, the replacement of the activator with MAO led to the formation of a mixture of oligomers (C_4-C_8) and diethyltoluenes. However, in the presence of systems with complexes **44b** – **e** under similar conditions, the only product of ethylene oligomerization was a mixture of butenes, hexenes and octenes. The catalytic activity of the systems based on Ni(II) complexes turned out to be much higher [up to 1084 kg mol(Ni)$^{-1}$ h^{-1}] than that of similar complexes of Co(II) [up to 339 kg mol(Co)$^{-1}$ h^{-1}] or Fe(II) [467 kg mol(Fe)$^{-1}$ h^{-1}]. The replacement of the activator with Me_3Al led to the selective dimerization of ethylene with low activities [about 100 kg mol(M)$^{-1}$ h^{-1}, in all experiments $p_{ethylene}$ = 9.9 atm]. The use of hexane or chlorobenzene as a solvent resulted only in ethylene oligomerization to mixtures of butenes and hexenes. However, in the presence of complex **43b**, trimers were mainly formed (> 80%). At the same time, the activity of all catalytic systems was higher when using chlorobenzene, which is likely related to the better solubility of catalysts in a more polar solvent.

It is worth noting that cobalt complexes **45e** – **h** activated by MAO are more active in ethylene oligomerization [resulting in a mixture of C_4-C_{18} oligomers, activity up to 338 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 19.7 atm] in comparison with similar nickel compounds **45a** – **d**.[92] The systems with complexes **45e** – **h** were characterized by a much lower chain termination rate (the butene fraction is 35 – 37% *vs* 62 – 83% for nickel compounds **45a** – **d**). In addition, cobalt complexes were thermally more stable. The catalytic activity of the complexes of both metals decreased in the series of solvents toluene > hexane > cyclohexane and with an increase in the number of OMe substituents in the ligand: **45a** > **45b** > **45c** > **45d** and **45e** > **45f** > **45g** > **45h**.

Binuclear complexes of iron triad metals **46** stabilized by hyperbranched iminopyridine ligands were also studied in ethylene oligomerization.[93] As expected, a higher activity

Structures 43 – 45



was observed for systems based on nickel complexes **46a–c** [MAO, 289–603 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 4.9 atm]. For similar compounds of Co(II) **46d** and Fe(II) **46e** the activity turned out to be 244 kg mol(Co)$^{-1}$ h^{-1} and 217 kg mol(Fe)$^{-1}$ h^{-1}, respectively, under the same conditions. The activity of these complexes was shown to depend strongly on the solvent properties. For example, for **46a** it decreased in the toluene > methylcyclohexane > cyclohexane series, which is apparently related to the decrease in the precatalyst solubility. The selectivity of the systems towards the light oligomer fractions increased in the series Ni (C_4–C_{22}, C_4 = 47–55%) < Co (C_4–C_{18}, C_4 = 66%) < Fe (C_4–C_8, C_4 = 70%). The replacement of MAO with Et_2AlCl or $EtAlCl_2$ in a system with complex **46a** led to the formation of polyalkyltoluenes in significant amounts among the reaction products along with a significant rise in activity [up to 4000 and 9000 kg mol(Ni)$^{-1}$ h^{-1}, respectively, $p_{ethylene}$ = 4.9 atm]

Bimetallic complexes **47**, activated with MAO, demonstrated a rather low activity in ethylene oligomerization (10–71 kg mol^{-1} h^{-1}, $p_{ethylene}$ = 19.7 atm).[94] Among them, iron complex **47a** turned out to be the most active and thermally stable one, whereas nickel complex **47c** was the worst in this context. In contrast to **46**, the activity of these compounds in cyclohexane was somewhat higher than that in toluene; however, the fraction of light olefins among the reaction products depended in a similar way on the metal nature, *i.e.*, increased in the Ni < Co < Fe series. The replacement of MAO with Et_3Al increased the activity and shifted the selectivity towards ethylene dimerization.

The catalytic properties of Ni(II) and Co(II) complexes with tetradentate NNNO-heteroscorpionate ligand **48** have been investigated recently.[95] The activity of cobalt complex **48a** in ethylene oligomerization reached 610 kg mol(Co)$^{-1}$ h^{-1} ($p_{ethylene}$ = 2.9 atm) accompanied with an increase in the fraction of heavy oligomers in the activator series Et_2AlCl < $Et_3Al_2Cl_3$ < $EtAlCl_2$. The same dependence of selectivity on the activator type was observed for nickel complex **48b**; however, its activity was much higher: up to 5550 kg mol(Ni)$^{-1}$ h^{-1} and (when using 1 mol. equiv. of PPh_3) even 12100 kg mol(Ni)$^{-1}$ h^{-1} at the same ethylene pressure. Addition of PPh_3 to cobalt complex **48a** did not change its catalytic activity. However, when using the catalytic systems **48b**–$EtAlCl_2$ and **48b**–$EtAlCl_2$–PPh_3, the most interesting and unexpected result was the formation of olefins with an odd number of carbon atoms (up to 5 mol.%) (see Section 4.2 for details).

Systemizing the above-considered data (Table 1), we can note several main consistent patterns of ethylene oligomerization, directly dependent on the nature of the metal in use and draw the following conclusions about its influence on the catalytic properties of discussed complexes:

— Ni(II) and Co(II) complexes, in contrast to Fe(II) complexes, do not tend to catalyze the formation of mixtures of polyethylene and ethylene oligomers. However, for systems with Co(II) compounds, a variation in the reaction conditions (systems with complex **33**[84]) or an increase in the steric hindrance around the metal centre (systems with complex **35**[87]) change much more rapidly the reaction direction towards polymerization;

— the catalytic activity of Ni(II) and Fe(II) complexes often exceed that of cobalt analogues;

— systems with Co(II) and Fe(II) complexes catalyze the formation of linear oligomers with a high fraction of terminal double bonds, whereas the systems based on Ni(II) complexes exhibit the formation of branched oligomers with a lower content of α-olefins;

— most of the above-considered Ni(II) complexes depend to a smaller extent on the type of activator in use compared to Fe(II) complexes that are activated mainly by MAO or MMAO. It allows one to control the composition of oligomeric products by changing the type of an organoaluminium activator. The maximum efficiency for these systems was obtained using chlorine-containing organoaluminium activators (Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlCl_2$);

— catalytic systems based on complexes of all three metals (**43**–**44**,[90,91] **46**,[93] **48**[95]) can catalyze Friedel–Crafts alkylation of toluene with *in situ* obtained ethylene oligomers in the presence of activators with a strong Lewis acidity;

— the fraction of heavy (C_{8+}) olefins in oligomer mixtures increases in the series Fe < Co < Ni for the catalytic systems capable of oligomerizing ethylene;

— addition of triphenylphosphine positively affects the catalytic activity only for the systems based on Ni(II) complexes.

These conclusions were formulated disregarding the cases standing out from the total data array, such as the inactivity of iron complexes **5** in the reactions of ethylene oligo-/polymerization or the large fraction of α-olefins obtained with nickel complex **30** activated by $Et_3Al_2Cl_3$.

It should also be noted that the catalytic properties of the systems under consideration are not determined only by the metal nature and depend to a great extent on the type and structure of the organic ligand and activator in use, as well as on the catalysis conditions (temperature, pressure and solvent). This circumstance makes it possible to increase the efficiency of the systems based on any of the three metals by changing the conditions for formation of a catalytic system. For example, the catalytic activity of up to 89 500 kg mol(Fe)$^{-1}$ h^{-1} was reached for Fe(II) compounds with iminophenanthroline ligands.[41,96] Nevertheless, most of Ni(II) complexes had a higher activity than similar Co(II) and Fe(II) complexes, and thus much more attention is being currently paid to these compounds.

Structures 46–48

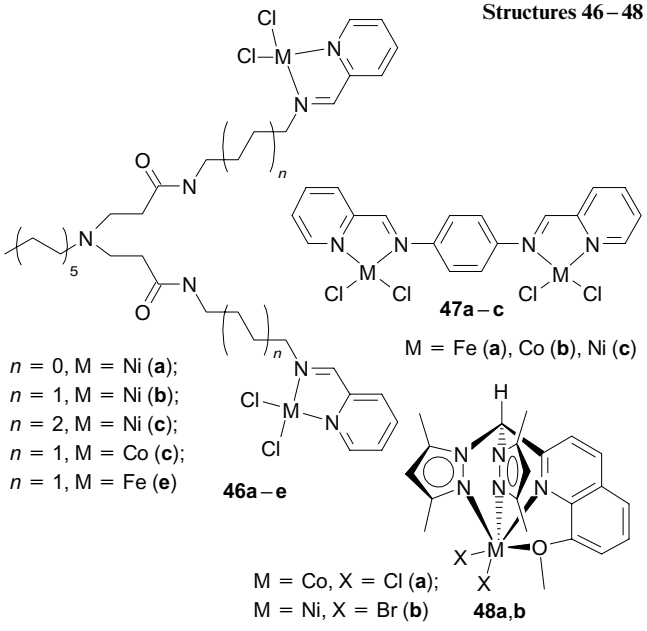


Table 1. Influence of the metal nature on the catalytic properties of complexes during ethylene oligomerization.[58]

Comparison parameters	Ni	Ni	Co	Fe	Ref.
Catalytic system	**7** – MAO	–	6 – MAO	**5** – MAO	58
Activity, kg mol(M)$^{-1}$ h^{-1}	2000 – 3300		700 – 930	0	58
Selectivity (mol.%)	C_4 (27 – 72%) C_6 (25 – 50%) C_{8+} (3 – 23%) + PE (≈1 wt.%)	–	C_4 (87 – 100%) C_6 (0 – 13%) C_8 (0 – 2%) + PE (1 – 13 wt.%)	–	58
Catalytic system	**9** – MAO	–	**8** – MAO	–	59
Activity, kg mol(M)$^{-1}$ h^{-1}	up to 210		≈ 1	–	59
Selectivity (mol.%)	C_4 (50 – 77%) C_6 (23 – 31%) C_{8+} (0 – 22%)		C_4 (100%)	–	59
Catalytic system	**10a** – MAO	**10a** – Et_2AlCl	–	**10b** – MAO	60
Activity, kg mol(M)$^{-1}$ h^{-1}	⩽240	⩽724	–	⩽414	60
Selectivity (mol.%)	C_4 (100%)	C_4 (100%)	–	C_4 (100%)	60
Catalytic system	**13c** – MAO		**13b** – MAO	**13a** – MAO	61
Activity, kg mol(M)$^{-1}$ h^{-1}	≈5	–	398	1250	
Selectivity (mol.%)	C_4 (100%)		C_4 (86%) C_6 (12%) C_{8+} (2%)	PE + C_4 – C_{20}	61
Catalytic system	**14**, **17**, **20a** – MAO, MMAO	**14**, **17**, **20a** – Et_2AlCl	**15**, **18**, **20b** – Et_2AlCl	**16**, **19**, **20c** – Et_2AlCl, MAO, MMAO	62, 63
Activity, kg mol(M)$^{-1}$ h^{-1}	58 – 2240	208 – 590	152 – 282	156 – 1030	62, 63
Selectivity (mol.%)	C_4 (32 – 96%) C_6 (4 – 68%)	C_4 (47 – 95%) C_6 (5 – 53%)	C_4 (37 – 82%) C_6 (18 – 63%)	C_4 (54 – 97%) C_6 (3 – 46%)	62, 63
Catalytic system	**21** – Et_2AlCl	–	**22** – Et_2AlCl, MAO, MMAO	**23** – MAO, MMAO	62, 63
Activity, kg mol(M)$^{-1}$ h^{-1}	750 – 10200 ⩽56400 (+ PPh_3)		56 – 354	321 – 14310 660 (+ PPh_3)	62, 63
Selectivity (mol.%)	C_4 (75 – 95%) C_6 (5 – 21%) C_8 (0 – 4%)		C_4 (71 – 100%) C_6 (0 – 29%)	C_4 (26 – 95%) C_6 (5 – 29%) C_{8+} (0 – 51%) + PE wax: 0 – 20 wt.%	62, 63
Catalytic system	**24** – Et_2AlCl	–	**25** – Et_2AlCl	**26** – MAO, MMAO	73
Activity, kg mol(M)$^{-1}$ h^{-1}	308 – 1200		56 – 178	141 – 824	73
Selectivity (mol.%)	C_4 (90 – 100%) C_6 (0 – 10%) α-C (48 – 98)		C_4 (90 – 100%) C_6 (0 – 10%) α-C (86 – 99)	C_4 (26 – 100%) C_6 (0 – 35%) C_{8+} (0 – 53%) α-C (98 – 99) PE wax: 5 – 41 wt.%	73
Catalytic system	**27** – Et_2AlCl	–	**28** – MAO, MMAO	**29** – MAO, MMAO	80, 81
Activity, kg mol(M)$^{-1}$ h^{-1}	190 – 3030 ⩽9310 (+ PPh_3)		36 – 151	160 —4110	80, 81
Selectivity (mol.%)	C_4 (80 – 100%) C_6 (0 – 18%) C_{8+} (0 – 6%) α-C (76 – 99)		C_4 (80 – 100%) C_6 (0 – 20%) α-C (78 – 98)	C_4 (27 – 70%) C_6 (14 – 27%) C_{8+} (11 – 51%) α-C (98 – 99) + PE wax: 3 – 52 wt.%	80, 81
Catalytic system	**30** – Et_2AlCl	**30** – $Et_3Al_2Cl_3$	–	**31** – MAO, MMAO	82, 83
Activity, kg mol(M)$^{-1}$ h^{-1}	540 – 2590	2200 – 8800	–	560 – 3030	82, 83
Selectivity (mol.%)	C_4 (88 – 97%) C_6 (3 – 12%) α-C (61 – 95)	C_4 (75 – 91%) C_6 (9 – 22%) α-C (> 99)	–	C_4 (28 – 75%) C_6 (5 – 29%) C_{8+} (16 – 59%) α-C (96 – 99)	82, 83

Table 1 (continued).

Comparison parameters	Ni	Ni	Co	Fe	Ref.
Catalytic system	**32** – Et_2AlCl	–	**33** – MAO	–	84, 85
Activity, kg mol(M)$^{-1}$ h^{-1}	359 – 1450 ⩽7190 (+ PPh_3)		50 – 752	–	84, 85
Selectivity (mol.%)	C_4 (93 – 100%) C_6 (0 – 7%) α-C (77 – 100)		C_4 (95 – 100%) C_6 (0 – 5%) α-C (93 – 100)	–	84, 85
Catalytic system	**34** – $Et_3Al_2Cl_3$	–	**35** – MMAO	**36** – MAO, MMAO	86 – 88
Activity, kg mol(M)$^{-1}$ h^{-1}	28 – 170		120 – 9870	2430 – 22400	86 – 88
Selectivity (mol.%)	C_4 (93 – 100%) C_6 (0 – 7%) α-C (94 – 99)		PE	PE	86 – 88
Catalytic system	**37** – Et_2AlCl	–	**38** – MAO	**39** – MAO, MMAO	72
Activity, kg mol(M)$^{-1}$ h^{-1}	3680 – 6150 (+ PPh_3)		2800 – 7330	5 – 2690	72
Selectivity (mol.%)	C_4 (95 – 100%) C_6 (0 – 5%) α-C (36 – 63)		C_4 (72 – 96%) C_6 (4 – 34%) C_{8+} (0 – 19%) α-C (97 – 100)	C_4 (98.5 – 100%) C_6 (0 – 1.5%) α-C (100)	72
Catalytic system	**40b**, **41b** – Et_2AlCl, MAO, MMAO	–	**40a**, **41a**, **42** – Et_2AlCl, MAO, MMAO	–	89
Activity, kg mol(M)$^{-1}$ h^{-1}	18 – 323		1 – 53	–	89
Selectivity (mol.%)	C_4 (83 – 89%) C_6 (11 – 17%) α-C (19 – 67)		C_4 (92 – 100%) C_6 (0 – 8%) α-C (7 – 99)	–	89
Catalytic system	**43a**, **43b**, **43e**, **44a**, 44b, **44e** – Et_2AlCl, MAO	–	**43c, 43f, 44c, 44f** – Et_2AlCl, MAO	**43d**, **44d** – Et_2AlCl, MAO	90, 91
Activity, kg mol(M)$^{-1}$ h^{-1}	⩽1084		⩽339	⩽467	90, 91
Selectivity (mol.%)	Toluene: alkyltoluenes 100% (Et_2AlCl), 8 – 22% + C_4 – C_8 (MAO) Hexane (Et_2AlCl): C_4 (91 – 98%), C_6 (2 – 9%) Chlorobenzene (Et_2AlCl): C_4 (84 – 87%), C_6 (13 – 17%)				90, 91
Catalytic system	**45a – d** – MAO	–	**45e – h** – MAO	–	92
Activity, kg mol(M)$^{-1}$ h^{-1}	⩽226		⩽338	–	92
Selectivity (mol.%)	C_4 (62 – 83%) C_6 (8 – 12%) C_{8+} (8 – 25%)		C_4 (35 – 36%) C_6 (14 – 36%) C_{8+} (28 – 50%)	–	92
Catalytic system	**46a – c** – MAO	**46a** – Et_2AlCl	**46d** – MAO	**46e** – MAO	93
Activity, kg mol(M)$^{-1}$ h^{-1}	289 – 603	4000	244	217	93
Selectivity (mol.%)	C_4 (47 – 55%) C_6 (21 – 24%) C_{8+} (24 – 29%)	C_4 (58%) C_6 (21%) C_{8+} (21%)	C_4 (66%) C_6 (18%) C_{8+} (16%)	C_4 (70%) C_6 (17%) C_8 (13%)	93
Catalytic system	**47c** – MAO	–	**47b** – MAO	**47a** – MAO	94
Activity, kg mol(M)$^{-1}$ h^{-1}	10 – 57		20 – 71	10 – 56	94
Selectivity (mol.%)	C_4 (64 – 96%) C_6 (1 – 27%) C_{8+} (1 – 13%)		C_4 (60 – 92%) C_6 (6 – 32%) C_{8+} (0 – 4%)	C_4 (64 – 95%) C_6 (2 – 28%) C_{8+} (0 – 3%)	94
Catalytic system	**48b** – Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlCl_2$, MMAO	–	**48a** – Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlCl_2$, MMAO	–	95
Activity, kg mol(M)$^{-1}$ h^{-1}	260 – 5550 3210 – 12100 (+ PPh_3)		420 – 610	–	95
Selectivity (mol.%)	C_4 (15 – 87%) C_6 (13 – 81%) C_{8+} (0 – 56%) + alkyltoluenes (0 – 30%)		C_4 (45 – 86%) C_6 (11 – 47%) C_{8+} (0 – 8%) + alkyltoluenes (0 – 1%)	–	95

Note. Selectivity to components in mol.% of the oligomer mixture, selectivity to polymers (if present) in wt.% of the total product mass; α-C is the fraction of α-isomers in the oligomer mixture.

4. Promising areas of using complexes of iron triad metals for ethylene oligomerization and polymerization

In this section we consider only novel and potentially promising fields of application of iron triad metal complexes such as: ethylene trimerization (Section 4.1), synthesis of odd carbon number olefins (Section 4.2), one-step formation of high-molecular-weight ethylene oligomers (Section 4.3) and polyethylene waxes (Section 4.4). Methods for heterogenization of catalysts based on complexes of iron triad metals and their application in ethylene polymerization and oligomerization reactions are considered separately in Section 4.5.

