

# Indenyl nickel complexes: synthesis, characterization and styrene polymerization catalysis

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## Abstract

Neutral indenyl nickel complexes with the general formula  $(\eta\text{-}1\text{-R-Ind})\text{Ni}(\text{PPh}_3)\text{Cl}$  ( $\text{R}$  = cyclopentyl (**1**), benzyl (**2**)) have been prepared and characterized by  $^1\text{H-NMR}$  spectroscopy and single-crystal X-ray analysis. The results of X-ray crystal structural determination reveal that the hapticity of indenyl ligand in complex **1** or **2** is significantly distorted away from an idealized  $\eta^5$  mode to an unsymmetrical  $\eta^3$  mode. Furthermore, the structures of  $(\text{R-Ind})\text{Ni}(\text{PPh}_3)\text{Cl}$  exhibit a progressively more distorted coordination of the indenyl ring from cyclopentyl to benzyl. Both of them are inert toward the insertion of styrene, however, they are able to catalyze the polymerization of styrene effectively in the presence of  $\text{NaBPh}_4$  and  $\text{PPh}_3$  to give syndio-rich atactic poly(styrene) with  $M_w$  values in the range of  $10^4$ . The  $\text{NaBPh}_4 \cdot \mathbf{1} \cdot \text{PPh}_3$  system shows the higher catalytic activity than the  $\text{NaBPh}_4 \cdot \mathbf{2} \cdot \text{PPh}_3$  system.

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**Keywords:** Nickel complex; Indenyl ligand; Polymerization; Styrene; Crystal structure

## 1. Introduction

The research of metallocene chemistry has showed that the hapticity of a polyolefin ligand usually exerts a dominant influence on the reactivity of its metal complexes [1]. One such kind of ligand, namely indene and its substituted derivatives, is of special interest in Group IVB complexes owing to its easily coordination modification by substitution [1,2]. However, their applications in group 10 metal complexes have received less attention. Recently, Zargarian et al. have reported that  $(\text{Ind})(\text{PR}_3)\text{Ni-X}$  ( $\text{Ind}$  = indenyl and its substituted derivatives;  $\text{R}$  = Ph, Me, Cy, Bu, etc.;  $\text{X}$  = halide, alkyl, alkynyl, imidate, thiolate, etc.) [3–6] can act as effective precatalysts in a number of reactions, such as the oligomerizations or polymerizations of ethylene [4], styrene [5] and phenylacetylene [6], the dehydrogenative oligomerization and polymerization of phenylsilane [7] etc. Preliminary studies have implied that the in situ

generated cationic species  $[\text{Ind}(\text{PPh}_3)\text{Ni}]^+$  might be the active centers for these reactions and the Ind substituents have a major influence on the course of the catalysis, the later is in evidence by comparison the analogous styrene reactions catalyzed by in situ generated cations from  $(1\text{-Me-Ind})(\text{PPh}_3)\text{Ni-Cl}$  and  $(\eta^3, \eta^0\text{-Ind-CH}_2\text{CH}_2\text{NMe}_2)(\text{PPh}_3)\text{Ni-Cl}$  [5]. However, the knowledge about the structure–activity relationships of indenyl nickel complexes seems still insufficient.

Recently, we have reported the development of Pd(II) and Ni(II) acetylide complexes  $(\text{PR}'_3)_2\text{M}(\text{C}\equiv\text{CR})_2$  [ $\text{M}$  = Pd, Ni;  $\text{R}'$  = Ph<sub>3</sub>, *n*-Bu<sub>3</sub>;  $\text{R}$  = Ph, CH<sub>2</sub>OH, CH<sub>2</sub>OOCCH<sub>3</sub>, CH<sub>2</sub>OOCPh, CH<sub>2</sub>OOCPhOH-*o*, C≡CC<sub>6</sub>H<sub>4</sub>C≡CH, etc.] as high active initiators for polymerizations of a series of monomers, e.g. propargyl alcohol [8], *p*-diethynylbenzene [9], methyl methacrylate [10], styrene [11], and so on. To our some surprise, the nickelocene acetylides  $(\pi\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ni}(\text{C}\equiv\text{CR})_2$  showed no catalytic activity for styrene or methyl methacrylate polymerization. Considering the so-called ‘indenyl effect’, also as an extension of our continuous study in this area, we report herein the preparation and structural characterization of new indenyl nickel complexes  $(\eta\text{-}1\text{-R-Ind})(\text{PPh}_3)\text{Ni-Cl}$  ( $\text{R}$  = cyclopentyl (**1**),

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benzyl (**2**)) and their catalytic activities in styrene polymerization, which enlarge the list of analogous complexes already described [3–7] to such an extent that comparative studies of their structure–catalytic activity relationships may be possible.

