

DOI:10.1002/ejic.201500993



# Synthesis, Structures and Properties of Half-Sandwich Nickel(II) Complexes with Backbone-Modified NHC Ligands

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Keywords: Nickel / N-Heterocyclic carbenes / C-C coupling / Polymerization / Protecting groups

A series of seven nickel complexes  $[\rm Ni(\eta^5-C_5H_5)(X)(\rm NHC)]$  (X = Cl or Br; NHC = N-heterocyclic carbene) containing backbone-modified NHC ligands was prepared by treatment of nickelocene with the corresponding NHC·HX salts or, in the case of complex **1h** [Ni(\eta^5-C\_5H\_5)(Cl)(IMes^O)] (IMes^O = 4-oxo-1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene), by deprotection of the corresponding NHC ligand in complex **1g** [Ni(\eta^5-C\_5H\_5)(Cl)(IMes^{OPiv})] [IMes^{OPiv} = 4-(pivaloyloxy)-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]. Singlecrystal X-ray structures were determined for complexes **1d** [Ni(\eta^5-C\_5H\_5)(Cl)(Bn\_2-bimy)] (Bn\_2-bimy = 1,3-dibenzylbenz-

## Introduction

Over recent years N-heterocyclic carbenes (NHCs) have found vast areas of application in organometallic chemistry, catalysis and other areas of chemistry.<sup>[1]</sup> Their electronic and steric properties, as well as strong binding to metal centres, made them excellent ligands.<sup>[2]</sup> An interesting feature of NHC ligands is that their electronic and steric properties are influenced to a great extent by different structural features. Whereas spatial properties of NHCs depend generally on the nature of groups connected to the nitrogen atoms, their electronic properties are influenced mostly by substitution at the 4- and 5-positions of the imidazole ring and/or introduction of heteroatoms into the heterocycle.<sup>[3]</sup>

In the field of transition-metal NHC complexes, particular attention is paid to nickel compounds, due to their catalytic activity in a number of organic reactions.<sup>[4]</sup> The first NHC cyclopentadienyl nickel(II) complex –  $[Ni(\eta^{5}-C_{5}H_{5})(Cl)(IMes)]$  [1a, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] – was synthesized in a reaction between nickelocene and 1,3-dimesitylimidazolium chloride in THF at reflux.<sup>[5]</sup> This procedure, developed by Abernethy imidazolin-2-ylidene), **1g** and **1h**. The coordination spheres around the nickel atoms resemble those of  $d^8$  NiL<sub>4</sub> squareplanar complexes, with Ni–C(Cp) bond length differentiation and C–C bond alternation in Cp ligands being taken into account. Desymmetrization of the five-membered heterocyclic ring and a tautomeric equilibrium were observed for complex **1h**. All new complexes are efficient precatalysts in three C– C bond-forming reactions (polymerization of styrene, polymerization of methyl methacrylate, Suzuki–Miyaura crosscoupling).

et al., has proved to be versatile and has resulted in a considerable number of different NHC complexes of the general formula [Ni( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)(X)(NHC)] (1, R = H or alkyl; X = Cl, Br or I).<sup>[6,7]</sup> These complexes serve as precatalysts in a remarkably broad range of transformations, such as amination of aromatic halides,<sup>[6a,6i]</sup> polymerization of styrene,<sup>[6b,6f]</sup> polymerization of methyl methacrylate,<sup>[8]</sup> Suzuki– Miyaura cross-coupling,<sup>[6g,9,10]</sup> polymerization of phenylacetylene,<sup>[6f]</sup> regioselective hydrothiolation of alkynes,<sup>[11]</sup> hydrosilylation of aldehydes, ketones and imines,<sup>[12]</sup> and  $\alpha$ arylation of acyclic ketones.<sup>[13]</sup>

Our aim is to optimize the catalytic activity of  $[Ni(\eta^5 C_5H_4R(X)(NHC)$  complexes through suitable modifications of the ligands. Previously, significant efforts were devoted to modifications of N-substituents in these complexes.<sup>[6]</sup> More recently, we have explored exchange of the chloride in  $[Ni(\eta^5-C_5H_4R)(Cl)(NHC)]$  for a nitrile or an anionic (trifluoroacetate or nitrate) ligand.<sup>[14]</sup> In this report we examine synthesis, structures and properties of a number of complexes containing backbone-modified NHC ligands. The electron-donating properties of NHC ligands (Scheme 1) are systematically varied, from ligands that are significantly stronger  $\sigma$ -donors that the standard IMes ligand (e.g. IMes<sup>2Me</sup>) to those that are weak donors (e.g., IMes<sup>O</sup>). For comparison, the available experimentally measured or calculated  $v_{CO}$  frequencies quantifying the overall electronic strength of each studied ligand are shown in Scheme 1.

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/ 10.1002/ejic.201500993.



IMes<sup>OH.</sup>HCI

(R = Mes)IPr<sup>OH.</sup>HCI

(R = Dipp)

HC

R

b

1h



(R = Mes PivC С Mes Mes IMes<sup>OPiv.</sup>HCI 1q Scheme 3. The synthesis of complexes 1g and 1h. Reaction condi-

a

(R = Mes or Dipp)

Scheme 1. Ligands explored in this study (Mes = 2,4,6-trimethylphenyl, Bn = benzyl). The reported average experimentally measured or calculated  $v_{CO}$  frequencies in [Ir(Cl)(NHC)(CO)<sub>2</sub>] complexes (in cm<sup>-1</sup>) are shown: [a] experimentally measured value,<sup>[15]</sup> [b] experimentally measured value,<sup>[3b]</sup> [c] converted from experimentally measured  $v_{CO}$  frequencies in the [Rh(Cl)(NHC)(CO)<sub>2</sub>] complex<sup>[3f]</sup> by use of the equation developed by Wolf and Plenio,<sup>[16]</sup> [d] converted from calculated TEP (Tolman electronic parameter, this work) value by use of the reversed equation published by Glorius and co-workers,<sup>[15]</sup> [e] experimentally measured value for the 5,6-dimethyl derivative,<sup>[17]</sup> and [f] experimentally measured value;<sup>[18a]</sup> complex [Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(Cl)(IMes<sup>2O</sup>)] could not be obtained. The calculated TEP values for each ligand are listed in Table S5 in the Supporting Information.

