

## Catalyst Design of Novel Nickellacyclic Complexes for Ethylene Polymerization

Tanabiki, Masao  
Yokkaichi Research Laboratory, TOSOH CORPORATION

Matsubara, Kouki  
Faculty of Science, Fukuoka University

Sunada, Yusuke  
Institute for materials chemistry and engineering, Kyushu University

Nagashima, Hideo  
Institute for materials chemistry and engineering, Kyushu University

<https://hdl.handle.net/2324/17906>

---

出版情報 : Journal of Novel Carbon Resource Sciences. 1, pp.16-23, 2010-03. Kyushu University  
G-COE program "Novel Carbon Resource Sciences" secretariat

バージョン :

権利関係 :

# Catalyst Design of Novel Nickellacyclic Complexes for Ethylene Polymerization

Masao Tanabiki<sup>\*1</sup>, Kouki Matsubara<sup>\*2</sup>, Yusuke Sunada<sup>\*3</sup> and Hideo Nagashima<sup>\*3</sup>

<sup>\*1</sup>Yokkaichi Research Laboratory, TOSOH CORPORATION

<sup>\*2</sup>Faculty of Science, Fukuoka University

<sup>\*3</sup>Institute for Materials Chemistry and Engineering, Kyushu University

(Received December 7, 2009; accepted February 1, 2010)

Azanicelacyclopentene complexes were synthesized and their molecular structures are determined by X-ray crystallographic analysis. These complexes showed good reactivity toward polymerization of ethylene in the presence of pMAO as the cocatalyst to give polyethylene. The effect of increased rigidity of a nickellacycle skeleton and fixation of iminoacyl moiety in a coordination plane for catalytic activity is discussed.

## 1. Introduction for Catalytic Polyethylene Production in Industry

Polyethylene (PE) and polypropylene (PP) are representative polyolefins widely used in human life. For instance, they are seen in a shopping bag supplied at a grocery store, a bumper of automobiles, and plastics we are commonly using. Our society is not convenient without polyolefins. There are two methods for industrial production of PE at present. One is a radical polymerization of ethylene, which is initiated by a peroxidic initiator, under high pressure of ethylene at high temperature, whereas the other is coordination polymerization of ethylene catalyzed by transition metal complexes. In Japan, 2,500,000 ton of PE is produced per year by coordination polymerization of ethylene<sup>1</sup>). HP-LDPE produced by radical polymerization has excellent properties in transparency and elasticity, and easily undergoes processing due to its branched structure and wide molecular weight distribution. Approximately 50% of low density PE is produced by the radical process. Despite the utility of HP-LDPE by the radical process, there are demerits in consumption of energy for the synthetic process derived from extremely high pressures of ethylene (100~300 MPa) and high temperatures (150~300 °C). In contrast, coordination polymerization of ethylene by transition metal catalysts proceeding under much milder conditions can produce PE having a linear structure and high density with a small amount of energy supply. It is important that the transition metal catalysts can copolymerize ethylene (monomer) with other olefins (co-monomer) such as 1-butene and 1-hexene. Since the copolymerization provides branches derived from the alkyl moieties of co-monomers in linear PE, judicious choice of the monomer / co-monomer ratio resulted in selective production of PE having a variety of density. In typical examples, HDPE produced by homopolymerization of ethylene or copolymerization of ethylene with small amounts of co-monomers is used for a plastic drain and a polytank for oils due to its stiffness. LLDPE in which the increased co-monomer ratio was

introduced shows mechanically stronger than HP-LDPE.

There are two types of catalysts used for industrial production of PE. One is named the Ziegler-Natta catalyst, which was discovered by Ziegler and Natta in 1950s, composed of titanium halides (main catalyst) and alkylaluminum compounds (cocatalyst)<sup>2</sup>). Use of the Ziegler-Natta catalyst made possible PE production under low ethylene pressure (1 atm). Stereoselective polymerization of propylene first gave a method to produce isotactic-PP. Although long history of the investigation of the net catalytic species did not give any clear answer, the catalyst contains several different active sites (multi-site catalysts) and gives PE with broader molecular weight distribution. The improved Ziegler-Natta catalysts supported on MgCl<sub>2</sub>, which was later invented, is now used in the real industrial process<sup>3</sup>). The Kaminsky catalyst discovered in 1980 is composed of zirconocenes (main catalyst) and methylaluminoxane (MAO; cocatalyst)<sup>4</sup>). The active species is molecular and called a single site catalyst, which contributes to produce PE with narrow molecular weight distribution. By virtue of the molecular catalyst, appropriate catalyst design results in facile control of catalytic activity and molecular weight of the polyolefin. In case of PP production, stereoselective polymerization to isotactic and syndiotactic PP is achieved by the catalyst design. The Kaminsky catalyst has made possible copolymerization of ethylene with less reactive comonomers such as cycloalkenes.

