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Letter

Visible-Light-Promoted Photoredox Dehydrogenative Coupling of Phosphines and Thiophenols

Xianya Wang, Chungu Xia,* and Lipeng Wu*

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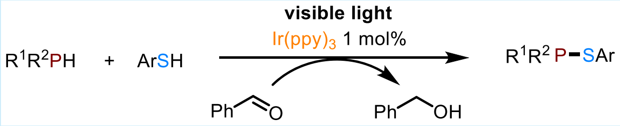
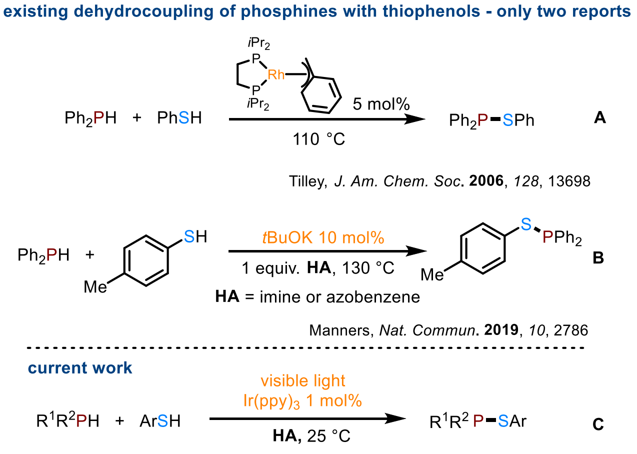
ABSTRACT: Herein, by applying visible-light photoredox catalysis, we have now achieved the first example of catalytic dehydrogenative coupling of phosphines and thiophenols that proceeds at room temperature. Key to our success is the use of benzaldehyde as a soft oxidant, which avoids the issue of phosphine oxidation. Furthermore, we observed the unexpected dealkylative coupling of secondary and tertiary alkylphosphine with thiophenols.



Catalytic bond formation and cleavage at the carbon centers play a pivotal role in the synthesis of bulk and fine chemicals.[1] In contrast, catalytic chemistry that involves the activation and transformation of main group substrates for E−E′ (E = *p*-block elements other than carbon) bond formation is considerably less developed.[2] Traditionally, the formation of main group element−element bonds has been achieved using methods such as salt metathesis[3] and Wurtz-type reductive coupling.[4] However, these approaches produce large amounts of salts as side products, and the harsh reaction conditions limit functional group tolerance. Consequently, the development of catalytic methods for E−E′ bond formation under mild reaction conditions with broad substrate tolerance is required.[5]

Over the past decade, visible-light photoredox catalysis has emerged as an enabling platform for the development of new organic reactions with high synthetic efficiency and broad functional group tolerance.[6] These reactions mainly focused on the bonds formation of C−C and C−E (E = N, S, Cl, Br, Si, B, Se).[7] In contrast, the application of photoredox catalysis for E−E′ bond formation is rare. In 2015, visible-light-catalyzed Si−O bond formation between hydrosilane and water, using rhodium porphyrin complexes, was reported.[8] In 2016, a visible-light-mediated oxidative cross-coupling of thiols with (P^V=O)−H compounds using air as the oxidant was developed.[9] Furthermore, the use of photoredox catalysis for S−S and N=N bond formation has also been achieved.[10] Notwithstanding these achievements, there is no application of photoredox catalysis on bond formation involving primary and secondary phosphines (P^{III}−H species: R^1R^2PH, R^2 = H or R^1) to date.[11] This is mainly because the P^{III}−H species is easily oxidized by common oxidants such as air,[9] dilauroyl peroxide,[12] or $K_2S_2O_8$,[13] which are otherwise required for the (P^V=O)−H compounds. Molecules containing P^{III} have numerous applications in coordination[5d,14] and synthetic chemistry.[15] In addition, compounds containing P^{III}−S bonds (thiophosphanes) are of great interest in medicinal chemistry and agrochemistry.[16] However, their direct synthesis from phosphines and thiophenols is very rare. To the best of our knowledge, there are only two examples reported in the literature, using rhodium catalyst at 110 °C[5b] (Scheme 1A) or

Scheme 1. (A) Rhodium Phosphido Complex-Catalyzed Dehydrocoupling of Phosphine with Thiophenols at 110 °C; (B) *t*BuOK-Catalyzed Dehydrocoupling of Phosphine with Thiophenols in the Presence of H_2 Acceptors at 130 °C; (C) Our Current Work Using Photoredox Catalyst Catalyzed Dehydrocoupling of Phosphines with Thiophenols under Visible-Light Condition[a]



[a]HA = hydrogen acceptor.

