

PAPER

View Article Online
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Cite this: DOI: 10.1039/d5dt01495f

FLP-type alkenylation of a phosphafluorene

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Received 25th June 2025,
Accepted 27th August 2025

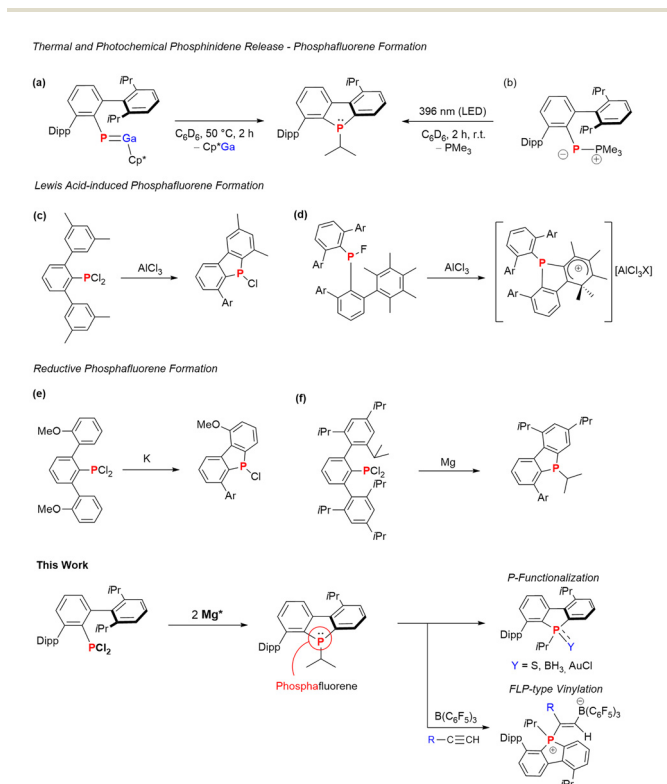
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Phosphafluorenes, in which the chemically vulnerable C-9 position of the fluorene core has been replaced with phosphorus, demonstrate enhanced stability compared to conventional fluorene-based materials and belong to the general class of dibenzophospholes (DBPs). Phosphafluorene formation is commonly observed in the reductive functionalization of terphenyl-based dihalophosphanes. Here, we outline a high-yielding route towards phosphafluorene **1**, starting from readily available ^{Dipp}TerPCL₂ (^{Dipp}Ter = 2,6-Dipp-C₆H₃; Dipp = 2,6-iPr₂-C₆H₃). Different functionalization strategies of **1** are outlined, including a complex with AuCl, its BH₃ adduct, and its corresponding sulphide. Interestingly, facile alkenylation of **1** was achieved in the presence of B(C₆F₅)₃ and various phenylacetylene derivatives. This FLP-type alkenylation is *E*-selective giving zwitterionic phosphonium borates.

Introduction

Phosphanylidene phosphoranes of the general form RP(PR')₃ are also referred to as phosphawittig reagents.¹ Specifically, aryl-substituted variants are commonly used in phosphalkene synthesis in the so-called phosphawittig reaction. The first aryl-substituted phosphanylidene phosphoranes, ArP(PMe₃), were synthesized by Protasiewicz and co-workers in 1998 through the combination of Ar-PCl₂ with an excess of PMe₃ and zinc powder.² To date a limited number of ArP(PMe₃) (Ar = 2,4,6-*t*Bu₃-C₆H₂, Mes*,² 2,6-(2,6-Cl₂C₆H₃)₂-C₆H₃, ^{Cl}Ter;³ 2,6-(2,4,6-Me₃-C₆H₂)₂-C₆H₃, ^{Mes}Ter;^{2,4} 2,6-(2,4,6-iPr₃-C₆H₂)₂-C₆H₃, ^{Tipp}Ter;⁵ 2,6-(2,6-iPr₂-C₆H₃)₂-C₆H₃, ^{Dipp}Ter;⁶ 1,1,3,3,5,5,7,7-octaethyl-1,2,3,5,6,7-hexahydro-s-indacen-4-yl, EIND⁷) have been reported and their utility in Wittig-type reactions has been explored. Moreover, it was shown that phosphawittig reagents offer a pathway for the generation of arylphosphinidenes, Ar-P, under photochemical conditions. For example, when ^{Tipp}TerP(PMe₃) was irradiated at 365 nm the formation of a phosphafluorene was described, through insertion of the phosphinidene into one of the C_{Ar}-C_{iPr} bonds of the Tipp groups.⁵ Our group observed ^{Dipp}Ter-P generation and deactivation to give phosphafluorene **1** via the thermal decomposition of the isolated phosphagallene, ^{Dipp}TerPGaCp* at 50 °C for 2 h (Scheme 1a), or through the irradiation (396 nm) of



Scheme 1 (a) Thermal phosphinidene release from a phosphagallene, (b) photochemical PMe₃ release from ^{Dipp}TerP(PMe₃); (c and d) Lewis acid induced phosphafluorene formation in terphenyl-substituted halo-phosphanes; (e and f) reductive approaches towards phosphafluorenes from dichlorophosphanes (e and f); and summary of this work.

