

# *N*-Heterocyclic carbene complexes of cyclopentadienylnickel(II): Synthesis, structure and catalytic activity in styrene polymerization

Włodzimierz Buchowicz<sup>a</sup>, Andrzej Koziół<sup>a</sup>, Lucjan B. Jerzykiewicz<sup>b</sup>, Tadeusz Lis<sup>b</sup>,  
Stanisław Pasynkiewicz<sup>a</sup>, Aleksandra Pęcherzewska<sup>a</sup>, Antoni Pietrzykowski<sup>a,\*</sup>

<sup>a</sup> *Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland*

<sup>b</sup> *University of Wrocław, Faculty of Chemistry, Joliot-Curie 14, 50-353 Wrocław, Poland*

Available online 5 July 2006

Dedicated to Professor Bogdan Marciniec on the occasion of his 65th birthday in recognition of his outstanding contributions to homogeneous catalysis and organometallic chemistry.

## Abstract

Cyclopentadienylnickel(II) complexes with *N*-heterocyclic carbenes [NiCp(X)(NHC)] (X = Cl, Br or CH<sub>3</sub>), combined with MAO have been used as catalysts for the polymerization of styrene. The catalytic activity of the systems depended mainly on the ease of the abstraction of X substituent by MAO and the stabilization of cationic species [NiCp(NHC)]<sup>+</sup>. The molecular structures of three title complexes have been determined by single-crystal X-ray diffraction. All three compounds crystallize in monoclinic crystal system with four molecules in the unit cell. Their structural parameters have been compared with data reported for similar complexes. Two of these complexes [NiCp(CH<sub>3</sub>)(IMes)] and [NiCp(CH<sub>3</sub>)(SIMes)] are the first examples of structurally characterized (unsubstituted)-cyclopentadienylnickel methyl compounds.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Nickel; Styrene; Polymerization; *N*-Heterocyclic carbene; Crystal structure

## 1. Introduction

*N*-Heterocyclic carbenes (NHC) (Fig. 1) are ubiquitous and versatile ligands in organometallic chemistry and homogeneous catalysis [1–4].

Complexes [NiCp(Cl)(NHC)] have been obtained recently by reacting nickelocene with a suitable carbene precursor [5,6]. Their catalytic activity in aryl dehalogenation and aryl amination reactions was demonstrated [6]. Related indenyl-nickel(II) complexes [Ni(Ind)(L)X] (Ind = indenyl; L = 1,3-diisopropylimidazole-2-ylidene; X = Cl or Br) with MAO as a co-catalyst displayed modest activity in oligomerization of ethylene [7]. Olefin polymerization was also reported with Ni(3-methyl-1-picolylimidazolin-2-ylidene)<sub>2</sub>Cl<sub>2</sub> or Ni(3-benzyl-1-picolylimidazolin-2-ylidene)<sub>2</sub>Cl<sub>2</sub> [8] as well as with Ni(II) *N*-heterocyclic carbene enolates [9]. On the other hand, substituted indenyl-nickel complexes [Ni(R-Ind)X(PR<sub>3</sub>)] are active catalysts for alkyne polymerization [10], dimerization and polymer-

ization of ethylene [11], polymerization of styrene [12–14] and hydrosilylation of styrene [14].

Here, we report the activity of cyclopentadienylnickel(II) complexes with *N*-heterocyclic carbenes in the polymerization of styrene in the presence of MAO.

## 2. Experimental

### 2.1. Techniques and materials

All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were distilled from potassium benzophenone ketyl. NHC ligands [15], SIMesBr [16], carbene IMes [17] nickelocene [18], 1,1'-dimethylnickelocene [19], [NiCp(Cl)(IMes)] **1** [5], [NiCp(Cl)(SIMes)] **2** and [NiCp(Cl)(SIPr)] **3** [6] were synthesized according to the literature procedures. Methylalumoxane (MAO), 10% in toluene, was purchased from Crompton GMBH. Styrene (Aldrich) was distilled from CaH<sub>2</sub> under reduced pressure and stored over MS 4A at –78 °C. Solutions of CH<sub>3</sub>Li were prepared from CH<sub>3</sub>I and Li in Et<sub>2</sub>O. <sup>1</sup>H NMR (400 MHz)

\* Corresponding author. Tel.: +48 22 6607116; fax: +48 22 6605462.  
E-mail address: [anpietr@ch.pw.edu.pl](mailto:anpietr@ch.pw.edu.pl) (A. Pietrzykowski).

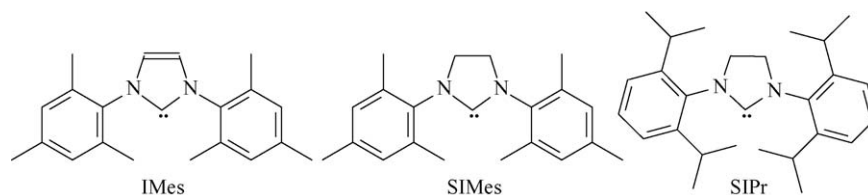


Fig. 1. NHC ligands used in this study.

and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Mercury-400BB spectrometer in  $\text{C}_6\text{D}_6$  at ambient temperature. Mass spectra (EI, 70 eV) were measured on an AMD-604 mass spectrometer. GPC analyses were performed on a LabAlliance chromatograph on a divinylbenzene column. THF was used as an eluent.