4.1. Ethylene trimerization

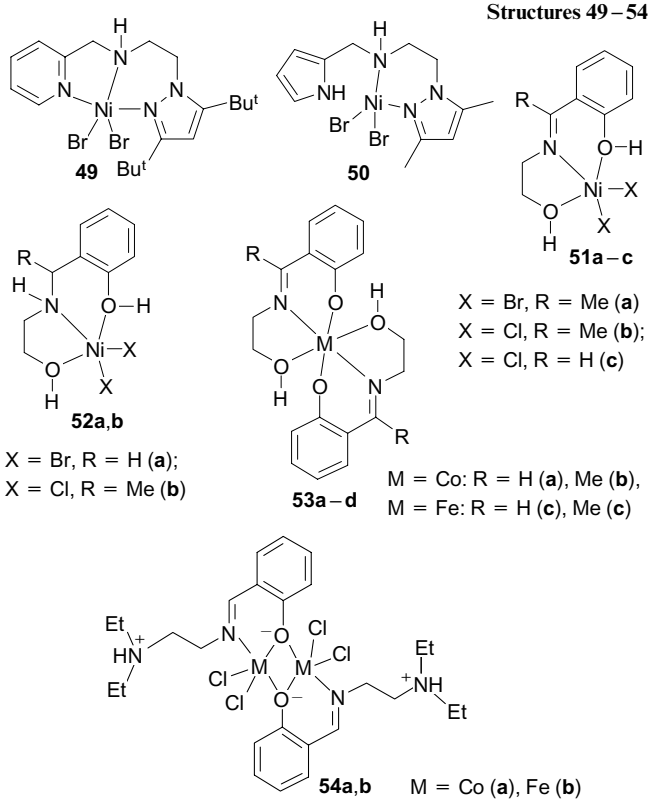
Selective oligomerization of ethylene is an important scientific and technological challenge, which is related to the great demand for linear hexenes in the synthesis of base engine oils and as comonomers in the production of linear low-density polyethylene (LLDPE) and other copolymers.[97] Currently, selective dimerization of ethylene can be successfully performed using titanium complexes.[98,99] Trimerization and tetramerization processes are generally conducted using catalytic systems based on chromium coordination compounds.[99–102] The main drawback of the latter is the formation of a small amount of polyethylene, which can rapidly clog the reactor in a large-scale process. It is known that complexes of late transition metals can also dimerize ethylene with a high selectivity.[35,55] However, until recently, there were only few publications on the use of these compounds in ethylene trimerization.

The high selectivity of the systems based on late transition metals complexes towards the formation of hexenes during ethylene oligomerization was noted for the first time by Ojwach and co-workers[90,91] and by Darkwa and co-workers.[103] Oligomerization of ethylene using nickel complex **43b** with a bidentate pyridinopyrazole ligand, activated by $EtAlCl_2$ in hexane or chlorobenzene, led to the formation of 80–93% branched (α-C_6 = 24–50%) hexenes. Complexes **49** and **50** after activation by $EtAlCl_2$ in chlorobenzene also favored the formation of hexenes during oligomerization process, but the compositions of oligomer mixtures were not studied. The catalytic activity was very high in the latter case and amounted to 9200 and 10 500 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 9.9 atm). However, the formation of a small amount of highly branched polyethylene was also observed along with the oligomers.

Subsequent studies showed that the use of (imino/amino)phenol complexes of nickel **51**, **52**,[104] cobalt and iron **53**, **54**,[105] activated by $EtAlCl_2$ in chlorobenzene, also led to predominant ethylene trimerization (C_6 = 56–80%). The fraction of α-C_6 olefins obtained using nickel catalysts is sufficiently larger (74–91%) in comparison with catalysts based on cobalt and iron complexes (23–28%). An increase in the reaction time from 0.5 to 2 h for compound **51c** led to a rise in the hexene fraction from 38 to 77%, whereas an increase in the ethylene pressure from 9.9 to 29.6 atm, *vice versa*, resulted in its decrease from 55 to 22%. Apparently, this dependence of selectivity indicates that hexenes are a product of codimerization of butene and ethylene (Fig. 4). The yield of hexenes depends on the molar fraction of butene, which increases in the reactor during the long-term catalytic process and, *vice versa*, decreases with an increase in ethylene pressure and, correspondingly, the concentration of dissolved ethylene in the reaction mixture.

However, the reason of the absence of oligomers with longer chains (octenes, decenes, *etc.*) is not clear. Assuming probability of their formation in the mixture according to the classical Cossee–Arlman mechanism, they should inevitably be accumulated during the process even if the chain termination rate significantly exceeds the chain growth rate after the formation of [Ni$^+$–Hex].

Structures 49 – 54



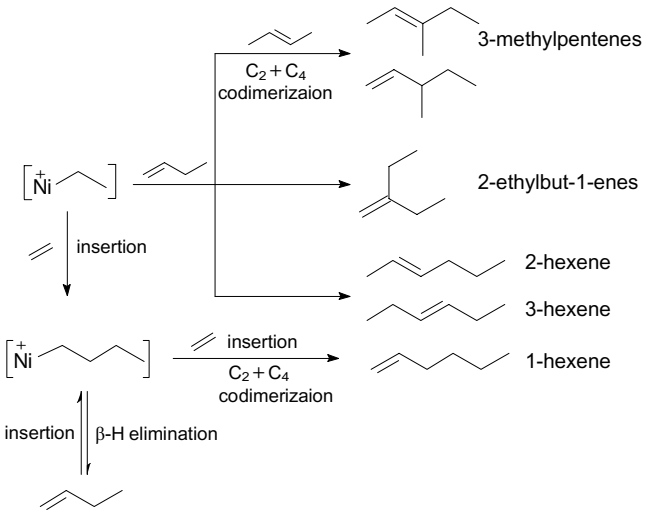


Figure 4. Schematic of isomeric hexene formation during ethylene oligomerization on nickel catalysts. The figure was created by the authors based on the data of Ref. 106, with permission from Wiley.

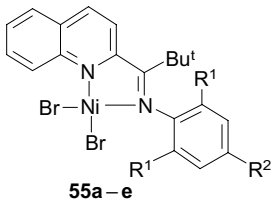
The use of toluene as a solvent in combination with $EtAlCl_2$ (**51c**) or MAO (**53**, **54**) increased the butene fraction in ethylene oligomerization products to 82–100%.

Sun *et al.* obtained a number of Ni(II) **55**–**58**[107–110] and Co(II) **59** complexes,[111] whose selectivity was also determined by the choice of activator. For example, systems with Ni(II) complexes **55**, after activation with $Et_3Al_2Cl_3$, catalyzed the formation of ethylene oligomers (C_4-C_{12}) with an activity of up to 4060 kg mol(Ni)$^{-1}$ h^{-1} (**55b**, $p_{ethylene}$ = 10 atm). After treatment with MAO, complexes **56**, **58**, **59** selectively dimerized ethylene with a moderate activity. However, in the presence of MMAO modified by Bu^i_3Al, complexes **55**–**59** trimerized ethylene with a high selectivity for hexenes (C_6): 71–90.5% (**55**), 84–98% (**56**), 81–87% (**57**), 88–96% (**58**), 52–86% (**59**). In this case, the 1-hexene fraction in the mixtures was 44–48.5% for systems based on nickel compounds and somewhat lower (34.6–49.2%) for cobalt complexes. The authors explained such selectivity by the steric influence of the isobutyl groups present in the activator. However, this explanation appears to be highly simplified, and additional studies should be performed to find the true reason. It is more likely that the mechanism of predominant hexene formation for these systems differs from the Cossee–Arlman coordination/migratory insertion mechanism, because about 90% of hexenes are formed even in a short-term (5 min) reaction; this fact excludes the version with accumulation of butenes in the reaction medium and their subsequent codimerization with ethylene.

At the same time, in the case of activation of complexes **57a**–**e** with Et_2AlCl, the hexene formation selectivity was also high (53–96%) and depended mainly on the organic ligand structure, reaching a maximum for complexes **57a**,**d** with methyl substituents in the ligand.[110] In this case, the dependence of the hexene amount on the reaction time, as for systems with complexes **51**–**54**, suggests hexene formation during ethylene and butene codimerization (see Scheme 1).

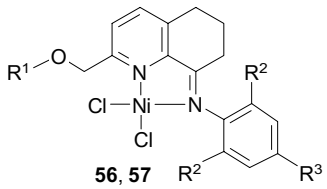
Heterogeneous systems **120a**,**c**,**e**–**h**–$EtAlCl_2$ catalyzed hexene formation with a selectivity of up to 89% during ethylene oligomerization.[112] Homogeneous and heterogeneous catalysts based on nickel phenoxyimine complex **124**[113] also showed the ability to trimerize ethylene with a high selectivity (up to 95%); note that the complex on a support demonstrated a much higher efficiency (see Section 4.5 for details).

Structures 55–59



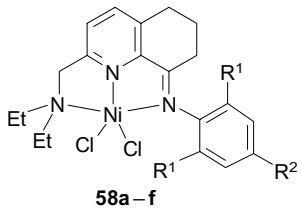
55a–e

55: R^1 = Me, R^2 = H (**a**)
R^1 = Et, R^2 = H (**b**)
R^1 = Pr^i, R^2 = H (**c**)
R^1 = Et, R^2 = Me (**c**)
R^1 = Me, R^2 = Et (**e**)



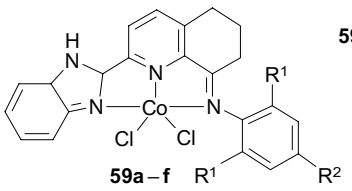
56, **57**

R^1 = MeC(O) (**56**), H (**57**):
R^2 = Me, R^3 = H (**a**);
R^2 = Et, R^3 = H (**b**)
R^2 = Pr^i, R^3 = H (**c**);
R^2 = R^3 = Me (**d**);
R^2 = Et, R^3 = Me (**e**);
R^2 = R^3 = Bu^t (**f**)



58a–f

58: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = R^2 = Me (**d**);
R^1 = Et, R^2 = Me (**e**);
R^1 = R^2 = Bu^t (**f**)



59a–f

59: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = R^2 = Me (**d**);
R^1 = Et, R^2 = Me (**e**)
R^1 = R^2 = Bu^t (**f**)

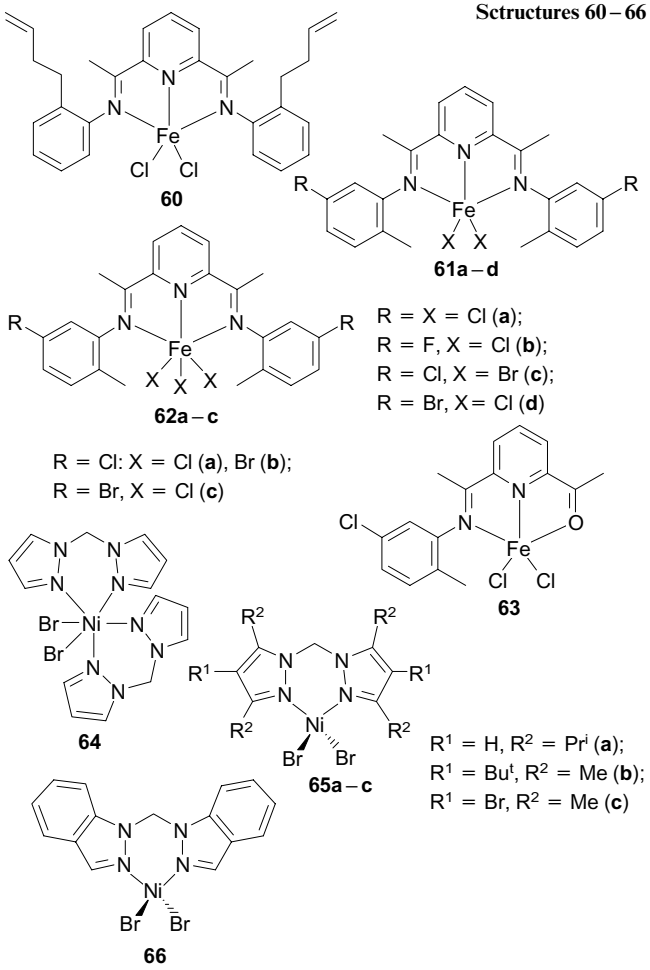
4.2. Production of odd carbon number olefins during catalytic ethylene oligomerization

Odd carbon number olefins are used in production of aviation engine oils, alcohol plasticizers, and polyalkyltoluenes.[114] These olefin fractions are generally isolated from a mixture of liquid products obtained during oil cracking or Fischer–Tropsch synthesis (Sasol production).[115] In addition, reactions of codimerization of olefins, for example, propene and butenes, can be used for their synthesis.[114, 115]

A possible alternative way to obtain these products is the formation of olefin isomers during ethylene oligomerization with the participation of systems based on iron and nickel complexes. The possibility of implementing such processes was demonstrated for the first time by Alt coworkers,[116, 117] who used bis(imino)pyridine iron complexes **60**–**62**. In particular, complex **60** activated with MAO, at ethylene pressure of 0.2 atm, catalyzed formation of about 29 mol.% odd number carbon olefins (C_9-C_{31}).[116] Complexes **61a**–**c** and **62a**–**b** activated with MAO also showed ability to catalyze formation of the aforementioned products; however, the activity of the systems based on these complexes does not exceed 100 kg mol(Fe)$^{-1}$ h^{-1} ($p_{ethylene}$ = 0.5 or 1 atm).[117] It is noteworthy that, in the case of the substituent R replaced with Br (complexes **61d**, **62c**) and in the absence of one imine moiety (complex **63**), no formation of odd-number olefins was observed, and the catalytic activity increased to 208 kg mol(Fe)$^{-1}$ h^{-1} (**63**, $p_{ethylene}$ = 0.5 atm).

Recently it was shown that odd carbon number olefins are also formed during ethylene oligomerization in the presence of nickel complexes with pyrazole-containing ligands **48b**[95] and **64**–**66**.[118] For example, oligomerization of ethylene in the presence of catalytic systems **48b**–$EtAlCl_2$ and **48b**–$EtAlCl_2$–PPh_3 was accompanied by the formation of 5 mol.% odd-number olefins (C_7-C_{19}); the catalytic activities of the systems [up to 12500 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3.8 atm] significantly exceeded the values obtained previously for the systems with iron complexes **60**–**63**. Activation of complexes **64**–**66** by ethylaluminium sesquichloride ($Et_3Al_2Cl_3$), which has a weaker Lewis acidity in comparison with ethylaluminium dichloride ($EtAlCl_2$), also led to the formation of odd-number olefins; however, their fraction did not exceed 0.8 mol.%. Moreover, carrying out the reaction in toluene (rather than in chlorobenzene, as in the case of **48b**), made it possible to detect the formation of light olefins (C_3, C_5) in the form of the corresponding alkyltoluenes. This can be explained by the fact that the aforementioned systems based on nickel complexes also catalyze tandem Friedel–Crafts alkylation of toluene.

Sctructures 60 – 66



There are several possible mechanisms of formation of odd carbon number olefins.

1) Transfer of the growing oligomeric chain to aluminium. This mechanism was previously proposed by Hey and Wass [119] to explain the formation of odd-number olefins during ethylene oligomerization using MAO-activated $Cr(acac)_3$ complexes.[120, 121] [Cr] – Me species, that emerge during activation of a complex and formation of a catalytic system, are considered to be responsible for the formation of these products. Due to the high rate of growing chain transfer to aluminium in the absence of the stabilizing bis(diphenylphosphino)amine ligand, they were continuously formed during the catalytic cycle (Fig. 5). Alt and co-workers [117] deny the possibility of this mechanism, because no formation of odd carbon number olefins was observed during oligomerization of 1-octene. In the case with nickel complexes **48b**, **64** – **66** this mechanism has no sense because only ethyl groups are present in the activator. However, experiments with oligomerization of 1-hexene in the presence of catalytic system **48b** – $EtAlCl_2$ showed formation of products (C_8, C_{14}, C_{20}, C_{26}) with a chain two carbon atoms longer than that expected for hexene isomers (C_6), its dimers (C_{12}), trimers (C_{18}) and tetramers (C_{24}), which may indicate transfer of the growing oligomeric chain to aluminium.

2) β-Alkyl elimination. Despite the fact that this mechanism is more typical of electron-deficient d_0 complexes of early transition metals, the occurrence of such reactions for nickel and palladium complexes has also been described.[122]

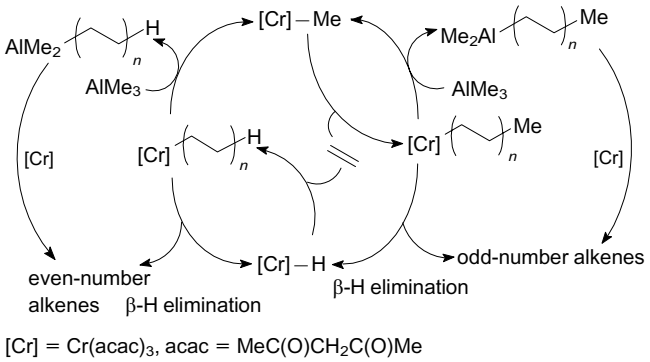
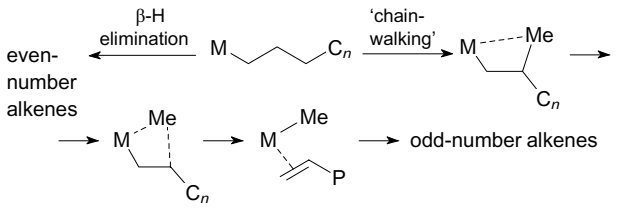


Figure 5. Mechanism of formation of odd carbon number olefins *via* chain transfer to aluminium using the catalytic system $Cr(acac)_3$ – MAO. The figure was created by the authors based on the data of Ref. 119, with permission from the American Chemical Society.

The process of β-Me elimination can be considered as competing with the β-H elimination, which is responsible for the growing chain termination and formation of ethylene oligomers (Scheme 1). This mechanism explains well the formation of odd-number olefins, in which the number of carbon atoms is lower by one than for the respective even carbon number ethylene oligomers.

Scheme 1



3) Metathesis of olefins. Alt and co-workers [117] considered this process as the most probable one for the formation of odd carbon number olefins using complexes **60** — **62** (Fig. 6). The probability of this mechanism for iron compounds is confirmed by both theoretical studies [123 – 125] and

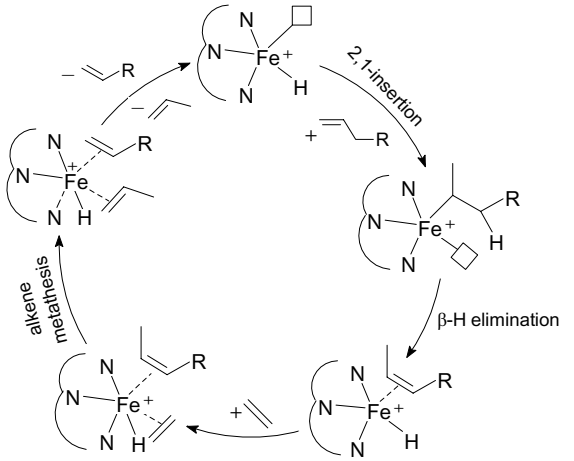


Figure 6. Mechanism of formation of odd carbon number olefins *via* metathesis reaction.[117] Published with permission from Elsevier.

the discovery of the first iron-based catalyst capable of ring-opening metathesis polymerization (ROMP) of norbornene.[126] However, the occurrence of metathesis of simple olefins has not yet been confirmed for nickel complexes **48b**, **64**–**66**. Nevertheless, this mechanism correlates well with the experimental results and, in the absence of disproving theoretical and experimental data, can be considered, along with the β-alkyl elimination, as one of possible ways of forming odd carbon number olefins in the presence of catalytic systems based on nickel complexes.

