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# Ionic Ni(II) complexes containing a triphenylphosphine ligand and an imidazolium cation: synthesis, structures and catalysis for aryl Grignard cross-coupling of aryl halides†

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Novel ionic Ni(II) complexes of general formula $[R_2im][Ni(PPh_3)Cl_3]$ ($R_2im$ = 1,3-bis(2,6-diisopropylphenyl)-imidazolium cation, IPrim, **1a**; $R_2im$ = 1,3-diisopropylimidazolium cation, $^iPrim$, **2a**) were easily prepared in high yields by the direct reaction of $Ni(PPh_3)_2Cl_2$ with 1 equiv. of *N*,*N*′-dihydrocarbylimidazolium salt, $[R_2im]Cl$. Their bromide analogs $[R_2im][Ni(PPh_3)Br_3]$ ($R_2im$ = IPrim, **1b**; $R_2im$ = $^iPrim$, **2b**) were synthesized by the same reaction in the presence of excess NaBr. The reaction of $Ni(DME)Cl_2$ (DME = 1,2-dimethoxy-ethane) with 2 equiv. of [IPrim]Cl led to the formation of the complex $[IPrim]_2[NiCl_4]$ (**3**) in an almost quantitative yield. All these complexes were characterized by elemental analysis, electrospray ionization mass spectrometry (ESI-MS), and $^1H$ NMR spectroscopy; X-ray crystallography was performed for **1a**, **1b**, **2a**, and **2b**. A catalytic study of the cross-coupling reactions of aryl Grignard reagents with aryl halides revealed that complexes **1a** and **1b** possessed the highest activities. In comparison, complexes **2a**, **2b**, **3**, and the related biscarbene Ni(II) complex $Ni(IPr)_2Cl_2$ [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] exhibited moderate activities; the least active complexes were $Ni(PPh_3)_2Cl_2$ and $[NEt_4][Ni(PPh_3)Cl_3]$.

## Introduction

Transition-metal-catalyzed cross-coupling reactions represent one of the most powerful and versatile tools for the construction of carbon–carbon bonds.[1] The development of highly efficient, yet robust and easy-to-access catalysts for applications to cross-coupling reactions continues to attract much interest. In this context, although most studies have their emphasis on palladium-based systems, nickel-based catalysts have attracted increasing attention, because nickel is much cheaper and easier to remove from the final products than palladium.[2] Several nickel-based catalysts perform particularly well compared with palladium systems in various reactions,[3] for example, the Grignard cross-coupling reaction of aryl chlorides.[4] One of the main breakthroughs in this area has been the application of *N*-heterocyclic carbenes (NHCs) as an alternative to traditional tertiary phosphine ligands to improve the stabilities and catalytic activities of the corresponding nickel complexes.[5] Imidazolium salts have also been widely used in a range of cross-coupling processes, because carbene ligands can be easily generated by *in situ* dehydrohalogenation of the corresponding imidazolium salts with various bases.[3a,b,4a,6]

Recently, research efforts have also been devoted to the synthesis of mixed phosphine–NHC complexes of nickel in order to combine activity and robustness in the corresponding complexes. The synergic effect between these two types of ligands, which has been successfully applied in palladium-based systems,[7] is mostly explained by the currently accepted view that the labile phosphine ligand is capable of reversible dissociation from the metal center to generate *in situ* a vacant coordination site that enables easy complexation of substrates, whereas the tightly bound NHC ligand is supposed to stabilize the active species as well as facilitate oxidative addition and/or reductive elimination during the catalytic coupling processes. In this context, bidentate phosphine–imidazolium precursors or their NHC derivatives, as well as mixtures of monodentate phosphines and monodentate NHCs, have been extensively used in catalysis. For example, Poli *et al.* showed that zwitterionic Ni(II) complexes containing a bidentate phosphine–imidazolium ligand (**Ni-I**) were very active catalysts for the cross-coupling of aryl Grignard reagents with aryl chlorides,[8] and Lee *et al.* demonstrated that cationic Ni(II) complexes of bidentate phosphine–NHC ligands (**Ni-II**) were very effective in the Suzuki cross-coupling reaction, and can even be superior to

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their Pd(II) counterparts.[3c] However, these bidentate ligands generally suffer from limitations such as multistep preparation, harsh conditions, and high costs.

Jamison *et al.* described a catalytic system, based on [Ni(cod)$_2$]/P(OPh)$_3$/IPr [cod = cyclooctadiene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], capable of highly selective coupling of alkenes and aldehydes,[9] and Sasaki *et al.* reported that [BMim]$_2$[NiCl$_4$] (BMim = 1-*n*-butyl-3-methylimidazolium cation) was active in the Suzuki cross-coupling reaction of chloroarenes in the presence of 2 equiv. of PPh$_3$.[10] In the latter case, a nickel carbenic species produced by pretreating [BMim]$_2$[NiCl$_4$] with K$_3$PO$_4$ was suggested to be the catalytically active species. However, a large amount of catalyst (up to 20 mol%)[9] or an excess of PPh$_3$ [10] is usually needed in these systems.

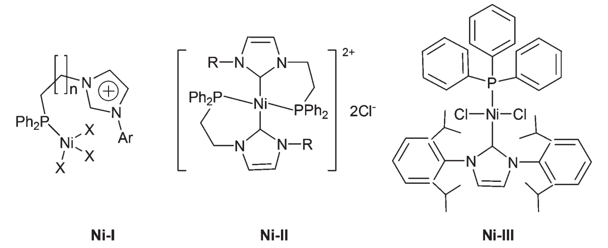
Notably, Matsubara *et al.* reported that a mixed Ni(II) complex bearing both a phosphine and an NHC ligand, Ni(PPh$_3$)(IPr)Cl$_2$ (**Ni-III**), showed distinctly higher catalytic activity in aryl Grignard cross-coupling, whereas the bis(NHC) complex of Ni(IPr)$_2$Cl$_2$ and the bisphosphine complex of Ni(PPh$_3$)$_2$Cl$_2$ showed much lower activities under the same conditions.[11a] Additionally, Ni(PPh$_3$)(IPr)Cl$_2$ can be used as a very efficient catalyst for other organic transformations, such as α-arylation of acyclic ketones,[11b] amination of haloarenes,[11b] and controlled polymerization of chlorothiophenes.[11c] A very recent study by Matsubara *et al.* also showed that a monovalent nickel complex, Ni(PPh$_3$)(IPr)Cl, was more effective than its biscarbene analog, Ni(IPr)$_2$Cl, in the aryl Grignard cross-coupling of aryl halides and amination of haloarenes.[12] All these results demonstrate that the combination of a monodentate phosphine ligand and a monodentate NHC ligand impart promising synergic effects to nickel-based catalysts. However, the fact that Ni(PPh$_3$)(NHC)Cl$_2$ could not be prepared unless the bulky IPr ligand was used might limit further investigations of the synthesis and applications of such complexes. We are therefore interested in exploring a versatile synthetic method for constructing a Ni(II)-based catalytic system with phosphine–NHC synergic effects.

