Synthesis, characterization and olefin polymerization of the nickel catalysts supported by [N,S] ligands

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ABSTRACT

The novel nickel (II) complexes (**2a**, **2b**) bearing 1-pyridyl-(3-substituedimidazole-2-thione) ligands were synthesized by the reaction of the corresponding ligands with $NiBr_2(DME)$. **2a** and **2b** have been characterized by IR, NMR and elemental analysis. The nickel complexes show high catalytic activities for norbornene polymerization in the presence of MAO (methylaluminoxane), although low activities for ethylene polymerization.

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1. Introduction

Since Brookhart discovered the α-diimine nickel and palladium catalysts which can produce high molecular weight polyethylene in 1995 [1], olefin polymerization of late transition metal catalysts has attracted considerable attention in academic and industrial fields over the past decade [2–6]. After activation with MAO, the pyridyl-imine based Ni[II] catalyst can produce mainly oligomer and methyl branched PE with good to moderate activity [7–11].

The NB (norbornene) addition polymerization product (PNB) displays a characteristic rigid random coil conformation, which shows restricted rotation about the main chain and exhibits high thermal stability ($T_g > 350\,°C$). In addition, it has excellent dielectric properties, optical transparency and unusual transport properties [2–3]. Therefore, it has been attracted many chemists to study the NB addition–polymerization. Up to now, catalytic systems based on titanium [12], zirconium [13], cobalt [14–17], chromium [14,18–19], nickel [20–33], palladium [33–35] and copper [31–32,36–37] have been mainly reported for the addition–polymerization of NB. Especially, the nickel complexes bearing [N,O] and [N,N] ligands using for norbornene polymerization exhibited high activity [21–22,25–27,29–32]. Recently, our group found that nickel complexes bearing soft atom donor ligands N-substituents imidazole-2-thione and imidazole-2-selone activated with MAO exhibited very high activity for norbornene polymerization [38]. Up to

now, there was no report of the nickel catalyst bearing [NS] ligands for olefin polymerization [2–6]. Herein, we report the synthesis and characterization of the nickel complexes with new hard–soft nitrogen–sulfur donor ligands 1-pyridyl-(3-[t]butylimidazole-2-thione) (**1a**) and 1-pyridyl-(3-(2,6-diisopropylphenylimidazole)-2-thione) (**1b**) and the test of the complexes for the polymerization of ethylene and norbornene.

2. Results and discussion

2.1. synthesis and characterization of the ligands and complexes

The bidentate ligands with N-substituents imidazole-2-thione and imidazole-2-selone can be easily prepared with moderate yields by the reaction of methylene and ethylene bridged N-substitutedimidazolium dibromide with sulfur or selenium powder and K_2CO_3 under reflux condition in MeOH solution [38–40]. The new hard–soft nitrogen–sulfur donor ligands 1-pyridyl-(3-[t]butylimidazole-2-thione) (**1a**) and 1-pyridyl-(3-(2,6-diisopropylphenylimidazole)-2-thione) (**1b**) were readily prepared by deprotonation of corresponding imidazolium salt with potassium *tert*-butoxide (Scheme 1) in THF solution, followed by adding the sulfur at room temperature. All the ligands were stable in the air and moisture, and were soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$ and THF. The ligands **1a** and **1b** were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. The formation of **1a** is conformed by the appearance of the ^{1}H signals at 1.87, 6.98 and 7.36 ppm, which can be assigned to the methyl, two
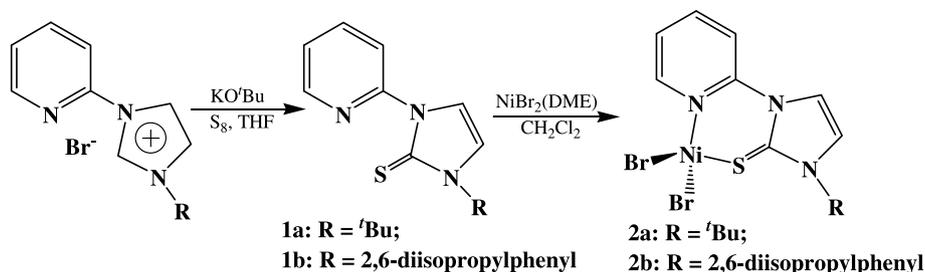
Scheme 1. Synthesis of ligands **1a** and **1b** and complexes **2a** and **2b**.

olefinic H protons of the imidazole, respectively, and the IR spectra exhibit intense C=S stretching at about 1158 cm^{-1}. Similarly, the structure of **1b** was conformed by the resonances at 1.13, 1.28, 6.77, 7.85 ppm in the ^{1}H NMR spectra. And the formation of C=S bond was further confirmed by ^{13}C NMR spectra which show singlet at about δ 164.6 ppm and δ 164.4 ppm for **1a** and **1b**, respectively.

