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Anion exchange in [Ni(η^5-C_5H_4R)(Cl)(NHC)]. Counterion effect on the structure and catalytic activity†

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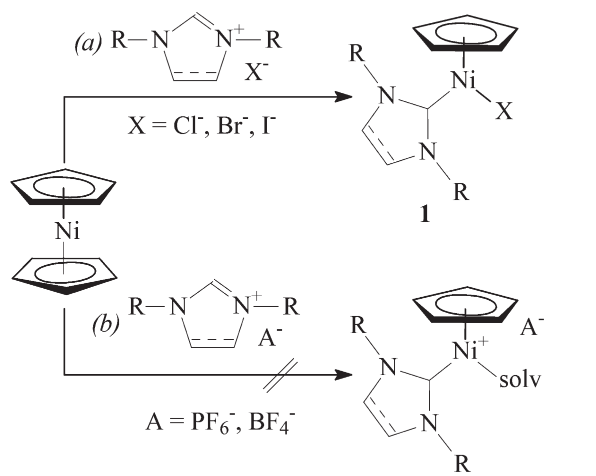
A series of novel complexes [Ni(η^5-C_5H_4R)(L)(NHC)]$^+$A$^-$ **2a–2j** and [Ni(η^5-C_5H_5)(A)(NHC)] **3a–3c** has been obtained by anion metathesis from the corresponding chlorides **1a–1d**, depending on the anion binding properties and reaction conditions. Solid-state structures of two cationic complexes (**2c**, **2j**) and two complexes with a coordinated anion (**3a**, **3c**) have been determined by X-ray diffraction revealing a trigonal planar geometry in all cases. Unexpectedly, **3c** displayed unprecedented for this type of compounds temperature-dependent NMR spectra that were interpreted in terms of spin equilibrium. The cationic complexes **2** were less efficient in styrene polymerization than the parent chlorides **1**. However, the activity of **2** and **3** in Suzuki cross-coupling did not depend considerably on the counterion.

Introduction

Transition metal N-heterocyclic carbene (NHC) complexes are a growing field of interest in organometallic chemistry, homogeneous catalysis, and other areas of chemistry.[1] Nickel(0), nickel(I), and nickel(II) NHC complexes have attracted substantial attention in recent years, mainly due to their application as catalysts in a number of important organic transformations.[2]

Abernethy *et al.* discovered that reaction of nickelocene with 1,3-dimesitylimidazolium chloride in refluxing THF afforded diamagnetic complex [Ni(η^5-C_5H_5)(Cl)(IMes)]‡ (**1a**) in high yield.[3] Following this original communication, a considerable variety of NHC complexes of the general formula [Ni(η^5-C_5H_4R)(X)(NHC)] (**1**, R = H or alkyl; X = Cl, Br, or I) has been prepared in this manner (Scheme 1, path a).[4–10] These Ni(II) complexes display promising catalytic activity in several reactions, including amination of aromatic compounds,[4] polymerization of styrene,[5,8] polymerization of methyl methacrylate,[11] Suzuki–Miyaura cross-coupling,[9,12] regioselective hydrothiolation of alkynes,[13] and hydrosilylation of aldehydes and ketones.[14]



Scheme 1 Reactions of nickelocene with NHC salts: (a) THF, heating; (b) THF or CH_3CN, heating.

Previously, we suggested that styrene polymerization catalysed by [Ni(η^5-C_5H_5)(X)(NHC)] in the presence of methylaluminoxane (MAO) proceeded *via* a cationic mechanism[15] involving intermediate species [Ni(η^5-C_5H_5)(L)(NHC)]$^+$ (L = styrene, solvent).[5] In order to further elucidate this process, we sought to approach these tentative intermediates *via* a different route.

Halogen substitution in complexes **1** with $AgBF_4$ or KPF_6 has been recently reported. In the case of complexes bearing

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‡ Standard abbreviations for NHC ligands are used throughout this manuscript: IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene, SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene, and Bn_2-bimy = 1,3-dibenzylbenzimidazolin-2-ylidene.

† Electronic supplementary information (ESI) available: Additional tables and figures. CCDC 972867–972870. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53352b

N-allyl functionalized NHC ligands, intramolecular cationic π-complexes $[Ni(\eta^5\text{-}C_5H_5)(\eta^3\text{-NHC})]^+A^-$ were obtained.[6] However, reactions of complexes with *N*-aryl substituted NHCs resulted in cationic complexes $[Ni(\eta^5\text{-}C_5R_5)(L)(NHC)]^+A^-$ (R = H or Me, L = CH_3CN or $(CH_3)_2CO$) in acetonitrile[12,16] or acetone.[17]

In this contribution, we explore the scope of halogen substitution in complexes $[Ni(\eta^5\text{-}C_5H_4R)(Cl)(NHC)]$ with various metal salts, including non-coordinating and weakly-coordinating anions, and catalytic properties of the resulting complexes.

Results and discussion

Synthesis

Nolan and co-workers reported that nickelocene did not react with NHC tetrafluoroborates or hexafluorophosphates in refluxing THF.[4a] Indeed, when we attempted to synthesize $[Ni(\eta^5\text{-}C_5H_5)(CH_3CN)(NHC)]^+(BF_4)^-$ directly from nickelocene and an imidazolium tetrafluoroborate in refluxing acetonitrile, a gradual decomposition of nickelocene was observed (Scheme 1, path b).

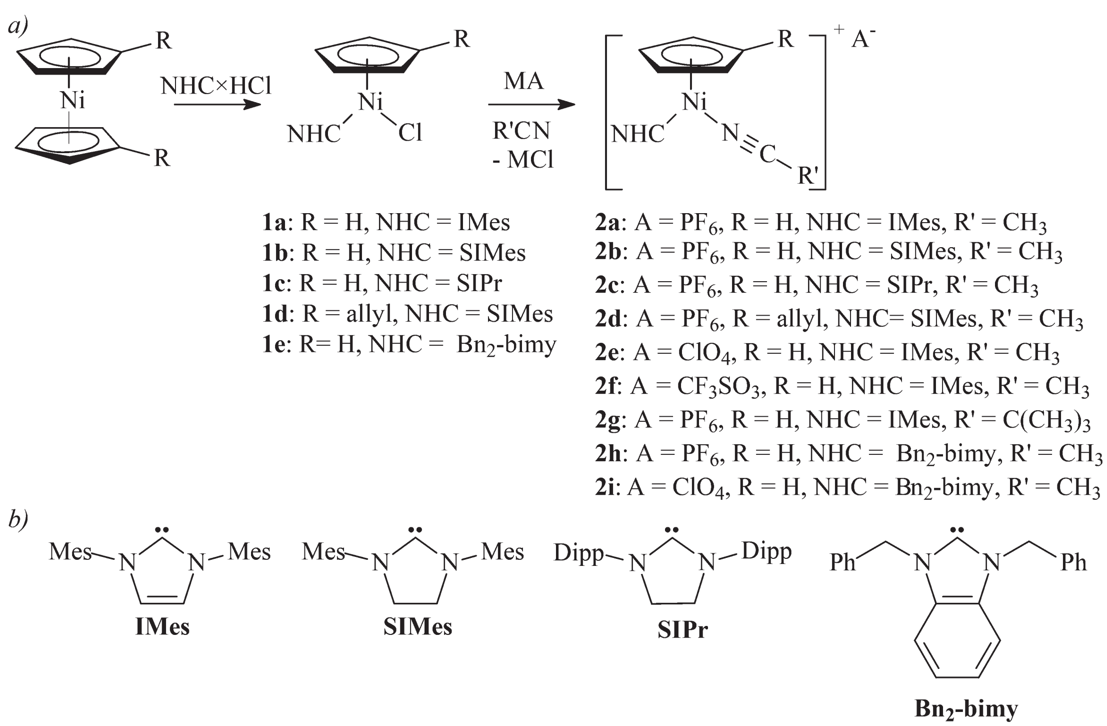
Accordingly, complexes $[Ni(\eta^5\text{-}C_5H_4R)(L)(NHC)]^+A^-$ (**2**) were obtained by the two-step route involving isolation of chlorides **1**.

Complexes **1a–1e** reacted cleanly with KPF_6, $AgClO_4$, $AgCF_3SO_3$, $AgCF_3CO_2$, or $AgNO_3$ in a nitrile solution (acetonitrile, pivalonitrile) at room temperature. The expected cationic complexes **2** were obtained as yellow-brown solids in high yields for KPF_6, $AgClO_4$, and $AgCF_3SO_3$ (Scheme 2). However, reactions of **1a** or **1b** with $AgCF_3CO_2$ in acetonitrile or toluene afforded complexes **3a** and **3b** with the coordinated carboxylate (Scheme 3). Attempts to extend this methodology to other carboxylates (acetate, pivalate) were not successful.