### 2.2. Synthesis of $[\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)(\text{Cl})(\text{SIMes})]$ **4**

A modified literature procedure was applied [5]. 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride [15] (0.94 g, 2.75 mmol) was added to a solution of 1,1'-dimethylnickelocene (0.45 g, 2.07 mmol) in THF (20 mL). The resulting mixture was refluxed for 24 h during which time the colour changed from dark green to red. The solvent was removed under vacuum to yield a deep red solid. This crude product was washed with hexane ( $3 \times 20$  mL) and subsequently extracted with hot toluene (60 mL). The solution was filtered, and the filtrate was evaporated to dryness. A red powder was obtained (0.702 g, 1.46 mmol, 70% yield). It was identified as  $[\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)(\text{Cl})(\text{SIMes})]$ :  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 1.26 (s,  $\text{C}_5\text{H}_4\text{CH}_3$ , 3H), 2.14 (s,  $p\text{-CH}_3$ , 6H), 2.34 (s,  $o\text{-CH}_3$ , 12H), 3.09 (s, NCH<sub>2</sub>, 4H), 4.39 (t,  $J=2.4$  Hz,  $\text{C}_5\text{H}_4\text{CH}_3$ , 2H), 4.71 (t,  $J=2.4$  Hz,  $\text{C}_5\text{H}_4\text{CH}_3$ , 2H), 6.87 (s,  $m\text{-H}$ , 4H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 13.40 (s, Cp-CH<sub>3</sub>), 18.76 (s,  $o\text{-CH}_3$ ), 21.06 (s,  $p\text{-CH}_3$ ), 50.60 (s, NCH<sub>2</sub>), 82.96; 99.49; 111.14 (Cp, ratio  $\sim 2:2:1$ ), 129.61 (s, C-3,5), 136.50 (s, C-2,6), 137.66 (s, C-4), 137.96 (s, C-1), 203.77 (s, NCN). EI-MS (70 eV)  $m/z$  (relative intensity) ( $^{58}\text{Ni}$ ): 478 ( $\text{M}^+$ , 57%), 442 ( $[\text{M}-\text{HCl}]^+$ , 95%), 364 ( $[\text{Ni}(\text{SIMes})]^+$ , 36%), 305 ( $[\text{SIMes}-\text{H}]^+$ , 80%), 303 ( $[\text{SIMes}-3\text{H}]^+$ , 100%). HRMS: Calcd. for  $\text{C}_{27}\text{H}_{33}\text{N}_2^{58}\text{Ni}^{35}\text{Cl}$ : 478.16857; Found: 478.16790. Crystals suitable for X-ray diffraction studies were obtained from a hexane/toluene solution.

### 2.3. Synthesis of $[\text{NiCp}(\text{Br})(\text{SIMes})]$ **5**

This compound was prepared in a similar way as described above for **4** from 1,3-bis-(2,4,6-trimethylphenyl)imidazolium bromide [16] (2.36 g, 6.1 mmol) and nickelocene (1.14 g, 6.06 mmol) in tetrahydrofuran (20 mL) under reflux for 12 h. Yield: 13% (0.410 g, 0.80 mmol).  $[\text{NiCp}(\text{Br})(\text{SIMes})]$ :  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 2.13 (s,  $p\text{-CH}_3$ , 6H), 2.33 (s,  $o\text{-CH}_3$ , 12H), 3.08 (s, NCH, 4H), 4.76 (s, Cp, 5H), 6.86 (s,  $m\text{-H}$ , 4H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 19.04 (s,  $o\text{-CH}_3$ ), 21.06 (s,  $p\text{-CH}_3$ ), 50.76 (s, NCH<sub>2</sub>), 92.87 (s, Cp), 129.72 (s, C-3,5), 137.04 (s, C-2,6), 137.54 (s, C-4), 138.12 (s, C-1), 203.17 (s, NCN); EI-MS (70 eV)  $m/z$  (rel. intensity) ( $^{58}\text{Ni}$ ,  $^{79}\text{Br}$ ): 508 ( $\text{M}^+$ , 48%), 428 ( $[\text{M}-\text{HBr}]^+$ ,

55%), 371 ( $[(\text{SIMes})\text{Cp}]^+$ , 92%), 361 ( $[\text{Ni}(\text{SIMes})-3\text{H}]^+$ , 70%), 305 ( $[\text{SIMes}-\text{H}]^+$ , 100%), 303 ( $[\text{SIMes}-3\text{H}]^+$ , 95%). HRMS: Calcd. for  $\text{C}_{26}\text{H}_{31}\text{N}_2^{58}\text{Ni}^{79}\text{Br}$ : 508.10241; Found: 508.10422.

