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New neutral nickel(II) complexes bearing pyrrole-imine chelate ligands: synthesis, structure and norbornene polymerization behavior

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Abstract

New neutral nickel(II) complexes bearing nonsymmetric bidentate pyrrole-imine chelate ligands (**4a**–**d**), [2-(ArNCH)C_4H_3N]Ni(PPh_3)Ph [Ar=2,6-diisopropylphenyl (**a**), 2-methyl-6-isopropylphenyl (**b**), 2,6-diethylphenyl (**c**), 2-*tert*-butylphenyl (**d**)], have been prepared in good yields from the sodium salts of the corresponding ligands and *trans*-Ni(PPh_3)$_2$(Ph)Cl, and the structure of complex **4a** has been confirmed by X-ray crystallographic analysis. These neutral Ni(II) complexes were investigated as catalysts for the vinylic polymerization of norbornene. Using modified methylaluminoxane (MMAO) as a cocatalyst, these complexes display very high activities and produce great mass polymers. Catalyst activity of up to 4.2×10^7 g (mol Ni h)$^{-1}$ and the viscosity-average molecular weight of polymer of up to 9.2×10^5 g mol^{-1} were observed. Catalyst activity, polymer yield, and polymer molecular weight can be controlled over a wide range by the variation of reaction parameters such as Al–Ni ratio, norbornene–catalyst ratio, monomer concentration, polymerization reaction temperature and time.

Keywords: Neutral Ni(II) complexes; Catalysts; Norbornene; Vinylic polymerization

1. Introduction

Norbornene is known to polymerize by ring-opening metathesis, cationic or vinylic polymerization [1–4]. Recently, the vinylic polymerization of norbornene has been considerably attracted because of the vinyl-type polynorbornene having unique physical properties, such as high glass transition temperature, optical transparency, and low birefringence [5]. The vinyl-type polynorbornene can be prepared using metal complexes based on nickel [6–10], chromium [11], zirconium [12–15], cobalt [16,17], and palladium [18–25] as catalyst. Zirconocenes and cationic palladium complexes are two types of important catalysts for the vinylic polymerization of norbornene. Zirconocenes exhibit only low catalytic activity and afford high polymers that decompose in air at high temperatures before they melt and are insoluble in organic solvents [12–15]. Cationic palladium complexes, such as [Pd(CH_3CN)$_4$][BF_4]$_2$, display extremely high catalytic activity and produce high polymers that are soluble in organic solvents such as chlorobenzene and *o*-dichlorobenzene, and exhibit high glass transition temperature ($T_g > 350$ °C). However, palladium is very expensive. Recently, Greiner reported the nickel(II) complexes bearing phosphoraneiminato ligands exhibiting high catalytic activity for the vinyl addition polymerization of norbornene and producing great mass polymer [9]. More recently, Grubbs reported that the neutral Ni(II) complexes bearing salicylaldiminato ligands can catalyze copolymerization of ethylene with norbornene derivatives and produce high copolymers [26]. We found Grubbs' neutral nickel complexes activated with methylaluminoxane (MMAO) display extreme activity for the vinylic polymerization of norbornene [27]. This urges us to investigate if other neutral Ni(II) complexes have high catalytic activity. Here, we would like to report the synthesis of novel neutral Ni(II) complexes bearing pyrrole-imine ligands and the catalysis properties for the vinylic polymerization of norbornene.

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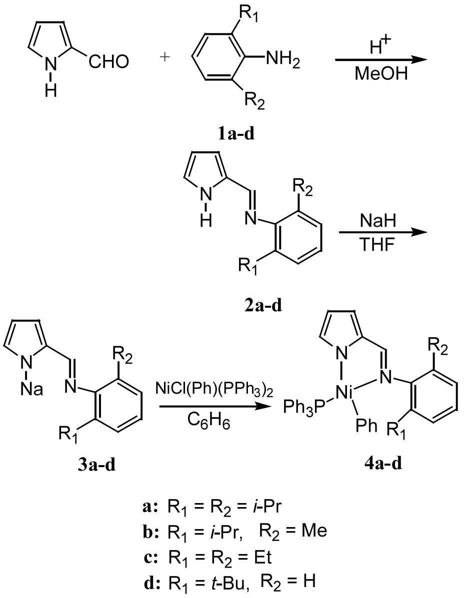
2. Results and discussion

2.1. *Synthesis and characterization complexes*

Grubbs and coworkers recently developed a family of neutral [N,O]Ni complexes capable of polymerizing ethylene and copolymerizing ethylene with norbornene derivatives [26]. Furthermore, we found Grubbs' neutral nickel complexes display extreme activity for the vinylic polymerization of norbornene [27]. This impels us to synthesize new neutral nickel complexes by modifying the structure of ligands. We report here the neutral Ni(II) complexes bearing pyrrole-imine ligands.

