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# A β-diketiminato-based pincer-type nickel(II) complex: Synthesis and catalytic performance in the cross-coupling of aryl fluorides with aryl Grignard reagents

Nobutaka Kurisu,[a] Erika Asano,[a] Yuki Hatayama,[a] Youji Kurihara,[a] Toru Hashimoto,[a] Kei Funatsu,[a] Kazuyoshi Ueda,[a] and Yoshitaka Yamaguchi*[a]

**Abstract:** A β-diketiminato-based tridentate pincer-type nickel(II) complex **Ni-NNP** was prepared by the reaction of the nickel(II) precursor [$NiCl_2$(2,4-lutidine)$_2$] with the lithiated NNP ligand, which was generated *in situ* by the reaction of the NNP pro-ligand **H-NNP** with *n*-BuLi. **H-NNP** was prepared by the condensation of 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one with 2-(diphenylphosphino)ethylamine. **Ni-NNP** was characterized spectroscopically and by X-ray diffraction, revealing a slightly distorted square-planar geometry around the nickel center. Density functional theory calculations indicated that the highest occupied molecular orbital in **Ni-NNP** is located at higher energy than those of three other homologous nickel(II) complexes, i.e., **Ni-ONN**, **Ni-ONP**, and **Ni-NNN**, which contain β-aminoketonato- or β-diketiminato-based pincer-type ligands. The electronic and steric properties of **Ni-NNP** effectively facilitated the cross-coupling of aryl fluorides with aryl Grignard reagents.

## Introduction

Fluorine is one of the most important elements in the development of materials and biologically active agents. The introduction of fluorine atom(s) into organic molecules often has a significant impact upon their physical, chemical, and biological properties. Thus, the installation of fluorine atom(s) in organic molecules is one of the most important challenges in synthetic chemistry.[1] Furthermore, the activation of C-F bonds, (i.e., the scission of C-F bonds) is also of great significance in organometallic chemistry and catalyst development because the C-F bond is one of the strongest single bonds present in organic compounds.[2] Therefore, C-F bond cleavage and subsequent C-C bond formation are some of the most attractive and challenging subjects in synthetic chemistry.[3] Research into these issues contributes to the fundamental understanding of the reactivity of highly stable bonds in organic molecules. Furthermore, such studies can potentially provide novel synthetic methodologies for organic chemists.

Nickel is one of the most attractive metals for catalyst development because it is significantly cheaper than group-10 metals such as palladium and platinum. Furthermore, nickel is one of the most fundamental metals in the development of cross-coupling reaction catalysts because its complexes show great potential for C-F bond activation.[4-6] During the last two decades, several effective nickel catalyst systems for the cross-coupling of fluorinated compounds as electrophiles have been reported.[7-24]

In order to achieve activation and smooth scission of the C-F bond located on the Ni center in a catalytic cycle, the enhancement of electron density at the metal center and the introduction of sterically bulky donor ligands such as alkylphosphines or *N*-heterocyclic carbenes to the metal are required. In an alternate approach, Nakamura and co-workers developed a bimetallic nickel/magnesium cooperation system featuring a hydroxylphosphine ligand. They demonstrated the effective activation of the C-F bond by the synergetic use of a group-10 nucleophilic metal (nickel) and a Lewis-acidic main-group element (magnesium).[13]

In recent years, tridentate pincer-type complexes have generated significant interest because the pincer-type ligand stabilizes the metal complex and its properties can be tuned to achieve optimal reactivity.[25] Naturally, extensive attention has been focused on the combination of pincer-type ligands with nickel,[26-28] and effective catalysts for cross-coupling reactions have been reported.[29-55] Aryl chlorides as electrophiles are effectively catalyzed by pincer-type Ni complexes. However, it remains difficult to activate aryl fluorides using pincer-type Ni catalysts.[56, 57]

We have recently reported the synthesis of β-aminoketonato-[58] and β-diketiminato-based tridentate pincer-type complexes of iron[59, 60] and nickel.[61] In our ongoing study of Ni(II) complexes, we have prepared three different types of Ni(II) complexes, **Ni-ONN**, **Ni-ONP**, and **Ni-NNN**, and their catalytic performances have been investigated (Figure 1).[61] Complex **Ni-ONP**, which has the β-aminoketonato framework tethering the phosphorus donor, acts as an effective catalyst for the cross-coupling of aryl chlorides with aryl Grignard reagents.

In this previous study, we revealed that the conjugated ligand framework (β-aminoketonato or β-diketiminato) and the third donor group have significant influences on catalytic performance. As a third donor, the phosphorus group shows superior catalytic activity over the nitrogen group. Intriguingly, the β-diketiminato framework increases the energy level of the highest occupied molecular orbital (HOMO) of the Ni(II) complex **Ni-NNN**, as revealed by density functional theory (DFT) calculations.[61] However, **Ni-NNN** is not an effective catalyst for cross-coupling reactions, and thus it can be considered that the combination of the pendant $NEt_2$ group with the β-diketiminato framework brings about a sterically and/or electronically unfavorable situation around the Ni center.