### 2.4. Synthesis of $[\text{NiCp}(\text{CH}_3)(\text{IMes})]$ **6**

A modified literature procedure was used [5]. A solution of  $\text{CH}_3\text{Li}$  in  $\text{Et}_2\text{O}$  (0.70 mL, 0.79 mmol) was added to a solution of  $[\text{NiCp}(\text{Cl})(\text{IMes})]$  (0.335 g, 0.722 mmol) in THF (17 mL) at  $-78^\circ\text{C}$ . The reaction mixture was warmed slowly to  $-20^\circ\text{C}$  when the solution changed colour from red to yellow. The solvents were removed under vacuum at this temperature. Green oil was obtained which was extracted with hexane (60 mL). These extracts were filtered through a pad of Celite, then kept for 24 h at  $-78^\circ\text{C}$  and filtered to remove residual LiCl. The resulting green filtrate was stored at  $-78^\circ\text{C}$  for 1 week. Small, green crystals of  $[\text{NiCp}(\text{CH}_3)(\text{IMes})]$  were formed. They were separated from the mother liquor and dried under vacuum. Yield: 0.031 g; 9.7%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm):  $-0.65$  (s, Ni-CH<sub>3</sub>, 3H), 2.12 (s,  $o$ - and  $p$ -CH<sub>3</sub>, 18H), 4.91 (s, Cp, 5H), 6.16 (s, NCH, 2H), 6.82 (s,  $m$ -H, 4H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm):  $-36.91$  (s, Ni-CH<sub>3</sub>), 18.56 (s,  $o$ -CH<sub>3</sub>), 21.04 (s,  $p$ -CH<sub>3</sub>), 89.94 (s, Cp), 122.36 (s, NCH), 129.23 (s, C-3,5), 135.78 (s, C-2,6), 137.87 (s, C-4), 138.23 (s, C-1), 186.92 (s, NCN). EI-MS (70 eV)  $m/z$  (relative intensity) ( $^{58}\text{Ni}$ ): 442 ( $\text{M}^+$ , 43%), 427 ( $[\text{M}-\text{CH}_3]^+$ , 28%), 362 ( $[\text{Ni}(\text{IMes})]^+$ , 37%), 305 ( $\text{IMesH}^+$ , 60%), 303 ( $[\text{IMes}-\text{H}]^+$ , 100%). Crystals suitable for X-ray diffraction were grown from a hexane solution at  $-20^\circ\text{C}$ .

### 2.5. Synthesis of $[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$ **7**

A solution of  $\text{CH}_3\text{Li}$  in  $\text{Et}_2\text{O}$  (0.40 mL, 0.43 mmol) was added to a solution of  $[\text{NiCp}(\text{Cl})(\text{SIMes})]$  (0.181 g, 0.389 mmol) in toluene (15 mL) at  $-78^\circ\text{C}$ . The mixture was slowly warmed to room temperature during which time the colour changed from red to green. Deoxygenated water (20 mL) was added and the mixture was stirred vigorously for 30 min. The organic layer was transferred to another Schlenk tube and dried over MS 4A overnight. The solvent was removed under vacuum and hexane (80 mL) was added to the green residue. The resulting suspension was filtered through a pad of Celite, and the filtrate was reduced in volume. This solution was stored at  $-78^\circ\text{C}$  for 48 h to yield green, fine crystals of  $[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$  (0.125 g, 72% yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm):  $-0.60$  (s, Ni-CH<sub>3</sub>, 3H), 2.13 (s,  $o$ -CH<sub>3</sub>, 6H), 2.26 (s,  $p$ -CH<sub>3</sub>, 12H), 3.07 (s, NCH<sub>2</sub>, 4H), 4.83 (s, Cp, 5H), 6.84 (s,  $m$ -H, 4H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm):  $-35.03$  (s, Ni-CH<sub>3</sub>), 18.53 (s,  $o$ -CH<sub>3</sub>), 21.05 (s,  $p$ -CH<sub>3</sub>), 50.57 (s, NCH<sub>2</sub>), 90.33 (s, Cp), 129.52 (s,

C-3,5), 136.61 (s, C-2,6), 137.34 (s, C-4), 138.43 (s, C-1), 217.75 (s, NCN). EI-MS (70 eV) *m/z* (relative intensity) ( $^{58}\text{Ni}$ ): 444 ( $\text{M}^+$ , 5.5%), 322 ( $[\text{M}-\text{NiC}_5\text{H}_4]^+$ , 48%), 321 ( $[\text{M}-\text{NiCp}]^+$ , 31%), 320 ( $[\text{M}-\text{NiCpH}]^+$ , 57%), 319 ( $[\text{M}-\text{NiC}_5\text{H}_7]^+$ , 100%), 305 ( $[\text{SIMes}-\text{H}]^+$ , 29%), 304 ( $[\text{SIMes}-2\text{H}]^+$ , 37%), 160 (48%), 146 (46%), 119 ( $[\text{C}_9\text{H}_{11}]^+$ , 16%), 105 ( $[\text{C}_8\text{H}_9]^+$ , 51%), 77 ( $[\text{C}_6\text{H}_5]^+$ , 29%). HRMS Calcd. for  $\text{C}_{27}\text{H}_{34}\text{N}_2^{58}\text{Ni}$ : 444.20755; Found: 444.20618. Mp: 133–134 °C. Crystals suitable for X-ray diffraction were grown from a hexane solution at  $-20$  °C.

