

DOI:10.1002/ejic.201201331

# *trans*-1,2-Diphenylethylene Linked Isoindoline– Salicylaldiminato Nickel(II) Halide Complexes: Synthesis, Structure, Dehydrogenation, and Catalytic Activity toward Olefin Homopolymerization

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Keywords: Tridentate ligands / Nickel / Solid-state structures / Oligomerization / Polymerization

Tridentate ligands 4-R<sup>1</sup>-6-R<sup>2</sup>-2-{[trans-2-(isoindolin-2-yl)-1,2diphenylethylimino]methyl}phenol  $[R^1 = R^2 = H, H(L^a); R^1 =$  $R^2 = tert$ -butyl,  $H(L^b)$ ;  $R^1 = Ph$ ,  $R^2 = H$ ,  $H(L^c)$ ] in which a substituted salicylaldimine moiety and an isoindoline are linked by a *trans*-1,2-diphenylethylene moiety have been prepared. Deprotonation of these tridentate ligands  $H(L^{a})-H(L^{c})$  by NaH at room temperature in tetrahydrofuran (THF), followed by treatment with 1 equiv. of  $[(PPh_3)_2NiX_2]$  (X = Cl, Br, I) at room temperature afforded the desired nickel complexes [(L)NiX] (X = Cl, L = L<sup>a</sup>, 1; X = Cl, L = L<sup>b</sup>, 2; X = Cl, L = L<sup>c</sup>, 3;  $X = Br, L = L^{b}, 4; X = I, L = L^{b}, 5$  in moderate yields. The structures of 2 and 4 were unequivocally confirmed by single-crystal X-ray diffraction in the solid state. The metal atom has a distorted square-planar coordination geometry and is coordinated to the two nitrogen atoms and one oxygen atom from the tridentate ligand and one halide atom. Dehydrogen-

## Introduction

The utilization of d<sup>8</sup> metal complexes for ethylene oligomerization and olefin (co)polymerization has been studied intensely in both academic and industrial fields over the past decades.<sup>[1]</sup> Traditionally, d<sup>8</sup> late-transition-metal catalysts were only found to produce dimers or low-molecularweight oligomers owing to chain termination by  $\beta$ -hydride elimination.<sup>[2]</sup> For example, the Shell higher olefin process (SHOP), based on the nickel catalyst [Ph<sub>2</sub>–PC(R)=C(R)O]-Ni(Ph)L, was developed to oligomerize ethylene to higher  $\alpha$ -olefins.<sup>[3]</sup> At the end of last century, Brookhart and coworkers developed a series of cationic bis(imino) nickel-(II)<sup>[4]</sup> and palladium(II)<sup>[5]</sup> catalysts, which have been successfully used as highly effective precatalysts for olefin (co)polymerization reactions in this field. Extensive investigations have subsequently favored the active species and re-

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oxygen afforded the corresponding nickel complexes [( $L^{b*}$ )-NiX] (X = Br, **6**; X = I, **7**). X-ray analysis showed that in these complexes the two bridged benzylic carbon atoms of ( $L^{b}$ )<sup>-</sup> were oxidized and a *cis*-stilbene moiety, which includes a C=C double bond (1.205–1.268 Å) was formed. These nickel complexes with such *trans*-1,2-diphenylethylene bridged tridentate ligands proved to be active catalysts for ethylene oligomerization in the presence of methylaluminoxane (MAO) and produced butene and hexene with catalytic activities of  $0.49 \times 10^5$ - $3.25 \times 10^5$  gmol<sup>-1</sup>Nih<sup>-1</sup> at 30 °C, under 20 bar of ethylene, and with an MAO/Ni ratio of 250. They were also active catalysts for the homopolymerization of norbornene and styrene and displayed activities of up to  $1.89 \times 10^5$  and  $7.36 \times 10^5$  gmol<sup>-1</sup>Nih<sup>-1</sup>, respectively.

ation of the chelate tridentate ligand (L<sup>b</sup>) in the presence of

action mechanisms, electronic and/or steric influence of these nickel and palladium derivatives because of better catalytic performances.<sup>[1a,1b]</sup> Functional olefin copolymers with hydroxy, epoxide, and carbohydrate groups were successfully controlled by copolymerization of ethylene with polar olefins by using a palladium–diimine chain-walking catalyst.<sup>[6]</sup> Soon after that, single-component neutral salicylaldiminato nickel catalysts<sup>[7]</sup> and SHOP-type phosphane–sulfonato palladium catalysts<sup>[8]</sup> were discovered in succession; they showed excellent performance in ethylene (co)polymerization.

To date, the quest for novel catalytic system involves the search for new ligand structures. However, this search was found to be empirical in nature; recent developments have provided somewhat more comprehensive guidelines for the design of metal catalysts. Several nickel and palladium complexes supported by tridentate [ONX] ligands [X = O, N, P, N-heterocyclic carbene (NHC)] have been found to be active for the oligomerization of ethylene and the polymerization of norbornene and acrylates to afford higher  $\alpha$ -ole-fins or vinyl-addition polymers.<sup>[9]</sup> As part of our ongoing research project on group 10 and group 4 metal complexes and their application as catalysts for olefin polymeriza-





tion,<sup>[10]</sup> we prepared a series of nickel complexes with chiral tridentate ligands, H(L<sup>a</sup>)-H(L<sup>c</sup>), in which a substituted salicylaldiminato moiety and an isoindoline are linked by a trans-1,2-diphenylethylene group (Scheme 1).<sup>[11]</sup> Initially, these chiral nickel complexes were tested in the polymerization of styrene. Unfortunately, the tacticity of the obtained polymer was very low. As the results were not good, we turned to the homogeneous polymerization of ethylene and norbornene. We found that this kind of monoanionic tridentate ligand L<sup>-</sup> can be used to create an appropriate environment around the coordination sphere of the nickel atom for ethylene oligomerization and norbornene polymerization. This tridentate fragment obviously results in a higher coordination number than an ordinary bidentate salicylaldiminato ligand. The third nitrogen donor atom of isoindoline will tend to compete against olefin monomers to coordinate the metal center during polymerization, and the trans-1,2-diphenylethylenediamine linker makes the coordination mode more flexible, which may or may not be beneficial to the polymerization reaction.

Herein, we wish to report the synthesis, characterization, and dehydrogenation of these nickel complexes and their catalytic activities toward ethylene oligomerization and norbornene and styrene homopolymerization with methylaluminoxane (MAO) as cocatalyst.