4.3. Production of heavy fractions of ethylene oligomers

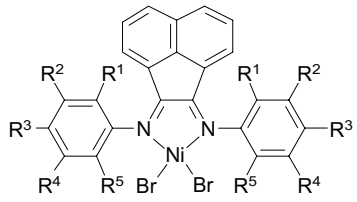
Poly-α-olefins (PAO) play an important role in the production of synthetic lubricating materials, because they have a number of competitive advantages over mineral products: a wider range of operating temperatures, high viscosity index (VI), thermal stability, resistance to oxidation, small values of corrosion activity and toxicity, compatibility with mineral oils, *etc.*[127] Generally, low-viscosity poly-α-olefin base oils (PAOO) are produced by oligomerization of 1-decene using the catalytic system BF_3 ROH; however, other LAOs (for example, C_8-C_{12}) can also be applied in this process. The BF_3 ROH catalytic system is highly valued for the predominant formation of 1-decene trimers, compared to other fractions of oligomers;[128] however, it also increases the branching of carbon chain. Different catalytic systems are used to produce more viscous PAOO, for example, $TiCl_4-AlR_3$ and $Et_3Al_2R_3-CH_2{=}CH-CH_2-CH_2Cl$.[127] Note also the constantly rising interest in the study of metallocene and post-metallocene catalysts, which can oligomerize α-olefins with the production of PAOO.[129]

The catalytic systems based on nickel and palladium complexes are characterized by a high rate of 'chain-walking' process, due to which they can be used to produce hyperbranched high-molecular-weight ethylene oligomers. This approach can theoretically be used to produce components of lubricating base oils directly from ethylene, which would greatly simplify and reduce the production cost.

In this subsection we consider only the Ni(II) compounds capable of conducting ethylene oligomerization with formation of branched heavy ($C_{20}-C_{60}$) olefins (M = 280–840 Da). In particular, Li and co-workers[130] investigated a series of systems based on mono- (**67**) and bisligated (**68**) α-diimine Ni(II) complexes, structurally similar to previously described complexes **3**. After the activation by MMAO, both series showed similar values of activity [4500–4600 kg mol(Ni)$^{-1}$ h^{-1}, complexes **67a**, **68b**, $p_{ethylene}$ = 10 atm] and selectivity (high-molecular-weight oligomers with a weight-average molecular weight M_w = 540–695 Da), which is indicative of possible destruction of biligand structures as a result of activation by organoaluminium compounds. However, the presence of two chlorine atoms in the positions proximate to the imine nitrogen atom in complexes **67d**,**e** led to an increase in the molecular weight of the product to 2700 and 4800 Da, respectively. This pattern confirms again that the presence of a bulky substituent near the metal complex centre decreases the reaction rates of β-H elimination and β-H transfer to monomer (see Section 1), which is the main reason for the increase in the chain length in the final product.

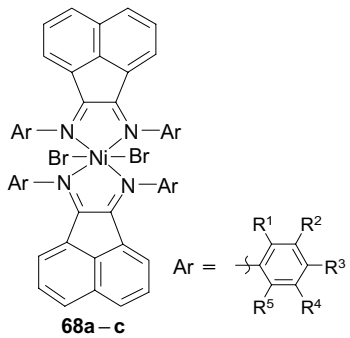
Gomes and co-workers[131,132] obtained phenyl complexes of Ni(II) **69a**–**e** with iminopyrrole ligands, which catalyzed ethylene oligomerization to hyperbranched oligomers with number-average molecular weights M_n = 500–1300 Da both in the absence of an activator and in the presence of $Ni(COD)_2$ [it should be noted that the use of $Ni(COD)_2$ rather often leads to a rise in the molecular weight of final products]. Complexes **69f** and **72** with a bulky substituent in the pyrrole moiety catalyzed ethylene polymerization under similar conditions [M_n = 11 000–20 000 Da (**69f**), M_n = 2000–3200 Da (**72**)], while complex **70** with an electron-withdrawing perfluoro-

Structures 67–74



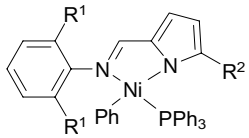
67a–e

$R^1 = R^2 = Cl$, $R^3 = R^4 = R^5 = H$ (**a**);
$R^1 = R^3 = Cl$, $R^2 = R^4 = R^5 = H$ (**b**);
$R^1 = R^4 = Cl$, $R^2 = R^3 = R^5 = H$ (**c**);
$R^1 = R^5 = Cl$, $R^2 = R^3 = R^4 = H$ (**d**);
$R^1 = R^3 = R^5 = Cl$, $R^2 = R^4 = H$ (**e**)



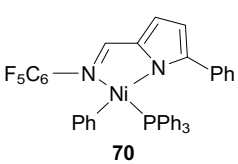
68a–c

$R^1 = R^2 = Cl$, $R^3 = R^4 = R^5 = H$ (**a**);
$R^1 = R^3 = Cl$, $R^2 = R^4 = R^5 = H$ (**b**);
$R^1 = R^4 = Cl$, $R^2 = R^3 = R^5 = H$ (**c**)

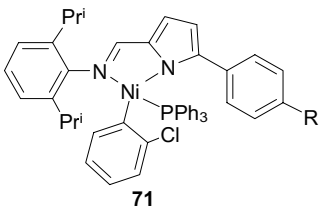


69a–f

R^2 = Ph: R^1 = Me (**a**), Pr^i (**b**);
R^2 = 3,5-$Me_2C_6H_3$: R^1 = Me (**c**);
$R^1 = Pr^i$ (**d**);
R^2 = 3,5-$(CF_3)_2C_6H_3$, $R^1 = Pr^i$ (**e**);
R^2 = 2,4,6-$Pr^i_3C_6H_2$: $R^1 = Pr^i$ (**f**)

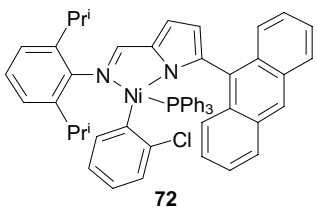


70

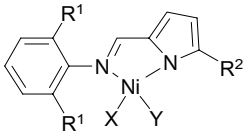


71

R = H (**a**), OMe (**b**), F (**c**)



72



73–74

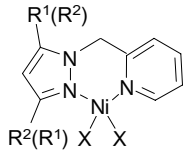
73: X = CH_2Ph; Y = PMe_3;
74: X, Y =

73, **74**: $R^1 = Pr^i$: R^2 = 3,5-$(CF_3)_2C_6H_3$ (**a**);
R^2 = 2,4,6-$Pr^i_3C_6H_2$ (**b**)

phenyl substituent, in contrast, catalyzed formation of light oligomers with rather low activity [17 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3 atm]. The highest catalytic activity [656 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9 atm] was observed for the system **69e** – Ni(COD)$_2$ with electron-withdrawing CF_3 groups at 50 °C. It was shown [133] that complexes **73a** [in the presence of Ni(COD)$_2$] and **74a**, structurally similar to that of **69e**, also catalyzed formation of highly branched (b = 100 – 115/1000C) oligomers with M_n = 900 – 1200 Da. The use of more sterically hindered catalysts **73b** – Ni(COD)$_2$ and **74b**, in contrast, led to the formation of viscous polyethylene oils with M_n = 10900 – 17000 Da. Microstructural analysis of the obtained PEs showed dominance of methyl and long ($> C_4$) branches in a ratio of 3 : 1 in the samples.

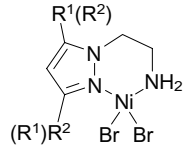
Obuah *et al.*[134] described Ni(II) complexes **75**, **76** with pyrazolylpyridines and pyrazolylamines, which consist of mixtures of two isomers, containing a ferrocenyl substituent in different positions of the pyrazole ring. After activation by $EtAlCl_2$ in chlorobenzene, these systems catalyzed formation of ethylene oligomers with a molecular weight of 380 – 600 Da; the use of toluene led to tandem ethylene dimerization and alkylation of solvent molecules with obtained butenes. Nickel bromide complexes exhibited a higher catalytic activity in comparison with chloride complexes [**75a** – $EtAlCl_2$ = 1776 kg mol(Ni)$^{-1}$ h^{-1}, **75c** – $EtAlCl_2$ = 823 kg mol(Ni)$^{-1}$ h^{-1}], while the replacement of hydrogen with a methyl group in the substituent R reduced the activity [**75a** – $EtAlCl_2$ = 1776 kg mol(Ni)$^{-1}$ h^{-1}, **75b** – $EtAlCl_2$ = 1023 kg mol(Ni)$^{-1}$ h^{-1}].

Structures 75, 76



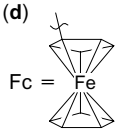
75a – d

R^2 = Fc, X = Br: R^1 = H (**a**), Me (**b**);
R^2 = Fc, X = Cl: R^1 = H (**c**), Me (**d**)



76a,**b**

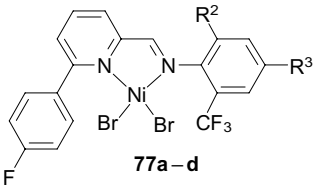
R^2 = Fc, X = Br:
R^1 = H (**a**), Me (**b**)



Complexes of Ni(II) **77** – **79**, containing fluorinated iminopyridine ligands, activated by MAO, catalyzed the formation of highly branched high-molecular-weight oligomers with M_n = 300 – 460 Da with wide distribution over chain lengths (C_n, average degree of polymerization n = 21.6 – 32.6).[135] Among them, the systems based on complexes **78** – **79** demonstrated the highest activity [6000 – 13 200 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 2 atm]. At the same time, the catalytic systems based on complexes **77** with a 4-fluorophenyl substituent in the pyridine moiety catalyzed formation of oligomers with the highest branching density (b = 168 – 229/1000C). Products obtained with complex **78d** were characterized by the largest number of long branches (C_n, $n > 5$), which made 84% of the total number of branches (b = 86/1000C).

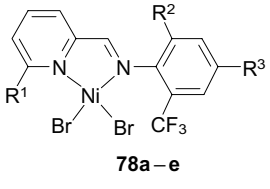
The Ni(II) α-diimine complex **80a**, containing CF_3 substituents, also demonstrated the ability to form high-molecular-weight oligomers; however, the latter were not

Structures 77 – 82



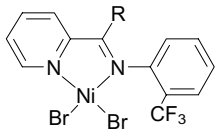
77a – d

R^2 = R^3 = H (**a**);
R^2 = F, R^3 = H (**b**);
R^2 = H, R^3 = F (**c**);
R^2 = H, R^3 = NO_2 (**d**)



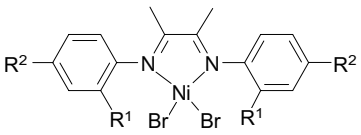
78a – e

R^2 = R^3 = H:
R^1 = 3-NCC_6H_4 (**a**),
4-NCC_6H_4 (**b**);
R^1 = R^2 = R^3 = H (**c**);
R^1 = R^3 = H, R^2 = F (**d**);
R^1 = H, R^2 = R^3 = Br (**e**)



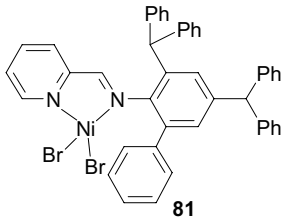
79a,**b**

R = Me (**a**), Ph (**b**)

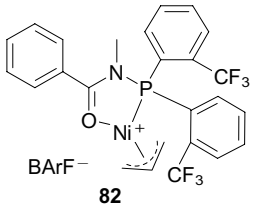


80a,**b**

R^1 = CF_3, R^2 = H (**a**);
R^1 = R^2 = Me (**b**)



81



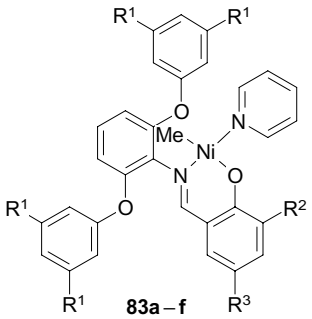
82

$BArF^-$ = $B[2,5\text{-}(CF_3)_2C_6H_3]^-$

characterized.[136] Complex **80b**, in contrast, catalyzed formation of mixtures of light and heavy oligomers with an average degree of oligomerization n = 6.1 – 8.6, which indicates importance of the presence of the CF_3 substituents for obtaining desired selectivity. The catalytic activity of both compounds was moderate [290 – 840 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3 atm]. The use of PPh_3 as a modifying additive led both to a rise in the catalytic activity and to a shift of selectivity towards the formation of low-molecular-weight products.

At the same time, complex **81**[137] without fluorinated substituents, after activation by Et_2AlCl, catalyzed the formation of viscous oils with M_n = 714 – 744 Da and a moderate number of branches (b = 66 – 72/1000C). Allyl nickel complex **82**[138] conducted ethylene oligomerization with a high catalytic activity (7000 – 11500 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 8 atm) and also led to the formation of viscous oils with

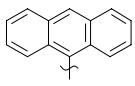
Structures 83



83a – f

R^2 = R^3 = I:
R^1 = Me (**a**), H (**b**), CF_3 (**c**);
R^2 = anthryl, R^3 = H:
R^1 = Me (**d**), H (**e**), CF_3 (**f**)

anthryl =



$M_w \approx 400$ Da, whose composition and microstructure have not been studied.

For nickel phenoxyimine complexes **83**,[139] introduction of CF_3 groups into the ligand structure resulted in an increase in molecular weight and in a decrease in the branching density in oligomer chains. Meanwhile, the use of complexes **83a**,**b**,**d**,**e** led to ethylene oligomerization giving branched oligomers ($b = 40-80$/1000C, $M_n = 270-380$ Da) isolated as liquid oils. The presence of complexes **83c**,**f** led to ethylene polymerization with formation of low-molecular-weight PE waxes ($M_n = 800-1400$ Da) having a significantly fewer side branches ($b = 16-35$/1000C).

It should also be noted that, like nickel complexes, cationic palldium complexes possess a similar ability to catalyze the formation of high-molecular-weight branched oligomers;[137, 140, 141] however, they are beyond the scope of this review. At the same time, it is obvious that the selectivity towards high-molecular-weight oligomers is intermediate between the selectivities towards the formation of light oligomers and low-molecular-weight polyethylene waxes, which are also of great practical importance.

4.4. Production of low-molecular-weight polyethylene waxes

Polyethylene waxes include linear and branched polyethylenes with intermediate molecular weights M_w in the range from 800 to 20 000 Da, which are in a solid aggregate state under ambient conditions. They are widely used in industry as adhesives, coatings for paper and wood, additives for fabricating plastic products, lubricants and packing materials; another range of applications is the production of candles, paints and cosmetics.[142] In addition, recent studies have shown good prospects of these materials as additives for UHMWPE processing by melt forming,[143] and as adhesives in fabrication of composite materials containing UHMWPE fibres.[144]

There are three main ways to produce PE waxes:[142]

(1) isolation of low-molecular-weight fractions arising as minor products when producing high-molecular-weight polyethylene;

(2) controlled thermal decomposition of high-molecular-weight polyethylene (this approach is generally used in waste processing);[145]

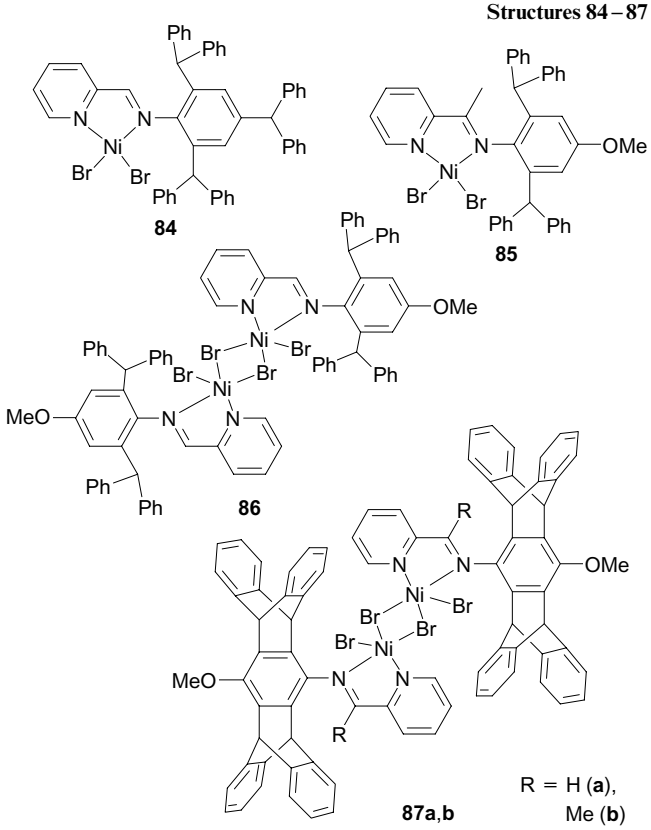
(3) directed synthesis from ethylene (with possible use of various comonomers: α-olefins, acrylic acid, vinyl acetate, *etc.*), which may occur both in the presence of Ziegler–Natta catalysts (or metallocenes[127]) and *via* free-radical high-pressure polymerization, in particular, using polar comonomers.

In this review we will consider the latest results, which were not included in the earlier reviews,[16, 22, 24, 26, 34, 37, 42, 56] devoted to the directed synthesis of PE waxes using catalysts based on iron triad metal complexes, and estimate the development prospects for this field of chemistry.

In view of the difference in the character of ethylene polymerization, nickel complexes catalyze the formation of waxes with medium and large branching numbers, whose properties are closer to the properties of their commercial analogues obtained by high-pressure radical polymerization, and cobalt and iron complexes catalyze the formation of linear products. Moreover, in the case of ethylene copolymerization with polar monomers, some catalytic systems based on nickel and palladium complexes also form products with a molecular weight in the characteristic range of PE waxes;[28–33] however, these catalytic systems often have low activity.

Iminopyridine complex **84**,[137] containing a more bulky substituent in comparison with its analog **81**, activated by Et_2AlCl, catalyzed formation of low-molecular-weight waxes ($M_n \approx 1100-1200$ Da) with a moderate branching ($b = 55-60$/1000C). Structurally similar complexes with dibenzhydryl (**85**, **86**) and pentiptycenyl (**87**) substituents,[147] with Et_2AlCl, MAO or MMAO used as activators, demonstrated similar catalytic properties, also leading to the formation of low-molecular-weight polyethylene ($M_w \approx 900-4000$ Da), but with a smaller branching degree ($b = 14-56$/1000C) than for the system based on complex **84**. The obtained PEs contained mainly internal double bonds. The activity of all catalytic systems based on complexes **84**–**87** was in the range of 1800–4700 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene} = 5-7.9$ atm). With a decrease in the reaction temperature to 5 °C, the activity of complexes **86**, **87** increased significantly: up to 14 500 kg mol(Ni)$^{-1}$ h^{-1}, which may indicate conservation of their binuclear structure during activation and manifestation of the cooperative effect.

Structures 84–87

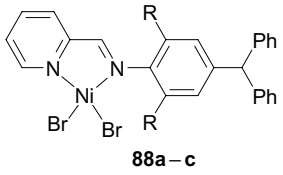


It was shown that, with a decrease in the volume of substituents R near the metal centre of compound **88**, the molecular weight of the obtained PE waxes ($M_n \approx 2300-11200$ Da) decreased in the series of systems with complexes **84** > **88a** > **88b** > **88c**.[148] In this case the number of branches ($b = 95-131$/1000C), *vice versa*, increased. All aforementioned compounds had comparable catalytic activities 4700–7100 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene} = 6$ atm). Comparing the activator effect, we should note that the use of Et_2AlCl[137] for activation of complex **84** leads to lower-molecular-weight PE waxes with

a moderate branching degree, whereas the application of MAO [148] allows one to obtain high-molecular-weight highly branched PE waxes and reach higher values of catalytic activity. A similar dependence of the catalyst properties on the activator type ($Et_3Al_2Cl_3$ or MAO) and substituents near the metal centre was observed for iminopyridine nickel complexes **89**.[149] For example, the M_w value of the obtained polymers changed in the ranges of 2200 – 16 500 Da (MAO) and 1400 – 14 400 Da ($Et_3Al_2Cl_3$), decreasing in the series of complexes **89c** > **89b** > **89a** > **89d** > **89e**. At the same time, their activity was somewhat higher when using MAO [2100 – 7900 kg mol(Ni)$^{-1}$ h^{-1} *vs* 2000 – 6750 kg mol(Ni)$^{-1}$ h^{-1} in the case of $Et_3Al_2Cl_3$ ($p_{ethylene}$ = 10 atm)]. It should be noted that the polymers formed in the presence of complexes **89d**,**e** with electron-withdrawing F and Cl groups had the largest fraction of terminal vinyl groups.

