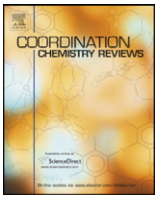
Coordination Chemistry Reviews 253 (2009) 827–861

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Metal catalysts for the vinyl/addition polymerization of norbornene

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Contents

Abbreviations: ^{n}Bu, *n*-butyl, C_4H_9; ^{t}Bu, *tert*-butyl, Me_3C; COC, cycloolefin copolymer; Cp, cyclopentadienyl; MAO, methylalumoxane; dMAO, dried MAO; MMAO, modified MAO; dppb, diphenylphosphinobutane; dppe, diphenylphosphinoethane; dppp, diphenylphosphino-propane; dpppt, diphenylphosphinopentane; Et, ethyl, C_2H_5; Me, methyl, CH_3; NB, norbornene, C_7H_{10}; NMR, nuclear magnetic resonance; ODCB, *ortho*-dichlorobenzene, $C_6H_4Cl_2$; PNB, poly(norbornene); py, pyridine, C_5H_5N; Ph, phenyl, C_6H_5; ^{i}Pr, *iso*-propyl, C_3H_7, $(CH_3)_2CH$-; ROMP, ring opening metathesis polymerization; TOPAS, thermoplastic olefin polymer of amorphous structure.

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doi:10.1016/j.ccr.2008.05.010

ARTICLE INFO

Article history:
Received 12 March 2008
Accepted 17 May 2008
Available online 23 May 2008

Keywords:
Catalysis
Norbornene
Polynorbornene
Polymerization
Vinyl/addition
Catalysts
Titanium
Chromium
Iron
Cobalt
Nickel
Palladium
Copper
Methylalumoxane
MAO
Boranes
Perfluorinated

ABSTRACT

A full literature account is given on work describing the transition-metal catalyzed vinyl or addition polymerization to polynorbornene covering the years of 2001 to the beginning of 2008. The interest in vinyl polynorbornene is driven by its dielectric and mechanical properties for the technical application in microelectronics applications. Metal catalysts of Ti, Cr, Fe, Co, Ni, Pd and Cu with methylalumoxane (MAO) or perfluorinated borane, e.g. $B(C_6F_5)_3$, cocatalysts are presented in terms of their activity and ligand effects. Among the ligands Schiff bases, tridentate *N*,*N*,*N*-bis(imino)pyridyl, bidentate *N*,*N*-anilido-imin, *N*,*O*-β-ketoiminato, *N*,*O*-salicylaldiminato (=salicylideneiminato), *O*,*O*-β-diketonato (=acetylacetonato), *P*,*P*-bis(phosphino)alkane, multidentate carbon ligands, e.g. allyl, cyclopentadienyl, aryl, and monodentate halo, especially chloro, triphenylphosphane (PPh_3) and phenyl feature prominently.

1. Introduction

This review is a follow-up to a review on the same topic published in 2001 [1]. Since then the number of publications dealing with metal complexes on the vinyl polymerization of norbornene (NB) has increased drastically. The progress on the vinyl/addition polymerization to (homo)polynorbornene (PNB) from 2001 to the beginning of 2008 is summarized here.

1.1. Modes of NB polymerization

Bicyclo[2.2.1]hept-2-ene, better known by its trivial name norbornene (NB, **1**) and its derivatives can be polymerized in three different ways (Fig. 1). Each route leads to its own polymer type and can be differentiated through the choice of catalyst.

The best-known polymerization of norbornene is the ring-opening metathesis polymerization (ROMP) technically applied in the Norsorex process [2]. The commercial polymerization process uses a $RuCl_3$/HCl catalyst in butanol. Other technical ROMP processes generally employ tungsten, molybdenum, rhenium or ruthenium catalysts as metal halides, metal oxides or metal oxo-chlorides in combination with alkylating agents (e.g. R_4Sn, Et_2AlCl) and promoting agents (e.g. O_2, EtOH, PhOH) [2]. While the industrial catalysts are usually heterogenous, academic ROMP research has focused on molecular single-component catalysts with metal–carbene complexes featuring prominently. Examples are tungsten–(carbene) complexes [3–10], molybdenum–(carbene) complexes [11–17] and ruthenium–(carbene) complexes [18–24]. The possibility of a ring-opening metathesis polymerization of norbornene with catalyst systems based on titanium [25], zirconium and hafnium [26], vanadium [27,28], niobium [29], tantalum [29–32], osmium [33] and rhenium [34] has been reported.

Little is known about the cationic and the radical polymerization of norbornene [35–38]. The result is a low molecular mass oligomeric material with 2,7-connectivity of the monomer. Initiators for the radical polymerization were, for example, azoisobutyronitrile (AIBN), *tert*-butyl peracetate or *tert*-butyl perpivalate. The cationic polymerization was started with $EtAlCl_2$ [35].

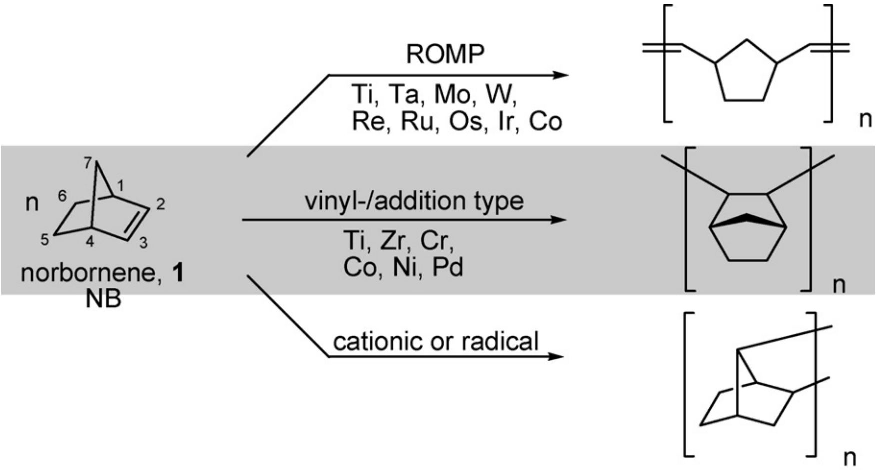


Fig. 1. Schematic representation of the three different types of polymerization of norbornene.

It is also possible to polymerize norbornene and to leave the bicyclic structural unit intact, i.e., to open only the double bond of the π-component. Such a polymerization which is akin to the classical olefin polymerization is termed a vinyl or addition polymerization here. The product does not contain double bonds any more. The vinyl polymerization of norbornene can take place as a homo- or as a copolymerization [39–41].

1.2. *Vinyl norbornene copolymerization*

In general, polycycloalkenes from a vinyl polymerization show extremely high melting points which lie above their decomposition temperatures (in air). Under vacuum the melting points were found (by DSC) to be 485 °C for polycyclobutene, 395 °C for polycyclopentene, and over 600 °C for polynorbornene [1,42]. Such high melting points make the homopolymers difficult to process. To lower the melting points, the cycloolefin can be copolymerized with ethene or propene. Of interest is the vinyl copolymerization of cyclic norbornene and acyclic α-olefins, especially ethene [43–47] and propene [48–50], to yield cycloolefin copolymers (COCs). Such a copolymerization can be carried out with metallocene, in particular zirconocene and half sandwich titanium/MAO-catalysts [51–56]. The COCs can be melt-processed, extruded to foils, tubes, pipes, fibers, etc. Their high transparency makes them ideally suited for optical applications. Cycloolefin copolymers have high refractive indices close to crown glass [57]. Thus, they can be applied as a glass substitute in lenses, prisms, carrier plates and foils for optical data storage, video and compact discs. They are envisioned as cover and focusing plates for solar cells or in glass fiber optics [58]. The norbornene/ethene copolymer features a high glass-transition temperature, excellent transparency, thermal stability and chemical resistance. It is suggested that these materials could be used for optical discs and fibers. With $C_2H_4(Ind'H_4)ZrCl_2$/MAO, ethene is inserted only 1.5–3.2 times faster than norbornene and copolymers containing more than 50 mol% of norbornene units can be made; if the norbornene concentration is higher than 60 mol%, a glass transition point of about 120 °C can be reached [59]. Hoechst (now Ticona) and Mitsui Sekka-have jointly developed a highly transparent technical plastic: a *t*hermoplastic *o*lefin *p*olymer of *a*morphous *s*tructure (TOPAS) [60]. TOPAS® COC is a copolymer from norbornene and ethene made through metallocene catalysis. The properties of TOPAS open applications in the market of compact discs, magneto-optic storage discs, packaging materials and especially as toner binder in color printers [61–65]. Cycloolefin copolymerization and COCs have in part been included in some overviews on metallocene catalysts [66–72].

1.3. *Substituted norbornenes*

In this review we focus on metal complexes which have been described in connection with the vinyl *homo*polymerization of *unsubstituted* norbornene. However, the same metal complexes can also be used for the polymerization of *substituted* norbornenes or for the *co*polymerization of different *substituted* norbornenes, provided the substituent does not contain deactivating functional groups. Substituents with donor atoms, like in esters, may slow down the chain propagation through metal coordination. Usually the norbornene derivatives are functionalized in the 5-position.

For the norbornene derivatives 5-vinyl-2-norbornene ($NB{-}CH{=}CH_2$), 5-ethylidene-2-norbornene ($NB{=}CHCH_3$) and dicyclopentadiene (Fig. 2) the activities in the homopolymerization with the half sandwich titanium/MAO-catalyst ($(^tBuNSiMe_2Flu)TiMe_2$/dMAO were two orders of magnitude lower than that for norbornene. Yet, the copolymerization of ethene and $NB{=}CHCH_3$ proceeded with better activity than the homopolymerization of the substituted norbornene. The glass transition temperature of the ethene/$NB{=}CHCH_3$ copolymer changed from 70 °C to 155 °C with the increase in 5-ethylidene-2-norbornene content from 27 to 68 mol%. Addition of norbornene as a third monomer to the ethene/$NB{=}CHCH_3$ copolymerization yielded a terpolymer with a glass transition temperature $T_g > 200$ °C [73].

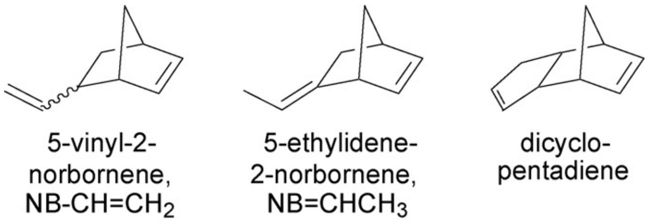


Fig. 2. The NB derivatives $NB{-}CH{=}CH_2$, $NB{=}CHCH_3$ and dicyclopentadiene.

Co- and terpolymerizations of 5-norbornene-2-methanol ($NB{-}CH_2OH$) and 5-norbornene-2-carboxylic acid (NB–COOH) were carried out with ethene and norbornene, respectively, using the homogeneous catalyst system $^iPr[CpInd]ZrCl_2$/MAO. From ^{13}C NMR the mol% of the substituted norbornene in the co- or terpolymer was 5–12% at a content of 50–30 mol% of the derivative in the feedstock composition. For the ethene copolymerization and the ethene/norbornene terpolymerization with 5-methyleneoxytriethylsilane-2-norbornene and 5-methyleneoxy-*tert*-butyldimethylsilane-2-norbornene their incorporation rate in the polymer was 5–6 mol% at a content of 20 mol% in the monomer feedstock (Fig. 3) [74].

Late transition metals are more tolerant to polar functionalities in the monomer and the formed polymer. On the other hand later transition metals are often ineffective for the copolymerization of ethene with norbornene because the former as well as other 1-alkenes act as a chain transfer agent through β-hydrogen elimination. Hence, a catalyst for the copolymerization of ethene with functionalized norbornenes most be both tolerant of functional groups and resistant to β-hydrogen elimination. Yet in particular with nickel-based systems for the copolymerization of ethene with functionalized norbornenes the extent of incorporation of the norbornene derivative monomer is less than 25 mol% [75].

Co- and terpolymerization of norbornene, 5-norbornene-2-carboxylic acid ethyl ester ($NB{-}CO_2Et$), 5-norbornene-2-methyl

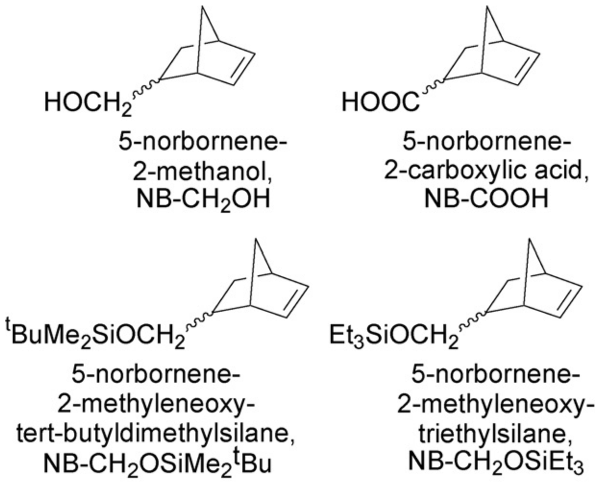


Fig. 3. The NB derivatives $NB{-}CH_2OH$, NB–COOH, $NB{-}CH_2OSiMe_2{}^tBu$ and $NB{-}CH_2OSiEt_3$.

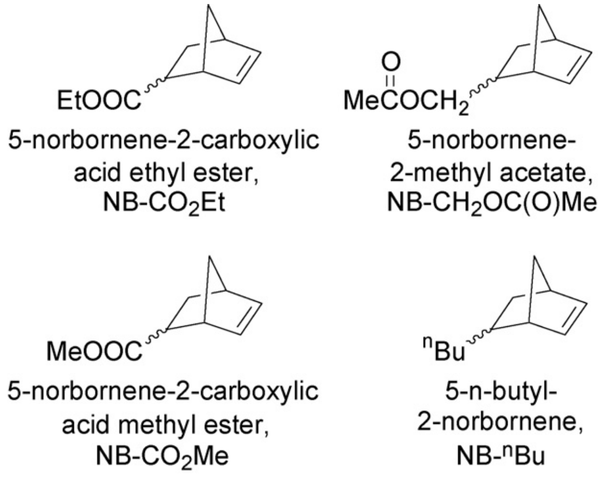


Fig. 4. The NB derivatives NB–CO$_2$Et, NB–CH$_2$OC(O)Me, NB–CO$_2$Me and NB–^{n}Bu.

acetate (NB–CH$_2$OC(O)Me), 5-norbornene-2-carboxylic acid methyl ester (NB–CO$_2$Me) and 5-*n*-butyl-2-norbornene (NB–^{n}Bu) with ethene and 1-alkenes, respectively, using square-planar nickel complexes with anionic *P*,*O*-chelate ligands (Figs. 4 and 5) gave up to 50 mol% incorporation only for norbornene, leading to an essentially alternating copolymer. NB derivatives with oxygen functionalities are noted to give lower (<19 mol%) incorporation and reaction rates, as well as polymer molecular weights. In the terpolymerization with 1-alkenes the additional chain-transfer pathways following 1-alkene insertion also decrease the polymer molar mass. The T_g values increase with the norbornene content [76].

Copolymerization of norbornene or the functional derivatives NB–CO$_2$Et, NB–CH$_2$OC(O)Me, NB–CH$_2$OH and 5-norbornene-2-acetate (NB–O$_2$CMe) with ethene using palladium allyl complexes with anionic *P*,*O*-ligands gave up to 40 mol% incorporation of norbornene. The copolymerization could even be carried out in the presence of water (Fig. 6) [75].

It is noteworthy that the *endo*-functionalized norbornenes are polymerized more slowly compared to the *exo*-analogues because of the possible coordination of the donor-containing substituent to the metal atom (Fig. 7), which attenuates the polymerization activity. Since the synthesis of substituted norbornenes is accomplished in a Diels–Alder reaction, always a mixture of *endo*- and *exo*-isomers is obtained. Hence, the polymerization of substituted derivatives proceeds slower than in the case of the unsubstituted norbornene monomer [77,78]. Examples for the polymerization of substituted norbornenes are given in [77–85].

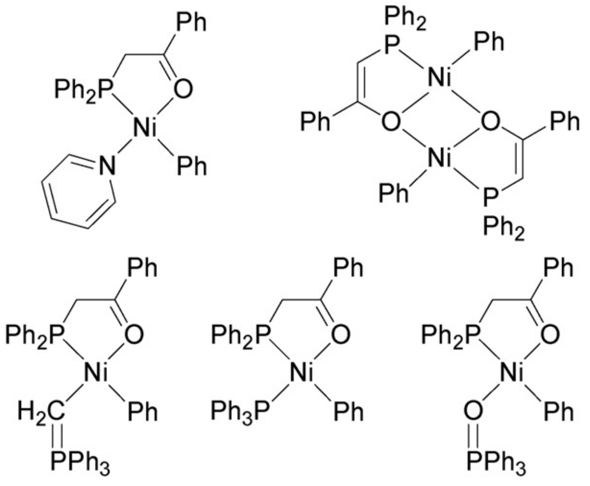


Fig. 5. Square-planar nickel complexes with anionic *P*,*O*-chelate ligands used for the co- and terpolymerization of NB, NB–CO$_2$Et, NB–CH$_2$OC(O)Me, NB–CO$_2$Me and NB–^{n}Bu with ethene and 1-alkenes.

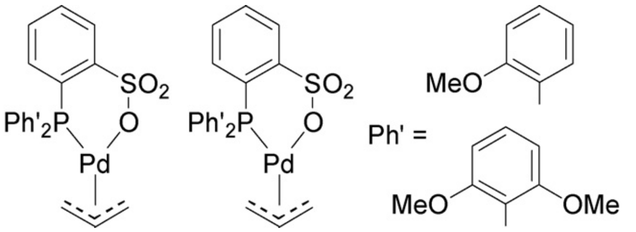


Fig. 6. Palladium allyl complexes used for the copolymerization of NB or the functional derivatives NB–CO$_2$Et, NB–CH$_2$OC(O)Me, NB–CH$_2$OH and NB–O$_2$Cme with ethene.

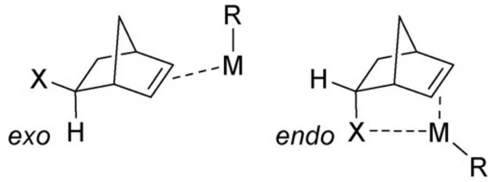


Fig. 7. Modes of bonding for functionalized norbornene derivatives (X = coordinating functionality).

1.4. Properties and applications of vinyl polynorbornene (PNB)

The vinyl addition norbornene (derivatives) (co-)polymer is a specialty polymer. PNBs from norbornene and its functional derivatives possess high glass transition and decomposition temperatures. Furthermore, they show a low water uptake, a small optical birefringence and dielectric loss [86]. Vinyl polynorbornene is investigated inter alia as a deep UV photoresist and interlevel dielectric in microelectronics applications. High glass transition temperature polynorbornenes exhibit many of the key performance criteria necessary for these demanding applications, which include good adhesion to a variety of films and substrates, thermal stability, high elongation-to-break values, and low stress [87]. Films made from norbornene vinyl polymer are excellent in transparency and heat resistance and have unchanged viscoelastic and electric characteristics to markedly high temperatures. Such a film is suitable for a condenser or an insulator [88] Polynorbornene films are applied as cover layers for liquid-crystal displays. The polymer is developed by Promerus (www.promerus.com) under the trade name Avatrel® dielectric polymer [87]. The sometimes poor adhesion of polynorbornene can be improved by attaching triethoxysilyl groups on the backbone to lower the rigidity of the system and result in higher elongation-to-break values and a decrease in residual stress [87]. The addition polymerization of substituted norbornenes was adopted for the preparation of electroactive polymers, in particular polymers designed as electrooptical materials [89]. Bis(trifluoromethyl)carbinol-substituted polynorbornenes are promising materials for future 157 nm photoresist resins [90].

2. Metal complexes for the vinyl NB polymerization

From their metal composition the catalysts for vinyl polymerization can be divided into three groups: (a) the early transition metal, especially metallocene catalysts of zirconium, which also give excellent results for ethene/norbornene copolymerization [1,51–53,91–93]; (b) the less used and seldom mentioned complexes of chromium, iron, cobalt and copper; (c) the often highly active late transition-metal nickel(II) and palladium(II) catalysts.

Research on metallocenes for norbornene homopolymerization seems to have ceased since 2001 [94]. Metallocenes are still actively investigated for norbornene–olefin copolymerization [51–56].

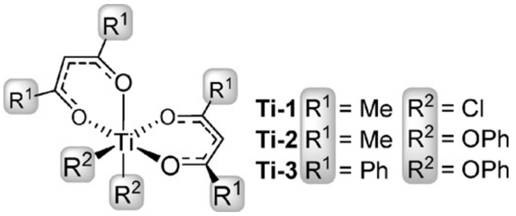
Usually, the metal complexes need to be activated by a cocatalyst for NB polymerization.

2.1. Cocatalysts

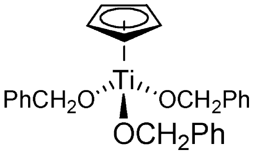
Cationic palladium complexes of the general formula $[Pd(NCR)_4]^{2+}2X^-$ are active without a cocatalyst [95]. These palladium systems contain weakly bound nitrile ligands and weakly coordinating counter ions, such as BF_4^-. Most other metal complexes are inactive as such (precatalysts) and require a cocatalyst for their activation. Most frequently, methylalumoxane (MAO) is used as cocatalyst, followed by perfluorinated boranes, such as tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ and trityl-tetrakis(pentafluorophenyl)borate, $Ph_3C^+B(C_6F_5)_4^-$. Recently, boron trifluoride/etherate, $BF_3{\cdot}Et_2O$ was also employed. Non-perfluorinated boranes, such as triphenylborane, $B(C_6H_5)_3$ were tested as cocatalysts for comparison but usually did not generate active species. The perfluorinated boranes were either employed alone or together with aluminum alkyls as cocatalyst. The aluminum alkyls, mainly triethylaluminum, $AlEt_3$ are added as scavengers towards impurities. Importantly, the combination of $B(C_6F_5)_3$ and $AlMe_3$ leads to a facile aryl/alkyl group exchange and for an equimolar ratio results in the formation of BMe_3 and $Al(C_6F_5)_3$ [96,97]. Accordingly, $B(C_6F_5)_3$ and $AlEt_3$ undergo an analogous ligand exchange reaction [98] The reaction between $B(C_6F_5)_3$ and the higher aluminum alkyls tri(*iso*-butyl)aluminum and tri(*n*-hexyl)aluminum (AlR_3 with R = *i*-Bu, *n*-C_6H_{13}) is slower and requires excess AlR_3 to shift the $C_6F_5 \leftrightarrow R$ exchange equilibria to almost complete formation of $Al(C_6F_5)R_2$ and BR_3. At equimolar ratio the equilibrium lies on the side of the unchanged borane together with its boranate $[B(C_6F_5)_3R]^-$ anion. For tri(*n*-octyl)aluminum even at large $Al(n\text{-}C_8H_{17})_3$ excess no $C_6F_5 \leftrightarrow$ alkyl exchange can be observed, but boranate anions form [98].

2.2. Titanium and zirconium catalysts

There are a few studies dealing with titanium catalysts for the vinyl homopolymerization of norbornene in recent years. Polynorbornene (PNB) was obtained with the β-diketonate titanium complexes **Ti-1** to **Ti-3** after being activated with MAO, with **Ti-3** showing the highest activity of 8×10^3 $g_{polymer}/mol_{Ti}$ h in the series [99].

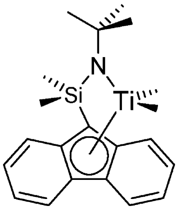


With the half-sandwich titanocene precatalyst **Ti-4** in combination with MAO pure vinyl-type PNB, soluble in common organic solvents, was obtained when the temperature did not exceed 80 °C and for an Al/Ti ratio of ≤60. In this case the highest monomer conversion of 69% was found for a temperature of 60 °C and an Al/Ti ratio of ~40. The polymer products obtained at temperatures higher than 80 °C and Al/Ti ratios larger than 60 contained certain amounts of the ring-opened polymer. At these conditions part of the titanium species were pyrolized to form an alkylidene compound which was able to catalyze ROMP [100].

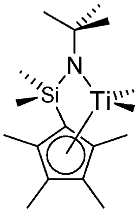


Ti-4

The half-sandwich titanocene precatalysts (^{t}BuN–Me_2Si–Flu)$TiMe_2$ (**Ti-5**) and (^{t}BuN–Me_2Si–Me_4Cp)$TiMe_2$ (**Ti-6**) could be activated with Me_3Al-free MAO (dried MAO, dMAO) for the addition polymerization of norbornene [101] Dried MAO is prepared by drying ordinary MAO (toluene solution) in vacuo to remove toluene and $AlMe_3$. From its synthesis, MAO contains residual trimethylaluminum. About 5% $AlMe_3$ is stated in commercial MAO-toluene solutions in company certificates, although other studies suggest up to 25–50% of partly free and "associated" $AlMe_3$ to MAO [102,103]. The $AlMe_3$ content is important for the solubility of MAO in aromatic hydrocarbons [104]. The agreement appears to be that the MAO/$AlMe_3$ oligomers are fluxional molecules with a dynamic equilibrium, which changes their size and structure [102,105,106]. Compound **Ti-5** showed good activities in a region of 10^6 $g_{polymer}/mol_{Ti}$ h for temperatures of 20 °C and 40 °C, but only a low activity at 0 °C, whereas precatalyst **Ti-6** showed only very low activities even at 40 °C. It was assumed that **Ti-5** provides a larger aperture of the coordination sphere [107–109] that favors an easier access of norbornene for propagation. The living nature of this catalyst system was investigated by changing the monomer concentration and by postpolymerization experiments at 20 °C indicating a living polymerization [110].



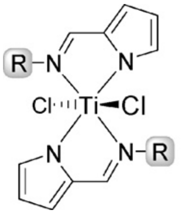
Ti-5



Ti-6

The norbornene polymerization with **Ti-5** exhibited only poor or no activity with MAO or $Ph_3C^+B(C_6F_5)_4^-$ at a wide range of temperatures (20–80 °C) [111]. Therefore a more detailed investigation with the cocatalysts dMAO, modified MAO (MMAO) and $Ph_3C^+B(C_6F_5)_4^-$ in combination with Al^iBu_3 was performed. With dMAO and MMAO the activity and M_n values increased with increasing Al/Ti ratios. System **Ti-5**/MMAO showed a better performance than **Ti-5**/dMAO, especially at the highest Al/Ti ratio of 800. Each catalyst **Ti-5**/dMAO, **Ti-5**/MMAO, and **Ti-5**/borate/$AlOct_3$ showed good activity over a wide range of reaction temperatures. For the dMAO and MMAO systems the activity improved with increasing temperature, being highest at 60 °C, whereas the borate system showed the maximum activity at 20 °C. The catalyst system **Ti-5**/borate/AlR_3 showed the overall highest activities of up to 4.8×10^6 $g_{polymer}/mol_{Ti}$ h compared to the dMAO and MMAO system which both exhibited activities of around 10^6 $g_{polymer}/mol_{Ti}$ h [111].

The titanium catalysts **Ti-7** to **Ti-10** bearing bis(pyrrolide-imine) ligands were predominantly applied for the copolymerization of norbornene and ethylene with high activities of more than 10^6 $g_{polymer}/mol_{Ti}$ h when activated with MAO. Complex **Ti-7**/MAO interestingly showed practically no reactivity towards the norbornene homopolymerization [112].



Ti-7 R = cyclohexyl
Ti-8 R = phenyl
Ti-9 R = 4-^{t}Bu-cyclohexyl
Ti-10 R = cyclooctyl

With the system $TiCl_4/AlEt_2Cl$ norbornene was *oligomerized* at 0 °C at a molar monomer/titanium ratio of about 11 leading to an X-ray amorphous fraction, soluble in Et_2O, and a crystalline fraction, insoluble in Et_2O. Single crystal X-ray analysis indicated that the crystalline compound was a norbornene heptamer with a stereoregular 2,3-*exo*-disyndiotactic structure, containing a terminal ethyl group, which originates from the first monomer insertion into the Ti–Et bond of the catalyst [113] (Fig. 8).

