

Deazaflavin-Catalyzed Arylation of White Phosphorus with Aryl Bromides and Chlorides

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Abstract: A substantial improvement in the challenging photocatalytic arylation of white phosphorus (P_4) with aryl chlorides and bromides is reported. Using the readily accessible deazaflavin-based photocatalyst *o*-Me-dFl, valuable triarylphosphines (PAR_3) and tetraarylphosphonium salts ($[PAR_4]X$, $X = Br, Cl$) are synthesized from P_4 under near UV-LED (365 nm) irradiation in up to 87% combined yield with drastically reduced reaction times compared to previous protocols. ^{31}P nuclear magnetic resonance spectroscopic monitoring studies and density functional theory calculations provide insights into the reaction pathway. The results represent an important step toward more atom-efficient and economical photocatalytic P_4 functionalization reactions.

Keywords: 5-aryldeazaflavin, organophosphorus compounds, photocatalysis, tetraarylphosphonium salts, triarylphosphines, white phosphorus

1. Introduction

Organophosphorus compounds (OPCs) such as triarylphosphines (PAR_3) and tetraarylphosphonium salts ($[PAR_4]X$) offer significant commercial value and academic interest.^[1] Their applications range from simple synthetic reagents to specialized ligands for industrial-scale metal-catalyzed transformations.^[2] However, their current industrial synthesis relies on a wasteful and inefficient multistep procedure. This process involves first the oxidation of white phosphorus (P_4) with chlorine gas and second the conversion of the intermediary chlorophosphines into the desired monophosphorus species.^[3] Thus, developing direct methods for transforming P_4 into OPCs and other phosphorus-based compounds—while avoiding chlorinated intermediates—is a highly desirable, yet challenging objective.^[4] Major breakthroughs have been achieved in recent years involving electrochemical,^[5] transition-metal mediated,^[6] main-group

synthetic,^[7] and other approaches.^[8] Building on the pioneering studies by Barton et al. demonstrating the ability of P_4 to trap carbon-centered radicals,^[9] photochemical and photocatalytic methods have been developed that convert P_4 into OPCs, such as di- and trialkylphosphine(oxide)s, benzylphosphines, and phosphoryltriacetates (**Figure 1a**).^[10]

We have been interested in the arylation of P_4 to yield tertiary arylphosphines and quaternary arylphosphonium salts (**Figure 1b**).^[11] By employing the photocatalyst $[Ir(ppy)_2(dtbbpy)]PF_6$, we successfully generated PAR_3 and $[PAR_4]I$ with aryl iodides as substrates in a single step (**Figure 1c**). Due to the limited commercial availability and high cost of both the aryl iodides and the iridium-based photocatalyst, we sought to extend our protocol to more abundant and cost-effective aryl bromides and chlorides in combination with organic photocatalysts. Recently, we reported the photocatalytic