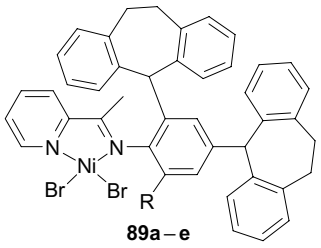
A comparison of the catalytic properties of mono- (**90**) and bisligated (**91**) nickel complexes showed that the latter activated by MAO exhibited lower activity than the monoligated ones but demonstrated higher thermal stability.[150] The PE waxes obtained in this case had a low molecular weight (M_n = 1400 – 7400 Da) and a branched microstructure (b = 40 – 100/1000C). With a decrease in reaction temperature to 5 °C, the systems with bisligated complexes **91** led to the formation of higher-molecular-weight PE waxes ($M_n \leqslant$ 19 000 Da) with fewer branches in the polymer chain (b = 20 – 30/1000C).

Structures 88 – 91



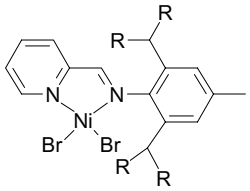
88a – c

R = Pr^i (**a**), Et (**b**), Me (**c**)



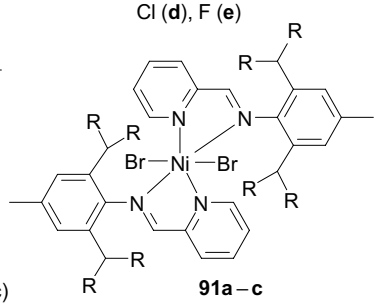
89a – e

R = Me (**a**), Et (**b**), Pr^i (**c**), Cl (**d**), F (**e**)



90a – c

90, **91**: R = 4-MeC$_6$H$_4$ (**a**), 4-Bu^{t}C$_6$H$_4$ (**b**), 4-MeOC$_6$H$_4$ (**c**)

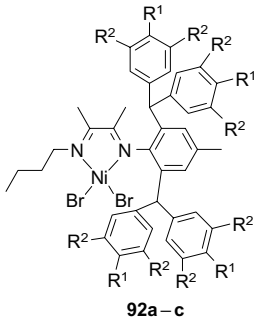


91a – c

Asymmetric α-diimine complexes **92** [151] in combination with MAO catalyzed the formation of higher-molecular-weight (M_n = 3400 – 13700 Da) and more branched (b = 66 – 95/1000C) products. However, the waxes with the lowest molecular weight were obtained at a temperature of 80 °C and isolated as viscous oils. The products with the highest weight were synthesized using complex **92a** with unsubstituted ligand. The catalytic activity of all systems based on complexes **92** was 1800 – 4500 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 5 atm).

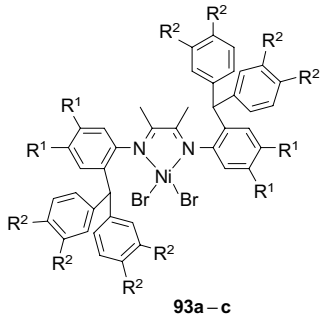
Nickel complexes **93**, **94**,[152] exist in the form of *trans*-isomers. After activation by MAO at temperature in the

Structures 92 – 94



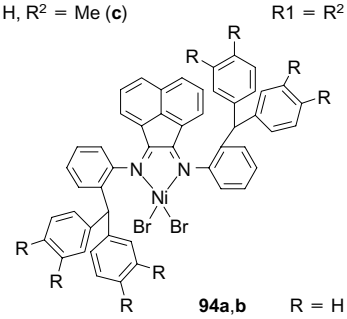
92a – c

R1 = R^2 = H (**a**);
R^1 = F, R^2 = H (**b**);
R^1 = H, R^2 = Me (**c**)



93a – c

R^1 = R^2 = H (**a**);
R1 = H, R^2 = OMe (**b**);
R1 = R^2 = OMe (**c**)



94a,**b** R = H (**a**), OMe (**b**)

range of 30 – 70 °C, they catalyze the formation of branched PE waxes with a molecular weight M_n ranging from 1100 to 8310 Da. The highest activity [10000 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 7.9 atm] was observed for the system with complex **93a**, and the lowest branching degree (b = 8 – 25/1000C) was observed for the system with complex **94b**. Moreover, when carrying out the reaction in toluene or anisole, one could observe, respectively, complete or partial functionalization of produced PE waxes due to the tandem Friedel – Crafts alkylation of the solvent with oligomers containing terminal vinyl or vinylene groups (Fig. 7). It should be noted that a decrease in the reaction temperature to −10 °C led to the formation of almost linear (b < 5/1000C) higher-molecular-weight (M_n = 6600 – 20 000 Da) polyethylenes, which do not undergo the Friedel – Crafts reaction.

Binuclear nickel complexes **95** [153] exhibited different dependences of the weight-average molecular weight M_w of produced PE waxes on the activator type. For example, when activating complexes by MAO, the polymer weight increased in the series **95d** < **95c** < **95a** < **95b**, reaching

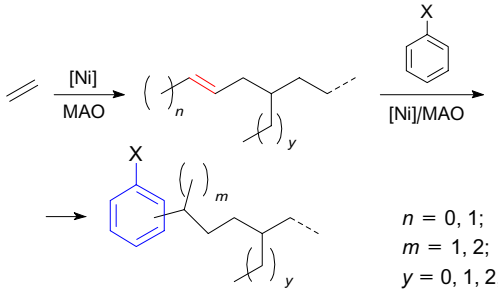
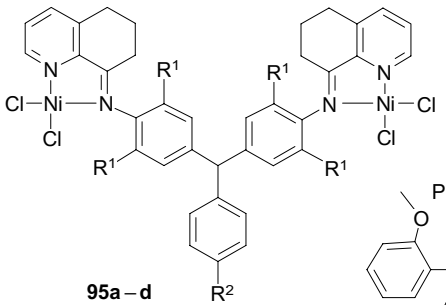


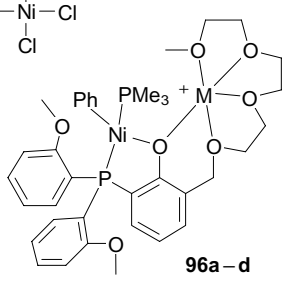
Figure 7. Alkylation of toluenes with polyethylene waxes.[152] Published with permission from the Royal Society of Chemistry.

Structures 95 – 98



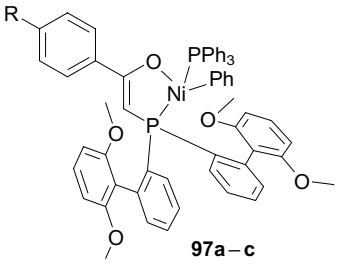
95a – d

R^1 = Me, R^2 = OH (**a**);
R^1 = Et, R^2 = OH (**b**);
R^1 = Me, R^2 = H (**d**);
R^1 = Me, R^2 = OMe (**c**)



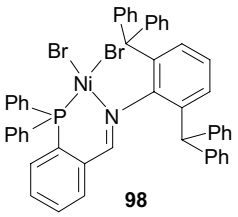
96a – d

M = Na (**a**), K (**b**), Li (**c**), Cs (**d**)



97a – c

R = H (**a**), OMe (**b**), CF_3 (**d**)



98

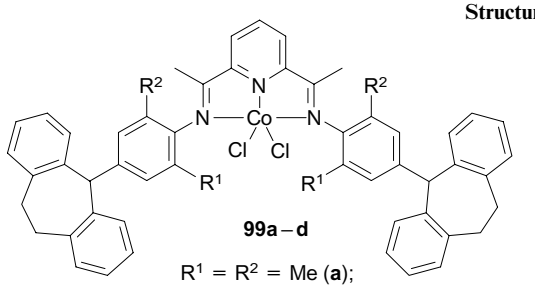
12000 Da. When using Et_2AlCl, the corresponding increase in weight (to 10500 Da) was observed in the series **95a** < **95c** < **95b** < **95d**. The catalytic systems containing Et_2AlCl were more active [to 3300 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm]; they initiated the formation of products with nonuniform branching and correspondingly, two melting peaks.

Tran *et al.*[154] revealed that the nature of alkali metal cations coordinated to nickel complexes **96** affects their catalytic properties. In particular, the presence of Na^+ or K^+ cations in the systems led to the formation of PE waxes with M_n = 1700 – 4500 Da even at a low polymerization temperature. An increase in temperature to 50 – 90 °C facilitated a decrease in the polymer molecular weight for all catalysts, except for the system based on complex **96d** containing a Cs^+ ion. Complexes **96a – c** exhibited very high activities [up to 38 000 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 30.5 atm] and a narrow molecular-weight distribution (MWD) (< 2) of produced polymers over the entire temperature range.

The SHOP-type complexes **97** with a bulky substituent near the metal centre led to the formation of PE waxes with low molecular weight (M_n = 840 – 3700 Da) and narrow MWD (≈ 1.5 – 2.5), demonstrating at the same time a moderate catalytic activity [80 – 390 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 8 atm].[155] The high melting temperatures of produced polymers correlate with their linear microstructure, proposed by the authors. Iminophosphine complex **98**, in contrast, after activation by Et_2AlCl, catalyzed the formation of higher-molecular-weight branched waxes with M_n = 3900 – 7000 Da.[156]

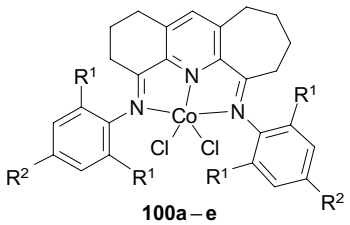
In contrast to Ni(II) complexes (except for compound **97**), all Co(II) complexes, activated by MAO or MMAO, catalyzed the formation of polyethylene waxes with a linear microstructure. In particular, linear waxes with low molecular weights (M_w = 1500 – 3200 Da, activator MMAO or MAO) and moderately narrow MWD ≈ 1.5 – 2.5 were obtained in the presence of systems based on bis(imino)pyridine cobalt complexes **99**.[157] However, the use of a bulkier substituent in the ligand near the metal centre of **99c** led to a significant rise in the molecular weight (M_w ≈ 20 000 Da). The obtained polymers contained both vinyl and saturated terminal groups in a ratio of ~4 : 1, which indicates a polymer chain transfer to the aluminium atom. The presence of flexible carbocyclic moieties in the structure of the ligand **100**[158] resulted in a narrower MWD (< 2) for the produced PE waxes. The molecular weights M_w remained approximately the same, whereas the catalytic activity somewhat decreased [~5000 kg mol(Co)$^{-1}$ h^{-1} (**100**) *vs* ~7000 kg mol(Co)$^{-1}$ h^{-1} (**99**) at $p_{ethylene}$ = 10 atm]. The polymers obtained in this case contained mainly terminal double bonds, and saturated PEs were not formed. Similar iron complexes under the same conditions catalyzed the formation of much higher-molecular-weight polyethylenes with a wide MWD ≈ 5 – 20.[159] The catalytic properties of cobalt complexes **101**,[160] containing two 7-membered carbocyclic moieties in the ligand structure, turned out to be close to those of compounds **99**, **100**. Complexes **101a – c**, activated by MAO or MMAO, were the least active [300 – 1000 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm]; sterically crowded complex **101c** catalyzed the formation of polyethylene with M_w > 40 000 Da. The formation of high-molecular-weight PE waxes (M_w ≈ 9000 – 22 000 Da) was observed for complexes **101a**,**b**,**d**, whereas the other systems, based on complexes **101e – h**, catalyzed the forma-

Structures 99 – 101



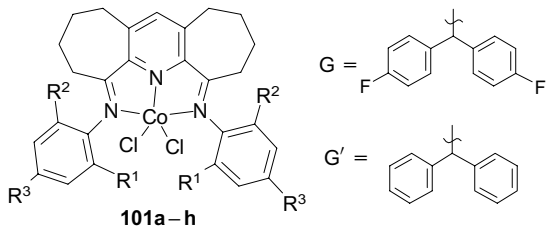
99a – d

R^1 = R^2 = Me (**a**);
R^1 = R^2 = Et (**b**);
R^1 = R^2 = Pr^i (**c**);
R^1 = Me, R^2 = Et (**e**)



100a – e

R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = R^2 = Me (**d**);
R^1 = Et, R^2 = Me (**e**)



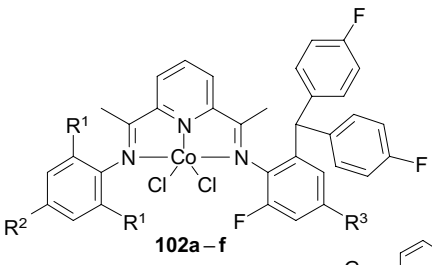
101a – h

R^2 = R^3 = G: R^1 = Me (**a**), Et (**b**), Pr^i (**c**), Cl (**d**), F (**e**);
R^2 = R^3 = G′, R^1 = F (**f**);
R^1 = R^2 = Me, R^3 = G (**g**)
R^1 = Me, R^2 = G, R^3 = Me (**h**)

tion of low-molecular-weight waxes [$M_w \approx 2000-5500$ Da) with activities of up to 8400 kg mol(Co)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm]. The obtained polyethylenes exhibited the prevalence of terminal vinyl groups over saturated ones; judging by this parameter, they are intermediate between the PEs produced using systems with complexes **99** and **100**.

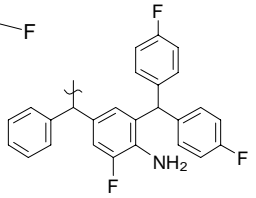
Complexes **102**, stabilized by fluorine-substituted bis(imino)pyridine ligands and activated by MAO or MMAO, initiated formation of the lowest-molecular-weight PE waxes (800–1200 Da) among the above-considered systems based on cobalt compounds. The activity of **102**–MAO(MMAO) was 11700 kg mol(Co)$^{-1}$ h^{-1} ($p_{ethylene}$ = 10 atm).[161] With an increase in the volume of the substituent R^1, one could observe a rise in M_w to 1450–2200 Da (**102b**,**d**) and 4800–10 000 Da (**102c**,**f**) and a relatively narrow MWD < 2.5 (except for **102f**, MWD ≈ 3–4.6) of PE waxes with a dominant fraction of terminal vinyl groups. After activation, Co(II) complexes **103**[162] catalyzed ethylene polymerization with the formation of PE waxes with medium and high molecular weights ($M_w \approx 4000-16\,000$ Da) (except for complex **103f** containing bulky substituents), which exceed the weights of polymers produced by their analogues, having no methyl substituents in the carbocyclic moiety.[163] In addition, the

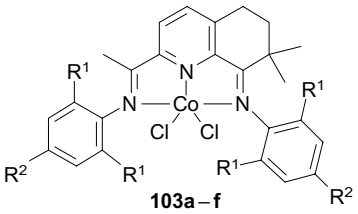
Structures 102–105



102a–f

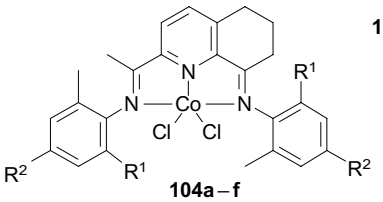
R^2 = H, R^3 = G: R^1 = Me (**a**), Et (**b**), Pr^i (**c**);
R^2 = Me, R^3 = G: R^1 = Me (**d**), Et (**e**);
R^2 = H, R^3 = G′: R^1 = Pr^i (**f**)





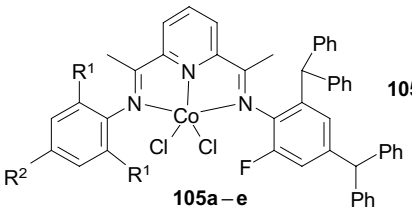
103a–f

103: R^1 = Me, R^2 = H (**a**);
R^1 = Et, R^2 = H (**b**);
R^1 = Pr^i, R^2 = H (**c**);
R^1 = R^2 = Me (**d**);
R^1 = Et, R^2 = Me (**e**);
R^1 = Bu^t, R^2 = Bu^t (**f**)



104a–f

104: R^2 = H:
R^1 = cyclo-C$_5$H$_9$ (**a**), cyclo-C$_6$H$_{11}$ (**b**), cyclo-C$_8$H$_{15}$ (**c**);
R^2 = Me:
R^1 = cyclo-C$_5$H$_9$ (**d**), cyclo-C$_6$H$_{11}$ (**e**), cyclo-C$_8$H$_{15}$ (**f**)



105a–e

105: R^2 = H:
R^1 = Me (**a**), Et (**b**), Pr^i (**c**);
R^2 = Me:
R^1 = Me (**d**), Et (**e**)

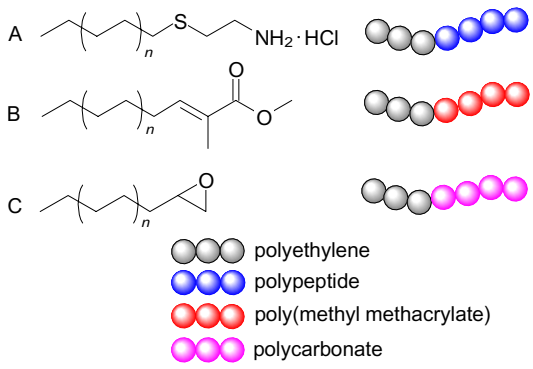


Figure 8. Functionilized polyethylene waxes and possible block copolymers on their basis.

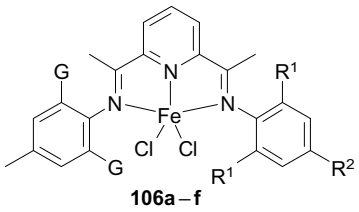
polyethylenes obtained using complexes **103a–e** were characterized by a wider MWD. The use of flexible carbocyclic substituents in arylimine moieties of ligand **104**[164] made it possible to obtain PE waxes with $M_w \approx 600-2000$ Da (MAO) and $M_w \approx 1000-2500$ Da (MAO); however, the catalytic activity reached 17 000 kg mol(Co)$^{-1}$ h^{-1} ($p_{ethylene}$ = 10 atm) in this case. These PE samples were also characterized by a high content of terminal vinyl groups (95%), due to which the polymer can be functionalized *via* the attachment of cysteamine hydrochloride (**A**), cross-metathesis with methyl methacrylate (**B**) or as a result of epoxidation reaction (**C**) (Fig. 8). This approach expands the possibilities of applying the obtained waxes in the synthesis of previously inaccessible block copolymers of different composition and structures, containing a terminal polyethylene moiety (or several moieties).

In one of recent studies by Sun and co-workers[165] devoted to the properties of fluorine-containing bis(imino)pyridine Co(II) complexes **105**, a fairly high (for such compounds) catalytic activity was achieved: up to 13200 kg mol(Co)$^{-1}$ h^{-1} (**105d**–MAO, $p_{ethylene}$ = 10 atm). The obtained polyethylene waxes had a very narrow MWD (1.2–2.4), which confirms homogeneity of active centres in the catalytic system. The synthesized polyethylenes were characterized by a linear structure with a predominant content of terminal vinyl groups (87%) and moderately low M_w values (1110–8230 Da).