The green complexes **2a** and **2b** were obtained by the reaction of **1a** and **1b** with NiBr$_2$(DME) in dichloromethane in good yields. In the IR spectra of complexes **2a**–**2b**, the C=S stretching vibrations shift toward lower frequencies (**2a**: from 1158 to 1156; **2b**: from 1178 to 1154) and were greatly reduced in intensity, which indicated the coordination interaction between the S atoms and the metal nickel ions. Elemental analysis is in all cases consistent with the stoichiometry (ligand)NiBr$_2$. ^{1}H NMR spectroscopy of complexes **2a** and **2b** exhibited paramagnetic properties indicating that the complexes possess a tetrahedral geometry as seen for (α-diimine)NiBr$_2$ complexes [1].

Green single crystals of **2b** bearing N-2,6-diisopropylphenyl substituted ligand were grown in CH$_3$CN/ether (1:10) at room temperature and the corresponding X-ray crystallographic data were given in Table 1. As depicted in Fig. 1, the complex **2b** forms a

mononuclear structure configuration, which not like the pyridylimine nickel complexes that crystallize as centrosymmetric dimers with two ligand nitrogen atoms, one terminal bromine and two bridging bromine atoms forming the coordination sphere around each five-coordinate nickel center [7–11]. The nickel center of complex **2b** adopted a distorted tetrahedral geometry, which further confirmed the paramagnetic results of the NMR measurements. A bulky steric interactions was created by the 2,6-diisopropyl of the phenyl within the nickel center (Fig. 1), which could be prevent the β-H transfer. The bond length of Ni–N (2.008(8) Å) was shorter than that of the pyridylimine nickel complexes (2.023(5)–2.086(3) Å) (Ni–N(pyridine)) [8] and pyridine functionalized chelate N-heterocyclic carbene nickel complexes (2.032(5)–2.103(5) Å) [41]. And the Ni–S (2.282(3) Å) bond distance was also shorter than that the nickel complexes bearing different N-substituents imidazole-2-thione (2.2837(15)–2.3155(18) Å) [38]. The dihedral angel of the pyridine ring and the imidazole plane was 36.2°, and do not possess in the same plane. The phenyl ring of the N-substituent was oriented essentially orthogonal to the imidazole plane (89.1°). And the dihedral angle of the phenyl ring and the pyridine ring is 60.6°.

2.2. Olefin polymerization

The α-diimine Ni and Pd complexes with bulky aryl substituents ligands, which can prevent β-H transfer, can produce high

Table 1
Crystallographic data of the complex **2b**.

Empirical formula	C$_{20}$H$_{23}$N$_3$SNiBr$_2$
Formula weight	556.00
Crystal system	Triclinic
Space group	P$\bar{1}$
a (Å)	8.041(7)
b (Å)	8.796(7)
c (Å)	16.330(14)
α (°)	77.158(12)
β (°)	85.275(10)
γ (°)	80.194(10)
V (Å^3)	1108.4(16)
Z	2
$D_{calcd.}$ (mg m^{-3})	1.666
Crystal size (mm^3)	0.12 × 0.10 × 0.08
μ (mm^{-1})	4.584
$F(000)$	556
θ_{max}, θ_{min} (°)	27.41, 2.40
Index range	
h	−10 → 9
k	−11 → 8
l	−19 → 20
[$R_{(int)}$]	0.0469
No. of independent reflections	4546
No. of observed reflections	3071
No. of variables	160
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0842$, $wR_2 = 0.2497$
R indices (all data)	$R_1 = 0.1084$, $wR_2 = 0.2589$
Goodness-of-fit (GOF)	1.078
Largest difference peak*(hole) (e Å^{-3})	1.786 (−0.881)
Δ/σ	0.000, 0.000

