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Mixed NHC/Phosphine Ni(II) Complexes: Synthesis and Their Applications as Versatile Catalysts for Selective Cross-Couplings of ArMgX with Aryl Chlorides, Fluorides, and Methyl Ethers

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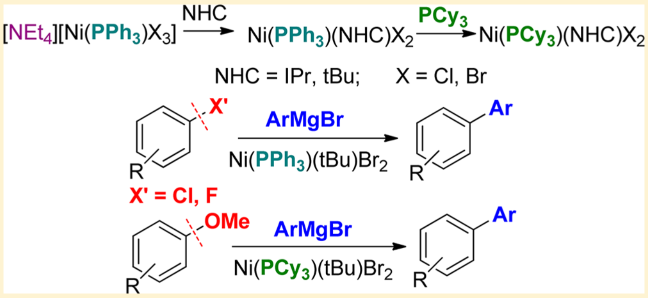
S *Supporting Information*



ABSTRACT: New methods for the preparation of mixed NHC/phosphine Ni(II) complexes have been developed. It was shown that the quaternary ammonium cation in the easily available Ni(II) complexes $[NEt_4][Ni(PPh_3)X_3]$ (X = Cl and Br) can act as a good leaving group in reactions of $[NEt_4][Ni(PPh_3)X_3]$ with the bulky ItBu (ItBu = 1,3-ditertbutylimidazol-2-ylidene) or IPr [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] ligand, resulting in the corresponding mixed NHC/PPh_3 Ni(II) complexes $Ni(PPh_3)(ItBu)X_2$ (X = Cl, **1**; X = Br, **2**) or $Ni(PPh_3)(IPr)Br_2$ (**3**) in high yields. The PPh_3 ligand in these obtained mixed NHC/PPh_3 Ni(II) complexes can be easily substituted by a more electron-donating phosphine ligand, i.e., PCy_3, resulting in the corresponding mixed NHC/PCy_3 Ni(II) complexes $Ni(PCy_3)(ItBu)Br_2$ (**4**) and $Ni(PCy_3)(IPr)Br_2$ (**5**) in high yields. The crystal structures of these Ni(II) complexes have been characterized, which revealed a *trans* disposition of the NHC ligand to the phosphine ligand. The catalytic behaviors of them on varying the carbene ligand (ItBu vs IPr) as well as the phosphine ligand (PPh_3 vs PCy_3) were investigated in the cross-coupling of aryl Grignard reagents with a wide range of electrophiles. In addition to a significant synergic effect on their catalytic activities, high selectivity for the activation and transformation of C−Cl, C−F and C−O bonds was achieved based on the rational structural design. Complex **2** showed the highest catalytic activity for the cross-coupling of aryl chlorides and fluorides with aryl Grignard reagents, but exhibit little activity for the cross-coupling of aryl methyl ethers with aryl Grignard reagents. On contrast, complex **4** showed great potential for the aryl methyl ethers involved cross-coupling reactions, although its reactivity for the activation of the C−X bond is very poor. The difference in catalytic activity between **2** and **4** has been successfully employed to construct oligoarenes by selective cross-coupling reactions.

■ INTRODUCTION

In recent years, *N*-heterocyclic carbenes (NHCs) have become an intensively studied class of ligands for the development of late-transition metal-based homogeneous catalysts.[1] While one main area of these studies has been directed toward the application of NHCs as alternatives to traditional phosphine ligands, another significant part of the investigations has focused on the potential to make these two types of ligands work together in order to construct highly active and/or selective, yet robust catalysts.[2] In this context, various mixed NHC/phosphine Pd(II) complexes, for example, have been successfully designed for a variety of cross-coupling reactions.[3] Mechanistic investigations have generated the explanation for the synergic effect between the two types of ligands that the labile phosphine ligand is capable of reversibly dissociating from the palladium to generate in situ a vacant coordination site readily for substrate binding, whereas the tightly bound NHC ligand is supposed to stay with the palladium to stabilize the active species as well as facilitate the oxidative addition and/or reductive elimination in the catalytic processes. On this basis, the mixed NHC/phosphine complexes of Pd(II) have been well developed and applied commonly in cross-coupling reactions.[3]

On the other hand, the replacement of palladium by nickel in transition metal-catalyzed cross-coupling reactions has also attracted increasing attention since it represents significant cost savings.[4] Mechanistic features of nickel-catalyzed cross-coupling reactions favor elemental steps which are considerably similar to those of palladium mediated ones. However, in comparison with the intensively studied mixed NHC/phosphine Pd(II) complexes, the related Ni(II) complexes are still less explored.[5−10]

To date, only several kinds of well-defined mixed NHC/phosphine Ni(II) complexes have been reported involving monodentate NHC/phosphine Ni(II) complexes,[6,8] bidentate phosphine-functionalized imidazolium cations[9] or derived NHCs[7] supported Ni(II) complexes and tridentate fluoroalkoxy-functionalized NHC-based Ni(II) complex.[10] Among them, the monodentate NHC/phosphine Ni(II) complex, i.e.,

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$Ni(PPh_3)(IPr)Cl_2$ [IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene], has become more appealing, not only due to its superior activity in the Kumada cross-coupling reaction as compared to those of $Ni(IPr)_2Cl_2$ and $Ni(PPh_3)_2Cl_2$,[6a] but also due to its remarkable catalytic performances for α-arylation of acyclic ketones,[6b] amination of haloarenes,[6b] and controlled cross-coupling of 2-substituted[6c] or 3-substituted thiophenes.[6d] These results show that a promising synergic effect can be achieved by the combining of a monodentate phosphine ligand and a monodentate NHC in nickel-catalyzed reactions. Furthermore, it is also reasonable that, in the case of complexes of type $Ni(PPh_3)(IPr)X_2$, the use of different pairs of mixed monodentate ligands could favor a fine-tuning of catalytic performances in a more facile and variable fashion, as those observed in palladium-based catalysis.[2a,3a] However, the scope of such kind of Ni(II) complexes remains extremely narrow. This limitation is due principally to the fact that $Ni(PPh_3)(IPr)Cl_2$ and its bromide analogue were occasionally isolated from the substitution reaction of the phosphine ligands in $Ni(PPh_3)_2X_2$ only with IPr ligand,[6a] which once was a well-known preparative approach to biscarbene Ni(II) complexes of the type $Ni(NHC)_2X_2$.[11] Thus, the development of a facile synthetic approach to such kind of mixed NHC/phosphine Ni(II) complexes is highly desired.

