Ethylene Polymerization by Self-Immobilized Neutral Nickel Catalysts Bearing Allyl Groups

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Dedicated to Professor Fo-Song Wang on the occasion of his 70th birthday

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[Ni(Ph)(PPh$_3$)(N,O)] complexes containing phenylimino-phenolato ligands (N,O) (**1**: N,O = **A**; **2**: N,O = **B**; **3**: N,O = **C**; **4**: N,O = **D**; **5**: N,O = **E**) have been synthesized and characterized. The molecular structure of **4** was determined by single-crystal X-ray analysis. Complexes **2**–**5** bearing allyl groups have been investigated as self-immobilized catalysts for ethylene polymerization without the use of co-catalysts. The high ethylene polymerization activities of ca. 10^5 g·PE mol^{-1} Ni·h^{-1} and high molecular weight ($M_w \approx 10^5$) of polyethylene could be accomplished by changing the ligand structures and reaction conditions. The self-immobilization of catalysts brings about a dramatic increase in the catalytic activities of ethylene polymerization.

Introduction

The polymerization of ethylene with late-transition-metal catalysts has attracted much interest because they not only catalyze the polymerization or oligomerization of ethylene and α-olefins, but they can also co-polymerize ethylene with α-olefins containing functional groups.[1−12] More recently, Grubbs et al. reported a new family of neutral late-transition-metal catalysts that are capable of polymerizing ethylene to high-molecular-weight linear polyethylene, even in the presence of a broad range of polar additives .[13] At the same time, this new family of catalysts based on neutral Ni^{II} complexes of substituted salicylaldiminato N,O ligands are highly active systems that can polymerize functionalized olefins. More importantly, the neutral, single-component nickel(II) catalysts require no co-catalysts, such as MAO, B(C$_6$F$_5$)$_3$ or Ni(COD)$_2$. The substantial cost incurred in the hyper-purification of the monomer feed in the production of polyolefin along with the use of co-catalysts has gone. People have been attracted by the potential for using them as active polymerization catalysts as a result of their low cost and ready availability.[1,2,14,15]

In order to be applied in conventional gas-phase or slurry reactors, homogeneous catalysts have to be heterogenized because soluble catalysts cause "fouling" which means that the polyolefin that is formed is deposited on the reactor walls and causes a "boiler scale effect". Inorganic supports such as silica or alumina[16a] and also organic supports such as polystyrene and starch,[16] have been used to heterogenize soluble polymerization catalysts. Many research groups have reported on the heterogenization of metallocene catalysts.[16] As a different heterogenization strategy, Alt et al. developed the self-immobilization of metallocene catalysts, which is the synthesis of metallocene catalysts with an olefin or alkyne functional group that can be used as a comonomer in the polymerization process.[17] Recently, our group[18] and also Herrmann et al.[19] reported the self-immobilization of Ni and Fe catalysts, respectively, for olefin polymerization. The homogenous self-immobilized catalyst can be transferred to a heterogeneous catalyst by itself during the ethylene polymerization. Herein, we report on neutral (benzaldehyde-phenylimine)nickel(II) complexes with allyl groups as self-immobilized catalysts, which exhibit excellent activities in ethylene polymerization, without co-catalysts, resulting in linear polymers.

Results and Discussion

Synthesis of Nickel Complexes as Self-Immobilized Catalysts

In this study, we utilized nickel complexes that possess phenylimino-phenolato chelate ligands bearing allyl groups. A general synthetic route for these complexes is shown in Scheme 1. The allyl group was introduced in dialkylaniline