### **Results and Discussion**

#### Synthesis

Complexes 1b-1f were obtained as red solids in yields varying from 41% to 87% by use of the straightforward procedure originally published by Abernethy et al.,<sup>[5]</sup> with minor modifications (Scheme 2). However, attempts to use 4-hydroxy-1,3-dimesitylimidazolium chloride (IMes<sup>OH</sup>. HCl)<sup>[3c,3f]</sup> or its 1,3-bis(2,6-diisopropylphenyl) analogue IPr<sup>OH</sup>•HCl<sup>[3c,3f]</sup> in this procedure were unsuccessful (Scheme 3, path a). In both cases light blue paramagnetic solids were obtained; they could not be fully identified, due to uninformative NMR spectra and absence of signals characteristic of organonickel species in the EI MS spectra.<sup>[19]</sup> Therefore, we decided to protect the OH group in IMes<sup>OH</sup>·HCl. Thus, IMes<sup>OH</sup>·HCl was deprotonated with Et<sub>3</sub>N by the published procedure<sup>[3f]</sup> and subsequently treated with pivaloyl chloride to give the desired ester IMes<sup>OPiv</sup>·HCl.<sup>[20]</sup> Gratifyingly, IMes<sup>OPiv</sup>·HCl appeared to be very reactive towards nickelocene, providing complex 1g within 2 h at room temperature in 84% yield (Scheme 3). The target complex 1h was then obtained from 1g upon hydrolysis of the ester protecting group in the NHC ligand. In this reaction  $NH_{3(aq.)}/MeOH$  was the most suitable rea-



1b: NHC = IMes<sup>2Me</sup>, X = C 1c: NHC = IMes<sup>Me</sup>, X = CI 1d: NHC = Bn<sub>2</sub>-bimy, X = Cl 1e: NHC = Bn<sub>2</sub>-bimy, X = Br 1f: NHC = <sup>1,2,4</sup>TBn, X = Br

Scheme 2. Synthesis of complexes 1b-1f. Reaction conditions: THF, reflux, 2.5-12 h.

tions: a THF, reflux, b Et<sub>3</sub>N, then pivaloyl chloride (ref.<sup>[3f]</sup>), c THF, room temp.,  $d \operatorname{NH}_{3(aq.)}/MeOH$ , room temp (Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl, Piv = trimethylacetyl).

gent,<sup>[21]</sup> giving much better results than HCl<sub>(aq.)</sub> or K<sub>2</sub>CO<sub>3</sub>/ MeOH, which caused decomposition of the substrate.

In the case of the diamidocarbene IMes<sup>2O</sup>, which is one of the poorest NHC donors reported to date,<sup>[18]</sup> heating of its precursor (2-chloro-1,3-dimesitylimidazolidine-4,5-dione) with nickelocene in THF at reflux resulted in ill-defined, brownish solids. NMR spectra of these materials did not feature any signals assignable to a Ni-bound cyclopentadienyl ligand.[19]

#### Characterization

The NMR spectra of complexes 1b-1h were conventionally recorded in CDCl<sub>3</sub> at ambient temperature. These spectra consist of signals originating from the cyclopentadienyl (Cp) moiety and the appropriate NHC ligand. In all cases the Cp protons are represented by sharp singlets appearing either from 4.52 ppm to 4.63 ppm for the imidazole-based NHC complexes 1b, 1c, 1g and 1h, or from 5.10 ppm to 5.15 ppm for the benzimidazole- and 1,2,4-triazole-derived NHC complexes 1d-1f. Whereas the presence of signals for the Cp protons in the range from 4.5 ppm to 4.8 ppm is common for N, N'-diaryl- or mixed N, N'-alkylaryl-nickel NHC complexes of this type,<sup>[6]</sup> its occurrence downfield from 5 ppm is usual for N,N'-dialkyl analogues.<sup>[6d,6g,6h,22]</sup> Our results confirm that the chemical shifts of Cp protons are influenced by N-substituents rather than by the structure of the heterocycle.

Upon coordination to the nickel centre, signals for all  $C(sp^2)$ -bonded protons from the NHC ligand core are shifted upfield in comparison with their precursors (e.g.,  $\Delta\delta$ = -1.38 ppm for the CH proton in the 1,2,4-triazole heterocycle in 1f). This could be a result of reduced ring current caused by transfer of electron density to the metal centre.

The <sup>1</sup>H NMR spectra of **1d** and **1e** each feature two intriguing, well-resolved (separated by ca. 0.7 ppm) doublets (1d:  $\delta = 6.92$  ppm and 6.22 ppm, J = 16.2 Hz; 1e:  $\delta =$ 6.89 ppm and 6.14 ppm, J = 16.0 Hz). Because in both cases  $\Delta v/J > 10$  (17.3 for 1d and 18.8 for 1e) those signals represent "the roof effect" (i.e., the inner peaks of two



1h-D-

neighbouring doublets are higher than the external peaks). Analysis of the spectra for 1d and 1e leads to the conclusion that these doublets represent diastereotopic methylene protons from the benzyl groups. Non-equivalence of these hydrogen atoms bonded to the same carbon atom originates from the restricted rotation of the Ni-C<sub>carbene</sub> or N-C<sub>Bn</sub> bonds. Similar dynamic behaviour was observed for some dialkyl or mixed alkyl-aryl nickel NHC complexes.[6c,6f,10,23] The nature of such restricted rotation has been attributed mainly to steric factors related to the bulkiness of halogen or Cp ligands, although electronic factors cannot be completely excluded.<sup>[6d,6f]</sup> Restricted rotation of the Ni-Ccarbene and N-C<sub>R</sub> bond could be also caused by a CH···XNi interaction, as observed in the solid state for  $[Ni(\eta^5 C_5H_5$ (Cl)(NHC)] [NHC = 1-cyclohexyl-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene].[6f] Another explanation for such a phenomenon could be anagostic CH...Ni interactions reported for the square-planar nickel complexes  $[Ni(Br)_2(NHC)_2]$  (NHC = 1,3-diisopropylbenzimidazolin-2-ylidene).<sup>[24]</sup> Although the occurrence of large downfield shifts for the benzyl methylene protons upon coordination (e.g.,  $\Delta \delta = -0.45$  ppm and -1.15 ppm for 1d) suggests possible anagostic interactions in solution, no such short contacts are observed in the solid state for 1d (vide infra). If it is assumed that the Ni<sup>II</sup> centres are saturated in complexes [Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(X)(NHC)], we do not at this point have a satisfactory explanation for this interesting behaviour.

Similar spectroscopic features as for 1d and 1e are observed for the 1,2,4-triazole-derived complex 1f. However, in 1f all four methylene protons are inequivalent, due to the restricted rotation and desymmetrization of the NHC core owing to the presence of a nitrogen atom at the 4-position of the heterocycle. The Ph- $CH_2$ - signals appear as unresolved and partially overlapping multiplets from 5.9 ppm to 6.3 ppm at room temperature.

The unsymmetrical nature of other ligands substituted at the NHC backbone (i.e., IMes<sup>Me</sup>, IMes<sup>OPiv</sup> and IMes<sup>O</sup>) demonstrates itself in the <sup>1</sup>H NMR spectra through nonequivalence of the methyl groups from the mesityl substituents. The methyl groups appear as three singlets, with a 6:6:6 intensity ratio in the cases of **1c** and **1h**, or as four singlets with a 3:3:6:6 ratio in that of **1g**. Thus, only in the latter case do the *para*-methyl groups resonate as two separate singlets.

In the case of **1h** a keto–enol tautomeric equilibrium could be expected (Scheme 4). Nonetheless, only two singlets appear in the diagnostic part of the <sup>1</sup>H NMR spectrum, at  $\delta = 4.30$  ppm and at  $\delta = 4.63$  ppm with a 2:5 intensity ratio. We assign these to the heterocycle -*CH*<sub>2</sub>- and Cp protons, respectively. Moreover, no signal that could be assigned to a single C(*sp*<sup>2</sup>)-bonded proton was present in this spectrum. Thus we conclude that only the keto form of **1h** is present in CDCl<sub>3</sub> at room temperature, similarly to what was observed for [Rh(Cl)(COD)(IMes<sup>O</sup>)]<sup>[3f]</sup> in CD<sub>2</sub>Cl<sub>2</sub> and for [Ir(Cl)(NHC)(CO)<sub>2</sub>] in CDCl<sub>3</sub> when related NHC ligands derived from 4-hydroxy-5-alkyl- or 5-arylimidazoles were used.<sup>[25]</sup>

Scheme 4. Deuterium exchange in 1h via the enol tautomer (R = 2,4,6-trimethylphenyl).

