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Phosphine-functionalized NHC Ni(II) and Ni(0) complexes: synthesis, characterization and catalytic properties†

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Two families of nickel complexes bearing chelating diphenylphosphine-functionalized NHC ligands [Ni^{II}(ArNHCPPh$_2$)(allyl)]Cl **1a** (Ar = Mes); -**1b**, (Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$) and [Ni^0(ArNHCPPh$_2$)(alkene)] **2a** (Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$, alkene = styrene); -**2b** (Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$, alkene = diethyl fumarate) have been prepared and fully characterized. VT-NMR experiments in solution reveal that the allyl derivatives **1a-b** are stereochemically nonrigid. The solid-state structure of the Ni^0 derivative **2b** is also reported. These complexes display interesting catalytic properties in various cross-coupling reactions. The precatalyst [Ni^0(ArNHCPPh$_2$)(styrene)] **2a** was found to be the most active system. The bulkiness of the N-substituent on the imidazole ring and the low oxidation state of the metal center in **2a** accounted for its enhanced catalytic performance. This system catalyzed effectively the coupling of (hetero)aryl chlorides with a range of nucleophiles including Grignard reagents, boronic acids, seconday amines and indoles.

Introduction

The field of organic chemistry, largely dominated by palladium catalysis, is gradually giving way to more sustainable transition metal catalysts, such as those based on earth-abundant 3*d* metals.[1] Nickel represents a very good example of this tendency, as evidenced by the significant progress achieved in Ni-mediated C-C and C-heteroatom bond formation and other coupling reactions over the last decade.[2] Not only is nickel a cheaper alternative to palladium, but it also offers diverse reactivity and novel catalytic transformations.[2,3]

Within the area of cross-coupling chemistry, nickel catalysis has enabled the efficient coupling of reluctant electrophiles under palladium catalysis, such as phenol derivatives.[4] Most of these compelling results have been achieved with the use of N-heterocyclic carbenes (NHC) as supporting ligands.[5] The remarkable σ-donor character of the NHCs ligands and the efficient steric protection provided by the substituents on the N atoms enhance the stability of the catalyst and its activity, when compared to phosphines.[6-7] In the last years, several groups have reported the beneficial effect of using mixed NHC/PPh_3 complexes in cross-coupling reactions.[8,9] The enhanced activity of such systems is ascribed to the synergistic effect between the two ligands, i.e., the dissociation of the more labile phosphine ligand provides a vacant coordination site for the oxidative addition, whereas the tightly bound NHC ligand facilitates the oxidative addition and the reductive elimination, the latter being accelerated by phosphine recoordination. This kind of dynamic behavior has been also attributed to bidentate phosphine-functionalized N-heterocyclic carbenes (NHCP).[10,11]

Palladium-based catalysts bearing bidentate NHCP ligands have not been extensively applied in cross-coupling reactions.[12,13] Regarding to nickel, we are aware of only two reports on the applications of NHCP/Ni complexes as catalysts for C-C couplings. Poli and co-workers have described the use of zwitterionic Ni(II) complexes with phosphine-functionalized imidazolium ligands as catalysts in the Kumada-Tamao-Corriu coupling reaction.[14] Lee and co-workers have shown that mono- and bis-NHCP Ni(II) chelates are effective catalysts for Suzuki coupling of aryl chlorides.[15] So far, the application of this type of ligand in Ni-catalyzed C-heteroatom cross-coupling reactions remains largely unexplored.

Part of our research interest is focused on the development of molecularly defined Ni catalysts for cross-coupling reactions. We have described the efficiency of two monodentate NHC/Ni catalyst precursors, [Ni^{II}(IPr)(allyl)Cl] and [Ni^0(IPr)(styrene)$_2$] (IPr = N,N'-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene), in C-C[16] and C-heteroatom couplings reactions.[17] We became interested in phosphine-functionalized NHC ligands since Ni-based catalyst systems containing these ligands have been underexplored in cross-coupling chemistry. For this purpose, we decided to prepare monochelate NHCP-Ni compounds analogues to those of monodentate IPr complexes above mentioned. In this work, we account the synthesis and structural characterization of two

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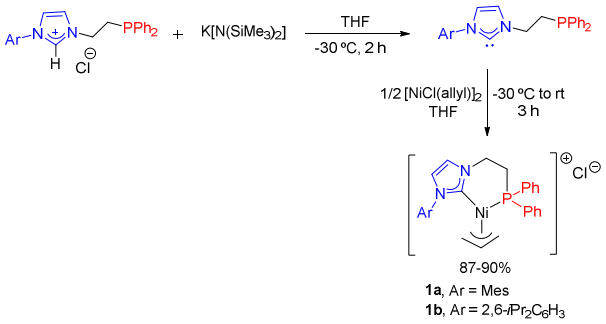
families of Ni(II) and Ni(0) complexes containing diphenylphosphine-functionalized NHC ligands. These complexes are active catalysts in the coupling of Grignard reagents and boronic acids with aryl chlorides. Moreover, the performance of NHCP/Ni complexes in the arylation of N-nucleophiles has been evaluated for the first time.

Results and Discussion

Synthesis and Characterization of Cationic ArNHCPPh$_2$-Ni^{II}(allyl) Complexes. In this study, we chose two chelating NHCP ligands containing a diphenylphosphine arm. The ligand bulkiness was then controlled by the substituents on the N atom of the imidazolyl moiety. The target ionic Ni^{II} complexes **1a** and **1b** were synthesized following a two-step procedure (Scheme 1). First, the phosphine-imidazolium salt, prepared as reported,[8c,18] was conveniently deprotonated at -30ºC in THF using 1 equiv of K[N(SiMe$_3$)$_2$]. Subsequently, a solution of the Ni(II) precursor [NiCl(allyl)]$_2$ in THF was added to the previous mixture leading to the isolation of the complexes **1a-b** as yellow-orange solids in 87-90% yield.