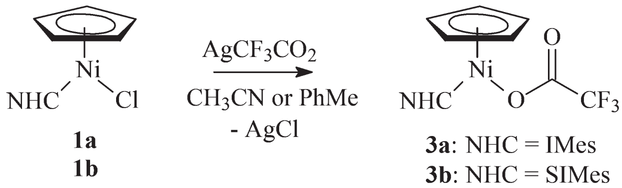
In contrast to $AgCF_3CO_2$, reaction of **1a** with $AgNO_3$ in acetonitrile afforded cationic complex **2j**. However, when this reaction was repeated in toluene/THF, neutral complex **3c** with a coordinated nitrate was isolated. Moreover, complex **2j** could be also obtained by dissolving **3c** in acetonitrile (Scheme 4). In contrast to **2a–2i** that were stable in $CDCl_3$ solutions (see below), dissolving **2j** in $CDCl_3$ resulted in a red solution giving NMR spectra corresponding to **3c**. A detailed inspection of these spectra revealed also a residual broad singlet at 4.77 ppm that could be assigned to **2j**. This behaviour suggests that **2j** and **3c** exist in equilibrium in a polar solvent, with **3c** being the major species.[18]

Characterization

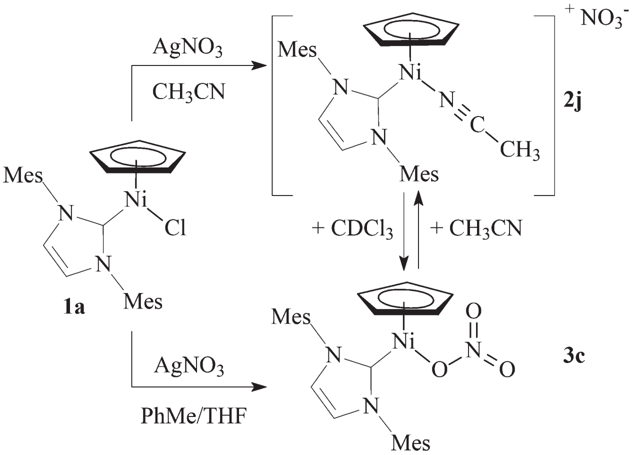
NMR studies. The NMR spectra of **2a–2i** were routinely recorded in $CDCl_3$ at ambient temperature. These spectra featured all expected resonances, *i.e.* that of the cyclopentadienyl, of the carbene, and of the coordinated nitrile. The Cp protons appeared as singlets from 4.67 ppm to 4.76 ppm for **2a–2c** and **2e–2g**. For the weaker-donating benzimidazole-based NHC ligand Bn_2-bimy,[19] the Cp resonances were shifted significantly downfield to 5.22 and 5.24 ppm for **2h** and **2i**. An interesting feature of the proton NMR spectra of these benzimidazole-based NHC complexes was the presence of the



Scheme 2 (a) The synthesis of cationic complexes **2a–2i** (M = K or Ag; complex **2a** has been reported by Chetcuti *et al.*[12]). (b) Structures of NHC ligands used in this work (Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl).



Scheme 3 The synthesis of trifluoroacetate complexes **3a** and **3b**.



Scheme 4 The synthesis of nitrates **2j** and **3c** (Mes = 2,4,6-trimethylphenyl).

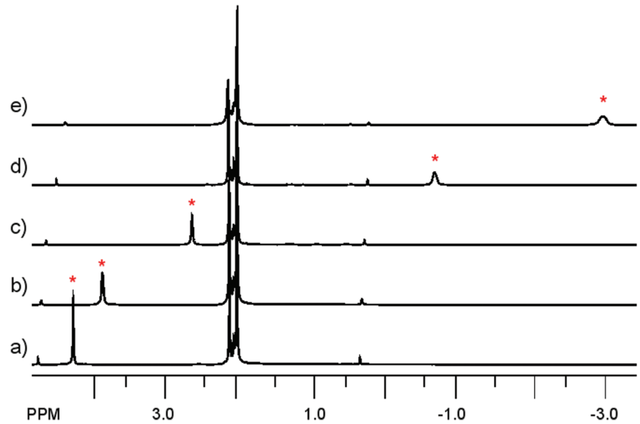


Fig. 1 VT ^{1}H NMR (500 MHz, toluene-d$_8$) spectra of complex **3c** (high-field range) at temperatures: (a) −55 °C, (b) −30 °C, (c) 10 °C, (d) 70 °C, and (e) 100 °C. Asterisk (*) indicates the Cp resonance.

Ph-CH_2-signals as two doublets with chemical shifts in the range from 6.19 to 6.45 ppm (^2J = 13.5 Hz) which suggests their diastereotopic character. The resonances of the co-ordinated acetonitrile molecule were observed as singlets from 2.03 to 2.26 ppm in $CDCl_3$.

The carbene carbon atom chemical shift varied from 159.9 ppm to 199.4 ppm, depending on the type of NHC ligand. For IMes complexes (**2a**, **2e–2g**, **2j**, and **3a**), the carbene carbon atom signal appeared from 159.9 to 166.2 ppm. The ^{13}C NMR spectra of Bn$_2$-bimy complexes **2h** and **2i** displayed their carbene atom signals at 174.1 ppm and 174.2 ppm, respectively. The highest chemical shift of the carbene carbon atom in the range of 195.6–199.4 ppm was observed for SIMes complexes (**2b**, **2d** and **3b**). While the spectra of trifluoro-acetates **3a** and **3b** were unexceptional, the spectra of nitrates **2j** and **3c** deserve a further comment.

In contrast to the other ionic complexes, NMR spectra of **2j** could be recorded only in CD_3CN since **2j** appeared to easily dissociate the nitrile ligand in a polar solvent (*e.g.* in $CDCl_3$) to form the neutral complex **3c** (see Scheme 4). Thus, NMR spectra of **2j** featured all expected signals within the usual ranges, *e.g.* a sharp singlet of Cp protons at 4.77 ppm.

However, NMR spectra of **3c** were far from routine: we first noticed rather unusual chemical shift and linewidth of the Cp signal: in $CDCl_3$ at ambient temperature it appeared at 3.53 ppm with $\nu_{1/2}$ = 5.6 Hz, and at 35 °C it appeared at higher field at 2.77 ppm with $\nu_{1/2}$ = 13 Hz. Moreover, the parameters of the Cp signal varied considerably also with the solvent used: it appeared at 2.34 ppm ($\nu_{1/2}$ = 8.9 Hz) in C_6D_6 at ambient temperature.[20]

In the ^{13}C NMR spectrum of **3c** no carbene carbon atom signal was detected; moreover, the Cp signal at 97.1 ppm was unusually broad with $\nu_{1/2}$ = 6.2 Hz, while for the other complexes $\nu_{1/2}$ was in the range 1.6–2.1 Hz. VT NMR studies in toluene-d$_8$ in the temperature range from −55 °C to 100 °C were therefore performed (Fig. 1). The Cp signal appeared as a singlet at 4.31 ppm at −55 °C and shifted to −3.01 ppm at 100 °C. This upfield shift with increasing temperature was accompanied by signal broadening from $\nu_{1/2}$ = 5 Hz to $\nu_{1/2}$ = 36 Hz. At the same time the imidazole singlet shifted downfield slightly from 5.81 ppm to 7.33 ppm. We explain this behaviour of **3c** in terms of spin equilibrium, *i.e.* equilibrium between a diamagnetic singlet ground state and a paramagnetic triplet excited state.[21] The absence of an observable carbene carbon atom signal might be explained by its merging with the baseline as a result of the paramagnetic broadening.

The spin equilibrium was further modelled by using a Boltzmann distribution of spins[22] (for details, see the ESI†) and the thermodynamic parameters for **3c** thus obtained were as follows: ΔH° = (15.15 ± 0.43) kJ mol^{-1}, ΔS° = (16.7 ± 4.0) J (mol K)$^{-1}$. The value of the high-spin species to low-spin species equilibrium constant K_{eq} of 0.02 calculated at 298.15 K shows that at this temperature there is a large excess of the diamagnetic form of **3c**. This value also explains why the magnetic susceptibility measurement by Evans' method[23] that we had attempted failed to give any significant result. At the same time such a placement of the equilibrium substantiates the observed chemical shift for Cp protons in **3c**. For nickelocene (two unpaired electrons, μ_{eff} = 2.88μ_B)[24] the magnitude of paramagnetic ^{1}H NMR chemical shift (δ = *ca.* −250 ppm)[25] is considerably larger than for **3c** even though both in nickelocene and in **3c** the distances between the nickel atom and the Cp plane are comparable (1.8177(4) Å[26] and 1.765(3) Å, respectively), and therefore the paramagnetic contribution to the

