



# Synthesis and catalytic activity of neutral salicylaldiminato nickel(II) complexes bearing a single *N*-heterocyclic carbene ligand

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## ABSTRACT

Neutral salicylaldiminato Ni(II) complexes bearing a single *N*-heterocyclic carbene (NHC) ligand [3,5-*t*Bu<sub>2</sub>-2-(O)C<sub>6</sub>H<sub>2</sub>CH=NAr]Ni(C{RNCHCHN<sup>i</sup>Pr})Ph [Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R = Bn (**1**); Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R = <sup>t</sup>Bu (**2**)], have been synthesized via a one-pot procedure in high yield. The X-ray structure analysis reveals that both of **1** and **2** adopt distorted square-planar coordination geometry and NHC carbon (C<sub>carbene</sub>) is *trans* to the ketimine nitrogen. Preliminary study indicates that complex **1** is inert toward the insertion of ethylene, however, it can catalyze the dimerization of ethylene in the presence of modified methylaluminumoxane (MMAO) with a moderate activity of 3.05 × 10<sup>4</sup> g(mol Ni)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> in a highly selective fashion.

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## 1. Introduction

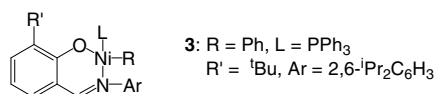
In recent years, *N*-heterocyclic carbenes (NHCs) are being used increasingly in late transition metal-based organometallic chemistry as a valuable alternative to traditional phosphine ligands [1]. Due to their strong donor properties, easily tuned in electronic and steric effect by the diversity of nitrogen substituents, the use of NHCs ligands has opened new opportunities in late transition metal-based catalysis [2]. In particular, nickel-based NHC systems have been widely employed in a series of reactions such as C–F bond [3] or C–H bond activation [4], and various coupling reactions for the formation of C–C bond [5] or C–N [5a] bond and so on. However, the application of such kind of NHC complexes in olefin polymerization has been relatively limited [6–12]. Up to date, only several kinds of NHC complexes of Ni(II) have been tested, mainly including: the bis-NHC dihalides [6], the picolyl-functionalized NHC complexes [7], the enol-functionalized NHC complexes [8], the salicylaldiminato-functionalized NHC complexes [9], and a single NHC co-supported cyclopentadienylnickel(II) [10], indenylnickel(II) [11] or allylnickel(II) [12] complexes. Furthermore, most of them are predominantly capable of catalyzing olefin oligomerizations [6,8,11,12] rather than olefin polymerization [7,9,10], espe-

cially the ethylene oligomerization [6,11,12]. The quite different behaviors in olefin polymerization showed by NHC-based systems, as compared with their phosphine analogues, may be attributed to the facile decomposition of the active species stabilized by NHC via the hydrocarbyl-imidazolium elimination [6a]. In line with this notion are recent reports of several NHC-based Ni(II) complexes showing somewhat good selectivity control either in ethylene oligomerization [6,11] or in styrene oligomerization [12].

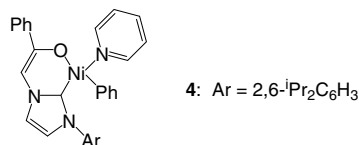
On the other hand, the salicylaldimine framework (N–O), as a common motif in organometallic chemistry, has been extensively applied in Ni(II)-based olefin polymerization and oligomerization catalysts [13]. The leading example is Grubbs' neutral salicylaldiminato Ni(II) complexes of the type (N–O)Ni(R)(L) (R = phenyl or methyl, L = triphenylphosphine or acetonitrile) (Scheme 1) [13a] for the polymerization of ethylene. In general, the catalytic activity and selectivity, *i.e.* ethylene polymerization vs. ethylene oligomerization, are greatly affected by steric and electronic properties of salicylaldimine framework as well as the nature of the L ligand. Very recently, neutral Ni(II) complexes supported by enolate chelating NHC ligand (**4**) (Scheme 2) have been reported to be capable of polymerizing ethylene in a highly linear fashion [8a]. This prompted us to develop novel neutral Ni(II) complexes bearing a single NHC ligand (instead of a phosphine ligand) and to understand further their catalytic behaviors for ethylene polymerization. Herein, we describe the synthesis, structure and catalytic behaviors of two neutral salicylaldiminato Ni(II) complexes stabilized

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Scheme 1. Reported salicylaldimine framework.