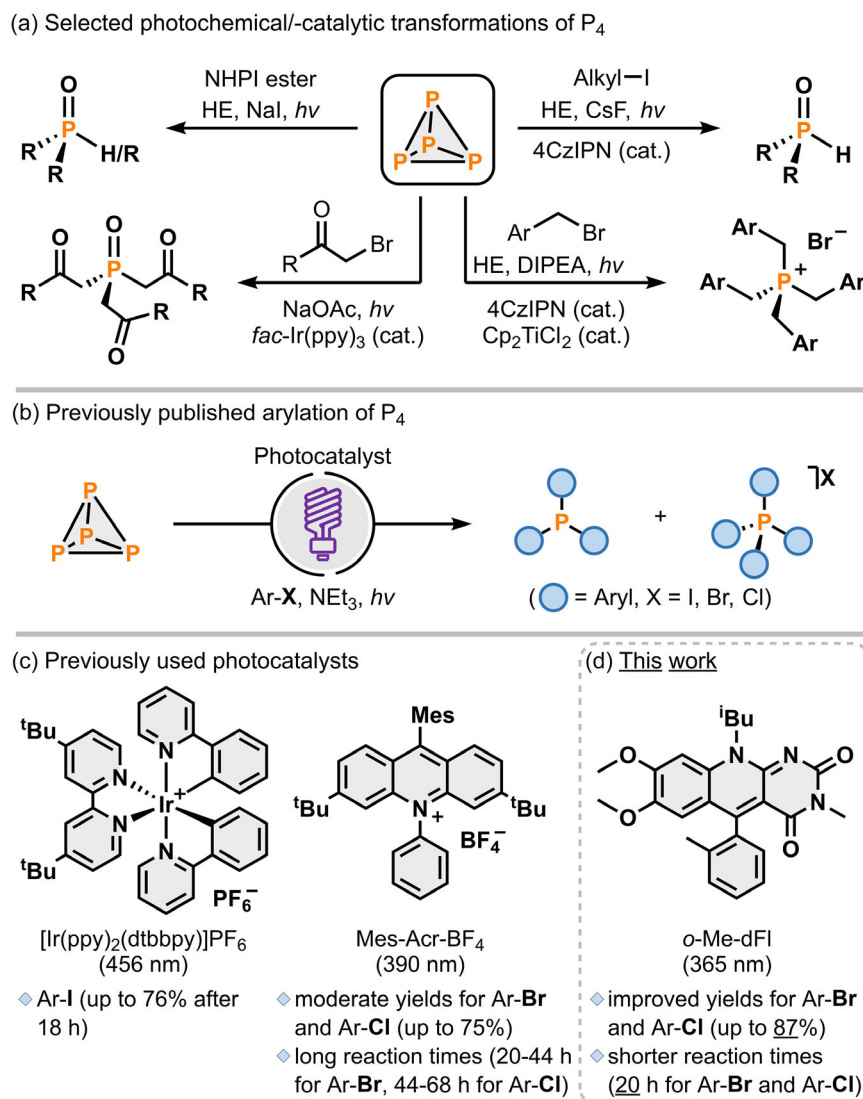


Figure 1. a) Selected examples for the photochemical or photocatalytic transformation of P_4 into relevant OPCs; HE = Hantzsch ester; b) General reaction scheme for the photocatalytic arylation of P_4 ; c) Previously used photo-catalysts in the photocatalytic arylation of P_4 with yields of $PAR_3/[PAR_4]X$; d) Photocatalyst presented in this work.

functionalization of P_4 into PAR_3 and $[PAR_4]X$ ($X = Br, Cl$) using the photocatalyst Mes-Acr- BF_4 (Figure 1c).^[12] This method is based on a consecutive photoinduced electron-transfer (conPET)^[13] strategy which facilitates the direct activation of otherwise resistant carbon–halogen bonds, allowing for the stepwise arylation of P_4 . This methodology afforded many desired products in moderate to good yields, but suffered from extraordinary long reaction times, especially for aryl chlorides (44–68 h).

Recently, 5-aryldeazaflavins (dFl) have been successfully used for the reductive photodehalogenation of electron-rich aryl bromides and chlorides.^[14] This class of compounds is structurally related to flavins, well-known photocatalysts frequently used for oxidative transformations.^[15] The remarkable reducing power of 5-aryldeazaflavins arises from a conPET mechanism, involving the presence of deazaflavin semiquinone

radicals.^[14] These radicals exhibit extreme reduction potentials after initial photoexcitation, enabling them to reduce electron-rich aryl halides with $E_{red} < -3$ V. Based on these considerations, we have screened a series of 5-aryldeazaflavin catalysts, which can be easily accessed through a three-component condensation of commercially available *N*-substituted anilines, aromatic aldehydes, and *N*-methylbarbituric acid (Figure 2). The preparation of these compounds has been previously described in literature (see SI for synthetic details).^[14b]

2. Results and Discussion

Among the tested catalysts, *o*-Me-dFl was most promising (Figure 1d). After optimization, we obtained $[P(C_6H_4-p-OMe)_4]Br$ and $P(C_6H_4-p-OMe)_3$ in 64%

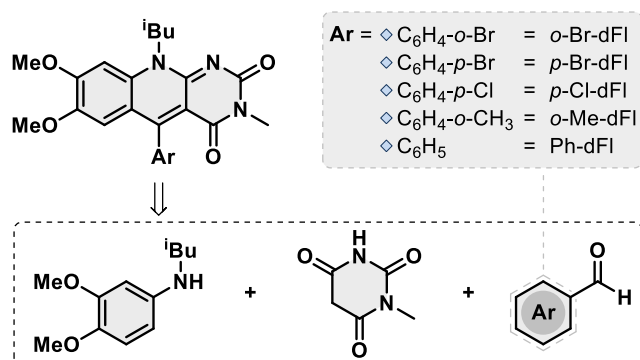


Figure 2. General structure and synthetic building blocks of 5-aryldeazaflavin photocatalysts.

and 8% nuclear magnetic resonance (NMR) spectroscopic yield, respectively, using P₄, *o*-Me-dFI (15 mol%), 4-bromoanisole, *N,N*-diisopropylethylamine (DIPEA), Cs₂CO₃, and near-UV LED (365 nm, 10 W) irradiation in a MeCN/benzene solvent mixture for 20 h.