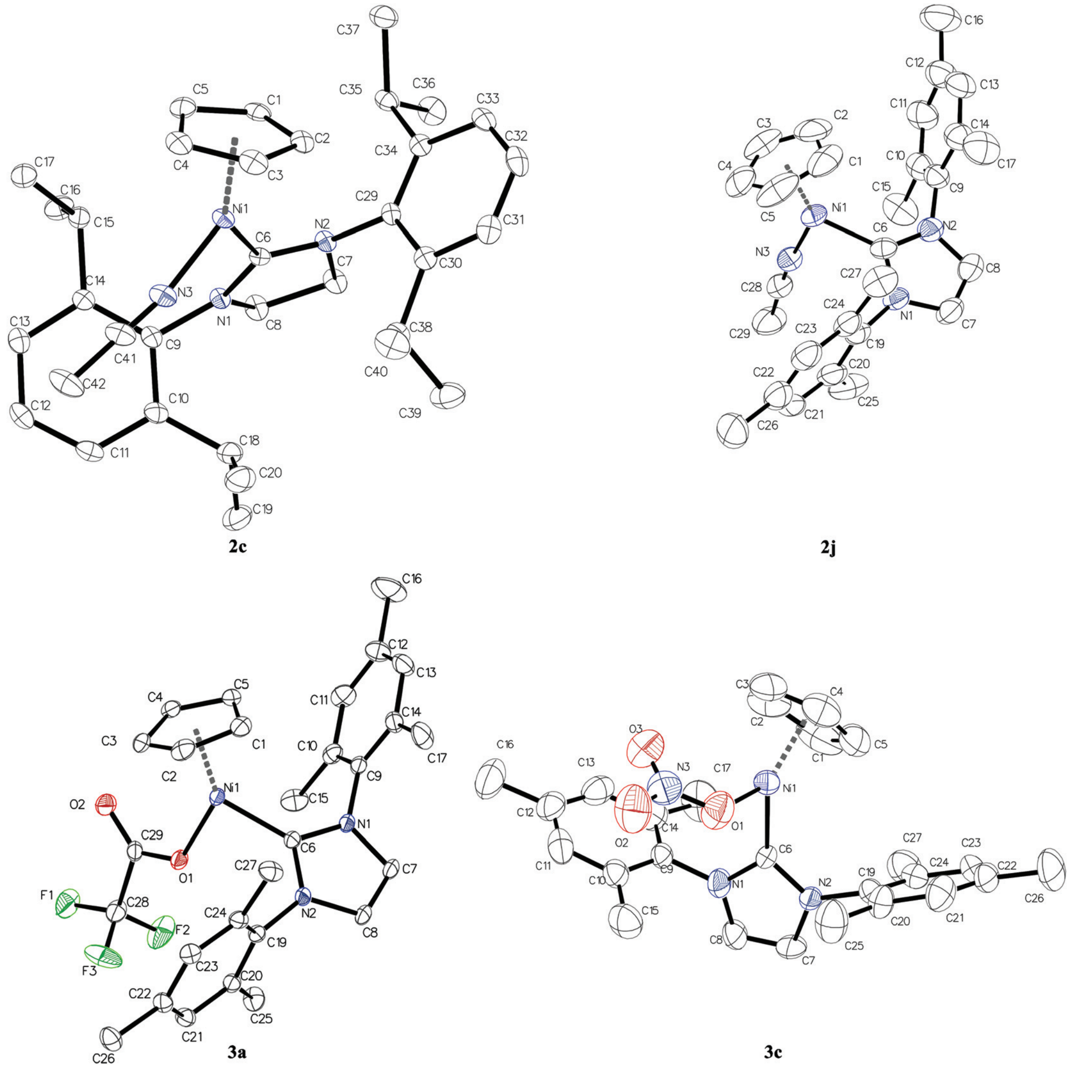


Fig. 2 The molecular structure of cations of complexes **2c** and **2j** and of neutral complexes **3a** and **3c**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. In the case of complexes **2c** and **3c**, where two independent molecules are present in the asymmetric unit, only one of them is presented. See Fig. S3 in the ESI† for the second ones of **2c** and **3c**.

chemical shifts in both compounds should be of a similar order of magnitude. In the case of **3c** this contribution is relatively small, creating a downfield shift of only several ppm. While it is not clear why the nitrate anion modifies the electronic properties of **3c** in comparison with the other studied anions, the solid state structure of **3c** (see below) revealed the expected, three-coordinate geometry.

Solid-state structures. We have focused our efforts to grow X-ray quality crystals on complexes with novel structural features, mainly on those with anions that have not been reported previously for [Ni(η^5-C_5H_5)(A)(NHC)] complexes. In particular, the intriguing solution properties of nitrates prompted us to study them in detail. Gratifyingly, the solid-state structures of complexes **2c**, **2j**, **3a**, and **3c** have been determined by single-crystal X-ray diffraction (Fig. 2). Selected crystallographic data, the parameters for data collection and refinement procedures are presented in Table 1. Selected bond lengths and angles are given in Table 2, and in Tables S2 and S3 in the ESI.†

Single crystal X-ray structure analysis reveals that compounds **2c**, **3a** and **2j** crystallise in the triclinic $P\bar{1}$ (no. 2) space group whereas complex **3c** is the only one to yield non-centrosymmetric crystal structure in the orthorhombic $Pca2_1$ (no. 29) space group. While crystal structures of compounds **3a** and **2j** contain one molecule and a pair of cation and anion, respectively, in the asymmetric unit, there are two independent molecules or two independent pairs of cations and anions in crystal structures of complexes **3c** and **2c**, respectively. The sum of bond angles around Ni atoms, that is, X–Ni–$C_{(NHC)}$, $C_{(NHC)}$–Ni–C_g and C_g–Ni–X angles, where C_g denotes the centre of gravity of Cp rings and X stands for N or O, amounts to 360° within 3 s.u.'s in all studied compounds which indicates planar trigonal coordination of nickel atoms (see Table S2 in the ESI†).

Table 1 Crystal data and structure refinement for complexes **2c**, **3a**, **2j**, and **3c**

Compound	2c	3a	2j	3c
Chemical formula	$NiC_{34}H_{46}N_3^+ \cdot PF_6^-$	$NiC_{28}H_{29}F_3N_2O_2$	$NiC_{28}H_{32}N_3^+ \cdot NO_3^-$	$NiC_{26}H_{29}N_3O_3$
Formula mass	700.42	541.24	531.28	490.23
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
a/Å	10.3048(8)	7.9276(3)	8.5478(3)	17.6218(3)
b/Å	18.3915(10)	9.6611(5)	8.8564(3)	12.2104(3)
c/Å	19.1066(10)	20.5983(8)	17.8908(5)	22.7534(4)
α/°	75.910(5)	78.742(4)	89.233(3)	90
β/°	86.934(5)	89.700(3)	80.886(3)	90
γ/°	81.371(5)	69.643(4)	85.015(3)	90
Unit cell volume/Å^3	3471.8(4)	1447.25(11)	1332.22(7)	4895.80(16)
Temperature/K	100(2)	100(2)	293(2)	293(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pca2_1$
Z	4	2	2	8
No. of reflections measured	97 217	55 160	26 005	53 880
No. of independent reflections	17 567	10 462	6117	9968
R_{int}	0.0708	0.0547	0.0361	0.0323
Final R_1 values ($I > 2\sigma(I)$)	0.0468	0.0488	0.0386	0.0532
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.1051	0.1233	0.0964	0.1444
Final R_1 values (all data)	0.0646	0.0578	0.0488	0.0606
Final w$R(F^2)$ values (all data)	0.1151	0.1279	0.1020	0.1516
Goodness of fit on F^2	1.021	1.135	1.019	1.067

Table 2 Selected bond lengths involving nickel atoms in **2c**, **3a**, **2j**, and **3c**

d/Å	2c	3a	2j	3c
Ni1–C1	2.033(2)	2.0388(17)	2.002(2)	2.032(7)
Ni1–C2	2.157(2)	2.1252(17)	2.138(2)	2.123(7)
Ni1–C3	2.181(2)	2.1245(17)	2.174(2)	2.139(6)
Ni1–C4	2.122(2)	2.1980(17)	2.152(2)	2.181(7)
Ni1–C5	2.134(2)	2.1895(17)	2.125(2)	2.163(7)
Ni1–C6 (NHC)	1.9013(19)	1.8835(16)	1.9020(19)	1.874(5)
Ni1–X (N3, O1)[a]	1.8644(18)	1.9104(12)	1.8693(17)	1.910(4)

[a] N3 denotes the nitrogen atom of the coordinated acetonitrile for **2c** and **2j**; O1 denotes the oxygen atom of the trifluoroacetate or nitrate anions for complexes **3a** and **3c**, respectively (see Fig. 2 for the atom numbering scheme).

The plane of the carboxylate group in complex **3a** deviates considerably from the Ni coordination plane (Ni, C_g, X, $C_{(NHC)}$) as evidenced by the value of C6–Ni1–O1–C29 torsion angle equal to −153.50(14)°. This is even more pronounced for nitrate anions in compound **3c** where C6–Ni1–O1–N3 and C36–Ni2–O31–N33 torsion angles are −116.2(4) and 115.2(5)°, respectively. This twist results in the monodentate binding of carboxylate and nitrate ligands to nickel (Ni⋯O distances for unbound oxygen atoms amount to 3.2238(13) Å in **3a** and 2.905(6) Å on average in **3c**). As shown in Table 2, the distances from nickel to Cp carbon atoms differ significantly from each other within every complex. The Ni–C_{Cp} bond *trans* to the *L* ligand (acetonitrile molecule for complexes **2c** and **2j**, trifluoroacetate anion for **3a** and nitrate anion for **3c**) is shorter by *ca.* 0.1 Å compared to the other ones. This variation in the Ni–C_{Cp} distances can be attributed to the *trans* effect of the NHC ligand which leads to the elongation of Ni–C_{Cp} bonds *trans* to the carbene and, consequently, shortening of the Ni–C_{Cp} bonds *trans* to the *L* ligand. The C–C bond lengths in cyclopentadienyl ligands vary from 1.35 to 1.45 Å which is typical for Ni complexes comprising both Cp and NHC ligands deposited in the Cambridge Structural Database (1.35–1.46 Å).[27]

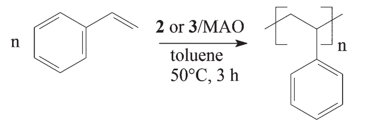
Catalytic activity

Styrene polymerization. The activity of complexes **2a**–**3c** in styrene polymerization was examined under conditions similar to those described in our previous reports.[5,8] Briefly, an excess of MAO (Al : Ni = 100 : 1) was added to a toluene suspension of complex **2** or **3**. After stirring for 30 min at ambient temperature, neat styrene (styrene : Ni = 1000 : 1) was added and the polymerization was run in a sealed Schlenk tube for 3 h at 50 °C. The results of styrene polymerization are summarized in Table 3.