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $RW = \{\sum [w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$.
* Largest peak(hole) in difference Fourier map.
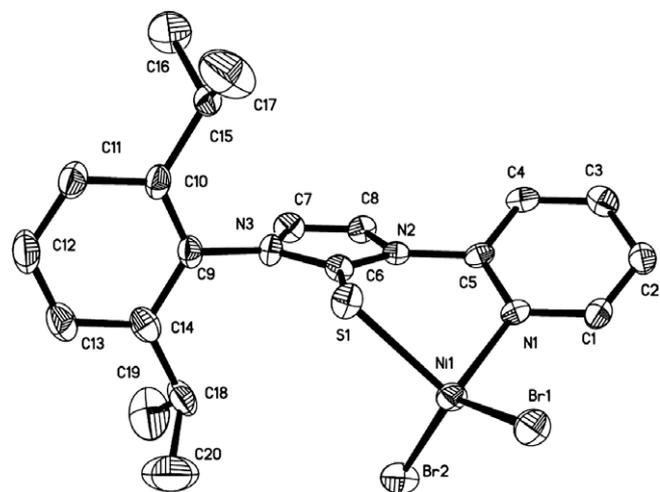
Fig. 1. Crystal structure of **2b**. For clarity, the hydrogen atoms are omitted. The ellipsoids are drawn at 30% probability level. Selected bond length (Å) and angles (°): Ni(1)–N(1), 2.008(8); Ni(1)–S(1), 2.282(3); Ni(1)–Br(1), 2.337(2); Ni(1)–Br(2), 2.342(3); S(1)–C(6) 1.690(9); N(1)–Ni(1)–S(1), 94.0(2); Br(1)–Ni(1)–Br(2), 133.80(8); N(1)–Ni(1)–Br(1), 107.0(2); S(1)–Ni(1)–Br(1), 103.51(9); N(1)–Ni(1)–Br(2), 103.1(2); S(1)–Ni(1)–Br(2), 108.47(9); C(5)–N(1)–Ni(1), 122.8(7); C(6)–S(1)–Ni(1), 94.1(4); C(6)–N(2)–C(5), 126.2(8); C(10)–C(9)–N(3), 118.6(9); C(14)–C(9)–N(3), 118.8(10).

molecular weight polyethylene [1]. The nickel complexes **2a** and **2b** bearing bulkyl N-substituents possess potentially reactive sites susceptible to ethylene polymerization. However, unfortunately, after activation with MAO, the bulkier steric hindrance nickel complex **2b** with N-2,6-diisopropylphenyl substituent catalyzed ethylene to a few wax with low activity at atmosphere pressure, even under 7 bar of ethylene press only obtained a few high molecular weight PE, while the complex **2a** bearing N-ᵗbutyl substituent obtained a few wax under the same condition. The catalyst activity for ethylene transform to high molecular weight PE was lower than that of the pyridylimine nickel complexes [7] and α-diimine nickel catalysts [1]. The reasons may be that only one bulky arm side (imidazole N-substituent) resulted in the chain propagation was quite slow than chain transfer which different from the α-diimine nickel catalysts (two bulky arm sides) [1]. And also the pyridine ring and the imidazole ring were not positioned in a square, which caused the introduction of the steric bulk deviates the axial sites, may be responsible for the low activity for ethylene transform to high molecular weight PE [2].

