Note

Synthesis and characterization of indenyl-functionalized N-heterocyclic carbene complex of Ni(II)

Hong-Mei Sun, Dong-Mei Hu, Yong-Sheng Wang, Qi Shen *, Yong Zhang

The Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, China

Abstract

A new type of Ind-NHC ligand precursor (Ind = indenyl), $[C_9H_7-(CH_2)_3-(CH\{NCHCHN^iPr\})]Br$ (HL·HBr, **1**), was designed and prepared. The reaction of in situ generated anionic indenyl-functionalized NHC ligand LLi with $(DME)NiCl_2$ affords a novel mono-ligand Ni(II) bromide, $[C_9H_6-(CH_2)_3-(C\{NCHCHN^iPr\})]NiBr$ (**2**), which was characterized by elemental analysis, NMR and X-ray crystal determination. Complex **2** in combination with $NaBPh_4$ can catalyze the polymerization of styrene at 80 °C.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Functionalized N-heterocyclic carbene; Nickel(II) complex; Indenyl; Styrene; Polymerization

1. Introduction

Since the first isolation of a stable imidazol-2-ylidene in pure form [1], the application of N-heterocyclic carbenes (NHCs) in ligand designs and modifications has played a crucial role for developing late transition metal-based organometallic catalysis [2]. In particular a number of Ni-based NHC systems have recently emerged as effective catalysts for a variety of coupling reactions [3]. However, their application in polymerization reaction has been quite limited [4]. The reason for it was supposed to the broken of the Ni–$C_{carbene}$ bond and then the decomposition of the active species via the reductive elimination of the hydrocarbyl and carbene moiety, as free NHC trends to 1,2-alkyl migration in Ni(II) complexes [4a,5]. Such a mode of decomposition is often more facile with cationic complexes [6]. The problem might be solved by use of the pendant functionalized bidentate or polydentate NHCs ligands developed recently, in which an anionic [7] or neutral group [8] acts as an anchor and the NHC is hemilabile. In general, these hemil-

abile ligands have been prone to provide an opportunity to control the stability [7c,7d],[8a] and reactivity of active centers more efficiently [7a,7h,8c]. As an inference to this, such pendant functionalized NHC ligands should also be useful in the design of late transition metal-based catalysts for polymerization reactions. In fact, two kinds of functionalized NHC complexes of Ni(II), i.e. pyridine [8c] or enol [7b]-functionalized NHC complexes of Ni(II), have been investigated for the polymerization of norbornene [8c] or ethylene [7b,8c]. Very recently, we reported the synthesis of the salicylaldimine-functionalized NHC complex of Ni(II) and its good catalytic activity for the polymerization of styrene in the presence of $NaBPh_4$ [9]. Inspired by the rich chemistry stemming from half-sandwich metallocene catalysts [10] and indenylnickel(II) complexes [11], we have modified the NHC ligand by introducing the indenyl group to the nitrogen atom of the five-member ring by an propenylene spacer and successfully synthesized the first Ni(II) complex (**1**) with the hemilabile NHC ligand. Preliminary study indicates that this complex also shows good catalytic activity for the polymerization of styrene in the presence of $NaBPh_4$. Herein we report these results. In a comparable approach, there has only been one example published so far that half-sandwich complexes of the type (FI-

---
* Corresponding author. Tel.: + 86 512 65880306; fax: +86 512 65880305.

E-mail address: qshen@suda.edu.cn (Q. Shen).

NHC)Ti(NMe$_2$)Cl or (Ind-NHC)V(NMe$_2$)Br (Fl = fluorenyl, Ind = indenyl) have been synthesized [12].

2. Results and discussion

The synthesis of the indene-functionalized imidazolium bromide [C$_9$H$_7$-(CH$_2$)$_3$-(CH{NCHCHN^{i}Pr})]Br (HL·HBr 1) is outlined in Scheme 1 (Eq. 1). The reaction of 3-bromopropylindene with 1-isopropyl-imidazole at room temperature for 24 h afforded the desired imidazolium salt of 1 in ca. 90% yield as pale-yellow oil. This synthetic route is also suitable for other alkyl-substituted imidazole, i.e. 1-methylimidazole, and the corresponding imidazolium salt could be obtained almost quantitatively. However, attempts to prepare analogous aryl-substituted imidazolium salts has met with obstruction due to the very poor reactivity of 2,6-diisopropylphenylimidazole or mesitylimidazole with 3-bromopropylindene. For example, almost no desired imidazolium salt was obtained after the stirring of 2,6-diisopropylphenylimidazole with 3-bromopropylindene at room temperature for several days, even in refluxing THF [13]. Compound 1 has been fully characterized. The ^{1}H NMR spectrum of 1 exhibits the characteristic resonances of imidazolium C$_2$–H signal at 10.98 ppm and the CH$_2$CH$_2$CH$_2$ protons signals in the region of 2.21–2.40 ppm.