Disappointingly, hexafluorophosphates **2a** and **2b** (entries 1 and 4) were one order of magnitude less active than the neutral parent complexes.[5] In control experiments we established that **2a** without MAO gave no polymer (entry 2). Similarly, MAO itself did not yield polystyrene (entry 3). Analogously to what was observed for the chloride series, introduction of the more bulky NHC ligand (SIPr *vs.* SIMes, entry 5) or a substituent on the Cp ligand (entry 6) resulted in significantly lower yields than for **2b**.

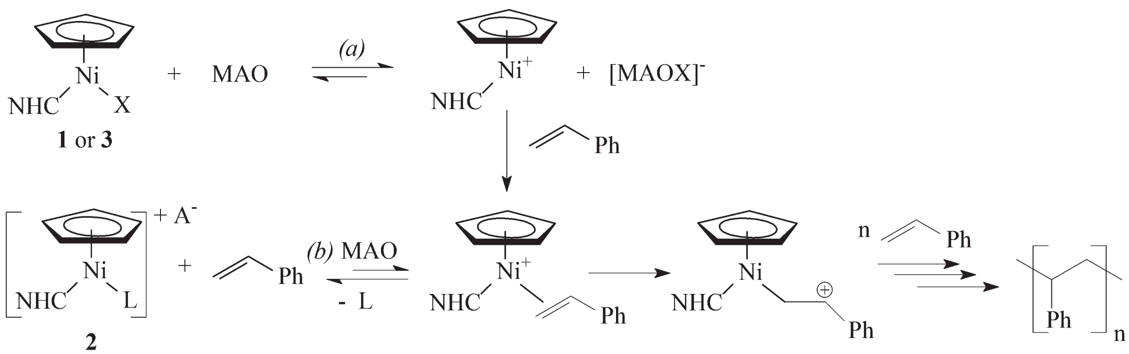
Other weakly- or non-coordinating anions (ClO_4^-, $CF_3SO_3^-$, and NO_3^-) had no significant effect on the activity (entries 7, 8, and 11). Complex **2g** with the more bulky nitrile (entry 9) provided the same efficiency as **2a**. Introduction of the weaker donating benzimidazole-based NHC ligand resulted in a low yield of the polymer (entry 10). The highest activity was achieved with complexes **3a** and **3b** (entries 12 and 13) bearing covalently bound carboxylates; however, neutral nitrate **3c** was less effective (entry 14). These findings show that strongly

Table 3 Styrene polymerization catalysed by $[Ni(Cp)(L)(NHC)]^+A^-$ (**2a–2j**)/MAO or [Ni(Cp)(A)(NHC)] (**3a–3c**)/MAO[a]



Entry	Complex (NHC)	A	L	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	**2a** (IMes)	PF_6^-	CH_3CN	22	14 000	2.0
					1300	1.1
2[d]	**2a** (IMes)	PF_6^-	CH_3CN	0	—	—
3[e]	—	—	—	0	—	—
4	**2b** (SIMes)	PF_6^-	CH_3CN	35	13 000[g]	2.0
					800	1.2
5	**2c** (SIPr)	PF_6^-	CH_3CN	13	10 000	2.3
6	**2d** (SIMes)[f]	PF_6^-	CH_3CN	10	11 000	2.0
7	**2e** (IMes)	ClO_4^-	CH_3CN	31	1300[g]	7.0
8	**2f** (IMes)	$CF_3SO_3^-$	CH_3CN	21	1300[g,h]	11
9	**2g** (IMes)	PF_6^-	$(CH_3)_3CCN$	20	1000[g]	6.9
10	**2h** (Bn_2-bimy)	PF_6^-	CH_3CN	14	14 600[g]	1.6
					800	1.5
11	**2j** (IMes)	NO_3^-	CH_3CN	42	1500[g]	6.7
12	**3a** (IMes)	$CF_3CO_2^-$	—	94	11 300	2.0
13	**3b** (SIMes)	$CF_3CO_2^-$	—	100	10 500	2.0
14	**3c** (IMes)	NO_3^-	—	45	1600[g]	7.3

[a] All reactions in duplicate; conditions: [Ni] = 1.30 mmol L^{-1}, 3 h, 50 °C, styrene : Ni = 1000 : 1, Al : Ni = 100 : 1. [b] Isolated yield. [c] Determined with GPC in CH_2Cl_2 (target M_n = 100 000). [d] Control experiment without MAO. [e] Control experiment without Ni, styrene : Al = 10 : 1. [f] Allyl substituted Cp. [g] Bimodal distribution with low M_n oligomers. [h] High molecular fraction (M_n 800 000) was also present.



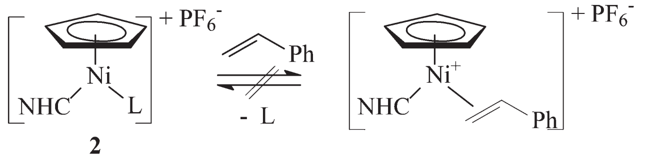
Scheme 5 Proposed pathways of the styrene polymerization with complexes **1–3** (X = halogen or $CF_3CO_2^-$, A = non- or weakly-coordinating anions used in this study, L = RCN).

coordinating anions, *i.e.* chloride or trifluoroacetate, are the most efficient in this type of polymerization.

The obtained polystyrenes were examined by ^{13}C NMR, GPC, and MALDI-TOF MS. The ^{13}C NMR spectra were consistent with atactic microstructure of all polymers.[28] GPC analyses showed that in most cases M_n was lower than that obtained with the corresponding chlorides, while M_w/M_n was higher than for the chlorides. The trifluoroacetates **3a** and **3b** produced polystyrenes with similar M_n and M_w/M_n to those obtained with **1a**.[5] MALDI-TOF MS (see the ESI†) suggested that the polystyrene chains were terminated with C═C double bonds.

Previously, we proposed that the initial reaction of complexes **1** with MAO resulted in cationic species $[Ni(\eta^5\text{-}C_5H_5)(NHC)]^+$ (Scheme 5, path a).[29] Consequently, the efficiency of styrene polymerization with **1**/MAO depended mainly on the stabilization of these intermediate species, meaning that the strongly coordinating chloride that irreversibly reacts with MAO was the most suitable counterion.[5] In this study, we anticipated that the labile nitrile ligand[12,30] in complexes **2** would be readily displaced with styrene (Scheme 5, path b) to produce the same intermediates as with **1**. However, the low efficiency of complexes **2** in the styrene polymerization suggests that the nitrile binds to the Ni centre rather strongly and actually inhibits the polymerization. To further address this issue, we studied reactions of complexes **2** with styrene (Scheme 6).

However, despite our best efforts to use as many various reaction conditions as possible (type of the nitrile ligand, solvent and temperature), the exchange of the nitrile ligand



Scheme 6 Attempted reactions of complexes **2** with styrene (L = CH_3CN or $(CH_3)_3CN$).

with styrene has not been accomplished. Complexes **2b** and **2g** remained unchanged in the presence of an excess of styrene, while **2h** upon stirring in neat styrene at 35 °C partially transformed into an inseparable mixture of green nickel complexes. We note that an intramolecular analogue of $[Ni(\eta^5\text{-}C_5H_5)(\eta^2\text{-alkene})(NHC)]^+$ has been fully characterized by Hahn and co-workers.[6,31]

Suzuki cross-coupling. The activity of neutral $[Ni(\eta^5\text{-}C_5R_5)(Cl)(NHC)]$ and cationic $[Ni(\eta^5\text{-}C_5R_5)(CH_3CN)(NHC)]^+PF_6^-$ (R = H or Me) complexes in Suzuki cross-coupling has been recently reported.[9,12] Surprisingly, chloride complexes and the corresponding hexafluorophosphates provided almost identical conversions. Encouraged by these results, we decided to test our new complexes **2** and **3** in the cross-coupling of 4′-bromoacetophenone with phenylboronic acid. The results are summarized in Table 4.

All studied complexes provided high yields of the expected cross-coupling product, *i.e.* 4-acetylbiphenyl (**A**), with excellent selectivity. The highest yield was achieved with cationic nitrate **2j** (entry 10); however, the advantageous effect of this counterion was not confirmed with neutral nitrate **3c** (entry 13). The weakly donating Bn_2-bimy ligand was consistently less efficient (entries 8 and 9) than the other NHC ligands. With the more challenging substrate, 4′-chloroacetophenone, complex **2e** was significantly less efficient than with 4′-bromoacetophenone (entry 14). The absence of a pronounced structure–activity relationship for the studied series of complexes is consistent with previous hypothesis that the Ni(II) complexes **2–3** serve as a convenient source of Ni(0) in this catalytic reaction.[9,12]

Conclusions

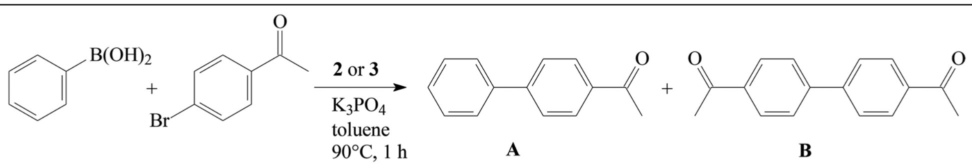
In summary, we have shown that, depending on the anion binding properties and reaction conditions, cationic **2** or neutral complexes **3** were obtained by anion metathesis in complexes **1**. In the case of nitrate, both cationic complex **2j** and neutral **3c** could be isolated. Complexes **2j** and **3c** were found to easily interconvert with each other in a solution. This facile exchange of ligands opens up prospects for further optimization of electronic and catalytic properties of these complexes, in particular discovery of systems with switchable magnetic properties and plausible applications in spintronics.