Control experiments demonstrated that the photocatalyst, the sacrificial electron donor DIPEA, and LED light are needed to obtain the desired products (Table S1, Supporting Information). Cs₂CO₃ enhances the photo-physical properties of the deazaflavin semiquinone, which is formed within the photocatalytic cycle (*vide infra*).^[14a] A strong increase in product formation was achieved by using *n*-hexane as an additional solvent (Table S1, Supporting Information). This amplifying effect of the ternary solvent mixture (MeCN/*n*-hexane/benzene) is substrate-dependent (e.g., 8% higher yield with 4-bromoanisole vs. 22% higher yield with bromobenzene). We reason that the addition of *n*-hexane affects the solubility of certain reactants, leading to an overall positive effect on the reaction outcome.

The scope of the photocatalytic arylation of P₄ using *o*-Me-dFI was investigated with various aryl bromides and chlorides as substrates (**Figure 3**). These studies demonstrated that aryl halides with electron-donating or neutral substituents (e.g., -H, -OMe, or -Me) led

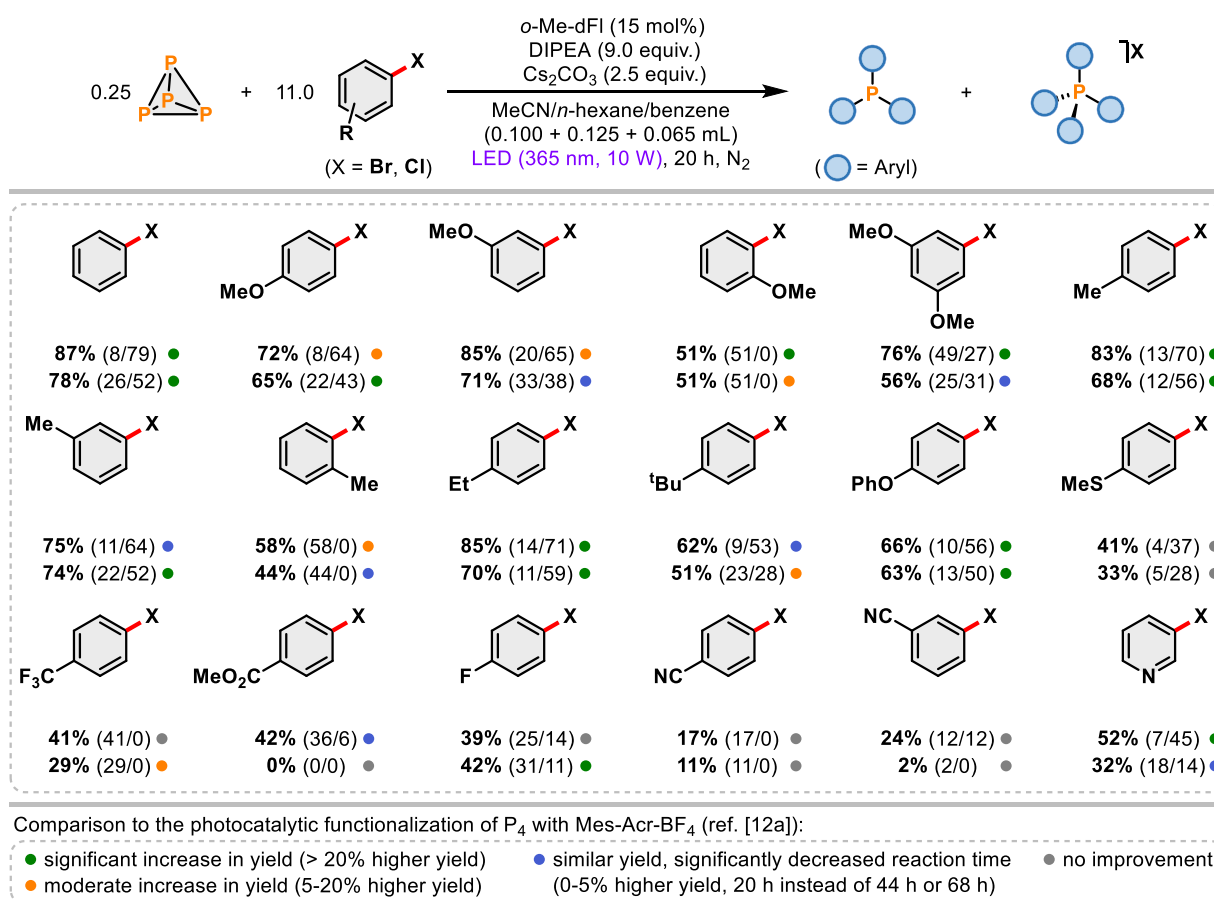


Figure 3. Substrate scope for the photocatalytic arylation of white phosphorus into triarylphosphines (PAR₃) and tetraarylphosphonium salts ([PAR₄]X, X = Br, Cl) with aryl bromides and chlorides. Standard conditions: P₄ (0.01 mmol), aryl halide (0.44 mmol), DIPEA (0.36 mmol), Cs₂CO₃ (0.10 mmol), *o*-Me-dFI (15 mol% based on a P-atom), MeCN (0.100 mL), *n*-hexane (0.125 mL), and C₆H₆ (0.065 mL). The samples were prepared under inert N₂-atmosphere and irradiated with near-UV LEDs (365 nm, 10 W) for 20 h. Yields (PAR₃/[PAR₄]X) were determined by quantitative ³¹P{¹H} NMR spectroscopy using triphenylphosphine oxide (PPh₃O, 0.02 mmol) as the internal standard.

to very good combined yields of PAr_3 and $[\text{PAr}_4]\text{X}$. The tetraarylphosphonium salts were usually the major product for aryl halides bearing substituents in the *meta*- or *para*-position. Triarylphosphines were formed as “by-products” except for the reactions with *ortho*-substituted aryl halides, where they were generated exclusively. This is probably due to the sterically hindered arylation of the tertiary phosphine PAr_3 . In contrast, aryl halides bearing electron-withdrawing substituents (e.g., $-\text{CF}_3$ or $-\text{CN}$) generally gave the desired products only in poor yields.