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In this contribution, we report on different functionalization products of phosphafluorene **1** using BH_3 , S_8 or AuCl . Moreover, the reactivity of **1** towards terminal alkynes (4-R- $\text{C}_6\text{H}_4\text{-C}\equiv\text{C-H}$) in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ was investigated, proving an FLP-type alkenylation strategy for DBPs (Scheme 1, bottom).

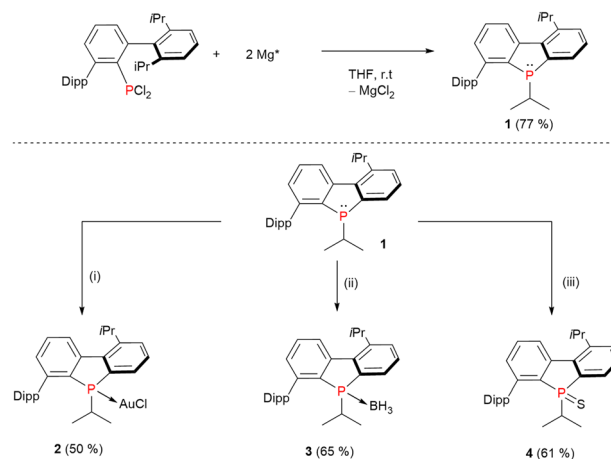
Results and discussion

Rather than starting from $\text{DippTerP}=\text{GaCp}^*$ or $\text{DippTerP}(\text{PMe}_3)$, phosphafluorene **1** is conveniently prepared through reduction

of ^{Dipp}TerPCl₂ with two equivalents of activated magnesium (Mg*, also see Scheme 1f).⁹ After work-up, **1** was afforded as light orange, fluffy solid in 77% yield (Scheme 2, top). The formation of **1** was confirmed by ³¹P NMR spectroscopy in C₆D₆ ($\delta(^{31}\text{P}\{\text{H}\}) = -1.1$ ppm) and a complex ¹H NMR spectrum, which shows a characteristic upfield-shifted pseudo-triplet ($\delta(^1\text{H}) = 0.26$ ppm) for one of Me-groups of the P-iPr moiety, in line with C₁ symmetry in solution.

Next, chemical modifications at the P-center of **1**, particularly through coordination to transition metals, sulfurization, and reactions with Lewis acids were targeted (Scheme 2, bottom). The combination of **1** with (Me₂S)AuCl in toluene afforded complex **2** (Scheme 2,i), which was recrystallized from a 1 : 5 CH₂Cl₂ : *n*-hexane solution at –30 °C giving colourless single crystals suitable for single crystal X-ray diffraction (SCXRD) analysis and **2** was isolated in 50% yield. The ³¹P{¹H} NMR shift in C₆D₆ at 32.4 ppm indicated the formation of complex **2** and a tetracoordinate P atom. Upon coordination of AuCl, the ³J_{P-H} coupling constant of the shielded Me-group (δ(¹H) = 0.04 ppm) increases and results in a clear doublet of doublet splitting of the signal. Phosphafluorene BH₃ adduct **3** (Scheme 2,ii) was obtained when stirring **1** and H₃B·SMe₂ in *n*-hexane. After crystallization from *n*-heptane at –30 °C **3** was isolated as colourless single crystalline material in 65% yield. The ³¹P{¹H} and ¹¹B{¹H} NMR spectra of **3** in C₆D₆ displayed characteristic signals at 37.3 ppm and –38.4 ppm, respectively, indicating tetracoordinate P and B atoms. Additionally, the BH₃ moiety is detected in the IR spectrum, with B–H stretching modes centred at 2345 cm^{–1}.²⁹

In the ^1H NMR spectrum, the expected quartet resonance for BH_3 is significantly broadened and overlaps with the signals of the iPr-Me groups and could therefore not be unambiguously assigned. Similarly to **2**, the shielded Me-groups of the iPr -groups on the P atom changes into a doublet of doublets.



