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Isolation of (Aryl)-(Imino) Phosphide, and (Aryl)-(Phosphaalkene) Amide Complexes of Alkali Metals from Carbene-Phosphinidenes under Reductive-Thermal Rearrangements

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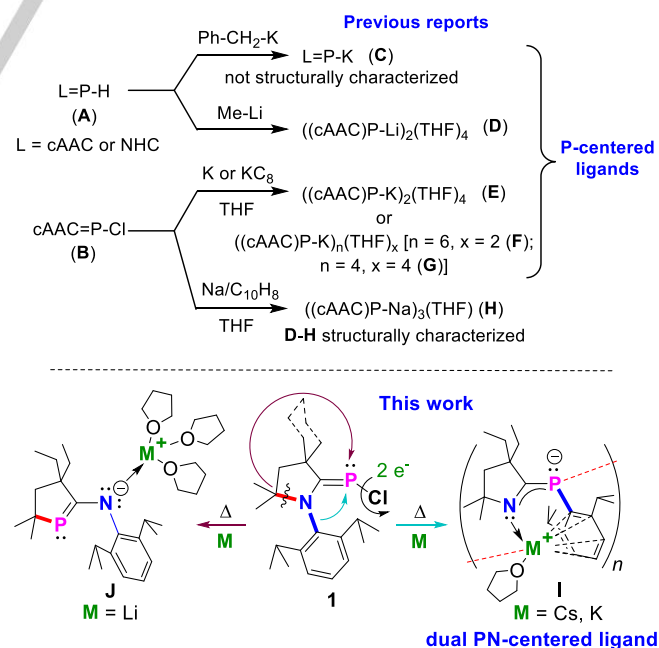
Abstract: Two-electron reduction of cyclic alkyl(amino) carbene (cAAC)-supported chloro-phosphinidene cAAC=P-Cl (**1**) followed by unprecedented thermal rearrangements afforded the alkali metal complexes of (aryl)-(cyclic alkyl(imino)) phosphides (**3a-3c**, **4a-4b**) via migration of the dipp group (dipp = 2,6-diisopropylphenyl) from N to the P center; and (aryl)-(cyclic alkyl(phosphaalkene)) amide (**5**) via the cleavage of the CMe₂-N bond followed by energetically favored 5-*exo-tet* ring-closure in presence of the alkali metals Cs (**3a-3c**), K (**4a**, **4b**), and Li (**5**), respectively. **3a** was found to be photoluminescent (PL), emitting bright orange light under a long UV lamp (365 nm) with PL quantum yield (Φ_{PL}) of 2.6% (λ_{em} = 600 nm), and an average lifetime (τ) of 4.8 μs . Reaction of **3a** with CuCl, and AgOTf afforded the (aryl)-(cyclic alkyl(imino)) phosphide-stabilized tetra-nuclear Cu(I) (**6**), and octa-nuclear Ag(I) (**7**) clusters, respectively. Moreover, the complexes **3a-3c** provided a direct route for the stabilization of cyclic alkyl(aminoboryl) phosphaalkenes **8a-8c** when treated with 1-bromo-N,N,N',N'-tetraisopropylboranediamine.

Introduction

Phosphinidenes (R-P) are the reactive group 15 analogs of carbenes with two lone pairs of electrons on the phosphorus atom, which have been initially stabilized under the coordination sphere of transition metals.^[1] Later on, carbenes [N-heterocyclic carbenes (NHCs); cyclic alkyl(amino) carbenes (cAACs)], and carbene-anchored silylenes have been successfully employed for the solid state isolation of the corresponding phosphinidene adducts.^[2,3] The donor-base (L)-stabilized parent-phosphinidenes L=P-H (**A**) have been synthesized either by the reduction of the bis-phosphorus compound L=P-P=L (L = NHC)^[4] or by treating the imidazolium salt with heptaphosphides Na₃P₇, and (Me₃Si)₃P₇^[5] in presence of a strong base. The zwitterionic half-parent phosphasilene LSi=PH [L = CH((C=CH₂)CMe(NAr)₂); Ar = 2,6-diisopropylphenyl] has been synthesized from LSi(IV)Br₂.^[6] Replacement of the hydrogen from the parent phosphinidene L=P-H with a phenyl group^[7] or chlorine^[8] afforded phenyl-, and chloro-phosphinidenes, respectively, which are useful synthons for the isolation of various functionalized phosphinidene derivatives. De-protonation of L=P-H (**A**, L = NHC, cAAC) using strong bases^[9] or reductive de-halogenation of carbene-chloro-phosphinidenes L=P-Cl (L = cAAC) (**B**)^[10] afforded the corresponding carbene-supported metal-phosphinidenides **C-G** (Scheme 1). In 2022 Liu group reported the synthesis of base-stabilized cyano-phosphinidenes,

and their reduction to the corresponding alkali metal phosphinidenide using KC₈.^[11] Recently, it has been shown that the alkali metal phosphinidenides (**E-G**) can be utilized as the source of carbene-supported mono-anionic phosphorus; an excellent ligand with three available lone pairs of electrons on the P atom, and thereby capable of μ_3 -P type coordination to the metal centers (Scheme 1).^[12]

Herein, we report on the alkali metal-mediated reductive dehalogenation of carbene-chloro-phosphinidenes (**1**), followed by unprecedented thermal rearrangements^[13] leading to either thermodynamically favored migration of the dipp group (dipp = 2,6-diisopropylphenyl)^[14] from the N to the P center of **1** (**I**) or the cleavage of the CMe₂-N bond of the five-membered ring of cAAC ligand in **1**, and the subsequent ring-closure in presence of the *in situ* generated P⁻ to form a new five-membered ring containing the divalent phosphorus as the heteroatom (**J**), generating the alkali metal complexes of (aryl)-(cyclic alkyl(imino)) phosphides (**3a-3c**, **4a-4b**), and (aryl)-(cyclic alkyl(phosphaalkene)) amide (**5**) (Scheme 1, aryl = dipp group).



Scheme 1. Top: Reported synthetic routes for generation of metal-phosphinidenides. Bottom: Schematic representation of the present work showing reductive-thermal rearrangements of **1** in presence of alkali metals (M = Cs, K, Li).

