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# Mono- and bimetallic ethylene polymerization catalysts having an azanickellacyclopentene skeleton

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#### ABSTRACT

A series of azanickellacyclopentene complexes having iodo, bromo, chloro, or triflate ligand on the Ni center were prepared, and are subjected to studies on ethylene polymerization catalysis. Activity of these mononuclear azanickellacyclopentene complexes was increased in the order, Ni–Cl < Ni–I  $\approx$  Ni–Br < Ni–OTf; this is explained by the performance of (pseudo)halogeno ligand as a leaving group from the nickel center. Methylalminoxane (MAO) and inexpensive AlEt<sub>2</sub>Cl can be used as the cocatalyst. Mechanistic consideration suggested the involvement of neutral Ni–alkyl intermediates as proposed in the SHOP type catalytic system. Interestingly, the catalytic activity is significantly increased by incorporating the second metals into the diimino moiety of mononuclear complex. Two factors should be considered to explain this activity enhancement. One is the increased rigidity of the azanickellacyclopentene ligand backbone, and the other is the possibility of the presence of the two active centers in one molecule.

## 1. Introduction

It is well known that organonickel complexes exhibit excellent catalytic activity for oligomerization and polymerization of alkenes, in which appropriate selection of auxiliary ligands of nickel is important for increasing the catalytic activity and molecular weight of the polymer formed [1]. One of the typical ethylene polymerization catalysts is Brookhart's  $\alpha$ -diimine complex, which shows an excellent catalytic activity with the aid of methylaluminoxane (MAO), providing relatively high molecular weight polyethylene  $(M_n = 30\ 000-1\ 000\ 000)$  [2]. Detailed experiments suggest that a key to forming high molecular weight polyethylene is introduction of sterically bulky 2,6-diisopropylphenyl groups as the N-aryl group as shown in Chart 1, A. In contrast, the SHOP catalysts typically shown in Chart 1, B, give oligomers of ethylene, which are actually used in industrial production of  $\alpha$ -olefins [3]. Studies stimulated by success of the Brookhart catalyst revealed that introduction of the sterically demanding substituents on the phosphorus atom leads to the formation of high molecular weight polyethylene with high efficiency. Nitrogen analogues of the SHOP catalyst bearing sterically bulky substituents on the N atoms were also investigated, giving polyethylene with high molecular weights [4].

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In 2004 we found NiX<sub>2</sub>(CNAr)<sub>2</sub> to be a unique ethylene polymerization catalyst in the presence of MAO [5]. This catalyst does not belong to a category of conventional nickel-based ethylene polymerization catalysts such as the Brookhart catalyst or the SHOP catalyst. In the course of our mechanistic considerations, we got the idea that oligomerization of isocyanide ligands on the nickel atom might be involved to generate catalytically active species. It is known that activation of isocyanides by a catalytic amount of nickel complexes leads to polymerization of isocyanides [6]. A complex shown in Chart 1, **D** ( $R = {}^{t}Bu$ ), which is formed by trimerization of <sup>t</sup>BuNC on the nickel atom, is considered to be an intermediate for the isocyanide polymerization. Complex D is prepared by treatment of Ni(<sup>t</sup>BuNC)<sub>4</sub> with CH<sub>3</sub>I or reaction of trans-Ni(PMe<sub>3</sub>)<sub>2</sub>MeCl with <sup>t</sup>BuNC [7]. The complex has an interesting structural feature in comparison with the Brookhart catalyst and SHOP catalyst. First is that it is analogous to the N-type SHOP catalyst C, which has a nickellacyclopentane structure with a Ni-O and a Ni  $\leftarrow$  N bond. Complex **D** has a nickellacyclopentane structure with a Ni–C and a Ni  $\leftarrow$  N bond. In other words, **D** is a novel class of the N-type SHOP catalyst having a Ni-C bond. The second unique structural feature of **D** is an  $\alpha$ -diimine substructure, which potentially coordinates with other transition metal fragments. Namely, introduction of nickel or other transition metal species gives a new type of Brookhart's  $\alpha$ -diimine complex (Scheme 1).

With these concepts in mind, we examined catalytic ethylene polymerization with azanickellacyclopentene complexes. Although the original complex shown in Chart 1, **D** ( $R = {}^{t}Bu$ ) did not exhibit catalytic activity, we found that its C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> analogues, **1–4**,

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SHOP-type catalysts Azanickellacyclopentene and its bimetallic complex

Chart 1. Previously reported ethylene polymerization catalysts.



Scheme 1. Strategy for construction of the new ethylene polymerization catalysts.

behaved as a good catalyst for production of polyethylene with  $M_{\rm p}$  = 61 000–130 000 in the presence of MAO or Et<sub>2</sub>AlCl. Furthermore, introduction of the second metal to the  $\alpha$ -diimine part of **1** significantly enhanced the catalytic activity. In this paper, we wish to report the catalytic behavior of these mono- and bimetallic catalysts for ethylene polymerization activated by organoaluminum cocatalysts in detail, and discuss the polymerization mechanisms [8].

# 2. Results and discussion

# 2.1. Synthesis and characterization of azanickellacyclopentene derivatives 1-4

The azanickellacyclopentene complex bearing a C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> group on the nitrogen atoms was synthesized by treatment of Ni(CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)<sub>4</sub>, which was generated in situ by the reaction of Ni(COD)<sub>2</sub> with 4 equivalent of CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>, with excess amounts of MeI in boiling C<sub>6</sub>H<sub>6</sub> for 24 h (95% yield) (Scheme 2). The OTf, Br, and Cl homologues of **1** were synthesized as follows: treatment of 1 with 1 equivalent of AgOTf in CH<sub>2</sub>Cl<sub>2</sub> for 3-4 h afforded azanickellacyclopentene triflate 2 in 89% yield as orange powder. The triflate 2 was allowed to react with LiBr or LiCl in acetone for 16 h, and gave rise to the formation of bromo- and chlorohomologue 3 and 4 in 72% and 63% yield, respectively (Scheme 2).

Spectroscopic data of 1-4 are summarized in Table 1. NMR spectrum of **1** shows four <sup>1</sup>H resonances as a singlet at 1.95, 2.09, 2.29, and 2.32 ppm and four <sup>13</sup>C resonances at 18.6, 18.7, 19.1, and 19.2 ppm due to methyl groups of four C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> moieties. The methyl signal of the azanickellacyclopentene skele-

ton was observed at 2.20 ppm (<sup>1</sup>H NMR) and 17.3 ppm (<sup>13</sup>C NMR). The IR spectrum shows a strong absorption band at 2161 cm<sup>-1</sup>, which is assigned to the C $\equiv$ N stretching vibration of coordinated CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ligand, along with a strong bands at 1640 cm<sup>-1</sup> derived from the C=N stretching mode of imino groups of the azanickellacyclopentene skeleton. These spectroscopic data are consistent with the molecular structure of **1** determined by X-ray diffraction analysis (vide infra). Spectroscopic data of bromo and chloro homologues of 1, i.e. 3 and 4, are almost identical with those of 1. The triflate 2 also gives similar spectra to 1; however, it is worthwhile to point out that <sup>1</sup>H resonance of the methyl group of the azanickellacyclopentene backbone shows significant upfield shift, and  $v_{C} \equiv_{NAr}$  absorption is shifted to a higher wavenumber compared with those of  $1(0.48 \text{ ppm}, \text{ and } 14 \text{ cm}^{-1}, \text{ respectively})$ . The dissociation of OTf anion from 2 in the solution state was suggested by low temperature <sup>19</sup>F NMR spectra. In fact, the single <sup>19</sup>F resonance at -78.8 ppm is consistent with a typical chemical shift due to the uncoordinated OTf anion in the literature, which generally appears around -79 ppm in CD<sub>2</sub>Cl<sub>2</sub> shifted to higher field by 1–2 ppm compared with the coordinated OTf [9]. Since no dynamic behavior was observed at the temperature range between room temperature to  $-90 \,^{\circ}$ C, **2** is likely to exist in the solvent stabilized form shown in Chart 2.

