Cross-Coupling

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Nickel- and Photoredox-Catalyzed Cross-Coupling Reactions of Aryl Halides with 4-Alkyl-1,4-dihydropyridines as Formal Nucleophilic Alkylation Reagents

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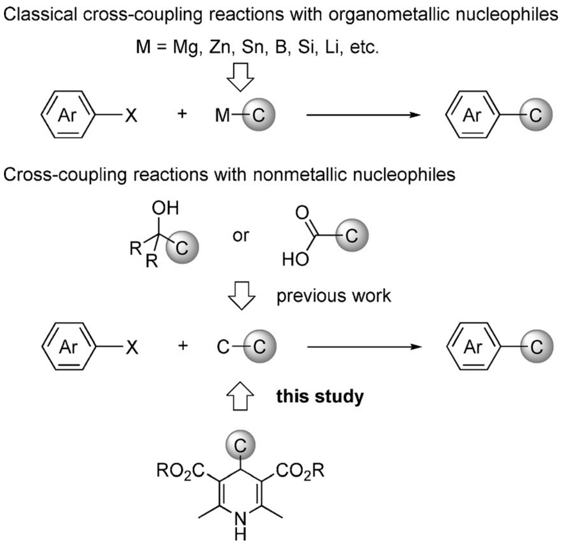
Abstract: *A combination of nickel and photoredox catalysts promoted novel cross-coupling reactions of aryl halides with 4-alkyl-1,4-dihydropyridines. 4-Alkyl-1,4-dihydropyridines act as formal nucleophilic alkylation reagents through a photoredox-catalyzed carbon–carbon (C–C) bond-cleavage process. The present strategy provides an alternative to classical carbon-centered nucleophiles, such as organometallic reagents.*

Transition-metal-catalyzed cross-coupling reactions of aryl halides with various nucleophilic reagents have been one of the most powerful synthetic strategies for decades.[1] In these reactions, the use of organometallic reagents (e.g. organomagnesium, organozinc, organotin, organoboron, organosilicon, and organolithium reagents) as nucleophiles has played a central role to date. In sharp contrast, less attention has been paid to the use of fully organic compounds as formal nucleophiles on the basis of the cleavage of unstrained C–C bonds.[2] In representative studies, cross-coupling reactions of aryl halides with tertiary alcohols through β-elimination-type C–C bond cleavage of alkoxymetal intermediates have been reported.[3–6] Cross-coupling reactions of aryl halides with carboxylic acids (or carboxylates) through decarboxylation under photochemical and thermal conditions have also been studied extensively.[7–9] However, the use of organic compounds as formal nucleophiles has been quite limited.

In relation to enzymatic synthesis, 1,4-dihydropyridine derivatives are recognized as formal hydride donors in a variety of reaction systems.[10] Furthermore, the synthetic use of 4-alkyl-1,4-dihydropyridines as alkylation reagents has emerged as a new strategy for alkylation reactions.[11,12] These alkylation reagents have been used in photochemical reactions[11a,12] and thermal reactions with Lewis acid catalysts[11b] or radical initiators.[11c] Quite recently, our research group succeeded in the development of photoredox-catalyzed[13] aromatic substitution reactions of cyanoarenes with 4-alkyl-1,4-dihydropyridines as formal nucleophilic alkylation reagents.[12,14] In this reaction system, a key step is the generation of alkyl radicals as reactive intermediates by single-electron oxidation of 4-alkyl-1,4-dihydropyridines. However, no successful example of the use of 4-alkyl-1,4-dihydropyridines as alkylation reagents in transition-metal-catalyzed transformations has been reported until now.

We envisaged that a combination of nickel and photoredox catalysts[8,15–17] might enable the use of 4-alkyl-1,4-dihydropyridines as formal nucleophilic alkylation reagents in transition-metal-catalyzed cross-coupling reactions. In this reaction system, photoredox-catalyzed C–C bond cleavage at the 4-position of 4-alkyl-1,4-dihydropyridines provides an alternative to classical organometallic reagents (Scheme 1). We describe herein our preliminary results in the successful nickel- and photoredox-catalyzed cross-coupling reactions of aryl halides with 4-alkyl-1,4-dihydropyridines as formal nucleophilic alkylation reagents.