The studies of iron complexes as precatalysts for the synthesis of PE waxes from ethylene are also actively continued. Some of these complexes exhibit high catalytic activity comparable to the most active iron-based bis(imino)pyridine catalysts, used in ethylene oligomerization,[41] and commercial heterogeneous titanium–magnesium Ziegler–Natta catalysts.

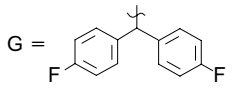
Iron complexes with fluorine-substituted ligands **106**[166] are most active in this reaction [3500–17 200 kg mol(Fe)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm] at a temperature of 80–90 °C; they catalyze wax formation even in the presence of bulky substituents (**106c**). The use of MAO made it possible to obtain products with M_w = 5500–12 600 Da and MWD ≈ 2–3, whereas activation by MMAO led to the formation of waxes with medium molecular weights (M_w = 5800–9200 Da) and a narrower MWD ≈ 1.7–2.5. The synthesized polymers are characterised by the presence of terminal vinyl, propyl and isobutyl groups, thereby indicating an essential contribution of the polymer chain transfer to aluminium when its growth is terminated; this is especially pronounced in the case of

Structures 106 – 109

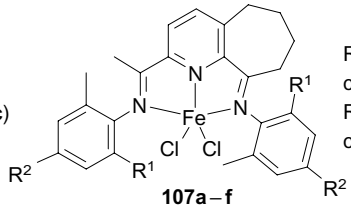


106a – f

G =

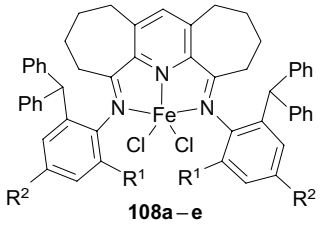


R^2 = H: R^1 = Me (**a**), Et (**b**), Pr^i (**c**)
R^2 = Me: R^1 = Me (**d**), Et (**e**);
R^1 = G, R^2 = Bu^t (**f**)



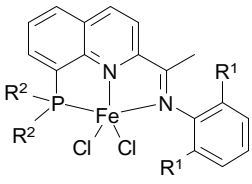
107a – f

R^2 = H: R^1 = cyclo-C_5H_9 (**a**), cyclo-C_6H_{11} (**b**), cyclo-C_8H_{15} (**c**);
R^2 = Me: R^1 = C_5H_9 (**d**), cyclo-C_6H_{11} (**e**), cyclo-C_8H_{15} (**f**)



108a – e

R^1 = R^2 = Me (**a**);
R^2 = $CHPh_2$: R^1 = Me (**b**), Et (**c**), Pr^i (**d**), Cl (**e**)



109a – j

R^1 = R^2 = Pr^i (**a**);
R^1 = Me, R^2 = Pr^i (**b**);
R^1 = Pr^i, R^2 = Bu^t (**c**);
R^1 = Pr^i, R^2 = Ph (**d**);
R^1 = Me, R^2 = Ph (**e**);
R^1 = Pr^i, R^2 = 4-$MeOC_6H_4$ (**f**);
R^1 = Me, R^2 = 4-$MeOC_6H_4$ (**g**);
R^1 = Pr^i, R^2 = 4-$CF_3C_6H_4$ (**h**);
R^1 = Me, R^2 = 4-$CF_3C_6H_4$ (**i**);
R^1 = Pr^i, R^2 = 2-$MeOC_6H_4$ (**j**)

activation by MMAO. It should be noted that the systems based on complex **106f** turned out to be inactive.

Complexes **107** with a flexible carbocyclic substituent in the arylimine moiety of the ligand demonstrated even higher catalytic activity [14000 – 19 100 kg mol(Fe)$^{-1}$ h^{-1}, T = 80°C, $p_{ethylene}$ = 10 atm].[167] The dependence of the properties of the obtained waxes on the activator composition retained; however, the maximum values of their molecular weight increased to 21 000 and 24 000 Da in the presence of MAO and MMAO, respectively. The MWD values for the produced polyethylenes were fairly high: they ranged from 2.3 to 8.0. An analysis of the polymer microstructure also showed the presence of both saturated and unsaturated terminal groups.

The higher thermal stability of complexes **106**, **107** allows reactions to be performed at temperatures above 80 °C and thus ensures high catalytic activity of the systems accompanied by lower-molecular-weight products in comparison with the previously described analogues.[16, 56]

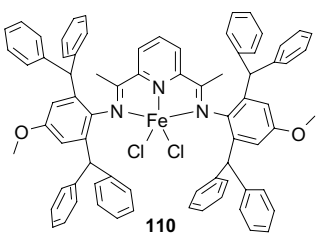
Iron complexes **108**[168] are analogues of cobalt complexes **101**, differing from them by only the type of substituents in phenyl groups. The PE waxes obtained using systems based on precatalysts **108** were characterized by low or intermediate M_w values [1000 – 3000 Da (MMAO) or 2000 – 8000 Da (MAO), respectively] with a fairly narrow MWD ≈ 1.1 – 1.5. The catalytic activity of the systems reached 30 000 kg mol(Fe)$^{-1}$ h^{-1} (**108a** – MMAO, $p_{ethylene}$ = 10 atm). Along with saturated and unsaturated terminal groups, some of produced polymers contained internal double bonds, which are extremely rare for catalysts based on iron complexes.

Complexes **109**[169] activated by MMAO exhibited the highest catalytic activity among all iron compounds considered in this subsection: up to 56 000 kg mol(Fe)$^{-1}$ h^{-1} ($p_{ethylene}$ = 13.5 atm, T = 20 °C). The polyethylenes obtained with their participation had either low or high molecular weights (M_w = 1000 – 20 000 Da) depending on the ligand substituents, and MWD varying in a fairly wide range (≈1.5 – 19). Moreover, according to the GPC data, many polymers had a pronounced low-molecular-weight peak with a wide high-molecular-weight shoulder; a bimodal distribution of molecular weights was observed in some cases. In addition, these systems demonstrated ability to catalyze ethylene copolymerization with 1-octene with activities of up to 6500 kg mol(Fe)$^{-1}$ h^{-1} ($p_{ethylene}$ = 1 atm). As a result, branched low-molecular-weight waxes (M_w = 700 – 1700 Da) with MWD = 1.8 – 2.3 and octene content of up to 8.8% were formed.

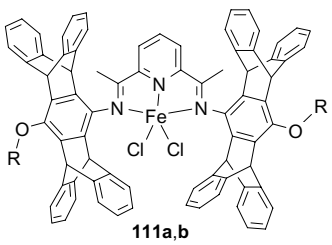
The use of bulky substituents does not always improve the catalytic properties of bis(imino)pyridine iron complexes.[170] Complex **110**, as well as previously considered complex **106f**, turned out to be practically inactive, thus indicating that the presence of four dibenzhydryl substituents in the ligand hinders ethylene coordination and insertion. At the same time, the systems based on complexes **111**, whose ligand contains structurally rigid and even more bulky pentiptycenyl substituents, in contrast, turned out to be very active: up to 25 500 kg mol(Fe)$^{-1}$ h^{-1} (MAO, $p_{ethylene}$ = 7.9 atm, 40 °C); however, instead of expected high-molecular-weight PE, they led to the formation of waxes with M_w = 1000 – 2000 Da and MWD < 2. The low-temperature (20 – 40 °C) polymerization resulted in the exclusive formation of terminal vinyl groups, whereas polymerization at elevated temperatures (60 – 80 °C) or a larger MAO excess led to tandem alkylation of toluene with obtained PE waxes (see Fig. 7), by analogy with nickel complexes **93** – **94**.

In the last few years the number of catalysts based on nickel complexes for copolymerization of ethylene and polar monomers (olefins containing different functional groups) has been constantly increasing. The low-molecular-weight copolymers, synthesized with their aid, despite the fact that they often have a linear microstructure, are most similar to the commercial PE waxes produced by radical copolymerization of ethylene with methyl acrylate or vinyl chloride. The functionalized polyethylenes obtained with the aid of the aforementioned Ni catalysts have not

Structures 110 , 111



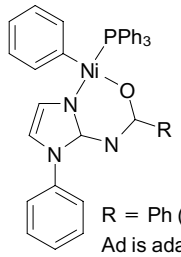
110



111a,b

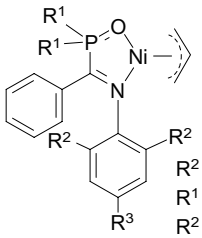
R = Me (**a**), H (**b**)

Structures 112 – 118



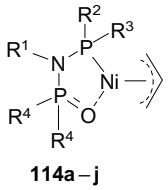
R = Ph (**a**), Ad (**b**);
Ad is adamantyl

112a,**b**



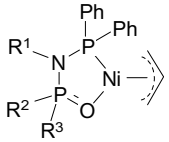
R^2 = Pr^i, R^3 = H:
R^1 = Ph (**a**), OEt (**b**);
R^2 = $CHPh_2$, R^3 = Me:
R^1 = Ph (**c**), OEt (**d**)

113a – d

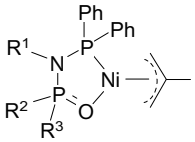


114a – j

R^1 = Ph, R^2 = Ph,
R^3 = 2-[2′,6′-$(MeO)_2C_6H_3$]C_6H_4:
R^4 = piperidinyl (**a**), morpholino (**b**),
Et_2N (**c**), MeO (**d**), Pr^{i}O (**e**);
R^1 = R^4 = Ph, R^2 = R^3 = 2-$MeOC_6H_4$ (**f**);
R^3 = 2-[2′,6′-$(MeO)_2C_6H_3$]C_6H_4:
R^1 = Ph, R^2 = Ph, R^4 = Ph (**g**);
R^1 = Ph, R^2 = Ph, R^4 = Pr^i (**h**);
R^1 = 4-$MeOC_6H_4$, R^2 = R^4 = Ph (**i**);
R^1 = 4-$CF_3C_6H_4$, R^2 = R^4 = Ph (**j**)

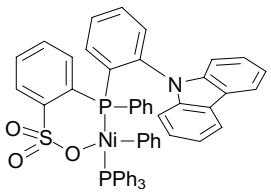


115a – c

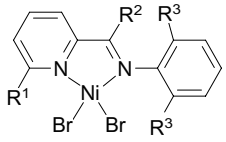


116a – c

115, **116**: R^1 = Ph, R^2 = R^3 = 2-$MeOC_6H_4$ (**a**);
R^1 = R^2 = Ph, R^3 = 2-[2′,6′-$(MeO)_2C_6H_3$]C_6H_4 (**b**);
R^1 = 4-$MeOC_6H_4$, R^2 = Ph,
R^3 = 2-[2′,6′-$(MeO)_2C_6H_3$]C_6H_4 (**c**)



117



118a – d

R^1 = 2,6-$Me_2C_6H_3$: R^2 = Me, R^3 = Pr^i (**a**),
R^2 = H, R^3 = Me (**b**);
R^1 = Me: R^2 = Me, R^3 = Pr^i (**c**);
R^2 = H, R^3 = Me (**d**)

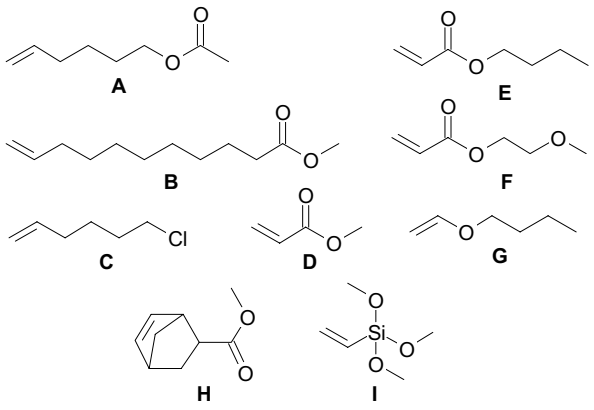
found their potential application yet. Most probably, this is due to their low catalytic activity as a significant drawback of these catalysts.

The use of catalytic systems based on complexes **112** led to the formation of low-molecular-weight waxes (M_n = 1400 – 4200 Da) with MWD < 2.3 and low branching degree (b = 5 – 25/1000C).[171] It was found that these complexes can catalyze ethylene copolymerization with 5-hexenyl acetate (monomer **A**). The content of the inserted comonomer did not exceed 1.3%, the MWD increased to 3.3, and the molecular weight barely changed.

Allyl complexes **113c – d** can also catalyze the formation of PE waxes (M_n = 3000 – 6400 Da) with MWD ≈ 2 – 3 and different degrees of branching (b = 25 – 80/1000C), depending on the synthesis temperature.[172] In particular, a system based on complex **113b** catalyzed copolymerization of ethylene with methyl 10-undecenoate (monomer **B**) and 6-chloro-1-hexene (monomer **C**) with the comonomer content of 1.4 – 3.4% and 0.9 – 1.8% in the resulting copolymers, respectively. The polyethylene wax obtained with the use of methyl 10-undecenoate (**B**) has a lower molecular weight (M_n = 2200 – 3900 Da) in comparison with copolymer based on 6-chloro-1-hexene (**C**), which can be assigned to both PE waxes and low-molecular-weight polyethylene (M_n = 7100 – 13 400 Da).

The application of allyl nickel complexes **114 – 116** made it possible to obtain medium- and high-molecular-weight linear PE waxes (M_n = 3000 – 10000 Da, MWD ≈ 2 – 3) based on wide series of functionalizing comonomers (**B – I**). The comonomers were located both in the middle and on the ends of polymer chain.[173 – 175] A maximum catalytic activity was observed for complex **114d** in ethylene copolymerization with methyl 10-undecenoate (monomer **B**) and 6-chlor0-1-hexene (**C**) (180 and 160 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 8 atm). The degree of comonomer incorporation varied from 1 to 7% and depended on the comonomer nature, precatalyst type and catalytic process conditions. In the case of ethylene copolymerization with the same monomers, a system based on complex **117** showed comparable values of catalytic activity [42 – 310 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 7.9 atm] and degrees of comonomer incorporation (0.6 – 4.9%); the copolymers also had a linear structure.[176]

Structures of polar monomers A – I



A **E** **B** **F** **C** **D** **G** **H** **I**

Iminopyridine nickel complexes **118** should be considered separately, because after activation they catalyzed formation of both oligomers (M_n = 300 – 700 Da) and low-molecular-weight ethylene copolymers with methyl acrylate (monomer **D**) (M_n = 900 – 11 700 Da).[177] Because of a high degree of branching (b = 66 – 141/1000C), most reaction products were isolated as oils. The low-molecular-weight functionilized products were also characterized by a controllable degree of incorporation of methyl acrylate (0.2 – 35%) and a narrow MWD (1.1 – 2.3). When carrying out the process in *o*-dichlorobenzene, using Et_2AlCl as an activator, methyl acrylate was introduced into only the polymer chain, whereas the use of dichloromethane gave rise to many possible ways for incorporation of the comonomer both into the main chain and into side branches. The degree and type of comonomer incorporation also depended on the activator nature and composition.

4.5. Oligo- and polymerization of ethylene on immobilized metal-complex catalysts

In some cases the application of heterogeneous catalysts makes it possible to significantly simplify the processes of their isolation from the reaction medium, regeneration and repeated use. This is especially important for commercial production. At the same time, these catalysts, compared to homogeneous ones, provide much less possibilities for studying such fundamental properties as the composition and structure of active centres, as well as the mechanisms of specific catalytic stages. One can state that impressive progress has been achieved to date in the field of technologies involving heterogeneous catalysts; however, the understanding of the nature of their catalytic action is incomplete as previously.[178] The best results were obtained when studying the processes involving one-component catalysts. In the case of multicomponent catalytic mixtures or supported catalysts, it is highly difficult to understand the occurring processes, because rather often the support itself has catalytic properties and affects greatly the overall selectivity of the process, for example, due to the isomerization of olefins on acid centres.[36] The immobilization of transition-metal complexes from solutions on various supports and their subsequent activation is one of the main approaches to study the properties of heterogenized metal-complex catalysts. The conclusions on the structure and the composition of active centres may differ and be ambiguous.

It is noteworthy that, in the case of nickel complexes, heterogenization on a support makes it possible to affect the selectivity of ethylene oligomerization, because the monomer, reaction products and catalyst are in different phases; this circumstance allows one to restrict the isomerization of reaction products on active centres.

This review considers the iron triad metal complexes grafted on such supports as silica gels, zeolites, alumina, carbon materials, *etc*., as well as the influence of heterogenization on their catalytic properties in ethylene (oligo)-polymerization processes [the use of ionic liquids and metal-organic frameworks (MOFs) in olefin oligomerization and polymerization were considered in detail in the reviews;[36, 179] review [180] was devoted to supported catalysts for olefin polymerization based on diimine complexes of late transition metals (Ni, Pd); the immobilization of iron complexes was considered in the review [181]].

There are three main approaches to immobilization of metal complexes on solid supports:[178]

— ligand grafting on the support surface with the formation of covalent chemical bonds and subsequent synthesis of a complex with the grafted ligand;

— direct grafting of complex,[182] generally *via* oxygen groups of the dehydroxylated surface of the oxide support;

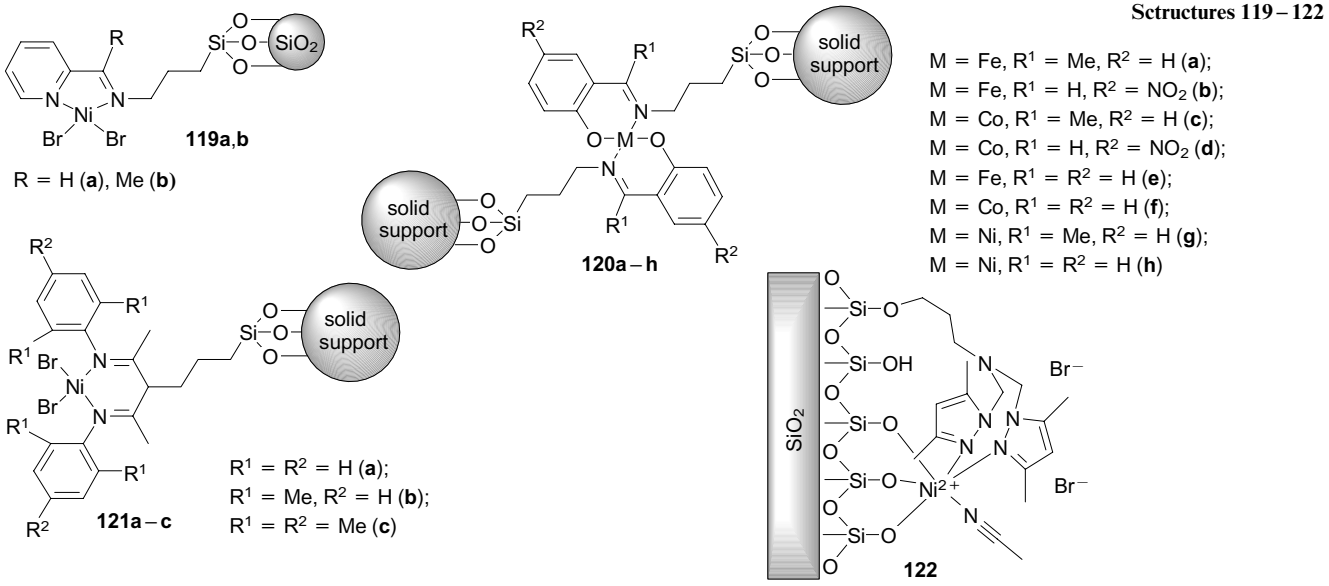
— formation of ionic bonds or occurrence of different noncovalent interactions between the complex and support, such as encapsulation, chemisorption, physical adsorption, *etc*.

