A visible-light activated secondary phosphine oxide ligand enabling Pd-catalyzed radical cross-couplings

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Although transition metal-catalyzed reactions have evolved with ligand development, ligand design for palladium-catalyzed photoreactions remains less explored. Here, we report a secondary phosphine oxide ligand bearing a visible-light sensitization moiety and apply it to Pd-catalyzed radical cross-coupling reactions. The tautomeric phosphinous acid coordinates to palladium in situ, allowing for pseudo-intramolecular single-electron transfer between the ligand and palladium. Molecular design of the metal complexes aided by time-dependent density functional theory calculations enables the involvement of allyl radicals from π-allyl palladium(II) complexes, and alkyl and aryl radicals from the corresponding halides and palladium(0) complex. This complex enables radical cross-couplings by ligand-to-Pd(II) and Pd(0)-to-ligand single-electron transfer under visible-light irradiation.
Pd-catalyzed cross-coupling is an important C–C bond formation methodology for the synthesis of pharmaceuticals, bioactive molecules, agrochemicals, and other functional molecules\(^1\)–\(^3\). Transition metal catalysts have evolved along with ligand development. Ligand tuning expands the reactivity of transition metals, increases turnover number, and allows for reactions under mild conditions; therefore, the design and synthesis of electronically and sterically controlled ligands have created major breakthroughs in palladium chemistry\(^4\).

Owing to the development of LED light and visible-light photocatalysts, transition metal-catalyzed photoreactions have recently attracted the increased attention of many chemists. The Pd-catalyzed photoreactions can be classified into three modes (Fig. 1a), as follows: (1) those in which the external photocatalyst is the sole light-absorbing species to proceed along three pathways: oxidative single electron transfer (SET), reductive SET, and energy transfer\(^5\)–\(^7\); (2) those in which a Pd catalyst absorbs light\(^8\)–\(^10\); and (3) those in which the external photocatalyst and Pd catalyst absorb light and the energy transfers from the photocatalyst to the Pd-containing intermediate\(^11\) (Fig. 1a). The generation of such a highly active palladium species enables versatile transformations. Moreover, although UV-light irradiation causes nonselective excitation of almost all materials, visible-light irradiation can selectively excite photocatalysts or Pd complexes. Thus, reports of Pd-catalyzed photoreactions have increased in recent years. Although the reaction mechanisms of photoreactions are quite different from those of thermal reactions, phosphine ligands, which are well-studied and designed for thermal reactions, have been applied for photoreactions. The development of ligands that orient photoreactions is limited\(^12\). In addition, the absorption coefficient of the d → p transition\(^13,14\) of the Pd(0) complex in the visible-light region is much smaller than that of other transition metals such as Ru and Ir photoredox catalysts (Fig. 1b). Hence, we expected that the development of ligands that absorb visible light will enhance the applications of transition metals.

To develop a ligand for photoreactions, we planned to synthesize a phosphine ligand with a photosensitive moiety. We first attempted to synthesize a tertiary phosphine bearing 9,10-diphenylanthracene (DPA), but it was unstable and thus easily oxidized under air (Supplementary Fig. 25). Therefore, we used a secondary phosphine oxide (DPAsphox (1)) as a pre-ligand (Fig. 1c), which acts as a ligand through the phosphorus atom after in situ tautomerization to phosphinous acids (DPAphos (1'))\(^15,16\). This ligand design enables the efficient absorption of visible light and pseudo-intramolecular electron or energy transfer to the metal center. Moreover, unlike photoredox catalysts, this metal complex enables a ligand-centered π → π* transition on DPAphos because the DPA moiety does not directly coordinate to palladium. Thus, we hypothesized that the excited DPAphos would generate Pd(I) by one-electron oxidation of Pd(0) via metal-to-ligand charge transfer (MLCT) or one-electron reduction of Pd(II) via ligand-to-metal charge transfer (LMCT) to promote further various radical reactions. The yielded DPA(·−) or (·+) exhibits opposite reactivities, indicating that different oxidation states of Pd(0 or II) can produce quite different reactivities.

Herein, we report the design and synthesis of DPAsphox and describe two different Pd-catalyzed radical cross-coupling reactions using Pd(0) or Pd(II) under visible-light irradiation.

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**Fig. 1 Pd-catalyzed photoreactions.** a Classification of photo-induced Pd-catalyzed reactions. b Absorption coefficient of Pd(0) complex is smaller than Ir and Ru photoredox complexes in visible region. UV-Vis spectra were measured in N,N-dimethylacetamide (DMA). c Concept of visible-light-activated secondary phosphine oxide ligand (DPAsphox (1)). PC photocatalyst, dbppy 4,4′-di-tert-butyl-2,2′-bipyridyl, ppy 2-phenylpyridine, bpy 2,2′-bipyridine.