#### **Results and Discussion**

# Synthesis of Tridentate Ligands and Their Nickel Complexes

The tridentate ligands 4,6-disubstituted-2-{(trans-2-(isoindolin-2-yl)-1,2-diphenylethylimino)methyl}phenol  $[H(L^{a})-H(L^{c})]$  were synthesized as outlined in Scheme 1. Racemic trans-diphenylethylenediamine (DPEDA) was used as the starting material. One of the amine groups of DPEDA was firstly protected with 1,3-dimethyl-5-acetylbarbituric acid<sup>[12]</sup> to form compound A, followed by alkylation of the other primary amine group with o-xylylene dibromide to give **B** in high yield.<sup>[13a]</sup> Deprotection of the amine group of **B** with ethanolamine gave the monoamine compound C,<sup>[13b]</sup> and further straightforward Schiff base condensation of the terminal primary amine with 3,5-disubstituted salicylaldehyde gave the corresponding crude products, which were purified by silica gel chromatography to afford the pure tridentate ligands  $H(L^a)-H(L^c)$  as yellowish solids in good yields (57-89%).

The ligands  $H(L^a)-H(L^c)$  were treated with excess sodium hydride in tetrahydrofuran (THF) at room temperature under argon to afford the corresponding sodium salts [(L)Na(THF)], which subsequently reacted with  $[(PPh_3)_2-$ NiX<sub>2</sub>] (X = Cl, Br, I) to give the desired nickel complexes [(L)NiX] (X = Cl, L = L<sup>a</sup>, 1; X = Cl, L = L<sup>b</sup>, 2; X = Cl, L = L<sup>c</sup>, 3; X = Br, L = L<sup>b</sup>, 4; X = I, L = L<sup>b</sup>, 5) in moderate yields (56–67%, Scheme 1). All nickel complexes were characterized by NMR and FTIR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of tridentate ligands  $H(L^a)-H(L^c)$  and their nickel complexes 1–5; reaction conditions: (i) THF, 3 d, yield: 91%. (ii) (1,2-Dibromomethyl)benzene, diisopropylethylamine, *N*,*N*-dimethylformamide (DMF), 40 °C, 2 d, yield: 72%. (iii) Ethanolamine, ethanol, yield: 77%. (iv) 3,5-Disubstituted salicylaldehyde, ethanol, reflux, yields: 57 [H(L<sup>a</sup>)], 86 [H(L<sup>b</sup>)], and 89% [H(L<sup>c</sup>)]. (v) a) NaH, THF, room temp.; b) [(PPh\_3)<sub>2</sub>NiX<sub>2</sub>] (X = Cl, Br, I), THF, room temp., yields: 56 (1), 63 (2), 69 (3), 67 (4), and 65% (5).

The <sup>1</sup>H NMR spectra of the ligands H(L) are indicative of a *trans*-1,2-diphenylethylene linked isoindoline–salicylaldiminato fragment. For example, ligand H(L<sup>b</sup>) exhibits two doublets at  $\delta = 4.27$  and 4.93 ppm with a coupling constant of J = 1.7 Hz that is attributable to the two inequivalent protons (H<sup>a</sup> and H<sup>b</sup>) of the CH group adjacent to the nitrogen atoms, and this <sup>1</sup>H NMR spectrum also displays two doublets at  $\delta = 3.98$  and 3.99 ppm (J = 11.1 Hz), which is characteristic of the CH<sup>c</sup>H<sup>d</sup>N protons of a five-member heterocyclic ring (Figure 1).

From the IR spectra, the  $v_{C=N}$  band obviously shifts from 1628–1630 cm<sup>-1</sup> for H(L) to 1599–1605 cm<sup>-1</sup> for nickel complexes 1–5. The NMR spectra of these nickel complexes showed no complexity; the broad singlet resonance assigned to the ArOH protons was not present and the resonances corresponding to the ligand protons were observed. It





Figure 1. Selected region ( $\delta = 6.5$ –3.5 ppm) of the <sup>1</sup>H NMR spectra of ligand H(L<sup>b</sup>) (above) and complex **2** (below) in CDCl<sub>3</sub> solutions at 20 °C. <sup>1</sup>H Chemical shifts referenced to residual undeuterated chloroform solvent signal ( $\delta = 7.26$  ppm).

should be noted that the CH and CH<sub>2</sub>N groups of the nickel complexes revealed six broad singlets in the range  $\delta$ = 6.12-3.88 ppm, which are quite different from those of free ligands (Figure 1). It is the inability of this ligand fragment to rotate with regard to the C-N bond (as a consequence of coordination) that causes the inequivalence of these nuclei. Variable-temperature NMR experiments revealed that the rotation of this part of the ligand could not proceed even at higher temperatures. As complexes of Ni(II) with square-planar geometry are expected to be diamagnetic, this observation implies that these complexes are distorted from the ideal geometry in solution. We tried but failed to observe an electron paramagnetic resonance (EPR) signal at room temperature. Inspection of 2 in the solid state also indicates a somewhat distorted structure, which is in agreement with this observation (see below).

#### X-ray Crystal Structural Analysis

Crystals of **2** and **4** suitable for single-crystal X-ray diffraction analysis were obtained as orange blocks by diffusing hexane into the corresponding toluene solution of the metal complexes. The ORTEP drawings of **2** and **4** are presented in Figures 2 and 3, and selected bond lengths and angles for these complexes are summarized in Table 1. ORTEP views reveal that the molecular structures of these two complexes are similar to each other. Each consists of one tridentate chelate ligand and a halide anion that form a distorted square-planar coordination geometry, and the nickel atoms are nearly coplanar.

For 2, the N<sub>imine</sub>–Ni–Cl [178.0(2)°] and O<sub>phenol</sub>–Ni– N<sub>amine</sub> [174.8(4)°] angles are close to linear, and the two angles are almost perpendicular to each other. The C(9) phenyl ring and C(16) phenyl ring of the tridentate ligand (L<sup>b</sup>) are in a staggered configuration with regard to the C(8)–C(15) bond, and the C(9)–C(8)–N(1) [115.8(7)°] and C(16)–C(15)–N(2) [115.9(8)°] bond angles are similar. The Ni–O<sub>phenol</sub> distance of 1.866(10) Å is within the typical range for Ni–O distances in square planar salicylaldiminato



Figure 2. Molecular structure of 2.



Figure 3. Molecular structure of 4.

Table 1. Selected bond lengths [Å] and angles [°] for 2, 4, 6, and 7.