The molecular structures of 1, 2, 3, and 4 were unequivocally determined by X-ray diffraction analysis; molecular structures of 2 and 3 are shown in Fig. 1, and representative bond lengths and angles are summarized in Table 1. Although OTf ligand in 2 is dissociated in the solution state, it is coordinated to the nickel center in the solid state. All of these four complexes have an azanickellacyclopentene framework, in which one nitrogen atom of the imino



Scheme 2. Synthesis of azanickellacyclopentene complexes 1-4.

Table 1	
Spectroscopic data of complexes 1-4	

		1	2	3	4
<sup>1</sup> H	CH₃ of xylyl CH₃ of nickellacycle	1.95, 2.09, 2.29, 2.32 2.20	1.97, 2.03, 2.21, 2.26 1.72	1.93, 2.05, 2.23, 2.35 2.18	1.94, 2.06, 2.23, 2.36 2.18
	Ph	6.53–6.58 (m, 1H), 6.62–6.65 (m, 2H), 6.88–6.94 (m, 3H), 7.00–7.09 (m, 3H), 7.15–7.16 (m, 3H)	6.43-6.47 (m, 3H), 6.51-6.58 (m, 1H), 6.62-6.66 (m, 1H), 6.83-6.94 (m, 5H), 6.96-7.00 (m, 1H)	6.50–6.56 (m, 1H), 6.60–6.67 (m, 2H), 6.86–6.95 (m, 3H), 6.98–7.03 (m, 2H), 7.05–7.11 (m, 1H), 7.13– 7.14 (m, 3H)	6.48–6.54 (m, 1H), 6.61–6.67 (m, 2H), 6.87–7.11 (m, 6H), 7.13–7.14 (m, 3H)
<sup>13</sup> C	(CH <sub>3</sub> ) Ph(C≡N)(C=N)	17.3, 18.6, 18.7, 19.1, 19.2 123.8, 124.1, 124.4, 126.1, 127.2, 127.7, 127.8, 128.0, 128.5, 128.9, 129.2, 134.7, 146.8, 148.6, 149.4, 164.5, 179.4, 186.4	16.1, 18.2, 18.3, 18.7, 19.1 124.1, 124.6, 125.8, 127.6, 128.1, 128.2, 128.9, 129.5, 135.8, 142.2, 148.6, 148.6, 163.7, 177.8, 179.9	17.2, 18.5, 18.6, 18.9, 19.2 123.8, 124.1, 124.4, 126.1, 127.2, 127.8, 127.9, 128.0, 128.4, 129.1, 129.3, 134.9, 148.7, 149.8, 164.7, 179.5	17.1, 18.5, 18.6, 18.8, 19.2 123.7, 124.0, 124.4, 126.0, 127.1, 127.7, 127.9, 128.4, 128.6, 129.1, 129.4, 134.9, 144.1, 148.7, 150.1, 164.9, 179.4, 184.1
IR	(C≡N) (C=N)	2161 1627	2175 1640	2164 1628	2175 1633



Chart 2. Possible dissociation/coordination process.

moiety and a carbon atom are bonded to the square planar nickel center. The complex 1, 2, and 3 exhibit a small distortion from the square planar geometry of nickel: the C(5) atoms of 1, 2, and 3 lie slightly out of the least square plane around Ni, and the deviation from the plane is 0.2258 Å, 0.2183 Å, and 0.1521 Å, respectively. In contrast, the C(5) atom of **4** lies completely on the square plane around Ni, and the sum of the angles around Ni is 360.0°. Conformation of the five-membered azanickellacyclopentene ring can be described as an envelope form, in which the C(4) atom is out of the plane defined by Ni, N(1), C(2), and C(3) (deviation from the plane is 0.6614 Å for 1, 0.6176 Å for 2, 0.6429 Å for **3**, 0.5374 Å for **4**, respectively). In the molecular structure of Carmona's azanickellacyclopentene chloride complex bearing 'Bu-imino moieties, the five-membered azanickellacycle adopts the similar envelope form, however, the deviation of the C(4) atom from the plane is more significant than our complexes 1-4 (Carmona's complex reportedly contains two independent molecules in the unit cell, and the deviations from the plane are 1.0193 and 1.0299 Å) [7]. This may be due to the more crowded steric environment given by the <sup>t</sup>Bu group. In contrast, in the previously reported azapalladacycle complexes bearing iodide or chloride ligands on palladium prepared by triple insertion of CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> [10], the five-membered azapalladacycles also have an envelope conformation with the deviation of the C(4) atom ca. 0.55 Å. The torsion angle of N(2)–C(3)–C(4)–N(3) is 58.37° (1), 51.28° (2), 58.67° (3) and 42.52° (4), respectively. The Ni–X (X = I, OTf, Br, Cl) bond length is decreased in the order, 1 [2.5770(8) Å] > 3 [2.3803(4) Å] > 4 [2.2287(5) Å] > 2 [1.988(2) Å]. Other bond lengths and angles of 1–4 are nearly identical, and the C–N bond length of the coordinated CNC<sub>6</sub>H<sub>3</sub>–2,6-Me<sub>2</sub> ligand (ca. 1.16 Å) is similar to those of the known Ni(II)-isocyanide complexes [11]. The C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ring on the N(1) atom of 4 is nearly perpendicular to the square plane around nickel, and the dihedral angle is 87.39°, while that of the others is slightly more acute than 4 (82.56° for 1, 75.04° for 2, and 80.44° for 3). In all complexes, the phenyl ring of the CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ligand (Table 2).

As mentioned in the introduction, the nickellacyclopentane complexes have a diimino moiety of the azanickellacyclopentene backbone, which is capable of coordinating to the second metal "MBr<sub>2</sub>" fragment; this leads to the formation of (hetero)bimetallic complexes (Scheme 3). As a typical example, treatment of **1** with ZnBr<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>/EtOH at room temperature for 24 h, followed by recrystallization from CH2Cl2/hexane gave rise to Ni-Zn (hetero)bimetallic complex 5a in 77% yield, which was characterized by NMR, IR, X-ray crystallographic study, and elemental analysis (vide infra). Similarly, the Ni-Zn (5b) homologue was synthesized in 67% yield, and characterized by spectroscopy. Studies on the reactions of the nickellacyclopentane with CoBr<sub>2</sub>, FeBr<sub>2</sub>, or NiBr<sub>2</sub> were hampered due to the paramagnetism of the products; however, consumption of almost all of the starting complex 1 or 3 checked by NMR spectroscopy strongly suggests the formation of the corresponding (hetero)bimetallic complexes. In the reaction of 1 with CoBr<sub>2</sub>, a formed Ni-Co (6a) complexes was isolated and characterized by crystallography.

In the <sup>1</sup>H NMR spectrum of the Ni–Zn (hetero)bimetallic complexes, four singlets due to the  $C_6H_3$ -2,6-Me<sub>2</sub> groups appeared at 2.24, 2.34, 2.47, and 2.69 ppm for **5a**, and 2.23, 2.33, 2.46, and 2.68 ppm for **5b**, respectively, whereas four signals were observed



Fig. 1. Molecular structures of 1, 2, 3, and 4 with 50% probability ellipsoids. Hydrogen atoms were omitted for clarity.