Complexes **1a-b** are quite robust in solid-state and in solution. Their elemental analyses were in agreement with the expected compositions. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of both complexes showed the presence of only one configurational isomer in solution. The ^{31}P resonances for **1a-b**, in CD_2Cl_2, were observed as singlets at 20.6 and 22.9 ppm, respectively. Upon coordination, these resonances were shifted at higher frequency with respect to the corresponding for the free imidazolium salts (-23.2 and -24.0, respectively). In addition to this, the carbene carbon resonance appeared as a doublet (δ 171.0, J_{CP} = 20 Hz, for **1a** and 172.5, J_{CP} = 24 Hz, for **1b**) as a result of the bidentate coordination of the ligands. At room temperature, the ^{1}H NMR spectra of these compounds showed three distinct resonances for the five allyl protons: a multiplet for the central proton (at 4.97 ppm for **1a** and 4.96 ppm for **1b**), a broad singlet for the syn protons (ca. 3.48 and 3.46 ppm for **1a** and **1b** respectively) and a doublet for the anti protons (ca. 1.99 and 1.95 ppm for **1a** and **1b**, respectively). Furthermore, resonances due to the CH_2-CH_2- bridge of the ArNHCPPh$_2$ ligands were also very broad. From these data, it was clear that a fluxional process involving the exchange between *syn-syn* and *anti-anti* protons takes place in solution. VT NMR studies were then carried out (see ESI). On cooling the CD_2Cl_2 solution of complex **1a** to -30 ºC five distinct resonances for the allyl protons were clearly observed, indicating that the *syn-syn* and *anti-anti* exchange was inhibited. At this temperature, it was also possible to observe independent broad resonances for each of the protons of ethylene bridge of the bidentate ligand (ca. 5.11, 4.47,



Scheme 1 Synthesis of cationic Ni^{II}-allyl complexes **1a-b**.

2.65 and 2.53 ppm). In addition, the rotation of the mesityl substituent of the NHC moiety around the C-N bond was hindered, as inferred from the observation of a singlet for each type of methyl protons of the mesityl ring.

The chemical shifts of the allyl group in **1a** deserve further comments. The resonances of the allyl terminal protons of the carbon atom *trans* to the NHC moiety at low temperature (δ 3.53 and 1.88 for H_{syn} and H_{anti}, respectively) were slighted shifted to higher frequencies than those corresponding to the carbon atom *trans* to the phosphine arm (δ 3.45 and 1.82 for H_{syn} and H_{anti}, respectively). Since the difference in chemical shift between the two *syn* (or the two *anti*) protons depends on the σ-donor properties of the ligands attached to the metal center,[19] the small variance observed was a consequence of minor differences in the σ-donation capabilities of both NHC and phosphine arms of this ligand. The similarity in the electronic character of both donors was also reflected in the small difference in chemical shift between the two terminal allyl ^{13}C resonances (4 ppm), appearing the CH_2 *trans* to P at slightly higher frequency (δ 67.1, J_{CP} = 29.1 Hz) than that of the CH_2 group *trans* to C (δ 63.1).[20]

For complex **1b** the temperature had to be lowered to -50 ºC to stop the *syn-syn*, *anti-anti* exchange (see ESI). The presence of isopropyl groups on the NHC bound phenyl ring did not produce significant changes in the chemical shifts of the allyl moiety with regard to those of derivative **1a**.

It has been proposed that the *syn-syn* and *anti-anti* exchange proceeds through apparent allyl rotation, which can involve the dissociation of one arm of the chelate[21] or the coordination of solvent or other donor molecules.[22] To test which pathway was responsible for the observed fluxional behavior of **1a-b** at room temperature, complex **1b** was treated with stoichiometric amounts of silver hexafluoroantimonate, affording the isolation of **1b-SF$_6$**.

Unlike in the case with the chloride derivative, the room-temperature ^{1}H NMR of **1b-SF$_6$** showed five nonequivalent allyl protons (Figure 1). This result suggests that the apparent rotation proceed through an associative pathway involving the coordination

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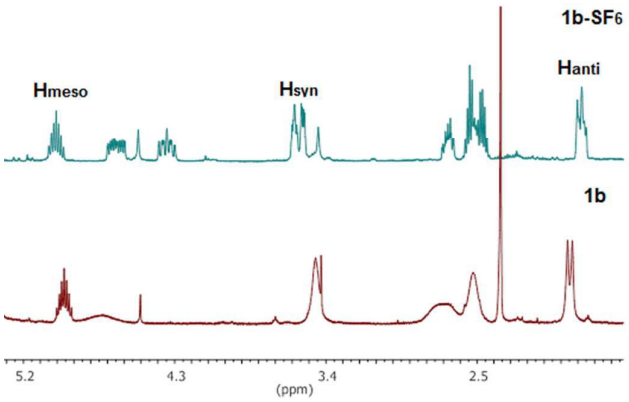


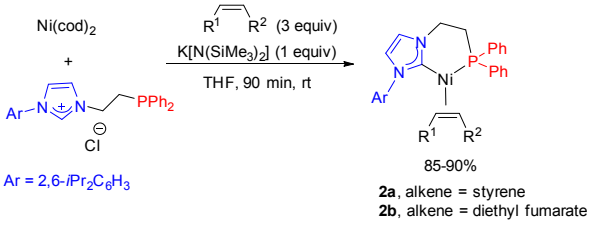
Fig. 1 Room temperature ^{1}H NMR (CD_2Cl_2) spectra of **1b-SF$_6$** (top) and **1b** (bottom).

of chloride anion. When heating a toluene-d_8 solution of **1b**, a second fluxional process was detected. At 80 ºC, all terminal allyl protons exchanged between them, simultaneously. This *syn-anti* exchange, occurring at both sides of the allyl ligand, is linked to η^3-η^1-η^3 allyl rearrangement.[20b,22b,23]

The coalescence temperatures for the *syn-syn* and *anti-anti* interconversion processes were determined from the variable temperature ^{1}H NMR studies carried out with **1a**-**b**. Thus, the coalescence of the signals of the *syn* protons occurred at 288 and 283 K for **1a** and **1b**, respectively, whereas that of the *anti* protons was observed at 258 K for complex **1b**. It was not possible to determine the coalescence of the *anti* proton resonances for **1a** due to strong overlap with the signal of the methyl groups. With the coalescence temperatures and the separation of the allylic resonances (see ESI for details) the estimated free energies of activation for the interconversion processes (kJ mol^{-1}) were as follows: **1a**, *syn-syn*, 58.9; **1b**, *syn-syn*, 57.5; **1b**, *anti-anti,* 53.3. These values are similar to those reported for apparent allyl rotation processes.[22c-d,23c]