The preparation of the mono-ligand half-sandwich Ni(II) bromide [C$_9$H$_6$-(CH$_2$)$_3$-(C{NCHCHN^{i}Pr})]NiBr (2) was attempted by reaction of (DME)NiCl$_2$ with the double deprotonated indene-functionalized imidazolium bromide [C$_9$H$_6$-(CH$_2$)$_3$-(C{NCHCHN^{i}Pr})]Li (LLi), which was generated in situ by the reaction of the corresponding salt HL·HBr (1) with two equivalents of n-C$_4$H$_9$Li at 0 °C. Thus, reacting LLi with (DME)NiCl$_2$ in THF at room temperature gave a dark red solution [14]. After workup, the complex 2 could be isolated from cool toluene solution as dark red crystals (suitable for X-ray structural analysis) in ca. 40% yield (Scheme 1, Eq. 2). Attempts to prepare analogous nickel(II) complex, i.e. N-methyl derivative, were hampered by the lack of synthetic methods leading to pure desired complexes, which might be due to the poor solubility of the products and the presence of byproducts [14]. Such difficulty also has arisen in the synthesis of indenyl-functionalized NHC complex of titanium, i.e. the low

yield of desired product was observed [12]. Initial characterization of 2 was supported by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectrum of complex 2 exhibits the characteristic resonance similar to those of the corresponding salt, except the disappearance of a singlet signal at 10.98 ppm assigned to the imidazolium C$_2$–H of the preligands. In the ^{13}C NMR spectrum, the characteristic resonance of the carbenic carbon (C$_{carbene}$) signal appears at 170.9 ppm, while compares with 166.8 ppm for (C$_9$H$_7$)NiBr[C(^{i}PrNCHCHN^{i}Pr)] (3), an indenylnickel(II) complex bearing a free 1,3-diisopropylimidazole-2-ylidene ligand, reported previously [15]. The small variation of the chemical shift of the C$_{carbene}$, i.e. from 166.8 ppm of 3 to 170.9 ppm of 2, should be caused by the chelate formation presented in complex 2.

The complex 2 is thermally stable and will melt at 165 °C (the melt point of 3 is 125 °C). It is worth mention that complex 2 is much less sensitive to air and moisture as compared to complex 3 [15]. In fact, complex 2 is extremely air stable in the solid state as can even remain unchanged for several days in open air, whereas 3 will decompose after several hours. Somewhat to our surprise, the solubility of complex 2 is much poor than that of 3, and the former one is sparing soluble in hot toluene.

The molecular structure of 2 is shown in Fig. 1, along with selected bond lengths and angles. The crystallographic data for 2 are listed in Table 1.

X-ray structural analysis reveals that the complex 2 crystallizes in the monoclinic system with a monomeric structure in P2$_1$/c space group. As seen in Fig. 1, the nickel
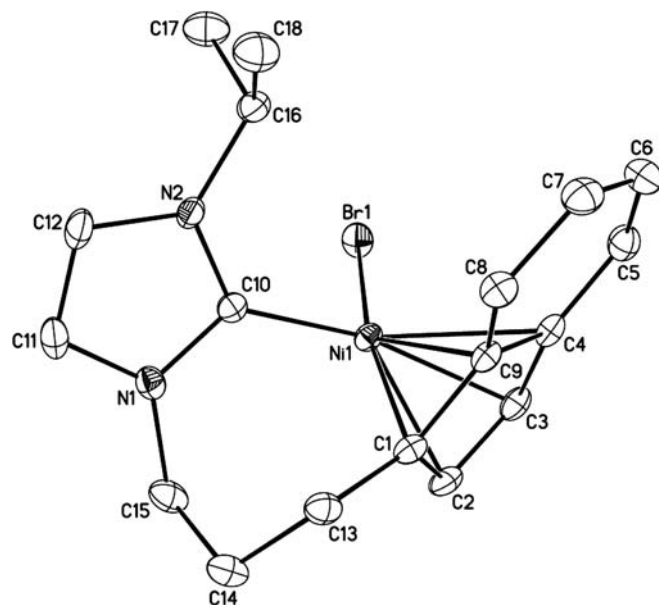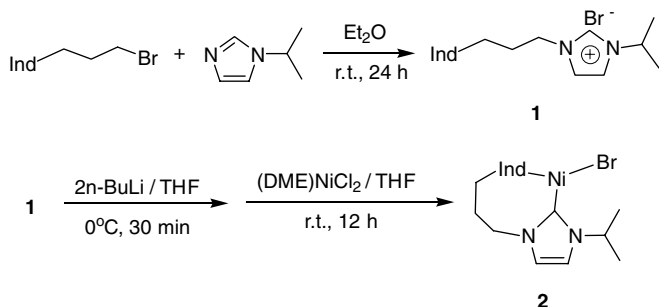

