DOI:10.1002/ejic.201500852

1,2,4-Triazole-Based N-Heterocyclic Carbene Nickel Complexes – Synthesis and Catalytic Application

Linus P. Bheeter,[a][‡] Duo Wei,[a][‡] Vincent Dorcet,[b] Thierry Roisnel,[b] Prasenjit Ghosh,[c] Jean-Baptiste Sortais,*[a] and Christophe Darcel*[a]

Keywords: Homogenous catalysis / Cross-coupling / Nickel / Carbene ligands / Borylation

Four nickel complexes bearing 1,2,4-triazole-based N-heterocyclic carbene backbones and a cyclopentadienyl ligand were prepared from the corresponding 1,2,4-triazolium salts and nickelocene in tetrahydrofuran (THF) under reflux. The obtained complexes were fully characterized, including by X-ray diffraction analysis. They were then used as catalysts (5 mol-%) for the borylation of aryl bromide derivatives with bis(pinacolato)diboron in the presence of Cs_2CO_3 as the base in THF at 70 °C for 20 h to form the corresponding borylated products in moderate yields.

Introduction

Aryl- and alkylboronic acid and ester derivatives are important starting materials in molecular synthesis[1] and are well-known partners for classical transformations such as the Petasis reaction,[2] Chan–Lam coupling,[3] conjugate addition reactions,[4] and, most impressively, Suzuki–Miyaura cross-coupling reactions.[5] To prepare such boronic acid derivatives efficiently, there are currently several methodologies, including the traditional route involving a metal–halogen exchange with an organolithium or Grignard reagent and trialkylborates.[6] Interesting alternatives have emerged involving transition-metal-catalyzed C–H activation/borylation, the major drawback of which is the control of the regioselectivity,[7,8] and the catalyzed Miyaura borylations of aryl and heteroaryl halides, mainly developed with palladium,[9] copper,[10] nickel,[11] or other earth-abundant transition metals.[12] For their selectivity and functional-group tolerance, bis(pinacolato)diboron (B_2pin_2, **1**), pinacolborane (H-Bpin, **2**), or neopentylglycolborane (**3**) were classically used as boron cross-coupling partners.

In comparison with those with palladium catalysts, the nickel-catalyzed borylations of aryl- and alkyl halides have been reported less frequently. In a pioneering work, Tour described the use of $Ni(dppp)Cl_2$ [dppp = bis(diphenylphosphanyl)propane] as a catalyst (6 mol-%) in the presence of a stoichiometric amount of NEt_3 for the borylation of aryl bromides with **2** to form the corresponding boronic acid derivatives after a hydrolysis step.[13] The addition of 10 mol-% of dppf [dppf = bis(diphenylphosphanyl)ferrocene] to $Ni(dppm)Cl_2$ [5 mol-%; dppm = 1,1-bis(diphenylphosphanyl)methane] favored the borylation of aryl chlorides, mesylates, and tosylates with **3** at 100 °C.[14–17] It must be noted that the use of bis(neopentylglycolato)diboron as the coupling partner permitted the borylation of aryl carbamates and *N*-arylamides with $NiCl_2(PCy_3)_2$ or [$Ni(cod)_2$/IMes·HCl] (cod = cyclooctadiene, IMes·HCl = 1,3-dimesitylimidazolium chloride) as the catalyst.[18,19] Examples of nickel catalysts for the borylation of alkyl halides are scarce. In 2011, Fu et al. described the coupling of alkyl halides and **1** catalyzed by $NiBr_2$·diglyme/pybox or 2,2′;6′,2"-terpyridine (terpy).[20,21] Substituted allylic boronates can also be prepared from allylic acetates in the presence of catalysts based on $Ni(cod)_2$ and PCy_3.[22] It is surprising that only one report deals with the use of nickel N-heterocyclic carbene (NHC) catalysts, as they are good candidates for catalytic applications,[23] in particular in hydroelementation reactions such as hydrosilylation.[24]

In this report, as a continuation of our work exploring the catalytic potential of nickel complexes in catalysis[25] and more especially those derived from N-heterocyclic carbene ligands, notably with a 1,2,4-triazole scaffold,[26] we

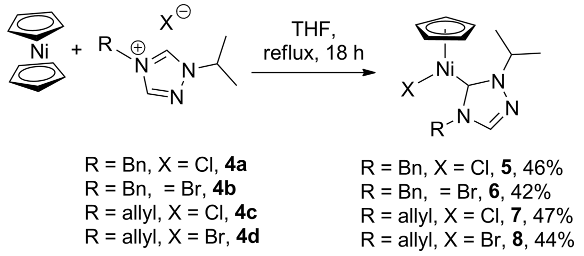
---

[a] UMR 6226 CNRS, Institut des Sciences Chimiques de Rennes, Team Organometallics: Materials and Catalysis, Centre for catalysis and Green Chemistry, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France
E-mail: jean-baptiste.sortais@univ-rennes1.fr
christophe.darcel@univ-rennes1.fr
http://sciencechimiques.univ-rennes1.fr/catalyse/
[b] UMR 6226 CNRS, Institut des Sciences Chimiques de Rennes, Centre de Diffraction X, Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex, France
[c] Department of Chemistry, Indian Institute of Technology Bombay,
Powai, Mumbai 400076, India
[‡] Equal contribution
Supporting Information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejic.201500852.

describe herein the synthesis of new 1,2,4-triazole-based NHC cyclopentadienyl (Cp) nickel complexes and their use in the catalytic borylation reactions of bromoaryl derivatives with bis(pinacolato)diboron.