Similar reactivity trends were also observed in some of our preceding investigations on the photocatalytic or photochemical arylation of white phosphorus.^[11d,12a] However, the yields of the desired products were substantially improved with *o*-Me-dFI up to 87% combined spectroscopic yield of $\text{PAr}_3/[\text{PAr}_4]\text{X}$ starting from aryl bromides and 78% starting from aryl chlorides (see the color code in Figure 3). Furthermore, the irradiation times could be drastically reduced to 20 h for all substrates (from 20–44 h with Ar–Br and 44–68 h with Ar–Cl).^[12a] To illustrate the synthetic utility of this method, we have isolated tetrakis(4-methoxyphenyl) phosphonium chloride (40% yield, representative of *para*-substituted aryl halides), tetrakis(3-methylphenyl) phosphonium chloride (51% yield, representative of *meta*-substituted aryl halides), and tris(2-methoxyphenyl)phosphine (45% yield, representative of *ortho*-substituted aryl halides). We have also evaluated alkyl and silyl substrates, such as benzyl, cyclohexyl, trimethylsilyl, and octyl halides (Table S13, Supporting Information). ^{31}P NMR spectroscopic data indicate the formation of triorganophosphines for benzyl bromide, benzyl chloride, and 2-phenylethyl chloride, but only in small amounts (up to 16% yield).

Other phosphorus-atom sources instead of P_4 could successfully engage in the reaction as well (Table S14, Supporting Information). The PH_3 -surrogates NaPH_2 and $\text{K}[\text{P}(\text{SiMe}_3)_2]$ gave the $\text{PAr}_3/[\text{PAr}_4]\text{X}$ mixtures in 50% and 64% combined spectroscopic yield, respectively. The arylation of H_2PPh and HPPH_2 with bromobenzene mainly produced PPh_3 . In contrast, the diphosphine P_2Ph_4 gave $[\text{PPh}_4]\text{Br}$ in a 47% yield, accompanied by 28% PPh_3 . In all reactions a loss of P-atom intensity was observed according to $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, indicating product decomposition. For example, only 43% PPh_3 remained after 20 h when we attempted the arylation of PPh_3 with bromobenzene, while $[\text{PPh}_4]\text{Br}$ was not detected.

