Complexes LNi(Cp)X with alkylamino-substituted N-heterocyclic carbene ligands (L) and their catalytic activity in the Suzuki—Miyaura reaction

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New nickel(II) complexes of the general formula LNi(Cp)X (L is an N-heterocyclic carbene (NHC) ligand of the 1,2,4-triazole or imidazole series; Cp is the cyclopentadienyl anion; X = Cl, I) are reported. In these complexes, the NHC ligands (L) contain an alkylamino group at the 3 or 4 position of the heterocycle. The synthesized complexes and structurally similar complexes without an alkylamino group were tested for catalytic activity in the Suzuki—Miyaura reaction. The introduction of an alkylamino group into the NHC ligand leads to the enhancement of the catalytic activity of complexes with *N,N′*-diaryl-substituted NHC ligands of the imidazole series and a decrease in the activity of the complexes with *N,N′*-dialkyl-substituted NHC ligands of the 1,2,4-triazole series.

Key words: N-heterocyclic carbenes, nickel, catalysis, Suzuki—Miyaura reaction.

Metal-catalyzed cross-coupling reactions serve as an indispensable tool for state-of-the-art organic synthesis.[1—6] Palladium plays a significant role in the catalysis of various cross-coupling reactions.[1,3,6—8] However, a drawback of palladium is its high cost. Hence, great efforts are being made to develop new efficient catalysts based on more available non-noble metals. Nickel is considered as a promising alternative for palladium in many reactions of organic synthesis.[1,9—11] Ligands have a significant effect on the efficiency of nickel catalysts.[1,4,10,11] For instance, nickel complexes with N-heterocyclic carbenes (NHC) are becoming increasingly popular in the catalysis of many cross-coupling reactions,[1,9,10,12] including the Suzuki—Miyaura reaction commonly employed for the carbon—carbon bond formation.[13—17] Advantages of NHCs over many other ligands, for example, phosphines, are the relative ease of the preparation, lower toxicity, high variability of the steric and electronic parameters, and considerable stability of the Ni—NHC bond due to high σ-donor ability of these ligands.[18—21] Readily available and air-stable complexes LNi(Cp)X (Cp is the cyclopentadienyl anion, X is halogen, L is a NHC ligand),[17,22—27] produced in one step from the azolium salts NHC · HX (NHC proligands) and nickelocene [$Ni(Cp)_2$],[14] are widely used in the catalysis of the Suzuki—Miyaura reaction.

Special electron-donating or -withdrawing groups, which are either ionizable or charge-bearing, are often introduced into NHC ligands in order to change the electronic and steric parameters, polarity, solubility, and other properties of the complexes, in particular their catalytic activity.[28] For example, the introduction of alkylamino and dialkylamino groups as substituents at the 4 and 5 positions of the imidazole ring makes it possible to increase the activity of Pd complexes with NHC ligands in the Buchwald—Hartwig reaction due to the electron-donating effect of alkylamino groups and the so-called buttressing effect of *N*-aryl substituents.[29—33] Palladium complexes with 3-arylamino-substituted NHC ligands of the 1,2,4-triazole series exhibit high activity in the Suzuki—Miyaura reaction.[34] It is assumed that the electron-donating and buttressing effects of a substituted amino group accelerate the oxidative addition of aryl halide and the subsequent reductive elimination of the cross-coupling product.[29—33] However, the effect of the alkylamino group, which is capable of conjugation with the aromatic system of the NHC ligand, on the catalytic activity of nickel complexes has not been investigated, and Ni complexes with 3(4)-alkylamino-substituted NHC ligands of the 1,2,4-triazole and imidazole series are not described in the literature.

Herein, we report the synthesis of new complexes LNi(Cp)X with 3(4)-alkylamino-substituted NHC ligands of the 1,2,4-triazole and imidazole series and the investigation of the effect of the alkylamino group on the catalytic activity of the complexes in the Suzuki—Miyaura reaction.

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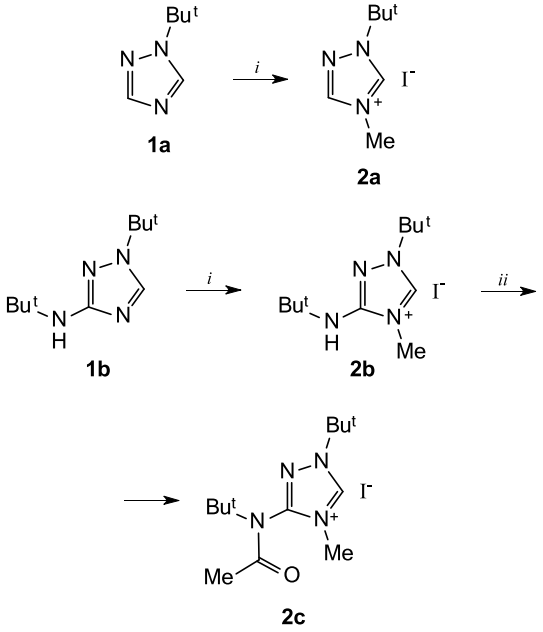
To evaluate the effect of alkylamino groups on the catalytic activity, it was reasonable to compare the catalytic properties of structurally similar complexes, which differ only by the presence of the corresponding alkylamino group in the NHC ligand. Therefore, we synthesized *N*,*N*′-dialkyl-1,2,4-triazolium and *N*,*N*′-diarylimidazolium salts as NHC proligands needed for the synthesis of the corresponding Ni complexes.

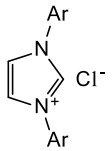
The alkylation of triazoles **1a,b**[35,36] with iodomethane afforded NHC proligands of the 1,2,4-triazole series **2a,b**, and the acylation of compound **2b** with acetic anhydride gave compound **2c** (Scheme 1).

Scheme 1



Reagents and conditions: *i*. CH_3I, acetonitrile, 80 °C, 12 h; *ii*. Ac_2O, reflux, 2 h.