The first approach is most commonly used in the synthesis of immobilized catalysts with the participation of iron triad metal complexes. For example, iminopyridine nickel complexes, containing a propyltriethoxysilane linker at the imine nitrogen, were grafted on the surface of silica gel (structure **119**).[183] After activation by $EtAlCl_2$ they were only slightly inferior in catalytic activity to their homogeneous analogues [maximum value 913 kg mol(Ni)$^{-1}$ h^{-1} *vs* 957 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 14.8 atm]; however, they turned out to be more thermally stable and surpassed them in ability to catalyze toluene alkylation with the obtained oligomers (polyalkyltoluene fraction of 89–100%). These precatalysts can be used repeatedly; however, in the third catalytic cycle their activity decreases by a factor of 4 in comparison with the initial value. Jayamani *et al*.[184] applied a similar procedure to prepare grafted phenoxyimine cobalt and iron complexes **120a**–**d**, where mesoporous material MCM-41 rather than a conventional silica gel was used as a solid support. After activation by $EtAlCl_2$ the obtained heterogeneous precatalysts also initiated predominant formation of polyalkyltoluenes with an admixture of ethylene dimers. It should be noted that the immobilization, as in the case of nickel complexes **119**, reduced the catalytic activity from 97–184 to 74–97 kg mol(M)$^{-1}$ h^{-1} ($p_{ethylene}$ = 9.9 atm), but for complexes **120a**–**d** it allowed to significantly increase the shares of dibutyl- (from ~10% to ~50%) and tributyltoluenes (from 5–10% to 15–20%). Ngcobo and Ojwach[112] used Fe_3O_4 as a support for phenoxyimine complexes of iron (**120a**,**e**), cobalt (**120c**,**f**) and nickel (**120g**,**h**); this approach made it possible to isolate the catalyst from the reaction mixture by a magnet for repeated use. After activation by $EtAlCl_2$ the supported precatalysts demonstrated activity from 67 (**120e**) to 98 (**120g**) kg mol(M)$^{-1}$ h^{-1} ($p_{ethylene}$ = 19.7 atm) under optimized conditions. It should be noted that the activity decreased by no more than 5% up to the third use of the catalyst, subject to the introduction of a new portion of $EtAlCl_2$ into the regenerated system. The selectivity of the catalytic process depended strongly on the solvent in use: a mixture of corresponding alkylation products and ethylene oligomers was formed in toluene and chlorobenzene, whereas only a mixture of olefins C_4-C_{10} was formed in n-hexane and n-heptane; the hexenes were the main fraction and ranged from 56 to 89%.

Bernardo-Gusmão and co-workers [185] obtained β-diimine nickel complexes **121** grafted on different supports: hybrid xerogels,[185] mesoporous structured materials SBA-15 [186] and MCM-41,[187] including aluminium-modified ones,[188] and delaminated ITQ-2 zeolites.[189] The standard grafting scheme was used for all supports, except for xerogels; according to this scheme, the β-diimine ligand was successively treated with NaH and 3-chloropropyltrimethoxysilane, after which the linker formed was grafted on the surface (upon heating in toluene) with the formation of Si–O bonds. Xerogels with a grafted ligand were obtained by the sol–gel method from a similarly modified β-diimine ligand and tetraethoxysilane in the presence of HF.

Complexes **121a**–**c** grafted on xerogels, activated by $Et_3Al_2Cl_3$, were much less active [50–386 kg mol(Ni)$^{-1}$ h^{-1}] in comparison with homogeneous analogues [512–5800 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 15 atm], but they selectively dimerized ethylene with the formation of 1-butene, with an almost quantitative output in the case of **121b**.[185] During the second and third cycles of catalyst use, its activity decreased by 40% and 60%, respectively, with retention of selectivity. Complexes **121a**,**b**, grafted on mesoporous materials and activated by $Et_3Al_2Cl_3$, were also inferior in activity to homogeneous catalytic systems. The catalysts supported on SBA-15 [186] were characterized by lower activity [75–200 kg mol(Ni)$^{-1}$ h^{-1}] but higher selectivity to 1-butene [96% (C_4), 76–90% (α-C_4)], in comparison with similar catalysts grafted on MCM-41 [activity: 355–510 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 15 atm, selectivity: 97–98% (C_4), 98% (α-C_4)]. The catalysts based on SBA-15,

Sctructures 119 – 122



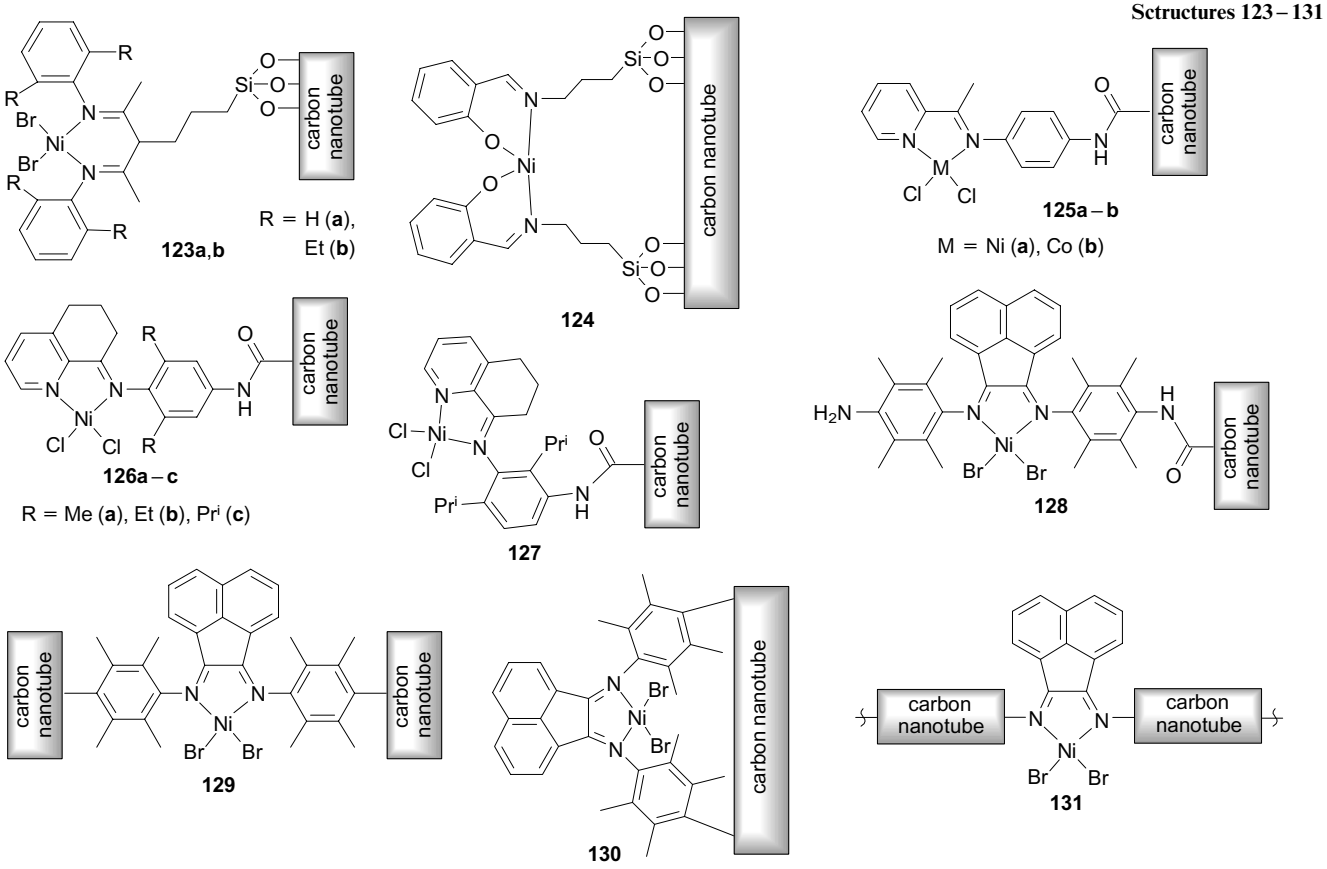
retained their activity and selectivity on the second use; however, in the third catalytic cycle these characteristics significantly deteriorated with respect to the butene formation. In contrast, the productivity of the complexes grafted on MCM-41 under similar catalytic conditions decreased by more than 50% after the first use; however, afterwards it retained on the same level up to the fourth catalytic cycle. It should be noted that the loss of activity as a result of heterogenization is smaller for complexes **121b**,**c**, containing substituents located near the metal centre, as compared with their unsubstituted analogue **121a**.

The deposition of complex **121a** on aluminium-modified supports MCM-41 and SBA-15 made it possible to increase the efficiency of heterogeneous catalysts after their activation by $Et_3Al_2Cl_3$ in comparison with a catalyst on an unmodified support.[188] For example, the activity of the obtained catalysts was in the range of 860 – 1050 kg mol(Ni)$^{-1}$ h^{-1}, ($p_{ethylene}$ = 15 atm) with a selectivity of 79 – 86% to 1-butene, whereas for the catalysts on unmodified supports it was 500 – 700 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 15 atm) with a selectivity to 1-butene of 69 – 74%. Delaminated ITQ-2 zeolite turned out to be the most efficient support for β-diimine nickel complexes.[189] In particular, complex **121a** grafted on its surface, being activated by $Et_3Al_2Cl_3$, was barely inferior to the homogeneous analogue in terms of activity under identical process conditions [1780 *vs* 2000 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 14.8 atm] and had a fairly high selectivity to butenes (92% for C_4, 69% for α-C_4). The main drawback of this catalytic system is that the catalyst reuse led to a significant decrease in activity.

The use of ligands with a spatial structure not so rigid as that of β-diimines, grafted on a silica gel surface, may lead to simultaneous coordination of metal by both donor ligand atoms and support surface.[190] According to the EXAFS/XANES (Extended X-ray Absorption Fine Structure/X-ray Absorption Near Edge Structure) spectroscopy data, complexes **122**, synthesized on the surface of silica gels having different porosities and modified by aminopropyl groups, had only oxygen and nitrogen atoms in the metal centre environment, whereas bromine atoms were apparently located in the outer coordination sphere. Such type of metal coordination caused a significant rise in catalytic activity [150 – 1450 kg mol(Ni)$^{-1}$ h^{-1}] in ethylene oligomerization in comparison with the homogeneous analogues [180 – 220 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 2.9 atm]. In addition, the selectivity to 1-butene increased as well (from 47% to 65% of the entire oligomer mixture).

The immobilization of the β-diimine ligand on the carbon nanotube surface, oxidized with the aid of H_2O_2 or HNO_3, with the subsequent synthesis of nickel complex **123**[191] and its activation by $Et_3Al_2Cl_3$, gave rise to a moderately active catalyst [in the former case, 80 – 130 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 14.8 atm]. It was inferior in activity to the homogeneous analogue, but retained selectivity to the formation of butene [≈80 – 90% (C_4), 96 – 100% (α-C_4)]. In contrast, after the direct immobilization of phenoxyimine complex **124** on the nanotube surface and activation by $Et_3Al_2Cl_3$, the obtained catalyst significantly surpassed the homogeneous analogue in activity [530 – 7610 kg mol(Ni)$^{-1}$ h^{-1} *vs* 200 – 1400 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 4.9 atm].[113] It is of interest that immobilized complex **124**, activated by MAO or $EtAlCl_2$ in cyclohexane or $AlEt_3$ in toluene, exhibited an unusually high selectivity to the formation of hexenes (∼80%). A similar effect was described previously for homogeneous catalytic systems based on nickel complexes in the presence of MMAO, Et_2AlCl or $EtAlCl_2$ (see Section 4.1 for more details). However, in the case under consideration, specifically heterogenization provided such high values of selectivity. The selectivity to hexenes for the homogeneous catalytic systems with a ligand structure similar to that of **124** did not exceed 60%. Moreover, it increased with an increase in the MAO : Ni ratio from 300 to 700 for heterogeneous catalytic systems and from 300 to 900 for homogeneous ones; the maximum value was 95% (**124**). The 1-hexene fraction amounted to 90 – 97% of the entire hexene fraction. It should also be noted that complexes **123**, **124** immobilized on nanotubes, lost their catalytic activity to some extent but retained selectivity when they were reused. In particular, the system **124** – MAO lost only 27% activity up to the fourth catalytic cycle, and its selectivity to hexene decreased by 11% (from 95% to 84%).

Sctructures 123 – 131



Iminopyridine nickel and cobalt complexes **125** were immobilized on carbon nanotubes, oxidized previously with a $H_2SO_4-HNO_3$ mixture, and tested as precatalysts for ethylene (oligo)polymerization.[192] A gradual increase in the amount of MAO equivalents from 200 to 2000 not only increased the catalytic activity of the catalytic systems (from 300 to 1900 kg mol^{-1} h^{-1}, $p_{ethylene}$ = 4.9 atm), but also shifted their selectivity towards the ethylene polymerization. The metal nature barely affected both the activity and selectivity of the process, in contrast to the most data in the literature.

Heterogenized complexes **126**, **127** were obtained in the same way as compound **125**.[193] After the activation by MAO they turned out to be much more active than their homogeneous analogues [to 6500 *vs* to 1300 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 10 atm] and catalyzed formation of higher-molecular-weight branched polyethylenes (M_w = 3670 – 15 300 Da *vs* 1090 – 12 700 Da). The MWD value for these products turned out to be somewhat wider than for those formed using homogeneous systems (2.6 – 5.2 *vs* 1.4 – 4.0).

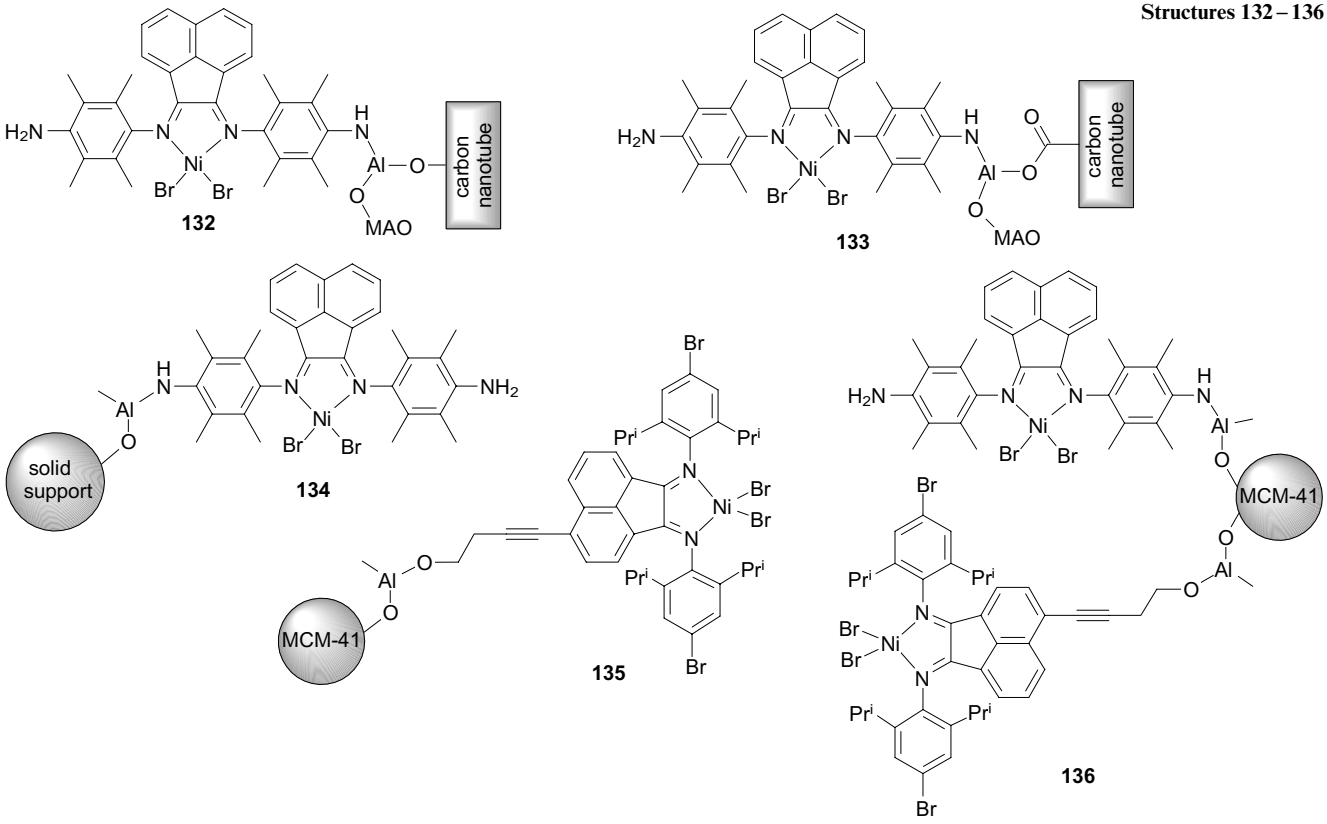
Complex **128** was grafted on the surface of carbon nanotubes after their preliminary oxidation and formation of acid chloride groups as a result of treatment with thionyl chloride.[194] The catalytic activity of complex **128** in the ethylene polymerization after treatment with MAO was 5800 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 9.9 atm), which is 2 – 3 times lower than for a homogeneous catalytic system. In this case, the weight-average molecular weight (M_w = 9.8 – 18 × 10^4 Da) of the obtained polymer exceeded significantly the molecular weight of the polymer produced under homogeneous conditions (0.53 – 1.17 × 10^4 Da), while maintaining a very wide MWD (6.7 – 14.1).

Direct ligand grafting on the nanotube surface *via* C – C bond formation for complexes **129** – **131** led to the formation of precatalysts, which, after activation by MAO, demonstrated a low activity [100 – 200 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm] in the synthesis of high-molecular-weight polyethylenes (M_w = 2.3 – 3.74 × 10^5 Da).[195] In view of the low catalyst activity, the obtained polyethylene samples are in essence filled composites, because carbon nanotubes make 14 – 20% of the total polyethylene weight.

The method of heterogenization of complexes **132** – **135** can be considered as a combined one, because it implies grafting of the previously synthesized complex *via* the functional group of its ligand on the support surface, treated with various organoaluminium compounds.

The structure of complexes **132**, **133** is similar to that of above-considered precatalysts **128**. However, the systems formed as a result of activation of complexes **132**, **133** by MAO demonstrated lower catalytic activity [1250 – 1440 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm] in comparison with the systems based on **128**, but they did not cause any changes in the properties of the final polymer.[194] The use of supports in the form of mesoporous silicates SBA-15[196] with different morphologies and spherical zeolite ZSM-5[197] led to the formation of supported complexes **134** and, after the treatment with MAO or $AlMe_3$, provided fairly active catalysts. For example, the activity of the catalyst supported on SBA-15 was lower than that of its homogeneous analogue [631 – 2613 kg mol(Ni)$^{-1}$ h^{-1} *vs* 960 – 4510 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3.9 atm, reaction time 10 – 30 min], whereas the precatalyst immobilized on ZSM-5, after addition of $AlMe_3$ or MAO, was not inferior in this respect and led to the formation of polyethylene with characteristics (crystallinity, melting point) practically iden-

Structures 132 – 136



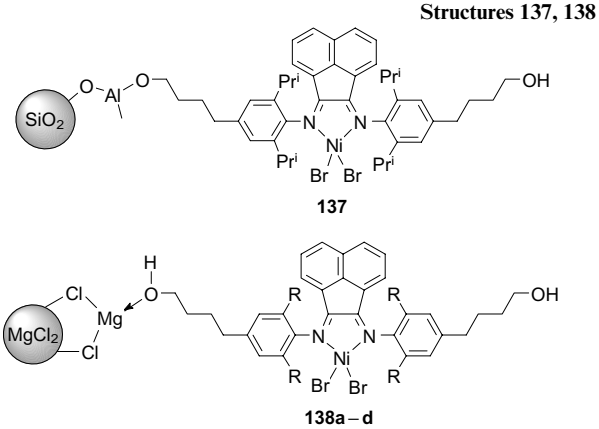
tical to those of homogeneous systems. This fact is indicative of very similar structure of active polymerization sites in the homogeneous and heterogenized states.

