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Synthesis, Structure, and Polymerization Activity of Cyclopentadienylnickel(II) N-Heterocyclic Carbene Complexes: Selective Cross-Metathesis in Metal Coordination Spheres

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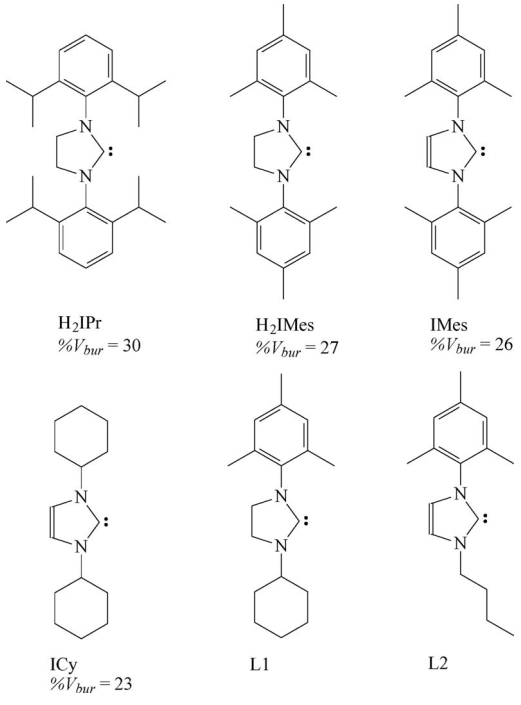
The N-heterocyclic carbene (NHC) complexes [(RC_5H_4)Ni(X)(NHC)] (**2**–**5**) have been prepared by treating nickelocene [or 1,1′-bis(alkenyl)nickelocene] with a suitable carbene precursor. The alkenylcyclopentadienido complexes **4** and **5** undergo chemoselective cross-metathesis with methyl acrylate or methyl vinyl ketone in the presence of the seocnd-generation Grubbs catalyst to yield complexes **6**–**8**, which bear an α,β-unsaturated carbonyl substituent on the cyclopentadienido ligand. The X-ray crystal structure of **2** [monoclinic, $P2_1/n$, Ni–$C_{carbene}$ 1.879(3) Å] and **7** [triclinic, $P\bar{1}$, Ni–$C_{carbene}$ 1.8874(6) Å] reveal undistorted trigonal-planar Ni coordination. VT-NMR studies of complexes **2** and **3**, which possess an *N*-alkyl substituent, show hindered rotation of the carbene ligand. Complexes [(RC_5H_4)Ni(X)(NHC)], in the presence of an excess of MAO, display high activity in the polymerization of styrene and moderate activity in the oligomerization of phenylacetylene.

Introduction

The complex [CpNi(Cl)(IMes)] (**1**; IMes = 1,3-dimesitylimidazol-2-ylidene; see Scheme 1) was synthesized for the first time by Abernethy et al. from nickelocene and 1,3-dimesitylimidazolium chloride.[1] A number of complexes of the general formula [(RC_5H_4)Ni(X)(NHC)] (X = Cl, Br, I; NHC = N-heterocyclic carbene) have since been prepared by us[2] and others[3] in a similar fashion since this seminal publication. Complexes of this type display catalytic activity in aryl dehalogenation and aryl amination,[3a] styrene polymerization in the presence of MAO,[2] and hydrothiolation of alkynes.[4] The related indenyl complexes [$(\eta^3$-$C_9H_7)$Ni(X)(NHC)] are moderately active in the oligomerization of ethylene[5] and styrene polymerization[6] in the presence of MAO or $NaBPh_4$, respectively. Other NHC-supported Ni^{II} complexes have also been tested for olefin polymerization[7] and carbon–carbon coupling reactions.[8]

Compound **1** and its saturated counterpart [CpNi(Cl)(H_2IMes)] (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) display the highest activity in styrene polymerization. The polystyrenes obtained are atactic, and a cationic mechanism has been proposed to explain the observed reactivity.[2] We reasoned that judicious modification of the ligands may lead to the discovery of more efficient and stereospecific polymerization catalysts, and re-



Scheme 1. NHC ligands discussed in this manuscript. The values of the steric parameter $\%V_{bur}$ are taken from ref.[9a]

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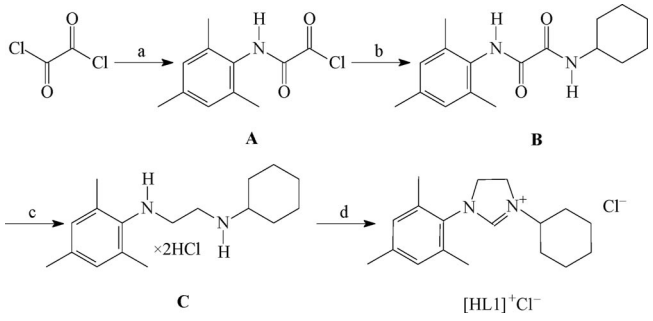
port herein the synthesis of novel complexes of this type bearing two different substituents in the carbene ligand (Scheme 4). Moreover, α,β-unsaturated carbonyl moieties have been attached to the cyclopentadienido ligand by means of selective cross-metathesis (Scheme 5). The activity of these new complexes in the polymerization of styrene or phenylacetylene is explored under optimized conditions.

Results and Discussion

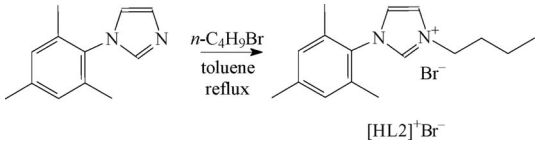
Ligand Synthesis

The electronic and steric ($\%V_{bur}$) properties of NHC ligands (see Scheme 1) have been studied in detail,[9] and it is now widely accepted that the differences in the electronic parameters of known NHC ligands are relatively small. Significant differences in the chemical behavior of NHC complexes are therefore more likely to arise from steric factors. Accordingly, carbene precursors bearing two different substituents on the N atoms have been considered in an attempt to enhance the polymerization activity, in particular to observe a possible tacticity in the resulting polystyrene. We have previously established that increased steric bulk (2,6-diisopropylphenyl vs. 2,4,6-trimethylphenyl) of the NHC ligand results in a decrease of the polymerization yield,[2] therefore a cyclohexyl group was chosen to replace one 2,4,6-trimethylphenyl group. The saturated carbene precursor [HL1]Cl was synthesized analogously to the method developed by Mol and co-workers[10] for an adamantyl-substituted ligand (Scheme 2).



Scheme 2. Synthesis of ligand precursor [HL1]Cl. Reagents and conditions: (a) $MesNH_2$, CH_2Cl_2, 0 °C to room temp. 12 h (ref.[10]); (b) $CyNH_2$, Et_3N, CH_2Cl_2, 0 °C to room temp. 2 h; (c) (i) $BH_3{\cdot}SMe_2$, toluene, reflux, 3 h, (ii) aq. HCl; (d) $HC(OEt)_3$, HCOOH, 130 °C, 3 h.

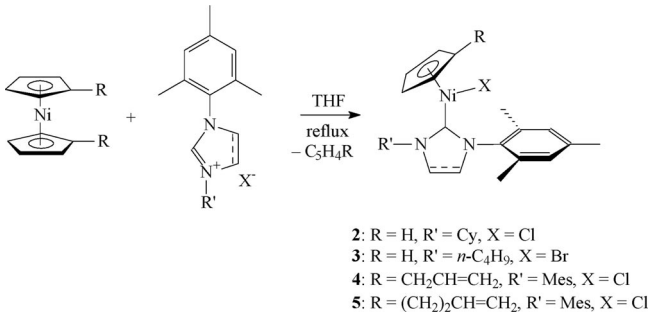
We also prepared the unsaturated carbene precursor [HL2]Br, which contains a primary alkyl group, in one step from *N*-mesitylimidazole and 1-bromobutane (Scheme 3)[11].