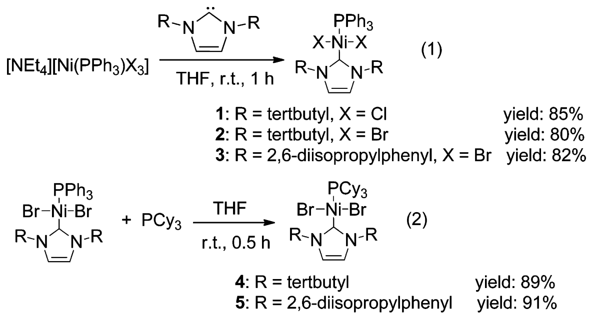
As a continuation of our studies on the development of nickel-based catalysis of NHCs,[12] herein we describe the facile synthesis of a series of mixed NHC/PR_3 Ni(II) complexes **1**−**5**. Notably, these Ni(II) complexes, possessing different pairs of NHC/phosphine ligands, can be used as efficient catalysts for the selective cross-coupling of aryl Grignard reagents with a wide range of electrophiles including aryl chlorides, aryl fluorides and aryl methyl ethers.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. We selected the bulky 1,3-ditertbutylimidazol-2-ylidene (ItBu) to synthesize the new target Ni(II) complex because the steric bulkiness of a NHC ligand is generally of benefit to high catalytic activity,[13] and the use of ItBu as a bulky coligand is rare in Ni(II) complexes.[14]

As shown in Scheme 1 (1), the reaction of the readily available $[NEt_4][Ni(PPh_3)X_3]$ (X = Cl and Br) with one equivalent of in situ generated ItBu occurred quickly in THF at room temperature, and afforded the desired Ni(II) complexes $Ni(PPh_3)(ItBu)X_2$ (X = Cl, **1**; X = Br, **2**) as dark purple crystals in high yields (85 and 80%, respectively). A similar reaction with another NHC ligand, i.e., IPr, also occurred quickly, giving complex **3** in 82% yield, which is much higher than that obtained from the substitution reaction of $Ni(PPh_3)_2Br_2$ with IPr reported previously, whereas only a 21% yield was reached.[6a] Of note, there is trace amount of biscarbene Ni(II) complexes observed in these reactions, mostly due to the difference in reactivity between the phosphine ligand and the quaternary ammonium cation. The formation of complexes **1**−**3** were supported by elemental analysis, NMR spectroscopy, and X-ray diffraction studies. In C_6D_6, the NMR data of complexes **1**−**3** are similar to those of $Ni(PPh_3)(IPr)Cl_2$ reported previously.[6a] The carbenic carbon resonances in **1**−**3** were observed as doublets with large coupling constants centered at 153.0 (J_{CP} = 128.7 Hz), 156.1 (J_{CP} = 124.0 Hz) and 171.1[15] (J_{CP} = 131.4 Hz) ppm, respectively, suggesting the *trans* position of the PPh_3 ligand with respect to the NHC ligand.[6a,8,11] At room temperature, the ^{31}P NMR resonances due to the PPh_3 ligand of **1**−**3** were observed as sharp singlet at 7.9, 14.0, and 19.5 ppm, respectively. Interestingly, the resonances due to the carbenic carbon atom together with the phosphorus atom in **2** are obviously shifted upfield with respect to the corresponding signals observed for **3**, which might reflect the difference of electronic properties between the ItBu ligand and the IPr ligand, such that the carbenic carbon atom in **3** might be more electrophilic.[3b,14a]

Scheme 1. Synthesis of the Mixed NHC/PR_3 Ni(II) Complexes



Complexes **1**−**3** are air and moisture stable in solid state. However, the color of their solutions changed in several minutes upon expositing to open air, resulting in white solids. The solubility of complex **3** is relatively better compared with those of **1** and **2**. Complex **3** is soluble in toluene, $CHCl_3$ and THF, whereas both **1** and **2** merely dissolve in $CHCl_3$ and THF.

With respect to the phosphine ligand, we selected PCy_3 (Cy = cyclohexyl) to broaden the scope of the mixed NHC/phosphine Ni(II) complexes since recent reports showed that it was an excellent ligand for the currently intensively explored nickel-catalyzed cross-coupling of phenolic derivatives.[16] As shown in Scheme 1 (2), the desired Ni(II) complexes, i.e., $Ni(PCy_3)(ItBu)Br_2$ (**4**) and $Ni(PCy_3)(IPr)Br_2$ (**5**), were readily prepared by the substitution reaction of the PPh_3 ligand in **2** and **3** with PCy_3, respectively. After workup pure complexes were obtained as violet crystals in excellent yields (89% and 91%, respectively). Similar protocol has been previously reported by Lee et al. for the synthesis of the mixed NHC/PR_3 Pd(II) complexes of the type $Pd(PCy_3)(NHC)X_2$, whereas the target Pd(II) complexes were obtained in ca. 50% yields.[3b,c] The NMR spectra of **4** and **5** exhibit the characteristic resonances similar to those of the corresponding PPh_3-based Ni(II) complexes, except the resonances assigned to the PCy_3 ligand. Notably, the ^{31}P NMR resonance shifts from 14.0 in **2** to 5.9 ppm in **4**, meanwhile that shifts from 19.5 in **3** to 9.0 ppm in **5**. Complexes **4** and **5** show the desirable air and moisture stability and, their behaviors in solution are very close to those of **2** and **3**. Notably, the solubility of **4** and **5** is obviously better than that of **2** and **3**, such that dissolve readily even in hexane.

Structural Description. The formation of complexes **1**−**5** was further confirmed by X-ray crystallography. The molecular structures of these complexes are shown in Figures 1 (**1** and **2**), 2 (**3**) and 3 (**4** and **5**), respectively. The selected bond lengths and angles are listed in Table 1.

These data reveal that the structures of these complexes are similar to each other, wherein the nickel atom adopts a slightly distorted square planar geometry with a *trans* arrangement of the NHC and phosphine ligand, similar to the only known

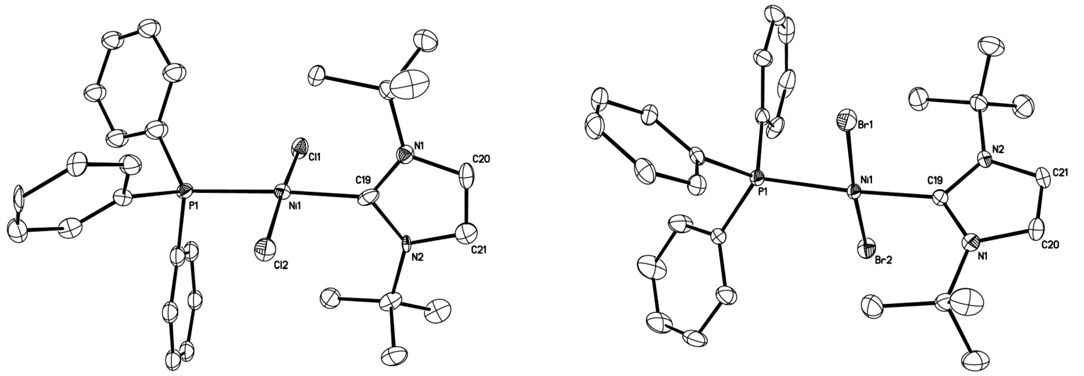


Figure 1. Molecular structures of **1** (left) and **2** (right) with thermal ellipsoids at the 30% probability level. Hydrogens are omitted for clarity.