## 2. Results and discussion

### 2.1. Synthesis and characterization of the indenylnickel complexes

The indenyl nickel complexes **1** and **2** are synthesized by the reactions of  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  with the corresponding lithium R-indenyl as shown in Scheme 1. Because the reaction of 1-cyclopentylindene or 1-benzylindene with an equimolar amount of *n*-BuLi in  $\text{Et}_2\text{O}$  give a quantitative yield of cyclopentyl or benzyl indenyl lithium, so freshly prepared solution of indenyl lithium is directly used in the following metathesis reactions. Thus, 1-cyclopentylindene or 1-benzylindene reacted with *n*-BuLi in  $\text{Et}_2\text{O}$  for 40 min at  $0^\circ\text{C}$ , the resulting solution was slowly added into a stirring suspension of  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  in 1:1.8 molar ratio. After workup, the expected complexes (R-Ind)Ni(PPh<sub>3</sub>)Cl (R = cyclopentyl (**1**), benzyl (**2**)) were isolated as dark red crystals in ca. 45% (**1**) or 65% (**2**) yield, supported by elemental analysis and  $^1\text{H-NMR}$  spectroscopy. Suitable crystals of **1** and **2** for X-ray diffraction studies are grown from cold hexane–DME solution.

Both of **1** and **2** have good thermal stability, they are air- and moisture-sensitive, and soluble in toluene,  $\text{CH}_2\text{Cl}_2$ , DME, THF and diethyl ether, but insoluble in hexane.

The crystal structures of **1** and **2** were determined in order to see the influence of substituted groups on indenyl ring on the structures of these complexes. The molecular structures of **1** and **2** are presented in Figs. 1 and 2, respectively. The crystallographic data and selected bond lengths and angles for **1** and **2** are listed in Tables 1 and 2, respectively. Molecular structures of **1** and **2** are analogues, and both are monomeric in the solid state, but they crystallize in different space groups (triclinic for **1** and orthorhombic for **2**). Each Ni in the two complexes is bound to P, Cl, C2, C3 and C4 based on the bond distances of Ni to these atoms, while the bond distances of the other two carbon atoms of the five-membered ring, i.e. C1 and C5, to Ni are significantly longer. The geometry of these complexes around Ni can be described as a distorted square planar with

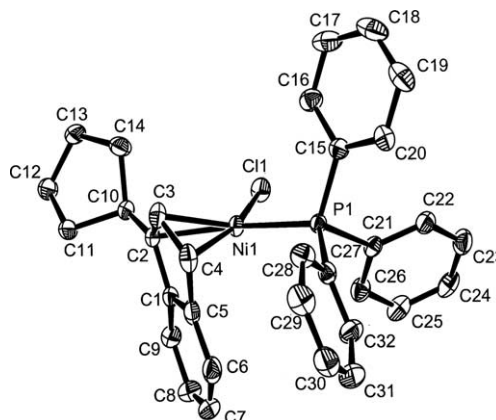


Fig. 1. The crystal structure of complex **1**.

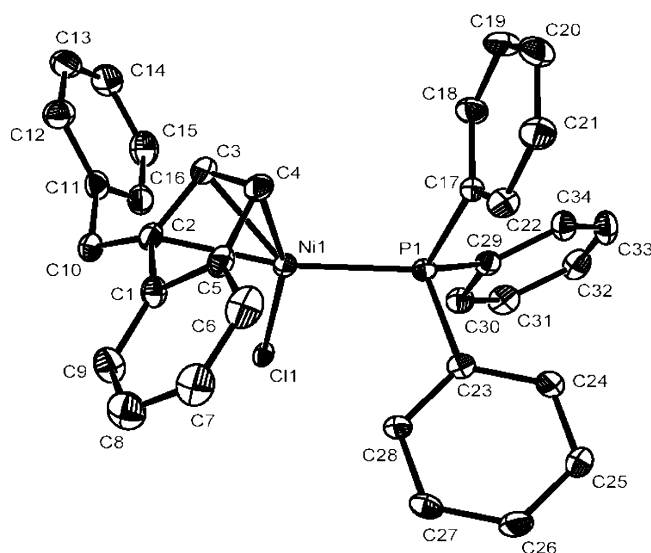
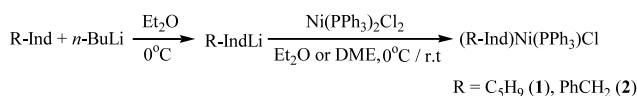


Fig. 2. The crystal structure of complex **2**.