Early transition metals such as titanium and zirconium are good catalyst components for the Ziegler-Natta catalyst and the Kaminsky catalyst to give linear, high density PE with high molecular weight. In contrast, efforts to polymerize ethylene by late transition metal catalysts opened the way to produce C<sub>4</sub> ~ C<sub>30</sub> oligomers. Typical catalysts are organonickel complexes, which showed high reactivity towards β-hydrogen elimination to produce 1-olefins from Ni-alkyl species. The β-hydrogen elimination accelerates chain transfer reactions rather than propagation; this causes facile production of oligomers rather than PE as shown in Fig. 1. Typical industrial

oligomerization process of ethylene is called SHOP (Shell Higher Olefin Process). In Fig. 2 is illustrated a typical example of the SHOP catalyst which often has nickelacyclic structure<sup>5</sup>). This particular catalyst has a five-membered ring structure having a Ni-O bond and coordination of P stabilizes the Ni center. The catalyst has high catalytic activity and durability to give a mixture of  $\alpha$ -olefins having  $C_4$ ~ $C_{30}$  (300,000 ton / year), which are widely used as starting materials for industrially useful materials. One of the typical examples is comonomers for polyolefins described above.

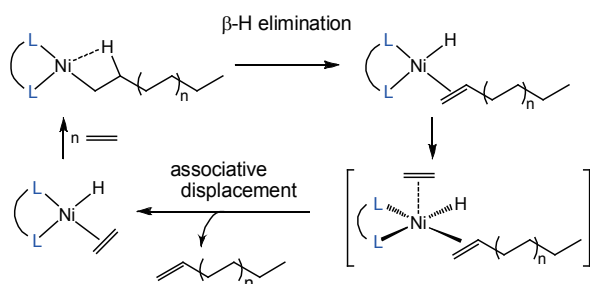


Fig. 1 Chain transfer reaction of late metal catalysts.

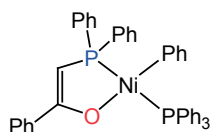


Fig. 2 SHOP(Shell Higher Olefin Process).

Of interest is whether there is no way to obtain PE with high molecular weights from ethylene monomer by nickel catalysts. A breakthrough was discovered in 1995 by Brookhart and coworkers who found certain nickel complexes bearing  $\alpha$ -diimine ligands to be a good catalyst for production of PE in the presence of MAO<sup>6</sup>). In particular, introduction of sterically bulky N-substituents to the  $\alpha$ -diimine ligand is a key to form PE with high molecular weights; catalytic activity is comparable to the metallocene catalysts. As described above, rapid chain transfer is a problem to obtain PE in the nickel catalyzed reaction with ethylene; this is due to the high reactivity of alkyl-nickel moieties towards  $\beta$ -hydrogen atom elimination followed by exchange of the resulting coordinating higher olefin by ethylene.

The role of sterically bulky group to suppress olefin exchange is illustrated in Fig. 3 and Fig. 4, in which the four R groups protect the metal center for coordination of ethylene at the axial position of square-planer nickel species, which facilitate exchange process of coordinated higher olefin shown in II of Fig. 4 by ethylene. "The chain walking" was found to be a characteristic feature of ethylene polymerization by certain nickel complexes, which is promoted by reactions involving  $\beta$ -hydrogen elimination, reinsertion, and propagation as shown in I-III in Fig. 4. The chain walking facilely takes place with nickel catalysts having bulkier N-substituents, providing a synthetic route of hyperbranched polyethylene<sup>7</sup>.

Discovery of Brookhart catalysts and the concept that sterically bulky group protecting the axial positions of square planer nickel species results in formation of PE with high molecular weights stimulated the improvement of SHOP catalysts for ethylene polymerization. Ligand design suitable for Brookhart's concept has provided a salicylaldimine nickel complex shown in Fig. 5, which successfully gives PE with high molecular weights<sup>8,9</sup>).

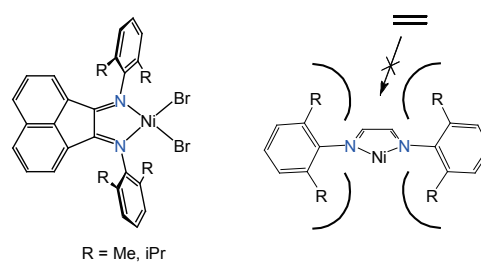


Fig.3  $\alpha$ -Diimine Ni complexes.

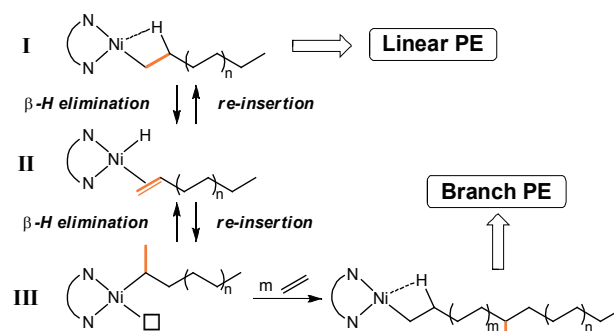


Fig. 4 Chain walking reaction.

