

Carbene-Anchored Boryl- and Stibanyl-Phosphaalkenes as Precursors for Bis-Phosphaalkenyl Dichlorogermane and Mixed-Valence Ag^I/Ag^{II} Phosphinidenide

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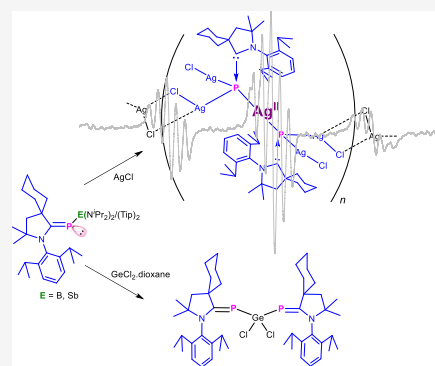
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ABSTRACT: Cyclic alkyl(amino) carbene (cAAC)-anchored boryl- and stibanyl-phosphaalkenes with general formula $cAAC = P-ER_2$ [$E = B, R = (N^iPr_2)_2$ (**3a-c**); $E = Sb, R = 2,4,6$ -triisopropylphenyl (**5a-b**)] have been synthesized and utilized as precursors for the bis-phosphaalkenyl dichlorogermane [$(cAAC = P)_2GeCl_2$] (**6**) and the first molecular example of a neutral polymeric mixed-valence Ag^I/Ag^{II} phosphinidenide complex [$(cAAC = P)_2Ag^I Ag^II Cl_4$]_n (**7**). All compounds have been characterized by single-crystal X-ray diffraction and further investigated by nuclear magnetic resonance (NMR), mass spectrometric analysis, and UV-vis/fluorescence measurements. The paramagnetic complex **7** has been characterized by ESR spectroscopy. Cyclic voltammetry studies of compounds **3/5** have suggested possible one-electron quasi-reversible reductions, indicating their redox noninnocent behavior in solution. Quantum chemical studies revealed the electron-sharing nature of the P–B and P–Sb σ bonds in compounds **3** and **5**, and the polar $C_{cAAC} = P$ bonds in compounds **3**, **5**, and **6** prevailing their phosphaalkene structures over phosphinidenes.



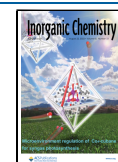
INTRODUCTION

Phosphinidenes (RP) are the species with two available lone pairs on phosphorus in their singlet ground state, which have been first detected in the gas phase by mass spectrometry¹ and in low-temperature matrices by various spectroscopic techniques.² The first stable and structurally characterizable phosphinidene was initially reported by the group of Mathey in the form of its terminal transition metal complexes (A) in 1982³ and later in 1996 by the group of Bertrand.³ In 2010, Robinson's group employed N-heterocyclic carbenes (NHCs) as the stabilizing ligands to isolate the corresponding parent phosphinidene complexes, $L' = P-H$ (B),⁴ followed by other groups who stabilized phosphinidenes⁵ in various forms, such as bis-carbene adduct of P₂,⁶ chloro-phosphinidenes (C),⁷ and silylene-phosphinidenes (D),⁸ utilizing the σ -donating and π -accepting ligands, such as cyclic alkyl(amino) carbenes (cAACs) (E) (Figure 1). Recently, Bertrand's group reported the existence of highly reactive (phosphino)phosphinidene (F), featuring a P–P multiple bond.⁹ In 2017, Cummins' group reported the generation of transient phosphinidene intermediates upon heating dibenzo-7 λ^3 -phosphanorbornadiene derivatives.¹⁰ Experimental results¹¹ and theoretical calculations¹² revealed that phosphinidenes can be regarded as phosphaalkenes with the predominant $C_{carbene} = P$ bond having inverse electron distribution ($C^{\delta+} - P^{\delta-}$), whereas the Lewis basic behavior of the former can be established by its coordination chemistry¹³ prevailing the presence of two lone pairs on phosphorus. Recently, the chemistry of carbene-

stabilized phosphaalkenyl species ($R_2C = \bar{P}$), known as the phosphinidenides,¹⁴ has greatly attracted the attention of the synthetic main group chemists. In this context, stabilization of the carbene-phosphinidenide complexes of the group 14 elements^{14b,15} by the von H \ddot{a} nisch and Inoue groups and transition metals¹⁶ by the Tamm group is noteworthy. However, the reports on coordination chemistry of cAAC-stabilized phosphinidenides are scarce.¹⁷ In our recent work, we focused on the syntheses of $[R_2CP]M$ salts.¹⁸ As a part of our research interest, we aimed to incorporate the Lewis acidic boryl and stibanyl functionalities at the phosphorus atom of cAAC-anchored phosphinidene to study the effect of the heteroatoms ($E = B, Sb$) on the nature of the $C_{cAAC} = P$ and P–E bonds and their interim reactivities toward inorganic and transition metal halides. Although, in recent times, low valent boron^{19–22} and antimony²³ compounds have attracted significant interest, incorporation of the boryl- and stibanyl-substituents²⁴ into the cAAC-stabilized phosphaalkenes is not documented. Herein, we report on the first syntheses of cAAC-anchored boryl- and stibanyl-phosphaalkenes with the general formula $cAAC = P-ER_2$ [$cAAC = P-B(N^iPr)_2$] (**3**) Cy-