$\text{C2}=\text{C3}$  occupying a single coordination site. In both structures, the Ind hapticity of the Ind ligand is significantly distorted away from an idealized  $\eta^5$  mode toward a fairly unsymmetric  $\eta^3$  coordination, which is common in this family of complexes [3b]. These distortions can be mainly attributed to the tendency of Ni(II) to avoid forming 18-electron complexes and the unequal *trans* influences of the  $\text{PPh}_3$  and Cl groups [3b,d]. On the other hand, the influence of substituted groups on indenyl ring on the solid state structure of **1** and **2** is also observed in the following manner. For instance, different Ni–Ind interactions occurred in present case. The Ni–Ind interaction can be compared quantitatively by calculating the parameters such as the slip value ( $\Delta\text{M}-\text{C}$ ) =  $[\text{M}-\text{C}_{\text{av}}(\text{for C}_1, \text{C}_5)] - [\text{M}-\text{C}_{\text{av}}(\text{for C}_2, \text{C}_4)]$  [3a]. In **1**,  $\Delta\text{M}-\text{C} = 0.27$ , more close to the value found in **3** (0.25) [3b], meanwhile in **2**,  $\Delta\text{M}-\text{C} = 0.31$  (Table 2), indicating a less slip-fold distortion of Ind ligand in **1** compared to that in **2**, as well as an increase of the Ind hapticity from **3** to **1** to **2**. Furthermore, as the observed



Scheme 1.

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

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>32</sub> H <sub>30</sub> NiPCl	C <sub>38</sub> H <sub>38</sub> O <sub>2</sub> PClNi
Formular weight	539.72	651.84
Temperature(K)	193(2)	193(2)
$\lambda$ (Mo–K $\alpha$ ) (Å)	0.71070	0.71070
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions		
<i>a</i> (Å)	9.061(3)	9.0898(5)
<i>b</i> (Å)	10.351(4)	13.6106
<i>c</i> (Å)	15.333(6)	26.450(2)
$\alpha$ (°)	80.137(13)	90.00
$\beta$ (°)	81.981(10)	90.00
$\gamma$ (°)	66.410(10)	90.00
<i>V</i> (Å <sup>3</sup> )	1294.5(8)	3272.3(4)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.385	1.323
Absorption coefficient (mm <sup>-1</sup> )	0.934	0.756
<i>F</i> (000)	564	1368
Crystal size (mm <sup>3</sup> )	0.26 × 0.66 × 0.13	0.45 × 0.80 × 0.10
2 $\theta$ <sub>max</sub> (°)	55.0	55.0
Reflections collections	10246	32921
Independent reflections	5650 [ <i>R</i> <sub>int</sub> = 0.022]	4159 [ <i>R</i> <sub>int</sub> = 0.042]
Data/restraints/parameters	4607/0/346	3644/0/426
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.00	1.00
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.033	0.0510
<i>R</i> <sub>w</sub>	0.097	0.1510

Table 2  
Select bond lengths (Å), bond angles (°) and structural parameters<sup>a</sup> (Å) for **1** and **2**