Results and Discussion

Cyclic voltammetry (CV) studies of the cyclic alkyl(amino) carbene (cAAC)-stabilized chloro-phosphinidene $\text{Et}_2\text{-cAAC=P-Cl}$ (**1a**) [$\text{Et}_2\text{-cAAC} = \text{:C(N-2,6-Pr}_2\text{C}_6\text{H}_3)(\text{C}_5\text{H}_{10})(\text{CMe}_2)(\text{CH}_2)$] [8] in 0.1 M solution of the electrolyte [$n\text{-Bu}_4\text{N}(\text{PF}_6)$] in THF showed one electron quasi-reversible reduction at -3.56 V, suggesting the *in situ* generation of the corresponding radical anion intermediate **1a⁻** (see SI), which was later on proved by the electron spin resonance (ESR) studies of the dark red color reaction mixture containing a 1:2.1 molar ratio of compound **1a**, and K metal in THF at 293 K (Figure 1). The X-band ESR spectrum suggests that the unpaired electron of **1a⁻** couples with the P (^{31}P ; $I = 1/2$; $a = 17.8$ G), and Cl ($^{35/37}\text{Cl}$; $I = 3/2$; $a = 4.2$ G) nuclei ($\text{P}\cdots\text{Cl}^-$) producing eight hyperfine lines ($a =$ hyperfine coupling constant).

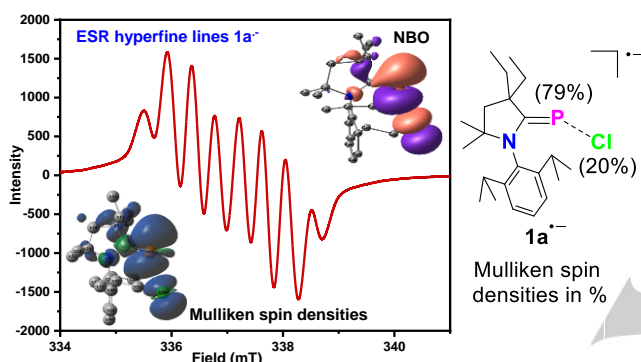
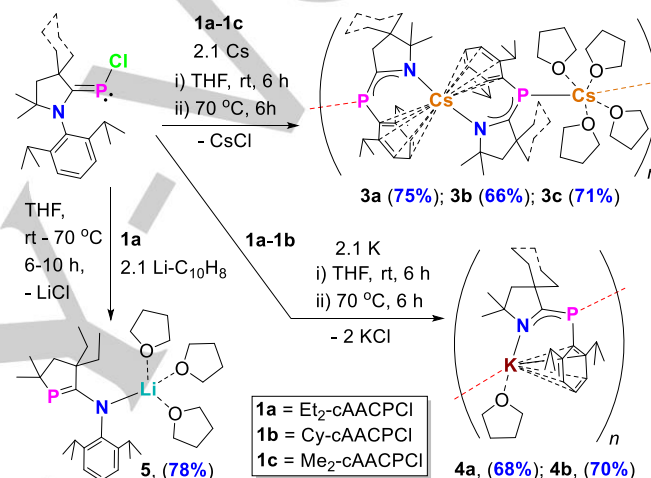


Figure 1. X-band ESR spectrum of the reaction mixture containing **1a**, and K in 1:2.1 molar ratio in THF at 293 K, indicating *in situ* generation of the radical anion **1a⁻**. $g = 1.9971$, $a(^{31}\text{P}; I = 1/2) = 17.8$ G and $a(^{35/37}\text{Cl}; I = 3/2) = 4.2$ G; Inset: SOMO of **1a⁻** (0.15 eV, calculated at BP86/def2-TZVPP level of theory).

The bright yellow THF solution of one equiv of $\text{Et}_2\text{-cAAC=P-Cl}$ (**1a**) was added to 2.1 equiv of the Cs metal at room temperature (rt), and stirred for 6 h until the color of the reaction mixture changed to reddish-brown. Afterwards, the temperature of the reaction mixture was raised to 70 °C, and stirred for another 6 h until the color changed from reddish-brown to bright orange. The reaction mixture was then filtered, and the filtrate was concentrated up to 1-2 mL under a reduced pressure. The orange-red colored concentrated THF solution was kept at -40 °C in a freezer for 2-3 days to obtain the light-orange block shaped, air and moisture sensitive single crystals of a polymeric chain of the Cs-complex $[\text{((Et}_2\text{-cAl)P(dipp))}_2\text{Cs}_2(\text{THF})_4]_n$ (**3a**) in 75% yield (Scheme 2). The ^{31}P NMR spectrum of the THF- d_8 solution of pure crystals of **3a** showed a sharp singlet at -55.5 ppm (See SI), which is much upfield shifted when compared to those of **1a** [+160.3 (phosphinidene), and +131.0 (phosphaalkene) ppm],^[8] dimeric Li-phosphinidene $[\text{cAACPLi}(\text{THF})_2]_2$ (+177.3 ppm),^[9c] and the tetrameric K-phosphinidene (+207.3 ppm),^[10] indicating the phosphide (P^-) nature of the P atoms in **3a** (Scheme 2). X-ray single-crystal diffraction of **3a** revealed that the dipp group (dipp = 2,6-diisopropylphenyl) has migrated from N to the P atom along with the elimination of Cl atom, resulting in a formal divalent mono-anionic P centre with longer C-P bond lengths of 1.779(2)/1.775(2) Å; and shorter $\text{C}_{\text{cAAC}}\text{-N}$ bond lengths of

1.313(3)/1.301(3) Å, which are comparable with those of a P-C electron sharing σ bond, and an imine (C=N) bond, respectively [for **1a**: C-P = 1.615(4), and C-N = 1.363(18) Å, representing a C=P double bond, and a C-N single bond, respectively;^[8] for $\text{((Me}_2\text{-cAAC)P-K)}_4(\text{THF})_4$: C-P = 1.703(3),^[10] C-N = 1.402(3) Å, representing a donor-acceptor type C=P double bond, and a C-N single bond, respectively]. **3a** possesses a 1D-chain like polymeric structure. Under similar reaction conditions, when K metal was employed instead of Cs, the air and moisture sensitive yellow blocks of the polymeric 1D-chains of the corresponding K-complexes $[\text{((Et}_2\text{-cAl)P(dipp))K}(\text{THF})]_n$ (**4a**), and $[\text{((Cy-cAl)P(dipp))K}(\text{THF})]_n$ (**4b**) stabilized by the rearranged phosphinidene, i.e., the (aryl) (cyclic alkyl(imino)) phosphide ligand $[(\text{Ar})(\text{cAl)P}^-]$ (Ar = dipp) were obtained in 68-70% yields, respectively (Scheme 2).