The hydrooligomerization of norbornene, that is the norbornene polymerization in the presence of H_2, with *rac*-$Me_2C(Ind')_2ZrCl_2$/MAO was used to deliberately obtain oligomers in order to gain insight into the microstructure of polynorbornene. The oligomers were separated by preparative HPLC and their structures, e.g. that of a norbornene pentamer (Fig. 9), determined by single-crystal X-ray diffraction. These studies show that in-between the regular *cis*-2,3-*exo* vinyl/addition insertions a metallocene-catalyzed σ-bond metathesis can take place. The *syn*-hydrogen on C7 (the bridgehead) of the previous to last inserted monomer interacts with the Zr atom which in the σ-bond metathesis becomes now bound to C7. Thus, the chain continues with the next insertion on the C7-bridgehead carbon atom of the previous to last monomer [114]. The pentamer X-ray structure with the same bridgehead (C7) substitution in a central trisubstituted norbornene unit (Fig. 9) had already been described earlier, where it was isolated from the hydrooligomerization of norbornene catalyzed by *rac*-$C_2H_4(Ind'H_4)_2ZrCl_2$/MAO [115].

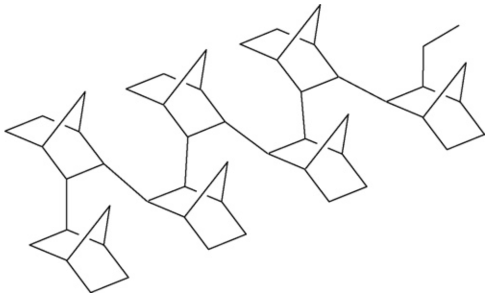


Fig. 8. Norbornene heptamer obtained with the system $TiCl_4/AlEt_2Cl$ having a 2,3-*exo*-disyndiotactic structure.

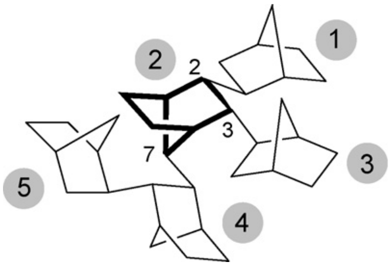
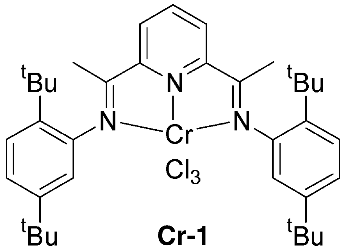


Fig. 9. Norbornene pentamer from a hydrooligomerization. The norbornene which was part of the σ-bond metathesis is highlighted for better visibility; the order of monomer insertion is given in the gray circles.

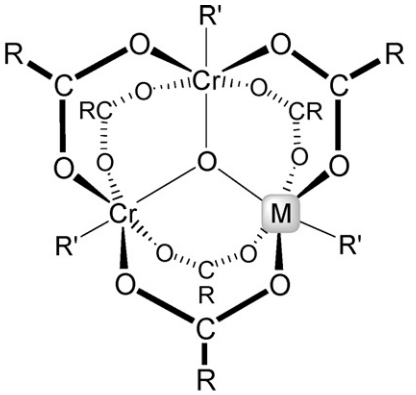
2.3. Chromium catalysts

The chromium(III) complex **Cr-1**, bearing a bulky bis(imino) pyridyl ligand, catalyzed the addition polymerization of norbornene with the moderate activity of 3.5×10^2 $g_{polymer}/mol_{Cr}$ h when activated with MAO (Al/Cr ratio = 500). Compound **Cr-1** was also applied for the ethylene polymerization with higher activities [116].



Cr-1

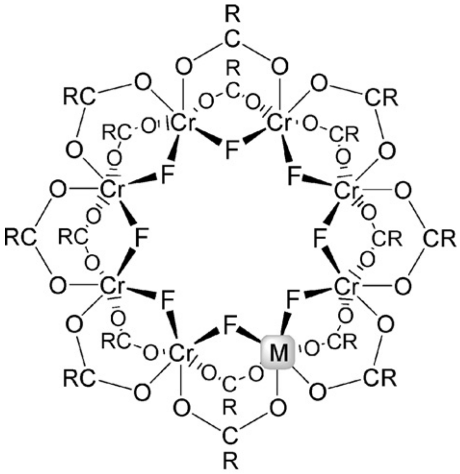
Furthermore, polynuclear homo- and heterometallic carboxylate complexes were used for the vinyl polymerization of norbornene [117]. It is noteworthy that the presence of nickel played an important role for the activity of those systems. The activity of the homometallic $\{Cr_3\}$, Ni-free triangles **Cr-2** and **Cr-3** was much less (by factor 10^2–10^3) than the heterometallic $\{Cr_2Ni\}$-triangle **Cr-4**, which exhibited a very high activity of 1.5×10^7 $g_{polymer}/mol_{metal}$ h. The activation was accomplished with MAO. Interestingly, even the less active $\{Cr_3\}$-cages **Cr-2** and **Cr-3** are 5–10 times more active than mononuclear $Cr(acac)_3$/MAO under the same conditions. More detailed investigations of the polymerization behavior were performed with the $\{Cr_2Ni\}$-triangle **Cr-4** using MAO and $B(C_6F_5)_3$ with or without $AlEt_3$ as cocatalysts and different kinds of addition sequences for the cocatalytic system. The addition sequence of the cocatalytic compounds influenced the polymerization activity. Higher activities are obtained using the addition sequence "**Cr-4** → $AlEt_3$ → $B(C_6F_5)_3$" compared to "**Cr-4** → $B(C_6F_5)_3$ → $AlEt_3$" (5.1×10^6 vs. 8.2×10^5 $g_{polymer}/mol_{metal}$ h) which may be reasoned by differences in $C_6F_5 \leftrightarrow$ ethyl exchange [98]. When $AlEt_3$ is added first such ligand exchange reaction can take place rapidly upon the subsequent addition of $B(C_6F_5)_3$ to the catalyst mixture and the metal complexes will then be activated with the stronger Lewis acid $Al(C_6F_5)_3$.



Cr-2 M = Cr, $[Cr_3O(O_2CPh)_6(H_2O)_3]ClO_4$
Cr-3 M = Cr, $[Cr_3O(O_2C^tBu)_6(H_2O)_3]O_2C^tBu$
Cr-4 M = Ni, $[Cr_2NiO(O_2C^tBu)_6(pip)_3]$
pip = piperidine, mor = morpholine

When $B(C_6F_5)_3$ is added first to the metal complex the boron atom may coordinate to the donor atom of a ligand to increase its coordination number to four [118], which completes the coordination sphere of the small boron atom and slows down the C_6F_5/Et-ligand exchange with the subsequently added $AlEt_3$ [98,119] Also, the borane $B(C_6F_5)_3$ alone could be used as an effective activator (tested for **Cr-4** and **Fe-5**) leading to similar activities of 3.1×10^5 $g_{polymer}/mol_{metal}$ h.

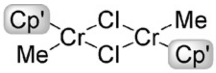
The activities of **Cr-5** to **Cr-10** showed the same trend as mentioned above for the precatalysts **Cr-2** to **Cr-4** [117]. With no nickel present (**Cr-5**, **Cr-8**, **Cr-9** and **Cr-10**) the activity of the $\{Cr_7M(\mu\text{-}F)_8\}$-wheels was mediocre around 10^5 $g_{polymer}/mol_{metal}$ h. Incorporation of Ni(II) as in $\{Cr_7Ni(\mu\text{-}F)_8\}$, **Cr-6** and **Cr-7** increased the activity by almost two orders of magnitude to 10^7 $g_{polymer}/mol_{metal}$ h.



$(Cation)[Cr_7MF_8(O_2C^tBu)_{16}]$

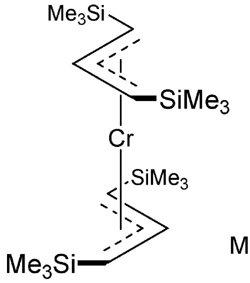
Cr-5 no cation M = Cr(III)
Cr-6 Cation = $Me_2NH_2^+$ M = Ni(II)
Cr-7 Cation = $Et_2NH_2^+$ M = Ni(II)
Cr-8 Cation = $Et_2NH_2^+$ M = Co(II)
Cr-9 Cation = $Et_2NH_2^+$ M = Mn(II)
Cr-10 Cation = $^nBu_2NH_2^+$ M = Fe(II)

The binuclear chromium(III) complexes **Cr-11** to **Cr-14** of the general type $[Cp'CrMeCl]_2$ [Cp′ = cyclopentadienyl, pentamethylcyclopentadienyl (Cp*), indenyl, fluorenyl] were synthesized to investigate both the electronic nature and the steric demand of substituted cyclopentadienyl ligands [107] on the polymerization activity of norbornene when activated with MAO [120]. The catalyst activity increased with the electron donating character of the Cp′-ligands (up to 88% yield, calculated activity 1.8×10^4 $g_{polymer}/mol_{Cr}$ h [121] for Cp′ = fluorenyl), whereas the steric demand affected the crystallinity of the obtained polynorbornenes. A monomer conversion of 88% was obtained with **Cr-14**/MAO (reaction time 1 h in toluene at 25 °C, monomer/Cr = 400, Al/Cr = 100). Catalyst **Cr-11**/MAO afforded only 2% conversion under the same reaction conditions. By increasing the steric demand of the cyclopentadienyl substituent docking of norbornene becomes more and more selective. As a result the crystallinity of polynorbornene is highest with Cp* as ligand. Furthermore, the copolymerization of norbornene and ethylene and the homopolymerization of ethylene were successfully performed with these chromium(III)/MAO catalysts [120].

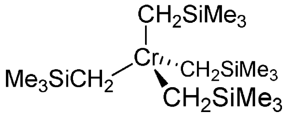


Cr-11 Cp′= cyclopentadienyl
Cr-12 Cp′= pentamethylcyclopentadienyl
Cr-13 Cp′= indenyl
Cr-14 Cp′= fluorenyl

The chromium(III) allyl complex **Cr-15** and the alkyl complex **Cr-16** were able to polymerize norbornene in moderate to good yields of up to 100% (activity 7.6×10^4 $g_{polymer}/mol_{Cr}$ h [121]) once activated with MAO. The polymer produced with the system **Cr-15**/MAO was not soluble in organic solvents. In contrast the polynorbornene generated with **Cr-16**/MAO was soluble in 1,1,2,2-tetrachlorethane-d_2 and 1,2,4-tetrachlorobenzene and was found to consist of norbornene oligomers. There was no evidence of unsaturated end-groups (by ^{1}H NMR). However, NMR and mass spectrometric evidence showed that the oligomers contained methyl end-groups and, thus, must have arisen by norbornene insertion into Cr–Me bonds, followed by rapid chain transfer to aluminum. When complex **Cr-15** was activated with the Lewis acid $B(C_6F_5)_3$ instead of MAO, no catalytic activity was observed [122].



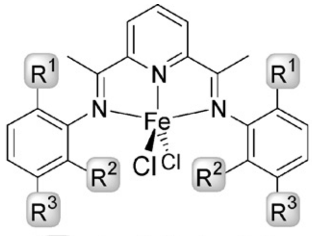
Cr-15



Cr-16

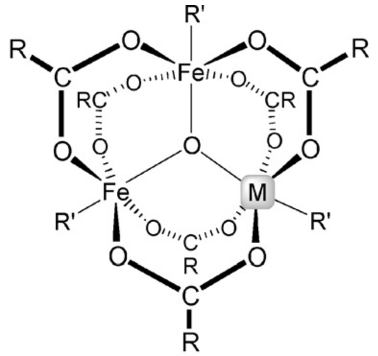
2.4. Iron catalysts

Complexes **Fe-1** and **Fe-2**, bearing bulky chelating tridentate bis(imino)pyridyl ligands, showed hardly any polymerization activity with MAO [123]. Interestingly, the closely related precursor complex **Fe-3** gave an activity of 9.25×10^3 $g_{polymer}/mol_{Fe}$ h once activated with MAO [116].



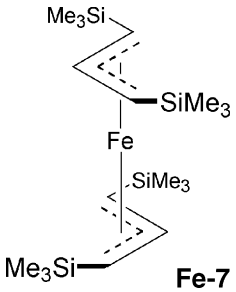
Fe-1 R^1 = ^{i}Pr R^2 = ^{i}Pr R^3 = H
Fe-2 R^1 = ^{t}Bu R^2 = H R^3 = H
Fe-3 R^1 = ^{t}Bu R^2 = H R^3 = ^{t}Bu

The polynuclear carboxylate complexes **Fe-4** to **Fe-6** showed a similar polymerization behavior like the chromium complexes **Cr-2** to **Cr-4**. The Ni-free $\{Fe_3\}$-triangle **Fe-4** gave an activity (6.4×10^3 $g_{polymer}/mol_{metal}$ h) more than 3 orders of magnitude lower compared to the heterometallic $\{Fe_2Ni\}$-triangles **Fe-5** and **Fe-6** with activities around 10^7 $g_{polymer}/mol_{metal}$ h after activation with MAO [117].



Fe-4 M = Fe, $[Fe_3O(O_2C^tBu)_6(H_2O)_3]O_2C^tBu$
Fe-5 M = Ni, $[Fe_2NiO(O_2C^tBu)_6(pip)_3]$
Fe-6 M = Ni, $[Fe_2NiO(O_2C^tBu)_6(mor)_3]$
pip = piperidine, mor = morpholine

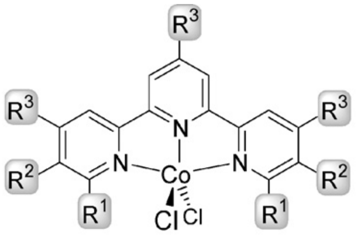
The Fe(II) allyl complex **Fe-7**/MAO exhibited a poor activity and only traces of monomer (1.2%) were converted [122].



Fe-7

2.5. Cobalt catalysts

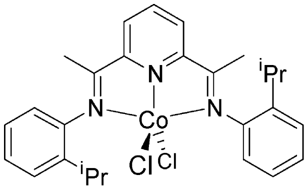
For a {Cr_7Co}-wheel, see **Cr-8**. A series of cobalt(II) complexes **Co-1** to **Co-5**, having terpyridine derivatives as tridentate *N*-donor ligands, showed very low conversions (∼5% yield) [124] when activated with MMAO. Thus, dMAO was chosen as cocatalyst and applied as a solution in chlorobenzene which led to a drastic increase of the conversion and activities (up to >99% for a reaction time of 12 h, activity calculated as 1.6×10^3 $g_{polymer}/mol_{Co}$ h [121]) [125].



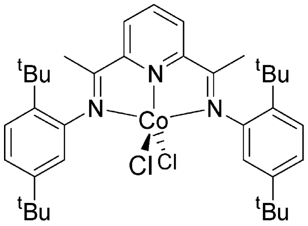
Co-1 R^1 = H R^2 = H R^3 = H
Co-2 R^1 = H R^2 = H R^3 = ^tBu
Co-3 R^1 = H R^2 = Me R^3 = H
Co-4 R^1 = Me R^2 = H R^3 = H
Co-5 R^1 = 3,5-$Me_2C_6H_3$ R^2 = H R^3 = H

Polymerization of norbornene with the system **Co-4**/dMAO at room temperature resulted in quantitative conversion within 3 h (activity calculated as 6.7×10^3 $g_{polymer}/mol_{Co}$ h [121]), whereas other systems required more than 12 h to achieve complete conversion of the monomer. The polymer yield decreased with increasing steric hindrance around the cobalt center. Complex **Co-5** with its bulky substituents showed the lowest activity among these terpyridine complexes (activity calculated as 1.5×10^3 $g_{polymer}/mol_{Co}$ h [121]). The effect of varying the molar NB/Co ratio was investigated with **Co-4**/dMAO. The NB/Co ratios covered a range from 117 to 1170. As a general trend the monomer conversion decreased with increasing norbornene/Co ratio. At the same time the average molecular weights of the generated polynorbornenes increased [125].

The complexes **Co-6** to **Co-13** bearing bulky bis(imino)pyridyl ligands are further examples for tridentate *N*-chelating cobalt complexes. Complex **Co-6** in combination with MAO showed a solvent dependency for the polymerization. Little activity was observed when toluene was used as solvent and only traces of polynorbornene were obtained. When *o*-dichlorobenzene was chosen, a low activity of 2.8×10^2 $g_{polymer}/mol_{Co}$ h was found. Investigations by ^1H NMR showed that a certain amount of ROMP polymer (383 ROMP units per 10 000 insertions) was generated during the polymerization process [123]. Complex **Co-7**/MAO showed a catalytic activity of 1.14×10^4 g_{PNB}/mol_{Co} h [116].

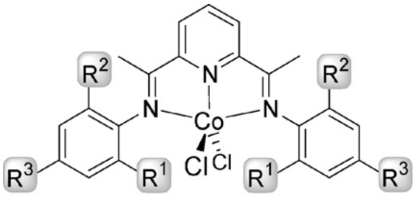


Co-6



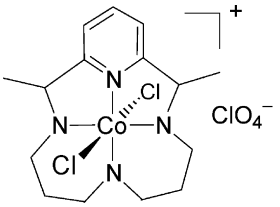
Co-7

Different substituents were introduced on the aryl groups of the imine functions in the closely related precatalysts **Co-8** to **Co-13** in order to modify either the electron density at the metal atom or the steric demand around the catalytic center [126,127]. All precatalysts were activated with MAO and afforded the norbornene polymerization in moderate yields in a range of 4.7×10^3 (**Co-11**/MAO) to 1.3×10^4 $g_{polymer}/mol_{Co}$ h (**Co-9**/MAO). $CoCl_2$/MAO was able to catalyze the polymerization with a higher activity than catalytic systems **Co-8** to **Co-13**/MAO. All polymers obtained were of high molecular weight (10^5–10^6 g mol^{-1}). Different polymerization parameters were studied in more detail—*NB concentration*: For **Co-8**/MAO, the monomer conversion increased linearly with the norbornene concentration and no difference was observed for the PNB molar masses. *Al/Co ratio*: With $CoCl_2$/MAO a maximal activity was reached for low Al/Co ratios (around 100), whereas the maximum activities for **Co-8**/MAO and **Co-9**/MAO were reached for much higher ratios (around 500–2000) [126,127]. For **Co-9**/MAO and $CoCl_2$/MAO the PNB molar masses decreased with increasing Al/Co ratios and the molar mass distribution was always monomodal. In contrast, **Co-8**/MAO showed a bimodal molar mass distribution, indicating the presence of at least two different active sites. *Reaction temperature*: With $CoCl_2$/MAO the activity increased with temperature and reached a plateau around 40 °C. With **Co-8**/MAO the activity increased to reach the plateau around 80 °C. With **Co-9**/MAO the activity first increased to a temperature of around 50 °C and then decreased with increasing temperatures, perhaps due to the thermal instability of this complex. For $CoCl_2$/MAO the molar mass distribution is monomodal up to 80 °C with an increase for higher temperatures. For temperatures above 80 °C the distribution became bimodal. This was shown being due to norbornene polymerization by MAO alone under these conditions. Complex **Co-9**/MAO gave a monomodal molar mass distribution below 60 °C and bimodal ones above 60 °C. In contrast, **Co-8**/MAO yielded a bimodal molar mass distribution even at 20 °C [126,127].

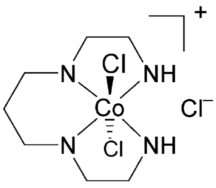


Co-8	R^1 = ${}^tBu$	R^2 = H	R^3 = H
Co-9	R^1 = CF_3	R^2 = H	R^3 = H
Co-10	R^1 = CF_3	R^2 = H	R^3 = Cl
Co-11	R^1 = Me	R^2 = Me	R^3 = Br
Co-12	R^1 = ${}^iPr$	R^2 = ${}^iPr$	R^3 = H
Co-13	R^1 = Ph	R^3 = Ph	R^3 = Ph

For the catalyst precursors **Co-14** and **Co-15** (MAO activation) only the latter gave a modest activity of 1.06×10^3 $g_{polymer}/mol_{Co}$ h and always a certain amount of ROMP polymer was produced with toluene as solvent [123]. When the solvent was changed from toluene to the more polar ODCB the activity increased, so that even the formerly inactive catalyst **Co-14**/MAO became modestly active, and the amount of ROMP product decreased. When the reaction temperature was changed from 30 °C to 50 °C both catalyst systems showed an increased activity with little variation in ROMP percentage. The average molar mass could be controlled for the system **Co-15**/MAO by addition of different amounts of 1-hexene. The more 1-hexene was added to the polymerization mixture, the lower the molar mass of the PNB. Furthermore, the addition of 1-hexene led to a noticeable decrease of the amount of ROMP product [123].

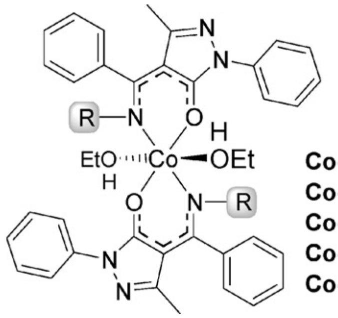


Co-14



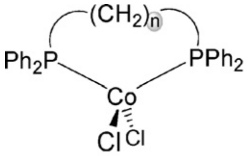
Co-15

The Co complexes with *N,O*-chelating trans bis(β-ketoiminato) ligands **Co-16** to **Co-20** could be activated with MAO towards norbornene polymerization [128,129]. The activity of **Co-16**/MAO strongly depended on the molar Al/Co ratio. For a ratio of 800 no monomer conversion could be detected, whereas an increase of this ratio to 1200 lead to an activity of almost 3×10^4 $g_{polymer}/mol_{Co}$ h. The polymer obtained was of high molecular weight of around 10^6 g mol^{-1} [128]. The iminato-R substituent had a strong influence on the catalytic activity which was of the order of **Co-19** > **Co-18** > **Co-17** [129]. The highest activity with **Co-19**/MAO (4.37×10^4 $g_{polymer}/mol_{Co}$ h) was attributed to both the steric and conjugating effects of the bulky naphthyl ring. Complex **Co-20** with its electron-withdrawing *p*-nitrophenyl group in combination with MAO exhibited a slightly higher activity of 3.05×10^4 $g_{polymer}/mol_{Co}$ h than the complexes **Co-17** and **Co-18**. All PNBs produced featured high molecular weights in the area of 10^5 g mol^{-1}. ^1H NMR spectra showed that those β-ketoiminato cobalt systems mainly afforded vinyl-type polynorbornene. However, a small amount of the ROMP polymer could be detected with the amount depending on the ligand type. The catalytic system **Co-20**/MAO was chosen to study the effect of polymerization conditions on the catalytic activity and the ROMP percentage. Both, activity and the ROMP polymer incorporation monotonically increased with increasing the Al/Co ratio from 600 to 3000. For system **Co-20**/MAO the activity increased from 0 °C to 80 °C, as did the ROMP percentage in the polymer (from 0.47% to 3.87%) [129].



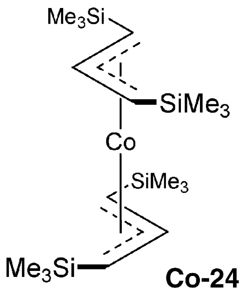
Co-16	R = *p*-fluorophenyl
Co-17	R = phenyl
Co-18	R = *o*-tolyl
Co-19	R = 1-naphthyl
Co-20	R = *p*-nitrophenyl

The dichloro(diphosphane)cobalt(II) complexes **Co-21** to **Co-24** catalyzed the vinyl type polymerization of norbornene when activated with MAO with moderate activities in a range of 3.0×10^2–1.6×10^3 $g_{polymer}/mol_{Co}$ h. The PNB molecular weight was between 10^5 and 10^6 g mol^{-1}. **Co-22** could also be activated with $B(C_6F_5)_3/AlEt_3$, however, only traces of polymeric material were obtained with an activity of 5.7×10^2 $g_{polymer}/mol_{Co}$ h [119].



Co-21	n = 2, $Co(dppe)Cl_2$
Co-22	n = 3, $Co(dppp)Cl_2$
Co-23	n = 4, $Co(dppb)Cl_2$
Co-23	n = 5, $Co(dpppt)Cl_2$

The cobalt allyl complex **Co-24** showed practically no activity with MAO [122].



Co-24

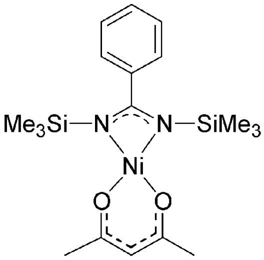
2.6. Nickel catalysts

Nickel(II) complexes constitute a large group of compounds for the polymerization of norbornene. Hence, for a better overview the Ni complexes are grouped according to the ligand type. In heteroleptic complexes of the type Ni(A^B)CD the bidentate A^B chelate ligand was usually viewed as the major ligand. A chelate ligand is more likely to remain bound upon activation by the cocatalyst and, therefore, can affect the metal catalyst properties, whereas the unidentate (C, D) ligands are probably lost to create the necessary vacant sites for norbornene coordination.

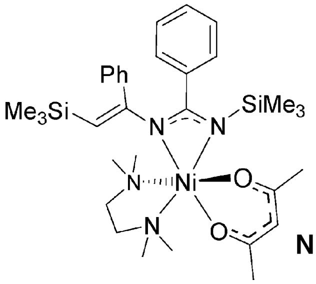
Four-coordinated nickel(II) atoms can be in a square planar or tetrahedral ligand environment, depending on the steric demand of the ligands. In the absence of an X-ray crystallographic, UV/vis or magnetic study it is not evident which coordination polyhedron will be formed. Hence, also for simplicity the nickel structure drawings with all ligands in the paper plane do *not* imply a square planar coordination.

2.6.1. N,N-Chelate and bis(N) ligands

Precatalyst **Ni-1** could be activated with MAO to show moderate activities around 10^5 g_{PNB}/mol_{Pd} h depending on the reaction conditions [130]. Two different catalyst activation processes were tested. In the first procedure, the precatalyst and MAO were mixed, generating the active species before the addition of norbornene. In the second procedure the active sites were generated by the activation of complex **Ni-1** in the presence of the monomer with the first procedure giving higher activities [130]. Furthermore, it was shown that the activities increased with a rising Al/Ni ratio up to 500 and then decreased again. The molecular weights of the polynorbornenes increased up to a molar Al/Ni ratio of ~100. Higher MAO to precatalyst ratios caused a lowering of the average molecular weight values, which reached a plateau around 2×10^5 g mol^{-1}. Furthermore, there was a first-order dependence in monomer indicating that the chain to olefin transfer pathway is plausible as the main operative chain termination mechanism. A decrease in temperature from 70 °C to 0 °C resulted in an augmentation of the polymer yield while a maximum was again observed at 25 °C in the molecular weights of the PNBs. This result indicated that higher temperatures induced some deactivation of the active sites in addition to more effective termination pathways [130].



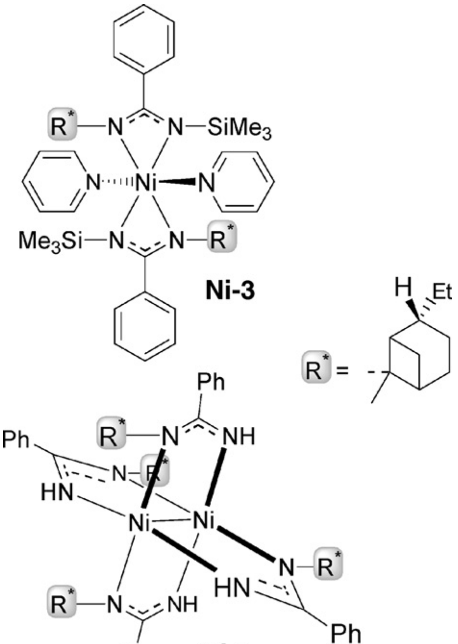
Ni-1



Ni-2

Compound **Ni-2** was less active than **Ni-1** when activated with MAO and an Al/Ni ratio of 100, yet when the molar Al/Ni ratio was raised to 200, **Ni-2**/MAO became the more active system [131].

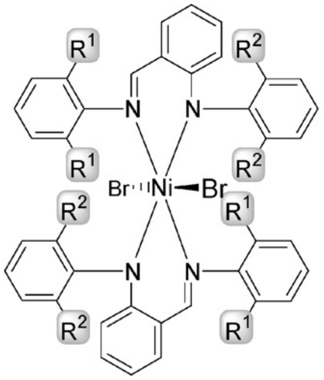
In addition, the chiral benzamidinato nickel complexes trans-**Ni-3** and **Ni-4** could catalyze the addition polymerization of norbornene when activated with MAO with conversions of 42% and 59% [124,132].