	<b>1</b>	<b>2</b>	<b>3</b> <sup>a</sup>
<i>Bond lengths</i>			
Ni–P	2.1810(10)	2.1860(10)	2.1782(11)
Ni–Cl	2.187(10)	2.2390(10)	2.1865(10)
Ni–C2	2.135(2)	2.144(5)	2.137(2)
Ni–C3	2.053(2)	2.053(5)	2.072(2)
Ni–C4	2.031(2)	2.020(5)	2.026(3)
Ni–C5	2.336(2)	2.377(5)	2.308(2)
Ni–C1	2.367(2)	2.410(5)	2.351(2)
C2–C3	1.418(3)	1.393(8)	1.403(4)
C3–C4	1.423(3)	1.442(8)	1.421(4)
C4–C5	1.457(3)	1.466(8)	1.451(4)
C1–C2	1.463(3)	1.467(7)	1.457(4)
C1–C5	1.423(3)	1.427(7)	1.4179(4)
<i>Bond angles</i>			
P–Ni–Cl	98.01(4)	102.80(5)	98.82(4)
P–Ni–C2	165.98(6)	163.2(2)	165.62(7)
P–Ni–C4	99.03(7)	96.5(2)	99.33(8)
Cl–Ni–C2	96.01(6)	93.9(2)	95.48(8)
C2–Ni–C4	66.96(9)	66.8(2)	62.79(9)
<i>Structural parameters</i>			
$\Delta$ M–C	0.27	0.31	0.25

<sup>a</sup> Taken from Ref. [3b].

values of the C2–C3, C3–C4, Ni–C2 and Ni–C4 bond lengths reflect the delocalization of the allyl moiety of Ind ligand, so the local symmetry in the coordination of the allyl moiety are also different in **1** and **2**, and indicate a more symmetric Ni–Ind interaction in **1**. Additionally, the Ni–P and Ni–Cl distance are apparently shorter in **1** (2.1810(10) and 2.187(10), respectively) than in **2** (2.1860(10) and 2.2390(10), respectively). Thus, Ni–Ind interaction together with Ni–Cl and Ni–P interactions are stronger in **1** than those in **2**, and seem closely between **1** and **3**. In the present case, we propose these differences mainly arising from the different substitution on the Ind ligand, and a ‘soft’, electron donating substituent such as cyclopentyl may do good to the stronger coordination between the nickel atom vis à vis the ancillary ligands in these indenyl nickel complexes. Alternatively, besides PPh<sub>3</sub> and Cl<sup>-</sup>, the substitution of the Ind ligand also be able to affect the relative ligand trans effects, and then on the hapticity of the Ind ligand.

Since the nature of the Ni–Ind interaction in solution is believed to be able to influence substantially the reactivity of Ind complexes, it is important to understand Ind hapticity in solution. Zargarian’s group [3b] have observed that, for **3** and its methyl derivative, the direct correlation between structural and solution NMR spectra data and used the <sup>1</sup>H-NMR resonances for the symmetry-related pairs of protons (H2/H4, H6/H9, and H7/H8) as a convenient indicator of Ind hapticity. Accordingly, they concluded that the solid state structures of these complexes were maintained in the solution. Herein, the above conclusion can also be reached from the paired comparisons of the <sup>1</sup>H-NMR spectra of these complexes (i.e. 1/3 and 2/3), as their <sup>1</sup>H-NMR spectra are very similar in pairs. For example, the H4 resonance in **1** (3.37 ppm) or in **2** (3.50 ppm) is very close to the corresponding resonance for **3** (3.37 ppm).

## 2.2. The polymerization of styrene

To the best of our knowledge, the catalytic activity of indenyl nickel complexes for styrene reactions has been reported only by Zargarian’s group, a chelating amino–indenyl cationic nickel complex in situ generated from ( $\eta^3$ ,  $\eta^0$ -Ind-CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)Ni(PPh<sub>3</sub>)Cl and AgBPh<sub>4</sub> (or AgBF<sub>4</sub>) for styrene polymerization or a 3/AgBF<sub>4</sub> system for oligomerization of styrene [5]. In the present paper, the catalytic behavior of (R–Ind)Ni(PPh<sub>3</sub>)Cl (R = cyclopentyl (**1**), benzyl (**2**)) for the polymerization of styrene in toluene has been tested. The preliminary results are listed in Table 3. The results show that complex **1** or **2** without NaBPh<sub>4</sub> is inert toward the insertion of styrene, however, together with NaBPh<sub>4</sub> and PPh<sub>3</sub>, they show highly catalytic activity for the polymerization of styrene. The purpose of the reaction between complex **1** or **2** with NaBPh<sub>4</sub> is to abstract the Cl<sup>-</sup> ligand from these complexes and facilitate the

Table 3  
Polymerization of styrene initiated by (R-Ind)Ni(PPh<sub>3</sub>)Cl/NaBPh<sub>4</sub>/PPh<sub>3</sub><sup>a</sup>