## 2.6. Typical procedure for the polymerization of styrene

A solution of MAO (0.43 mL, Al/Ni = 100) was added to a solution of  $[\text{NiCp}(\text{Cl})(\text{IMes})]$  (0.010 g, 0.0216 mmol) in toluene (5.0 mL). The resulting mixture was stirred for 30 min at room

temperature. The solution changed colour from green to yellow-brown. Styrene (neat, 11.50 g, 0.11 mol, styrene/Ni = 5000) was added and the mixture was vigorously stirred at 50 °C for 3 h. After cooling to room temperature, 9% aq. HCl was slowly added to decompose the remaining MAO; the organic layer was separated and poured into an excess of methanol (200 mL). The resulting polystyrene was collected by filtration, washed with methanol and dried at 80 °C.

## 2.7. Crystal structure determination

Crystal data, data collection and refinement parameters for  $[\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)(\text{Cl})(\text{SIMes})]$  **4**,  $[\text{NiCp}(\text{CH}_3)(\text{IMes})]$  **6** and  $[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$  **7** are given in Table 1. The molecular structures of these compounds are presented in Figs. 2–4, respec-

Table 1  
Crystal data and structure refinement for  $[\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)(\text{Cl})(\text{SIMes})]$ ,  $[\text{NiCp}(\text{CH}_3)(\text{IMes})]$ ,  $[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$

	$[\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)(\text{Cl})(\text{SIMes})]$	$[\text{NiCp}(\text{CH}_3)(\text{IMes})]$	$[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$
Empirical formula	$\text{C}_{27}\text{H}_{33}\text{ClN}_2\text{Ni}$	$\text{C}_{27}\text{H}_{32}\text{N}_2\text{Ni}$	$\text{C}_{27}\text{H}_{34}\text{N}_2\text{Ni}$
Crystal size (mm)	$0.257 \times 0.142 \times 0.037$	$0.25 \times 0.10 \times 0.06$	$0.48 \times 0.35 \times 0.30$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Unit cell dimensions:			
<i>a</i> (Å)	9.271(5)	13.700(4)	13.938(4)
<i>b</i> (Å)	19.756(5)	10.994(4)	10.941(3)
<i>c</i> (Å)	14.318(5)	16.216(5)	16.094(4)
$\beta$ (°)	107.83(1)	108.11(4)	109.85(3)
Volume (Å <sup>3</sup> )	2496.5(17)	2321.4(13)	2308.4(11)
Z	4	4	4
Formula weight	479.71	443.26	445.27
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.276	1.268	1.281
Temperature (K)	100(2)	100(2)	85(2)
Absorption coefficient (mm <sup>-1</sup> )	0.900	0.851	0.856
$F(000)$	1016	944	952
Radiation		Mo K $\alpha$ ( $\lambda = 0.71073$ Å, graphite monochromator)	
$\theta$ range (°)	3.10–28.07	3.13–27.00	4.66–28.00
Scan type	$\omega$	$\omega$	$\omega$ and $\varphi$
Absorption correction			
$T_{\text{min}}, T_{\text{max}}$	0.71, 0.93	0.838, 0.949	0.700, 0.793
Index ranges	$-12 \leq h \leq 12$ $-23 \leq k \leq 26$ $-18 \leq l \leq 18$	$-9 \leq h \leq 17$ $-14 \leq k \leq 14$ $-20 \leq l \leq 20$	$-16 \leq h \leq 18$ $-14 \leq k \leq 14$ $-20 \leq l \leq 21$
Reflections collected	34902	14138	30482
Unique data	6044, $R_{\text{int}} = 0.0556$	4966, $R_{\text{int}} = 0.0785$	5551, $R_{\text{int}} = 0.0380$
Refinement method		Full-matrix least-squares on $F^2$	
Data/restraints/parameters	6044/0/287	2571/3/340	4933/0/326
Goodness-of-fit on $F^2$ <sup>a</sup>	1.018	0.903	1.102
Final <i>R</i> indices [ $I > 2\sigma(I)$ ] <sup>b</sup>	$R1 = 0.0312$ $wR2 = 0.0760$	$R1 = 0.0527$ $wR2 = 0.0402$	$R1 = 0.0359$ $wR2 = 0.0901$
<i>R</i> indices (all data)	$R1 = 0.0463$ $wR2 = 0.0798$	$R1 = 0.1382$ $wR2 = 0.0483$	$R1 = 0.0402$ $wR2 = 0.0931$
Largest resid. (e Å <sup>-3</sup> )	0.39/–0.31	0.36/–0.37	0.73/–0.33
Weights <i>a</i> ; <i>b</i> <sup>c</sup>	0.0471; 0.0	0.0; 0.0	0.048; 1.48

<sup>a</sup> GooF =  $S = \{\sum [w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$ .

