

Allenic Phosponium Borate Zwitterions via a Transient Phosponium Allenylidene

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Abstract

We describe the synthesis of alkynyl phosphanes of the type $R_2P-C\equiv C-(OCH_3)Ph_2$ ($R = Ph, Cy$) and investigate their transformation to geminally substituted phosponium borato-allene zwitterions upon their reaction with $B(C_6F_5)_3$. The mechanism for this transformation was studied experimentally and by density functional theory computations (DFT), suggesting the intermediacy of an unsaturated 3-coordinate phosponium electrophile akin to a methylene phosponium cation.

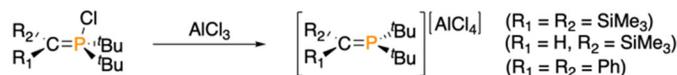
Introduction

The iminium functional group has been thoroughly studied and is ubiquitous in organic chemistry.¹ By comparison, the phosphorus containing congener, known as the methylene phosponium cation, is considerably less explored. Whereas iminium salts typically react as carbon-based electrophiles,² methylene phosponium cations are fierce phosphorus-centered Lewis acids.³ In the late 1980s, Bertrand and co-workers reported the original preparation of a methylene phosponium cation of the formulation $[(iPr_2N)_2P=C(SiMe_3)_2]^+$ by the silylation of a phosphinocarbene precursor (Scheme 1).^{3a} A synthetic route later reported by Grützmacher and Pritzkow yielded methylene phosponium salts of the general form $[tBu_2P=CR_2]^+$ via halogen abstraction from *P*-chloromethylenephosphoranes.⁴ The Erker group recently demonstrated a frustrated Lewis pair (FLP) pathway to methylene phosponium systems from the reaction of a vinyl substituted phosphane and electrophilic boranes.⁵

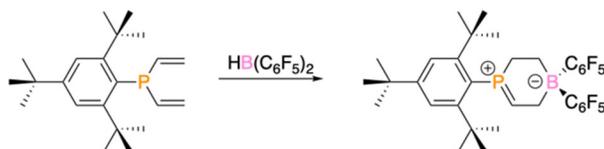
(a) Bertrand: Addition of TMSOTf to phosphino-carbenes



(b) Grützmacher and Pritzkow: Chloride abstraction of *P*-chloromethylenephosphoranes



(c) Erker: FLP pathway to methylene phosponium salts



Scheme 1 – Synthesis of early methylene phosponium systems.

An alternate bonding description for the methylene phosphonium cation **II** is the phosphanyl-substituted carbenium ion **I** (Scheme 2).^{3d, 6} In a review published over 20 years ago, Bertrand et al. discussed the feasibility of accessing methylene phosphonium salts **II** by employing precursor phosphanes with abstractable functional groups in the position α to the phosphorus center.^{6a} The authors noted that a considerable energetic barrier disfavors the formation of planarized phosphonium salts **II** from pyramidal cationic phosphanes **I**, evidence of the inferior p-donor properties of phosphorus when compared to nitrogen.



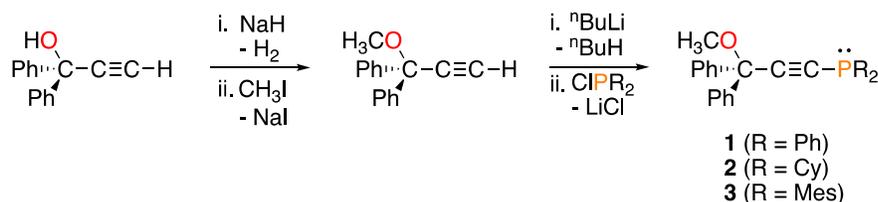
Scheme 2: Structural models for methylene phosphonium cations. Phosphanyl-substituted carbenium ion (**I**) and a methylene phosphonium cation (**II**). Alkynyl phosphane linked carbenium ion (**III**) and a proposed cumulenic methylene phosphonium cation (**IV**)