Favero *et al.*[198] performed a comparative study of the catalytic properties of two different α-diimine complexes **134**, **135**, supported on MCM-41, and binary precatalyst **136**, consisting of the two aforementioned diimine complexes, immobilized on the same support. Precatalysts **134**, **135** activated by $AlMe_3$ or MAO were inferior in activity to their homogeneous analogues, whereas binary precatalyst **136** activated by $AlMe_3$ surpassed other heterogeneous catalytic systems [1300 kg mol(Ni)$^{-1}$ h^{-1} *vs* 500 – 1000 kg mol(Ni)$^{-1}$ h^{-1} (**134** – **135**), $p_{ethylene}$ = 3.9 atm]. However, when $Et_3Al_2Cl_3$ was used as an activator, the highest efficiency was demonstrated by heterogenized precatalysts **135**, **136** [3950 – 3900 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3.9 atm]. It should be noted that the catalytic systems **134** – $Et_3Al_2Cl_3$ and **135** – $Et_3Al_2Cl_3$ facilitate the preferential formation of linear and highly branched (b = 50/1000C) polyethylenes, respectively. At the same time, the system **136** – $Et_3Al_2Cl_3$ catalyzes the formation of polyethylene with averaged characteristics, which is apparently a mixture of products obtained with the participation of two different catalytic sites. This conclusion is further confirmed by the wide MWD (5.5) of the obtained polymer samples.

The grafted α-diimine nickel complex **137** was obtained by analogy with compounds **134** – **136**.[199] After its activation by $Et_3Al_2Cl_3$, branched polyethylenes were obtained (b = 30 – 115/1000C, mainly Me branches); the productivity of this catalyst depended on the reaction temperature and OAC excess and turned out to be 1100 – 4100 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 6 atm).

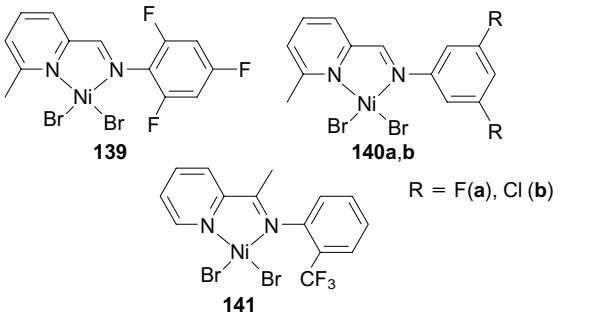
Complexes **138** (with a ligand of similar structure) were grafted on thermally activated supports $MgCl_2$ and $MgCl_2 - SiO_2$ through the formation of Mg – O donor bonds.[200] After activation by $Et_3Al_2Cl_3$ these compounds demonstrated fairly high values of catalytic activity in ethylene polymerization: 11100 – 25 700 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 9.9 atm), which only slightly differed from the activities of similar homogeneous catalytic systems. However, the MWD value for polymers obtained using the supported systems increased significantly (from 1.7 – 2.8 to 5.8 – 8.3), which indicates inhomogeneity of the catalytically active sites formed on the support surface. In addition, the use of a support made it possible to increase the molecular weight of produced polymers, which reached 4.2×10^6 Da (**138d** – $MgCl_2 - SiO_2$).

Structures 137, 138



R = Me (**a**), Pr^i (**b**), Ph (**c**), 4-Bu^{t}C$_6$H$_4$ (**d**)

Structures 139 – 141



In recent years the second approach to the formation of supported catalysts, including direct grafting of a transition-metal complex onto an activated dehydroxylated support surface in the abscence of specific functional groups in the ligand structure, has become increasingly popular. This approach often provides a higher concentration of active sites per unit surface area and, correspondingly, a higher catalytic activity.

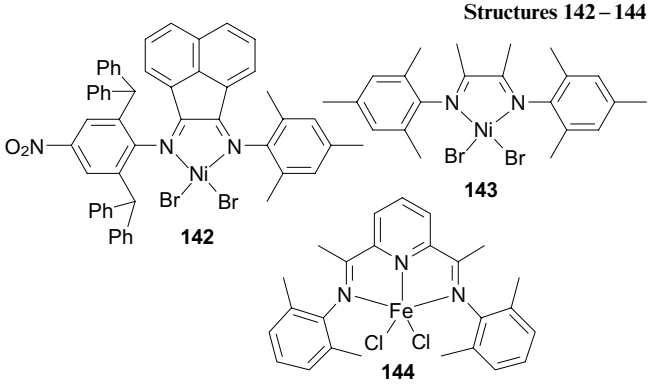
Iminopyridine nickel complexes **139** – **141**, grafted onto aluminium modified SiO_2, have been reported.[201] Systems **139** – **141** – MAO (or Et_2AlCl) led to the oligomerization of ethylene with activities of up to 9700 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 1 atm, **139** – MAO), which are comparable with the corresponding parameters of similar homogeneous systems. Moreover, the retention of selectivity to butenes (~93 – 98%) of the aforementioned systems made it possible to obtain up to 79% of 1-butene (of the total butene amount), which exceeded 41% of 1-butene, obtained using the homogeneous system. Activation of complexes **139** – **141** by $Et_3Al_2Cl_3$ led to the formation of polyalkyltoluenes for both homogeneous and heterogeneous catalytic systems due to the occurrence of competing processes of ethylene oligomerization and Friedel – Crafts alkylation of toluene with obtained oligomers. The system with immobilized complex **141**, activated by MAO, MMAO or $AlBu^i_3$,[135] was inferior in activity to homogeneous analogue **79a** [315 *vs* 960 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm, MAO] but surpassed it when activated by Et_2AlCl [470 *vs* 240 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm], leading in this case to the formation of even higher-molecular-weight polymers with a very broad MWD (M_w = 3000 – 29 000 Da, MMP = 6.2 – 45).

α-Diimine nickel complexes **142**, **143**[202, 203] and bis(imino)pyridine iron complex **144**[204] were heterogenized in a similar way. The homogeneous catalytic system **142** – Et_2AlCl demonstrated very high activity in ethylene polymerization [3350 – 16 800 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 2.5 – 9.9 atm], leading to the formation of ultra-high-molecular-weight branched polyethylene (viscosity-average molecular weight $M_v = 1.4 – 2.1 \times 10^6$ Da; b = 22 – 77/1000C). When using $Et_3Al_2Cl_3$, which has a stronger Lewis acidity, the activity of the system increased to 21 000 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 4.9 atm) with retention of polymer properties.[202] The heterogenized catalysts based on complex **142** demonstrated a lower activity after activation by either Et_2AlCl [7850 – 10400 kg mol(Ni)$^{-1}$ h^{-1}] or $AlBu^i_3$ [2600 – 10 000 kg mol(Ni)$^{-1}$ h^{-1}] at $p_{ethylene}$ = 9.9 atm. However, the latter system made it possible to produce higher-molecular-weight polyethylene (M_v = 1.8 – 2.4 × 10^6 Da). These heterogeneous systems allow one to obtain polymers in the form of spherical particles with a good morphology, in contrast to homogeneous systems, which give rise to small polymer particles, adhering to the walls of the reactor and contaminating it. Sun and co-workers[203] found that, in contrast to homogeneous systems, supported precatalysts **142**, **143**, activated by $AlBu^i_3$, catalyzed formation of polyethylenes with only methyl branches. The use of the catalytic system **143** – $AlBu^i_3$ led to the formation of lower-molecular-weight products (M_w = 2.1 × 10^5 Da, MMP = 2.6) than in the case of **142** – $AlBu^i_3$ with mechanical properties similar to those of commercial LLDPE samples.

Iron complex **144** was grafted on silica gels with different aluminium contents [SiO_2, SiO_2(nAl), Al_2O_3].[204] The catalytic activity of the system **144** – $AlBu^i_3$ [**410** – 1100 kg mol(Fe)$^{-1}$ h^{-1}, $p_{ethylene}$ = 4.9 atm] was shown to depend on the complex concentration on the support surface; this concentration, in turn, is determined by the amount and density of aluminium acid sites on this surface, because the complex is coordinated to them. The polyethylenes obtained using this system had a moderate molecular weight (M_w = 1.8 – 2.4 × 10^5 Da) and a wide MWD (7.5 – 16.6).

Various porous organic structures can also be used as supports to heterogenize catalysts; however, the catalytic systems formed with their participation exhibit low activity. When covalent organic frameworks (COFs) are used, nickel halides are coordinated directly to the donor centres present in them to form complexes **145** or **146**.[205] In other words,

Structures 142 – 144



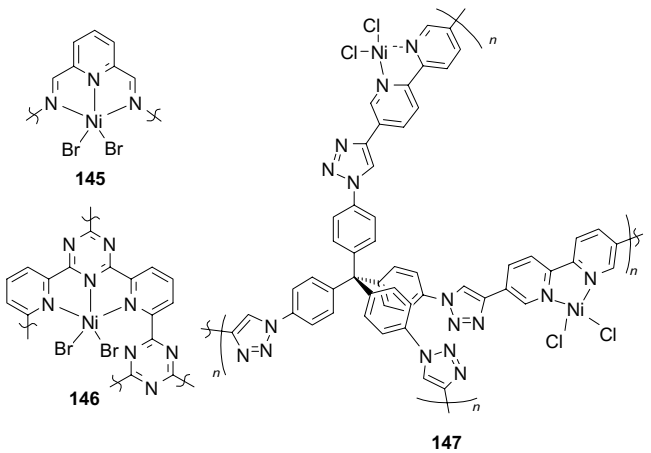


Figure 9. Coordination modes of nickel halides in covalent organic frameworks **145**, **146**[205] and porous organic polymer **147**[206] used as supports.

COFs simultaneously play the roles of a support and an organic ligand (Fig. 9). After activation by $AlEt_3$ these systems oligomerized ethylene with the preferred formation of light oligomers (C_4-C_8); the activity did not exceed 33 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 14.8 atm) in this case. Nevertheless, they demonstrated good stability at multiple use, losing less than half its activity up to the fifth catalytic cycle (**146**).

After activation of heterogeneous precatalyst **147** (consisting of nickel chloride immobilized on a porous organic polymer) by Et_2AlCl (see Fig. 9), the obtained catalytic system oligomerized ethylene to C_4-C_{10} olefin mixtures with an activity not higher than that for complexes **145**, **146**.[206] Moreover, the polyethylene formed during the catalytic process encapsulates catalyst particles, making impossible their repeated use.

Along with the two above-considered aproaches to covalently bind complexes to the support, various methods based on electrostatic or noncovalent interactions have also been applied. In particular, ethoxylated $MgCl_2$ treated with $AlBu^i_3$ was described by Ahmadjo *et al.*[207] as a support for α-diimine nickel complex **148** (Fig. 10). According to the authors, the complex is grafted onto the support surface *via* electrostatic interaction. However, the exchange reaction between the complex and grafted $AlBu^i_2$ appears to be the most probable way, leading to the formation of ion pairs **149** (see Fig. 10); *i.e.*, the support plays simultaneously the role of an activator. Unfortunately, the catalytic properties of these potentially active species have not been studied. The immobilized complex was instead additionally activated by $AlEt_3$ and then tested in the ethylene polymerization reaction. Its activity was in the range of 325–980 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 3.9 atm), and the molecular weight of the resulting PE amounted to 1.69×10^6 Da. The homogeneous precursor, activated by MAO, was more active [580–1290 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3.9 atm] but catalyzed the formation of lower-molecular-weight polyethylenes ($3.17-5.11 \times 10^5$ Da).

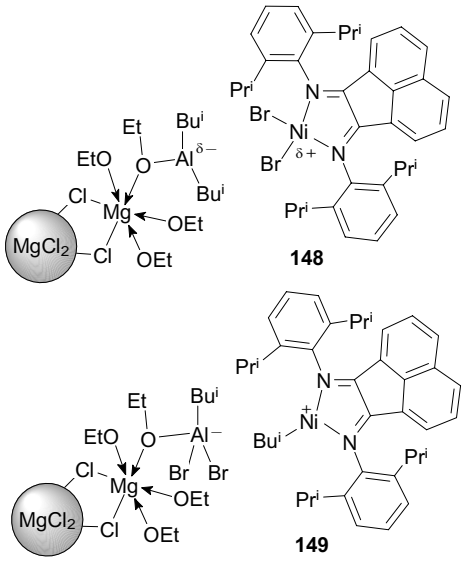
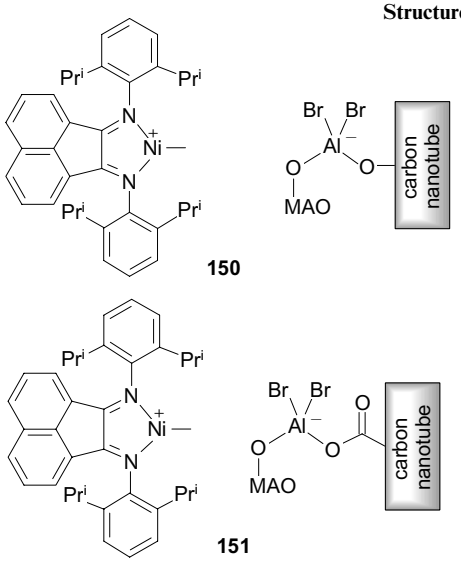


Figure 10. Possible structures of the α-diimine nickel complex immobilized on the surface of ethoxylated $MgCl_2$ treated with by $AlBu^i_3$.

Structures 150, 151

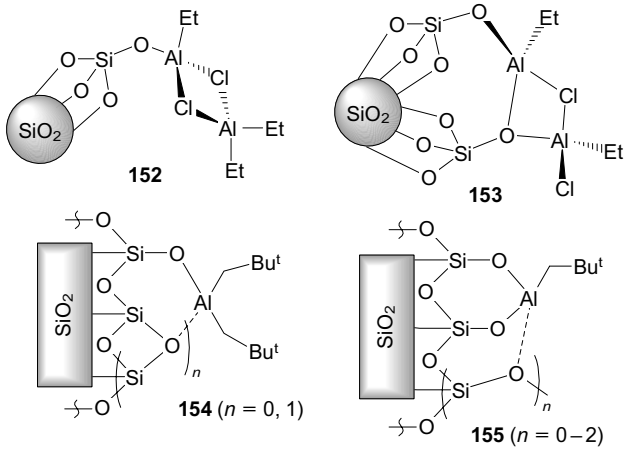


α-Diimine nickel complexes **150**, **151**, were supported onto the surface of MAO-treated carbon nanotubes in a similar way.[194] However, both systems (after additional activation by MAO) demonstrated low catalytic activity [105–204 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm] and led to the formation of high-molecular-weight polyethylenes ($M_w \leqslant 3.15 \times 10^5$ Da) filled with 11–25% nanotubes.

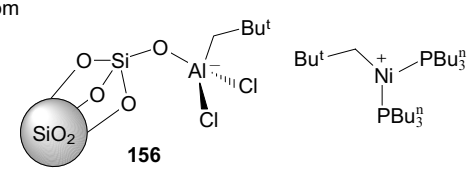
The questions of the formation of silica gel-supported OACs and their use in fabrication of heterogeneous catalysts for ethylene oligomerization were considered in detail.[208, 209] In particular, grafted organoaluminium dimeric particles of different composition and structure (in particular, **152** and **153**) were obtained as a result of the interaction of SBA-15, MCM-41 or Aerosil SiO_2 with Et_2AlCl. A detailed analysis of the formation of supported Et_2AlCl was conducted using ^{27}Al NMR, supplemented with the DFT simulation results. It showed that the above mentioned species amount to 20% (**152**) and 50% (**153**) of the total number of aluminium sites on the silica gel surface. After the interaction of grafted activator with $NiCl_2(PBu^n_3)_2$, the newly formed heterogeneous catalysts were involved in ethylene oligomerization with an activity of up to 14 000 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 4.9 atm), calculated based on the data of a 5-min experiment. The homogeneous system $NiCl_2(PBu^n_3)_2-Et_2AlCl$ turned out to be much more active: 24 800 kg mol (Ni)$^{-1}$ h^{-1} under similar conditions; however, heterogeneous catalysts exhibited excellent stability. For example, after a 1-h reaction their activity reduced to only 11900 kg mol(Ni)$^{-1}$ h^{-1}, without any changes in selectivity to butenes (94–99%), the majority of which was 2-butene.

A similar treatment of the surface of silica gel previously dehydroxylated at 700 °C with tris(neopentyl) aluminium $Al(CH_2Bu^t)_3$ leads to the formation of two types of aluminium-containing species: **154** (20%) and **155** (80%).[209] In the authors' opinion, when these species interact with $NiCl_2(PBu^n_3)_2$, only **154** sites act as an activator leading to the formation of ion pairs **156**. After activation of $NiCl_2(PBu^n_3)_2$ by a heterogeneous cocatalyst (consisting of a mixture of **154** and **155**), the *in situ* obtained catalytic system demonstrated an activity of up to 263 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 4.9 atm), whereas the preparatively obtained catalyst **156** was less active

Structures 152 – 156



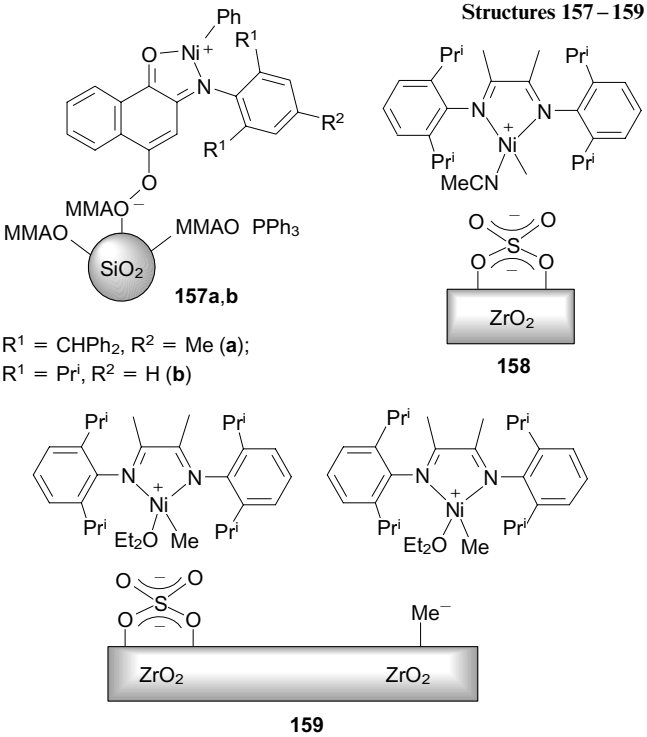
n is the number of O atoms located on the SiO_2 surface and coordinated to the Al atom



[110 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 4.9 atm]. Nevertheless, the activity of both catalytic systems exceeded that of $NiCl_2(PBu^n_3)_2$, activated by Et_2AlCl and grafted onto the same silica gel [78 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 4.9 atm]. The preparatively obtained catalyst **156** was also characterized by a high selectivity to butenes (96%) and 1-butene (72%).

A possibility of using MMAO (grafted onto a silica gel surface) as an activator has also been shown.[210] The activation occurs *via* the interaction between the ligand and the support with formation of zwitter-ionic complexes **157**.