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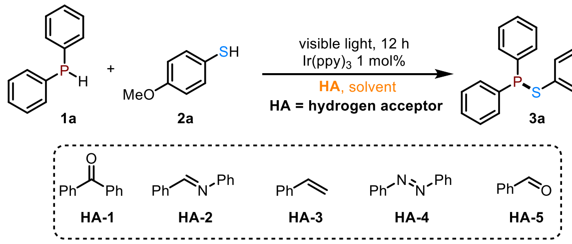
*t*BuOK at 130 °C (Scheme 1B),[17] both of which require high temperatures and fall short in terms of substrate generality studies. Consequently, the development of a milder and more convenient approach for the direct synthesis of thiophosphanes remains underdeveloped. Herein, we report the first example of a general dehydrocoupling of phosphines with thiophenols enabled by photoredox catalysis under visible-light irradiation to produce a series of thiophosphanes (Scheme 1C). More interestingly, we also observed an unexpected dealkylative coupling process in the reaction of secondary and tertiary alkylphosphine with thiophenols.

We chose diphenylphosphine **1a** (0.2 mmol) coupled with 4-methoxythiophenol **2a** (0.24 mmol) as the model reaction and Ir(ppy)$_3$ (1 mol %) as the photoredox catalyst (see Table S1 for photoredox catalyst screening), under ambient conditions, with a 22 W white LED plate as the light source. The results of our initial investigations revealed that, without any H$_2$-acceptor (**HA**), only a trace amount of **3a** was produced (Table 1, entry 1). Then, in an effort to promote the dehydrocoupling process, we added 1 equiv of various **HAs** to the MeCN solution. To our delight, we obtained improved results. With benzophenone (**HA-1**), we obtained 29% of the dehydrocoupling product **3a** (Table 1, entry 2). With an imine (**HA-2**), we obtained 32% of **3a** (Table 1, entry 3). With styrene (**HA-3**), only a trace amount of **3a** was observed; this was due to the competing hydrophosphination of styrene (Table 1, entry 4). With azobenzene (**HA-4**), we obtained 65% of **3a** (Table 1, entry 5). Finally, benzaldehyde (**HA-5**) was found to be the best **HA**, which afforded **3a** in 96% yield (Table 1, entry 6, and Figure S1). Then, changing the reaction solvent from MeCN to other solvents was conducted, and all the tested solvents gave inferior results (Table 1, entries 7−12), while it is worth mentioning that THF, dioxane, and DMSO gave similar results (Table 1, entries 9−11).

Table 1. Ir(ppy)$_3$-Catalyzed Dehydrogenative Coupling of Diphenylphosphine (1a) with 4-Methoxythiophenol (2a) under Visible-Light: Condition Optimization[a]

