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Room Temperature C–P Bond Formation Enabled by Merging Nickel Catalysis and Visible-Light-Induced Photoredox Catalysis

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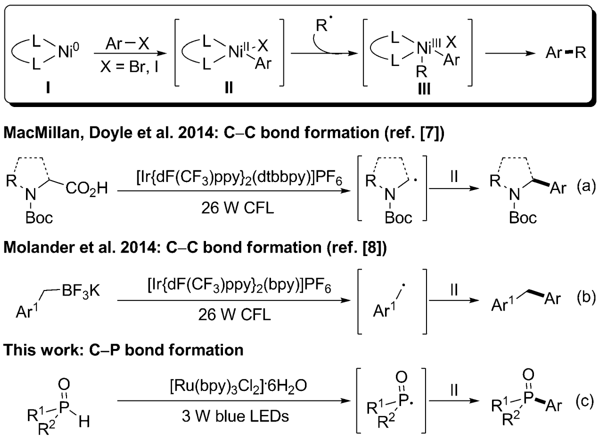
Abstract: A novel and efficient C–P bond formation reaction of diarylphosphine oxides with aryl iodides was achieved by combining nickel catalysis and visible-light-induced photoredox catalysis. This dual-catalytic reaction showed a broad substrate scope, excellent functional group tolerance, and afforded the corresponding products in good to excellent yields. Compared with the previously reported use of photoredox/nickel dual catalysis in the construction of C–C bonds, the methodology described herein was observed to be the first to allow for C-heteroatom bond formation.

Over the past several years, transition-metal-catalyzed cross-coupling reactions have been established as one of the most useful and efficient methods for creating new C–C and C–heteroatom bonds.[1] More intriguingly, dual catalysis realized by merging transition-metal catalysis with visible-light-induced photoredox catalysis has recently attracted considerable attention.[2] Exploration of this dual-catalytic strategy has allowed for the development of various useful chemical transformations, which are unfeasible or not easily accessible by a single catalytic system. In 2011, Sanford and co-workers published a seminal contribution on the arylation of unactivated arenes by combining palladium catalysis and visible-light photoredox catalysis.[3a] Since that study, many other transition metals, such as copper,[4] gold,[5] and rhodium,[6] have been subsequently introduced to this emerging research area. However, very recently, a milestone was reached in the field of photoredox/nickel dual catalysis when two elegant examples of this catalytic process appeared simultaneously. One example was the coupling of α-carboxyl sp^3-carbons with aryl halides (Scheme 1 a),[7] and the other was the coupling of benzylic trifluoroborates with aryl bromides (Scheme 1 b).[8] In each study, the photogenerated carbon-centered radical was intercepted by a Ni^{II} intermediate **II** to yield Ni^{III} complex **III**, followed by a reductive elimination to give the final product of C–C bond formation. Despite these impressive advances, further exploration of the photoredox/nickel dual-catalytic system to develop other useful chemical transformations, especially the formation of new C–heteroatom bonds, remains a highly desirable but challenging goal.



Scheme 1. Photoredox/nickel dual catalysis. Boc = *tert*-butyloxy carbonyl, {dF(CF_3)ppy} = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, bpy = 2,2′-bipyridine, CFL = compact fluorescent light.

Organophosphine compounds are an important class of chemicals that have been widely used in organic synthesis, medicinal chemistry, polymers, photoelectric materials, and coordination chemistry.[9] Consequently, great effort has been devoted to the development of new and efficient catalytic methods for their synthesis.[10] Generally, the visible-light-mediated C–P bond formation reaction can be divided into two categories. One is the utilization of a phosphite ester as the nucleophile to capture the photogenerated reactive species, such as iminium ion[11] and arylgold(III) intermediates,[12] to create new C–P bonds. The other strategy has been reported by the Kobayashi group and involves the visible-light-induced hydrophosphinylation of unactivated alkenes.[13] In the study by Kobayashi and co-workers, a P-centred radical, generated by reductive quenching of the excited state of the photoredox catalyst with diarylphosphine oxide, was considered the key intermediate. Inspired by these elegant studies, we hypothesized