Our group is interested in 3-cumulenic analogues of methylene phosphonium species **IV**, which have yet to be reported. To attempt the synthesis of **IV**, we envisioned a suitable pathway that first involves the generation of a carbenium ion **III**, accessed *via* a heterolytic bond cleavage reaction at the γ carbon of a propargyl- substituted phosphane.⁷ We chose to employ phosphane precursors with a p-electron stabilizing diphenylacetylene substituent, which upon methoxide anion abstraction had the anticipated effect of delocalizing the phosphorus atom lone pair and providing salts akin to **IV**. We reasoned that the formation of **IV** over the carbenium ion **III** could be favourable if the positive charge were delocalized from the main group center over several atoms, possibly counteracting the energetic penalty associated with the planarization of the phosphorus center. This synthetic approach draws direct inspiration from the preparation of cationic allenylidene complexes $[L_nM=C=C=CR_2][X]$ accessed from the ionization of neutral acetylide complex.⁸

This communication will detail the synthesis of phosphanes substituted with the $(-C\equiv C-C(OCH_3)Ph_2)$ moiety. Abstraction of the $-OCH_3$ by $B(C_6F_5)_3$ led to the serendipitous discovery of a reaction that produces allenic phosphonium borate salts in high yield. While we have been unsuccessful in isolating a 3-cumulenic analogue of a methylene phosphonium cation, the isolated zwitterionic products described in this report suggest that the species we initially pursued are likely a transient reaction intermediate. Additionally, we will discuss dichotic results that arise from the ambidentate nature of phosphanes $R_2P-C\equiv C-C(OCH_3)Ph_2$.

Results and Discussion

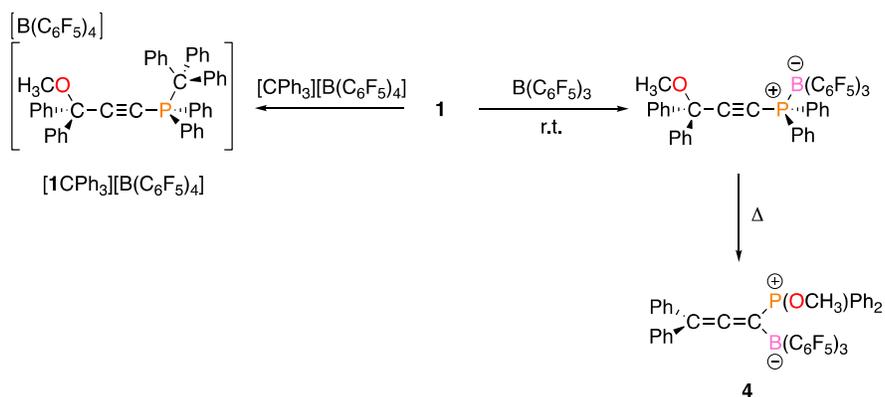
Phosphanes $R_2P-C\equiv C-C(OCH_3)Ph_2$ ($R = Ph$ **1**, Cy **2**, Mes **3**) were synthesized in two steps in moderate yields from commercially available 1,1-diphenyl-2-propyn-1-ol (Scheme 3).^{8,9} **1**, **2**, and **3** were characterized by multinuclear NMR spectroscopy (see ESI), high-resolution mass spectrometry (HRMS) and the solid-state structure of **1** was determined by single crystal X-ray diffraction (Fig 1, a).



Scheme 3: Synthesis of phosphanes 1-3

With **1** in hand, we targeted its transformation to the $[R_2P=C=C=CR_2]^+$ cation, initially employing trifluoromethylsulfonate (TMSOTf) as a methoxide abstraction reagent.⁷ Addition of a stoichiometric excess of TMSOTf (~ 1.5 equiv) to a chloroform-*d* solution of **1** at -78 °C, in the absence of light, resulted in a gradual change from colorless to bright yellow. Monitoring the reaction by ¹H NMR spectroscopy indicated conversion to a single major product, identified by the generation of a diagnostic doublet resonance at $\delta = 4.11$ ppm with a small ³J_{PH} coupling constant of 12.5 Hz, further confirmed by 2D ¹H-³¹P {H} heteronuclear multiple bond coherence experiments. The corresponding ³¹P {¹H} spectrum displayed a singlet resonance at $\delta = + 60.7$ ppm, shifted to a considerably higher frequency with respect to **1** ($\Delta \delta$ of ~ 95 ppm). Taken together, the spectroscopic features of this reaction mixture were strongly suggestive of methoxide abstraction (C_g-O bond cleavage) of **1** and subsequent alkoxylation at phosphorus producing methoxy-phosphonium of the general form $[Ph_2P(OCH_3)R]^+$ (see ESI).¹⁰ We encountered difficulties with attempting to isolate or to crystallize the reaction product of **1** and TMSOTf to determine its atom connectivity. This prompted us to explore alternative Lewis acidic reagents to facilitate the methoxy group abstraction of phosphane **1**.

