

Ethylene Polymerization Promoted by Nickel Complexes¹

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Received July 11, 2005

Abstract—The nickel complexes are of special relevance to catalysis for ethylene oligomerization and polymerization. Beyond the famous commercial SHOP process for ethylene oligomerization, among recent progress of nickel catalysts, various nickel complexes containing different ligands such as the bidentate and tridentate ligands are of interest. In contrast to the importance of heterogeneous catalysis, the homogeneous catalyst is a small share for polyolefins, while the well-defined complexes affect the microstructure of the resultant polyolefin. The nickel catalysts often perform ethylene activations for inner olefins and the branched polyethylene with broad or bimodal molecular weight distribution. The catalytic behavior will be affected by adaptation of ligands coordinating around the nickel center. In addition, the auxiliary ligand Ph_3P can improve the catalytic activity by one order of magnitude, and its active center can be confirmed through isolating and characterizing the reliable intermediate.

DOI: 10.1134/S0023158406020194

The oligomerization and polymerization of ethylene are important processes to convert the basic feedstock into useful value-added products such as linear α -olefins, wax, and polyethylene. The late-transition-metal catalysts have long been established to produce dimers or low-molecular-weight oligomers by chain termination via β -hydride elimination [1–3]. The steric demand of bulky groups of ligands is understood to be important for the chain propagations for ethylene polymerization with the competition of β -hydride elimination. Ethylene oligomerization and polymerization by nickel complexes is particularly well developed on the basis of the commercialized SHOP process [4, 5]; moreover, the easily synthesized nickel catalysts showed various catalytic properties influenced by the characteristics of the attached ligands. In 1995, the pioneering work by Brookhart’s group on α -diimino nickel complexes (complex **1**, Fig. 1) for high-molecular-weight polyethylene broke the silence on late-transition-metal catalysts for polyolefins [6–10] and resulted in a remarkable increase in the number of academic publications and patents for polyolefins and oligomers obtained with Group VIII metal catalysts [11–13]. Various nickel complexes containing chelating ligands such as [O–P] [14, 15], [O–N] [16–19], [N–N] [20–30], [N–P] [31–36], [N–N–O] [20–30] and [N–N–N] [37–42] ligands have been extensively studied and observed for their unique properties. The nickel complexes usually show activities for both ethylene oligomerization and polymerization, and a considerable amount of inner olefins as well as branched polyethylene can be produced. There are numerous reviews focusing on the

various complexes as catalysts for oligomerization and polymerization; however, the insights of structural features of precursors and catalytic intermediates will give a train of thought for advanced catalysts. In this paper, we wish to summarize our primary results and understanding of nickel catalytic precursors and active intermediates for ethylene oligomerization or polymerization with the assistance of the cocatalyst methylaluminoxane (MAO), and their advantage and disadvantage for ethylene oligomerization and polymerization are also listed with future potentials in academic research and industrial applications.

[N–N] Bidentate Nickel Complexes

The pioneering work on diimine nickel complexes reported by Brookhart’s group was a milestone for late-transition-metal complexes as catalysts for ethylene polymerization [6–10], in which those diimine ligands are symmetrical. That leads to a question about unsymmetrical complexes as catalysts for ethylene activation; the asymmetrical microstructure of those complexes will be helpful for chain propagation in a catalytic system with absorbing ethylene on one side and giving products on another side. Driven by this consideration, the commercial chemical 8-iminoquinoline and its derivatives were investigated by our group. Fortunately, the nickel complexes (complex **2**) containing 8-iminoquinoline derivatives indeed showed positive results of considerable to good activities for ethylene oligomerization at ambient ethylene pressure, up to $1.2 \times 10^7 \text{ g (mol Ni)}^{-1} \text{ h}^{-1}$ [43]. In 1999, the unsymmetrical nickel complex **3** containing pyridinylimino ligand was reported by Laine’s group [44–46]. The conjugated systems between two coordi-

¹ The text was submitted by the authors in English.