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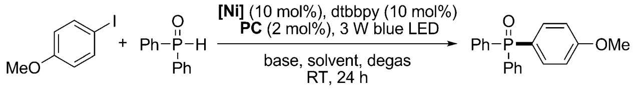
that the photogenerated P-centred radical can also be added to the metal center of the Ni^{II} intermediate **II** in the photoredox/nickel dual-catalytic system, thus providing an efficient alternative method for forging C–P bonds in a controllable manner. As part of our ongoing research interest in the development of new photocatalytic chemical transformations,[14] we herein describe an efficient redoxneutral C–P bond formation reaction by merging nickel catalysis with visible-light photoredox catalysis (Scheme 1 c). To the best of our knowledge, this is the first example of a C–heteroatom bond formation reaction by using the combination of visible-light photoredox catalysis and nickel catalysis.

Our proposed dual-catalytic C–P formation reaction was initially evaluated by using 4-iodoanisole (**1 a**) and diphenylphosphine oxide **2 a** along with 10 mol % [Ni(cod)$_2$], 10 mol % dtbbpy as the ligand, 2 mol % [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ photoredox catalyst, Cs$_2$CO$_3$, and a 3 W blue LED at room temperature (Table 1).[15] To our delight, we observed the desired C–P bond formation product **3 a** when using DMSO as the reaction media, albeit in a modest 16 % yield (entry 1). It was observed that the solvent selection had a significant effect on the yield of the coupling reaction (entries 2–4), with MeOH being the best choice (entry 3, 65 % yield). Moreover, the use of a number of commonly used nickel catalysts did not improve the reaction efficiency (entries 5 and 6). Further investigations revealed that the GC yield of **3 a** could be slightly increased when [Ru(bpy)$_3$Cl$_6$]·6 H$_2$O was used as the photoredox catalyst (entry 7, 72 % yield). Next, we examined the influence of the base on this C–P bond formation reaction. Compared with the reaction involving Cs$_2$CO$_3$, the reaction proceeded less efficiently with other bases, such as K$_2$CO$_3$, KOH, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; entries 8–10). Other reaction parameters, including the ratio of **1 a** to **2 a** and the catalyst loading, were also carefully screened (entries 11–13). A similar GC yield was obtained when 2.0 equivalents of **1 a** were employed (entry 11). To our delight, the yield of **3 a** could be increased to 83 % when a 1:2 ratio of **1 a** to **2 a** was used. Finally, 91 % GC yield (90 % isolated yield) was achieved when the reaction was performed in the presence of 5 mol % [Ru(bpy)$_3$Cl$_6$]·6 H$_2$O and 2 mol % [Ni(cod)$_2$]/dtbbpy with 2.0 equivalents of Cs$_2$CO$_3$ (entry 13). The critical role of the nickel catalyst, the photoredox catalyst, light irradiation and the base, as well as the degassing procedure were demonstrated through control experiments in which no or only a trace amount of the desired product was detected upon omission of any of these components (Table 1, entries 14–18).

Table 1. Optimization of the reaction conditions.[a]



1a **2a** **3a**

Entry	[Ni]	PC	Solvent	Base	Yield [%][b]
1	Ni(cod)$_2$	**[Ir]**	DMSO	Cs$_2$CO$_3$	16
2	Ni(cod)$_2$	**[Ir]**	CH$_3$CN	Cs$_2$CO$_3$	6
3	Ni(cod)$_2$	**[Ir]**	MeOH	Cs$_2$CO$_3$	65
4	Ni(cod)$_2$	**[Ir]**	DCM	Cs$_2$CO$_3$	4
5	NiCl$_2$(PPh$_3$)$_2$	**[Ir]**	MeOH	Cs$_2$CO$_3$	45
6	NiCl$_2$·glyme	**[Ir]**	MeOH	Cs$_2$CO$_3$	42
7	Ni(cod)$_2$	**[Ru]**	MeOH	Cs$_2$CO$_3$	72
8	Ni(cod)$_2$	**[Ru]**	MeOH	K$_2$CO$_3$	63
9	Ni(cod)$_2$	**[Ru]**	MeOH	KOH	39
10	Ni(cod)$_2$	**[Ru]**	MeOH	DBU	71
11[c]	Ni(cod)$_2$	**[Ru]**	MeOH	Cs$_2$CO$_3$	70
12[d]	Ni(cod)$_2$	**[Ru]**	MeOH	Cs$_2$CO$_3$	83
13[e]	Ni(cod)$_2$	**[Ru]**	MeOH	Cs$_2$CO$_3$	91 (90)[f]
14	–	**[Ru]**	MeOH	Cs$_2$CO$_3$	6
15	Ni(cod)$_2$	–	MeOH	Cs$_2$CO$_3$	0
16	Ni(cod)$_2$	**[Ru]**	MeOH	–	trace
17[g]	Ni(cod)$_2$	**[Ru]**	MeOH	Cs$_2$CO$_3$	0
18[h]	Ni(cod)$_2$	**[Ru]**	MeOH	Cs$_2$CO$_3$	0