The unselective arylation of these primary and secondary phosphines prompted us to investigate the stability of the triarylphosphines and tetraarylphosphonium salts under photocatalytic conditions by quantitative $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Section S7, Supporting Information). A first test reaction showed that PPh_3 is formed in 66% yield when a MeCN solution containing $[\text{PPh}_4]\text{I}$, *o*-Me-dFI, DIPEA, and Cs_2CO_3 is irradiated

with near-UV light for 20 h (Figure 4a, left chart). Furthermore, a $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring study (0–20 h irradiation time) revealed that $[\text{PPh}_4]\text{I}$ is already completely degraded after 6 h reaction time. Simultaneously, the formation of PPh_3 can be observed, which reaches its maximum after 6 h. Further irradiation leads to some decomposition of PPh_3 into undetected compounds, presumably oligo- and polyphosphorus species. Overall, a total loss of $\approx 30\%$ of the initial P-atom intensity was detected after 20 h. Similar observations were made with the tetraanisylphosphonium salt $[\text{P}(\text{C}_6\text{H}_4\text{-}i\text{-OMe})_4]\text{I}$ (Figure 4a, middle chart). The starting material is almost entirely degraded after 6 h, while the formation of the corresponding phosphine can be observed. Compared to $[\text{PPh}_4]\text{I}$, the degradation process is slightly slower, and a total loss of $\approx 20\%$ of the initial P-atom intensity was observed.

In contrast, a phosphonium salt with electron-withdrawing arene substituents, such as $[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CF}_3)_4]\text{I}$, was significantly less stable under the reaction conditions (Figure 4a, right chart). Irradiation for 1 h resulted in a degradation of $\approx 90\%$ $[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CF}_3)_4]\text{I}$ and after 20 h irradiation time, a total loss of around 65% of the initial P-atom intensity was detected.

Similarly, triarylphosphines also showed limited stability (Figure 4b). In the case of PPh_3 and $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})_3$, $\approx 80\%$ of the starting material remained intact, while only around 40% of $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CF}_3)_3$ could be detected after 20 h of irradiation. Trace amounts of diarylphosphines could also be detected during the reaction.

Based on these experimental results, two trends can be identified: First, an electron-withdrawing group attached to the arene unit drastically decreases the stability of the corresponding phosphorus compound under the applied photocatalytic conditions. Second, triarylphosphines are less prone to decomposition than the corresponding tetraarylphosphonium salts. Thus, we concluded that the decreased stability of PAr_3 and $[\text{PAr}_4]^+$ bearing electron-deficient arene groups could account for the lower yields obtained in the photocatalytic arylation reactions (Figure 3). The fact that $[\text{PAr}_4]^+$ decomposes faster than PAr_3 plausibly rationalizes why the phosphonium salts are never formed as exclusive products, but always as mixtures with the corresponding phosphine.

To elucidate possible reasons for the observed experimental trends, we have performed density functional theory (DFT) calculations on the stability of the investigated species (PBE-D3BJ/def2-TZVP level of theory, Section S8, Supporting Information). In a first approach, we sought to explain the variations in stability by differences in the bond dissociation energy of the corresponding $\text{P}-\text{C}_{\text{Ar}}$ bond. For the homolytic bond cleavage of $[\text{PAr}_4]^+$ into $[\text{PAr}_3]^{++}$ and the corresponding aryl radical, DFT calculations revealed dissociation energies of 82.6, 82.2, and 79.1 kcal mol^{-1} for the aryl moiety being phenyl, anisyl, and trifluoromethylphenyl, respectively.