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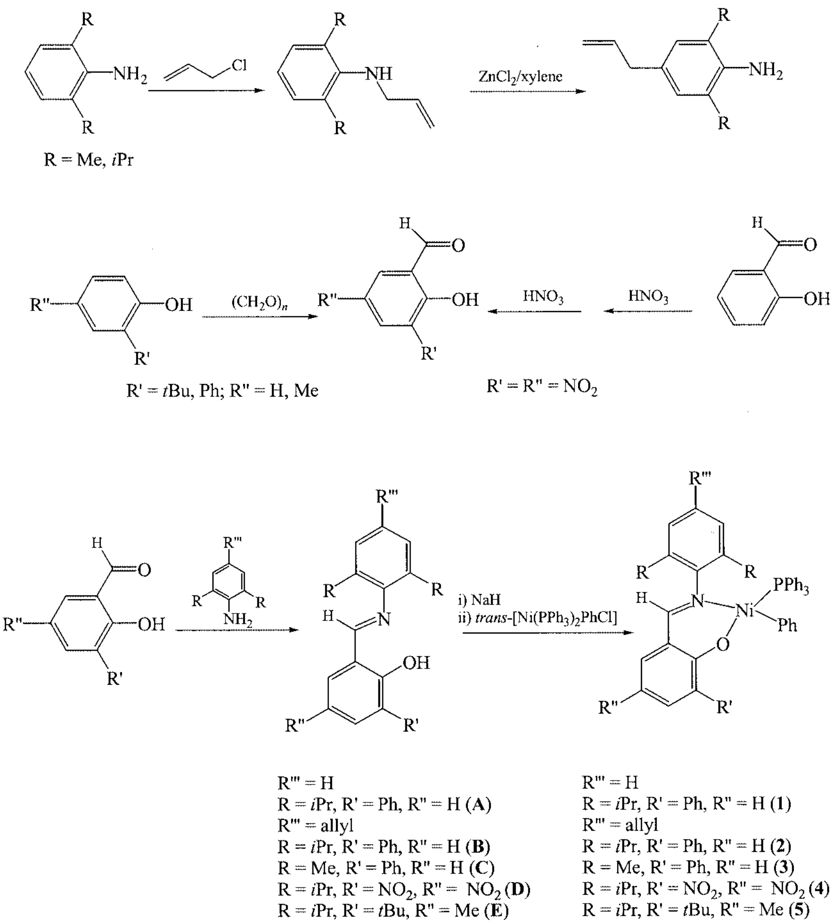


Scheme 1. Preparation of allyl-functionalized (phenylimino-phenolato)nickel complexes

by treating it with allyl chloride, giving *N*-allyl-dialkylaniline. The colorless oil was rearranged to 4-allyl-2,6-dialkylaniline in refluxing xylene in the presence of zinc chloride. Treatment of a phenol derivative with paraformaldehyde in the presence of tin(IV) chloride produced an *ortho*-formylated phenol in high yields. However, phenols containing electron-withdrawing groups barely reacted at all. Dinitrobenzaldehyde was obtained by performing the nitrogenation of benzaldehyde twice.

Ligands **B**−**E** were produced by the condensation of benzaldehyde derivatives with an equimolar amount of the allyl-substituted aniline derivative in alcohol in the presence of formic acid.[15,24,25] All phenylimino-phenolato ligands were characterized by ^{1}H NMR spectroscopy.

The (phenyl)(phenylimino-phenolato)nickel(II) complexes **1**−**5** (Scheme 1) were synthesized according to known procedures.[15,24] The phenylimino-phenolato ligand was dissolved in THF and treated with an excess of NaH. The sodium salt of the corresponding ligand was obtained in benzene and then combined with *trans*-[NiCl(Ph)(PPh$_3$)$_2$] to form the (benzaldehyde-phenylimine)(phenyl)nickel(II) complex in high yield. The ^{1}H NMR spectroscopic characterization and elemental analyses of complexes **2**−**5** have confirmed the composition of the complexes. The EI mass spectra generally contain the peaks of the molecular ion [M]$^+$. A particularly intense signal is observed for the [Ni(L)(Ph)]$^+$ ion which has lost the two-electron ligand PPh$_3$.

Molecular Structure

An X-ray crystallographic structure analysis was carried out for catalyst **4** (Figure 1). The unit cell in the solid state contains two crystallographically independent, but chemically similar molecules (**4a** and **4b**) that are related by a non-crystallographic pseudo-inversion center. Table 1 summarizes selected bond lengths and angles.

Complex **4** contains a chelating phenylimino-phenolato ligand, a triphenylphosphane group and a phenyl group. The Ni atoms are arranged in a distorted square-planar geometry made up of four atoms of the ligands (P1, O1, N1, C1 and P2, O6, N4, C47). The PPh$_3$ group and the imine nitrogen atom are *cis* to one another. The distances between Ni and the imine-N {phenoxy-O} are shorter [1.883(14)−1.967(15) Å] {1.912(12)−1.917(13) Å} than those in other complexes with N−O bidentate ligands [1.926(6)−1.945(4) Å] {1.911(5)−1.931(3) Å}[26b] and N−N bidentate ligands [2.010(5)−2.022(5) Å],[26a] while the distance between Ni and PPh$_3$ [2.207(5)−2.121(6) Å] is much