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Results

Computational studies of Pd complexes. We first calculated the absorption wavelength of the Pd(II)-DPAsphox complex using time-dependent density functional theory (TD-DFT) calculations (Fig. 2a). The \( S_0 \rightarrow S_1 \) absorption of Pd(II) complex (2) was calculated as the ligand-centered \( \pi \rightarrow \pi^* \) transition on DPA, and its wavelength expanded up to 500 nm, indicating that visible-light irradiation enables selective excitation of the DPA moiety. We concluded that this excited DPA moiety in the Pd(II) complex enabled intramolecular one-electron reduction of Pd(II) to afford Pd(I) and DPA\(^{+}\) via LMCT. Thus, we next individually compared the reduction potential of DPA and Pd(II). The reduction potential of DPA\(^{+}\) \( (E_{1/2} \text{[DPA]\(^{+}\)/DPA\(^{-}\]} = -1.68 \text{ V vs. SCE}) \) (Supplementary Information, Section 1–7) was lower than that of allyl Pd(II) complex \( 3 \ (E_{1/2} \text{[3\(^{+}\)/3]} = -1.35 \text{ V vs. SCE}) \)\(^{13} \) and the one-electron reduction of 3 afforded 11.3 kcal/mol stable states (Fig. 2b), indicating that a rapid LMCT in the excited state of 2 would proceed to afford Pd(I) and DPA\(^{+}\) \( (E_{1/2} \text{[DPA]\(^{+}\)/DPA\(^{-}\]} = -0.93 \text{ V vs. SCE}) \) (Supplementary Information, Section 1–7), which is higher than that of Pd(PPh\(_3\))\(_4\) \( (E_{1/2} \text{[Pd(0)/Pd(I)]} = -0.03 \text{ V vs. SCE}) \)\(^{18} \). Therefore, the most favorable ligand-centered excitation \( S_0 \rightarrow S_2 \) facilitates the formation of \( 4 (S_0 \rightarrow S_1) \) and its high reduction potential \( (E_{\text{scale}} [4^{+}/4(S_1)] = -2.80 \text{ V vs. SCE}) \) may cause a further radical reactions such as one-electron reduction of alkyl and aryl halides to generate the carbon-centered radicals.

Synthesis and experimental analysis of DPAsphox. DPAsphox 1 was synthesized, and the stability, spectroscopic and electrochemical properties, and coordination ability to palladium were evaluated. Pd-catalyzed C–P cross-coupling and esterification of 2-bromo-9,10-diphenylanthracene (5) with anilinium hypophosphite afforded ethyl phosphinate 6 in 79% yield\(^{19} \), and the subsequent nucleophilic substitution with phenyl magnesium bromide produced DPAsphox in 86% yield (Fig. 2g). The stability of DPAsphox was tested, and the purity was maintained for at least 1 week under refrigeration (Supplementary Table 7). Absorption and emission spectra of the synthesized DPAsphox revealed \( S_0 \rightarrow S_1 \) absorption at 405 nm and \( S_1 \rightarrow S_0 \) emission at 435 nm (2.85 eV) (Fig. 2h). In addition, cyclic voltammetry showed that the oxidation potential of DPAsphox was +1.33 V (vs. SCE) (Fig. 2i). Thus, the reduction potential of excited DPAsphox was estimated to be −1.52 V (vs. SCE) by Rehm-Weller formalism\(^{20} \). The coordination of DPAsphox to Pd(II) and Pd(0) complexes was next investigated by \(^{31}\)P NMR (Fig. 2j). Stirling DPAsphox with [PdCl(allyl)]\(_2\) and PPh\(_3\) in DMF-d\(_7\) for 1 hour led to the disappearance of the doublet peak at 18.5 ppm of DPAsphox, and the emergence of new peaks between 79.1 and 92.8 ppm, suggesting that DPAsphox (1) derived from DPAsphox coordinates to palladium\(^{15} \). In addition, stirring with Pd(PPh\(_3\))\(_4\) also caused a peak shift between 79.1 and 79.8 ppm. Therefore, as we expected, DPAsphox can be a stable pre-ligand for DPAsphox to become a Pd-DPAsphox complex.