As a continuation of our research on the nickel chemistry of NHCs,[13] we report here the facile synthesis of a new type of ionic Ni(II) complex, containing a triphenylphosphine ligand and an imidazolium cation, [R$_2$im][Ni(PPh$_3$)X$_3$] (R$_2$im = 1,3-dihydrocarbylimidazolium cation; X = Cl and Br), and their catalytic potential in aryl Grignard cross-coupling of aryl halides. Notably, the easily available [R$_2$im][Ni(PPh$_3$)X$_3$] is very effective, whereas the related Ni(II) complexes such as [R$_2$im]$_2$[NiCl$_4$], Ni(NHC)$_2$X$_2$, Ni(PPh$_3$)Cl$_2$ and [NEt$_4$][Ni(PPh$_3$)Cl$_3$] showed obviously lower activities under the same conditions.

## Results and discussion

### Synthesis and characterization of ionic Ni(II) complexes

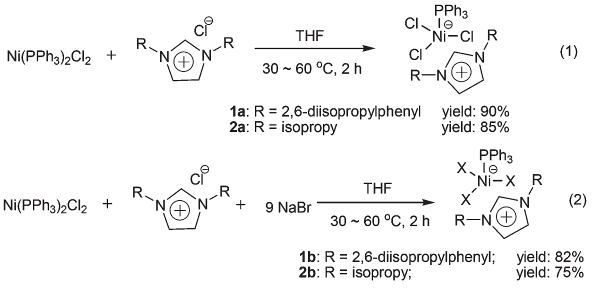
The target ionic Ni(II) complexes **1a–2b** were readily synthesized using Ni(PPh$_3$)$_2$Cl$_2$ as the starting material. As shown in Scheme 1 (1), at 30 °C, the reaction of Ni(PPh$_3$)$_2$Cl$_2$ with 1 equiv. of the *N*,*N*′-diarylimidazolium salt [R$_2$im]Cl [R$_2$im = 1,3-bis(2,6-diisopropylphenyl)imidazolium cation, IPrim] occurred smoothly in tetrahydrofuran (THF) and gave the desired complex **1a** in 90% yield as bright blue crystals. In addition, even when more than 1 equiv. of [IPrim]Cl was added, only **1a** was obtained, with recovery of some [IPrim]Cl. To assess the potential of the new synthetic approach, a similar reaction with another imidazolium salt was tested. It was found that the substitution reaction of one PPh$_3$ ligand in Ni(PPh$_3$)$_2$Cl$_2$ with the *N*,*N*′-dialkylimidazolium salt [R$_2$im]Cl (R$_2$im = 1,3-diisopropylimidazolium cation, $^i$Prim) also occurred smoothly and afforded the analogous complex **2a** in high yield. The latter reaction, however, proceeded at a slower rate than that using [IPrim]Cl, and an elevated temperature (60 °C) was required to obtain the high yield.



**Scheme 1** Typical mixed Ni(II) complexes.

Notably, the exchange of the [Ni(PPh$_3$)Cl$_3$]$^-$ anion for the [Ni(PPh$_3$)Br$_3$]$^-$ anion also proceeded smoothly by the addition of sodium bromide (NaBr). As seen in Scheme 2 (2), the treatment of Ni(PPh$_3$)$_2$Cl$_2$ with 1 equiv. of [IPrim]Cl in the presence of excess NaBr afforded the analogous complex **1b** in 82% yield as bright green crystals, and a similar reaction with [$^i$Prim]Cl produced the bromide **2b** in 75% yield at an elevated temperature (60 °C).

Complexes **1a** and **1b** are air stable, whereas complexes **2a** and **2b** are somewhat sensitive to moisture (stable in dry air) and decompose slowly to white solids in a moist atmosphere.[14] Better solubility profiles were observed for these Ni(II) complexes than for the corresponding *N*,*N*′-dihydrocarbylimidazolium salts [R$_2$im]X, and all of them dissolved easily in THF. The difference in solubility between the Ni(II) complex and the corresponding [R$_2$im]X facilitated effective purification of the target product.

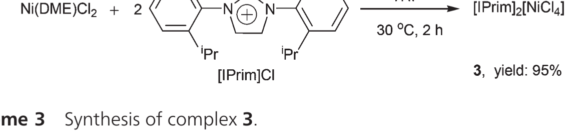


**Scheme 2** Synthesis of ionic nickel(II) complexes **1a–2b**.

Attempts to synthesize the corresponding neutral mixed Ni(II) complexes bearing both a $PPh_3$ ligand and an NHC ligand by dehydrohalogenation of **1a**–**2b** with various bases, following procedures similar to those for their palladium analogs[7d,15] or zwitterionic Ni(II) complexes **Ni-I**,[8] were investigated. Typically, the addition of a strong base such as $^nBuLi$[8] or $KO^tBu$[11a] to a THF solution of **1a** induced a color change to dark red, indicating the formation of a nickel carbenic species, very similar to the change observed in the dehydrohalogenation of **Ni-I**.[8] However, our attempts to isolate the expected mixed Ni(II) complex, $Ni(PPh_3)(IPr)Cl_2$, were unsuccessful, and the pure biscarbene Ni(II) complex of $Ni(IPr)_2Cl_2$ together with some amounts of $PPh_3$ were isolated from the reaction solution. This was mostly caused by the substitution reaction of $Ni(PPh_3)(IPr)Cl_2$, which was generated by *in situ* dehydrohalogenation of **1a**, with an *in situ* generated IPr ligand during the reaction procedure. Matsubara *et al.* demonstrated that $Ni(PPh_3)(IPr)Cl_2$ could be converted to $Ni(IPr)_2Cl_2$ in quantitative yield by the addition of more than 1 equiv. of IPr ligand.[11a]

Stirring a sample of $Ni(DME)Cl_2$ (DME = 1,2-dimethoxyethane) with 2 equiv. of [IPrim]Cl in THF at 30 °C, an alternative procedure with mild conditions relative to those used in the previously reported methods,[16] led to the formation of the complex $[IPrim]_2[NiCl_4]$ (**3**) in 95% yield as blue crystals (Scheme 3). The reported methods, which used anhydrous $NiCl_2$[16a–c] or $NiCl_2·6H_2O$[16d,f] as nickel sources, usually proceeded above 70 °C and needed a much longer reaction time. Complex **3** dissolved in THF, but was insoluble in toluene and hexane. Similar to previously described imidazolium tetrachloronickelate(II) complexes,[16] complex **3** is hygroscopic, and was immediately converted to a green solid when water was added deliberately, but the blue color could be regenerated on heating under vacuum.