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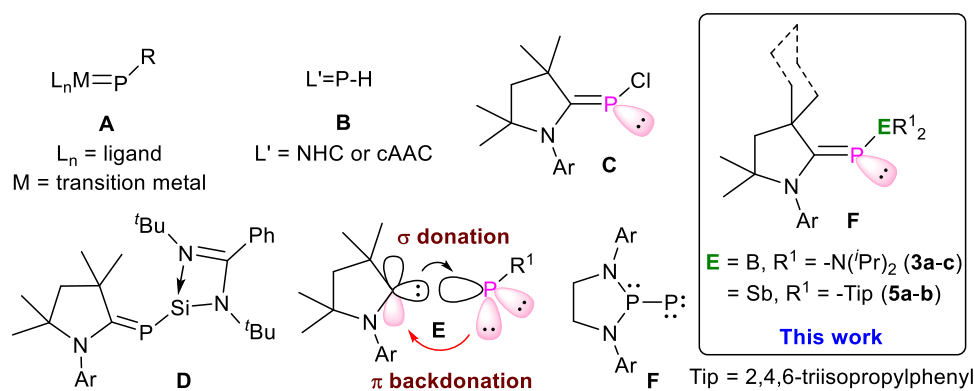
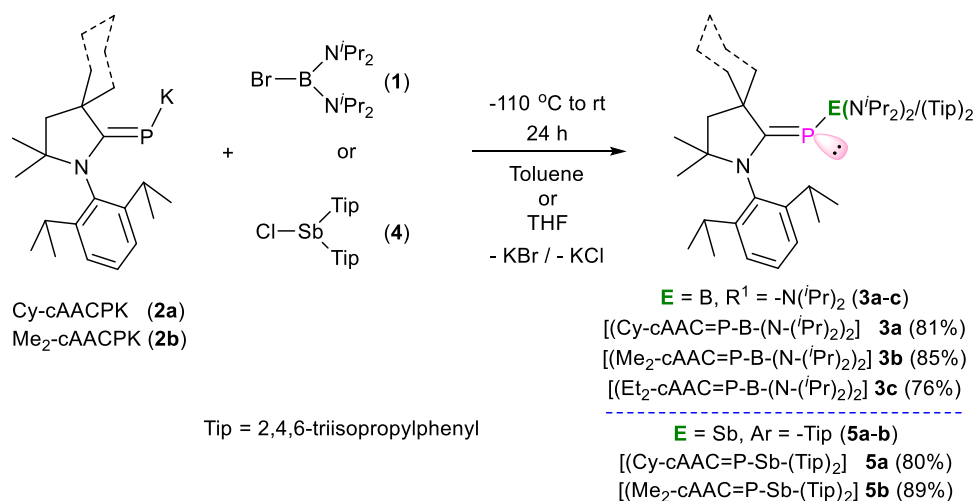


Figure 1. Selective examples of stable phosphalkenes.

Scheme 1. Syntheses of cAAC-Stabilized Boryl- and Stibanyl-Phosphaalkenes, 3a-c/5a-b



cAAC=:(C(N-2,6-ⁱPr₂C₆H₃)(C₆H₁₀)(CMe₂)(CH₂)) (**3a**); Me₂-cAAC=:(C(N-2,6-ⁱPr₂C₆H₃)(CMe₂)₂(CH₂)) (**3b**); Et₂-cAAC=:(C(N-2,6-ⁱPr₂C₆H₃)(CEt₂)(CMe₂)₂(CH₂)) (**3c**); cAAC=P-Sb(Tip)₂ (**5**) (Tip = 2,4,6-triisopropylphenyl); Cy-cAAC (**5a**); Me₂-cAAC (**5b**) by treating cAAC-stabilized potassium phosphinidenides (cAAC=PK)¹⁸ with halo-borane²⁵ and halo-stibane,²⁶ respectively. Moreover, we explored the reactivity of **3/5** and successfully utilized these compounds as precursors to bis-phosphaalkenyl dichlorogermane [(cAAC=P)₂GeCl₂] (**6**) and a polymeric chain of the mixed-valence Ag^I/Ag^{II}-phosphinidenide complex [(Cy-cAAC-P)₂Ag^IAg^{II}Cl₄]_n (**7**) upon treatment with GeCl₂·dioxane and AgCl, respectively.

RESULTS AND DISCUSSION

Initially, the dark red crystals of various cyclic alkyl(amino) carbene (cAAC)-stabilized potassium phosphinidenides (cAAC=PK, **2**)¹⁸ were synthesized and isolated in good yields. The toluene solution of 1.3 equiv (a little excess is required for an improved yield of the intended product, **3a**) of the dark red crystalline compound Cy-cAAC=PK (**2a**)¹⁸ cooled to 0 °C (using an ice bath) was added to the toluene solution (cooled to -110 °C using a THF/liquid N₂ bath) of 1.0 equiv of 1-bromo-*N,N,N',N'*-tetraisopropylboranediamine (**1**). After, the resultant reaction mixture was stirred for 30 min at low temperature (-110 °C); then, the temperature was slowly raised to room temperature (rt) and the mixture was stirred for 24 h, while the color of the reaction mixture turned