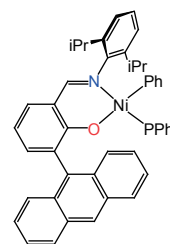
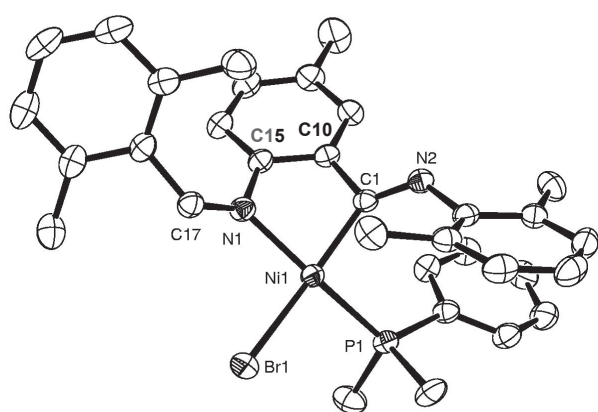
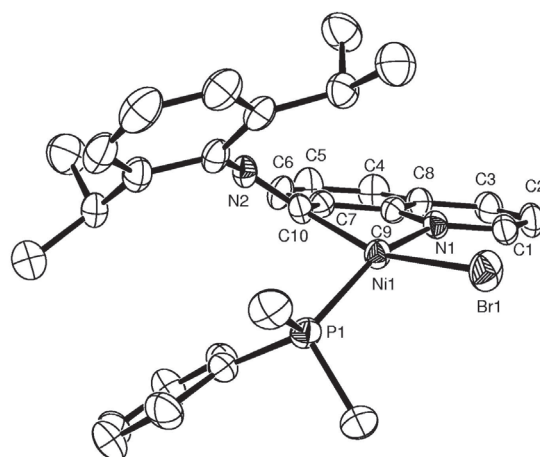


Fig. 5 Salicylaldimine Ni complex.

We have recently discovered nickel complexes shown as **A** in Fig. 6 to be a catalyst for ethylene polymerization in the presence of MAO<sup>10</sup>). The complex **A** is easily synthesized by trimerization of arylisocyanide on the nickel atom, having an azanickellacyclopentene skeleton. The aryl group on the nitrogen atom in **A** is important for changing molecular weight and number of branches in PE produced. Interestingly, **A** contains  $\alpha$ -diimine moiety in the molecule which potentially coordinates to other metals. Introduction of the second metal such as  $ZnBr_2$ ,  $CoBr_2$ , and  $FeBr_2$  (Fig. 6, **B**) results in dramatic increase of the catalytic activity, which is considered to be promoted by the fact that the second metal reinforces the metallacyclic structure.



Fig. 8 ORTEP drawing of **C1**.Fig. 9 ORTEP drawing of **C2**.Table 1-1 Crystallographic data, bond distances and bond angles of **C1**

		<b>C1</b>			
Crystallographic data		Bond distances		Bond angles	
Formula	C <sub>33</sub> H <sub>36</sub> N <sub>2</sub> BrNiP	Ni(1)-C(1)	1.900(3)	C(1)-Ni(1)-N(1)	81.50(11)
Crystal system	Triclinic	Ni(1)-N(1)	1.962(2)	Br(1)-Ni(1)-P(1)	95.87(7)
Space group	P-1 (#2)	Ni(1)-Br(1)	2.3877(5)	C(1)-Ni(1)-P(1)	94.78(9)
a[Å]	10.9082(7)	Ni(1)-P(1)	2.1647(8)	N(1)-Ni(1)-Br(1)	95.87(7)
b	15.4658(7)	N(1)-C(15)	1.437(4)	C(1)-N(2)-C(2)	127.5(3)
c	10.2929(7)	C(1)-C(10)	1.488(4)	C(1)-Ni(1)-Br(1)	165.79(9)
α[°]	106.253(4)	C(10)-C(15)	1.392(4)	N(1)-Ni(1)-P(1)	163.20(8)
β	115.943(2)	N(1)-C(17)	1.285(4)		
γ	81.801(2)	C(1)-N(2)	1.269(4)		
V[Å <sup>3</sup> ]	1498.66(16)	N(2)-C(2)	1.412(4)		
Z	2				
R, Rw	0.0426, 0.1065				

Table 1-2 Crystallographic data, bond distances and bond angles of **C2**

		<b>C2</b>			
Crystallographic data		Bond distances		Bond angles	
Formula	C <sub>30</sub> H <sub>34</sub> N <sub>2</sub> BrNiP	Ni(1)-C(10)	1.899(4)	C(10)-Ni(1)-N(1)	84.41(17)
Crystal system	Triclinic	Ni(1)-N(1)	1.969(4)	Br(1)-Ni(1)-P(1)	96.04(11)
Space group	P-1 (#2)	Ni(1)-Br(1)	2.3959(8)	C(10)-Ni(1)-P(1)	96.48(13)
a[Å]	9.1564(8)	Ni(1)-P(1)	2.1830(13)	N(1)-Ni(1)-Br(1)	96.04(11)
b	17.7859(15)	N(1)-C(9)	1.369(6)	C(10)-N(2)-C(11)	128.2(4)
c	9.1190(9)	C(10)-C(7)	1.495(6)	C(10)-Ni(1)-Br(1)	159.32(14)
α[°]	95.706(3)	C(7)-C(9)	1.411(6)	N(1)-Ni(1)-P(1)	154.31(12)
β	105.318(3)	N(1)-C(1)	1.326(6)		
γ	99.124(4)	C(10)-N(2)	1.280(6)		
V[Å <sup>3</sup> ]	1398.5(2)	N(2)-C(11)	1.405(6)		
Z	2				
R, Rw	0.0557, 0.1385				