 Table 2

 Representative bond lengths and angles for azanickellacyclopentene complexes 1-4.

	1	2	3	4
Bond length (Å)				
Ni-X	2.5770(8)	1.988(2)	2.3803(4)	2.2287(5)
Ni-N(1)	1.969(4)	1.942(2)	1.968(2)	1.937(2)
Ni-C(4)	1.906(5)	1.882(2)	1.892(2)	1.899(2)
Ni-C(5)	1.821(4)	1.838(2)	1.816(2)	1.814(2)
N(1)-C(2)	1.317(8)	1.290(3)	1.284(3)	1.290(2)
C(2) - C(3)	1.480(6)	1.484(4)	1.483(2)	1.480(2)
C(3) - C(4)	1.505(9)	1.499(3)	1.504(3)	1.512(2)
N(2)-C(3)	1.274(8)	1.272(3)	1.264(3)	1.273(2)
N(3)-C(4)	1.255(6)	1.261(3)	1.269(2)	1.267(2)
N(4)-C(5)	1.159(6)	1.154(3)	1.153(2)	1.161(2)
Bond angles (°)				
X-Ni-N(1)	97.2(1)	89.39(8)	96.41(5)	94.15(5)
X-Ni-C(4)	173.2(2)	171.54(9)	174.45(7)	178.00(6)
X-Ni-C(5)	91.4(2)	97.71(9)	92.23(8)	87.73(6)
N(1)-Ni-C(5)	169.2(3)	167.12(11)	169.21(11)	177.90(8)
Ni-N(1)-C(2)	113.9(3)	114.6(2)	114.71(12)	116.36(13)
N(1)-C(2)-C(3)	111.8(5)	112.4(2)	112.4 (2)	112.6(2)
C(2)-C(3)-C(4)	111.0(5)	110.9(2)	109.7(2)	110.8(2)
Ni-C(4)-C(3)	103.9(3)	105.4(2)	104.99(13)	106.62(14)
Ni-C(5)-N(4)	178.1(6)	174.3(2)	177.2(2)	173.2(2)

at around 20 ppm in the <sup>13</sup>C NMR spectrum. It should be noted that a <sup>1</sup>H resonance due to the methyl group of the azanickellacyclopentene backbone appeared at around 1.45 ppm for both **5a** and **5b**, which was higher by ca. 0.75 ppm than that of mononuclear azanickellacyclopentene precursor **1**. This significant upfield shift is attributed to effective shielding of the methyl group of the nickellacyclopentene skeleton by one of the phenyl rings of the C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> groups of the diimino moiety (*vide infra*). The absorption band due to the coordinated CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ligand is sensitive to the halogen ligand, which appeared at  $2165 \text{ cm}^{-1}$  for **5a** and  $2183 \text{ cm}^{-1}$  for **5b**. Although the NMR data of the CoBr<sub>2</sub> homologue **6a** gave only broad signals, the formation of the expected bimetallic complex was confirmed by IR and elemental analysis. IR spectrum of **6a** shows a strong absorption band at  $2159 \text{ cm}^{-1}$ , which is assigned to the C=N stretching vibration of coordinated CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ligand. The result of the elemental analysis is consistent with the formulation of the Ni–Co (hetero)bimetallic complex.

The crystals of **5a** and **6a** suitable for X-ray diffraction analysis were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane. The ORTEP drawing (Fig. 2) reveals that the coordination geometry around the nickel is square planar, and the arrangement around the zinc or cobalt center can be described as slightly distorted tetrahedral. Interestingly, the orientation of the  $C_6H_3$ -2,6-Me<sub>2</sub> group on the N(2) atom is flipped to the opposite side compared with that of the parent complex **1**, which leads to the effective shielding of the methyl group of the azanickellacyclopentene backbone as observed in the <sup>1</sup>H NMR spectrum. In addition, coordination of ZnBr<sub>2</sub> or CoBr<sub>2</sub> fragments also triggers the structural change over the nickellacyclopentene framework, in which planarity of the five-membered ring is increased. Thus, the C(4) atom lies nearly on the leastsquare plane defined by Ni, N(1), C(2), and C(3) (deviation from the plane is 0.1613 Å for **5a** and 0.1510 Å for **6a**) (Table 3). The dihedral angle between the Ni–N(1)–C(2) and Ni–C(4)–C(3) plane is 19.597° for 5a and 20.284° for 6a. The planarity around Ni is decreased by formation of the (hetero)bimetallic complex; the C(5)atom is out of the least-square plane around Ni for 0.6606 Å (5a) and 0.6411 Å (**6a**), and the sum of the angles around Ni is 366° (5a) and  $365.9^{\circ}$  (6a), respectively. The torsion angle of N(2)-C(3)-C(4)-N(3) is 2.45° (5a) and 1.11° (6a), respectively, both of which are significantly decreased due to the complexation of the



Scheme 3. Synthesis of bimetallic complexes 5-8.



Fig. 2. Molecular structures of 5a (left) and 6a (right) with 50% probability ellipsoids. Hydrogen atoms were omitted for clarity.

 Table 3

 Representative bond lengths and angles for bimetallic complexes 5a and 6a.

	5a	6a
Bond length (Å)		
Ni–I	2.481(1)	2.493(1)
M-Br(1)	2.394(1)	2.387(1)
M-Br(2)	2.354(1)	2.358(1)
Ni-N(1)	1.941(8)	1.918(7)
Ni-C(4)	1.863(8)	1.863(7)
Ni-C(5)	1.824(9)	1.821(8)
M-N(2)	2.115(7)	2.053(6)
M-N(3)	2.062(7)	2.034(7)
N(1)-C(2)	1.27(1)	1.30(1)
C(2)-C(3)	1.48(1)	1.47(1)
C(3)-C(4)	1.53(1)	1.53(1)
N(2)-C(3)	1.28(1)	1.28(1)
N(3)-C(4)	1.29(1)	1.288(9)
N(4)-C(5)	1.16(1)	1.17(1)
Bond angles (°)		
X-Ni-N(1)	97.9(2)	97.7(2)
X-Ni-C(4)	162.8(2)	162.8(2)
X-Ni-C(5)	87.8(3)	87.6(3)
N(1)-Ni-C(5)	159.6(3)	160.1(3)
N(2)-M-N(3)	79.1(3)	79.9(2)
Br(1)-M-Br(2)	112.18(5)	108.62(5)
Ni-N(1)-C(2)	116.5(6)	117.6(5)
N(1)-C(2)-C(3)	113.6(8)	111.6(7)
C(2)-C(3)-C(4)	110.6(7)	111.4(6)
Ni-C(4)-C(3)	111.5(5)	111.5(5)
Ni-C(5)-N(4)	168.6(7)	168.5(7)

diimino moieties with the second transition metal fragments. The bond lengths of Ni–I (2.481(1) Å for **5a** and 2.493(1) Å for **6a**) are significantly shorter than that of **1** (2.5770(8) Å), which may be due to the effective delocalization of the  $\pi$ -electron over the nick-ellacyclopentene skeleton containing a heterometal at the diimino substructure. The C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ring on the N(1) atom of **5a** and **6a** is nearly perpendicular to the square plane around nickel (dihedral angles are 88.409° (**5a**) and 81.592° (**6a**)). Two C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> rings of the diimino moieties are also arranged perpendicularly to the least-square plane defined by M–N(2)–C(3)–C(4)–N(3) atoms, and the dihedral angles are 83.502° and 86.746° for **5a**, and 82.767° and 86.712° for **6a**, respectively. The bond lengths of C N bond (1.16(1) Å for **5a** and 1.17(1) Å for **6a**) are comparable to that of **1**.