slowly from dark brownish-red to golden-yellow over a period of 2 h. The reaction mixture was filtered after 24 h. The filtrate was concentrated under high vacuum, resulting in the formation of the yellow crystalline solid, which was then extracted in *n*-hexane to obtain the boryl-phosphaalkene **3a** [Cy-cAAC=P-B(N(ⁱPr)₂)₂]. Compound **3a** was crystallized at rt from the concentrated *n*-hexane solution to obtain the yellow needle-shaped single crystals in 81% yield (Scheme 1). Similarly, compounds **3b** [Me₂-cAAC=P-B(N(ⁱPr)₂)₂] and **3c** [Et₂-cAAC=P-B(N(ⁱPr)₂)₂] were isolated in 85 and 76% yields, respectively, when the corresponding potassium phosphinidenides **2b** (Me₂-cAAC=PK)¹⁷ and **2c** (Et₂-cAAC=PK) reacted with **1** in 1.3:1 molar ratio (Scheme 1). Reduced yields (64–72%) of **3a–3c** were observed when **1** and **2** reacted in 1:1 molar ratio under similar reaction conditions. **3a–3c** were structurally characterized by single-crystal X-ray diffraction and NMR spectroscopic studies. When similar reactions were performed using cAAC=PK, **2** (Cy-cAAC, **2a**; Me₂-cAAC, **2b**)¹⁷ and the chlorostibane **4**, (Tip)₂Sb-Cl (Tip = 2,4,6-triisopropylphenyl, **4**) in 1:1 molar ratio in THF at -110 °C, golden-yellow blocks of the corresponding stibanyl-phosphaalkenes, **5a–b** [cAAC=P-Sb(Tip)₂], were isolated in 80 and 89% yields, respectively, from the corresponding concentrated *n*-hexane solutions at rt after 4–6 days (Scheme 1). The crystals of **3a–c/5a–b** were found to be soluble in THF, toluene, and *n*-hexane and stable in both solution and solid state at rt for more than six months under an inert atmosphere. **3a–c/5a–b** melted at 161–163 °C (**3a**), 123–125 °C (**3b**),

148–150°C (**3c**), 190–192°C (**5a**), and 178–180°C (**5b**). **3a-c/5a-b** were characterized by ^1H , ^{13}C $\{^1\text{H}\}$, ^{11}B , ^{31}P NMR spectroscopy and high-resolution mass spectrometry (HRMS) in solution (see Supporting Information (SI)). The ^{13}C $\{^1\text{H}\}$ NMR spectra of **3a-c** exhibited doublets at 204.3 ($J_{\text{C-P}} = 59.6$ Hz), 204.3 ($J_{\text{C-P}} = 57.5$ Hz), and 205.3 ($J_{\text{C-P}} = 61.6$ Hz) ppm, respectively, for C_{AAC} , which is comparable with those of **2a** (207 ppm, $J_{\text{C-P}} = 81$ Hz)¹⁸ and $\text{Cy-cAAC} = \text{P-Cl}$ ⁸ (210 ppm, $J_{\text{C-P}} = 104.4$ Hz). The ^{11}B spectra of **3a-c** exhibited broad singlets at $\delta = 41.8$, 40.8, and 42.1 ppm, respectively (theoretically calculated $\delta = 37.5$ (**3a**) and 39.0 ppm (**3b**) at the BP86-D3(BJ)/def2-TZVPP level), which is found to be downfield shifted when compared with the same for **1** (29.48 ppm). The ^{31}P spectra of **3a-c** exhibited much upfield-shifted singlets at $\delta = 28.6$, 22.3, and 17.9 ppm, respectively, when compared with those of **2a** (206.9 ppm)¹⁸ and $\text{Cy-cAAC} = \text{P-Cl}$ (163.4, 160.3 ppm).⁸ The 1,3-bond correlated ^1H - ^{15}N HMBIC spectrum of **3a** showed two singlets at $\delta = -273.11$ (N^iPr_2) and -239.91 ($:\text{C}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$) ppm, indicating a decreased back donation from P to C_{AAC} as expected.²⁷ The ^{13}C $\{^1\text{H}\}$ NMR spectra of **5a-b** exhibited doublets at $\delta = 211.0$ ($J_{\text{C-P}} = 98.9$ Hz) and 211.4 ($J_{\text{C-P}} = 96.9$ Hz) ppm, respectively, for C_{AAC} , which is slightly downfield shifted when compared with the same for **3a-b**. ^{31}P resonances of **5a-b** were observed as singlets at $\delta = 49.1$ and 45.8 ppm, respectively, which are slightly downfield shifted when compared with those of **3a-c**.

Compound **3a** [$\text{Cy-cAAC} = \text{P-B}(\text{N}^i\text{Pr}_2)_2$] crystallizes in the monoclinic space group $P2_1/c$ (Figure 2). The molecular structure of **3a** consists of a Cy-cAAC group attached to the P atom with bent geometry and bonded to a B atom attached to two N^iPr_2 substituents. The B atom of **3a** exhibits a distorted trigonal planar geometry with the sum of the bond angle of 358.28° , whereas the P atom with a lone pair possesses the