Moderate heating has negligible effect on the <sup>1</sup>H NMR spectra of complex 1h (e.g., the  $-CH_2$ - singlet shifts from 4.30 ppm in CDCl<sub>3</sub> at ambient temperature to 4.28 ppm at 50 °C). However, the chemical shift of the heterocycle  $-CH_2$ - singlet varies considerably with the solvent polarity: from 3.41 ppm in  $C_6D_6$  to 4.61 ppm in  $(CD_3)_2CO$ . This could be a result of the tautomeric equilibrium in polar solvents that is fast on the NMR timescale. In order to confirm the presence of the elusive enol form of 1h, H/D exchange experiments were performed in (CD<sub>3</sub>)<sub>2</sub>CO/D<sub>2</sub>O. The -CH<sub>2</sub>- singlet at  $\delta$  = 4.67 ppm disappeared completely upon treatment of **1h** with an excess of D<sub>2</sub>O overnight at room temperature. Moreover, the corresponding -CH2- resonance at  $\delta = 54.27$  ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum turned into a broad band due to splitting with D atoms (Scheme 4, see also Figure S2 in the Supporting Information).

Interestingly, during these studies on **1h** we noticed that the sharp  $-CH_2$ - singlet at  $\delta = 4.67$  ppm broadened upon cooling and split at -50 °C into two broad resonances centred at  $\delta = 4.83$  and 4.77 ppm. At the same time, the two signals of non-equivalent *meta* aromatic protons at  $\delta =$ 7.14 and 7.11 ppm also significantly broadened (Figure S3 in the Supporting Information). These observations could be explained in terms of a dynamic process that becomes slow on the NMR timescale at low temperature (vide supra), most likely the hindered rotation of the *N*-mesityl substituents.

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of complexes **1b–1h** the Cp singlets are present in a narrow range from 92.1 to 93.8 ppm. The carbene carbon chemical shifts in complexes **1b–1h** varied from 161.7 ppm for **1b** to 220.1 ppm for **1h**. Although these complexes feature the most- and the least-electron-donating carbene ligands, respectively, no correlation of C<sub>carbene</sub> chemical shifts with the electronic properties of ligands is observed within the series of complexes **1a–1h** (Figure S4 in the Supporting Information).

#### X-ray Studies

Compound **1d** crystallizes in the triclinic  $\overline{I}$  space group (no. 2) whereas compound **1g** crystallizes in the  $P2_1/n$  space group (no. 14) of the monoclinic crystal system. Both of the crystal structures contain two independent molecules in the asymmetric unit. However, the conformational differences in the substituents in the NHC ligands do not exert significant influence either on the nickel coordination sphere or on the imidazolium ring geometry, so only one molecule from the asymmetric unit is presented in Figure 1 and Figure 2.



Figure 1. Molecular structure of complex 1d. See the Supporting Information for the other molecule from the asymmetric unit. Thermal ellipsoids are drawn at the 50% level of probability and hydrogen atoms are omitted for clarity. Selected interatomic distances and angles: Ni1…Cp<sub>Cg</sub> 1.7646(8) Å [Ni1…Cp<sub>plane</sub> 1.7630(3) Å], Ni1–Cl1 2.2005(4) Å, Ni1–C6 1.8700(13) Å, N1–C6–N2 105.85(11)°, C6–N1 1.3606(17) Å, C6–N2 1.3600(17) Å, N2–C8 1.3945(17) Å, N1–C7 1.3931(18) Å, C7–C8 1.393(2) Å.



of the benzimidazole plane as the chloride anion, whereas in the other molecule the phenyl rings are on the opposite side of the plane. The C18–C17–C16–N1 and C11–C10– C9–N2 torsion angles, describing the orientation of the phenyl rings within the latter structure, amount to 2.96(16)° and 24.35(14)°, respectively, and the analogous C48–C47– C46–N31 and C41–C40–C39–N32 torsion angles in the former one are 52.18(14)° and –71.85(14)°, respectively.

The conformational differences between independent molecules of complex 1g are twofold. Firstly, the NHC ligand is oriented differently with respect to the Ni–Cl bonds, as evidenced by the values of the torsion angles Cl1–Ni1–C6–N1 and Cl41–Ni41–C46–N41 of  $58.87(12)^{\circ}$  and  $-60.17(12)^{\circ}$ , respectively. Secondly, the orientations of the pivaloyl group with respect to the imidazolium ring of the NHC are different, as can be seen from the values of the C27–O1–C7–C8 and C67–O41–C47–C48 torsion angles, which equal –91.5(2)° and 91.8(2)°, respectively. Compound 1h crystallizes in the orthorhombic *Pbca* space group (no. 61) and there is one molecule in the asymmetric unit (Figure 3). The C7–O1 and C7–C8 bond lengths of 1.197(3) and 1.507(3) Å, respectively, indicate unequivocally that the NHC ligand exists in the keto form in this complex.



Figure 2. Molecular structure of complex **1g**. See the Supporting Information for the other molecule from the asymmetric unit. Thermal ellipsoids are drawn at the 50% level of probability and hydrogen atoms are omitted for clarity. Selected interatomic distances and angles: Ni1…Cp<sub>Cg</sub> 1.7727(11) Å [Ni1…Cp<sub>plane</sub> 1.7708(3) Å], Ni1–Cl1 2.1880(6) Å, Ni1–C6 1.888(2) Å, N1–C6–N2 103.65(18)°, C6–N1 1.361(3) Å, C6–N2 1.362(3) Å, N2–C7 1.388(3) Å, N1–C8 1.396(3) Å, C7–C8 1.339(3) Å.

In one of the molecules of complex **1d** the phenyl rings from both benzyl substituents are located on the same side

Figure 3. Molecular structure of complex **1h**. Thermal ellipsoids are drawn at the 50% level of probability and hydrogen atoms are omitted for clarity. Selected interatomic distances and angles: Ni1····Cp<sub>Cg</sub> 1.7720(13) Å [Ni1···Cp<sub>plane</sub> 1.7698(6) Å], Ni1-Cl1 2.1829(7) Å, Ni1-C6 1.872(2) Å, N1-C6-N2 107.09(19)°, C6-N1 1.386(3) Å, C6-N2 1.328(3) Å, N2-C8 1.469(3) Å, N1-C7 1.409(3) Å, C7-C81.507(3) Å, C7-O11.197(3) Å.

Interestingly, the amidocarbene NHC ligand in **1h** features significant elongation of the N2–C8 and C6–N1



bonds and shortening of the C6–N2 bond with respect to the analogous bonds in complexes 1d and 1g (see Figure 1, Figure 2 and Figure 3 captions for numerical values). This indicates localization of electrons in the  $\pi$  orbitals of C6– N2 bond in complex 1h, whereas in molecules 1d and 1g they are delocalized over N1, C6 and N2 atoms. Consequently, the mesomeric formula A depicted on Scheme 5 is dominant in the imidazolium ring electronic structure in compound 1h.