Radical cross-couplings using a Pd(II) complex. We performed Pd-catalyzed radical cross-coupling reactions under visible-light irradiation to demonstrate the utility of DPAsphox. We first verified the reactivity of the allyl-Pd(II)-DPAsphox complex (Table 1 and Fig. 3). Using N-phenyl-1,2,3,4-tetrahydroisoquinoline (7a) and allyl methyl carbonate (8a), C-allylated product 9a was obtained in 75% yield under purple-light irradiation (400 nm) (Table 1, entry 1)\(^{21} \). Irradiation with blue LED light (450 nm) showed the similar performance to give the product (9a) in 76 % yield (entry 2). Control experiments in entries 3 and 4 indicated that Pd catalyst and visible-light irradiation are essential for the allylation reaction. When using ligands such as PPh\(_3\), DPEphos, and Xantphos, which cannot absorb visible light by themselves, no allylated compound (9a) was obtained (entries 5 and 6). The reaction with Pd instead of DPAsphox also afforded 9a in 25% yield (entry 7), suggesting that the pseudo-intramolecular electron transfer of DPAsphox improved the yield in comparison with intermolecular SET with DPA.

Thus, we next carried out a fluorescence quenching study of DPAsphox and DPA to investigate the efficiency of the SET from DPAsphox to Pd(II) (Fig. 3a, b). The absorption spectrum of the mixture of DPAsphox, [PdCl(allyl)]\(_2\), and PPh\(_3\) (solid red line) at around 400 nm, meaning that the DPA moiety of DPAsphox absorbs the light (Fig. 3a). In contrast, the emission intensity was strongly suppressed by the coordination of DPAsphox to palladium, clearly suggesting that quenching proceeded via LMCT from excited DPAsphox to Pd(II). On the other hand, no quenching was observed when we performed the same spectroscopic study using DPA instead of DPAsphox (Fig. 3b). The results of these quenching studies suggest that coordination of DPAsphox to Pd(II) enables highly efficient LMCT by pseudo-intramolecular electron transfer.

We therefore investigated the substrate scope of Pd-catalyzed α-allylation of amines (Fig. 3c). Amine 7a and 1.5 equivalents of allyl methyl carbonate 8a yielded the product 9a in 97% yield under 5 W blue LED lights. The desired 9a was also obtained with 1.0 mmol of 7a in the same yield. Furthermore, the reaction proceeded using allyl alcohol instead of 8a to provide 9a in 95% yield. Substituents at the para position of aniline were examined (9b–g): acetyl (77%), fluoride (quant.), chloride (96%), bromide (61%), methyl (48%), and methoxy (52%). A bromo group was applicable for this allylation in the presence of a Pd catalyst (9e). Electron-donating groups, however, decreased the yields (9f, g), and the product 9g with a methoxy group was obtained in 52% yield when 2,4,6-collidine was added as a Brønsted base to facilitate deprotonation at the α-position of amine\(^{21} \). 6,7-Dimethoxy tetrahydroisoquinoline derivative (9h) and indole- and thiophene-fused piperidine derivatives (9i, j) were obtained in 76%, 84%, 69% yields, respectively. The C-allylation of amino acids also proceeded to give 9k (46%) and 9l (25%). Next, we investigated the substrate scope of allyl methyl carbonate (9m–r). Allyl methyl carbonate with β-methyl, benzy1, n-butyl, and isopropyl groups yielded the product in 93%, 62%, 55%, and 70%, respectively. In addition, using γ-substituted allyl methyl carbonate 8q and 8r, allylic alkylation proceeded in a linear-selective manner to afford 9q (52%) and 9r (56%).