Results and Discussion

According to the procedure of Cowley,[27] the 1,2,4-triazole NHC nickel complexes CpNi(NHC)X (X = Cl, Br) **5**–**8** were prepared from their corresponding 1,2,4-triazolium chloride and bromide salts **4a**–**4d** by reaction with nickelocene in THF under reflux for 20 h; the complexes were obtained as crystals in 42–47 % isolated yields after recrystallization from THF/pentane mixtures (Scheme 1).



Scheme 1. Synthesis of 1,2,4-triazole NHC CpNi(NHC)X complexes.

All of the complexes were fully characterized through classical techniques, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, X-ray diffraction analysis, HRMS, and elemental analysis.

The $^{13}C\{^{1}H\}$ NMR spectra of the diamagnetic complexes **5**–**8** exhibited characteristic Ni–$C_{carbene}$ resonances at δ = 165.9–167.0 ppm and characteristic Cp resonances at δ = 92.1 ppm. These results are in good accordance with those for previously described structures such as CpNi(IMes)Cl (δ = 167.2 and 92.3 ppm, respectively).[26a,28] Complexes **5**–**8** gave suitable crystals for X-ray diffraction analysis, and the obtained molecular structures are strikingly similar; the nickel atom is bonded to an η^5-Cp ring, a triazole moiety, and a chlorido (**5** and **7**) or bromido (**6** and **8**) ligand in a two-legged piano-stool geometry (Figure 1 and Table 1).

In **5**–**8**, the Ni–$C_{carbene}$ bond lengths [**5**, 1.870(3) Å; **6**, 1.865(3) Å; **7**, 1.876(2) Å; **8**, 1.875(3) Å] are not significantly different from each other or from those of CpNi(NHC)Cl complexes bearing imidazol-2-ylidene or 2,5-dihydroimidazol-2-ylidene ligands [1.85(2)–1.917(9) Å].[26a,28] They are slightly shorter than the sum of the individual covalent radii of nickel and carbon (Ni–C 1.926 Å).[29] The Ni–Cl bond lengths of 2.2037(8) Å in **5** and 2.2084(7) Å in **7** are slightly longer than those reported for CpNi(NHC)Cl [2.1795(5)–2.199(5) Å]. The differences