planar geometry, in which the nickel atom is bonded with a carbon of the iminoacyl group, bromine, a nitrogen atom of the imino or quinoline group, and phosphorous atom of  $\text{PMe}_2\text{Ph}$ . The carbon and the bromine are in the trans-position. The xylyl group in the iminoacyl moiety in **C1** takes part in giving some steric influence around the nickel center; however, that in the imino group is far from the metal center. The molecular structure of **C1** suggests that nickellacyclopentene structure is flexible and the substituents connected to the non-planer metallacycle freely rotated to avoid the steric repulsion; this leads to only small steric bias is available for the circumstance of the nickel center from the ligand structure. In contrast, **C2** has a planer structure due to the planarity of the quinoline ring, and sterically more bulky 2,6-diisopropylphenyl group exists in the iminoacyl moiety effectively protect the axial position of the nickel square. In other words, we prepared two complexes, **C1** and **C2**, having a similar ligand arrangement consisting of a carbon, bromine, nitrogen, and phosphorous; however, **C1** has a small effect on the protection of the axial positions of the nickel square, whereas **C2** has a relatively large effect.

$^1\text{H}$  NMR spectra of **C1** and **C2** in  $\text{C}_6\text{D}_6$  at 60 °C indicate that the molecular structures determined by crystallography are maintained in solution states. Interestingly, the spectra sometimes showed dynamic behavior; at room temperature, the signals due to the iminoacyl group and  $\text{PMe}_2\text{Ph}$  are broaden. For instance, a signal due to the methyl group of the iminoacyl moiety in **C1** appears as a singlet ( $\delta$  2.8) at 60 °C, whereas it was seen as a broad bump ( $\delta$  2~3) at room temperature. This indicates that the benzene ring of the iminoacyl moiety has a rotational barrier in the NMR time scale; this may affect the rotation of  $\text{PMe}_2\text{Ph}$  along the Ni-P bond. In sharp contrast, the diastereotopic two methyl groups of the two isopropyl moieties in **C2** appeared as a independent sharp doublets at both 60 °C and at room temperature. This suggest that the benzene ring connected to the isopropyl moieties does not rotate, but affect to slow down the rotation of  $\text{PMe}_2\text{Ph}$  ( $\delta$  0.84). In considering the catalytic species,  $\text{PMe}_2\text{Ph}$  in **C1** and **C2** should dissociate from the nickel center to provide a coordination site for ethylene. In the absence of MAO, free  $\text{PMe}_2\text{Ph}$  was not observed; this indicates the importance of the action of MAO for generation of the active species.

### 2.3 Polymerization of ethylene by **C1** and **C2** in the presence of MAO.

The results of ethylene polymerization by **C1** and **C2** are shown in Table 2. The catalyst was prepared in situ by treating with MAO (200 eq. to the catalyst) in toluene at room temperature for 30 min. Then, the reaction vessel was put into a 100 mL stainless steel autoclave, and 0.8 MPa of ethylene was applied. After 20 min, the reaction was quenched, and the formed PE was subjected to GPC analysis. The molecular weight of the formed polyethylene was  $M_n > 10^5$  in either the catalyst. The melting point of the formed PE indicates existence of branches. The catalytic activity of **C2** was 73 g PE/ mmol·hr, which is comparable to those seen in the ethylene polymerization

by the catalyst A. In contrast, **C1** was not a reactive catalyst (5 g PE/mmol·hr). These differences between **C1** and **C2** will be discussed later.

**Table 2** Catalytic activities of azanickellacycle complexes for polymerization of ethylene

Run	Complex	Activity g/mmol·hr	$M_n$ $\times 10^4$	$M_w/M_n$	$T_m$ °C
1	<b>C1</b>	5	10.9	7.9	128.5
2	<b>C2</b>	73	22.1	2.3	103.8
3	<b>A</b>	76	10.0	3.3	128.0
4	<b>B</b>	1620	0.6	3.4	127.4

cocatalyst: pMAO (200 equiv, run 3:100 equiv),  
ethylene: 0.8 MPa, solvent: toluene 50 mL (total volume)  
temperature: r.t., time: 20 min