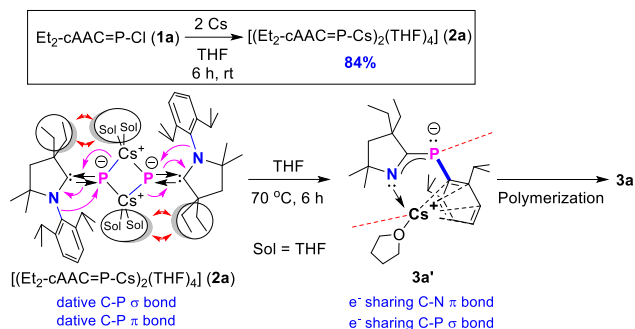


Scheme 2. Syntheses of (aryl) (cyclic alkyl(imino)) phosphide complexes of alkali metals (Cs: **3a-3c**; K: **4a-4b**; Li: **5**).

The ^{31}P NMR spectrum of the THF- d_8 solutions of **4a-4b** showed sharp singlets at -56.3, and -62.1 ppm, respectively (See SI), which are comparable with that of **3a**. The ^{13}C NMR spectra of **3a**, and **4a** showed a doublet corresponding to C_{CP} atom at 199.2 ($J_{\text{C-P}} = 73.7$ Hz), and 201 ($J_{\text{C-P}} = 75.7$ Hz) ppm, respectively, which are found to be slightly upfield shifted when compared to that of the chloro-phosphinidene **1a** (208.2 ppm, $J_{\text{C-P}} = 102.6$ Hz),^[8] and comparable with that of $\text{((Me}_2\text{-cAAC)P-K)}_4(\text{THF})_4$ (202.9 ppm, $J_{\text{C-P}} = 81.9$ Hz).^[10] To have a deeper insight into the reaction mechanism, we crystallized the reaction mixture containing a 1:2.1 molar ratio of **1a**, and Cs metal after 6 h of initial stirring at rt, when the first color change took place from yellow to dark brownish-red. The concentrated THF solution kept at -40 °C in a freezer afforded the dark red blocks of the dimeric Cs-phosphinidene $[\text{((Et}_2\text{-cAAC=P)}_2\text{Cs}_2(\text{THF})_4]$ (**2a**) in 84% yield after 4-5 days (Scheme 3, top).

The ^{31}P NMR spectrum of the THF- d_8 solution of dark red crystals of **2a** exhibited a sharp singlet at +233.8 ppm (See SI), which is downfield shifted when compared to that of **3a** (-55.5 ppm). The ^{13}C NMR spectrum of **2a** showed a doublet corresponding to C_{cAAC} at 203.8 ppm ($J_{\text{C-P}} = 86.0$ Hz), which is slightly downfield shifted when compared to that of **3a**. Next, the isolated pure crystals of **2a** were dissolved in THF and heated to

70 °C for 6 h, which led to a color change of the reaction solution from brownish-red to bright-orange, which was then concentrated under reduced pressure, and kept for crystallization at -40 °C, which led to the formation of the orange color single crystals of the rearranged Cs-complex **3a**. The monomeric unit of complex **3a** is represented as **3a'** in Scheme 3, bottom for simplicity.



Scheme 3. Synthesis of cAAC-supported dimeric Cs-phosphinidenide $[(Et_2cAAC=P)_2Cs_2(THF)_4]$ (**2a**), and its rearrangement to the monomeric unit **3a'** of the complex **3a**.

Interestingly, when one equiv of the chloro-phosphinidene **1a** was treated with freshly prepared dark green colored THF solution of Li/Naphthalenide (Li-C₁₀H₈) at rt to 70 °C for 6-10 h, the air and moisture sensitive reddish-orange block shaped crystals of monomeric complex $[(dipp)(cAPA)N]Li(THF)_3$ (**5**) stabilized by (aryl) (cyclic alkyl(phosphaalkene)) amide ligand $[(Ar)(cAPA)N^-]$ (aryl = dipp) were obtained in 78% yield (Scheme 2). The ³¹P NMR spectrum of the THF-*d*₆ solution of **5** showed a sharp singlet at -31.7 ppm (See SI), which is much upfield shifted when compared to that of $[cAACPLi(THF)_2]_2$ (+177.3 ppm),^[9c] and also to that of **1a** (+160.3/+131.0 ppm),^[8] but downfield shifted when compared to those obtained for complexes **2a-4a**. This observation indicates a comparatively lower electron density at the P centre in **5**, which is not coordinated to the Li metal. The ⁷Li NMR spectrum of **5** showed a singlet at 0.4 ppm. The single-crystal X-ray diffraction of **5** revealed that the C-P bond length is 1.7538(15) Å, which is longer than that of the reported dimeric complex $[cAACPLi(THF)_2]_2$ (1.7036(12) Å),^[9c] but shorter when compared to those of the reported oligomeric K-phosphinidenides (average C-P bond length = 1.78 Å).^[10] The C-N bond length in **5** is found to be 1.3327(19) Å, which is longer when compared to those observed in complexes **2a-4a** (average C-N bond length = 1.31 Å), but shorter than that of $[cAACPLi(THF)_2]_2$ (1.3955(14) Å).^[9c]

From the above observations, we proposed that upon generation **2a** by two-electron reduction of the chloro-phosphinidene **1a** in the presence of comparatively more electropositive (and softer) alkali metal Cs, the excess electron density on the P atom of the carbene-phosphinidenide, $cAACP^-$ anion (**A**) drives the migration of the dipp group from the sp³ N to the P centre, resulting in the formation of a divalent N with sp² hybridization, keeping one of the p orbitals available for the extended delocalization of the negative charge from P to C_{cAAC} to the N centres, thus affording the aryl (cyclic alkyl(imino)) phosphide anion $[(dipp)(cAl)P^-]$ **B** (Figure 2). On the other hand, in presence of a harder alkali metal Li, the demand for a harder

donor atom of the ligand led to the cleavage of the CMe₂-N bond of the initially generated carbene-phosphinidenide anion **A**, followed by the energetically favoured 5-*exo-tet* ring-closure. This led to the isolation of the (aryl)-(cyclic alkyl(phosphaalkene)) amide $[(Ar)(cAPA)N^-]$ **C** (aryl = dipp) with a newly formed five-membered ring consisting of the heteroatom P (Figure 2). To have a better understanding of the electron densities distribution in various canonical forms of the rearranged anions **B** and **C** (Figure 3) of the complexes **4a-4b**, **5**, respectively; we have performed NBO analysis at BP86-D3(BJ)/def2-TZVPP//BP86-D3(BJ)/def2-TZVPP level of theory (see SI). The NBO results revealed that in **B** with the dipp group migrated from the N to the P atom, the C_{cAAC}-P bond is an electron-sharing σ bond with Wiberg bond index (WBI) of 1.24. The two-coordinate P atom has a lone pair of electrons with 64% of s-character and 36% of π -character, located mostly on the P atom with a slight polarization towards the C_{cAAC}, the overall negative charge on the species is delocalized through the p orbitals of the P-C-N backbone with a major contribution from the N atom (HOMO-5; see SI).