After activation with MAO, the Ni complexes **2a–2b** exhibit high catalytic activity for norbornene polymerization. The norbornene polymerization results of the nickel complexes **2a** and **2b** are summarized in Table 2. The norbornene polymerization was typical addition-vinyl type through the FT-IR spectra and ^{1}H NMR and ^{13}C NMR spectra of the obtained PNB. In the FT-IR spectra (IR, KBr, cm^{-1}): 2947, 2869, 1474, 1453, 1375, 1294, 1258, 1222, 1190, 1148, 1107, 1039, 942, 893, 805), there are no absorptions at 1680–1620 cm^{-1}, especially around 960 and 735 cm^{-1}, assigned to the *trans* and *cis* form of double bonds, respectively, which are characteristic of the ROMP (ring-opening metathesis polymerization) structure of PNB [23]. ^{1}H NMR and ^{13}C NMR spectra confirmed the above conclusions. ^{1}H NMR spectra (^{1}H NMR: δ 0.9–2.7 ppm (m, maxima at 0.96, 1.36, 2.11, 2.50) show signals in the 0.9–3.0 ppm range, where no resonances are displayed at about 5.1 and 5.3 ppm in the ^{1}H NMR spectrum of the PNB, assigned to the *cis* and *trans* form of the double bonds, which generally indicates the presence of the ROMP structure [23]. The ^{13}C NMR spectrum shows the main four broad groups of resonances (^{13}C NMR (*o*-dichlorobenzene-d_4): δ = 28–52 ppm (m, maxima at 48.7, 39.4, 35.6, 31.8)), attributed to carbons 2 and 3, carbons 1 and 4, carbon 7, and carbons 5 and 6, respectively (Chart 1). These data indicate that the obtained PNB was an addition-type (2,3-linked) product, which was not 2-exo, 7′-syn linked norbornene polymer [42–43]. Their ^{13}C NMR spectra show that the PNB are *exo* enchained; the spectra do not exhibit resonances in the 20–24 ppm region [23]. Unfortunately, the broad, unresolved nature of the spectra (PNB is more stiff with hindered rotation than the ethene-norbornene copolymer) made it difficult to assign exact stereochemistry to the enchainment of norbornene in the polymers with absolute certainty [23–24,44–46]. All of the obtained PNB are soluble in chlorobenzene, *o*-dichlorobenzene and cyclohexane solvents, which indicate low stereoregularity [47]. Attempted to determine the
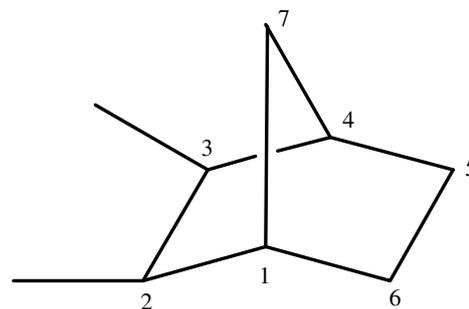

Chart 1.

glass transition temperature (T_g) of PNB failed, and the DSC studies did not give an endothermic signal upon heating to the decomposition temperature (above 450 °C).

The complex **2a** (3.56×10^7 gPNBmol^{-1} Nih^{-1}) bearing N-ᵗbutyl substituent exhibited higher activity than that of **2b** (3.14×10^7 gPNBmol^{-1}Nih^{-1}) containing N-2,6-diisopropylphenyl substituent under the same conditions (Entry 1 and 2, Table 2). The reason may be that norbornene is a sterically encumbered monomer, and it need more sterically open nature [38,48]. Although these Ni complexes **2a–2b** exhibited a little lower activity than the nickel complexes bearing N-substituents imidazole-2-thione ligands (1.36×10^8 gPNBmol^{-1}Nih^{-1}) [38], they are as highly active as nickel complexes bearing [N,O] and [N,N] ligands [21–22,25–27,29–32] and show a very higher activity polymerization than other transition metal catalysts [12–20,23–24,28,33–37]. The amount of the co-catalyst MAO affects obviously the activity and molecular weight of the PNB obtained by the complex **2a** (Entry 3–5, Table 2). When MAO/Ni = 500, there is almost no polymer. The catalytic activity sharply increases from 2.12×10^7 to 3.56×10^7 gPNBmol^{-1}Nih^{-1} when MAO/Ni increases from 1000/1 to 2000/1. In contrast, the viscosity-average molecular weight (M_v) of the polymer decreases from 6.76×10^5 to 5.91×10^5 gmol^{-1} with the increase in the molar ratio of MAO to **2a** due to the chain transfer to MAO [44]. When the amount of the MAO continues increase, the activity increases a little (Entry 5, Table 2). The temperature also influences the catalytic activity of **2a** and the molecular weights of the PNB. As shown in Table 2, with the increase the polymerization temperature from 0 °C to 50 °C, the activity increase from 0.98×10^7 to 3.72×10^7 gPNBmol^{-1}Nih^{-1}. However, when the temperature increases to 80 °C, the nickel complex displayed no activation which may be the complex decomposes at high temperature [38].

3. Conclusions

In conclusion, the nickel complexes bearing hard–soft nitrogen–sulfur donor ligands 1-pyridyl-(3-substituedimidazole-2-thione)

Table 2
Results of norbornene polymerization^a initiated by nickel catalyst **2a** and **2b**.