General synthetic route for the neutral Ni(II) complexes bearing pyrrole-imine ligands **2a**–**d** used in this study is shown in Scheme 1. The pyrrolide-imine ligands were prepared (yields: **2a**, 75; **2b**, 70; **2c**, 72; **2d**, 67%) by the condensation of the corresponding aniline derivatives **1a**–**d** and pyrrole-2-carboxaldehyde. The sodium salts **3a**–**d** were obtained by treatment of **2a**–**d** with NaH in THF. The neutral Ni(II) complexes **4a**–**d** were obtained as yellow powers (yields: **4a**, 76; **4b**, 79; **4c**, 73; **4d**, 69%) by the reaction of **3a**–**d** with *trans*-[NiCl(Ph)(PPh$_3$)$_2$]. According to NMR spectra, these neutral Ni(II) complexes with pyrrole-imine ligands, similar to those neutral salicylaldiminato Ni(II) complexes [29], are diamagnetic and adopt a square-planar geometry. In the ^{1}H-NMR spectra of **4a**–**d** the imine protons show a characteristic ^{31}P coupling, which corresponds to PPh$_3$ bound in a *trans* relationship to ketimine. The signals for the triphenylphosphine ligand in the ^{31}P-NMR spectra of complexes **4a**–**d** are observed between 28.0 and 28.6 ppm.



Scheme 1.

Crystals of **4a** suitable for X-ray structure determination were grown from a benzene–pentane (1:1) solution. The data collection and refinement data of the analysis are summarized in Table 1, and the molecule structure is shown in Fig. 1. In the solid state, the molecule adopts nearly ideal square-planar coordination geometry. The bulky 2,6-diisopropylbenzimine occupies the position *trans* to the triphenylphosphine ligand with a P–Ni–N2 angle of 168.53(7)°. The phenyl group attached to Ni lies *trans* to N1 with a N1–Ni–C1 angle of 167.05(12)°. The N2–Ni–N1, N2–Ni–C1, P–Ni–N1, and P–Ni–C1 bond angles are 82.70(10), 93.92(11), 100.09(7) and 85.69(9)°, respectively. The torsion angle of the plan (N1, C7, C11, N2, Ni) and the plan (Ni, P, C1) is 17.8°. The Ni–C1, Ni–N1, and Ni–N2 bond distances are 1.910(3), 1.952(2), and 1.982(2) Å, respectively. The Ni–P bond of **4a** (2.148(1) Å) is shorter than that of the neutral salicylaldiminato Ni(II) complex (2.172(2) Å) [29] (Table 2).

2.2. *Polymerization*

The structure of the neutral nickel complexes **4a**–**d** is similar to that of Grubbs' catalysts that can catalyze the polymerization of ethylene and produce great mass polymers [26]. However, attempt to polymerize ethylene with complexes **4a**–**d** did not success whether phosphine scavengers or cocatalysts such as MMAO were used or not, which is similar to the case of the neutral palladium complexes reported by Novak and coworkers [30]. It is very interesting, nevertheless, that complexes **4a**–**d**, like the neutral salicylaldiminato Ni(II) complexes [27], exhibit extremely high catalytic activity for the vinylic

Table 1
Crystal data and structure refinements for **4a**

Empirical formula	$C_{41}H_{41}N_2NiP$
Formula weight	651.44
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.177(4)
b (Å)	17.857(6)
c (Å)	18.059(4)
β (°)	104.79(3)
V (Å^3)	3485(2)
Z	4
ρ_{calc} (g cm^{-3})	1.242
μ(Mo–K$_\alpha$) (cm^{-1})	0.71073
F(000)	1376
θ Range (°)	1.63–25.03
Independent reflections	6133 ($R_{int}=0.0269$)
Absorption correction	ψ-scan
Max. and min. transmission	0.4188 and 0.3786
Parameters	410
Final R indices [$I>2\sigma(I)$]	$R_1=0.0380$, $wR_2=0.0583$
Goodness-of-fit on F^2	0.812
Largest peak/hole in final difference map (e Å^{-3})	+0.235/−0.294