Scheme 3. Synthesis of ligand precursor [HL2]Br.

Complex Synthesis

Complexes **2**–**5** were synthesized by treating nickelocene or 1,1′-disubstituted nickelocene with an appropriate imidazolium or dihydroimidazolium halide in refluxing thf (Scheme 4). A prolonged reaction time (11–13 h) was needed to complete the reaction for compounds containing a substituted cyclopentadienido ligand (**4**, **5**), as well as for the bromide **3**. Complexes **2**–**5** were isolated as red solids in good to moderate yields (52–33%).



Scheme 4. Synthesis of complexes **2**–**5** (Mes = 2,4,6-trimethylphenyl).

Whilst NMR characterization of **4** and **5** was straightforward, the room-temperature ^1H NMR spectra of **2** and **3** feature a number of broad signals. For example, the aromatic singlet at δ = 7.07 ppm for complex **3** (Figure 1) is somewhat broad, and the multiplets assigned to the methylene groups of the *n*-butyl substituent are not resolved. Interestingly, only one singlet of the mesitylene methyl groups is observed, and no signal could be assigned to the NCH_2 group (Figure 1b). The NCH_2 signal appears at 50 °C as a broad singlet centered at δ = 5.02 ppm (Figure 1a).

The low-temperature spectra of **3** (–50 °C, Figure 1c) reveal all expected signals, especially three singlets for the mesitylene methyl groups at δ = 1.71, 2.41, and 2.47 ppm. The three methylene groups of the *n*-butyl moiety appear as pairs of non-equivalent multiplets, thus indicating that these protons are diastereotopic. Noticeably, the NCH_2 signals are 1.15 ppm apart (δ = 4.39 and 5.54 ppm). This large difference in the values of the chemical shift suggests that one of the protons interacts with the bromide. Moreover, the ^{13}C NMR spectrum of **3** at –50 °C features six aromatic carbon resonances and three signals for the mesitylene methyl groups. We can therefore conclude that at low temperature complex **3** exists as a single rotamer with hindered rotation around the Ni–$C_{carbene}$ and N–C_{Ar} bonds.

A similar behavior was observed for complex **2**, with all aromatic and cyclohexyl signals being non-equivalent at low temperature (see Supporting Information). It is also interesting to note the low-field signal (δ = 6.07 ppm) for the proton bonded to C1 of the cyclohexyl ring. This phenomenon could be explained by an interaction of this hydrogen atom with the halogen atom. Indeed, the solid-state structure of **2** (see below) provides support for the presence of an interaction between this proton and the chloride

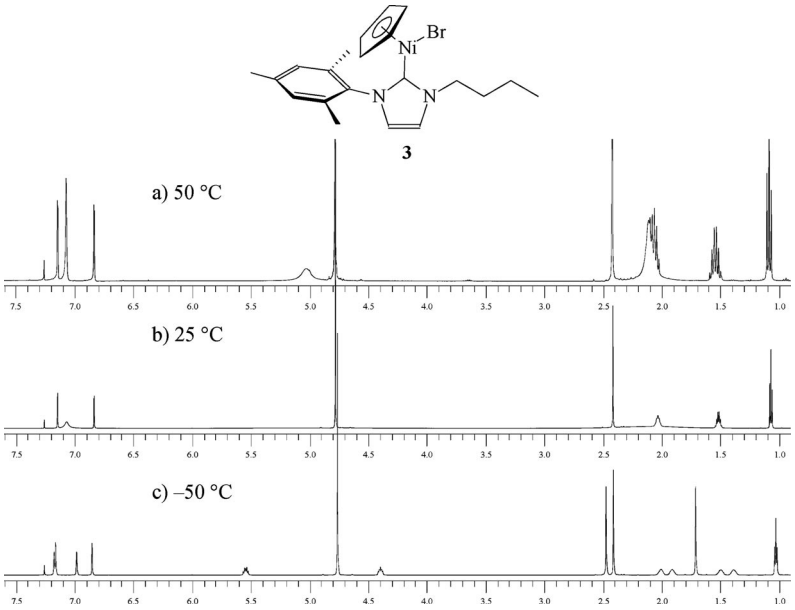


Figure 1. VT ^{1}H NMR spectra of complex **3** in $CDCl_3$: (a) 400 MHz; (b) and (c) 700 MHz.

[H···Cl 2.84(4), C···Cl 3.566(4) Å]. In this context, we note that an extensive search of crystallographic data showed that transition metal–Cl moieties are good hydrogen-bond acceptors.[12] Moreover, published data indicate that L1 is smaller than IMes [$\%V_{bur}$ = 23 for 1,3-dicyclohexylimidazol-2-ylidene (ICy) and 26 for IMes; see Scheme 1].[9] Taking into account that IMes rotates freely in complex **1**, the hindered rotation of carbene L1 in complex **2** cannot be explained on the grounds of steric hindrance. Thus, we attribute the restricted rotation in **2** to the presence of an N–CH···Cl–Ni interaction. Likewise, we assume that electronic effects are also a plausible explanation for the observed behavior of **3** in solution. Some examples of NHC complexes bearing an alkyl substituent with a restricted metal–carbene bond rotation have already been reported,[3b,13] although no comprehensive explanation of this phenomenon was given.[3b]

The solid-state structure of **2** was unambiguously confirmed by single-crystal X-ray diffraction (Figure 2). Complex **2** crystallizes in the monoclinic crystal system (space group $P2_1/n$). The nickel coordination is trigonal-planar (considering the Cp centroid), with Ni–$C_{carbene}$ 1.879(3), Ni–Cl 2.1934(11), and Ni–Cp(c) 1.768(6) Å. The presence of ligand L1 does not produce a significant distortion in the Ni coordination sphere when compared with related complexes.[1–3]

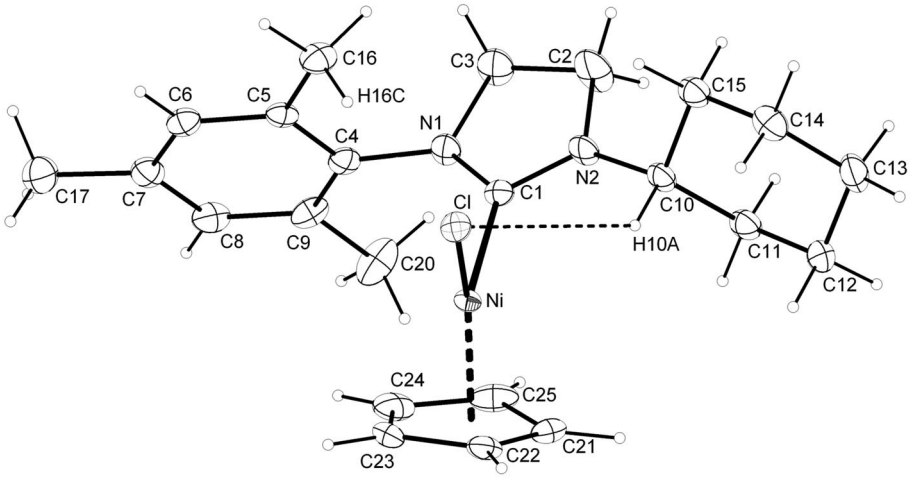


Figure 2. Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni–C(1) 1.879(3), Ni–Cl 2.1934(11), Ni–Cp(c) 1.768(6), N(1)–C(1) 1.346(4), C(1)–N(2) 1.325(3), C(2)–C(3) 1.522(5); Cp(c)–Ni–Cl 131.6(1), C(1)–Ni–Cp(c) 131.0(2), C(1)–Ni–Cl 97.14(8); H(10A)···Cl 2.84(4), C(10)–Cl 3.566(4).