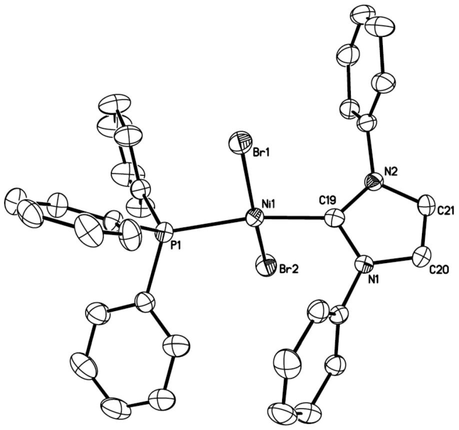


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity.

example of $Ni(PPh_3)(IPr)Cl_2$.[6a] The Ni−$C_{carbene}$ bond lengths were found to lie in a narrow range of 1.905−1.931 Å, whereas the Ni−P bond lengths and Ni-X bond lengths were 2.249(2)-2.308(2) Å and 2.190(2)-2.3346(6) Å, respectively. These structural data are within the expected range for similar Ni(II) complexes.[6−8,10]

On the other hand, as expected, a detailed structural analysis reveals that there are some structural differences among these complexes. For example, the complex bearing the PCy_3 ligand has a longer Ni−$C_{carbene}$ bond length and a longer Ni−P bond length (compare **4** with **2**, and **5** with **3**), a similar trend previously observed with Pd(II) analogues,[3d,e] which is consistent both with the stronger σ-donor ability and the larger steric bulkiness of the PCy_3 ligand relative to the PPh_3 ligand. In terms of NHC ligand, complexes bearing IPr ligand display a more distorted square coordination geometry with $C_{carbene}$−Ni−P angle smaller than the ideal 180° (compare **2** with **3**, and **4** with **5**). Notably, despite the large differences in the electronic and steric properties of NHC ligands (ItBu vs IPr) and phosphine ligands (PPh_3 vs PCy_3), no clear trend with Ni-X bond length was observed, revealing that both electronic effect and steric hindrance do have an influence.

Catalytic Behaviors. The Group 10 metal catalyzed Kumada cross-coupling reaction is one of the most powerful tools for the formation of C−C bonds.[17] In this field, despite the undoubted success of palladium-based systems, recent reports indicate that some effective nickel-based catalysts also particularly promote the cross-coupling of more challenging substrates, such as the less reactive, yet the less expensive and most widely available aryl chlorides,[9c,13b,14c,18−20] the inert aryl fluorides,[13a,19−21] and aromatic ether derivatives.[14c,22]

To disclose any effect due to the coordination variation of a center metal on catalysis, we initially tested the catalytic performance of complexes **1**−**5** and related Ni(II) complexes in the cross-coupling of phenylmagnesium bromide with phenyl chloride or phenyl fluoride.

As seen from Table 2, there are significant differences in catalytic activities of these Ni(II) complexes under conditions similar to those reported previously.[6a] For example, by using 4-chlorotoluene as a substrate, complex **2** is the most effective catalyst precursor, affording a 93% yield of 4-methylbiphenyl

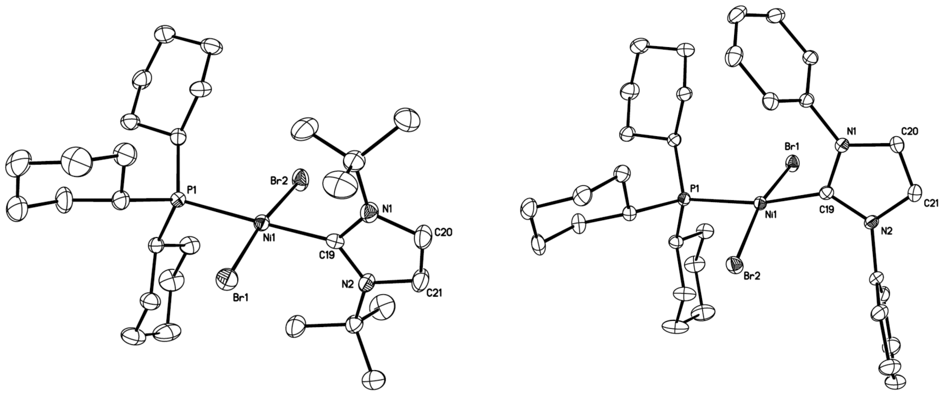


Figure 3. Molecular structures of **4** (left) and **5** (right) with thermal ellipsoids at the 30% probability level. Hydrogens and isopropyl groups are omitted for clarity.

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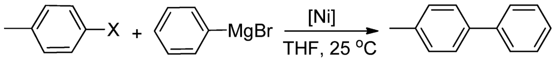
Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**−**5**

	1	**2**	**3**	**4**	**5**
Ni(1)−P(1)	2.249(2)	2.250(1)	2.242(2)	2.308(2)	2.292(1)
Ni(1)−C(19)	1.911(8)	1.905(4)	1.922(5)	1.927(7)	1.931(2)
Ni(1)−X(1)	2.190(2)	2.335(1)	2.298(1)	2.334(1)	2.312(1)
Ni(1)−X(2)	2.203(2)	2.329(1)	2.311(1)	2.351(1)	2.306(1)
C(19)−Ni(1)−P(1)	176.7(3)	175.59(12)	170.25(15)	178.6(2)	169.07(6)
C(19)−Ni(1)−X(1)	91.6(2)	87.34(11)	94.11(13)	88.0(2)	87.25(6)
C(19)−Ni(1)−X(2)	87.3(2)	89.77(11)	88.23(13)	86.8(2)	91.48(6)
P(1)−Ni(1)−X(1)	89.14(8)	92.17(3)	92.80(4)	92.90(6)	89.61(3)
P(1)−Ni(1)−X(2)	91.74(8)	87.34(11)	87.14(4)	92.39(6)	94.08(2)
X(1)−Ni(1)−X(2)	174.83(10)	174.76(2)	163.29(4)	172.97(5)	165.83(2)

Table 2. Cross-Coupling of 4-MeC_6H_4X with C_6H_5MgBr Catalyzed by Ni(II) Complexes[a]



6 **7a** **8a**

entry	catalyst (mol %)	X	*T* (h)	yield (%)
1	**1** (1)	Cl	3	97
2	**1** (0.5)	Cl	5	78
3	**1** (2)	F	5	85
4	**2** (1)	Cl	3	99 (98)[b]
5	**2** (0.5)	Cl	5	93
6	**2** (2)	F	5	92
7	**3** (1)	Cl	5	77
8	**3** (2)	F	10	72
9	**4** (1)	Cl	5	9
10	**5** (1)	Cl	5	8
11	$Ni(PPh_3)(IPr)Cl_2$ (1)	Cl	5	63
12	$Ni(PPh_3)(IPr)Cl_2$ (2)	F	10	65
13	$Ni(PPh_3)_2Br_2$ (1)	Cl	5	14
14	$Ni(IPr)_2Br_2$ (1)	Cl	5	26

[a] Reaction conditions: 4-MeC_6H_4X (1.0 mmol), C_6H_5MgBr (1.5 mmol, 1.0 M in THF) was added in one portion, THF (total volume: 2.0 mL), 25 °C, GC yield using *n*-hexadecane as internal standard, average of two trials. [b] Isolated yield.