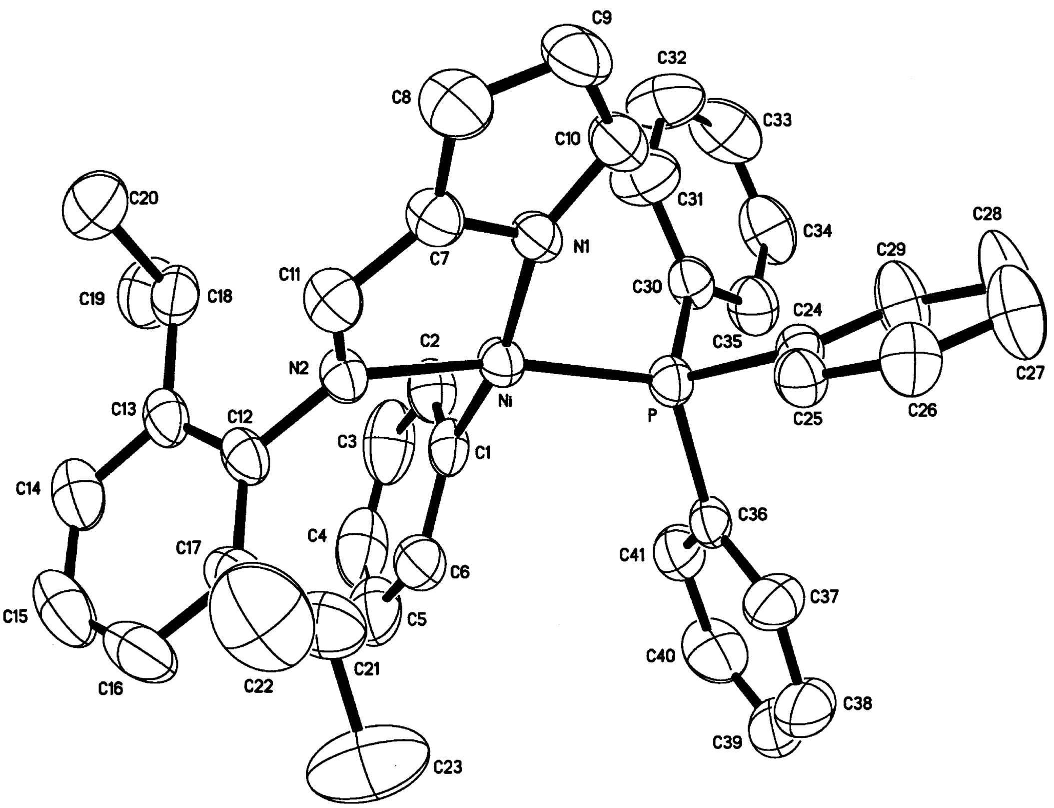


Fig. 1. Molecular structure of complex **4a**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

polymerization of norbornene and produce great mass polynorbornene, in the presence of MAO or modified MAO (MMAO) under moderate conditions.

Polymer yields and molecular weights as well as catalyst activities depended significantly on the reaction conditions. MMAO was essential for the polymerization of norbornene catalyzed by the neutral Ni(II) complexes. Variation of the molar ratio of MMAO–**4a**, which is expressed here as Al–Ni ratio, showed considerable effects on the polymer yields, molecular weights and catalyst activities. When the mole ratio of Al–Ni was 1000/1, the catalytic activity is 3.6×10^6 g polym (mol Ni h)$^{-1}$, and a significant increase of the activity of up to 8.8×10^6 g polym (mol Ni h)$^{-1}$ was observed by increase of the ratio of Al–Ni to 2000/1 as shown in Fig. 2. In contrast, the viscosity-average molecule weights ($\bar{M}_v$) of the polymers decrease with increase of the Al–Ni ratio.

Table 2
Selected bond lengths (Å) and angles (°) for complex **4a**

Bond lengths	
Ni–C(1)	1.910(3)
Ni–N(1)	1.952(2)
Ni–N(2)	1.982(2)
Ni–P	2.148(1)
N(1)–C(10)	1.346(3)
N(2)–C(11)	1.295(3)
N(1)–C(7)	1.392(3)
P–C(24)	1.832(3)
P–C(30)	1.829(3)
P–C(36)	1.837(3)
Bond angles	
C(1)–Ni–N(1)	167.05(12)
C(1)–Ni–N(2)	93.92(11)
N(1)–Ni–N(2)	82.70(10)
C(1)–Ni–P	85.69(9)
N(1)–Ni–P	100.09(7)
N(2)–Ni–P	168.53(7)
C(30)–P–Ni	113.38(10)
C(30)–P–C(24)	102.83(13)
C(30)–P–C(36)	106.45(14)
C(24)–P–C(36)	100.44(13)

As shown in Fig. 3, the reaction temperature also affects considerably on the catalytic activity of **4a** and molecular weights of the polymers. With increase of the reaction temperature, the catalytic activities and viscosity-average molecule weights ($\bar{M}_v$) of the polymers increase first and then decrease. As for the catalytic activity, the optimum reaction temperature is ca. 30 °C.