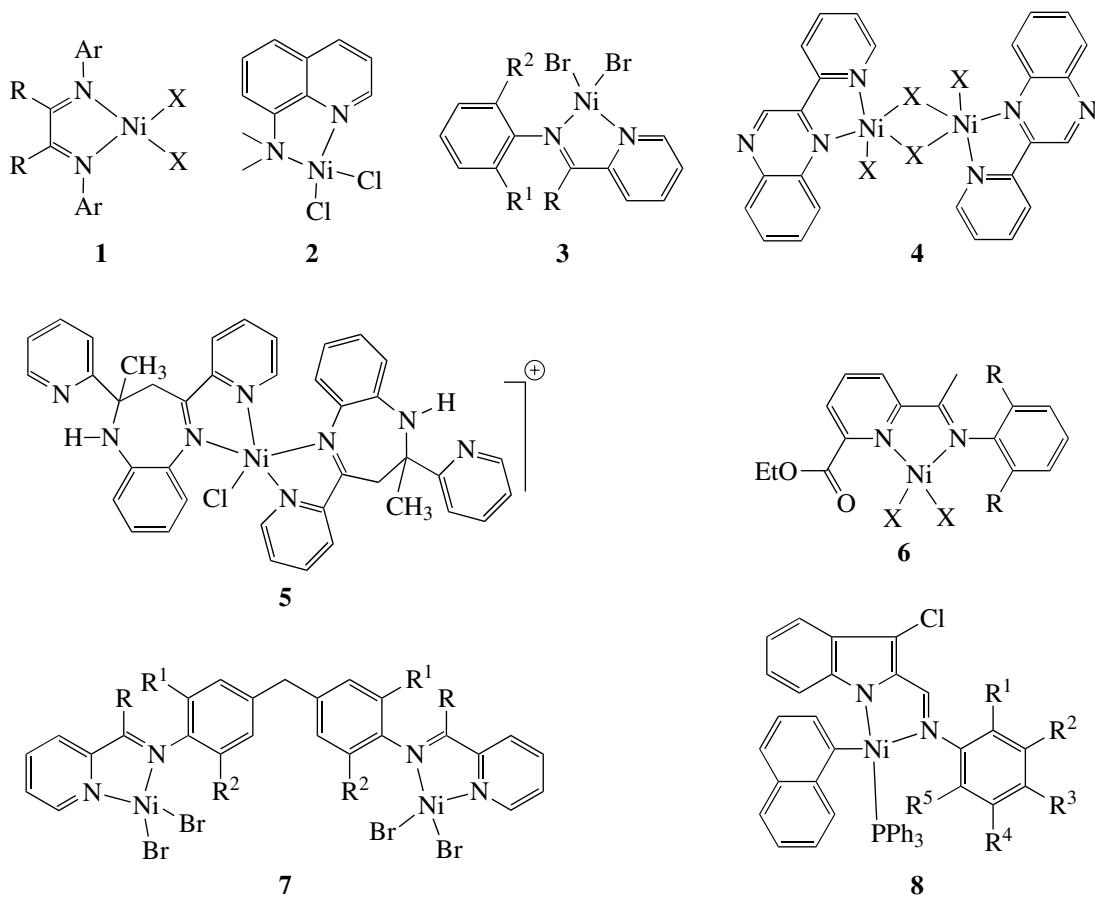


Fig. 1. [N–N] bidentate nickel complexes.

nated nitrogen atoms are different for ligands in **2** and **3**. Therefore, variations of bidentate ligands were pursued. The nickel complexes **4** showed ethylene oligomerization activity up to 7.1×10^5 g (mol Ni) $^{-1}$ h $^{-1}$ [47], and the nickel complexes **5** produced both oligomers from C4 to C10 and high branched polymers with bimodal molecular weight distributions [48]. Complex **6** also showed good activities for both oligomerization and polymerization of ethylene, and the ethylene oligomerization activity was significantly improved in the presence of PPh_3 as an auxiliary ligand [29]. For dinickel complex **7**, the activity for ethylene oligomerization was up to 3.3×10^5 g (mol Ni) $^{-1}$ h $^{-1}$, and it was up to 2.8×10^6 g (mol Ni) $^{-1}$ h $^{-1}$ for ethylene polymerization; the polymer obtained was branched polyethylene with bimodal molecular weight distributions [30]. Typical NMR spectra for the polyethylene from complex **7** were illustrated in Fig. 2. The neutral nickel complex **8** containing bidentate nitrogen ligands showed low activity for ethylene oligomerization without cocatalyst [49].