Entry	Catalyst	MAO/Ni	T (°C)	Yield (g)	Activity (10^7 gPNBmol^{-1}Nih^{-1})	M_v (10^5 gmol^{-1})
1	**2a**	2000	27	1.78	3.56	5.91
2	**2b**	2000	27	1.57	3.14	4.82
3	**2a**	500	27	Trace	–	–
4	**2a**	1000	27	1.06	2.12	6.76
5	**2a**	3000	27	1.81	3.62	4.35
6	**2a**	2000	0	0.49	0.98	6.52
7	**2a**	2000	50	1.86	3.72	3.17
8	**2a**	2000	80	Trace	–	–

^{a} *Polymerization conditions*: [Ni] = 0.2 μmol, [NB] = 3.76 g; time = 15 min; V_{total} = 15 mL; solvent: chlorobenzene.

exhibit high activities for norbornene addition polymerization, although show poor activity for ethylene polymerization to produce high molecular weight PE.

4. Experimental

4.1. General

All experiments and manipulations were carried out under argon using standard Schlenk techniques. All solvents were purified by standard procedures. NB was purchased from Alfa Aesar and purified by distillation over sodium. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. Other chemicals were analytical grade and used as received. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer. ^{1}H NMR spectra were obtained using Bruker DMX-400 spectrophotometer in CDCl$_3$, CD$_3$CN for complexes and o-dichlorobenzene-d_4 solution for PNB using TMS as an internal standard. N-^{t}butyl-N′-2-pyridylimidazolium bromide and N-2,6-diisopropylphenyl-N′-2-pyridylimidazolium bromide were synthesized according to the public literature [49]. The intrinsic viscosity [η] was measured in chlorobenzene at 25 °C using an Ubbelohde viscometer. Viscosity average molecular weight (M_v) values of polymer were calculated by the following equation [50]: $[\eta] = 5.97 \times 10^{-4} M_v^{0.56}$.

4.2. Synthesis of ligands (1a–1b)

4.2.1. 1-Pyridyl-(3-^{t}butylimidazole-2-thione) (1a)

To a solution of N-^{t}butyl-N′-2-pyridylimidazolium bromide (2.62 mmol) in THF (50 ml) and potassium tert-butoxide (3.0 mmol) was added at r.t. The mixture was stirred for 10 min and then sulphur (3.0 mmol) was added. After 12 h the solution was filtered and the solvent was removed to give a pure product 1a which was flash chromatography (CH$_2$Cl$_2$). (0.46 g, 75% yield). Anal. Calc. for C$_{12}$H$_{15}$N$_3$S: C, 61.77; H, 6.48; N, 18.01. Found: C, 61.75; H, 6.47; N, 18.04%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 1.87 (s, CH$_3$, 9H), 6.98 (d, J = 2.92, 1H, H4-Im), 7.36 (d, J = 2.92, 1H, H5-Im), 7.28 (m, 1H, H5-Py), 7.86 (t, 1H, H3-Py), 8.51 (m, 1H, H4-Py), 8.68 (d, J = 8.32, 1 H, H6-Py). ^{13}C NMR (CDCl$_3$, ppm): 28.2 (CH$_3$), 59.8 (^{t}C), 115.3 (C5-Im), 115.8 (C3-Py), 120.6 (C4-Im), 122.7 (C5-Py), 137.4 (C4-Py), 147.2 (C2-Py), 148.5 (C6-Py), 164.6 (C2-Im). IR (KBr cm^{-1}): 1158 (C=S).

4.2.2. 1-Pyridyl-(3-(2,6-diisopropylphenylimidazole)-2-thione) (1b)

