

## Highly Active Nickel Complexes Containing Functionalized Bipyridine Ligands for Norbornene Polymerization

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Polynorbornenes have drawn much attention due to their unique physical properties such as high glass transition temperature, optical transparency, low dielectric properties and birefringence.<sup>1</sup>

Due to higher tolerance toward oxygen functionalities in the monomer and the polymer than early transition metals, recent research activities have focused on the development of late transition metal catalysts with enhanced performance.<sup>2</sup> Reported catalytic systems are mainly based on Ni and Pd complexes containing various bidentate P<sup>^</sup>O, N<sup>^</sup>O, P<sup>^</sup>P and N<sup>^</sup>N ligands with bulky aryl substituents. The complexes with tri or higher dentate ligands are generally known to be inactive or less active for olefin polymerizations than ones with bidentate ligands.<sup>3</sup>

Bipyridines, especially 2,2'-bipyridines utilized as a metal chelating ligand due to its robust redox stability and ease of functionalization are extensively reviewed.<sup>4</sup>

For the potentially tetradentate bipyridine derivatives, the following advantages are expected; higher stability of starting metal complexes and polymerization intermediates due to increased chelate effect, conservation of symmetry around the active center to produce stereospecific  $\alpha$ -olefin polymer, and blocking or retardation of  $\beta$ -hydrogen elimination to produce high molecular weight polymers. Therefore, we could expect the new type of complexes with high activity and stability.

Herein we report the novel and well-characterized nickel complexes containing potentially tetradentate bipyridine ligands, which are highly active towards norbornene polymerization.

6,6'-bis(alkoxymethyl)-2,2'-bipyridines were prepared with moderate yields by the substitution reaction of mesyl compounds with alkoxides<sup>5</sup> (Scheme 1).

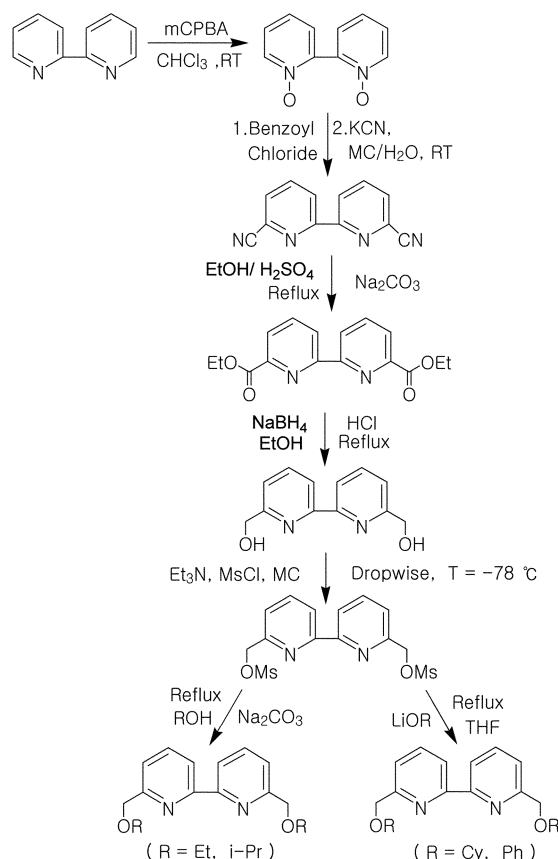
Ni(DME)Br<sub>2</sub> (DME = dimethoxyethane) has been generally used as a starting material.<sup>6</sup> However, due to higher solubility of NiCl<sub>2</sub> than the products, new nickel complexes had been conveniently prepared by the simple reaction between NiCl<sub>2</sub> and functionalized bipyridine ligands refluxed in EtOH with moderate yields (Scheme 2).<sup>7</sup> Unfortunately, due to paramagnetic character, these can be characterized only by elemental analysis and X-ray crystallography. Ni(bpy)Cl<sub>2</sub> was prepared for the comparison.<sup>8</sup>

Contrary to our expectation, the structure of complex **3** can be described as a 5-coordinate, distorted trigonal bipyramid, where one of alkoxy oxygen atom coordinates to

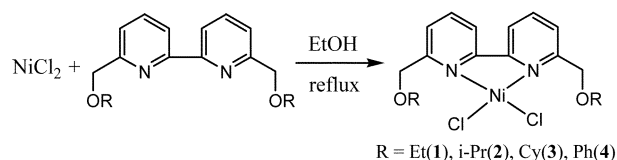
metal (Figure 1). Bipyridine rings are a little twisted by 5.9(4)°. Detailed bond lengths and bond angles are listed in the supporting information.

These complexes are very active in norbornene polymerization on activation with MMAO (modified methylaluminoxane)<sup>9</sup> and preliminary results are summarized in Figure 2.