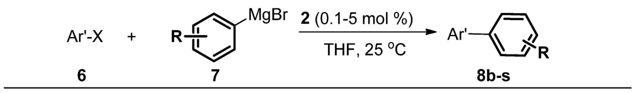
even when its loading was reduced to 0.5 mol % (entry 5), whereas its chloride analogue **1** exhibited an obviously lower activity and afforded a 78% yield with the same loading (entry 2). Meanwhile, complex **3** showed moderate activity compared with that of **2**, affording the product in 77% yield at a 1 mol % loading (entry 7). Also $Ni(PPh_3)(IPr)Cl_2$ showed moderate activity catalytic activity (entry 11, 63% yield) compared with that of the ItBu-derivative **1**. In comparison, the catalytic activity of $Ni(PPh_3)_2Br_2$ (entry 13) or $Ni(IPr)_2Br_2$ (entry 14) is much lower than that of complex **3**, similar to the previously reported pattern with $Ni(PPh_3)(IPr)Cl_2$.[6a] To our surprise, it is found that the least reactive complexes were **4** and **5**, which afforded the product in merely 9% (entry 9) and 8% (entry 10) yields, respectively. The differences in catalytic activity among **1**−**5** and related Ni(II) complexes clearly show that both of the NHC ligand and the phosphine ligand can exert a significant influence on the catalytic activity of the mixed NHC/PPh_3 Ni(II) complexes, in which a significant synergic effect on their catalytic activity can also be observed. The fact that the catalytic activities of **1** and **2** are higher than those of $Ni(PPh_3)(IPr)Cl_2$ and **3**, respectively, can possibly be ascribed to both the larger steric bulkiness and the stronger electron-donating property of the ItBu ligand compared to the IPr ligand, which may help in a number of ways such as facilitate the reductive elimination for the formation of the desired biaryl products together with the regeneration of the catalytic active species,[13] and accelerate the initial reduction step as well as the oxidative addition step during the catalytic cycle.[23] The Ni(II) bromides, i.e., **2** and **3**, exhibited catalytic activities higher than those of their chloride partners, which are the same as those previously reported.[24] However, the reason for the significant difference on catalytic activity between the PPh_3-based Ni(II) complexes and the PCy_3-based ones is unclear.

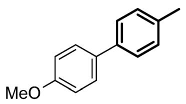
Interestingly, **2** also displays a high activity toward less reactive aryl fluorides, i.e., 4-fluorotoluene, affording the desired product in 92% yield after 5 h with a 2 mol % loading at room temperature (entry 6), and the same trend in catalytic activity, i.e., **2** ≥ **1** ≫ **3** ≥ $Ni(PPh_3)(IPr)Cl_2$, was observed in turn. Despite the increasing attention on the activation of C−F bond and related transformation, the catalytic activation of the inert C−F bond remains challenging because of the inherent strength of the C−F bond.[13a] With respect to the reported nickel catalysts for the cross-coupling of aryl fluorides with aryl Grignard reagents, **2** shows higher catalytic activity than $Ni(IPr)_2$,[13a] $Ni(acac)_2$/phosphine oxide,[19a,d] $Ni(acac)_2$/phosphites,[19b] $Ni(PR_2R')_2X_2$,[19c] NHC-based pincer Ni(II) complexes,[19e] and Ni(I) complexes of $Ni(PPh_3)(NHC)X$,[19f] but lower than $Ni(acac)_2$/hydroxyphosphine system,[20a,b] bidentate NHC-based Ni(II) complex,[20c] and *P*,*N*,*N*-pincer Ni(II) complexes.[20d]

We also investigated the scope of **2** with a representative set of coupling partners. As shown in Table 3, a variety of aryl chlorides, aryl fluorides and heteroaryl chlorides were capable of cross-couplings with arylmagnesium bromides to give the corresponding coupling products in good to excellent yields.

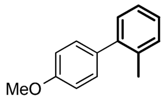
To our delight, the steric hindrance and functional group compatibility are considerably well-tolerated by this system, especially in the formation of di-*ortho*-substituted biaryls (**8d**,**e**, **8f** and **8n**), ketal-functionalized biaryls (**8l**−**n**), pyridine derivatives (**8o**−**r**), and the ester-functionalized biaryl (**8s**). Interestingly, with only 0.1 mol % of **2**, the cross-coupling of 2-chloroquinoline with 4-methoxyphenylmagnesium bromide was completed in 2 h (97% isolated yield) at room temperature. For this type of reaction, the catalytic activity of complex **2** is very close to that of Ni(IPr)(allyl)Cl, which possesses of the highest catalytic activity for such a Kumada reaction with heteroaromatic chlorides catalyzed by nickel-based catalysts.[14c] Moreover, it is noteworthy that this protocol could also be extended to the synthesis of triaryl compounds either from 1-chloro-3-fluorobenzene via a sequential cross-coupling (**8j**) or from 1,3-dichlorobenzene via a simultaneous process (**8k**).

Table 3. Cross-Coupling of Aryl Chlorides and Fluorides with ArMgBr Catalyzed by **2**[a]

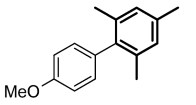




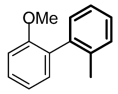
8b, (X = Cl), 4 h, 98%



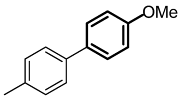
8c, (X = Cl), 5 h, 98%
(X = F), 10 h, 96%[c]



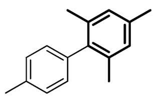
8d, (X = Cl), 24 h, 90%[b]



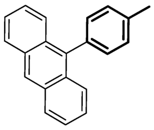
8e, (X = Cl), 4 h, 98%[c,d]



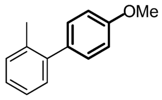
8b, (X = Cl), 4 h, 95%



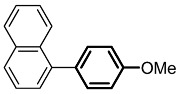
8f, (X = Cl), 24 h, 86%[b]



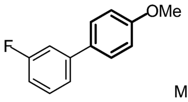
8g,(X = Cl), 5 h, 85%[d]