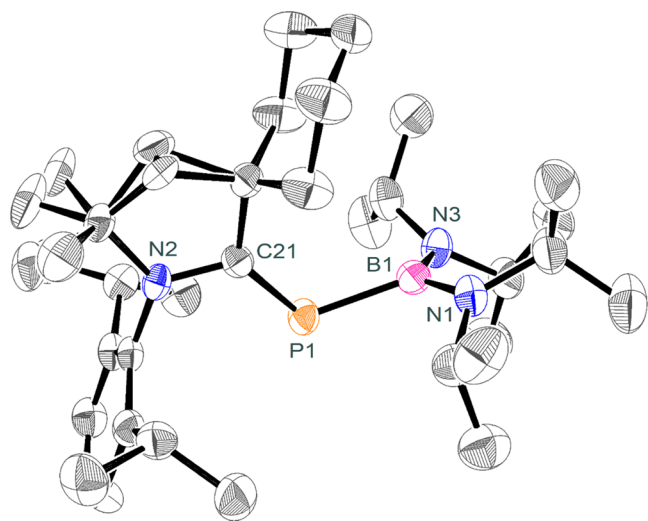


Figure 2. Molecular structure of compound **3a** [$\text{Cy-cAAC} = \text{P-B}(\text{N}^i\text{Pr}_2)_2$]. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. The positions of C22/C22A, C24/C24A, and C25/C25A (left, top, CH_2 and CMe_2 groups) are slightly disordered. Selected experimental [calculated at BP86/Def2-TZVPP] bond lengths [Å] and bond angles [$^\circ$]: C21-P1 1.731(3) [1.739], C21-N2 1.379(4) [1.378], P1-B1 1.994(4) [1.980], B1-N1 1.433(5) [1.446], B1-N3 1.445(5) [1.468], C21-P1-B1 113.88(16) [113.3], N1-B1-P1 121.5(3) [116.1], N3-B1-P1 113.9(3) [119.4], and N3-B1-N1 122.9(3) [122.6].

bent geometry with the bond angle of $114.0(2)^\circ$ (C21-P1-B1). The C21-P1 bond length in **3a** is 1.731(3) Å, which is very close to those of $\text{Cy-cAAC} = \text{P-Cl}$ ⁸ (1.735(1) Å), $(\text{Cy-cAAC})_2\text{P}_2$ (1.719(7) Å), and $(\text{Cy-cAAC})_2\text{P}_4$ (1.747(2) Å),⁶ containing a $\text{C}_{\text{carbene}} = \text{P}$ double bond. The B1-P1 distance in **3a** is 1.994(4) Å, which is significantly longer when compared with the same for $[(\text{Me}_2\text{-CAAC})\text{B}(\text{PMe}_3) = \text{B}(\text{NMe}_2)]$ (1.904(2) Å)²² and the B-P covalent bonds (1.96 Å).²⁸ The C21-N2 bond distance in the Cy-cAAC unit of **3a** is longer (1.379(4) Å) than that in $\text{Cy-cAAC} = \text{P-Cl}$ ⁸ (1.3632(18) Å), which is in between a C-N single and double bond. The molecular structures of **3b** and **3c** are similar to that of **3a** and are given in the Supporting Information (SI). **3b** [$\text{Me}_2\text{-cAAC} = \text{P-B}(\text{N}^i\text{Pr}_2)_2$] and **3c** [$\text{Et}_2\text{-cAAC} = \text{P-B}(\text{N}^i\text{Pr}_2)_2$] crystallize in the orthorhombic $P2_12_12_1$ and monoclinic $P2_1/n$ space groups, respectively, and the detailed structural descriptions are given in the SI.

Compound **5a** crystallizes in the orthorhombic space group $Pccn$, and the asymmetric unit contains one molecule of **5a** and half of a lattice n -hexane molecule (Figure 3). The Sb-atom

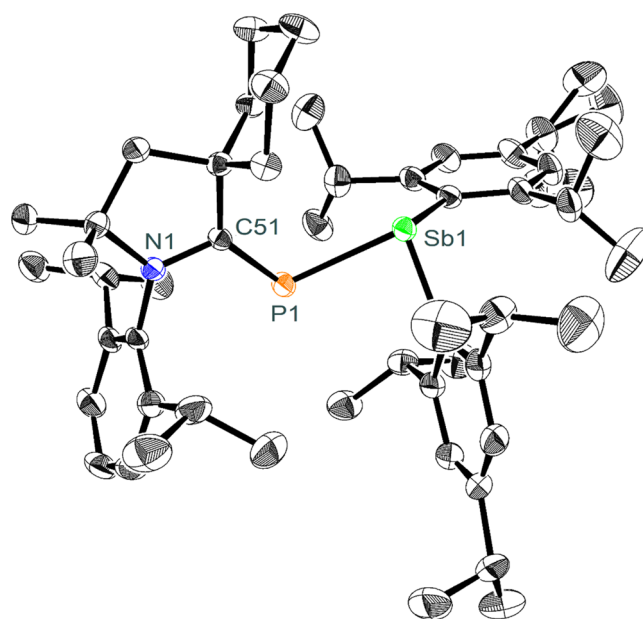


Figure 3. Molecular structure of compound **5a** [$\text{Cy-cAAC} = \text{P-Sb}(\text{Tip})_2$]. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. The solvated n -hexane molecule is shown. Selected experimental [calculated at BP86/def2-TZVPP] bond lengths [Å] and bond angles [$^\circ$]: N1-C51 1.360(3) [1.362], C51-P1 1.736(3) [1.724], P1-Sb1 2.5385(8) [2.555], N1-C51-P1 118.06(19) [117.37], and C51-P1-Sb1 107.43(9) [108.7].

adopted a distorted trigonal pyramidal geometry and bonded to one P atom and two Tip groups. The C51-P1-Sb1 bond angle is found to be $107.43(9)^\circ$. The torsion angle, N1-C51-P1-Sb1, was found to be $165.04(6)^\circ$, indicating the *anti*-orientation of the heteroatoms across the C51-P1 bond. The C51-P1 bond length is found to be 1.736(3) Å, which is longer than that of **3a** and $\text{Cy-cAAC} = \text{PK}$ (1.703(4) Å)¹⁸ but similar to $(\text{Cy-cAAC})_2\text{P}_4$ (1.747(2) Å)^{6a} and $(^i\text{PrNHC})_2\text{P}_2$ (1.7502(11) Å). The Sb1-C22 and Sb1-C55 bond lengths are found to be 2.205(3) and 2.188(3) Å, respectively, which are significantly longer than the reported Sb-C bond lengths of 2.09(3)–2.171(4) Å.²⁹ The C1-N1 bond length in **5a**

