



# Synthesis, characterization and ethylene oligomerization behavior of *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylamino nickel(II) dichlorides

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## ARTICLE INFO

### Article history:

Received 2 October 2011  
Received in revised form 7 December 2011  
Accepted 8 December 2011  
Available online 16 December 2011

### Keywords:

*N*-(2-Alkyl-5,6,7-trihydroquinolin-8-ylidene)arylamine  
Nickel(II) complex  
Ethylene oligomerization

## ABSTRACT

A series of *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylamino nickel(II) dichloride complexes were synthesized in a one-pot reaction with nickel dichloride. All nickel complexes were characterized by elemental and spectroscopic analysis. The molecular structures of representative nickel complexes, as determined by the single crystal X-ray diffraction, are reported. All nickel complexes, when treated with ethylaluminum sesquichloride (Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>), showed high activities (up to  $1.1 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup>) for ethylene oligomerization, with good thermal stability at 80 °C at 10 atm ethylene. The influence of the reaction parameters on the catalytic behavior was investigated for these nickel-based systems, including variation of Al/Ni molar ratio and reaction temperature.

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## 1. Introduction

$\alpha$ -Olefins originally manufactured by the Ziegler (Alfen) process are key intermediates for the synthesis of a wide range of chemical products. Over the past few decades, the preparation of ethylene oligomers catalyzed by transition metal complexes has undergone significant development, especially for those systems based on nickel. By the end of the 1970s, nickel complexes had been developed as catalysts for ethylene oligomerization by Keim et al. [1], which, in the 1980s, was industrialized in the form of the Shell Higher Olefin Process (SHOP), and is now a major process for the production of linear  $\alpha$ -olefins via the oligomerization of ethylene [2]. In the 1990s, Brookhart et al. found that cationic diimino-nickel complexes performed with very good activity during ethylene polymerization and oligomerization [3–4], and this encouraged further extensive investigation into new pre-catalysts of other late-transition metal complexes [5]. Moreover, to improve catalyst performance, efforts were paid to both the modification of the original ligand set as well as exploration of new ligand types capable of producing high activity nickel catalysts, and numerous nickel complexes bearing bidentate ligands such as N<sup>N</sup> [6–13], N<sup>O</sup> [14–20], P<sup>N</sup> [21–25], P<sup>O</sup> [26–29] and tridentate ligands such as N<sup>P</sup>N [30–32], N<sup>N</sup>O [33–35], P<sup>N</sup>N [30,36,37], and N<sup>N</sup>N [38–43], have been prepared. A num-

ber of recent review articles have covered the progress of nickel complexes as catalysts for ethylene reactivity [44–47].

Within the *N,N*-bidentate Ni(II) family of complexes, the 2-iminopyridinyl nickel halides showed good activities for both ethylene oligomerization and polymerization [48–51]. Previous work in our group has reported a fused-cycloalkanylpyridine for such 2-iminopyridine ligation, viz *N*-(2-chloro-/2-phenyl-5,6,7-trihydroquinolin-8-ylidene)arylamino nickel dichlorides [52], which showed high activity in ethylene oligomerization. The nickel pre-catalysts bearing *N*-(5,6,7-trihydroquinolin-8-ylidene)arylamines, which have no substituent at the ortho-position of the 5,6,7-trihydroquinoline, however, performed high activities in ethylene polymerization [53]; moreover, their nickel analogs solely showed ethylene polymerization with verified substituents on the aryl groups within of *N*-(5,6,7-trihydroquinolin-8-ylidene)arylamines [54]. In comparison with the results obtained by nickel pre-catalysts ligated with *N*-(2-chloro- or 2-phenyl-5,6,7-trihydroquinolin-8-ylidene)arylamines, the scope of the nickel complexes bearing *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylamines are necessarily investigated. Therefore, 2-alkyl-5,6,7-trihydroquinolin-8-ones are synthesized, reacted with various anilines and nickel dihalides to form the corresponding *N*-(2-alkyl-5,6,7-trihydroquinolin-8-ylidene)arylamino nickel dichlorides. The molecular structures of representative complexes have been determined by single-crystal X-ray crystallography. Upon activation with ethylaluminum sesquichloride (Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, EASC), all the nickel pre-catalysts showed good activity towards ethylene oligomerization. The influence of the reaction parameters on the catalytic performance has been investigated in detail.

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## 2. Results and discussion

### 2.1. Synthesis and characterization

Initially, the preparation of the nickel compounds was attempted by first synthesizing the ligand set (2-methyl/isopropyl-5,6,7-trihydroquinolin-8-one plus aniline) followed by subsequent reaction with the nickel salts; however, this resulted in two compounds, namely cyclic 4,5-dihydroquinolin-8-arylamines, which were very unstable. To conquer this problem, a one-pot process involving 2-methyl- or 2-isopropyl-5,6,7-trihydroquinolin-8-one and the corresponding aniline together with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in acetic acid, was undertaken to synthesize the target nickel complexes (Scheme 1).

All nickel complexes, which were formed in good yield, were characterized by FT-IR spectroscopy and by elemental analysis. In the FT-IR spectra, there is a strong band in the range 1550–1600  $\text{cm}^{-1}$ , which can be ascribed to the stretching vibration of C=N. The molecular structures of complexes **Ni1**, **Ni4** and **Ni10** were confirmed by single crystal X-ray crystallography.

### 2.2. X-ray crystallographic studies

Single crystals of the nickel complexes **Ni1** and **Ni4** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into methanol solution, while crystals of the complex **Ni10** were obtained by diffusion of diethyl ether into dichloromethane solution. The ORTEP diagrams of the molecular structures are shown in Figs. 1–3. The selected bond lengths and angles are listed in Table 1.