Scheme 5. The mesomeric structures of the NHC ligand in complex **1h**.

Similarly to those in in compounds 1d and 1g, the Ni- $C_{Cp}$  bond lengths in **1h** show a pronounced *trans* effect of the NHC ligand. The Ni-C<sub>Cp</sub> bond length with carbon lying cis to the NHC ligand (trans to the chloride ligand) is ca. 0.1 Å shorter than the bond lengths to carbons on the opposite side of Cp (see Table S2 in the Supporting Information). The slippage of Cp rings is very small in all compounds and does not exceed 0.095 Å. The C-C bond lengths in the Cp rings are varied in an analogous way as in the Cp\* complexes of Ni with tertiary phosphine ligands  $[Ni(X)(Cp^*)(PEt_3)]$ :<sup>[26]</sup> that is, the two bonds approximately parallel to the C<sub>NHC</sub>-Ni-Cl plane are shorter than the others, resulting in the so-called "diene distortion" (see Table S3 in the Supporting Information). Detailed analysis of the electronic structure presented by Holland et al.<sup>[26]</sup> and references cited therein indicates that the coordination sphere of the nickel atom resembles the square-planar geometry characteristic of d<sup>8</sup> NiL<sub>4</sub> complexes. The overlap of Ni d and Cp  $\pi$  orbitals results in the observed C–C bond length alternation in the non-slipped Cp ring.

### Catalysis

#### Styrene Polymerization

We reported in 2006 that complexes [Ni( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)(X)(NHC)] bearing the standard NHC ligands initiate polymerization of styrene in the presence of an excess of methylaluminoxane (MAO).<sup>[6b]</sup> A significant effect of the steric bulk of NHC and Cp ligands on the catalytic activity was concluded from those experiments. The results of styrene polymerization with all the new complexes are listed in Table 1. All studied complexes polymerize styrene with comparable yields (90–98%), with the exception of the triazole-derived complex **If** (Entry 5), which provided a somewhat lower yield (82%). Under more challenging conditions (i.e., at Al/Ni ratio 100:1) the reference complex **Ia** performed considerably better (95% yield) than **1c** (67% yield).

Table 1. Polymerization of styrene with  $[Ni(\eta^5\text{-}C_5H_5)(X)(NHC)]$   $(1a\text{-}1h)/MAO^{[a]}$ 

n Ph	1. <b>1a–1h</b> /MAO toluene, 30 m 2. toluene, 50 °C	in, r.t. ►	· /	n
Complex		Yield <sup>[b]</sup>	M <sub>n</sub> <sup>[c]</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>[c]</sup>
[Ni(ŋ <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(C	[])(IMes)] (1a) <sup>[d]</sup>	98	11100	1.8
[Ni(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(C	$(1)(1Mes^{2Me})$ (1b)	94	8000	3.0
[Ni(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(C	(I)(IMes <sup>Me</sup> )] (1c)	96	8000	2.9
[Ni(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(C	(l)(Bn <sub>2</sub> -bimy)] (1d)	90	7400	3.0
$[Ni(\eta^{5}-C_{5}H_{5})(B$	r)( <sup>1,2,4</sup> TBn)] ( <b>1f</b> )	82	430/18000 [e]	2.0/1.9 <sup>[e]</sup>
[Ni(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(C	I)(IMes <sup>OPiv</sup> )] (1g)	94	6000	4.0
$[Ni(\eta^{5}-C_{5}H_{5})(C_{5}H_{5})]$	[l)(IMes <sup>O</sup> )] (1h)	96	7600	2.8
	n  Ph Complex [Ni( $\eta^5-C_5H_5$ )(C [Ni( $\eta^5-C_5H_5$ )(C [Ni( $\eta^5-C_5H_5$ )(C [Ni( $\eta^5-C_5H_3$ )(B [Ni( $\eta^5-C_5H_3$ )(C [Ni( $\eta^5-C_5H_5$ )(C	$\begin{array}{c} n \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	$\begin{array}{c c} n & \text{Ph} & \begin{array}{c} 1. \ \textbf{1a-1h/MAO} \\ \text{toluene, 30 min, r.t.} \\ \hline 2. \ \text{toluene, 50 °C, 3 h} \\ \hline \\ $	$\begin{array}{c c} n & \text{Ph} & \begin{array}{c} 1. \ \textbf{1a-1h/MAO} \\ toluene, 30 \ \text{min, r.t.} \\ \hline 2. \ toluene, 50 \ ^{o}\text{C}, 3 \ h \end{array} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array} \\ \hline \text{Ph} \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} Complex & \begin{array}{c} 2. \ toluene, 50 \ ^{o}\text{C}, 3 \ h \end{array} & \begin{array}{c} & \begin{array}{c} & \end{array} \\ \hline \end{array} \\ \hline \begin{array}{c} Ni(\eta^5-C_3H_3)(\text{Cl})(\text{IMes})] \ \textbf{(1a)}^{[d]} & 98 \\ Ni(\eta^5-C_3H_3)(\text{Cl})(\text{IMes}^{2Me})] \ \textbf{(1b)} & 94 \\ Ni(\eta^5-C_3H_3)(\text{Cl})(\text{IMes}^{Me})] \ \textbf{(1c)} & 96 \\ Ni(\eta^5-C_3H_3)(\text{Cl})(\text{IMes}^{-h}\text{Im})] \ \textbf{(1f)} & 82 \\ Ni(\eta^5-C_3H_3)(\text{Cl})(\text{IMes}^{O^{\text{Piv}}})] \ \textbf{(1g)} & 94 \\ Ni(\eta^5-C_3H_3)(\text{Cl})(\text{IMes}^{O^{\text{Piv}}})] \ \textbf{(1g)} & 96 \\ \end{array} $

[a] Reaction conditions: styrene/Ni 15000:1, Al/Ni 300:1, toluene, 30 min at room temp., then 3 h at 50 °C. [b] Isolated yield. [c] Determined by GPC. [d] Data from ref.<sup>[6f]</sup> [e] Bimodal distribution.

The GPC measurements indicate that low-molecularweight polystyrene (PS,  $M_n$  from 6000 to 8000 Da, in comparison with the target  $M_n$  of 1560 kDa) with rather broad  $M_w/M_n$  ratios were obtained. In the case of complex **1f** lowmolecular-weight oligomers were also present. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra of PS were consistent with atactic microstructure in all cases.