### 2.4 The relationship between the catalyst structure and activity and branching.

In Fig. 10 are summarized valued of  $\omega$ ,  $\theta$ , and  $\tau$  for **C1** and **C2**. The  $\omega$  is defined as sum of inner angles of the five membered nickellacycle, which is an indicator of planarity of the azametallacycle. The dihedral angle between the least square plane defined by the five-membered nickellacycle and iminoacyl moiety was defined by  $\theta$ , which shows deviation of the iminoacyl group from the nickel square. The  $\tau$  is defined as dihedral angle between the nickellacycle plane and the imino moiety, which shows deviation of the ligand containing a coordinating nitrogen atom from the nickel square. The  $\omega = 534.7^\circ$  of **C2** is close to that of **C1** ( $\omega = 521.9^\circ$ ). The iminoacyl moieties of **C1**, **C2**, and **B** are not coplanar with the nickel square, giving  $\theta > 36^\circ$ , which is much different from  $\theta$  of **B** ( $16.4^\circ$ ). The  $\tau$  of **C1** is  $43.9^\circ$ , which is much larger than those of **C2** ( $6.4^\circ$ ), **A** ( $10.8^\circ$ ), and **B** ( $4.5^\circ$ ); only **C1** has a coordinating nitrogen-containing ligand which is not coplanar with the nickel square. The bond distances around the imino group in **C2** are the following features; the N(1)-C(9) bond in the nickellacycle is 1.369 Å, whereas the N(1)-C(1) at the exo position is 1.326 Å; these are apparently shorter than a typical N-C single bond distance (1.45 Å), suggesting multiple bond interaction. In the complex **C1**, the N(1)-C(15) in the metallacycle is close to a N-C single bond (1.47 Å), whereas the N(1)-C(17) bond distance of 1.285 Å is similar to a typical N=C bond (1.26 Å); these makes  $\tau$  larger. The structural feature of **C1** having larger  $\theta$  and  $\tau$  provides two important factors for the polymerization mechanisms; one is the aromatic group on the imino moiety is too remote and too flexible to give steric influence to the nickel center compared with other three nickellacyclic complexes. Compared with the structure of **C1**, **C2** and **A** have relatively rigid structure. In particular, the quinoline ring in **C2** takes part in increasing  $\omega$ , namely the planarity of the metallacycle, which is an indicator of rigidity of the

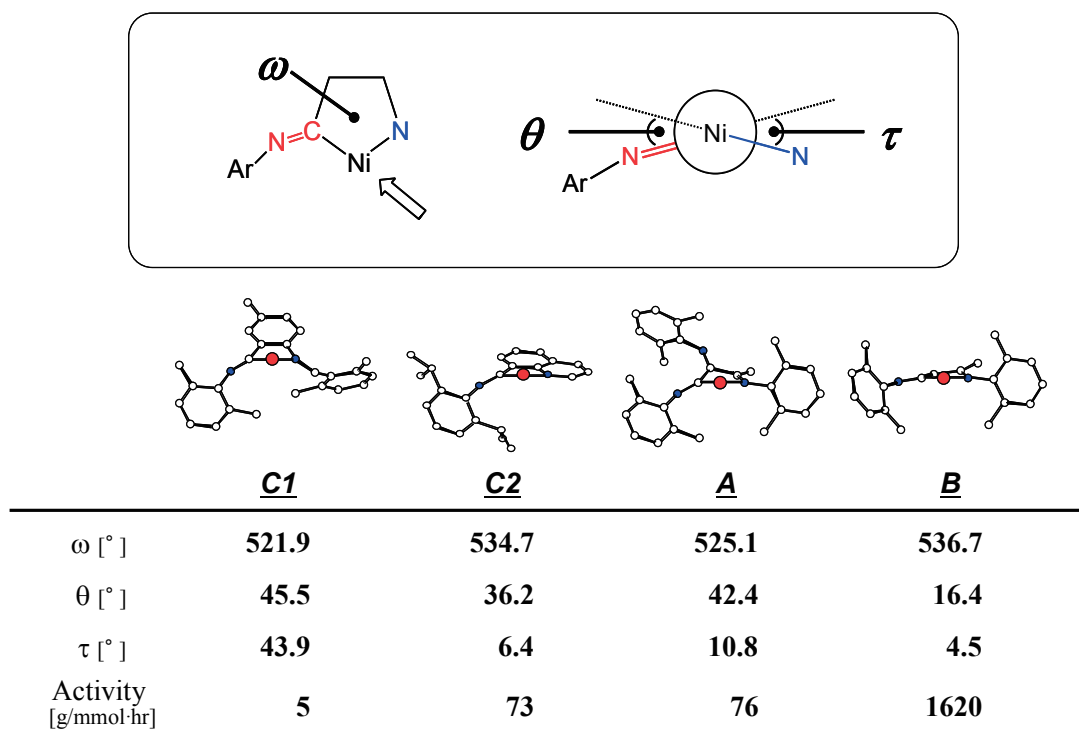


Fig 10 Structure and catalytic activity.

complex. Straight comparison of the effective blocking of the axial positions of the nickel atom by the substituents of the metallacycle is difficult between **C2** and **A**, because **C2** has a single more bulky 2,6-diisopropylphenyl ring, whereas **A** possesses two less bulky *o*-xylyl groups. However, it is of interest as rough estimation that both of them contribute to providing good steric factor for blocking the axial positions of the nickel atom. Compared with **C1**, **C2**, and **A**, **B** has the largest  $\omega$  and the smallest  $\theta$  and  $\tau$ ; this means that the complex has a planer and rigid structure, taking part in effective blocking of the axial positions of the nickel atom by two *o*-xylyl moieties.