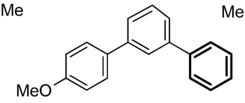
8c, (X = Cl), 4 h, 98%
(X = F), 10 h, 92%[f]



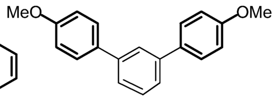
8h, (X = F), 10 h, 88%[c]



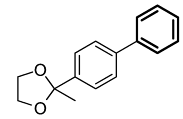
8i, (X = Cl), 5 h, 80%



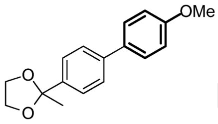
8j, (X = F), 10 h, 90%[c]



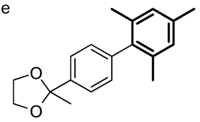
8k, (X = Cl), 5 h, 79%[e]



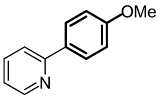
8l, (X = Cl), 20 h, 94%[c,d]



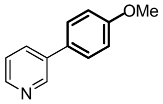
8m, (X = Cl), 3 h, 96%[c,d]



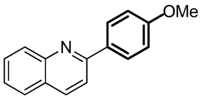
8n, (X = Cl), 20 h, 89%[c,d]



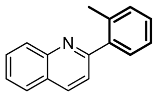
8o, (X = Cl), 3 h, 97%



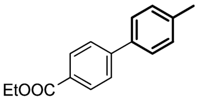
8p, (X = Cl), 3 h, 93%



8q, (X = Cl), 2 h, 97%[g]



8r, (X = Cl), 2 h, 88%[g]



8s, (X = Cl), 4 h, 85%[h]

[a]Conditions: **2** (1 mol %), aryl halides (1.0 mmol), ArMgBr (1.5 mmol, 1.0 M in THF), THF, (total volume: 2.0 mL), 25 °C, isolated yield. [b]**2** (5 mol %). [c]**2** (2 mol %). [d]60 °C. [e]**2** (3 mol %), ArMgBr (3 mmol, 1.0 M in THF), total volume (4.0 mL). [f]**2** (3 mol %). [g]**2** (0.1 mol %). [h]**2** (5 mol %), $ZnCl_2$ (10 mol %), LiCl (1.2 mmol), NMP (1.5 mL), ArMgBr (2.0 mmol, 1.0 M in THF), THF (total volume: 4.5 mL), 1.3 equiv of 4-MeC_6H_4MgBr was used, after the reaction mixtures were stirred for 2 h, additional 0.66 equiv of 4-MeC_6H_4MgBr was added, and stirring was continued for 2 h.

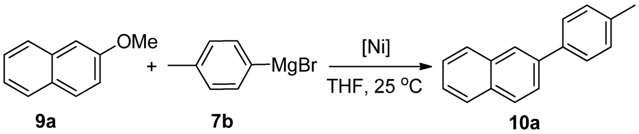
In recent years phenolic derivatives have received increasing attention as an attractive alternative to traditional aryl halides in various cross-coupling reactions through C−O bond activation.[16] Among the unconventional groups reacted in this way, the activation of an inert C(aryl)−OMe bond is even more attractive in terms of its easy availability and high atom economy.[16d,f] However, the application of aryl methyl ethers in the Kumada cross-coupling still remain limited,[21] which mostly be attributed to the higher bond dissociation energy (BDE) of the C(aryl)−OMe bond compared with that of the corresponding C(aryl)−Cl bond.[16a]

Since PCy_3 has been particularly used as the effective ligand in the nickel-catalyzed cross-coupling of Grignard reagents with aryl methyl ethers,[16,21] we are interested in whether $Ni(PCy_3)(NHC)X_2$ represents an alternative catalytic precursor for such cross-coupling reaction. As far as we are aware, mixed NHC/phosphine Ni(II) complexes have not been used as precatalysts in this type of reaction. Hence, we tested the catalytic performance of complexes **4**, **5** and related Ni(II) complexes in the cross-coupling between 2-methoxynaphthalene and 4-MeC_6H_4MgBr, which is a prototype cross-coupling of aryl methyl ethers with aryl Grignard reagents.[14g,21c,e]

As shown in Table 4, we encountered significant differences in the catalytic behavior of these Ni(II) complexes, which were also quite different from those observed from Table 3. Interestingly, complex **4**, $Ni(PCy_3)(ItBu)Br_2$, effectively promoted this type of reaction with a 1 mol % loading, resulting in the desired cross-coupling product in almost quantitative yield (entry 4), meanwhile its IPr-based analogue **5** afforded a slightly lower yield of 90% (entry 5) with the same loading. On contrast, all of PPh_3-based complexes, i.e., **1**−**3**, performed poorly under the same reaction conditions, affording very low yields around 2−10% (entries 1−3). The bisphosphine Ni(II) complex exhibited moderate activity (entries 6 and 7), whereas, in comparison, the biscarbene Ni(II) complex exhibited a lower activity, and furnished 21% yield of the desired cross-coupling product (entry 8). Thus, these results discussed above show clearly that the present structural variations of these mixed NHC/phosphine Ni(II) complexes can also exert significant influences on their catalytic selectivities. Notably, the replacement of the PPh_3 ligand by the PCy_3 ligand allows an easy exchange of the activation of the C(aryl)-X bond by a nickel center for the activation of the C(aryl)-OMe bond by the corresponding nickel center.

The catalytic performance of **4** was also compared with other nickel-based catalysts reported in the literature. In general, 2−5 mol % loadings of Ni(II) complexes or a large excess of the Grignard reagents are required to achieve satisfactory yields for the reaction shown in Table 4.[14c,21c,e] Therefore, the present results suggest that complex **4** might be among the most efficient precatalysts for the cross-coupling reaction of aryl

Table 4. Cross-Coupling of 2-$MeOC_8H_7$ with 4-MeC_6H_4MgBr Catalyzed by Ni(II) Complexes[a]



entry	complex (mol %)	*T* (h)	yield (%)
1	**1** (1)	10	2
2	**2** (1)	10	3
3	**3** (1)	10	10
4	**4** (1)	10	99 (98)[b]
5	**5** (1)	10	90
6	$Ni(PCy_3)_2Cl_2$ (1)	10	82
7	$Ni(PCy_3)_2Br_2$ (1)	10	86
8	$Ni(IPr)_2Br_2$ (1)	10	21

[a]Reaction conditions: 2-methoxynaphthalene (1.0 mmol), 4-MeC_6H_4MgBr (1.5 mmol, 1.0 M in THF) was added in one portion, THF (total volume: 2.0 mL), 25 °C, GC yield using *n*-hexadecane as internal standard, average of two trials. [b]Isolated yield.