Synthesis and Characterization of neutral ArNHCPPh$_2$-Ni^0(alkene) Complexes. Due to their enhanced stability towards oxidation, Ni^{II} complexes are commonly employed as catalyst precursors in most Ni-mediated cross-coupling processes. To avoid the in situ reduction step associated with the catalyst activation, the use of Ni^0 complexes can be advantageous. However, examples of catalyst systems based on molecularly defined Ni^0 complexes are scarce.[17b,24] Having this in mind, we tackled the synthesis of ArNHCPPh$_2$-Ni^0 derivatives. The preparation of the title compounds [Ni(ArNHCPPh$_2$)(alkene)] (Ar = 2,6-*i*Pr^2-C$_6$H$_3$, alkene = styrene, **2a**; alkene = diethyl fumarate, **2b**) was accomplished following a modified procedure to that we reported for the complex [(IPr)Ni(styrene)$_2$].[17b] We observed that the purity of the nickel products was higher when carrying out the reactions in a one-pot fashion. Thus, an equimolar mixture of [Ni(cod)$_2$], the ligand salt and the base were reacted in THF in the presence of an excess of the alkene (3 equiv), at room temperature (Scheme 2). After the workup procedure, complexes **2a** and **2b** were obtained in high yields as yellow-orange solids.

Alternatively, the styrene-derivative **2a** could also be prepared by the reduction of the cationic complex 1b with di-*n*-butylmagnesium in THF, in the presence of 2 equiv of styrene (see ESI for experimental details). Complexes **2a-b** are stable in solid state under an inert atmosphere, but they are degraded in solution when exposing to air. Both complexes are very soluble in common polar solvents, like THF or diethyl ether and sparingly soluble in non-polar solvents, such as hexane or toluene. Compounds **2a-b** represent the first examples of



Scheme 2 Synthesis of Ni^0-alkene complexes **2a-b.**

zerovalent NHCPPh$_2$-Ni derivatives stabilized by coordination to alkenes. It is worth mentioning that attempts to prepare the corresponding ethylene derivatives failed. ^{1}H and ^{13}C{^{1}H} of **2a** in C_6D_6 displayed four distinct signals for the four methyl groups of the isopropyl substituents and two resonances for the two methine groups, indicating that both isopropyl substituents were in different chemical environment. In addition, the methylene protons of the fragment N-CH$_2$-CH$_2$-P were also inequivalent and appeared as four multiplets. The olefinic protons of the styrene appeared as three multiplets (ca. 3.71, 2.15 and 1.89 ppm) in the ^{1}H NMR spectrum, and a singlet (δ 52.2) and a doublet due to the coupling with the ^{31}P nucleus (δ 33.4, J_{CP} = 24 Hz) were observed for the olefinic carbons in the ^{13}C{^{1}H} NMR. The resonances attributed to the alkene, both in the ^{1}H and ^{13}C{^{1}H} NMR, appeared at lower frequencies than those of the free styrene,[25] as expected for a strong metal-alkene π back-bonding. Finally, in the ^{13}C{^{1}H} NMR spectrum the carbenic carbon signal was observed at δ 195.5 and appeared as a doublet (J_{CP} = 7.5 Hz) due to the coupling with the phosphorus. The ^{31}P{^{1}H} NMR displayed a singlet at 15.2 ppm, indicative of the coordination of the phosphine arm to the nickel center (see above).

The ^{31}P resonance for the diethyl fumarate complex **2b** appeared at 23.7 ppm in C_6D_6. Its ^{1}H and ^{13}C NMR features were very similar to those already discussed for **2a** and deserve no further comments (see ESI).

The structure of compound **2b** was confirmed by X-ray diffraction studies. Figure 2 shows the molecular structure of **2b** together with the most relevant bond distances and angles. To the best of our knowledge, this is the first reported structure of a phosphine-functionalized Ni^0-alkene complex. The nickel center is bonded to the phosphorus and carbenic carbon atoms of the bidentate ArNHCPPh$_2$ ligand and to one molecule of diethylfumarate, in a distorted trigonal planar environment. The C=C double bond distance of the coordinated alkene (1.434(4) Å) is longer than that of free alkene (1.318(2) Å)[26] as a result of the strong π back-donation. Interestingly, both Ni–C (alkene) bond distances are very

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similar (1.976(3) and 1.965(3) Å), indicating that the phosphorus and the carbenic carbon donors have comparable electron-donating properties. A similar situation is encountered in a series of alkene-Pd^0 complexes reported recently with structurally related phosphine-functionalized NHC ligands.[12g] The Ni–carbene distance (1.898 (3) Å) is within the range of values reported for other NHC–Ni^0 complexes.[27] The alkene double bond is almost coplanar with the nickel, the phosphorus and the carbenic carbon atoms (with a slight deviation of 15.64(0.12)° between the two planes Ni1–C31–C3 and P1–Ni1–C1).