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Therefore, we reasoned that the introduction of a pendant phosphorus donor into the β-diketiminato framework would create a sterically and electronically favorable environment at the Ni center and thus a highly active Ni catalyst for the activation of the C-F bond will be realized (Figure 1). Accordingly, in the current report we describe the synthesis and structure of the pincer-type Ni(II) complex bearing the β-diketiminato-based NNP ligand and its application as a catalyst for the cross-coupling of aryl fluorides with aryl Grignard reagents.

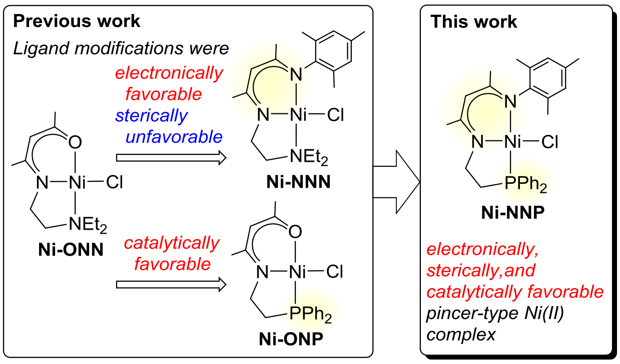


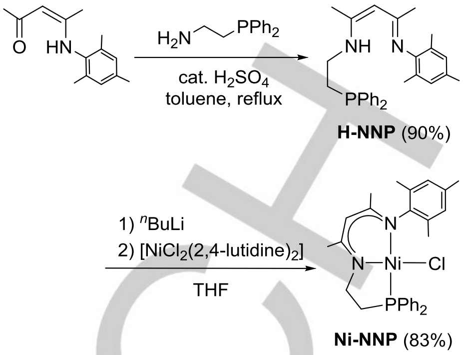
**Figure 1.** Conceptual rationale for a pincer-type Ni(II) complex bearing a β-diketiminato-based NNP ligand.

## Results and Discussion

### Synthesis and characterization

The synthetic procedures for the preparation of the β-diketiminato-based tridentate pro-ligand **H-NNP** and its Ni(II) complex **Ni-NNP** are shown in Scheme 1. The pro-ligand **H-NNP** was prepared by the condensation of 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one with 2-(diphenylphosphino)ethylamine in the presence of a catalytic amount of $H_2SO_4$ and 4-Å molecular sieves in toluene at reflux.[62] Compound **H-NNP** was isolated as a red liquid in 90% yield. This compound was characterized by NMR spectroscopy. In the $^1H$ NMR spectrum, the characteristic broadened signal of the N-H proton was observed downfield at 10.84 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet signal assignable to the $PPh_2$ moiety was observed at -20.9 ppm.

Next, we investigated the preparation of the Ni(II) complex **Ni-NNP**. Treatment of the Ni(II) precursor $[NiCl_2(2,4\text{-lutidine})_2]$ with the lithiated ligand, which was prepared *in situ* by the reaction of **H-NNP** with *n*-BuLi in tetrahydrofuran (THF), afforded complex **Ni-NNP** as a green solid in 83% yield. Elemental analysis, NMR spectroscopy, and X-ray diffraction analysis confirmed the formation of the desired pincer-type Ni(II) complex **Ni-NNP**. Comparison of $^1H$ NMR and $^{31}P$-decoupled $^1H$ NMR ($^1H\{^{31}P\}$ NMR) spectra of **Ni-NNP** was highly effective for the characterization of this complex (see Experimental section). The $^{31}P\{^1H\}$ NMR spectrum of **Ni-NNP** showed a singlet signal at 35.6 ppm. The downfield shift suggests that the $PPh_2$ moiety is coordinated to the Ni center (-20.9 ppm for **H-NNP**).



**Scheme 1.** Synthetic procedures for the pro-ligand **H-NNP** and complex **Ni-NNP**.

The structure of **Ni-NNP** was determined by X-ray analysis. The ORTEP representation of **Ni-NNP** is shown in Figure 2. This complex has a slightly distorted square-planar geometry around the Ni center in which the ligand coordinates in a tridentate pincer-type fashion. For the ligand binding to the Ni center in the mutually *cis* position, the angles are in the range 83.56(3)°–95.64(8)° and the sum of the angles around the Ni center is almost 360° (360.21°). For the ligand binding to the Ni center in the mutually *trans* position, the Cl1-Ni1-N1 and P1-Ni1-N2 angles are 169.61(7)° and 175.68(6)°, respectively. The Ni1-P1 and Ni1-N1 bond lengths are 2.1465(8) and 1.8921(16) Å, respectively.

In our previous study on a series of pincer-type Ni(II) complexes (**Ni-ONN**, **Ni-ONP**, and **Ni-NNN**), complex **Ni-NNN** was found to exhibit a more sterically crowded Ni center than **Ni-ONN** and **Ni-ONP** due to the presence of bulky substituent(s) on the ligand.[61] The structural parameters for this series of Ni(II) complexes are summarized in Table 1. The observed trend does seem to follow the steric demands. The $Ni\text{-}NEt_2$ bond length (1.994(3) Å) in **Ni-NNN** is shorter than the $Ni\text{-}PPh_2$ bond length (2.1465(8) Å) in **Ni-NNP**, and thus complex **Ni-NNP** does not exhibit significant distortion from the ideal square-planar geometry around the Ni center. Therefore, the structural features around the Ni center of **Ni-NNP** are similar to those of **Ni-ONP** and the NNP ligand framework provides a sterically favorable situation around the Ni center in complex **Ni-NNP**. In addition, in the β-diketiminato framework, the N-C (N1-C2 = 1.322(3) and N2-C4 = 1.328(3) Å) and C-C (C2-C3 = 1.387(4) and C3-C4 = 1.387(3) Å) bond lengths are within the mean value ranges of N-C/C-C single and double bonds. Furthermore, the sum of the angles around N1, N2, C2, and C4 atoms are almost 360° (359.86° for N1, 360.01° for N2, 359.9° for C2, and 360.0° for C4). Therefore, these results indicate that the π-electrons are delocalized over the N1-C2-C3-C4-N2 framework.