Fig. 1. The crystal structure of 2 showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–Br, 2.3308(3); Ni–C10, 1.885(2); Ni–C1, 2.033(2); Ni–C2, 2.055(2); Ni–C3, 2.083(2); Ni–C4, 2.349(2); Ni–C9, 2.320(2); C1–C2, 1.425(3); C1–C9, 1.468(3); C2–C3, 1.410(3); C3–C4, 1.459(3); C4–C9, 1.421(3); Br–Ni–C10, 100.89(6); Br–Ni–C3, 99.65(6); C1–Ni–C3, 67.55(8); C10–Ni–C1, 91.90.

Scheme 1.

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

	2
Empirical formula	$C_{18}H_{21}BrN_2Ni$
Formular weight	403.99
Temperature (K)	193(2)
λ(Mo Kα) (Å)	0.71070
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.3988(7)
b (Å)	9.6223(6)
c (Å)	18.7130(1)
β (°)	93.619
V (Å^3)	1689.0(2)
Z	4
D_{calcd} (g/cm^3)	1.598
Absorption coefficient (mm^{-1})	3.512
$F(000)$	824
Crystal size (mm)	$0.58 \times 0.20 \times 0.19$
$2\theta_{max}$ (°)	27.48
Number of reflections collected	18497
Number of independent reflections	3882 ($R_{int} = 0.0306$)
Goodness-of-fit on F^2	1.092
Final R indices $[I > 2\sigma(I)]$	0.0269

center is within reasonable bonding distance from the C10 (1.885 Å), Br (2.331 Å), C1 (2.033 Å), C2 (2.055 Å) and C3 (2.083 Å), while considerably farther away from the other two carbon atoms of the five-membered ring of the indenyl group, i.e. C4 (2.349 Å) and C9 (2.320 Å). The geometry around the nickel center is obviously irregular and can be described as a distorted square planar with C2=C3 (i.e. C1–C2 > C2–C3) occupying a single coordination site [15,16].

The Ni–C10 distance of 1.885 Å in **1** is within the expected range for Ni(II)–C$_{carbene}$ bonds reported [7–9], and is almost equal to 1.888 Å in **3**. The strain imposed by the chelation of the tether is reflected in the small C10–Ni–C1 angle of 91.90° (compared to ca. 98.8° for the same angle in **3**), whereas the large C10–Ni–Br angle of 100.99° (compared to ca. 96.6° in **3**) and the large C3–Ni–Br angle of 99.65° (compared to ca. 97.9° in **3**). The chelation can also be invoked to explain why Ni–Br distance in **2** (2.3308 Å) is slightly longer than the corresponding distance in **3** (2.3160 Å) [15]. The similar effects of the tether on the solid structure also have been observed in the phosphine-based Ni(II) complex containing a chelating amino-indenyl ligand, $\{[C_9H_6-(CH_2)_2-NMe_2]Ni(PPh_3)\}[BPh_4]$ [16].

The coordination of the indenyl moiety with nickel center in **2** is intermediate between η^5 and η^3, as inferred from the significantly shorter Ni–C1, Ni–C2 and Ni–C3 distances compared to Ni–C4 and Ni–C9 distances. It is worthy noticing that the chelation of the tether also raised obvious effect on the Ni–Ind interaction. As compared with the Ni–C distances presented in **3**, it is observed that the length of Ni–C3 or Ni–C4 bond in **2** is shorter (by ca. 0.024 Å for Ni–C3 bond, and 0.028 Å for Ni–C4 bond) than that of **3**, and the length of N–C9 bond in **2** is longer