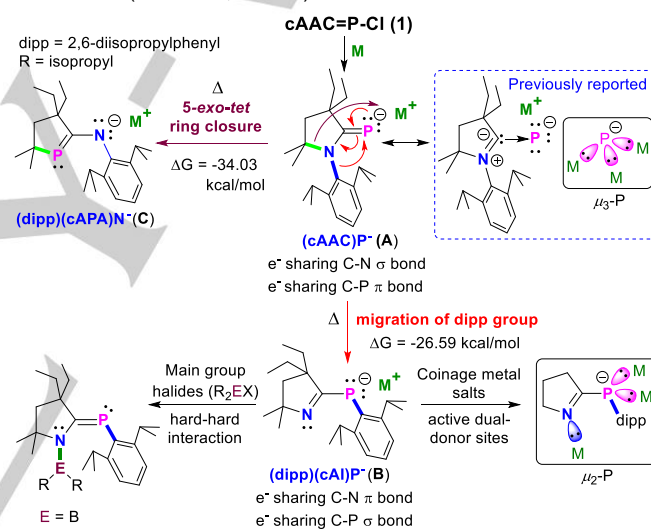


Figure 2. Synthetic routes for generation of (aryl) (cyclic alkyl(imino)) phosphide $[(Ar)(cAl)P^-]$ (**B**), and (aryl) (cyclic alkyl(phosphaalkene)) amide $[(Ar)(cAPA)N^-]$ (**C**). ΔG^{298K} values are calculated at BP86/def2-tzvpp level of theory. Ar = dipp group.

The HOMO-4 of **B** indicates the π type bond between N and C_{cAAC}, which is slightly extended towards the lone pair on P atom. HOMO-17 features the σ type bond between the P and C_{cAAC} atoms (see SI).

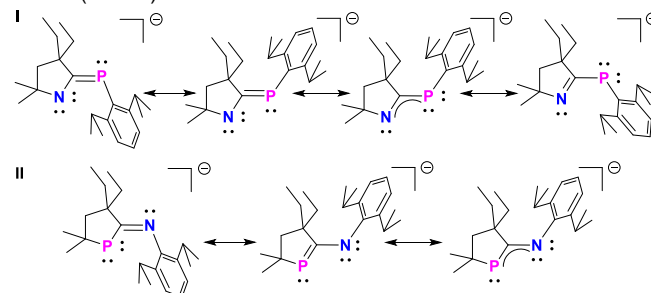
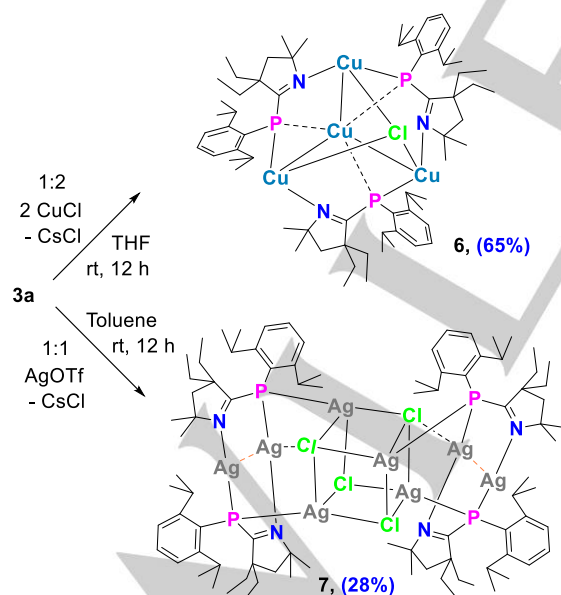


Figure 3. (I): Canonical structures of the dipp group migrated anionic part of complex **3a** (denoted as anion **B**). (II): Canonical structures of the rearranged anionic part of complex **5** (denoted as anion **C**).

The anion **C** (Figure 2) is also found to have a similar type of electron densities distribution with the dipp group attached to the N atom (see SI). In this case, the HOMO-4 represents the σ type bond between P and C_{cAAC}. HOMO-5 shows a delocalization of the electron density over the P-C-N backbone. HOMO-10 features the σ type bond between P, and C centre. All the above observations suggest the presence of P=C_{carbene}, and C_{carbene}=N partial double bonds in anions **B-C**. This is also supported by the respective WBI values (see SI). The calculated proton affinity values of the anions **A-C** were found to be +368, +342, and +335 kcal/mol, which are approximately 57-90 kcal/mol lower than that of ⁿBu-Li (425 kcal/mol, see SI).

The complexes **3a-3c**, **4a**, and **5** have been structurally characterized by single-crystal X-ray diffraction (Figures 4-6). Corroborated by the NBO analysis, we envisioned that the anion **B** once generated in the form of complex **3**, could be efficiently exploited as a ligand with dual donor sites, i.e., the Lewis basic N and the P centres, thereby capable of reacting with both hard Lewis acidic main group halides, and soft coinage metals salts (Figure 2). Accordingly, we conducted the reactivity studies of complex **3a** in presence of various coinage metal salts and a dialkylboroborane (Schemes 4, 5).

A 1:2 molar ratio of the pure crystals of complex $[(Et_2-cAl)P(dipp)]_2Cs_2(THF)_4$ (**3a**), and CuCl in THF was stirred overnight at rt. The color of the reaction mixture was changed from reddish-brown to golden yellow. Afterwards, the reaction mixture was filtered to remove the insoluble salt CsCl, and the filtrate was concentrated up to 1-2 mL under reduced pressure. The resulting concentrated filtrate was stored in a freezer at -40 °C for 2-3 days to obtain the golden yellow rod-shaped crystals of tetrameric Cu(I)₄ cluster $[(Et_2-cAl)P(dipp)]_3Cu_4Cl$ (**6**) in 65% yield (Scheme 4).