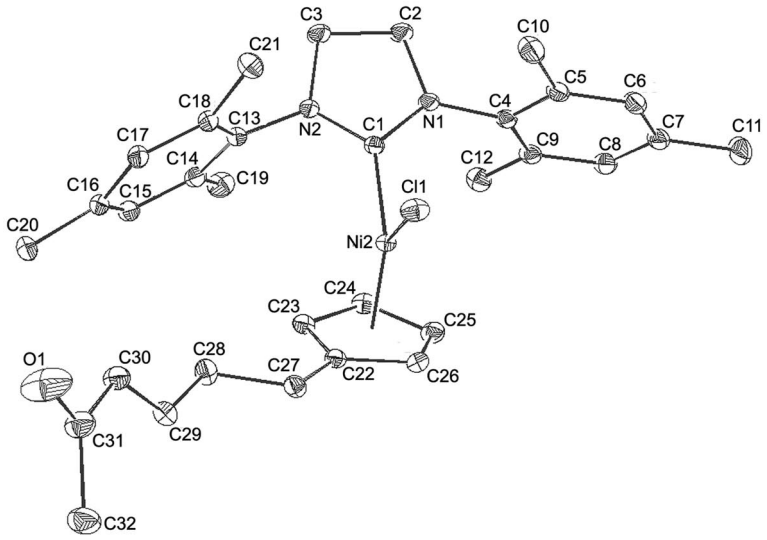
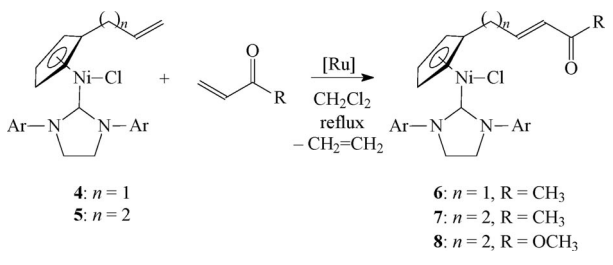


Figure 3. Molecular structure of complex **7**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni(2)–C(1) 1.8874(6), Ni(2)–Cl(1) 2.1941(2), Ni(2)–Cp(c) 1.778(1), C(3)–C(2) 1.5273(11), N(2)–C(1) 1.3419(9), N(1)–C(1) 1.3391(8); Cp(c)–Ni–Cl 126.32(3), C(1)–Ni(2)–Cl(1) 98.67(2), C1–Ni(2)-Cp(c) 134.65(3). Hydrogen atoms have been omitted for clarity.

Selective Cross-Metathesis in Metal Coordination Spheres

A pronounced influence of the cyclopentadienido ligand on the reaction outcome could be expected if the styrene polymerization proceeds by a coordination/insertion mechanism. Thus, we sought to synthesize complexes $[(RC_5H_4)Ni(X)(NHC)]$ with a cyclopentadienido ligand bearing a functional group. Because such complexes are obtained from nickelocene (Scheme 4), their synthesis is restricted by the availability of substituted nickelocenes. In particular, polar functional groups (e.g. carbonyl) are not compatible with the lithium or sodium cyclopentadienide derivatives used in the metallocene synthesis.[14] Unlike ferrocene, nickelocene is not stable to lithiation,[15] and functionalization of the cyclopentadienido ligand in nickelocene has not been reported.[16] On the other hand, olefin metathesis has been used successfully to synthesize a number of organometallic compounds, most often as a ring-closing reaction between two ligands at a coordination centre.[17] Several examples of a cross-metathesis between two transition metal complexes,[18] or between a complex and an organic molecule,[18b,18c,19] have also been reported. Therefore, we decided to apply selective cross-metathesis[20] to attach a carbonyl group to complexes **4** and **5** (Scheme 5).



Scheme 5. Selective cross-metathesis for complexes **4** and **5** (Ar = 2,4,6-trimethylphenyl).

Complexes **6**–**8** were obtained in high yields (78–51%) by refluxing complex **4** or **5** with an α,β-unsaturated carbonyl compound (methyl acrylate, methyl vinyl ketone) in CH_2Cl_2 in the presence of $[RuCl_2(=CHPh)(PCy_3)(H_2IMes)]$.[21] The ^1H NMR spectra of the crude reaction mixtures showed that a single organometallic product had formed. Large coupling constants for the olefinic protons ($^3J_{H,H}$ = 15–16 Hz) indicated an (*E*) configuration for the double bonds. The structure of complex **7** was confirmed by X-ray crystallographic analysis (Figure 3).

Complex **7** crystallizes in the $P\bar{1}$ space group of the triclinic crystal system. The nickel coordination is trigonal-planar (considering the Cp centroid), with an Ni–$C_{carbene}$ bond length of 1.8874(6) Å. Whereas the two methylene bridging groups are coplanar with the cyclopentadienido ring, the plane of the α,β-unsaturated carbonyl system is nearly perpendicular to the cyclopentadienido ring plane.

Polymerization

The activity of complexes **1**–**8** in styrene polymerization was investigated under conditions similar to those in our previous report.[2]

The most active complex polymerized up to 15000 equiv. of styrene at 50 °C in 3 h (Table 1, Entry 1). Substitution of one mesitylene group in **1** for an alkyl group (cyclohexyl or *n*-butyl) resulted in a significantly lower activity (Table 1, Entries 2 and 3). Similarly, the allylcyclopentadienido and butenylcyclopentadienido complexes **4** and **5** were less efficient than **1**. The presence of a carbonyl group had a beneficial effect on the activity (Table 1, Entries 6–8). However, addition of MAO in these runs resulted in precipitation of a dark solid that remained insoluble during the entire reaction, in other words these polymerizations appeared to proceed under heterogeneous conditions. GPC analysis of the

Table 1. Styrene polymerization with complexes **1**–**8** in the presence of an excess of MAO.[a]

Entry	Complex	Yield [%]	M_n	M_w/M_n
1	[CpNi(Cl)(IMes)] (**1**)	98	11100	1.8
2	[CpNi(Cl)(L1)] (**2**)	49	12550	1.8
3	[CpNi(Br)(L2)] (**3**)	52	12100	1.9
4	[($C_5H_4CH_2CH=CH_2$)Ni(Cl)(H_2IMes)] (**4**)	72	13000	1.8
5	[{$C_5H_4(CH_2)_2CH=CH_2$}Ni(Cl)(H_2IMes)] (**5**)	42	13200	1.8
6	[{$C_5H_4CH_2CH=CHC(O)CH_3$}Ni(Cl)(H_2IMes)] (**6**)	90	13400	1.9
7	[{$C_5H_4(CH_2)_2CH=CHC(O)CH_3$}Ni(Cl)($H_2$IMes)] (**7**)	94	12300	1.9
8	[{$C_5H_4(CH_2)_2CH=CHC(O)OCH_3$}Ni(Cl)($H_2$IMes)] (**8**)	92	13300	1.9

[a] All runs in duplicate. Conditions: styrene/Ni = 15000:1, Al/Ni = 300:1, [Ni] = 4.0 mM in toluene, 50 °C, 3 h; L1 = 1-cyclohexyl-3-mesityl-4,5-dihydroimidazol-2-ylidene; L2 = 1-(*n*-butyl)-3-mesitylimidazol-2-ylidene; IMes = 1,3-dimesitylimidazol-2-ylidene; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (see Scheme 1).

resulting polystyrenes showed similar results (M_n = 11100–13400 Da, DP = 110–130, M_w/M_n = 1.8–1.9) for all the complexes studied. The ^{13}C NMR spectra indicated that the obtained polymers were isotactic-rich atactic.[22] The MALDI-TOF mass spectra of the polymer produced with complex **2** featured peaks corresponding to the molecular formula $[(C_8H_8)_nAg]^+$ (e.g. for n = 16 peak centered at m/z = 1774). Accordingly, we conclude that the methyl groups from MAO were not incorporated into the polymer chains.