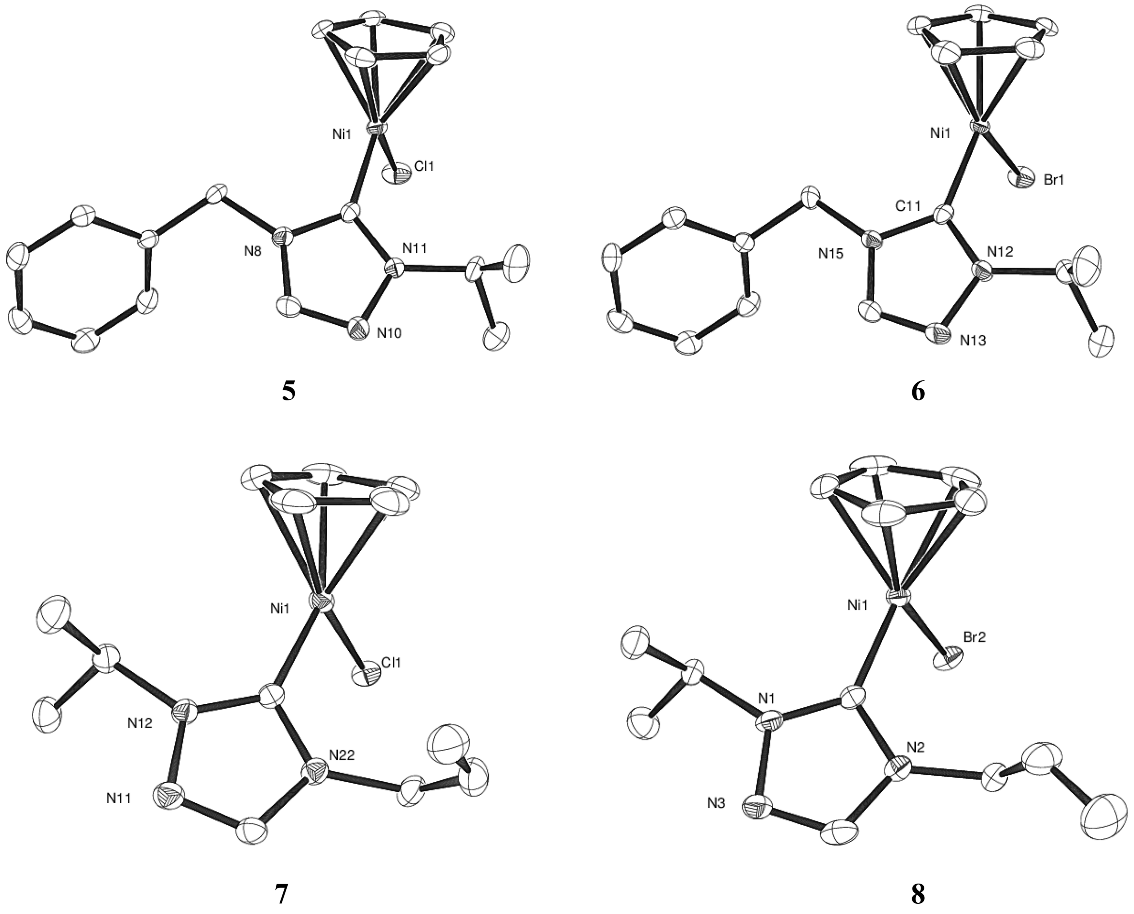


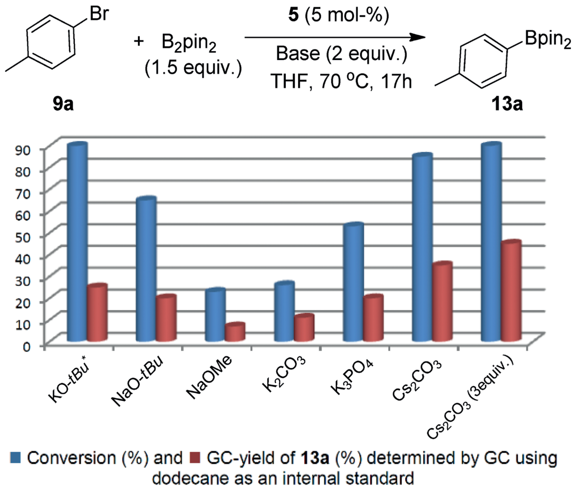
Figure 1. ORTEP views of **5**–**8** with thermal ellipsoids at the 50 % probability level. The hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **5**–**8**.

	5 (X = Cl)	**6** (X = Br)	**7** (X = Cl)	**8** (X = Br)
Ni–X	2.2037(8)	2.3294(5)	2.2084(7)	2.3410(5)
Ni–$C_{carbene}$	1.870(3)	1.865(3)	1.876(2)	1.875(3)
Ni–C(Cp) average	2.138	2.130	2.138	2.130
Ni–C(Cp) max	2.169(3)	2.162(3)	2.169(3)	2.183(3)
Ni–C(Cp) min	2.056(3)	2.048(3)	2.038(3)	2.059(3)
$C_{carbene}$–N	1.350(4), 1.370(4)	1.343(4), 1.377(3)	1.348(3), 1.365(3)	1.339(3), 1.363(3)
N–$C_{carbene}$–Ni	130.0(2), 127.3(2)	129.6(2), 127.7(2)	129.6(2), 127.7(2)	130.5(2), 126.4(2)
N–$C_{carbene}$–N	102.7(2)	102.7(3)	102.30(19)	103.1(2)
$C_{carbene}$–Ni–X	96.23(9)	95.45(8)	96.16(7)	94.91(8)
$C_{carbene}$–Ni–Cp_{cent}	131.36	132.50	132.15	131.97
X–Ni–Cp_{cent}	132.28	131.93	131.51	133.07

between the carbenoid C–Ni–X angles and those of the CpNi(NHC)Cl analogues are unimportant [94.91(8)–96.23(9) vs. 92.06(5)–99.4(6)°]. Thus, the use of triazole ligands instead of imidazole ligands did not induce strong differences in the molecular structures of the nickel complexes.

Borylation is an important reaction in molecular synthesis, and examples of NHC–nickel complexes as catalysts in the borylation of halide derivatives to form the corresponding borylated compounds are scarce.[23] This prompted us to examine **5**–**8** as potential catalysts for the coupling of **1** with aryl bromides. As the nature of the base can have a crucial effect on the selectivity of such cross-coupling reactions, we studied the borylation of **9a** with B_2pin_2 (1.5 equiv.), 5 mol-% of **5**, and 2 equiv. of different types of bases such as alkoxide, carbonate or phosphate bases to evaluate the reaction (Scheme 2).

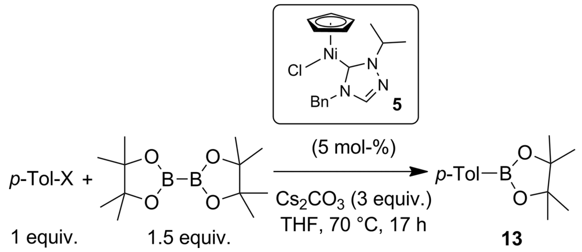


Scheme 2. Influence of the base on the selectivity.