Imidazolium NHC proligands **2d—f** containing alkyl- and dialkylamino groups at the 4 position of the imidazole ring were synthesized based on the approach proposed previously (Scheme 2)[37,38] by the alkylation of formamidines **3a,b** with chloroacetic acid amides **4a,b** followed by the cyclization of alkylation products **5a,b** with trifluoromethanesulonic anhydride. The use of *N*,*N*-diisopropylethylamine (DIPEA) instead of Et_3N as a base made it possible to significantly reduce the time of synthesis compared to the procedure described previously.[37,38]



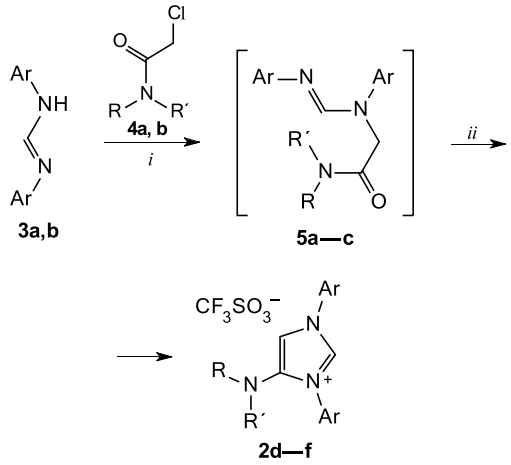
2g,h

Ar = Mes (**g**), DiPP (**h**)

Proligands **2g** and **2h** were synthesized by known procedures.[39]

The complexes LNi(Cp)X (**6a—h**) were prepared by heating proligands **2a—h** with nickelocene in THF using

Scheme 2

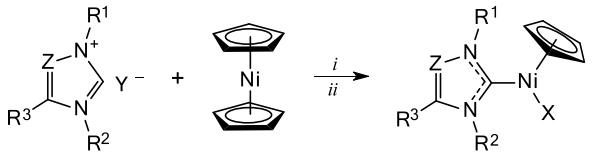


2, 3: Ar is 2,4,6-trimethylphenyl (Mes) (**2d,e**, **3a**), 2,6-diisopropylphenyl (DiPP) (**2f**, **3b**);
2, 4, 5: R = H, R′ = Bu^t (**2d,f**, **4a**, **5a,b**); R—R′ = $(CH_2)_4$ (**2e**, **4b**, **5c**)

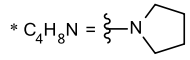
Reagents and conditions: *i*. DIPEA, DMA, 140 °C; *ii*. $(CF_3SO_2)_2O$, CH_2Cl_2, 2,4,6-trimethylpyridine, –75 °C.

a general procedure[26,40] (Scheme 3). The synthesis of complexes **6d—f** from triflates **2d—f** was accomplished in the presence of tetraethylammonium chloride as a source of chloride ions (see Scheme 3).

Scheme 3



Compound **2**, **6**	Z	**2**, **6** R^1	R^2	R^3	**2** Y	**6** X
a	N	Bu^t	Me	H	I	I
b	N	Bu^t	Me	Bu^{t}NH	I	
c	N	Bu^t	Me	Ac(Bu^t)N	I	I
d	CH	Mes	Mes	Bu^{t}NH	CF_3SO_3	Cl
e	CH	Mes	Mes	C_4H_8N*	CF_3SO_3	Cl
f	CH	DiPP	DiPP	Bu^{t}NH	CF_3SO_3	Cl
g	CH	Mes	Mes	H	Cl	Cl
h	CH	DiPP	DiPP	H	Cl	Cl

* C_4H_8N = 

Reagents and conditions: *i*. THF, 70 °C for **2a—c,g,h**; *ii*. $[Et_4N]Cl$, THF, 70 °C for **2d—f**.

The synthesized complexes are air-stable red-purple crystalline compounds. The structures of new complexes **6a—f** were confirmed by ^1H and ^{13}C NMR spectroscopy

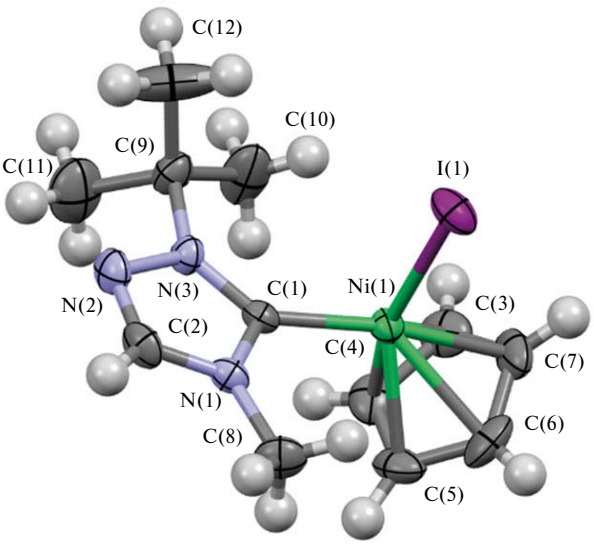


Fig. 1. X-ray molecular structure of compound **6a**.

and elemental analysis. The structures of compounds **6a—c** were also determined by X-ray diffraction (Figs 1—3). The ^{1}H NMR spectra show characteristic signals of substituents of the NHC ligands and a singlet of the Cp ligand at δ_H 4.5—5.3. The complexes containing the Bu^{t}NH substituent give a singlet of NH at δ_H 3.5 (**6b**) or 2.8 (**6d,f**), which disappears upon deuteration. In the ^{1}H NMR spectrum of complex **6c**, the signals of the acetyl and N-methyl groups and the signal of the Cp ligand are split due apparently to hindered rotation of the Ac(Bu^t)N group.