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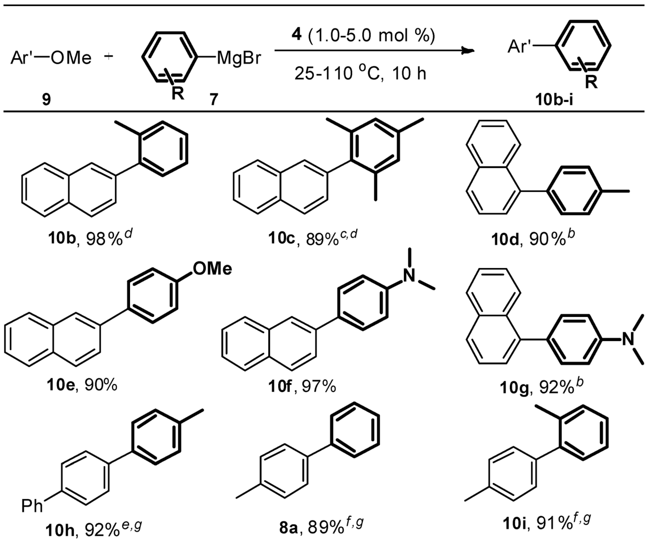
methyl ethers with aryl Grignard reagents, possibly due to a synergic effect between ItBu and PCy_3.

We then briefly investigated the versatility of complex **4** with other coupling partners. As seen from Table 5, substantial kinds of substrates including 1- or 2-methoxynaphthalene, 4-methoxybiphenyl and 4-methylanisole are applicable. For example, both 1-methoxynaphthalene and 2-methoxynaphthalene reacted smoothly with a variety of aryl Grignard reagents with yields varying from 89 to 98% (**10b**−**10g**), wherein hindered Grignard reagents such as 2-MeC_6H_4MgBr and $2,4,6\text{-Me}_3C_6H_2MgBr$ participated also in the reaction to give the desired products in excellent to good yields (98% for **10b**, 89% for **10c**) by increasing reaction temperature to 60 °C and/or by using 5 mol % loading of **4**. For the less reactive biphenyl methyl ethers and the least reactive phenyl methyl ethers,[14c] cross-coupling reactions achieved completely (92% for **10h**, 89% for **8a**, and 91% for **10i**) at a higher temperature (110 °C). These results indicate a broad generality of the substrate scope.

Table 5. Cross-Coupling of Methoxyarenes with ArMgBr Catalyzed by 4[a]



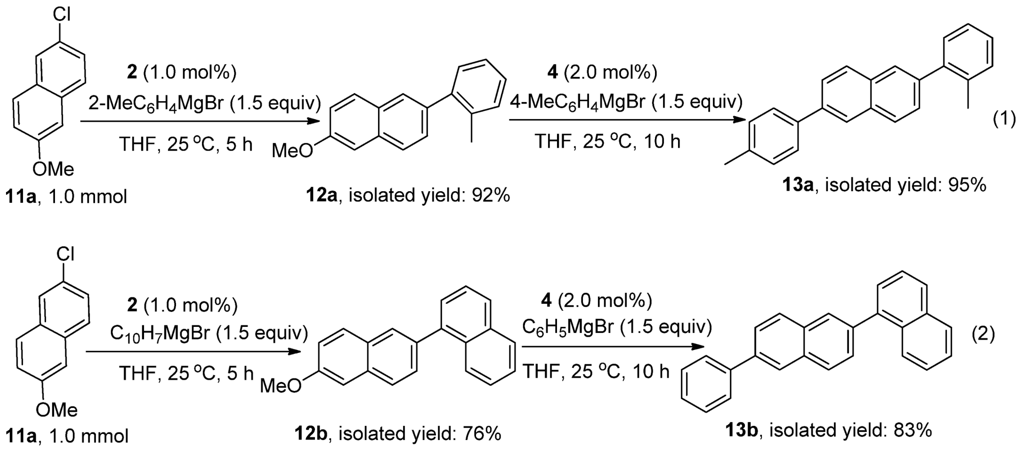
[a]Conditions: **4** (1 mol %), aryl ethers (1.0 mmol), ArMgBr (1.5 mmol, 1.0 M in THF), THF, (total volume: 2.0 mL), 25 °C, isolated yield. [b]**4** (2.5 mol %). [c]**4** (5 mol %). [d]60 °C. [e]**4** (2 mol %). [f]**4** (3 mol %). [g]Toluene was used instead of THF, 110 °C.

Finally, the difference in catalytic activity between **2** and **4** has been successfully applied to the selective cross-coupling of the chloride moiety or the methoxy group for the construction of oligoarenes, which are important building blocks of advanced materials, natural products and drug molecules.[22] As shown in Scheme 2, in the first cross-coupling procedure, treatment of the naphthalene compound **11a** with 2-MeC_6H_4MgBr and $C_{10}H_7MgBr$ in the presence of **2** (1 mol %) led to the selective cross-coupling of the aryl chloride to afford biaryl products **12a** and **12b**, respectively, whereas the C(aryl)-OMe bond remaining intact. Next, with a 2 mol % loading of **4**, **12a** and **12b** reacted smoothly with 4-MeC_6H_4MgBr and C_6H_5MgBr to give naphthalene derivatives **13a** and **13b**, respectively.

CONCLUSION

The present work provides facile synthetic methods for the synthesis of novel mixed NHC/phosphine Ni(II) complexes of the type $Ni(PR_3)(NHC)X_2$ (**1**−**5**) via controlled ligand substitution reactions using easily available Ni(II) complexes $[NEt_4][Ni(PPh_3)X_3]$ as the starting materials. Under mild conditions, these complexes have great potential as versatile catalysts for the selective cross-coupling of aryl Grignard reagents with a wide range of electrophiles including aryl chlorides, aryl fluorides and aryl methyl ethers. Among them, complex **2** showed the highest catalytic activity and great potential in the cross-coupling reactions of aryl Grignard reagents with aryl chlorides and fluorides, while the catalytic activity of complex **4** is largely superior to those of **1**−**3** and **5** in the aryl Grignards cross-coupling of aryl methyl ethers. The significant difference in catalytic activity between **2** and **4** has been successfully applied in the synthesis of oligoarenes by the selective cross-coupling reaction. Since a variety of NHC ligands as well as phosphine ligands are available, this work confirmed that the installation of a robust NHC ligand and a labile phosphine ligand on one nickel atom can be used as an excellent strategy for building highly active and/or selective, yet robust catalysts of nickel. The research on further fine-tuning their catalytic activity by surveying well-matched pairs of NHC/PR_3 ligands, the scope of these Ni(II) complexes in other cross-coupling reactions, and related mechanism study are currently under investigation in our laboratory.