Scheme 2. Reported enolate chelating NHC framework.

by a single NHC ligand (**1** and **2**). To our best knowledge, this is the first example of neutral salicylaldiminato Ni(II) phenyl complexes bearing a single NHC ligand.

## 2. Experimental

### 2.1. General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Ni(PPh<sub>3</sub>)<sub>2</sub>PhCl [**14**], 3,5-<sup>t</sup>Bu<sub>2</sub>-2-(HO)C<sub>6</sub>H<sub>2</sub>CH=NAr (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [**15**] and 1,3-diisopropylimidazolium bromide (iPr · HBr) [**16**] were prepared by published methods. All other chemicals were obtained commercially and used as received unless stated otherwise. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. NMR (CDCl<sub>3</sub>) spectra were measured on a Unity Inova-400 spectrometer at 25 °C.

### 2.2. Synthesis of 1-benzyl-3-isopropylimidazolium bromide (Bn-<sup>i</sup>Pr · HBr)

To a THF solution (30 mL) of 1-isopropyl-imidazole (2.34 g, 20 mmol) was added equivalent of benzyl bromide (2.38 mL, 20 mmol). After stirring 3 h, the white powder was collected through filtration, washed with ether and dried *in vacuo*. The yield is almost quantitative (3.77 g, 95%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ: 8.77 (s, 1H, NCHN), 7.49 (s, 1H, Ph-H), 7.32–7.39 (6H, Ph-H and NCH), 5.29 (s, 2H, NCH<sub>2</sub>), 4.52 (m, 1H, NCH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (m, 6H, 2CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calc. for C<sub>13</sub>H<sub>17</sub>BrN<sub>2</sub>: C, 55.53; H, 6.09; N, 9.96. Found: C, 55.18; H, 6.49; N, 10.34%.

### 2.3. Synthesis of **1**

A Schlenk flask was charged with 1-benzyl-3-isopropylimidazolium bromide (0.28 g, 1.0 mmol), 3,5-<sup>t</sup>Bu<sub>2</sub>-2-(HO)C<sub>6</sub>H<sub>2</sub>CH=NAr (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (0.39 g, 1.0 mmol), THF (20 mL) and a stir bar. To this suspension was added dropwise the solution of NaN(SiMe<sub>3</sub>)<sub>2</sub> (1.0 M, 2.0 mL) in THF at 0 °C. The reaction was stirred for 2.5 h at 0 °C and gradually warmed to room temperature for additional 30 min. The resulted mixture was added slowly to the solution of Ni(PPh<sub>3</sub>)<sub>2</sub>PhCl (0.70 g, 1.0 mmol) in 20 mL toluene under stirring at room temperature. The solution was stirred overnight, filtered, and evaporated to dryness. The residue was extracted with toluene and recrystallized from toluene/DME at –10 °C yielded yellow crystals (0.58 g, 80%) suitable for X-ray diffraction studies and elemental analysis. Melt point: 227–228 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.02 (s, 1 H, N=CH), 7.82 (1H, d, Ph-

H), 7.52 (2H, d, Ph-H), 6.91–7.11 (10H, Ph-H), 6.59–6.81 (2H, Ph-H), 6.13 (1H, s, NCH), 6.18 (1H, s, NCH), 5.47 (1H, m, NCH(CH<sub>3</sub>)<sub>2</sub>), 4.32 (2H, m, NCH<sub>2</sub>), 0.94–1.60 (38H, CH(CH<sub>3</sub>)<sub>2</sub>, NCH(CH<sub>3</sub>)<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub> or C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR: δ 22.9, 23.4, 24.2, 26.3, 26.6, 29.5, 30.3, 32.0, 32.2, 35.9, 52.6, 55.3, 116.3, 120.5, 121.9, 123.3, 125.5, 126.2, 128.3, 128.5, 128.7, 129.0, 129.4, 139.0, 141.1, 141.3, 168.0. Anal. Calc. for C<sub>46</sub>H<sub>59</sub>N<sub>3</sub>NiO: C, 75.82; H, 8.16; N, 5.76. Found: C, 75.80; H, 8.17; N, 5.73%.