Experimental section

General

All manipulations (except polymer separation and purification, and work-up of the Suzuki cross-coupling reactions) were performed under an inert atmosphere of argon using Schlenk techniques. Solvents were purified with conventional methods.[32] Styrene (*ReagentPlus*®, Aldrich) was distilled from

Table 4 Suzuki cross-coupling of phenylboronic acid with 4′-bromoacetophenone catalysed by $[Ni(Cp)(L)(NHC)]^+A^-$ (**2a–2j**) or [Ni(Cp)(A)(NHC)] (**3a–3b**)[a]



Entry	Complex (NHC)	A	L	Yield[b] (%)	Selectivity[c]
1	**2a** (IMes)	PF_6^-	CH_3CN	78	99 : 1
2	**2b** (SIMes)	PF_6^-	CH_3CN	73	99 : 1
3	**2c** (SIPr)	PF_6^-	CH_3CN	69	98 : 2
4	**2e** (IMes)	ClO_4^-	CH_3CN	74	99 : 1
6	**2f** (IMes)	$CF_3SO_3^-$	CH_3CN	62	99 : 1
7	**2g** (IMes)	PF_6^-	$(CH_3)_3CCN$	67	99 : 1
8	**2h** (Bn_2-bimy)	PF_6^-	CH_3CN	56	97 : 3
9	**2i** (Bn_2-bimy)	ClO_4^-	CH_3CN	47	98 : 2
10	**2j** (IMes)	NO_3^-	CH_3CN	88	99 : 1
11	**3a** (IMes)	$CF_3CO_2^-$	—	57	99 : 1
12	**3b** (SIMes)	$CF_3CO_2^-$	—	60	99 : 1
13	**3c** (IMes)	NO_3^-	—	38	99 : 1
14	**2e** (IMes)[d]	ClO_4^-	CH_3CN	47	99 : 1

[a] All runs in duplicate; reaction conditions: [Ni] = 10.2 mM (3 mol%), 90 °C, 1 h, toluene. [b] Determined with GC. [c] Determined with GC as the ratio A : B. [d] Run with 4′-chloroacetophenone.

CaH_2 under reduced pressure and passed through a column with neutral Al_2O_3. Other reagents were purchased from commercial suppliers and were used without further purification. Complexes **1a–1e** were prepared from nickelocene[33] or 1,1′-bis(allyl)nickelocene[34] and the appropriate imidazolium salt according to the published method with minor modifications.[3]

NMR spectra were recorded, unless otherwise noted, at ambient temperature on a Mercury-400BB spectrometer operating at 400 MHz for ^1H NMR, at 101 MHz for ^{13}C NMR, at 376 MHz for ^{19}F NMR, and at 162 MHz for ^{31}P NMR. ESI MS were measured on a Mariner spectrometer. EI MS (70 eV) were measured on a AutoSpec Premier (Waters) spectrometer. MALDI-TOF MS of polystyrenes were acquired with a Bruker Daltonics ultrafleXtreme™ mass spectrometer (DCTB matrix with $AgCF_3CO_2$). The average molecular weights of PS were measured on a LabAlliance liquid chromatograph equipped with a Jordi Gel DVB Mixed Bed column (250 mm × 10 m) using CH_2Cl_2 as the mobile phase at 30 °C and calibrated with standard PS. Conversion and selectivity of Suzuki reactions were determined on 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 cationic complexes 2a–2j

General procedure (the reported method[12] was modified). To a solution of $[Ni(\eta^5\text{-}C_5H_5)(Cl)(IMes)]$ (**1a**) (100 mg, 0.216 mmol) in acetonitrile (3.0 mL), solid $AgClO_4$ was added (44.8 mg, 0.216 mmol, 1 eq.). The colour of the reaction mixture changed immediately from red to yellow. After stirring for 1 h at room temperature (with protection from light when silver salts were used) the reaction mixture was filtered through Celite and evaporated to dryness *in vacuo*. The resulting solid was washed with diethyl ether (2 × 6 mL) and dried *in vacuo* to give 120.3 mg (0.212 mmol, 98% yield) of $[Ni(\eta^5\text{-}C_5H_5)(IMes)(CH_3CN)]^+ (ClO_4)^-$ (**2e**) as a yellow solid.

$[Ni(\eta^5\text{-}C_5H_5)(CH_3CN)(IMes)]^+(PF_6)^-$ (2a).[12] Obtained from **1a** (186.0 mg, 0.401 mmol) and KPF_6 (73.0 mg, 0.397 mmol, 1 eq.) in acetonitrile (5.0 mL). Yield: 73%, yellow solid (180.0 mg, 0.293 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.20 (2H, s, $HC{=}CH$), 7.13 (4H, s, *m*-Ar*H*), 4.76 (5H, s, C_5H_5), 2.43 (6H, s, *p*-ArCH_3), 2.14 (3H, s, CH_3CN), 2.11 (12H, s, *o*-ArCH_3).[12] **^1H NMR** (400 MHz, CD_3CN) δ(ppm): 7.43 (2H, s, $HC{=}CH$), 7.21 (4H, s, *m*-Ar*H*), 4.79 (5H, s, C_5H_5), 2.43 (6H, s, *p*-ArCH_3), 2.16 (3H, s, CH_3CN), 2.12 (12H, s, *o*-ArCH_3).

$[Ni(\eta^5\text{-}C_5H_5)(CH_3CN)(SIMes)]^+(PF_6)^-$ (2b). Obtained from **1b** (160.0 mg, 0.343 mmol) and KPF_6 (63.0 mg, 0.342 mmol, 1 eq.) in acetonitrile (5.0 mL). Yield: 62%, yellow-brown solid (130.0 mg, 0.211 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.06 (4H, s, *m*-Ar*H*), 4.70 (5H, s, C_5H_5), 3.98 (4H, s, NCH_2–CH_2N), 2.38 (6H, s, *p*-ArCH_3), 2.33 (12H, s, *o*-ArCH_3), 2.20 (3H, s, CH_3CN). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ(ppm): 195.6 (NCN), 139.2 (^{Ar}C), 136.9 (^{Ar}C), 135.7 (^{Ar}C), 129.7 (^{Ar}C), 116.4 (CH_3CN), 93.8 (C_5H_5), 51.5 (NCH_2–CH_2N), 21.1 (*p*-ArCH_3), 18.5 (*o*-ArCH_3), 1.9 (CH_3CN). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −73.48 (d, *J* = 708.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ(ppm): −143.47 (sep, *J* = 708.7 Hz). **ESI MS** *m/z* (^{58}Ni): 470 ($[M - PF_6]^+$), 429 ($[M - CH_3CN - PF_6]^+$). **Anal.** Calc. for $C_{28}H_{34}F_6N_3NiP$: C, 54.57; H, 5.56; N, 6.82. Found: C, 54.38; H, 5.87; N, 7.34%.

$[Ni(\eta^5\text{-}C_5H_5)(CH_3CN)(SIPr)]^+(PF_6)^-$ (2c). Obtained from **1c** (219.0 mg, 0.398 mmol) and KPF_6 (72.8 mg, 0.396 mmol, 1 eq.) in acetonitrile (5.0 mL). Yield: 74%, yellow-brown solid (260.0 mg, 0.371 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.50 (2H, m, *J* = 7.6 Hz, *p*-Ar*H*), 7.35 (4H, d, *J* = 7.6 Hz, *m*-Ar*H*), 4.67 (5H, s, C_5H_5), 4.10 (4H, s, NCH_2–CH_2N), 3.15 (4H, m, *J* = 6.8 Hz, $CH(CH_3)_2$), 2.13 (3H, s, CH_3CN), 1.45 (12H, d, *J* = 6.8 Hz, $CH(CH_3)_2$), 1.30 (12H, d, *J* = 6.8 Hz, $CH(CH_3)_2$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ(ppm): 198.0 (NCN), 147.0 (^{Ar}C), 136.1 (^{Ar}C), 130.1 (^{Ar}C), 124.8 (CH_3CN), 94.1 (C_5H_5), 54.1 (NCH_2–CH_2N), 28.7 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 1.0 (CH_3CN). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −73.40 (d, *J* = 709.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ(ppm): −143.49 (sep, *J* = 709.1 Hz). **ESI MS** *m/z* (^{58}Ni): 513 ($[M - CH_3CN - PF_6]^+$). **Anal.** Calc. for $C_{34}H_{46}F_6N_3NiP$: C, 58.30; H, 6.62; N, 6.00. Found: C, 58.34; H, 6.66; N, 6.01%.

$[Ni(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)(CH_3CN)(SIMes)]^+(PF_6)^-$ (2d). Obtained from **1d** (104.0 mg, 0.206 mmol) and KPF_6 (37.0 mg, 0.203 mmol, 1 eq.) in acetonitrile (5.0 mL). Yield: 75%, yellow-brown solid (100.0 mg, 0.152 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.07 (4H, s, *m*-Ar*H*), 5.42 (1H, m, $=CH$), 4.89, 4.91, and 4.93 (2H, m, $=CH_2$), 4.73 (2H, m, *J* = 2.2 Hz, C_5H_4), 4.30 (2H, t, *J* = 2.4 Hz, C_5H_4), 4.00 (4H, s, NCH_2–CH_2N), 2.38 (6H, s, *p*-ArCH_3), 2.32 (12H, s, *o*-ArCH_3), 2.26 (3H, s, CH_3CN), 2.19 (2H, d, *J* = 6.8 Hz, $C_5H_4CH_2$). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ(ppm): 197.4 (NCN), 139.2 (^{Ar}C), 135.9 (*ipso*-^{Ar}C), 133.4 (^{Ar}C), 130.2 ($=CH$), 129.7 (^{mAr}C), 128.7 (CH_3CN), 116.8 ($=CH_2$), 114.8 ($C_5H_4CH_2$), 97.9 ($C_5H_4CH_2$), 86.7 ($C_5H_4CH_2$), 51.5 (NCH_2–CH_2N), 31.4 ($C_5H_4CH_2$), 21.1 (*p*-ArCH_3), 18.1 (*o*-ArCH_3), 3.9 (CH_3CN). **ESI MS** *m/z* (^{58}Ni): 510 ($[M - PF_6]^+$). 469 ($[M - CH_3CN - PF_6^-]^+$). **Anal.** Calc. for $C_{31}H_{38}N_3NiPF_6$: C, 56.7; H, 5.79; N, 6.40. Found: C, 56.4; H, 5.75; N, 6.28%.