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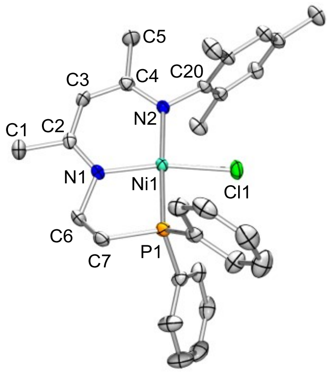
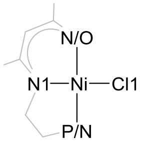


**Figure 2.** ORTEP drawing of **Ni-NNP** (thermal ellipsoids drawn at 30% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1-Cl1, 2.1951(7); Ni1-P1, 2.1465(8); Ni1-N1, 1.8921(16); Ni1-N2, 1.916(2); N1-C2, 1.322(3); N1-C6, 1.484(3); N2-C4, 1.328(3); C1-C2, 1.519(3); C2-C3, 1.387(4); C3-C4, 1.387(3); C4-C5, 1.509(4); Cl1-Ni1-P1, 83.56(3); Cl1-Ni1-N1, 169.61(7); Cl1-Ni1-N2, 94.32(5); P1-Ni1-N1, 86.69(7); P1-Ni1-N2, 175.68(6); N1-Ni1-N2, 95.64(8); Ni1-N1-C2, 125.13(17); Ni1-N1-C6, 117.29(15); C2-N1-C6, 117.44(18); Ni1-N2-C4, 124.00(16); Ni1-N2-C20, 121.81(14); C4-N2-C20, 114.2(2).

**Table 1.** Structural parameters for Ni(II) complexes relevant to the current study.

| | **Ni-NNP** | **Ni-ONN**[a] | **Ni-ONP**[a] | **Ni-NNN**[a] |
|---|---|---|---|---|
| ΣNi (°)[b] | 360.21 | 359.93 | 360.30 | 362.89 |
| Cl1-Ni-N1 (°) | 169.61(7) | 177.20(7) | 174.50(6) | 163.43(6) |
| N/O-Ni-P/N (°) | 175.68(6) | 178.36(9) | 174.16(5) | 169.29(9) |
| Ni-N1 (Å) | 1.8921(16) | 1.8696(18) | 1.896(2) | 1.860(2) |
| Ni-P/N (Å) | 2.1465(8) | 1.980(2) | 2.1292(6) | 1.994(3) |



[a] Reference [61]. [b] Sum of angles around the Ni atom.

As a matter of course, an ancillary ligand is often used to provide an appropriate steric and electronic environment around the metal center. In our previous study on pincer nickel(II) complexes, we revealed that the β-diketiminato framework provides a more electronically donating environment, i.e., it increases the energy level of the HOMO more than the β-aminoketonato framework.[61] Thus, to elucidate the electronic properties of **Ni-NNP**, theoretical calculations were performed on this complex.

Computational study was carried out using Gaussian 09 at the B3LYP level of theory with the LANL2DZ basis set for the Ni atom and the 6-311++G(d,p) basis set for the other atoms. The LANL2DZ pseudopotential was used for the Ni center. Geometrical optimization of **Ni-NNP** was performed successfully. The optimized molecular structure is shown in Figure S2 in the Electronic Supplementary Information (ESI). Selected geometrical parameters for **Ni-NNP** are summarized in Table S3 (ESI). The geometrical parameters determined by DFT calculations were found to be in good agreement with those obtained by X-ray analysis, but the calculations predicted slightly longer bond lengths.

Representations of the HOMO and LUMO orbitals of **Ni-NNP** are given in Figure 3. **Ni-NNP** shows similar HOMO and LUMO orbitals to those of the series of Ni(II) complexes reported previously.[61] The HOMO orbital of **Ni-NNP** resides on the six-membered ring comprising the Ni-β-diketiminato unit. The energies of the HOMO and LUMO for **Ni-NNP** together with those of the previously reported Ni(II) complexes are summarized in Table 2. The HOMO of **Ni-NNP** (-5.17 eV) is slightly higher than that of **Ni-NNN** (-5.23 eV) in energy, while the energy level of the **Ni-NNP** HOMO is significantly higher than those of the **Ni-ONN** (-5.68 eV) and **Ni-ONP** (-5.68 eV) HOMOs. In contrast, these Ni(II) complexes present similar LUMO energy values. We reasoned that the β-diketiminato framework has a significant electronic influence on the Ni center and that complex **Ni-NNP** is more electron rich than the β-aminoketonato-based pincer complexes **Ni-ONN** and **Ni-ONP**. From the results of the X-ray diffraction and DFT analyses of **Ni-NNP**, this complex most likely provides a structurally and electronically favorable environment for the cross-coupling reaction at the Ni center.