Catalytic Results. We began our catalytic survey by examining the performances of complexes **1a-2b** in the room temperature Kumada-Tamao-Corriu (KTC) coupling of 4-chlorotoluene with phenylmagnesium bromide. As depicted in Table 1, all precatalysts were active in this reaction, with complex **2a** affording the highest yield (entry 3). Full selectivity towards the coupling product was observed in all cases. A similar trend in the catalytic behavior of **1a-2b** was obtained when 4-ethyl-chlorobenzene was used as the coupling partner (entries 5-8). Next, we gauged the catalytic activity of the most active catalyst system **2a** in the challenging coupling of 2-chloropyridine with phenylmagnesium bromide. Full conversion

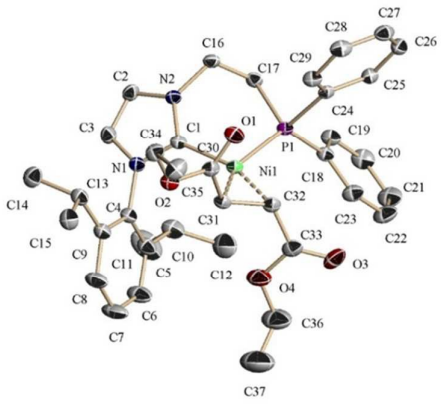
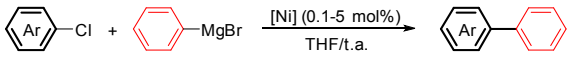


Fig. 2 Molecular structure of **2b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (º) for **2b**: Ni(1)-C(1), 1.898(3); Ni(1)-P(1), 2.1527(7); Ni(1)-C(31), 1.977(2); Ni(1)-C(32), 1.965(2); C(31)-C(32), 1.435(4); C(32)-Ni(1)-C(31), 42.69(11); C(1)-Ni(1)-P(1), 96.78(7); C(32)-Ni(1)-P(1), 107.35(8); C(1)-Ni(1)-C(31), 113.39(11); C(1)-Ni(1)-C(32), 155.78(11).

was attained using 5 mol % of the Ni precatalyst (entry 9). The catalyst loading was subsequently decreased to 1 mol% and the reaction was complete within 1 hour (entry 11). However, a further reduction of the catalyst loading to 0.1 mol% produced lower yield (76%) of the couple product (entry 12). Under the optimized catalytic conditions, other heteroaryl chlorides such as 2-chloroquinoline and 2-chloroquinoxaline afforded 81% and 41% yields of product, respectively, in the reaction with phenylmagnesium bromide (entries 13-14).

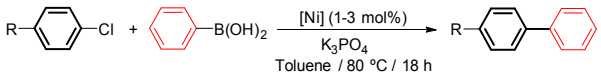
Table 1 Cross-Coupling of (Hetero)aromatic Chlorides with PhMgBr Catalyzed by Ni Complexes.[a]



entry	precatalyst (mol %)	Ar	time (h)	yield (%)[b]
1	**1a** (5)	*p*-Me-C_6H_4	18	80
2	**1b** (5)	*p*-Me-C_6H_4	18	92
3	**2a** (5)	*p*-Me-C_6H_4	18	98
4	**2b** (5)	*p*-Me-C_6H_4	18	95
5	**1a** (5)	*p*-Et-C_6H_4	18	82
6	**1b** (5)	*p*-Et-C_6H_4	18	88
7	**2a** (5)	*p*-Et-C_6H_4	18	92
8	**2b** (5)	*p*-Et-C_6H_4	18	84
9	**2a** (5)	2-pyridyl	18	97
10	**2a** (1)	2-pyridyl	18	91
11	**2a** (1)	2-pyridyl	1	94
12	**2a** (0.1)	2-pyridyl	1	76
13	**2a** (1)	2-quinolyl	1	81
14	**2a** (1)	2-quinoxalyl	1	41

[a]Reaction conditions: ArCl (0.5 mmol), PhMgBr (0.75 mmol), precatalyst (0.1-5 mol%), THF (1 mL). [b]Yields determined by ^{1}H NMR using an internal standard.

Table 2. Cross-Coupling of Aromatic Chlorides with $PhB(OH)_2$ Catalyzed by Ni Complexes.[a]



entry	precatalyst (mol%)	R	yield (%)[b]
1	**1a** (3)	Me	68
2	**1b** (3)	Me	70
3	**2a** (3)	Me	98
4	**2b** (3)	Me	68
5	**2a** (1)	Me	72
6	**1a** (3)	COMe	90
7	**1b** (3)	COMe	92
8	**2a** (3)	COMe	95
9	**2b** (3)	COMe	79

[a]Reaction conditions: ArCl (0.5 mmol), $PhB(OH)_2$ (0.65 mmol), K_3PO_4 (1.3 mmol), precatalyst (1-3 mol%), toluene (2 mL), 18 h at 80 ºC. [b]Yields determined by ^{1}H NMR using an internal standard.

Next, we explored the activities of the NHCP-Ni complexes in the Suzuki-Miyaura coupling of *p*-chlorotoluene with phenylboronic acid (Table 2). These complexes showed moderate to high activities (69-98% conversions) under somewhat standard conditions, e.g. 3 mol% of the Ni precatalyst, K_3PO_4 and toluene at 80 ºC (entries 1-4). As in the previous case, the styrene derivative **2a** afforded the highest yield of the biaryl product. When the catalyst loading was reduced to 1 mol %, complex **2a** exhibited only moderate activity. Using more reactive 4-chloroacetophenone as the coupling partner led to excellent yields of product with **1a-b** and **2a** and good yield (79%) with **2b** at 3 mol% loading of catalysts (entries 6-9)

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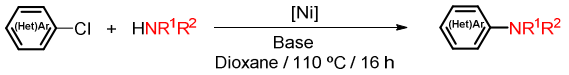
Having demonstrated the good activities of compounds **1a**-**2b**, and in particular, that of the styrene-Ni^0 derivative **2a** in the C-C cross-coupling reactions examined, we focused on the Buchwald-Hartwig amination reaction. At stated above, the application of phosphine-functionalized NHCs ligands in the amination of aryl halides have received scant attention. We have found only two examples of use of phosphine-functionalized imidazolium ligands with palladium in Buchwald-Hartwig aminations.[13] However, no report on the performance of this type of ligand in nickel-catalyzed Buchwald-Hartwig aminations has yet been described. Hence, we evaluated the performance of NHCP-Ni complexes **1a**-**2b** in the amination of 2-chloropyridine with morpholine following catalytic conditions reported by us previously,[17b] i.e., NaO*t*Bu as base, 5 mol% catalyst loading, THF (1 mL), at 110 ºC. Complexes **1a**-**2b** displayed poor to moderate yields in reactions carried out for 16 hours (Table 3, entries 1-4). A more reactive substrate, 2-chloroquinoline, was then employed as the coupling partner and, as expected, the activities of these NHCP-Ni systems were significantly enhanced (entries 5-8). Once again, the styrene-derivative **2a** displayed the best catalytic behavior, leading to complete conversion of the substrates. Good conversion was also obtained for 2-chloroquinoxaline as substrate (entry 9).