	2 (X = Cl)	4 (X = Br)	<b>6</b> (X = Br)	7 (X = I)
Bond lengths				
Ni–N <sup>[a]</sup>	1.976(10)	1.960(12)	1.988(5)	1.984(5)
Ni–N <sup>[b]</sup>	1.850(8)	1.817(13)	1.822(6)	1.849(5)
Ni–O <sup>[c]</sup>	1.866(10)	1.815(9)	1.819(5)	1.833(4)
Ni–X	2.215(3)	2.362(2)	2.3647(13)	2.5485(11)
$C-C^{[d]}$	1.473(13)	1.481(13)	-	
$C=C^{[e]}$	-	-	1.205(9)	1.268(10)
Bond angles				
N <sup>[a]</sup> -Ni-N <sup>[b]</sup>	86.5(4)	85.6(5)	85.8(2)	85.9(2)
N <sup>[b]</sup> -Ni-O <sup>[c]</sup>	92.9(4)	93.6(4)	93.6(2)	94.43(19)
O <sup>[c]</sup> -Ni-X	87.3(3)	86.0(3)	86.86(14)	84.96(13)
X–Ni–N <sup>[a]</sup>	87.3(3)	94.8(3)	94.63(15)	94.78(15)
N <sup>[a]</sup> -Ni-O <sup>[c]</sup>	174.8(4)	174.6(5)	172.9(2)	177.0(2)
X-Ni-N <sup>[b]</sup>	178.0(2)	179.4(3)	172.2(3)	177.71(19)

[a] Amine nitrogen atom. [b] Imine nitrogen atom. [c] Phenol oxygen atom. [d] C–C single bond of two bridged benzylic carbon atoms. [e] C=C double bond of *cis*-stilbene moiety in ( $L^{b*}$ ).

nickel complexes.<sup>[7,9]</sup> The Ni–N<sub>amine</sub> distance of 1.976(10) Å is longer than the Ni–N<sub>imine</sub> distance [1.850(8) Å]. The former is close to the Ni–N(1) distance [2.005(2) Å] in  $[(\eta^3:\eta^1-indenyl(CH_2)_2NMe_2)Ni(PPh_3)]$ [BPh<sub>4</sub>],<sup>[14]</sup> and the latter is comparable to that of Ni–N(2) in [(L)NiCl] {1.858(8) Å, L



= 4,6-di-*tert*-butyl-2-[*N*-(quinolin-8-yl)iminomethyl]phenolato}.<sup>[9d]</sup> The C(8)–C(15) distances of 1.473 (13) Å are normal for a C–C single bond.

For 4, the Ni–Br distance [2.36(2) Å] is naturally longer than the Ni–Cl distance [2.215(3) Å] of 2. Noticeably, the Ni–N<sub>imine</sub>, Ni–N<sub>amine</sub>, and Ni–O<sub>phenol</sub> bond lengths in 4 are shorter than those in 2, and the differences are in the order Ni–N<sub>amine</sub> (0.016 Å) < Ni–N<sub>imine</sub> (0.033 Å) < Ni–O<sub>phenol</sub> (0.051 Å). Complex 4 has a less ideal coordination plane surrounding the metal center than that of 2; the N<sub>amine</sub>–Ni– N<sub>imine</sub> [85.6(5)°], N<sub>amine</sub>–Ni–O<sub>phenol</sub> [93.6(4)°], O<sub>phenol</sub>–Ni– Br [86.0(3)°], and Br–Ni–N<sub>amine</sub> [94.80°] bond angles deviate from the ideal 90° more seriously than the equivalent angles in 2 [86.5(4), 92.9(4), 87.3(3), and 87.3(3)°, respectively]. The trend of bond length shortening and bond angle deviation is attributed to the bromide coligand as it has a relatively large atomic radius.

#### Dehydrogenation of the Chelated Ligand (L<sup>b</sup>)

Unlike nickel chloride complexes 1–3, when the bromide (4) and iodide (5) complexes bearing (L<sup>b</sup>) ligands were prepared in the presence of O<sub>2</sub> at an elevated temperature of 40 °C or were exposed to air at 40 °C, complexes of the type [(L<sup>b\*</sup>)NiX] (X = Br, 6; X = I, 7) could be obtained (Scheme 2). The <sup>1</sup>H NMR spectra of these complexes apparently lack signals attributable to methyne protons (CH) on the diamine moiety, which are observed in the spectra of H(L<sup>b</sup>) at  $\delta$  = 4.27 and 4.93 ppm. This indicates that dehydrogenation of the coordinated tridentate ligand took place at the bridged carbon atoms to form the *cis*-stiblene moiety.



Scheme 2.

Single-crystal X-ray diffractions analyses (Table 1, Figures 4 and 5) were performed to confirm the dehydrogenation of the chelate ligand. Complexes 6 and 7 have similar solid-state structures to those of 2 and 4. Four atoms coordinate to the Ni<sup>II</sup> center to create five- and six-member metallacycles. Notably, the two benzylic carbon atoms were oxidized and a C=C double bond [1.205 Å for C(9)–C(16) of 6, 1.268(10) Å for C(1)–C(8) of 7] formed in the five-membered metal–chelate ring.

Similar dehydrogenation of coordinated tetradentate salen-like ligands derived from 1,2-diphenyl-1,2-ethanediamine by using oxidation reagents such as molecular oxygen and heating of their nickel complexes for prolonged periods has been reported.<sup>[15]</sup> This kind of dehydrogenation reaction is usually considered to involve the prior oxidation



Figure 4. Molecular structure of **6**.



Figure 5. Molecular structure of 7.

of a metal ion to an unstable higher oxidation state, followed by oxidation of the ligand and reduction of the metal ion. Therefore, oxidation reagents are necessary for the oxidation of the metal ion. We also found that the dehydrogenation reactions of L<sup>b</sup> in 4-5 did not directly occur under an argon atmosphere, but that oxygen is necessary for the oxidation. Control NMR-tube experiments showed that heating the THF solution of 4 for a long time in the presence of  $O_2$  could give 6 very slowly, whereas a relatively short time is sufficient for 5. This result suggested that, in addition to oxygen, something else (e.g., coordinated anionic groups Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) might play a role in the above one-pot dehydrogenation of 4. Moreover, several control experiments were performed to exclude the influence of NaH in the first step. Ligand  $H(L^b)$  reacted with excess NaH in THF at elevated temperature (less than 60 °C) in the presence of oxygen to give the salt [(L<sup>b</sup>)Na(THF)]; no corresponding salt of the dehydrogenated chelate ligand could be detected by <sup>1</sup>H NMR spectroscopy. However, the role of  $O_2$ , coordinated halides, and the nickel centers in these complexes still remains unclear.