Scheme 1. Novel concept of the use of formal nucleophilic alkylation reagents in cross-coupling reactions.

We first evaluated the reaction conditions with the substrates 4-iodobiphenyl (**1a**) and 4-benzyl-3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine (**2a**; Table 1). We found that the reaction of **1a** with **2a** (3 equiv) in the presence of *fac*-[Ir(ppy)$_3$] (1 mol %), anhydrous NiCl$_2$ (10 mol %), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbbpy; 15 mol %), and sodium acetate (1.5 equiv) in 1,3-dimethyl-2-imidazolidinone (DMI) under visible-light illumination with a white LED (14 W) gave the desired product 4-benzylbiphenyl (**3a**) in 97 % yield (Table 1, entry 1). In this reaction, formation of the aromatized pyridine derivative **4** was observed. When [Ir(ppy)$_2$(bpy)][BF$_4$] was used as the photoredox catalyst, **3a** was obtained in slightly lower yield (Table 1, entry 2). The use of

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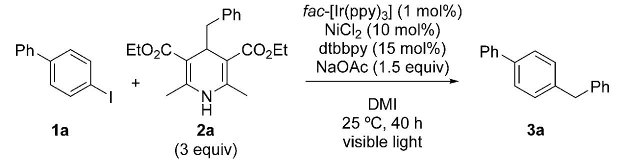
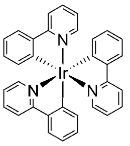
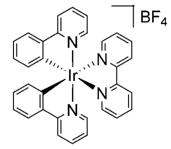
Table 1: Reactions of 4-iodobiphenyl (**1a**) with 4-benzyl-3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine (**2a**).[a]

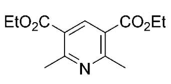


Entry	Variation from standard conditions	Yield [%][b]
1	none	97
2	$[Ir(ppy)_2(bpy)][BF_4]$ instead of *fac*-$[Ir(ppy)_3]$	83
3	$NiBr_2$ instead of $NiCl_2$	84
4	$[Ni(acac)_2]$ instead of $NiCl_2$	25
5	$[Ni(cod)_2]$ instead of $NiCl_2$	72
6	$[NiCl_2(dtbbpy)]$ (10 mol%) instead of $NiCl_2$ and dtbbpy	70
7	in the absence of *fac*-$[Ir(ppy)_3]$	0
8	in the absence of $NiCl_2$	0
9	no light	0
10	in the absence of dtbbpy	19
11[c]	in the absence of NaOAc	60

[a] Standard reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), *fac*-$[Ir(ppy)_3]$ (0.0025 mmol), anhydrous $NiCl_2$ (0.025 mmol), dtbbpy (0.038 mmol), NaOAc (0.38 mmol), DMI (2.5 mL), 14 W white LED illumination, 25 °C, 40 h. [b] Yield of the isolated product. [c] Reaction time: 90 h.


fac-$[Ir(ppy)_3]$


$[Ir(ppy)_2(bpy)][BF_4]$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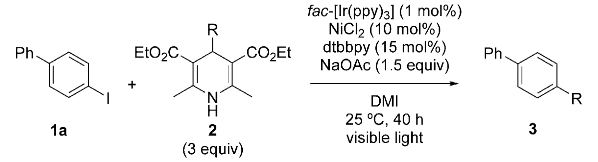
other nickel(II) and nickel(0) complexes, such as $NiBr_2$, $[Ni(acac)_2]$ (acac = acetylacetonato), $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene), and separately prepared $[NiCl_2(dtbbpy)]$ gave **3a** in lower yields (Table 1, entries 3–6). When the reaction was carried out in the absence of *fac*-$[Ir(ppy)_3]$ or anhydrous $NiCl_2$, no **3a** was obtained at all (Table 1, entries 7 and 8). We also confirmed that the reaction did not proceed in the absence of light (Table 1, entry 9). These results clearly show that the reaction is promoted by both the photoredox and the nickel catalyst. Furthermore, in the absence of dtbbpy or NaOAc, the yield of **3a** was decreased (Table 1, entries 10 and 11), thus indicating that all the components in this reaction system are required for the formation of **3a** in high yield.