$[Ni(\eta^5\text{-}C_5H_5)(CH_3CN)(IMes)]^+(ClO_4)^-$ (2e). Obtained from **1a** (100 mg, 0.216 mmol) and $AgClO_4$ (44.8 mg, 0.216 mmol, 1 eq.) in acetonitrile (3.0 mL). Yield: 98%, yellow solid (120.3 mg, 0.212 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.21 (2H, s, $HC{=}CH$), 7.13 (4H, s, *m*-Ar*H*), 4.77 (5H, s, C_5H_5), 2.43 (6H, s, *p*-ArCH_3), 2.23 (3H, s, CH_3CN), 2.12 (12H, s, *o*-ArCH_3). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ(ppm): 161.5 (NCN), 140. 4 (^{Ar}C), 135.6 (^{Ar}C), 135.0 (^{Ar}C), 129.8 (^{Ar}C), 130.1 (CH_3CN), 125.7 ($HC{=}CH$), 93.7 (C_5H_5), 21.4 (*p*-ArCH_3), 18.2 (*o*-ArCH_3), 4.5 (CH_3CN). **Anal.** Calc. for $C_{28}H_{31}ClN_3NiO_4$: C, 59.24; H, 5.50; N, 7.40. Found: C, 59.18; H, 5.64; N, 7.39%.

$[Ni(\eta^5\text{-}C_5H_5)(CH_3CN)(IMes)]^+(CF_3SO_3)^-$ (2f). Obtained from **1a** (100.0 mg, 0.216 mmol) and $AgCF_3SO_3$ (60.0 mg, 0.248 mmol, 1.15 eq.) in acetonitrile (3.0 mL). Yield: 98%, yellow solid (127.4 mg, 0.212 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.21 (2H, s, $HC{=}CH$), 7.13 (4H, s, *m*-Ar*H*), 4.76 (5H, s, C_5H_5), 2.43 (6H, s, *p*-ArCH_3), 2.22 (3H, s, CH_3CN), 2.11 (12H, s, *o*-ArCH_3). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ(ppm): 161.2 (NCN), 140.4 (^{Ar}C), 135.6 (^{Ar}C), 134.9 (^{Ar}C), 129.7 (^{Ar}C), 130.0 (CH_3CN), 125.7 ($HC{=}CH$), 93.7 (C_5H_5), 21.3 (*p*-ArCH_3), 18.2 (*o*-ArCH_3). 4.4 (CH_3CN). **^{19}F NMR** (376 MHz, $CDCl_3$)

δ(ppm): −78.65 (s). **Anal.** Calc. for $C_{29}H_{32}F_3N_3NiO_3S$: C, 56.33; H, 5.22; N, 6.80. Found: C, 56.31; H, 5.30; N, 6.79%.

[Ni(η^5-C$_5$H$_5$)((CH$_3$)$_3$CCN)(IMes)]$^+$(PF$_6$)$^-$ (2g). Obtained from **1a** (117.0 mg, 0.253 mmol) and KPF_6 (62.0 mg, 0.336 mmol, 1.33 eq.) in pivalonitrile (3.0 mL). Yield: 96%, yellow solid (159.3 mg, 0.243 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.26 (2H, s, *H*C=C*H*), 7.13 (4H, bs, *m*-Ar*H*), 4.75 (5H, s, C$_5$*H*$_5$), 2.44 (6H, s, *p*-ArC*H*$_3$), 2.09 (12H, s, *o*-ArC*H*$_3$), 1.24 (9H, s, (C*H*$_3$)$_3$CCN). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm): 159.9 (N*C*N), 140.2 (^{Ar}*C*), 138.2 (*C*N), 135.7 (^{Ar}*C*), 134.8 (^{Ar}*C*), 129.8 (^{Ar}*C*), 126.1 (H*C*=*C*H), 93.9 (*C*$_5$H$_5$), 30.9 ((CH$_3$)$_3$*C*CN), 27.6 ((*C*H$_3$)$_3$CCN), 21.4 (*p*-Ar*C*H$_3$), 18.2 (*o*-Ar*C*H$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −73.55 (d, *J* = 709.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ(ppm): −143.35 (sep, *J* = 709.0 Hz). **ESI MS** *m/z* (^{58}Ni): 427 ([M − (CH$_3$)$_3$CN − PF$_6$]$^+$). **Anal.** Calc. for $C_{31}H_{38}F_6N_3NiP$: C, 56.73; H, 5.84; N, 6.40. Found: C, 56.70; H, 5.77; N, 6.40%.

[Ni(η^5-C$_5$H$_5$)(CH$_3$CN)(Bn$_2$-bimy)]$^+$(PF$_6$)$^-$ (2h). Obtained from **1e** (112.1 mg, 0.245 mmol) and KPF_6 (55.0 mg, 0.299 mmol, 1.22 eq.) in acetonitrile (2.5 mL). Yield: 41%, yellow solid (60.8 mg, 0.100 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.37 (4H, m, Ar*H*), 7.33 (2H, m, Ar*H*), 7.30–7.24 (4H, m, Ar*H*), 7.11 (4H, bd, *J* = 7.1 Hz, Ar*H*), 6.45 (2H, bd, *J* = 13.5 Hz, C*H*$_2$), 6.19 (2H, bd, *J* = 13.8 Hz, C*H*$_2$), 5.22 (5H, s, C$_5$*H*$_5$), 2.03 (3H, s, C*H*$_3$CN). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm): 174.3 (N*C*N), 135.7 (^{Ar}*C*), 129.3 (^{Ar}*C*), 129.1 (CH$_3$*C*N), 128.23 (^{Ar}*C*), 126.2 (^{Ar}*C*), 125.4 (^{Ar}*C*), 124.2 (^{Ar}*C*), 111.5 (^{Ar}*C*), 93.82 (*C*$_5$H$_5$), 53.1 (*C*H$_2$Ph), 3.8 (*C*H$_3$CN). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −73.06 (d, *J* = 709.2 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ(ppm): −143.36 (sep, *J* = 709.2 Hz). **ESI MS** *m/z* (^{58}Ni): 421 ([M − CH$_3$CN − PF$_6$]$^+$). **Anal.** Calc. for $C_{28}H_{26}F_6PN_3Ni$: C, 55.30; H, 4.31; N, 6.91. Found: C, 55.14; H, 4.41; N, 6.90%.

[Ni(η^5-C$_5$H$_5$)(CH$_3$CN)(Bn$_2$-bimy)]$^+$(ClO$_4$)$^-$ (2i). Obtained from **1e** (70.0 mg, 0.153 mmol) and $AgClO_4$ (33.3 mg, 0.160 mmol, 1.05 eq.) in acetonitrile (1.5 mL). Yield: 68%, yellow solid (58.5 mg, 0.104 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.40–7.27 (10H, m, Ar*H*), 7.12 (4H, bd, *J* = 7.2 Hz, Ar*H*), 6.46 (2H, bd, C*H*$_2$), 6.23 (2H, bd, C*H*$_2$), 5.24 (5H, s, C$_5$*H*$_5$), 2.14 (3H, s, C*H*$_3$CN). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm): 174.2 (N*C*N), 135.7 (^{Ar}*C*), 129.6 (CH$_3$*C*N), 129.3 (^{Ar}*C*), 128.5 (^{Ar}*C*), 128.2 (^{Ar}*C*), 126.2 (^{Ar}*C*), 124.1 (^{Ar}*C*), 111.5 (^{Ar}*C*), 93.9 (*C*$_5$H$_5$), 53.2 (*C*H$_2$Ph), 4.4 (*C*H$_3$CN). **Anal.** Calc. for $C_{28}H_{26}ClN_3NiO_4\cdot 2H_2O$: C, 56.17; H, 5.05; N, 7.02. Found: C, 56.74; H, 4.95; N, 7.23%.

[Ni(η^5-C$_5$H$_5$)(CH$_3$CN)(IMes)]$^+$(NO$_3$)$^-$ (2j). This compound was prepared according to the general procedure for cationic complexes from **1a** (150.0 mg, 0.324 mmol) and $AgNO_3$ (55.5 mg, 0.327 mmol, 1 eq.) in acetonitrile (4.5 mL). Yield: 68%, yellow-green solid (116.7 mg, 0.220 mmol). **^{1}H NMR** (400 MHz, CD_3CN) δ(ppm): 7.42 (2H, s, *H*C=C*H*), 7.19 (4H, s, *m*-Ar*H*), 4.77 (5H, s, C$_5$*H*$_5$), 2.42 (6H, s, *p*-ArC*H*$_3$), 2.21(1.6H due to exchange with CD_3CN, bs, C*H*$_3$CN), 2.11 (12H, s, *o*-ArC*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN) δ(ppm): 160.0 (N*C*N), 140.8 (^{Ar}*C*), 136.8 (^{Ar}*C*), 136.3 (^{Ar}*C*), 130.2 (^{Ar}*C*), 127.0 (H*C*=*C*H), 94.24 (*C*$_5$H$_5$), 21.2 (*p*-Ar*C*H$_3$), 18.3 (*o*-Ar*C*H$_3$). **Anal.** Calc. for $C_{28}H_{32}N_4NiO_3$: C, 63.30; H, 6.07; N, 10.55. Found: C, 62.99; H, 6.07; N, 10.64%.