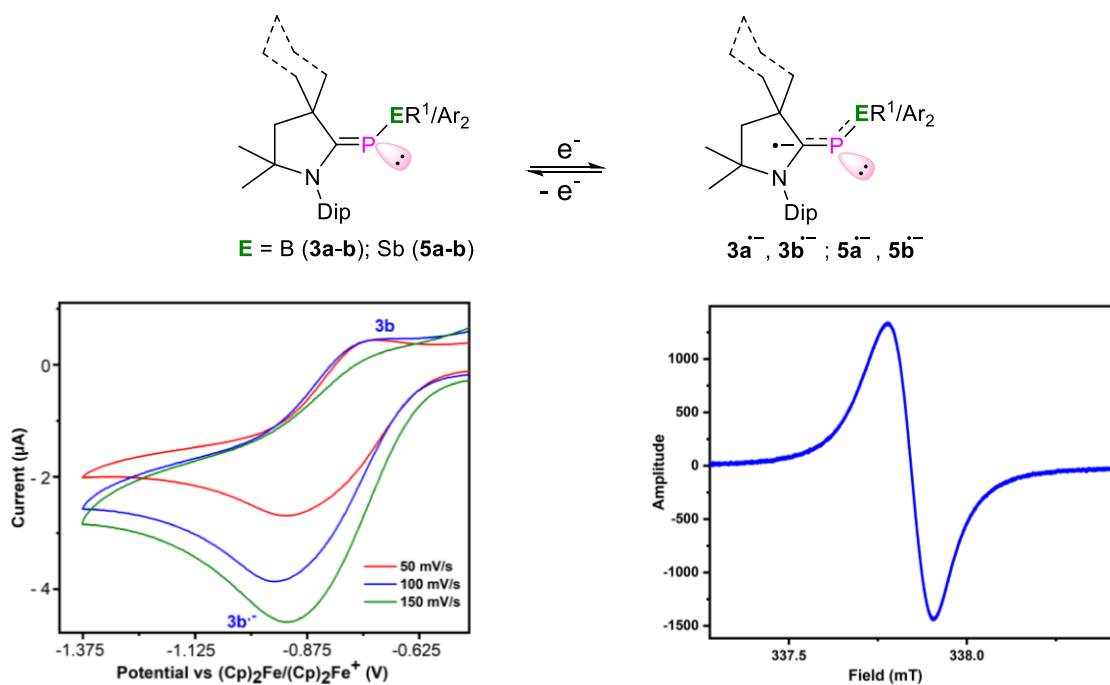
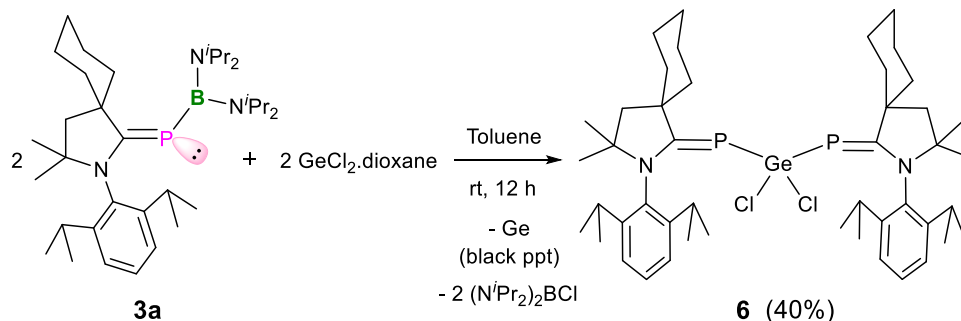


Figure 4. Left: cyclic voltammograms of $[(\text{Me}_2\text{-cAAC})\text{P}-\text{B}(\text{N}(\text{iPr})_2)_2]$ (**3b**) in THF containing 0.1 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ as the electrolyte (CE: Pt, WE: GC, RE: Ag). Right: (top) the concomitant chemical process involved; (bottom) X-band ESR spectrum of the reaction mixture containing $[(\text{Cy-cAAC})\text{P}-\text{B}(\text{N}(\text{iPr})_2)_2]$ (**3a**) and KC_8 in 1:1 molar ratio in THF at 293 K (*in situ*).

Scheme 2. Synthesis of Bis-Phosphaalkenyl Dichlorogermane $[(\text{cy-cAAC} = \text{P})_2\text{GeCl}_2]$ (**6**)



(1.360(3) Å) is found to be shorter than that of **3a**. The molecular structure of **5b** is given in the SI.