#### 2.2. Ethylene polymerization catalyzed by 1-8

As described earlier, the azanickellacyclopentene complex **1** having  $N-C_6H_3-2$ ,  $6-Me_2$  groups showed good reactivity towards catalytic ethylene polymerization in the presence of MAO, though no polyethylene was formed with the  $N-^tBu$  homologue of **1** reported by Otsuka [7c] under similar conditions. A series of ethylene

 Table 4

 Catalytic activities of azanickellacyclopentene complexes using MAO as activator<sup>a</sup>.

polymerization reactions were carried out to figure out the effect of halogeno ligand on the nickel and the aluminum activator as shown in Table 4. Polymerization was typically performed in a 100 mL stainless autoclave fitted with a Teflon inner tube in toluene (20 mL) for 20 min under 8 atm of ethylene gas in the presence of an Al activator at room temperature. When the polymerization was carried out with Cp<sub>2</sub>ZrCl<sub>2</sub> under similar conditions, the activity reached ca 2.0 kg/mmolZr h. This suggests that the activity over 1.0 kg/mmolNi h is a benchmark for the polymerization catalyst showing good activity. As shown in entries 1-3, Lewis acidic aluminum activators, Et<sub>2</sub>AlCl, Me<sub>2</sub>AlCl, and MAO, are well assist the polymerization with 1 to form polyethylene with similar melting points. Under similar conditions, almost no polymerization occurred using AlEt<sub>3</sub> (activity: 6 g/mmolNi h) or AlMe<sub>3</sub> (activity: 69 g/mmolNi h). A halogen or OTf ligand on the nickel atom also affects the activity. As shown in Table 4, the order of catalytic activity is  $2 > 3 \approx 1 > 4$  with MAO, whereas it is 2 > 1 > 3 > 4 with Et<sub>2</sub>AlCl. Activity of polymerization reached over 1 kg/mmolNi h in the case of 2/MAO, 2/Et<sub>2</sub>AlCl, and 1/Et<sub>2</sub>AlCl. It is of interest that inexpensive Et<sub>2</sub>AlCl showed better activity than MAO. The activity of polymerization is reproducible (672-1059 g/mmolNi h) when 200 equiv. of the aluminum activator is used based on 1. Careful removal of moisture is necessary for reproducible ethylene polymerization; however, it is worthwhile to point out that polymerization proceeds well in the presence of even 20 equiv. of the aluminum activator. In the polymerization assisted by 20 equiv. of MAO, the activity of 1 is 242 g/mmolNi h, and that of 2 is 395 mmolNi h.

Polyethylene obtained in the polymerization summarized in Table 4 has  $M_n$  = 61 000–130 000 with PDI = 2.4–4.2. The GPC profile is monomodal. <sup>13</sup>C{1H} NMR spectroscopy suggests that the polyethylene formed has relatively low branching content (~10C/ 1000C). Increase of polymer branches lowers  $T_m$  as shown in entries 1, 7, and 8.

In Table 5 are summarized the data for ethylene polymerization catalyzed by (hetero)bimetallic complexes. In entries 1-5 of this table, the experiments were performed under the same conditions as used in the polymerization shown in Table 4. Introduction of a second metal, ZnBr<sub>2</sub>, CoBr<sub>2</sub>, FeBr<sub>2</sub>, or NiBr<sub>2</sub>, to the diimino moiety of **1** apparently increased the catalytic activity (1.2–3.6 times as much as the activity of 1) as shown in entries 1-5. The high catalytic activity of the bimetallic catalysts prompted us to lower the amount of the aluminum activator (see Table 5 entry 6-13). Since the catalyst is sensitive to moisture and oxygen, the experiments with 20 equiv. of Al activator to the catalyst required higher bimetallic catalyst contents (10 µmol) to obtain reproducible TON data for the experiment using a 100 mL autoclave system. The activity of the (hetero)bimetallic catalysts [entries 7-9 (MAO), 11-13 (Et<sub>2</sub>AlCl)] was 2.5-5.2 times that of the monometallic catalyst [entries 6 (MAO) and 10 (Et<sub>2</sub>AlCl)]. Thus, the bimetallic catalysts, in particular those containing Fe as the second metal, apparently show excellent catalytic activity even in the presence of smaller

Entry	Catalyst	Al-cocatalyst	Yield (g)	Activity (g/mmol h)	$M_{\rm n}~( imes 10^4)$	$M_{ m w}( imes 10^4)$	$M_w/M_n$	$T_{\rm m}(^{\circ}{\rm C})$	Branch/1000C
1	1	MAO	0.197	591	7.9	26	3.3	125.0	8.3
2	1	AlEt <sub>2</sub> Cl	0.353	1059	8.2	30	3.7	128.3	6.6
3	1	AlMe <sub>2</sub> Cl	0.407	1221	-	-	-	127.4	-
4	2	MAO	0.385	1155	7.9	33	4.2	127.3	5.9
5	3	MAO	0.232	696	13.0	32	2.4	133.0	2.4
6	4	MAO	0.174	522	12.0	37	3.0	132.1	3.4
7	2	AlEt <sub>2</sub> Cl	0.413	1239	6.1	23	3.9	123.4	11.5
8	3	AlEt <sub>2</sub> Cl	0.329	987	6.6	28	4.2	122.6	9.7
9	4	AlEt <sub>2</sub> Cl	0.201	603	8.0	30	3.7	128.1	6.1

<sup>a</sup> All reactions were carried out in a 100 mL stainless-steel autoclave in the presence of 200 equiv. of Al-cocatalysts based on the charged nickel catalysts (1 µmol) at room temperature for 20 min. Ethylene (0.8 MPa) was applied.

Table	5
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Catalytic	activities	of	bimetallic	complexes <sup>a</sup> .
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Entry	Catalyst	Cat (µmol)	A-cocatalyst	Al/Ni	Yield (g)	Activity (g/mmol h)	$M_{\rm n}( imes 10^4)$	$M_{ m w}~( imes 10^4)$	$M_w/M_n$	$T_{\rm m}(^{\circ}{\rm C})$	Branch/1000C
1	1	1	MAO	200	0.197	591	7.9	26	3.3	125.0	8.3
2	5a	1	MAO	200	0.344	1032	8.8	29	3.3	128.1	4.2
3	6a	1	MAO	200	0.234	702	9.7	28	2.9	128.1	4.3
4	7a	1	MAO	200	0.540	1620	5.6	19 <sup>b</sup>	3.4	127.4	7.6
5	8	1	MAO	200	0.709	2127	6.7	24 <sup>b</sup>	3.6	132.9	4.4
6	3	10	MAO	20	0.329	99	-	-	-	-	-
7	5b	10	MAO	20	0.918	275	6.9	21	3.1	126.0	9.9
8	6b	10	MAO	20	0.946	284	7.5	22	2.9	127.9	8.3
9	7b	10	MAO	20	1.545	464	2.8	13	4.7	126.2	6.5
10	3	10	AlEt <sub>2</sub> Cl	20	0.314	102	-	-	-	-	-
11	5b	10	AlEt <sub>2</sub> Cl	20	0.946	284	6.3	18	2.9	122.3	28.1
12	6b	10	AlEt <sub>2</sub> Cl	20	0.833	250	7.3	20	2.8	120.4	24.1
13	7b	10	AlEt <sub>2</sub> Cl	20	1.756	527	3	15	4.9	121.3	17.6

<sup>a</sup> All reactions were carried out in a 100 mL stainless-steel autoclave in the presence of 20 or 200 equiv. of Al-cocatalysts based on the charged nickel catalysts (1 or 10 μmol) at room temperature for 20 min. Ethylene (0.8 MPa) was applied.