In summary, the order of the rigidity of the complex is: **B** > **C2** > **A** > **C1**, whereas the order of effective blocking of the nickel atom by the ligands is: **B** > **C2**  $\geq$  **A** > **C1**. These two factors are known to provide catalytic activity for ethylene oligomerization and polymerization; the higher rigidity and the more effective blocking of the axial positions generally give higher catalytic activity. In the SHOP catalysts, the catalytic activity is decreased in the order, nickellacyclopropane, nickellacyclohexane, and nickellacycloheptane. This is explained by the decreased planarity and rigidity of the metallacycle in increasing the ring size of the metallacycle<sup>12</sup>. The decreased planarity and rigidity in the order, **B** > **C2** > **A** > **C1**, described above are consistent with the order of the catalytic activity. Sterically bulky ligands which effectively block the axial positions of the nickel center suppress the chain transfer to contribute to producing PE with high molecular weight as described above. The other sterically bulky ligand effect which was proposed in literature regarding to the Brookhart catalyst is destabilization of alkylnickel intermediates coordinating to ethylene (resting state) which

facilitates the propagation. In the mechanism of Grubbs' salicylaldimine complex, sterically bulky ligand was proposed to accelerate dissociation of  $\text{PPh}_3$  to open the coordination site for ethylene and to suppress the formation of inactive salicylaldimine dimer<sup>13</sup>. These may be effective for high catalytic activity of **B**, too.

Measurement of DSC of the formed PE showed melting points of PE produced by **C1**, **C2**, **A**, and **B** to be 128.5, 103.8, 128.0, and 127.4 °C, respectively. In general, linear PE is crystalline and its melting point is around 138 °C. Introduction of branches to PE results in lowering of the crystallinity to decrease the melting point. For instance, the melting point of PE produced by the Brookhart catalyst is dependent on the steric bulkiness of the ligand; higher steric bulkiness gives lower melting point. This is a side effect of destabilization of the resting state as described above; "Chain Walking" pathway is predominant over the propagation from the alkyl cation intermediates (complex I of Fig. 4). It is known that two diimine complexes shown in Fig. 3, where R = Me and *i*Pr, gave PE with  $T_m$  = 128 and 110 °C, respectively, which are corresponding to the ratio of branched carbon in the PE chain of 13/1000C and 24/1000C, respectively, when polymerization was performed at 35 °C for 10 min under 200 psi of ethylene pressure.<sup>7</sup>) Similar effect of sterically bulky ligand is apparently involved in the mechanisms to give PE with different  $T_m$  in **C1**, **C2**, **A**, and **B**. In particular, it is of interest in comparison with the Brookhart catalyst of R = *i*Pr which have four isopropyl groups in the molecule that only two isopropyl groups effectively gave significantly low  $T_m$  of 103 °C.

In summary, we have synthesized two novel complexes, **C1** and **C2** having an iminoacyl moiety and found their

catalytic activity towards PE production in the presence of MAO. This is the second example that the iminoacyl moiety is effective partial structure in the SHOP type catalyst. Higher catalytic activity of **C2** is ascribed to appropriate planarity and rigidity of the complex associated with the steric bulkiness of the ligand affecting blocking of the nickel center. In the same line of these catalyst design, we anticipate further examples of active polymerization catalyst having the iminoacyl moiety, and further investigation is in progress.

### 3. Experimental

All of the experiments were carried out under nitrogen atmosphere. Anhydrous toluene and pentane were purchased from commercial source. Benzene- $d_6$  was distilled from benzophenone ketyl. Other reagents, 2,6-dimethylbenzaldehyde, and 2-bromo-4-methylaniline were purchased from TCI, whereas 8-bromoquinoline and PMAO-S were from Aldrich and TOSOH Fine Chem, respectively. NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) were measured by JEOL GSX 270. Mw and Mw/Mn were determined by GPC (TOSOH HLC-8121GPC/HT) at 140 °C by *o*-dichlorobenzene as an eluent. Tm was measured by DSC (Seiko DSC-200).