Radical cross-couplings using a Pd(0) complex. The reactivity and spectroscopic properties of the Pd(0) complex were next
Fig. 2 Calculated excited states of Pd-DPAphos complexes and synthesis of DPAsphox (1). a UV-Vis spectrum of Pd(II) complex (2) calculated with ωB97X-D/SDD, 6-311 + G(d,p)//MN15/SDD, 6-31 G(d) in DMF (PCM). b Intermolecular SET from DPA* to Pd(II) complex (3) is a thermodynamically favored pathway. c LMCT after π → π* transition on complex 2 produces Pd(I) and DPA++. d UV-Vis spectrum of Pd(0) complex (4) calculated with ωB97X-D/SDD, 6-311 + G(d,p)//MN15/SDD, 6-31 G(d) in DMA (PCM). e Calculation of the first singlet excited state of 4. f MLCT after π → π* transition on complex 4 produces Pd(I) and DPA−. g Synthesis of DPAsphox. h UV-Vis spectra of DPAsphox in DMF. i Cyclic voltammogram and redox potential of DPAsphox. j 31P NMR studies of the mixture of Pd(0 or II) complex and DPAsphox. DPA 9,10-diphenylanthracene, SET single electron transfer, LMCT ligand-to-metal charge transfer, MLCT metal-to-ligand charge transfer, dppp 1,3-Bis(diphenylphosphino)propane, THF tetrahydrofuran, SCE saturated calomel electrode.
evaluated under blue-light irradiation (Table 2 and Fig. 4). Control experiments of the Heck reaction were performed with styrene (10a) and unactivated tertiary alkyl bromide (11a) (Table 2).23–26 The addition of 5 mol % of Pd(PPh₃)₄ and DPAsphox provided β-alkylated styrene (12a) in 79% yield under 5 W blue LED lights (entry 1). In situ generation of Pd(0) complex from 5 mol % of Pd(PPh₃)₂Cl₂, PPh₃, and DPAsphox improved the yield of 12a in 93% (entry 2). Under conditions without DPAsphox (entry 3) and with DPA instead of DPAsphox (entry 4), 12a was produced in low yield, indicating that DPAsphox plays an important role as a visible-light–activated ligand. Shang and Fu reported this kind of photo-induced Heck reaction, in which they achieved a high yield and broad substrate generality using Xantphos.25 The reaction required intense light, however, such as a 36 W blue LED light, because Xantphos does not absorb visible light. Thus, under our 5 W blue LED condition, the photo-reaction with Xantphos gave the product in 57% yield (entry 5).

Thus, we next carried out a UV-Vis spectroscopic and fluorescence quenching study using Pd(0) and DPAsphox to clarify the interaction between them (Fig. 4a). The absorption intensity of the mixture of Pd(PPh₃)₄ and DPAsphox was stronger (solid red line) than that of Pd(PPh₃)₄ alone (blue line) because of the π → π* transition of DPAsphox (dotted red line). The emission of DPAsphox (dotted red line) was clearly suppressed in the presence of Pd(PPh₃)₄ (solid red line), indicating that pseudo-intramolecular quenching occurred in the Pd(0)-DPAsphox complex. Additionally, tert-BuBr (11a) did not affect the absorption and emission spectra (Supplementary Figs. 37, 38), suggesting that no EDA complex formed between Pd(0) and 11a. Furthermore, the mixture of Pd(PPh₃)₄ and DPA (solid black line) showed almost no change in the absorption and emission spectra compared with DPA alone (dotted black line) (Fig. 4b) similar to the Pd(II) complex. Together, these results support the high efficiency of our visible-light–activated ligand.

The substrate scope of the photo-Heck reaction was investigated (Fig. 4c). The β-alkylated styrene 12a was also obtained in 94% yield with 1.0 mmol of styrene. The para-substituted styrenes were examined next, and styrenes with acetoxyl (90%), tert-butyl (91%), and fluoro groups (70%) afforded the corresponding alkylated styrenes (12b–d). The yield was decreased by electron-withdrawing groups at the para-position26, but the addition of triphenyl phosphite improved the yield (12e, f). This effect was also observed using Xantphos as a ligand (Supplementary Information, Section 1–15). 1,1-Diphenylethylene (10g) and a piperonal derivative (10h) were applicable to this photo-Heck reaction. Other tertiary alkyl bromides, such as 1-adamantyl and 2-methylbutyl bromides, gave the products in 84% (12i) and 94% (12j) yields. Secondary butyl (92%) and cyclic alkyl groups (88%-96%) were also introduced at the β-position of styrene (12k–n). In addition, primary alkyl bromides afforded the products with high E/Z selectivity (>20:1) (12o–q), and the radical clock experiment using (bromomethyl)cyclopropane yielded the ring-opened product 12r, indicating that this reaction involves a radical process.

We next applied this photo-ligand-Pd(0) system to a one-electron reduction of aryl bromide and chloride, examples for which are quite limited in Pd-catalyzed photoreactions.27 Cross-coupling of aryl halide and pyrroles was performed with PdCl₂(PPh₃)₂, PPh₃, and DPAsphox under blue-light irradiation (Fig. 5a). Biarene 15a was obtained from 2-chlorobenzonitrile and N-methyl pyrrole in 80% (from 0.2 mmol of 13a) and 81% yield from 1.0 mmol of 13a). 15a was also obtained from 2-bromobenzonitrile in 84% yield. Biaryl compounds (15b–e) were also afforded by 4-chlorobenzonitrile (74%), 2-chloro-5-trifluoromethyl benzonitrile (72%), methyl 4-chlorobenzoate (43%), and methyl 5-chlorothiophene-2-carboxylate (73%). This reaction was also applicable for coupling using aryl bromide; 3-bromo-4-fluorobenzaldehyde (74%) and 2-bromoanisole (32%) gave the corresponding products (15f, g). The substrate scope of radical acceptors was examined next, and various pyroles were applicable: N-H pyrrole (15h, 75%), 2,4-dimethyl pyrrole (15i, 83%), 3-ethyl-2,4-dimethyl pyrrole (15j, 86%), N-Ph-pyrrole (15k, 42%), and 1,3-dimethylindole (15l, 31%).