Because the steric demands of *N*-mesityl- and *N*-benzylsubstituted NHCs are different,<sup>[27]</sup> the effects of the electronic properties of the NHC ligands on this catalytic process could be compared in the series of *N*,*N'*-dimesityl complexes **1b**, **1c**, **1a**, **1g** and **1h**: that is, in the order of decreasing donor strength of ligands (IMes<sup>2Me</sup> > IMes<sup>Me</sup> > IMes  $\approx$  IMes<sup>OPiv</sup> > IMes<sup>O</sup>). Because all of them provide the same yields of polystyrene, these results suggest that factors other than the electronics of the NHCs define the overall efficiency of this catalytic system.<sup>[28]</sup>

#### Methyl Methacrylate Polymerization

We have recently described methyl methacrylate (MMA) polymerization in the presence of a series of  $[Ni(\eta^5 C_5R_5$ (X)(NHC)] complexes together with MAO.<sup>[8]</sup> Our findings, supported by literature precedents, allowed us to suggest a coordinative-anionic mechanism in which the monomer molecule is activated through coordination to the Ni centre.<sup>[29]</sup> The highest level of conversion was achieved with complex [Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(Cl)(SIPr)], bearing the bulky N,N'-2,6-diisopropylphenyl NHC ligand (Table 2, Entry 1). In the present work, we have found that MMA polymerization in the presence of complexes 1/MAO can be preferably carried out at room temperature. The results of MMA polymerization under the optimized conditions are shown in Table 2. Initially, complex  $[Ni(\eta^5-C_5H_5)(Cl)(SIPr)]$  was tested (Entry 2), and provided PMMA [poly(methyl methacrylate)] with 47% yield and slightly higher content of rr triad than in previous runs at 50 °C. Then, complexes 1a-1h were tested and gave up to 61% yields of PMMA (1g, Entry 9). The same syndiotactic-rich polymer microstructure was obtained for all studied complexes.



Table 2. Polymerization of methyl methacrylate in the presence of  $[Ni(\eta^5\text{-}C_5H_5)(X)(NHC)]$   $(1a\text{--}1h)/MAO.^{[a]}$ 

	$n \qquad \qquad$		$\mathcal{A}_{n}^{\circ}$
Entry	Complex	Yield <sup>[b]</sup>	Triad fractions <sup>[c]</sup> rr:mr:mm
1	$[Ni(\eta^5-C_5H_5)(Cl)(SIPr)]^{[d]}$	34	67:25:8
2	$[Ni(\eta^5-C_5H_5)(Cl)(SIPr)]$	47	74:20:6
3	$[Ni(\eta^{5}-C_{5}H_{5})(Cl)(IMes)]$ (1a)	34	72:21:7
4	$[Ni(\eta^{5}-C_{5}H_{5})(Cl)(IMes^{2Me})]$ (1b)	44	75:19:6
5	$[Ni(\eta^{5}-C_{5}H_{5})(Cl)(IMes^{Me})]$ (1c)	55	75:20:5
6	$[Ni(\eta^{5}-C_{5}H_{5})(Cl)(Bn_{2}-bimy)]$ (1d)	58	72:22:6
7	$[Ni(\eta^{5}-C_{5}H_{5})(Br)(Bn_{2}-bimy)]$ (1e)	24	73:20:7
8	$[Ni(\eta^5-C_5H_5)(Br)(^{1,2,4}TBn)]$ (1f)	36	71:22:7
9	$[Ni(\eta^{5}-C_{5}H_{5})(Cl)(IMes^{OPiv})]$ (1g)	61	73:21:6

[a] Reaction conditions: MMA/Ni 1000:1, Al/Ni 100:1, toluene, 30 min at room temp., then 20 h at room temp. [b] Isolated yield. [c] Determined by <sup>1</sup>H NMR. [d] Data from ref.<sup>[8]</sup> (30 min at room temp., then 3 h at 50 °C, MMA/Ni 1000:1, Al/Ni 100:1); SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene.

Determination of the molecular weights of these polymers by GPC proved to be troublesome owing to unexplained back pressure increases. However, measurements of representative samples indicate that these polymers are of complex, multimodal composition with two major fractions: one with  $M_n$  ca. 100 kDa and the second one with  $M_n > 1000$  kDa. These data were further verified with dynamic light scattering (DLS) measurements that show the presence of two fractions corresponding to sizes of roughly 5 nm and 25 nm.

Because ligand modification had no effect on the microstructure of the polymers, we conclude that Ni species do not participate in the propagation steps. Collectively, these findings provide further evidence for an anionic MMA polymerization mechanism.

Table 3. Suzuki cross-coupling between phenylboronic acid and 4'-haloacetophenones.<sup>[a]</sup>

#### **Cross-Coupling Reactions**

Both neutral complexes [Ni( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)(X)(NHC)] and cationic complexes [Ni( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)(RCN)(NHC)]<sup>+</sup>A<sup>-</sup> are efficient precatalysts for Suzuki–Miyaura cross-coupling between aryl halides and phenylboronic acid.<sup>[6g,9,14]</sup> The backbone-modified complexes **1b–1h** were tested under standard conditions in toluene with K<sub>3</sub>PO<sub>4</sub> as a base (Table 3). All of the new complexes catalyze formation of the cross-coupling product from 4'-bromoacetophenone and phenylboronic acid with yields from 52% to 78%, with excellent selectivity. Moreover, complex **1g** was significantly less efficient when 4'-chloroacetophenone was used as a substrate (33% yield, Entry 8). Surprisingly, phenylboronic acid pinacol ester (Entry 10), which has often been used as a substrate in Suzuki cross-couplings, did not react under these conditions.

Previously, a considerable number of tested complexes  $[Ni(\eta^5-C_5R_5)(X)(NHC)]$  and their ionic congeners have given similar levels of conversion in Suzuki–Miyaura cross-couplings. Therefore, it has been suggested that complexes 1 are probably reduced in situ to provide catalytically active Ni<sup>0</sup> complexes.<sup>[6g,9]</sup> Our findings could be explained consistently with this proposal because the electronic and steric properties of NHC ligands tested in this study do not significantly influence the outcome of these cross-coupling reactions.

In preliminary tests, we have also found that complexes  $[Ni(\eta^5-C_5H_5)(X)(NHC)]$  are active in Kumada–Corriu cou-



Scheme 6. Kumada-Corriu coupling catalyzed by complex 1b.



[a] Reaction conditions: 3 mol-% [Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(X)(NHC)] in toluene, K<sub>3</sub>PO<sub>4</sub> (2.6 equiv.), 90 °C, 1 h. [b] Determined by GC. [c] Data from ref.<sup>[9]</sup> (reaction time 30 min). [d] Run with phenylboronic acid dimethyl ester; phenylboronic acid pinacol ester did not react.



pling. For example, the reaction between phenylmagnesium bromide and *meta*-bromotoluene in the presence of 3 mol-% of complex **1b** (90 min, room temp.) gives a 92% yield of the cross-coupling product (Scheme 6).

# Conclusions

A number of backbone-functionalized NHC precursors have been successfully applied in the direct synthesis of complexes  $[Ni(\eta^5-C_5H_5)(X)(NHC)]$ . In the case of 4hydroxy-substituted NHC precursor IMes<sup>OH</sup>·HCl we have developed a protection/deprotection strategy to obtain the desired 4-oxo complex 1h. Crystallographic data for complexes 1d, 1g and 1h show that the backbone substituents influence the structure of the heterocycle ring but do not significantly modify the overall geometry of the Ni coordination sphere. All new complexes are catalytically active in three C–C bond-forming reactions: polymerization of styrene (TON up to 14400), polymerization of methyl methacrylate (TON up to 610) and Suzuki-Miyaura cross-coupling (TON up to 24). However, the effect of variable properties of the NHC ligands on the reactivity of the studied complexes is not pronounced.