Table 3. Cross-Coupling of Heteroaryl Chorides and N-Nucleophiles Catalyzed by Ni Complexes.[a]



entry	precatalyst (mol%)	(Het)Ar	HNR^{1}R^2	Yield (%)[b]
1	**1a** (5)	2-pyridyl	morpholine	24
2	**1b** (5)	2-pyridyl	morpholine	35
3	**2a** (5)	2-pyridyl	morpholine	46
4	**2b** (5)	2-pyridyl	morpholine	40
5	**1a** (5)	2-quinolyl	morpholine	80
6	**1b** (5)	2-quinolyl	morpholine	83
7	**2a** (5)	2-quinolyl	morpholine	96
8	**2b** (5)	2-quinolyl	morpholine	82
9	**2a** (5)	2-quinoxalyl	morpholine	82
10	**2a** (5)	2-pyridyl	indole	60[c]
11	**2a** (10)	2-pyridyl	indole	94[c]
12	**2a** (10)	2-quinolyl	indole	94[c]
13	**2a** (10)	2-quinoxalyl	indole	95[c]

[a]Reaction conditions: Heteroaryl chloride (0.5 mmol), N-nucleophile (0.6 mmol), NaO*t*Bu (0.6 mmol), catalyst (5 or 10 mol%), dioxane, 16 h at 110 ºC. [b]Yields determined by ^{1}H NMR using an internal standard. [c]Reaction using LiO*t*Bu (0.6 mmol) as the base.

Then, we surveyed the activity of **2a** in the *N*-arylation of indoles,[17c] a challenging substrate due to its poor nucleophilicity, high acidity and strong coordination ability of the NH group. 2-Chloropyridine and indole were the substrates selected for the catalytic tests. Carrying out the reaction with 5 mol% Ni at 110 ºC for 16 h, provided moderate yield of the N-coupled product (Table 3, entry 10). Increasing the catalyst loading up to 10 mol% resulted in the complete conversion of the substrate into the couple product (entry 11). Under these conditions, **2a** also catalyzed competently the coupling of other heteroaryl chlorides such as, 2-chloroquinoline and 2-chloroquinoxaline affording the products in excellent yields (entries 12-13).

The outcomes of the catalytic studies presented in Tables 1-3 demonstrate that the NHCP-Ni complexes **1a-2b**, prepared in this work, are all active in the cross-coupling processes examined. The best catalyst among them is the styrene-Ni^0 complex **2a**. Its superior performance not only can be ascribed to the larger steric bulkiness of the substituent 2,6-*i*Pr$_2$-C$_6$H$_3$ on the imidazolyl moiety, but also to a faster rate of activation since the metal precursor is in its zero oxidation state. The good catalytic activity showed by **2a** in the C-C couplings compares well to those reported by Poli at al.[16] and Lee et al.[17] for their Ni^{II} systems bearing bidentate NHCP ligands. Furthermore, this catalyst system is also applicable for the coupling of challenging heteroaryl chlorides with secondary amines (morpholine) and indole.

Conclusions

Two sets of nickel complexes [Ni^{II}(ArNHCPPh$_2$)(allyl)]Cl, [Ni^0(ArNHCPPh$_2$)(alkene)] have been easily prepared from the corresponding Ni precursor and phosphine-functionalized imidazolium salt. The fluxional behavior observed for the allyl-Ni^{II} derivatives at room temperature can be attributed to an apparent allyl rotation facilitated by the chloride anion. At high temperature, a η^3-η^1-η^3 allyl isomerization is also taking place. The diethylfumarate-Ni^0 complex, **2b**, has been characterized by X-ray diffraction. This represents the first reported structure of ArNHCPPh$_2$-Ni^0-alkene complex. These complexes have been tested for catalytic activity in cross-coupling processes. The complex [Ni^0(ArNHCPPh$_2$)(styrene)] (Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$), **2a**, has shown its potential as a versatile catalyst for the coupling of (hetero)aryl chlorides with a range of nucleophiles including phenyl Grignard, phenylboronic acid, morpholine and indole. The bulkiness of the N-substituent on the imidazole ring and the low oxidation state of the metal center in complex **2a** have found to be beneficial for its enhanced catalytic activity. This is the first example of NHCP/Ni catalyst system applied in Buchwald-Hartwig aminations.

Experimental Section

General Procedures.

All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques or under nitrogen atmosphere in an Mbraun glovebox. All substrates were purchased from Aldrich and used without further purification. Solvents were distilled and degassed before use. [Ni(cod)$_2$],[28] [Ni(allyl)Cl]$_2$[29] and the phosphine-functionalized NHCPPh$_2$ ligands[8c,18] were prepared according to literature methods. NMR spectra were recorded on Agilent 400 MR or Agilent 500 DD2. FTIR spectra were recorded on a Nicolet IR200 FTIR spectrometer. ^{1}H and ^{13}C NMR shifts were measured relative to deuterated solvents peaks but are reported relative to tetramethylsilane. Elemental analyses were performed on a PerkinElmer Series II CHNS/O Analyzer 2400.