#### **Ethylene Oligomerization**

The catalytic performances of the obtained nickel complexes in the homopolymerization of ethylene and nor-



bornene have been evaluated with MAO as cocatalyst. To show the differences in catalytic behavior of the present complexes and previously known Ni catalysts, we prepared a simpler nickel complex **8** with a similar NNO ligand (ethylenediamine-linked salicilaldiminato-diethylamine) according to ref.<sup>[16]</sup>

As shown in Table 2, nickel complexes 1–5 catalyzed ethylene oligomerization with activities of  $0.49 \times 10^{5}$ –  $3.25 \times 10^{5}$  gmol<sup>-1</sup>Nih<sup>-1</sup> at 30 °C under 20 bar of ethylene with an MAO/Ni ratio of 250. Complexes 6 and 7 with chelated ligand (L<sup>b\*</sup>) revealed much lower activity and only trace C<sub>6</sub> product could be detected (Table 2, Entries 6 and 7). The ethylenediamine-bridged [ONN] nickel complex 8 showed good catalytic activity of  $1.02 \times 10^{5}$  gmol<sup>-1</sup>Nih<sup>-1</sup> for ethylene dimerization (Table 2, Entry 12).

Table 2. Ethylene oligomerization with 1-7/MAO system.<sup>[a]</sup>

Entry	Cat.	Al/Ni	P [atm]	Activity <sup>[b]</sup>	$\begin{array}{c} \text{Selectiv} \\ \text{C}_4^{[c]} \end{array}$	vity [%] 1-C <sub>4</sub>	$C_6^{[d]}$
1	1	250	20	1.59	97.8	75.3	2.2
2	2	250	20	3.14	98.3	86.3	1.7
3	3	250	20	3.30	97.1	83.2	2.9
4	4	250	20	3.28	97.9	85.5	2.1
5	5	250	20	3.25	97.2	85.5	2.1
6	6	250	20	0.77	>99	_	_
7	7	250	20	0.49	>99	_	_
8	2	250	5	0.55	98.0	64.2	2.0
9	2	250	40	3.28	98.5	92.1	1.5
10 <sup>[e]</sup>	2	500	5	0.34	97.0	42.6	3.0
11	2	500	5	0.06	99.8	66.9	0.2
12	8	250	40	1.02	>99	-	_

[a] Reaction conditions: 50 mL of toluene, 10  $\mu$ mol of Ni, 30 °C, 30 min. The results shown are representative of at least duplicated experiments. [b]  $\times 10^5$  g mol<sup>-1</sup> Ni h<sup>-1</sup>, as determined by quantitative gas–liquid chromatography (GLC). [c] Butene. [d] Several isomers of hexene were detected by GLC. [e] 60 °C.

Complex **2** was carefully studied for further optimization, and the influence of temperature, Al/Ni mol ratio, and ethylene pressure was investigated (Table 2, Entries 8–11). From the representative results, several points can be concluded. Firstly, the oligomerization rate logically increased with ethylene pressure; the activities varied from  $0.55 \times 10^5$ to  $3.28 \times 10^5$  gmol<sup>-1</sup> Ni h<sup>-1</sup> from 5 to 40 bar (Table 2, Entries 8 and 9). Secondly, increasing the oligomerization temperature caused an increase of the selectivity for 1-butene, along with a more balanced 2-butene isomeric ratio (*cis* vs. *trans*, Table 2, Entries 10 and 11). Finally, a greater load of MAO led to lower activity (Table 2, Entries 11 and 8). At the same time, increasing the ration from 250 to 500 equiv. led to slightly improved selectivity for both the C<sub>4</sub> fraction (98.0 to 99.8%) and 1-butene (64.2 to 66.9%).

#### Norbornene Addition Polymerization

On the basis of the preliminary results for ethylene oligomerization, complex 2 was selected for further investigation in norbornene polymerization (Table 3). In the presence of MAO, complex 2 proved to be an active catalyst for the polymerization of norbornene (NB). Polynorbornene (PNB) formed immediately after MAO was added to a mixture of norbornene and nickel complex in toluene. The steric effect of the diphenyl-substituted C–C linker negatively impacts the catalytic activity. Under the same polymerization conditions, complex **2** showed a catalytic activity of  $0.12-1.89 \times 10^5$  gmol<sup>-1</sup> Nih<sup>-1</sup>, which is much lower than that of **8** [ $5.90 \times 10^5$  gmol<sup>-1</sup> Nih<sup>-1</sup>] and other previously known Ni catalysts [ $>10^6$  gmol<sup>-1</sup> Nih<sup>-1</sup>].<sup>[9d]</sup>

Table 3. Norbornene	polymerization	with	2/MAO	system.[a]
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Entry	Ni [µmol]	<i>Т</i> [°С]	Yield [g]	Activity <sup>[b]</sup>	$M_{ m w}^{ m [c]}$ (×10 <sup>6</sup> )	$M_{\rm w}/M_{\rm n}^{\rm [c]}$
1	4	50	0.070	0.17	_	_
2	4	30	0.355	0.89	0.82	1.59
3	4	10	0.753	1.89	1.06	1.72
4 <sup>[d]</sup>	4	10	0.421	1.05	1.32	2.07
5	2	10	0.048	0.12	_	_
6 <sup>[e]</sup>	0	10	0	_	_	_
7 <sup>[f]</sup>	4	10	1.180	5.90	-	_

[a] Polymerization conditions: [Ni]:  $1.0 \times 10^{-3}$  M in CH<sub>2</sub>Cl<sub>2</sub>, MAO: 2.2 M in toluene, Al/Ni: 1100, norbornene: 2 g, time: 30 min,  $V_{\text{total}} = 15$  mL. [b]  $\times 10^{5}$  g mol<sup>-1</sup>Ni h<sup>-1</sup>. [c] Determined by high temperature GPC at 150 °C. [d] Al/Ni: 550. [e] Blank experiment with only MAO. [f] Complex 8 as precatalyst.

Further study showed that the polymerization conditions strongly influenced the activities (Table 3). For example, decreasing the reaction temperature from 50 to 10 °C resulted in an improvement of activity from 0.17 to  $1.89 \times 10^5$  gmol<sup>-1</sup>Nih<sup>-1</sup> (Table 3, Entries 1–3). A low activity of  $1.05 \times 10^5$  gmol<sup>-1</sup>Nih<sup>-1</sup> was observed in the presence of a low Al/Ni molar ratio of 550 (Table 3, Entries 3 and 4), which indicates that more MAO was required to stabilize the active species for norbornene polymerization. Moreover, a low initial nickel catalyst concentration caused a low polymer yield (Table 3, Entry 5). The blank experiments showed that no polymers were produced in the absence of **2** (Table 3, Entry 6).