All the obtained complexes were characterized by elemental analysis, electrospray ionization mass spectrometry (ESI-MS), and $^1H$ NMR spectroscopy, and by X-ray crystallography for complexes **1a**–**2b**. The positive ion ESI-MS of **1a**–**3** were used to establish the presence of the imidazolium cation, and in all cases a peak with an intensity of almost 100% indicative of the imidazolium cation was observed. The $^1H$ NMR spectra of complexes **1a**–**2b** exhibited characteristic resonances similar to those of the corresponding imidazolium salts, except that slightly down-field chemical shifts, together with three broad and weak signals at ranges of $\delta = -4.11$–2.69, 3.81–5.08, and 18.74–19.04 ppm, respectively, were observed. Such shift variations and broadening are very similar to those observed for previously reported bidentate phosphine–imidazolium salts and their derived zwitterionic Ni(II) complexes **Ni-I**, as a result of the paramagnetic properties of the metal ion.[8] The $^{13}P$ NMR spectra of **1a**–**2b** exhibited no signal in $CD_3OCD_3$, indicating direct bonding of the $PPh_3$ ligand to the nickel. The relatively sharp resonances in the $^1H$ NMR spectra of **1a**–**2b** can be rationalized by the hypothesis that there is no strong coordination between the imidazolium cation and the nickel center, which can be further confirmed by X-ray crystallography. The $^1H$ NMR spectrum of **3** is also very similar to that of [IPrim]Cl, and only minor differences in the chemical shifts were observed.



**Scheme 3** Synthesis of complex **3**.

Crystals suitable for X-ray diffraction studies were grown from a concentrated THF solution (**1a** and **2a**) or a THF–toluene solution (**1b** and **2b**) of the obtained Ni(II) complexes at 0 °C. The crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2, respectively. The molecular structures of these complexes are shown in Fig. 1 (**1a** and **1b**) and 2 (**2a** and **2b**).

As shown in Fig. 1 and 2, each of the four molecular structures contains one imidazolium $[R_2im]^+$ cation and one $[Ni(PPh_3)X_3]^-$ anion. The structures of the $[R_2im]^+$ cations do not change significantly upon reaction of the imidazolium salts with $Ni(PPh_3)_2Cl_2$, as the bond distances and angles within the imidazolium ring differ only slightly, and these parameters are comparable to those of previously reported imidazolium salts.[8,17] For complexes **1a** and **1b**, each plane of the phenyl ring is oriented nearly perpendicular to the imidazolium ring, with dihedral angles ranging between 84.2 and 85.6° in **1a** and between 85.2 and 86.0° in **1b**, as well as at an angle of 23.2° (**1a**) or 24.6° (**1b**) to the plane of the other phenyl ring in the system. In all four $[Ni(PPh_3)X_3]^-$ anions, each nickel atom is coordinated by three halogen atoms and one phosphorus atom in a distorted tetrahedral geometry, with Ni–Cl, Ni–Br, and Ni–P bond lengths in the ranges 2.209(2)–2.254(2) Å, 2.308(2)–2.332(2) Å, and 2.308(2)–2.318(1) Å, respectively. The mean values of the Ni–Cl bond lengths are 2.240 Å for **1a** and 2.225 Å for **2a**, whereas the mean values of the Ni–Br bond lengths are 2.364 Å and 2.349 Å for **1b** and **2b**, respectively. These values are unexceptional and lie within the ranges found for other complexes containing $[Ni(PR_3)X_3]^-$ anions.[8,18] Nevertheless, it is worth noting that complexes **1a**–**2b** have very similar Ni–P bond lengths [2.318(1), 2.310(2), 2.314(1), and 2.308(2) Å in **1a**, **1b**, **2a**, and **2b**, respectively], even though they bear either a different imidazolium cation or a different halide atom. The angles at nickel are in the ranges 99.14(6)–121.22(6)° for **1a**, 99.60(6)–123.38(5)° for **1b**, 102.44(5)–120.68(6)° for **2a**, and 102.60(6)–124.11(5)° for **2b**. In the structures of both **1a** and **1b**, the X(3)–Ni–X(1) angle is significantly wider [121.22(6)° for **1a** and 123.38(5)° for **1b**] than the other two X–Ni–X angles. A similar trend, *i.e.*, a much wider X(2)–Ni–X(3) angle [120.68(6)° for **2a** and 124.11(5)° for **2b**], is observed in the structures of **2a** and **2b**. Such a trend has been observed in the structures of the previously reported zwitterionic Ni(II) complexes **Ni-I**, and may be related to the C–H···X interaction between the $[R_2im]^+$ cation and the $[Ni(PR_3)X_3]^-$ anion.[8] Indeed, a number of hydrogen contacts less than 3 Å are observed in all the structures, and the shortest distance,