Next, we examined the cross-coupling of aryl fluorides with aryl Grignard reagents using the Ni(II) complexes as catalysts.

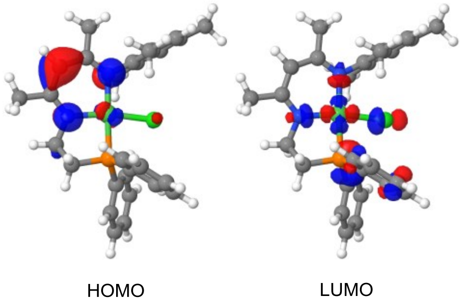


**Figure 3.** HOMO and LUMO orbitals of **Ni-NNP** prepared using the Jmol software package.[63]

**Table 2.** HOMO and LUMO energies for the Ni(II) complexes in this study.

| | **Ni-NNP** | **Ni-ONN**[a] | **Ni-ONP**[a] | **Ni-NNN**[a] |
|---|---|---|---|---|
| HOMO (eV) | -5.17 | -5.68 | -5.61 | -5.23 |
| LUMO (eV) | -1.74 | -1.84 | -1.86 | -1.80 |

[a] Reference [61].

### Cross-coupling reaction catalyzed by Ni(II) complexes

In order to evaluate the catalytic properties of the four Ni(II) complexes, cross-coupling reactions were conducted using 1 mmol of fluorobenzene (**1a**) with 1.2 equivalents of *p*-tolylmagnesium bromide (**2b**) in the presence of 5 mol% of the Ni(II) complex in THF at room temperature for 6 h (Table 3).

Complexes **Ni-ONN** and **Ni-NNN** exhibit poor activity (entries 1 and 2). Conversely, **Ni-ONP** performs effectively as a catalyst for the coupling reaction to give the cross-coupled product 4-methylbiphenyl (**3ab**) in 66% yield (entry 3). Complex **Ni-NNP** also acts as an effective catalyst to give 4-methylbiphenyl (**3ab**) in 67% yield (entry 4). Thus, **Ni-ONP** and **Ni-NNP** present similar performances in this reaction.

Therefore, we next performed the reaction of 4-fluorotoluene (**1b**), which has an electron-donating group on the aromatic ring, with phenylmagnesium bromide (**2a**) using these complexes under the same conditions (entries 5 and 6). Complex **Ni-NNP** exhibits superior performance to **Ni-ONP** and affords 4-methylbiphenyl (**3ba**) in 52% yield along with the homo-coupled products 4,4'-dimethylbiphenyl (**4bb**, 4%) and biphenyl (**5aa**, 18%).

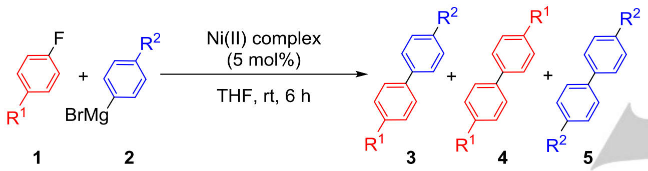


**Table 3.** Comparison of the catalytic performances of the Ni(II) complexes in this study for the cross-coupling reaction.[a]

| Entry | Ni(II) complex | R$^1$ | R$^2$ | **3** (%)[b] | **4** (%)[b] | **5** (%)[b] |
|---|---|---|---|---|---|---|
| 1 | **Ni-ONN** | H | Me | 17 | 6 | 23 |
| 2 | **Ni-NNN** | H | Me | 9 | 1 | 14 |
| 3 | **Ni-ONP** | H | Me | 66 | 4 | 10 |
| 4 | **Ni-NNP** | H | Me | 67 | 2 | 13 |
| 5 | **Ni-ONP** | Me | H | 44 | 2 | 22 |
| 6 | **Ni-NNP** | Me | H | 52 | 4 | 18 |

[a] The reaction was carried out with 1.0 mmol of fluoroarene **1** and 1.2 mmol of arylmagnesium bromide **2** in the presence of Ni(II) complex (0.05 mmol) in THF (5 mL) at room temperature for 6 h. [b] The yields were determined by gas-liquid chromatography (GLC) analysis using octadecane as an internal standard. The yields of **3**, **4**, and **5** are based on **1**, **1**, and **2**, respectively.

To optimize the reaction conditions, we preformed the reaction with fluorobenzene (**1a**) and *p*-tolylmagnesium bromide (**2b**) in the presence of a catalytic amount of **Ni-NNP** at room temperature for 6 h under various conditions. The results are summarized in Table 4.

Initially, we investigated the influence of the solvent on the reaction (entries 1–5). In the case of Et$_2$O, the yield of the cross-coupled product **3ab** increases to 71% (entry 1). In 1,2-dimethoxyethane (DME) and 1,4-dioxane, the desired product is formed in low and moderate yields, respectively (entries 2 and 3). Cyclopentyl methyl ether (CPME) provides the best result, affording the product in 87% yield (entry 4). Toluene is also as an effective solvent, providing the desired product in 85% yield (entry 5). Regarding the optimal amounts of Grignard reagent and the catalyst **Ni-NNP**, we found that 1.5 equivalents of the Grignard reagent and 2.5 mol% of the catalyst provide good yields of **3ab** (entries 6–9). In these reactions, concomitant formation of the homo-coupled products **4aa** and **5bb** in approximately 10% yields occurs.