<sup>b</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = \{\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]\}^{1/2}$ .

<sup>c</sup>  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = [2F_c^2 + \max(F_o^2, 0)] / 3$ .

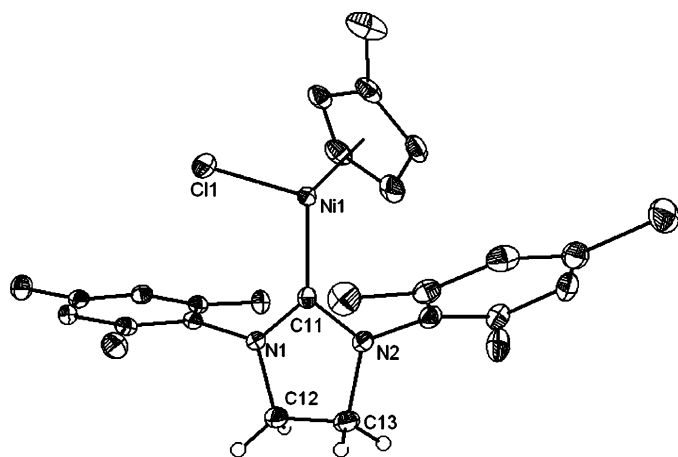


Fig. 2. ORTEP drawing of the molecular structure of  $[\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)(\text{Cl})(\text{SIMes})]$  **4**. Hydrogen atoms, except for the imidazole ones, have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni(1)–Cl(1) 2.1915(9), Ni(1)–C(11) 1.889(2), Ni(1)–Cp(c) 1.778(1), N(1)–C(11) 1.340(2), N(1)–C(12) 1.484(2), N(2)–C(11) 1.352(2), N(2)–C(13) 1.476(2), C(12)–C(13) 1.525(2), Cl–Ni–C(11) 100.67(5), Cl(1)–Ni(1)–Cp(c) 125.98(2), C(11)–Ni(1)–Cp(c) 133.04(7), N(2)–C(11)–N(1) 107.32(14).

tively. Selected bond lengths and angles are given in the figure captions.

Crystallographic data for the structural analysis of **4**, **6** and **7** have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 299129, 299130 and 299131, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax: +44 1223 336 033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>).

Preliminary examination and intensities data collections for **4**, **6** and **7** were carried out on a CCD KUMA KM4 diffractometer with graphite-monochromated Mo K $\alpha$ . Data were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods and refined by the full-matrix

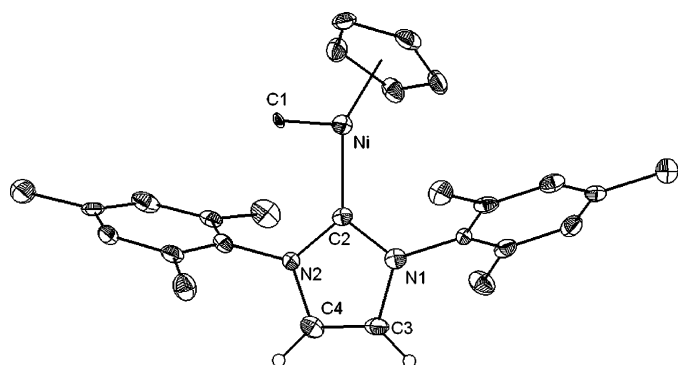


Fig. 3. ORTEP drawing of the molecular structure of  $[\text{NiCp}(\text{CH}_3)(\text{IMes})]$  **6**. Hydrogen atoms, except for the imidazole ones, have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni(1)–C(1) 2.033(3), Ni(1)–C(2) 1.854(3), Ni(1)–Cp(c) 1.798(1), C(2)–N(2) 1.376(3), C(2)–N(1) 1.382(3), C(3)–C(4) 1.334(4), C(4)–N(2) 1.390(3), N(1)–C(3) 1.409(3), C(2)–Ni(1)–C(1) 93.06(12), C(1)–Ni(1)–Cp(c) 127.91(9), C(2)–Ni(1)–Cp(c) 138.67(9), N(2)–C(2)–N(1) 102.6(2).

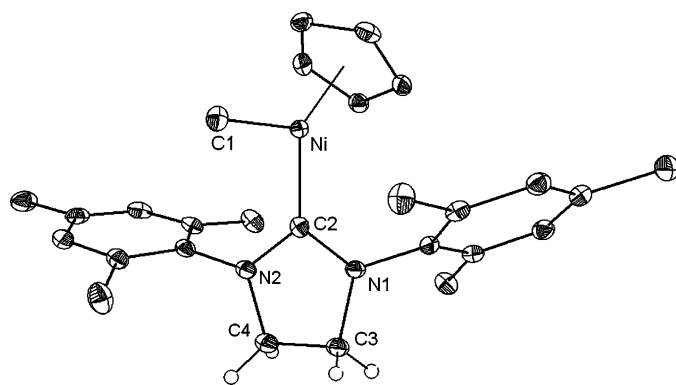
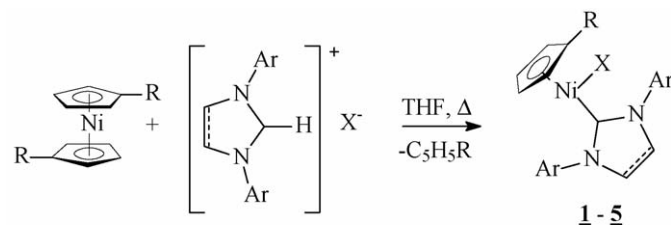