The molecular weights  $(M_w)$  of the polynorbornenes obtained range from  $0.82 \times 10^5$  to  $1.32 \times 10^5$  gmol<sup>-1</sup> with very low molecular weight distribution (1.59 to 2.07). The absence of resonances at  $\delta = 5.0$ –6.0 ppm in the <sup>1</sup>H NMR spectra revealed that the obtained polynorbornene possesses a vinyl addition structure but not a ring opening metathesis polymerization (ROMP) structure.<sup>[17]</sup> In the <sup>13</sup>C NMR spectra, the main four groups of resonances at  $\delta =$ 52.8–47.7 ppm for the backbone carbon atoms and 39.8– 35.5, 31.5, and 30.0–29.8 ppm for the bridge carbon atoms also agree with this.<sup>[18]</sup>

#### **Styrene Polymerization**

Nickel complex **2** was found to actively catalyze the polymerization of styrene in the presence of MAO (Table 4). The activities decreased with prolongation of the polymerization time probably owing to the increased viscosity of the quickly formed polystyrene solution, which might block



catalytic species (Table 4, Entries 1-4). Increased polymerization temperature slightly improved the activity (Table 4, Entries 4 and 5). Further study showed that the Al/Ni molar ratio strongly influenced the activities, which decreased quickly from  $3.24 \times 10^5$  to  $0.49 \times 10^5$  gmol<sup>-1</sup> Nih<sup>-1</sup> with a decrease of MAO loading (Table 4, Entries 5-7). The optimum Al/Ni value was about 1100 and lower catalyst loading decreased the catalytic ability (Table 4, Entries 5–8). Unlike norbornene polymerization, complex 2 revealed a slightly higher activity  $[3.57 \times 10^5 \text{ gmol}^{-1} \text{ Ni h}^{-1}]$  than the ethylenediamine-linked salicylalidiminato-diethylamine Ni complex 8  $[2.94 \times 10^5 \text{ gmol}^{-1} \text{ Ni} \text{ h}^{-1}]$  under the same conditions (Table 4, Entries 4 and 9). Although the nickel complex is active for styrene polymerization, the tacticity of the obtained polystyrene is very low because these polymer are very soluble in 2-butanone.<sup>[19]</sup> Polystyrene samples at the various Al:Ni ratios as well as reaction temperature were analyzed by gel permeation chromatography (GPC, Table 4). Both the molecular weight  $(M_w)$  and polydispersity index (PDI,  $4.20 \times 10^4$  gmol<sup>-1</sup> and 1.54, respectively) of the polymer obtained increase with a decrease of polymerization temperature from 60 to 5 °C ( $6.67 \times 10^4$  g mol<sup>-1</sup> and 1.62) and a decrease of the Al/Ni molar ratio from 1100 to 550 (4.72×  $10^5$  gmol<sup>-1</sup> and 1.714).

Table 4. Styrene polymerization with 2/MAO system.[a]

Entry	Ni [µmol]	Al/ Ni	Time [min]	Yield [g]	Activity <sup>[b]</sup>	$M_{ m w}^{ m [c]} \ ( imes 10^4)$	$M_{\rm w}/M_{\rm n}^{\rm [c]}$
1	2	1100	15	0.368	7.36	_	_
2	2	1100	30	0.503	5.03	_	_
3	2	1100	45	0.621	4.14	_	_
4	2	1100	60	0.713	3.57	4.20	1.54
5 <sup>[d]</sup>	2	1100	60	0.757	3.79	6.67	1.62
6	2	550	60	0.097	0.49	4.72	1.71
7	2	2200	60	0.648	3.24	_	_
8	1	1100	60	0.654	3.27	-	_
9[e]	8	1100	60	0.588	2.94	-	_

[a] Polymerization conditions: [Ni]:  $1.0 \times 10^{-3}$  M in CH<sub>2</sub>Cl<sub>2</sub>, MAO: 2.2 M in toluene, styrene: 1 mL, temperature: 24 °C,  $V_{\text{total}} = 4.0$  mL. [b]  $10^5$  g mol<sup>-1</sup> Ni h<sup>-1</sup>. [c] Determined by GPC at 40 °C. [d] Polymerization temperature: 5 °C. [e] Complex **8** as precatalyst.

# Conclusions

We have synthesized a class of *trans*-1,2-diphenylethylenediamine-linked salicylaldiminato-isoindoline ligands and their nickel complexes. These compounds were characterized by NMR and FTIR spectroscopy and elemental analysis. Single-crystal X-ray analysis confirms the formation of complexes in which the metal center is coordinated with the oxygen and nitrogen atoms of the tridentate ligands. Dehydrogenation of the chelated tridentate ligand took place and the two bridged benzylic carbon atoms of a CH–CH single bond were oxidized to form the *cis*-stilbene moiety with a C=C double bond. The nickel complexes were active for ethylene oligomerization and the homopolymerization of norbornene and styrene with MAO as cocatalyst.

# **Experimental Section**

**General:** Unless otherwise noted, all manipulations of air- and/or water-sensitive compounds were carried out under an inert atmosphere by using standard Schlenk techniques. Toluene, THF, and hexane were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from CaH<sub>2</sub>. CDCl<sub>3</sub> was dried and distilled before use. 1,3-Dimethyl-5-acetylbarbituric acid (DAB),<sup>[12]</sup> **B**<sup>[13a]</sup>, **C**<sup>[13b]</sup> (Scheme 1), 3,5-disubstituted salicylalde-hyde,<sup>[20]</sup> [(PPh<sub>3</sub>)<sub>2</sub>NiX<sub>2</sub>] (X = Cl, Br, I),<sup>[21]</sup> and **8**<sup>[16]</sup> were prepared according to published procedures. MAO was purchased from Akzo Chemical as a 2.2 m toluene solution. Other commercially available reagents were purchased and used without further purification.

NMR spectra were recorded with Bruker DMX-500 (500 MHz, <sup>1</sup>H; 125 MHz, <sup>13</sup>C) and Jeol ECA 400 spectrometers (400 MHz, <sup>1</sup>H; 100 MHz, <sup>13</sup>C). Chemical shifts ( $\delta$ ) for <sup>1</sup>H and <sup>13</sup>C spectra are referenced to internal solvent resonances and are reported relative to tetramethylsilane (TMS). NMR experiments on air-sensitive samples were conducted in Teflon-valve-sealed sample tubes (J. Young). IR spectra were recorded with a Nicolet AV-360 spectrometer. Elemental analyses for C, H, and N were performed with a Vario EL III analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of polymers were acquired in 1,2-[D<sub>4</sub>]dichlorobenzene at 120 °C. GPC for polynorbornenes was carried out in 1,2,4-trichlorobenzene at 150 °C with a Waters high-temperature GPC 2000 instrument equipped with a set of three PLgel 10  $\mu$ m mixed-B columns. GPC for polystyrenes was carried out in THF at 40 °C with a Waters Ultrastyra GPC instrument.