#### 3.1 Preparation of **C1**.

##### 3.1.1 Preparation of the ligand precursor L1.

In a Schlenk tube (300 mL) was dissolved 2,6-dimethylbenzaldehyde (3.37 g, 25.2 mmol) in toluene (250 mL). To this solution, *p*-toluenesulfonic acid monohydrate (PTSA) (4.8 g, 25.2 mmol), 2-bromo-4-methylaniline (3.2 mL, 25.8 mmol) was added. Suspension was formed. Dean-Stark trap was attached to the Schlenk tube and the reaction vessel was heated under reflux of toluene with removal of formed water. Reddish brown homogeneous solution was formed. After 6 h, the mixture was cooled to room temperature. The toluene solution was washed with  $\text{NaHCO}_3$  aq. and brine, and dried over  $\text{MgSO}_4$ . Concentration of the organic solution gave brown solid, which was washed with hexane to remove impurities. The ligand precursor L1 was obtained as a yellow solid (3.49 g, 29 %).  $^1\text{H}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 1.95(s, 3H, tolyl- $\text{CH}_3$ ), 2.51(s, 6H, 2,6-( $\text{CH}_3$ ) $_2$  $\text{C}_6\text{H}_3$ ) imine), 6.65(d, 1H, tolyl), 6.80(d, 1H, tolyl), 6.89(d, 2H, m-2,6-( $\text{CH}_3$ ) $_2$  $\text{C}_6\text{H}_3$ )), 7.01(t, 1H, p-2,6-( $\text{CH}_3$ ) $_2$  $\text{C}_6\text{H}_3$ )), 7.34(s, 1H, tolyl), 8.50(s, 1H, N=C-H).

##### 3.1.2 Preparation of **C1**.

To  $\text{Ni}(\text{cod})_2$  (0.18g, 0.66mmol) dissolved in toluene (10 ml) was added a toluene solution of  $\text{PMe}_2\text{Ph}$  (95  $\mu\text{L}$ , 0.66mmol) and 2,6-dimethylphenyl isocyanide (0.5 M, 1.3 mL, 0.65 mmol), and the mixture was stirred at room temperature for 1 h. Then, L1 (0.20 g, 0.66 mmol) dissolved in toluene (10 mL) was added. The mixture was heated at 50 °C for 6 h. The solvents were removed in vacuo, and the resulting solids were washed with pentane. Dissolution of the obtained solid in toluene was followed by filtration for removal of insoluble materials. The complex **C1** was obtained by concentration as red solids. (0.31 g, 75.8 %).  $^1\text{H}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 1.48(br, 6H,  $\text{P}(\text{CH}_3)_2\text{Ph}$ ), 1.87(s, 3H, tolyl- $\text{CH}_3$ ), 1.91(br s, 6H, 2,6-( $\text{CH}_3$ ) $_2$  $\text{C}_6\text{H}_3$ )

imine), 1.98(br s, 6H, 2,6-( $\text{CH}_3$ ) $_2$  $\text{C}_6\text{H}_3$ ) iminoacyl), 6.36(d, 1H), 6.44(d, 1H).  $^{31}\text{P}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): -2.18.  $^{13}\text{C}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 20.32, 20.40, 20.78, 118.82, 123.04, 123.79, 128.31, 128.67, 129.67, 129.77, 134.82, 138.93, 147.59, 147.96, 148.28, 171.17 (several peaks were not observable due to the poor solubility of the complex)

#### 3.2 Preparation of **C2**

To a  $\text{Ni}(\text{cod})_2$  (0.28 g, 1.0 mmol) dissolved in toluene (10 mL) was added a toluene solution of  $\text{PMe}_2\text{Ph}$  (0.15 mL, 1.05 mmol) and 2,6-diisopropylphenyl isocyanide (0.5 M, 2.1 mL, 1.05 mmol), and the mixture was stirred at room temperature for 1 h. Then, 8-bromoquinoline (0.223 g) dissolved in toluene (10 mL) was added, and the mixture was heated at 50 °C for 6h. After removal of the solvent in vacuo, the crude material was washed with pentane and redissolved in toluene. Insoluble by-products were removed by filtration, and the filtrate was concentrated. The complex **C2** was obtained as red solids. (0.454 g, 74.4 %).  $^1\text{H}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 0.91(d, 6H), 1.29(d, 6H), 1.53(s, 6H), 3.74(br, 2H), 6.59(m, 1H), 6.83(t, 1H), 7.01-7.10(m, 7H), 7.37(t, 2H, 7.66(br, 2H), 10.00(d, 1H).  $^{31}\text{P}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 0.84.  $^{13}\text{C}$  NMR( $\delta$ ,  $\text{C}_6\text{D}_6$ ): 23.30, 23.41, 29.28, 122.43, 123.38, 123.85, 124.04, 127.04, 128.09, 136.28, 136.51, 153.78 (several peaks were not observable due to the poor solubility of the complex)

#### 3.3 Polymerization of Ethylene

In a 100 mL Schlenk tube, the catalyst (10 mmol) was dissolved in toluene (50 mL). To this solution, MAO (PMAO-S, 2.0 mmol) was treated at room temperature for 1 h. The solution was placed a stainless autoclave (100 mL), and ethylene was applied at room temperature. During the polymerization, the pressure of ethylene was kept at 0.8 MPa. After 20 min, ethylene was purged, and the reaction was quenched by methanol (10 mL). The reaction mixture was poured into a solution of HCl in methanol for removal of aluminum residues. The formed PE was filtered and dried in vacuo at 80 °C for 12 h.