### 2.4. Synthesis of **2**

Following the procedure similar to the synthesis of **1**, 1,3-diisopropylimidazolium bromide (0.19 g, 1.0 mmol) was added to the Schlenk flask instead of 1-benzyl-3-isopropylimidazolium bromide. After workup, complex **2** was obtained as orange crystals in ca. 82% yield (0.56 g), which was suitable for X-ray diffraction studies and elemental analysis. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 8.01 (s, 1H, N=CH), 7.67 (1H, s, Ph-H), 7.50 (2H, d, Ph-H), 7.04 (1H, s, Ph-H), 6.91 (2H, m, Ph-H), 6.61 (4H, m, Ph-H), 6.22 (2H, s, NCH), 4.40 (2H, m, NCH(CH<sub>3</sub>)<sub>2</sub>), 1.34–1.50 (32H, CH(CH<sub>3</sub>)<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub> or C(CH<sub>3</sub>)<sub>3</sub>), 1.10 (12H, m, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR: δ 23.2, 28.6, 29.4, 30.7, 32.2, 51.9, 52.4, 115.5, 116.3, 119.2, 122.5, 123.0, 124.6, 125.1, 127.8, 128.0, 128.2, 129.0, 138.2, 138.6, 140.7, 151.5, 165.0, 167.7, 174.0. Anal. Calc. for C<sub>42</sub>H<sub>59</sub>N<sub>3</sub>NiO: C, 74.11; H, 8.74; N, 6.17. Found: C, 74.08; H, 8.70; N, 6.14%.

### 2.5. X-ray structural determination of **1** and **2**

Suitable single crystals of **1** and **2** were sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 153(2) K for **1** and 193(2) K for **2**, respectively. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on F<sup>2</sup>. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively. Crystal data and collection and main refinement parameters are given in Table 1. Selected bond lengths (Å) and angles (°) for **1** and **2** are given in Table 2.

### 2.6. A typical procedure for ethylene dimerization

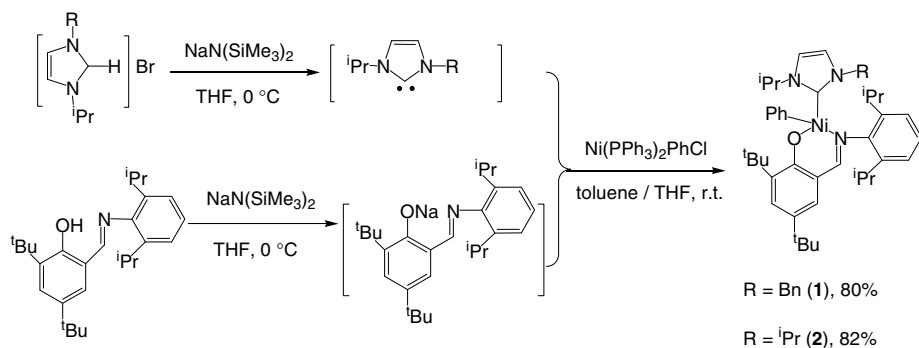
In a typical run, a Schlenk flask was charged with toluene (30 mL, saturated by ethylene (1 atm)) and MMAO (500 equiv.), a toluene solution (5 mL) of complex **1** (5.0 μmol) was added via syringe under N<sub>2</sub> at room temperature. After 60 min the ethylene was bled off and the reaction quenched with 10% HCl at –20 °C. The toluene phase was analyzed by GC–MS with *n*-heptane (0.8 mL) as an internal standard.

## 3. Results and discussion

### 3.1. Synthesis and characterization of **1** and **2**

The procarbene ligand, 1-benzyl-3-isopropylimidazolium bromide was prepared in quantitative yield by the alkylation reaction of the 1-isopropyl-imidazole with benzyl bromide. The formation of 1-benzyl-3-isopropylimidazolium bromide was supported by its <sup>1</sup>H NMR spectrum, particularly by the characteristic resonance at 8.77 ppm for the imidazolium proton.

Up to date, the substitution of phosphine ligands in Ni(II) halides by NHC ligands is one of the most common route to prepare NHC complexes of Ni(II) [5c]. Herein, a one-pot procedure was developed for the preparation of complexes **1** and **2** in high

Scheme 3. Synthesis of **1** and **2**.