The results presented in Table 1 show that the structure of the Ni complex significantly affects the polymerization yield, although it has very little or no effect on the structure of the polystyrene produced. These observations are in agreement with a cationic mechanism for styrene polymerization,[2,23] although a coordination/insertion mechanism involving an Ni–H species cannot be ruled out.[22,24]

Selected complexes were also tested in the polymerization of phenylacetylene in the presence of an excess of MAO (Table 2). Moderate activities (TONs up to 600) were obtained under conditions similar to those for styrene. The presence of an alkyl substituent in the NHC moiety (Table 2, Entry 3) resulted in a significantly lower activity than for the bis(aryl) counterparts. Phenylacetylene oligomers (M_n = 1200–1600 Da) were obtained in most runs with the exception of [CpNi(Cl)(H_2IPr)] (Table 2, Entry 4), where a bimodal distribution was detected with a high molecular weight fraction (M_n = 13600 Da). Accordingly, we conclude that the increased steric bulk in the NHC ligand (H_2IPr vs. H_2IMes) affects the course of the polymerization.

Table 2. Phenylacetylene polymerization with selected complexes in the presence of an excess of MAO.[a]

Entry	Complex	Yield [%]	M_n	M_w/M_n
1	[CpNi(Cl)(IMes)] (**1**)	60	1200	1.2
2	[CpNi(Cl)(H_2IMes)]	56	1600	1.1
3	[CpNi(Br)(L2)] (**3**)	23	1400	1.1
4	[CpNi(Cl)(H_2IPr)]	50	1200[b]	1.2
			13600	1.4

[a] All runs in duplicate. Conditions: phenylacetylene/Ni = 1000:1, Al/Ni = 300:1, [Ni] = 2.7 mM in toluene, 75 °C, 5 h. IMes = 1,3-dimesitylimidazol-2-ylidene; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; L2 = 1-(*n*-butyl)-3-mesitylimidazol-2-ylidene; H_2IPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (see Scheme 1). [b] Bimodal distribution.

Conclusions

We have synthesized and fully characterized seven new [(RC_5H_4)Ni(X)(NHC)] complexes. Complexes **2** and **3**, which bear an alkyl substituent in the NHC ligand (L1 and L2, respectively), display restricted rotation of this ligand in solution due to the presence of an N–CH···Cl–N interaction rather than to steric hindrance. The studied complexes, in the presence of an excess of MAO, efficiently polymerize styrene with an activity up to 8700 g PS/g Ni h. The polymerization yield depends strongly on the composition of both the cyclopentadienido and NHC ligands, whereas the tacticity of the resulting polystyrenes is not affected by the structure of the nickel complexes.

Experimental Section

General: All manipulations involving organometallic complexes were performed by using standard Schlenk techniques under argon. All solvents were purified by appropriate methods.[25] A commercial solution of MAO in toluene (10 wt.-%) from Aldrich was used in all experiments. Styrene, phenylacetylene, methyl vinyl ketone, and methyl acrylate (Aldrich) were dried with CaH_2 and distilled under reduced pressure. Cyclohexylamine (Aldrich) and 1-bromobutane (POCh) were distilled under argon. Nickelocene,[14] 1,1′-bis(allyl)nickelocene and 1,1′-bis(but-3-enyl)nickelocene,[17i] previously described ligands,[26] NHC complexes,[1–3] and *N*-mesitylimidazole[27] were synthesized according to reported methods. All other reagents were purchased from commercial sources (Aldrich, POCh) and used as received. EI (70 eV) mass spectra were recorded with an AMD-604 spectrometer and ESI mass spectra with an ESI Mariner spectrometer. Unless otherwise noted, NMR spectra were recorded at ambient temperature with a Mercury 400BB spectrometer at 400 MHz for ^1H and at 101 MHz for ^{13}C with chemical shifts reported relative to the residual deuterated solvent. M_w and M_n of polymers were determined with a LabAlliance liquid chromatograph equipped with a Jorgi Gel DVB Mixed Bed column (250 mm × 10 m) with thf (polystyrenes) or $CHCl_3$ (polyphenylacetylenes) as the mobile phase. MALDI TOF mass spectra of the polymers were recorded with a Kratos Kompakt 4 V 5.2.1 instrument by using the DHB/THF (30 mg/mL) matrix (CF_3COOAg was added).

Ligand Synthesis.

***N*-Cyclohexyl-*N*′-(2,4,6-trimethylphenyl)oxalamide (B):** A solution of cyclohexylamine (4.0 mL, 36.7 mmol) and triethylamine

(5.0 mL, 35.8 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a CH_2Cl_2 (200 mL) solution of oxo(2,4,6-trimethylphenylamino)acetyl chloride[10] (**A**; 8.131 g, 36.3 mmol) at 0 °C and the resulting yellow mixture stirred at room temp. for an additional 1.5 h. Water (200 mL) was added, and the organic layer was separated and dried with $MgSO_4$. The solvent was removed under reduced pressure to afford a yellow residue, which was crystallized from CH_2Cl_2 (50 mL) and Et_2O (12 mL) to give the title compound as a white solid (6.63 g, 23.0 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.98 (m, 10 H, Cy), 2.19 (s, 6 H, *o*-CH_3), 2.28 (s, 3 H, *p*-CH_3), 3.78 (m, 1 H, 1-H of Cy), 6.91 (s, 2 H, Ar), 7.48 (d, J = 8.8 Hz, 1 H, NH-Cy), 8.77 (s, 1 H, NH-Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.33 (*o*-CH_3), 20.92 (*p*-CH_3), 24.75, 25.28, 32.63, 49.08 (Cy), 129.00, 129.75, 134.71, 137.46 (Ar), 158.44, 158.80 (C=O) ppm. ESI MS: m/z = 289 $[M + H]^+$, 311 $[M + Na]^+$, 599 $[2M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 1656 (C=O), 1505 (N–H), 1448 (CH_2), 1375 (CH_3), 1230 [C(O)–N], 844, 746, 710 (2,4,6-C–H) cm^{-1}. $C_{17}H_{24}N_2O_2$ (288.39): calcd. C 70.80, H 8.39, N 9.72; found C 70.77, H 8.36, N 9.78.