Even though *t*BuOK and NaO*t*Bu led to 90 and 65% conversion, respectively, the expected borylated product **13a** was obtained in low GC yields (25%). The transformation was not selective as significant amounts of dehalogenation product and *p*-bitolyl were obtained from a homocoupling reaction. With NaOMe, K_2CO_3, and K_3PO_4, the reaction was more selective, as no homocoupling adduct was observed, but the cross-coupling product **13a** was still obtained in low GC yields (7, 11, and 20%, respectively). Finally, Cs_2CO_3 was found to be the best base and afforded the product **13a** in a moderate GC yield (35%) at 85% conversion. An increase of the quantity of Cs_2CO_3 to 3 equiv. led to the formation of 45% of **13a** at 90% conversion; an increased quantity of base did not improve the reaction.

The nature of the electrophile (1 equiv.) was then evaluated for the reaction with 1.5 equiv. of **1** in the presence of 3 equiv. of Cs_2CO_3 as the base and 5 mol-% of **5** in THF at 70 °C for 17 h (Table 2). With *p*-tosyltoluene (**12**), no conversion was observed (Table 2, Entry 4). The use of *p*-iodo- and *p*-chlorotoluene (**10** and **11**) led to good conversions (97 and 85%, respectively), but the borylated compound **13** was obtained in poor yield (11%) in both cases (Table 2, Entries 2 and 3). The best electrophile was *p*-bromotoluene, which was converted in 90% and furnished the borylated compound **13** in 45% yield (Table 2, Entry 1). The four prepared complexes (**5**–**8**) were then tested in this reaction, and complexes **5** and **6** bearing a 1-isopropyl-4-benzyl-1,2,4-triazole ligand led to the borylated product in satisfactory yields (45–50%; Table 2, Entries 1 and 5–7).

Table 2. Borylation reactions with different electrophiles.[a]

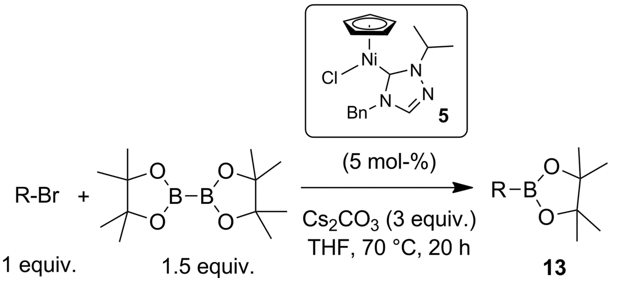


Entry	Cat.	Substrate		Conv. [%][b]	Yield [%][b]
1	**5**	*p*-Me-C_6H_4-Br	**9a**	90	45
2	**5**	*p*-Me-C_6H_4-I	**10**	97	11
3	**5**	*p*-MeO-C_6H_4-Cl	**11**	85	11
4	**5**	*p*-Me-C_6H_4-Tos	**12**	0	0
5	**6**	*p*-Me-C_6H_4-Br	**9a**	> 98	50
6	**7**	*p*-Me-C_6H_4-Br	**9a**	95	40
7	**8**	*p*-Me-C_6H_4-Br	**9a**	92	40

[a] Typical procedure: *p*-Tol-X (1 equiv.), **1** (1.5 equiv.), Cs_2CO_3 (3 equiv.), catalyst (5 mol-%), THF, 70 °C for 17 h. [b] Conversion and yield determined by GC analysis with dodecane as an internal standard. The difference between the conversions and GC yields can be attributed to the formation of toluene as a result of the dehalogenation of halotoluene; Tos = *p*-Me-C_6H_4-SO_3.

The scope of the cross-coupling borylation reaction was then explored with **5** as the catalyst and Cs_2CO_3 as the base (3 equiv.) in THF at 70 °C for 20 h (Table 3). The reaction led to the corresponding borylated derivatives in 29–40% yields for electron-donating groups on the arene rings. Indeed, 90–98% conversions were obtained from *para*- and *ortho*-bromotoluene, and the corresponding borylated products were obtained in 40 and 29% yields (determined by NMR spectroscopy), respectively; therefore an *ortho* substituent slightly hampered the reactivity (Table 3, Entries 3 and 4). For the aryl bromide substituted with an electron-donating methoxy group, the corresponding cross-coupling product was obtained in 40 % yield (Table 3, Entry 5).

Table 3. Borylation reactions with different electrophiles.[a]



Entry	Aryl bromide	Conv. [%][b]	Product	Yield [%][c]
1	Ph-Br	94	Ph-Bpin	37
2	*p*-F-C_6H_4-Br	93	*p*-F-C_6H_4-Bpin	35
3	*p*-Me-C_6H_4-Br	90	*p*-Me-C_6H_4-Bpin	40
4	*o*-Me-C_6H_4-Br	98	*o*-Me-C_6H_4-Bpin	29
5	*p*-MeO-C_6H_4-Br	88	*p*-MeO-C_6H_4-Bpin	40
6	*p*-(MeO_2C)-C_6H_4-Br	71	*p*-(MeO_2C)-C_6H_4-Bpin	25
7	*p*-(Et-OC)-C_6H_4-Br	76	*p*-(Et-OC)-C_6H_4-Bpin	23
8	*o*-(CF_3) -C_6H_4-Br	76	*o*-(CF_3) -C_6H_4-Bpin	31
9	*p*-(NC)-C_6H_4-Br	79	*p*-(NC)-C_6H_4-Bpin	8
10	Ph-CH_2–CH_2–Br	98	Ph-CH_2–CH_2–Bpin	18