# **Experimental Section**

**General:** All manipulations (except polymer separation and purification and workup of the Suzuki cross-coupling reactions) were performed under inert atmosphere (argon) with use of Schlenk techniques. Solvents were purified by conventional methods.<sup>[30]</sup> Styrene (ReagentPlus<sup>®</sup>, Aldrich) was distilled from CaH<sub>2</sub> under reduced pressure and passed through a column with neutral Al<sub>2</sub>O<sub>3</sub>. Methyl methacrylate (Aldrich, 99%) was distilled from CaH<sub>2</sub> under reduced pressure. Ligand precursors IMes<sup>2Me</sup>·HCl,<sup>[31]</sup> IMes<sup>Me</sup>·HCl,<sup>[31]</sup> <sup>1,2,4</sup>TBn·HBr,<sup>[32]</sup> IMes<sup>OH</sup>·HCl, IPr<sup>OH</sup>·HCl and IMes<sup>OPi</sup>·HCl,<sup>[3f]</sup> Bn<sub>2</sub>-bimy·HCl,<sup>[33]</sup> Bn<sub>2</sub>-bimy·HBr<sup>[34]</sup> and 2-chloro-1,3-dimesitylimidazolidine-4,5-dione<sup>[18a]</sup> were prepared by literature procedures. Other reagents were purchased from commercial suppliers and used without further purification.

NMR spectra were recorded at ambient temperature with a Mercury-400BB spectrometer operating at 400 MHz for <sup>1</sup>H NMR and at 101 MHz for <sup>13</sup>C NMR spectroscopy. The average molecular weights of PS and PMMA were measured with a LabAlliance liquid chromatograph equipped with a Jordi Gel DVB Mixed Bed column (250 mm × 10 m) with CH<sub>2</sub>Cl<sub>2</sub> as the mobile phase at 30 °C and calibrated with the appropriate standard (PS or PMMA). Dynamic light scattering (DLS) experiments with PMMA were performed with a Malvern ZetaSizer Nano instrument in CH<sub>2</sub>Cl<sub>2</sub>. Levels of conversion and selectivity of Suzuki reactions were determined with an Agilent Technologies 7820 GC System equipped with a FID detector and an Agilent 19091J-413 column. Tetradecane was used as an internal standard.

Synthesis of Complexes: Complexes 1b–1g were each prepared from nickelocene and the appropriate imidazolium salt in THF by the published method<sup>[5]</sup> with minor modifications. Briefly, a THF solution of nickelocene was added to NHC·HX. The resulting mixture was heated at reflux for the specified time (or vigorously stirred at ambient temperature in the case of 1g). The solvent was then removed under vacuum, and the solid residue was treated with tolu-

ene and filtered. The desired complexes were obtained by crystallization from the filtrate.

[Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(Cl)(IMes<sup>2Me</sup>)] (1b): This complex was obtained from nickelocene (388.0 mg, 1.053 mmol) and IMes<sup>2Me</sup>·HCl (198.0 mg, 1.053 mmol) in THF (10.0 mL) with use of a reaction time of 3 h, yield 56%, red solid (289.3 mg, 0.589 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.12 (s, 4 H, *m*-Ar*H*), 4.52 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.44 (s, 6 H, *p*-ArCH<sub>3</sub>), 2.08 (s, 12 H, *o*-ArCH<sub>3</sub>), 1.86 (s, 6 H, <sup>Im</sup>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.7 (NCN), 138.9 (<sup>Ar</sup>C), 136.2 (<sup>Ar</sup>C), 135.3 (<sup>Ar</sup>C), 129.4 (<sup>Ar</sup>C), 128.0 (<sup>Im</sup>C), 92.1 (C<sub>5</sub>H<sub>5</sub>), 21.5 (*p*-ArCH<sub>3</sub>), 18.6 (*o*-ArCH<sub>3</sub>), 9.6 (<sup>Im</sup>CH<sub>3</sub>) ppm. EI MS: *m/z* (<sup>58</sup>Ni, <sup>35</sup>Cl, %) = 490 (39) [M]<sup>+</sup>, 455 (31) [M - Cl]<sup>+</sup>, 425 (16) [M - Cp]<sup>+</sup>, 331 (100) [IMes<sup>2Me</sup> - H]<sup>+</sup>. C<sub>28</sub>H<sub>33</sub>ClN<sub>2</sub>Ni·H<sub>2</sub>O (509.8): calcd. C 65.98, H 6.92, N 5.50; found C 66.45, H 6.72, N 5.69.

**[Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(Cl)(IMes<sup>Me</sup>)] (1c):** This complex was obtained from nickelocene (260.0 mg, 1.38 mmol) and IMes<sup>Me</sup>·HCl (480.0 mg, 1.35 mmol) in THF at reflux (13.0 mL) with use of a reaction time of 2.5 h, yield 47%, red solid (307.0 mg, 0.647 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.13 (s, 2 H, *m*-Ar*H*), 7.10 (s, 2 H, *m*-Ar*H*), 6.82 (s, 1 H, <sup>Im</sup>CH), 4.54 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.44 (br. s, 6 H, *p*-ArCH<sub>3</sub>), 2.16 (s, 6 H, *o*-ArCH<sub>3</sub>), 2.11 (s, 6 H, *o*-ArCH<sub>3</sub>), 1.92 (s, 3 H, <sup>Im</sup>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.0 (NCN), 139.2 (<sup>Ar</sup>C), 139.0 (<sup>Ar</sup>C), 137.0 (<sup>Ar</sup>C), 136.4 (<sup>Ar</sup>C), 136.0 (<sup>Ar</sup>C), 134.7 (<sup>Ar</sup>C), 132.6 (<sup>Im</sup>C), 129.4 (<sup>Ar</sup>C), 129.3 (<sup>Ar</sup>C), 121.6 (<sup>Im</sup>C), 92.1 (*C*<sub>5</sub>H<sub>5</sub>), 21.5 (*p*-ArCH<sub>3</sub>), 21.4 (*p*-ArCH<sub>3</sub>), 18.6 (*o*-ArCH<sub>3</sub>), 18.5 (*o*-ArCH<sub>3</sub>), 10.1 (<sup>Im</sup>CH<sub>3</sub>) ppm. EI MS: *m*/*z* (<sup>58</sup>Ni, <sup>35</sup>Cl, %) = 476 (10) [M]<sup>+</sup>, 411 (1) [M - Cp]<sup>+</sup>, 317 (100) [IMes<sup>M</sup> - H]<sup>+</sup>. C<sub>27</sub>H<sub>31</sub>ClN<sub>2</sub>Ni·0.5 H<sub>2</sub>O (486.7): calcd. C 66.63, H 6.63, N 5.76; found C 66.68, H 6.53, N 5.73.