***N*-Cyclohexyl-*N*′-(2,4,6-trimethylphenyl)ethane-1,2-diamine Dihydrochloride (C):** $BH_3{\cdot}SMe_2$ (46.5 mL, 2.0 M solution in toluene, 93 mmol) was added to a solution of **B** (6.54 g, 22.68 mmol) in toluene (165 mL) and the resulting mixture heated at reflux for 4 h. After cooling to room temp., 1 M aq. HCl (ca. 200 mL) was added until the solution became acidic, then 10% aq. NaOH (ca. 150 mL) until it became basic. The mixture was transferred to a separating funnel and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic extracts were reduced to about 1/4 of the original volume. Acetone (40 mL) was added to the yellow solution followed by 12 M aq. HCl until a white solid appeared. This mixture was stirred at room temp. for 12 h. The resulting solid was collected by filtration, washed with diethyl ether, and dried in air to give the title compound as a white, crystalline solid (5.45 g, 20.97 mmol, 89%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.23–1.78 (m, 10 H, Cy), 2.07 (s, 6 H, *o*-CH_3), 2.21 (s, 3 H, *p*-CH_3), 3.06 (br. t, J = 10 Hz, 1 H, 1-H of Cy), 3.36 (br. s, 2 H, CH_2NHCy), 3.55 (br. s, 2 H, CH_2NHAr), 6.95 (s, 2 H, Ar), 9.62 (br. s, 2 H, both NH) ppm. ^{13}C NMR (101 MHz, [D$_6$]-DMSO): δ = 18.00 (*o*-CH_3), 20.26 (*p*-CH_3), 23.78, 24.72, 28.46, 30.71 (Cy), 45.66, 56.02 (NCH_2CH_2N), 130.27, 131.60, 137.26 (br., Ar) ppm. ESI MS: m/z = 261 $[M + H]^+$. IR (KBr): $\tilde{\nu}$ = 3304 (N–H), 2938 (Cy), 1021 (C–N) cm^{-1}. $C_{17}H_{28}N_2{\cdot}2HCl{\cdot}2H_2O$ (369.39): calcd. C 55.28, H 9.28, N 7.58; found C 56.67, H 8.81, N 7.77.

1-Cyclohexyl-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolinium Chloride ([HL1]Cl): A suspension of **C** (5.254 g, 20.21 mmol) in triethyl orthoformate (80 mL) with a few drops of formic acid was heated at reflux for 3 h. During this time the white solid dissolved, and the solution turned orange. After cooling to room temp., the volatiles were removed under reduced pressure. The brown residue was treated with CH_2Cl_2 (10 mL) and hexane (25 mL). Two phases separated; the upper layer was collected, and the solvents were evaporated to dryness to yield a yellow solid that was crystallized twice from thf to give the title compound as a white solid (0.385 g, 1.25 mmol, 6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14–1.86 (m, 10 H, Cy), 2.26 (s, 3 H, *p*-CH_3), 2.30 (s, 6 H, *o*-CH_3), 4.16 (m, J = 4.4 Hz, 2 H, NCH_2CH_2N), 4.19 (m, J = 4.2 Hz, 2 H, NCH_2CH_2N), 4.34 (m, 1 H, 1-H of Cy), 6.91 (s, 2 H, Ar), 9.77 (s, 1 H, NCHN) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.03 (*o*-CH_3), 20.97 (*p*-CH_3), 24.59, 24.80, 31.17, 45.82 (Cy), 50.43, 57.56 (NCH_2CH_2N), 129.95, 130.73, 135.19, 140.16 (Ar), 158.79 (NCN) ppm. ESI MS: m/z = 271 $[M - Cl]^+$. This compound was used in the next step without further purification.

(2,4,6-Trimethylphenyl)N(CHO)CH$_2$CH$_2$N(CHO)Cy was also isolated as a yellow solid (0.693 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32–1.90 (m, 10 H, Cy), 2.19 (s, 6 H, *o*-CH_3), 2.28 (s, 3 H, *p*-CH_3), 3.29 (m, 1 H, 1-H of Cy), 3.52 (m, J = 4.0 Hz, 2 H, NCH_2CH_2N), 3.60 (m, J = 4.0 Hz, 2 H, NCH_2CH_2N), 6.92 (s, 2 H, Ar), 8.00 (m, 1 H, CHO), 8.10 (m, 1 H, CHO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.39 (*o*-CH_3), 20.87 (*p*-CH_3), 24.96, 25.73, 32.42, 38.67 (Cy), 45.06, 58.53 (NCH_2CH_2N), 129.63, 135.98, 136.08, 138.30 (Ar), 162.58 (CHO), 164.03 (CHO) ppm. ESI MS: m/z = 339 $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 2931 (Cy), 2856 [C(O)–N], 1672 (C=O) cm^{-1}. $C_{19}H_{28}N_2O_2$ (316.45): calcd. C 72.12, H 8.92, N 8.85; found C 71.92, H 8.87, N 8.90.

1-Butyl-3-(2,4,6-trimethylphenyl)imidazolium Bromide ([HL2]Br): *N*-Mesitylimidazole[27] (1.984 g, 10. 6 mmol) and 1-bromobutane (1.15 mL, 10.7 mmol) were heated at reflux in toluene (30 mL) for 16 h. Et_2O (60 mL) was then added and the resulting suspension filtered to afford the title compound (1.169 g, 34%) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.92 (t, J = 7.2 Hz, 3 H, CH_3), 1.27 (sext, J = 8.0 Hz, 2 H, CH_2), 1.87 (quint, J = 7.2 Hz, 2 H, CH_2), 2.00 (s, 6 H, *o*-CH_3), 2.32 (s, 3 H, *p*-CH_3), 4.28 (t, J = 7.2 Hz, 2 H, N-CH_2), 7.14 (s, 2 H, Ar), 7.94 (t, J = 1.6 Hz, 1 H, imidazole), 8.11 (t, J = 1.6 Hz, 1 H, imidazole), 9.47 (d, J = 6.8 Hz, 1 H, NCHN) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 13.28 (CH_3), 16.87 (CH_2), 18.75 (*o*-CH_3), 20.59 (*p*-CH_3), 21.06 (CH_2), 49.02 (NCH_2), 123.17, 123.94, 129.25 (imidazole), 131.16, 134.28, 137.26, 140.24 (Ar) ppm. ESI MS: m/z = 243 $[M - Br]^+$. $C_{16}H_{23}BrN_2{\cdot}0.4H_2O$ (330.48): calcd. C 58.15, H 7.26, N 8.48; found C 58.42, H 6.66, N 8.52.