Ni-3

Ni-4

When the complexes **Ni-5** to **Ni-8** were activated with MAO they exhibited high activities for norbornene polymerization of around 10^6 $g_{polymer}/mol_{Ni}$ h [133]. The steric demand of the ligands slightly influenced the catalytic activities, which increased with increasing bulk in the substituents. This resulted in an activity order of **Ni-8** > **Ni-7** ~ **Ni-6** > **Ni-5**.



Ni-5 R^1 = Me R^2 = Me
Ni-6 R^1 = Me R^2 = ^{i}Pr
Ni-7 R^1 = ^{i}Pr R^2 = Me
Ni-8 R^1 = ^{i}Pr R^2 = ^{i}Pr

increasing steric demand ↓

When the temperature was varied from 0 °C to 90 °C the activities were highest at 70 °C for all precatalysts **Ni-5** to **Ni-8** [134]. Surprisingly, low average molecular masses and broad molecular weight distributions were observed at lower polymerization temperatures. The molar mass increased and the distribution narrowed with increasing temperature. The presence of two different active species LNi(II)(μ-Me)$_2$AlMe$_2$ (**Ni–Me–Al**) and LNi(II)Me (**Ni–Me**) (L = anilido-imin ligand) was assumed for the broad molecular weight distribution that indicated that two actives sites generated two types of polynorbornene (Fig. 10). There was an equilibrium (**Ni–Me–Al** ⇆ **Ni–Me** + (1/2)Al$_2$Me$_6$) between the two active species because the solid MAO used contained small amounts of trimethylaluminum. Species **Ni–Me–Al** was stable below 50 °C, but only monometallic **Ni–Me** could exist at higher temperatures [134].

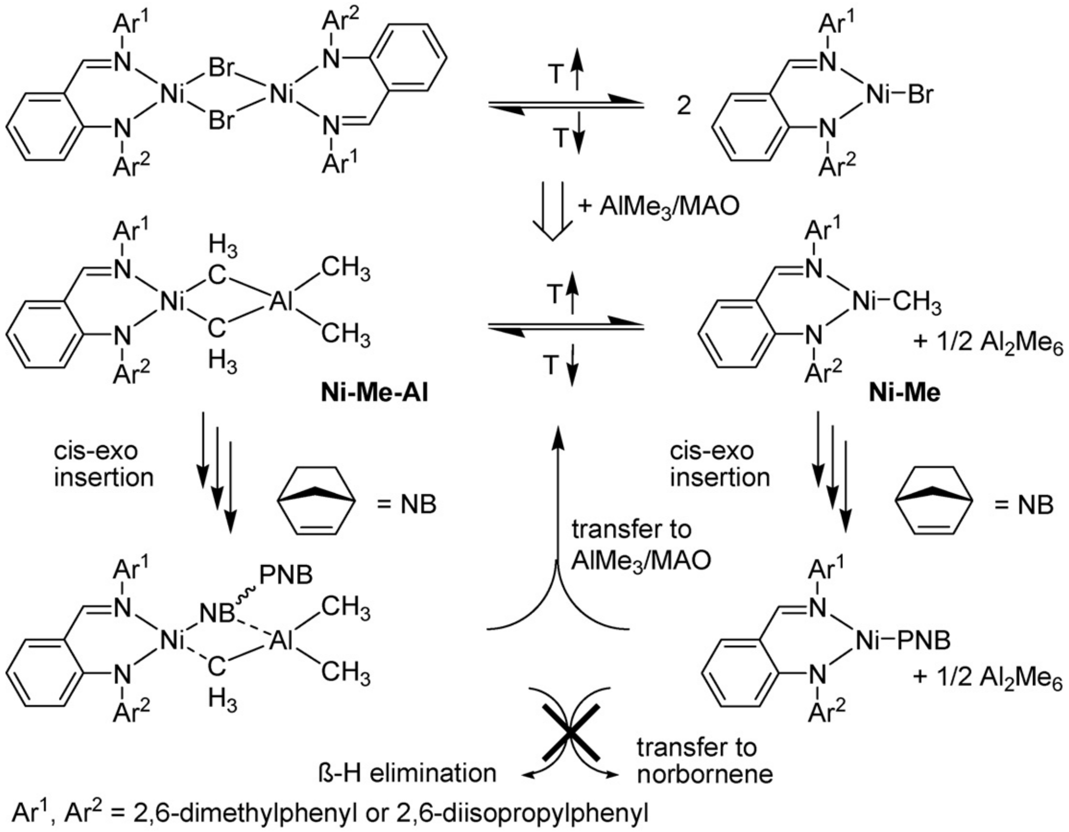
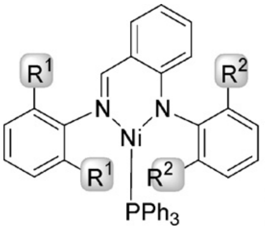


Fig. 10. Proposed coordination mechanism for norbornene polymerization catalyzed by the anilido-imin complexes **Ni-5** to **Ni-8** activated with MAO.

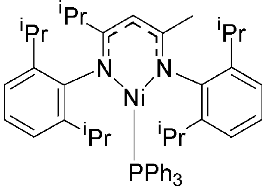
Further investigations were performed with the catalytic system **Ni-5**/MAO with 70 °C as polymerization temperature since in this case the catalyst showed a single-site character. The polymer yields increased with reaction time and the polymerization rate gradually slowed down with the monomer consumed. The activity increased both with increase in norbornene concentration or catalyst concentration, with the monomer concentration having a greater influence than the catalyst concentration on the activity [134].

Activated with MAO the closely related Ni(I) precatalysts **Ni-9** and **Ni-10** could reach high activities in the order of 10^7 g_{PNB}/mol_{Ni} h [135]. When the molar Al/Ni ratio was varied from 1000 to 10 000 the activity steadily increased. For a ratio of 1000, only traces of polynorbornene were generated, but for higher ratios higher activities were obtained. With increasing reaction temperature, the catalytic activity first increased and then decreased (highest activity at 60 °C). The system **Ni-10**/MAO exhibited slightly higher activities than **Ni-9**/MAO which could be attributed to the steric hindrance in complex **Ni-9** making the monomer insertion more difficult [135].



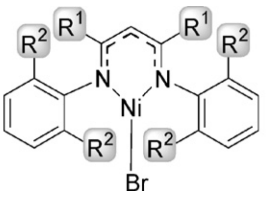
Ni-9 R^1 = ^{i}Pr R^2 = ^{i}Pr
Ni-10 R^1 = Me R^2 = ^{i}Pr

When the nickel(I) complex **Ni-11**, bearing a β-diketiminato ligand, was activated with MMAO it was able to perform the polymerization with high activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h [136]. The catalyst was active over a wide range of temperatures. There was practically no loss in activity when the temperature was varied from 0 °C to 60 °C.



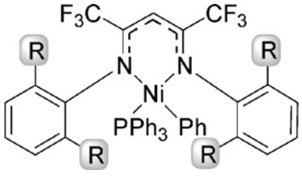
Ni-11

Compounds **Ni-12** to **Ni-15** in the presence of MAO performed with activities of around 10^6 g_{PNB}/mol_{Ni} h. The substituents slightly influenced the catalytic activities. The fluorinated complexes exhibited higher activities than the nonfluorinated analogues (**Ni-14** > **Ni-12** and **Ni-15** > **Ni-13**). The same trend was observed for the bulkiness of the substituent, which showed higher activities with increasing steric demand (**Ni-12** > **Ni-13** and **Ni-14** > **Ni-15**). The catalytic system **Ni-14**/MAO was investigated more detailed. The optimal Al/Ni ratio was shown to be 1500. Variation of the polymerization temperatures from 0 °C to 90 °C caused a steady increase in the activities, whereas the molecular weights of the PNB decreased at the same time [137].



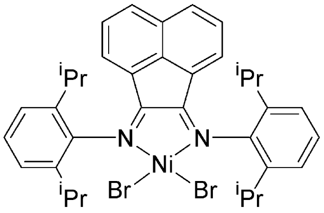
Ni-12 R^1 = Me R^2 = ^{i}Pr
Ni-13 R^1 = Me R^2 = Me
Ni-14 R^1 = CF_3 R^2 = ^{i}Pr
Ni-15 R^1 = CF_3 R^2 = Me

Precatalysts **Ni-16** and **Ni-17** with fluorinated β-diketiminato ligands yielded activities of more than 10^6 $g_{polymer}/mol_{Ni}$ h in combination with MAO [138]. When the temperature was raised from 30 °C to 90 °C the activity increased and the average molecular weight decreased. When the Al/Ni ratio was changed from 200 to 1200 the activity first increased and then decreased with an optimal ratio of 800 for both precatalysts **Ni-16** and **Ni-17**. Under the same conditions **Ni-17** exhibited higher catalytic activities and produced PNB with higher molecular weight than **Ni-16** [138].

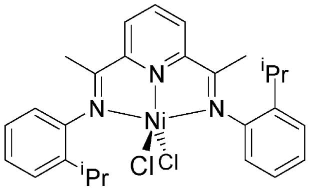


Ni-16 R = Me
Ni-17 R = ^{i}Pr

The compounds **Ni-18** and **Ni-19** with bulky diimine ligands exhibited low activities of around 10^3 g_{PNB}/mol_{Pd} h when activated with MAO as cocatalyst [123]. The structure of the ligands did not influence the activities. It is noteworthy that the generated polynorbornenes contained a certain amount of ROMP units. The effect of the solvent was tested using toluene and the more polar *o*-dichlorobenzene (ODCB). The activity increased when the polymerizations were performed in ODCB. Additionally there was a noticeable decrease of the detectable ROMP units when ODCB was used as solvent. The effect of the reaction temperature was investigated for the system **Ni-18**/MAO. An increase from 30 °C to 50 °C caused higher activities. Finally, it was possible to control the molecular weight of the polynorbornenes by the addition of 1-hexene. With increasing amounts of 1-hexene the molecular weight could be lowered significantly [123].

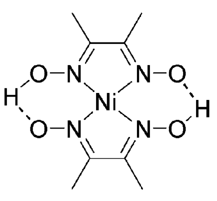


Ni-18

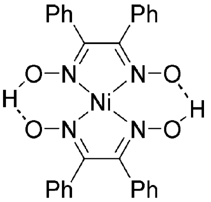


Ni-19

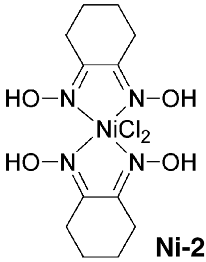
Compounds **Ni-20** to **Ni-22** bearing α-dioxime ligands could be activated with both cocatalysts MAO and $B(C_6F_5)_3/AlEt_3$ [139,140] In general, the activities were moderate with values between 10^3 and 10^5 g_{PNB}/mol_{Ni} h (to the high end with MAO). Compounds **Ni-21** and **Ni-22** also showed low activities with $AlEt_3$ alone. In all cases, the activity increased with an increase of polarity of the solvent (toluene vs. toluene/methylene chloride 1:1) which may indicate a complex-cation/MAO-anion pair as the active species. For the system **Ni-21**/$B(C_6F_5)_3/AlEt_3$ the influence of the concentration of the borane was tested. The maximum activity was obtained for a B/Ni ratio of around 3, higher amounts of the borane caused a decrease in activity. In addition, the role of $AlEt_3$ was investigated. For this, a B/Ni ratio of 1 was set and the Al/Ni ratio was varied from 1 to 100. An increase in the amount of aluminum from Ni/B/Al = 1/1/1 lead to a strong increase in polymerization activity up to a molar ratio of 1/1/5. From there the increase leveled off but continued steadily with a small gradient up to a ratio of 1/1/100. The molecular weight of the polynorbornenes could be controlled with the addition of the chain transfer agent 1-dodecene [139].



Ni-20

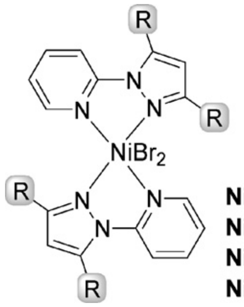


Ni-21



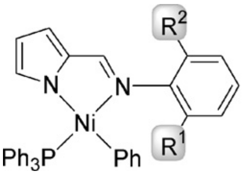
Ni-22

A series of Ni(II) *cis*-(dibromo) complexes **Ni-23** to **Ni-26**, containing pyridyl-pyrazolylato ligands, afforded the norbornene polymerization with activities of more than 10^5 g_{PNB}/mol_{Pd} h in combination with MAO. An exception was the system **Ni-23**/MAO which exhibited noticeable lower activity [141].



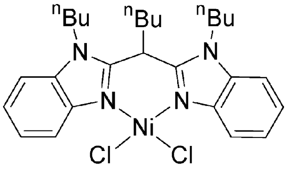
Ni-23 R = Me
Ni-24 R = Ph
Ni-25 R = ^{t}Bu
Ni-26 R = *p*-methoxyphenyl

The nickel(II) imino-pyrrolylato chelate complexes **Ni-27** to **Ni-30** performed the vinyl polymerization of norbornene with very high activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h in the presence of MMAO [142] (for **Ni-27** also [143]). Bulky substituents in the *ortho*-position of nitrogen hindered the insertion of norbornene and lowered the activity. This fact is reflected in the activity sequence **Ni-30** > **Ni-29** > **Ni-28** > **Ni-27**. Variation of the molar Al/Ni ratio from 1000 to 2000 led to an increase of the catalytic activity in all cases. Meanwhile, the molecular weights of the polynorbornenes decreased at the same time. For the system **Ni-27**/MMAO the activity and molecular weights were highest at a temperature of 30 °C. In addition, an increase of the monomer concentration caused a linear increase of the activity for **Ni-27**/MMAO. At the same time, the molecular weight values first increased and then kept constant with increase of norbornene concentration [142].

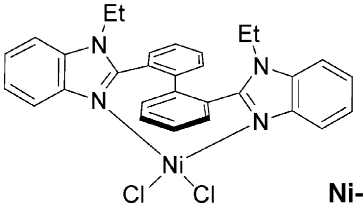


Ni-27 R^1 = ^{i}Pr R^2 = ^{i}Pr
Ni-28 R^1 = ^{i}Pr R^2 = Me
Ni-29 R^1 = Et R^2 = Et
Ni-30 R^1 = ^{t}Bu R^2 = H

Compounds **Ni-31** and **Ni-32**, bearing benzimidazole ligands, were activated with MAO to catalyze the norbornene polymerization [144]. Both complexes exhibited similar monomer conversions of 77–99% (activities calculated by us as 10^5 g_{PNB}/mol_{Ni} h [121]) under the same reaction conditions and it was shown that an increase in both reaction time and molar Al/Ni ratio led to slightly higher monomer conversions.

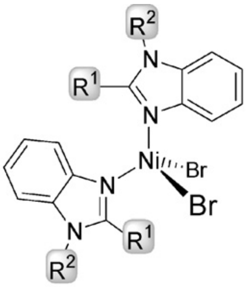


Ni-31



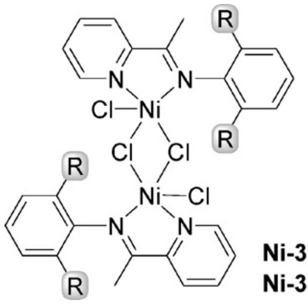
Ni-32

The nonchelating monodentate pseudo-tetrahedral benzimidazole nickel(II) catalysts **Ni-33** to **Ni-36**/MAO showed very high catalytic activities in a range of 5×10^8 (**Ni-35**/MAO) to 1.7×10^9 g_{PNB}/mol_{Ni} h (**Ni-36**/MAO) depending on the reaction conditions. The lower activity of the system **Ni-35**/MAO was due to its lower steric demand and electronic poor nature. Catalyst **Ni-36** was used for further investigation and it was found that the optimal polymerization temperature was 25 °C. Furthermore, the activity dramatically decreased by several orders of magnitude when the solvent was changed from the polar ODCB to a ODCB/toluene mixture [145].



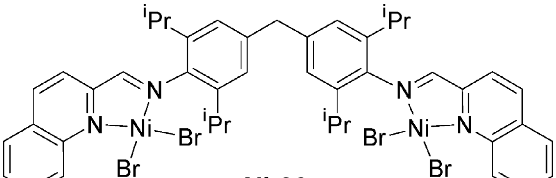
Ni-33 R^1 = 2,6-difluorophenyl R^2 = H
Ni-34 R^1 = 2,6-difluorophenyl R^2 = 2,6-difluorobenzyl
Ni-35 R^1 = Me R^2 = H
Ni-36 R^1 = 2-methoxyphenyl R^2 = 2-methoxybenzyl

The dinuclear complexes **Ni-37** and **Ni-38** were both active towards norbornene polymerization in the presence of MAO. Under the same conditions, **Ni-37**/MAO showed higher activities than **Ni-38**/MAO although both catalysts still exhibited moderate activities in the order of 10^5 g_{PNB}/mol_{Ni} h. The activities for **Ni-37**/MAO varied slightly with the amount of MAO when the molar Al/Ni ratio was changed from 100 to 1600. Here, small MAO amounts of Al/Ni = 100 were found sufficient to create the catalytic active species. At the same time, the molecular weights increased first and then decreased with the Al/Ni ratio. Furthermore, in the more polar solvent mixture toluene/dichloromethane higher activities were generated than in pure toluene for **Ni-37**/MAO. For a temperature of 0 °C the optimal activity was observed and an increase in temperature lowered the activity [146].



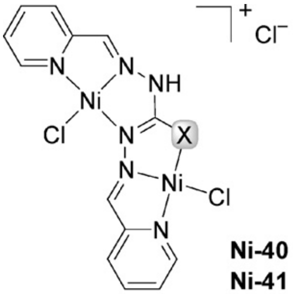
Ni-37 R = ⁱPr
Ni-38 R = Me

The dinuclear diimine complex **Ni-39**, activated with MAO, generated polynorbornene with moderate activity in the range of 10^5 $g_{polymer}/mol_{Ni}$ h and was also applied for the copolymerization of norbornene with styrene [147].



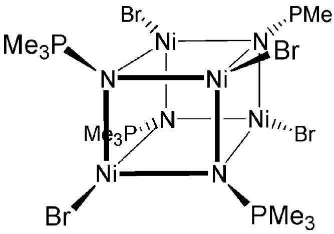
Ni-39

The dinuclear bis(2-pyridylmethylene)-carbonodihydrazide and -thiocarbonodihydrazide complexes **Ni-40** and **Ni-41** were applied in the presence of the cocatalysts MAO and $B(C_6F_5)/AlEt_3$. Activities were between 10^4 and 10^5 g_{PNB}/mol_{Ni} h. With $B(C_6F_5)_3$ alone no polymerization activity was observed [140,148].



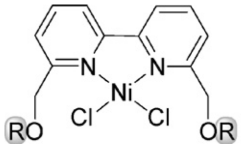
Ni-40 X = O, +4MeOH
Ni-41 X = S, +MeOH

The tetranuclear nickel complex $[NiBr(NPMe_3)]_4$ **Ni-42**, in which the Ni- and N-atoms form a heterocubane, required MAO to create an active species [149]. The catalytic activity depended on the monomer/Ni ratio, which was varied from 5000 to 60 000. For the latter value a high activity of 10^7 $g_{polymer}/mol_{Ni}$ h was observed. This is due to the high monomer excess, which at the same time leads to rather low polymer yields of 10–18% only. Higher yields were possible by increasing the reaction time or the amount of catalyst. In addition, it was shown that the molar masses could be controlled by addition of styrene after certain reaction times. The MAO [150] or $B(C_6F_5)_3$ [151] activated complex $[NiBr(NPMe_3)]_4$ was also applied for the copolymerization of norbornene with different olefins to produce olefin-terminated polynorbornene chains.

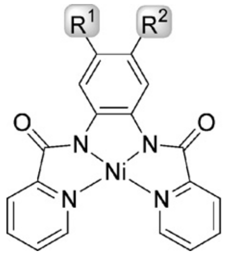


Ni-42

Precatalysts **Ni-43** to **Ni-46**, bearing bipyridine ligands, were highly active in the presence of MMAO with activities in the range of 10^7–10^8 g_{PNB}/mol_{Ni} h [152]. The activities increased slightly with the bulkiness of the substituent.

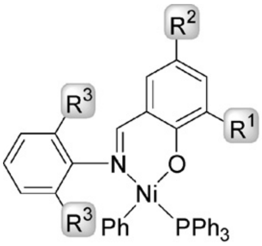

Ni-43 R = Et
Ni-44 R = ^{i}Pr
Ni-45 R = cyclohexyl
Ni-46 R = Ph

Compounds **Ni-47** to **Ni-53** with tetradentate *N*,*N*,*N*,*N*-chelating ligands were also activated with MMAO. The catalytic activities were found to depend on the substituents, temperature, and solvents [153]. The catalysts with electron-withdrawing substituents generally showed higher activities. In general, the activities for these catalysts covered a range from 10^5 to 10^6 g_{PNB}/mol_{Ni} h. In all cases an increase of activity was obtained when the polymerization was conducted in chlorobenzene instead of toluene. For **Ni-52**/MMAO and **Ni-53**/MMAO the temperature was changed from 25 °C to 100 °C. In both cases, the optimal temperature was 70 °C [153].

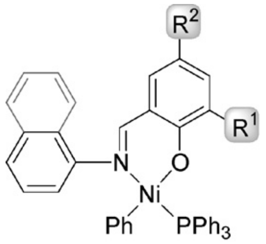

Ni-47 R^1 = H R^2 = NO_2
Ni-48 R^1 = H R^2 = F
Ni-49 R^1 = Cl R^2 = Cl
Ni-50 R^1 = H R^2 = H
Ni-51 R^1 = H R^2 = Me
Ni-52 R^1 = Me R^2 = Me
Ni-53 R^1 = H R^2 = OMe

2.6.2. *N,O-(N,S-)Chelate ligands*

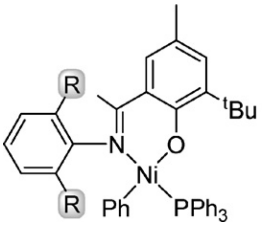
Complexes **Ni-54** to **Ni-61** with a salicylaldiminato ligand afforded very high activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h in combination with MMAO as cocatalyst [154] (for **Ni-54** also [143]). High molecular weight polynorbornenes were obtained in all cases. Except for **Ni-55**, showing a threefold lower activity, the structures of these complexes did not greatly affect the polymer yields under the same reaction conditions. A more detailed study for the system **Ni-61**/MMAO revealed that variation of the molar Al/Ni ratio from a value of 100–10 000 was followed by an increase of the activity. Simultaneously, the molecular weights of the polymers first increased and then decreased. With an increase of the reaction temperature from 0 °C to 50 °C, a significant increase of the activity was obtained, and a significant decrease of the molecular weights was observed. An increase of the monomer/Ni ratio caused a dramatic increase of the catalytic activity of **Ni-61**/MMAO [154].


Ni-54 R^1 = H R^2 = H R^3 = ^{i}Pr
Ni-55 R^1 = H R^2 = H R^3 = Me
Ni-56 R^1 = ^{t}Bu R^2 = H R^3 = ^{i}Pr
Ni-57 R^1 = ^{t}Bu R^2 = H R^3 = Me
Ni-58 R^1 = Ph R^2 = H R^3 = ^{i}Pr
Ni-59 R^1 = Ph R^2 = H R^3 = Me
Ni-60 R^1 = ^{t}Bu R^2 = ^{t}Bu R^3 = ^{i}Pr
Ni-61 R^1 = ^{t}Bu R^2 = ^{t}Bu R^3 = Me

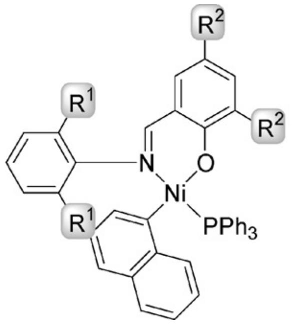
The precatalysts **Ni-62** to **Ni-66** afforded activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h when activated with MAO. In addition, complex **Ni-63** showed very good activities over a wide range of temperatures [155].


Ni-62 R^1 = H R^2 = H 1-naphthyl
Ni-63 R^1 = ^{t}Bu R^2 = H 1-naphthyl
Ni-64 R^1 = H R^2 = OMe 1-naphthyl
Ni-65 R^1 = NO_2 R^2 = NO_2 1-naphthyl
Ni-66 R^1 = H R^2 = H phenyl

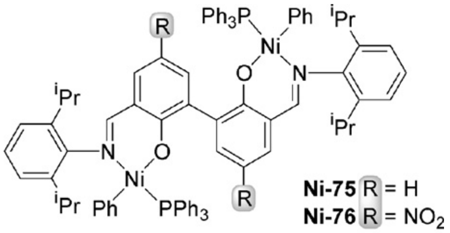
Precatalysts **Ni-67** and **Ni-68** were activated with MMAO and catalyzed the norbornene polymerization in very good activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h [136].


Ni-67 R = Me
Ni-68 R = ^{i}Pr

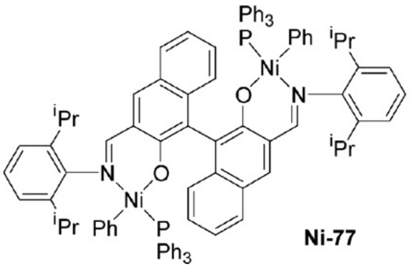
When activated with MAO compounds **Ni-69** to **Ni-74** were very efficient catalysts with activities of more than 10^8 $g_{polymer}/mol_{Ni}$ h. There was practically no influence of the ligand structures on the polymer yields [156]. The system **Ni-69**/MAO was used for further investigations concerning the polymerization parameters. It was found that a large excess of MAO was necessary for high activities. There was a remarkable increase between an Al/Ni ratio of 500 and 1000, whereas the activity difference for the Al/Ni ratio from 1000 to 2500 was not impressive. To the contrary, a ratio of more than 2000 led to a decrease in activity. **Ni-69**/MAO showed good activities over a wide temperature range from 0 °C to 100 °C. The temperature influenced the activities only slightly, whereas the NB/Ni ratio greatly affected the activity. It was shown that at least a NB/Ni ratio of 10 000 was required to give polynorbornene in good yields and for a ratio of 25 000 an excellent activity of 2.6×10^8 g_{PNB}/mol_{Ni} h was obtained [156].


Ni-69 R^1 = ^{i}Pr R^2 = I
Ni-70 R^1 = ^{i}Pr R^2 = Cl
Ni-71 R^1 = Et R^2 = I
Ni-72 R^1 = Et R^2 = Cl
Ni-73 R^1 = Me R^2 = I
Ni-74 R^1 = Me R^2 = Cl

The dinuclear (salicylaldiminato)nickel(II) complexes **Ni-75** to **Ni-77** exhibited very high activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h in combination with MMAO [157]. Although there is a profound difference in the steric structures of the complexes **Ni-75** and **Ni-77**, the obtained activities were almost the same. This indicates that the size of the substituents on the phenoxy fragment did not influence the catalytic activity. The system **Ni-75**/MAO was used for further investigations. The molar Al/Ni ratio was increased from 500 to 2500 and a constant increase of the activity was observed. At the same time the molecular masses of the produced polymers decreased. When the reaction temperature was changed from 10 °C to 50 °C both the activities and the average molar masses decreased slightly. Furthermore, an increase of the monomer concentration caused an increase of both activities and molar masses [157].

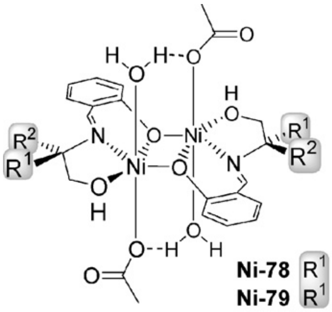


Ni-75 R = H
Ni-76 R = NO$_2$

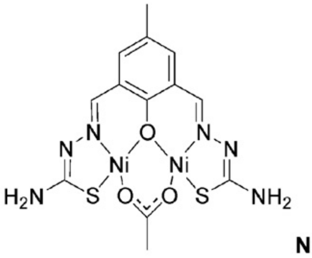


Ni-77

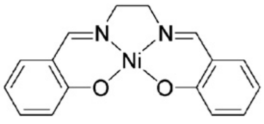
The dinuclear salicylaldiminato Schiff-base complexes **Ni-78** to **Ni-80** were applied in the presence of the cocatalysts MAO, $B(C_6F_5)/AlEt_3$ or $B(C_6F_5)_3$ alone [140,148]. Systems **Ni-78**/MAO and **Ni-79**/MAO performed with high activities of more than $10^7\ g_{PNB}/mol_{Ni}$ h. The system **Ni-80**/MAO was close to the $10^7\ g_{PNB}/mol_{Ni}$ h benchmark. The mononuclear Ni–salen complex **Ni-81** was included for comparison and it was found that the dinuclear complexes **Ni-78**, **Ni-79** and **Ni-80** could reach higher activities [140].