**Table 1** X-ray crystallographic data for **1a–2b**

| | **1a** | **1b** | **2a** | **2b** |
|---|---|---|---|---|
| Formula | $C_{45}H_{52}Cl_3N_2NiP$ | $C_{45}H_{52}Br_3N_2NiP$ | $C_{27}H_{32}Cl_3N_2NiP$ | $C_{27}H_{32}Br_3N_2NiP$ |
| Formula weight | 816.92 | 950.30 | 580.58 | 713.96 |
| Temperature/K | 223(2) | 223(2) | 293(2) | 223(2) |
| Radiation used | Mo-Kα | Mo-Kα | Mo-Kα | Mo-Kα |
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | *Pna*21 | *Pna*21 | *P*21/*c* | *P*21/*c* |
| **Unit cell dimensions** | | | | |
| $a$/Å | 17.270(7) | 17.4911(18) | 15.958(4) | 16.0114(5) |
| $b$/Å | 14.224(5) | 14.3761(14) | 9.663(2) | 9.7678(8) |
| $c$/Å | 17.322(7) | 17.6688(19) | 19.083(4) | 19.4056(3) |
| $\beta$/° | 90 | 90 | 90.547(4) | 91.043(11) |
| $V$/Å$^3$ | 4255(3) | 4442.9(8) | 2942.4(11) | 3034.5(3) |
| $Z$ | 4 | 4 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.275 | 1.421 | 1.311 | 1.563 |
| $\mu$/mm$^{-1}$ | 0.715 | 3.202 | 1.004 | 4.660 |
| $F$(000) | 1720 | 1936 | 1208 | 1424 |
| $\theta$ range/° | 3.00–25.50 | 3.06–27.47 | 3.25–25.35 | 3.24–25.50 |
| Reflection collected | 19 706 | 24 646 | 22 080 | 15 163 |
| Independent reflections, $R_{int}$ | 7031, 0.0427 | 8189, 0.0494 | 5339, 0.0841 | 5628, 0.0448 |
| Goodness-of-fit on $F^2$ | 1.114 | 1.092 | 0.936 | 1.087 |
| $R_1$, w$R_2$ [$I > 2\sigma(I)$] | 0.0531, 0.1322 | 0.0651, 0.1601 | 0.0558, 0.1357 | 0.0736, 0.1837 |
| $R_1$, w$R_2$ (all data) | 0.0592, 0.1487 | 0.0828, 0.1732 | 0.1044, 0.1651 | 0.1069, 0.2047 |

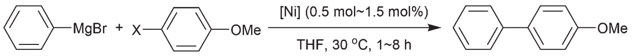
**Table 2** Selected bond lengths (Å) and angles (°) for **1a–2b**

| | **1a** | **1b** | **2a** | **2b** |
|---|---|---|---|---|
| Ni(1)–X(1) | 2.254(2) | 2.392(1) | 2.226(1) | 2.340(1) |
| Ni(1)–X(2) | 2.226(2) | 2.332(2) | 2.209(2) | 2.346(1) |
| Ni(1)–X(3) | 2.239(2) | 2.368(1) | 2.240(2) | 2.361(1) |
| Ni(1)–P(1) | 2.318(1) | 2.310(2) | 2.314(1) | 2.308(2) |
| N(1)–C(19) | 1.340(7) | 1.336(9) | 1.329(6) | 1.332(11) |
| N(1)–C(20) | 1.389(6) | 1.369(9) | 1.360(7) | 1.373(11) |
| N(2)–C(19) | 1.324(7) | 1.318(9) | 1.323(6) | 1.301(10) |
| N(2)–C(21) | 1.379(6) | 1.4009) | 1.362(6) | 1.378(11) |
| C(20)–C(21) | 1.336(8) | 1.321(11) | 1.334(7) | 1.328(13) |
| X(2)–Ni(1)–X(3) | 115.72(8) | 118.81(8) | 120.68(6) | 124.11(5) |
| X(2)–Ni(1)–X(1) | 108.18(7) | 100.49(7) | 110.05(7) | 106.70(6) |
| X(3)–Ni(1)–X(1) | 121.22(6) | 123.38(5) | 113.53(6) | 111.56(5) |
| X(2)–Ni(1)–P(1) | 105.88(5) | 109.09(7) | 104.68(5) | 106.22(6) |
| X(3)–Ni(1)–P(1) | 99.14(6) | 99.60(6) | 102.44(5) | 102.60(6) |
| X(1)–Ni(1)–P(1) | 104.46(6) | 104.20(7) | 103.13(5) | 103.62(6) |

2.52 Å, is found in **1a**. In **1a** and **1b**, each $[R_2im]^+$ cation is close to three halide atoms belonging to two different $[Ni(PPh_3)X_3]^-$ anions, whereas in **2a** and **2b**, five and four hydrogen contacts, which stem from four and three different $[Ni(PPh_3)X_3]^-$ anions, are observed, respectively. Such hydrogen bonding interaction between the imidazolium cation and the metal-containing anion has been well established and explains to some degree their markedly higher melting points relative to, for example, those of the corresponding imidazolium salts.[8,16,17]

### Catalysis by ionic Ni(II) complexes

To disclose any synergic effects resulting from the ionic Ni(II) complexes of $[R_2im][Ni(PPh_3)X_3]$, the standard Kumada–Corriu reaction, outlined in eqn (1), was chosen as a test reaction[8,11a,19] for comparisons among $[R_2im][Ni(PPh_3)X_3]$ (**1a–2b**), $[IPrim]_2[NiCl_4]$ (**3**), $Ni(IPr)_2Cl_2$, $Ni(PPh_3)Cl_2$, and $[NEt_4][Ni(PPh_3)Cl_3]$. The experiments were performed using 4-bromoanisole and its analogous chloride, respectively, as starting reagents, in order to highlight activity differences. The results obtained are summarized in Table 3.



(1)

As can be seen from Table 3, there are significant differences among the catalytic activities of these Ni(II) complexes under the present conditions. The catalytic activities of **1a** and **1b** are higher than the other Ni(II) complexes. For example, the cross-coupling reaction of 4-bromoanisole with phenylmagnesium bromide afforded a quantitative yield of 4-methoxybiphenyl with 0.5 mol% of **1a** or **1b** in 1 h at 30 °C (entries 1 and 3), and for **1a** the yield still reached 95% even when the reaction time was reduced to 30 min. In comparison, complexes **2a**, **2b**, **3**, and $Ni(IPr)_2Cl_2$ showed moderate activities, and respectively furnished 64% (entry 5), 67% (entry 7), 80% (entry 9), and 75% (entry 11) yields of 4-methoxybiphenyl. The least reactive complexes were $Ni(PPh_3)_2Cl_2$ and $[NEt_4][Ni(PPh_3)Cl_3]$, which afforded the product in merely 26% (entry 13) and 33% (entry 15) yields, respectively. The apparent difference in catalytic activity between **1a** and $[NEt_4][Ni(PPh_3)Cl_3]$ indicates clearly that the imidazolium cation plays an important role in the activity of the present ionic Ni(II) complex, *i.e.* acts as a precursor to an active Ni-NHC species. Using less reactive 4-chloroanisole as the starting reagent, the same trend in catalytic activity was observed when the catalyst loading was increased to 1.5 mol%. Notably, the catalytic activity of **1a** was found to be very close to that of a mixed Ni(II) complex bearing both a phosphine and an NHC ligand, $Ni(PPh_3)(IPr)Cl_2$ (**Ni-III**), which afforded a quantitative yield of 4-methylbiphenyl by using