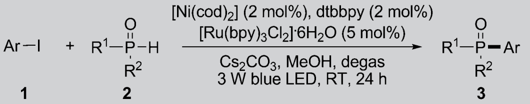
[a] Reaction conditions: **1 a** (0.36 mmol), **2 a** (0.3 mmol), Ni catalyst (10 mol %), dtbbpy (10 mol %), **PC** (2 mol %), base (0.6 mmol), and solvent (3 mL) at RT for 24 h under the irradiation of a 3 W blue LED. [b] GC yield by using tetradecane as the internal standard. [c] **1 a** (0.6 mmol), **2 a** (0.3 mmol). [d] **1 a** (0.3 mmol), **2 a** (0.6 mmol). [e] [Ni(cod)$_2$] (2 mol %), dtbbpy (2 mol %), photocatalyst (5 mol %). [f] Isolated yield in parentheses. [g] Without visible-light irradiation. [h] Without the degassing procedure. **[Ir]**: [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$, **[Ru]**: [Ru(bpy)$_3$Cl$_2$]·6 H$_2$O, cod = 1,5-cyclooctadiene, glyme = 1,2-dimethoxyethane, DMSO = dimethyl sulfoxide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. **PC** = photocatalyst.

With the optimal reaction conditions in hand, we next probed the scope of this dual catalytic C–P formation process. As shown in Table 2, a series of diversely substituted aryl iodides reacted readily with diphenylphosphine oxide **2 a** under the optimal conditions. Incorporation of electron-donating (-Me, -OMe) or electron-withdrawing groups (-F, -Cl, -Br) at the *para*-position of iodobenzene were tolerated well, affording the corresponding coupling products **3 a**–**f** in generally high yields (entries 1–6, 71–91 % yields). In addition, this dual catalytic reaction allowed for a broad range of functional groups on the aryl ring (e.g., phenols, amines, amides, and ethers) to be accommodated (entries 7–11, 81–86 % yield). More significantly, the sterically encumbered 1-iodonaphthalene **1 l** proved to be a viable partner, affording the C–P formation product **3 l** in 90 % yield (entry 12). To our delight, the methyl-modified secondary phosphine oxide **2 b** also proved to be a competent reactant to provide triarylphosphine oxide **3 m** in 69 % yield (entry 13). It is well documented that electron-rich secondary phosphine oxides exist nearly exclusively in their pentavalent tautomeric form, which prevents them from participating in the photo-oxidation step to give the key P-centered radical intermediates.[13,16] As expected, no desired C–P bond formation products were detected when dicyclohexylphosphine oxide **2 c** and ethyl phenylphosphinate **2 d** were utilized under the best reaction conditions (entries 14 and 15).

Notably, this photoredox/nickel dual-catalytic process could be extended further to the coupling of diarylphosphine oxide with heteroaryl iodides. For example, 5-iodo-1*H*-indole (**1 m**) and 2-iodopyridine (**1 n**) can facilely react with diphenylphosphine oxide **2 a**, giving the corresponding C–P bond formation products **3 p** and **3 q** in 84 and 75 % yield, respectively [Eq. (1) and (2)]. It is worth noting that the photoredox catalyst [Ir(ppy)$_2$(bpy)]PF$_6$ was observed to be superior in the latter case.