**[Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(Cl)(Bn<sub>2</sub>-bimy)] (1d):** This complex was obtained from nickelocene (170.0 mg, 0.901 mmol) and Bn<sub>2</sub>-bimy·HCl (300 mg, 0.897 mmol) in THF at reflux (8.5 mL) with use of a reaction time of 12 h, yield 41%, red solid (167.1 mg, 0.365 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.37 (m, 6 H, C<sub>6</sub>H<sub>5</sub>), 7.27 (m, 4 H, C<sub>6</sub>H<sub>5</sub>), 7.10 (m, 4 H, <sup>bimy</sup>C), 6.92 (d, *J* = 16.2 Hz, 2 H, PhCH<sub>2</sub>), 6.22 (d, *J* = 16.2 Hz, 2 H, PhCH<sub>2</sub>), 6.22 (d, *J* = 16.2 Hz, 2 H, PhCH<sub>2</sub>), 5.10 (s, 5 H, C<sub>5</sub>H<sub>5</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 179.9 (NCN), 136.0 (<sup>bimy</sup>C), 135.4 (C<sub>6</sub>H<sub>5</sub>), 129.0 (C<sub>6</sub>H<sub>5</sub>), 127.9 (C<sub>6</sub>H<sub>5</sub>), 126.6 (C<sub>6</sub>H<sub>5</sub>), 122.9 (<sup>bimy</sup>CH), 110.7 (<sup>bimy</sup>CH), 92.3 (C<sub>5</sub>H<sub>5</sub>), 53.6 (PhCH<sub>2</sub>) ppm. EI MS: *mlz* (<sup>58</sup>Ni, <sup>35</sup>Cl, %) = 456 (7) [M]<sup>+</sup>, 91 (100) [PhCH<sub>2</sub>]<sup>+</sup>. C<sub>26</sub>H<sub>23</sub>ClN<sub>2</sub>Ni·0.5H<sub>2</sub>O: calcd. C 66.92, H 5.18, N 6.00; found C 67.08, H 5.25, N 5.95.

**[Ni(\eta^5-C<sub>5</sub>H<sub>5</sub>)(<b>Br**)(**Bn**<sub>2</sub>-**bimy**)] (1e): This complex was obtained from nickelocene (500.0 mg, 2.645 mmol) and Bn<sub>2</sub>-bimy·HBr (940 mg, 2.478 mmol) in THF at reflux (25 mL) with use of a reaction time of 10 h, yield 29%, red solid (360 mg, 0.717 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38–7.33 (m, 6 H, C<sub>6</sub>H<sub>5</sub>), 7.25–7.23 (m, 4 H, C<sub>6</sub>H<sub>5</sub>), 7.08 (s, 4 H, <sup>bimy</sup>C), 6.89 (d, *J* = 16 Hz, 2 H, PhCH<sub>2</sub>), 6.14 (d, *J* = 16 Hz, 2 H, PhCH<sub>2</sub>), 5.15 (s, 5 H, C<sub>5</sub>H<sub>5</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 181.5 (NCN), 136.0 (<sup>bimy</sup>C), 135.5 (*C*<sub>6</sub>H<sub>5</sub>), 129.0 (*C*<sub>6</sub>H<sub>5</sub>), 127.9 (*C*<sub>6</sub>H<sub>5</sub>), 126.5 (*C*<sub>6</sub>H<sub>5</sub>), 122.8 (<sup>bimy</sup>CH), 110.7 (<sup>bimy</sup>CH), 92.32 (*C*<sub>5</sub>H<sub>5</sub>), 53.80 (PhCH<sub>2</sub>) ppm. EI MS: *m/z* (<sup>58</sup>Ni, <sup>79</sup>Br, %) = 500 (4) [M]<sup>+</sup>, 435 (1) [M – Cp]<sup>+</sup>, 91 (100) [PhCH<sub>2</sub>]<sup>+</sup>. C<sub>26</sub>H<sub>23</sub>BrN<sub>2</sub>Ni·0.5 C<sub>7</sub>H<sub>8</sub> (548.2): calcd. C 64.64, H 4.96, N 5.11; found C 64.21, H 5.00, N 5.61.

[Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(Br)(<sup>1,2,4</sup>TBn)] (1f): This complex was obtained from nickelocene (220.0 mg, 1.16 mmol) and <sup>1,2,4</sup>TBn·HBr (410.0 mg, 1.24 mmol) in THF at reflux (12.0 mL) with use of a reaction time of 12 h, yield 87%, red solid (460.0 mg, 1.01 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.85 (s, 1 H, <sup>Triaz</sup>CH), 7.41–7.32 (m, 10 H, C<sub>6</sub>H<sub>5</sub>), 6.15–6.04 (b, 4 H, PhCH<sub>2</sub>), 5.15 (s, 5 H, C<sub>5</sub>H<sub>5</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.8 (NCN), 143.58 (<sup>Triaz</sup>CH), 135.65 (C<sub>6</sub>H<sub>5</sub>), 134.82 (C<sub>6</sub>H<sub>5</sub>), 129.44 (C<sub>6</sub>H<sub>5</sub>), 128.97



 $(C_6H_5)$ , 128.40  $(C_6H_5)$ , 128.21  $(C_6H_5)$ , 128.10  $(C_6H_5)$ , 92.46  $(C_5H_5)$ , 57.13  $(PhCH_2)$ , 53.60  $(PhCH_2)$  ppm. EI MS: m/z (<sup>58</sup>Ni, <sup>79</sup>Br, %) = 451 (14) [M]<sup>+</sup>, 386 (5) [M - Cp]<sup>+</sup>, 307 (25) [M - Cp Br]<sup>+</sup>, 202 (6) [M - NHC]<sup>+</sup>, 91 (100) [PhCH<sub>2</sub>]<sup>+</sup>. C<sub>21</sub>H<sub>20</sub>BrN<sub>3</sub>Ni (453.02): calcd. C 55.68, H 4.45, N 9.28; found C 55.76, H 4.64, N 8.93.

 $[Ni(\eta^5-C_5H_5)(Cl)(IMes^{OPiv})]$  (1g): This complex was obtained from nickelocene (347.0 mg, 1.839 mmol) and IMes<sup>OPiv</sup>·HCl (793.2 mg, 1.801 mmol) in THF (17.0 mL) with use of a reaction time of 2 h at ambient temperature, yield 84%, red solid (852. 9 mg, 1.514 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.11 (s, 2 H, m-ArH), 7.08 (s, 2 H, m-ArH), 6.99 (s, 1 H, ImCH), 4.56 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.43 (s, 3 H, p-ArCH<sub>3</sub>), 2.41 (s, 3 H, p-ArCH<sub>3</sub>), 2.23 (s, 6 H, o-ArCH<sub>3</sub>), 2.15 (s, 6 H, o-ArCH<sub>3</sub>), 1.02 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 173.2 (CO<sub>2</sub>), 163.0 (NCN), 139.9 (<sup>Im</sup>CH), 139.5 (<sup>Ar</sup>C), 139.3 (<sup>Ar</sup>C), 137.0 (<sup>Ar</sup>C), 136.7 (<sup>Ar</sup>C), 136.2 (<sup>Ar</sup>C), 132.5 (<sup>Ar</sup>C), 129.3 (<sup>Ar</sup>C), 129.2 (<sup>Ar</sup>C), 111.3 (<sup>Im</sup>C–O), 92.3 (C5H5), 39.2 [C(CH3)3], 26.6 [C(CH3)3], 21.5 (p-ArCH3), 21.4 (p-ArCH<sub>3</sub>), 18.6 (o-ArCH<sub>3</sub>), 18.5 (o-ArCH<sub>3</sub>) ppm. EI MS: m/z (<sup>58</sup>Ni, <sup>35</sup>Cl, %) = 562 (81) [M]<sup>+</sup>, 497 (7) [M - Cp]<sup>+</sup>, 469 (100) [M -NiCl]<sup>+</sup>. C<sub>31</sub>H<sub>37</sub>ClN<sub>2</sub>NiO<sub>2</sub> (563.81): calcd. C 66.04, H 6.61, N 4.97; found C 66.09, H 6.54, N 4.98.