As shown in Fig. 4, the concentration of norbornene also considerably affects the polymerization reaction. An increase of the monomer concentration caused a linear increase of the catalyst activity of **4a**. Viscosity-average molecule weights ($\bar{M}_v$) increase first and then keep steady with increase of the monomer concentration.

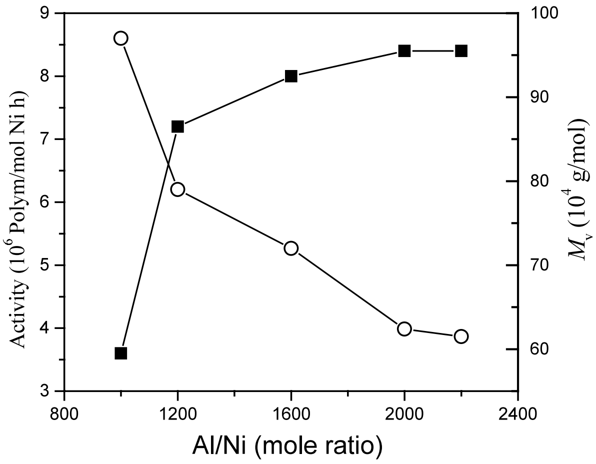


Fig. 2. Plot of activity (■) and $\bar{M}_v$ (○) vs. Al–Ni (molar ratio). 0.5 μmol **4a**, [norbornene]–[Ni] = 47 800, V_{total} = 30 ml, polymerization reaction at 30 °C for 30 min.

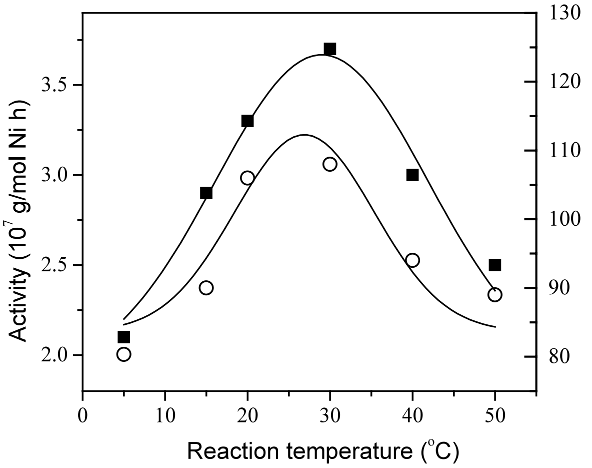


Fig. 3. Plot of activity (■) and $\bar{M}_v$ (○) vs. reaction temperature. 0.5 μmol **4a**, Al–Ni = 2000, [norbornene]–[Ni] = 47 800, V_{total} = 30 ml, polymerization reaction for 15 min.

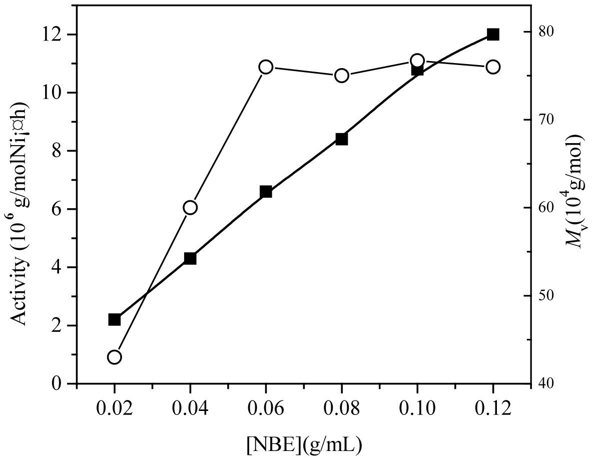


Fig. 4. Plot of activity (■) and $\bar{M}_v$ (○) vs. norbornene concentration. 0.5 μmol **4a**, Al–Ni = 2000, V_{total} = 30 ml, polymerization reaction at 30 °C for 30 min.

The polymerization results using complexes **4a**–**d** activated with MMAO are summarized in Table 3. The structures of the neutral Ni(II) complexes affect on the polymer yields and activities under the same experimental conditions. Bulky substituents in the *ortho* position of nitrogen atom hinder the insertion of norbornene. The decrease of steric hindrance is favorable to the insertion reaction of norbornene. Hence, **4a** with two big substituents displays the lowest catalytic activity and produces the smallest mass polymers, and **4c** with only one substituents displays the highest catalytic activity and produces the greatest mass polymers among the four catalysts. All polymers display high molecular weights ($\bar{M}_v$ up to 1.3×10^6 g mol^{-1}). It is worthy to notice that the viscosity-average molecule weights ($\bar{M}_v$) of the polymers are almost independent of the structure of catalyst used. The glass transition temperatures (T_g) of the polymers are in the range of 395.0–410.0 °C as shown in Fig. 5.