Run	R	Yield <sup>b</sup> (%)	$M_n$ ( $\times 10^{-3}$ )	$M_w$ ( $\times 10^{-3}$ )	$M_w/M_n$ <sup>c</sup>	Catalytic activity (kg PE/mol Ni h)
1	C <sub>5</sub> H <sub>9</sub>	83	4.09	11.7	2.86	1.8
2 <sup>d</sup>	C <sub>5</sub> H <sub>9</sub>	55	–	–	–	0.71
3	PhCH <sub>2</sub>	58	8.68	34.1	3.93	1.3
4	CH <sub>3</sub>	78	5.96	28.0	4.70	1.7

<sup>a</sup> General polymerization conditions: [Ni] = 25 mM; [M]/[Ni] = 300;  $T = 80^\circ\text{C}$ ;  $t = 24$  h; NaBPh<sub>4</sub>/(R-Ind)Ni(PPh<sub>3</sub>)Cl/PPh<sub>3</sub> = 7:1:1.

<sup>b</sup> Yield = weight of polymer obtained/weight of monomer used.

<sup>c</sup> Measured by GPC calibrated with standard polystyrene samples.

<sup>d</sup> NaBPh<sub>4</sub>/(R-Ind)Ni(PPh<sub>3</sub>)Cl/PPh<sub>3</sub> = 7:1:4.

formation of cationic species [3d,4a,e], while the addition of moderate PPh<sub>3</sub> is of benefit to suppress the decomposition of the cationic species (as shown below). For example, when the styrene polymerization was carried out in toluene at 80 °C with NaBPh<sub>4</sub>/1/PPh<sub>3</sub> = 7:1:4 (mole ratio), [styrene]/[1] = 500 (mole ratio), the polymer yield could reached 83% after 24 h (run 1, Table 3). The obtained polystyrene is soluble in THF with  $M_w = 11700$  and  $M_w/M_n = 2.86$ . Fig. 3 shows the <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>) of the phenyl C-1 carbon of the obtained polymer. According to reported results, the phenyl C-1 carbon signal is the most important signal for determining stereoregularity of polystyrene [15a]. The present spectrum shows characteristically broad signals of atactic polystyrene in the range of ca. 145–147 ppm [15b]. Furthermore, the phenyl C-1 spectrum can be analyzed in term of triads, the three main peaks from higher magnetic field (ca.  $\delta = 145.8$  ppm) to lower magnetic field (ca.  $\delta = 146.7$  ppm) are assigned to syndiotactic triad (rr), heterotactic triad (mr) and isotactic triad (mm), respectively. Thus, it is obviously that the polystyrene obtained with NaBPh<sub>4</sub>/1/PPh<sub>3</sub> system is a syndio-rich atactic polymer [15].

The influence of the substituents on Ind ligand on the catalytic activity of the corresponding complexes are also observed (runs 1, 3 and 4, Table 3), with (1-(C<sub>5</sub>H<sub>9</sub>)Ind)Ni(PPh<sub>3</sub>)Cl being the most active one (according to the polymer yield). Similar higher activity is

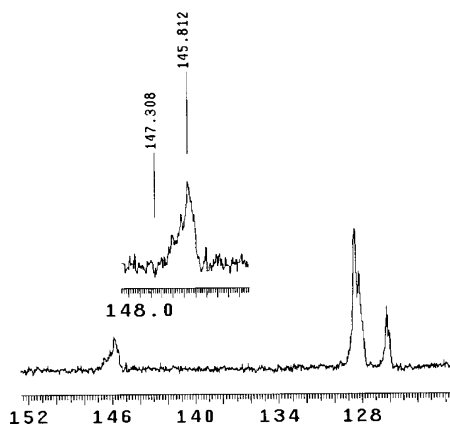


Fig. 3. <sup>13</sup>C-NMR spectrum of polystyrene (CDCl<sub>3</sub>, 100 MHz).

obtained with 3. On the contrary, the polymer with the most high molecular weight is obtained with 2, as well as polymers with similar molecular weight are obtained with 1 or 3. Apparently, the differences between their catalytic activities are in accord with those of between their Ind hapticities as shown above, indicating a close relationship between structure–activity of these indenyl nickel complexes. In the present case, it is suggested that a ‘soft’, electron donating substituent on the Ind ligand is of benefit to increase the catalytic activity of the indenyl nickel complex for styrene polymerization.