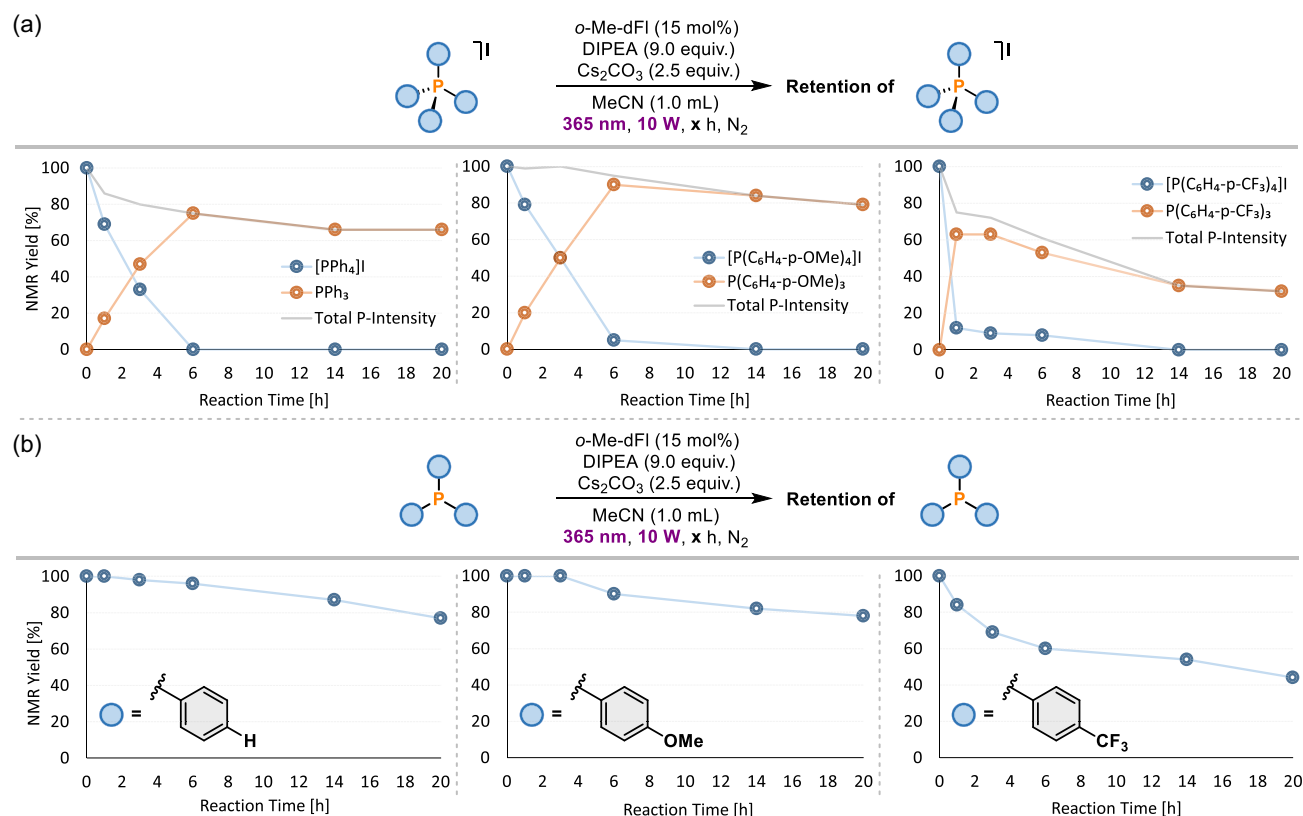


Figure 4. Stability of selected a) tetraarylphosphonium salts and b) triarylphosphines under photocatalytic conditions. Standard conditions: [PAr₄]⁺I⁻ or PAr₃ (0.04 mmol), DIPEA (0.36 mmol), Cs₂CO₃ (0.10 mmol), *o*-Me-dFl (15 mol%), MeCN (1.0 mL). The samples were prepared under inert N₂-atmosphere and irradiated with near-UV LEDs (365 nm, 10 W) for the given time (0–20 h). Yields were determined by quantitative ³¹P{¹H} NMR spectroscopy using triphenylphosphine oxide (PPh₃O, 0.02 mmol) as the internal standard.

To model the likely reaction pathway, we have calculated the bond dissociation energies starting from a hypothetical [PAr₄]⁺, which will be generated via reduction within the reductive photoredox quenching cycle.

The DFT calculations for the homolysis of [PAr₄]⁺ into PAr₃ and Ar[•] revealed surmountable reaction energies of 10.6, 11.0, and 13.3 kcal mol⁻¹ for phenyl, anisyl, and trifluoromethylphenyl substituents, respectively,

indicating that homolysis can occur at ambient temperature. The facile decomposition of the phosphonium salts can be explained by the calculated reduction potentials (obtained in the gas phase and referenced to the ferrocene/ferrocenium redox couple). Thereby, the weakest reduction potential was found for [P(C₆H₄-*p*-CF₃)₄]⁺ (*E*_{red} = −1.63 V), then [PPh₄]⁺ (*E*_{red} = −2.67 V), and finally [P(C₆H₄-*p*-OMe)₄]⁺ (*E*_{red} = −3.18 V) (Figure 5).