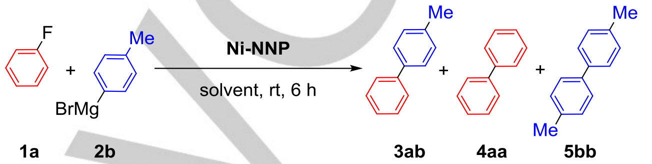


**Table 4.** Optimization of the cross-coupling reaction catalyzed by **Ni-NNP**.[a]

| Entry | **Ni-NNP** (mol%) | *p*-TolMgBr (equiv.) | solvent | **3ab** (%)[b] | **4aa** (%)[b] | **5bb** (%)[b] |
|---|---|---|---|---|---|---|
| 1 | 5 | 1.2 | Et$_2$O | 71 | 5 | 11 |
| 2 | 5 | 1.2 | DME | 4 | -[c] | 8 |
| 3 | 5 | 1.2 | 1,4-dioxane | 49 | 1 | 6 |
| 4 | 5 | 1.2 | CPME | 87 | 7 | 11 |
| 5 | 5 | 1.2 | toluene | 85 | 6 | 10 |
| 6 | 2.5 | 1.2 | CPME | 87 | 7 | 10 |
| 7 | 1 | 1.2 | CPME | 81 | 7 | 10 |
| 8 | 2.5 | 1.5 | CPME | 90 | 7 | 11 |
| 9 | 2.5 | 2.0 | CPME | 88 | 7 | 11 |

[a] The reaction was carried out a 1.0 mmol scale of 4-fluorobenzene (**1a**). [b] The yields were determined by GLC analysis using octadecane as an internal standard. [c] Product **4aa** was not detected.

To further demonstrate the efficiency of **Ni-NNP** as a catalyst for cross-coupling reactions, we investigated the substrate scope of the protocol using different aryl fluorides and arylmagnesium bromides in CPME. The results are summarized in Table 5.

The reaction of 4-fluorotoluene with phenylmagnesium bromide under the optimized reaction conditions, i.e., in the presence of 2.5 mol% of **Ni-NNP** at room temperature for 6 h, affords the desired product, 4-methylbiphenyl, in 78% yield (entry 1). An increase in the yield of 4-methylbiphenyl is observed after 24 h (90%, entry 2). Based on the result in entry 2, all subsequent reactions were conducted for 24 h. In the case

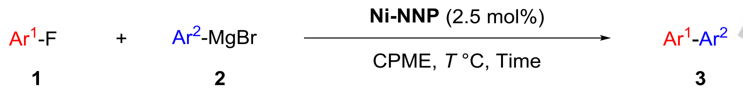
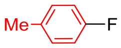
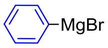
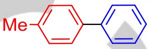
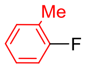
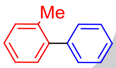
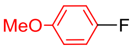
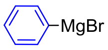
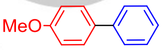
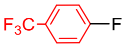
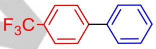
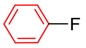
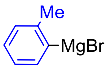
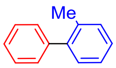
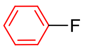
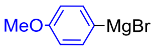
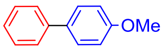
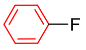
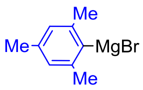
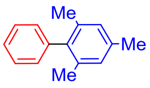


**Table 5.** Results of cross-coupling reaction catalyzed by **Ni-NNP**. [a]

| Entry | $Ar^1$–F (**1**) | $Ar^2$–MgBr (**2**) | *T* (°C) | Time (h) | $Ar^1$–$Ar^2$ (**3**) | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 |  |  | rt | 6 |  | 78 |
| 2 |  |  | rt | 24 |  | 90 |
| 3 |  |  | rt | 24 |  | 16 |
| 4 |  |  | 60 | 24 |  | 23 |
| 5 |  |  | rt | 24 |  | 48 |
| 6 |  |  | 60 | 24 |  | 91 |
| 7 |  |  | rt | 24 |  | 55 |
| 8 |  |  | 60 | 24 |  | 61[c] |
| 9 |  |  | rt | 24 |  | 30[c] |
| 10 |  |  | 60 | 24 |  | 72[c] |
| 11 |  |  | 60 | 24 |  | 30[d] |

[a] The reaction was carried out with fluoroarene (1.0 mmol) and arylmagnesium bromide (1.5 mmol) in the presence of the catalyst **Ni-NNP** (0.025 mmol). [b] The yield was determined by GLC analysis using octadecane as an internal standard. [c] Isolated yield. [d] The yield was determined by $^1$H NMR analysis using pyrazine as an internal standard.

of 2-fluorotoluene, 2-methylbiphenyl is obtained in 16% yield (entry 3). When the reaction is conducted at higher temperature (60 °C) for 24 h, the product yield does not increase drastically (23%, entry 4). The reaction with 4-fluoroanisole at room temperature leads to the formation of 4-methoxybiphenyl in 48% yield (entry 5). In contrast, at 60 °C, the yield of the product increases to 91% (entry 6). The reaction of 4-fluorobenzotrifluoride with phenylmagnesium bromide affords the coupled product in 55% yield (entry 7).