Fig. 4. ORTEP drawing of the molecular structure of  $[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$  **7**. Hydrogen atoms, except for the imidazole ones, have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni(1)–C(1) 1.967(2), Ni(1)–C(2) 1.864(2), Ni(1)–Cp(c) 1.801(1), C(2)–N(2) 1.354(2), C(2)–N(1) 1.348(2), C(3)–C(4) 1.523(2), C(4)–N(2) 1.476(2), N(1)–C(3) 1.473(2), C(2)–Ni(1)–C(1) 91.65(7), C(1)–Ni(1)–Cp(c) 128.56(6), C(2)–Ni(1)–Cp(c) 139.48(5), N(2)–C(2)–N(1) 106.80(13).

least-squares method on all  $F^2$  data using the SHELXTL-NT V5.1 software [20]. Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode. All non-hydrogen atoms were refined with anisotropic displacement parameters.

### 3. Results and discussion

The activity of cyclopentadienylnickel(*N*-heterocyclic carbene) complexes in the polymerization of alkenes has not been tested up to now. We have synthesized three new complexes (**4**, **5**, **7**) and four complexes (**1–3**, **6**) described earlier in the literature [5,6], and have checked their activity in the polymerization of styrene, using MAO as a co-catalyst. The complexes were prepared as shown in Schemes 1 and 2.

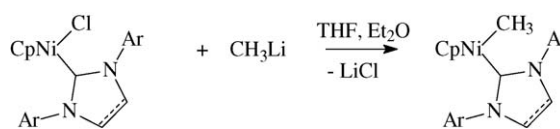


R = H or CH<sub>3</sub>

X = Cl<sup>−</sup> or Br<sup>−</sup>

Ar = 2,4,6-trimethylphenyl or 2,6-diisopropylphenyl

Scheme 1. Synthesis of catalysts [5,6].



Ar = 2,4,6-trimethylphenyl

Scheme 2. Synthesis of complexes  $[\text{NiCp}(\text{CH}_3)(\text{IMes})]$  **6** [5] and  $[\text{NiCp}(\text{CH}_3)(\text{SIMes})]$  **7**.

The molecular structure of **4** is depicted in Fig. 2. The coordination geometry at the nickel centre can be described as trigonal planar considering the Cp(centroid), the carbene and the chloride ion (sum of bond angles = 359.7°). These angles and the bond lengths between nickel atom and its substituents are almost identical with those reported for [CpNi(Cl)(SIMes)] [6]. This indicates that the methyl substituent in the cyclopentadienyl ring has no influence on the coordination sphere of [Ni(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)(Cl)(SIMes)].

Two methylnickel compounds, i.e. the previously reported methyl complex [Ni(Cp)(CH<sub>3</sub>)(IMes)] **6** [5] and its saturated counterpart [Ni(Cp)(CH<sub>3</sub>)(SIMes)] **7** were prepared in the reactions of their chloride analogues **1** and **2** with methyllithium (Scheme 2).

While we found the isolation of [NiCp(CH<sub>3</sub>)(IMes)] **6**, described in the literature [5], somewhat problematic, the complex [NiCp(CH<sub>3</sub>)(SIMes)] **7** proved to be stable to the hydrolytic work-up and was isolated in a 72% yield. The structures of **6** and **7** determined by single crystal X-ray diffraction are shown in Figs. 3 and 4, respectively. To the best of our knowledge, the complexes are the first examples of structurally characterized (unsubstituted)-cyclopentadienylnickel methyl compounds. Both complexes display trigonal planar geometry at the nickel centre considering the Cp(centroid), the carbene, and the methyl group (sum of bond angles = 359.7°). The Ni–C(carbene) bond lengths of 1.854(3) and 1.864(2) Å, respectively, are similar to those reported for [NiCp(η<sup>1</sup>-Cp)(1,3-bis(2,6-dimethyl-4-bromophenyl)imidazol-2-ylidene)] (1.885(4) Å [21]), [NiCp(Cl)(IMes)] **1** (1.917(9) Å [5]), and [NiCp(Cl)(SIMes)] **2** (1.85(2) Å and 1.89(2) Å [6]), but are shorter than those in nickel carbonyl complexes: [Ni(CO)<sub>3</sub>(IMes)] (1.971(3) Å [22]) and [Ni(CO)<sub>3</sub>(SIMes)] (1.960(2) Å [22]). The Ni–CH<sub>3</sub> distances in [NiCp(CH<sub>3</sub>)(IMes)] **6** and [NiCp(CH<sub>3</sub>)(SIMes)] **7** (2.033(3) and 1.967(2) Å, respectively) are within the upper limit of Ni–CH<sub>3</sub> bond lengths determined for [Cp\*Ni(CH<sub>3</sub>)(PEt<sub>3</sub>)] 1.96(1) Å [23] and substituted indenyl–Ni(II) phosphine complexes: [Ind–(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>Ni(CH<sub>3</sub>)PPh<sub>3</sub>] 1.950(2) Å, [Ind–