Scheme 2 Synthesis of phosphaphluorene **1** (top). Functionalization of the phosphorus center in **1**: (i) AuCl-SMe₂, toluene, 16 h, r.t.; (ii) H₃B-SMe₂, *n*-hexane, 16 h, r.t.; (iii) 1/8 S₈, CH₂Cl₂, 16 h, r.t.

(2,6-diisopropylphenyl)-5,9-diisopropyl-9-phosphafluorene) and was isolated in 61% yield. Compound **5** features a ^1H NMR resonance at 7.84 ppm (d, $^3J_{\text{P-H}} = 38.0$ Hz) assigned to the alkenyl C=CH moiety (*cf.* $\text{Ph}_3\text{P}(\text{PhC}=\text{CH})\text{B}(\text{C}_6\text{F}_5)_3$: $\delta(^1\text{H}) = 8.32$ ppm, $^3J_{\text{P-H}} = 36.0$ Hz).²⁶ The ^{31}P NMR signal at 36.1 ppm is in line with a phosphonium center, whereas the ^{19}F NMR spectrum showed three sets of signals for the *o*-, *p*-, and *m*-fluorine atoms of the C_6F_5 groups located at $\delta(^{19}\text{F})$ −130.5, −161.7, and −166 ppm, respectively, in line with reported FLP-type activations of phenylacetylene and free rotation about the B–C axis.²⁶ In the ^{11}B NMR spectrum, a signal at −15.4 ppm (d, $^3J_{\text{P-B}} = 18.0$ Hz) is in line with a four-coordinate boron center and a zwitterionic phosphonium borate species. Collectively these data suggested that **5** is exclusively the 1,2-addition product (Scheme 3, bottom). This assumption was confirmed by X-ray crystallography showing that the phosphine and borane added to the alkyne in (*E*)-fashion with the B adding to the CH terminus of the alkyne (Fig. 2, left).²⁷ The solid-state structure reveals P–C_{Ar} (1.792(2), 1.801(2) Å) and P–C_{iPr} (1.828(2) Å) distances similar to those found in **2** and **3** (*vide supra*). The P–C_{C=C} distance (1.828(2) Å) is in the range of a contracted P–C single bond ($\sum r_{\text{cov}}(\text{P-C}) = 1.86$ Å)³² and minimally longer than in $\text{Ph}_3\text{P}(\text{PhC}=\text{CH})\text{B}(\text{C}_6\text{F}_5)_3$ (*cf.* 1.806(1) Å).²⁶ The C31–C32 distance (1.344(2), *cf.* $\sum r_{\text{cov}}(\text{C}=\text{C}) = 1.34$ Å)³² clearly indicates activation of the alkyne unit, with the P and B atoms being in *trans*-orientation with respect to the C=C bond. Notably, the

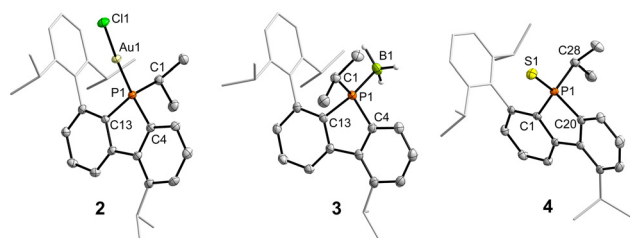
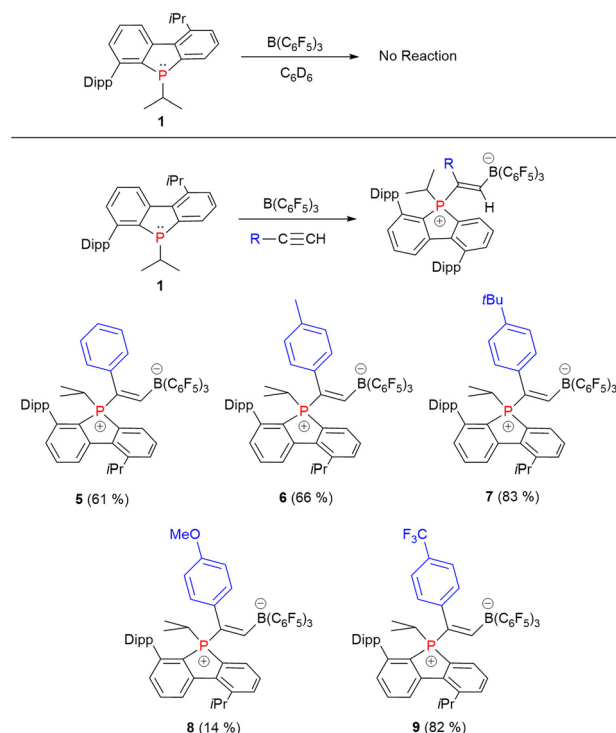