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Synthesis

[Ni(ArNHCPPh$_2$)(allyl)]Cl (Ar = Mes (1a), (2,6-^{i}Pr-C$_6$H$_3$ (1b)). The imidazolium salt (1.5 mmol) and potassium bis(trimethylsilyl)amide (0.3 g, 1.5 mmol) were stirred in THF (10 mL) at -30 ºC for 2 hours. A solution of [Ni(allyl)Cl]$_2$ (0.2 g, 0.75 mmol) in THF (5 mL) cooled at -30 ºC was added to the former suspension, and the mixture was allowed to reach room temperature. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and filtered through a Celite pad. The solution was taken to dryness and the solid washed with diethyl ether and dried under vacuum. Recrystallization from toluene afforded the complexes as dark orange solids. Yields: 0.72 g, 90 % for **1a**; 0.81 g, 87 % for **1b**. Data for **1a**: ^{1}H NMR (500 MHz, CD_2Cl_2, -30 ºC) δ 8.13 (s, 1H, C*H*$_{imid}$), 7.56-7.41 (m, 10 H, C*H*$_{Ar}$), 7.03 (s, 1 H, C*H*$_{imid}$), 7.01 (s, 1 H, C*H*$_{Ar}$), 6.95 (s, 1 H, C*H*$_{Ar}$), 5.11 (m, 1 H, NC*H*$_2$), 4.99 (m, 1 H, H$_{meso}$), 4.48 (m, 1 H, NC*H*$_2$), 3.53 (m, 1 H, H$_{syn}$), 3.45 (m, 1 H, H$_{syn}$), 2.65 (m, 1 H, PC*H*$_2$), 2.53 (m, 1 H, PC*H*$_2$), 2.32 (s, 3 H, C*H*$_3$), 1.94 (s, 3 H, C*H*$_3$), 1.92 (s, 3H, C*H*$_3$), 1.88-1.80 (m, 2 H, H$_{anti}$). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, -30 ºC) δ 171.0 (d, J_{CP} = 20 Hz, N*C*N), 139.6 (*C*$_{Ar}$), 136.3 (*C*$_{Ar}$), 133.4 (d, J_{CP} = 13 Hz, *C*$_{Ar}$), 131.8 (*C*$_{Ar}$), 131.6 (*C*$_{Ar}$), 131.1 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 129.4 (*C*$_{Ar}$), 129.2 (d, J_{CP} = 3 Hz, *C*$_{Ar}$), 125.0 (*C*$_{Ar}$), 122.6 (*C*$_{Ar}$), 115.5 (*C*H$_{allyl}$), 67.1 (d, J_{CP} = 29 Hz, *C*H$_{2allyl}$), 63.1 (*C*H$_{2allyl}$), 46.6 (d, J_{CP} = 3 Hz, N*C*H$_2$), 26.7 (d, J_{CP} = 26 Hz, P*C*H$_2$), 21.2 (*C*H$_{3Ar}$), 18.4 (*C*H$_{3Ar}$), 18.2 (*C*H$_{3Ar}$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 20.6. Anal. Calcd for $C_{29}H_{32}N_2PNiCl$: C, 65.26; H, 6.04; N, 5.25. Found: C, 64.74; H, 5.96; N, 5.21. Data for **1b**: ^{1}H NMR (500 MHz, CD_2Cl_2, -50 ºC) δ 8.31 (s, 1 H, C*H*$_{imid}$), 7.59-7.41 (m, 11 H, C*H*$_{Ar}$), 7.31-7.14 (m, 2 H, C*H*$_{Ar}$), 7.10 (s, 1 H, C*H*$_{imid}$), 5.16 (m, 1 H, NC*H*$_2$), 4.99 (m, 1 H, H$_{meso}$), 4.38 (m, 1 H, NC*H*$_2$), 3.53 (m, 1 H, H$_{syn}$), 3.41 (m, 1 H, H$_{syn}$), 2.66 (m, 1 H, PC*H*$_2$), 2.53-2.41 (m, 3 H, C*H*-*i*Pr and PC*H*$_2$), 1.76 (m, 1 H, H$_{anti}$), 1.69 (m, 1 H, H$_{anti}$), 1.19 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, C*H*$_3$-*i*Pr), 1.05 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$-*i*Pr), 1.01 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, C*H*$_3$-*i*Pr), 0.82 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$-*i*Pr). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, -70 ºC) δ 172.5, (d, J_{CP} = 24 Hz, N*C*N), 145.1 (*C*$_{Ar}$), 144.6 (*C*$_{Ar}$), 137.7 (*C*$_{Ar}$), 135.5 (*C*$_{Ar}$), 133.1 (d, J_{CP} = 13 Hz, *C*$_{Ar}$), 131.5 (*C*$_{Ar}$), 131.0 (*C*$_{Ar}$), 130.9 (*C*$_{Ar}$), 130.6 (*C*$_{Ar}$), 129.9 (*C*$_{Ar}$), 129.1-128.9 (m, *C*$_{Ar}$), 128.7 (*C*$_{Ar}$), 127.9 (*C*$_{Ar}$), 124.9 (*C*$_{Ar}$), 124.5 (*C*$_{Ar}$), 123.8 (*C*$_{Ar}$), 123.6 (d, J_{CP} = 16 Hz, *C*$_{Ar}$), 114.7 (*C*H$_{allyl}$), 66.4 (d, J_{CP} = 22 Hz, *C*H$_{2allyl}$), 62.8 (*C*H$_{2allyl}$), 45.8 (N*C*H$_2$), 28.0 (*C*H-*i*Pr), 27.9 (*C*H-*i*Pr), 26.2 (d, J_{CP} = 27 Hz, P*C*H$_2$), 25.6 (*C*H$_3$-*i*Pr), 22.9 (*C*H$_3$-*i*Pr), 22.2 (*C*H$_3$-*i*Pr), 21.1 (*C*H$_3$-*i*Pr). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 22.9. Anal. Calcd for $C_{32}H_{38}N_2PNiCl{\cdot}0.5C_7H_8$: C, 68.57; H, 6.81; N, 4.50. Found: C, 68.94; H, 6.79; N, 4.25.