Table 2

Styrene polymerization with [Ni(Cp)X(NHC)]/MAO

Entry	Precatalyst	Yield (%)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
1	[NiCp(Cl)(IMes)] <b>1</b>	89	165000	2.0
2	[NiCp(Cl)(SIMes)] <b>2</b>	81	158000	2.0
3	[NiCp(Cl)(SIPr)] <b>3</b>	23	16100	4.0
4	[NiCp(Br)(SIMes)] <b>5</b>	18	19450	2.9
5	[Ni(C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> )(Cl)(SIMes)] <b>4</b>	16	9370	3.0
6	[NiCp(CH <sub>3</sub> )(SIMes)] <b>7</b>	33		
7	[NiCp(Cl)(SIMes)] <sup>a</sup> <b>2</b>	–		

All reactions were performed in duplicate at 50 °C in toluene for 3 h, [Ni] = 4.32 mmol/L, Ni:styrene = 1:5000, Ni:Al = 1:100.

<sup>a</sup> Reaction at 20 °C.

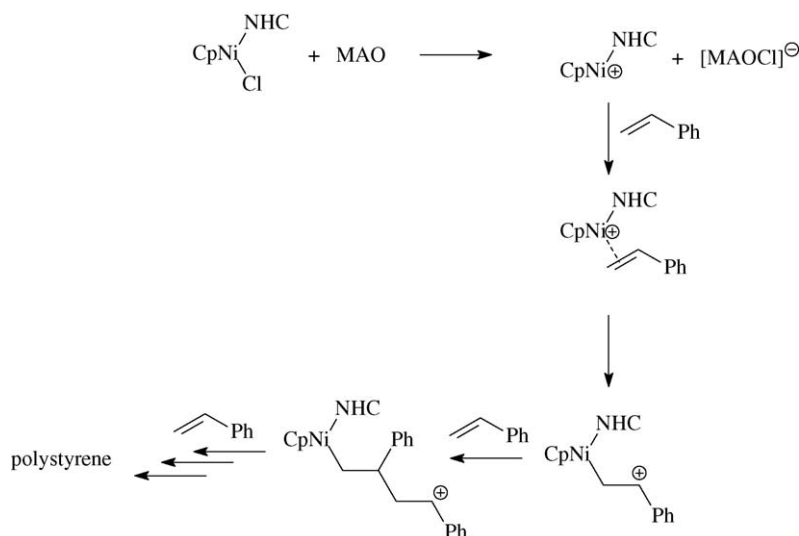
(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>Ni(CH<sub>3</sub>)P(CH<sub>3</sub>)<sub>3</sub>] 1.983(4) Å [12]; [(1-CH<sub>3</sub>–Ind)Ni(CH<sub>3</sub>)(PCy)<sub>3</sub>] 1.965(4) Å, [(1-CH<sub>3</sub>–Ind)Ni(CH<sub>3</sub>)(PCH<sub>3</sub>)<sub>3</sub>] 1.955(4) Å [24].

The catalytic activity of cyclopentadienylnickel(*N*-heterocyclic carbene) complexes was tested in the polymerization of styrene under standard conditions: all reactions were carried out at 50 °C in toluene for 3 h, [Ni] = 4.32 mmol/L, Ni:styrene = 1:5000, Ni:Al = 1:100. The results are shown in the Table 2.

In control experiments all precatalysts (without MAO), MAO itself and the free carbene combined with MAO were inactive.

Polystyrene obtained in the above reactions was atactic, what was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra, melting point determination and its solubility in toluene.

The highest catalytic activity (yield 80–90%) was observed for cyclopentadienylnickel chloride complexes with IMes and SIMes ligands, **1** and **2** (entries 1 and 2). On the other hand the complex **2** was inactive at room temperature (entry 7). Introducing more bulky isopropyl groups in the carbene significantly reduced the activity (entry 3). Rather unexpected decrease in the activity was observed for the complex **4** with a methyl substituent at the cyclopentadienyl ligand (entry 5). The bromo analogue of **2** also displayed low activity (entry 4).



Scheme 3. Proposed course for the cationic polymerization of styrene.

We presumed that activation of the precatalyst with MAO led to the formation of a Ni–methyl bond. Therefore, the low activity of the methyl analogue of **2** was a somewhat unexpected result. Moreover, MALDI-ToF spectra of the polystyrene obtained in all reactions clearly showed that there were no methyl groups present as the end-groups of the polymer. This indicated that the mechanism of the polymerization was not a coordination-insertion one.