Dehalogenative hydrogenations of aryl chloride and bromide were demonstrated (Fig. 5b). The hydrogenation of 2-chlorobenzonitrile proceeded in 87% yield using N-methylpyrrolidone (NMP) as a solvent and a hydrogen donor (17a).28 9-Bromophenanthrene and methyl 2-bromobenzoate yielded the corresponding amines in 93% and 89% yields (17b, c). In addition, our reaction system selectively hydrogenated halide on amines in the presence of terminal olefin and benzyl ether in the substrates (17d, e).

Table 1 Establishment of the reaction condition.

| Entry | Ligand and additive | Yield (%)a of 9a |
|-------|---------------------|----------------|
| 1     | PPh₃ (5 mol %), DPAsphox (5 mol %) | 75 |
| 2b    | PPh₃ (5 mol %), DPAsphox (5 mol %) | 76 |
| 3c    | PPh₃ (5 mol %), DPAsphox (5 mol %) | n.d. |
| 4d    | PPh₃ (5 mol %), DPAsphox (5 mol %) | n.d. |
| 5     | PPh₃ (10 mol %)          | trace |
| 6     | DPEphos or Xantphos (5 mol %) | n.d. |
| 7     | PPh₃ (10 mol %), DPA (5 mol %) | 25 |

| Reaction mechanisms of Pd-catalyzed radical cross-couplings. Finally, the reaction mechanisms of α-alkylation of amines with Pd(II) (Fig. 3) and a photo-Heck reaction with Pd(0) (Fig. 4) are
considered and compared in Fig. 6. The process involving light is the ligand-centered excitation for both reactions, namely the $\pi \rightarrow \pi^*$ transition of the DPA moiety, but the subsequent quenching path differs between them: a one-electron reduction of Pd(II) (LMCT) and a one-electron oxidation of Pd(0) (MLCT).

In the allylation reaction, oxidative addition of allyl methyl carbonate $8$ to Pd(0) complex $A$ forms redox-active $\pi$-allyl Pd(II) complex $B$ at room temperature.$^{29}$ Although the direct reduction pathway of $8$ by excited Pd(0) complex $A$ cannot be excluded, the formation of $\pi$-allyl Pd(II) complex $B$ is plausible because no ligands other than DPAphox functioned (Table 1) and allyl alcohol was also applicable for this allylation reaction (Fig. 3c)$^{30}$. The eliminated methyl carbonate generates methoxide anions through decarboxylation and acts as a base. The highly efficient pseudo-intramolecular one-electron reduction (LMCT) from the $S_1$ state ($C$) generated the biradical state $D$; fluorescence quenching supported this process (Fig. 3b). The following one-electron oxidation of amine ($7$) by DPA afforded the corresponding $7^+$. Then, the free radical $[7^- H]$ generated from $7^+$ by deprotonation reacted with the allyl-Pd(I) complex ($E$) (path A) or free allyl radical (path B) to give the product $9$ and complex $A^{21}$.

On the other hand, in the reaction mechanisms of the Pd-catalyzed photo-Heck reaction, Pd(I) cation species ($H$) would be
### Table 2 Control experiments.

| Entry | Pd catalyst | Ligand and additive | Yield (%)<sup>a</sup> of 12a |
|-------|-------------|---------------------|-----------------------------|
| 1     | Pd(PPh<sub>3</sub>)<sub>4</sub> | DPAsphox (5 mol %) | 79                          |
| 2     | PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> | PPh<sub>3</sub> (5 mol %), DPAsphox (5 mol %) | 93                          |
| 3     | PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> | PPh<sub>3</sub> (5 mol %) | 19                          |
| 4     | PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> | PPh<sub>3</sub> (5 mol %), DPA (5 mol %) | 31                          |
| 5     | PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> | Xantphos (5 mol %) | 57                          |

<sup>a</sup>Isolated yields were shown. DMA N,N-dimethylacetamide, DPA 9,10-diphenylanthracene, Xantphos 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthenec.