#### References

- 1) Japan Petrochemical Industry Association, statistical data
- 2) a) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.*, **67**, 541 (1955), b) G. Natta, *Angew. Chem. Int. Ed.*, **68**, 393 (1956). c) A. J. Peacock, *Handbook of Polyethylene: Structures, Properties, and Applications*; Marcel Dekker: New York, 534 (2000), d) L. L. Böhm, *Angew. Chem. Int. Ed. Engl.*, **42**, 5010 (2003).
- 3) N. Kashiwa, *Polym. J.*, **12**, 603 (1980).
- 4) H. Sinn, W. Kaminsky, H. J. Vollmer, R. Woldt, *Angew. Chem. Int. Ed.*, **19**, 390 (1980).
- 5) a) W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl.*, **17**, 466 (1978), b) M. Peuckert, W. Keim, *Organometallics*, **2**, 594 (1983), c) W. Keim, *Angew. Chem. Int. Ed. Engl.*, **29**, 235 (1990), d) P. Kuhn, D. Sémeril, D. Matt, M. J. Chetcuti, P. Lutz, *Dalton. Trans.*, 515 (2007).
- 6) a) M. Brookhart, *J. Am. Chem. Soc.*, **117**, 6414 (1995), b) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.*, **118**, 267 (1996), c) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.*, **120**, 267 (1998)



- 7) a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.*, **100**, 1169 (2000), b) D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromolecules*, **33**, 2320 (2000).
- 8) a) T. R. Youkin, E. F. Conner, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science*, **287**, 460 (2000), b) C. M. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben, M. W. Day, *Organometallics*, **17**, 3149 (1998), c) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.*, **103**, 283 (2003).
- 9) a) F. M. Bauers, S. Mecking, *Macromolecules*, **34**, 1165 (2001), b) F. A. Hicks, M. Brookhart, *Organometallics*, **20**, 3217 (2001), c) J. C. Jenkins, M. Brookhart, *Organometallics*, **22**, 250 (2003), d) F. A. Hicks, J. C. Jenkins, M. Brookhart, *Organometallics*, **22**, 3533 (2003), e) S. Y. Desjardins, K. J. Cavell, J. L. Hoare, B. W. Skelton, A. N. Sobolev, A. H. White, W. Keim, *J. Organomet. Chem.*, **544**, 16 (1997), f) C. B. Shim, Y. H. Kim, B. Y. Lee, Y. Dong, H. Yun, *Organometallics*, **22**, 4278 (2003), g) B. Y. Lee, Y. H. Kim, H. J. Shin, C. H. Lee, *Organometallics*, **21**, 3481 (2002), h) G. A. Luinstra, J. Queisser, B. Bildstein, H. -H. Görtz, C. Amort, M. Malaun, A. Krajete, G. Werne, M. O. Kristen, N. Huber, C. Gernert, In *Late Transition Metal Polymerization Catalysis*; Rieger, B., Saunders Baugh, L., Kacker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, Germany, 59 (2003), i) M. P. Batten, A. J. Canty, K. J. Cavell, T. Rütther, B. W. Skelton, A. H. White, *Inorg. Chim. Acta.*, **359**, 1710 (2006), j) J. D. Azoulay, K. Itigaki, G. Wu, G. C. Bazan, *Organometallics*, **27**, 2273 (2008), k) R. S. Rojas, J. -C. Wasilke, G. Wu, J. W. Ziller, G. C. Bazan, *Organometallics*, **24**, 5644 (2005), l) R. S. Rojas, G. B. Galland, G. Wu, J. W. Ziller, G. C. Bazan, *Organometallics*, **26**, 5339 (2007).
- 10) a) M. Tanabiki, K. Tsuchiya, Y. Motoyama, H. Nagashima, *Chem. Commun.*, **27**, 3409 (2005), b) D. Noda, M. Tanabiki, K. Tsuchiya, Y. Sunada, H. Nagashima, *Polyhedron*, **28**, 3935 (2009).
- 11) a) F. Millich, *Chem. Rev.*, **72**, 101 (1972), b) R. J. M. Nolte, *Chem. Soc. Rev.*, **23**, 11 (1994), c) P. C. J. Kamer, R. J. M. Nolte, W. Drenth, H. L. L. M. Nijs, J. A. Kanters, *J. Mol. Cat.*, **49**, 21 (1988), d) T. J. Deming, B. M. Novak, *J. Am. Chem. Soc.*, **115**, 9101 (1993), e) T. J. Deming, B. M. Novak, *Macromolecules*, **26**, 7092 (1993), f) M. Yamamoto, K. Onitsuka, S. Takahashi, *Organometallics*, **19**, 4669 (2000).
- 12) W. Keim, R. P. Schulz, *J. Mol. Catal.*, **92**, 21 (1994).
- 13) a) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science*, **287**, 460 (2000), b) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben, M. W. Day, *Organometallics*, **17**, 3149 (1998).