[N–P] Bidentate Nickel Complexes

Inspired by the SHOP process with **9** (Fig. 3) containing a ligand of phosphine [4–5], one came to an

interesting point with analogues of the same frame with coordinative atoms of nitrogen and phosphine to the 8-iminoquinoline ligand of **2**. However, although the desired ligand **10** was prepared, the expected complex **11** was not formed; instead, the six-coordinated complex **12** was isolated, in which the P(III) was oxidized into P(V) and oxygen coordinated to the nickel center [50]. Complex **12** showed no ethylene catalytic activity, which was ascribed to the fact that two leaving groups of halides are *trans*-form and there is no interaction between coordinated ethylenes on the nickel center for carbon–carbon bond formation. Therefore, it is necessary to design and synthesize a nickel complex with its two leaving groups in *cis*-form. The target complex **13** was finally synthesized [51]; it can oligomerize ethylene to afford oligomers of butenes and hexenes. However, the catalytic system of **13** showed no activation at 80°C with the potential of deactivating the active nickel site by reasons of the lower solubility of ethylene or unstable nickel complex at higher temperature. Therefore, the substituent methyl group was added through synthesis at the ortho position to nitrogen of quinoline in order to stabilize the nickel complex. Its dinickel complex **14** was obtained and characterized [51]. Indeed, such modification stabilized the nickel active

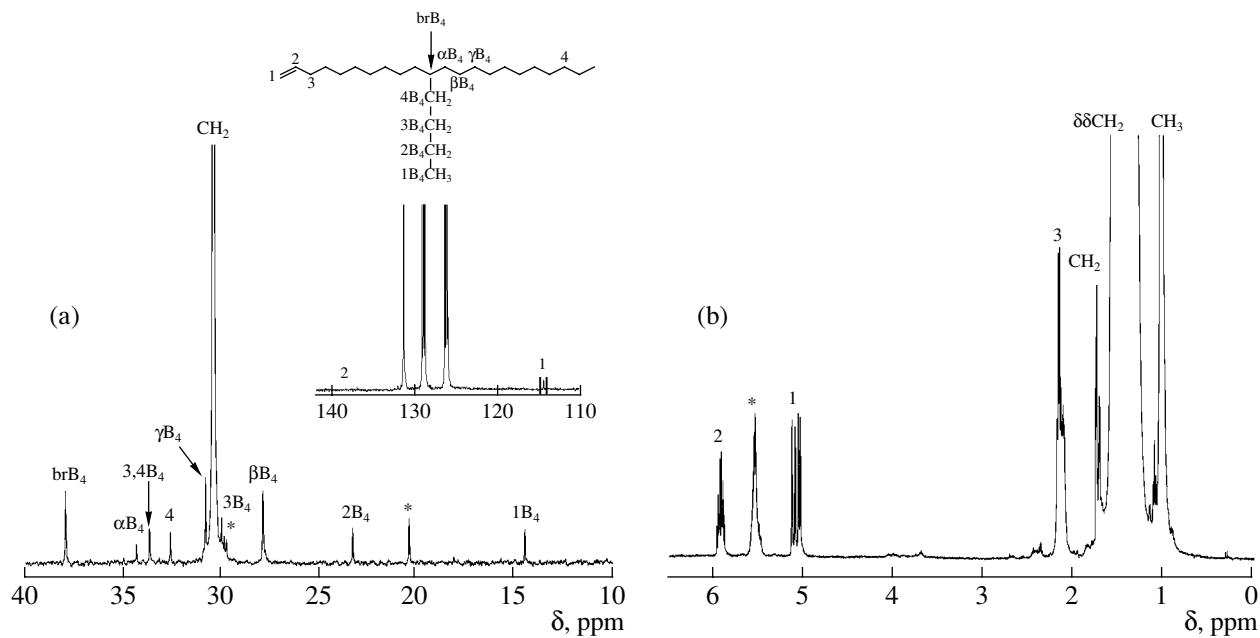


Fig. 2. NMR spectra of polyethylene obtained by complex **7**: (a) ^{13}C NMR; (b) ^1H NMR. Peaks marked with an asterisk were not assigned.

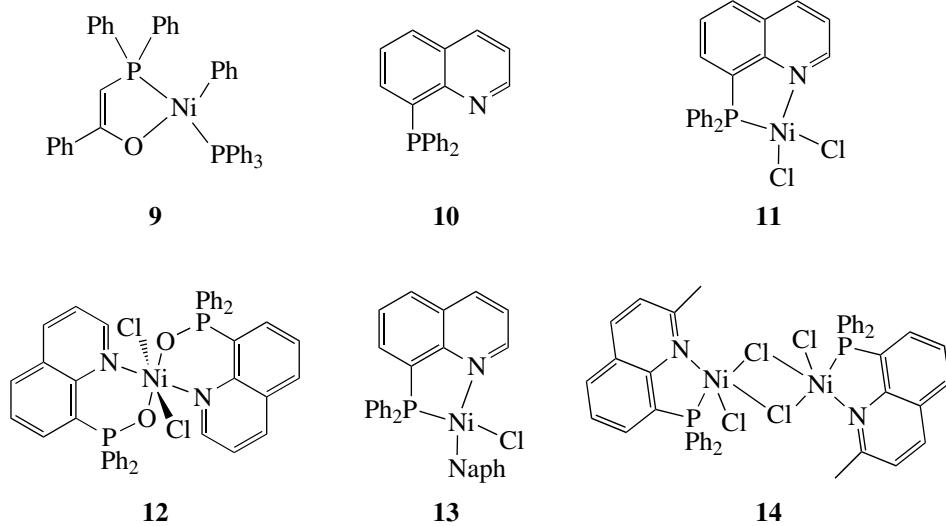


Fig. 3. Nickel complexes containing phosphine in the ligands.