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**Fig. 4 Pd-catalyzed Heck reaction of unactivated alkyl bromide.**

- **a** UV-Vis analysis with DPAsphox in DMA (0.05 mM).
- **b** UV-Vis analysis with DPA in DMA (0.05 mM).
- **c** Substrate scope. **1.**0 mmol scale. **2**. Yield determined by <sup>1</sup>H NMR analysis. **3**. <sup>3</sup>F(OPh)<sub>3</sub> (5 mol %) was added. DMA N,N-dimethylacetamide, DPA 9,10-diphenylanthracene.

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**R = H (12a)** 93% (94%<sup>a</sup>)

**OAc (12b)** 90%

**tert-Bu (12c)** 91%

**F (12d)** 70%

**CHO (12e)** 15%<sup>b</sup> (64%)<sup>c</sup>

**CN (12f)** 67%

**12g 96%**

**12h 56%**

**12i 84%**

**12j 94%**

**12k 92%**

**12l 95%**

**12m 88%**

**12n 96%**

**12o 78%**

**12p 76%**

**12q 54%**

**12r 29%<sup>b</sup>**

(from Br) 11r
generated as the $S_1$ state by pseudo-intramolecular one-electron oxidation of Pd(0) from an excited DPA moiety via an $S_0 \rightarrow S_2 \rightarrow S_1$ transition. Although the $S_0 \rightarrow S_1$ transition directly produces cationic Pd(I) (H), the oscillator strength of the transition was 32 times smaller than that of the $S_0 \rightarrow S_2$ transition (Fig. 2d), indicating that the $S_0 \rightarrow S_2 \rightarrow S_1$ transition would be the primary excitation mechanism of this complex. Because the DPA$^-$ moiety of H has a high reduction potential, alkyl bromide 11 ($E_{1/2}$ [11/11$^{-}$] = −2.1 to −2.4 V) is readily reduced to give alkyl radical and Pd(I) complex I. After the addition of alkyl radical to styrene 10 (I $\rightarrow$ J) and the following bromo atom transfer from Pd(I) to the benzyl radical (J $\rightarrow$ K), Pd(0) complex F is regenerated, and β-alkylated styrene 12 is provided by elimination of HBr, which is supported by the KIE experiment (Supplementary Information, Section 1–15$^{25,26}$).

**Discussion**

A visible-light–activated secondary phosphine oxide ligand was developed for Pd-catalyzed radical cross-couplings. The ligand-centered $\pi \rightarrow \pi^*$ transition of DPAsphox promoted allyl radical-mediated cross-coupling via LMCT in the allyl Pd(II) complex, and alkyl and aryl radical-mediated cross-couplings via MLCT in the Pd(0) complex. The efficient SET was observed by spectroscopic studies as a strong quenching of the fluorescence emission of DPAsphox. This was achieved by the visible-light–sensitizing moiety (DPA) in the secondary phosphate oxide ligand. Our strategy for designing a visible-light–activated ligand and metal complexes showed potential for tuning the electronic state of transition metals under visible-light irradiation. Further development of ligands to orient transition-metal-catalyzed photocouplings is expected.

**Methods**

**General information.** NMR spectra were recorded on JEOL-JMN-ECS 400 or ECZ 400 spectrometers. Data for NMR are reported as follows: chemical shift ($\delta$, ppm), multiplicity (s singlet, br-s broad singlet, d doublet, t triplet, q quartet, and m multiplet), coupling constants (Hz), and integration. Chemical shifts are reported in the scale relative to TMS (0.0 ppm) for $^1$H NMR and the solvent signal (CHCl$_3$ (77.0 ppm)) for $^{13}$C NMR. $^{19}$F and $^{31}$P NMR spectra are referenced to external hexafluorobenzene and 85% phosphoric acid. Infrared (IR) spectra were recorded on a Fourier transform infrared spectrophotometer equipped with ATR. High-resolution mass spectra were measured on a JMS-T100LP instrument (ionization method: ESI). Melting points were measured with a SIBATA NEL-270 melting point apparatus. The absorption and emission spectra generated as the $S_0$ state by pseudo-intramolecular one-electron oxidation of Pd(0) from an excited DPA moiety via an $S_0 \rightarrow S_2 \rightarrow S_1$ transition. Although the $S_0 \rightarrow S_1$ transition directly produces cationic Pd(I) (H), the oscillator strength of the transition was 32 times smaller than that of the $S_0 \rightarrow S_2$ transition (Fig. 2d), indicating that the $S_0 \rightarrow S_2 \rightarrow S_1$ transition would be the primary excitation mechanism of this complex. Because the DPA$^-$ moiety of H has a high reduction potential, alkyl bromide 11 ($E_{1/2}$ [11/11$^{-}$] = −2.1 to −2.4 V) is readily reduced to give alkyl radical and Pd(I) complex I. After the addition of alkyl radical to styrene 10 (I $\rightarrow$ J) and the following bromo atom transfer from Pd(I) to the benzyl radical (J $\rightarrow$ K), Pd(0) complex F is regenerated, and β-alkylated styrene 12 is provided by elimination of HBr, which is supported by the KIE experiment (Supplementary Information, Section 1–15$^{25,26}$).

