



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-substitutedimidazole-2-thione) ligands were synthesized by the reaction of the corresponding ligands with NiBr₂(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

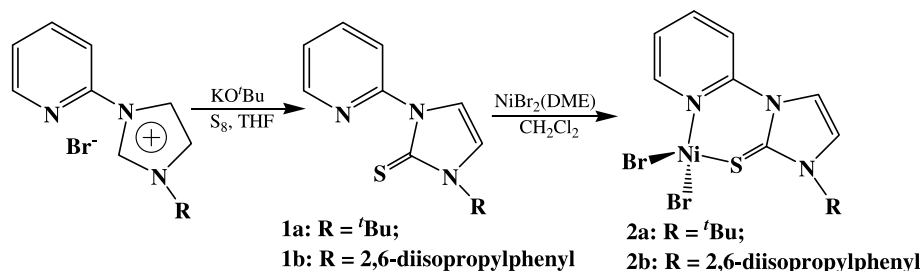
now, there was no report of the nickel catalyst bearing [NS] ligands for olefin polymerization [2–6]. Herein, we report the synthesis and characterization of the nickel complexes with new hard-soft nitrogen-sulfur donor ligands 1-pyridyl-(3-*t*-butylimidazole-2-thione) (**1a**) and 1-pyridyl-(3-(2,6-diisopropylphenylimidazole)-2-thione) (**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 K₂CO₃ 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 CH₂Cl₂, CHCl₃ and THF. The ligands **1a** and **1b** were characterized by ¹H NMR, ¹³C NMR, IR spectroscopy and elemental analysis. The formation of **1a** is conformed by the appearance of the ¹H signals at 1.87, 6.98 and 7.36 ppm, which can be assigned to the methyl, two

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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 confirmed by the resonances at 1.13, 1.28, 6.77, 7.85 ppm in the ^1H 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 $\text{NiBr}_2(\text{DME})$ 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 . ^1H 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 $\text{CH}_3\text{CN}/\text{ether}$ (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 angle 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	$\text{C}_{20}\text{H}_{23}\text{N}_3\text{S}\text{NiBr}_2$
Formula weight	556.00
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	8.041(7)
<i>b</i> (Å)	8.796(7)
<i>c</i> (Å)	16.330(14)
α (°)	77.158(12)
β (°)	85.275(10)
γ (°)	80.194(10)
<i>V</i> (Å ³)	1108.4(16)
<i>Z</i>	2
<i>D</i> _{calcd.} (mg m ⁻³)	1.666
Crystal size (mm ³)	0.12 × 0.10 × 0.08
μ (mm ⁻¹)	4.584
<i>F</i> (000)	556
θ_{max} , θ_{min} (°)	27.41, 2.40
Index range	
<i>h</i>	–10 → 9
<i>k</i>	–11 → 8
<i>l</i>	–19 → 20
<i>R</i> _(int)	0.0469
No. of independent reflections	4546
No. of observed reflections	3071
No. of variables	160
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0842, <i>wR</i> ₂ = 0.2497
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1084, <i>wR</i> ₂ = 0.2589
Goodness-of-fit (GOF)	1.078
Largest difference peak ^a (hole) (e Å ⁻³)	1.786 (–0.881)
Δ / σ	0.000, 0.000

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad RW = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum w(F_o^2)} \right\}^{1/2}$$

^a Largest peak(hole) in difference Fourier map.

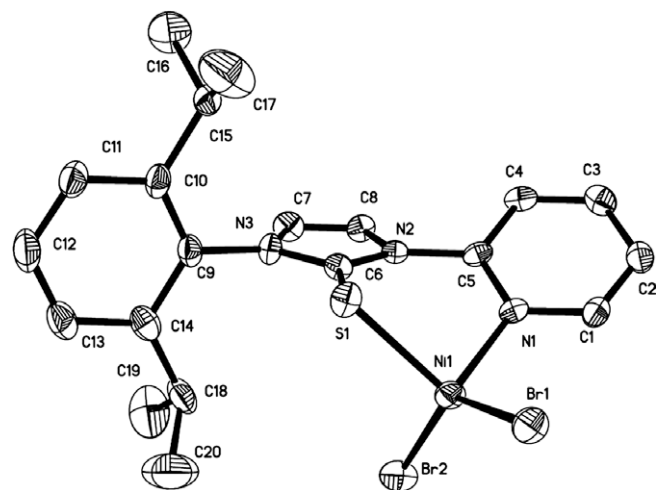


Fig. 1. Crystal structure of **2b**. For clarity, the hydrogen atoms are omitted. The ellipsoids are drawn at 30% probability level. Selected bond length (Å) and angles (°): Ni(1)–N(1), 2.008(8); Ni(1)–S(1), 2.282(3); Ni(1)–Br(1), 2.337(2); Ni(1)–Br(2), 2.342(3); S(1)–C(6), 1.690(9); N(1)–Ni(1)–S(1), 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).

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