Fascinated by the bright luminescence exhibited by **3/5** under a laboratory UV lamp of wave length 254 nm, we have studied the photophysical properties in solution and solid state (see SI for details). The redox properties of **3, 5** have been studied by cyclic voltammetry (CV, see SI). The cyclic voltammograms of **3a-3b**, measured in 0.1 M THF solution of $[\text{n-Bu}_4\text{N}]\text{ClO}_4$, showed quasi-reversible one-electron processes at $E_{1/2} = -0.88$ V (**3a**) and -0.83 V (**3b**), suggesting the generation of the corresponding radical anions **3a** $^{\bullet-}$ and **3b** $^{\bullet-}$ respectively, (Figures 4 and SI), which is a characteristic feature for most of the cAAC-containing main group compounds. The calculated electron affinity values of **3a/3b** were found to be -1.35 eV/ -1.19 eV. The cyclic voltammograms of **5a/5b**, measured in 0.1 M THF solution of $[\text{n-Bu}_4\text{N}]\text{ClO}_4$, also showed a quasi-reversible one-electron process at $E_{1/2} = -1.07$ V/ -1.14 V, suggesting the generation of the corresponding radical anion **5a** $^{\bullet-}/\text{5b}^{\bullet-}$ (see SI). The natural bond orbital (NBO) analysis of the radical anion, **3a** $^{\bullet-}$ (at the BP86/def2-TZVPP level of theory), reveals that the incoming electron occupies the LUMO ($\pi^*_{\text{N}=\text{C}-\text{P}}$) of **3a** (α -

SOMO of **3a** $^{\bullet-}$, see SI). The *in situ* generation of the carbene-centered radical has been proved by the observed broad EPR resonance at $g = \sim 2$ ($g = 1.9982$) at 293 K (Figure 4, right), suggesting the coupling with other nuclei (^{11}B , ^{14}N , ^{31}P) (see SI).

Geometry optimizations of **3/5** (at the BP86/Def2-TZVPP level of theory) revealed the singlet states as the electronic ground state in all the cases. The natural bond orbital (NBO) analysis (at the BP86/def2-TZVPP level of theory) of **3a/b** infers the presence of a $\text{C}_{\text{cAAC}}=\text{P}$ bond where the σ bond is polarized toward the C_{cAAC} atom (65%) with an occupancy of 1.96 e and the π bond is polarized toward the P atom (57%) with an occupancy of 1.89 e (see SI for details). The energy decomposition analysis coupled with natural orbitals for chemical valence (EDA-NOCV) for **3a, 5a** shows that the interaction of the neutral $\text{cAAC}=\text{P}$ and $\text{B}(\text{N}(\text{iPr})_2)_2/\text{Sb}(\text{Tip})_2$ fragments in their electronic doublet states form the electron-sharing σ -bonds, depicting the best bonding description with the lowest ΔE_{orb} values (see SI).³⁰ Previously reported EDA-NOCV analyses³¹ have shown that the nature (covalent vs. dative) of the $\text{C}_{\text{cAAC}}-\text{P}$ bond can change depending upon the chemical fragment bonded to the other side of the P atom.

It is evident that the steric and electronic properties of carbene-stabilized phosphinidenes could be varied using different substituents on the phosphorus atom and also by varying the carbene fragment.^{5,32} However, the coordination properties of this class of molecules, especially with cAACs, have not been well explored. In recent past, the Lavoie,³³ Tamm,^{4c} and Dias^{13a} groups described the syntheses of the N-heterocyclic carbene-phosphinidene transition metal complexes. We explored the possibility of utilizing these compounds as cAACP[−] transfer reagents to the main group and transition metal halides, considering the presence of the potential halide abstracting Lewis acidic boron and antimony centers in **3** and **5**, respectively. Initially, we chose N-heterocyclic carbene (NHC, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)-stabilized dichlorosilylene [(NHC)SiCl₂] and dichlorogermylene [(NHC)GeCl₂] as the source of main group halides. Separate reaction mixtures of 1:1 molar ratio of **3a**, [(NHC)SiCl₂] and **3a**, [(NHC)GeCl₂] in toluene stirred for 12 h at rt did not give any new product. However, the reaction of a 1:1 molar ratio of **3a** and GeCl₂·dioxane in toluene at rt gave the bis-phosphaalkenyl dichlorogermene [(Cy-cAAC = P)₂GeCl₂] (**6**) in 40% yield after 12 h of stirring (Scheme 2). The needle-shaped orange-colored single crystals of **6** were obtained from a concentrated DCM solution kept in a −40 °C freezer. The formation of **6** can be described by the disproportionation of the Ge^{II} species to Ge^{IV} (**6**) and Ge⁰ (black ppt) along with the formation of the byproduct (NⁱPr₂)₂BCl, which was confirmed by the NMR spectroscopic analysis of the crude reaction mixture (see SI).

Compound **6** [(Cy-cAAC = P)₂GeCl₂] crystallizes in the monoclinic space group C2/c (Figure 5). The molecular structure of compound **6** consists of two Cy-cAAC units, and each Cy-cAAC unit is linked to a bent P atom with a bond angle of 110.3(2)°. Both the Cy-cAACP units are bonded to a Ge(IV) center with a pyramidal geometry containing two Cl atoms and a P-Ge-P bond angle of about Ge1 143.29(3)°, suggesting the presence of a lone pair.³⁴ The Ge–Cl unit is

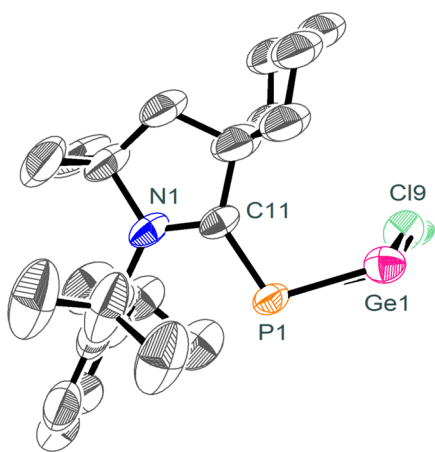


Figure 5. Crystallographic asymmetric unit of compound **6** [(Cy-cAAC = P)₂GeCl₂]. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. The positions of Ge1/Ge2 and C11/Cl9 are slightly disordered. Selected experimental [calculated at BP86/def2-TZVPP] bond lengths [Å] and bond angles [°]: N1–C11 1.338(7) [1.361], C11–P1 1.749(5) [1.750], P1–Ge1 2.302(3) [2.309], Ge1–Cl9 2.380(5) [2.246]. C11–P1–Ge1 107.1(10) [111.88], and P1–Ge1–Cl9 105.9(13) [110.84].