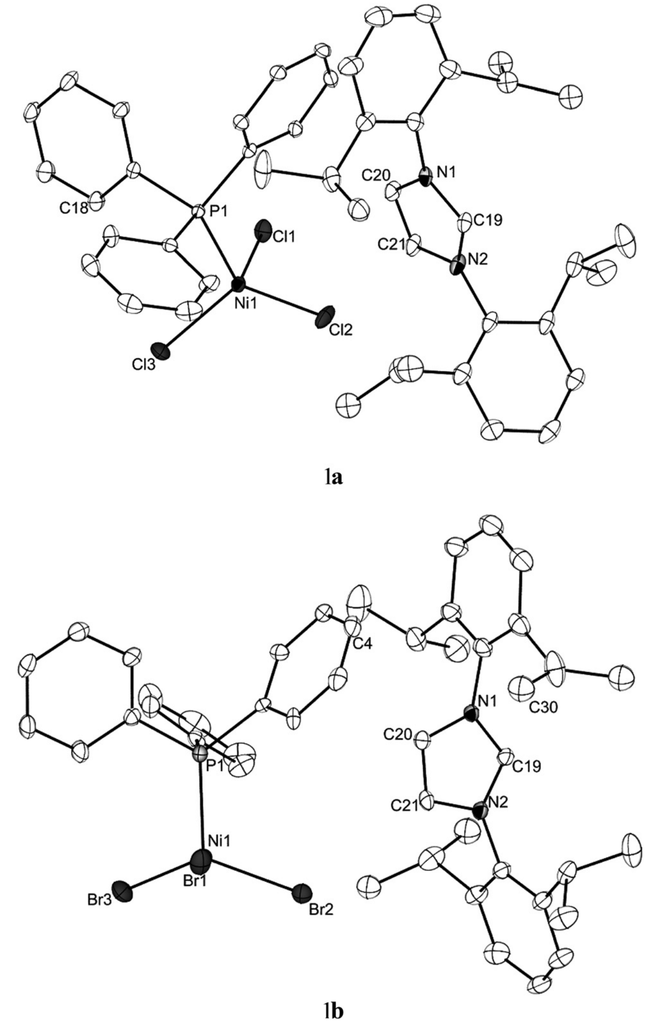


**Fig. 1** Molecular structures of **1a** and **1b** with thermal ellipsoids at the 15% probability level. All hydrogens are omitted for clarity.

4-bromoanisole as starting material with a 0.5 mol% loading in 30 min at 18 °C, and 39% yield of the desired product when 4-chloroanisole was used instead of 4-bromoanisole.[11a] The catalytic activity of **1b** was comparable to that of a zwitterionic Ni(II) complex bearing a bidentate phosphine–imidazolium salt ligand (**Ni-I**), reported by Poli *et al.*[8b] The present work therefore clearly shows that the simple, easily accessible ionic Ni(II) complexes of [R$_2$im][Ni(PPh$_3$)X$_3$] can exert a significant synergic effect on their catalytic activity. The high catalytic activities of **1a** and **1b** are mainly the result of the stability provided by the *in situ*-generated bulky IPr ligand and the hemilability of the PPh$_3$ ligand on the nickel center.[11] The fact that the catalytic activities of **1a** and **1b** are higher than those of **2a** and **2b**, respectively, could be ascribed more to a result of the steric bulkiness provided by the *in situ*-generated NHC ligand,[4a] which can facilitate reductive elimination to form the desired cross-coupling product as well as to regenerate the catalytically active species, than the acceleration of oxidative addition brought about by the strong σ-donating ability of the *in situ*-generated NHC ligand.[4c]

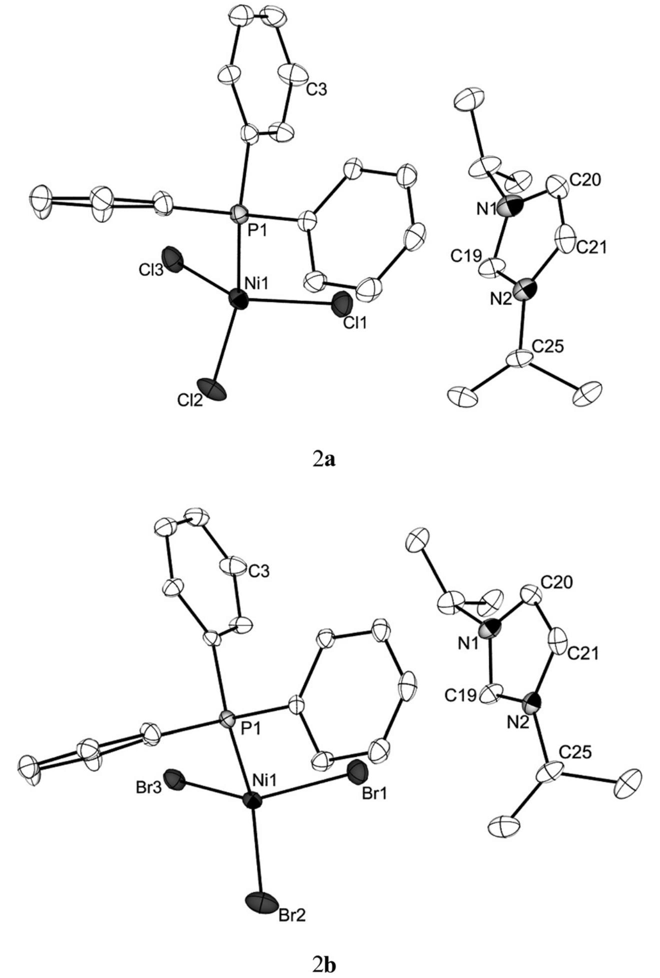


**Fig. 2** Molecular structures of **2a** and **2b** with thermal ellipsoids at the 15% probability level. All hydrogens are omitted for clarity.