In addition, it is noteworthy that the proper quantity of PPh<sub>3</sub> is necessary to initiate a higher active polymerization of styrene. In the present system, the optimal Ni:PPh<sub>3</sub> ratio seems to be about 1:1 for the Ni–Cl precursor, and a large excess of PPh<sub>3</sub> leads to a dramatic decrease in polymer yield (runs 1 and 2, Table 3). However, a rapid decomposition of the Ni–Cl complex is observed at the polymerization temperature in the reaction system in the absence of PPh<sub>3</sub>. By the way, PPh<sub>3</sub> has no catalytic activity for the present polymerization in blank experiment. On the other hand, Zargarian et. al. have reported that a bis(phosphine) cationic species [(1-Me-Ind)Ni(PPh<sub>3</sub>)PPh<sub>3</sub>]<sup>+</sup> was obtained in 90% yield when equimolar quantities of 3, AgBF<sub>4</sub> and PPh<sub>3</sub> are stirred in CH<sub>2</sub>Cl<sub>2</sub> [4a], similar results were also observed when PPh<sub>3</sub> was added to the mixture of ( $\eta^3$ ,  $\eta^0$ -Ind-CH<sub>2</sub>CH<sub>2</sub>Ni-Pr<sub>2</sub>)Ni(PPh<sub>3</sub>)Cl and NaBPh<sub>4</sub> (>90%) [4e]. In fact, the highly electrophilic ‘naked’ cation [(1-Me-Ind)Ni(PPh<sub>3</sub>)]<sup>+</sup>, which is generated from the reaction between 3 and AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> in the absence of any donor, is nonstabilized and coordinates any residual PPh<sub>3</sub> from 3. Thus, combination with the reported results indicate that the present styrene polymerization mainly be catalyzed by the in situ generated cationic species [1-R-Ind(PPh<sub>3</sub>)Ni(PPh<sub>3</sub>)]<sup>+</sup>. An excess of PPh<sub>3</sub> could suppress the effective competition of styrene for coordination to Ni, and leads to a dramatic decrease in polymer yield. It is not clear, however, why the bis(phosphine) cationic species [(1-Me-Ind)Ni(PPh<sub>3</sub>)PPh<sub>3</sub>]<sup>+</sup> is catalytically inert toward ethylene polymerization [5], yet it shows moderate activity for the polymerization of styrene. We

suggest it might be due to the fact that styrene is a more electron-rich monomer than ethylene.

### 3. Conclusion

Indenyl nickel complexes (R-Ind)Ni(PPh<sub>3</sub>)Cl (R = cyclopentyl (**1**), benzyl (**2**)) can be easily prepared by the reactions of R-IndLi (R = cyclopentyl, benzyl) with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in 1:1.8 molar ratio, respectively. Moreover, the NaBPh<sub>4</sub>/(R-Ind)Ni(PPh<sub>3</sub>)Cl/PPh<sub>3</sub> systems were found to be able to initiate the polymerization of styrene with high activity to give moderate molecular weight, syndio-rich atactic polystyrene. A close relationship between the structure–activity of these indenyl nickel complexes is observed. Although the mechanistic details of the styrene polymerization are not known with certainty, the involvement of cationic species such as [(1-R-Ind)Ni(PPh<sub>3</sub>)PPh<sub>3</sub>]<sup>+</sup> in the reaction has been suggested. Further investigations focus on the detailed structure–activity relationships and mechanistic aspects of the polymerization using these complexes are now in progress.

### 4. Experimental

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 prior to use. Indene (Fluka) (dried over 4 Å molecular sieves) and styrene (dried over CaH<sub>2</sub>) were distilled before use. The (PPh<sub>3</sub>)<sub>2</sub>NiCl<sub>2</sub> [12] and the ligands 1-cyclopentylindene [13], 1-benzylindene [14] and complex **3** [3b] were prepared by published methods. Carbon and hydrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Molecular weight and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-3 and HR-4); THF was used as an eluent at 30 °C. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>) and <sup>13</sup>C-NMR (CDCl<sub>3</sub>) spectra were measured on a Unity Inova-400 spectrometer.