<sup>b</sup> The GPC profile is bimodal.

amounts of Al activator. Use of Et<sub>2</sub>AlCl provides somewhat higher activity than MAO. There is no significant difference in  $M_n$  (28 000–97 000) among the polymers obtained by the experiments shown in Table 5. Although the polyethylene formed in most of the experiments in this table has only a small number of polymer branches (<10, entries 1–5, 7–9), it may be worthwhile to point out that polyethylene formed by the experiments shown in entry 11–13 has relatively lower  $T_m$  (120–122 °C), of which the <sup>13</sup>C NMR spectrum showed the existence of a significantly higher number of branches (17.6–28.1). Of interest is the bimodal GPC profile of the polymer obtained in the experiments using Ni–Fe and Ni–Ni bimetallic catalysts (See Supplementary data in detail), which will be discussed later.

#### 2.3. Mechanistic considerations

The above described features of mono- and bimetallic nickellacyclopentanes as an ethylene polymerization catalyst can be summarized as follows: (1) catalytic activity of the monometallic catalyst **3** (X = Br) is 380 times higher than trans-( $CNC_6H_3$ -2,6-Me<sub>2</sub>)NiBr<sub>2</sub> under the same conditions; however, that is ca. one third of the Brookhart catalyst, [(C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)N=C(Me)C(Me)=N(C<sub>6</sub>H<sub>3</sub>- $2,6-Me_2$ ]NiBr<sub>2</sub>; (2) the N-<sup>t</sup>Bu analogue of the monometallic catalyst 1 (X = I) showed no catalytic activity towards ethylene polymerization, (3) activity is affected by the halogeno ligand of the monometallic catalysts, **1–4**, and the order is  $X = OTf > I \approx Br > Cl$ . This order is consistent with the ease of dissociation of X from the nickel center, which is estimated by solution dynamics using variable temperature NMR; (4) enhancement of the catalytic activity is achieved by introduction of the second metal. The order is Ni > Fe > Co = Zn; (5) In supporting experiments, it was confirmed that iron, cobalt, and zinc homologues of the Brookhart catalyst,  $[(C_6H_3-2,6-Me_2)N=C(Me)C(Me)=N(C_6H_3-2,6-Me_2)]-MBr_2$  (M=Fe, Co, Ni), showed no catalytic activity towards ethylene polymerization [12,13].

As a possible mechanism to explain all of the features described above, we proposed catalytic mechanism shown in Scheme 4. Reaction of the monometallic catalyst with the alkylaluminum activator results in dissociation of an isocyanide ligand and displacement of a halogeno ligand by an alkyl group to give a coordinatively unsaturated intermediate I. The dissociation of the isocyanide would be assisted by Lewis acidity of MAO or Et<sub>2</sub>AlCl, whereas the halogeno ligands are good leaving group that will be readily displaced by Me or Et groups leading to formation of the Ni-C bond. Coordination of ethylene to I forms an intermediate II; insertion of ethylene between the Ni–C bond in II initiates the polymerization. Although the chain propagation takes place on the cationic nickel species in the Brookhart catalyst, the catalytic species for the chain propagation is neutral in the mononuclear nickel complexes presented in this paper. It is well known from mechanistic studies on the Brookhart catalyst that steric demands around the nickel center, which are produced by the ortho-substituents of the N-aryl moieties nearby, are important for the smooth propagation to form polymer. This clearly explains the dramatic increase of the catalytic activity by changing the N-<sup>t</sup>Bu groups in Otsuka's complex [7c] by the N-C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> groups; a structure of the intermediate II shows effective blocking of the coordination sphere by 2,6-dimethyl groups in the N-C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> ligand. One explanation for the rate enhancement is that the second metal species acts as the promoter for the polymerization. Introduction of ZnX<sub>2</sub> or CoX<sub>2</sub> species to the mononuclear nickel complex provides an activity enhancement, while the GPC profile of formed polyethylene is monomodal. Since Zn and Co diimines showed no catalytic activity towards ethylene polymerization in the presence of MAO, both of Zn and Co center are not involved in the catalytic cycle. It should be noted that the molecular structures of 5 and 6 were determined by crystallography, indicating that the incorporation of the second metal fragment to the diimino moiety makes the ring structure more rigid. The increased rigidity of the azanickellacyclopentene backbone would lead to an effective stabilization of the azanickellacyclopentene framework during polymerization. Similar influence of the rigidity of the ligand backbone was reported by Wass et al., in which the nickel complexes having NMe, CH<sub>2</sub>, and phenylene-bridged diphosphine ligand show some



Scheme 4. Possible reaction mechanism for ethylene polymerization.

catalytic activity for polymerization of ethylene, whereas ethyl- or propyl-bridged diphosphine complexes exhibited no activities [14]. The incorporation of the second metal results in increased planarity of the azanickellacyclopentene skeleton and increased steric repulsion between the  $C_6H_3$ -2,6-Me<sub>2</sub> ring on N(3) and the second metal. These two factors force two  $C_6H_3$ -2,6-Me<sub>2</sub> rings connected to N(3) and N(1) close to the nickel center. It is known that ortho-substituents in the Brookhart catalyst play a key role in increasing activities by blocking the apical coordination sites of the square-planar nickel species. In similar fashion, the orthomethyl groups on the  $C_6H_3$ -2,6-Me<sub>2</sub> rings close to the nickel center could effectively produce the sterically suitable circumstances around the nickel center in the active species.

The rate enhancement mechanism in which the second metal acts as the promoter also explains the second metal effect of NiX<sub>2</sub> giving significantly higher activity. However, it may be worthwhile to speculate that the Ni<sub>2</sub> bimetallic catalysts may have two active centers inside and outside of the metallacylic skeleton; the active species of the former is neutral similar to that produced from **1**, whereas the cationic active center would be formed from the second NiBr<sub>2</sub> species deduced from the analogy to the Brookhart catalyst. Bimodal GPC profiles may support this speculation. The polymerization with the Ni–Fe bimetallic catalyst **7** may involve similar bimetallic active centers, which showed high catalytic activity to give polyethylene having a bimodal GPC profile.

#### 3. Conclusion

As described above, we have been successful in preparing new ethylene polymerization catalysts, which have a special structural feature with an azanickellacyclopentene skeleton. The catalytic activity of the monometallic catalyst 1-4 is ca. one third of the Me<sub>2</sub>)]NiBr<sub>2</sub>; however, it is significantly higher than trans-(CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)NiBr<sub>2</sub> under the same conditions. It should be noted that inexpensive AlEt<sub>2</sub>Cl can be used as the cocatalyst of this catalyst system. Activities of mononuclear azanickellacyclopentene complexes is increased in the order,  $M-Cl < M-I \approx M-Br < M-I$ OTf; this is explained by the order of X as a leaving group from the nickel center. The active species for the polymerization is suggested to be neutral, in other words, the catalyst is more close to the SHOP catalyst but the Brookhart catalyst. The catalytic activity is significantly increased by introduction of the second metal to the diimio moiety of 1, which forms a series of heterobimetallic complexes. Order of the polymerization activity is Ni-Ni > Fe-Ni > Co-Ni=Zn-Ni. Increased rigidity of the azanickellacyclopentene skeleton provided by incorporation of the second metals at the diimino moiety is a key factor in understanding the catalytic activity. In the case of Ni-Ni and Fe-Ni bimetallic catalysts, two metals in the catalyst molecule may produce individual active centers leading to high catalytic activity and formation of polyethylene having bimodal GPC features. The present results clearly demonstrate the mono and bimetallic new C-N SHOP type compounds as an unique postmetallocene ethylene polymerization catalyst.