(by ca. 0.029 Å) than that of **3**, whereas the length of Ni–C1 or Ni–C2 bond is almost equal to that found in **3**. These results reflect that the nickel center in **2** should coordinate with the indenyl ligand in a more symmetric mode. This Ni–Ind interaction also could be quantitatively calculated by the main geometrical parameters such as the slip value represented by $\Delta M–C$ $\{1/2[M–C_{av}$ (for C4, C9)] $- 1/2[M–C_{av}$ (for C1, C3)]$\}$ [11]. For example, $\Delta M–C$ values close to zero indicate little distortion from η^5 hapticity, whereas the values above ca. 0.5 Å indicate nearly η^3 hapticity. Here, in complex **2**, the $\Delta M–C$ value is 0.28, which is slight larger than that of **3** ($\Delta M–C = 0.30$). This data further indicates that the Ni–Ind bonding fashion here is somewhat more symmetric than that of **3**, and can be described as an intermediate hapticity between η^5- and η^3-mode. Meanwhile, the hinge angle (HA: the angle formed between the planes formed by the atoms C1, C2, C3 and C1, C3, C4, C9) and the fold angle (FA is the angle formed between the planes formed by the atoms C1, C2, C3 and C4, C5, C6, C7, C8, C9) of **2** are 11.03° and 13.38°, respectively. The values of the two parameters are slightly larger than those of **3** (HA = 9.52, FA = 12.33). This difference in these parameters between the hemilabile NHC or free NHC co-supported indenylnickel(II) complexes should attributed to the presence of the $CH_2CH_2CH_2$ tether in **2**, which caused a less unequal *trans* influences between NHC moiety and halogen group [17]. Besides, as mentioned above, the Ni–Br bond distance in **2** is slightly longer than the corresponding distance in **3**. Thus, it is reasonable that the hemilabile NHC should be a stronger donor ligand than the free NHC, which stabilizes the center metal more efficiently.

To the best of our knowledge, the catalytic activity of NHC co-supported indenylnickel(II) complexes for styrene reaction has not been reported previously. Herein, the catalytic activity of **2** for styrene polymerization was examined. The preliminary results showed that complex **2** alone is inactive and inert toward the insertion of styrene. However, it exhibited considerable activity in the presence of NaBPh$_4$ for the polymerization of styrene. The purpose of the reaction between complex **2** and NaBPh$_4$ is to abstract the Br ligand from **2** and facilitate the formation of cationic species [16] which are active toward the insertion of styrene [18]. For example, when the styrene polymerization was carried out under the conditions of styrene/NaBPh$_4$/**2** = 300:7:1 (molar ratio) in toluene at 80 °C, the polystyrene of ca. 75% yield with number-average molecular weight (M_n) of 27000 (PDI = 1.89) could be obtained after 24 h. On the basis of the polymer yield, this catalytic activity is much higher than that of the indenylnickel(II) bromide co-supported by free 1,3-diisopropylimidazole-2-ylidene ligand, i.e. a polystyrene yield of 35% ($M_n = 43000$, PDI = 3.08) was obtained with **3** under the same conditions. These results demonstrated the introduce of indenyl-functionalized NHC ligand by a $CH_2CH_2CH_2$ tether is benefit to stabilize the Ni(II)-based catalytic active species for the styrene polymerization. The detailed

polymerization behaviors together with other cocatalysts are proceeding in our laboratory.

3. Conclusion

A novel type of neutral half-sandwich Ni(II) complex **2** derived from anionic hemilabile NHC ligand, i.e. indenyl-functionalized NHC by a $CH_2CH_2CH_2$ spacer, has been synthesized and structural characterized. The present results demonstrate that the role of the pendant indenyl moiety not only could increase the NHC complex stability by chelation formation, but also could enhance its catalytic activity, i.e. for the polymerization of styrene in the presence of $NaBPh_4$. Thus, this work has provided a useful hypothesis for guiding future NHC-based catalyst development.

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 under pure argon prior to use. Indene (Fluka) (dried over 4 Å molecular sieves) was distilled immediately before use. 1-Isopropyl-imidazole and 1-methyl-imidazole were obtained commercially and used as received. 3-bromopropylindene [19] and $(DME)NiCl_2$ [20] were prepared by published methods. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. NMR (CD_3Cl or C_6D_6) spectra were measured on a Unity Inova-400 spectrometer at 25 °C. Molecular weight and molecular weight distribution were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-3, HR-4).