**Table 3** The cross-couplings of C$_6$H$_5$MgBr with *p*-MeOC$_6$H$_4$X catalyzed by Ni(II) complexes[a]

| Entry | Catalyst (mol%) | X | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | **1a** (0.5) | Br | 1 | 100 (95[b]) |
| 2 | **1a** (1.5) | Cl | 8 | 85 |
| 3 | **1b** (0.5) | Br | 1 | 100 |
| 4 | **1b** (1.5) | Cl | 8 | 86 |
| 5 | **2a** (0.5) | Br | 1 | 64 |
| 6 | **2a** (1.5) | Cl | 8 | 65 |
| 7 | **2b** (0.5) | Br | 1 | 67 |
| 8 | **2b** (1.5) | Cl | 8 | 63 |
| 9 | **3** (0.5) | Br | 1 | 80 |
| 10 | **3** (1.5) | Cl | 8 | 55 |
| 11 | Ni(IPr)$_2$Cl$_2$ (0.5) | Br | 1 | 75 |
| 12 | Ni(IPr)$_2$Cl$_2$ (1.5) | Cl | 8 | 52 |
| 13 | Ni(PPh$_3$)$_2$Cl$_2$ (0.5) | Br | 1 | 26 |
| 14 | Ni(PPh$_3$)$_2$Cl$_2$ (1.5) | Cl | 8 | 27 |
| 15 | [NEt$_4$][Ni(PPh$_3$)Cl$_3$] (0.5) | Br | 1 | 33 |
| 16 | [NEt$_4$][Ni(PPh$_3$)Cl$_3$] (1.5) | Cl | 8 | 32 |

[a] Reaction conditions: C$_6$H$_5$MgBr (1.5 mmol, 1.0 M in THF), *p*-MeOC$_6$H$_5$X (1.0 mmol), total volume (2.0 mL), 30 °C, GC yield. [b] 0.5 h.

The performances of the catalytic systems with other coupling partners were investigated and are summarized in Table 4.

As can be seen from Table 4, a host of aromatic bromides and chlorides reacted smoothly with various arylmagnesium halides to give the corresponding coupling products in good to excellent yields. Notably, complex **1a** displayed good activity toward aryl chlorides, which is less reactive and yet the most attractive substrate among the aryl halides from the standpoints of cost and availability.[4,20] In particular, the electronic properties exert the expected influences, that is the electron-poor arenes being the most active (entries 8–10, 22),

**Table 4** The cross-couplings of aryl Grignard reagents with aryl halides catalyzed by **1a**[a]

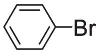
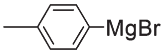
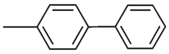
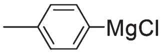
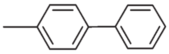
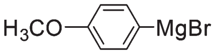
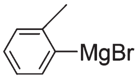
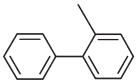
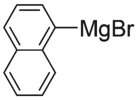
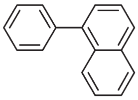
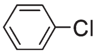
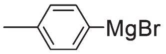
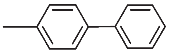
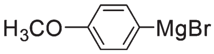
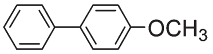
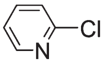
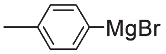
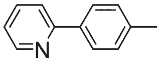
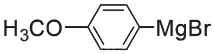
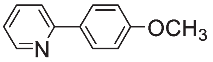
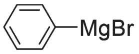
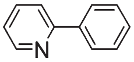
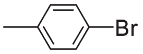
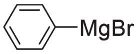
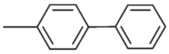
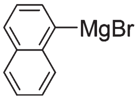
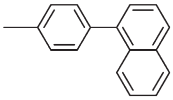
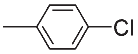
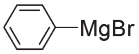
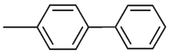
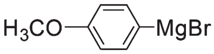
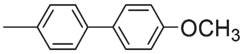
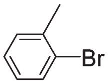
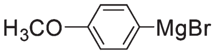
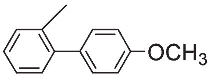
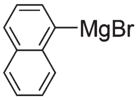
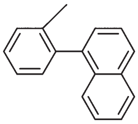
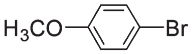
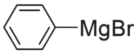
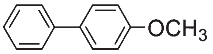
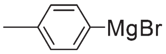
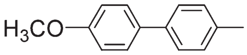
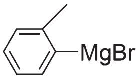
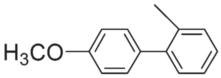
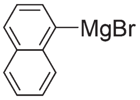
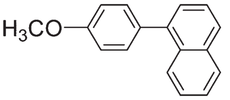
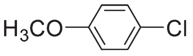
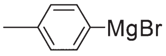
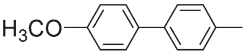
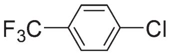
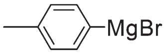
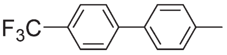
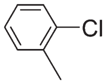
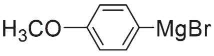
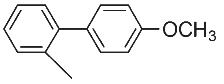
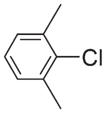
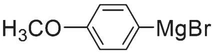
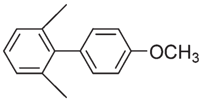
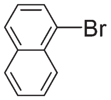
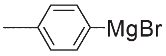
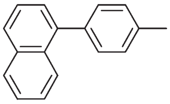
| Entry | ArX | Ar′MgX | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  |  |  | 96 (100[b]) |
| 2 | |  |  | 89 |
| 3 | |  |  | 72 |
| 4 | |  |  | 72 |
| 5[c] | |  |  | 82 |
| 6[d] |  |  |  | 85 (90[b]) |
| 7[d] | |  |  | 67 |
| 8[e] |  |  |  | 94 (99[b]) |
| 9[e] | |  |  | 99[b] |
| 10[e] | |  |  | 98[b] |
| 11 |  |  |  | 100[b] |
| 12[c] | |  |  | 83 |
| 13[d] |  |  |  | 81 |
| 14[d] | |  |  | 65 |
| 15 |  |  |  | 60 |
| 16[c] | |  |  | 88 |
| 17 |  |  |  | 95 (100[b]) |
| 18 | |  |  | 72 |
| 19 | |  |  | 68 |

**Table 4** *(Contd.)*

| Entry | ArX | Ar′MgX | Product | Yield (%) |
|---|---|---|---|---|
| 20[c] | |  |  | 58 |
| 21[d] |  |  |  | 83 |
| 22 |  |  |  | 42 (99[b,c]) |
| 23[d] |  |  |  | 52 |
| 24[d] |  |  |  | ~0 |
| 25 |  |  |  | 85 |

[a] Conditions: **1a** (0.5 mol%), aryl Grignard reagents (1.5 mmol, 1.0 M in THF), aryl bromide (1.0 mmol), total volume (2.0 mL), 30 °C, 1 h, isolated yield. [b] GC yield. [c] Grignard reagents (1.2 mmol, 0.3 M in THF), total volume (4.8 mL). [d] **1a** (1.5 mol%), 8 h. [e] **1a** (1.0 mol%), 5 h.

meanwhile the steric hindrance is partially tolerated by the system as demonstrated by 2-chlorotoluene, but 2-chloro-*m*-xylene showed little activity (entries 6, 23, 24). This is similar to the previously reported pattern with the Ni(acac)$_2$/[IPrim]Cl catalytic system.[4] Therefore, these results suggest the great potential of the new type of Ni(II) complex of [R$_2$im][Ni(PPh$_3$)X$_3$] as a suitable precatalyst for C–C cross-coupling applications.