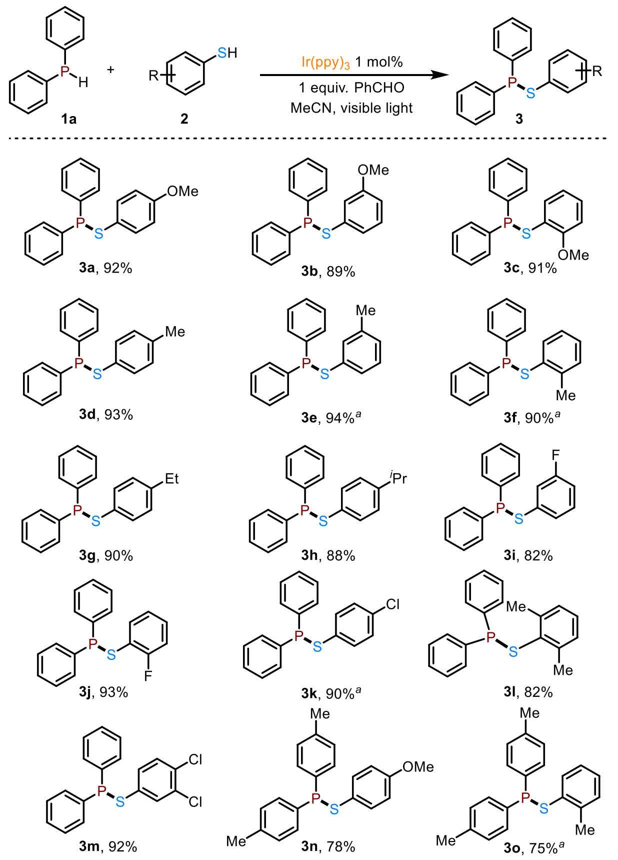


entry	HAs	solvent	yield[b] (%)
1		MeCN	2
2	HA-1	MeCN	29
3	HA-2	MeCN	32
4	HA-3	MeCN	trace
5	HA-4	MeCN	65
6	**HA-5**	**MeCN**	**96**
7	HA-5	EtOH	20
8	HA-5	DCM	78
9	HA-5	THF	88
10	HA-5	DMSO	92
11	HA-5	dioxane	92
12	HA-5	toluene	76

[a] Reactions were performed in a 20 mL vial with **1a** (0.2 mmol), **2a** (0.24 mmol), Ir(ppy)$_3$ (1 mol %), **HA** (0.2 mmol), and solvents (1.0 mL) under N$_2$ atmosphere with light irradiation. [b] Yields were determined by ^{31}P NMR spectroscopy.

With the optimized reaction conditions in hand (Table 1, entry 6), we evaluated the generality of our methodology for the synthesis of various thiophosphanes. First, thiophenols with different substituents on the phenyl ring were applied in the reaction with diphenylphosphine (**1a**) (Scheme 2). In general, good to excellent yields were obtained. For example, thiophenols with −OMe, −Me, −Et, and −^{i}Pr groups on the phenyl ring reacted smoothly with **1a** and afforded the corresponding thiophosphanes **3a**−**3h** in yields ranging from 88% to 94%. We also found that the position of the substituents on the phenyl ring had no obvious effect on the results. Furthermore, fluoride- and chloride-substituted thiophenols also participated in the dehydrogenative coupling reaction without side reactions arising from the C−X bonds (X = F, Cl) (**3i**−**3k**). Apart from the monosubstituted thiophenols, the multisubstituted thiophenols also worked well in our system; **3l** with 2,6-dimethyl groups and **3m** with 3,4-dichloro groups were obtained in yields of 82% and 92%, respectively. Finally, by changing the phosphine to 4-Me-substituted diphenylphosphines we could obtain the corresponding products in 78% and 75% yields when coupling with different thiophenols (**3n** and **3o**).

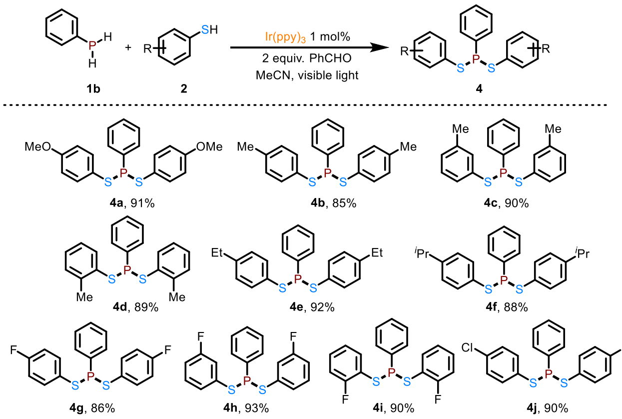
Scheme 2. Ir(ppy)$_3$-Catalyzed Dehydrogenative Coupling of Diphenylphosphine with Various Thiophenols under Visible-Light Irradiation*



*Reactions were performed in a 20 mL vial with **1a** (0.2 mmol), thiophenols (0.24 mmol), benzaldehyde (0.2 mmol), Ir(ppy)$_3$ (1 mol %), and MeCN 1.0 mL under N$_2$ and light irradiation for 12−24 h; isolated yields are given. [a] Isolated yields after complexation with BH$_3$.

We then turned our attention to the use of a primary phenylphosphine in the dehydrogenative coupling reactions. Phenylphosphine ($PhPH_2$) has two P−H bonds; therefore, upon reaction with thiophenols, it is possible that a mixture of mono- and bis-dehydrocoupling products will be formed. To our delight, we selectively obtained the bis-dehydrocoupling product by using 3 equiv of thiophenols in the reaction with phenylphosphine. Scheme 3 shows that a series of thiophenols could readily react with phenylphosphine and afford the corresponding bis-thiophosphanes in excellent yields (85−93%). As in the case of diphenylphosphine, the position of the substituents on the phenyl ring of thiophenol had hardly any effect on the reaction outcome. Apart from the various alkyl substituents, the halogen groups (such as fluoride and chloride) remained intact.