[Ni(η^5-C$_5$H$_5$)(CF$_3$COO)(IMes)] (3a). To a solution of [Ni(η^5-C$_5$H$_5$)(IMes)Cl] (**1a**) (80 mg, 0.173 mmol) in acetonitrile (2.0 mL) a solution of CF_3CO_2Ag (39 mg, 0.173 mmol, 1 eq.) in THF (1.0 mL) was added. The colour of the reaction mixture changed immediately from red to yellow. After 1 h of stirring at room temperature with protection from light the reaction mixture was filtered through Celite and evaporated *in vacuo*. The resulting red solid was washed with diethyl ether (2 × 3 mL) and dried *in vacuo* to give 63.5 mg of [Ni(C$_5$H$_5$)(CF$_3$COO)(IMes)] as a red solid (0.117 mmol, 68%). Toluene could be used instead of acetonitrile, providing **3a** in 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.11 (6H, s, *m*-Ar*H* and *H*C=C*H* overlapping), 4.62 (5H, s, C$_5$*H*$_5$), 2.44 (6H, s, *p*-ArC*H*$_3$), 2.09 (12H, s, *o*-ArC*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm): 166.2 (N*C*N), 163.8 (q, *J* = 35.6 Hz, *C*O), 139.34 (^{Ar}*C*), 136.3 (^{Ar}*C*), 135.6 (^{Ar}*C*), 129.3 (^{Ar}*C*), 124.6 (H*C*=*C*H), 114.1 (q, *J* = 291.4 Hz, *C*F$_3$), 91.3 (*C*$_5$H$_5$), 21.5 (*p*-Ar*C*H$_3$), 18.0 (*o*-Ar*C*H$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −74.73 (s). **EI MS** (70 eV) *m/z* (^{58}Ni): 540 (M$^+$, 24%), 475 ([M − Cp]$^+$, 29), 427 ([M − CF$_3$CO$_2$]$^+$, 29), 303 (IMes$^+$, 100). **Anal.** Calc. for $C_{28}H_{29}F_3N_2NiO_2$: C, 62.14; H, 5.40; N, 5.18. Found: C, 62.18; H, 5.51; N, 5.20%.

[Ni(η^5-C$_5$H$_5$)(CF$_3$COO)(SIMes)] (3b). This compound was prepared similarly as described for **3a** from **1b** (90.0 mg, 0.194 mmol) and CF_3CO_2Ag (43.0 mg, 0.195 mmol, 1 eq.). Yield: 63%, red solid (66.3 mg, 0.122 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.07 (4H, s, *m*-Ar*H*), 4.62 (5H, s, C$_5$*H*$_5$), 3.93 (4H, s, *H*$_2$C–C*H*$_2$), 2.40 (6H, s, *p*-ArC*H*$_3$), 2.31 (12H, s, *o*-ArC*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm): 199.4 (N*C*N), 163.8 (q, *J* = 35.4 Hz, *C*O), 138.5 (^{Ar}*C*), 136.6 (^{Ar}*C*), 136.5 (^{Ar}*C*), 129.6 (^{Ar}*C*), 114.1 (q, *J* = 291.5 Hz, *C*F$_3$), 91.6 (*C*$_5$H$_5$), 51.2 (NH$_2$*C*–*C*H$_2$N), 21.4 (*p*-Ar*C*H$_3$), 18.0 (*o*-Ar*C*H$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$) δ(ppm): −74.30 (s). **EI MS** (70 eV) *m/z* (^{58}Ni): 542 (M$^+$, 17%), 477 ([M − Cp]$^+$, 16), 429 ([M − CF$_3$CO$_2$]$^+$, 26), 305 (SIMes$^+$, 100). **Anal.** Calc. for $C_{28}H_{31}F_3N_2NiO_2$: C, 61.91; H, 5.75; N, 5.16. Found: C, 61.71; H, 5.83; N, 5.18%.

[Ni(η^5-C$_5$H$_5$)(NO$_3$)(IMes)] (3c). This compound was prepared similarly as described for **3a** from **1a** (64.0 mg, 0.138 mmol) and $AgNO_3$ (24.0 mg, 0.141 mmol, 1 eq.) in toluene–THF (1.8 mL/1.8 mL) with overnight stirring. Yield: 98%, red solid (66.1 mg, 0.135 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm): 7.24 (2H, s, *H*C=C*H*), 7.12 (4H, s, *m*-Ar*H*), 3.53 (5H, s, C$_5$*H*$_5$), 2.43 (6H, s, *p*-ArC*H*$_3$), 2.16 (12H, s, *o*-ArC*H*$_3$). **^{1}H NMR** (400 MHz, C_6D_6) δ(ppm): 6.86 (4H, s, *m*-Ar*H*), 6.40 (2H, s, *H*C=C*H*), 2.34 (5H, s, C$_5$*H*$_5$), 2.15 (6H, s, *p*-ArC*H*$_3$), 2.06 (12H, s, *o*-ArC*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm): 139.5 (^{Ar}*C*), 136.5 (^{Ar}*C*), 135.5 (^{Ar}*C*), 129.4 (^{Ar}*C*), 126.8 (H*C*=*C*H), 97.1 (*C*$_5$H$_5$), 21.4 (*p*-Ar*C*H$_3$), 18.1 (*o*-Ar*C*H$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ(ppm): 139.5 (s, ^{Ar}*C*), 136.5 (s, ^{Ar}*C*), 135.5 (s, ^{Ar}*C*), 129.4 (d, *J* = 151.8 Hz, Mes), 126.6 (d, *J* = 195.1 Hz, H*C*=*C*H), 96.9 (d, *J* = 169.3 Hz, *C*$_5$H$_5$), 21.4 (q, *J* = 127.3 Hz, *p*-Ar*C*H$_3$), 18.1 (q, *J* = 127.5 Hz, *o*-Ar*C*H$_3$). **EI MS** (70 eV) *m/z* (^{58}Ni): 424 ([M − Cp]$^+$, 80%), 378 ([M − Cp − NO$_2$]$^+$, 19), 320 (100), 302 (84). **Anal.** Calc. for $C_{26}H_{29}N_3NiO_3 \cdot H_2O$: C, 61.44; H, 6.15; N, 8.27. Found: C, 61.85; H, 5. 92; N, 8.52%. Magnetic susceptibility measurements by Evans' method in toluene-d_8 up to 100 °C gave $\mu \approx 0$.

Attempted exchange of nitrile with styrene in 2

Complex $[Ni(\eta^5\text{-}C_5H_5)(SIMes)(CH_3CN)]^+PF_6^-$ (**2b**) (40.0 mg, 65.0 μmol) was dissolved in THF (1.0 mL) in a Schlenk tube and styrene (neat, 0.3 mL, 2.6 mmol, 40 eq.) was added. This solution was stirred at 50 °C for 4 h. The reaction mixture was evaporated *in vacuo* and the solid residue was washed with hexane (2.0 mL) and diethyl ether (2.0 mL), and dried *in vacuo* at room temperature. The solid thus obtained, according to ^1H NMR analysis, appeared to be substrate **2b**. When CH_2Cl_2 (0.3 mL) was used instead of THF at 35 °C, no reaction occurred. Stirring of **2b** (107.0 mg, 173.9 μmol) in styrene (neat, 1.5 mL, 13.0 mmol, 74.8 eq.) at 50 °C gave the same result. Attempts to exchange the pivalonitrile ligand in **2g** under conditions analogous to those for **2b** in THF also failed. Complex **2h** (20.0 mg, 32. 9 μmol) stirred in styrene (neat, 1.0 mL, 8.7 mmol, 967 eq.) at 35 °C underwent transformation to an inseparable mixture of green nickel complexes (by ^1H NMR).

Catalytic activity

General procedure for styrene polymerization. To a suspension of $[Ni(\eta^5\text{-}C_5H_5)(IMes)(CH_3CN)]^+(ClO_4)^-$ (**2e**) (9.3 mg, 16.4 μmol) in toluene (10.0 mL) a solution of MAO in toluene (10% wt. from Aldrich) was added (1.15 mL, Al/Ni = 100). The colour of the reaction mixture changed immediately from pale yellow to brown and white fumes appeared. After stirring for 30 min at room temperature, styrene was added (neat, 1.95 mL, 17.0 mmol). The resulting mixture was immersed in a preheated oil bath maintained at 50 °C and stirred vigorously for 3 h at this temperature. After cooling to the room temperature the reaction mixture was poured into methanol (*ca.* 200 mL). The resulting polystyrene was isolated by filtration, washed with methanol, and dried *in vacuo*. Yield: 1.77 g, 31%. **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ(ppm): 146.3–145.1 (*ipso*-C_6H_5), 128.6–126.7 (C_6H_5), 126.1–125.6 (C_6H_5), 44.1–41.5 (CH), 40.5, 40.3 (CH_2). MALDI-TOF MS (DCTB, $AgCF_3CO_2$) *m/z*: 1459.7 $[(C_8H_8)_{13}{}^{107}Ag]^+$, 1563.8 $[(C_8H_8)_{14}{}^{107}Ag]^+$, 1667.8 $[(C_8H_8)_{15}{}^{107}Ag]^+$.