[Ni(ArNHCPPh$_2$)(allyl)]SbF$_6$ (Ar = 2,6-*i*Pr-C$_6$H$_3$ (1b-SbF$_6$)). One equivalent of $AgSbF_6$ (0.123 g, 0.35 mmol) was added to a solution of complex **1b** (0.2 g, 0.35 mmol) in dichloromethane (5 mL). The reaction stirred for 10 min and then filtered through a pad of Celite. The solvent was removed under reduce pressure to afford a pale yellow solid in quantitative yield. Data for **1b-SbF$_6$**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.63-7.44 (m, 10 H, C*H*$_{Ar}$), 7.36-7.28 (m, 2 H, C*H*$_{Ar}$), 7.16 (d, 1 H, $^3J_{HH}$ = 1.8 Hz, C*H*$_{imid}$), 5.00 (m, 1 H, H$_{meso}$), 4.65 (m, 1 H, NC*H*$_2$), 4.35 (m, 1 H, NC*H*$_2$), 3.59 (m, 1 H, H$_{syn}$), 3.54 (m, 1 H, H$_{syn}$), 2.68 (m, 1 H, PC*H*$_2$), 2.57-2.44 (m, 3 H, C*H*-*i*Pr and PC*H*$_2$), 1.90-1.85 (m, 2 H, H$_{anti}$), 1.21 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr), 1.09 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr), 1.07 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr), 0,95 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 172.9, (d, J_{CP} = 19 Hz, N*C*N), 145.6 (*C*$_{Ar}$), 145.1 (*C*$_{Ar}$), 136.0 (*C*$_{Ar}$), 132.9 (d, J_{CP} = 14 Hz, *C*$_{Ar}$), 131.9 (d, J_{CP} = 3 Hz, *C*$_{Ar}$), 131.5 (d, J_{CP} = 11 Hz, *C*$_{Ar}$), 131.3 (d, J_{CP} = 3 Hz, *C*$_{Ar}$), 130.6 (*C*$_{Ar}$), 129.6, (d, J_{CP} = 2 Hz, *C*$_{Ar}$), 129.5 (d, J_{CP} = 2 Hz, *C*$_{Ar}$), 124.9 (*C*$_{Ar}$), 124.3 (d, J_{CP} = 6 Hz, *C*$_{Ar}$), 123.6 (*C*$_{Ar}$), 115.3 (*C*H$_{allyl}$), 67.6 (d, J_{CP} = 18 Hz, *C*H$_{2allyl}$), 63.2 (d, J_{CP} = 5 Hz, *C*H$_{2allyl}$), 47.1 (d, J_{CP} = 4 Hz, NCH$_2$), 28.5 (d, J_{CP} = 18 Hz, PCH$_2$), 27.0 (*C*H-*i*Pr), 26.8 (*C*H-*i*Pr), 25.4 (*C*H$_3$-*i*Pr), 24.9 (*C*H$_3$-*i*Pr), 22.9 (*C*H$_3$-*i*Pr), 22.6 (*C*H$_3$-*i*Pr). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 21.3. Anal. Calcd for $C_{32}H_{38}F_6N_2PNiSb{\cdot}0.4CH_2Cl_2$: C, 48.04; H, 4.83; N, 3.46. Found: C, 47.83; H, 4.83; N, 3.46.

[Ni(ArNHCPPh$_2$)(alkene)] (Ar = (2,6-iPr-C$_6$H$_3$; alkene = styrene (2a), diethyl fumarate, (2b)). The imidazolium salt (0.48g, 1 mmol), potassium bis(trimethylsilyl)amide (0.2 g, 1 mmol), Ni(cod)$_2$ (0.27 g, 1 mmol) and 3 equivalents of the corresponding alkene were dissolved in THF (5 mL). The mixture was stirred for 90 minutes at room temperature and then, it was filtered through a pad of Celite. The volatiles were removed under reduced pressure. The yellow-orange solid was washed with hexane to give the desired product. Yield: 0.54 g, 90 % for **2a**; 0.57 g, 85 % for **2b**. Data for **2a**: ^{1}H NMR (500 MHz, C_6D_6) δ 7.60 (t, 2 H, J_{HH} = 8.5 Hz, C*H*$_{Ar}$), 7.27-7.14 (m, 3 H, C*H*$_{Ar}$), 7.10-6.85 (m, 13 H, C*H*$_{Ar}$), 6.41 (s, 1 H, C*H*$_{imid}$), 6.13 (s, 1 H, C*H*$_{imid}$), 3.78-3.68 (m, 1 H, NC*H*$_2$ and C*H*$_{olefin}$), 3.39 (m, 1 H, NC*H*$_2$), 2.95 (hept, 1 H, $^3J_{HH}$ = 7 Hz, C*H*-*i*Pr), 2.66 (hept, 1 H, $^3J_{HH}$ = 7 Hz, C*H*-*i*Pr), 2.15 (m, 1H, C*H*$_{olefin}$), 1.94-1.85 (m, 2 H, PC*H*$_2$ and C*H*$_{olefin}$), 1.57 (m, 1 H, PC*H*$_2$), 1.30 (d, 3 H, $^3J_{HH}$ = 7 Hz, C*H*$_3$-*i*Pr), 1.11 (d, 3 H, $^3J_{HH}$ = 7 Hz, C*H*$_3$-*i*Pr), 1.05 (d, 3 H, $^3J_{HH}$ = 7 Hz, C*H*$_3$-*i*Pr), 0.89 (d, 3 H, $^3J_{HH}$ = 7 Hz, C*H*$_3$-*i*Pr). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 195.5 (d, J_{CP} = 8 Hz, N*C*N), 150.3 (*C*$_{Ar}$), 146.3 (*C*$_{Ar}$), 145.8 (*C*$_{Ar}$), 139.6 (d, J_{CP} = 23 Hz, *C*$_{Ar}$), 138.1 (*C*$_{Ar}$), 135.9 (d, J_{CP} = 25 Hz, *C*$_{Ar}$), 133.3 (d, J_{CP} = 15 Hz, *C*$_{Ar}$), 131.7 (d, J_{CP} = 13 Hz, *C*$_{Ar}$), 129.1 (*C*$_{Ar}$), 128.3 (*C*$_{Ar}$), 128.0 (*C*$_{Ar}$), 127.6 (*C*$_{Ar}$), 123.6 (*C*$_{Ar}$), 123.3 (*C*$_{Ar}$), 123.2 (*C*$_{Ar}$), 121.0 (*C*$_{Ar}$), 120.1 (*C*$_{Ar}$), 119.8 (*C*$_{Ar}$), 52.2 (*C*H$_{2olefin}$), 47.0 (d, J_{CP} = 8 Hz, NCH$_2$), 33.4 (d, J_{CP} = 24 Hz, *C*H$_{olefin}$), 28.4 (*C*H-*i*Pr), 28.3 (*C*H-*i*Pr), 27.7 (d, J_{CP} = 23 Hz, PCH$_2$), 25.4 (*C*H$_3$-*i*Pr), 24.6 (*C*H$_3$-*i*Pr), 23.7 (*C*H$_3$-*i*Pr), 22.6 (*C*H$_3$-*i*Pr). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 15.2. Attempts to obtain elemental analysis or the molecular mass by HRMS have failed with this compound.