According to the X-ray diffraction data, the geometric parameters of molecules **6a—c** are similar to those of the complexes LNi(Cp)X with NHC ligands of the triazole series described previously.[41,42] The nickel atom is nearly in the plane of the triazole ring; the maximum deviation (0.209(8) Å) from the mean C(1),N(1),C(2),N(2),N(3) plane is observed in compound **6b**. The Ni(1)—I(1) bond is nearly perpendicular to the C(1)—Ni(1) bond. The I(1)—Ni(1)—C(1) bond angle is 92.9(1)° in compound **6a**, 98.2(2)° in compound **6b**, and 93.8(2)° in compound **6c**. The C(1)—Ni(1) bond length (1.890(5), 1.888(5), and 1.882(9) Å in molecules **6a**, **6b**, and **6c**, respectively) only slightly depends on the nature of the alkylamino group in the NHC ligand and is quite similar to the typical values published in the literature (1.860—1.876 Å).[41,42] In compound **6b**, the alkylamino group adopts a planar configuration (the sum of the bond angles at the N(4) atom is 360°) and is nearly coplanar with the triazole ring (the C(9)—N(4)—C(2)—N(2) torsion angle is 4.6(8)°, the deviation of the N(4) atom from the mean plane of the triazole ring is as small as 0.050(8) Å). This is indicative of the possible conjugation of the N atom lone pair of the alkylamino group with the π system of the NHC ligand. In compound **6c**, the N(4) atom of the Ac(Bu^t)N group is significantly flattened (the sum of the bond angles at the N(4) atom is 359.1°). However, unlike the *tert*-butylamino group of compound **6b**, the Ac(Bu^t)N group of molecule **6c** is nearly orthogonal to the plane of the triazole ring; the C(9)—N(4)—C(2)—N(2) torsion angle is 84.8(9)°.

To evaluate the effect of the alkylamino group of the NHC ligand on the catalytic activity of Ni/NHC complexes, compounds **6a—f** were tested in the catalysis of the cross-coupling of 4-chloroacetophenone (**7a**) with phenylboronic acid (**8a**) in dioxane containing H_2O (1 vol.%) in the presence of KOH as a base (Scheme 4, Table 1). The conditions for the preliminary evaluation of the catalytic activity of the complexes were chosen taking into account that the aqueous dioxane—KOH system proved to be highly efficient in the Ni/L-catalyzed Suzuki—Miyaura

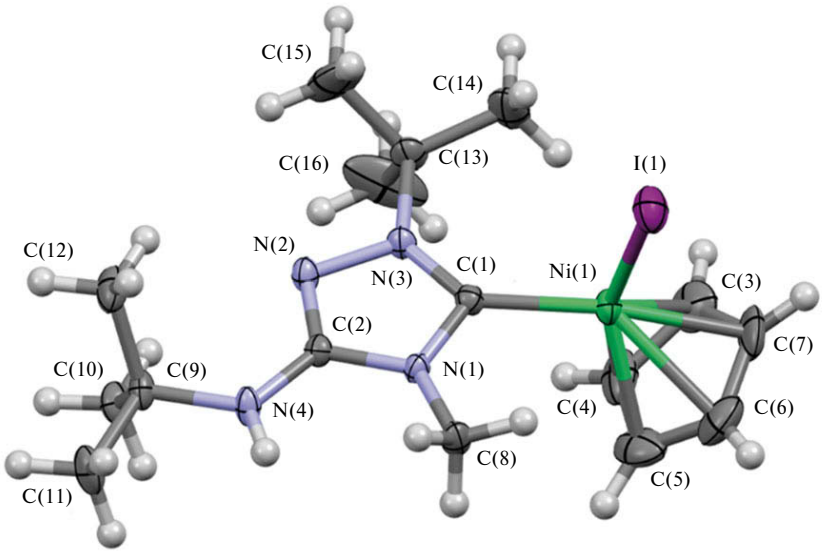


Fig. 2. X-ray molecular structure of compound **6b**.

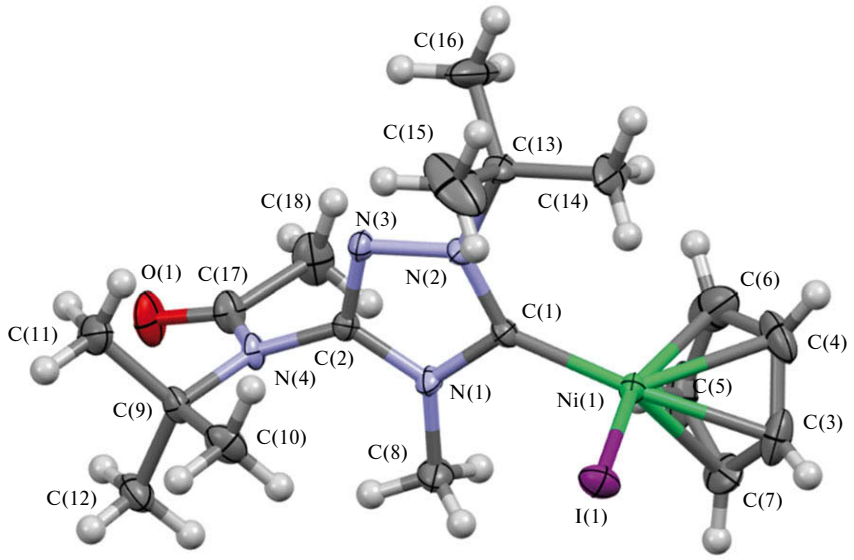
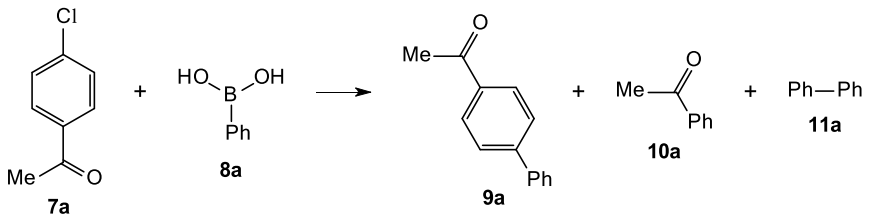