## Conclusions

A new type of ionic Ni(II) complex, of general formula [R$_2$im][Ni(PPh$_3$)X$_3$] (**1a**–**2b**), was easily synthesized *via* the simple reaction of Ni(PPh$_3$)$_2$Cl$_2$ with 1 equiv. of *N*,*N*′-dihydrocarbyl-imidazolium salt. It is of interest that the monophosphine Ni(II) complexes of [IPrim][Ni(PPh$_3$)X$_3$] (X = Cl, **1a**; X = Br, **1b**) showed much higher catalytic activities in the cross-coupling of aryl Grignard reagents with aryl halides than did other related Ni(II) complexes, *i.e.*, [$^i$Prim][Ni(PPh$_3$)X$_3$] (X = Cl, **2a**; X = Br, **2b**), [IPrim]$_2$[NiCl$_4$] (**3**), Ni(IPr)$_2$Cl$_2$, Ni(PPh$_3$)Cl$_2$, and [NEt$_4$][Ni(PPh$_3$)Cl$_3$]. This apparently high catalytic activity is possibly due to the stabilization effect of an *in situ*-generated bulky IPr ligand and the hemilability of the PPh$_3$ ligand on the catalytically active species. Since a variety of bisphosphine Ni(II) dihalides and imidazolium salts are available, we reasoned that the construction of the ionic Ni(II) complex of general formula [R$_2$im][Ni(PR$_3$)X$_3$] can be used as an alternative strategy to significantly improve the catalytic activity of Ni(II) complexes with phosphine/NHC synergic effects. A detailed structure–reactivity relationship study of this new type of Ni(II) complex, the isolation of the expected monophosphine monocarbene complexes of nickel, and the scope of these Ni(II) complexes in other carbon–carbon coupling reactions are currently under investigation in our laboratory.

## Experimental section

### General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Ni(PPh$_3$)$_2$Cl$_2$,[21] [IPrim]Cl,[22] [$^i$Prim]Cl,[23] Ni(IPr)$_2$Cl$_2$ [13g] and [NEt$_4$][Ni(PPh$_3$)Cl$_3$][24] were prepared by published methods. Organic reagents used for cross-coupling reactions were purchased from Acros Organics, Sigma-Aldrich and Alfa Aesar. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. NMR spectra were measured on a Varian Unity INOVA 400 or a VNMRS 300 MHz spectrometer at 25 °C. Electrospray Ionization-Mass spectrum (ESI-MS) data were recorded on a 6220 Accurate-Mass TOF LC/MS instrument. The melt points were determined on a Diamond DSC (Perkin Elmer) using powder samples under an N$_2$ atmosphere (50 mL min$^{-1}$). The system was heated from 50 °C to 350 °C at 20 °C min$^{-1}$. Gas chromatographic (GC) analysis was performed using a Varian CP-3800 instrument equipped with an FID detector and a capillary column AT.OV-101 (30 m × 0.32 mm i.d., 0.10 μm film). The oven program temperature was 80 °C for 2 min, increased to 280 °C at 10 °C min$^{-1}$, and held for 2 min.

### Synthesis

**[IPrim][Ni(PPh$_3$)Cl$_3$] (1a).** A Schlenk flask was charged with Ni(PPh$_3$)$_2$Cl$_2$ (0.65 g, 1.00 mmol), [IPrim]Cl (0.43 g, 1.00 mmol), THF (15 mL) and a stir bar. The resulting mixture was stirred for 2 h at 30 °C, filtered, and evaporated to dryness. The residue was washed with toluene and extracted with hot THF and crystallized from concentrated THF at 0 °C. The product was precipitated as bright blue crystals in a yield of 90% (0.74 g). M.p. 285.3 °C. Anal. calcd for $C_{45}H_{52}Cl_3N_2NiP$: C, 66.16; H, 6.42; N, 3.43. Found: C, 66.22; H, 6.53; N, 3.43. $^1$H NMR ($\delta$, 400 MHz, $(CD_3)_2CO$): −2.69 (br s, Ph-*H*), 1.41 (d, *J* = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.43 (d, *J* = 4.0 Hz, 12H, $CH(CH_3)_2$), 2.98 (m, 4H, $CH(CH_3)_2$), 5.07 (br s, Ph-*H*), 7.63 (d, *J* = 8.0 Hz, 4H, *m*-Ar-*H*), 7.76–7.79 (m, 2H, *p*-Ar-*H*), 9.61 (s, 2H, NC*H*C*H*N), 9.96 (s, 1H, NC*H*N), 18.83 (br s, Ph-*H*). MS (ESI+): *m*/*z* 389.29 $[C_{27}H_{37}N_2]^+$ (100%).

**[IPrim][Ni(PPh$_3$)Br$_3$] (1b).** A Schlenk flask was charged with $Ni(PPh_3)Cl_2$ (0.65 g, 1.00 mmol), [IPrim]Cl (0.43 g, 1.00 mmol), NaBr (0.93 g, 9 mmol), THF (15 mL) and a stir bar. The resulting mixture was stirred for 2 h at 30 °C, filtered, and evaporated to dryness. The residue was washed with toluene and extracted with hot THF and crystallized from concentrated THF–toluene at 0 °C. The product was precipitated as bright green crystals in a yield of 82% (0.78 g). M.p. 294.8 °C. Anal. calcd for $C_{45}H_{52}Br_3N_2NiP$: C, 56.88; H, 5.52; N, 2.95. Found: C, 56.84; H, 5.59; N, 2.95. $^1$H NMR ($\delta$, 400 MHz, $(CD_3)_2CO$): −3.56 (br s, Ph-*H*), 1.33 (d, *J* = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.38 (d, *J* = 8.0 Hz, 12H, $CH(CH_3)_2$), 2.75 (m, 4H, $CH(CH_3)_2$), 4.29 (br s, Ph-*H*), 7.61 (d, *J* = 8.0 Hz, 4H, *m*-Ar-*H*), 7.75–7.78 (m, 2H, *p*-Ar-*H*), 8.96 (s, 2H, NC*H*C*H*N), 9.92 (s, 1H, NC*H*N), 19.04 (br s, Ph-*H*). MS (ESI+): *m*/*z* 389.30 $[C_{27}H_{37}N_2]^+$ (100%).