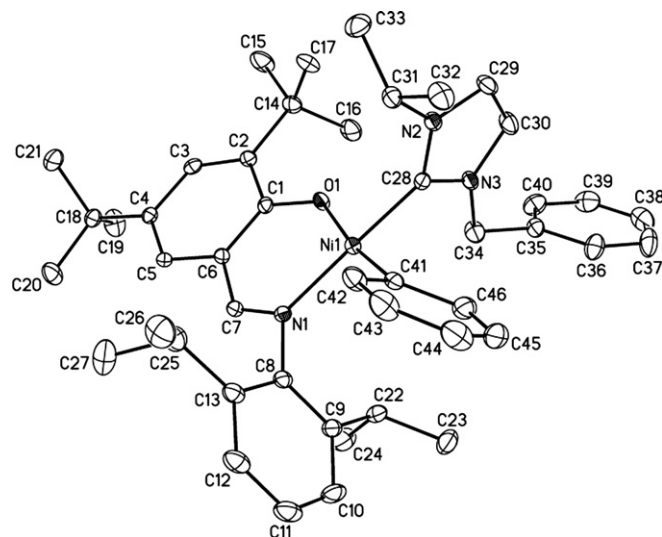
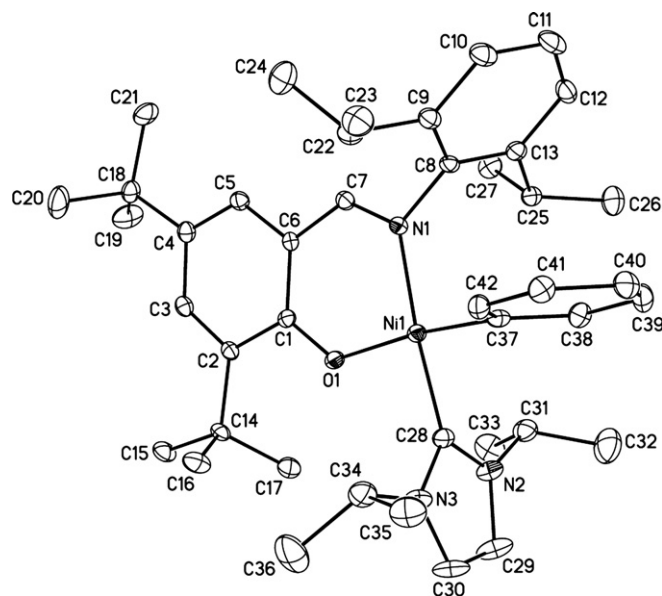
yield (Scheme 3). This procedure has the advantage to avoid the preparation of the phosphine-based neutral salicylaldimino Ni(II) complexes beforehand. Thus, the mixture of 3,5-*t*Bu<sub>2</sub>-2-(HO)-C<sub>6</sub>H<sub>2</sub>CH=NAr (Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), Bn-*i*Pr · HBr and NaN(SiMe<sub>3</sub>)<sub>2</sub> (1:1:2 molar ratio), which had stirred at 0 °C for 2.5 h, was directly reacted with an equivalent of Ni(PPh<sub>3</sub>)<sub>2</sub>PhCl at room temperature. After workup, the target product **1** was isolated as yellow crystals with analytical purity in *ca.* 80% yield. The similar one-pot procedure employing the imidazolium salt *i*Pr · HBr afforded the complex **2** as orange crystals in *ca.* 82% yield. The formation of **1** or **2** was initially supported by elemental analysis and NMR spectroscopy. The <sup>1</sup>H NMR spectra of complexes **1** and **2** exhibit the characteristic resonances of *iso*-propyl and *tert*-butyl protons, meanwhile disappear the characteristic resonances of the imidazolium proton. In their <sup>13</sup>C NMR spectra, the singlet NHC carbon (C<sub>carbene</sub>) signals appear at δ 168.0 ppm for **1** and δ 174.0 ppm for **2**, respectively. These chemical shifts of C<sub>carbene</sub> signals in <sup>13</sup>C NMR spectra are in good agreement with those reported for monocarbene Ni(II) complexes [11]. Further determination of the molecular structures of **1** and **2** were obtained by X-ray structural analysis. Complexes **1** and **2** represent one of only two examples of a stable phenyl Ni(II) complex bearing a single NHC ligand published. The other one is Ni(tm<sub>iy</sub>)<sub>2</sub>(*o*-tolyl)Br which was synthesized via the oxidative addition of Ni(tm<sub>iy</sub>)<sub>2</sub> with *o*-tolyl bromide (tm<sub>iy</sub> = 1,3,4,5-tetramethylimidazol-2-ylidene) [17].

In fact, it should be noted that the Ni(II) complexes presented in this work are quite stable, which is very similar to Ni(tm<sub>iy</sub>)<sub>2</sub>(*o*-tolyl)Br [17]. For example, complexes **1** and **2** are thermally stable and will melt (not decompose) at 227–228 °C and 232–234 °C, respectively. Besides, both of **1** and **2** are showed greatly enhanced air-stability in solid-state, as compared with their phosphine analogous, and even can remain unchanged for several days in open dry air. However, they are sensitive to water, especially in solution. For example, the color of their THF solution changed immediately during the addition of water. Complexes **1** and **2** are soluble in CHCl<sub>3</sub>, THF, DME, toluene and diethyl ether, sparingly soluble in hexane.