Synthesis of [(RC$_5$H$_4$)Ni(X)(NHC)] Complexes

[CpNi(Cl){1-cyclohexyl-3-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene}] (2): Nickelocene (0.229 g, 1.21 mmol) and [HL1]Cl (0.385 g, 1.26 mmol) were refluxed in thf (12 mL) for 2.5 h. The usual workup[1] provided 0.279 g (0.652 mmol, 52%) of complex **2** as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.61–1.80 (m, 10 H, Cy), 1.98 (br. s, 3 H, *o*-CH_3), 2.37 (s, 3 H, *p*-CH_3), 2.61 (br. s, 3 H, *o*-CH_3), 3.67 (s, 4 H, NCH_2CH_2N), 4.73 (s, 5 H, Cp), 6.07 (br., 1 H, 1-H of Cy), 6.94 and 7.11 (2 overlapping br. s, 2 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 17.61 (br., *o*-CH_3), 19.22 (br., *o*-CH_3), 21.09 (*p*-CH_3), 25.54 (Cy), 31.16 (br., Cy), 43.72 (NCH_2CH_2N), 50.09 (NCH_2CH_2N), 60.16 (Cy), 91.57 (Cp), 128.59 (b), 130.00 (b), 137.12, 138.05 (Ar), 196.00 (NCN) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, –60 °C): δ = 1.47–1.99 (m, 10 H, Cy), 1.84 (s, 3 H, *o*-CH_3), 2.37 (s, 3 H, *p*-CH_3), 2.60 (s, 3 H, *o*-CH_3), 3.70 (br. s, 4 H, NCH_2CH_2N), 4.72 (s, 5 H, Cp), 6.00 (br. s, 1 H, 1-H of Cy), 6.96 (s, 1 H, Ar), 7.12 (s, 1 H, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, –60 °C): δ = 17.50 (*o*-CH_3), 19.10 (*o*-CH_3), 21.16 (*p*-CH_3), 25.02, 25.20, 25.44, 30.69, 31.11 (Cy), 43.53, 49.75 (NCH_2CH_2N), 59.80 (Cy), 91.20 (Cp), 128.38, 129.69, 134.90, 136.63, 137.99, 138.60 (Ar), 194.10 (NCN) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ = 1.53–2.40 (m, 16 H, Cy and *o*-CH_3), 2.37 (s, 3 H, *p*-CH_3), 3.67 (s, 4 H, NCH_2CH_2N), 4.73 (s, 5 H, Cp), 6.11 (t, J = 3.2 Hz, 1 H, 1-H of Cy), 7.03 (br.s, 2 H, Ar) ppm. EI MS (70V): m/z (%) [^{58}Ni, ^{35}Cl] = 428 (64) $[M^+]$, 392 (83) $[M - HCl]^+$, 335 (70) $[C_{23}H_{31}N_2]^+$, 323 (55) $[NiC_{18}H_{21}N_2]^+$, 269 (88) $[L1 - H]^+$, 245 (43) $[NiC_{12}H_{15}N_2]^+$, 187 (100) $[C_{12}H_{15}N_2]^+$, 123 (8) $[NiCp]^+$, 65 (16) Cp. HR EI MS: calcd. for $C_{23}H_{31}N_2{}^{35}Cl{}^{58}Ni$ 428.15292; found 428.15384. Complex decomposes at 180 °C. $C_{23}H_{31}ClN_2Ni$ (429.66): calcd. C 64.29, H 7.27, N 6.52; found C 63.92, H 7.17, N 6.51. Crystals suitable for X-ray analyses were obtained by slow concentration of a hexane solution at room temp.

[CpNi(Br){1-butyl-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene}] (3): Nickelocene (0.51 g, 2.70 mmol) and [HL2]Br (0.90 g, 2.78 mmol)

were stirred at reflux in thf (25 mL) for 12 h and then at room temp. for 2 d. The usual workup[1] provided 0.53 g (1.19 mmol, 44%) of complex **3** as a red, microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.07 (t, J = 7.2 Hz, 3 H, CH_3), 1.51 (m, J = 7.6 Hz, 2 H, CH_2), 2.03 (br.m, 2 H, CH_2), 2.42 (s, 3 H, p-CH_3), 4.78 (s, 5 H, Cp), 6.84 (d, J = 1.6 Hz, 1 H, imidazole), 7.07 (br. s, 2 H, Ar), 7.15 (d, J = 2.0 Hz, 1 H, imidazole) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): δ = 1.08 (t, J = 7.4 Hz, 3 H, CH_3), 1.54 (sext, J = 7.6 Hz, 2 H, CH_2), 2.06 (m, overlapped with a br. s centered at δ = 2.1 ppm, 8 H, CH_2 and o-CH_3), 2.42 (s, 3 H, p-CH_3), 4.78 (s, 5 H, Cp), 5.02 (br., 2 H, N-CH_2), 6.83 (d, J = 1.6 Hz, 1 H, imidazole), 7.07 (br. s, 2 H, Ar), 7.14 (d, J = 2.0 Hz, 1 H, imidazole) ppm. ^{1}H NMR (700 MHz, $CDCl_3$, –50 °C): δ = 1.03 (t, J = 7.7 Hz, 3 H, CH_3), 1.39 and 1.48 (2 m, 2 H, CH_2), 1.71 (s, 3 H, o-CH_3), 1.91 and 2.01 (2 m, 2 H, CH_2), 2.41 (s, 3 H, p-CH_3), 2.47 (s, 3 H, o-CH_3), 4.39 (m, 1 H, NCH_2), 4.76 (s, 5 H, Cp), 5.54 (dt, J = 13.3, 7.7 Hz, 1 H, NCH_2), 6.85 (d, J = 1.4 Hz, 1 H, imidazole), 6.98 (s, 1 H, Ar), 7.16 (d, J = 1.4 Hz, 1 H, imidazole), 7.17 (s, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 13.99 (CH_3), 18.5 (br., o-CH_3), 19.97 (CH_2), 21.14 (p-CH_3), 33.34 (CH_2), 52.34 (NCH_2), 91.56 (Cp), 122.41, 123.68 (imidazole), 129.0 (br., m-Ar), 136.74, 138.99 (Ar), 163.19 (NCN) ppm. ^{13}C NMR (176 MHz, $CDCl_3$, –50 °C): δ = 14.49 (CH_3), 17.85 (o-CH_3), 19.97 (CH_2), 20.14 (o-CH_3), 21.54 (p-CH_3), 33.42 (CH_2), 52.37 (NCH_2), 91.59 (Cp), 122.67, 123.94 (imidazole), 128.59, 129.76, 134.34, 136.60, 137.73, 139.19 (Ar), 161.50 (NCN) ppm. EI MS (70 eV): m/z (%) [^{58}Ni, ^{79}Br] = 444 (32) [M^+], 364 (28) [M – HBr]$^+$, 307 (100) [M – NiBr]$^+$, 295 (20) [$C_{10}H_{10}BrN_2Ni$]$^+$, 242 (19) [L2]$^+$, 185 (17) [L2 – C_4H_9]$^+$, 123 (4) [NiCp]$^+$, 91 (11) [C_7H_7]$^+$, 65 (7) [Cp^+]. HR EI MS: calcd. for $C_{21}H_{27}{}^{79}BrN_2{}^{58}Ni$ 444.07111; found 444.07265. $C_{21}H_{27}BrN_2Ni$ (446.05): calcd. C 56.55, H 6.10, N 6.28; found C 56.61, H 5.65, N 6.51.

[($C_5H_4CH_2CH=CH_2$)Ni(Cl){1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene}] (4): 1,1′-Bis(allyl)nickelocene[17i] (0.90 g, 3.34 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolinium chloride[26] (1.15 g, 3.35 mmol) were stirred at reflux in thf (35 mL) for 13 h and then at room temp. for 3 d. The usual workup provided 0.85 g (1.68 mmol, 50%) of complex **4** as a red, crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (d, J = 6.8 Hz, 2 H, $C_5H_4CH_2$), 2.38 (s, 18 H, o- and p-CH_3), 3.92 (s, 4 H, NCH_2CH_2N), 4.26 (t, J = 2.4 Hz, 2 H, C_5H_4), 4.47 (m, J = 2.2 Hz, 2 H, C_5H_4), 4.83, 4.85, 4.90 (m, 2 H, =CH_2), 5.85 (m, 1 H, =CH), 7.06 (s, 4 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.54 (o-CH_3), 21.10 (p-CH_3), 31.61 ($C_5H_4CH_2$), 50.89 (NCH_2CH_2N), 83.03, 97.91, 113.35 ($C_5H_4CH_2$), 115.05 (=CH_2), 129.36 (m-Ar), 135.95 (=CH), 136.91 (o or p-Ar), 136.9 (br., $ipso$-Ar), 138.11 (o or p-Ar), 202.25 (NCN) ppm. EI MS (70 eV): m/z (%) [^{58}Ni, ^{35}Cl] = 504 (12) [M^+], 468 (59) [M – HCl]$^+$, 364 (27) [NiL]$^+$, 305 (100) [L – H]$^+$, 304 (69) [L – 2 H]$^+$, 303 (82) [L – 3 H]$^+$, 146 (40), 103 (15) [C_8H_7]$^+$, 91 (21) [C_7H_7]$^+$, 77 (18) [C_6H_5]$^+$. HR EI MS: calcd. for $C_{29}H_{35}{}^{35}ClN_2{}^{58}Ni$ 504.18422; found 504.18263. $C_{29}H_{35}ClN_2Ni$ (505.76): calcd. C 68.87, H 6.97, N 5.54; found C 68.90, H 6.88, N 5.45.