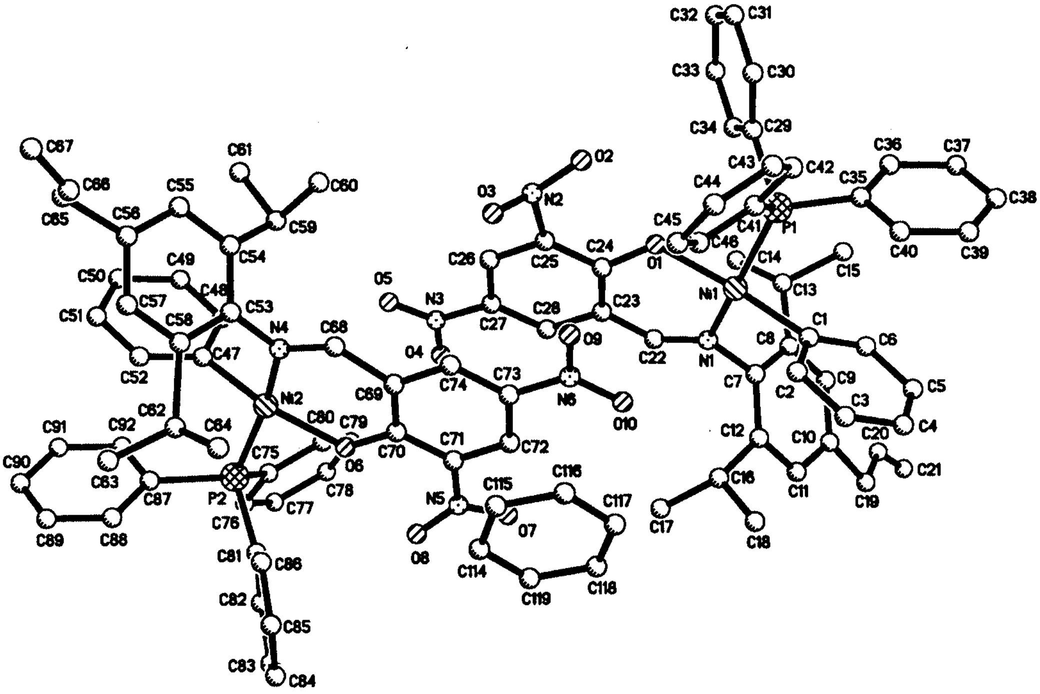


Figure 1. View of the molecular structure of complex **4**; hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths [Å] and bond angles [°] for **4** (**4a** and **4b**, respectively) with estimated standard deviations

	Bond lengths [Å]			Bond angles [°]	
	4a	**4b**		**4a**	**4b**
Ni−P	2.207(5)	2.121(6)	C(1)−Ni−N(1)	95.1(6)	94.8(6)
Ni−N	1.883(14)	1.967(15)	C(1)−Ni−O(1)	164.9(7)	160.2(6)
Ni−C	1.883(11)	1.857(10)	N(1)−Ni−O(1)	91.9(6)	93.4(6)
Ni−O	1.912(12)	1.917(13)	C(1)−Ni−P	89.0(4)	86.5(4)
N−C(imine)	1.23(2)	1.369(19)	N(1)−Ni−P	164.6(6)	164.3(5)
N−C(Ph)	1.451(16)	1.389(16)	O(1)−Ni−P	87.8(4)	90.5(4)
O−C	1.313(13)	1.324(13)	Ni−N(1)−C(22)	121.0(14)	125.6(13)
C(20)−C(21)	1.182(9)	1.194(9)	Ni−O−C	125.7(9)	130.5(9)

longer than those in other complexes [2.148(2)−2.163(2) Å,[26b] 2.172(2) Å[24]]. However, the dihedral angles defined by the C24 phenyl ring and N3−O4−O5 and also the C69 phenyl ring and N6−O9−O10 are 6.6° and 7.3°, respectively, which indicates that each nitro group is coplanar with its corresponding phenyl ring. At the same time, the dihedral angle of the C24 phenyl ring and C69 phenyl ring is only 4.9° and the distances between the atoms of the nitro groups of **4a** and the phenyl ring plane of **4b** are in the range 3.240−3.510 Å, which means that there is some interaction between the nitro group and the phenyl ring (Figure 2).

Catalysis

The (phenyl)(phenylimino-phenolato)nickel(II) complexes **1−5** were tested for ethylene polymerization without any co-catalysts. A significant difference in the activities was observed for the different complexes (Table 2). For example, complex **2** displays an activity of $1.8 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1} while complex **5** shows no activity for ethylene polymerization. Attachment of a methyl group (complex **3**), which is sterically smaller than an isopropyl group, at the R position, dramatically decreases the activity. The reason for this is that the bulky substituents surrounding the active center shield the axial faces and retard chain termination. Complex **4**, which contains electron-withdrawing groups such as the nitro groups, shows an enhanced catalytic activity.