Ni-78 R^1 = Me R^2 = Me
Ni-79 R^1 = H R^2 = Et

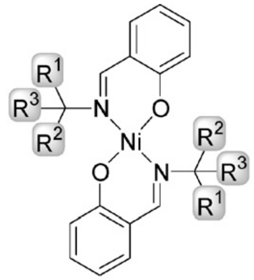


Ni-80



Ni-81

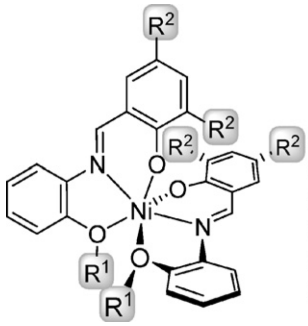
The activities of the MAO activated catalysts **Ni-82** to **Ni-85** were in the order **Ni-82 > Ni-83 > Ni-84 > Ni-85**, which indicated that complexes with higher steric hindrance can afford higher activities [158]. The systems **Ni-82**/MAO and **Ni-83**/MAO showed very high activities of more than $10^8\ g_{polymer}/mol_{Ni}$ h. The reaction parameters such as the Al/Ni ratio, polymerization temperature and monomer/catalyst ratio were varied for the system **Ni-82**/MAO. An Al/Ni ratio of 2000 was optimal. For higher values the activity decreased. Variation of the temperature from 0 °C to 100 °C led to a slight decrease in activity. An increase in the NB/Ni ratio from 2500 to 40 000 dramatically increased the activity [158].



Ni-82 R^1 = Ph R^2 = Ph R^3 = H
Ni-83 R^1 = Me R^2 = Ph R^3 = H
Ni-84 R^1 = Me R^2 = Me R^3 = Me
Ni-85 R^1 = Me R^2 = Me R^3 = H

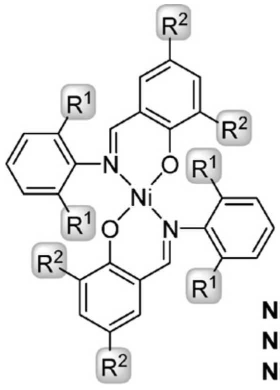
↑ increased steric demand

The neutral nickel(II) complexes **Ni-86** to **Ni-91** performed with activities in the area of $10^5\ g_{polymer}/mol_{Ni}$ h in combination with MAO [159]. **Ni-86**/MAO was chosen for further investigations. The Al/Ni ratio was varied from 500 to 2500 and an increase of the MAO amount led to higher monomer conversion. In addition, a temperature of 75 °C was found optimal. Furthermore, an increase in monomer concentration led to higher catalytic activities [159].



Ni-86 R^1 = Me R^2 = H
Ni-87 R^1 = Et R^2 = H
Ni-88 R^1 = Me R^2 = I
Ni-89 R^1 = Et R^2 = I
Ni-90 R^1 = Me R^2 = Cl
Ni-91 R^1 = Et R^2 = Cl

Precatalyst **Ni-93** could be activated with MAO-W (containing 28 mol% free $AlMe_3$) for the polymerization of norbornene [160]. Moderate activities of $10^5\ g_{polymer}/mol_{Ni}$ h were reached with this system. To investigate the influence of the content of free $AlMe_3$ in the cocatalyst, MAO-A (containing ca. 15 mol% $AlMe_3$) was used instead of MAO-W. The polymerization results were similar [160]. It was found that the polarity of the solvent played an important role. When dichlorobenzene or chlorobenzene were used instead of toluene in the presence of MAO-W the polymerization activity increased by about one order of magnitude. When MAO-W was replaced by MAO-A, the productivity significantly increased with an increasing Al/Ni ratio. Compound **Ni-94**, containing also the electron-withdrawing nitro groups, showed the same activity as **Ni-93** while compound **Ni-92** with no electron-withdrawing groups exhibited a significant decrease of activity which indicated that the nitro groups played an important role [160]. In other work **Ni-92**/MAO was reported with an activity of $10^{7}\,g_{PNB}/mol_{Ni}\,h$ [143].

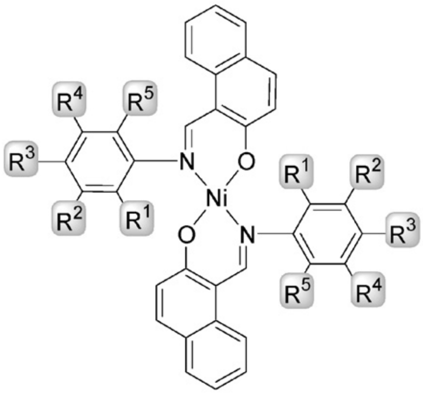


Ni-92 $R^1 = {}^iPr$ $R^2 = H$
Ni-93 $R^1 = {}^iPr$ $R^2 = NO_2$
Ni-94 $R^1 = H$ $R^2 = NO_2$

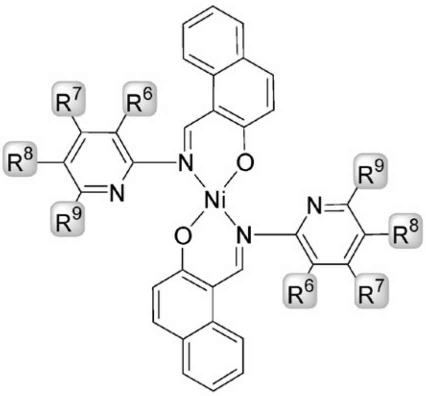
The series of bis(1-arylimino-methylenyl-naphthalen-2-oxy)nickel(II) complexes **Ni-95** to **Ni-113** was active with MAO and showed similar moderate activities of almost $10^{5}\,g_{polymer}/mol_{Ni}\,h$ [161]. The catalytic system **Ni-101**/MAO was chosen for deeper investigations concerning the reaction parameters and their influence upon the catalytic activity. The molar Al/Ni ratio was varied from 1000 to 3000 and a value of 2000 was found best. The activity decreased with increasing temperature from 0 °C to 100 °C. Also, the activity decreased with increasing reaction volume or with a decrease of the norbornene/catalyst ratio [161].

The bis(salicylideneiminato)nickel(II) complexes **Ni-82**, **Ni-83**, **Ni-95**, **Ni-98** and **Ni-100** were supported on spherical $MgCl_2$ and silica [162]. The activities of the supported precatalysts **Ni-82**, **Ni-83** and **Ni-98** were in the range of $10^{5}\,g_{polymer}/mol_{Ni}\,h$ and significantly higher than those of the supported compounds **Ni-95** and **Ni-100**. MAO was required as cocatalyst. The polymerizations of norbornene were performed in toluene and hexane with the former producing slightly higher yields. In general, the polynorbornenes produced with the supported catalyst had higher molecular weights and slightly broader molecular weight distributions than with the respective homogeneous catalyst [162].

Complexes **Ni-114** to **Ni-117** afforded good activities in the presence of MMAO as cocatalyst [143]. The structures of the complexes affected the activity. **Ni-116** and **Ni-117** with electron-withdrawing CF_3-groups gave activities of more than $10^{7}\,g_{PNB}/mol_{Ni}\,h$, higher than for **Ni-114** and **Ni-115** without such substituents (activities of 6.2 and $7.0 \times 10^{6}\,g_{PNB}/mol_{Ni}\,h$, respectively). In addition, the activities could be slightly increased by bulky substituents in the *ortho*-position of the *N*-aryl group. So the order of activity was **Ni-117** > **Ni-116** > **Ni-115** > **Ni-114**. Polymer yields and molecular weights depended significantly on the reaction conditions. For the system **Ni-116**/MMAO the effects of Al/Ni ratio, polymerization temperature and monomer concentration were investigated. The activity first increased rapidly with an increase of the Al/Ni ratio up to a value of 2500 and then kept steady upon further increase. In contrast, the molecular weight decreased at the same time. The optimal temperature was shown to be 25 °C. The molecular weights increased with raising the temperature from 0 °C to 50 °C. With increasing norbornene concentration both the activity and molecular weights increased [143]. For **Ni-115** the activities increased

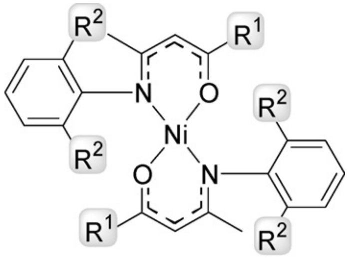


Ni-95 $R^1 = {}^iPr$ $R^2 = H$ $R^3 = H$ $R^4 = H$ $R^5 = H$
Ni-96 $R^1 = Et$ $R^2 = H$ $R^3 = H$ $R^4 = H$ $R^5 = H$
Ni-97 $R^1 = Me$ $R^2 = H$ $R^3 = H$ $R^4 = Me$ $R^5 = H$
Ni-98 $R^1 = Me$ $R^2 = H$ $R^3 = H$ $R^4 = H$ $R^5 = Me$
Ni-99 $R^1 = Me$ $R^2 = Me$ $R^3 = Br$ $R^4 = H$ $R^5 = H$
Ni-100 $R^1 = {}^iPr$ $R^2 = H$ $R^3 = H$ $R^4 = H$ $R^5 = {}^iPr$
Ni-101 $R^1 = Me$ $R^2 = H$ $R^3 = Me$ $R^4 = H$ $R^5 = Me$
Ni-102 $R^1 = F$ $R^2 = H$ $R^3 = H$ $R^4 = H$ $R^5 = H$
Ni-103 $R^1 = F$ $R^2 = H$ $R^3 = H$ $R^4 = H$ $R^5 = F$
Ni-104 $R^1 = F$ $R^2 = F$ $R^3 = F$ $R^4 = H$ $R^5 = H$
Ni-105 $R^1 = F$ $R^2 = F$ $R^3 = H$ $R^4 = H$ $R^5 = F$
Ni-106 $R^1 = Cl$ $R^2 = H$ $R^3 = Cl$ $R^4 = Cl$ $R^5 = H$
Ni-107 $R^1 = Cl$ $R^2 = H$ $R^3 = Cl$ $R^4 = H$ $R^5 = Cl$



Ni-108 $R^6 = OCH_2Ph$ $R^7 = H$ $R^8 = H$ $R^9 = H$
Ni-109 $R^6 = H$ $R^7 = H$ $R^8 = H$ $R^9 = H$
Ni-110 $R^6 = H$ $R^7 = Me$ $R^8 = H$ $R^9 = H$
Ni-111 $R^6 = H$ $R^7 = Me$ $R^8 = H$ $R^9 = Me$
Ni-112 $R^6 = Br$ $R^7 = H$ $R^8 = Br$ $R^9 = Me$
Ni-113 $R^6 = H$ $R^7 = H$ $R^8 = NO_2$ $R^9 = H$

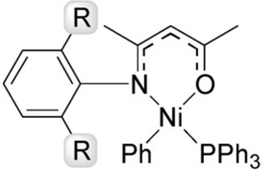
sharply with an increase in the Al/Ni ratio to an optimal value and then decreased again [163].



Ni-114 R^1 = Ph R^2 = Me
Ni-115 R^1 = Ph R^2 = ^{i}Pr
Ni-116 R^1 = CF_3 R^2 = Me
Ni-117 R^1 = CF_3 R^2 = ^{i}Pr

Compared with β-diketonato ligands, β-ketoiminato ligands have an increased steric demand, so the bis(β-ketoiminato)nickel complexes **Ni-115** and **Ni-114** produced higher molecular weight polymers than the corresponding bis(β-diketonato)nickel complex **Ni-159** under the same conditions. At the same time steric hindrance makes the insertion step more difficult. As a consequence, **Ni-115** and **Ni-114** exhibited slightly lower activities than **Ni-159**. When the phenyl group in **Ni-114** and **Ni-115** was replaced by the smaller and stronger electron-withdrawing CF_3 group, complexes **Ni-117** and **Ni-116** displayed both higher activities and molecular weights, as did the corresponding complex **Ni-160** over **Ni-159**. This fact indicates that the bis(β-diketoiminato)nickel complexes are more favorable catalysts for norbornene polymerization than the bis(β-diketonato)nickel complexes [143].

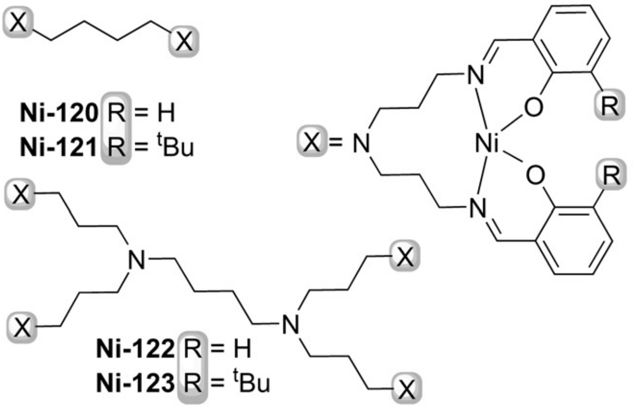
When the β-ketoiminato complexes **Ni-118** and **Ni-119** were activated with MMAO they afforded high activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h and high molecular weight polymers [136].



Ni-118 R = Me
Ni-119 R = ^{i}Pr

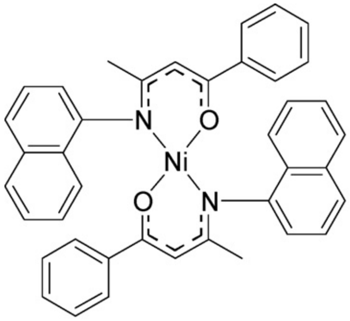
The steric structure of compounds **Ni-116** to **Ni-119** slightly influenced their catalytic activities in the order of **Ni-118 > Ni-116 > Ni-119 > Ni-117** [164]. Complex **Ni-1118** with its 2,6-dimethylphenyl group displayed a higher activity than complex **Ni-119** with the bulkier 2,6-diisopropylphenyl substituent, because an increase in steric hindrance makes the insertion of the monomer more difficult. The catalytic system **Ni-118**/MAO was chosen for further investigations. A value of 5000 for the molar Al/Ni ratio allowed the highest activity of 5.2×10^7 g_{PNB}/mol_{Ni} h. The minimum value to afford good yields was 3000. The reaction temperature was varied from 0 °C to 90 °C with 30 °C to be optimal [164].

The multinuclear dendrimeric complexes **Ni-120** to **Ni-124** exhibited activities around 5×10^5 g_{PNB}/mol_{Ni} at optimized Al/Ni ratios of about 4000 [164b].

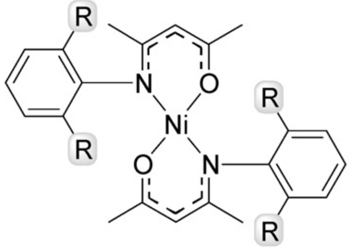


Ni-120 R = H
Ni-121 R = ^{t}Bu
Ni-122 R = H
Ni-123 R = ^{t}Bu

Activities of more than 10^6 g_{PNB}/mol_{Ni} h were observed when the precatalysts **Ni-124**, **Ni-125** and **Ni-126**, in comparison with **Ni-127**, **Ni-128** and **Ni-115** were used in the presence of MAO [163]. The polymerization results were strongly dependent on the Al/Ni ratio. For **Ni-126** the activities increased sharply with an increase in the Al/Ni ratio to a respective optimal value, and then decreased again. For **Ni-124**, a fast increase of the activity was observed with increasing ratios up to 600 and then a slight decrease for higher values was noticeable. For **Ni-125** a molar Al/Ni ratio of 1000 was necessary to obtain activity. The highest yields and activities were achieved in a range from 50 °C to 70 °C. It was found that steric effects of the ligands did not play a role concerning the activities. Instead, the ligand electronic effect obviously influenced the monomer conversion. A stronger electron-conjugated substituent connected to the imino group was more favorable for increasing the activities than an electron-donating one. So **Ni-128** and **Ni-124** with their conjugating naphthyl substituents showed higher activities than complex **Ni-125** bearing an electron-donating 2,6-dimethylphenyl group [163].

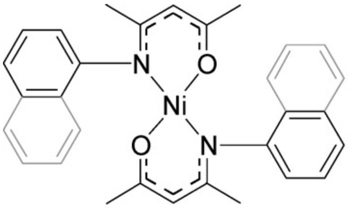


Ni-124



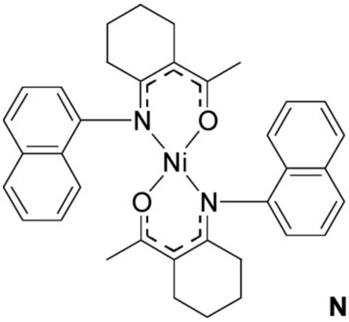
Ni-125 R = Me
Ni-126 R = ^{i}Pr

Precatalysts **Ni-127** and **Ni-128** showed high polymerization activities of more than 10^7 g_{PNB}/mol_{Ni} h and high molecular weights of more than 10^6 g mol^{-1} once activated with $B(C_6F_5)_3$. Both catalytic systems required at least a B/Ni ratio of 10 and for higher values up to 20 the activities increased. The average molecular weights increased first and then decreased at the same time. Furthermore, both compounds showed good activities over a wide range of temperatures (20–100 °C). The molecular weight values reached the maximum at 75 °C. The NB concentration caused a decrease in activity when the NB/Ni ratio was changed from 600 to 3800, whereas the molecular weights increased until a ratio of 1800 was reached [165]. Precatalyst **Ni-127** and **Ni-128** performed with activities of around 10^6 $g_{polymer}/mol_{Ni}$ h with MAO as cocatalyst depending on the polymerization temperature. This catalytic system had a good thermostability and generated the highest activity at a temperature of 60 °C [166]. The polymerization results were strongly dependent on the Al/Ni ratio. For **Ni-128**, a maximal activity was reached for a ratio of 600, and the activity decreased rapidly for ratios higher than 600 [163]. The system **Ni-128**/MAO was also applied for the copolymerization of norbornene and its derivative norbornene carboxylic acid methyl ester [166].



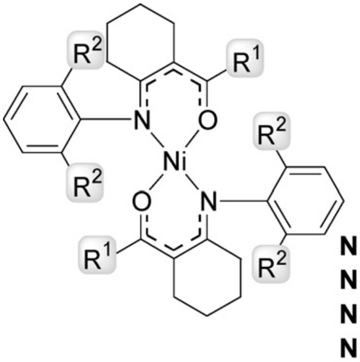
Ni-127 phenyl
Ni-128 1-naphthyl

Compound **Ni-129** was tested in the presence of MAO under various reaction conditions leading to activities in the area of 10^6 g_{PNB}/mol_{Ni} h. The amount of MAO was essential and the optimal Al/Ni ratio was found to be 1000. Higher or lower values caused a decrease in activity. This system showed good activities over a wide range of temperatures from 20 °C to 80 °C. An increase of the catalyst concentration first led to a significant increase of activity which later decreased [167].



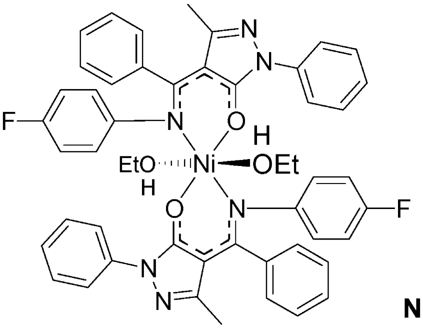
Ni-129

Complexes **Ni-130** to **Ni-133** were activated with MAO [168]. The complexes with 2,6-diisopropyl-substituted *N*-aryl had higher activities than the corresponding complexes bearing 2,6-dimethyl-substituted *N*-aryl, i.e., **Ni-130** > **Ni-131** and **Ni-132** > **Ni-133**, especially at high temperatures. In addition, compounds **Ni-132** and **Ni-133** with benzoyl moieties were more active than **Ni-130** and **Ni-131** with acetyl groups. This result could be attributed to the more effective conjugation of the benzoyl group for stabilizing the insertion transition state. In general, activities obtained with complexes **Ni-130** to **Ni-133** were in the range of 10^5–10^6 $g_{polymer}/mol_{Ni}$ h [168].



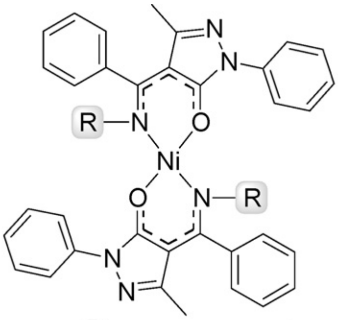
Ni-130 R^1 = Me R^2 = ^iPr
Ni-131 R^1 = Me R^2 = Me
Ni-132 R^1 = Ph R^2 = ^iPr
Ni-133 R^1 = Ph R^2 = Me

The catalytic system **Ni-134**/MAO showed very high activities in the area of 10^7 g_{PNB}/mol_{Ni} h [128]. The activity increased by almost a factor of 4 when the temperature was varied from 0 °C to 80 °C. At the same time the molecular weight decreased sharply. In addition, the monomer conversion increased monotonically when the molar Al/Ni ratio was changed from 600 to 2400 [128].



Ni-134

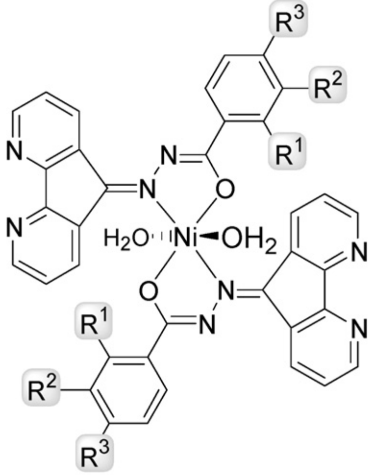
The catalytic activity sequence **Ni-138** > **Ni-137** > **Ni-136** > **Ni-135** indicated again that steric ligand effects play an important role for activities [169]. Activities obtained with these complexes in combination with MAO exceeded 10^7 g_{PNB}/mol_{Ni} h. The activity of **Ni-138**/MAO as the most active among these catalytic systems could be attributed to both the steric and the conjugating effect of the large naphthyl ring. Also, the activity increased with higher norbornene/Ni ratios as shown for **Ni-138**/MAO. The PNBs generated by complexes **Ni-135** to **Ni-138** were of high molecular weights and molecular weight distributions around 2 indicated an active species with single site character in all cases. The influence of MAO was examined with **Ni-136**. An increase of the molar Al/Ni ratio from 500 to 3000 was followed by a linear increase of the activity. An increase in the polymerization temperature from 0 °C to 70 °C led to an increase of the activity and to a decrease of the molar weight of the polynorbornenes [169].



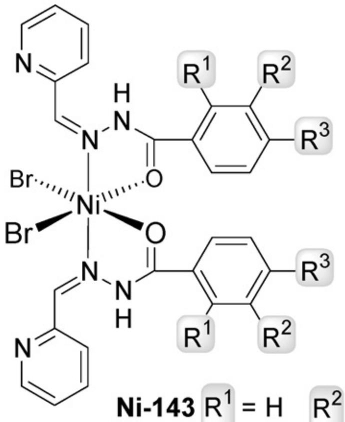
Ni-135 R = phenyl
Ni-136 R = *o*-tolyl
Ni-137 R = *p*-nitrophenyl
Ni-138 R = 1-naphthyl

increase of steric demand ↓

The acylhydrazone nickel(II) complexes **Ni-139** to **Ni-147** showed similar activities upon activation with MAO in the range of almost 10^6 g_{PNB}/mol_{Ni} h depending on the reaction conditions [170]. Interestingly, the *cis*-compounds **Ni-143** to **Ni-147** required higher Al/Ni ratios for a complete monomer conversion than the trans-compounds **Ni-139** to **Ni-142**. This result illustrates that the pyridyl ligand lowered the activities of its complex. In addition, complexes **Ni-139** to **Ni-142** produced higher molecular weight polynorbornenes. For a systematic investigation of the reaction parameters the system **Ni-139**/MAO was tested under various conditions such as the solvent, Al/Ni ratio, reaction time, temperature, and norbornene/catalyst ratio [170]. The activity increased when the Al/Ni ratio was changed from 100 to 500 and then decreased with further increase. At the same time, the average molecular weights of the polymers increased as well. The activities in the polar solvent dichloromethane were higher than those obtained in toluene. For both solvents a dependency of the polymerization temperature was investigated and 25 °C was found to be optimal in both cases. Furthermore, the activity could be increased by increasing the monomer/Ni ratio for both solvents until a value of 5000 was reached. For higher ratios the activities started to decline [170].

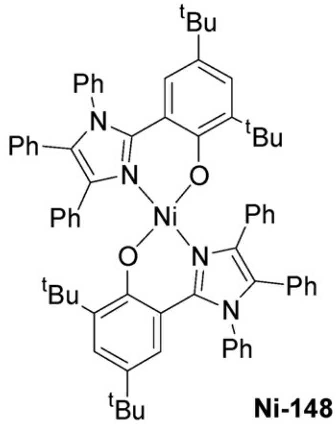


Ni-139 R^1 = H R^2 = H R^3 = H
Ni-140 R^1 = Me R^2 = H R^3 = H
Ni-141 R^1 = H R^2 = Me R^3 = H
Ni-142 R^1 = H R^2 = H R^3 = Me



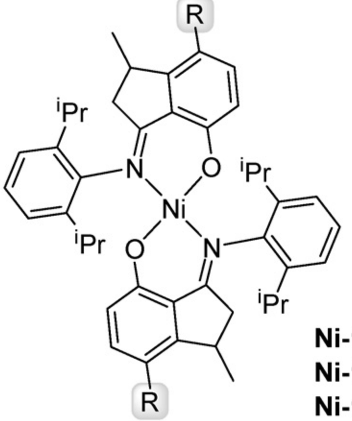
Ni-143 R^1 = H R^2 = H R^3 = H
Ni-144 R^1 = Cl R^2 = H R^3 = H
Ni-145 R^1 = Me R^2 = H R^3 = H
Ni-146 R^1 = H R^2 = OMe R^3 = H
Ni-147 R^1 = H R^2 = H R^3 = Me

Very high activities could be obtained with **Ni-148** containing a phenoxy-imidazole ligand in the presence of MAO. The activity values exceeded 10^8 $g_{polymer}/mol_{Ni}$ h. The optimal Al/Ni ratio was 10 000 and the best polymerization temperature was 45 °C. All PNBs generated with this system were of high molecular weight [171].

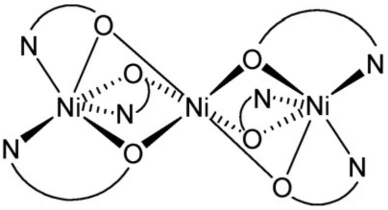


Ni-148

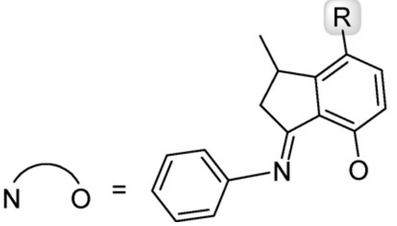
The mono- and trinuclear complexes **Ni-149** to **Ni-154** bearing indanimine ligands were activated with MAO to catalyze the norbornene polymerization with high yields of more than 10^7 g_{PNB}/mol_{Ni} h and high molecular weights (up to 10^6 g mol^{-1}). Both compounds **Ni-149** and **Ni-152** were studied under various reaction conditions. For **Ni-152**/MAO the optimal temperature was found to be 35 °C and a molar Al/Ni ratio of 7500 was optimal. The system **Ni-149**/MAO performed best for a temperature of 40 °C and an Al/Ni ratio of 4500. In general, the activities of the mononuclear complexes **Ni-149**, **Ni-150** and **Ni-151** were slightly higher than those of the trinuclear compounds **Ni-152**, **Ni-153** and **Ni-154** [172].