center and improved the catalytic activity of **14** at higher temperature up to 80°C. Moreover, the ethylene oligomerization by **14** produced oligomers with parts of longer carbon chains such as octene. Increasing the bulk of ligands resulted in the stability of the active center along with higher order oligomers (enforcement of chain propagation in the catalytic mechanism). However, the complexes containing phosphine ligands did not improve their catalytic activities. This is consistent with the result of theoretical prediction of catalytic activity affected by ligands, in which it was concluded

that the more electrophilic the metal center, the higher the rate of ethylene insertion [52].

[N–O] Bidentate Nickel Complexes

The nickel complexes containing ligands of N–O also showed promising results in ethylene oligomerization and polymerization. The significant neutral nickel complex **15** (Fig. 4) could run ethylene polymerization without MAO as the cocatalyst [53, 54]. However, our efforts ended in the formation of nickel complex **16**

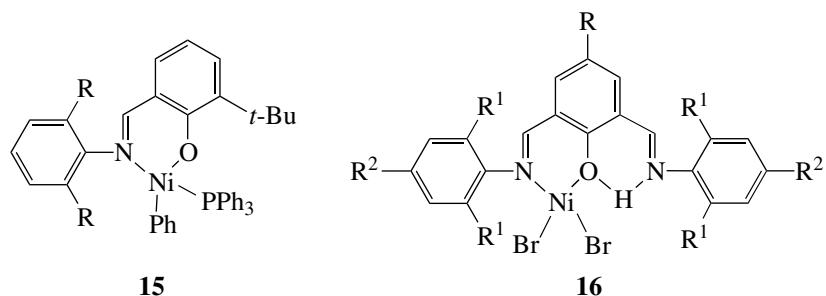
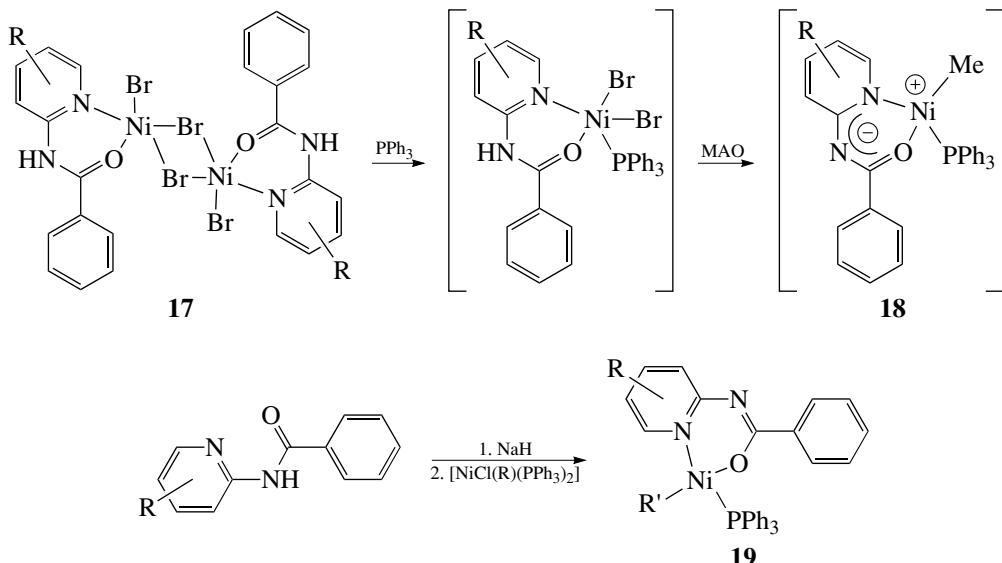


Fig. 4. Nickel complexes containing nitrogen and oxygen in the ligands.



Scheme. The proposed active intermediate **18** and synthesis of its active catalytic model **19**.

[55], which showed ethylene oligomerization and polymerization with the cocatalyst MAO.