General Procedure for the Synthesis of 4,6-Disubstituted 2-{(*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethylimino)methyl}phenol [H(L<sup>a</sup>)–H(L<sup>c</sup>)]: To a mixture of 1,3-dihydro- $\alpha$ , $\beta$ -diphenyl-2*H*-isoindole-2-ethanamine C, 3,5-disubstitutedsalicylaldehyde (equivalent to C), and several 4 Å molecular sieves in a septum capped Schlenk tube was added anhydrous ethanol (ca. 10 mL per mmol of C) with a syringe at 20 °C with stirring under nitrogen. After the resulting mixture was stirred overnight, the solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel ( $V_{\text{ethyl acetate}}/V_{\text{petroleum ether}} = 1:20$ ) to give the yellow to brown target ligands H(L<sup>a</sup>)–H(L<sup>c</sup>).

**2-{(***trans***-2-(Isoindolin-2-yl)-1,2-diphenylethylimino)methyl}phenol [H(L<sup>a</sup>)]:** Yellowish white crystalline solid, yield: 0.422 g, 57%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.99 (d, *J* = 12.0 Hz, 2 H, CHH'), 4.11 (d, *J* = 12.0 Hz, 2 H, CHH'), 4.22 (s, 1 H, NCHCHN=CH), 4.96 (s, 1 H, NCHCHN=CH), 6.87 (t, *J* = 7.0 Hz, 1 H, ArH), 6.98 (d, *J* = 8.0 Hz, 1 H, ArH), 7.08 (s, 2 H, ArH), 7.09 (d, *J*<sub>H,H</sub> = 2.0 Hz, 2 H, ArH), 7.13–7.17 (m, 7 H, ArH), 7.19 (s, 4 H, ArH), 7.32 (t, *J* = 7.0 Hz, 1 H, ArH), 8.49 (s, 1 H, N=CH), 13.41 (br. s, 1 H, OH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 58.5, 76.1, 117.0, 122.2, 128.1, 129.7, 137.0, 140.1, 161.1, 165.1 ppm. FTIR (Nujol):  $\tilde{\nu}$  = 1629 (v<sub>C=N</sub>) cm<sup>-1</sup>. C<sub>29</sub>H<sub>26</sub>N<sub>2</sub>O (418.53): calcd. C 83.22, H 6.26, N 6.69; found C 83.19, H 6.31, N 6.75.

**4,6-Di-***tert***-butyl-2-**{*(trans***-2-(isoindolin-2-yl)-1,2-diphenylethyl-imino)methyl}phenol [H(L<sup>b</sup>)]:** Yellowish white crystalline solid, yield: 0.630 g, 86%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.29$  [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.47 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 4.01 (d, J = 12.0 Hz, 2 H, CHH'), 4.10 (d, J = 12.0 Hz, 2 H, CHH'), 4.22 (d, J = 6.0 Hz, 1 H, NCHCHN=CH), 4.93 (s, J = 6.0 Hz, 1 H, NCHCHN=CH), 7.08–7.18 (m, 15 H, ArH), 7.39 (d, J = 2.0 Hz, 1 H, ArH), 8.52 (s, 1 H, N=CH), 13.64 (s, 1 H, OH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 21.4$ , 29.4, 31.4, 33.7, 35.2, 59.1, 64.2, 74.0, 78.9, 121.3, 127.0, 128.5, 129.4, 136.6, 137.3, 159.5, 163.3 ppm. FTIR (Nujol):  $\tilde{v} =$ 



1628 ( $\nu_{C=N})~cm^{-1}.~C_{37}H_{42}N_2O$  (530.74): calcd. C 83.73, H 7.98, N 5.28; found C 83.69, H 8.00, N 5.41.

**6-Phenyl-2-{**[*trans*-2-(isoindolin-2-yl)-1,2-diphenylethylimino]methyl}phenol [H(L<sup>c</sup>)]: Yellowish white crystalline solid, yield: 0.478 g, 89%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.98 (d, *J* = 11.0 Hz, 2 H, CHH'), 4.08 (d, *J* = 11.0 Hz, 2 H, CHH'), 4.27 (d, *J* = 6.7 Hz, 1 H, NCHCHN=CH), 4.93 (d, *J* = 6.7 Hz, 1 H, NCHCHN=CH), 6.95 (t, *J* = 7.5 Hz, 1 H, ArH), 7.07–7.17 (m, 15 H, ArH), 7.35 (t, *J* = 8.5 Hz, 2 H, ArH), 7.41 (d, *J* = 7.5 Hz, 1 H, ArH), 7.45 (t, *J* = 7.5 Hz, 2 H, ArH), 7.65 (d, *J* = 8.5 Hz, 1 H, ArH), 8.55 (s, 1 H, N=CH), 13.91 (s, 1 H, OH) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 58.3, 77.7, 118.7, 119.2, 122.2, 126.7, 127.1, 127.4, 127.8, 128.0, 128.1, 128.2, 128.3, 128.5, 129.3, 129.4, 129.7, 129.8, 131.2, 133.6, 137.8, 140.3, 158.5 ppm. FTIR (Nujol):  $\tilde{v}$  = 1630 ( $v_{C=N}$ ) cm<sup>-1</sup>. C<sub>35</sub>H<sub>30</sub>N<sub>2</sub>O (494.63): calcd. C 84.99, H 6.11, N 5.66; found C 85.03, H 6.17, N 5.74.

General Synthesis of Complex {*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethyl]-[3,5-bis(substituent)salicylaldiminate]}Ni<sup>II</sup>X (1–5): To a stirred suspension of NaH (5.0 mmol) in THF (5 mL) at 0 °C was added dropwise a solution of H(L) (1.0 mmol) in THF (10 mL). After the resulting mixture was warmed to room temperature and stirred for 2 h, the excess NaH was removed by centrifugation. The resultant clear yellow-green THF solution of sodium complex of H(L) was transferred into a Schlenk tube containing [(PPh<sub>3</sub>)<sub>2</sub>NiX<sub>2</sub>] (X = Cl, Br, I, 1.0 mmol). After the mixture was stirred overnight, the solvent was evaporated under vacuum to afford a solid residue, which was washed with hexane (2×5 mL). The residue was extracted with toluene (2×5 mL) to afford a dark red solution. The toluene was removed in vacuo to give pure nickel complexes 1–5.

{*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethyl]-(salicylaldiminate)}Ni<sup>II</sup>Cl (1): Orange-red solid, yield: 0.286 g, 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.13 (br. s, 1 H, CH=N), 7.35 (s, 6 H, Ar*H*), 7.17 (d, *J* = 6.4 Hz, 2 H, Ar*H*), 7.05 (s, 3 H, Ar*H*), 6.90 (m, 2 H, Ar*H*), 6.80 (m, 1 H, Ar*H*), 6.72 (m, 2 H, Ar*H*), 6.12 (br. s, 1 H), 5.80 (br. s, 1 H), 5.35 (br. s, 1 H), 4.92 (br. s, 1 H), 4.28 (br. s, 1 H), 3.88 (br. s, 1 H) ppm. FTIR (Nujol):  $\tilde{v}$  = 1603 ( $v_{C=N}$ ) cm<sup>-1</sup>. C<sub>29</sub>H<sub>25</sub>ClN<sub>2</sub>NiO (511.67): calcd. C 68.07, H 4.92, N 5.47; found C 67.88, H 5.17, N 5.63.