A plausible reaction mechanism was proposed in Scheme 2 to explain this dual catalytic C–P bond formation process. The photocatalytic cycle starts with the reductive quenching of ex-

Table 2. Substrate scope.[a]



2a: R^1 = R^2 = phenyl; **2b**: R^1 = R^2 = tosyl
2c: R^1= R^2= cyclohexyl; **2d**: R^1 = phenyl, R^2 = ethoxyl

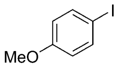
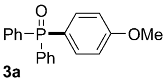
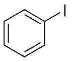
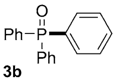
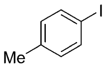
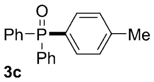
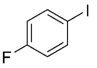
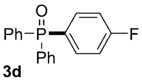
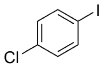
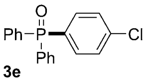
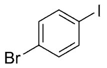
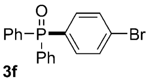
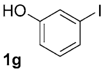
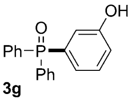
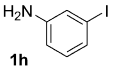
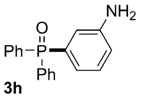
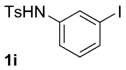
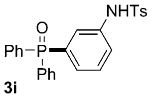
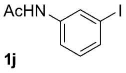
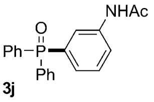
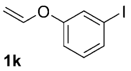
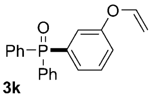
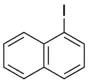
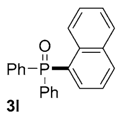
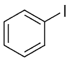
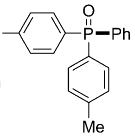
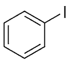
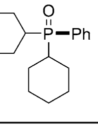
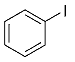
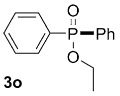
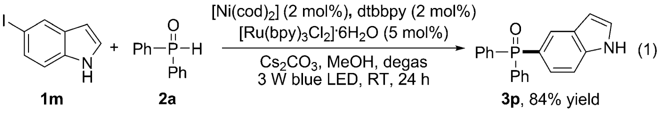
Entry	1	2	Product	Yield [%][b]
1	 **1a**	**2a**	 **3a**	90
2	 **1b**	**2a**	 **3b**	91
3[c]	 **1c**	**2a**	 **3c**	71
4	 **1d**	**2a**	 **3d**	83
5	 **1e**	**2a**	 **3e**	88
6	 **1f**	**2a**	 **3f**	81
7	 **1g**	**2a**	 **3g**	84
8	 **1h**	**2a**	 **3h**	85
9	 **1i**	**2a**	 **3i**	86
10	 **1j**	**2a**	 **3j**	81
11	 **1k**	**2a**	 **3k**	83
12	 **1l**	**2a**	 **3l**	90
13[d]	 **1b**	**2b**	 **3m**	69
14	 **1b**	**2c**	 **3n**	n.d.[e]

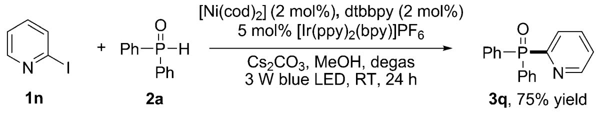
Table 2. (Continued)

Entry	1	2	Product	Yield [%][b]
15	 **1b**	**2d**	 **3o**	n.d.[e]

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), [Ni(cod)$_2$] (2 mol%), dtbbpy (2 mo%), [Ru(bpy)$_3$Cl$_2$]·6H$_2$O (5 mol%), Cs$_2$CO$_3$ (0.6 mmol), and MeOH (3 mL) at RT for 24 h under the irradiation of a 3 W blue LED. [b] Yield of the isolated product. [c] **1c** (0.6 mmol), **2a** (0.3 mmol). [d] **1b** (0.6 mmol), **2b** (0.3 mmol). [e] n.d. = not detected. Ts = *p*-toluenesulfonyl, Ac = acetyl.