IR, ^{1}H- (Fig. 6) and ^{13}C-NMR spectra (Fig. 7) are characteristic for polynorbornene and reveal no traces of double bonds, which are typical for metathesis-type polynorbornene. All polymers are soluble at room temperature in chlorobenzene, *o*-dichlorobenzene, and dichloroethylene, which indicate low stereoregularity. It is confirmed by ^{1}H- and ^{13}C-NMR spectra. Indeed, analysis by wide-angle X-ray diffractometry shows no indication of crystallinity.

3. Experimental

3.1. General procedures and materials

All work involving air and moisture sensitive compounds was carried out using standard Schlenk techniques. NMR analyses of polymers were performed on a Varian Unity 400 MHz spectrometer at 135 °C, using *o*-$C_6D_4Cl_2$ as solvent. Other NMR data of ligands and complexes were obtained on a Varian Unity 400 MHz spectrometer at ambient temperature, C_6D_6 or $CDCl_3$ as solvent. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. DSC measurements were performed with a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter. Viscosity-average molecular weights were calculated from the intrinsic viscosity by using the Mark–Houwink coefficients: $a = 0.56$, $K = 5.97 \times 10^{-4}$ dl g^{-1} [28].

2,6-Dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline and 2-*tert*-butylaniline were obtained from Acros and purified by distillation before use. Pyrrole-2-carboxaldehyde and triphenylphosphine were obtained from Aldrich and used without purification. Norbornene was dried over Na, vacuum-transferred, and degassed by repeated freeze–pump–thaw cycles. Benzene-d_6 was dried over CaH_2, vacuum-transferred,

Table 3
The results of the vinylic polymerization of norbornene [a]

Entry	Catalyst	Al–Ni (mol ratio)	Norbornene (g)	Polymer (g)	Yield (%)	Activity (10^7 g (mol Ni h)$^{-1}$)	$\bar{M}_v$ (10^4 g mol^{-1})
1	**4a**	1200	2.40	1.39	58	3.3	85
2	**4b**	1200	2.40	1.49	62	3.6	87
3	**4c**	1200	2.40	1.58	66	3.8	90
4	**4d**	1200	2.40	1.68	70	4.0	92
5	**4a**	2000	2.40	1.61	67	3.9	65
6	**4b**	2000	2.40	1.68	70	4.0	67
7	**4c**	2000	2.40	1.78	74	4.3	69
8	**4d**	2000	2.40	1.85	77	4.4	71

[a] 0.5 μmol catalyst, $V_{total} = 30$ ml, polymerization reaction for 5 min at 30 °C.

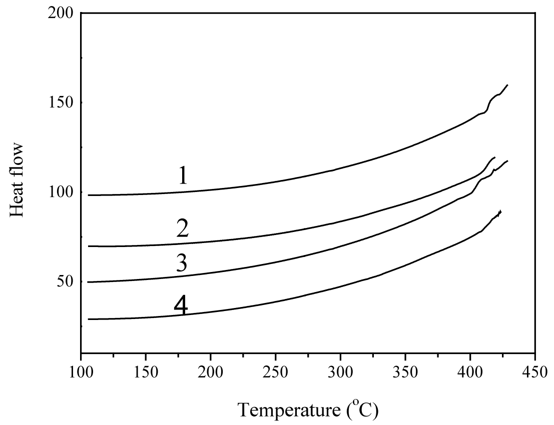


Fig. 5. The glass transition temperature (T_g) of polymers by DSC with a heating rate of 20 °C min^{-1}. **1**, **2**, **3**, and **4** correspond to entries 5, 6, 7, and 8 in Table 3, respectively.

degassed by repeated freeze–pump–thaw cycles, and stored over 4Å molecular sieves. o-Dichlorobenzene-d_4 was obtained from Aldrich and used without further purification.

3.2. Synthesis of ligands **2a–d**

To a stirred solution of pyrrole-2-carboxyaldehyde (1.90 g, 20 mmol) in dried MeOH (30 ml), 2,6-diisopropylaniline (3.6 g, 20 mmol) and formic acid (0.5 ml), as a catalyst, were added. The reaction mixture was stirred for 24 h at room temperature (r.t.). Subsequently, the white precipitate was separated by filtration, and then recrystallized from MeOH to yield **2a** as white crystals in 75% yield (3.81 g). The other ligands **2b–d** were prepared by the same procedure with similar yields.