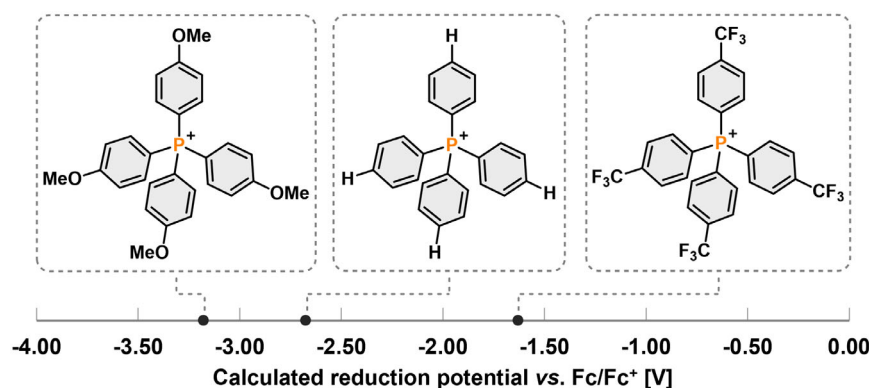


Figure 5. Calculated reduction potentials for selected tetraarylphosphonium salts (Ar = phenyl, anisyl, or trifluoromethylphenyl). Reduction potentials were referenced against ferrocene/ferrocenium.

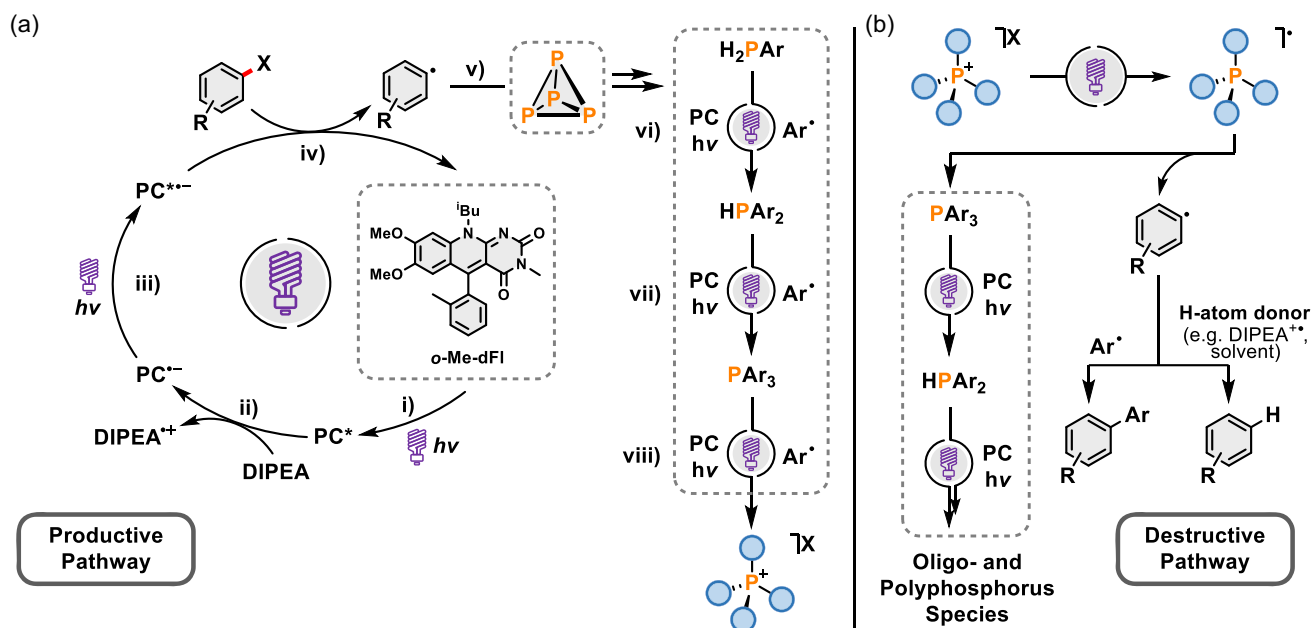


Figure 6. a) Proposed simplified mechanism for the photocatalytic arylation of P_4 with *o*-Me-dFl using aryl bromides and chlorides to generate tetraaryldiphosphonium salts (= productive pathway). For simplification, excited spin states and intersystem crossing processes involving 5-aryldeazaflavin semiquinone species are not displayed. b) Proposed pathway for the degradation of tetraaryldiphosphonium salts under photocatalytic conditions (= destructive pathway); possible H-atom donors are $DIPEA^{•+}$ or the solvent.