### 4. Experimental

#### 4.1. General procedures

The manipulation of air and moisture sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line. All solvents were distilled over appropriate drying reagents prior to use (toluene, ether, THF, hexane, Ph<sub>2</sub>CO/Na, acetone, MS

4A). <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR chemical shifts ( $\delta$  values) were given in ppm relative to the solvent signal (<sup>1</sup>H, <sup>13</sup>C) or standard resonances (<sup>19</sup>F; external CF<sub>3</sub>COOH). IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Melting points were measured on a Yanaco micro melting point apparatus. HRMS spectrum was recorded on a JEOL Mstation JMS-70 apparatus. Elemental analyses were performed by a Perkin–Elmer 2400/CHN analyzer. Starting material, Ni(COD)<sub>2</sub> [15], CNC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub> and complex **1** [8], were synthesized by the method reported in the literature.

#### 4.2. Preparation of Iodo [1,2,3-tris(2,6-

#### dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel (1)

To a solution of Ni(COD)<sub>2</sub> (5.8 g, 21.2 mmol) in benzene (50 mL) was added a solution of 2,6-xylylisocyanide (11.1 g, 85.2 mmol) in benzene (100 mL), the mixture was stirred at room temperature for 2 h, and the resulting solution was concentrated in vacuo. The obtained pale yellow residue was washed with hexane three times (in total 150 mL), and dissolved in benzene (100 mL). To this benzene solution of crude Ni(CN-C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)<sub>4</sub> was added methyl iodide (6.6 mL, 106 mmol). After heating under reflux for 24 h, the reaction mixture was concentrated in vacuo, and the brown residue was washed with hexane (250 mL). Purification by recrystallization from dichloromethane/hexane gave the desired complex 1 in 95% yield (11.1 g) as dark red platelets. Mp 141 °C (dec). Anal. Calc. for C<sub>37</sub>H<sub>39</sub>N<sub>4</sub>I<sub>1</sub>Ni<sub>1</sub>: C, 61.27; H, 5.42; N, 7.72. Found: C, 61.48; H, 5.44; N, 7.61%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  1.95 (s, 6H, CH<sub>3</sub> of xylyl), 2.09 (s, 6H, CH<sub>3</sub> of xylyl), 2.20 (s, 3H, CH<sub>3</sub>), 2.29 (s, 6H, CH<sub>3</sub> of xylyl), 2.32 (s, 6H, CH<sub>3</sub> of xylyl), 6.53-6.58 (m, 1H, Ph), 6.62-6.65 (m, 2H, Ph), 6.88-6.94 (m, 3H, Ph), 7.00-7.09 (m, 3H, Ph), 7.15-7.16 (m, 3H, Ph). <sup>13</sup>C{1H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): *δ* 17.3 (s, CH<sub>3</sub>), 18.6 (s, CH<sub>3</sub>), 18.7 (s, CH<sub>3</sub>), 19.1 (s, CH<sub>3</sub>), 19.2 (s, CH<sub>3</sub>), 123.8, 124.1, 124.4, 126.1, 127.2, 127.7, 127.8, 128.0, 128.5, 128.9, 129.2, 134.7, 146.8. 148.6. 149.4. 164.5. 179.4. 186.4. IR (KBr):  $v_{C=N}(cm^{-1}) = 2161 (s), v_{C}=_{N}(cm^{-1}) = 1627 (s).$ 

# 4.3. Preparation of trifluoromethanesulfonate[1,2,3-tris(2,6dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel (2)

In a 50 mL Schlenk tube were placed complex 1 (800 mg, 1.10 mmol) and AgOTf (330 mg, 1.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The resulting solution was stirred for 4 h at room temperature, during which the color of the solution turned red. The solution was filtered through a pad of celite, then the solvent was removed in vacuo. The remaining dark red solid was dissolved in toluene (30 mL) and layered with hexane (60 mL), from which orange crystals of 2 were obtained in 89% yield (730 mg). Mp 105 °C (dec). Anal. Calc. for C<sub>38</sub>H<sub>39</sub>N<sub>4</sub>O<sub>3</sub>S<sub>1</sub>F<sub>3</sub>Ni: C, 61.27; H, 5.42; N, 7.72. Found: C, 61.48; H,5.44; N, 7.61%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  1.72 (s, 3H, CH<sub>3</sub>), 1.97 (s, 6H, CH<sub>3</sub> of xylyl), 2.03 (s, 6H, CH<sub>3</sub> of xylyl), 2.21 (s, 6H, CH<sub>3</sub> of xylyl), 2.26 (s, 6H, CH<sub>3</sub> of xylyl), 6.43-6.47 (m, 3H, Ph), 6.51-6.58 (m, 1H, Ph), 6.62-6.66 (m, 1H, Ph), 6.83-6.94 (m, 5H, Ph), 6.96-7.00 (m, 1H, Ph). <sup>13</sup>C{1H} NMR (150 MHz,  $C_6D_6$ , room temperature):  $\delta$  16.1 (s, CH<sub>3</sub>), 18.2 (s, CH<sub>3</sub>), 18.3 (s, CH<sub>3</sub>), 18.7 (s, CH<sub>3</sub>), 19.1 (s, CH<sub>3</sub>), 124.1, 124.6, 125.8, 127.6, 128.1, 128.2, 128.9, 129.5, 135.8, 142.2, 148.6, 148.6, 163.7, 177.8, 179.9. <sup>19</sup>F{1H} NMR (565 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  –78.8 (s, CF<sub>3</sub>). IR (KBr):  $v_{C} \equiv N(cm^{-1}) = 2175$  (s),  $v_{C} = N(cm^{-1}) = 1640(s), v_{S} = 0(cm^{-1}) = 1320, 1233, 1016 (s).$ ESI-(HI)-MS. Calc. for  ${}^{12}C_{37}{}^{1}H_{39}{}^{14}N_{4}{}^{59}Ni_{1}$ : 597.2528. Found: 597.2531.