As expected a self-immobilization effect,[17−19] similar to that found for metallocenes, could be observed during the polymerization processes. The self-immobilized catalyst **2** bearing allyl substituents displays an ethylene polymerization activity of $1.8 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1}, while complex **1**, without allyl group, only exhibits an ethylene polymerization activity of $0.10 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1} under the same polymerization conditions. When ethylene was applied

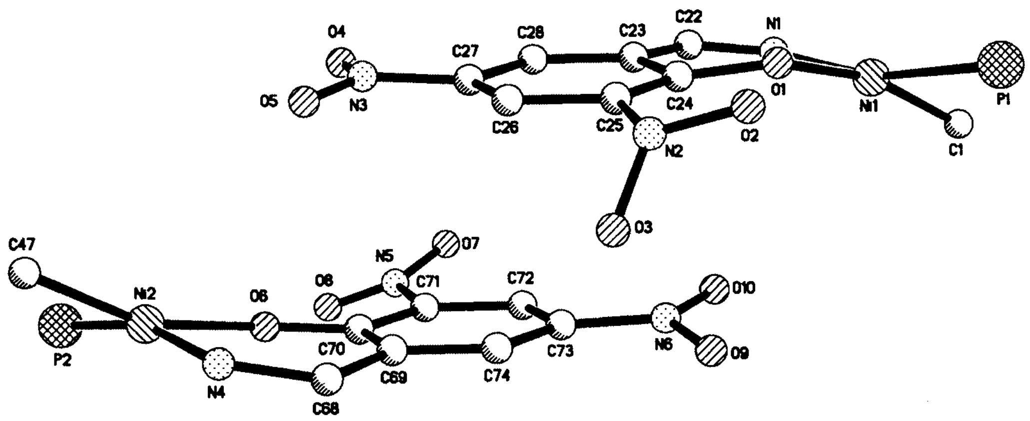


Figure 2. A plot showing the interaction between **4a** and **4b**

Table 2. Results of the ethylene polymerization with complexes **1**−**5**

Complex[a]	Activity[b]	*M*w[c]	*M*w/*M*n[c]
1	0.1	207.0[f]	2.2[f]
2	1.81	66.4	12.8
2[d]	1.32	n.d.[e]	n.d.[e]
3	0.90	121.8	4.6
4	2.90	192.4	32.0
5	0	−	−

[a] Polymerization conditions: 65.4 μmol of the appropriate catalyst, toluene (120 mL), 27 °C, 500-mL autoclave reactor, 4.0 bar ethylene pressure, reaction time 1 h. [b] 10^5 g PE·mol^{-1}Ni·h^{-1}. [c] *M*w ($\times 10^{-3}$) and *M*w/*M*n values were determined by GPC measurement. [d] Polymerization in the presence of 3 mL of methacrylate (MA). [e] Not determined.

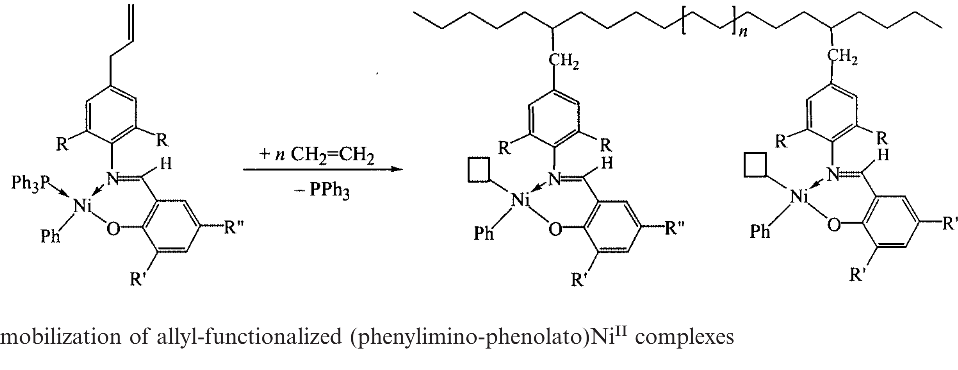
to the solution of the self-immobilized catalysts **2**−**5**, the ethylene was polymerized and the catalyst molecules were simultaneously incorporated into the growing chain of polyethylene due to their allyl functions (Scheme 2). At the beginning the color of the reaction mixture became deep and soon a large number of dark-red particles appeared in the polymerization system. These particles still displayed high activities after they were separated to be re-used as heterogeneous catalysts. That is to say, the homogenous catalysts were transformed into heterogeneous systems without any supports. Thus, active centers distributed along the polymer chain prevent catalysts from losing their effectiveness and help to make their catalytic activities more efficient. When complex **1** was used in the polymerization the "self-immobilization" of the nickel catalysts did not occur.

Complex **2** showed a slight drop in activity of ethylene polymerization when 3 mL of methyl acrylate (MA) was added to the polymerization system. This indicates that the self-immobilized neutral nickel catalysts are tolerant towards polar monomers. The IR spectra show that the methyl acrylate was not incorporated into the polymer chain, which suggests that the addition of MA does not destroy the catalytic activity.