Fig. 1 Molecular structures of **2** (left), **3** (middle) and **4** (right). Ellipsoids drawn at 50% with C–H-atoms omitted, Dipp- and one of the iPr-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] of **2**: C1–P1 1.845(2), C4–P1 1.798(2), C13–P1 1.805(2), P1–Au1 2.2247(6), Cl1–Au1 2.2885(6); C4–P1–C13 91.83(10), C4–P1–C1 106.46(10), C13–P1–C1 105.84(10), C4–P1–Au1 114.61(7), C13–P1–Au1 121.62(7), C1–P1–Au1 113.71(8); C5–C4–P1–C13 179.9(2). **3**: P1–C4 1.7991(13), P1–C13 1.8102(13), P1–C1 1.8435(14), P1–B1 1.9269(16); C4–P1–C13 91.52(6), C4–P1–C1 108.29(6), C13–P1–C1 107.20(6), C4–P1–B1 111.38(7), C13–P1–B1 121.08(6), C1–P1–B1 114.62(7); C13–P1–C4–C9–178.84(12); **4**: P1–C1 1.809(1), P1–C20 1.797(1), P1–C28 1.866(1), P1–S1 1.9462(5), C20–P1–C1 91.78(6), C20–P1–C28 106.39(6), C1–P1–C28 104.83(6), C28–P1–S1 112.84(5), C20–P1–C1–C2 175.58(12).



Scheme 3 Reactivity of **1** towards $\text{B}(\text{C}_6\text{F}_5)_3$ in the absence (top) and presence of phenylacetylene derivatives, giving alkenyl phosphonium borates **5–9**.

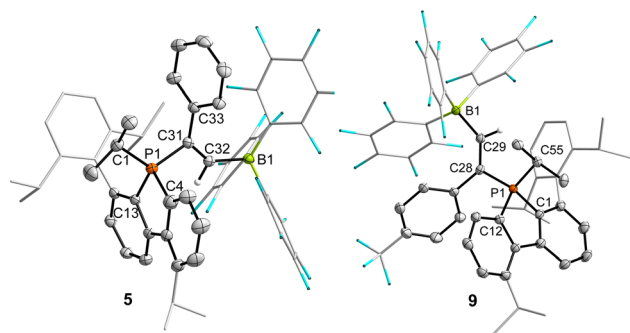


Fig. 2 Molecular structures of **5** and **9**. Ellipsoids drawn at 50% with C-H-atoms omitted (except those at C32 (**5**) and C29(**9**)), Dipp-, C₆F₅-, CF₃- and one of the iPr-groups rendered as wire-frame for clarity. Selected bond lengths [Å] and angles [°] of **5**: P1–C4 1.7915(18), P1–C13 1.8014(16), P1–C1 1.8282(18), P1–C31 1.8282(17), B1–C32 1.648(2), C31–C32 1.344(2); C4 P1 C13 93.34(8), C4–P1–C1 110.49(8), C13–P1–C1 113.17(8), C4–P1–C31 107.19(8), C13–P1–C31 112.12(7), C1–P1–C31 117.64(8), C32–C31–P1 112.79(12), C31–C32–B1 138.96(15); C4–P1–C31–C32 65.08(14). **9**: C1–P1 1.8007(14), C12–P1 1.7807(14), C28–P1 1.7969(13), C55–P1 1.8326(14), C28–C29 1.3433(19), C29–B1 1.642(2); C12–P1–C28 108.96(6), C12–P1–C1 93.52(6), C28–P1–C1 122.55(6), C12–P1–C55 108.64(7), C28–P1–C55 113.19(6), C1–P1–C55 107.71(6), C29–C28–P1 116.86(10), C28–C29–B1 136.79(13); C29–C28–P1–C12 137.25(11).

C=CH proton is oriented towards the phosphafluorene moiety.