Next, we investigated the reaction of fluorobenzene with different arylmagnesium bromides. In the case of *o*-tolylmagnesium bromide, the cross-coupled product 2-methylbiphenyl is obtained in 61% yield at 60 °C (entry 8). With 4-methoxyphenylmagnesium bromide at room temperature, 4-methoxybiphenyl is obtained in 30% yield (entry 9). At 60 °C, the yield of 4-methoxybiphenyl increases to 72% (entry 10). In the reaction of 2-mesitylmagnesium bromide at 60 °C, the cross-coupled product is obtained in 30% yield. Thus, from the results in entries 4 and 8, **Ni-NNP** shows low activity towards sterically bulky electrophiles, whereas this complex tolerates sterically congested nucleophiles. Further investigation into the development of effective catalysts that activate sterically hindered electrophiles is currently underway in our group.

## Conclusions

In this work, we investigated the synthesis, structure, and electronic properties of the β-diketiminato-based pincer-type Ni(II) complex **Ni-NNP** and compared its catalytic performance in the cross-coupling of aryl fluorides with arylmagnesium bromides with those of a previously reported series of pincer-type Ni(II) complexes.[61] The pincer ligand based on the β-diketiminato framework with a phosphorus tether enabled the Ni center to activate the C-F bond in aromatic fluorides. The β-aminoketonato-based pincer complex **Ni-ONP** also showed considerable performance in the cross-coupling of aryl fluorides. In the case of **Ni-ONP**, the β-aminoketonato oxygen atom may interact with magnesium, and thus synergistic bimetallic Ni/Mg cooperation could not be ruled out.[13] In contrast, we assume that such bimetallic cooperation cannot occur with **Ni-NNP**. Therefore, the design of the ligand framework and its combination with the metal play crucial roles in the development of highly active catalysts. Further investigations into the modification of the ligand framework, the mechanistic aspects of the catalytic system, and the coupling of various organometallic reagents with organic electrophiles are currently underway in our group.

## Experimental Section

**General procedures:** All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an atmosphere of nitrogen, which was dried with SICAPENT (Merck Co., Inc.), using standard Schlenk tube or high vacuum techniques. All solvents were distilled over the appropriate drying agents prior to use. 4-((2,4,6-Trimethylphenyl)amino)pent-3-en-2-one,[64] 2-(diphenylphosphino)ethylamine,[65] [$NiCl_2$(2,4-lutidine)$_2$],[66] **Ni-ONN**,[61] **Ni-ONP**,[61] and **Ni-NNN**[61] complexes were prepared according to literature methods. All other reagents employed in this study are commercially available and were used without further purification. $^1H$, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on BRUKER DRX-300, DRX-500, or JEOL ECX-400 spectrometers at ambient temperature. $^1H$, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR chemical shifts are presented in ppm relative to $Me_4Si$ as an internal standard. $^{31}P\{^1H\}$ NMR chemical shifts are presented in ppm relative to $H_3PO_4$ as an external standard. All coupling constants are presented in Hz. Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet), dt (doublet of triplets), and m (multiplet). Thin layer chromatography (TLC) was performed using Merck silica gel 60F-254 plates and visualized under UV (254 nm) irradiation. Column chromatography was performed using Silica Gel 60N (spherical, neutral, 63–210 μm, Kanto Chemical Co., Inc.). High-resolution mass spectra (HRMS) were recorded using fast atom bombardment (FAB) ionization with a JEOL JMS-700 mass spectrometer. Elemental analyses were performed on a Vario EL elemental analyzer. GLC was performed on a Shimadzu GC-17A gas chromatographer using a ULBON HR-1 capillary column (0.25 i.d. × 25 m, Shinwa Chemical Industries Ltd.).