Influence of the Polymerization Conditions with Self-Immobilized Catalyst 2

It is well known that the conditions of the polymerization reaction influence the productivity of the self-immobilized catalyst system and the nature of the polymer produced. To study these effects, we carried out polymerization over ranges of catalyst concentration, ethylene pressure, reaction temperature, polymerization time and solvent, employing the self-immobilized catalyst **2**. The results are summarized in Table 3.

To examine the effect of the catalyst concentration on the polymerization of ethylene, we carried out several tests in which the amount of catalyst **2** was systematically varied from 65.4 to 11.3 μmol. At 65.4 μmol of catalyst a broad molecular weight distribution (12.8) was observed, centered at 67213 (M_{pk}s). As the amount of catalyst is decreased to 32.7 μmol, a narrow distribution (9.9) is observed, with an



Scheme 2. Self-immobilization of allyl-functionalized (phenylimino-phenolato)Ni$^{\mathrm{II}}$ complexes

Table 3. Results of ethylene polymerization with self-immobilized catalyst **2**

No.[a]	Catalyst [μmol]	T [°C]	10^{-5} P [Pa]	Activity[b]	M_v [c]
1	65.4	27	4.0	1.81	82.8
2	65.4	27	3.0	1.30	87.2
3	65.4	27	2.0	0.93	129.3
4	49.1	27	4.0	2.07	31.1
5	32.7	27	4.0	3.14	96.0
6	15.1	27	4.0	2.41	372.4
7	11.3	27	4.0	1.26	196.4
8[d]	11.3	27	4.0	1.14	247.3
9	32.7	27	3.0	0.45	238.0
10[e]	32.7	27	4.0	3.70	171.5
11	32.7	37	3.0	1.81	265.3
12	32.3	47	3.0	2.23	74.2
13	32.7	57	3.0	2.18	11.8
14	32.7	67	3.0	2.00	4.4

[a] Polymerization conditions: 500-mL autoclave reactor, 120 mL of toluene, 800 rpm stirring, reaction time 1 h. [b] 10^5 g PE·mol^{-1}Ni·h^{-1}. [c] M_v ($\times 10^{-3}$) was determined with an Ubbelohde viscometer in decalin at 135±0.1 °C. [d] 120 mL of hexane was used instead of toluene. [e] Reaction time 36 min.

M_{pk}s of 71968. At 15.1 μmol the distribution (3.1) becomes very narrow with an M_{pk}s of 138061.

The ethylene pressure also has an effect on both the activity and the molecular weight distribution of the polyethylene. For example, employing 65.4 μmol of catalyst **2** at 2.0 bar of ethylene, a polymer with a distribution of 7.471 and a peak centered at 73042 was produced. On increasing the pressure to 4.0 bar, a broad distribution (12.8) was observed.

A series of experiments was undertaken to determine the effect of temperature variation on the performance of the catalyst. First, polymerization performed at 47 °C had a higher activity of $2.23 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1} than those at 27, 37, 57, and 67 °C. These results parallel the effect observed by Grubbs et al.[13] Secondly, with the increase of temperature, the molecular weight M_η varied from 238000 at 27 °C to 4400 at 67 °C, while the molecular weight distribution of PE decreased from 4.2 to 2.3. Moreover, as the reaction time increased from 36 to 60 min the activity decreased slightly from $3.70 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1} due to partial loss of catalytic activity. The solvent used for the polymerization had a slight influence, for example, when toluene solvent was replaced by hexane the activity decreased from $1.26 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1} to $1.14 \cdot 10^5$ g PE·mol^{-1} Ni·h^{-1} and M_η increased from 196400 to 247300.

Characterization of the Polyethylene Products

The ^{13}C NMR spectra of polyethylene produced by the self-immobilized catalysts **2**, **3**, and **4** have similar resonances, which can be seen in Table 4. Methyl branches were identified by the resonances at δ = 30.1 (CH_2), 20.1 (CH_3), 30.3 (CH), 37.7 (α-CH_2), 30.5 (γ-CH_2), and 27.6 ppm (β-CH_2).[27,13] The methyl branches were estimated as 0.41% (catalyst **2**), 0.55% (catalyst **3**), and 0.65% (catalyst **4**) in the spectra of PE. No other types of short branches are observed in the ^{13}C NMR spectra. The similar microstructures of polyethylene indicate that the self-immobilized catalysts keep the same arrangement around the active center as that of the original catalysts. The bulk densities of the PE produced by these self-immobilized catalysts are in the range of 0.148−0.278 g·cm^{-3}, which suggests that self-immobilization can improve the morphology of polymer products. The DSC results for the PE produced by catalysts **2**, **3**, and **4**, indicate that the self-immobilized catalysts convert ethylene to linear polyethylene with high crystallinity. The melting point temperatures (*T*m [°C]) of the polyethylene produced are 131 °C (catalyst **2**), 130 °C (**3**), and 129 °C (**4**), indicating the high-density nature of the polyethylene.