Under the optimized reaction conditions, reactions of **1a** with other 4-alkyl-1,4-dihydropyridines were investigated (Table 2). A variety of benzyl groups bearing a *tert*-butyl, methoxy, phenyl, chloro, fluoro, or methyl group at the 4-position of the benzene ring were applicable in this reaction system, and the corresponding coupling products were obtained in good yields (Table 2, entries 1–6). The introduction of a methyl group at the 3- or 2-position led to the successful synthesis of **3h** and **3i** (Table 2, entries 7 and 8). As examples of nonbenzylic alkyl groups, methoxymethyl, benzyloxymethyl, (*N*,*N*-dibenzylamino)methyl, and 2-pentyl groups were also transferred to give the corresponding products in moderate yields (Table 2, entries 9–12).

Table 2: Reactions of 4-iodobiphenyl (**1a**) with 4-alkyl 1,4-dihydropyridines **2**.[a]



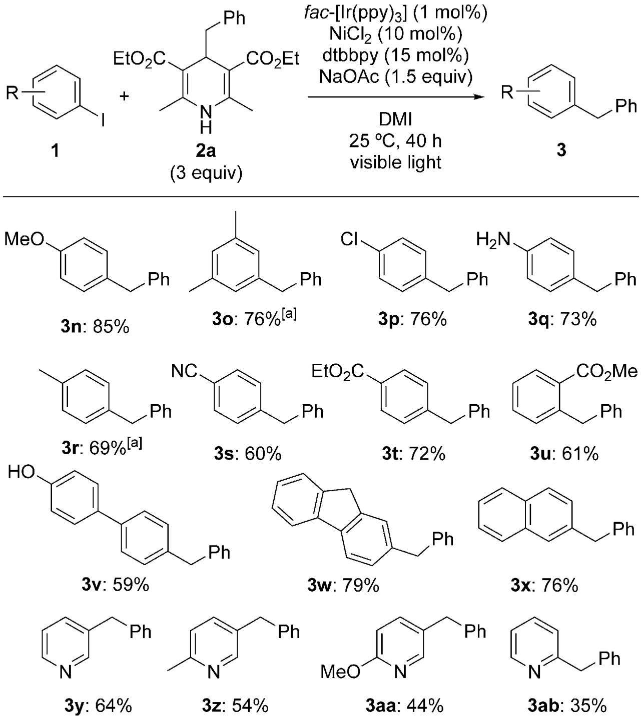
Entry	R in **2**	Yield [%][b]
1	$CH_2(4\text{-}tBuC_6H_4)$ (**2b**)	74 (**3b**)
2	$CH_2(4\text{-}MeOC_6H_4)$ (**2c**)	71 (**3c**)[c]
3	$CH_2(4\text{-}PhC_6H_4)$ (**2d**)	72 (**3d**)
4	$CH_2(4\text{-}ClC_6H_4)$ (**2e**)	70 (**3e**)
5	$CH_2(4\text{-}FC_6H_4)$ (**2f**)	79 (**3f**)
6	$CH_2(4\text{-}MeC_6H_4)$ (**2g**)	61 (**3g**)
7	$CH_2(3\text{-}MeC_6H_4)$ (**2h**)	77 (**3h**)
8	$CH_2(2\text{-}MeC_6H_4)$ (**2i**)	70 (**3i**)
9	CH_2OMe (**2j**)	57 (**3j**)
10	CH_2OCH_2Ph (**2k**)	42 (**3k**)
11	$CH_2N(CH_2Ph)_2$ (**2l**)	41 (**3l**)
12	2-pentyl (**2m**)	17 (**3m**)[c]

[a] All reactions of **1a** (0.25 mmol) with **2** (0.75 mmol) were carried out in the presence of *fac*-$[Ir(ppy)_3]$ (0.0025 mmol), anhydrous $NiCl_2$ (0.025 mmol), dtbbpy (0.038 mmol), and NaOAc (0.38 mmol) in DMI (2.5 mL) with 14 W white LED illumination at 25 °C. [b] Yield of the isolated product. [c] The yield was determined by NMR spectroscopy.