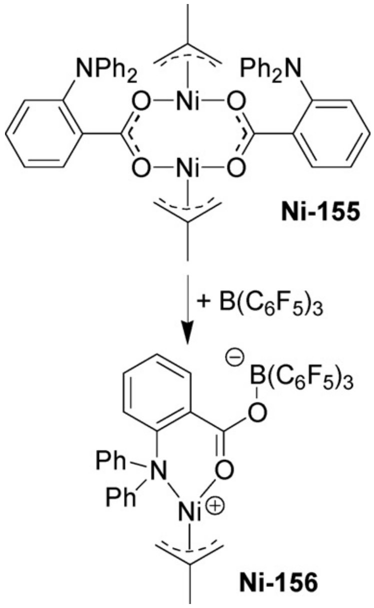
Ni-149 R = Me
Ni-150 R = H
Ni-151 R = Cl



Ni-152 R = Me
Ni-153 R = H
Ni-154 R = Cl



The dinuclear Ni(II)–carboxylate complex **Ni-155** did not show any activity towards the polymerization of norbornene, but could be transformed into the active compound **Ni-156** by reaction with $B(C_6F_5)_3$, which showed a high activity of up to $3.6 \times 10^6\ g_{polymer}/mol_{Ni}$ h. The variation of reaction temperature from room temperature to 70 °C did not show an effect on the activity but on the molecular weights which declined at the same time [173].



Ni-155

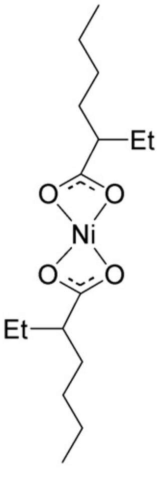
Ni-156

2.6.3. *O,O-Chelate ligands*

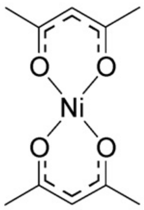
An acetylacetonato ligand was already part of the nickel complexes **Ni-1** and **Ni-2**.

Multinuclear mixed-metal chromium–nickel and iron–nickel $\{M_2Ni\}$-triangles and $\{M_7Ni\}$-wheels (M = Cr, Fe) with carboxylato-κ*O*:*O*′ ligands were already reported in the section on chromium and iron catalysts, respectively. The nickel content was important to reach high activities of $10^7\ g_{polymer}/mol_{metal}$ h. Without Ni, the polymerization activities were about three order of magnitude lower. For a $\{Cr_2Ni\}$-triangle see **Cr-4**, for $\{Cr_7Ni(\mu\text{-}F)_8\}$-wheels see **Cr-6** and **Cr-7**, for $\{Fe_2Ni\}$-triangles see **Fe-5** and **Fe-6** [117].

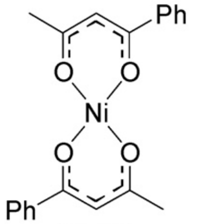
The Ni(II) complexes bis(acetylacetonato)nickel (**Ni-157**) and bis(2-ethylhexanoato)nickel (**Ni-158** [174]) were both activated with different cocatalysts such as MAO, $B(C_6F_5)_3$ with or without $AlEt_3$ for norbornene polymerization [175]. Attempts to activate with $AlEt_3$ alone or with triphenylborane $B(C_6H_5)_3$ with or without $AlEt_3$ failed. Both catalysts **Ni-157** and **Ni-158** exhibited a slightly higher or comparable activity with $B(C_6F_5)_3/AlEt_3$ than with MAO of more than $10^6\ g_{polymer}/mol_{Ni}$ h. Changing the sequence of addition of the cocatalytic compounds had effects on the catalytic activities. When the sequence of addition was changed from **Ni-157** + $B(C_6F_5)_3$ + $AlEt_3$ to **Ni-157** + $AlEt_3$ + $B(C_6F_5)_3$, a decrease of the activity was observed. When **Ni-158** was chosen as precatalyst changing the sequence of addition from **Ni-158** + $B(C_6F_5)_3$ + $AlEt_3$ to **Ni-158** + $AlEt_3$ + $B(C_6F_5)_3$ caused a decrease of the activity by a factor of 4 [175].



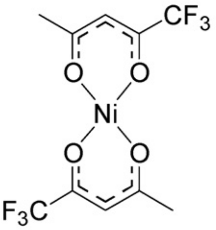
Ni-158



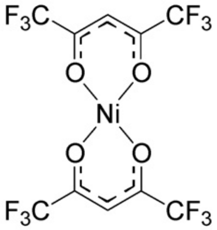
Ni-157



Ni-159



Ni-160



Ni-161

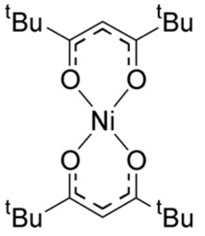
The activity of **Ni-157** and **Ni-158** with MAO also depended on the monomer/catalyst ratio [176]. For **Ni-157**/MAO the activity passed through a maximum for a monomer/Ni ratio of about 4100. A further increase of the norbornene concentration lowered the activity again. For the system **Ni-158**/MAO a continuous increase of activity was obtained when the norbornene/Ni ratio was changed from 770 to 5060. Both nickel catalysts **Ni-157** and **Ni-158** exhibited a steady increase of molar mass for the PNB formed with increasing monomer/Ni ratio [176].

Compound **Ni-158** in the presence of $B(C_6F_5)_3$ in combination with MAO led to a complete monomer conversion within 1 h of reaction time (activity calculated as $10^5\ g_{polymer}/mol_{Ni}$ h [121]) [177].

In a later publication different cocatalysts for the activation of **Ni-158** were tested again such as MAO, $B(C_6F_5)_3$/MAO, $B(C_6H_5)_3$/MAO, BEt_3/MAO, $BF_3\cdot OBu_2$/MAO and $B(C_6F_5)_3/AlEt_3$. The system **Ni-158**/$B(C_6F_5)_3$/MAO showed the highest activity of more than $10^5\ g_{PNB}/mol_{Ni}$ h, whereas **Ni-158**/$B(C_6F_5)_3/AlEt_3$ only performed with an activity of $3.6 \times 10^3\ g_{PNB}/mol_{Ni}$ h. The other 4 mentioned catalytic systems were in a short range between 2.1 and $2.8 \times 10^4\ g_{polymer}/mol_{Ni}$ h [178]. As **Ni-158**/$B(C_6F_5)_3$/MAO was the most active among these systems it was used for further investigations. The optimal B/Ni ratio was found to be 5 and good yields were already obtained for a value of 3. At the same time, the average molecular weights of the polynorbornenes decreased with increasing B/Ni ratio from a value of 1–10. Also the Al/Ni ratio greatly influenced the polymerization activity. Changing the values from 20 to 100 enhanced the monomer conversion by a factor of 36. A variation of the temperature from 0 °C to 80 °C showed no influence on the activity but on the molecular weights of the polymers, which declined linearly with an increase in the polymerization temperature. Furthermore, both the activities and the molecular weight values increased with the polarity of the used solvents in the order of heptane < cyclohexane < toluene < chlorobenzene. Finally, the addition of 1-decene made it possible to control the molecular weights. With an increase of 1-decene amount both the molecular weights and the monomer conversion declined [178].

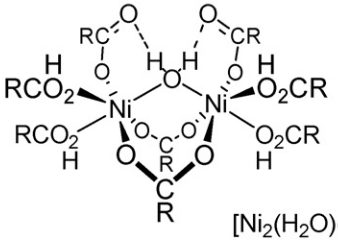
Complexes **Ni-157** and **Ni-159** to **Ni-161** were compared under the same polymerization conditions. The order of activities for the substituted acetylacetonato complexes was found to be **Ni-161** > **Ni-160** > **Ni-159** > **Ni-157**, indicating that electron-withdrawing groups and bulky substituents on β-diketonato ligands can increase the catalytic activities. Bulky substituents are capable of controlling chain transfer reactions. As a result, **Ni-159** produced higher molecular weight polymers than **Ni-157** [151].

Compound **Ni-162** was applied in the presence of different cocatalysts [179]. The addition of $B(C_6F_5)_3$ was essential for the polymerization. When the boranes $BF_3{\cdot}OEt_2$, $B(OEt)_3$ or $B(OC_6F_5)_3$ were used no monomer conversion was observed. Also, the addition of $AlEt_3$ to the system **Ni-162**/$B(C_6F_5)_3$ was not necessary for better activities as both systems produced PNB with the same activity under the same conditions in the area of 10^5 $g_{polymer}/mol_{Ni}$ h. In addition the effect of water on the polymerization system was investigated and the presence of certain amounts of water was found to double the monomer conversion. Also, the average molecular weights of the polymers obtained with the water containing catalytic system **Ni-162**/$B(C_6F_5)_3$ were significantly lower [179].



Ni-162

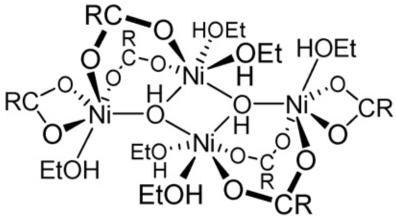
Activated with MAO, the di- and tetranuclear compounds **Ni-163** to **Ni-166** showed similar high polymerization activities of around 1.5×10^7 g_{PNB}/mol_{Ni} h. Compound **Ni-164** also was activated with $B(C_6F_5)_3/AlEt_3$ using different kinds of addition sequences for the cocatalytic system. When the sequence of addition was **Ni-164** + $AlEt_3$ + $B(C_6F_5)_3$ a slightly higher activity of 7.6×10^6 g_{PNB}/mol_{Ni} h was observed than for the sequence **Ni-164**+$B(C_6F_5)_3$ + $AlEt_3$ with 4.5×10^6 g_{PNB}/mol_{Ni} h. When the borane alone was used for activation, the activity decreased to a value of 7.5×10^5 g_{PNB}/mol_{Ni} h [117].



Ni-163

R = ^tBu

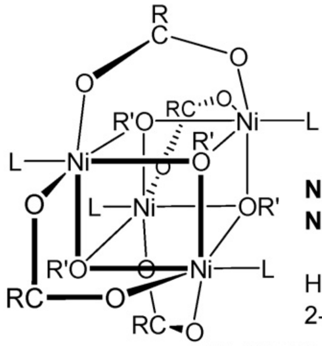
$[Ni_2(H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$



Ni-164

R = ^tBu

$[Ni_4(OH)_2(O_2C^tBu)_6(EtOH)_6]$



R = ^tBu

Ni-165 R' = CH_3, L = MeOH
Ni-166 R' = (O-)Mq, L = N(-Mq)

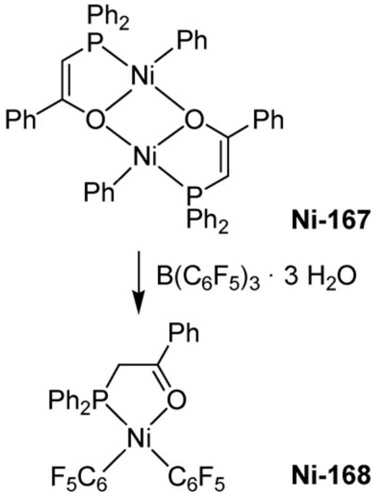
HOMq = 6-hydroxy-2-methylquinoline

Ni-165 $[Ni_4(OCH_3)_4(O_2C^tBu)_4(MeOH)_4]$
Ni-166 $[Ni_4(O_2C^tBu)_4(OMq)_4]$

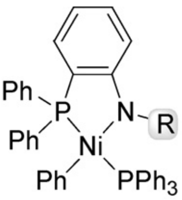
2.6.4. Phosphane (arsane, stibane) ligands

Nickel complexes with a single PPh_3 ligand are reported in the sections on *N*,*N*-, *N*,*O*- and *O*,*O*-chelate ligands (see complexes **Ni-9**, **Ni-10**, **Ni-16**, **Ni-17**, **Ni-27** to **Ni-30**, **Ni-54** to **Ni-77**, **Ni-118, Ni-119**) and in the section on multidentate carbon ligands (see **Ni-188**, **Ni-189**). In this section the focus is mainly on complexes with two or more phosphane ligands, including chelating bisphosphanes. In addition, complexes with *P*,*O*- and *P*,*N*-chelate ligands are included.

The dimeric complex **Ni-167** formed an active species with $B(C_6F_5)_3$ and showed a low activity of 7.9×10^4 g_{PNB}/mol_{Ni} h for norbornene polymerization. However, the activity of the complex was boosted by almost an order of magnitude by addition of two equivalents of $B(C_6F_5)_3{\cdot}3H_2O$ and increased to 4.1×10^5 g_{PNB}/mol_{Ni} h , which was known from previous work to react with **Ni-167** to form compound **Ni-168** via an unprecedented transfer of two pentafluorophenyl groups from B to Ni [179,180].

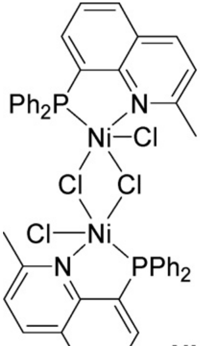


High polymerization activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h were afforded with the *P*,*N*-chelate complexes **Ni-169** and **Ni-170** with MAO as cocatalyst [181]. The optimal Al/Ni ratio was found to be 3000 for both precatalysts. The reaction temperature was investigated for **Ni-169**. When changed from 0 °C to 90 °C the maximum activity was observed for a temperature of 30 °C. In addition, the activity increased with higher monomer concentrations until a plateau was reached for a norbornene concentration of 3 mol/l.



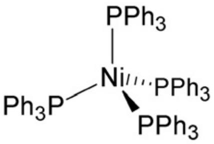
Ni-169 R = H
Ni-170 R = Me

Precatalyst **Ni-171** could be activated with MAO as cocatalyst. The optimal molar Al/Ni ratio here was 600. An increase in norbornene concentration greatly enhanced the polymerization activity. When the NB/Ni ratio was varied from 1062 to 20 000 an increase of the activity by more than factor 10^3 was observed and a very high catalytic activity of more than 10^8 $g_{polymer}/mol_{Ni}$ h was obtained. The effect of the reaction temperature was also investigated and 25 °C was found to be the optimized temperature [182].

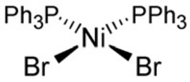


Ni-171

Tetrakis(triphenylphosphane)nickel(0), **Ni-172** was used in combination with $BF_3{\cdot}OEt_2$ for norbornene polymerization with good activities in the range of 10^6 $g_{polymer}/mol_{Ni}$ h [183]. The molar B/Ni ratio greatly influenced the polymerization activity and a variation of this ratio from 50 to 500 led to a steep increase until for a value of 300 an activity plateau was reached. **Ni-172**/$BF_3{\cdot}OEt_2$ was active over a wide range of temperature with 65 °C to be optimal. At the same time, the average molecular mass of the polymers increased with an increase in the B/Ni ratio and decreased with higher temperatures. Furthermore higher monomer concentration caused an increase of the activity [183].

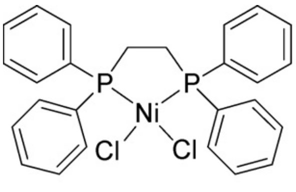


Ni-172

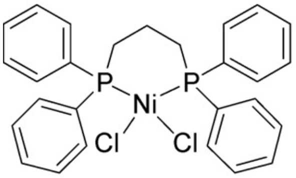


Ni-173

The phosphane complexes **Ni-172**, **Ni-173** and **Ni-174**, were compared for NB polymerization [177]. **Ni-172** was used in the presence of $B(C_6F_5)_3$ leading to a 65% monomer conversion for a B/Ni ratio of 5 (activity calculated as 6.5×10^4 g_{PNB}/mol_{Ni} h [121]). Compounds **Ni-173** and **Ni-174** were used in combination with the cocatalytic system $B(C_6F_5)_3$/MAO. For **Ni-173** only traces of norbornene were converted and **Ni-174** performed with 39% conversion (activity calculated by 3.9×10^4 g_{PNB}/mol_{Ni} h [121]) [177,178].



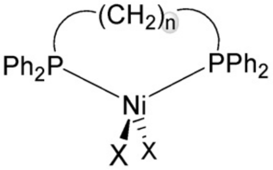
Ni-174



Ni-175

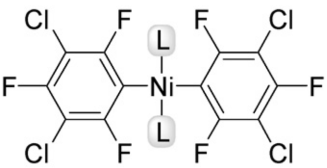
Precatalysts **Ni-174** and **Ni-175** gave rise to norbornene polymerization catalysts when activated with MAO or $B(C_6F_5)_3/AlEt_3$. When the borane was used as the activator, $AlEt_3$ had to be simultaneously applied for the halide/alkyl exchange to create the active species and as a scavenger for impurities. The activities obtained were rather low in a range from 3.9×10^3 to 2.9×10^4 g_{PNB}/mol_{Ni} h. Higher activities were observed with MAO than with $B(C_6F_5)_3/AlEt_3$ and **Ni-175** was slightly more active than **Ni-174** [184].

The diphosphane complexes **Ni-174**, **Ni-175** and **Ni-176** to **Ni-178** were used with moderate activities when activated with MAO [119]. Only complexes **Ni-176** and **Ni-178** containing the six- or seven-membered dppb and dpppt ligands exhibited activities around or above 10^5 $g_{polymer}/mol_{Ni}$ h. For the compounds **Ni-174** and **Ni-175** the conversion and activity with MAO was unremarkable. The same trend with similar activities was observed when compounds **Ni-174**, **Ni-175**, **Ni-176** and **Ni-178** were activated with $B(C_6F_5)_3$ in combination with $AlEt_3$. **Ni-176** and **Ni-178** could also be activated with the borane alone to moderate activities. Precatalyst **Ni-177** containing bromine instead of chlorine catalyzed the norbornene polymerization after activation with MAO or $B(C_6F_5)_3/AlEt_3$. With the latter cocatalytic system the activity exceeded 10^5 g_{PNB}/mol_{Ni} h [119].



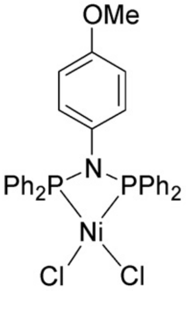
Ni-174 n = 2, X = Cl, Ni(dppe)Cl_2
Ni-175 n = 3, X = Cl, Ni(dppp)Cl_2
Ni-176 n = 4, X = Cl, Ni(dppb)Cl_2
Ni-177 n = 2, X = Br, Ni(dppe)Br_2
Ni-178 n = 5, X = Br, Ni(dpppt)Br_2

Among the Ni(II) precatalysts **Ni-179** to **Ni-183**, only compounds **Ni-179**, **Ni-180** and **Ni-181** polymerized norbornene, with yields between 72% and 90% (activities calculated as $2.7–3.4 \times 10^5$ g_{PNB}/mol_{Ni} h [121]) and with L = $SbPh_3$ showing the highest conversion. Interestingly, no cocatalysts were required to perform the polymerization [185]. With **Ni-182** and **Ni-183** only traces of PNB were obtained under the same conditions.



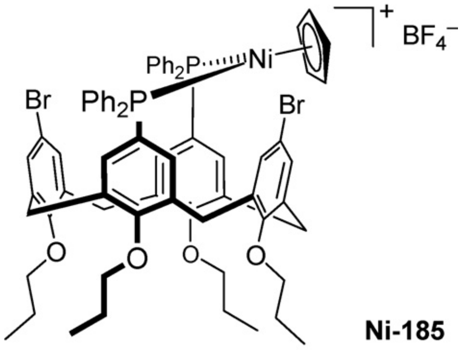
Ni-179 L = $SbPh_3$
Ni-180 L = $AsPh_3$
Ni-181 L = $AsCyPh_2$
Ni-182 L = $AsMePh_2$
Ni-183 L = PPh_3
Cy = cyclohexyl

The (diphosphinoamine)nickel(II) complex **Ni-184** exhibited activities in the range of $10^5–10^6$ g_{PNB}/mol_{Ni} h under various reaction conditions [186]. The optimal temperature was 20 °C. The best Al/Ni ratio was 500 and required was at least a value of 300.

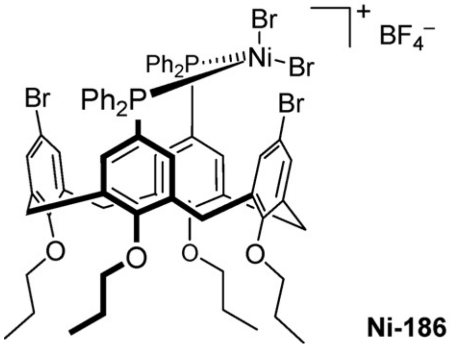


Ni-184

The complexes *cis-P,P′*-(η^5-cyclopentadienyl)-{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}nickel(II) tetrafluoroborate (**Ni-185**) and dibromo-{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxy-calix[4]arene}nickel(II) (**Ni-186**), both of which contain a constrained chelating diphosphine built upon a calix[4]arene skeleton produced polynorbornene with activities of up to 7.5×10^5 g_{PNB}/mol_{Ni} h under the same conditions and activated with MAO [187]. For further investigations the system **Ni-186**/MAO was used. The molar Al/Ni ratio was best for a value of 1000. The influence of the reaction time was also investigated. It was found that within 5 min the maximum conversion was almost reached. When the reaction times were varied from 5 min to 24 h, the monomer conversion slightly increased from 83% to 90% and the molar mass of the polymer did not vary significantly [187].



Ni-185



Ni-186

2.6.5. Multidentate carbon-bonded ligands

The previous sections on chelating ligands already featured nickel–carbon bound complexes with ligands like phenyl (**Ni-16**, **Ni-17**, **Ni-27** to **Ni-30**, **Ni-54** to **Ni-68**, **Ni-75** to **Ni-77**, **Ni-118**, **Ni-119**, **Ni-167**), naphthyl (**Ni-69** to **Ni-74**), allyl (**Ni-156**) and perfluorophenyl (**Ni-168**). The last section on phosphane ligands included nickel complexes with carbon-bound ligands such as phenyl (**Ni-169**, **Ni-170**), chlorofluorophenyl (**Ni-179** to **Ni-183**) and cyclopentadienyl (**Ni-185**).

The allyl, η^6-toluene and cyclopentadienyl nickel complexes would belong in this section, here. Yet, in combination with the *N,O*-chelating ligand for allyl (**Ni-156**) and a *P,P*-chelating ligand for cyclopentadienyl (**Ni-185**) the multidentate carbon group is probably the labile ligand which is lost upon activation.

A readily active catalyst, without the need of a cocatalyst, should contain pentafluorophenyl ligands and one or two labile ligands that can be readily displaced by norbornene. A prototype is complex **Ni-187** with the weakly coordinating η^6-toluene ligand, which was applied for the copolymerization of norbornene with 5-triethoxysilylnorbornene (the substituted norbornene was incorporated for polymer solubility) [179].

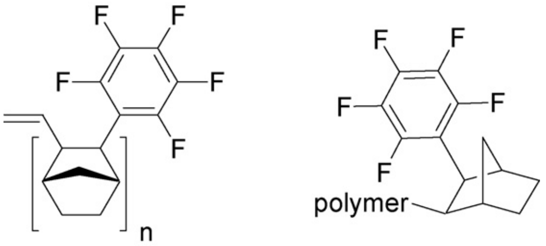
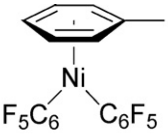


Fig. 11. End-group structure of the PNB polymer obtained with **Ni-187** in the presence of ethylene, based upon ^{1}H- and ^{13}C NMR investigations [179].

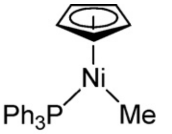


Ni-187

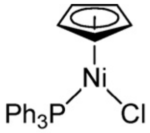
Complex **Ni-187** was also used to investigate the mechanism of the norbornene polymerization, whose initiation step is of high interest. The most direct proof of the initiation mechanism would come from elucidation of the end-group structure of the polymer. The norbornene/5-triethoxysilylnorbornene copolymers produced by **Ni-187** were of too high molecular weight to determine the end-group by NMR. Thus, norbornene was polymerized in the presence of ethylene at a 500:1 norbornene to nickel ratio. ^{1}H NMR and ^{19}F NMR showed that the polynorbornene obtained had the end-groups $-CH{=}CH_2$ and $-C_6F_5$ with an *exo*-enchainment of the latter (Fig. 11) [179].

This allowed the suggestion of a mechanism of chain initiation and termination (Fig. 12): The chain start occurs via insertion of the *exo* face of the norbornene monomer into the $Ni-C_6F_5$ bond. Presumably, coordination of norbornene to Ni takes place prior to insertion. This explains the higher activity observed for **Ni-187** with its labile toluene ligand compared to complex **Ni-168** containing a chelate ligand [179]. After the first norbornene insertion, propagation ensues. After insertion of ethylene, a $(C_6F_5)Ni-CH_2-CH_2-(NB)_n-C_6F_5$ capped norbornene polymer intermediate is formed. Free rotation about the $-CH_2-CH_2-$ bond of this intermediate offers two β-hydrogen atoms that can be readily eliminated to form a neutral species and a vinyl-terminated poly(norbornene) chain. The $(C_6F_5)Ni-H$ moiety decomposes via reductive elimination of pentafluorobenzene and nickel(0).

Complex **Ni-188** was activated with the cocatalysts $B(C_6F_5)_3$, $Ph_3C^+B(C_6F_5)_4^-$ or MMAO. For **Ni-189** MMAO, $B(C_6F_5)_3/AlMe_3$ or $Ph_3C^+B(C_6F_5)_4^-/AlMe_3$ were applied as cocatalysts [188]. For **Ni-188** the cocatalytic system $Ph_3C^+B(C_6F_5)_4^-$ afforded the highest activity of more than 10^6 $g_{polymer}/mol_{Ni}$ h. With the borane or MAO the activities were rather low. For **Ni-189** the activities were moderate on the order of 10^5 $g_{polymer}/mol_{Ni}$ h in all cases. Both catalysts were also able to catalyze the copolymerization of norbornene with 5-norbornene-2-carboxylic acid methyl ester [188].



Ni-188



Ni-189

From the two *cis N*-heterocyclic carbene complexes **Ni-190** and **Ni-191** the former could catalyze the norbornene polymerization in the presence of MAO with excellent activities of more than 10^7 $g_{polymer}/mol_{Ni}$ h and high molecular weights in the range of 10^6 g/mol. A polymerization temperature of at least 40 °C was

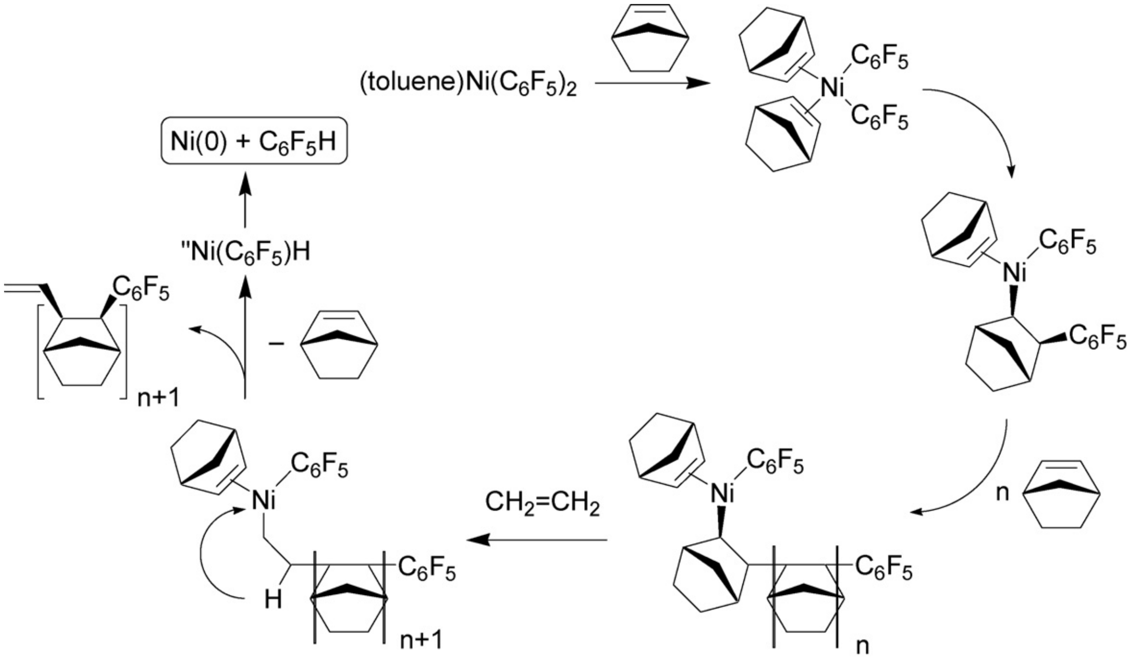
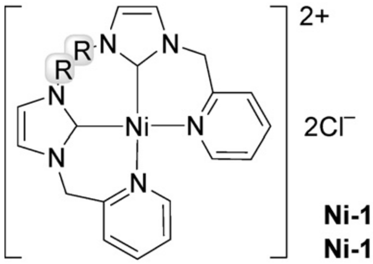


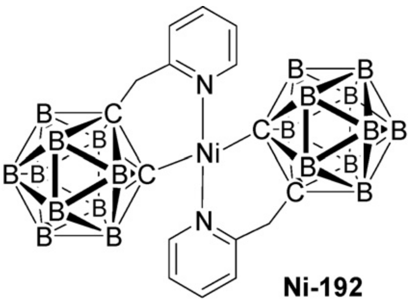
Fig. 12. Suggested polymerization mechanism of norbornene with **Ni-187** in the presence of ethylene [179].

required. The optimum was 80 °C, but also at 100 °C good activities were obtained. At the same time, the average molar weights of the polymers decreased with increasing temperature. Variation of the reaction time showed that the monomer conversion increased with longer reaction times and the catalytic activities decreased at the same time due to the decreasing norbornene concentration during the reaction [189].