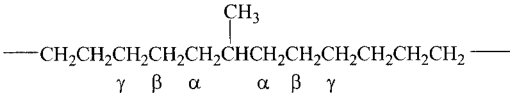
Conclusion

In this study, we have demonstrated that neutral nickel complexes bearing allyl groups as self-immobilized single-component catalysts display very high ethylene polymerization activities. The activities can be improved by changing the substituents of the benzaldehyde-phenylimine ligand and the polymerization reaction conditions. The results clearly indicate that self-immobilized neutral nickel complexes possess great potential as new olefin polymerization catalysts.

Experimental Section

General: All experiments with metal complexes and phenyliminophenolato ligands were carried out under argon using standard Schlenk and vacuum-line techniques. Solvents were dried by re-

Table 4. ^{13}C NMR spectroscopic data of polyethylene employing self-immobile catalysts **2**, **3**, and **4**



$$-\mathrm{CH_2CH_2}\underset{\gamma}{\mathrm{CH_2}}\underset{\beta}{\mathrm{CH_2}}\underset{\alpha}{\mathrm{CH_2}}\overset{\mathrm{CH_3}}{\mathrm{CH}}\underset{\alpha}{\mathrm{CH_2}}\underset{\beta}{\mathrm{CH_2}}\underset{\gamma}{\mathrm{CH_2}}\mathrm{CH_2CH_2CH_2}-$$

Catalyst	CH_2 (ppm)	CH_3 (ppm)	CH (ppm)	α-CH_2 (ppm)	β-CH_2 (ppm)	γ-CH_2 (ppm)	Branches per 1000 C
2	30.15	20.06	33.36	37.71	27.59	30.53	4
3	30.11	20.06	33.25	37.67	27.55	30.53	6
4	30.11	20.08	33.27	37.71	27.55	30.49	7

fluxing with appropriate drying agents (sodium/benzophenone for toluene, benzene, diethyl ether, THF, and hexane; CaH_2 for dichloromethane; magnesium for methanol) and distilled under argon prior to use. ^1H NMR spectra were recorded with a Varian Unity-400 spectrometer. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, q = quadruplet, m = multiplet, br = broad. IR spectra of the complexes were measured with a Bio-Rad FTS135 spectrometer. EI-MS spectra were recorded with a Finnigan MAT 8500 spectrometer (electron energy 70 eV) and elemental analyses were performed with a Perkin−Elmer Series II CHN/O Analyzer 2400. The ^{13}C NMR spectroscopic data for polyethylene were obtained using *o*-dichlorobenzene as the solvent with an FX-100 NMR spectrometer at 130 °C. The intrinsic viscosity [η] was measured in decalin at 135 °C using an Ubbelohde viscometer. The viscosity average molecular weight (M_v) was calculated by the following equation $[\eta] = 67.7 \cdot 10^{-3}\ M_v^{0.67}$. Average molecular weight (M_w) and molecular weight distribution (M_n/M_w) values of polyethylene products were determined using a PL GPC-220 gel permeation chromatograph at 150 °C using a narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 μm MIXED-B LS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL/min. Melting points were determined by DSC with a Perkin−Elmer 7 Series Thermal Analysis System. The starting materials 3-*tert*-butyl-5-methylbenzaldehyde and 3-phenylbenzaldehyde,[20] 3,5-dinitrobenzaldehyde,[21] 4-allyl-2,6-dimethylaniline,[22] *trans*-$[Ni(PPh_3)_2(Ph)Cl]$[23] and complex **1**[13] were prepared according to literature procedures and characterized by ^1H NMR spectra. Other commercially available reagents were purchased and used without purification.

General Procedure for Ethylene Polymerization: A 500-mL autoclave was charged with 100 mL of toluene under argon. A solution of the self-immobilized nickel(II) complex (10−65 μmol) in toluene (20 mL) was added. After three times of ethylene gas exchange, the ethylene pressure was raised to the specified value and maintained for a certain time. The polymerization was terminated by the addition of methanol and dilute HCl (10%). The solid polyethylene was filtered, washed with methanol and dried at 40 °C in vacuo.