Along this note, we proceeded to employ $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ as potential -OCH₃ abstracting reagent. Addition of an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ to **1** gave the Lewis adduct $[1CPh_3][B(C_6F_5)_4]$ as determined by ³¹P, ¹⁹F, ¹³C and ¹¹B spectroscopic methods (Scheme 4).¹¹ Formation of the trityl phosphonium borate $[1CPh_3][B(C_6F_5)_4]$ demonstrates Lewis adduct formation at the phosphorus lone pair of **1**, while the C_g-O bond remains intact. Combining **1** with a stoichiometric quantity of $B(C_6F_5)_3$ at room temperature in benzene, resulted in no obvious colour change upon dissolution. After 3 hours, analysis of a reaction aliquot by ³¹P {¹H} NMR spectroscopy indicated complete consumption of **1** and the formation of a major species in solution (*ca.* 94%), which displayed a broadened singlet centered at $\delta = 3.71$ ppm. The corresponding ¹H NMR spectrum retained the diagnostic singlet resonance of the -OCH₃ moiety in **1**. Taken together, we likened the product to be the phosphane Lewis adduct **1**- $B(C_6F_5)_3$. However, heating this mixture to 60 °C resulted in quantitative conversion to a new product **4**, evidenced by the generation of a ³¹P {¹H} NMR resonance at $\delta = 67.0$ ppm. The corresponding ¹H NMR spectrum showed a doublet resonance at $\delta = 2.93$ ppm (³J_{PH} = 11.4 Hz), which collapsed to a singlet upon ³¹P decoupling. In the ¹¹B {¹H} NMR spectrum, a sharp signal was observed at $\delta = - 13.6$ ppm, and the ¹⁹F NMR spectrum showed a set of signals at $\delta = - 129.6$ ppm (*o*-F), $- 159.7$ ppm (*p*-F) and $- 165.1$ ppm (*m*-F), supporting the structure of **4** as a zwitterion containing a phosphonium cation and tetracoordinate boron center.¹² The C{¹H} NMR spectrum showed a resonance at $\delta = + 214$ ppm diagnostic of an sp-hybridized allenic carbon atom. Upon work up, **4** was isolated as an analytically pure yellow solid in 67% yield. Recrystallization from a layered solution of CH₂Cl₂ and pentane afforded X-ray crystallographic quality single crystals of **4** confirming its structure (Scheme 4). The allene fragment of **4** is almost completely linear (C1-C2-C3 of *ca.* 176.0 (2)°). The P1-C1 bond distance of **4** is 1.779(2) Å, longer with respect to the P1-C1 of **1** 1.762(2) Å. Elongation of the C1-C2 bond is observed upon salt formation from 1.210(3) Å to 1.311(2) Å, in agreement with an overall decreased bond order from 3 (alkyne) to 2 (alkene). Contraction of the C2-C3 bond was observed from 1.476(3) Å in **1** to 1.317(2) Å in **4**. The bond angles around C1 and C3 sum to 359.0(3)° and 360 (3)° respectively. Additionally, the substituents on C1 and C3 lie within orthogonal planes, confirming an allene type structure with extended tetrahedral geometry.



Scheme 4: Synthesis of salt $[1\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ and zwitterion **4**.