Scheme 3. Ir(ppy)$_3$-Catalyzed Dehydrogenative Coupling of Phenylphosphine with Various Thiophenols under Visible-Light Irradiation[a]

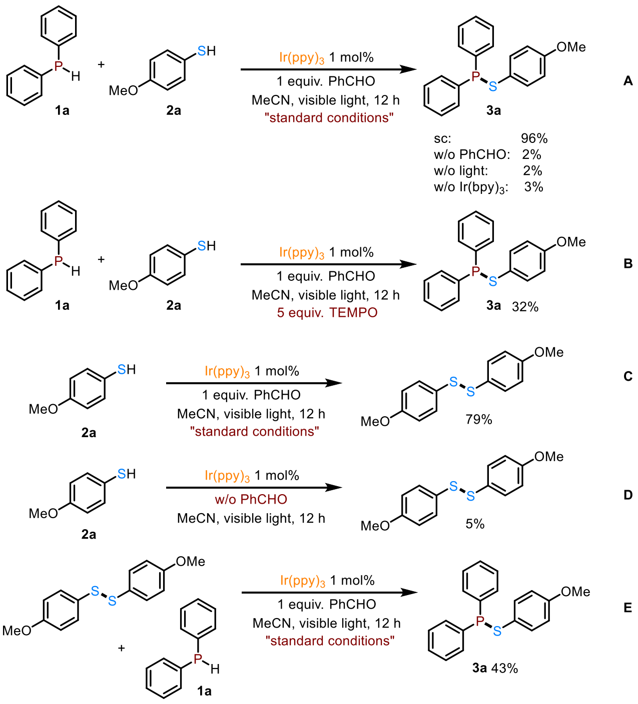


[a]Reactions were performed in a 20 mL vial with **1b** (0.2 mmol), thiophenols (0.6 mmol), benzaldehyde (0.4 mmol), Ir(ppy)$_3$ (1 mol %), and MeCN 1.0 mL under N_2 and light irradiation for 12−24 h; isolated yields are given.

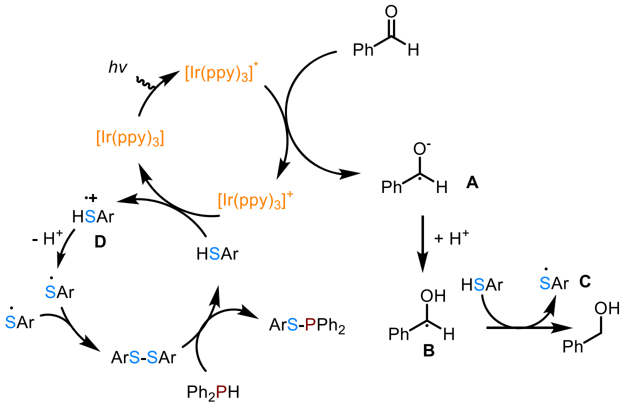
To understand the reaction mechanism, we carried out several control experiments. First, we observed that the omission of benzaldehyde or light yielded only a trace amount of **3a**, hence indicating the crucial role of both the H_2-acceptor and light in the reaction (Scheme 4A, Figures S2 and S3). Second, we observed that the reaction without Ir(ppy)$_3$ gave only 3% of the product (Scheme 4A, Figure S4), hence ruling out the possibility of benzaldehyde itself acting as the photoredox catalyst in the reaction.[18] Furthermore, the addition of 5 equiv of TEMPO to the reaction largely suppressed the reaction with only 32% of **3a** obtained (Scheme 4B). Further control experiments with only thiophenol in the catalytic system showed that disulfide was formed in 79% yield (Scheme 4C) but required the presence of benzaldehyde as only 5% of disulfide was produced without benzaldehyde (Scheme 4D). In addition, disulfide reacted with diphenylphosphine to produce **3a** in 43% yield (Scheme 4E).