 $[Ni(\eta^{5}-C_{5}H_{5})(Cl)(IMes^{O})]$  (1h): Complex  $[Ni(\eta^{5}-C_{5}H_{5})(Cl)-$ (IMes<sup>OPiv</sup>)] (1g, 215.5 mg, 0.383 mmol) was dissolved in methanol (9.5 mL) and the resulting solution was placed in an acetone/dry ice cooling bath. Aqueous ammonia solution was added (1.1 mL, 14.72 mmol NH<sub>3</sub>), which was followed by an immediate change of colour from red to orange-yellow. After 5 min the cooling bath was removed and stirring was continued at room temperature for 10 min. Solvents were evaporated in vacuo and the remaining crude product was dissolved in toluene and filtered through Celite. The filtrate was concentrated in vacuo and applied to silica gel on a chromatography column. Complex 1h was eluted with diethyl ether/ hexane [gradient from 1:4 to 1:1 (v/v)], yield 63%, red solid (115.0 mg, 0.240 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.11 (s, 2 H, m-ArH), 7.10 (s, 2 H, m-ArH), 4.63 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.31 (s, 2 H, CH<sub>2</sub>), 2.40 (s, 6 H, p-ArCH<sub>3</sub>), 2.35 (s, 6 H, o-ArCH<sub>3</sub>), 2.30 (s, 6 H, *o*-ArCH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 220.1 (NCN), 170.7 (C=O), 139.9 (ArC), 136.5 (ArC), 135.7 (ArC), 131.5 (ArC), 130.0 (ArC), 129.7 (ArC), 129.2 (ArC), 128.3 (ArC), 93.8  $(C_5H_5)$ , 54.5  $(CH_2)$ , 21.5  $(p-ArCH_3)$ , 21.4  $(p-ArCH_3)$ , 18.9  $(o-ArCH_3)$ , 18.9 ArCH<sub>3</sub>), 18.6 (*o*-ArCH<sub>3</sub>) ppm. EI MS: m/z (<sup>58</sup>Ni, <sup>35</sup>Cl, %) = 478 (64)  $[M]^+$ , 159 (100)  $[CpNiCl + H]^+$ .  $C_{26}H_{29}ClN_2NiO$  (479.69): calcd. C 65.10, H 6.09, N 5.84; found C 65.21, H 6.12, N 5.81.

X-ray Diffraction Studies: Single crystals of 1d suitable for X-ray measurements were obtained from hexanes/toluene at 4 °C. Single crystals of 1g were obtained from toluene/hexanes at 4 °C. Single crystals of 1h were grown from toluene/n-heptane at -20 °C. Diffraction data were collected with an Agilent κ-CCD Gemini A Ultra diffractometer and use of graphite-monochromated Mo- $K_{\alpha}$  radiation at 100 K for compounds 1d and 1h and at 120(1) K for 1g. Cell refinement and data collection, as well as data reduction and analysis, were performed with the CrysAlis<sup>PRO</sup> software.<sup>[35]</sup> The structures were solved by direct methods and subsequent Fourierdifference synthesis with ShelXS and refined by full-matrix leastsquares against  $F^2$  with ShelXL within the Olex2 program suite.<sup>[36,37]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions and refined as riding atoms with isotropic displacement parameters related to that of the parent atoms. Data analysis was carried out by use of Olex2 and Mercury.<sup>[38,39]</sup> Crystal data and structure refinement parameters are given in Table S1 in the Supporting Information.

CCDC-1039261 (for 1d), -1039262 (for 1g) and -1039263 (for 1h) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

#### Catalysis

General Procedure for Styrene Polymerization: Reactions were run in duplicate as described previously.<sup>[6e]</sup> In a typical experiment, a solution of MAO in toluene (1.80 mL, 2.70 mmol) was added to a solution of complex **1a** (4.2 mg, 0.0090 mmol) in toluene (0.45 mL) and the resulting solution was stirred at room temp. for 30 min. Styrene (neat, 15.5 mL, 0.135 mol) was added, and the reaction mixture was placed in an oil bath maintained at 50 °C with vigorous stirring for 3 h. After cooling to room temp. the reaction mixture was poured into methanol (ca. 200 mL). The precipitated polymer was filtered off, washed with methanol and dried under high vacuum, yield 11.9 g (85%).

General Procedure for Methyl Methacrylate Polymerization: A solution of MAO in toluene (10wt.-%, Aldrich, 0.80 mL) was added to a solution of  $[Ni(\eta^5-C_5H_5)(Cl)(IMes^{2Me})]$  (1b, 6.4 mg, 13.0 µmol, Al/Ni 100) in toluene (10.0 mL). The colour of the reaction mixture changed immediately from red to dark brown and white fumes appeared. After the system had been stirred for 30 min at room temperature, methyl methacrylate was added (neat, 1.40 mL, 13.0 mmol). The resulting mixture was stirred vigorously for 20 h at room temperature. Next, methanol (ca. 200 mL) was added to the reaction mixture. The resulting precipitate was isolated by filtration, washed with methanol and dried in vacuo. This crude product was redissolved in CH2Cl2 (40 mL) and stirred overnight with hydrochloric acid (10%, ca. 40 mL). After phase separation, the organic solution was concentrated in vacuo and poured into methanol (ca. 200 mL). The resulting white precipitate was isolated by filtration, washed with methanol and dried in vacuo, yield 0.59 g, 44%.

**General Procedure for Suzuki Cross-Coupling:** These reactions were carried out similarly to those described previously.<sup>[14]</sup> 4'-Bromo-acetophenone (55.1 mg, 0.277 mmol) and phenylboronic acid (44 mg, 0.361 mmol) were dissolved in toluene (0.80 mL). K<sub>3</sub>PO<sub>4</sub> (153 mg, 0.722 mmol) and tetradecane (internal standard, 7.0  $\mu$ L) were then added, followed by complex **1h** (4.0 mg, 8.4  $\mu$ mol). The reaction was maintained at 90 °C for 1 h with stirring. The reaction was quenched with cold water, and the reaction mixture was then diluted with diethyl ether, washed with water and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The substrate conversion and selectivity were determined by GC.

**Computational Details:** The TEP parameters for ligands were obtained by scaling the  $v_{CO}(A_1)$  calculated for [Ni(NHC)(CO)<sub>3</sub>] complexes.<sup>[3d]</sup> Geometry optimizations and frequency calculations for [Ni(NHC)(CO)<sub>3</sub>] were carried out by use of the mPW1PW91<sup>[40]</sup> functional in the Gaussian suite of programs<sup>[41]</sup> with the 6–311+G(2d) basis set for nickel and 6–311+G(d,p) for all other atoms.<sup>[42]</sup> All optimized geometries were verified to have real harmonic frequencies.

## Acknowledgments

The authors thank the National Science Centre, Poland for financial support of this work (grant number DEC-2011/01/B/ST5/ 06297). Financial support was also provided by Warsaw University of Technology (P. A. G. and J. Z.). The authors thank Dr. M. Koszytkowska-Stawińska for helpful discussion on the synthesis and de-





protection of the pivaloyl esters, and Dr. I. Wielgus for DLS measurements and data interpretation. Calculations were carried out at the Interdisciplinary Centre for Mathematical and Computational Modelling (grant number G59-0).

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Received: October 5, 2015 Published Online: November 9, 2015