Fig. 3. X-ray molecular structure of compound **6c**.

reaction.[16] It is worth noting that the complexes containing the *tert*-butylamino group (**6b**) or the *N*-acetyl-*N*-*tert*-butylamino group (**6c**) showed lower catalytic activity (runs *2* and *3*) than complex **6a**, in which the NHC ligand at the 3 position is not replaced (run *1*). The opposite effect of the alkylamino group is observed in complexes **6d—h** containing the imidazol-2-ylidene NHC ligands with aryl substituents at the nitrogen atoms of the imidazole ring. The introduction of an alkylamino group leads to a significant increase in the activity of the complexes with N-mesityl substituents at the nitrogen atoms of the NHC ligand. For example, the yield of compound **9a** in the reaction catalyzed by complex **6g**, which does not contain an alkylamino group at the 4 position of the imidazole ring, is 62% (run *4*), whereas the yield in the reaction catalyzed by complexes **6d,e** with functionalized NHC ligands is 90% and 89%, respectively (runs *5* and *6*). A comparison of the activity of complexes **6h** (run *7*) and **6f** (run *8*) shows that in the case of the bulkier 2,6-diisopropylphenyl substituents at the nitrogen atoms of the NHC ligand, the introduction of an alkylamino group (complex **6f**) also leads to a slight increase in the catalytic activity.

The factors responsible for the different effects of the alkylamino group on the catalytic activity of the complexes with 1,2,4-triazol-5-ylidene and imidazol-2-ylidene ligands are unclear. In our opinion, the opposite effects of the alkylamino group on the activity of complexes **6b,c** and **6e,f,h** can be attributed primarily to the nature of substituens at the nitrogen N atoms of the NHC ligand rather than to the structure of the heterocycle. Complexes **6a—c** contain aliphatic substituents at the N atoms. Apparently, steric interactions between the alkylamino group and *N*-alkyl substituents in the 1,2,4-triazolylidene ligands induce destabilizing steric hindrance in the transition state of the Suzuki—Miyaura reaction. However, according to the literature data, specific non-covalent interactions can occur in complexes with *N,N′*-diarylimidazol-2-ylidene ligands between *N*-aryl substituents and aryl groups coordinated to the metal.[43,44] These interactions reduce the energy of the transition state.[43,44] The alkylamino group can exert the buttressing effect of *N*-aryl substituents, thereby enhancing non-covalent interactions in the transition state, which can lead to the acceleration of the Suzuki—Miyaura reaction.[32] The

Scheme 4



Reaction conditions: 7a (0.25 mmol), **8a** (0.35 mmol), base (0.35 mmol), catalyst **6a—h**, solvent (2 mL), argon, 120 °C, 12 h.

Table 1. Catalytic activity of complexes **6a—h** in the reaction of 4-chloroacetophenone (**7a**) with phenylboronic acid (**8a**)

Run	Catalyst (mol.%)[a]	Solvent	Base	C^b (%)	Yield (%)[c]		
					9a	**10a**	**11a**
1	**6a** (1)	Dioxane + 1% H_2O	KOH	81	79	2	—[d]
2	**6b** (1)	The same	KOH	77	75	2	—[d]
3	**6c** (1)	»	KOH	45	42	3	—[d]
4	**6g** (1)	»	KOH	65	62	3	0
5	**6d** (1)	»	KOH	91	90	1	—[d]
6	**6e**(1)	»	KOH	90	89	1	—[d]
7	**6h** (1)	»	KOH	91	89	2	—[d]
8	**6f** (1)	»	KOH	93	92	1	—[d]
9	**6f** (3)	»	KOH	96	92	3	—[d]
10	**6f** (0.5)	»	KOH	68	68	0	—[d]
11	**6f** (0.1)	»	KOH	34	34	0	—[d]
12	**6f** (1)	Dioxane	KOH	65	52	8	0
13	**6f** (1)	Dioxane	K_3PO_4	5	5	0	—[d]
14	**6f** (1)	Dioxane	Cs_2CO_3	25	24	—[d]	1
15	**6f** (1)	Dioxane	$NaOBu^t$	26	25	0	0
16	**6f** (1)	Toluene	KOH	44	42	—[d]	2
17	**6f** (1)	Toluene	K_3PO_4	42	40	—[d]	2

[a] The amount of the catalyst (mol.%) relative to aryl halide **7a**.
[b] The conversion of compound **7a**.
[c] GC-MS data.
[d] Traces.

mechanism of the effect of the alkylamino group on the catalytic activity of the complexes under study requires an additional more detailed investigation.

Among the characterized complexes, compound **6f** showed the highest activity (see Table 1, run *8*). Since the variation of the used amounts of the catalyst, solvent, and base did not lead to an increase in the yield of the target product **9a** (see Table 1, runs *9—17*), the conditions of run *8* were accepted as optimal. Under the optimized conditions, the coupling of aryl chlorides **7a—f**

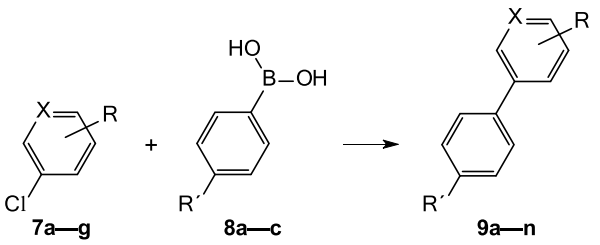
Table 2. Yields of biaryls **9a—n** in the reaction of aryl halides **7a—f** and 3-chloropyridine **7g** with arylboronic acids **8a—c** catalyzed by complex **6f**[a]