Data for **2b**: ^{1}H NMR (500 MHz, C_6D_6): δ 8.07 (t, 2 H, $^3J_{HH}$ = 8.7 Hz, C*H*$_{Ar}$), 7.49 (t, 2 H, $^3J_{HH}$ = 8.7 Hz, C*H*$_{Ar}$), 7.24-7.12 (m, 7 H, C*H*$_{Ar}$), 7.08-7.01 (m, 2 H, C*H*$_{Ar}$), 6.46 (s, 1H, C*H*$_{imid}$), 6.09 (br. s, 1 H, C*H*$_{imid}$), 4.05 (dq, 1 H, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, COOC*H*$_2$CH$_3$), 3.97 (dq, 1 H, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, COOC*H*$_2$CH$_3$), 3.90-3.81 (m, 2 H, COOC*H*$_2$CH$_3$ and NC*H*$_2$), 3.71 (dq, 1 H, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, COOC*H*$_2$CH$_3$), 3.54 (m, 1 H, C*H*$_{olefin}$), 3.33-3.21 (m, 2 H, C*H*$_{olefin}$ and NC*H*$_2$), 3.09 (sept, 1 H, $^3J_{HH}$ = 6.5 Hz, CH-*i*Pr), 3.08 (sept, 1 H, $^3J_{HH}$ = 6.5 Hz, CH-*i*Pr), 1.72 (m, 1 H, PC*H*$_2$), 1.60 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH$_3$-*i*Pr), 1.39 (m, 1 H, PC*H*$_2$), 1.12 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH$_3$-*i*Pr), 0.99 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH$_3$-*i*Pr), 0.97 (t, 3 H, $^3J_{HH}$ = 7 Hz, COOCH$_2$C*H*$_3$), 0.84 (t, 3 H, $^3J_{HH}$ = 7 Hz, COOC*H*$_2$C*H*$_3$), 0.70 (d, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$-*i*Pr). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 192.0 (N*C*N), 173.8 (d, J_{CP} = 5 Hz, *C*=O), 145.9 (*C*$_{Ar}$), 144.9 (*C*$_{Ar}$), 137.4 (*C*$_{Ar}$), 137.2 (*C*$_{Ar}$), 136.9 (*C*$_{Ar}$), 135.1 (d, J_{CP} = 31 Hz, *C*$_{Ar}$), 133.3 (d, J_{CP} = 14 Hz, *C*$_{Ar}$), 132.2 (d, J_{CP} = 13 Hz, *C*$_{Ar}$), 129.4 (*C*$_{Ar}$), 129.1 (*C*$_{Ar}$), 128.9 (*C*$_{Ar}$), 128.4 (d, J_{CP} = 9 Hz, *C*$_{Ar}$), 128.1 (d, J_{CP} = 9 Hz, *C*$_{Ar}$), 128.0 (*C*$_{Ar}$), 127.2 (*C*$_{Ar}$), 123.8 (d, J_{CP} = 5 Hz, *C*$_{Ar}$), 123.3 (*C*$_{Ar}$), 119.8 (*C*$_{Ar}$), 57.9 (COO*C*H$_2$CH$_3$), 57.8 (*C*H$_{olefin}$), 46.2 (d, J_{CP} = 7 Hz, NCH$_2$), 41.2 (d, J_{CP} = 20 Hz, *C*H$_{olefin}$), 34.0 (COO*C*H$_2$CH$_3$), 27.4 (d, J_{CP} = 25 Hz, PCH$_2$), 26.3 (*C*H-*i*Pr), 24.5 (*C*H-*i*Pr), 23.3 (*C*H$_3$-*i*Pr), 22.4 (*C*H$_3$-*i*Pr), 22.3 (*C*H$_3$-*i*Pr), 21.8 (*C*H$_3$-*i*Pr), 14.4 (d, J_{CP} = 20 Hz, COOCH$_2$*C*H$_3$),

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13.9 ($COOCH_2CH_3$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 23.7. IR (KBr): ν(C-O) = 1668 cm^{-1} (str). Anal. Calcd for $C_{37}H_{45}N_2O_4PNi$: C, 66.19; H, 6.76; N, 4.17. Found: C, 66.28; H, 6.49; N, 4.29.

General procedure for Kumada-Tamao-Corriu reactions.

To a mixture of the catalyst (0.1 to 5 mol%) and the (hetero)aryl chloride (0.5 mmol) in THF (1 mL), phenylmagnesium chloride (0.75 mmol, 1 M in THF) was added under a nitrogen atmosphere. The reaction mixture was stirred at a room temperature for 16 h. A saturated solution of NH_4Cl was added and the mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solven was evaporated to dryness. The yield of product was determined by ^1H NMR using anisole as internal standard.

General procedure for Suzuki-Miyaura reactions.

The catalyst (1 or 3 mol%), the base K_3PO_4 (1.3 mmol), phenylboronic acid (0.65 mmol) and toluene (2 mL) were added in turn to a vial equipped with a J Young tap and containing a magnetic bar. The aryl chloride (0.5 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred for 18 h at 80 ºC in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through celite. After evaporation of the solvent, the crude was analyzed by ^1H NMR using anisole as internal standard.

General procedure for Buchwald-Hartwig amination reactions.

The catalyst (2.5-10 mol%), the base NaO*t*Bu or LiO*t*Bu (0.6 mmol) and dioxane (1 mL) were added in turn to a vial equipped with a J Young tap and containing a magnetic bar. The N-nucleophile (0.6 mmol) and the (hetero)aryl chloride (0.5 mmol) were added under a nitrogen atmosphere. The reaction mixture was stirred at 110ºC for 16 h in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through celite. The clean solution was evaporated to dryness, and the residue was analyzed by ^1H NMR using anisole as internal standard.

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