[($C_5H_4(CH_2)_2CH=CH_2$)Ni(Cl){1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene}] (5): 1,1′-Bis(but-3-enyl)nickelocene[17i] (2.23 g, 7.51 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolinium chloride[26] (3.22 g, 9.39 mmol) were stirred at reflux in thf (70 mL) for 11 h. The usual workup provided 1.28 g (2.47 mmol, 33%) of complex **5** as a red, crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (t, J = 7.8 Hz, 2 H, $C_5H_4CH_2CH_2$), 2.00 (m, J = 7.8, J = 1.2 Hz, 2 H, $C_5H_4CH_2CH_2$), 2.38 (s, 18 H, o- and p-CH_3), 3.91 (s, 4 H, NCH_2CH_2N), 4.25 (t, J = 2.4 Hz, 2 H, C_5H_4), 4.46 (t, J = 2.2 Hz, 2 H, C_5H_4), 4.83, 4.85, 4.88, 4.93 (m, 2 H, =CH_2), 5.71 (m, 1 H, =CH), 7.06 (s, 4 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.57, 21.12 (o- and p-CH_3), 26.40 ($C_5H_4CH_2CH_2$), 31.57 ($C_5H_4CH_2CH_2$), 50.92 (NCH_2CH_2N), 82.86, 97.56 ($C_5H_4CH_2$), 113.95 (=CH_2), 115.57 ($C_5H_4CH_2$), 129.37, 136.9 (br.), 136.98, 138.15 (Ar), 139.04 (=CH), 202.59 (NCN) ppm. EI MS (70 eV): m/z (%) [^{58}Ni, ^{35}Cl] = 518 (19) [M^+], 482 (47) [M – HCl]$^+$, 364 (20) [Ni(L)]$^+$, 305 (100) [L – H]$^+$, 304 (35) [L – 2H]$^+$, 303 (54) [L – 3 H]$^+$, 146 (24), 117 (6), 91 (12), 77 (9). HR EI MS: calcd. for $C_{30}H_{37}{}^{35}ClN_2{}^{58}Ni$ 518.19987; found 518.19887. $C_{30}H_{37}ClN_2Ni$ (519.79): calcd. C 69.32, H 7.17, N 5.39; found C 68.92, H 7.06, N 5.46.

Selective Cross-Metathesis

[($C_5H_4CH_2CH=CHC(O)CH_3$]Ni(Cl){1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene}] (6): Neat methyl vinyl ketone (100 μL, 0.086 g, 1.23 mmol) was added to a solution of complex **4** (0.20 g, 0.39 mmol) and [$RuCl_2$(=CHPh)(PCy_3)(H_2IMes)] (0.0161 g, 0.0190 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at reflux for 3 h after which time the reaction was incomplete as judged by ^{1}H NMR spectroscopy. Further methyl vinyl ketone (100 μL) and catalyst (0.0111 g) were added and the reaction mixture was refluxed for a further 3.5 h. The volatiles were removed under vacuum to yield a red solid, which was redissolved in toluene (15 mL). This solution was filtered through a pad of Celite, and the solvents were evaporated to dryness. This crude product was washed several times with hexane at –78 °C and crystallized from CH_2Cl_2/hexane. Yield: 0.11 g (0.20 mmol, 51%), red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 [s, 3 H, $C(O)CH_3$], 2.32 (d, J = 6.8 Hz, 2 H, $C_5H_4CH_2$), 2.37 and 2.38 (2 overlapped s, 18 H, o- and p-CH_3), 3.90 (s, 4 H, NCH_2CH_2N), 4.26 (t, J = 2.4 Hz, 2 H, $C_5H_4CH_2$), 4.53 (t, J = 2.4 Hz, 2 H, $C_5H_4CH_2$), 5.92 [d, J = 16 Hz, 1 H, =CHC(O)], 6.64 (dt, J = 16, J = 7.2 Hz, 1 H, CH_2CH=), 7.06 (s, 4 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.52 (o-CH_3), 21.12 (p-CH_3), 26.51 [$C(O)CH_3$], 30.69 ($C_5H_4CH_2$), 50.97 (NCH_2CH_2N), 83.65, 98.08, 109.95 ($C_5H_4CH_2$), 129.41, 129.74, 136.7 (br.), 136.86, 138.25, 145.83 (Ar and C=C), 199.05 (C=O), 200.84 (NCN) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 1671, 1486, 1433, 1256, 1019, 984, 852, 795 cm^{-1}. EI MS (70 eV): m/z [^{58}Ni, ^{35}Cl] = 546 [M^+], 510 [M – HCl]$^+$. $C_{31}H_{37}ClN_2NiO$ (547.80): calcd. C 67.97, H 6.81, N 5.11; found C 67.79, H 6.66, N 5.16.

[($C_5H_4(CH_2)_2CH=CHC(O)CH_3$]Ni(Cl){1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene}] (7): Complex **5** (0.21 g, 0.40 mmol) and [$RuCl_2$(=CHPh)(PCy_3)(H_2IMes)] (0.0192 g, 0.0226 mmol, 5.6 mol-%) were dissolved in CH_2Cl_2 (11 mL). Freshly distilled methyl vinyl ketone (100 μL, 1.23 mmol, 3.1 equiv.) was added and the resulting solution stirred at reflux for 3 h, after which time the volatiles were removed under vacuum to yield a red solid. This was redissolved in toluene (20 mL), the solution filtered through a short pad of Celite, and the solvents were evaporated to dryness. The residue was washed with hexane (2 × 3 mL) at –78 °C and crystallized from CH_2Cl_2/hexane at –78 °C. Yield: 0.17 g (0.30 mmol, 75%). M.p. 137–140 °C (CH_2Cl_2/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (t, J = 8.0 Hz, 2 H, $C_5H_4CH_2CH_2$), 2.17 (m, 2 H, $C_5H_4CH_2CH_2$), 2.20 [s, 3 H, C(O)-CH_3], 2.38 (s, 18 H, o- and p-CH_3), 3.92 (s, 4 H, NCH_2CH_2N), 4.27 (t, J = 2.4 Hz, 2 H, $C_5H_4CH_2$), 4.48 (t, J = 2.4 Hz, 2 H, $C_5H_4CH_2$), 5.96 [dt, J = 16 Hz, 1 H, =CHC(O)], 6.70 (dt, J = 16, J = 7.2 Hz, 1 H, CH_2CH=), 7.06 (s, 4 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.52 (o-CH_3), 21.11 (p-CH_3), 26.60 [C(O)-CH_3], 25.51 ($C_5H_4CH_2CH_2$), 30.30 ($C_5H_4CH_2CH_2$), 50.88 (NCH_2CH_2N), 83.08, 97.47, 113.88 ($C_5H_4CH_2$), 129.34 (Ar), 131.13 [=CHC(O)], 136.89, 138.20, 145.43 (Ar), 148.90 (CH_2CH=), 198.97 (C=O), 201.85 (NCN) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 1671, 1487,