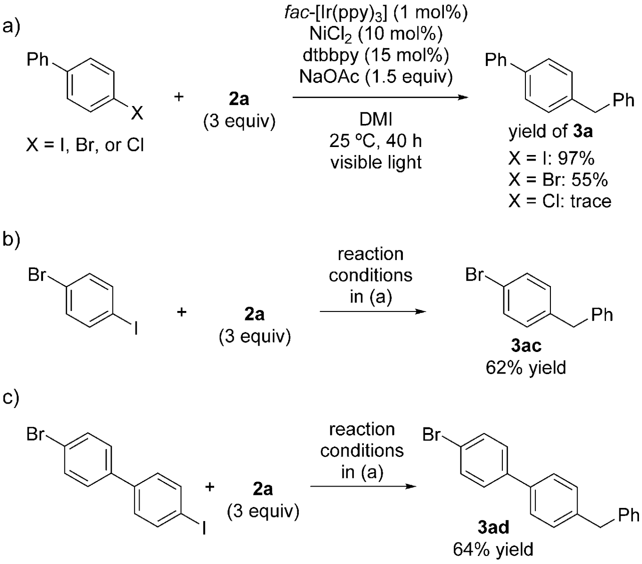
Next, we investigated the use of a variety of aryl iodides **1** in this reaction system (Scheme 2). Aryl iodides bearing various functional groups were compatible with this reaction system, and the corresponding benzylated arenes **3n**–**v** were obtained in high yields. Notably, very polar and strongly coordinating functional groups, such as amino, cyano, and hydroxy goups, were tolerated by this reaction system (products **3q**, **3s**, and **3v**). Reactions of 3-iodo-9*H*-fluorene and 2-iodonaphthalene also proceeded smoothly to give **3w** and **3x**. Besides iodobenzene derivatives, iodopyridines were also suitable substrates. They were converted into the corresponding products **3y**, **3z**, **3aa**, and **3ab** in moderate to good yields.

We also investigated the use of aryl bromides and chlorides as the aryl halide substrate under the same reaction conditions (Scheme 3a). When 4-bromobiphenyl was used, **3a** was obtained in 55% yield, thus indicating that aryl bromides are also applicable in this reaction system. However, the use of 4-chlorobiphenyl did not afford **3a** at all. In reactions of 4-bromo-1-iodobenzene and 4′-bromo-4-iodobiphenyl with **2a**, alkylation occurred selectively at the position of the iodine substituent to give **3ac** and **3ad** in good yields (Scheme 3b,c).

To obtain mechanistic information, we carried out a reaction of **1a** with **2a** in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; 2 equiv; Scheme 4). In this reaction, the formation of **3a** was completely inhibited, and 1-benzyloxy-2,2,6,6-tetramethylpiperidine (**5**) was obtained. Furthermore, when we carried out the reaction in the presence of galvinoxyl (2 equiv), **3a** was not observed at all. These results suggest the involvement of a benzyl radical as a reactive intermediate. The quantum yield of the typical reaction of **1a** with **2a** was determined to be $\Phi = 0.04$. The

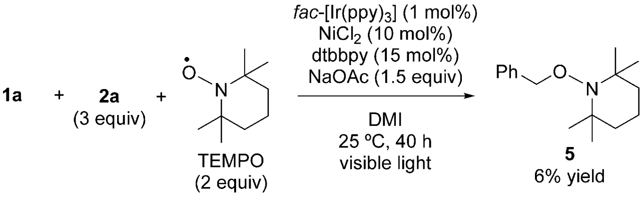


Scheme 2. Reactions of aryl iodides **1** with **2a**. All reactions of **1** (0.25 mmol) with **2a** (0.75 mmol) were carried out in the presence of *fac*-[Ir(ppy)$_3$] (0.0025 mmol), anhydrous NiCl$_2$ (0.025 mmol), dtbbpy (0.038 mmol), and NaOAc (0.38 mmol) in DMI (2.5 mL) with 14 W white LED illumination at 25 °C. Yields are for the isolated product. [a] The yield was determined by NMR spectroscopy.