From the control experiments and the fact that we could detect disulfide and benzyl alcohol in the reaction (Figure S5), we proposed the reaction mechanism as depicted in Scheme 5. Ir(ppy)$_3$ is first excited under visible light to yield its excited-state species, [Ir(ppy)$_3$]*, which then undergoes a single-electron transfer with benzaldehyde to yield [Ir(ppy)$_3$]$^+$ and radical anion of benzaldehyde (**A**), which produced ketyl radical (**B**) with H$^+$, the ketyl radical then interacted with thiophenols to yield the *S*-based radical (**C**) and benzyl alcohol. On the other hand [Ir(ppy)$_3$]$^+$ was reduced by another thiophenol to regenerate Ir(ppy)$_3$ and produce radical cation of thiophenol (**D**), which produced *S*-based radical after deprotonation. Coupling of *S*-based radical generated ArS−SAr, which reacted with Ph_2PH to generate ArS−PPh$_2$ and thiophenol.

Scheme 4. Mechanism Study Reactions

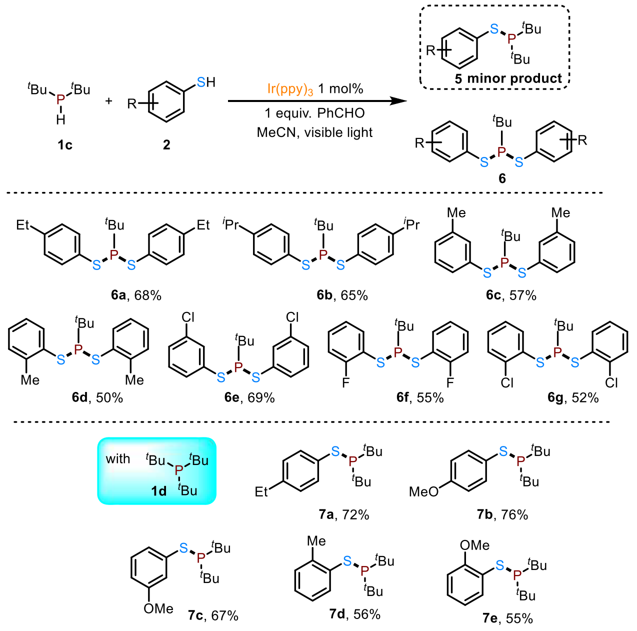


Scheme 5. Plausible Reaction Mechanism for Photoredox Dehydrocoupling of Phosphines with Thiophenols



We then carried out experiments to determine whether an alkylphosphine could undergo the catalytic photoredox dehydrocoupling reaction with thiophenols. Di-*tert*-butylphosphine **1c** was used in the above-described system. To our surprise, we found that only ∼30% dehydrogenative coupling product **5** was formed with its further dealkylcoupling product **6** as the major product (Scheme 6). This unexpected transformation is applicable to various thiophenols with an alkyl substituent on the phenyl ring to produce the dealkylative coupling products **6a**−**6d** in 50−68% yields. Halides such as −Cl and −F were also tolerant as demonstrated by products

Scheme 6. Photoredox Dealkylcoupling of Alkyl Phosphines with Thiophenols



6e−6g. More interestingly, this dealkylative coupling approach could extend to tri-*tert*-butylphosphine **1d**, in which case the dealkylative coupling of one −^{t}Bu group was found to be the major products, and substituents on the *para*-, *ortho*-, and *meta*-position of the phenyl ring were all applicable with yields ranging from 55 to 76% (**7a−7e**).

In conclusion, we have developed the first visible-light-promoted photoredox dehydrogenative coupling of phosphines with thiophenols. The application of visible light and the use of benzaldehyde as H_2-acceptor are key to our success. Our system offers the mildest conditions (25 °C) for the dehydrogenative coupling of phosphines with thiophenols. Prior to this, the only two existing catalytic thermal reactions required temperatures >110 °C. A series of thiolphosphanes was successfully synthesized in excellent yields. Moreover, the unexpected dealkylative coupling of alkylphosphine with thiophenols was observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02746.

Experimental details, initial condition optimization table, product characterizations (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Chungu Xia − *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P.R. China*; Email: cgx@licp.cas.cn

Lipeng Wu − *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P.R. China*; orcid.org/0000-0003-0583-4832; Email: lipengwu@licp.cas.cn

Author

Xianya Wang − *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P.R. China; University of Chinese Academy of Sciences, Beijing 100049, P.R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c02746

Notes

The authors declare no competing financial interest.

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