## 4.4. Preparation of bromo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel (**3**)

In a 20 mL Schlenk tube were placed complex 2 (490 mg, 0.66 mmol) and LiBr (88 mg, 1.01 mmol) in acetone (5 mL). The resulting solution was stirred for 16 h at room temperature. The solution was filtered through a pad of celite, then the solvent was removed in vacuo. The remaining red solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and layered with hexane (30 mL), from which red crystals of **3** were obtained in 72% yield (320 mg). Mp 156 °C (dec). Anal. Calc. for C<sub>37</sub>H<sub>39</sub>N<sub>4</sub>Br<sub>1</sub>Ni<sub>1</sub>: C, 65.51; H, 5.80; N, 8.26. Found: C, 65.48; H, 5.94; N, 8.13%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  1.93 (s, 6H, CH<sub>3</sub> of xylyl), 2.05 (s, 6H, CH<sub>3</sub> of xylyl), 2.18 (s, 3H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub> of xylyl), 2.35 (s, 6H, CH<sub>3</sub> of xylyl), 6.50-6.56 (m, 1H, Ph), 6.60-6.67 (m, 2H, Ph), 6.86-6.95 (m, 3H, Ph), 6.98-7.03 (m, 2H, Ph), 7.05-7.11 (m, 1H, Ph), 7.13-7.14 (m, 3H, Ph). <sup>13</sup>C{1H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  17.2 (s, CH<sub>3</sub>), 18.5 (s, CH<sub>3</sub>), 18.6 (s, CH<sub>3</sub>), 18.9 (s, CH<sub>3</sub>), 19.2 (s, CH<sub>3</sub>), 123.8, 124.1, 124.4, 126.1, 127.2, 127.8, 127.9, 128.0, 128.4, 129.1, 129.3, 134.9, 148.7, 149.8, 164.7, 179.5. IR (KBr):  $v_{C=N}(cm^{-1}) = 2164$  (s),  $v_{C=N}(cm^{-1}) = 1628$  (s). HR-MS. Calc. for  ${}^{12}C_{37}{}^{1}H_{39}{}^{14}N_{4}{}^{81}Br_{1}{}^{59}Ni_{1}$ : 678.1690. Found: 678.1700.

#### 4.5. Preparation of chloro[1,2,3-tris(2,6-dimethylphenylimino)butyl]-(2,6-dimethylphenylisocyanide)nickel (**4**)

In a 50 mL Schlenk tube were placed complex 2 (1290 mg, 1.73 mmol) and LiCl (88 mg, 2.08 mmol) in acetone (40 mL). The resulting solution was stirred for 16 h at room temperature. The solution was filtered through a pad of celite, then the solvent was removed in vacuo. The remaining red solid was dissolved in toluene (20 mL) and layered with hexane (50 mL), from which red crystals of 4 were obtained in 63% yield (639 mg). Mp 160 °C (dec). Anal. Calc. for C37H39N4Cl1Ni1: C, 70.11; H, 6.20; N, 8.84. Found: C, 70.10; H, 6.35; N, 8.82%.  $^1\mathrm{H}$  NMR (600 MHz,  $\mathrm{C_6D_6}$ , room temperature):  $\delta$  1.94 (s, 6H, CH<sub>3</sub> of xylyl), 2.06 (s, 6H, CH<sub>3</sub> of xylyl), 2.18 (s, 3H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub> of xylyl), 2.36 (s, 6H, CH<sub>3</sub> of xylyl), 6.48-6.54 (m, 1H, Ph), 6.61-6.67 (m, 2H, Ph), 6.87-7.11 (m, 6H, Ph), 7.13–7.14 (m, 3H, Ph). <sup>13</sup>C{1H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  17.1 (s, CH<sub>3</sub>), 18.5 (s, CH<sub>3</sub>), 18.6 (s, CH<sub>3</sub>), 18.8 (s, CH<sub>3</sub>), 19.2 (s, CH<sub>3</sub>), 123.7, 124.0, 124.4, 126.0, 127.1, 127.7, 127.9, 128.4, 128.6, 129.1, 129.4, 134.9, 144.1, 148.7, 150.1, 164.9, 179.4, 184.1. IR (KBr):  $v_C \equiv N(cm^{-1}) = 2175$  (s),  $v_C = N(cm^{-1}) = 1633$ (s). ESI-(HI)-MS. Calc. for  ${}^{12}C_{37}{}^{1}H_{39}{}^{14}N_{4}{}^{35}Cl_{1}{}^{59}Ni_{1}$ : 632.2217. Found: 632.2218.

# 4.6. Preparation of {iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel}(dibromo)zinc(II) (**5a**)

To a solution of ZnBr<sub>2</sub> (170 mg, 0.75 mmol) in EtOH (10 mL) was added a solution of 1 (530 mg, 0.73 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). After it was stirred at room temperature for 24 h, the reaction mixture was concentrated under a reduced pressure. The remaining crude product was used for ethylene polymerization without further purification. For the characterization of the product, purification by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane gave the desired complex **5a** in 77% (540 mg) yield as dark red crystals. Mp 139 °C (dec). Anal. Calc. for C<sub>37</sub>H<sub>39</sub>N<sub>4</sub>Br<sub>2</sub>Cl<sub>1</sub>Ni<sub>1</sub>Zn<sub>1</sub>: C, 46.75; H, 4.53; N, 5.89. Found: C, 46.45; H, 4.53; N, 5.68%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  1.45 (s, 3H, CH<sub>3</sub>), 2.24 (s, 6H, CH<sub>3</sub> of xylyl), 2.34 (s, 6H, CH<sub>3</sub> of xylyl), 2.47 (s, 6H, CH<sub>3</sub> of xylyl), 2.69 (s, 6H, CH<sub>3</sub> of xylyl), 6.48-6.52 (m, 1H, Ph), 6.82-6.86 (m, 2H, Ph), 6.95-6.97 (m, 2H, Ph), 6.98–7.00 (m, 1H, Ph), 7.11–7.17 (m, 6H, Ph). <sup>13</sup>C{1H} NMR (150 MHz,  $C_6D_6$ , room temperature):  $\delta$  18.5 (s,  $CH_3$ ), 19.2 (s,  $CH_3$ ), 19.4 (s, CH<sub>3</sub>), 20.0 (s, CH<sub>3</sub>), 20.8 (s, CH<sub>3</sub>), 127.2, 127.2, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.4, 128.6, 128.7, 128.8,

129.2, 129.3, 129.4, 133.7, 142.7, 148.3, 167.9, 176.2. IR (KBr):  $v_{C \equiv N}(cm^{-1}) = 2165$  (s).

### 4.7. Preparation of {bromo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel}(dibromo)zinc(II) (**5b**)

In a 20 mL Schlenk tube were placed complex 3 (71 mg, 0.11 mmol) and ZnBr<sub>2</sub> (30 mg, 0.13 mmol) in Et<sub>2</sub>O (10 mL). The resulting suspension was stirred for 8 h at room temperature. The solvent was removed in vacuo, and the residue was washed with hexane (30 mL). The remaining dark red solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), centrifuged to remove the remaining solid, and layered with hexane (60 mL), from which red crystals of 5b were obtained in 67% yield (68 mg). The crystals were used for the ethylene polymerization. Mp 144 °C (dec). <sup>1</sup>H NMR (600 MHz,  $C_6D_6$ , room temperature):  $\delta$  1.46 (s, 3H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub> of xylyl), 2.33 (s, 6H, CH<sub>3</sub> of xylyl), 2.46 (s, 6H, CH<sub>3</sub> of xylyl), 2.68 (s, 6H, CH<sub>3</sub> of xylyl), 6.48-6.52 (m, 1H, Ph), 6.82-6.86 (m, 2H, Ph), 6.92-7.01 (m, 2H, Ph), 7.09-7.14 (m, 4H, Ph), 7.15-7.16 (m, 3H, Ph). <sup>13</sup>C{1H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature):  $\delta$  17.1 (s, CH<sub>3</sub>), 18.5 (s, CH<sub>3</sub>), 18.6 (s, CH<sub>3</sub>), 18.8 (s, CH<sub>3</sub>), 19.2 (s, CH<sub>3</sub>), 123.7, 124.0, 124.4, 126.0, 127.1, 127.7, 127.9, 128.4, 128.6, 129.1, 129.4, 134.9, 144.1, 148.7, 150.1, 164.9, 179.4, 184.1. IR (KBr):  $v_{C=N}(cm^{-1}) = 2183$  (s),  $v_{C}=_{N}(cm^{-1}) = 1632$  (s).