Run	**7**	**8**	C^b (%)	Product	X	R	R′	Yield of **9** (%)[c]
1	**7a**	**8a**	92	**9a**	CH	COMe	H	92
2	**7b**	**8a**	93	**9b**	CH	H	H	92
3	**7c**	**8a**	63	**9c**	CH	Me	H	61
4	**7d**	**8a**	59	**9d**	CH	OMe	H	56
5	**7e**	**8a**	92	**9e**	CH	CN	H	86
6	**7f**	**8a**	99	**9f**	CH	CF_3	H	98
7	**7g**	**8a**	90	**9g**	N	H	H	87
8	**7a**	**8b**	63	**9h**	CH	COMe	CF_3	61
9	**7b**	**8b**	55	**9f**	CH	H	CF_3	52
10	**7e**	**8b**	65	**9i**	CH	CN	CF_3	63
11	**7f**	**8b**	66	**9j**	CH	CF_3	CF_3	65
12	**7g**	**8b**	85	**9k**	N	H	CF_3	83
13	**7a**	**8c**	73	**9l**	CH	COMe	OMe	71
14	**7e**	**8c**	65	**9m**	CH	CN	OMe	64
15	**7g**	**8c**	60	**9n**	N	H	OMe	58

[a] Reaction conditions: halide **7a—g** (0.25 mmol), arylboronic acid **8a—c** (0.35 mmol), KOH (0.35 mmol), complex **6f** (1.5 mg, 2.5 μmol, 1 mol.%), aqueous dioxane (1 vol.% H_2O, 2 mL), 120 °C, 12 h.
[b] The conversion of aryl halide **7a—g**.
[c] GC-MS data.

and 3-chloropyridine **7g** with arylboronic acids **8a—c** afforded biaryls **9a—n** in 52—98% yields (Scheme 5, Table 2). Therefore, complex **6f** can serve as a new catalyst for the Suzuki—Miyaura reaction involving aryl chlorides.

Scheme 5



Reagents and conditions: 6f (1 mol.%), KOH, aqueous dioxane (1 vol.% H_2O), 120 °C, 12 h.

In summary, we developed methods for the synthesis of new (NHC)Ni(Cp)X complexes with NHC ligands containing alkylamino and *N*-acetyl-*N*-alkylamino groups at the 3 or 4 position of the NHC ligand. The introduction of an alkylamino group into the NHC ligand was found to increase the catalytic activity of the complexes with *N*,*N*′-diaryl-substituted NHC ligands of the imidazole series and decrease the activity of the complexes with *N*,*N*′-dialkyl-substituted NHC ligands of the 1,2,4-triazole series in the Suzuki—Miyaura reaction. Synthesized complex **6f** was proposed as a new efficient catalyst for the cross-coupling of aryl halides with arylboronic acids.

Experimental

The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV-300 spectrometer (300 and 75 MHz, respectively) using residual signals of the solvent as the internal standard. High-resolution electrospray ionization (ESI) mass spectra were obtained on a Bruker maXis Q-TOF mass spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 analyzer. Gas chromatography mass spectrometry (GC-MS) was carried out on an Agilent 7890A chromatograph equipped with an Agilent 5975C mass-selective detector (EI, 70 eV) and an HP-5MS capillary column (30 m×0.25 mm×0.25 μm). The cross-coupling products were identified by comparing their mass spectra with those of the reference samples and the NIST mass spectral library. The melting points were determined in sealed capillary tubes on a PTP-1 instrument. Triazoles **1a,b**,[35] salts **2d,e**,[39] complexes **6g,h**,[40,45] *N*-(*tert*-butyl)chloroacetamide (**4a**),[46] 2-chloro-1-(pyrrolidin-1-yl)ethanone (**4b**),[47] and authentic samples of cross-coupling products **9a—n**[48—51] were prepared according to procedures described in the literature. Other reagents were commercially available.

1-*tert*-Butyl-4-methyl-1*H*-1,2,4-triazolium iodides (2a,b). A solution of 1-*tert*-butyl[1,2,4]triazole (**1a**) or 1-*tert*-butyl-3-(*tert*-butylamino)[1,2,4]triazole (**1b**) (1 mmol) and MeI (0.21 g, 1.5 mmol) in MeCN (3 mL) was heated with stirring at 80 °C in a closed tube (*high pressure*!) for 16 h. Then the solvent was distilled off *in vacuo*, and the residue was recrystallized from acetone, washed on a filter with Et_2O, and dried *in vacuo*.

1-*tert*-Butyl-4-methyl-1*H*-1,2,4-triazolium iodide (2a). The yield was 0.18 g (67%), colorless crystals, m.p. 196—198 °C (acetone). High-resolution MS: found *m/z* 140.1186 $[M - I]^+$; calculated for $C_7H_{14}N_3^+$ 140.1182. ^1H NMR (DMSO-d_6), δ: 1.60 (s, 9 H, Bu^t); 3.88 (s, 3 H, Me); 9.15 (s, 1 H, $C_{arom}H$); 10.19 (s, 1 H, $C_{arom}H$). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 28.0, 33.9, 62.5, 141.4, 145.1. Found (%): C, 31.54; H, 5.31; N, 15.66. $C_7H_{14}N_3I$. Calculated (%): C, 31.48; H, 5.28; N, 15.73.

1-*tert*-Butyl-3-(*tert*-butylamino)-4-methyl-1*H*-1,2,4-triazolium iodide (2b). The yield was 0.25 g (74%), colorless crystals, m.p. 174—176 °C (EtOAc). High-resolution MS: found *m/z* 211.1913 $[M - I]^+$; calculated for $C_{11}H_{23}N_4^+$ 211.1917. ^1H NMR ($CDCl_3$), δ: 1.48 (s, 9 H, Bu^t); 1.65 (s, 9 H, Bu^t); 4.04 (s, 3 H, Me); 5.70 (s, 1 H, NH); 10.25 (s, 1 H, $C_{arom}H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 28.5, 28.7, 33.7, 53.8, 62.4, 136.6, 153.0. Found (%): C, 39.16; H, 6.74; N, 16.51. $C_{11}H_{23}IN_4$. Calculated (%): C, 39.06; H, 6.85; N, 16.56.