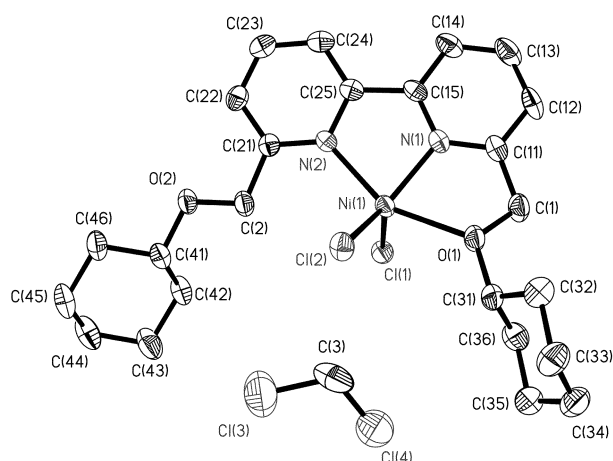
Activity increases with bulkiness of the substituent,



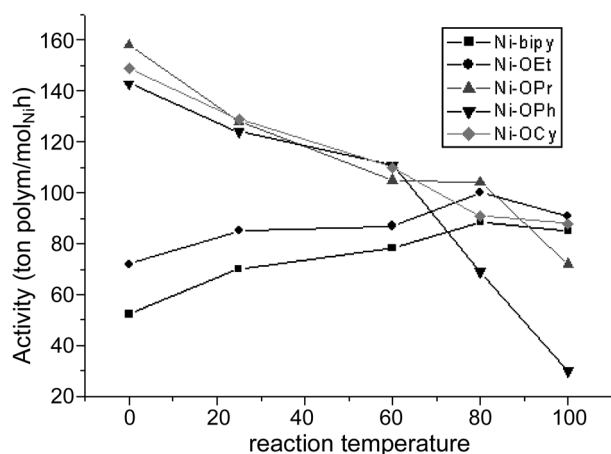
**Scheme 1.** Ligand Synthesis.



**Scheme 2.** Complex Synthesis.



**Figure 1.** ORTEP drawing of complex **3**.



**Figure 2.** The Effects of temperature and substituents on the catalytic activity catalyst:  $0.23 \times 10^{-3}$  mmol, solvent : chlorobenzene 15 mL, reaction time : 2 min, monomer: 2 g ([monomer]/[cat.] = 100,000), MAO: 1,000eq.

especially at lower temperatures but the differences are not great. Since these complexes have 5-coordinate structure, the substituents cannot be very efficient to protect the active sites and termination reaction. Thermal stability was monitored by checking the activities in higher temperatures and it seems to be improved, but the improvement is not great over 80 °C. Even worse activities are observed in cases of *i*-Pr and Ph derivatives in this range, while Et derivatives showed almost same behavior as Ni(bpy)Cl<sub>2</sub>. It appears that increased thermal motion of bulky substituents would induce lower thermal stability.

In conclusion, we have prepared a series of new nickel complexes with functionalized bipyridine ligands and these complexes are found to be highly active catalysts for norbornene polymerization on activation with MAO. New catalysts showed higher activities than Ni(bpy)Cl<sub>2</sub> but complicated thermal properties were resulted in depending on the bulkiness of the substituents.

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- General Procedure: 0.649 mmol of 6,6'-bis(alkoxymethyl) 2,2'-bipyridine (detailed data will be published elsewhere) and 0.084 g (0.649 mmol) of NiCl<sub>2</sub> were suspended in 60 mL of EtOH and refluxed for 12 h. The solvent was removed under reduced pressure. The pale green solid was obtained by washing with cold 10 mL of EtOH and washed with 10 mL of ether and recrystallized in the mixture of methylene and n-hexane. Yield = (**1**, 50%; **2**, 55%; **3**, 40%; **4**, 75%) Anal. **1** (Found: C, 47.63; H, 5.39; N, 7.15%. Required for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> NiCl<sub>2</sub>: C, 47.81; H, 5.02; N, 6.97%). **2** (Found: C, 49.82; H, 5.66; N, 6.26%. Required for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>NiCl<sub>2</sub>: C, 50.28; H, 5.63; N, 6.51%). **3** (Found: C, 56.25; H, 6.45; N, 5.34%. Required for C<sub>24</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub>NiCl<sub>2</sub>: C, 56.51; H, 6.32; N, 5.49%). **4** (Found: C, 57.38; H, 4.55; N, 6.04%. Required for C<sub>24</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>NiCl<sub>2</sub>: C, 57.88; H, 4.05; N, 5.62%).
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- In an inert (N<sub>2</sub>) atmosphere, MMAO (catalyst : cocatalyst = 1 : 1000) was placed into a small vial. To this was added approximately 5 mL of solvent, and the mixture gently shaken to dissolve the solids. This solution was then added to 0.001 g of catalyst, 100000 equivalent of norbornene dissolved in approximately 10 mL of solvent in a vial containing a stirring bar. The solution was stirred rapidly for about 2 min. The product was quenched by adding acidified methanol. The solid was washed with methanol and dried under vacuum.