### 3.2. Crystal structures of **1** and **2**

Crystals of **1** and **2** suitable for an X-ray crystal structure determination were grown from hexane/DME for **1** and toluene/DME for **2** at –10 °C. The solid structures for **1** and **2** were shown in Figs. 1 and 2, respectively. The crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively.

The X-ray structural analysis revealed complexes **1** and **2** have the similar solid-state structure. The center nickel atom of each complex coordinated to phenyl carbon (C<sub>phenyl</sub>), O, N and C<sub>carbene</sub> to form a distorted square-planar geometry with a sum of the four

Fig. 1. The crystal structure of **1** showing 20% probability ellipsoids. The hydrogen atoms are omitted for clarity.Fig. 2. The crystal structure of **2** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

**Table 1**  
X-ray crystallographic data for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>46</sub> H <sub>59</sub> N <sub>3</sub> NiO	C <sub>42</sub> H <sub>59</sub> N <sub>3</sub> NiO
Formula weight	728.67	680.63
Temperature (K)	193(2)	153(2)
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71070	0.71070
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21/n
<i>a</i> (Å)	15.2641(18)	12.3136(9)
<i>b</i> (Å)	17.519(2)	14.0031(9)
<i>c</i> (Å)	15.7000(17)	22.8218(17)
$\beta$ (°)	94.460(3)	99.167(2)
<i>V</i> (Å <sup>3</sup> )	4185.7(8)	3884.9(5)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.156	1.164
Absorption coefficient (mm <sup>-1</sup> )	0.500	0.533
<i>F</i> (000)	1568	1472
Crystal size (mm)	0.39 × 0.20 × 0.05	0.28 × 0.20 × 0.18
2 $\theta$ <sub>max</sub> (°)	50.7	50.7
Number of reflections collected	40850	37589
Number of independent reflections ( <i>R</i> <sub>int</sub> )	7641 (0.0904)	7107 (0.0760)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.198	1.124
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0783	0.0607

**Table 2**  
Selected bond distances (Å) and angles (°) for **1** and **2**

<b>1</b>			
Ni(1)–C(28)	1.861(4)	Ni(1)–C(41)	1.891(4)
Ni(1)–O(1)	1.905(2)	Ni(1)–N(1)	1.927(3)
C(28)–Ni(1)–C(41)	86.9(2)	C(28)–Ni(1)–O(1)	85.1(1)
C(41)–Ni(1)–O(1)	171.3(1)	C(28)–Ni(1)–N(1)	176.2(1)
C(41)–Ni(1)–N(1)	95.6(1)	O(1)–Ni(1)–N(1)	92.6(1)
<b>2</b>			
Ni(1)–C(28)	1.875(3)	Ni(1)–C(37)	1.889(3)
Ni(1)–O(1)	1.905(2)	Ni(1)–N(1)	1.924(2)
C(28)–Ni(1)–C(37)	86.1(1)	C(28)–Ni(1)–O(1)	87.8(1)
C(37)–Ni(1)–O(1)	170.5(1)	C(28)–Ni(1)–N(1)	173.7(1)
C(37)–Ni(1)–N(1)	93.5(1)	O(1)–Ni(1)–N(1)	93.4(1)