Structures 157 – 159

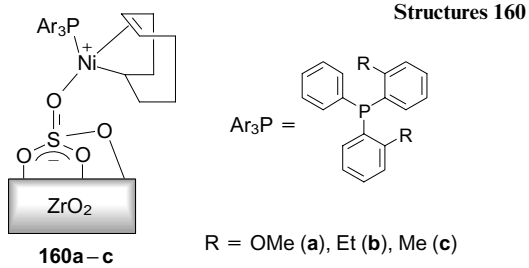


The activity of heterogeneous catalysts **157** was 1.5 – 2 times higher than that of ungrafted complexes, activated by dry MMAO, both in cases of ethylene homopolymerization [up to 5900 kg mol(Ni)$^{-1}$ h^{-1} *vs* 3000 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm] and of its copolymerization with 5-hexene-1-yl acetate and allyl acetate [up to 4700 kg mol(Ni)$^{-1}$ h^{-1} *vs* 3060 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 9.9 atm]. As a result higher-molecular-weight products with similar MWD values were formed and the degree of comonomer incorporation at a level of 0.19 – 0.94% was retained.[210] However, it should be noted that the duration of the catalytic process in this case often does not exceed 5 – 7 min; therefore, the real activity values measured during 1 h experiment may be significantly lower due to the catalyst deactivation.

Dehydroxylated ZrO_2, treated with sulfuric acid and thus containing Brønsted acid sites, can be used as an alternative support for noncovalent binding of transition metal complexes. The interaction of the methylated α-diimine nickel complex with such a support, depending on the solvent chosen, resulted in the formation of compounds **158** – MeCN and **159** – Et_2O.[211] Both heterogeneous catalysts initiated ethylene polymerization; complex **159** surpassed **158** in activity by a factor of more than 2 [to 586 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3 atm] and led to the formation of a much higher-molecular-weight polyethylene (M_n = 5.4 – 15.3 × 10^4 Da *vs* 1.46 – 2.85 × 10^4 Da) with the retention of MWD (1.8 – 2.4) and polymer microstructure (*b* = 71 – 92/1000C) compared to polymers obtained using **158**. Catalyst **159** also demonstrated ability to copolymerize ethylene with methyl 10-undecenoate; however, the comonomer incorporation was only 0.4% in this case, and the catalytic activity did not exceed 5 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 3 atm).

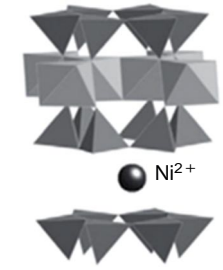
Moderately active ethylene polymerization catalysts **160** [3 – 4 kg mol(Ni)$^{-1}$ h^{-1}, $p_{ethylene}$ = 3 atm)] were formed as a result of the successive treatment of sulfated zirconia with PAr_3 and $Ni(COD)_2$.[212] The catalytic process led to the formation of polyethylene with a small branching degree (*b* = 20 – 35/1000C). One can suggest that further modification of the metal centre environment in these systems will make it possible to increase the catalytic activity and to enable the copolymerization of ethylene with polar monomers.

Structures 160

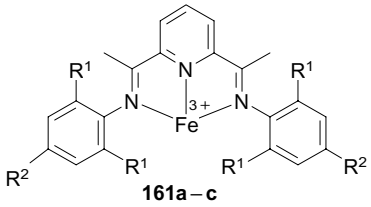


Another way to implement noncovalent immobilization of iron triad metal complexes is to intercalate cations of these metals into layered clays or fluorotetrasilicon mica with the subsequent treatment of the intercalate with the ligand. The thus obtained bis(imino)pyridine iron complexes **161**, located in the interlayer space, being activated by MAO, $AlEt_3$ or $AlBu^i_3$, polymerized ethylene with an activity of up to 1643 kg mol(Fe)$^{-1}$ h^{-1} ($p_{ethylene}$ = 2 atm).[213] The less sterically hindered complexes

Structures 161 – 168

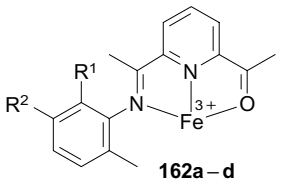


M = Ni^{2+}, Co^{2+}, Fe^{2+} or Fe^{3+}



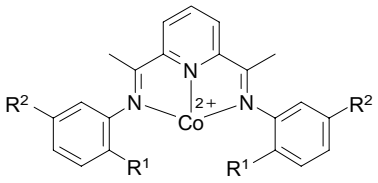
161a – c

R^1 = Me, R^2 = H (**a**);
R^1 = R^2 = Me (**b**);
R^1 = Pr^i, R^2 = H (**c**)



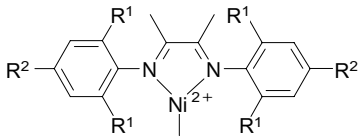
162a – d

R^1 = Me, R^2 = H (**a**);
R^1 = H, R^2 = Me (**b**);
R^1 = R^2 = H (**c**);
R^1 = H, R^2 = Cl (**d**)



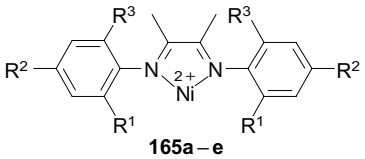
163a – c

R^1 = R^2 = Me (**a**);
R^1 = Me, R^2 = F (**b**);
R^1 = CF_3, R^2 = H (**c**)



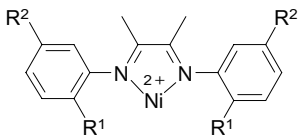
164a – d

R^1 = Me, R^2 = H (**a**);
R^1 = R^2 = Me (**b**);
R^1 = Et, R^2 = Me (**c**);
R^1 = Pr^i, R^2 = Me (**d**)



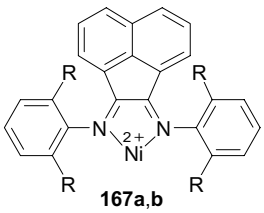
165a – e

R^1 = F, R^2 = R^3 = H (**a**);
R^1 = R^3 = H, R^2 = F (**b**);
R^1 = R^2 = F, R^3 = H (**c**)
R^1 = R^2 = R^3 = F (**d**);
R^1 = R^2 = R^3 = H (**e**)



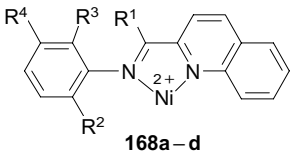
166a,b

R^1 = Me:
R^2 = H (**a**), Me (**b**)



167a,b

R = H (**a**), Me (**b**)



168a – d

R^1 = R^4 = H, R^2 = R^3 = Me (**a**);
R^1 = R^2 = R^3 = Me, R^4 = H (**b**);
R^1 = R^2 = Me, R^3 = R^4 = H (**c**);
R^1 = R^2 = R^4 = Me, R^3 = H (**d**)

162 catalyzed (under similar conditions) the formation of a mixture of oligomeric (C_4-C_{20}) and polymeric products with an activity of up to 39000 kg mol(Fe)$^{-1}$ h^{-1} ($p_{ethylene}$ = 3.9 atm),[214] which exceeds that of the homogeneous analogue by a factor of more than 4. Intercalated cobalt complexes with bis(imino)pyridine ligands **163**, treated with $AlEt_3$, also turned out to be more active by a factor of more than 2 [to 2310 kg mol(Co)$^{-1}$ h^{-1} (**163c**), $p_{ethylene}$ = 6.9 atm] than their homogeneous analogues activated by MAO. They also catalyzed formation of a mixture of oligomeric (C_4-C_{20}) and polymeric products.[215] Intercalates of nickel complexes with α-diimine ligands **164** polymerized ethylene with an activity of up to 2300 kg mol(Ni)$^{-1}$ h^{-1} (**164a** – $AlBu^i_3$, $p_{ethylene}$ = 6.9 atm).[216] Precatalysts **165** were obtained using both unsubstituted and fluorine-substituted α-diimine ligands; the application of these precatalysts after their activation by $AlEt_3$ or $AlBu^i_3$ led mainly to ethylene oligomerization with Schulz – Flory distribution of products (C_4-C_{22}).[217] However, as well as in the case of previously considered complexes of cobalt (**163**) and iron (**162**), wax like polyethylenes (from 4 to 23%) were observed among the reaction products. The same pattern was observed for grafted nickel complexes **166** and **167a**; however, solid reaction products dominated in this case (72 – 95%).[218] Precatalysts **164a** and **167b**, treated with $AlEt_3$, also demonstrated ability to catalyze copolymerization of ethylene with 1-hexene, 1-octene and cyclopentene; complex **164a** turned out to be much more efficient.[219]

A method for formation of precatalysts by intercalation of a cation and subsequent template synthesis of a ligand in coordination sphere of this cation was described.[220, 221] The catalytic activity of Fe(III) complexes **161** immobilized on different supports and treated with $AlEt_3$ was lower by a factor of more than two as compared with that of their analogues obtained using the classical approach.[221] At the

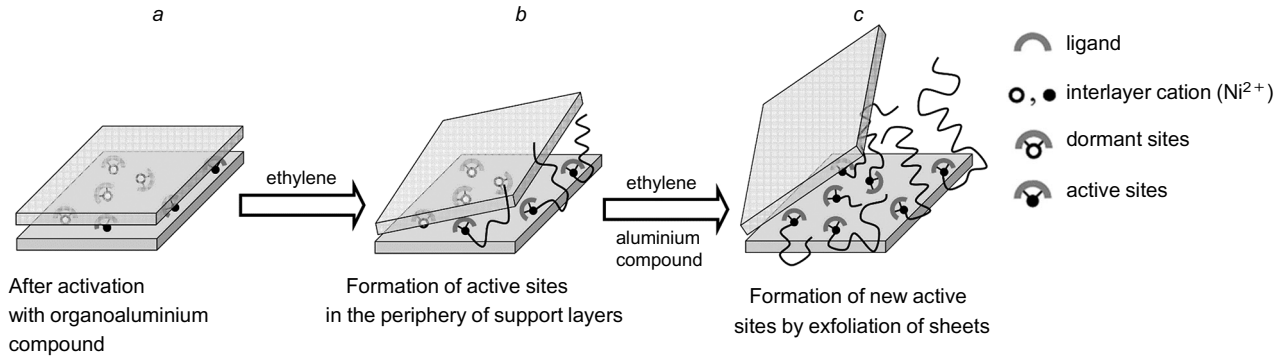


Figure 11. Proposed mechanism of activation of precatalysts intercalated in layered supports.[220] Published with permission from Elsevier.

same time, grafted Ni(II) complexes **168** with iminoquinoline ligands, obtained in a one-step process, surpassed the corresponding analogues. After activation by $AlEt_3$, catalysts **168** initiated ethylene oligomerization with an activity of up to 80 kg mol(Ni)$^{-1}$ h^{-1} ($p_{ethylene}$ = 9.9 atm).[220] However, PE waxes were formed as a minor product at a reaction temperature below 60 °C.

Despite the large values of catalytic activity obtained in some cases, all intercalated precatalysts have two main drawbacks: low selectivity and a long-term induction period. The former drawback, apparently, can be explained by the difference in the nature of newly formed active sites, due to which PE waxes are formed during oligomerization as a by-product, and the obtained polymers are characterized by a wide MWD. The latter drawback is directly related to the activation of intercalated complexes. In particular, the compounds located in the periphery of interlayer space are activated first, and then gradual exfoliation of support layers is observed during the catalysis, which is accompanied by a significant rise in the catalytic activity (Fig. 11).[220] The duration of induction period depends strongly on the activator choice and may reach 1.5–2 h (Et_2AlCl). It should also be noted that polymers obtained using the above-described catalytic systems are in fact composites, because encapsulation of a layered support occurs during the catalytic process.[216, 219]

5. Conclusion

Many studies devoted to the catalytic properties of iron triad metal complexes have been published in the last five years, which indicates the emergence of new lines of research in this field. These studies become even more crucial in view of the new advances in the synthesis of light olefins from easily accessible methane.[222] Many investigations are devoted to the catalytic systems based on nickel complexes, which is related to their high activity, ability to catalyze structural isomerization of a polymer chain *via* 'chain-walking' process and some other unusual catalytic properties (Table 2).

For example, the catalytic systems based on nickel, cobalt and iron complexes showed the ability to be involved in ethylene trimerization with a high selectivity (up to 98%) and, therefore, compete with chromium complexes in selective formation of 1-hexene.[102] In addition, these complexes do not catalyze the polyethylene formation as a by-product, which is an important technological advantage, because even trace amounts of polyethylene clog the reactor and thus must be removed. However, the use of different activators (MMAO or $Et_2AlCl/EtAlCl_2$) leads, apparently, to implementation of different mechanisms of hexene synthesis, which affects significantly not only the total selectivity but also the relative content of 1-hexene in the oligomer mixture. Hence, a detailed study of the mechanism of ethylene trimerization with the participation of the aforementioned systems is of key importance for selecting and optimizing the experimental technology.

The second, no less interesting area of research in the development of catalytic chemistry of late transition metals is the formation of odd carbon number olefins. The first-row transition-metal complexes are actively investigated as catalysts and components of catalytic systems, which can

Table 2. Promising directions in the use of iron triad metal complexes for ethylene oligomerization and polymerization.

Research area	Precatalysts (by metal atom)			Priority development pathways
	Ni	Co	Fe	
Ethylene trimerization (Section 4.1)	**49**–**52** [103, 104] **55**–**58** [107–110]	**53**, **54** [105] **59** [111]	**53**, **54** [105]	Determination of mechanism. Increase in 1-hexene yield. Catalyst heterogenization.
Formation of odd carbon number olefins (Section 4.2)	**48b** [95] **64**–**66** [118]	–	**60**–**63** [116, 117]	Determination of mechanism: metathesis, β-alkyl elimination, *etc*. Increase in selectivity
Formation of high-molecular-weight ethylene oligomers (Section 4.3)	**67**, **68** [130] **69**–**74** [131–133] **75**, **76** [134] **77**–**82** [135–138] **83** [139]	–	–	Systematic study of the structure–catalytic properties relationship for complexes. Study of the composition, structure and properties of high-molecular-weight fractions. Increase in the target product output
Formation of polyethylene waxes (Section 4.4)	**84**–**87** [137, 147] **88**–**91** [148–150] **92**–**94** [151, 152] **95** [153] **96** [154] **97** [155] **98** [156] **112** [171] **113** [172] **114** [173, 174] **115**, **116** [175] **117** [176] **118** [177]	**99** [157] **100** [158] **101** [160] **102** [161] **103** [162] **104** [164] **105** [165]	**106** [166] **107** [167] **108** [168] **109** [169] **110**, **111** [170]	Development of catalysts for synthesis of PE waxes functionilized by polar monomers. Postfunctionilization of PE waxes and formation of block copolymers on their basis.

implement the olefin metathesis reaction.[223] The first iron complex, capable of catalyzing ring-opening metathesis polymerization (ROMP) of norbornene was discovered recently.[126] Improvement of the selectivity to 'odd' olefins and study of the mechanism of this reaction catalyzed by systems based on nickel complexes should become an important step in the development of this line of research. Studies in this field may lead to a breakthrough in the concepts of formation of metathesis catalysts based on iron triad metal compounds or explain the formation of unusual products in a more conventional way.

A possible promising approach to obtaining the base oils is their direct synthesis from ethylene. Some systems based on post-metallocene nickel complexes can catalyze formation of high-molecular-weight branched ethylene oligomers. These unique properties of nickel catalysts (high activity, ability to catalyze structural isomerization of the carbon chain of oligomeric products, high fraction of heavy oligomers) again confirm the conclusions on the influence of the metal centre nature, which were reported in Section 2. However, the efficiency of these systems is still insufficiently high, and the properties, composition and structure of the oligomers obtained with their use have been poorly studied. The degree of ethylene oligomerization is controlled to a certain extent by a balanced change in the steric crowding and electron-donating properties of the ligand; the best results were observed for asymmetric structures. At the same time, the factors determining the synthesis of oligomers with a large number of long branches in the oligomer chain, which prevent wax crystallization and provide necessary viscosity of produced oil, have not been established yet. Important directions in the development of this area should be a systematic study of the relationship between the structure of complexes and their ability to catalyze the formation of oligomeric oils, as well as a more detailed analysis of the microstructure and viscosity properties of the products.

Another direction in the study of catalytic systems based on iron triad metal complexes is related to the formation of polyethylene waxes. Catalytic systems based on nickel compounds allow one to obtain highly branched polyethylene waxes, whose structure is close to that of the polyethylenes obtained by radical polymerization; however, these systems provide a controlled microstructure and molecular weights of the obtained products. Linear PE waxes are produced using catalytic ethylene polymerization on Ziegler–Natta catalysts and metallocenes; the chain length is controlled by adding hydrogen to the reaction medium, which not only terminates the chain growth but leads also to the formation of saturated polyethylenes. The catalytic systems considered within this review, which are based on cobalt and (partly) iron, make it possible to obtain PE waxes with a high content of terminal vinyl groups, which opens a possibility for their further functionalization and use as building blocks for synthesizing block copolymers. There is also a need in new high-efficiency catalysts in order to produce PE waxes with statistically distributed functional groups, because the existing systems have low activity and cannot provide a high level of polar comonomer incorporation.

To date, most of commercial catalytic processes of olefin polymerization and oligomerization have been implemented with application of heterogeneous catalysts, including immobilized metal complexes; this technology not only provides a better control over the polymer morphology and oligomerization selectivity but also allows one to reuse a catalyst, isolating it from the reaction medium. The number of publications devoted to the so-called 'surface organometallic chemistry' has been constantly increasing in the last years.[178, 182] This approach makes it possible to graft a metal centre directly on the support surface, thus avoiding the multistep ligand synthesis and its subsequent grafting. Moreover, the activity of the immobilized catalyst increases due to the increase in the density of active sites. The latest studies show that this approach allows one to form the heterogenized cocatalysts, which can be used to activate various complexes and obtain highly efficient heterogeneous catalytic systems. One would expect further development of the methods for modifying solid supports and deeper understanding of the processes occurring on their surface when a complex or activator is grafted. These developments are needed in order to design more efficient immobilized catalytic systems characterized by high selectivity and wide action range.

To conclude, we should note that the catalytic activity of transition metal complexes is often not limited by a particular catalytic process. In particular, complexes demonstrating rather moderate results in olefin oligomerization or polymerization may find application in some other catalytic processes in organic chemistry. For example, iron complexes can be used in catalysis of a number of organic transformations,[224] whereas iron, nickel and cobalt complexes are applied as catalysts in chemistry of diamondoids.[225]

The study was funded by the Russian Foundation for Basic Research (Project No. 20-13-50074), the Ministry of Science and Higher Education of the Russian Federation (Project No. AAAA-A16-116053110012-5) and the Russian Science Foundation (Project No. 18-13-00375).

6. List of abbreviations and designations

$b = n/1000C$ — number of branches per 1000 carbon atoms of polymer chain,
COD — cyclooctadiene,
DME — dimethoxyethane,
EXAFS — extended X-ray absorption fine structure,
GPC — gel permeation chromatography,
LAO — linear α-olefins,
LLDPE — linear low-density polyethylene,
LPPE — low-pressure polyethylene,
MAO — methylaluminoxane,
MMAO — modified methylaluminoxane,
M_n — number-average molecular weight,
M_v — viscosity-average molecular weight,
M_w — weight-average molecular weight,
MWD — molecular-weight distribution,
PAO — poly-α-olefins,
PAOO — poly-α-olefin oils,
PE — polyethylene,
PP — polypropylene,
OAC — organoaluminium compounds,
ROMP — ring opening metathesis polymerization,
SHOP — Shell higher olefin process,
UHMWPE — ultra-high-molecular-weight polyethylene,
VI — viscosity index,
XANES — X-ray absorption near-edge structure.

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