(1)



(2)

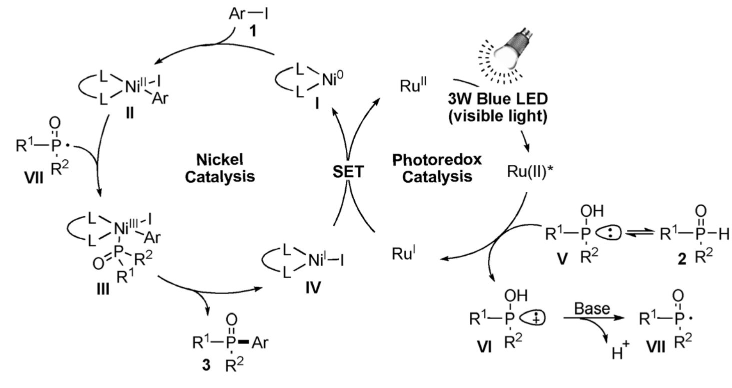
cited state Ru^{II}* with phosphinous acid **V** to yield the corresponding radical-cation intermediate **VI** and the low-valence Ru^{I} complex. Then, the base-promoted deprotonation of **VI** delivers the key P-centered radical **VII**.[13] Meanwhile, the oxidative addition of the Ni^{0} species **I** to aryl halide **1** would give the Ni^{II} intermediate **II**, which rapidly intercepts the P-centered radical **VII** to afford the organometallic Ni^{III} complex **III**.[7,8] Reductive elimination of **III** gives the final C–P bond formation product **3**, as well as the Ni^{I} species **IV**. Finally, single-electron reduction of the Ni^{I} species **IV** by the low-valence photocatalyst Ru^{I} completes both of the catalytic cycles. Another reaction pathway involving the addition of P-centered radical **VII** to the Ni^{0} species might be possible and cannot be totally ruled out at the current stage (see Section S4 in the Supporting Information for details).

In conclusion, we have developed an efficient dual-catalytic C–P formation reaction by combining nickel catalysis and visible-light-induced photoredox catalysis. The method takes advantage of the visible-light photoredox catalytic cycle to generate P-centered radicals from diarylphosphine oxides under very mild reaction conditions (room temperature, visible-light irradiation) and combines the reaction with the nickel-catalyzed functionalization of aryl iodides. These reactions are compatible with a wide range of functional groups (e.g., phenols, amines, amides, and ethers) and give the corresponding important triarylphosphine oxides in good to excellent yields.

Experimental Section

Representative procedure

To a 10 mL Schlenk flask equipped with a magnetic stir bar **1a** (0.3 mmol), **2a** (0.6 mmol), [Ru(bpy)$_3$Cl$_2$]·6H$_2$O (0.015 mmol),



Scheme 2. Plausible reaction mechanism.

[Ni(cod)$_2$] (0.006 mmol), dtbbpy (0.006 mmol), Cs_2CO_3 (0.6 mmol), and dry MeOH (3.0 mL) were added. The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of ~5 cm from a 3 W blue LED and stirred at room temperature for 24 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 μm; eluent: petroleum ether/ethyl acetate 3:1 to 1:1) to provide the pure product **3a** as a white solid in 90% (83.2 mg, 0.27 mmol) yield.

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Keywords: C–P bond formation · dual catalysis · nickel · photochemistry · radicals

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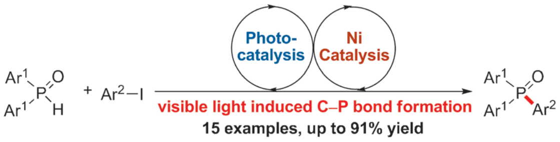

Dual catalysis: A novel and efficient C–P bond formation reaction of diarylphosphine oxides with aryl iodides was achieved by combining nickel catalysis and visible-light-induced photoredox catalysis (see scheme). This dual-catalytic reaction showed a broad substrate scope, excellent functional-group tolerance, and afforded the corresponding products in good to excellent yields. Compared with previously reported photoredox/nickel dual catalytic systems, this methodology is the first to allow for C–heteroatom bond formation.

Synthetic Methods

J. Xuan, T.-T. Zeng, J.-R. Chen, L.-Q. Lu, W.-J. Xiao**

■■ – ■■

Room Temperature C–P Bond Formation Enabled by Merging Nickel Catalysis and Visible-Light-Induced Photoredox Catalysis