#### 4.1. Synthesis of (1-C<sub>5</sub>H<sub>9</sub>C<sub>9</sub>H<sub>6</sub>)Ni(PPh<sub>3</sub>)Cl (**1**)

A Schlenk flask was charged with 1-cyclopentylindene (0.55 g, 3 mmol), DME (50 ml) and a stir bar. *n*-BuLi (2.3 mL, 3 mmol, 1.30 M in hexane) was added dropwise to this solution via syringe at 0 °C. The solution was stirred for 30 min and then added slowly to a stirring suspension of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3.53 g, 5.4 mmol) in DME at 0 °C. The color of the solution gradually changed to dark red. The resultant solution was then stirred for

another 40 min at room temperature, filtered, and evaporated to dryness. The residue was washed with hexane (3 × ca. 20 ml) to remove PPh<sub>3</sub> and other byproducts and recrystallized from DME–hexane solution at 0 °C yielded crystals (728 mg, 45%) suitable for X-ray diffraction studies and elemental analysis. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.72 (m, 5H, PPh<sub>3</sub>), 7.36 (m, 1H, H8), 7.02 (m, 11H, PPh<sub>3</sub> and H9), 6.91 (t, 1H, H7), 6.45 (br s, 1H, H3), 6.22 (d, 1H, H6), 3.37 (br s, 1H, H4), 0.89–2.91 (m, 9H, C<sub>5</sub>H<sub>9</sub>). Anal. Calc. for C<sub>32</sub>H<sub>30</sub>ClNiP: C, 71.25; H, 5.56. Found: C, 71.28; H, 5.71%.

#### 4.2. Synthesis of (1-C<sub>7</sub>H<sub>7</sub>C<sub>9</sub>H<sub>6</sub>)Ni(PPh<sub>3</sub>)Cl (**2**)

Following the procedure similar to the synthesis of **1**, (1-C<sub>7</sub>H<sub>7</sub>C<sub>9</sub>H<sub>6</sub>)Li (5.2 ml, 3 mmol, 0.58 M in Et<sub>2</sub>O) was added slowly to a stirring suspension of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3.53 g, 5.4 mmol) in Et<sub>2</sub>O (60 ml) at room temperature (r.t.). The color of the solution gradually changed to dark red. The resulting solution was then stirred for another 40 min, filtered, and evaporated to dryness. The residue was washed with hexane (3 × ca. 20 ml) to remove PPh<sub>3</sub> and other byproducts and recrystallized from Et<sub>2</sub>O–hexane at –30 °C to give the product as dark red crystals (986 mg, 65%) for elemental analysis and <sup>1</sup>H-NMR. Recrystallization of a small portion of this solid from a cold DME–hexane solution yielded crystals suitable for X-ray diffraction studies. The result of the X-ray diffraction analysis showed the crystal cell contained a solvent molecular. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, δ): 7.68 (t, 1H, H8), 7.46 (m, 20H, Ar), 7.23 (m, 1H, H9), 6.93 (t, 1H, H7), 6.36 (br s, 1H, H3), 6.17 (br s 1H, H6), 3.50 (br s, 1H, H4), 1.63 (br s, 2H, –CH<sub>2</sub>–ph). Anal. Calc. for C<sub>34</sub>H<sub>28</sub>ClNiP: C, 72.70; H, 5.02. Found: C, 72.93; H, 5.11%.

#### 4.3. A typical procedure for polymerization of styrene

The procedures for the polymerization of styrene are the same, and a typical polymerization reaction is given as follows. Under dry argon, the solid initiator **1** (11.3 mg, 0.02 mmol), PPh<sub>3</sub> (21 mg, 0.08 mmol), NaBPh<sub>4</sub> (48 mg, 0.14 mmol), toluene (0.2 ml) and styrene (1.2 ml, 0.01 mol) were added into a dry glass ampule in turn. Then, the sealed ampule was placed into a water bath held at 80 °C. After a definite reaction time, the polymerization was stopped by adding 1 ml of 5% HCl–ethanol. After evaporation of solvent and unreacted monomer, the resulted polymer was dissolved in THF, followed by precipitation in 95% ethanol. After filtration, the white polymer was dried in vacuum at room temperature overnight. The polymer yield was determined gravimetrically.

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

A suitable crystal was mounted in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Bruker SMART CCD area detector using phi and omega scans. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on  $|F|^2$ . 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.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 207234 and 207235 for complexes **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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