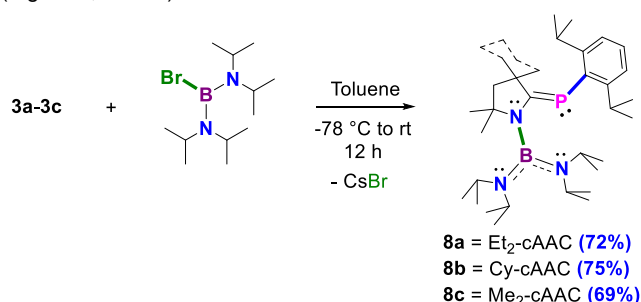


Scheme 4. Syntheses of Cu(I)₄ (**6**), and Ag(I)₈ (**7**) clusters.

Similarly, the reaction of a 1:1 molar ratio of **3a** with AgOTf in toluene at rt for 12 h afforded colorless block shaped crystals of Ag(I)-cluster $[(Et_2-cAl)P(dipp)]_4Ag_8Cl_4$ (**7**) with Ag(I)₈ core in 28% yield upon extraction and crystallization in DCM (Scheme

4). We assumed that the incorporation of the Cl atoms in the **7** takes place via the activation of the C-Cl bonds of DCM. Both **6**, and **7** were found to be air and moisture sensitive. However, the crystals of **6**, **7** were found to be stable under an inert atmosphere for more than 6 months at rt. **6**, and **7** were found to be soluble in polar organic solvents, e.g., THF, DCM, etc. and the respective solutions were also found to be stable under an inert atmosphere for more than one month at rt. Both the complexes have been thoroughly characterized by NMR, ESI-MS, and single-crystal X-ray diffraction (Figures 7, 8; see SI). The ³¹P NMR spectra of DCM-*d*₂ solutions of pure crystals of **6**, and **7** exhibited a singlet at -66.2, and a triplet at -87 (*J*_{P-Ag} = 468.1 Hz) ppm (See SI), respectively, which is slightly upfield shifted when compared to that of **3a** (-55.5 ppm).

Complexes **3a-3c** reacted with (NⁱPr)₂B-Br in a 1:1 molar ratio using toluene as solvent at -78 °C to rt for 12 h to produce the corresponding cyclic alkyl(aminoboryl) phosphalkenes ((R₂-cAl)P(dipp)B(NⁱPr)₂ [R₂ = Et₂ (**8a**) Cy (**8b**), Me₂ (**8c**)] in 69 to 75% yield (Scheme 5). The ³¹P NMR spectra of C₆D₆ solutions of pure crystals of **8a-8c** exhibited singlets at 35.1, 43.1, and 41.7 ppm (See SI), respectively, which are very much downfield shifted when compared to those of the Cs-complexes **3a-3c** (-55.5, -60.9, and -63.3 ppm, respectively); and upfield shifted when compared to that of the chloro-phosphinidenes **1a-1c**;^[8] and Cy-cAAC-phenyl-phosphinidene (Cy-cAAC)P-Ph^[7] (68.9 ppm). The ¹¹B NMR spectra of C₆D₆ solutions of **8a-8c** exhibited singlets at 29.8, 24.2, and 29.6 ppm (See SI), respectively, which are upfield shifted when compared to those of the previously reported boryl-phosphalkenes [cAAC=P-B(NⁱPr)₂]₂ (40.8-42.1 ppm).^[15] The ¹³C NMR spectra of C₆D₆ solutions of **8a-8c** exhibited doublets corresponding to C_{cAAC} at 206.3 (*J*_{C-P} = 64.64 Hz), 204.7 (*J*_{C-P} = 60.6 Hz), and 205.5 (*J*_{C-P} = 60.6 Hz) ppm (See SI), respectively, which are upfield shifted when compared to those of the chloro-phosphinidenes **1a-1c** (208.2 (**1a**); 210.0 (**1b**), and 210.9 (**1c**) ppm, respectively),^[8] and upfield shifted when compared to that of (Cy-cAAC)P-Ph (208.1 ppm).^[7] Compounds **8a-8c** have also been structurally characterized by ESI-MS, and the single-crystal X-ray diffraction (Figure 8, see SI).



Scheme 5. Syntheses of cyclic alkyl(aminoboryl) phosphalkenes **8a-8c** from complexes **3a-3c**.

X-ray single-crystal diffraction revealed that **2a** [(Cy-cAAC-P)₂Cs₂(THF)₄] crystallizes in the monoclinic crystal system, and *P*₂/*1*/*n* space group (see SI). The asymmetric unit of **2a** possesses two anionic units of Et₂-cAACP⁻, two Cs⁺ ions, and two terminal THF molecules. Both the monoanionic phosphorus atoms P⁻ of Et₂-cAACP⁻ are bridged together by two Cs⁺ ions,

thus creating a planar four-membered ring, P_2Cs_2 . The P_2Cs_2 core is further strengthened by the coordination of four terminal THF molecules. The P1–Cs1 and P1–Cs1' bond distances are found to be 3.5286(5) and 3.6497(5) Å, respectively, which are much longer than the P–Li bond distances of 2.562(2)/2.563(2) Å in $[(Me_2cAAC=P)Li(THF)_2]_2^{[10]}$ as expected. The P–Cs–P and Cs–P–Cs bond angles are found to be 84.933(10)°, and 95.067(10)°, respectively. The P atom of the $Et_2cAAC=P^-$ unit possesses a trigonal pyramidal geometry and coordinated to two Cs^+ ions. The bond distance of P– C_{cAAC} is 1.7068(17) Å, which is comparable to that of $[(cAAC=P)Li(THF)_2]_2$ (1.7042(12) Å), and the alkali metal-phosphinidenides reported by our group (1.702(3), 1.703(4) Å).^[10] **2a** possess an inversion centre, glide plane and the 2-fold screw axis of symmetry.

3a, and **4a** crystallize in triclinic $P-1$ and orthorhombic $P2_12_12_1$ space groups, respectively (Figure 4).

3a possesses a one-dimensional polymeric 1D-chain having an asymmetric unit consisting of two anionic units of $Et_2cAACP(dipp)^-$, two Cs^+ , and THF molecules. The three-coordinated P atom of the anionic unit is having a trigonal planar geometry (the sum of the bond angles is close to 360°), which is bonded to the C_{Et_2cAAC} , and C atom of the dipp group, and further coordinated to the Cs^+ ion. Each Cs^+ ion coordinated to P atom in the asymmetric unit of **3a** is having an occupancy of 0.5. The Cs1–P1 bond distance (3.6753(6) Å) is found to be longer than that of **2a** (3.5286(6) Å), whereas the P2–Cs3 bond length (3.5486(6) Å) is found to be comparable to that of **2a**.