[a] Typical procedure: Ar-Br (1 equiv.), Cs_2CO_3 (3 equiv.), **1** (1.5 equiv.), **5** (5 mol-%), 70 °C for 20 h. [b] Conversion of the aryl bromide determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene (0.5 equiv.) as an internal standard. [c] Yields determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene (0.5 equiv.) as an internal standard.

By contrast, although good conversions (71–79 %) can be reached with electron-deficient aryl bromides after 20 h of reaction at 70 °C, the borylated compounds were obtained in lower yields (8–31 %): the significant decrease of the yield was mainly due to an increase of the level of debromination (Table 3, Entries 6–9). Interestingly, functional groups such as esters, ketones, and nitriles can be tolerated during the coupling process. However, for *para*-nitrobromobenzene or 3-bromopyridine, no conversion was observed under similar conditions. Noticeably, the reaction can also be performed with alkyl bromides, for example, 2-phenylethyl bromide, which led to full conversion but only 18 % of the corresponding alkylBpin (Table 3, Entry 10).

Notably, this family of half-sandwich NHC catalysts showed better activities than those of the parent $Ni(NHC)_2Cl_2$ square-planar complexes.[26c]

Conclusions

A series of nickel complexes bearing 1,2,4-triazole-based N-heterocyclic carbene backbones and cyclopentadienyl ligands were prepared from the corresponding 1,2,4-triazolium salts by reaction with nickelocene in THF under reflux. The complexes have been fully characterized, including by X-ray diffraction analysis. In the catalytic borylation reactions of aryl bromide derivatives with bis(pinacolato)diboron in the presence of Cs_2CO_3 as the base in THF at 70 °C for 20 h, the prepared complexes led to the corresponding borylated compounds with moderate activities and yields.

Experimental Section

General Procedures: All reagents were obtained from commercial sources and used as received. THF and pentane were dried with a Braun MB-SPS-800 solvent-purification system. All solvents were stored with molecular sieves under an argon atmosphere. All reactions were performed under an argon atmosphere. Technical-grade petroleum ether and diethyl ether (Et_2O) were used for chromatography.

^1H NMR spectra were recorded with samples in $CDCl_3$ at ambient temperature with Bruker AVANCE 300 and Bruker 400 spectrometers at 300 and 400 MHz, respectively, and the solvent resonance was used as the internal standard (δ = 7.26 ppm for $CHCl_3$). The ^{13}C NMR spectra were recorded with samples in $CDCl_3$ or CD_2Cl_2 and obtained at 75 or 100 MHz. The chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively. The peak patterns are indicated as follows: s singlet, d doublet, t triplet, q quartet, m multiplet, and br. broad.

GC analyses were performed with a GC-2014 (Shimadzu) instrument equipped with a 30 m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 m × 0.25 mm × 0.25 mm film thickness), which was used with N_2/air as the vector gas.

GC–MS was performed with a GCMS-QP2010S (Shimadzu) instrument with a GC-2010 chromatograph equipped with a 30 m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 m × 0.25 mm × 0.25 mm film thickness), which was used with helium as the vector gas. The following GC conditions were used: initial temperature 80 °C for 2 min, 10 °C/min to 225 °C, 225 °C for 15 min.

The HRMS and microanalysis were performed by the corresponding facilities at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), University of Rennes 1, France.

The X-ray diffraction data were collected with an APEXII (Bruker-AXS) diffractometer equipped with a CCD detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at T = 150(2) K. The structures were solved by direct methods with the SIR97 program[30] and then refined through full-matrix least-square methods based on F^2 (SHELXL-97)[31] with the aid of the WINGX[32] program.

CCDC-1414345 (for **5**), -1414343 (**6**), -1414346 (for **7**), and -1414344 (for **8**) 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.

1-Isopropyl-4-allyl-1,2,4-triazolium and 1-isopropyl-4-benzyl-1,2,4-triazolium salts were synthesized according to literature procedures.[26a,26b]

General Procedure for the Preparation of 1,2,4-Triazole NHC CpNi(NHC)X Complexes: In a Schlenk tube, nickelocene (1 equiv.) and 4-alkyl-1-isopropyl-1,2,4-triazolium halide salt (1 equiv.) were dissolved in THF (10 mL) under argon atmosphere. The mixture was heated under reflux for 20 h, and the solution slowly turned from dark green to dark red. The mixture was then filtered through a Celite pad and rinsed with THF (3 × 15 mL). The solvent was then removed under vacuum, and the resulting solid was washed with pentane (3 mL), dried, and recrystallized from a THF/pentane mixture at room temperature. The (cyclopentadienyl)(4-alkyl-1-isopropyl-1,2,4-triazol-5-ylidene)nickel halide complex was obtained as a solid.