**[$^i$Prim][Ni(PPh$_3$)Cl$_3$] (2a).** A Schlenk flask was charged with $Ni(PPh_3)Cl_2$ (0.65 g, 1.00 mmol), [$^i$Prim]Cl (0.19 g, 1.00 mmol), THF (15 mL) and a stir bar. The resulting mixture was stirred for 2 h at 60 °C, filtered, and evaporated to dryness. The residue was washed with toluene and extracted with hot THF and crystallized from concentrated THF at 0 °C. The product was precipitated as bright blue crystals in a yield of 85% (0.49 g). M.p. 172.5 °C. Anal. calcd for $C_{27}H_{32}Cl_3N_2NiP$: C, 55.86; H, 5.56; N, 4.83. Found: C, 55.77; H, 5.56; N, 4.96. $^1$H NMR ($\delta$, 400 MHz, $(CD_3)_2CO$): −2.81 (br s Ph-*H*), 2.96 (d, *J* = 32 Hz, 12H, $CH(CH_3)_2$), 5.08 (br s, Ph-*H*), 7.61–7.81 (m, 2H, $CH(CH_3)_2$), 8.91 (s, 2H, NC*H*C*H*N), 12.41 (s, 1H, NC*H*N), 18.74 (br s, Ph-*H*). MS (ESI+): *m*/*z* 153.14 $[C_9H_{17}N_2]^+$ (100%).

**[$^i$Prim][Ni(PPh$_3$)Br$_3$] (2b).** A Schlenk flask was charged with $Ni(PPh_3)Cl_2$ (0.65 g, 1.00 mmol), [$^i$Prim]Cl (0.19 g, 1.00 mmol), NaBr (0.93 g, 9 mmol), THF (15 mL) and a stir bar. The resulting mixture was stirred for 2 h at 60 °C, filtered, and evaporated to dryness. The residue was washed with toluene and extracted with THF and crystallized from concentrated THF–toluene at 0 °C. The product was precipitated as bright green crystals in a yield of 75% (0.54 g). M.p. 154.6 °C (dec). Anal. calcd for $C_{27}H_{32}Br_3N_2NiP$: C, 45.42; H, 4.52; N, 3.92. Found: C, 45.33; H, 4.60; N, 3.89. $^1$H NMR ($\delta$, 400 MHz, $(CD_3)_2CO$): −4.11 (br s, Ph-*H*), 2.61 (d, *J* = 76 Hz, 12H, $NCH(CH_3)_2$), 3.81 (br s, Ph-*H*), 7.48 (m, 2H, $NCH(CH_3)_2$), 8.68 (s, 1H, NC*H*C*H*N), 8.86 (s, 1H, NC*H*C*H*N), 12.56 (s, 1H, NC*H*N), 18.80 (br s, Ph-*H*). MS (ESI+): *m*/*z* 153.14 $[C_9H_{17}N_2]^+$ (100%).

**[IPrim]$_2$[NiCl$_4$] (3).** A Schlenk flask was charged with $Ni(DME)Cl_2$ (0.22 g, 1.00 mmol), [DIPrim]Cl (0.86 g, 2.00 mmol), THF (15 mL) and a stir bar. The resulting mixture was stirred for 2 h at 30 °C, filtered, then crystallized from concentrated THF at 0 °C. The product was precipitated as blue crystals in a yield of 95% (0.94 g). M.p. 252.0 °C. Anal. calcd for $C_{54}H_{74}Cl_4N_4Ni$: C. 66.20; H, 7.61; N, 5.72. Found: C, 66.33; H, 7.62; N, 5.68. $^1$H NMR ($\delta$, 400 MHz, $(CD_3)_2CO$): 1.23 (d, *J* = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.39 (d, *J* = 6.8 Hz, 24H, $CH(CH_3)_2$), 2.37 (m, 8H, $CH(CH_3)_2$), 7.38 (s, 4H, NC*H*C*H*N), 7.51 (d, *J* = 7.6 Hz, 8H, *m*-Ar-*H*), 7.67–7.71 (m, 4H, *p*-Ar-*H*), 9.59 (s, 1H, NC*H*NAr). MS (ESI+): *m*/*z* 389.30 $[C_{27}H_{37}N_2]^+$.

### X-ray structural determination

Single crystals of **1a–2b** for X-ray diffraction studies were sealed in a thin-walled glass capillary. The data were collected on a Rigaku Mercury CCD area detector at 223(2) K (for **1a**, **1b**, and **2b**) or at 293(2) K (for **2a**). Structures were solved by direct methods and refined by full-matrix least-squares procedures based on $F^2$ using SHELXS-97 and SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

### General procedure for the cross-coupling reactions

In atypical example, complex **1a** (0.005 mmol), aryl bromide (1.0 mmol), and THF (0.5 mL) were added to a Schlenk tube, and the mixture was stirred at 0 °C for 2 minutes. To the solution was added a solution of PhMgBr (1.5 mL, 1.0 M in THF) at 0 °C with stirring. The color of the resulting solution turned to dark red immediately. Then, the resulting solution was stirred for 1 h in an oil bath at 30 °C. After the reaction mixture was quenched by addition of diluted hydrochloric acid (1 M, 0.5 mL), the mixture was extracted with acetic ether (3 × 3 mL) and dried over $MgSO_4$. The yield of the desired product is determined by GC analysis, using *n*-hexadecane as an internal standard substance.

Purification of the crude mixture by flash column chromatography [silica gel, 5.0% ethyl acetate–pet ether (60–90 °C)] gave the isolated yield of the desired coupling product. The identity of the product was confirmed by $^1$H NMR spectroscopy and TLC.

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