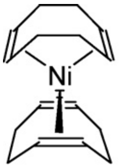
Ni-190 R = Me
Ni-191 R = benzyl

The picolyl-functionalized carborane Ni(II) complex **Ni-192** could be activated with MAO and showed activities up to 3×10^6 g_{PNB}/mol_{Ni} h and molar masses in the range of 10^5 g/mol. A variation of the molar Al/Ni ratio from 3000 to 10 000 showed a maximum activity for a value of 8000. At the same time, the molar masses of the polynorbornenes increased significantly with higher amounts of MAO. The reaction temperature was found to be optimal at 60 °C [190].



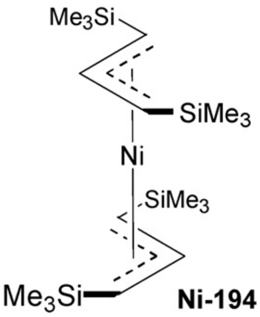
Ni-192

The bis(cyclooctadiene)nickel(0) compound, Ni(cod)$_2$ **Ni-193** was tested in the presence of the borane activators $B(C_6F_5)_3$, $B(C_6H_5)_3$, BEt_3 and $BF_3 \cdot OBu_2$, of which only $B(C_6F_5)_3$ produced PNB in high yields of 96% (activity calculated as 9.6×10^4 g_{PNB}/mol_{Ni} h [121]) [177]. In order to investigate the polymerization mechanism, a small amount of ethylene was added and the end groups analyzed by ^{1}H- and ^{19}F NMR. The resulting polymer was vinyl terminated on one side and C_6F_5-terminated on the other end of the PNB-chain. These results pointed to a polymerization mechanism very similar to that postulated by Goodall and co-workers in [179] (Fig. 12).



Ni-193

The bis(allyl)-Ni(II)-complex **Ni-194** was activated with MAO to catalyze the vinyl polymerization of norbornene with high yields (activity calculated as 2.3×10^5 g_{PNB}/mol_{Ni} h [121]) [122].



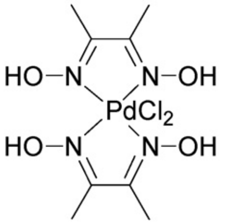
Ni-194

2.7. Palladium catalysts

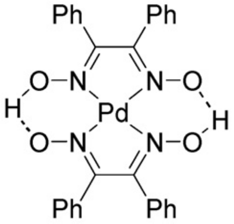
Palladium(II) complexes also constitute a large group of compounds for the polymerization of norbornene. For a better overview the Pd complexes are grouped according to the major ligand type just like the Ni complexes. In heteroleptic complexes of the type Pd(A^B)CD the bidentate A^B chelate ligand is usually viewed as the major ligand. A chelate ligand is more likely to remain bonded upon activation by the cocatalyst and, therefore, can affect the metal catalyst properties, whereas the monodentate (C, D) ligands are probably lost to create the necessary vacant sites for norbornene coordination.

2.7.1. N,N-Chelate ligands

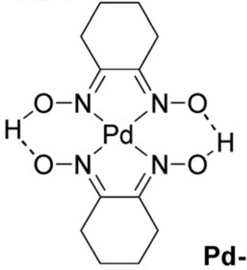
The Pd(II) complexes **Pd-1** to **Pd-3** with α-dioxime ligands were investigated with the different activators MAO, $B(C_6F_5)_3/AlEt_3$ and $B(C_6F_5)_3$ alone for norbornene polymerization. The activities covered a range between 1.2×10^4 and 3.2×10^7 $g_{polymer}/mol_{Pd}$ h. Compound **Pd-1** always showed the highest activity which was similar for MAO or $B(C_6F_5)_3/AlEt_3$ but lower for the borane. When the polarity of the solvent was decreased by going from a toluene/methylene chloride mixture (1:1, v/v) to pure toluene a slight decrease in polymerization activity was observed which suggested a complex-cation/MAO-anion pair as the active species [139].



Pd-1

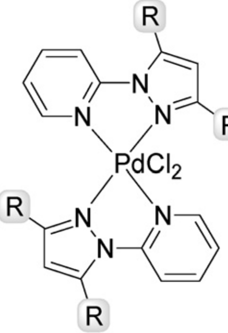


Pd-2



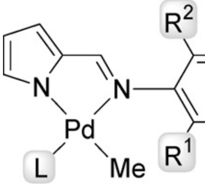
Pd-3

Among the compounds **Pd-4** to **Pd-7** with pyrazolylpyridine ligands in combination with MAO only the system **Pd-4**/MAO showed a moderate activity of 1.33×10^5 $g_{polymer}/mol_{Pd}$ h, whereas **Pd-5**/MAO and **Pd-6**/MAO produced only traces of polynorbornene and **Pd-7**/MAO was completely inactive [141].

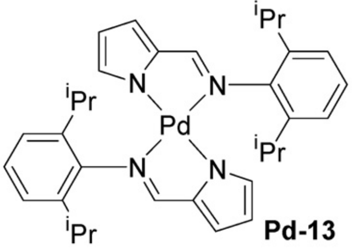


Pd-4 R = Me
Pd-5 R = Ph
Pd-6 R = ^{t}Bu
Pd-7 R = *p*-methoxyphenyl

The palladium(II) complexes **Pd-8** to **Pd-13** with pyrrole-iminato ligands gave high and similar activities of ~10^6 $g_{polymer}/mol_{Pd}$ h with MMAO. Detailed investigations for **Pd-8**/MMAO showed a maximum activity for a catalyst concentration of 0.025 μmol/ml and an Al/Pd ratio of 1500 (in the range 500–2500). For higher ratios the activity just increased slightly. An increase in NB/Pd ratio from 10 000 to 80 000 led to a decrease in polymerization activity [192].

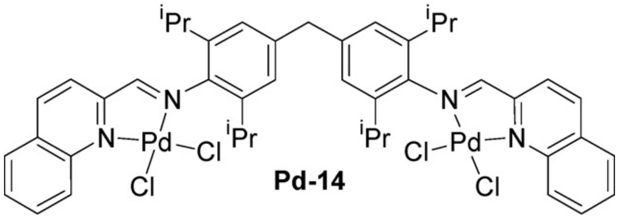


Pd-8 R^1 = ^{i}Pr R^2 = ^{i}Pr L = PPh_3
Pd-9 R^1 = Me R^2 = Me L = PPh_3
Pd-10 R^1 = H R^2 = ^{t}Bu L = PPh_3
Pd-11 R^1 = H R^2 = H L = PPh_3
Pd-12 R^1 = ^{i}Pr R^2 = ^{i}Pr L = py

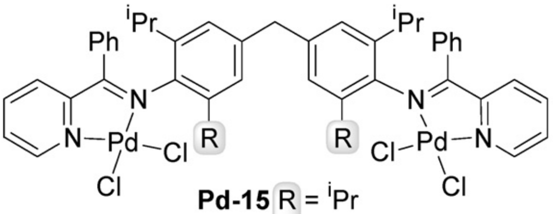


Pd-13

The dinuclear diimine palladium complexes **Pd-14** to **Pd-16** with MAO catalyzed the vinyl polymerization of norbornene with activities in the range of 10^6 g_{PNB}/mol_{Pd} h. The activity of **Pd-16**/MAO was slightly higher than that of **Pd-15**/MAO, which seems to be due to the smaller size of the methyl substituent. The system **Pd-16**/MAO was used to study the influence of the polymerization conditions on the catalytic activity. When the molar Al/Pd ratio was decreased from 525 to 35, the activity also decreased, but still remained in the area of 10^5 g_{PNB}/mol_{Pd} h. Furthermore, the activity decreased with a decrease of the monomer concentration [147].

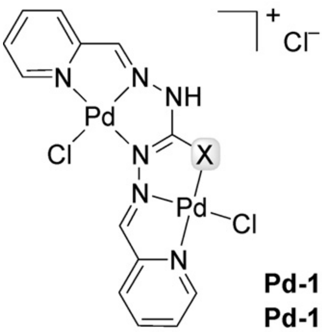


Pd-14



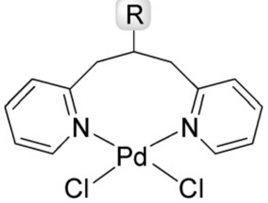
Pd-15 R = ^{i}Pr
Pd-16 R = Me

The dinuclear Pd(II) complexes **Pd-17** and **Pd-18** were applied for the polymerization of norbornene with MAO, $B(C_6F_5)_3$ or $B(C_6F_5)_3/AlEt_3$ as cocatalysts. When MAO or $B(C_6F_5)_3/AlEt_3$ were used, the activities were in the area of 10^7 $g_{polymer}/mol_{Pd}$ h. Compound **Pd-17** was slightly more active than **Pd-18** under the same conditions. With the borane alone the activity decreased drastically to 2.7×10^4 $g_{polymer}/mol_{Pd}$ h (**Pd-17**). The system **Pd-18**/$B(C_6F_5)_3$ exhibited even no monomer conversion [140,148].



Pd-17 X = O
Pd-18 X = S

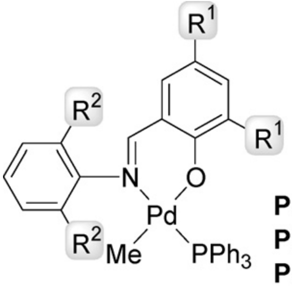
After activation with MAO, the Pd(II) complexes **Pd-19** to **Pd-23** yielded quantitative conversion of norbornene within a short period of time (5 min, activity 1.1×10^6 $g_{polymer}/mol_{Pd}$ h [121]). No further investigations on the homopolymerization of norbornene were conducted, but the precatalysts were also used for the copolymerization of norbornene with different norbornene derivatives [191].



Pd-19 R = H
Pd-20 R = n-pentyl
Pd-21 R = phenyl
Pd-22 R = *p*-tolyl
Pd-23 R = ferrocenyl

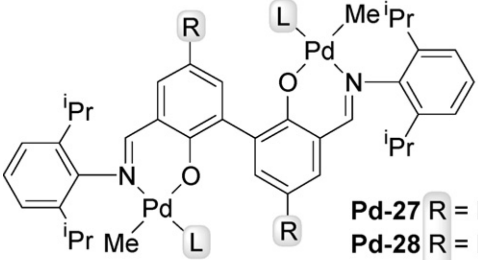
2.7.2. *N,O(N,S)-Chelate ligands*

The precatalysts **Pd-24** to **Pd-26** bearing salicylaldiminato substituents could be activated with MMAO. The activities were in the area of 10^6 $g_{polymer}/mol_{Pd}$ h and in the order of **Pd-24** > **Pd-25** > **Pd-26**. For **Pd-24**/MMAO an optimal reaction temperature of 30 °C was found [192].

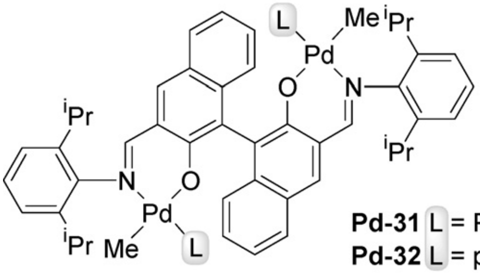


Pd-24 R^1 = ^tBu R^2 = Me
Pd-25 R^1 = ^tBu R^2 = ^iPr
Pd-26 R^1 = NO_2 R^2 = ^iPr

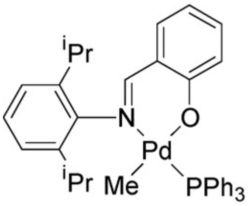
The neutral salicylaldiminato Pd(II) complexes **Pd-27** to **Pd-32** in combination with MMAO exhibited extremely high polymerization activities of more than 10^8 $g_{polymer}/mol_{Pd}$ h for **Pd-27**/MMAO, **Pd-29**/MMAO and **Pd-31**/MMAO, in particular [157]. To understand the high activities of **Pd-27** and **Pd-29** the mononuclear salicylaldiminato palladium complex **Pd-33** was synthesized and its catalytic behaviour was investigated under the same conditions. This mononuclear complex displayed much lower activities than the corresponding binuclear complexes **Pd-27** and **Pd-29**. Obviously, bulky groups in the 3-position of the salicylaldiminato fragment were responsible for the high catalytic activities of the binuclear palladium complexes [157]. It was also found that the palladium complexes with pyridine exhibited much lower activities than those with PPh_3. One would expect that Pd complexes bearing a more weakly bound pyridine ligand have higher activities than those bearing a more strongly bound PPh_3 ligand because of the need to dissociate the donor ligand to free a coordination site for the monomer. Therefore, it was assumed that the bulky PPh_3 dissociates more easily than the small pyridine under activation with MMAO [157]. The activity of **Pd-27**/MMAO depended on the amount of the cocatalyst. The activity slowly increased with an increase of the molar Al/Pd ratio and reached the highest value for a ratio of 2500. With a further increase of the Al/Pd ratio the activity decreased. An increase of the reaction temperature from 20 °C to 70 °C caused an increase in the activity. Also, the catalytic activity increased with higher monomer concentrations up to 7×10^7 g_{PNB}/mol_{Pd} h [157].



Pd-27 R = H L = PPh_3
Pd-28 R = H L = py
Pd-29 R = NO_2 L = PPh_3
Pd-30 R = NO_2 L = py

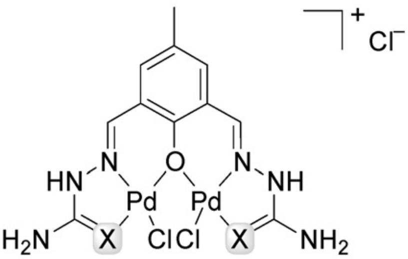


Pd-31 L = PPh_3
Pd-32 L = py



Pd-33

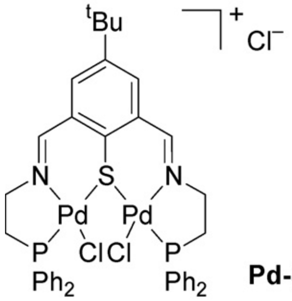
The dinuclear Pd(II) complexes **Pd-34** and **Pd-35** with Schiff-base hydrazone ligands were applied for the polymerization of norbornene with MAO, $B(C_6F_5)_3$ or $B(C_6F_5)_3/AlEt_3$ as cocatalysts. When MAO or $B(C_6F_5)_3/AlEt_3$ were used, the activities were in the area of 10^6–10^7 $g_{polymer}/mol_{Pd}$ h. With the borane alone the activity decreased drastically to 6.3×10^2 (**Pd-34**) or 5.3×10^2 $g_{polymer}/mol_{Pd}$ h [140,148].



Pd-34 X = S, +2DMF
Pd-35 X = O, +DMF

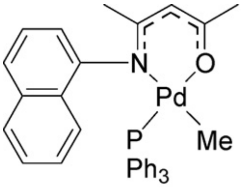
Compound **Pd-36** with its dinucleating P_2N_2S ligand was tested for the norbornene polymerization in combination with MAO or

$B(C_6F_5)_3/AlEt_3$ [193]. Activities between 10^5 and 10^6 g_{PNB}/mol_{Pd} h were obtained. So the activity of the dinuclear Pd complex **Pd-36** is lower than that of the related precatalysts **Pd-34** and **Pd-35**. This observation was attributed to the presence of the Ph_2P-ligating group which can shield the active center with its bulkiness and because the Pd-P bond is less likely to open even in the presence of the cocatalysts to create a required open coordination site.



Pd-36

The palladium(II) complex **Pd-37** in combination with MAO exhibited a very high activity of up to 8 × 10^7 g_{PNB}/mol_{Pd} h over a wide temperature range (0–80 °C) with 60 °C as the optimal temperature. This system was also active for the copolymerization of norbornene and norbornene carboxylic acid methylester [166].

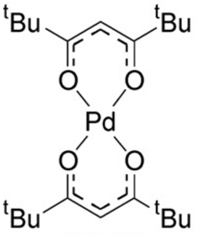


Pd-37

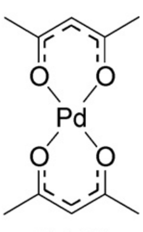
2.7.3. *O,O-Chelate ligands*

With complex **Pd-38** in combination with $B(C_6F_5)_3$ the activity increased by almost a factor of 10 (to 3.66 × 10^5 g_{PNB}/mol_{Pd} h) by raising the molar B/Pd ratio from 1 to 10 [179].

The system bis(acetylacetonato)palladium(II) (**Pd-39**) with borontrifluoride etherate ($BF_3{\cdot}OEt_2$) featured high activities up to 2 × 10^7 $g_{polymer}/mol_{Pd}$ h at an optimized B/Pd ratio of 25. The activities decreased dramatically with increasing the monomer/Pd ratio from 5600 to 56 000. The structure of the polymer from **Pd-39**/$BF_3{\cdot}OEt_2$ was found by NMR and FTIR spectroscopy to consist exclusively of 2,7-enchained repeating norbornene units (see Fig. 1) [194].

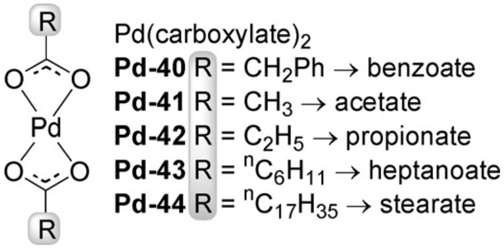


Pd-38



Pd-39

Palladium(II) carboxylates **Pd-40** to **Pd-44**, in particular $Pd(OAc)_2$, and $BF_3{\cdot}OEt_2$, gave high activities of more than 10^6 g_{PNB}/mol_{Pd} h [195].

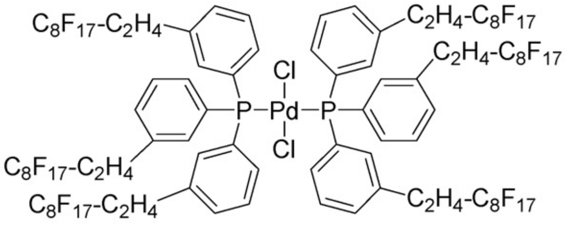


For the system **Pd-41**/$BF_3{\cdot}OEt_2$ the molar B/Pd ratio was varied between 5 and 60 and a ratio of 40 was found to be optimal. The average molecular weight of the generated PNBs increased at the same time. When the temperature was raised from 15 °C to 65 °C both the activity and molar mass decreased, which indicated an active species of low thermal stability. The NB/Pd ratio had no effect on the activity, thus, indicating zero order of the reaction rate with respect to monomer. A higher concentration of precatalyst led to higher monomer conversion and activities but the average molecular masses of the polymer decreased. The monomer conversion was not affected by the nature of the carboxylate ligand, whereas the PNB molecular weight showed a linear decrease with increasing acidity of the carboxylate ligands [195–197].

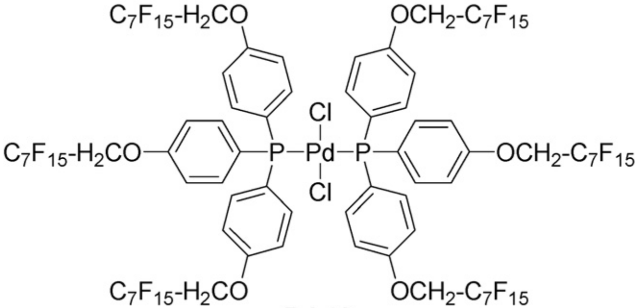
2.7.4. *Phosphane ligands*

Palladium complexes with a single PPh_3 ligand are reported in the sections on *N,N*-, *N,O*- and *O,O*-chelate ligands (see complexes **Pd-8** to **Pd-11**, **Pd-24** to **Pd-27**, **Pd-29**, **Pd-31**, **Pd-33**, and **Pd-37**) and in the section on multidentate carbon ligands (see **Pd-59**). A P_2N_2S-ligand was given in **Pd-36**. In this section the focus is on complexes with two phosphane ligands, including chelating bisphosphanes.

The two perfluorinated Pd(II) precatalysts **Pd-45** and **Pd-46** were designed for applying the *fluorous biphasic concept* (FBS) to the palladium-catalyzed addition polymerization of norbornene. The FBS concept should have allowed the chemical recovery of the active species by working in a biphasic system. Separation of the fluorous phase containing the perfluorinated (active) metal species would have opened the possibility to restart the polymerization by a simple addition of a new portion of monomer. Although the perfluorinated Pd(II) precatalysts **Pd-45** and **Pd-46** were proven to be highly active with the cocatalysts $B(C_6F_5)_3/AlEt_3$ or MAO, the aim to recycle the active species was not achieved. After each recycling step the addition of new cocatalyst was required and monomer conversions dropped considerably after the first recycling [198].



Pd-45



Pd-46

Compounds **Pd-47** to **Pd-50** with their bidentate 1,2-bis(diphenylphosphino)alkane ligands were used in combination with different cocatalysts [MAO and $B(C_6F_5)_3/AlEt_3$]. The activities were moderate around 10^3–10^5 $g_{polymer}/mol_{Pd}$ h except for the system **Pd-47**/$B(C_6F_5)_3/AlEt_3$, which showed an activity of more than 10^7 $g_{polymer}/mol_{Pd}$ h. It is noteworthy that the required cocatalyst quantities were much less with borane/$AlEt_3$ than with MAO for similar monomer conversions and activities. This leads to less

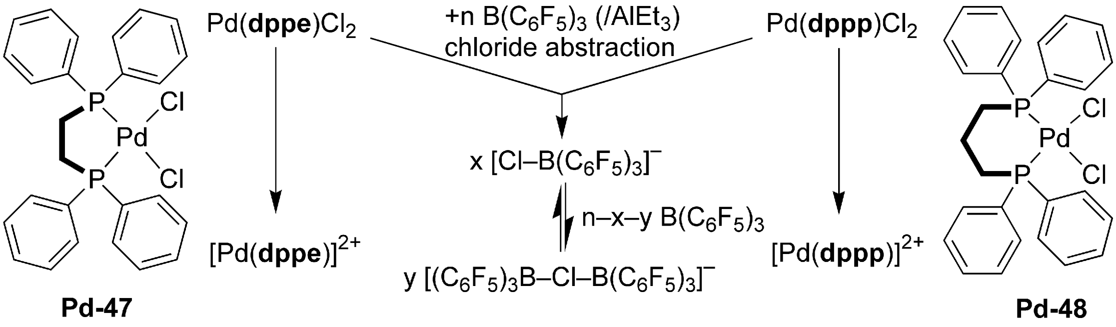
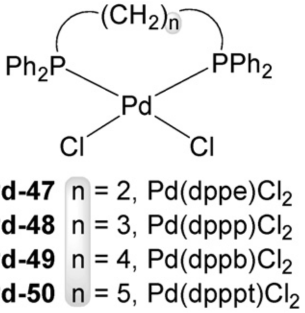


Fig. 13. Part of the activation process of precatalyst **Pd-47** and **Pd-48** with $B(C_6F_5)_3$ as elucidated by ^{19}F- and ^{31}P NMR [119,140].

cocatalyst residues in the polymer, which is highly advantageous for any prospective optical applications of polynorbornene [184].



The activity of compound **Pd-47** in comparison to the closely related compound **Pd-48** differed by a factor 6×10^3 when activated with $B(C_6F_5)_3/AlEt_3$ [119,140]. For both complexes two equivalents of borane were required to reach polymerization activity which then continued to increase somewhat with the borane ratio in combination with $AlEt_3$. A combined ^{19}F- and ^{31}P NMR study on the reaction of **Pd-47** and **Pd-48** with $B(C_6F_5)_3$ indicated chlorine abstraction with formation of a fast equilibrium between free excess borane and chloro-boranate, $[Cl–B(C_6F_5)_3]^-$ and a second slow equilibrium to chloro-diboranate, $[(F_5C_6)_3B–Cl–B(C_6F_5)_3]^-$ (Fig. 13). There was no indication of a phosphane ligand abstraction from **Pd-47** or **Pd-48**. These salient features did not change when the NMR-study was repeated with $B(C_6F_5)_3/AlEt_3$. On the other hand, the NMR-results did not explain the activity difference since apparently the same $[Pd(bisphosphane)]^{2+}$-species was initially formed. Results from X-ray structural investigations based on single-crystal products from the reactions of **Pd-47** and **Pd-48** with $B(C_6F_5)_3$ and Ag[*closo*-1-$CB_{11}H_{12}$], however, revealed a different stability and solution behavior of these $[Pd(phosphane)]^{2+}$-species: reaction with $B(C_6F_5)_3$ yielded crystals only for **Pd-47** and the X-ray structure showed a Pd^{2+}-cation with *two* dppe-bisphosphane ligands, $[Pd(dppe)_2]^{2+}$. In order to obtain crystalline products also based on **Pd-48**, the chloride abstraction was carried out with the silver salt of the monocarba-*closo*-dodecarborane(12) anion, Ag[*closo*-1-$CB_{11}H_{12}$]. Crystals from **Pd-47** again showed the Pd^{2+}-cation with two dppe ligands, $[Pd(dppe)_2]^{2+}$, while crystals from **Pd-48** contained the expected Pd^{2+}-cation with a single dppp ligand, $[Pd(dppp)]^{2+}$ (Fig. 14) [119,140].

The X-ray crystallographic results supported the notion from the NMR data of chloride abstraction and formation of $[Pd(bisphosphane)]^{2+}$-species. Yet, with bis(diphenylphosphino)ethane, dppe as a ligand, the $[Pd(bisphosphane)]^{2+}$-cation obviously is unstable with respect to a ligand redistribution (dismutation) reaction which yields a bis-dppe cation, $[Pd(dppe)_2]^{2+}$ together with an un-ligated Pd^{2+}-cation. The formation of an un-ligated Pd^{2+}-cation, which can be expected to be highly unstable, is supported by the formation of elemental palladium under non-polymerization conditions. There is no evidence that the cation from **Pd-48**, $[Pd(dppp)]^{2+}$, can enter in a similar ligand redistribution reaction. Hence, the activity difference was attributed to the formation of a highly reactive "naked" Pd^{2+}-cation

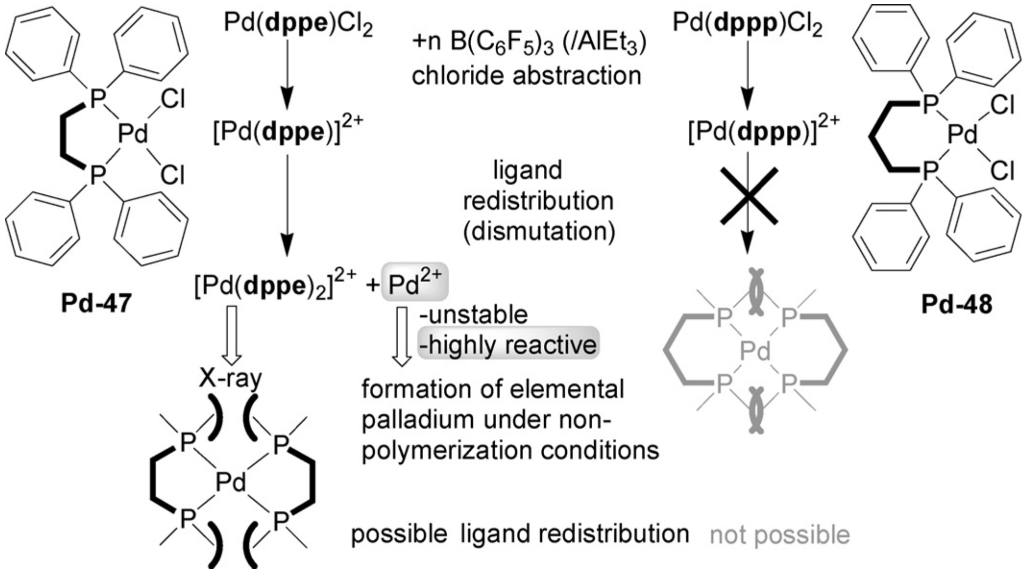


Fig. 14. Activation process of the precatalysts **Pd-47** and **Pd-48** with $B(C_6F_5)_3$ or $B(C_6F_5)_3/AlEt_3$ and the possibility of ligand redistribution for dppe and dppp ligands [119,140].