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were measured by a JASCO V-730 spectrophotometer and FP-8500 spectrofluorometer. Column chromatographic purification was performed with silica gel 60 N (spherical, neutral 40-50 μm), and preparative TLC purification was performed with TLC silica gel 60 F254. The Pd-catalyzed reactions were carried out with standard Schlenk techniques under Ar atmosphere. Unless otherwise noted, photochemical reactions were performed with degassed solvents by freeze-pump-thaw cycles three times.

**Computational methods.** All calculations were performed with the Gaussian 16 program. Structure optimizations were carried out at 298.15 K, using the MN15 functional with an ultrafine grid and the SDD (for Pd) and 6-31 G(d) (for the other atoms) basis sets. DMF (for Pd(II) complex) and N,N-dimethylacetamide (DMA) (for Pd(0) complex) were used as implicit solvents using PCM as a solvation model. Harmonic vibrational frequencies were computed at the same level of theory to confirm that no imaginary vibration was observed for the optimized structure. Single-point energy calculations were performed for all geometries at 298.15 K, using the ωB97X-D functional with an ultrafine grid and the SDD (for Pd) and 6-311+G(d,p) (for the other atoms) basis sets with the same solvation model. The Gibbs free energy was calculated by the sum of total electronic energy in the single-point energy calculation and the thermal correction energy in the frequency calculation. All molecular orbitals were computed at an isovalue of 0.02.

**Procedure for the synthesis of DPAsphox (1).** A 100 mL Schlenk tube containing a magnetic stirring bar was charged with 2-bromo-9,10-diphenylanthracene 5 (1.23 g, 3.0 mmol, 1.0 equiv.), anilinium hypophosphite (716 mg, 4.5 mmol, 1.5 equiv.), (3-aminopropyl)triethoxysilane (1.06 mL, 4.5 mmol, 1.5 equiv.), Pd(OAc)2 (20.2 mg, 0.090 mmol, 3.0 mol %), dppp (40.8 mg, 0.099 mmol, 3.3 mol %), and MeCN (18.0 mL, 0.17 M), and purged with argon. After stirring for 20 h at 90 °C, the reaction mixture was evaporated and EtOAc (20 mL) was added. The organic layer was washed with water (3.0 mL), 1 N HCl aq. (3.0 mL), sat. NaHCO3 aq. (3.0 mL), and brine (3.0 mL), dried over Na2SO4, and concentrated. The crude product was purified by column chromatography on silica gel (eluting with EtOAc/hexane and gradients of MeOH in EtOAc) and preparative TLC (eluting with hexane/ethyl acetate).

**Fig. 6 Proposed reaction mechanisms of Pd-catalyzed radical cross-couplings.** a Pd-catalyzed α-allylation of amines. b Pd-catalyzed photo-Heck reaction. DPA 9,10-diphenylanthracene, LMCT ligand-to-metal charge transfer, SET single electron transfer, MLCT metal-to-ligand charge transfer.
product was purified by flash column chromatography (n-hexane/EtOAc 2/1 to 1/1) to afford ethyl phosphonate 6 (998.2 mg, 2.36 mmol) in 79% yield as yellow amorphous. Next, an oven-dried 100 mL Schlenk tube containing a magnetic stirring bar was charged with 6 (998.2 mg, 2.36 mmol, 1.0 equiv.) and THF (11.8 mL, 0.20 M) under argon. To the solution cooling at −78 °C, 1 M PhMgBr in THF (7.1 mL, 3.0 equiv.) was added dropwise. After stirring for 2.5 h at the same temperature, the reaction was quenched with 6 N HCl aq. (5.9 mL, 0.40 M), and stirred for 1 h at room temperature. Then, the organic layer was washed with EtOAc (10 mL × 3), washed with brine (3 mL), dried over Na2SO4, and concentrated. The crude product was purified by flash chromatography (n-hexane/EtOAc = 1/1 to 1/4) to afford crude product 7 (290.9 mg, 2.03 mmol) in 86% yield as yellow amorphous.