Scheme 2. Selective Cross-Coupling Strategies for Synthesis of Oligoarenes



■ EXPERIMENTAL SECTION

General Experimental 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. $[NEt_4][Ni(PPh_3)Cl_3]$,[25] $[NEt_4][Ni(PPh_3)Br_3]$,[25] $Ni(PPh_3)_2Cl_2$,[26] $Ni(IPr)_2Cl_2$,[12d] $Ni(PCy_3)_2Cl_2$,[27b] $Ni(PCy_3)_2Br_2$,[27] 1,3-ditertbutylimidazol-2-ylidene[28] and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene[29] were prepared by published methods. The synthesis of $Ni(PPh_3)(IPr)Cl_2$ has been reported previously,[6a] it could also be prepared following the method similar to the synthetic procedure of **1** (see Supporting Information for details). 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 VNMRS 300 MHz spectrometer at 25 °C. The melt points were determined on a Diamond DSC (PerkinElmer) using powder samples under N_2 atmosphere (50 mL/min). The system was heated from 50 to 350 °C at 20 °C/min. Gas chromatographic (GC) analysis was performed on a Varian CP-3800 instruments equipped with an FID detector and a capillary column AT.OV-101 (30 m × 0.32 mm i.d., 0.10 μm film). High resolution mass spectra were obtained using GCT-TOF instrument with ESI or CI source.

*$Ni(PPh_3)(ItBu)Cl_2$ (**1**).* A Schlenk flask was charged with $[NEt_4][Ni(PPh_3)Cl_3]$ (0.56 g, 1.00 mmol), THF (10 mL) and a stir bar. To this solution was added 1,3-ditertbutylimidazol-2-ylidene (0.18 g, 1.00 mmol) in THF (10 mL) at room temperature. The color of the mixture changed into violet immediately. The solution was then stirred for 1 h at room temperature. Volatiles were removed in vacuo. The residue was washed with hexane (3 × 10 mL), extracted with THF (3 × 10 mL), and crystallized from concentrated THF solution at 0 °C. The product was precipitated as dark purple crystals in a yield of 85% (0.48 g), mp 187 °C; ^1H NMR (400 MHz, C_6D_6) δ = 2.39 (s, 18H, $C(CH_3)_3$), 6.43 (s, 2H, $CH{=}CH$), 7.05−7.12 (m, 9H, C_6H_5), 8.03−8.07 (m, 6H, C_6H_5). ^{13}C NMR (75 MHz, C_6D_6) δ = 153.0 (d, J_{PC} = 128.7 Hz, NCN), 134.9 (d, J_{PC} = 9.9 Hz, *ortho*-C_6H_5), 132.3 (d, J_{PC} = 38.5 Hz, *ipso*-C_6H_5), 129.7 (*para*-C_6H_5), 128.2 (*meta*-C_6H_5), 119.4 (d, J_{PC} = 3.8 Hz, $CH{=}CH$), 59.2 ($C(CH_3)$), 32.6 (CH_3). ^{31}P NMR (121 MHz, C_6D_6) δ = 7.9. Anal. Calcd for $C_{29}H_{35}Cl_2N_2NiP$: C, 60.87; H, 6.17; N, 4.90. Found: C, 60.75; H, 6.16; N, 4.88.

*$Ni(PPh_3)(ItBu)Br_2$ (**2**).* Following a procedure similar to the synthetic procedure of **1**, a THF (10 mL) solution of 1,3-ditertbutylimidazol-2-ylidene (0.18 g, 1.00 mmol) was added to a THF (10 mL) suspension of $[NEt_4][Ni(PPh_3)Br_3]$ (0.69 g, 1.00 mmol) at room temperature. After workup, the residue was washed with hexane (3 × 10 mL), extracted with THF (3 × 10 mL), and crystallized from concentrated THF solution at 0 °C. The product was precipitated as dark purple crystals in a yield of 80% (0.53 g), mp 195 °C; ^1H NMR (400 MHz, C_6D_6) δ = 2.32 (s, 18H, $C(CH_3)_3$), 6.45 (s, 2H, $CH{=}CH$), 7.04−7.14 (m, 9H, C_6H_5), 8.03−8.08 (m, 6H, C_6H_5). ^{13}C NMR (75 MHz, C_6D_6) δ = 156.1 (d, J_{PC} = 124.0 Hz, NCN), 134.9 (d, J_{PC} = 9.6 Hz, *ortho*-C_6H_5), 133.1 (d, J_{PC} = 40.2 Hz, *ipso*-C_6H_5), 129.6 (*para*-C_6H_5), 128.3 (*meta*-C_6H_5), 120.4 (d, J_{PC} = 4.0 Hz, $CH{=}CH$), 59.2 ($C(CH_3)$), 32.5 (CH_3). ^{31}P NMR (121 MHz, C_6D_6) δ = 15.0. Anal. Calcd for $C_{29}H_{35}Br_2N_2NiP$: C, 52.69; H, 5.34; N, 4.24. Found: C, 52.73; H, 5.39; N, 4.33.

*$Ni(PPh_3)(IPr)Br_2$ (**3**).* Following a procedure similar to the synthetic procedure of **1**, a THF (10 mL) solution of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (0.39 g, 1.00 mmol) was added to a THF (10 mL) suspension of $[NEt_4][Ni(PPh_3)Br_3]$ (0.69 g, 1.00 mmol) at room temperature. After workup, the residue was washed with hexane (3 × 10 mL), extracted with toluene (3 × 10 mL), and crystallized from concentrated toluene/hexane solution at 0 °C. The product was precipitated as dark purple crystals in a yield of 82% (0.71 g), mp 166 °C; ^1H NMR (400 MHz, C_6D_6) δ = 1.04 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.50 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$), 3.44−3.51 (m, 4H, $CH(CH_3)_2$), 6.63 (s, 2H, $CH{=}CH$), 6.96−6.97 (m, 9H, $P(C_6H_5)_3$), 7.39 (d, J = 7.6 Hz, 4H, *m*-C_6H_3: NHC), 7.46 (t, J = 7.2 Hz, 2H, *p*-C_6H_3: NHC), 7.59−7.66 (m, 6H, $P(C_6H_5)_3$). ^{13}C NMR (75 MHz, C_6D_6) δ = 171.1 (d, J_{PC} = 131.4 Hz, NCN), 147.3 (*ipso*-C_6H_3: NHC), 136.3 (*ortho*-C_6H_3: NHC), 135.1 (*ortho*-C_6H_5: PPh_3), 132.5 (d, J_{PC} = 39.4 Hz, *ipso*-C_6H_5: PPh_3), 130.1 (*para*-C_6H_5: PPh_3), 129.1 (*meta*-C_6H_5: NHC), 127.2 (*meta*-C_6H_5: PPh_3), 125.0 (*para*-C_6H_3: NHC), 124.0 ($CH{=}CH$), 29.0 ($C(CH_3)$), 26.4 (CH_3), 23.1 (CH_3). ^{31}P NMR (121 MHz, C_6D_6) δ = 19.5. Anal. Calcd for $C_{45}H_{51}Br_2N_2NiP$: C, 62.17; H, 5.91; N, 3.22. Found: C, 62.13; H, 5.88; N, 3.17.