1-*tert*-Butyl-3-[*tert*-butyl(acetyl)amino]-4-methyl-1*H*-1,2,4-triazolium iodide (2c). A solution of salt **2b** (0.34 g, 1 mmol) and Ac_2O (0.15 g, 1.5 mmol) in MeCN (3 mL) was refluxed for 2 h. Then the solvent was distilled off, and the residue was recrystallized from water and dried *in vacuo*. The yield was 0.32 g (84%), colorless crystals, m.p. 190—192 °C (EtOAc). High-resolution MS: found *m/z* 253.2019 $[M - I]^+$; calculated for $C_{13}H_{25}N_4O^+$ 253.2023. ^1H NMR (DMSO-d_6), δ: 1.35 (s, 9 H, Bu^t); 1.62 (s, 9 H, Bu^t); 1.78 (s, 3 H, Ac); 3.80 (s, 3 H, N—Me); 10.33 (s, 1 H, $C_{arom}H$). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 24.4, 27.5, 27.7, 32.7, 60.7, 63.3, 143.6, 50.1, 169.6. Found (%): C, 41.14; H, 6.64; N, 14.85. $C_{13}H_{25}N_4OI$. Calculated (%): C, 41.06; H, 6.63; N, 14.73.

Synthesis of 4-aminoimidazolium triflates 2d—f (general procedure). A mixture of *N,N*′-diarylformamidine **3a,b**[52] (0.5 mmol), chloroacetamide **4a,b** (0.6 mmol), DIPEA (97 mg, 0.75 mmol), and KI (5 mg, 0.03 mmol) in DMA (2 mL) was stirred in a tightly closed tube at 140 °C for 2 h. Then the solution was cooled and poured with stirring onto crushed ice (100 g). The amorphous precipitate that formed was filtered off, thoroughly washed with water, and dried to constant weight *in vacuo* at 40 °C. Amides **5a,b**[38] prepared by this procedure were used in the next step of the synthesis without additional purification. A solution of compound **5a,b** (0.5 mmol) and 2,4,6-trimethylpyridine (91 mg, 0.75 mmol) in dry CH_2Cl_2 (4 mL) was cooled to −75 °C, and trifluoromethanesulfonic anhydride $[(CF_3SO_2)_2O]$ (155 mg, 0.55 mmol) was added with stirring. The reaction mixture was stirred at −75 °C for 1 h and then at room temperature for 2 h. A saturated aqueous $NaHCO_3$ solution (5 mL) was added, and the mixture was stirred at room temperature for 30 min. The organic layer was separated, washed with a $NaHCO_3$ solution and water, and dried over Na_2SO_4. The solvent was distilled off *in vacuo*, and the residue was treated with diethyl ether (10 mL). The crystalline precipitate that formed was filtered off, washed with diethyl ether, recrystallized from EtOH, and dried *in vacuo* at 80 °C.

4-*tert*-Butylamino-1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazolium triflate (2d). The yield was 124 mg (47%), colorless powder, m.p. 157—159 °C (EtOH). High-resolution MS: found *m/z* 376.2745 $[M - CF_3SO_3^-]^+$; calculated for $C_{25}H_{34}N_3^+$ 376.2747. ^1H NMR (DMSO-d_6), δ: 1.23 (s, 9 H, Bu^t); 2.09

(s, 6 H, Me); 2.16 (s, 6 H, Me); 2.34 (s, 3 H, Me); 2.35 (s, 3 H, Me); 5.06 (s, 1 H, NH); 7.18 (s, 2 H, Ar); 7.19 (s, 2 H, Ar); 7.46 (d, 1 H, Ar, J = 1.8 Hz); 9.10 (d, 1 H, Ar, J = 1.8 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 16.8, 17.2, 20.65, 20.74, 27.9, 51.3, 103.6, 127.6, 129.3, 129.5, 131.6, 131.8, 134.3, 135.7, 138.3, 140.3, 140.6, the signal of CF_3 is at the background level. Found (%): C, 59.51; H, 6.60; N, 8.04. $C_{26}H_{34}N_3F_3SO_3$. Calculated (%): C, 59.41; H, 6.52; N, 7.99.

4-(Pyrrolidin-1-yl)-1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazolium triflate (2e). The yield was 84 mg (32%), colorless powder, m.p. 142—145 °C (EtOH). High-resolution MS: found m/z 374.2590 $[M - CF_3SO_3]^+$; calculated for $C_{25}H_{32}N_3^+$ 374.2591. ^1H NMR (DMSO-d_6), δ: 1.78 (m, 4 H, CH_2); 2.16 (s, 6 H, Me); 2.17 (s, 6 H, Me); 2.34 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.85 (m, 4 H, CH_2); 7.18 (s, 2 H, Ar); 7.19 (s, 2 H, Ar); 7.36 (d, 1 H, Ar, J = 2.0 Hz); 9.15 (d, 1 H, Ar, J = 2.0 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ: 16.7; 17.1; 20.6; 20.7; 24.6; 49.6; 103.9; 120.7 (q, CF_3, J = 322.7 Hz); 129.3; 129.4; 129.6; 131.4; 132.8; 134.2; 135.3; 140.3; 140.8; 142.4. Found (%): C, 59.68; H, 6.20; N, 8.09. $C_{26}H_{32}F_3N_3O_3S$. Calculated (%): C, 59.64; H, 6.16; N, 8.03.