Preparation of Complex 2. (a) Ligand Synthesis: 4-Allyl-2,6-diisoproylaniline was prepared from 2,6-diisoproylaniline by an analogous method according to ref.[22] The colorless liquid product was collected at 98.5 °C/0.6 Torr in 35% yield. ^1H NMR(400 MHz, $CDCl_3$): δ = 6.85 (s, 2 H, H-Ar), 5.98 (m, 1 H, CH=C), 5.09 (d, 1 H, $C{=}CH_{(E)}$), 5.03 (d, 1 H, $C{=}CH_{(Z)}$), 3.6 (br, 2 H, NH_2), 3.30 (d, 2 H, $CH_2C{=}C$), 2.92 [m, 2 H, $CH(Me)_2$], 1.26 [d, 12 H, $C(CH_3)_2$]. Formic acid (0.25 mL) was added to a methanol solution (5 mL) containing 4-allyl-2,6-diisopropylphenylamine (1.302 g, 6.0 mmol) and 3-phenylbenzaldehyde (1.148 g, 5.8 mmol). After stirring at room temperature for 12 h, the reaction mixture was poured into distilled water (25 mL), extracted with diethyl ether (25 mL × 2), washed with deionized water (25 mL × 2) and dried overnight with anhydrous sodium sulfate. After the solvent was removed by rotary evaporation a yellow solid was separated and dried under vacuum to afford 2.187 g of **B** in 95% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ = 13.68 (s, 1 H, OH), 8.35 (s, 1 H, N=CH), 7.71−7.05 (m, 8 H, Ar−H), 7.00 (s, 2 H, C=N−Ar−H), 6.00 (m, 1 H, CCH=C), 5.11 (q, 2 H, $C{=}CH_2$), 3.39 (d, 2 H, $CH_2C{=}C$), 2.99 (m, 2 H, $CHMe_2$), 1.16 (d, 12 H, CH_3 of *i*Pr). **(b) Complex Synthesis:** Sodium hydride (0.2 g, 5 mmol) was added to a solution of the ligand **B** (0.596 g, 1.5 mmol) in THF (20 mL). The mixture was stirred at room temp. for 2 h, and then centrifuged after which the upper clear solution was transferred and concentrated in vacuo to afford a pale-yellow solid residue. After washing with hexane (20 mL), the sodium salt of the corresponding ligand was obtained. A solution containing the sodium salt of **B** (0.629 g, 1.5 mmol) and *trans*-$[Ni(PPh_3)_2(Ph)Cl]$ (1.0 g, 1.44 mmol) in benzene (20 mL) was stirred at room temp. After 6 h, the reaction mixture was separated by filtration to remove NaCl. Hexane was slowly added to the top of the filtrate. Complex **2** was obtained as a yellow-orange solid. Yield: 0.95 g (83%). ^1H NMR (400 MHz, C_6D_6): δ = 8.13 (d, 1 H, N=CH), 7.89−6.34 (m, 30 H, Ar-H), 6.02 (m, 1 H, CH=), 5.11 (m, 2 H, $=CH_2$), 4.23 (m, 2 H, $CHMe_2$), 3.32 (d, $J_{H,H}$ = 6.4, 2 H, CH_2), 1.35 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.27 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH_3) ppm. EI-MS: *m*/*z* = 717 $[M - Ph]^+$, 455 $[M - Ph - PPh_3]^+$. $C_{52}H_{50}NNiOP$ (794.64): calcd. C 78.60, H 6.34, N 1.76; found C 78.88, H 6.22, N 1.73.

Complex 3: Ligand **C** as a yellow solid in 90% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ = 13.71 (s, 1 H, OH), 8.39 (s, 1 H, N=CH), 7.69−7.01 (m, 8 H, Ar-H), 6.93 (s, 2 H, C=N−Ar−H), 5.98(m, 1 H, CCH=C), 5.09(q, 2 H, $C{=}CH_2$), 3.37(d, 2 H, $CH_2C{=}C$), 2.19(s, 6 H, CH_3). **3** as a red crystalline solid. Yield: 0.95 g (86%). ^1H NMR (400 MHz, C_6D_6): δ = 8.07 (d, $J_{P,H}$ = 8.4 Hz, 1 H, N=CH), 7.78−6.44 (m, 30 H, Ar-H), 6.01 (m, 1 H, CH=), 5.10 (d, $J_{H,H}$ = 1.6, 2 H, $=CH_2$), 3.19 (d, $J_{H,H}$ = 6.4 Hz, 2 H, CH_2), 2.53 (s, 6 H, CH_3) ppm. EI-MS: *m*/*z* = 662 $[M - Ph]^+$, 400 $[M - Ph - PPh_3]^+$. $C_{48}H_{42}NNiOP$ (738.53): calcd. C 78.06, H 5.73, N 1.90; found C 77.99, H 5.73, N 1.91.