Thus, the reduction of $[P(C_6H_4-p-CF_3)_4]^+$ is expected to proceed the easiest, followed by $[PPh_4]^+$ and $[P(C_6H_4-p-OMe)_4]^+$. Subsequent P–C_{Ar} bond homolysis then leads to the degradation of the corresponding phosphonium salts. Based on these results and our previous studies using the acridinium catalyst Mes-Acr-BF₄, we propose the following mechanism for the arylation of white phosphorus (“productive pathway”, Figure 6a).

The first step involves the excitation of *o*-Me-dFl (step i), followed by the reduction with DIPEA (step ii), and a consecutive photoexcitation of the photocatalyst to give the excited radical anion ($PC^{•-}$ = photoexcited 5-aryldeazaflavin semiquinone, step iii). Next, aryl radicals are generated via single electron transfer from $PC^{•-}$ to the substrates (step iv). In analogy to our previous investigations,^[11,12a] the stepwise arylation of P_4 and all P_4 -derived intermediates (e.g., H_2PAr , $HPAr_2$) leads to PAR_3 and $[PAr_4]^+$ as final products (steps v–viii). Simultaneously, product decomposition starts (“destructive pathway”, Figure 6b). Besides aryl halides, reduction of the tetraaryldiphosphonium salts and triaryldiphosphines produced by the arylation of P_4 can occur and subsequent homolytic bond cleavage thereby leading to the degradation into undetectable oligo- and polyphosphorus species. Within our stability study, the formation of the corresponding arenes has been confirmed by gas chromatography-mass spectrometry (GC-MS) analysis (Section S7.4, Supporting Information).

3. Conclusion

In conclusion, we have improved our previous protocol for the arylation of P_4 with aryl bromides and chlorides by increasing the product yields for many substrates and simultaneously reducing the reaction times. PAR_3 and $[PAr_4]X$ ($X = Br, Cl$) have been obtained in up to 87% combined yield after 20 h. Using experimental and computational methods, our work provides valuable insights into the mechanistic details of the reaction and highlights the crucial importance of product stability in photocatalytic systems. The differences in the product formation for electron-donating and electron-withdrawing aryl halides and the product ratio (PAR_3 vs $[PAr_4]X$) are explained by the propensity of the products for P–C_{Aryl} bond cleavage under the strongly reducing conditions, limiting the selectivity. Strategies to increase the selectivity and further expand the substrate scope are currently under investigation in our laboratories.

4. Experimental Section

General Procedure for the Photocatalytic Arylation of P_4 : To a 10 mL stoppered tube equipped with a stirring bar were added the appropriate aryl bromide or aryl chloride (0.44 mmol, 11.0 equiv.), *N,N*-diisopropylethylamine (DIPEA, 62.7 μ L, 0.36 mmol, 9.0 equiv.), Cs₂CO₃ (0.10 mmol, 32.6 mg, 2.5 equiv.), *o*-Me-dFl (2.6 mg, 6.0 μ mol, 15 mol%), and P_4 (1.2 mg, 0.01 mmol P_4 = 0.04 mmol P-atom, 0.25 equiv., as a stock solution in 65 μ L benzene). The mixture was dissolved in acetonitrile

(0.100 mL) and *n*-hexane (0.125 mL). The tube was sealed under an inert N₂-atmosphere, placed in a water-cooled block to ensure a near-ambient temperature, and irradiated with UV light (365 nm, 10 W, 700 mA) for 20 h, unless stated otherwise. Ph₃PO (0.02 mmol, stock solution in benzene) was subsequently added as an internal standard. The resulting mixture was subjected to ³¹P{¹H} NMR analysis.

Single Crystal X-Ray Diffraction Data: Deposition number CCDC 2441682 (for [P(C₆H₄-*p*-CF₃)₄]⁺)] contains the supplementary crystallographic data for this article. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structure Service (<https://www.ccdc.cam.ac.uk/structures/>).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data supporting the findings of this study is available in the main text or the Supplementary Material. Primary research data for this study is openly accessible on Radar4Chem (<https://radar4chem.radar-service.eu/radar/de/home>) under the DOI 10.22000/dm18t7at8zhdw0ag.

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