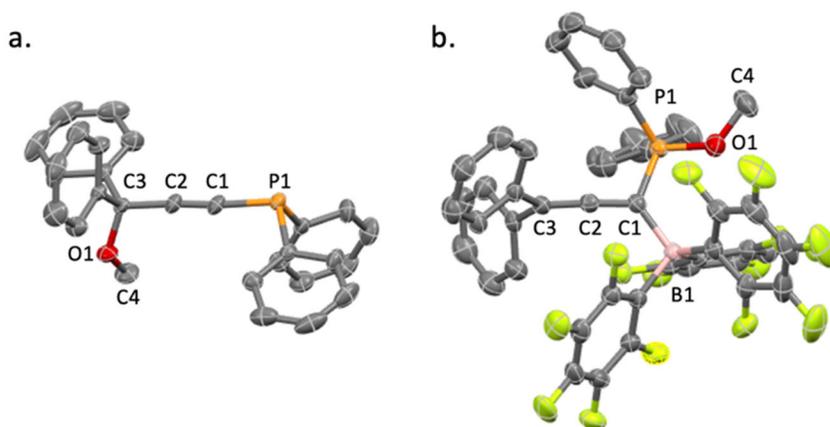


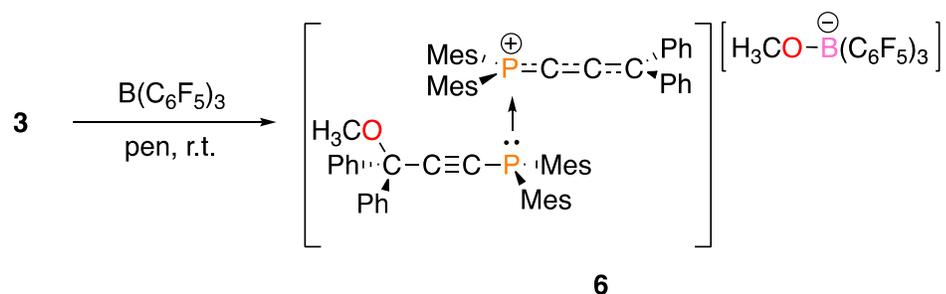
Figure 1: Solid state molecular structure of **1** (left) and **4** (right). All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

The analogous product **5** was prepared from **2** and $\text{B}(\text{C}_6\text{F}_5)_3$ in 63% yield as an orange solid. Notably, this reaction occurs relatively quickly when compared to the reaction of **1** and $\text{B}(\text{C}_6\text{F}_5)_3$, and even proceeds to completion in the absence of an external heat source (12 h, 25 °C). We attribute this difference in reactivity to the increased steric bulk of **2** imparted by larger cyclohexyl substituents, which may minimize competing phosphane-borane interactions. The spectroscopic features of **5** are virtually identical to **4** with diagnostic NMR features at $\delta_{\text{H}} = 2.71$ (d), $\delta_{\text{B}} = -13.4$, $\delta_{\text{P}} = +82.8$, $\delta_{\text{C}} = +212.5$. In no circumstance did we observe any evidence of 1,1 carboboration products arising from reactions of either **1** or **2** with $\text{B}(\text{C}_6\text{F}_5)_3$.¹³

The unprecedented rearrangement reaction leading to products **4** and **5** from their respective alkynyl phosphanes **1** and **2** was encouraging evidence for our hypothesized approach to $[\text{R}_2\text{P}=\text{C}=\text{C}=\text{CR}_2]^+$ cations. We suspect the intermediacy of an unsaturated 3-coordinate phosphonium electrophile may explain the connectivity of **4** and **5**. In an attempt to isolate this intermediate, we employed the bulkier substrate **3**, anticipating that mesityl substituents may provide a greater measure of kinetic stabilization. While mixing **3** with $\text{B}(\text{C}_6\text{F}_5)_3$ in benzene at room temperature gave an intractable mixture of reaction products, the same reaction in pentane led to the instantaneous formation of a light green precipitate. Isolating and dissolving this precipitate in benzene- d_6 revealed the formation of a single new product, evidenced by a pair of doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta = -5.36$ and -18.72 ppm, sharing identical coupling constants ($^1J_{\text{PP}} = 211$ Hz), and integrating in a ratio of 1:1. The large coupling constant and doublet splitting pattern

indicated a new species with two chemically distinct phosphorus environments connected through a single bond. A ^{11}B NMR signal at $\delta = -1.68$ ppm suggested the formation of the tetracoordinate borate counter anion $[\text{H}_3\text{CO-B}(\text{C}_6\text{F}_5)_3]^-$. Notable features of the ^1H NMR spectrum include two resonances for the $-\text{OCH}_3$ functionality, one singlet at $\delta = 2.75$ ppm, and a second broad singlet at $\delta = 3.55$ ppm, which integrate equally. Based on the above spectroscopic features, we have tentatively assigned this product to be the cationic phosphine phosphonium adduct **6** (as depicted in Scheme 5). Compound **6** decomposes slowly in solution ($\sim 90\text{-}95\%$ remaining after 2 days) and all attempts to grow single crystals for X-ray diffraction have been unsuccessful to date.