The above results led us to the conclusion that in the studied reactions, the styrene polymerized according to the cationic mechanism [14]. For the chloride complexes **1** and **2**, the anion  $\text{Cl}^-$  is permanently bonded by MAO, leading to the formation of a stable cation on nickel atom. Coordination of a styrene molecule to that cation is followed by a transfer of the positive charge to the carbon atom. Further polymerization proceeds on carbocationic centres of the growing polymer chain (Scheme 3).

If in the precatalyst the chloride substituent is replaced by the methyl group, the decrease of the polymer yield can be explained by a weaker bonding of  $\text{CH}_3^-$  than  $\text{Cl}^-$  by MAO. This is caused by lower affinity of aluminium to  $\text{CH}_3^-$  than to  $\text{Cl}^-$ . As the result of that the number and stability of the cationic centres  $\text{Ni}^+$  decrease and the yield of the polymer become lower. Decreasing of the polystyrene yield with the bromide analogue of the catalyst (Table 2, entry 4) can be explained similarly (lower affinity of aluminium to  $\text{Br}^-$  than to  $\text{Cl}^-$ ).

The reduced activity of precatalyst **4** with the methyl-substituted cyclopentadienyl ring is not fully understood (Table 2, entry 5). The possible explanations could be: reducing of the cationic character of  $\text{Ni}^+$  caused by an increase of the electron density on the cyclopentadienyl ring or an increase of the steric hindrance around catalytic active  $\text{Ni}^+$  centre.

#### 4. Conclusions

We have prepared a series of cyclopentadienylnickel(*N*-heterocyclic carbene) complexes. Molecular structures of three of these complexes were determined by single-crystal X-ray diffraction. The combination of MAO with the nickel complexes formed effective catalysts for the polymerization of styrene (the maximum TON was 4450). The results obtained indicated that polymerization proceeded probably according to the cationic mechanism. It was found that polystyrene yield depends on number and stability of cationic nickel centres. The polymer obtained was atactic.

#### Acknowledgement

The authors thank the Ministry of Education and Science for financial support of this work (Grant no. 4 T09A 012 25).

#### References

- [1] W.A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2163.
- [2] W.A. Herrmann, M. Elison, J. Fisher, C. Köcher, G.R.J. Artus, *Chem. Eur. J.* 2 (1996) 772.
- [3] W.A. Herrmann, C. Köcher, L.J. Gooßen, G.R.J. Artus, *Chem. Eur. J.* 2 (1996) 1627.
- [4] L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, *J. Organomet. Chem.* 690 (2005) 5407.
- [5] C.D. Abernethy, A.H. Cowley, R.A. Jones, *J. Organomet. Chem.* 596 (2000) 3.
- [6] R.A. Kelly III, N.M. Scott, S. Diez-Gonzales, E.D. Stevens, S.P. Nolan, *Organometallics* 24 (2005) 3442.
- [7] H.M. Sun, Q. Shao, D.M. Hu, W.F. Li, Q. Shen, Y. Zhang, *Organometallics* 24 (2005) 331.
- [8] X. Wang, S. Liu, G.-X. Jin, *Organometallics* 23 (2004) 6002.
- [9] B.E. Ketz, X.G. Ottenwaelder, R.M. Waymouth, *Chem. Commun.* (2005) 5693.
- [10] R. Wang, F. Bélanger-Gariépy, D. Zargarian, *Organometallics* 18 (1999) 5548.
- [11] M.-A. Dubois, R. Wang, D. Zargarian, J. Tian, R. Vollmerhaus, Z. Li, S. Collins, *Organometallics* 20 (2001) 663.
- [12] L.F. Groux, D. Zargarian, *Organometallics* 22 (2003) 4759.
- [13] M. Jimenez-Tenorio, M. Carmen Puerta, I. Salcedo, P. Valerga, S.I. Costa, L.C. Silva, P.T. Gomes, *Organometallics* 23 (2004) 3139.
- [14] D. Gareau, C. Sui-Seng, L.F. Groux, F. Brisse, D. Zargarian, *Organometallics* 24 (2005) 4003.
- [15] A.J. Arduengo III, R. Krafczyk, R. Schmutzler, *Tetrahedron* 55 (1999) 14523.
- [16] A. J. Arduengo, III, United States Patent 5,077,414.
- [17] A.J. Arduengo III, H.V. Rasika Dias, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 114 (1992) 5530.
- [18] K.W. Barnett, *J. Chem. Educ.* 51 (1974) 422.
- [19] M.F. Retting, R.S. Drago, *J. Am. Chem. Soc.* 91 (1969) 1361.
- [20] G.M. Sheldrick, SHELXTL. Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998.
- [21] C.D. Abernethy, J.A.C. Clyburne, A.H. Cowley, R.A. Jones, *J. Am. Chem. Soc.* 121 (1999) 2329.
- [22] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, *J. Am. Chem. Soc.* 127 (2005) 2485.
- [23] P.L. Holland, M.E. Smith, R.A. Andersen, R.G. Bergman, *J. Am. Chem. Soc.* 119 (1997) 12815.
- [24] F.-G. Fontaine, D. Zargarian, *Organometallics* 21 (2002) 401.