{*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethyl]-[3,5-bis(*tert*butyl)salicylaldiminate]}Ni<sup>II</sup>Cl (2): Orange-red solid, yield: 0.370 g, 63%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.24 (br. s, 1 H, CH=N), 7.35 (s, 6 H, Ar*H*), 7.17 (d, *J* = 6.4 Hz, 2 H, Ar*H*), 7.05 (s, 3 H, Ar*H*), 6.90 (m, 2 H, Ar*H*), 6.80 (m, 1 H, Ar*H*), 6.72 (m, 2 H, Ar*H*), 6.12 (br. s, 1 H), 5.80 (br. s, 1 H), 5.35 (br. s, 1 H), 4.92 (br. s, 1 H), 4.28 (br. s, 1 H), 3.88 (br. s, 1 H), 1.34 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.19 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. FTIR (Nujol):  $\tilde{v}$  = 1599 ( $v_{C=N}$ ) cm<sup>-1</sup>. C<sub>37</sub>H<sub>41</sub>CIN<sub>2</sub>NiO (623.88): calcd. C 71.23, H 6.62, N 4.49; found C 71.19, H 6.57, N 4.62.

{*N*-{*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethyl]-(3-phenylsalicylaldiminate)}Ni<sup>II</sup>Cl (3): Orange-red solid, yield: 0.430 g, 69%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.22 (br. s, 1 H, CH=N), 7.48–7.45 (m, 3 H, Ar*H*), 7.32–7.30 (m, 3 H, Ar*H*), 7.23–7.21 (m, 5 H, Ar*H*), 7.12 (d, *J* = 6.4 Hz, 4 H, Ar*H*), 7.07 (m, 2 H, Ar*H*), 6.94–6.92 (m, 5 H, Ar*H*), 6.14 (br. s, 1 H), 5.79 (br. s, 1 H), 5.37 (br. s, 1 H), 4.92 (br. s, 1 H), 4.27 (br. s, 1 H), 3.88 (br. s, 1 H) ppm. FTIR (Nujol):  $\tilde{v}$  = 1603 ( $v_{C=N}$ ) cm<sup>-1</sup>. C<sub>35</sub>H<sub>29</sub>ClN<sub>2</sub>NiO (587.76): calcd. C 71.52, H 4.97, N 4.77; found C 71.79, H 5.07, N 4.95.

{*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethyl]-[3,5-bis(*tert*-butyl)salicylaldiminate]}Ni<sup>II</sup>Br (4): Orange-red solid, yield: 0.447 g, 67%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81 (br. s, 1 H, CH=N), 7.35 (s, 6 H, Ar*H*), 7.17 (d, *J* = 6.4 Hz, 2 H, Ar*H*), 7.05 (s, 3 H, Ar*H*), 6.90 (m, 2 H, Ar*H*), 6.80 (m, 1 H, Ar*H*), 6.72 (m, 2 H, Ar*H*), 6.22 (br. s, 1 H), 5.82 (br. s, 1 H), 5.01 (br. s, 1 H), 4.30 (br. s, 2 H), 4.12 (br. s, 1 H), 3.55 (br. s, 1 H), 1.73 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.13 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. FTIR (Nujol):  $\tilde{v} = 1603 (v_{C=N}) \text{ cm}^{-1}$ . C<sub>37</sub>H<sub>41</sub>BrN<sub>2</sub>NiO (668.33): calcd. C 66.49, H 6.18, N 4.19; found C 66.24, H 6.39, N 4.28.

{*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylethyl]-[3,5-bis(*tert*-butyl)salicylaldiminate]}Ni<sup>II</sup> (5): Orange-red solid, yield: 0.464 g, 65%. <sup>1</sup>H NMR (500 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  = 7.76 (br. s, 1 H, CH=N), 7.34 (s, 6 H, Ar*H*), 7.14 (d, *J* = 6.4 Hz, 2 H, Ar*H*), 7.00 (s, 3 H, Ar*H*), 6.91 (m, 2 H, Ar*H*), 6.76 (m, 1 H, Ar*H*), 6.70 (m, 2 H, Ar*H*), 6.22 (br. s, 1 H), 5.83 (br. s, 1 H), 5.02 (br. s, 1 H), 4.25 (br. s, 2 H), 4.11 (br. s, 1 H), 3.53 (br. s, 1 H), 1.72 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.12 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. FTIR (Nujol):  $\tilde{v}$  = 1605 (v<sub>C=N</sub>) cm<sup>-1</sup>. C<sub>37</sub>H<sub>41</sub>IN<sub>2</sub>NiO (715.33): calcd. C 62.12, H 5.78, N 3.92; found C 62.09, H 5.80, N 4.00.

General Dehydrogenation Synthesis of Complex {*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylvinyl]-[3,5-bis(substituent)salicylaldiminate]}Ni<sup>II</sup>X (6–7): To a stirred suspension of NaH (5.0 mmol) in THF (5 mL) at room temperature was added dropwise a solution of H(L<sup>b</sup>) (1.0 mmol) in THF (10 mL). The resulting mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was centrifugated to remove excess NaH. The obtained clear yellow-green THF solution of the sodium salt was transferred to a Schlenk tube containing [(PPh<sub>3</sub>)<sub>2</sub>NiX<sub>2</sub>] (X = Br, I, 1.0 mmol) under an O<sub>2</sub> atmosphere. The resulting mixture was stirred overnight, and the solvent was removed under vacuum to afford a solid residue. The residue was washed with hexane (2×5 mL) and then extracted with toluene twice (2×5 mL) to produce a dark red solution, which was layered with hexane (10 mL) to give red crystals of pure product.

{*N*-[*trans*-2-(Isoindolin-2-yl)-1,2-diphenylvinyl]-[3,5-bis(*tert*-butyl)salicylaldiminate]}Ni<sup>II</sup>Br (6): Red crystals, yield: 0.379 g, 57% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.12 (br. s, 1 H, CH=N), 7.62–6.69 (m, 16 H, Ar*H*), 5.92 (br. s, 2 H, CH<sub>2</sub>), 4.18 (br., s, 2 H, CH<sub>2</sub>), 1.34 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.18 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. C<sub>37</sub>H<sub>39</sub>BrN<sub>2</sub>NiO (666.32 g): calcd. C 66.69, H 5.90, N 4.20; found C 66.77, H 5.97, N 4.30.