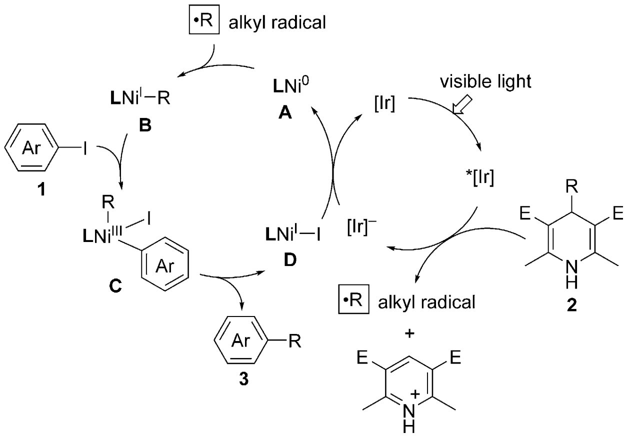


Scheme 3. Effect of halogen substituents.

value below unity suggests that the reaction proceeds through a sequential redox pathway rather than a radical chain process.[12,14,18]



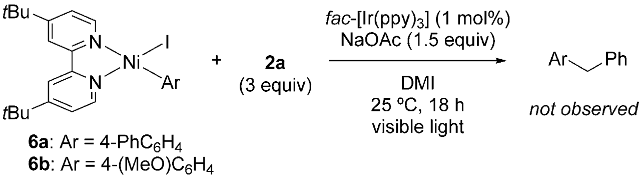
Scheme 4. Reaction in the presence of TEMPO.



Scheme 5. A plausible reaction pathway.

A plausible reaction pathway based on these results is described in Scheme 5. First, an excited-state iridium catalyst (*[Ir]; $E = -1.74$ and $+0.26$ V)[19,20] is formed by the absorption of visible light. Subsequent single-electron oxidation of the 4-alkyl-1,4-dihydropyridine **2** ($E_{pa} = +1.03$ V; pK_a(N–H) = 20.3)[21] proceeds to give the corresponding alkyl radical and aromatized pyridine derivative.[22] The addition of the generated alkyl radical to a nickel(0) complex **A** proceeds to give the corresponding nickel(I)–alkyl complex **B**. Oxidative addition of **B** with an aryl halide **1** occurs to give a nickel(III) complex **C**. Then, reductive elimination takes place to give the cross-coupling product **3**. Finally, the catalytic cycle is completed by single-electron transfer between the resulting nickel(I) halide complex **D** ($E_{pc} = -1.34$ V (Ni$^{II/0}$))[17e] and the reduced form of the iridium catalyst ([Ir]$^-$; $E = -2.24$ V).[20]

The present reaction pathway is similar to that proposed by Molander, Kozlowski, and co-workers for reactions of aryl halides with alkyl borates, in which a Ni^{III} complex **C** is considered to act as a key reactive intermediate.[15c] However, the same nickel(III) complex **C** might be generated by another reaction pathway: The oxidative addition of the nickel(0) complex **A** to the aryl halide would afford a Ni^{II}–aryl complex **6**, such as [(dtbbpy)Ni^{II}(Ar)I],[23] and subsequent addition of the alkyl radical to **6** could then give **C**. To get information on the reactivity of **6**, we carried out reactions of **6a** and **6b** with **2a** (3 equiv) in the presence of *fac*-[Ir(ppy)$_3$] (1 mol%) and NaOAc (1.5 equiv) under visible-light illumination (Scheme 6).[24] In these reactions, the corresponding cross-coupling products **3** were not observed at all. This result indicates that an Ni^{II}–aryl complex such as **6** does not participate in the present catalytic reactions. As a result, we consider that the reactions proceed by the pathway proposed in Scheme 5, in which the key intermediate Ni^{III} complex **C** is generated by oxidative addition of the Ni^{I}–alkyl complex **B** with **1**.[25]



Scheme 6. Reactions of Ni^{II}–aryl complexes **6** with **2a**.

In summary, we have developed novel cross-coupling reactions of aryl halides with 4-alkyl-1,4-dihydropyridines. In this reaction system, 4-alkyl-1,4-dihydropyridines can be used as formal nucleophilic alkylation reagents in transition-metal-catalyzed cross-coupling reactions. These results provide an alternative to the use of classical organometallic reagents as carbon-centered nucleophilic reagents. We consider that the method described herein opens up a novel synthetic strategy for the use of 4-alkyl-1,4-dihydropyridines as formal nucleophilic alkylation reagents in transition-metal-catalyzed transformations.

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