bond angles at Ni of 360.2° (**1**) and 360.8° (**2**). Steric congestion around the Ni center is relieved by rotation of the carbene ring, the phenyl ring and the arylamine ring. Dihedral angles of the above rings relative to the coordination plane are 72.5°, 64.1° and 78.4° in turn for **1** and 88.9°, 81.5° and 80.7° in turn for **2**. The more perpendicular dihedral angles presented in **2** reflect a bigger steric hindrance induced by the *iso*-propyl substituent on the carbene ring than by the benzyl moiety. The NHC ligand is *trans* to the arylamine group with a nearly linear C<sub>carbene</sub>–Ni–N angle of 176.1° for **1** or 173.7° for **2**, which is close to the reported value (172.2° for **3**) [13a]. The Ni–C<sub>carbene</sub> bond length of 1.861 Å for **1** or 1.875 Å for **2** is within the range for normal Ni–C<sub>carbene</sub> bonds. For example, both of them are shorter than that of 1.911–1.919 Å observed in Ni(tmy)<sub>2</sub>(*o*-tolyl)Br [17], and slightly longer than that of 1.848 Å observed in the phenyl Ni(II) complexes bearing enolate chelating NHC ligand (**4**) [8a]. The Ni–N bond length of 1.927 Å for **1** and 1.924 Å for **2** is very close to the reported value of 1.937 Å for PPh<sub>3</sub>-based neutral salicylaldiminato Ni(II) phenyl complex **3** [13a]. The phenyl group attached to Ni(II) lies approximately *trans* to phenoxide oxygen with a O–Ni–C<sub>phenyl</sub> angle of 171.3° for **1** or 170.5° for **2**, which is closer to linearity than that of 166.2° observed in **3** [13a]. The Ni–C<sub>phenyl</sub> bond length of 1.891 Å for **1** or 1.889(3) Å for **2** is almost the same as that of 1.895 Å observed in **3** [13a] and 1.891 Å in **4** [8a]. By the way, the same Ni–O bond length of 1.905 Å is observed in **1** and **2**, which is also just the same as 1.910 Å found in **3**, whereas a slightly shorter Ni–O bond of 1.891 Å was observed in **4** [8a]. The similarity of the typical bond

length between **1/2** and **3**, *i.e.* Ni–C<sub>phenyl</sub> and Ni–O bond, indicates that the PPh<sub>3</sub> and NHC ligand presented herein has little effect on the Ni–C<sub>phenyl</sub> and Ni–O interaction in the neutral salicylaldiminato Ni(II) phenyl complexes of the type (N–O)Ni(Ph)(L), whereas the slightly difference of Ni–N bond length between the two kinds of neutral Ni(II) complexes might be due to the stronger *trans* influence exerted by PPh<sub>3</sub> than by the NHC moiety [5d] in the salicylaldimine framework. Otherwise, the different substituents on the carbene ring of **1** and **2** showed only little effect on their solid structure, which might be due to the rotation of the carbene ring.

### 3.3. The catalytic activity of **1** for the dimerization of ethylene

Since complexes **1** and **2** have very similar solid structure, only complex **1** was tested as a catalyst for ethylene polymerization. Surprisingly, toluene solution of complex **1** is inert toward the insertion of ethylene (1–7 bar ethylene, 25–60 °C) in the absence of a co-catalyst such as MMAO, which is quite different from the PPh<sub>3</sub>-based analogues of **3** [13a]. Then, we studied the same polymerization reaction in the presence of MMAO. However, complex **1** still showed very low reactivity at room temperature under 1 bar ethylene when the molar ratio of MMAO to **1** varied from 1500 to 500. After 1 h only trace dimmer of ethylene was detected. When the pressure of ethylene being increased to 7 bar and the reaction temperature being increasing to 60 °C, complex **1** showed a modest activity of 3.05 × 10<sup>4</sup> g(mol Ni)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> after 60 min under a 500 molar ratio of MMAO to **1** (the oligomerization conditions were not optimized). Interestingly, GC/MS analysis of the final reaction solution showed the products to be unique 1-butene, indicating that β-H elimination from the putative Ni–Bu intermediate is too fast to chain propagation. It is worthy noticing that the catalytic system of **1** and MMAO is quite stable and no decomposition of **1**, *i.e.* the appearance of black powder in the reaction solution, was observed during the reaction process. Considering the greatly difference of catalytic behaviors for ethylene polymerization between **1** and **3**, it might be reasonable to assume that the resting state of the present system should be a NHC complex. We note that a recent report also assumed that the NHC ligand coordinated to the active species for the styrene oligomerization initiated by cationic allyl complexes of Ni(II) bearing a single NHC ligand, which also be studied as mimicking the analogous phosphine-based system [12].

## 4. Conclusion

In summary, we have prepared two neutral salicylaldiminato Ni(II) complexes bearing a single NHC ligand via a convenient one-pot procedure in high yield. Both of them show obviously enhanced thermal and air-stability as compared with their phosphine analogues. The preliminary study showed that complex **1** could catalyze the dimerization of ethylene in the presence of MMAO with a moderate activity of 3.05 × 10<sup>4</sup> g(mol Ni)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> in a highly selective fashion. Although complex **1** could not be used as single-component catalyst for the ethylene polymerization, the present work provide a directly characteristic comparison between NHC ligands and phosphine ligands, and provide an useful hypothesis for guiding future nickel-based catalyst construction, *i.e.* tuning the degree of olefin polymerization and so on.

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 665468 and 665469 contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.03.005.

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