2a: ^{1}H-NMR ($CDCl_3$): δ 10.8–10.2 (br, 1H, N–H), 7.91 (s, 1H, N=C–H), 7.17 (m, 3H, Ph–H), 6.67 (d, 1H, pyrrole-H), 6.25 (s, 1H, pyrrole-H), 3.07 (m, 1H, C–H), 1.15 (d, 12H, i-Pr–CH_3). ^{13}C-NMR ($CDCl_3$): δ 23.6, 27.9, 109.8, 116.7, 123.2, 124.1, 124.5, 129.8, 138.9,

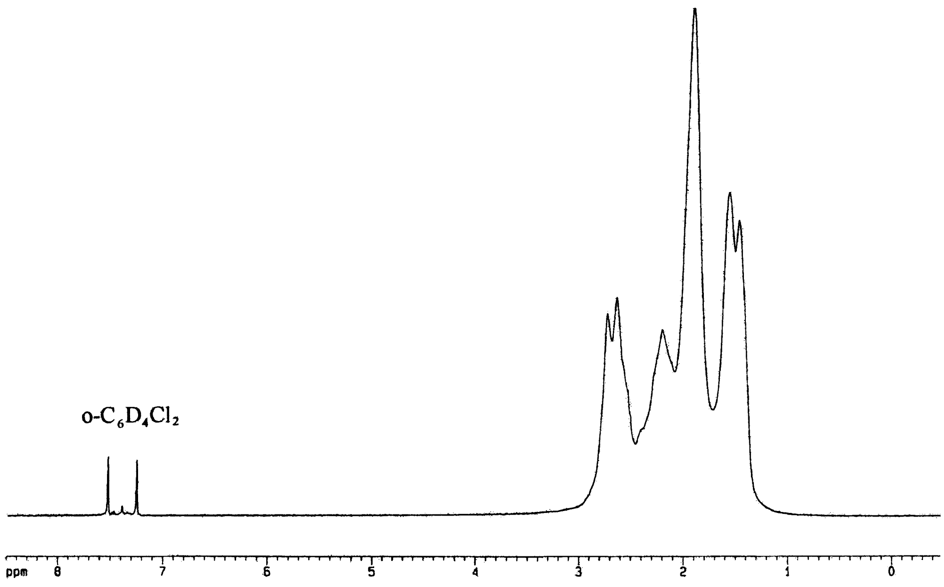


Fig. 6. ^{1}H-NMR spectra of polynorbornene recorded in o-$C_6D_4Cl_2$ at 135 °C.

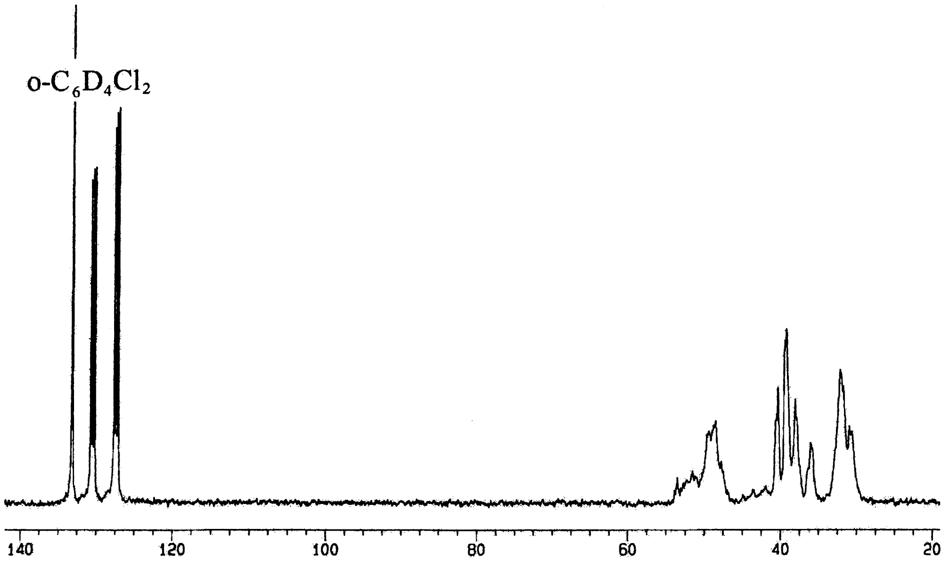


Fig. 7. ^{13}C-NMR spectra of polynorbornene recorded in *o*-$C_6D_4Cl_2$ at 135 °C.