(Cyclopentadienyl)(4-benzyl-1-isopropyl-1,2,4-triazol-5-ylidene)nickel Chloride (5): Persian red solid; yield 46 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.50–7.30 (m, 5 H), 6.23 (sept, J = 6.8 Hz, 1 H), 6.05 (br. s, 2 H), 5.17 (s, 5 H), 1.58 (d, J = 6.8 Hz, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 166.8, 144.0, 136.2, 129.9, 129.4, 128.9, 92.8, 56.2, 53.6, 22.9 ppm. $C_{17}H_{20}N_3Ni$ (325.08): calcd. C 56.64, H 5.59, N 11.66; found C 56.44, H 5.63, N 11.53. HRMS: calcd. for $C_{17}H_{20}N_3{}^{58}Ni$ $[M - HCl]^+$ 324.1011; found 324.1008.

(Cyclopentadienyl)(4-benzyl-1-isopropyl-1,2,4-triazol-5-ylidene)nickel Bromide (6): Persian red solid; yield 42 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1 H), 7.24–7.50 (m, 5 H), 6.19 (br. s, 1 H), 6.03 (br. s, 2 H), 5.21 (s, 5 H), 1.58 (br. s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 167.0, 143.0, 134.9, 129.2, 128.6, 128.0, 119.8, 92.1, 55.5, 53.1, 22.2 ppm. $C_{17}H_{20}BrN_3Ni$ (404.98): calcd. C 50.42, H 4.98, N 10.38; found C 50.86, H 5.04, N 10.41. HRMS: calcd. for $C_{17}H_{20}N_3{}^{79}Br^{58}Ni$ $[M]^+$ 403.0194; found 403.0197.

(Cyclopentadienyl)(4-allyl-1-isopropyl-1,2,4-triazol-5-ylidene)nickel Chloride (7): Firebrick solid; yield 47 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 6.25–6.10 (m, 2 H), 5.50–5.24 (m, 4 H), 5.23 (s, 5 H), 1.55 (br. s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 165.9, 142.7, 132.2, 119.8, 92.1, 55.4, 51.7, 22.4 ppm. $C_{13}H_{18}ClN_3Ni$ (310.47): calcd. C 50.28, H 5.85, N 13.53; found C 49.33, H 5.83, N 13.10. HRMS: calcd. for $C_{13}H_{18}N_3{}^{58}Ni$ $[M - Cl]^+$ 274.0854; found 274.0854.

(Cyclopentadienyl)(4-allyl-1-isopropyl-1,2,4-triazol-5-ylidene)nickel Bromide (8): Deep carmine pink solid; yield 44 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 6.18–6.07 (m, 2 H), 6.00–5.21 (m, 4 H), 5.26 (s, 5 H), 1.54 (br. s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 166.7, 142.8, 132.1, 119.7, 92.0, 55.4, 51.8, 22.2 ppm. $C_{13}H_{18}BrN_3Ni$ (354.92): calcd. C 43.99, H 5.11, N 11.84; found C 43.42, H 5.02, N 12.46. HRMS: calcd. for $C_{13}H_{18}N_3{}^{58}Ni$ $[M - Br]^+$ 274.0854; found 274.0853.

General Procedure for Borylation Reactions: A 10 mL Schlenk tube containing a stirring bar was loaded with Cs_2CO_3 (3 equiv.), B_2pin_2 (1.5 equiv.), **5** (5 mol-%), and dry THF (4 mL). The aryl bromide (1.5 equiv.) was then added, and the reaction mixture was stirred in a preheated oil bath at 70 °C for 20 h. The reaction mixture was then cooled, 2,4,6-trimethoxybenzene (0.5 equiv.) was added as the internal NMR standard, and the mixture was stirred for 5 min. The conversion and yield were then determined by ^{1}H NMR spectroscopy of the crude mixture. The product can be further purified by silica gel column chromatography with a petroleum ether/diethyl ether mixture.

Acknowledgments

The authors thank the Indo-French Centre for the Promotion of Advanced Research (IFCPAR), New Delhi (project number 4605-1, PhD grant to L. P. B.) for financial support of this research. C. D. and J. B. S. thank the French Ministère de l'Enseignement Supérieur et de la Recherche and the Centre National de la Recherche Scientifique (CNRS) for financial support.

---

[1] a) D. G. Hall (Ed.), *Boronic Acids*, Wiley-VCH, Weinheim, Germany, **2011**; b) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417.

[2] N. Candeias, F. Montalbano, P. M. S. D. Cal, P. Gois, *Chem. Rev.* **2010**, *110*, 6169.

[3] J. Qiao, P. Lam, *Synthesis* **2011**, 829.

[4] G. Berthon-Gelloz, T. Hayashi, *Rhodium- and Palladium-Catalyzed Asymmetric Conjugate Addition of Organoboronic Acid*, in: *Boronic Acids* (Ed.: D. G. Hall), Wiley-VCH, Weinheim, Germany, **2011**.