4-*tert*-Butylamino-1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazolium triflate (2f). The yield was 204 mg (67%), colorless powder, t.decomp. 245—250 °C (EtOH). High-resolution MS: found m/z 460.3689 $[M - CF_3SO_3]^+$; calculated for $C_{31}H_{46}N_3^+$ 460.3686. ^1H NMR (DMSO-d_6), δ: 1.13 (d, 6 H, CH$\underline{Me}_2$, J = 6.8 Hz); 1.18 (d, 6 H, CH$\underline{Me}_2$, J = 6.8 Hz); 1.25 (s, 9 H, Bu^t); 1.29 (d, 6 H, CH$\underline{Me}_2$, J = 6.8 Hz); 1.31 (d, 6 H, CH$\underline{Me}_2$, J = 6.9 Hz); 2.38—2.47 (m, 2 H, C$\underline{H}Me_2$); 2.38—2.47 (m, 2 H, C$\underline{H}Me_2$, overlaps with the signal of DMSO); 5.18 (s, 1 H, NH); 7.47—7.54 (m, 4 H, Ar); 7.61—7.70 (m, 3 H, Ar); 9.50 (d, 1 H, Ar, J = 1.9 Hz). $^{13}C\{^1H)$ NMR (DMSO-d_6), δ: 22.5; 23.4; 24.16; 24.24; 27.8; 28.6; 28.8; 51.5; 103.6; 120.7 (q, CF_3, J = 322.4 Hz); 124.4; 124.9; 126.5; 130.8; 131.4; 131.9; 132.3; 139.1; 144.9; 146.0. Found (%): C, 63.11; H, 7.62; N, 6.83. $C_{32}H_{46}F_3N_3O_3S$. Calculated (%): C, 63.03; H, 7.60; N, 6.

Synthesis of complexes 6a—h (general procedure). The reaction was performed under an argon atmosphere. A solution of salt **1a—f** (0.5 mmol) and nickelocene (104 mg, 0.55 mmol) in anhydrous THF (15 mL) was heated at 70 °C with stirring for 20 h (in the synthesis of compounds **6e,f,h**, $[Et_4N]Cl$ (166 mg, 1 mmol) was added to the reaction mixture). Then the reaction mixture was filtered, without cooling, through a thin layer of celite, and the solvent was distilled off *in vacuo*. The product was isolated by silica gel column chromatography (CH_2Cl_2 as the eluent) and additionally purified by recrystallization from an appropriate solvent.

(1-*tert*-Butyl-4-methyl-1*H*-1,2,4-triazol-3-ylidene)(iodo)-(η^5-cyclopentadienyl)nickel (6a). The yield was 107 mg (55%), purple needles, t.decomp. >150 °C (CH_2Cl_2—hexane, 1 : 5). ^1H NMR ($CDCl_3$), δ: 2.00 (s, 9 H, Bu^t); 4.40 (s, 3 H, Me); 5.31 (s, 5 H, C_5H_5); 7.97 (s, 1 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 31.3; 37.8; 62.3; 93.6; 142.7; 166.6. Found (%): C, 37.16; H, 4.60; N, 10.61. $C_{12}H_{18}N_3INi$. Calculated (%): C, 36.97; H, 4.65; N, 10.78.

[1-*tert*-Butyl-5-(*tert*-butylamino)-4-methyl-1*H*-1,2,4-triazol-3-ylidene](iodo)(η^5-cyclopentadienyl)nickel (6b). The yield was 99 mg (43%), dark-purple needles, t.decomp. >150 °C (CH_2Cl_2—hexane, 1 : 5). ^1H NMR ($CDCl_3$), δ: 1.36 (s, 9 H, Bu^t); 1.95 (s, 9 H, Bu^t); 3.51 (s, 1 H, NH); 4.18 (s, 3 H, N—Me); 5.28 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 28.8; 31.2; 34.8; 52.6; 60.8; 93.4; 151.9; 159.4. Found (%): C, 41.72; H, 6.01; N, 12.05. $C_{16}H_{27}N_4INi$. Calculated (%): C, 41.69; H, 5.90; N, 12.15.

{1-*tert*-Butyl-5-[*N*-acetyl-*N*-*tert*-butylamino]-4-methyl-1*H*-1,2,4-triazol-3-ylidene}(η^5-cyclopentadienyl)(iodo)nickel (6c). The yield was 168 mg (67%), dark-purple needles, t.decomp. >150 °C (CH_2Cl_2—hexane, 1 : 5). ^1H NMR ($CDCl_3$), δ: 1.35 (br.s, 9 H, Bu^t); 1.65 and 1.68 (both s, total 3 H, Ac); 1.99 (s, 9 H, Bu^t); 4.26 and 4.27 (both s, total 3 H, N—Me); 5.32 and 5.33 (both s, total 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 24.3; 24.6; 28.2; 28.3; 31.1; 36.2; 36.4; 60.4; 60.9; 62.8; 93.6; 151.0; 151.1; 169.8; 170.5; 170.7. Found (%): C, 43.07; H, 5.84; N, 11.05. $C_{18}H_{29}N_4INiO$. Calculated (%): C, 42.98; H, 5.81; N, 11.14.

[4-*tert*-Butylamino -1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene](η^5-cyclopentadienyl)(chloro)nickel (6d). The yield was 166 mg (62%). Lilac powder, t.decomp. >150 °C (toluene). ^1H NMR ($CDCl_3$), δ: 1.15 (s, 9 H, Bu^t); 2.16 (s, 6 H, Me); 2.22 (s, 6 H, Me); 2.42 (s, 3 H, Me); 2.44 (s, 3 H, Me); 2.80 (s, 1 H, NH); 4.50 (s, 5 H, C_5H_5); 6.31 (s, 1 H, Ar); 7.09 (s, 2 H, Ar); 7.13 (s, 2 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 18.5; 18.6; 21.4; 21.5; 29.0; 51.6; 92.1; 104.5; 129.2; 129.7; 132.3; 136.2; 137.4; 137.5; 138.8; 139.7; 156.8; 164.9. Found (%): C, 67.44; H, 7.19; N, 7.81. $C_{30}H_{38}N_3ClNi$. Calculated (%): C, 67.38; H, 7.16; N, 7.86.