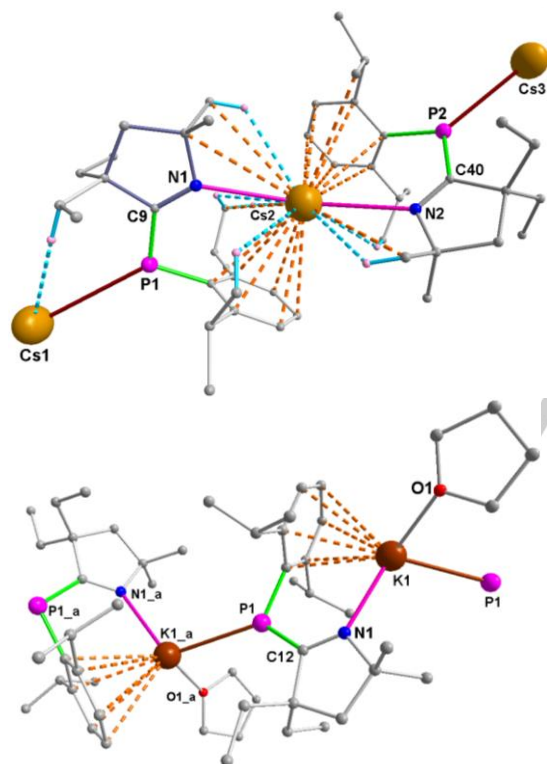


Figure 4. Asymmetric unit of complexes **3a** (top), and **4a** (bottom). Hydrogen atoms, and disordered moieties are omitted for clarity. Cs1 and Cs3 have 0.5 occupancies each. Selected bond lengths [Å], and bond angles [°]: **3a** (4 THF molecules were omitted from Cs1/Cs3 atoms); Selected bond distances [Å], and bond angles [°]: Cs1–P1 3.6753(6), P1–C9 1.779(2), N1–C9 1.313(3), Cs2–N1 3.1423(19), Cs2–N2 3.1777(18), N2–C40 1.301(3), P2–C40 1.775(2),

Cs3–P2 3.5486(6); C9–P1–Cs1 123.97(7), N1–C9–P1 128.46(17), N2–C40–P2 128.10(16), C40–P2–Cs3 128.12(7). **4a**; Selected bond lengths [Å], and bond angles [°]: P1–C12 1.791(4), N1–C12 1.309(5), K1–P1 3.2166(18), K1–N1 2.734(3); C12–P1–K1 126.97(12), N1–C12–P1 127.6(3), N1–K1–P1 112.02(8).

Both Cs1 and Cs3 are coordinated to four THF molecules from equatorial side, and the two axial sites are coordinated by P atoms to form the polymeric 1D-chain. The central Cs ion (Cs2) is sandwiched by the phenyl rings of the two dipp groups in η^6 fashion, and further coordinated by the five-membered ring nitrogen atoms N1, and N2. Additionally, one of the H_{CH_3} atoms of the CM_{e_2} group of five-membered rings are seen to have an interaction (3.212–3.440 Å) with the Cs2 ion. The bond length of C9–P1 is 1.779(2) Å, which is significantly elongated than that of **1a**,^[8] and can be attributed to an electron-sharing P–C single bond. A significant shortening of the N2–C40 bond (1.301(3) Å) is also observed in complex **3a** when compared to that of **2a** (1.401(2) Å) (see SI).

The repeating unit of 1D-chain of **4a** consists of one (aryl)-cyclic alkyl(imino)phosphide anion $[(Ar)(cAl)P^-]$ (Ar = dipp), one K^+ ion, and coordinated one THF molecule (Figure 4, bottom). The C12 atom (C_{cAAC}) of the $[(Ar)(cAl)P^-]$ unit is in trigonal planar geometry with an angular sum of 360°. The P1–C12 bond distance is 1.791(4) Å, which is similar to the reported $cAAC \rightarrow P^-$ dative bond.^[16] The K^+ ions interact with the phenyl ring of the dipp group in η^6 fashion, and also co-ordinated by one THF molecule. The P1–K1 bond distance is 3.2166(18) Å, which is very close to the P–K distance reported in $cAAC$ -supported alkali metal-phosphinidenides.^[10]

The molecular structure of **5** is depicted in Figure 5. Complex **5** crystallizes in the monoclinic $P2_1$ space group. The molecular unit of **5** consists of one aryl-cyclic alkyl(phosphaalkene) amide $[(Ar)(cAPA)N^-]$ (Ar = dipp) unit, one Li^+ ion, and three terminally coordinated THF molecules. The N-atom of the anion $[(Ar)(cAPA)N^-]$ is in trigonal planar geometry with a sum of bond angles close to 360°. The N–Li bond distance in **5** is 2.080(3) Å, which is comparable to the experimentally and theoretically reported N–Li complexes.^[17]

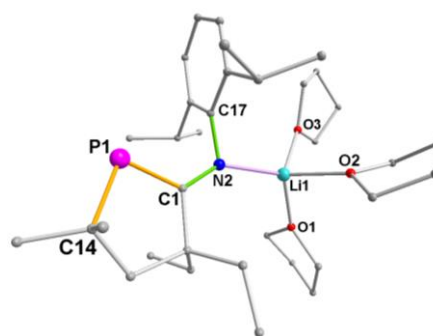


Figure 5. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Important bond lengths [Å] and bond angles [°]: P1–C1 1.7538(15), N2–C1 1.3327(19), N2–Li1 2.080(3); N2–C1–P1 127.07(11); C1–N2–Li1 142.93(12).