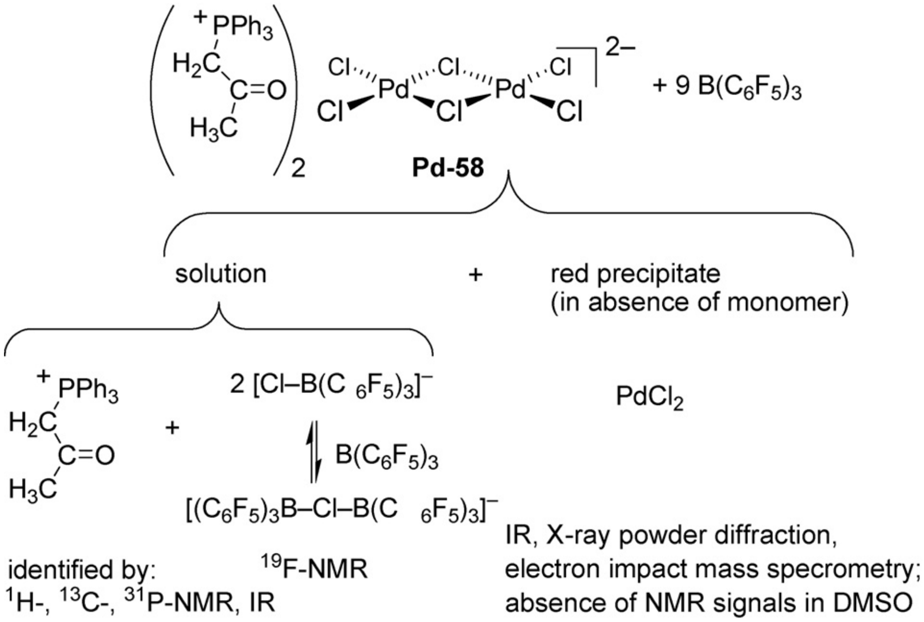
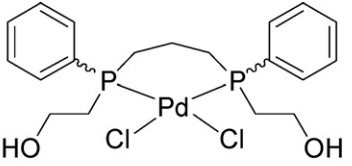


Fig. 15. Activation process of precatalyst **Pd-58** with $B(C_6F_5)_3$ [140,118].

in the case of **Pd-47** and the absence of the same for **Pd-48** (Fig. 14). The $[Pd(bisphosphane)]^{2+}$-cations themselves are apparently only of mediocre activity in the addition polymerization of norbornene [119,140].

The ligand redistribution with dppe in the case of **Pd-47** and the absence of this dismutation reaction with dppp for **Pd-48** can be explained with steric arguments due to the different bite angle and chelate ring size, which results in a different steric demand of the chelate ligand around the metal. The features of the dppe ligand allow for the formation of two five membered Pd(dppe)-rings around a square-planar Pd^{2+}-ion center. With the dppp ligand two six membered Pd(dppp)-rings in a square-planar geometry are not possible (and have not been structurally authenticated in the literature) because of inter-ligand repulsion between the sterically demanding phenyl groups [119,140].

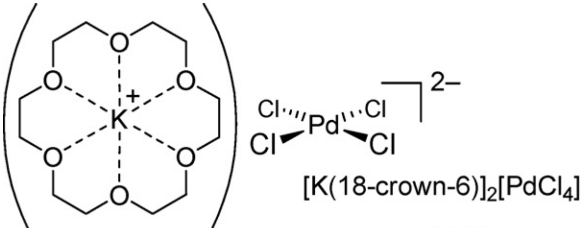
Precatalyst **Pd-51** was applied with MAO as cocatalyst and for two different Al/Pd ratios (500 and 1000) a ratio of 1000 gave the highest activity of 10^5 $g_{polymer}/mol_{Pd}$ h (better than the used reference substance $Pd(dppp)Cl_2$/MAO) [199].



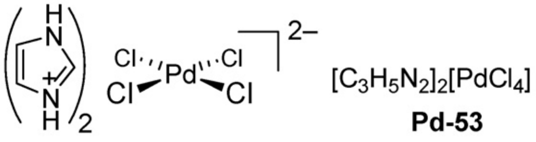
Pd-51

2.7.5. Homoleptic Pd complexes with chloro ligands

Palladium(II) salts containing the $[PdCl_4]^{2-}$ anion and the organic cations $[K(18\text{-crown-}6)]^+$ or $[imidazolium]^+$ such as **Pd-52** and **Pd-53** could be activated with MAO or $B(C_6F_5)_3/AlEt_3$. Precatalyst **Pd-52** exhibited a high activity of more than 10^7 g_{PNB}/mol_{Pd} h with the cocatalytic system $B(C_6F_5)_3/AlEt_3$ and a significant lower activity when MAO was used. Compound **Pd-53** showed high activities in the range of 10^6–10^7 g_{PNB}/mol_{Pd} h for both activators. Furthermore **Pd-52** and **Pd-53** also proved to be active with $B(C_6F_5)_3$ alone, yielding 10^4 $g_{polymer}/mol_{Pd}$ h. The inorganic Pd(II) compounds $PdCl_2$ (**Pd-54**) and K_2PdCl_6 (**Pd-55**) were tested under the same conditions and were considerably less active [140,118].



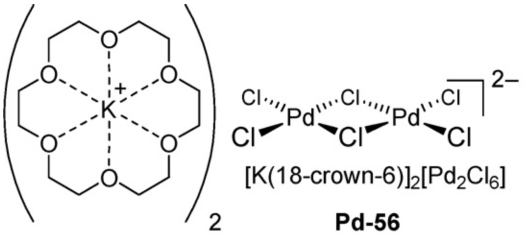
Pd-52



Pd-53

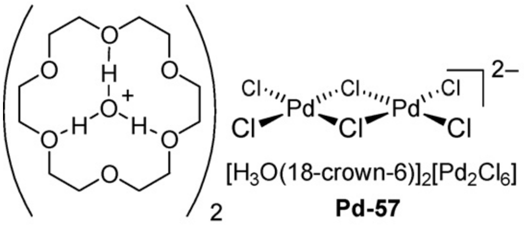
$PdCl_2$ **Pd-54** K_2PdCl_4 **Pd-55**

Palladium(II) salts **Pd-56** to **Pd-58** containing the $[Pd_2Cl_6]^{2-}$ anion and the organic cations $[K(18\text{-crown-}6)]^+$, $[H_3O(18\text{-crown-}6)]^+$ or $[Ph_3PCH_2C(O)CH_3]^+$ could be activated with MAO or $B(C_6F_5)_3/AlEt_3$ towards norbornene polymerization [140,118]. These catalytic systems gave very high activities of more than 10^7 g_{PNB}/mol_{Pd} h, except for **Pd-56**/MAO, which exhibited a lower activity of around 10^5 g_{PNB}/mol_{Pd} h. System **Pd-56**/MAO also proved to be active with $B(C_6F_5)$ alone, yielding almost 10^5 g_{PNB}/mol_{Pd} h. The inorganic Pd(II) compounds $PdCl_2$ (**Pd-54**) and K_2PdCl_6 (**Pd-55**) were tested under the same conditions and were considerably less active. The activation process of the precatalyst $[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]$ (**Pd-58**) in combination with the borane $B(C_6F_5)_3$ was followed by multinuclear (^1H, ^{13}C, ^{19}F, and ^{31}P)NMR investigations and pointed to the *in situ* formation of molecular $PdCl_2$ which may represent the active species in the polymerization process (Fig. 15) [140,118]. The higher activity of *in situ* prepared $PdCl_2$ from **Pd-58** over commercial, solid-state $PdCl_2$ (**Pd-54**) was attributed to a higher solubility, larger surface area or the polymer initiation by molecular $PdCl_2$ and its stabilization by the growing polymer chain.



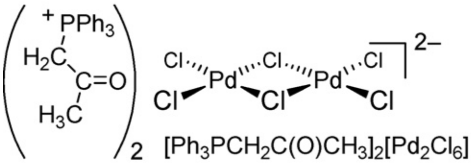
$[K(18\text{-crown-6})]_2[Pd_2Cl_6]$

Pd-56



$[H_3O(18\text{-crown-6})]_2[Pd_2Cl_6]$

Pd-57

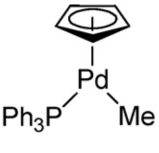


$[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]$ **Pd-58**

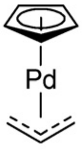
2.7.6. Multidentate carbon-bonded ligands

The sections on palladium catalysts with *N*,*N*- and *N*,*O*-chelate ligands also contained complexes with a Pd bound methyl group (Pd–Me) as carbon bonded ligand, namely **Pd-8** to **Pd-12**, **Pd-24** to **Pd-33**, and **Pd-37**. In this section the palladium-π complexes with the π-ligands cyclopentadienyl, allyl, alkene or with *N*-heterocyclic carbenes are summarized.

Compounds **Pd-59** and **Pd-60** were markedly affected in their activity by the cocatalyst. Activators used were $B(C_6F_5)_3$, MMAO (modified MAO containing isobutylalumoxane) and $Ph_3C^+B(C_6F_5)_4^-$ with an extremely high activity of more than 10^8 $g_{polymer}/mol_{Pd}$ h for **Pd-60**/$Ph_3C^+B(C_6F_5)_4^-$. With the other cocatalysts the activities decreased by several orders of magnitude for both precatalysts **Pd-59** and **Pd-60** covering a range from 10^4 to 10^6 $g_{polymer}/mol_{Pd}$ h [188].

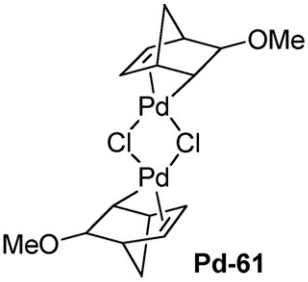


Pd-59



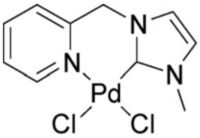
Pd-60

The vinyl polymerization of norbornene with **Pd-61** in combination with MAO was investigated by varying the molar Al/Pd ratio and the monomer/Pd ratio [176]. The Al/Pd ratio was varied from 30 to 200 and the activity increased at the same time. It was also shown that the MAO excess could be lowered without a significant loss in activity. Only when the molar Al/Pd ratio dropped below a value of 30 a significant decrease in activity occured. The optimal monomer/Pd ratio was found to be at around 2300; a further increase of this ratio then caused a decrease of the polymerization activity. This may be explained by impurities in the monomer which eventually decrease the number of active centers. In general, the activities exceeded 10^6 g_{PNB}/mol_{Pd} h [176].



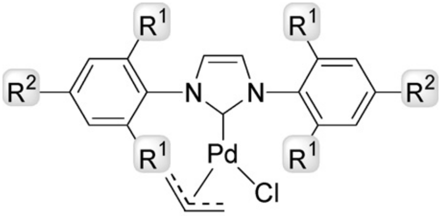
Pd-61

The palladium carbene complex **Pd-62** could be activated with MAO to catalyze the norbornene polymerization with very high activities of up to 10^8 $g_{polymer}/mol_{Pd}$ h. The molar ratio of Al to Pd greatly affected the activity; the activity increased rapidly as the molar Al/Pd ratio increased. Also, the polymerization temperature influenced the catalytic activity. When the temperature rose from 0 °C to 40 °C the activity increased as well [200].



Pd-62

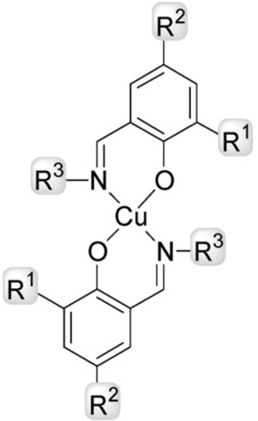
A series of *in situ* generated allyl palladium complexes bearing *N*-heterocyclic carbene ligands (**Pd-63** to **Pd-67**) were proven to be catalysts for the norbornene polymerization once activated with $AgBF_4$ or $AgSbF_6$. The catalytic activities were highly dependent on the counterion, the solvent, and the reaction temperature. High yields were obtained for the catalysts **Pd-64** to **Pd-67** (99% each [124]), whereas complex **Pd-63** exhibited only a poor monomer conversion of 30%. Catalysts **Pd-65** to **Pd-67** were also used for the polymerization of the norbornene derivatives 5-norbornene-2-carboxylic-acid methyl ester (NB–CO_2Me) and 5-norbornene-2-carboxylic-acid *n*-butyl ester (NB–$CO_2{}^n$Bu) [201].



Pd-63 R^1 = Me R^2 = Me
Pd-64 R^1 = Me R^2 = Br
Pd-65 R^1 = ^{i}Pr R^2 = H
Pd-66 R^1 = ^{i}Pr R^2 = I
Pd-67 R^1 = ^{i}Pr R^2 = Br

2.8. Copper catalysts

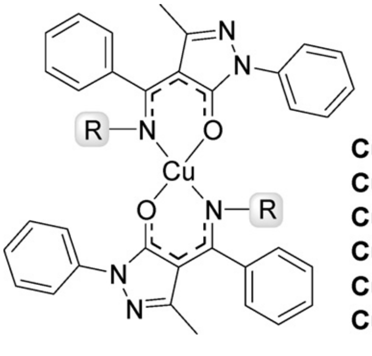
The bis(salicylaldiminato)copper(II) complexes **Cu-1** to **Cu-5** were activated with MAO-A (MAO-A contains about 15 mol% free TMA) to afford between 10^4 and 10^5 g_{PNB}/mol_{Cu} h. Relative high temperatures of 60–80 °C and a rather high molar Al/Cu ratio of 2500 were needed to afford a significant monomer conversion. The presence of electron-withdrawing nitro substituents on the chelate ligand markedly increased the activity [202].



Cu-1 $R^1 = NO_2$ $R^2 = NO_2$ R^3 = 2,6-diisopropylphenyl
Cu-2 $R^1 = NO_2$ $R^2 = NO_2$ R^3 = phenyl
Cu-3 $R^1 = H$ $R^2 = H$ R^3 = 2,6-diisopropylphenyl
Cu-4 $R^1 = NO_2$ $R^2 = H$ R^3 = 2,6-diisopropylphenyl
Cu-5 $R^1 = NO_2$ $R^2 = NO_2$ $R^3 = {}^tBu$

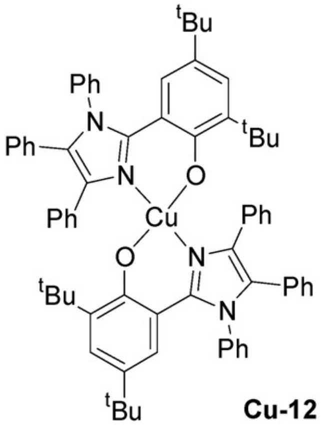
For the complexes **Cu-6** to **Cu-9** with *N*,*O*-chelating *β*-ketoiminato ligands in combination with MAO both steric and electronic effects contribute to the catalytic activities which were in the order of **Cu-7** > **Cu-9** > **Cu-8** > **Cu-6** and between 1.31×10^4 and 6.35×10^4 $g_{polymer}/mol_{Cu}$ h [203,204]. The sequence of decreasing activity correlated with the decrease in the bulkiness of the iminato-R-substituent. In addition, an almost fivefold increase of activity of **Cu-7**/MAO over **Cu-6**/MAO was attributed to the large π-system of the naphthyl ring. The system **Cu-9**/MAO with its electron-withdrawing *p*-nitrophenyl group and more electron-deficient Cu(II) center gave a similar high activity than **Cu-7**/MAO [203]. The catalytic system **Cu-73**/MAO showed the lowest activity among this group of β-ketoiminato Cu(II) complexes [204].

The precatalysts **Cu-6** to **Cu-10** in combination with MAO were also tested for the copolymerization of norbornene and styrene and featured the same activity sequence as for the homopolymerization of norbornene. Complex **Cu-11** activated with MAO exhibited a moderate catalytic activity for norbornene polymerization of $\sim 10^4$ $g_{polymer}/mol_{Cu}$ h. An increase in the molar Al/Cu ratio from 300 to 700 led to an increase in activity. When the temperature was raised from 20 °C to 100 °C a linear decrease of the polymer molecular weights and a linear increase of the activity was observed [205].



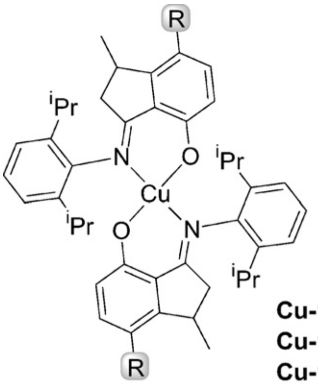
Cu-6 R = phenyl
Cu-7 R = 1-naphthyl
Cu-8 R = *o*-tolyl
Cu-9 R = *p*-nitrophenyl
Cu-10 R = benzyl
Cu-11 R = *m*-tolyl

The copper complex **Cu-12** with its bidentate phenoxy-imidazol ligands in combination with MAO catalyzed the norbornene polymerization with moderate yields up to 3.16×10^5 $g_{polymer}/mol_{Cu}$ h depending on the reaction conditions. The Al/Cu ratio was varied from 500 to 3000 with a ratio of 2000 found to be best. The optimal temperature was 60 °C [171].



Cu-12

The activities of the copper complexes **Cu-13** to **Cu-15** with *N*,*O*-chelating hydroxyindaniminato ligands covered a range from 4.7×10^4 to 1.1×10^5 $g_{polymer}/mol_{Cu}$ h, with **Cu-15** being the most active one after activation with MAO. For **Cu-13**/MAO variation of the molar Al/Cu ratio from 300 to 1500 showed the highest activity at a ratio of 750. Further investigations of the reaction temperatures for **Cu-13**/MAO showed similar activities from 16 to 60 °C and an optimal temperature of 30 °C [206].



Cu-13 R = H
Cu-14 R = Cl
Cu-15 R = Me

3. Supported catalysts

Unlike the classical Ziegler–Natta polymerization of ethene or propene, norbornene polymerization is usually started as a homogeneous solution polymerization. Within a short time the precitation of polynorbornene often renders the polymerization procedure inherently heterogeneous.

There are examples in the literature of supported nickel complexes applied in norbornene polymerization. Layered double hydroxides of Al and Zn of the hydrotalcite-type, were applied as support for $Ni(acac)_2$ (**Ni-157**). These functional inorganic hydroxide frameworks possess anion-exchange properties, high polarity and are selective towards polar molecules. The activity of immobilized **Ni-157** was found to be higher than that of the homogeneous one [207].

The bis(salicylideneiminato)nickel(II) complexes **Ni-82**, **Ni-83**, **Ni-95**, **Ni-98** and **Ni-100** were supported on spherical $MgCl_2$ and silica to yield activities in the range of 10^5 $g_{polymer}/mol_{Ni}$ h. MAO was required as cocatalyst. In general, the polynorbornenes produced with the supported catalyst had higher molecular weights and slightly broader molecular weight distributions than with the respective homogeneous catalyst [162].

4. Di- and multinuclear metal complexes

The majority of metal complexes reported for norbornene polymerization are mononuclear, that is, possess only one metal atom. Some comparative studies showed significant activity differences between polynuclear and related mononuclear complexes (for details see in the individual metal sections):

The homo- and heterometallic nickel-containing wheels **Cr-4**, **Cr-6**, **Cr-7**, **Fe-5**, **Fe-6** revealed a higher activity *per nickel* when compared to mixtures of Ni(acac)$_2$ with Cr(acac)$_3$ or Fe(acac)$_3$ [117]. The dinuclear salicylaldiminato Schiff-base complexes **Ni-78** to **Ni-80** could reach higher activities than the related mononuclear Ni–salen complex **Ni-81** [140,148]. On the other hand, the general activities of the mononuclear complexes **Ni-149**, **Ni-150** and **Ni-151** were slightly higher than those of the trinuclear compounds **Ni-152**, **Ni-153** and **Ni-154** [172]. Again, the dinuclear salicylaldiminato complexes **Pd-27** and **Pd-29** exhibited much higher polymerization activities than the related mononuclear **Pd-33** under the same conditions [157].

5. Activity comparison

Fig. 16 shows an overview of the catalytic systems which are summarized in this review. It is obvious that the precatalysts based upon nickel and palladium show the highest activities. It is noteworthy that by far the largest number of publications deal with nickel. This fact is also reflected in the wide range of activity values. The majority of nickel catalysts exhibit activities of 10^5 g_{PNB}/mol_{Ni} h or higher (for the distribution see numbers in Fig. 16). A more detailed overview over the different ligand types for nickel is shown in Fig. 17. Precatalysts bearing *N*,*O*-coordinating salicylaldiminato or β-ketoiminato ligands showed activities of at least 10^6 g_{PNB}/mol_{Ni} h. Exceptions to this generalizations are **Ni-86** to **Ni-91**, **Ni-93**, **Ni-94** and **Ni-95** to **Ni-113** which have lower activities. The widest range in activities is observed for nickel complexes with an *N*,*N*-coordination. Such complexes give the highest activities observed, so far (>10^9 g_{PNB}/mol_{Ni} h with **Ni-33** to **Ni-36**) but can also exhibit rather low activities.

Palladium based precatalysts were also able to catalyze the vinyl polymerization of norbornene with high activities, whereas the activated precatalysts based upon titanium, chromium, iron, cobalt and copper showed rather low activities.

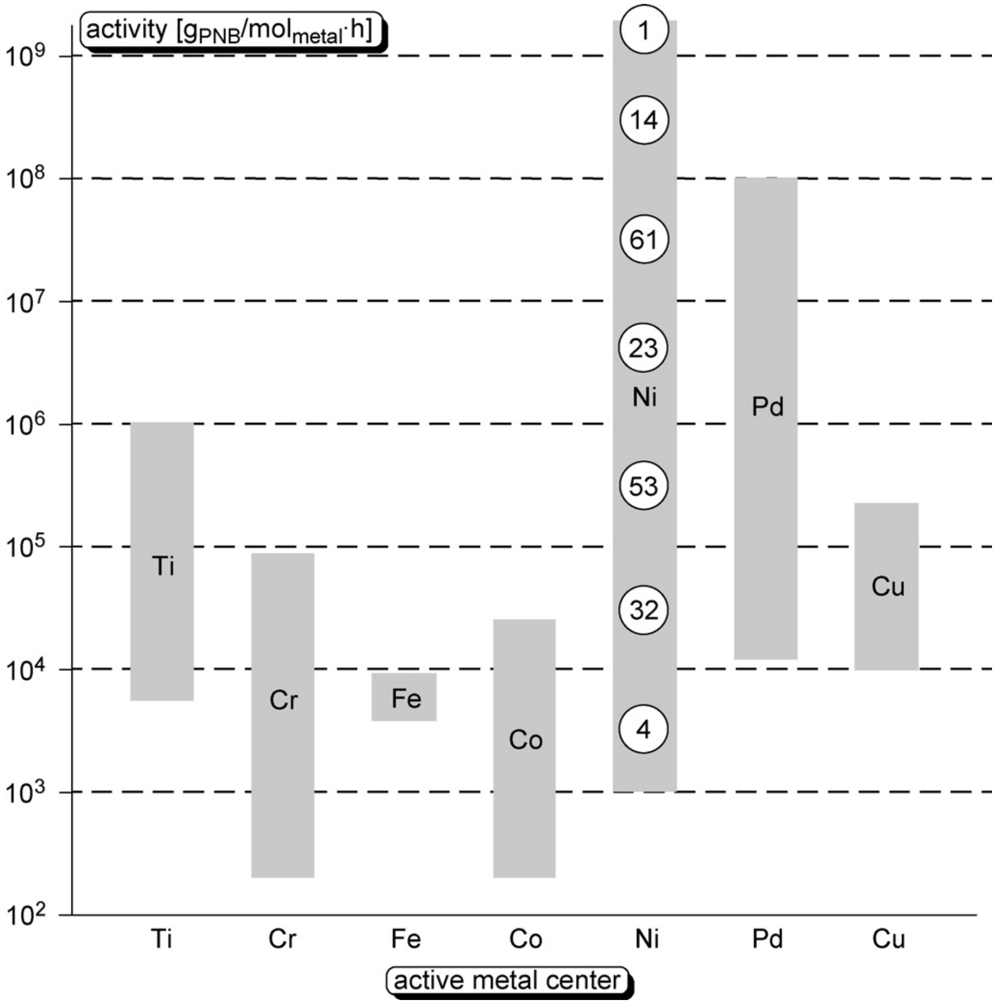


Fig. 16. Activity ranges of the different metal catalysts for the vinyl polymerization of norbornene. (The bimetallic, nickel-containing {M$_2$Ni}-triangles (M = Fe, Ni) and {Cr$_7$Ni(μ-F)$_8$}-wheels are counted towards nickel, as this metal was shown to be responsible for the high activity.) The numbers in the nickel column indicate the number of Ni-complexes in the respective activity range.

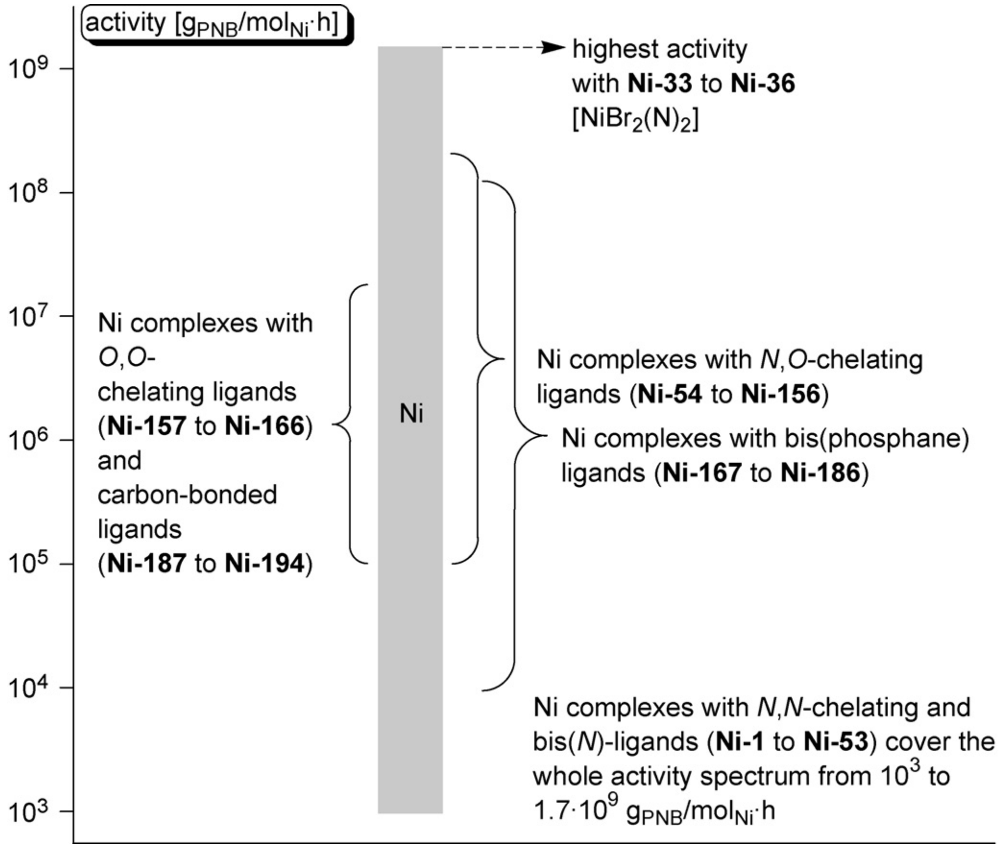


Fig. 17. A more detailed overview of the different ligand types of the adopted nickel precatalysts for the vinyl polymerization of norbornene.

6. Conclusions

Metal complexes with M = Ti, Zr, Cr, Fe, Co, Ni, Pd, and Cu and with almost any ligand type can be activated with MAO or perfluorinated borane, like $B(C_6F_5)_3$ towards the polymerization of norbornene. High activities of more than 10^7 $g_{polymer}/mol_{metal}$ h are obtained especially with Ni and Pd catalysts. Yet, the activity studies of the majority of complexes towards various ligand or substituent effects are rather empirical. There is, at large, still a lack of understanding on the activation mechanism and the nature of the active species to understand the activity trends. Studies on these questions are highly warranted in the future.