[4-(Pyrrolidin-1-yl)-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (6e). The yield was 224 mg (84%), dark-red crystals, t.decomp. >150 °C (CH_2Cl_2—hexane, 1 : 5). ^1H NMR ($CDCl_3$), δ: 1.71—1.79 (m, 4 H, 2 CH_2); 2.18 (s, 6 H, Me); 2.23 (s, 6 H, Me); 2.41 (s, 3 H, Me); 2.43 (s, 3 H, Me); 2.66—2.77 (m, 4 H, 2 CH_2); 4.48 (s, 5 H, C_5H_5); 6.30 (s, 1 H, Ar); 7.08 (s, 2 H, Ar); 7.09 (s, 2 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 18.6; 19.0; 21.4; 21.5; 24.8; 50.4; 92.2; 106.8; 129.2; 129.3; 135.7; 136.2; 137.1; 137.4; 138.8; 139.0; 145.6; 160.7. Found (%): C, 67.57; H, 6.83; N, 7.78. $C_{30}H_{36}N_3ClNi$. Calculated (%): C, 67.63; H, 6.81; N, 7.89.

[4-*tert*-Butylamino-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (6f). The yield was 167 mg (54%), red powder, t.decomp. >175 °C (CH_2Cl_2—hexane). ^1H NMR ($CDCl_3$), δ: 1.00—1.23 (m, 21 H, 4 CH_3 + Bu^t); 1.38—1.45 (m, 12 H, 4 CH_3); 2.80 (s, 1 H, NH); 2.84—3.07 (m, 4 H, 4 C$\underline{H}Me_2$); 4.46 (s, 5 H, C_5H_5); 6.30 (s, 1 H, Ar); 7.38 (d, 2 H, Ar, J = 7.7 Hz); 7.45 (d, 2 H, Ar, J = 7.7 Hz); 7.51 (t, 1 H, Ar, J = 7.7 Hz); 7.61 (t, 1 H, Ar, J = 7.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 22.8; 23.8; 25.4; 26.3; 28.3; 28.5; 28.8; 51.1; 92.1; 105.7; 124.0; 124.8; 129.8; 130.8; 132.5; 137.6; 139.5; 146.5; 148.3; 159.3. Found (%): C, 70.02; H, 8.19; N, 6.73. $C_{36}H_{50}N_3ClNi$. Calculated (%): C, 69.86; H, 8.14; N, 6.79.

Evaluation of catalytic activity of compounds 6a—h in the Suzuki—Miyaura reaction (general procedure). The reaction was performed under an argon atmosphere in a 7-mL glass tube equipped with a magnetic stirrer bar and a screw cap. A solution of the catalyst (7.5 μmol, 1 mol.%) in the appropriate solvent (1.5 mL) (see Tables 1 and 2) was added to a solution of the appropriate base (0.35 mmol), aryl halide 7a—g (0.25 mmol), and arylboronic acid 8a—c (0.35 mmol) in the corresponding solvent (0.5 mL). The tube was sealed and heated to the specified temperature with stirring during a required time (see Tables 1 and 2). Then the mixture was cooled to room temperature, and a solution of naphthalene (16 mg, 0.125 mmol) in acetonitrile (2 mL) was added as the internal standard. An aliquot (2 μL) of the resulting mixture was dissolved in acetonitrile (1 mL) and analyzed by GC-MS (see Tables 1 and 2).

Table 3. Crystallographic data and the structure refinement parameters for compounds **6a—c**

Parameter	**6a**	**6b**	**6c**
Molecular formula	$C_{12}H_{18}IN_3Ni$	$C_{16}H_{27}IN_4Ni$	$C_{18}H_{29}IN_4NiO$
M/g	389.90	461.02	503.06
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1$
a/Å	7.0225(2)	36.1170(14)	11.8453(6)
b/Å	17.1910(8)	10.9892(4)	8.0500(4)
c/Å	12.4220(3)	10.1206(4)	12.5201(7)
α/deg	90	90	90
β/deg	97.985(2)	90.010(8)	112.993(4)
γ/deg	90	90	90
V/Å^3	1485.09(10)	4016.8(3)	1099.00(10)
Z 4	8	2	
d_{calc}/g cm^{-3}	1.744	1.525	1.520
F(000)	768	1856	508
μ/mm^{-1}	3.37	2.51	2.3
R_{int}	0.092	0.118	0.101
θ_{max}/deg	28.3	28.3	28.2
θ_{min}/deg	2.0	1.9	1.8
Number of reflections			
measured	39352	26169	16155
unique	3613	4776	5068
with $I > 2\sigma(I)$	2178	2139	2756
Number of refined parameters	159	206	235
R_1	0.045	0.054	0.043
wR_2 ($I > 2\sigma(I)$)	0.105	0.130	0.069
S 0.89	0.87	0.81	
Residual electron density ($\Delta\rho_{max}/\Delta\rho_{min}$)/e Å^{-3}	0.74/−1.28	0.53/−1.01	0.58/−0.95

X-ray diffraction study. Single crystals of complexes **6a—c** were obtained by the crystallization from dichloromethane in hexane vapor. The unit cell parameters were measured on a StadiVari Pilatus 100K diffractometer using Cu-Kα radiation from a GeniX^{3D} generator equipped with a microfocus X-ray tube and a FOX3D HF Xenocs multilayer thin-film ellipsoidal monochromator. The X-ray diffraction data were collected, the unit cell parameters were determined and refined, and the diffraction data were processed using the STOE X-Area software package (STOE & Cie GmbH, Darmstadt, Germany, 2013). The intensities of reflections were scaled with the LANA module of the X-Area software suite to minimize the differences in the intensities of symmetry-equivalent reflections (multi-scan method). The crystal structures were solved by direct methods using the SHELXS-97 program package.[53,54] The positional and thermal parameters of nonhydrogen atoms were refined by the full-matrix method with anisotropic displacement parameters. The hydrogen atoms were positioned geometrically and refined using a riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.2U_{eq}(C)$).

Tables of atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic displacement parameters for all the compounds were deposited with the Cambridge Crystallographic Data Centre (CCDC 2041135 (**6a**), 2041141 (**6b**), 2041132 (**6c**)), and are available at www.ccdc.cam.ac.uk.

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