The five-coordinate complexes **Ni1** and **Ni4** are best described as distorted trigonal bipyramidal geometries at nickel, with the fifth coordination site occupied by the solvent (methanol) molecule.

Complex **Ni10** is a binuclear structure with centrosymmetric bridging Cl atoms, and the coordination geometry around the nickel center can again be described as a distorted trigonal bipyramidal. The ligands with a bulky *i*Pr group occupy more space around nickel, which for **Ni10** creates slight differences in the bond lengths and bond angles of N1–Ni–N2 from those of **Ni1** and **Ni4**, and larger bond angles for N2–Ni–Cl2, C11–Ni–Cl2.

### 2.3. Ethylene oligomerization

In order to find the most suitable co-catalyst, pre-catalyst **Ni3** was screened using different co-catalysts such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminum chloride ( $\text{AlEt}_2\text{Cl}$ ) and ethylaluminum sesquichloride ( $\text{Et}_3\text{Al}_2\text{Cl}_3$ , EASC) at 40 °C (only moderate activity was observed at 20 °C) under 10 atm ethylene (Table 2). In general, good observed activities were achieved on varying the co-catalysts, with the exception of the very low activity observed on combination with  $\text{AlEt}_2\text{Cl}$ . However, the benefit of using EASC was evident both in terms of

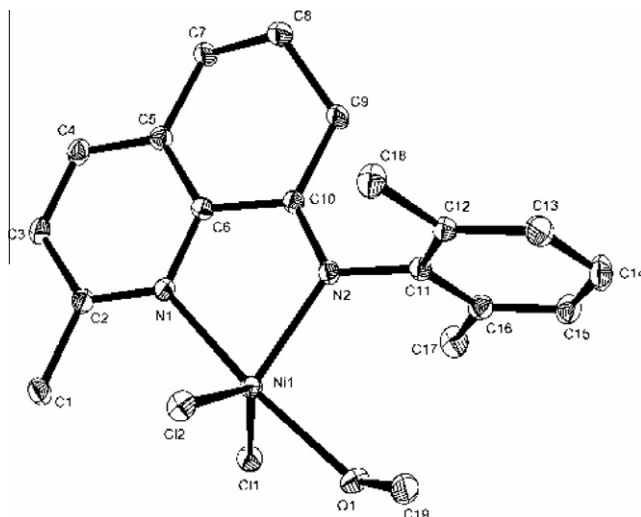


Fig. 1. ORTEP drawing of complex **Ni1** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

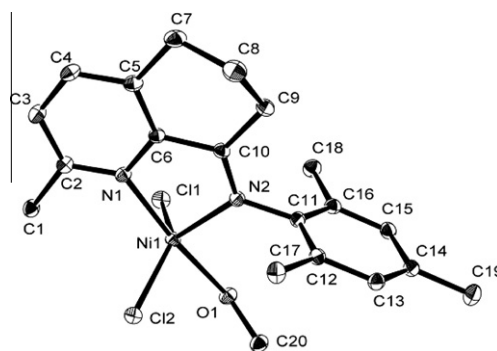


Fig. 2. ORTEP drawing of complex **Ni4** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

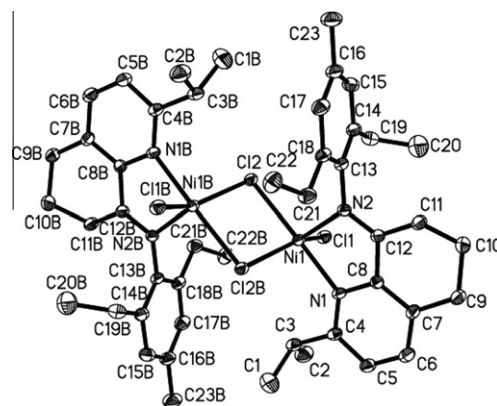
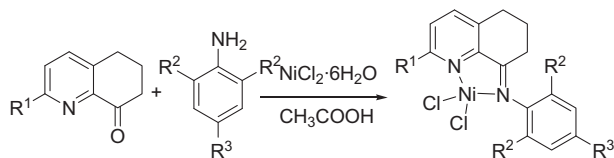


Fig. 3. ORTEP drawing of complex **Ni10** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

catalytic activity and economic considerations, thus EASC was chosen as the co-catalyst for further investigations.

To evaluate the effects of the reaction conditions on the catalytic performance, detailed investigations with complex **Ni3** were carried out using different Al/Ni ratios and reaction temperatures; results are summarized in Table 3.

For the **Ni3**/EASC system, on changing of the Al/Ni molar ratio from 100 to 400 at 40 °C, the highest activity ( $1.79 \times 10^5 \text{ g mol}^{-1} (\text{Ni})\text{h}^{-1}$ ) was achieved with a Al/Ni molar ratio of 200. Furthermore,



	<b>Ni1</b>	<b>Ni2</b>	<b>Ni3</b>	<b>Ni4</b>	<b>Ni5</b>	<b>Ni6</b>	<b>Ni7</b>	<b>Ni8</b>	<b>Ni9</b>	<b>Ni10</b>
R <sup>1</sup>	Me	Me	Me	Me	Me	<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr
R <sup>2</sup>	Me	Et	<i>i</i> Pr	Me	Et	Me	Et	<i>i</i> Pr	Me	Et
R <sup>3</sup>	H	H	H	Me	Me	H	H	H	Me	Me

Scheme 1. Synthetic procedure of nickel complexes.

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