Motivated by these findings, we next tested a series of *para*-substituted phenylacetylenes (4-R-C₆H₄-C≡CH where R = CH₃ (**6**), *t*Bu (**7**), OMe (**8**), CF₃ (**9**)) to investigate possible substituent effects on this FLP reactivity. Reaction of these alkynes with the 1/B(C₆F₅)₃ FLP system proceeded analogously to **5**, yielding diverse zwitterionic alkenyl phosphonium borate products (Scheme 3), which underlines the generality of this functionalization strategy.²⁷ This FLP-type alkenylation of a P-heterocycle is also related to the chemistry of phosphinine-borane adducts towards phenylacetylene.³³ The ³¹P NMR shifts for **6–9** are clustered near 36.0 ppm, clearly showing minimal influence of the *para*-substituent. All compounds (**6–9**) displayed ¹⁹F NMR signals for the B(C₆F₅)₃ moiety in the range of –130.5 (*ortho*-F), –161.7 (*para*-F), and –166.0 (*meta*-F), mirroring **5**, and thereby indicating a similar B(C₆F₅)₃ moiety in all alkenylation products **5–9**. Notably, **9** showed an additional singlet at –63.3 ppm in the ¹⁹F NMR spectrum assigned to the CF₃ group. The ¹¹B NMR spectra of **6–9** uniformly exhibited resonances near –15.0 ppm (d, ³J_{P-B} = 18 Hz) as expected for borate-type activation products. These observations suggest minimal electronic influence from the *para*-substituents of phenylacetylenes (EDG/EWG) on the regio- and chemoselectivity of the alkenylation. In all derivatives the C=CH resonance is deshielded at *ca.* 8 ppm and a ³J_{P-H} coupling constant of *ca.* 38 Hz.

These results underscore the robustness of FLP-mediated alkyne activation, where steric and electronic perturbations at the *para*-position are effectively reduced by the conjugated aro-

matic system, preserving the core electronic structure of the adducts.

Single crystals of **9** suitable for SCXRD were obtained from layering the C₆D₆ reaction mixture with *n*-heptane at room temperature. As previously observed in **5**, the alkyne activation is (*E*)-selective, with boron attached to the CH terminus (Fig. 2, right). All key structural parameters are similar to those found in **5**. However, the orientation of the C=CH proton is different, which is now oriented towards the P-*i*Pr group.

Lastly, the absorption and emission profiles of **1** and its derivatives in MeCN solution were investigated. Phosphafluorene **1** shows absorption maxima in the UVB region at 303 and 312 nm and weak blue fluorescence with a broad emission maximum at 369 nm. As a representative for P-functionalized species **2–4**, phosphafluorene **4** was studied and shows two bathochromically shifted absorption maxima at 313 and 323 nm, while the emission maximum is hypsochromically shifted to 361 nm (Fig. 3). A second emission maximum is evident at 453 nm. Notably, the emission band is rather broad and tails into the visible region, in line with blue fluorescence in MeCN solution. Interestingly, the absorption spectra of alkenylated species **5–9** are nearly identical with absorption maxima at *ca.* 330 nm (Fig. 4), indicating minimal influence of the *para*-substituent in the employed phenylacetylene derivatives. The emission spectrum of **5** features a maximum at 381 nm with a shoulder at 400 nm (Fig. S66). Broad emission maxima between 380–390 nm are detected for **6**, **7** and **9**. Compound **8** displays distinct photophysical characteristics, featuring a minor absorption shoulder at 385 nm, while the emission maximum is markedly red-shifted to 472 nm. In the absence of lifetime data, we tentatively attribute this pronounced red-shift to phosphorescence rather than fluorescence or a chemical transformation in the excited state. Generally, P-functionalization in **4** results in a red-shift of the absorption maximum, which is even more pronounced

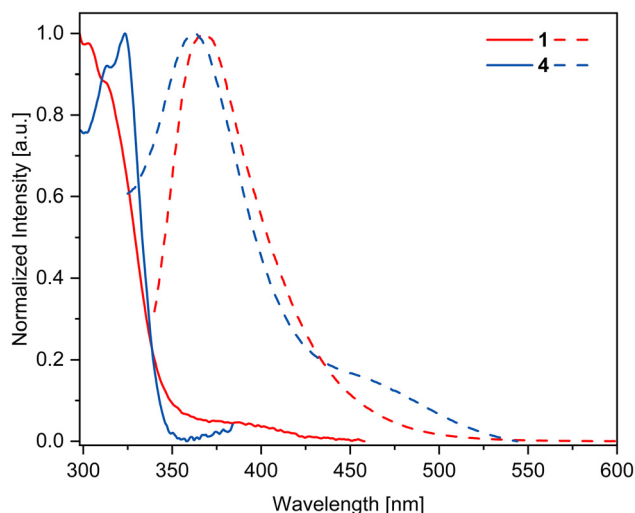


Fig. 3 Normalized absorption- (compact) and emission (dashed) spectra of **1** and **4**.

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