*$Ni(PCy_3)(ItBu)Br_2$ (**4**).* A Schlenk flask was charged with $Ni(PPh_3)(ItBu)Br_2$ (**2**) (0.68 g, 1.0 mmol), THF (10 mL) and a stir bar. To this solution was added PCy_3 (0.28 g, 1.0 mmol) in THF (10 mL) at room temperature. The mixture was stirred for 30 min and evaporated to dryness in vacuo. The residue was washed with hexane (3 × 10 mL), extracted with toluene (3 × 10 mL), and crystallized from concentrated toluene/hexane solution at 0 °C. The product was precipitated as violet crystals in a yield of 89% (0.60 g), mp 189 °C; ^1H NMR (400 MHz, C_6D_6) δ = 1.38−1.25 (m, 9H, $P(C_6H_{11})_3$), 1.73−1.70 (m, 3H, $P(C_6H_{11})_3$), 2.00−1.83 (m, 12H, $P(C_6H_{11})_3$), 2.22−2.19 (m, 6H, $P(C_6H_{11})_3$), 2.50−2.47 (m, 21H, $P(C_6H_{11})_3$ + $C(CH_3)_3$), 6.47 (s, 2H, $CH{=}CH$). ^{13}C NMR (100 MHz, C_6D_6) δ = 156.7 (d, J_{PC} = 110.5 Hz, NCN), 119.9 (d, J_{PC} = 3.6 Hz, $CH{=}CH$), 58.9 ($C(CH_3)$), 32.8 (CH_3), 31.4 (d, J_{PC} = 17.3 Hz, $P(C_6H_{11})_3$), 29.5 ($P(C_6H_{11})_3$), 27.9 (d, J_{PC} = 9.7 Hz, $P(C_6H_{11})_3$), 26.9 ($P(C_6H_{11})_3$); ^{31}P NMR (162 MHz, C_6D_6) δ = 5.9. Anal. Calcd for $C_{29}H_{53}Br_2N_2NiP$: C, 51.28; H, 7.87; N, 4.12. Found: C, 51.19; H, 7.79; N, 4.18.

*$Ni(PCy_3)(IPr)Br_2$ (**5**).* Following a procedure similar to the synthetic procedure of **4**, a THF (10 mL) solution of PCy_3 (0.28 g, 1.0 mmol) was added to a THF (10 mL) solution of $Ni(IPr)(PPh_3)Br_2$ (**3**) (0.87 g, 1.0 mmol) at room temperature. The mixture was stirred for 30 min and evaporated to dryness in vacuo. The residue was washed with hexane (3 × 10 mL), extracted with toluene (3 × 10 mL) and crystallized from concentrated toluene/hexane solution at 0 °C. The product was precipitated as violet crystals in a yield of 91% (0.81 g), mp 220 °C; ^1H NMR (400 MHz, C_6D_6) δ = 1.04 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.23−1.08 (m, 9H, $P(C_6H_{11})_3$), 1.65−1.60 (m, 27H, $CH(CH_3)_2$+ $P(C_6H_{11})_3$), 1.88−1.85 (m, 6H, $P(C_6H_{11})_3$), 2.16−2.11 (m, 3H, $P(C_6H_{11})_3$), 3.53−3.47 (m, 4H, $CH(CH_3)_2$), 6.61 (s, 2H, $CH{=}CH$), 7.41−7.34 (m, 6H, C_6H_3). ^{13}C NMR (100 MHz, C_6D_6) δ = 170.3 (d, J_{PC} = 118.4 Hz, NCN), 147.6 (*ipso*-C_6H_3), 136.3 (*ortho*-C_6H_3), 124.8 (d, J_{PC} = 3.5 Hz, *para*-C_6H_3), 123.8 ($CH{=}CH$), 32.7 (d, J_{PC} = 18.1 Hz, $P(C_6H_{11})_3$), 29.9 ($P(C_6H_{11})_3$), 29.0 ($C(CH_3)$), 27.8 (d, J_{PC} = 9.9 Hz, $P(C_6H_{11})_3$), 26.7 ($P(C_6H_{11})_3$), 26.6 (CH_3), 22.9 (CH_3). ^{31}P NMR (162 MHz, C_6D_6) δ = 9.0. Anal. Calcd for $C_{45}H_{69}Br_2N_2NiP$: C, 60.90; H, 7.84; N, 3.16. Found: C. 60.98; H, 7.79; N, 3.20.

X-ray Structural Determination. Single crystals of **1**−**5** 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 **1**, **3** and **5**) or at 293(2) K (for **2** and **4**). 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 of Ar′X with ArMgBr. In a typical example, complex **2** (0.01 mmol), Ar′X (1.0 mmol), and THF (0.5 mL) were added to a Schlenk tube, and the mixture was stirred at 0 °C for 2 min. To this stirred mixture was added ArMgBr solution (1.5 mL, 1.0 M in THF) at 0 °C by syringe. The color of the resulting mixture turned to brownish yellow immediately. Then, this mixture was stirred for 5 h in an oil bath at 25 °C. Diluted hydrochloric acid (1 M, 0.5 mL) was added. The resulting mixture was extracted with acetic ether (3 × 3 mL), dried over anhydrate $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography [silica gel (230−400 mesh), 5.0% ethyl acetate/pet ether]. The calibrated yield of desired product against *n*-hexadecane as the internal standard was obtained using GC spectroscopic analysis.

The identity of the product was confirmed by ^1H NMR spectroscopy and TLC.

General Procedure for the Cross-Coupling of Ar′OMe with ArMgBr. In a typical example, complex **4** (0.02 mmol), Ar′OMe (1.0 mmol), and THF (0.5 mL) were added to a Schlenk tube, and the mixture was stirred at 0 °C for 2 min. To this stirred mixture was added ArMgBr (1.5 mL, 1.0 M in THF) by syringe. The color of the resulting mixture turned to brownish yellow immediately. Then, the resulting mixture was stirred for 10 h in an oil bath at 25 °C. Diluted hydrochloric acid (1 M, 0.5 mL) was added. The resulting mixture was extracted with acetic ether (3 × 3 mL), dried over anhydrate $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography [silica gel (230−400 mesh), 5.0% ethyl acetate/pet ether]. The calibrated yield of desired product against *n*-hexadecane as the internal standard was obtained using GC spectroscopic analysis.

The identity of the product was confirmed by ^1H NMR spectroscopy and TLC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00874.

Synthesis of $Ni(PPh_3)(IPr)Cl_2$, characterization of complexes **1−5**, and characterization of cross-coupling products. (PDF)

Crystallographic information files (CIF) of complexes **1−5**. (ZIP)

Accession Codes

CCDC reference numbers: **1** (CCDC 971433), **2** (CCDC 971434), **3** (CCDC 971435), **4** (CCDC 1014572), and **5** (CCDC 983587).

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Notes

The authors declare no competing financial interest.

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