[5] a) For the Nobel Prize lecture, see: A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722; *Angew. Chem.* **2011**, *123*, 6854; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; c) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147; d) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417; e) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg, V. Percec, *Chem. Rev.* **2011**, *111*, 1346.

[6] a) D. G. Hall, in: *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine* (Ed.: D. G. Hall), Wiley-VCH, Weinheim, Germany, **2005**, p. 1–99; b) E. J. Corey, C.-M. Yu, S. S. Kim, *J. Am. Chem. Soc.* **1989**, *111*, 5495; c) P. G. M. Wuts, S. S. Bigelow, *J. Org. Chem.* **1982**, *47*, 2498; d) R. W. Hoffmann, B. Kemper, *Tetrahedron Lett.* **1982**, *23*, 845.

[7] For leading reviews, see: a) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992; b) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; c) T. Ishiyama, N. Miyaura, *Pure Appl. Chem.* **2006**, *78*, 1369; d) T. Ishiyama, N. Miyaura, *Chem. Rec.* **2004**, *3*, 271; e) T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2003**, *680*, 3.

[8] For recent examples with iron, see: a) T. Dombray, C. G. Werncke, S. Jiang, M. Grellier, L. Vendier, S. Bontemps, J.-B. Sortais, S. Sabo-Etienne, C. Darcel, *J. Am. Chem. Soc.* **2015**, *137*, 4062; b) Y. Ohki, T. Hatanaka, K. Tatsumi, *J. Am. Chem. Soc.* **2008**, *130*, 17174; c) T. Hatanaka, Y. Ohki, K. Tatsumi, *Chem. Asian J.* **2010**, *5*, 1657; d) G. Yan, Y. Jiang, C. Kuang, S. Wang, H. Liu, Y. Zhang, J. Wang, *Chem. Commun.* **2010**, *46*, 3170; for recent examples with iron and copper, see: e) T. J. Mazzacano, N. P. Mankad, *J. Am. Chem. Soc.* **2013**, *135*, *17258*; for a recent example with cobalt, see: f) J. V. Obligacion, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 4133; for examples with nickel, see: g) T. Furukawa, M. Tobisu, N. Chatani, *Chem. Commun.* **2015**, *51*, 6508.

[9] For selected examples, see: a) T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508; b) T. Ishiyama, K. Ishida, N. Miyaura, *Tetrahedron* **2001**, *57*, 9813; c) A. Fürstner, G. Seidel, *Org. Lett.* **2002**, *4*, 541; d) K. L. Billingsley, T. E. Barder, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2007**, *46*, 5359; *Angew. Chem.* **2007**, *119*, 5455; e) S. Kawamorita, H. Ohmiya, T. Iwai, M. Sawamura, *Angew. Chem. Int. Ed.* **2011**, *50*, 8363; *Angew. Chem.* **2011**, *123*, 8513; f) W. Tang, S. Keshipeddy, Y. Zhang, X. Wei, J. Savoie, N. D. Patel, N. K. Yee, C. H. Senanayake, *Org. Lett.* **2011**, *13*, 1366.

[10] a) W. Zhu, D. Ma, *Org. Lett.* **2006**, *8*, 261; b) C. Kleeberg, L. Dang, Z. Lin, T. B. Marder, *Angew. Chem. Int. Ed.* **2009**, *48*, 5350; *Angew. Chem.* **2009**, *121*, 5454; c) G. Yan, M. Yang, J. Yu, *Lett. Org. Chem.* **2012**, *9*, 71; d) C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder, L. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 528; *Angew. Chem.* **2012**, *124*, 543.

[11] For a recent review, see: a) F. S. Han, *Chem. Soc. Rev.* **2013**, *42*, 5270; b) S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874; for NHC–nickel(II) complexes, see: c) V. Ritleng, A. M. Oertel, M. J. Chetcuti, *Dalton Trans.* **2010**, *39*, 8153; d) A. M. Oertel, V. Ritleng, M. J. Chetcuti, *Organometallics* **2012**, *31*, 2829.

[12] Recent examples with iron, see: a) T. C. Atack, R. M. Lecker, S. P. Cook, *J. Am. Chem. Soc.* **2014**, *136*, 9521; b) R. B. Bedford, P. B. Brenner, E. Carter, T. Gallagher, D. M. Murphy, D. R. Pye, *Organometallics* **2014**, *33*, 5940; recent examples

with zinc: c) S. K. Bose, K. Fucke, L. Liu, P. G. Steel, T. B. Marder, *Angew. Chem. Int. Ed.* **2014**, *53*, 1799; *Angew. Chem.* **2014**, *126*, 1829; d) S. K. Bose, T. B. Marder, *Org. Lett.* **2014**, *16*, 4562.

[13] A. B. Morgan, J. L. Jurs, J. M. Tour, *J. Appl. Polym. Sci.* **2000**, *76*, 1257.