Complex 4: Ligand **D** as yellow-gold crystals in 95% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ = 16.27 (s, 1 H, OH), 9.07 (s, $^4J_{P,H}$ = 3.2 Hz, 1 H, N=CH), 8.50 (s, $^4J_{H,H}$ = 2.8 Hz, 1 H, Ar-H), 8.26 (s, 1 H, Ar-H), 7.10 (s, 2 H, C=N−Ar−H), 5.97 (m, 1 H, CCH=C), 5.16 (q, 2 H, $C{=}CH_2$), 3.43 (d, 2 H, $CH_2C{=}C$), 2.95 (m, 2 H, $CHMe_2$), 1.24 (d, 12 H, CH_3 of *i*Pr). **4** as a red solid. Yield: 1.05 g (90%). ^1H NMR (400 MHz, C_6D_6): δ = 8.34 (d, $J_{H,P}$ = 2.8 Hz, 1 H, N=CH), 7.84−6.34 (m, 24 H, Ar-H), 6.02 (m, 1 H, CH=), 5.12 (m, 2 H, $=CH_2$), 3.96 (m, 2 H, $CHMe_2$), 3.28 (d, $J_{H,H}$ = 6.0, 2 H, CH_2), 1.29 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.12 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH_3) ppm. EI-MS: *m*/*z* = 807 $[M^+]$, 545 $[M - PPh_3]^+$. $C_{46}H_{44}N_3NiO_5P$ (808.53): calcd. C 68.33, H 5.48, N 5.20; found C 68.97, H 5.41, N 5.10.

Complex 5: Ligand **E** as a yellow-green oil in 92% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ = 13.41 (s, 1 H, OH), 8.12 (s, 1 H, N=CH), 7.26−6.98 (m, 4 H, Ar-H), 6.02 (m, 1 H, CCH=C), 5.10 (q, 2 H, $C{=}CH_2$), 3.39 (d, 2 H, $CH_2C{=}C$), 2.99 (m, 2 H, $CHMe_2$), 2.32 (s, 3 H, CH_3Ar), 1.48 (s, 9 H, CH_3 of *t*Bu), 1.16 (d, 12 H, CH_3 of *i*Pr). **5** as a yellow-orange solid. Yield: 0.92 g (81%). ^1H NMR (400 MHz, C_6D_6): δ = 8.10 (d, 1 H, N=CH), 7.90−6.34 (m, 24 H, Ar-H), 6.04 (m, 1 H, CCH=C), 5.11 (q, 2 H, $C{=}CH_2$), 4.45 (m, 2 H, CH of *i*Pr), 3.32 (d, 2 H, $CH_2C{=}C$), 2.32 (s, 3 H, CH_3−Ar), 1.36 (d, 6 H, CH_3 of *i*Pr), 1.36 (d, 6 H, CH_3) 1.26 (d, 12 H, CH_3 of *i*Pr), 1.09 (s, 9 H, CH_3 of *t*Bu) ppm. EI-MS: *m*/*z* = 787 $[M]^+$. $C_{51}H_{56}NNiOP$ (788.67): calcd. C 77.67, H 7.16, N 1.78; found C 77.90, H 7.03, N 1.88.

X-ray Crystal Structure Determination of Complex 4: The crystallographic data for **4** (**4a**/**4b**) are summarized in Table 5. Dark-red single crystals were grown in toluene/hexane (1:1) at −15 °C. The crystal was sealed in a thin-walled glass capillary under argon. The intensity data were collected at 293 K with a Siemens P4 diffractometer using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). The stability of the primary beam was controlled by monitoring three check reflections every 100 reflections. Corrections for absorption based on the ψ-scan technique were applied. The structure was solved by direct methods using the SHELXTL-97 program and refined by full-matrix least-squares on F_o^2 using

Table 5. Crystallography data

	4
Empirical formula	$C_{59.50}H_{59}N_3NiO_5P$
Formula mass	985.78
Crystal description	Dark red plate
Crystal size [mm]	0.52 × 0.42 × 0.38
Crystal system	monoclinic
Space group	Cc
a [Å]	38.170(13)
b [Å]	10.477(4)
c [Å]	28.808(4)
β [deg]	102.45(4)
V [Å^3]	11250(6)
Z	8
Density (calcd.) [Mg·m^{-3}]	1.164
Absorption coefficient [mm^{-1}]	0.421
F(000)	4160
θ range for data collection [°]	1.99−22.50
Reflections collected	17155
Data/restraints/parameters	14620/24/791
Independent reflections	14620 (R_{int} = 0.0199)
Final R indices [$I > 2\sigma(I)$]	$R1^{[a]} = 0.0894$ $wR2^{[b]} = 0.2235$
R indices (all data)	$R1 = 0.2154$ $wR2 = 0.2669$
GOF on F^2	0.820
Absolute structure parameter	0.49(4)
$\rho_{max/min}$ [eÅ^{-3}]	0.821/−0.869

[a] $R1 = \Sigma|F_o| - \Sigma|Fc|/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F^2_o - F^2_c)]/\Sigma[w(F^2_o)^2]\}^{1/2}$.

SHELXTL-97.[28] All hydrogen atoms were included in idealized positions. CCDC-186490 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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