Concerning the mechanism for the formation of **4** and **5**, we believe that the reaction process is initiated by a borane-mediated $\text{C}_g\text{-OCH}_3$ bond cleavage event to generate an ion pair of a tri-coordinate phosphonium cation and the borate anion $[\text{H}_3\text{CO-B}(\text{C}_6\text{F}_5)_3]^-$ (Depicted as **Int2** in Figure 2). The methoxide moiety from the anion $[\text{H}_3\text{CO-B}(\text{C}_6\text{F}_5)_3]^-$ is delivered to the Lewis acidic phosphonium cation, to give phosphacumulene ylides (**Int4**). Products **4** and **5** are Lewis adducts of the aforementioned ylides and $\text{B}(\text{C}_6\text{F}_5)_3$, structurally resembling a P/B inner salt prepared by the Krempner group from Bestmann's ylide (Ph_3PCCO).¹² Compounds **1** and **2** can presumably form classical P-B Lewis adducts with $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 4), a process that competes with $\text{C}_g\text{-OCH}_3$ abstraction. Lastly, the generation of **6** from **3** and $\text{B}(\text{C}_6\text{F}_5)_3$ in pentane solution suggests cations like **Int2** may be involved in the reaction cascade that yields allenes **4** and **5** from their respective phosphanes.



Scheme 5: Formation of adduct **6** from **3** and $\text{B}(\text{C}_6\text{F}_5)_3$

To support the proposed mechanism for the formation of zwitterions **4** and **5**, density functional theory (DFT) computations at the BP86-D3/def2SVP level of theory in the gas phase for the reaction involving **1** and $\text{B}(\text{C}_6\text{F}_5)_3$ were performed.^{14,15} As a result, we found that the first step of this transformation involves coordination of the ether moiety in **1** to $\text{B}(\text{C}_6\text{F}_5)_3$, providing the B-O Lewis adduct **Int1**. This step is slightly exergonic ($\Delta G = -5.5$ kcal mol⁻¹) and highly exothermic ($\Delta H = -23.5$ kcal mol⁻¹). Heterolytic cleavage of the C-O bond leading to salt **Int2** is both exergonic ($\Delta G = -13.59$) and exothermic ($\Delta H = -7.44$ kcal mol⁻¹). The structural parameters of **Int2** suggest that the structure has some delocalization across the P-C-C-C vector with a shortened P-C bond length of 1.732 Å, compared to **1** (1.762(2) Å). Furthermore, the CC triple-bond length increased from 1.198(3) Å in **1** to 1.248 Å in **Int2**, with a related bond contraction between C2 and C3 (Figure 1) from 1.481(3) Å in **1** to 1.388 Å in **Int2**. Compared to the methylene phosphonium cation reported by Grützmacher and co-workers, $[\text{tBu}_2\text{P}=\text{CPh}_2]^+$ which has a P=C bond length of 1.683 Å, suggests that while delocalization is occurring in our system, we do not have complete P=C double bond formation and it is best described as a hybrid of structures **III** and **IV** in Scheme 1. Frontier orbital analysis indicate that both the HOMO and LUMO are found across the P-C-C-C fragment (ESI Figure 9) supporting the

observed bond parameters of **Int2**. From **Int2**, the P-O adduct formation producing intermediate **Int3** is barrierless. P-O bond formation and B-O bond breakage leading to phosphacumulene ylide **Int4** is an endergonic and endothermic reaction ($\Delta G = 5.84$ and $\Delta H = 7.44$ kcal mol⁻¹) and is the rate determining step with ΔG^\ddagger of 8.34 kcal mol⁻¹. The last step of this process, the association of **Int4** and B(C₆F₅)₃ to give **4** is highly exergonic ($\Delta G = -38.14$ kcal mol⁻¹). Overall, the formation of **4** from **1** and B(C₆F₅)₃ is very exergonic and exothermic ($\Delta G = -46.48$ and $\Delta H = -65.12$ kcal mol⁻¹). Despite this, in our experimentation, the reaction was very slow in the absence of heating. It is reasonable to assume that this is a consequence of the formation of **A1** which is a highly exergonic ($\Delta G = -19.2$ kcal mol⁻¹) and thus inhibits the reaction from proceeding. These calculations support our initial suggestion that this transformation possibly proceeds *via* an unsaturated tricoordinate P-centered electrophilic intermediate. However, the highly reactive nature of **Int2** has made the isolation of **Int2** impossible due to consequent reaction of this intermediate with the rather strong B–O bond ultimately leading to product **4**.