148.4, 152.7. Anal. Calc. for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 80.35; H, 8.69; N, 10.96%.

2b (70%): ^{1}H-NMR ($CDCl_3$): δ 10.3–10.1 (br, 1H, N–*H*), 7.96 (s, 1H, N=C–*H*), 7.17 (s, 1H, Ph–*H*), 7.08–7.02 (m, 2H, Ph–*H*), 6.68 (s, 1H, pyrrole-*H*), 6.62 (d, 1H, pyrrole-*H*), 6.25 (d, 1H, pyrrole-*H*), 3.07 (m, 1H, C–*H*), 2.15 (s, 3H, C*H*$_3$), 1.13 (d, 6H, *i*-Pr–C*H*$_3$). ^{13}C-NMR ($CDCl_3$): δ 18.7, 23.4, 27.8, 109.9, 116.6, 123.4, 123.9, 124.2, 127.8, 127.9, 129.9, 139.3, 149.5, 153.0. Anal. Calc. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.70; H, 7.98; N, 12.32%.

2c (72%): ^{1}H-NMR ($CDCl_3$): δ 10.5–10.3 (br, 1H, N–*H*), 7.97 (s, 1H, N=C–*H*), 7.13–7.07 (s, 3H, Ph–*H*), 6.59 (m, 1H, pyrrole-*H*), 6.44 (s, 1H, pyrrole-H), 6.19 (m, 1H, pyrrole-*H*), 2.54 (m, 4H, C*H*$_2$), 2.10 (m, 6H, C*H*$_3$). ^{13}C-NMR (400 MHz, C_6D_6): δ 15.4, 26.0, 109.9, 116.7, 123.3, 124.2, 124.5, 129.9, 139.0, 148.6, 152.9. Anal. Calc. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.60; H, 8.00; N, 12.40%.

2d (67%): ^{1}H-NMR ($CDCl_3$): δ 9.18–9.08 (br, 1H, N–*H*), 8.10 (s, 1H, N=C–*H*), 7.37 (dd, 1H, Ph–*H*), 7.21 (m, 1H, Ph–*H*), 7.14 (m, 1H, Ph–*H*), 6.82 (dd, 1H, pyrrole-*H*), 6.66 (d, 1H, pyrrole-*H*), 6.32 (m, 1H, pyrrole-*H*), 1.43 (s, 9H, *t*-Bu–C*H*$_3$). ^{13}C-NMR ($CDCl_3$): δ 30.6, 35.6, 110.4, 116.1, 120.3, 125.2, 126.1, 127.1, 131.0, 142.8, 148.6, 151.4. Anal. Calc. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.59; H, 8.06; N, 12.35%.

3.3. Synthesis of neutral Ni(II) complexes *4a–d*

A solution of ligand **2a** (0.51 g, 2.0 mmol) in THF (20 ml) was added to NaH (120 mg, 5 mmol). The resulting mixture was stirred at r.t. for 5 h, filtered, and evaporated. The solid residue was washed with C_5H_{12} (20 ml) and dried in vacuum. The Na salt **3a** (0.28 g, 1.0 mmol) and *trans*-[NiCl(Ph)(PPh$_3$)$_2$] (0.67 g, 0.97 mmol) were in a Schlenk flask dissolved in C_6H_6 (20 ml) and stirred at r.t. for 8 h. The resulting mixture was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ca. 5 ml. Pentane (30 ml) was added. Subsequently, a yellow–orange solid precipitated from solution and was isolated by cannula filtration, and was washed several times by cold C_5H_{12} to yield 0.51 g (76%) of **4a**. The other complexes **4b–d** were prepared by the same procedure with similar yields.

4a: ^{1}H-NMR (C_6D_6): δ 7.78 (s, 5H, NiPh–*H*), 7.68 (s, 1H, N=C–*H*), 7.16 (s, 1H, Ph–*H*), 6.99 (m, 15H, PPh–*H*), 6.46 (s, 3H, 2Ph–*H*+pyrrole-*H*), 6.31 (s, 1H, pyrrole-*H*), 6.12 (s, 1H, pyrrole-*H*), 4.11 (s, 2H, C–*H*), 1.46 (s, 6H, *i*-Pr–C*H*$_3$), 1.28 (s, 6H, *i*-Pr–C*H*$_3$). ^{13}C-NMR (C_6D_6): 23.0, 26.4, 29.2, 113.5, 113.7, 118.3, 122.0, 123.0, 124.4, 126.2, 126.4, 129.1, 130.1, 130.5, 132.2, 132.6, 132.7, 132.8, 133.0, 135.2, 135.3, 137.2, 140.7, 141.6, 142.8, 144.2, 146.9, 152.4, 152.9, 162.7. ^{31}P-NMR (C_6D_6): δ 28.6. Anal. Calc. for $C_{41}H_{41}N_2NiP$: C, 75.59; H, 6.34; N, 4.30. Found: C, 75.31; H, 6.36; N, 4.32%.