# 4.8. Preparation of {iodo[1,2,3-tris(2,6-dimethylphenylimino)butyl](2,6-dimethylphenylisocyanide)nickel}(dibromo)cobalt(II) (**6a**)

In a 100 mL Schlenk tube were placed complex **1** (240 mg, 0.33 mmol) and CoBr<sub>2</sub> (72 mg, 0.33 mmol) in benzene (20 mL) and THF (5 mL). The resulting mixture was stirred for 24 h at room temperature, and the solvent was removed *in vacuo*. The obtained crude product was used for ethylene polymerization without further purification. The crystals of **6a** suitable for X-ray diffraction analysis can be isolated by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane as dark red crystals. Mp 193 °C (dec). *Anal*. Calc. for C<sub>37</sub>H<sub>39</sub>Br<sub>2</sub>Co<sub>1</sub>. N<sub>4</sub>I<sub>1</sub>Ni<sub>1</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 44.35; H, 4.02; N, 5.44. Found: C, 44.59; H, 3.99; N, 5.47%. IR (KBr):  $v_{c} \equiv_{N} (cm^{-1}) = 2159$  (s).

# 4.9. Preparation of Ni–Fe (**7a**, **7b**) and Ni–Ni (**8a**) (hetero)bimetallic complexes

As a typical example, to a solution of **1** (220 mg, 0.31 mmol) in benzene was added a solution of FeBr<sub>2</sub> (66 mg, 0.31 mmol) in THF. After stirring for 3 h, the reaction mixture was evacuated under vacuum. The resulting solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the crude product was used for the ethylene polymerization without further purification. The Ni(Br)–Fe (**7b**), and Ni(I)–Ni (**8**) (hetero)bimetallic complexes were prepared according to the similar procedure using complex **3** (100 mg, 0.15 mmol) and FeBr<sub>2</sub> (30 mg, 0.14 mmol) in Et<sub>2</sub>O/THF (10 mL/ 1 mL) for **7b**, and complex **1** (131 mg, 0.18 mmol) and (DME)NiBr<sub>2</sub> (56 mg, 0.18 mmol) in benzene (20 mL) for **8a**.

## 4.10. Ethylene polymerization

In a 100 mL stainless autoclave fitted with a Teflon inner tube was placed the precatalyst **1–8** (1 or 10  $\mu$ mol) and toluene (20 mL). A toluene solution of MAO (PMAO-S available from TOS-OH-FINECHEM Corp. 2.85 M in toluene) or a toluene solution of AlEt<sub>2</sub>Cl (1.0 M in toluene) was added via syringe (20 equiv. or 200 equiv. for precursor **1–8**) and the mixture was stirred for 1 h at room temperature. Then ethylene (0.8 MPa) was introduced, and the mixture was stirred at room temperature for 20 min. Unreacted ethylene was released, and methanol (10 mL) was added to

Table 6									
Crystallographic	data	for	1,	2,	3,	4,	5a	and	6a.

	1	2	3	4	5a	6a
Empirical formula	C37H39IN4Ni	C38H39F3O3SN4Ni	C37H39BrN4Ni	C37H39ClN4Ni	C37H39Br2IN4NiZn·CH2Cl2	C37H39N4Br2CoINi·CH2Cl2
Formula weight	725.35	747.51	678.35	633.89	1035.47	1029.02
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Lattice type	C-centered	primitive	C-centered	primitive	primitive	primitive
Space group	$C_2/c$ (#15)	P1 (#2)	$C_2/c$ (#15)	Pbca (#61)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	29.374(9)	10.828(2)	29.111(7)	17.791(2)	15.091(2)	15.211(1)
b (Å)	14.767(4)	13.441(2)	14.872(3)	15.265(2)	11.585(2)	11.6798(8)
<i>c</i> (Å)	17.319(5)	13.623(2)	16.959(4)	24.375(3)	22.938(4)	22.888(2)
α (°)	90	72.866(5)	90	90	90	90
β (°)	116.5987(11)	82.243(6)	116.4000(9)	90	97.1574(8)	96.590(2)
γ (°)	90	74.594(6)	90	90	90	90
Volume, Å <sup>3</sup>	6718(3)	1823.2(4)	6576(3)	6619.9(13)	3979.1(11)	4039.5(5)
Z value	8	2	8	8	4	4
$D_{\rm calc},  {\rm g/cm^3}$	1.434	1.362	1.370	1.272	1.728	1.692
F(000)	2960.00	780.00	2816.00	2672.00	2048.00	2036.00
Crystal color, habit	Dark red, platelet	brown, prism	brown, prism	red, platelet	brown, chip	dark red, platelet
Crystal dimensions, mm	$0.24 \times 0.08 \times 0.06$	$0.15 \times 0.15 \times 0.10$	$0.21 \times 0.12 \times 0.11$	$0.25 \times 0.10 \times 0.03$	$0.15 \times 0.10 \times 0.05$	$0.50 \times 0.50 \times 0.03$
No of observations (all	7622	7982	7540	7572	5062	8837
reflections)	407	100	407	407	102	142
No of variables	427	490	427	427	483	443
Reflection/parameter ratio	17.85	16.29	17.66	17.73	10.48	19.95
R (all reflections)	0.092	0.0466	0.0659	0.0601		0.109
$R_1(I > 2\sigma(I))^{\circ}$	0.042	0.0628	0.0314	0.0406	$0.055(I > 3\sigma(I))$	0.069
$WK_2$ (all reflections) <sup>5</sup>	0.111	0.1394	0.0276	0.1069	$0.161(I > 3\sigma(I))$	0.225
Goodness of fit (GOF)	1.000	1.002	0.876	1.019	1.004	1.048
final cycle	0.000	0.000	0.000	0.000	0.000	0.002
Maximum peak in final	1.06	0.98	0.75	0.77	3.52	1.66
difference map, e/Å <sup>3</sup>						
Minimum peak in final difference map, e/Å <sup>3</sup>	-0.98	-0.86	-0.82	-0.37	-1.48	-2.09

<sup>a</sup>  $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ .

<sup>b</sup>  $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2}.$ 

stop the polymerization. Polyethylene was precipitated when the reaction mixture was poured into a methanol solution of HCl. The polymer was collected by filtration and dried in vacuo.

#### 4.11. X-ray data collection and reduction

X-ray crystallography for new complexes 2, 3, and 4 was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71070 A). The data were collected at 123(2) K using  $\omega$  scan in the  $\theta$  range of 3.0  $\leq$  $\theta \leq 27.5^{\circ}$  (2),  $3.0 \leq \theta \leq 27.5^{\circ}$  (3) and  $3.0 \leq \theta \leq 27.5^{\circ}$  (4). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structures were solved by direct methods [16], and expanded using Fourier techniques [17]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on  $F^2$  was based on 7982 observed reflections and 490 variable parameters for 2, 7540 observed reflections and 427 variable parameters for 3, and 7572 observed reflections and 427 variable parameters for 4. Neutral atom scattering factors were taken from Cromer and Waber [18]. All calculations were performed using the CRYSTALSTRUCTURE [19,20] crystallographic software package. Details of final refinement as well as the bond lengths and angles are summarized in Table 6 in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.

#### Supplementary data

CCDC 198229, 689689, 689690, 689691, 265483 and 265482 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, 5a

and **6a**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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