1435, 1267, 976, 852, 793 cm^{-1}. EI MS (70 eV): *m/z* [^{58}Ni, ^{35}Cl] = 560 [M^+], 524 [M – HCl]$^+$. HR EI MS: calcd. for $C_{32}H_{39}{}^{35}ClN_2{}^{58}NiO$ 560.21044; found 560.20949. $C_{32}H_{39}ClN_2NiO$ (561.84): calcd. C 68.34, H 7.00, N 4.99; found C 67.82, H 7.21, N 5.20. Crystals suitable for X-ray measurement were grown from a CH_2Cl_2/hexane solution at room temp.

[($C_5H_4(CH_2)_2CH{=}CHC(O)OCH_3$)Ni(Cl){1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene}] (8): Complex **5** (0.16 g, 0.31 mmol) and [$RuCl_2$(=CHPh)(PCy_3)(H_2IMes)] (0.0140 g, 0.0165 mmol, 5.3 mol-%) were dissolved in CH_2Cl_2 (8.0 mL). Freshly distilled methyl acrylate (90 μL, 1.00 mmol, 3.2 equiv.) was added and the resulting solution stirred at reflux for 3.5 h, after which time the volatiles were removed under vacuum to yield a red solid. This was redissolved in toluene (20 mL), the solution filtered through a short pad of Celite, and the solvents were evaporated to dryness. The residue was washed several times with hexane at 0 °C and at room temp. to obtain a bright-red solid. Yield: 0.14 g (0.24 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (t, *J* = 7.6 Hz, 2 H, $C_5H_4CH_2CH_2$), 2.14 (m, 2 H, $C_5H_4CH_2CH_2$), 2.38 (s, 18 H, *o*- and *p*-CH_3), 3.70 (s, 3 H, OCH_3), 3.92 (s, 4 H, NCH_2CH_2N), 4.27 (t, *J* = 2.4 Hz, 2 H, $C_5H_4CH_2$), 4.46 (t, *J* = 2.4 Hz, 2 H, $C_5H_4CH_2$), 5.72 [dt, *J* = 15.6, *J* = 1.6 Hz, 1 H, =CHC(O)], 6.70 (dt, *J* = 15.6, *J* = 6.8 Hz, 1 H, CH_2CH=), 7.06 (s, 4 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.52 (*o*-CH_3), 21.09 (*p*-CH_3), 25.29 ($C_5H_4CH_2CH_2$), 29.95 ($C_5H_4CH_2CH_2$), 50.88 (NCH_2CH_2N), 51.29 (O-CH_3), 83.12, 97.36, 114.14 ($C_5H_4CH_2$), 120.50 [=*C*HC(O)OCH_3], 129.34 (*m*-Ar), 136.90, 138.20 (Ar), 149.79 (CH_2CH=), 167.18 [*C*(O)OCH_3], 202.02 (NCN) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 1719, 1787, 1439, 1267, 1032, 855, 789 cm^{-1}. EI MS (70 eV): *m/z* [^{58}Ni, ^{35}Cl] = 576 [M^+], 540 [M – HCl]$^+$. HR EI MS: calcd. for $C_{32}H_{39}{}^{35}ClN_2{}^{58}NiO_2$ 576.20535; found 576.20450. $C_{32}H_{39}ClN_2NiO_2$ (577.83): calcd. C 66.52, H 6.80, N 4.85; found C 65.97, H 6.66, N 4.86.

Typical Procedure for the Polymerization of Styrene: A toluene solution of MAO (0.63 mL, 0.952 mmol) was added to a solution of complex **5** (0.00165 g, 0.00317 mmol) in toluene (0.16 mL) and the resulting mixture stirred at room temp. for 30 min. During this time the color of the solution changed from red to green (for complexes **6**–**8** a dark precipitate formed instantly after MAO was added). Styrene (neat, 5.50 mL, 48.0 mmol) was added and the reaction mixture placed in an oil bath maintained at 50 °C. The reaction mixture was stirred at this temperature for 3 h. After cooling to room temp., 9% aq. HCl (20 mL) was cautiously added to decompose the excess MAO. The organic layer was separated and poured into methanol (200 mL). The precipitated polymer was filtered off, washed with methanol, and dried under high vacuum. Yield: 2.47 g (49%). The reproducibility was within 5%.

Typical Procedure for the Polymerization of Phenylacetylene: A toluene solution of MAO was added to a toluene (2.0 mL) solution of complex **1** (0.0050 g). The resulting solution was stirred at room temp. for 30 min. An appropriate volume of neat phenylacetylene was added and the reaction mixture placed in an oil bath maintained at 75 °C. The reaction mixture was stirred at this temperature for 5 h. The resulting polymer was isolated as a yellow solid as described above for polystyrene.

Crystal Structure Determination: Crystal data collection and refinement parameters for complexes **2** and **7** are summarized in Table 3. Preliminary examination and intensity data were carried out with a Kuma KM4 κ-axis diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Lorentz, polarization and absorption corrections were applied for all collected reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data by using the SHELXTL 6.14 program.[28] CCDC-745005 (for **2**) and -745006 (for **7**) 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.

Supporting Information (see footnote on the first page of this article): ^{1}H-^{13}C HMBC spectrum of complex **2**, VT ^{1}H NMR spectra of complex **2**, and VT ^{13}C NMR spectra of complex **2**.

Table 3. Crystallographi data for complexes **2** and **7**.

	2	**7**
Empirical formula	$C_{23}H_{31}ClN_2Ni$	$C_{32}H_{39}ClN_2NiO$
M_r	429.66	561.81
Cell setting, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
Temperature [K]	100(2)	90
a [Å]	11.405 (5)	9.9453(3)
b [Å]	12.047 (5)	9.9480(3)
c [Å]	16.244 (6)	15.7420(4)
α [°]	90	91.404(2)
β [°]	105.77 (1)	106.358(1)
γ [°]	90	103.509(2)
V [Å^3]	2147.9 (15)	1446.24(7)
Z	4	2
Radiation type	Mo-K_α	Mo-K_α
μ [mm^{-1}]	1.04	0.790
Crystal size [mm]	0.18 × 0.18 × 0.11	0.09 × 0.18 × 0.22
Diffractometer	Kuma KM-4 CCD kappa-axis diffractometer	
Absorption correction	analytical CrysAlis CCD, Version 1.171.31, Oxford Diffraction Ltd., **2006**; analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R. C. Clark, J. S. Reid, *Comput. Phys. Commun.* **1998**, *111*, 243	
T_{min}, T_{max}	0.862, 0.914	0.889, 0.959
R_{int}	0.028	0.0339
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.0566, 0.1036, 1.501	0.0309, 0.0815, 1.072
R_{all}, $wR(F^2)$, S_{all}	0.0570, 0.1037, 1.501	0.0426, 0.0873, 1.072
No. of independent reflections	5170	17809
No. of parameters	263	341
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.53, –0.39	0.846, –0.364

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