General procedure for Suzuki cross-coupling. 4′-Bromoacetophenone (55.1 mg, 0.277 mmol) and phenyl-boronic acid (44.0 mg, 0.361 mmol, 1.3 eq.) were dissolved in toluene (0.80 mL) in a Schlenk tube. Solid K_3PO_4 (153 mg, 0.722 mmol, 2.6 eq.) and tetradecane (internal standard, 7.0 μL) were then added, followed by **2e** (5.0 mg, 8.8 μmol, $3.2\%_{mol}$). The tube was immersed in a preheated oil bath maintained at 90 °C and stirred for 1 h at this temperature. After cooling to the room temperature, the reaction mixture was diluted with diethyl ether, washed with water and dried over anhydrous Na_2SO_4. The substrate conversion (74%) and selectivity were determined with GC.

X-ray diffraction studies

Single crystals of **2c** suitable for X-ray studies were obtained from a CH_2Cl_2–hexanes (1 : 2) solution; single crystals of **3a** and **3c** were obtained from saturated toluene–hexane solutions at 4 °C; compound **2j** was crystallized from a mixture of acetonitrile and diethyl ether at 4 °C. Diffraction data of suitable single crystals were measured on an Agilent κ-CCD Gemini A Ultra diffractometer with graphite-monochromated Mo-Kα radiation at 100(2) K for compounds **2c** and **3a**, and at 293(2) K for **2j** and **3c**. Cell refinement and data collection as well as data reduction and analysis were performed with the CrysAlis^PRO software.[35] The structures were solved by direct methods and subsequent Fourier-difference synthesis with ShelXS and refined by full-matrix least-squares against F^2 with ShelXL within the Olex2 program suite.[36,37] 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. Asymmetric unit of complex **3a** contained one half of a severely disordered toluene molecule which was treated with the SQUEEZE procedure implemented in PLATON.[38] The structure model of compound **3c** was refined as an inversion twin with the twin ratio refined to 43 : 57. Attempts to refine the crystal structure in centrosymmetric space group failed giving unphysical ADPs. Data analysis was carried out using Olex2 and PLATON. Crystal data and structure refinement parameters are given in Table 1 and CCDC 972867–972870.

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Notes and references

1 (*a*) W. A. Hermann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*b*) L. Cavallo, A. Correa, C. Costabile and H. Jacobsen, *J. Organomet. Chem.*, 2005, **690**, 5407; (*c*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (*d*) S. Diez-Gonzales, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.

2 For selected recent examples, see: (*a*) C. J. E. Davies, M. J. Page, C. E. Ellul, M. F. Mahhon and M. K. Whittlesey, *Chem. Commun.*, 2010, **46**, 5151; (*b*) S. Miyazaki, Y. Koga, T. Matsumoto and K. Matsubara, *Chem. Commun.*, 2010, **46**, 1932; (*c*) K. Zhang, M. Conda-Sheridan, S. R. Cooke and J. Louie, *Organometallics*, 2011, **30**, 2546; (*d*) C. Lohre, T. Dröge, C. Wang and F. Glorius, *Chem.–Eur. J.*, 2011, **17**, 6052; (*e*) B. Liu, X. Liu, C. Chen, C. Chen and W. Chen, *Organometallics*, 2012, **31**, 282; (*f*) H. Song, D. Fan, Y. Liu, G. Hou and G. Zi, *J. Organomet. Chem.*, 2013, **729**, 40;

(*g*) K. Vin Tan, J. L. Dutton, B. W. Skelton, D. J. D. Wilsom and P. J. Barnard, *Organometallics*, 2013, **32**, 1913; (*h*) E. A. Bielinski, W. Dai, L. M. Guard, N. Hazari and M. K. Takase, *Organometallics*, 2013, **32**, 4025.

3 C. D. Abernethy, A. H. Cowley and R. A. Jones, *J. Organomet. Chem.*, 2000, **596**, 3.

4 (*a*) R. A. Kelly, N. M. Scott, S. Diez-Gonzalez, E. D. Stevens and S. P. Nolan, *Organometallics*, 2005, **24**, 3442; (*b*) A. R. Martin, Y. Makida, S. Meiries, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2013, **32**, 6265.

5 W. Buchowicz, A. Kozioł, L. B. Jerzykiewicz, T. Lis, S. Pasynkiewicz, A. Pęcherzewska and A. Pietrzykowski, *J. Mol. Catal. A: Chem.*, 2006, **257**, 118.

6 E. F. Hahn, B. Heidrich, A. Hepp and T. Pape, *J. Organomet. Chem.*, 2007, **692**, 4630.

7 V. Ritleng, C. Barth, E. Brenner, S. Milosevic and M. J. Chetcuti, *Organometallics*, 2008, **27**, 4223.

8 W. Buchowicz, W. Wojtczak, A. Pietrzykowski, A. Lupa, L. B. Jerzykiewicz, A. Makal and K. Woźniak, *Eur. J. Inorg. Chem.*, 2010, 648.

9 A. M. Oertel, V. Ritleng and M. J. Chetcuti, *Organometallics*, 2012, **31**, 2829.

10 O. R. Luca, B. A. Thompson, M. K. Takase and R. H. Crabtree, *J. Organomet. Chem.*, 2013, **730**, 79.

11 W. Buchowicz, J. Conder, D. Hryciuk and J. Zachara, *J. Mol. Catal. A: Chem.*, 2014, **381**, 16.

12 V. Ritleng, A. M. Oertel and M. J. Chetcuti, *Dalton Trans.*, 2010, **39**, 8153.

13 D. A. Malyshev, N. M. Scott, N. Marion, E. D. Stevens, V. P. Ananikov, I. P. Beletskaya and S. P. Nolan, *Organometallics*, 2006, **25**, 4462.

14 (*a*) L. Postigo and B. Royo, *Adv. Synth. Catal.*, 2012, **354**, 2613; (*b*) L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J.-B. Sortais and V. Ritleng, *Adv. Synth. Catal.*, 2012, **354**, 2619.

15 D. Gareau, C. Sui-Seng, L. F. Groux, F. Brisse and D. Zargarian, *Organometallics*, 2005, **24**, 4003.

16 A. M. Oertel, J. Freudenreich, J. Gein, V. Ritleng, L. F. Veiros and M. J. Chetcuti, *Organometallics*, 2011, **30**, 3400.

17 A. M. Oertel, V. Ritleng, A. Busiah, L. F. Veiros and M. J. Chetcuti, *Organometallics*, 2011, **30**, 6495.

18 As suggested by a referee, we tried to observe both **2j** and **3c** in coexistence; in a mixed solvent $CDCl_3$–CD_3CN both species were observed by ^1H NMR in a *ca.* 1 : 1 ratio (according to Cp integration).

19 H. V. Huynh, Y. Han, R. Jothibasu and J. A. Yang, *Organometallics*, 2009, **28**, 5395.

20 Typical values of ^1H NMR chemical shifts for η^5-Cp ligands in reported [Ni(Cp)(X)(NHC)] complexes are in the range from 4.5 to 4.8 ppm. See ref. 4–10.

21 For an example of spin equilibrium in a half-sandwich nickel complex [Cp*Ni(acac)] see: M. E. Smith and R. A. Andersen, *J. Am. Chem. Soc.*, 1996, **118**, 11119; for spin equilibria in square-planar/tetrahedral complexes [NiX_2L_2] see: R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, 1963, **2**, 1701; G. R. van Hecke and W. D. Horrocks, *Inorg. Chem.*, 1966, **5**, 1968; G. N. La Mar and E. O. Sherman, *J. Am. Chem. Soc.*, 1970, **92**, 2691.

22 P. Gütlich, B. R. McGarvey and W. Kläui, *Inorg. Chem.*, 1980, **19**, 3704.

23 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

24 G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton, *J. Am. Chem. Soc.*, 1953, **75**, 1011.

25 F. H. Köhler, *J. Organomet. Chem.*, 1976, **110**, 235.

26 P. Seiler; and J. D. Dunitz, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 2255.

27 The CSD (version 5.34, May 2013) search was restricted to complexes containing Ni cations with both Cp and NHC ligands. Only structures with *R* factor lower than 0.05 and containing neither errors nor disorder were considered. The resulting data set comprises 20 entries.

28 (*a*) L. F. Johnson, F. Heatley and F. A. Bovey, *Macromolecules*, 1970, **3**, 175; (*b*) N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi, *Macromolecules*, 1986, **19**, 2464.

29 In this "classical" cationic polymerization propagation occurs through addition of a monomer to the carbocation.

30 A. M. Oertel, V. Ritleng, L. Burr and M. J. Chetcuti, *Organometallics*, 2011, **30**, 6685.

31 A related Ni(0)–NHC–$(styrene)_2$ complex has been also reported; see M. J. Iglesias, J. F. Blandez, M. R. Fructos, A. Prieto, E. Álvarez, T. R. Belderrain and M. C. Nicasio, *Organometallics*, 2012, **31**, 6312.

32 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1988.

33 K. W. Barnett, *J. Chem. Educ.*, 1974, **51**, 422.

34 W. Buchowicz, L. B. Jerzykiewicz, A. Krasińska, S. Losi, A. Pietrzykowski and P. Zanello, *Organometallics*, 2006, **25**, 5076.

35 *CrysAlisPro Software system*, Agilent Technologies UK Ltd, Oxford, UK, 2011.

36 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.

37 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

38 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.