[14] a) B. M. Rosen, C. Huang, V. Percec, *Org. Lett.* **2008**, *10*, 2597; b) D. A. Wilson, C. J. Wilson, B. M. Rosen, V. Percec, *Org. Lett.* **2008**, *10*, 4879; c) C. Moldoveanu, D. A. Wilson, C. J. Wilson, P. Corcoran, B. M. Rosen, V. Percec, *Org. Lett.* **2009**, *11*, 4974; d) C. Moldoveanu, D. A. Wilson, C. J. Wilson, P. Leowanawat, A.-M. Resmerita, C. Liu, B. M. Rosen, V. Percec, *J. Org. Chem.* **2010**, *75*, 5438.

[15] P. Leowanawat, A.-M. Resmerita, C. Moldoveanu, C. Liu, N. Zhang, D. A. Wilson, L. M. Hoang, B. M. Rosen, V. Percec, *J. Org. Chem.* **2010**, *75*, 7822.

[16] D. A. Wilson, C. J. Wilson, C. Moldoveanu, A.-M. Resmerita, P. Corcoran, L. M. Hoang, B. M. Rosen, V. Percec, *J. Am. Chem. Soc.* **2010**, *132*, 1800.

[17] M. Murata, Y. Sogabe, T. Namikoshi, S. Watanabe, *Heterocycles* **2012**, *86*, 133.

[18] K. Huang, D.-G. Yu, S.-F. Zheng, Z.-H. Wu, Z.-J. Shi, *Chem. Eur. J.* **2011**, *17*, 786.

[19] M. Tobisu, K. Nakamura, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 5587.

[20] A. S. Dudnik, G. C. Fu, *J. Am. Chem. Soc.* **2012**, *134*, 10693.

[21] J. Yi, J.-H. Liu, J. Liang, J.-J. Dai, C.-T. Yang, Y. Fu, L. Liu, *Adv. Synth. Catal.* **2012**, *354*, 1685.

[22] P. Zhang, I. A. Roundtree, J. P. Morken, *Org. Lett.* **2012**, *14*, 1416.

[23] For recent references, see: a) A. P. Prakasham, P. Ghosh, *Inorg. Chim. Acta* **2015**, *431*, 61; b) M. Henrion, V. Ritleng, M. J. Chetcuti, *ACS Catal.* **2015**, *5*, 1283; c) M. Henrion, M. J. Chetcuti, V. Ritleng, *Chem. Commun.* **2014**, *50*, 4624; d) M. N. Rao, M. Haridas, M. K. Gangwar, P. Rajakannu, A. C. Kalita, P. Ghosh, *Eur. J. Inorg. Chem.* **2015**, 1604; e) M. Katari, G. Rajaraman, P. Ghosh, *J. Organomet. Chem.* **2015**, *775*, 109.

[24] a) L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J.-B. Sortais, V. Ritleng, *Adv. Synth. Catal.* **2012**, *354*, 2619; b) L. P. Beether, M. Henrion, M. J. Chetcuti, C. Darcel, V. Ritleng, J.-B. Sortais, *Catal. Sci. Technol.* **2013**, *3*, 3111; c) L. Postigo, B. Royo, *Adv. Synth. Catal.* **2012**, *354*, 2613; d) J. Zheng, T. Roisnel, C. Darcel, J.-B. Sortais, *ChemCatChem* **2013**, *5*, 2861; e) J. Zheng, C. Darcel, J.-B. Sortais, *Catal. Sci. Technol.* **2013**, *3*, 81.

[25] a) C. Dash, M. M. Shaikh, R. J. Butcher, P. Ghosh, *Dalton Trans.* **2010**, *39*, 2515; b) S. Kumar, A. Narayanan, N. Rao, M. M. Shaikh, P. Ghosh, *J. Organomet. Chem.* **2012**, *696*, 4159; c) M. K. Samantaray, M. M. Shaikh, P. Ghosh, *Organometallics* **2009**, *28*, 2267; d) S. Ray, M. M. Shaikh, P. Ghosh, *Eur. J. Inorg. Chem.* **2009**, 1932; e) M. Katari, G. Rajaraman, G. Ghosh, *J. Organomet. Chem.* **2014**, *775*, 109.

[26] a) C. Dash, M. M. Shaikh, P. Ghosh, *Eur. J. Inorg. Chem.* **2009**, 1608; b) C. Dash, M. M. Shaikh, R. J. Butcher, P. Ghosh, *Dalton Trans.* **2010**, *39*, 2515; c) A. Kumar, L. P. Bheeter, M. K. Gangwar, J.-B. Sortais, C. Darcel, P. Ghosh, *J. Organomet. Chem.* **2015**, *786*, 63.

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

[28] a) V. Ritleng, E. Brenner, M. J. Chetcuti, *J. Chem. Educ.* **2008**, *85*, 1646; b) V. Ritleng, C. Barth, E. Brenner, S. Milosevic, M. J. Chetcuti, *Organometallics* **2008**, *27*, 4223; c) R. A. Kelly III, N. M. Scott, S. Diez-Gonzalez, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 3442.

[29] L. Pauling, *The Nature of The Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**, p. 224–228, p. 256–258.

[30] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.

[31] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

[32] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.

Received: July 29, 2015