To simplify preparation of a suitable ligand and investigation of catalytic intermediates in an easier way, a series of *N*-(2-pyridyl)benzamides and their nickel complexes **17** (scheme) were synthesized [56]. These complexes showed considerable activity for ethylene oligomerization. It was reported that the existence of the auxiliary PR_3 ligand for the SHOP-type catalysts resulted in the stabilization of the catalytic species [57], and a further report claimed its influence on ethylene oligomerization [58]. Therefore, the addition of PPh_3 in the catalytic system showed a positive effect, a catalytic activity one order of magnitude higher. A more detailed investigation supported the possible catalytic intermediate **18** linking of neutral nickel complex [59]. To explain the formation of active intermediate **18**, a plausible mechanism was proposed as follows (scheme). To confirm the active intermediate **18**, it was realized that the proton of amine in the ligand should be removed to form an enolate anion, which coordinated with the nickel center. Therefore, the ligand first reacted

with NaH and then reacted with *trans*-[NiCl(Naph)(PPh₃)₂], and the expected neutral nickel complex **19** was isolated (scheme) [56]. To be sure of the active intermediate, the complex **19** performed the highest activity for ethylene oligomerization; when the auxiliary PPh₃ was added to the catalytic system, its catalytic activity decreased. This showed a typical example for clarifying the active center by designing complexes, which is one advantage of a homogeneous catalyst in understanding the catalytic site compared to a heterogeneous catalyst (such as Ziegler–Natta [60, 61], Philip [62], and supported metallocene catalysts [63]).

Those nickel complexes show the stepwise progress in designing nickel complexes as catalysts for ethylene oligomerization and polymerization. The variations of ligands with their steric bulk and electronic effects affected the complexes with different activity and stability and also changed their products. Therefore, the products could be controlled through tailoring the substituents of ligands. Comparing heterogeneous catalysts, the homogeneous catalyst could be single-molecule to show a clear catalytic model and active site.

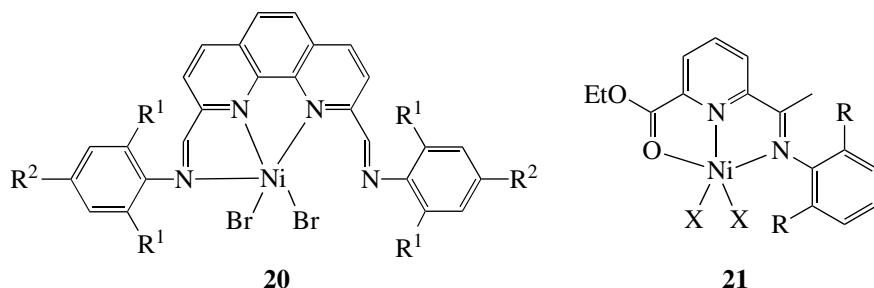


Fig. 5. Nickel complexes containing tridentate ligands.

Designing the suitable ligands will build the desired environment for the catalytic center and approach to the economic reaction with the expected product. Liking the complex **1** as the most effective nickel catalyst for ethylene polymerization, it was succeeded by the use of bulky aryl groups [6]. Activated by a cocatalyst, the nickel catalysts form different active sites in the catalytic system to produce bimodal or multimodal polyethylene.

Tridentate Nickel Complexes

In addition to the effective catalysts of bidentate nickel catalysts, it would be interesting with great potential in exploring tridentate nickel complexes. After the innovative works of tridentate ferrous complexes [14, 15], there are a few examples of tridentate nickel complexes for activating ethylene. It is worth mentioning that the nickel complexes bearing 2,9-bis(imino)-1,10-phenanthrolinyl ligands were first reported to perform ethylene oligomerization and polymerization [64, 65]. Those complexes **20** (Fig. 5) showed good activity for ethylene polymerization at a pressure of 1 atm, while wax was mainly produced in ethylene polymerization with elevated pressure of ethylene. In complex **21**, the ligands chelated with nickel in tridentate fashion with the carbonyl oxygen atoms coordinate to the metal centers. Upon activation with MAO, this complex was active for both ethylene oligomerization and polymerization, and mainly non- α -olefins and branched polyethylene with bimodal molecular weight distribution were obtained [29]. This might be initially motivating ethylene polymerization with tridentate nickel complexes.

CONCLUSIONS

Nickel complexes as catalysts for ethylene oligomerization and polymerization showed some unique properties. Beyond the SHOP process for oligomers, more effective catalysts will possibly be available with their imino ligands. In addition, the inner olefins and the branched polyethylene in most cases with bimodal molecular weight distribution are expectable in the polymerization process with nickel complexes.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China for financial support under grant no. 20473099, National 863 Foundation (2002AA333060).

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