References

[1] C. Janiak, P.-G. Lassahn, J. Mol. Catal. A: Chem. 166 (2001) 193.
[2] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, 1997, p. 407.
[3] J. Kress, M. Wesolek, J.A. Osborn, J. Chem. Soc. Chem. Commun. (1982) 514.
[4] J. Kress, J.A. Osborn, J. Am. Chem. Soc. 105 (1983) 6346.
[5] A. Aguero, J. Kress, J.A. Osborn, J. Chem. Soc., Chem. Commun. (1985) 793.
[6] J. Kress, J.A. Osborn, R.M.E. Greene, K.J. Ivin, J.J. Rooney, J. Chem. Soc., Chem. Commun. (1985) 874.
[7] J. Kress, J.A. Osborn, R.M.E. Greene, K.J. Ivin, J.J. Rooney, J. Am. Chem. Soc. 109 (1987) 899.
[8] R.R. Schrock, J. Feldman, L.F. Cannizzo, R.H. Grubbs, Macromolecules 20 (1987) 1172.
[9] Y. Takashima, Y. Nakayama, A. Harada, Chem. Lett. (2001) 488.
[10] A. Lehtonen, R. Sillanpää, Inorg. Chem. Commun. 5 (2002) 267.
[11] J.S. Murdzek, R.R. Schrock, Organometallics 6 (1987) 1373.
[12] J.S. Murdzek, R.R. Schrock, Macromolecules 20 (1987) 2642.
[13] G.C. Bazan, R.R. Schrock, H.N. Cho, V.C. Gibson, Macromolecules 24 (1991) 4495.
[14] V. Heroguez, M. Fontanille, J. Polym. Sci. (Part A) 32 (1994) 1755.
[15] C. Cazalis, V. Héroguez, M. Fontanille, Macromol. Chem. Phys. 202 (2001) 1513.
[16] K. Nomura, S. Takahashi, Y. Imanishi, Macromolecules 34 (2001) 4712.
[17] K. Hiya, Y. Nakayama, H. Yasuda, Macromolecules 36 (2003) 7916.
[18] P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem. Int. Ed. 34 (1995) 2039.
[19] P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.
[20] A. Hafner, P.A. van der Schaaf, A. Mühlebach, Chimia 50 (1996) 131.
[21] D. Amoroso, D.E. Fogg, Macromolecules 33 (2000) 2815.
[22] R. Castarlenas, D. Sémeril, A.F. Noels, A. Demonceau, P.H. Dixneuf, J. Organomet. Chem. 663 (2002) 235.
[23] D.M. Haigh, A.M. Kenwright, E. Khosravi, Tetrahedron 60 (2004) 7217.
[24] M. Bernechea, N. Lugan, B. Gil, E. lalinde, G. Lavigne, Organometallics 25 (2006) 684.
[25] L.R. Gilliom, R.H. Grubbs, J. Am. Chem. Soc. 108 (1986) 733.
[26] J.J. Eisch, A.A. Adeosun, Eur. J. Org. Chem. (2005) 993.
[27] K. Nomura, A. Sagara, Y. Imanishi, Macromolecules 35 (2002) 1583.
[28] J. Yamada, M. Fujiki, K. Nomura, Organometallics 24 (2005) 2248.
[29] Y. Nakayama, M. Tanimoto, T. Shiono, Macromol. Rapid Commun. 28 (2007) 646.
[30] K.C. Wallace, A.H. Liu, J.C. Dewan, R.R. Schrock, J. Am. Chem. Soc. 110 (1988) 4964.
[31] M.H.P. Rietveld, W. Teunissen, H. Hagen, L. van de Water, D.M. Grove, P.A. van der Schaaf, A. Mühlebach, H. Kooijman, W.J.J. Smeets, N. Veldman, A.L. Spek, G. van Koten, Organometallics 16 (1997) 1674.
[32] M.H.P. Rietveld, P. Lohner, M.G. Nijkamp, D.M. Grove, N. Veldman, A.L. Spek, M. Pfeffer, G. van Koten, Chem. Eur. J. 3 (5) (1997) 817.
[33] J.L. Burmaghim, G.S. Girolami, Organometallics 18 (1999) 1923.
[34] C.M. Frech, O. Blacque, H.W. Schmalle, H. Berke, C. Adlhart, P. Chen, Chem. Eur. J. 12 (2006) 3325.
[35] J.P. Kennedy, H.S. Makowski, J. Macromol. Sci. Chem. A1 (1967) 345.
[36] N.G. Gaylord, B.M. Mandal, M. Martan, J. Polym. Sci., Polym. Lett. Ed. 14 (1976) 555.
[37] N.G. Gaylord, A.B. Deshpande, B.M. Mandal, M. Martan, J. Macromol. Sci. Chem. A 11 (1977) 1053.
[38] N.G. Gaylord, A.B. Deshpande, J. Polym. Sci., Polym. Lett. Ed. 14 (1976) 613.
[39] S. Rush, A. Reinmuth, W. Risse, Macromolecules 30 (1997) 7375.
[40] L. Goodall, L.H. McIntosh III, L.F. Rhodes, Makromol. Chem. Macromol. Symp. 89 (1995) 421.
[41] N. Seehof, C. Mehler, S. Breunig, W. Risse, J. Mol. Catal. 76 (1992) 219.
[42] W. Kaminsky, A. Bark, I. Däke, in: T. Keii, K. Soga (Eds.), Catalytic Olefin Polymerization, Kodansha–Elsevier, Tokyo–Amsterdam, 1990, p. 425.
[43] I. Tritto, L. Boggioni, C. Zampa, D.R. Ferro, Macromolecules 38 (2005) 9910.

[44] P. Wehrmann, M. Zuideveld, R. Thomann, S. Mecking, Macromolecules 39 (2006) 5995.
[45] S.Y. Park, J. Lee, K.Y. Choi, Macromol. React. Eng. 1 (2007) 68.
[46] W. Zuo, W.-H. Sun, S. Zhang, P. Hao, A. Shiga, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 3415.
[47] M. Gao, C. Wang, X. Sun, C. Qian, Z. Ma, S. Bu, Y. Tang, Z. Xie, Macromol. Rapid. Commun. 28 (2007) 1511.
[48] T. Hasan, T. Ikeda, T. Shiono, Macromolecules 38 (2005) 1071.
[49] Z. Cai, Y. Nakayama, T. Shiono, Macromolecules 39 (2006) 2031.
[50] W. Kaminsky, S. Derlin, M. Hoff, Polymer 48 (2007) 7271.
[51] D. Ruchatz, G. Fink, Macromolecules 31 (1998) 4684.
[52] D. Ruchatz, G. Fink, Macromolecules 31 (1998) 4681.
[53] D. Ruchatz, G. Fink, Macromolecules 31 (1998) 4674.
[54] W. Kaminsky, A. Noll, Polym. Bull. 31 (1993) 175.
[55] H. Cherdron, M.-J. Brekner, F. Osan, Angew. Makromol. Chem. 223 (1994) 121.
[56] W. Kaminsky, R. Spiehl, Makromol. Chem. 19 (1989) 515.
[57] Crown glass is produced from alkali-lime silicates containing approximately 10% potassium oxide. It has low refractive index (∼1.52). www.wikipedia.org.
[58] J.M. Brekner, F. Osan, J. Rohrmann, M. Antberg, Patent EP0485893, Equivalents JP4268312, etc., Hoechst AG (Germany) (1992).
[59] W. Kaminsky, A. Bark, M. Arndt, Makromol. Chem., Macromol. Symp. 47 (1991) 83.
[60] Web page (in German) which explains the Acronym TOPAS: http://idw-online.de/pages/de/news21.
[61] Chem. Techn. 29 (2000) 14. http://www.chemietechnik.de/ai/resources/6088f5afd7a.pdf.
[62] H.G. Hauthal, Nachr. Chem. Techn. Lab. 43 (1995) 822.
[63] H. Vennen, Future-Hoechst Mag. IV (1995) 52.
[64] Mod. Plast. 72 (9) (1995) 137.
[65] For the Applications of TOPAS® COC, see http://www.topas.com/products-topas_coc.
[66] W. Kaminsky, J. Chem. Soc., Dalton Trans. (1998) 1413.
[67] W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907.
[68] W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 144.
[69] C. Janiak, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, Wiley, Weinheim, 1998, p. 547 (Chapter 9).
[70] G.G. Hlatky, Coord. Chem. Rev. 181 (1999) 243.
[71] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.
[72] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.
[73] T. Hasan, T. Ikeda, T. Shiono, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 4581.
[74] R.A. Wendt, G. Fink, Macromol. Chem. Phys. 201 (2000) 1365.
[75] S. Liu, S. Borkar, D. Newsham, H. Yennawar, A. Sen, Organometallics 26 (2007) 210, and references therein.
[76] G.M. Benedikt, E. Elce, B.L. Goodall, H.A. Kalamarides, L.H. McIntosh, L.F. Rhodes, K.T. Selvy, C. Andes, K. Oyler, A. Sen, Macromolecules 35 (2002) 8978.
[77] M. Kang, A. Sen, Organometallics 23 (2004) 5396.
[78] J.K. Funk, C.E. Andes, A. Sen, Organometallics 23 (2004) 1680.
[79] B. Liu, Y. Li, B.-B. Shin, D.Y. Yoon, I. Kim, L. Zhang, W. Yan, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 3391.
[80] M.K. Boggiano, D. Vellenga, R. Carbonell, V.S. Ashby, J.M. DeSimone, Polymer 47 (2006) 4012.
[81] K. Mueller, S. Kreiling, K. Dehnicke, J. Allgaier, D. Richter, L.J. Fetters, Y. Jung, D.Y. Yoon, A. Greiner, Macromol. Chem. Phys. 207 (2006) 193.
[82] D.P. Sanders, E.F. Connor, R.H. Grubbs, R.J. Hung, B.P. Osborn, T. Chiba, S.A. MacDonald, C.G. Willson, W. Conley, Macromolecules 36 (2003) 1534.
[83] B.-G. Shin, M.-S. Jang, D.Y. Yoon, W. Heitz, Macromol. Rapid Commun. 25 (2004) 728.
[84] J. Lipian, R.A. Mimna, J.C. Fondran, D. Yandulov, R.A. Shick, B.L. Goodall, L.F. Rhodes, Macromolecules 35 (2002) 8969.
[85] A.D. Hennis, J.D. Polley, G.S. Long, A. Sen, D. Yandulov, J. Lipian, G.M. Benedikt, L.F. Rhodes, Organometallics 20 (2001) 2802.
[86] T.F.A. Haselwander, W. Heitz, S.A. Krügel, J.H. Wendorff, Macromol. Chem. Phys. 197 (1996) 3435, and references therein.
[87] N.R. Grove, P.A. Kohl, S.A.B. Allen, S. Jayaraman, R. Shick, J. Polym. Sci., Part B: Polym. Phys. 37 (1999) 3003.
[88] A. Hideki, A. Satoshi, M. Hiroshi, M. Junichi, Patent EPO445755, Equivalents DE69129600, JP4063807, Idemitsu Kosan Co. (Jpn.) (1991).
[89] K.H. Park, R.J. Twieg, R. Ravikiran, L.F. Rhodes, R.A. Shick, D. Yankelevich, A. Knoesen, Macromolecules 37 (2004) 5163.
[90] T. Hoskins, W.J. Chung, A. Agrawal, P.J. Ludovice, C.L. Henderson, L.D. Seger, L.F. Rhodes, R.A. Shick, Macromolecules 37 (2004) 4512.
[91] M. Arndt, I. Beulich, Macromol. Chem. Phys. 199 (1998) 1221.
[92] S.Y. Park, K.Y. Choi, K.H. Song, B.G. Jeong, Macromolecules 36 (2003) 4216.
[93] E.-G. Kim, M.L. Klein, Organometallics 23 (2004) 3319.
[94] Based on a Scifinder search with the keywords "metallocene and norbornene polymerization".
[95] S. Mecking, Coord. Chem. Rev. 203 (2000) 325.
[96] M. Bochmann, M.J. Sarsfield, Organometallics 17 (1998) 5908.
[97] J. Klosin, G.R. Roof, E.Y.X. Chen, K.A. Abboud, Organometallics 19 (2000) 4684.
[98] C. Janiak, P.-G. Lassahn, Macromol. Symp. 236 (2006) 54.
[99] X. Mi, D. Xu, W. Yan, C. Guo, Y. Ke, Y. Hu, Polym. Bull. 47 (2002) 521.
[100] Q. Wu, Y. Lu, J. Polym. Sci., Part A: Polym. Chem. 40 (2002) 1421.
[101] T. Hasan, K. Nishii, T. Shiono, T. Ikeda, Macromolecules 35 (2002) 8933.
[102] H. Sinn, Macromol. Symp. 97 (1995) 27;
I. Tritto, M.C. Sacchi, P. Locatelli, S.X. Li, Macromol. Chem. Phys. 197 (1996) 1537.
[103] A.R. Barron, Organometallics 14 (1995) 3581;
For a different method to determine the content of "free" TMA in MAO upon complexation with $WOCl_4$, see E. Thorn-Csányi, J. Dehmel, O. Halle, W. Sciborski, Macromol. Chem. Phys. 195 (1994) 3017.
[104] D. Cam, E. Albizzati, P. Cinquina, Makromol. Chem. 191 (1990) 1641.
[105] C. Janiak, B. Rieger, R. Voelkel, H.-G. Braun, J. Polym. Sci., Polym. Chem. 31 (1993) 2959.
[106] C. Janiak, B. Rieger, Angew. Makromol. Chem. 215 (1994) 47.
[107] C. Janiak, K.C.H. Lange, U. Versteeg, D. Lentz, P.H.M. Budzelaar, Chem. Ber. 129 (1996) 1517.
[108] C. Janiak, U. Versteeg, K.C.H. Lange, R. Weimann, E. Hahn, J. Organomet. Chem. 501 (1995) 219.
[109] P.C. Möhring, N.J. Coville, Coord. Chem. Rev. 250 (2006) 18.
[110] T. Shiono, S. Yoshida, H. Hagihara, T. Ikeda, in: W. Kaminsky (Ed.), Metalorganic Catalysts for Synthesis and Polymerization, Springer-Verlag, Berlin, 1999, p. 264.
[111] T. Hasan, T. Ikeda, T. Shiono, Macromolecules 37 (2004) 7432.
[112] Y. Yoshida, J.-I. Mohri, S.-I. Ishii, M. Mitani, J. Saito, S. Matsui, H. Makio, T. Nakano, H. Tanaka, M. Onda, Y. Yamamoto, A. Mizuno, T. Fujita, J. Am. Chem. Soc. 126 (2004) 12023.
[113] L. Porri, V.N. Scalera, M. Bagatti, A. Famulari, S.V. Meille, Macromol. Rapid. Commun. 27 (2006) 1937.
[114] C. Karfilidis, H. Hermann, A. Rufiñska, B. Gabor, R.J. Mynott, G. Breitenbruch, C. Weidenthaler, J. Rust, W. Joppek, M.S. Brookhart, W. Thiel, G. Fink, Angew. Chem. Int. Ed. 43 (2004) 2444.
[115] M. Arndt, M. Gosmann, Polym. Bull. 41 (1998) 433.
[116] J. Chen, Y. Huang, Z. Li, Z. Zhang, C. Wie, T. Lan, W. Zhang, J. Mol. Catal. A: Chem. 259 (2006) 133.
[117] P.-G. Lassahn, V. Lozan, G.A. Timco, P. Christian, C. Janiak, R.E.P. Winpenny, J. Catal. 222 (2004) 260.
[118] P.-G. Lassahn, V. Lozan, C. Janiak, Dalton Trans. (2003) 927.
[119] P.-G. Lassahn, V. Lozan, B. Wu, A.S. Weller, C. Janiak, Dalton Trans. (2003) 4437.
[120] U. Peucker, W. Heitz, Macromol. Chem. Phys. 202 (2001) 1289.
[121] Calculated by us from the given yield, reaction time and molar catalyst amount.
[122] T.J. Woodman, Y. Sarazin, S. Garratt, G. Fink, M. Bochmann, J. Mol. Catal. A: Chem. 235 (2005) 88.
[123] M.C. Sacchi, M. Sonzogni, S. Losio, F. Forlini, P. Locatelli, I. Tritto, M. Licchelli, Macromol. Chem. Phys. 202 (2001) 2052.
[124] An activity calculation was not possible because no reaction time or monomer amount was given.
[125] Y. Sato, Y. Nakayama, H. Yasuda, J. Organomet. Chem. 689 (2004) 744.
[126] F. Pelascini, F. Peruch, P.J. Lutz, M. Wesolek, J. Kress, Macromol. Rapid Commun. 24 (2003) 768.
[127] F. Pelascini, F. Peruch, P.J. Lutz, M. Wesolek, J. Kress, Macromol. Symp. 213 (2004) 265.
[128] F. Bao, X. Lü, Y. Qiao, G. Gui, H. Gao, Q. Wu, Appl. Organomet. Chem. 19 (2005) 957.
[129] F. Bao, X.-Q. Lü, H. Gao, G. Gui, Q. Wu, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 5535.
[130] E. Nelkenbaum, M. Kapon, M.S. Eisen, Organometallics 24 (2005) 2645.
[131] E. Nelkenbaum, M. Kapon, M.S. Eisen, J. Organomet. Chem. 690 (2005) 2297.
[132] E. Nelkenbaum, M. Kapon, M.S. Eisen, J. Organomet. Chem. 690 (2005) 3154.
[133] H. Gao, W. Guo, F. Bao, G. Gui, J. Zhang, F. Zhu, Q. Wu, Organometallics 23 (2004) 6273.
[134] H. Gao, J. Zhang, Y. Chen, F. Zhu, Q. Wu, J. Mol. Catal. (2005) 178.
[135] H.-Y. Wang, X. Meng, G.-X. Jin, Dalton Trans. (2006) 2579.
[136] D. Zhang, G.-X. Jin, L.-H. Weng, F. Wang, Organometallics 23 (2004) 3270.
[137] Y. Li, M. Gao, Q. Wu, Appl. Organomet. Chem. 21 (2007) 965.
[138] Y. Li, L. Jiang, L. Wang, H. Gao, F. Zhu, Q. Wu, Appl. Organomet. Chem. 20 (2006) 181.
[139] B. Berchtold, V. Lozan, P.-G. Lassahn, C. Janiak, J. Polym. Sci., Part A: Polym. Chem. 40 (2002) 3604.
[140] C. Janiak, P.-G. Lassahn, V. Lozan, Macromol. Symp. 236 (2006) 88.
[141] H.Y. Cho, D.S. Hong, D.W. Jeong, Y.-D. Gong, S.I. Woo, Macromol. Rapid Commun. 25 (2004) 302.
[142] Y.-S. Li, Y.-R. Li, X.-F. Li, J. Organomet. Chem. 667 (2003) 185.
[143] Y.-Z. Zhu, J.-Y. Liu, Y.-S. Li, Y.-J. Tong, J. Organomet. Chem. 689 (2004) 1295.
[144] A.O. Patil, S. Zushma, R.T. Stibrany, S.P. Rucker, L.M. Wheeler, J. Polym. Sci., Part A: Polym. Chem. 41 (2003) 2095.
[145] N.H. Tarte, H.Y. Cho, S.I. Woo, Macromolecules 40 (2007) 8162.
[146] X. Mi, Z. Ma, N. Cui, L. Wang, Y. Ke, Y. Hu, J. Appl. Polym. Sci. 88 (2003) 3273.
[147] X. Mi, Z. Ma, L. Wang, Y. Ke, Y. Hu, Macromol. Chem. Phys. 204 (2003) 868.
[148] V. Lozan, P.-G. Lassahn, C. Zhang, B. Wu, C. Janiak, G. Rheinwald, H. Lang, Z. Naturforsch. 58b (2003) 1152.
[149] M. Schroers, C. Mast, K. Dehnicke, A. Greiner, Polym. Mater. Sci. Eng. 84 (2001) 761.
[150] C. Mast, M. Krieger, K. Dehnicke, A. Greiner, e-Polymers No. 016 (2001) 1.
[151] M. Schroers, J. Demeter, K. Dehnicke, A. Greiner, Macromol. Chem. Phys. 203 (2002) 2658.
[152] S.A. Lee, K.Y. Shin, B.J. Park, M.K. Choi, I.-M. Lee, Bull. Korean Chem. Soc. 27 (4) (2006) 475.

[153] D.H. Lee, J.Y. Lee, J.Y. Ryu, Y. Kim, C. Kim, I.-M. Lee, Bull. Korean Chem. Soc. 27 (7) (2006) 1031.
[154] X.-F. Li, Y.-S. Li, J. Polym. Sci., Part A: Polym. Chem. 40 (2002) 2680.
[155] W.-H. Wang, G.-X. Jin, Inorg. Chem. Commun. 8 (2005) 109.
[156] W.-H. Sun, H. Yang, Z. Li, Y. Li, Organometallics 22 (2003) 3678.
[157] T. Hu, Y.-G. Li, Y.S. Li, N.-H. Hu, J. Mol. Catal. A: Chem. 253 (2006) 155.
[158] H. Yang, W.-H. Sun, F. Chang, Y. Li, Appl. Catal. A: Gen. 252 (2003) 261.
[159] D.-H. Zhang, S.-Y. Jie, H.-J. Yang, F. Chang, W.-S. Sun, Chin. J. Polym. Sci. 23 (6) (2005) 619.
[160] C. Carlini, M. Martinelli, A.M.R. Galletti, G. Sbrana, J. Polym. Sci., Part A: Polym. Chem. 44 (2006) 1514.
[161] F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song, W.-H. Sun, J. Organomet. Chem. 689 (2004) 936.
[162] J. Hou, S. Jie, W. Zhang, W.-H. Sun, J. Appl. Polym. Sci. 102 (2006) 2233.
[163] X. He, Q. Wu, J. Appl. Polym. Sci. 101 (2006) 4172.
[164] (a) H.-Y. Wang, J. Zhang, X. Meng, G.-X. Jin, J. Organomet. Chem. 691 (2006) 1275;
(b) R. Malgas-Enus, S.F. Mapolie, G.S. Smith, J. Organomet. Chem. 693 (2008) 2279.
[165] X. He, Y. Chen, Y. Liu, S. Yu, S. Hong, Q. Wu, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 4733.
[166] L.Y. Wang, Y.F. Li, F.M. Zhu, Q. Wu, Eur. Polym. J. 42 (2006) 322.
[167] G. Gui, F. Bao, H. Gao, F. Zhu, Q. Wu, Appl. Organomet. Chem. 19 (2005) 627.
[168] G. Gui, F. Bao, H. Gao, F. Zhu, Q. Wu, J. Coord. Chem. 59 (1) (2006) 107.
[169] F. Bao, X. Lü, B. Kang, Q. Wu, Eur. Polym. J. 42 (2006) 928.
[170] J. Hou, W.-H. Sun, D. Zhang, L. Chen, W. Li, D. Zhao, H. Song, J. Mol. Catal. A: Chem. 213 (2005) 221.
[171] F.-T. Chen, G.-R. Tang, G.-X. Jin, J. Organomet. Chem. 692 (2007) 3435.
[172] G. Tang, Y.-J. Lin, G.-X. Jin, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 489.
[173] B.Y. Lee, Y.H. Kim, H.J. Shin, C.H. Lee, Organometallics 21 (2002) 3481.
[174] The structure of bis(2-ethylhexanoato)nickel is simplified. The compound has not been characterized by a single-crystal X-ray structure (negative search of the Cambridge Structure Data bank), yet it may consist of dimers and trimers and contain a substantial amount of free carboxylic acid.
[175] P.-G. Lassahn, C. Janiak, J.-S. Oh, Z. Naturforsch. 56b (2001) 1289.
[176] C. Janiak, P.-G. Lassahn, Polym. Bull. 47 (2002) 539.
[177] Y. Jang, H.-K. Sung, S. Lee, C. Bae, Polymer 46 (2005) 11301.
[178] Y. Jang, H.-K. Sung, H. Kwag, Eur. Polym. J. 42 (2006) 1250.
[179] D.A. Barnes, G.M. Benedikt, B.L. Goodall, S.S. Huang, H.A. Kalamarides, S. Lenhard, L.H. McIntosh III, K.T. Selvy, R.A. Shick, L.F. Rhodes, Macromolecules 36 (2003) 2623.
[180] H.A. Kalamarides, S. Iyer, J. Lipian, L.F. Rhodes, C. Day, Organometallics 19 (2000) 3983.
[181] H.-Y. Wang, G.-X. Jin, Eur. J. Inorg. Chem. (2005) 1665.
[182] H. Yang, Z. Li, W.-H. Sun, J. Mol. Catal. A: Chem. 206 (2003) 23.
[183] G. Myagmarsuren, O.-Y. Jeong, S.-K. Ihm, Appl. Catal. A: Gen. 255 (2003) 203.
[184] P.-G. Lassahn, C. Janiak, J.-S. Oh, Macromol. Rapid Commun. 23 (2002) 16.
[185] J.A. Casares, P. Espinet, J.M. Martín-Alvarez, J.M. Martínez-Ilarduya, G. Salas, Eur. J. Inorg. Chem. (2005) 3825.
[186] Z. Sun, F. Zhu, Q. Wu, S.-A. Lin, Appl. Organomet. Chem. 20 (2006) 175.
[187] M. Lejeune, C. Jeunesse, D. Matt, D. Sémeril, F. Peruch, L. Toupet, P.J. Lutz, Macromol. Rapid Commun. 27 (2006) 865.
[188] S. Kaita, K. Matsushita, M. Tobita, Y. Maruyama, Y. Wakatsuki, Macromol. Rapid. Commun. 27 (2006) 1752.
[189] X. Wang, S. Liu, G.-X. Jin, Organometallics 23 (2004) 6002.
[190] X. Wang, G.-X. Jin, Organometallics 23 (2004) 6319.
[191] D.M. Shin, S.U. Son, B.K. Hong, Y.K. Chung, S.-H. Chun, J. Mol. Catal. A: Chem. 210 (2004) 35.
[192] H. Liang, J. Liu, X. Li, Y. Li, Polyhedron 23 (2004) 1619.
[193] G. Siedle, P.-G. Lassahn, V. Lozan, C. Janiak, B. Kersting, Dalton Trans. (2007) 52.
[194] G. Myagmarsuren, K.-S. Lee, O.-Y. Jeong, S.-K. Ihm, Catal. Commun. 4 (2003) 615.
[195] G. Myagmarsuren, J.-I. Park, S.-K. Ihm, Polymer 47 (2006) 8474.
[196] G. Myagmarsuren, V.S. Tkach, D.S. Suslov, F.K. Shmidt, Russ. J. Appl. Chem. 80 (2) (2007) 252.
[197] V.S. Tkach, G. Myagmarsuren, D.S. Suslov, F.K. Shmidt, Russ. J. Gen. Chem. 77 (3) (2007) 489.
[198] P.-G. Lassahn, C. Tzschucke, W. Bannwarth, C. Janiak, Z. Naturforsch. 58b (2003) 1063.
[199] U.W. Meier, U. Thewalt, T. Debaerdemaeker, B. Rieger, Eur. J. Inorg. Chem. (2004) 3057.
[200] X. Wang, S. Liu, L.-H. Wenig, G.-X. Jin, Organometallics 25 (2006) 3565.
[201] I.G. Jung, J. Seo, Y.K. Chung, D.M. Shin, S.-H. Chun, S.U. Son, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 3042.
[202] C. Carlini, S. Giaiacopi, F. Marchetti, C. Pinzino, A.M.R. Galletti, G. Sbrana, Organometallics 25 (2006) 3659.
[203] X.-Q. Lü, F. Bao, B.-S. Kang, Q. Wu, H.-Q. Liu, F.-M. Zhu, J. Organomet. Chem. 691 (2006) 821.
[204] F. Bao, R. Ma, Y. Jiao, Appl. Organomet. Chem. 20 (2006) 368.
[205] F. Bao, R. Ma, R. Ma, Y. Jiao, J. Coord. Chem. (2007) 557.
[206] G. Tang, Y.-J. Lin, G.-X. Jin, J. Organomet. Chem. 692 (2007) 4106.
[207] I.A. Grafova, A.V. Grafov, U. Costantino, F. Marmottini, M.L. Dias, Z. Naturforsch. 58b (2003) 1069.