**Preparation of H-NNP:** 4-((2,4,6-Trimethylphenyl)amino)pent-3-en-2-one (1022 mg, 4.70 mmol), 2-(diphenylphosphino)ethylamine (1137 mg, 4.96 mmol), and toluene (20 mL) were placed in a Schlenk tube. A few drops of $H_2SO_4$ were added to the reaction mixture. After attaching a 4-Å molecular sieve column ($\phi$ = 20 mm, length = 50 mm) between the Schlenk tube and the reflux condenser the reaction mixture was refluxed for 24 h. After cooling to room temperature, aqueous NaOH (10 mL) was added to the reaction mixture and then the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were dried with $Na_2SO_4$, filtered, and concentrated *in vacuo* at 110 °C to give **H-NNP** as a red liquid (1809 mg, 4.22 mmol, 90%). $^1H$ NMR ($\delta$, $CDCl_3$): 1.59 (s, 3H, $CH_3$), 1.87 (s, 3 H, $CH_3$), 2.01 (s, 6H, N-*o*-$(C\mathit{H}_3)_3C_6H_2$), 2.24–2.28 (m, 2H, $NCH_2C\mathit{H}_2P$), 2.26 (s, 3H, N-*p*-$(C\mathit{H}_3)_3C_6H_2$), 3.27–3.32 (m, 2H, $NC\mathit{H}_2CH_2P$), 4.61 (s, 1H, CH), 6.85 (s, 2H, N-$(CH_3)_3C_6\mathit{H}_2$), 7.30–7.32 (m, 6H, $PPh_2$), 7.37–7.41 (m, 4H, $PPh_2$), 10.84 (s, 1H, NH). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$): 18.5 (s, N-*o*-$(\mathit{C}H_3)_3C_6H_2$), 19.3 (s, $NC\mathit{C}H_3$), 20.8 (s, N-*p*-$(\mathit{C}H_3)_3C_6H_2$), 21.2 (s, $NC\mathit{C}H_3$), 30.4 (d, $^1J_{PC}$ = 14.1 Hz, $NCH_2\mathit{C}H_2P$), 40.4 (d, $^2J_{PC}$ = 24.9 Hz, $N\mathit{C}H_2CH_2P$), 93.6 (s, $NC\mathit{C}CN$), 127.8 (s, N-*o*-$(CH_3)_3\mathit{C}_6H_2$), 128.3 (s, N-*m*-$(CH_3)_3\mathit{C}_6H_2$), 128.6 (d, $^3J_{PC}$ = 6.7 Hz, P-*m*-$C_6H_5$), 128.8 (s, P-*p*-$C_6H_5$), 131.1 (s, N-*p*-$(CH_3)_3\mathit{C}_6H_2$), 132.7 (d, $^2J_{PC}$ = 19.2 Hz, P-*o*-$C_6H_5$), 138.0 (d, $^1J_{PC}$ = 12.5 Hz, P-$\varepsilon$-$C_6H_5$), 147.0 (s, N-$\varepsilon$-$(CH_3)_3\mathit{C}_6H_2$), 155.0 (s, $N\mathit{C}CCN$), 166.1 (s, $NCC\mathit{C}N$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$): -20.9 (s). HRMS ($FAB^+$) *m*/*z* $[M + H]^+$ calc. for $C_{28}H_{34}N_2P$: 429.2460; found 429.2461.

**Preparation of Ni-NNP**: A solution of [$NiCl_2$(2,4-lutidine)$_2$] (1465 mg, 4.26 mmol) in THF (15 mL) was cooled to -78 °C, and then a THF solution of the lithiated ligand, which was prepared by the reaction of **H-NNP** (1876 mg, 4.38 mmol) with *n*-butyllithium (1.70 mL of a 2.54 M hexane solution, 4.32 mmol) at -78 °C, was added. The reaction mixture was allowed to warm to room temperature. After 18 h, the volatiles were removed under reduced pressure. The residual solid was extracted with toluene (30 mL), and the volatiles were removed under reduced pressure to give **Ni-NNP** as a green solid (1850 mg, 3.55 mmol, 83%). An analytically pure sample of **Ni-NNP** was obtained by recrystallization from toluene/hexane. Anal. Calc. for $C_{28}H_{32}ClN_2NiP$: C, 64.46; H, 6.18; N, 5.37%. Found: C, 64.51; H, 6.24; N, 5.30%. $^1H$ NMR ($\delta$, $C_6D_6$): 1.46 (dt, $J$ = 10.4, 6.6 Hz, 2H, $NCH_2C\mathit{H}_2P$), 1.67 (s, 3H, $CH_3$), 1.71 (s, 3H, $CH_3$), 2.16 (s, 3H, N-*p*-$(C\mathit{H}_3)_3C_6H_2$), 2.62 (s, 6H, N-*o*-$(C\mathit{H}_3)_3C_6H_2$), 2.83 (dt, $J$ = 27.1, 6.6 Hz, 2H, $NC\mathit{H}_2CH_2P$), 4.96 (s, 1H, CH), 6.87 (s, 2H, N-*m*-$(CH_3)_3C_6\mathit{H}_2$), 7.00–7.07 (m, 6H, $PPh_2$), 7.91–9.75 (m, 4H, $PPh_2$). $^1H\{^{31}P\}$ NMR ($\delta$, $C_6D_6$): 1.45 (t, $J$ = 6.7 Hz, 2H, $NCH_2C\mathit{H}_2P$), 1.67 (s, 3H, $CH_3$), 1.71 (s, 3H, $CH_3$), 2.16 (s, 3H, N-*p*-$(C\mathit{H}_3)_3C_6H_2$), 2.62 (s, 6H, N-*o*-$(C\mathit{H}_3)_3C_6H_2$), 2.83 (t, $J$ = 6.7 Hz, 2H, $NC\mathit{H}_2CH_2P$), 4.96 (s, 1H, CH), 6.87 (s, 2H, N-*m*-$(CH_3)_3C_6\mathit{H}_2$), 7.00–7.07 (m, 6H, $PPh_2$), 7.94 (d, $J$ = 7.0 Hz, 4H, $PPh_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $C_6D_6$): 19.9 (s, N-*o*-$(\mathit{C}H_3)_3C_6H_2$), 21.1 (s, N-*p*-$(\mathit{C}H_3)_3C_6H_2$), 23.9 (d, $^4J_{PC}$ = 4.6 Hz, $NC\mathit{C}H_3$), 23.9 (s, $NC\mathit{C}H_3$), 31.8 (d, $^1J_{PC}$ = 23.8 Hz, $NCH_2\mathit{C}H_2P$), 52. 9 (d, $^2J_{PC}$ = 11.0 Hz, $N\mathit{C}H_2CH_2P$), 98.9 (s, $NC\mathit{C}CN$), 128.5 (d, $^3J_{PC}$ = 10.1 Hz, P-*m*-$C_6H_5$), 128.8 (s, N-*m*-$(CH_3)_3\mathit{C}_6H_2$), 130.6 (d, $^4J_{PC}$ = 1.8 Hz, P-*p*-$C_6H_5$), 131.3 (d, $^1J_{PC}$ = 51.3 Hz, P-$\varepsilon$-$C_6H_5$), 132.3 (s, N-*o*-$(CH_3)_3\mathit{C}_6H_2$), 133.0 (s, N-*p*-$(CH_3)_3\mathit{C}_6H_2$), 133.7 (d, $^2J_{PC}$ = 10.1 Hz, P-*o*-$C_6H_5$), 147.8 (s, N-$\varepsilon$-$(CH_3)_3C_6H_2$), 159.1 (s, $N\mathit{C}CCN$), 159.8 (s, $NCC\mathit{C}N$). $^{31}P\{^1H\}$ NMR ($\delta$, $C_6D_6$): 35.6 (s).