**General procedure for α-allylation of amines.** A 20 mL Schlenk tube containing a magnetic stirring bar was charged with amine 7 (0.20 mmol, 1.0 equiv.), [PdCl(allyl)]2 (1.8 mg, 2.5 mol %), P(Ph)3 (4.5 mg, 5.0 mol %), allyl methyl carbonate (4.5 mg, 2.5 mol %), and DMA (1.0 mL, 0.20 M). After the reaction mixture was degassed by freeze-pump-thaw cycles three times, it was stirred with 5 W blue LED lights. Then, water (3.0 mL) was added to the reaction, and the aqueous layer was extracted with EtOAc (3.0 mL × 3). The combined organic layer was washed with water (3.0 mL × 3) and brine (3.0 mL), dried over Na2SO4, and concentrated. The crude product was purified by flash column chromatography (n-hexane/EtOAc = 1/1 to 1/4) to afford crude product 8 (290.9 mg, 2.03 mmol) in 86% yield as yellow amorphous.

**General procedure for Heck reaction of unactivated alkyl bromide.** A 20 mL Schlenk tube containing a magnetic stirring bar was charged with PdCl2(PPh3)2 (7.0 mg, 5.0 mol %), PPh3 (8.0 mg, 5.0 mol %), aryl halide (0.20 mmol, 1.0 equiv.), and solvent as specified. After the reaction mixture was degassed by freeze-pump-thaw cycles three times, it was stirred with 5 W blue LED lights. Then, water (3.0 mL) was added to the reaction, and the aqueous layer was extracted with EtOAc (3.0 mL × 3). The combined organic layer was washed with water (3.0 mL × 3) and brine (3.0 mL), dried over Na2SO4, and concentrated. The crude product was purified by flash column chromatography to afford the corresponding product 9.

**General procedure for Heck reaction of unactivated alkyl chloride.** A 20 mL Schlenk tube containing a magnetic stirring bar was charged with PdCl2(PPh3)2 (7.0 mg, 5.0 mol %), PPh3 (8.0 mg, 5.0 mol %), aryl halide (0.20 mmol, 1.0 equiv.), and solvent as specified. After the reaction mixture was degassed by freeze-pump-thaw cycles three times, it was stirred with 5 W blue LED lights. Then, water (3.0 mL) was added to the reaction, and the aqueous layer was extracted with EtOAc (3.0 mL × 3). The combined organic layer was washed with water (3.0 mL × 3) and brine (3.0 mL), dried over Na2SO4, and concentrated. The crude product was purified by flash column chromatography to afford the corresponding product 10.

**General procedure for biaryl synthesis.** A 20 mL Schlenk tube containing a magnetic stirring bar was charged with PdCl2(PPh3)2 (7.0 mg, 5.0 mol %), PPh3 (8.0 mg, 5.0 mol %), aryl halide 10 (0.20 mmol, 1.0 equiv.), pyrrole 14 (2.0 mmol, 1.0 equiv.), and DMA (1.0 mL, 0.20 M). After the reaction mixture was degassed by freeze-pump-thaw cycles three times, it was stirred at room temperature under irradiation with 5 W blue LED lights. Then, water (3.0 mL) was added to the reaction, and the aqueous layer was extracted with EtOAc (3.0 mL × 3). The combined organic layer was washed with water (3.0 mL × 3) and brine (3.0 mL), dried over Na2SO4, and concentrated. The crude product was purified by flash column chromatography to afford the corresponding product 11.

**General procedure for dehalogenative hydrogenation.** A 20 mL Schlenk tube containing a magnetic stirring bar was charged with PdCl2(PPh3)2 (7.0 mg, 5.0 mol %), PPh3 (8.0 mg, 5.0 mol %), PdCl2(PPh3)2 (7.0 mg, 5.0 mol %), PPh3 (8.0 mg, 5.0 mol %), [PtCl(allyl)]2 (1.8 mg, 2.5 mol %), P(Ph)3 (4.5 mg, 5.0 mol %), allyl methyl carbonate (4.5 mg, 5.0 mol %), and DMA (1.0 mL, 0.20 M). After the reaction mixture was degassed by freeze-pump-thaw cycles three times, it was stirred with 5 W blue LED lights. Then, water (3.0 mL) was added to the reaction, and the aqueous layer was extracted with EtOAc (3.0 mL × 3). The combined organic layer was washed with water (3.0 mL × 3) and brine (3.0 mL), dried over Na2SO4, and concentrated. The crude product was purified by flash column chromatography to afford the corresponding product 12.

**Data availability** All data generated in this study are provided in the Supplementary Information.

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Author contributions
T.K. and M.N. conceived, designed, and performed calculations. T.K. carried out the synthetic experiments. M.N. and T.N. guided this project. All authors discussed and co-wrote the manuscript.

Competing interests
The authors declare no competing interests.

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