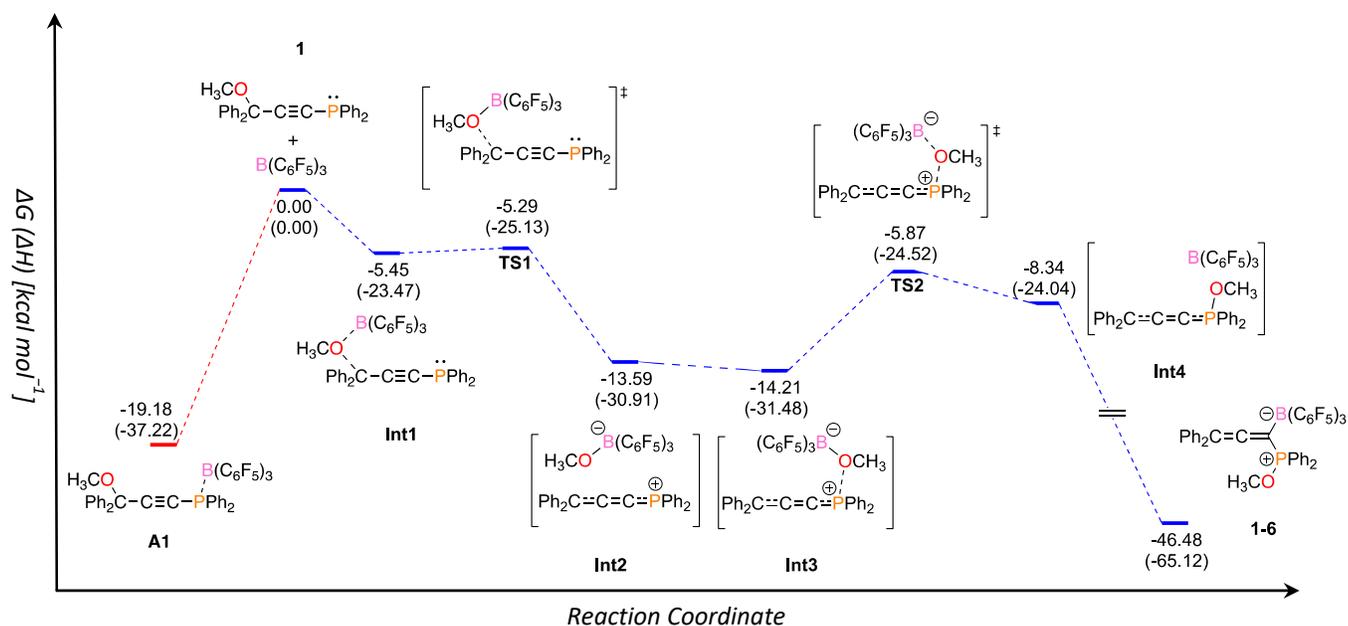


Figure 2: Potential energy surface calculated for a possible reaction mechanism for the formation of **4**. Energies are reported relative to the starting materials. Gibbs free energies and enthalpies (in parenthesis) given in kcal mol⁻¹.

Conclusion

In conclusion, we have prepared the geminal phosphonium borate zwitterions **4** and **5** through B(C₆F₅)₃ mediated methoxide abstraction of the alkynyl phosphanes **1** and **2**, respectively. We are currently exploring the potential applicability of this transformation towards the isolation of Lewis-base free phosphorus/carbon-based tricoordinate salts $[\text{R}_2\text{P}=\text{C}=\text{C}=\text{CR}_2]^+$, as well its general utility for synthesizing phosphorus/boron materials.

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Conflicts of Interest

The authors declare no conflicts of interest.

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