**Experimental procedure for X-ray crystallography:** A suitable single crystal of **Ni-NNP** was obtained by recrystallization from toluene/hexane at room temperature and was mounted on a glass fiber. All measurements were made on a Rigaku Mercury 70 diffractometer using graphite monochromated Mo-*K*α radiation ($\lambda$ = 0.71073 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum $2\theta$ value of 60.2°. A total of 744 oscillation images were collected. The crystal-to-detector distance was 45.00 mm. Readout was performed in 0.068-mm-pixel mode. Data were collected using CrystalClear[67] and processed using CrysAlisPro.[68] In the reduction of the data, an empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. Crystallographic data and the results of the measurements are summarized in Table S1 (ESI). The structure was solved by direct methods (SHELXT),[69] and expanded using Fourier techniques. Least-square refinements were carried out using SHELXL.[70] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at the ideal positions and refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package.[71] Crystal data for **Ni-NNP**: $C_{28}H_{32}ClN_2NiP$, $M$ = 521.70, monoclinic, $a$ = 18.0428(10), $b$ = 9.2258(5), $c$ = 16.1409(7) Å, $\beta$ = 101.477(5)°, $V$ = 2633.1(2) Å$^3$, space group $P2_1/c$ (#14), $Z$ = 4, $Dc$ = 1.316 g cm$^{-3}$, $F(000)$ = 1096.00, $T$ = 223(1) K, $\mu$(Mo-$K\alpha$) = 9.174 cm$^{-1}$, 19532 reflections measured, 6024 independent ($R$int = 0.0461). The final refinement converged to $R1$ = 0.0399 for $I > 2.0\sigma(I)$, w$R2$ = 0.0936 for all data. $S$ = 1.010. Maximum/minimum residual electron densities; 0.31/-0.25 e$^-$ Å$^{-3}$.

CCDC 1862649 (for **Ni-NNP**) contains the supplementary crystallographic data for this manuscript. This data can be obtained free of charge from The Cambridge Crystallographic Data Center.

**DFT calculations:** All geometry optimizations were carried out using Gaussian 09[72] at the B3LYP[73] level of theory[74] with the LANL2DZ basis set[75] for the nickel atom and the 6-311++G(d,p) basis set for other atoms. The LANL2DZ pseudo-potential was used for the nickel center.

**Typical procedure for cross-coupling reactions (taken from Table 4, entry 8): Ni-NNP** (13.0 mg, 0.025mmol), octadecane (129.8 mg, 0.51 mmol), CPME (5 mL), and fluorobenzene (96.4 mg, 0.094 mL, 1.00 mmol) were placed in a Schlenk tube. *p*-Tolylmagnesium bromide (1.5 mL of a 1.0 M THF solution, 1.5 mmol) was then added to the reaction mixture. After stirring for 6 h at room temperature, 1 M hydrochloric acid (5 mL) was added to quench the reaction. The products were extracted with $Et_2O$ and the yields of the products were determined by GLC analysis using octadecane as an internal standard.

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**Keywords:** Nickel • Pincer ligand • β-Diketiminato framework • Aryl fluorides • Cross-coupling reaction

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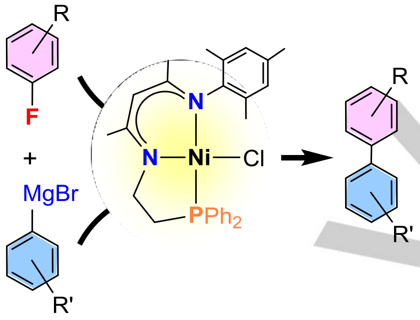
**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

## FULL PAPER

A β-diketiminato-based pincer-type nickel(II) complex was synthesized, and its catalytic performance in the cross-coupling of aryl fluorides with aryl Grignard reagents was investigated.



**Pincer Ni(II) Complex***

*Nobutaka Kurisu, Erika Asano, Yuki Hatayama, Youji Kurihara, Toru Hashimoto, Kei Funatsu, Kazuyoshi Ueda, and Yoshitaka Yamaguchi**

***Page No. – Page No.***

**A β-diketiminato-based pincer-type nickel(II) complex: Synthesis and catalytic performance in the cross-coupling of aryl fluorides with aryl Grignard reagents**

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