4b (79%): ^{1}H-NMR (C_6D_6): δ 7.89 (s, 1H, N=C–*H*), 7.77 (s, 5H, NiPh–*H*), 7.49 (s, 1H, Ph–*H*), 7.12 (s, 1H, Ph–*H*), 6.48 (s, 1H, pyrrole-*H*), 6.38 (s, 1H, Ph–*H*), 6.32 (s, 1H, pyrrole-*H*), 6.08 (s, 1H, pyrrole-*H*), 3.81 (s, 1H, C–*H*), 2.72 (s, 3H, PhC*H*$_3$), 1.34 (d, 3H, *i*-Pr–C*H*$_3$), 1.18 (s, 3H, *i*-Pr–C*H*$_3$). ^{13}C-NMR (C_6D_6): δ 20.5, 22.6, 26.4, 29.0, 113.5, 116.6, 118.3, 122.0, 123.1, 124.7, 125.9, 127.6, 129.0, 129.2, 130.1, 130.5, 132.1, 132.7, 132.8, 133.1, 135.3, 135.4, 136.8, 140.5, 141.9, 142.7, 148.2, 162.9. ^{31}P-NMR (C_6D_6): δ 28.0. Anal. Calc. for $C_{39}H_{37}N_2NiP$: C, 75.14; H, 5.98; N, 4.49. Found: C, 75.34; H, 6.01; N, 4.47%.

4c (73%): ^{1}H-NMR (C_6D_6): δ 7.79 (m, 6H, 5 NiPh–H+1 N=C–H), 7.38 (d, 1H, Ph–H), 7.19 (d, 1H, Ph–H), 7.09–6.85 (m, 15H, PPh–H), 6.52 (m, 1H, pyrrole-H), 6.41 (m, 1H, Ph–H), 6.18 (s, 1H, pyrrole-H), 6.09 (s, 1H, pyrrole-H), 3.20 (m, 2H, CH_2), 2.98 (m, 2H, CH_2), 1.35 (d, 6H, CH_3). ^{13}C-NMR (C_6D_6): δ 15.3, 26.0, 113.5, 118.3, 122.1, 125.5, 125.8, 130.5, 132.7, 133.1,135.3, 135.4, 136.9, 137.8, 140.4, 162.7. ^{31}P-NMR (C_6D_6): δ 28.5. Anal. Calc. for $C_{39}H_{37}N_2NiP$: C, 75.14; H, 5.98; N, 4.49. Found: C, 75.02; H, 5.95; N, 4.47%.

4d (69%): ^{1}H-NMR (C_6D_6): δ 7.89 (s, 5H, NiPh–H), 7.84 (s, 1H, N=C–H), 7.39 (d, 1H, Ph–H), 7.18 (s, 2H, Ph–H), 7.04 (m, 16H, 15 PPh–H+1 pyrrole-H), 6.35 (s, 1H, pyrrole-H), 6.14 (s, 1H, pyrrole-H), 1.58 (s, 9H, CH_3). ^{13}C-NMR (C_6D_6): δ 32.8, 36.9, 37.1, 114.5, 119.2, 119.9, 125.3, 125.5, 127.1, 130.7, 132.5, 132.9, 135.6, 141.1, 145.6, 156.4. ^{31}P-NMR (C_6D_6): δ 28.3. Anal. Calc. for $C_{39}H_{37}N_2NiP$: C, 75.14; H, 5.98; N, 4.49. Found: C, 75.04; H, 5.95; N, 4.51%.

3.4. *Typical polymerization procedure*

Fresh catalyst solution (2 ml) (C_6H_5Cl, 0.5 μmol catalyst), 3 ml of a solution of norbornene (20 mmol, 2.40 g) in C_6H_5Cl, and 24 ml of C_6H_5Cl were added under inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by the addition of 1 ml of a MMAO solution (0.4 mmol in C_6H_5Cl) at 30 °C. After 15 min, the reaction mixture was poured into 200 ml of acidic EtOH (EtOH–$HCl_{conc.}$ = 50/1). The polymer was isolated by filtration, washed with MeOH, and dried under vacuum at 80 °C for 24 h. Total reaction volume was 30 ml, unless otherwise stated. This was achieved by variation of the amount of C_6H_5Cl if necessary.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 184370 for compound **4a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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