twisted by 91.32(7)° with respect to the Cy-cAAC plane across the P–Ge bond. Compound **6** possesses a two-fold center of symmetry passing through the Ge atom. The Ge atom of **6** exhibits a pyramidal geometry. Both the Ge–Cl bond lengths are found to be 2.38(5) Å, which is little shorter when compared with the same of that in the reported [(NHC)–GeCl₂] adduct (2.295(8) Å).³⁴ The C11–P1 bond length in **6** is found to be 1.749(5) Å (comparable with the theoretically calculated value of 1.750 Å), which is longer than the C_{carbene}–P bond of Cy-cAAC=PCl (1.735(1) Å) and (Cy-cAAC)₂P₂ (1.719(7) Å) containing a C_{carbene}=P double bond. The P1–Ge1 bond length is found to be 2.302(3) Å, which is closer to the reported value of 2.298(2) Å.³⁴

We also explored the reactivity of **3a** with AgCl. So far, there are only a very few reports of the group 11 metal ion complexes of carbene-phosphinidenes, where the NHC-phosphinidenes have been utilized as the stabilizing ligands leading to the isolation of the interesting halide-bridged octanuclear molecule {[IMes-PPh]-(AgCl)₂}₄.^{13a} However, there are no reports on cAAC-phosphinidene-stabilized Ag^I complexes known so far. Treatment of **3a** with an equivalent amount of AgCl in toluene at rt gave the cAAC-phosphinidene-stabilized neutral mixed-valence Ag^{II}/Ag^I complex **7** [(Cy-cAACP)₂Ag^IAg^{II}Cl₄]_n in 46% yield. The block-shaped, yellow-colored single crystals of **7** were from a concentrated DCM solution kept in a −20 °C freezer (Scheme 3), which were found to be stable in solid state and solution for three months under an inert atmosphere. The amorphous powder of **7** was melted at 151–153 °C. Complex **7** was found to be NMR inactive at rt and even at low temperature (−60 °C) and showed ESR signals at 293 K (Figure 6). The formation of the byproduct (Cy-cAAC)₂P₂ was confirmed by ³¹P NMR spectroscopy (58.2 ppm).³⁵

Complex **7** [(Cy-cAACP)₂Ag^IAg^{II}Cl₄]_n crystallizes in the orthorhombic space group Pnma (Figure 6). The crystallographic asymmetric unit of complex **7** consists of one Cy-cAACP[−] anion, two and half of the Ag ions, and two Cl ions. The repeating molecular unit of complex **7** (see SI) possesses two Cy-cAACP[−] units, each containing a μ₃-P[−] ion, two terminal AgCl units with two coordinate Ag^I ions (Ag3), two bridging AgCl units (Ag2) with two μ-bridging Cl[−] ions (Ag2ⁱⁱ–Cl2–Ag2 89.82(8)° and Ag2ⁱⁱ–Cl1–Ag2 95.63(7)°), and one paramagnetic Ag^{II} ion (Ag1; Figure 6), which is bridged between two Cy-cAACP[−] ions (P1–Ag1–P1ⁱ 180.00(6)°). There is a center of inversion within this repeating unit of **7** passing through the Ag1 center (Ag^{II}, S = 1/2). The 1D chain of [(Cy-cAACP)₂Ag^IAg^{II}Cl₄]_n has been propagated in a zig-zag fashion along the *a*-axis (Figure 6, bottom). The experimental bond parameters revealed the phosphinidene nature of the cAACP unit with a C_{carbene}–N bond length of 1.326(8) Å, featuring a nearly C=N bond, and the C_{carbene}–P bond length of 1.763(5) Å, featuring a coordinate bond. The packing diagram of **7** along the *b*- and *c*-axes is shown in the SI.

The paramagnetic nature of **7** is confirmed by ESR measurements, which suggests that the unpaired electron couples with two ¹⁴N (*I* = 1) and ³¹P (*I* = 1/2) nuclei leading to multiple hyperfine lines (Figure 7).

CONCLUSIONS

In summary, we have demonstrated the facile syntheses and characterizations of five redox active, luminescent cAAC-stabilized boryl- and stibanyl-phosphaalkenes (**3a-c**, **5a-b**) in