4.1. Synthesis of [C_9H_7-(CH_2)_3-(CH{NCHCHN^iPr})]Br (HL·HBr 1)

To a solution of 3-bromopropylindene (7.11 g, 30.0 mmol) in 20 mL of Et_2O was added 1-isopropyl-imidazole (3.30 g, 30.0 mmol). After stirring at room temperature for one day, ether was removed in vacuo. The resulting viscous residue was washed with Et_2O (3 × ca. 15 mL). The product **1** was obtained as pale-yellow oil in ca. 90% yield (9.37 g). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.526 (d, 6H); 2.362 (m, 2H); 2.663 (m, 2H); 3.339 (t, 2H); 3.50 (m, 1H); 4.430 (t, 2H); 4.691 (m, 1H); 6.492 (m, 1H); 6.820(m, 1H); 7.173–7.424 (m, 4H), 10.978 (s, 1H). Anal. Calcd. for $C_{18}H_{23}BrN_2$: C, 62.25; H, 6.68; N, 8.07. Found: C, 62.20; H, 6.70; N, 8.05%.

4.2. Synthesis of [C_9H_6-(CH_2)_3-(C{NCHCHN^iPr})]NiBr (LNiBr, 2)

A Schlenk flask was charged with **1** (0.70 g, 2.0 mmol), THF (20 mL) and a stir bar. To this suspension solution was added dropwise the solution of n-C_4H_9Li (0.94 mL, 4.0 mmol) in THF at 0 °C. The solution was stirred for 30 min and gradually warmed to room temperature. Then a solution of $(DME)NiCl_2$ (0.44 g, 2.0 mmol) in 20 mL THF was added slowly to the reaction system at room temperature. The color of the solution immediately changed from pale-yellow to dark red, accompanied with the emergence of a large amount of yellowish precipitate. The resulting solution was then stirred for additional 12 h, filtered, and evaporated to dryness. The residue was extracted with hot toluene. The complex **2** was obtained as dark red crystals by cooling the concentrated toluene solution at −30 °C (0.32 g, 40%). ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 1.227 (d, 6H), 1.638 (m, 2H), 2.214 (m, 2H), 3.000 (m, 2H), 3.283 (m, 1H), 5.213 (m, 2H), 6.730–7.264 (m, 6H). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 170.9 (s, NCN). Anal. Calcd. for $C_{18}H_{21}BrN_2Ni$: C, 53.52; H, 5.24; N, 6.93. Found: C, 53.96; H, 5.30; N, 6.79%.

4.3. A typical procedure for the polymerization of styrene

A typical procedure for the polymerization of styrene is given as follows. Under dry argon, the solid initiator **2** (6.7 mg, 0.017 mmol), $NaBPh_4$ (41.1 mg, 0.12 mmol), toluene (0.2 mL) and styrene (0.6 mL, 0.005 mol) were added into a dry glass ampule in turn. Then, the sealed ampule was placed in 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 the 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 vacuo at room temperature overnight. The polymer yield was determined gravimetrically.

4.4. X-ray structural determination of 2

A suitable crystal was mounted in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(2) K. 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. Crystal data and collection and main refinement parameters are given in Table 1.

Appendix A. Supplementary material

CCDC 613900 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2006.09.044.

References

[1] A.J. Arduengo III, R.L. Harlou, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[2] (a) For selected references, see: D. Kremzow, G. Seidel, C.W. Lehmann, A. Fürstner, Chem. Eur. J. 11 (2005) 1833;
(b) N.M. Scott, S.P. Nolan, Eur. J. Inorg. Chem. (2005) 1815;
(c) K.J. Cavell, D.S. McGuinness, Coord. Chem. Rev. 248 (2004) 671;
(d) W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 41 (2002) 1290;
(e) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
(f) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.

[3] (a) R.A. Kelly, N.M. Scott, S. Díez-González, E.D. Stevens, S.P. Nolan, Organometallics 24 (2005) 3442 (and the references cited);
(b) B. Knapp-Reed, G.M. Mahandru, J. Montgomery, J. Am. Chem. Soc. 127 (2005) 13156.

[4] (a) D.S. McGuinness, W. Mueller, P. Wasserscheid, K.J. Cavell, B.W. Skelton, A.H. White, U. Englert, Organometallics 21 (2002) 175;
(b) A.L. Mackinnon, M.C. Baird, J. Organomet. Chem. 683 (2003) 114.

[5] (a) D.S. McGuinness, N. Saendig, B.F. Yates, K.J. Cavell, J. Am. Chem. Soc. 123 (2001) 4029;
(b) D.S. McGuinness, K.J. Cavell, B.W. Skelton, A.H. White, Organometallics 19 (2000) 1596.