The ligand 1b was prepared by similar procedures of ligand 1a using N-2,6-diisopropylphenyl-N′-2-pyridylimidazolium bromide. (0.65 g, 74% yield). Anal. Calc. for C$_{20}$H$_{23}$N$_3$S: C, 71.18; H, 6.87; N, 12.45. Found: C, 71.15; H, 6.89; N, 12.46%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 1.13 (d, J = 6.88, 6H, CH$_3$), 1.28 (d, J = 6.88, 6H, CH$_3$), 2.65(m, 2H, CH), 6.77 (d, J = 2.72, 1H, H4-Im), 7.29–7.31 (m, 3H, Ph), 7.47 (t, 1H, H5-Py), 7.85 (d, J = 2.72, 1H, H5-Im), 7.89 (m, 1H, H2-Py), 8.53 (m, 1H, H4-Py), 9.21 (d, J = 8.28, 1H, H6-Py). ^{13}C NMR (CDCl$_3$, ppm): 23.5 (CH$_3$), 28.8 (CH), 116.5 (C5-Im), 118.2 (C3-Py), 119.2 (C4-Im), 122.5 (C5-Py), 124.4 (C3-Ph), 130.3 (C4-Ph), 133.3 (C1-Ph), 138.0 (C4-Py), 146.6 (C2-Ph), 148.3 (C2-Py), 150.5 (C6-Py), 164.4 (C2-Im). IR (KBr cm^{-1}): 1178 (C=S).

4.3. Synthesis of complexes (2a–2b)

4.3.1. (1-Pyridyl-(3-^{t}butylimidazole-2-thione))NiBr$_2$ (2a)

Ligand 1a (1.0 mmol) was dissolved in CH$_2$Cl$_2$ (10 ml) and NiBr$_2$(DME) (1.0 mmol) was added the colorless solution. The reaction mixture was stirred at room temperature for 24 h which resulting in the formation of a green suspension. The green product

2a was obtained by filtration and washed twice with 10 mL of Et$_2$O and dried in vacuo. (0.35 g, 78% yield), Anal. Calc. for C$_{12}$H$_{15}$N$_3$SNiBr$_2$: C, 31.90; H, 3.35; N, 9.30. Found: C, 31.88; H, 3.34; N, 9.32%. IR (KBr cm^{-1}): 1156 (C=S).

4.3.2. (1-Pyridyl-((3-(2,6-diisopropylphenylimidazole))-2-thione)) NiBr$_2$ (2b)

The complex 2b was prepared by similar procedures of complex 2a using 1-pyridyl-(3-(2,6-diisopropylphenylimidazole))-2-thione. (0.42 g, 76% yield), Anal. Calc. For C$_{20}$H$_{23}$N$_3$SNiBr$_2$: C, 43.21; H, 4.17; N, 7.56. Found: C, 43.24; H, 4.19; N, 7.54%. IR (KBr cm^{-1}): 1154 (C=S).

4.4. Ethylene polymerization

The precatalyst was dissolved in toluene and MAO (10 wt% in toluene) added to the solution. The flamedried Schlenk flask (or stainless steel polymerization autoclave) was placed in a water bath and purged with ethylene, and the contents were magnetically stirred and maintained under 1 bar ethylene (or 7 bar ethylene press) for 1 h. The polymerization was terminated by the addition of 10% (by mass) acidified ethano1. The solid PE was recovered by filtration, washed with ethanol and dried under vacuum at 70 °C overnight.

4.5. Norbornene polymerization

In a typical procedure for norbornene polymerization, precatalyst nickel complex in chlorobenzene was added into a polymerization bottle (50 mL) with a stirrer under nitrogen atmosphere. Then MAO was charged into the polymerization system via syringe. At last the norbornene in chlorobenzene was added the polymerization system the reaction was started. After designated time, the acidic ethanol ($V_{ethanol}$:$V_{concd.HCl}$ = 10:1) was added to terminated the reaction. The PNB was isolated by filtration, washed with ethanol and dried at 80 °C for 48 h under vacuum. For all polymerization procedures, the total reaction volume was 15.0 mL, which can be achieved by the variation of the amount of chlorobenzene when necessary. Spectra of the obtained polynorbornenes: IR (KBr pellet, ν(cm^{-1})): 2947, 2869, 1474, 1453, 1375, 1294, 1258, 1222, 1190, 1148, 1107, 1039, 942, 893, 805. ^{1}H NMR (o-dichlorobenzene-d_4): δ = 0.9–2.7 ppm (m, maxima at 0.96, 1.36, 2.11, 2.50). ^{13}C NMR (o-dichlorobenzene-d_4): δ = 28–52 ppm (m, maxima at 31.8, 35.6, 39.4, 48.7).

4.6. X-ray crystallography

Diffraction data of complexes 2b were collected at room temperature on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [51], absorption corrections were applied to the data. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions.

Supplementary material

CCDC 699351 contains the supplementary crystallographic data for 2b. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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