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Ethylene Oligomerization Promoted by Nickel Complexes with 8-Iminoquinoline Derivatives

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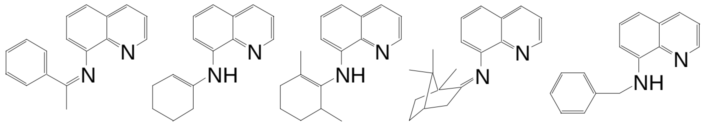
Abstract: A series of 8-iminoquinoline derivatives nickel complexes were synthesized to proceed high activity in ethylene oligomerization.

Keywords: Nickel Complex, iminoquinoline, ethylene oligomerization, homogeneous catalysis.

In the past decades, the great progress has been witnessed in chemical industry, and chain olefins have played important roles in substantial technical interests of detergents, plastics, lubricants, oil additives and a variety of fine chemicals. Ethylene oligomerization is the fast developing process to get chain olefins. Shell Company did the pioneer pilot process work[1], which was based on the nickel complexes with remarkable activity and selectivity. The chelating ligands are considered to play an important role in their high activities. Therefore alternating chelating ligands have drawn much attention in promoting both polymerization and oligomerization of ethylene[2]. Looking the ligands carefully, it is not difficult to find out that conjugated systems are commonly presented between the chelating atoms. It has been realized that the conjugated system will be helpful for the electronic adaptation of withdrawing or donating electrons at the stages of the proceeding catalytic system in order to create the high active species. In single site componsent catalysis, catalytic property is generally relied on the synergic effects of its core metal and ligands. For such metal complexes to promote specific reaction, the activity and selectivity of catalytic system could be improved by modifying the ligands with the electronic configuration and stereo-robustness. The numerous imine type ligands are particularly developed and demonstrated their great potential usefulness in forming late transition-metal complexes for oligomerization and polymerization[3]. Even there are several papers considered for polymerization or oligomerization by complexes containing unsymmetrical ligands[4], the full unsymmetrical ligands screening is necessary and helpful in promoting the catalysts design for polymerization and oilgomerization. Moreover, the fundamental view of multi-bond formation will easily proceed on unsymmetrical catalytic species due to the induced olefin-in and product-out pathway. Herein 8-iminoquinoline derivatives have been synthesized and their nickel complexes are found to be high active in oligomerization of ethylene.

The 8-iminoquinoline derivatives were synthesized following classical condensation methods of ketones and primary amines[5]. According to the NMR data of 8-iminoquinoline derivatives, their structures were shown in **Scheme 1**. In case of cyclohexanone used as the starting substrate, the nitrogen-carbon double bonds were immigrated into cyclohexanyl ring due to the more stability of double bonds in the ring.

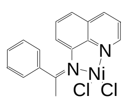
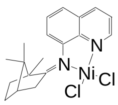
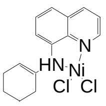
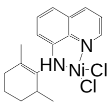
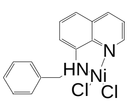
Scheme 1



The Schiff base, including the 8-aminoquinoline itself, and $NiCl_2 \cdot 6H_2O$ were stoichiometrically mixtured in 10 mL THF at room temperature under N_2 atmosphere, then stirred for 5 hours. The solvent was evaporated under vacuum, and the product nickel complex was washed with ether to give the yellow solid. According to the N-H stretch bands in IR spectrum, it was confirmed that the N-H was presented in their nickel complexes. Therefore (8-iminoquinoline derivatives) nickel dichlorides were the precatalysts for ethylene oligomerization.

Under ethylene atmosphere with normal pressure, 50mL of toluene was charged in the flask and stirring. When the reaction temperature was set up, cocatalyst methylalumoxane (MAO) with ratio of Ni/Al 1:2000 was added *via* syringe. After stirring for several minutes, the precatalyst nickel complex solved in dichloromethane was added to the flask *via* syringe. The oligomerization proceeded at 20°C for 20 minutes, the reaction was quenched with acidified ethanol. The products were analyzed by GC-MS for the distribution of olefins. The activities of the complexes for ethylene oligomerization were collected in the **Table 1**. It was noticed that high basity of the ligands showed lower activity for the catalysis, as well as the stereo effect is also considerable. The products are all chain olefins with 90% to 99% of C_8 and C_{10}. However, the alpha-olefins were only formed less than 40%. Further investigations are still being carried out for high activities, and especially for higher distribution of alpha-olefins.

Table 1 Ethylene Oligomerization

Precatalyst						
Activity g C_2H_4/(molNi· h)	1.2 x 10^7	5.0 x 10^5	7.0 x 10^4	1.0 x 10^5	6.5 x 10^5	3.0 x 10^4

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