The Li1–C17 distance is found to be 2.774 (3) Å, indicating a weak interaction. The C1 atom (C_{cAAC}) of the five-membered phosphaalkene ring also possesses a trigonal planar geometry with sum of bond angles of 360.01°. The C1–P1 bond length in **5** is 1.7538(15) Å, which is comparable to that of the chloro-

phosphinidene **1a** (1.7513(15) Å), but shorter than its corresponding conformational isomer (phosphaalkene) (1.615(4) Å).^[8]

The tetra-nuclear Cu(I) cluster **6** crystallizes in the trigonal *R3c* space group. The molecular structure of **6** is depicted in Figure 6, which possesses a three-fold rotational axis of symmetry that passes through Cu1 and Cl1 atoms; hence, the occupancies of these two atoms are 0.33 each. Complex **6** with Cu(I)₄ core contains three four-coordinate Cu(I) ions in the periphery, and one Cu(I) ion at the centre. Three P-atoms furnish μ -bridge between four Cu(I) ions. Cu1 is bonded to three Cu2 atoms, and three P2 atoms. The Cu1–Cu2 bond length is 2.6181(6) Å. The Cu1–P1 bond length is 2.4098(7) Å, which is slightly longer than those of the reported complexes {[IMes·PPh](CuCl)₂]₄ (2.1828(7)–2.2110(7) Å)^[18] and [(IPr·PPh)CuCl] (2.1654(6) Å).^[19]

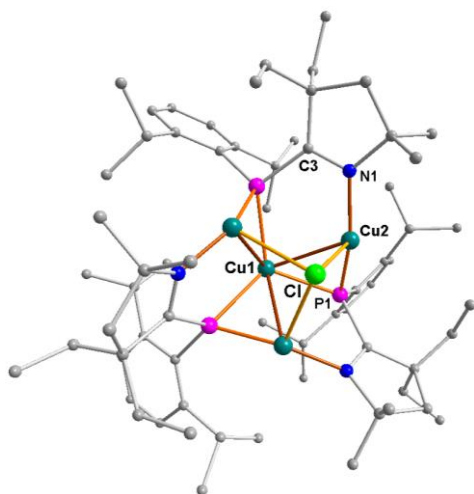


Figure 6. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Cu1 and Cl1 have 0.33 occupancy each. Important bond lengths [Å], and bond angles [°]: Cu1–P1 2.4098(7), P1–C3 1.823(3), N1–C3 1.291(4), N1–Cu2 1.923(3), Cu1–Cu2 2.6181(6), Cu2–Cl1 2.5212(9); P1–Cu1–Cu2 74.32(2), C3–P1–Cu1 120.06(10), C3–N1–Cu2 118.4(2).

All three Cu2 atoms in **6** are held together by the Cu1 and μ_3 -bridged Cl1 atoms. The central Cu(I) ion possesses three short Cu··Cu metallophilic-interactions (Cu–Cu 2.6181(6) Å), which is comparable with that of the reported tetranuclear complex [(IPr·PPh)₂Cu₄Cl₂][BARf]₂ (2.6381(6) Å) and considered as a closed-shell d¹⁰–d¹⁰ cuprophilic interaction.^[18] The central Cu(I) ion in complex **6** resides 0.31 Å above the plane containing the three coordinating P-atoms of the ligands. The P1–C3 bond distance is 1.823(3), which can be ascribed to the electron-sharing P–C single bonds.

The octa-nuclear Ag(I)₈ cluster **7** crystallizes in the triclinic *P*-1 space group having a central distorted-cubane of Ag₄Cl₄ unit, flanked by two ((Et₂-cAl)P(dipp))₂Ag₂ units with Ag··Ag short contacts,^[12] and two Cl bridges (Figure 7). The P and N atoms of the two ligands in **7** are bonded to the Ag–Ag bridge. The P atoms of the ligands are also coordinated to the Ag atom of the Ag₄Cl₄ core, thus providing stability to the overall structure. The average P–Ag bond length is 2.436 Å, which is in well agreement with the Ag–P distances seen in our recently reported Ag clusters-stabilized by cAAC-anchored mono-anionic phosphorous ligand.^[12]

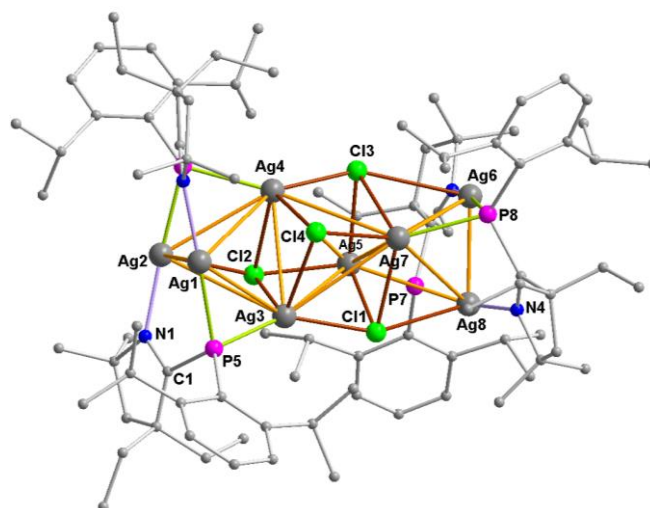


Figure 7. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. For selected bond lengths [Å], and bond angles [°] of **7** see SI.

The Ag–Cl bond length of the Ag₄Cl₄ core is in the range of 2.55–2.83 Å. This complex features the shortest C46–N3 bond distance of 1.251(12) Å among all the complexes discussed here.

The solid-state structures of **8a–8c** were confirmed by single-crystal X-ray diffraction. Due to structural similarities, only **8a**, which crystallizes in *P*₂/*1*/*n* monoclinic space group is discussed herein (Figure 8). The P atom of **8a** has a bent geometry, and bonded to the C_{cAAC}, and C_{dipp} atoms. The bond length of C7–P1 is found to be 1.7258(10) Å, which is similar to those of (Cy-cAAC)P–Ph (1.73 Å),^[7] Cy-cAAC₂P₂ (1.719(7) Å),^[20] and (Me₂-cAAC)P–Si(Cl₂)–L (L = benzamidinate) (1.732(2) Å) containing a C_{cAAC}=P double bond.^[3a]

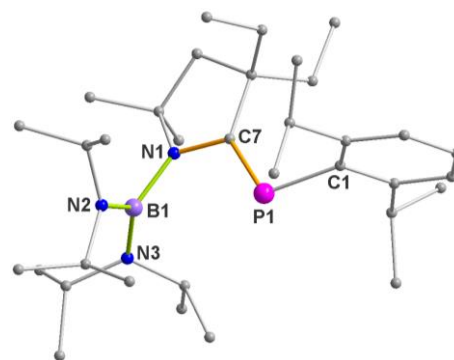


Figure 8. Molecular structure of compound **8a**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], and angles [°]: P1–C1 1.8563(10), P1–C7 1.7258(10), N1–C7 1.3722(13), N1–B1 1.5114(13), N2–B1 1.4248(14), N3–B1 1.4444(14); C7–N1–B1 125.77(8), N1–C7–P1 117.88(7), N2–B1–N1 117.90(9).