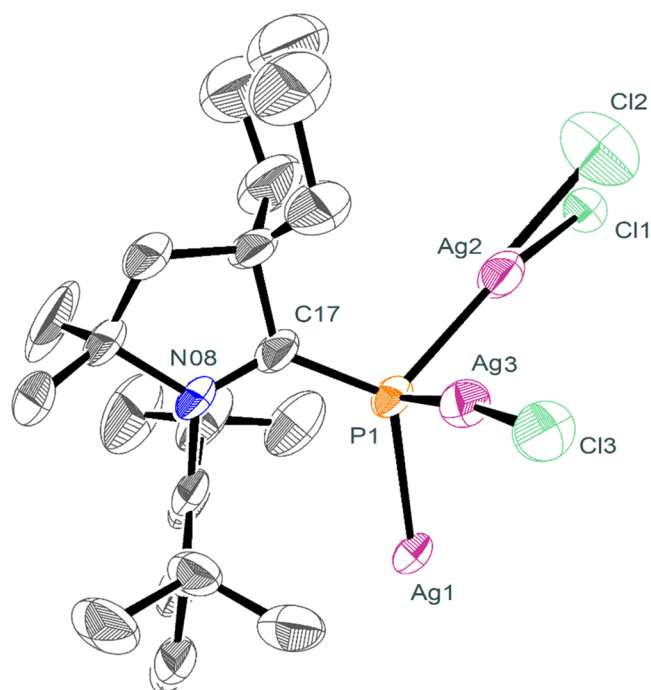
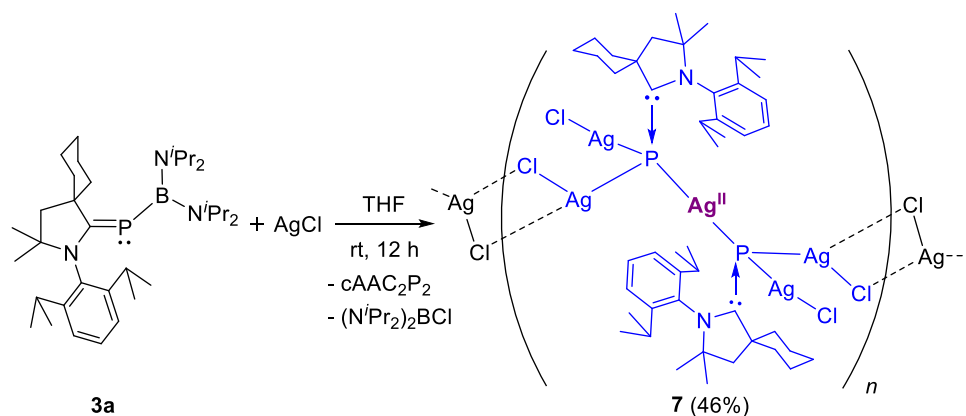
Scheme 3. Synthesis of cAAC-Stabilized Mixed-Valence Ag^{II}/Ag^I-Phosphinidenide [(Cy-cAACP)₂Ag₄Ag^ICl₄]_n (7)

Figure 6. Crystallographic asymmetric unit of complex 7. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected experimental bond lengths [Å] and bond angles [°]: N8–C17 1.325(8), C17–P1 1.763(5), Ag1–P1 2.3835(13), Ag1–P1ⁱ 2.3836(13), Ag3–Ag2 3.2814(8), Ag3–P1 2.3749(15), Ag3–Cl3, 2.3716(16), Ag2–Cl1 2.5219(13), Ag2–P1 2.3754(15), Ag2–Cl2 2.6470(18), P1–C17 1.763(5), N08–C17 1.325(8), N08–C4 1.460(8), N08–C13 1.524(7); P1–Ag1–P1ⁱ 180.00(6), Ag2ⁱⁱ–Cl2–Ag2 89.82(8), Ag2ⁱⁱ–Cl1–Ag2 95.63(7), Ag3–P1–Ag1 102.14(5), Ag3–P1–Ag2 87.38(5), and Ag2–P1–Ag1 122.28(5).

the solid state. The photophysical properties of compounds 3–5 have been investigated. Cyclic voltammetry studies of compounds 3–5 have suggested the *in situ* generation of the corresponding radical anions in solution, which has been proved experimentally by the observed EPR signal of the diluted reaction mixture of 3a in the presence of KCl₈. Upon exploring the reactivity of compounds 3/5 toward GeCl₂-dioxane and AgCl, 3a gave the bis-phosphaalkenyl dichloro-germane (6) and a neutral polymeric mixed-valence Ag^I/Ag^{II} phosphinidenide complex (7), respectively. Theoretical inves-

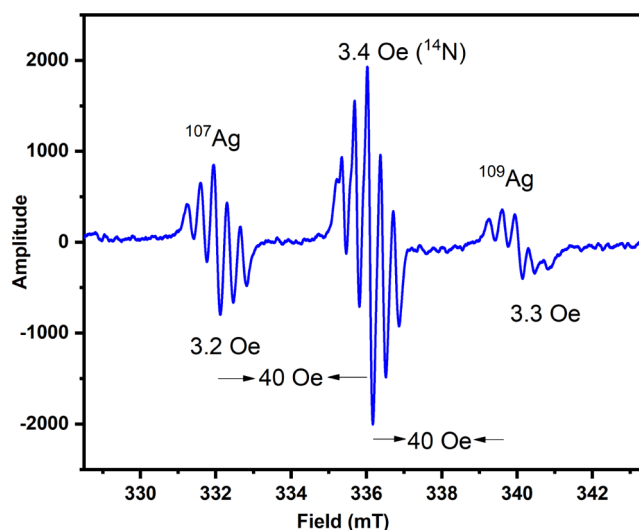


Figure 7. X-Band ESR spectrum of the complex 7³⁶ [(Cy-cAACP)₂Ag₄Ag^ICl₄]_n in the DCM solution at 293 K.

tigations revealed polar C_{cAAC}=P bonds in compounds 3–5, featuring the phosphalkene nature. However, experimental and theoretical bond parameters revealed donor- and acceptor-type bonds between the C_{cAAC} and P atoms in 6, 7.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01132>.

Experimental details, UV–vis, fluorescence, ESR and NMR spectra, HRMS data, crystallographic data, computational details, and optimized coordinates (PDF)

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CCDC 2079353–2079355, 2104745, 2130611, 2163309, and 2163339 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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