{*N*-[*trans*-2-(isoindolin-2-yl)-1,2-diphenylvinyl]-[3,5-bis(*tert*-butyl)salicylaldiminate]}Ni<sup>II</sup> (7): Red crystals, yield: 0.392 g, 55% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.11 (br. s, 1 H, CH=N), 7.62– 6.67 (m, 16 H, Ar*H*), 5.94 (br., s, 2 H, CH<sub>2</sub>), 4.13 (br., s, 2 H, CH<sub>2</sub>), 1.35 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.19 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. C<sub>37</sub>H<sub>39</sub>IN<sub>2</sub>NiO (713.32): calcd. C 62.30, H 5.51, N 3.93; found C 62.17, H 5.47, N 4.00.

General Procedure for Ethylene Oligomerization by Ni Catalysts 1– 7/MAO: A 150 mL stainless autoclave equipped with a mechanical stirrer and a continuous feed of ethylene was used. The reactors were dried in an oven at 120 °C for 12 h prior to each run and then placed under vacuum for 30 min. After toluene and the proper amount of MAO cocatalyst were introduced into the reactor under argon, the system was closed and saturated with ethylene, and the oligomerization reaction was started by introduction of the nickel complex dissolved in toluene. The ethylene was continuously fed in order to maintain the ethylene pressure at the desired value. After a certain time, the reaction was stopped by cooling the system to 0 °C, depressurizing, and introducing 1 mL of ethanol. An exact amount of cyclohexane was introduced (as an internal standard), and the mixture was analyzed by quantitative GLC.

General Procedure for Norbornene Addition Polymerization by Ni Catalysts 1–5/MAO: To a solution of norbornene (2 g) and precata-

	2	4.0.5(CH <sub>2</sub> Cl <sub>2</sub> )	6	<b>7</b> •0.5(C <sub>7</sub> H <sub>8</sub> )
Formula	C <sub>37</sub> H <sub>41</sub> ClN <sub>2</sub> NiO	C <sub>37,50</sub> H <sub>42</sub> BrClN <sub>2</sub> NiO	C <sub>74</sub> H <sub>78</sub> Br <sub>2</sub> N <sub>4</sub> Ni <sub>2</sub> O <sub>2</sub>	C <sub>40.50</sub> H <sub>43</sub> IN <sub>2</sub> NiO
Formula weight	623.88	710.80	1332.64	759.38
Crystal size [mm]	$0.32 \times 0.20 \times 0.10$	$0.25 \times 0.15 \times 0.06$	$0.20 \times 0.18 \times 0.16$	$0.12 \times 0.08 \times 0.01$
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P1	<i>P</i> 1	$P\overline{1}$	PĪ
a [Å]	10.808(4)	10.674(4)	12.807(6)	12.937(6)
<i>b</i> [Å]	12.766(5)	12.857(5)	16.046(8)	13.214(6)
c [Å]	14.958(6)	13.632(5)	21.378(10)	13.310(6)
a [°]	97.559(5)	86.610(5)	84.819(8)	89.462(5)
β [°]	99.404(5)	70.852(5)	78.323(7)	61.739(5)
γ [°]	105.708(5)	74.666(5)	74.385(8)	66.565(5)
V [Å <sup>3</sup> ]	1926.4(12)	1703.5(11)	4141(3)	1793.2(13)
Ζ	2	2	2	2
$\rho_{\rm calcd.}  [{\rm Mg}{\rm m}^{-3}]$	1.076	1.386	1.069	1.406
F(000)	660	738	1384	778
T [K]	293(2)	293(2)	293(2)	293(2)
$\mu \text{ [mm^{-1}]}$	0.599	1.852	1.458	1.435
$\theta$ range [°]	1.40 to 25.01	1.58 to 25.01	1.67 to 25.01	1.72 to 25.01
Reflections collected	8004	7092	17262	7451
Data/restraints/parameters	8004/9/770	7092/21/784	14301/37/746	6189/6/429
Goodness of fit	0.913	1.022	0.788	1.012
R indices $[I > 2\sigma(I)]$	$R_1 = 0.0621$	$R_1 = 0.0636$	$R_1 = 0.0773$	$R_1 = 0.0600$
	$wR_2 = 0.1496$	$wR_2 = 0.1805$	$wR_2 = 0.1718$	$wR_2 = 0.1495$
R indices (all data)	$R_1 = 0.0813,$	$R_1 = 0.0796$	$R_1 = 0.1472$	$R_1 = 0.0943$
	$wR_2 = 0.1599$	$wR_2 = 0.2059$	$wR_2 = 0.1868$	$wR_2 = 0.1653$
Largest diff. peak and hole $e Å^{-3}$	0.9425 and 0.8314	1.152 and -1.089	1.092 and -0.689	0.925 and -0.736

Table 5. Crystal data and structure refinements of complexes 2, 4, 6, and 7.

[a] 
$$R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$$
,  $wR_2 = [\Sigma (|F_0|^2 - |F_c|^2)^2 / \Sigma (F_0^2)]^{1/2}$ .

lyst (4  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> was added MAO (2.2  $\mu$  in toluene) by syringe. After the desired run time, the reactor was vented, and the reaction mixture was quickly quenched with 10% HCl in methanol. The precipitated polymer was stirred for several hours, collected by filtration, and washed with methanol. It was then dried under high vacuum at 40 °C overnight.

General Procedure for Polymerization of Styrene: To a solution of styrene (1 mL) and precatalyst (2  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> was added MAO (2.2 M in toluene) by syringe. After the desired time, the reaction mixture was quenched by adding acidified EtOH (5 mL, EtOH/concentrated HCl, 10:1 v/v). The mixture was poured into a solution of concentrated HCl in EtOH (5% v/v) and stirred for 12 h. The polymer was collected by filtration, washed with EtOH, and dried under reduced pressure at 40 °C to constant weight.

**X-ray Data Collection, Structure Solution, and Refinement:** Single crystals suitable for X-ray analysis were sealed in a glass capillary, and the intensity data of the single crystals were collected with a CCD Bruker Smart APEX system. The data obtained with a  $\omega$ -2 $\theta$  scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo- $K_a$  radiation ( $\lambda = 0.71073$  Å) at 293 K. The structures were solved by direct methods, and further refinement with full-matrix least squares on  $F^2$  was obtained with the SHELXTL program package.<sup>[22]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. The crystal data are summarized in Table 5.

CCDC-875835 (for 2), -875836 [for 4 $\cdot$ 0.5(CH<sub>2</sub>Cl<sub>2</sub>)], -875837 (for 6), and -875838 [for 7 $\cdot$ 0.5(C<sub>7</sub>H<sub>8</sub>)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

## Acknowledgments

This work was financially supported by National Natural Science Foundation of China (NSFC) (grant numbers 20972031 and 21272040).

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Published Online: February 12, 2013