[6] D.S. McGuinness, K.J. Cavell, Organometallics 19 (2000) 4918.

[7] (a) D. Patel, S.T. Liddle, S.A. Mungur, M. Rodden, A.J. Blake, P.L. Arnold, Chem. Commun. (2006) 1124;
(b) B.E. Ketz, X.G. Ottenwaelder, R.M. Waymouth, Chem. Commun. (2005) 5693;
(c) C.Y. Legault, C. Kendall, A.B. Charette, Chem. Commun. (2005) 3826;
(d) P.L. Arnold, M. Rodden, C. Wilson, Chem. Commun. (2005) 1743;
(e) W.F. Li, H.M. Sun, M.Z. Chen, Z.G. Wang, D.M. Hu, Q. Shen, Y. Zhang, J. Organomet. Chem. 690 (2005) 6227;
(f) A.O. Larsen, W.H. Leu, C.N. Oberhuber, J.E. Campbell, A.H. Hoveyda, J. Am. Chem. Soc. 126 (2004) 11130;
(g) L.P. Spencer, S. Winston, M.D. Fryzuk, Organometallics 23 (2004) 3372;
(h) A.W. Waltman, R.H. Grubbs, Organometallics 23 (2004) 3105;
(i) H. Aihara, T. Matsuo, H. Kawaguchi, Chem. Commun. (2003) 2204.

[8] (a) R.H. Wang, B. Twamley, J.M. Shreeve, J. Org. Chem. 71 (2006) 426;
(b) G. Steiner, H. Kopacka, K.-H. Ongania, K. Wurst, P. Preishuber-Pflügl, B. Bildstein, Eur. J. Inorg. Chem. (2005) 1325;
(c) X. Wang, S. Liu, G.X. Jin, Organometallics 23 (2004) 6002;
(d) S. Winston, N. Stylianides, A.A.D. Tulloch, J.A. Wright, A.A. Danopoulos, Polyhedron 23 (2004) 2813;
(e) H. Seo, H. Park, B.Y. Kim, J.H. Lee, S.U. Son, Y.K. Chung, Organometallics 22 (2003) 618;
(f) M. Frøseth, A. Dhindsa, H. Røise, M. Tilset, Dalton Trans. (2003) 4516;
(g) K.S. Coleman, H.T. Chamberlayne, S. Turberville, M.L.H. Green, A.R. Cowley, Dalton Trans. (2003) 2917;
(h) M.V. Baker, B.W. Skelton, A.H. White, C.C. Williams, Organometallics 21 (2002) 2674.

[9] W.F. Li, H.M. Sun, M.Z. Chen, Z.G. Wang, D.M. Hu, Q. Shen, Y. Zhang, Organometallics 24 (2005) 5925.

[10] (a) Y. Qian, J. Huang, M.D. Bala, B. Lian, H. Zhang, Chem. Rev. 103 (2003) 2633;
(b) U. Siemeling, Chem. Rev. 100 (2000) 1495;
(c) A.L. McKnight, P.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[11] D. Zargarian, Coord. Chem. Rev. 233–234 (2002) 157.

[12] S.P. Downing, A.A. Danopoulos, Organometallics 25 (2006) 1337.

[13] Very recently, an aryl-substituted imidazolium salt, which linked an indenyl ligand by an ethylene spacer, has been synthesized by the reaction of 2,6-diisopropylphenylimidazole with 2-bromoethylidene at 110 °C for one week in the yield of 61%, Ref. [12].

[14] During the reaction process, a large amount of yellowish precipitates was appeared. Similar phenomenon occurred during the reaction of Li^+ salts of Ind with nickel(II) dihalides, Ref. [11]. Such precipitate should be a mixture containing nickel halide salts.

[15] H.M. Sun, Q. Shao, D.M. Hu, W.F. Li, Q. Shen, Y. Zhang, Organometallics 24 (2005) 331.

[16] L.F. Groux, F. Bélanger-Gariépy, D. Zargarian, R. Vollmerhaus, Organometallics 19 (2000) 1507.

[17] L.F. Groux, D. Zargarian, Organometallics 20 (2001) 3811.

[18] (a) L.F. Groux, D. Zargarian, Organometallics 22 (2003) 3124;
(b) R. Vollmerhaus, F. Bélanger-Gariépy, D. Zargarian, Organometallics 16 (1997) 4762.

[19] M. Deppner, R. Burger, H.G. Alt, J. Organomet. Chem. 689 (2004) 1194.

[20] F.A. Cotton, Inorg. Syn. 13 (1972) 160.