The C7–N1 bond length is found to be 1.3722(13) Å, which is similar to that of Et₂-cAAC=PCl (**1a**) (1.375(12) Å), but longer than that of the free cAAC (1.309 Å). The C_{cAAC}–P bond consists of electron sharing covalent double bonds (σ , π) (see the EDANOCV analyses given in the SI). A similar bonding situation has been observed in the previously reported boryl- and stibanyl-phosphaalkenes cAAC=P-ER₂ [E = B, Sb].^[15] N1 is bonded to

two $B(NiPr_2)_2$ groups. The N1–B1 bond length is found to be 1.5114(13) Å, which is in well agreement with typical B–N single bond. The N2–B1, and N3–B1 bond lengths are 1.4248(14), and 1.4444(14) Å, respectively, indicating partial double bonds.^[21] We have performed optimization, and NBO analyses of **8a–8c** at BP86/def2-TZVPP level of theory (see SI). For all molecules the corresponding singlet states were found to be the spin ground states with an average singlet-triplet energy gap of 42 kcal/mol. NBO analysis on **8a** showed that the C_{CAAC} –P bond exhibits the s and p occupancies of 1.95 and 1.93 e. The electron density of the C_{CAAC} –P σ bond is found to be polarized towards C_{CAAC} (64%), while the same for the π bond is found to be more polarized towards the P atom (58%). WBI calculated for **8a** was found to be 1.50 suggesting a significant π bonding in C_{CAAC} –P bond. The calculated electron density $\rho(r)$ at the (3, -1) bond critical points (BCPs) of C_{CAAC} –P bonds (+0.168) along with the respective Laplacian $\nabla^2\rho(r)$ of +0.150 indicated a closed-shell interaction (see SI). However, the energy decomposition analysis coupled with natural orbital of chemical valence (EDA-NOCV) revealed that the bond between Et_2 -cAAC and P_{dipp} fragments in **8a** is best described when the fragments interact in a neutral triplet state, resulting in σ/π -electron-sharing bonds (see SI). CV of **8a** showed a quasi-reversible reduction leading to the formation of red coloured radical anion intermediate **8a⁻** in solution (see SI).

2a–5 have been further studied by UV-Vis spectroscopy (see SI). The UV-Vis absorption spectra of THF solutions of **2a**, **4a**, and **5** showed absorption bands at 328 (λ_{max}), 422 nm for **2a**; 319 (λ_{max}), 438 nm for **4a**; 315 (λ_{max}), 427 nm for **5** (see SI). Interestingly, the solid powder, and THF solution of **3a** was found to be bright luminescent, emitting orange light under a laboratory UV lamp of 365 nm wave length at rt (Figure 9, top (inset); also see SI). The UV-Vis absorption spectrum of a THF solution of **3a**, recorded at rt (300 K) under an argon atmosphere showed the absorption maximum (λ_{max}) at 320 nm with a shoulder at 439 nm (Figure 9, top, left). The photoluminescent (PL) spectrum of THF solution of **3a** at 300 K exhibited orange emission with λ_{em} at 600 nm (Figure 9, top, right) with a photoluminescent quantum yield (PLQY) Φ_{PL} of 2.6%, and an average lifetime, τ of 4.8 μ s (Figure 9, bottom). However, the complexes **2a**, **5**, **6**, and **7** were not emissive.

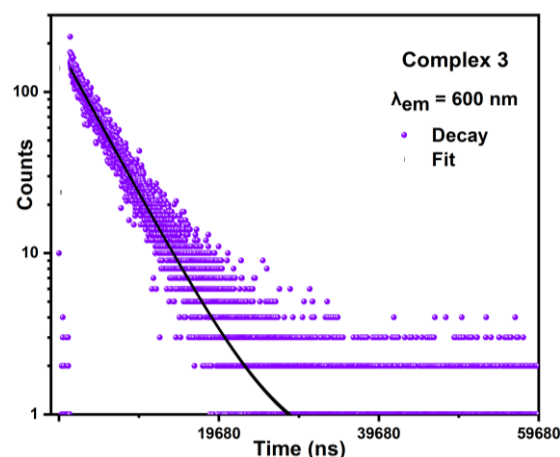
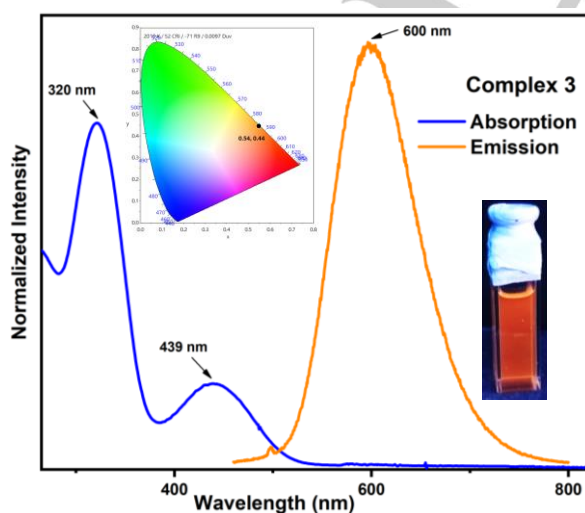


Figure 9. TOP: UV-Vis absorption (blue), and emission (orange) spectra of **3a** in THF at rt. The absorption bands were observed at 320, 439 nm. λ_{em} was observed at 600 nm for λ_{ex} at 435 nm. Inset: The PL color coordinates of **3a**, plotted in the CIE 1931 chromaticity diagram. The black dot corresponds to coordinates attributed to orange light emission (0.54, 0.44). Bottom: Lifetime decay of **3a** in THF at rt (λ_{em} = 600 nm). The exciting pulsed and emission are shown in blue color (τ_{av} = 4.80 μ s at 600 nm during excitation with light source VPLED 475 nm), and fitting in black color.

Conclusion

In conclusion, we have reported the unprecedented one-pot thermal rearrangements of various alkali metal ($M = Li, K, Cs$)-phosphinidenes generated upon two-electron reduction of cAAC-anchored chloro-phosphinidenes **1**, either via migration of the dipp group from N to the P center of **1**; or the cleavage of the CMe_2 -N bond of the five-membered ring of cAAC followed by energetically favourable 5-*exo-tet* ring-closure leading to the isolation of novel alkali metal complexes of (aryl) (cyclic alkyl(imino)) phosphide [(Ar)(cAl)P⁻] (Ar = dipp; Cs, **3a–3c**; K, **4a–4b**); and (aryl) (cyclic alkyl(phosphaalkene)) amide [(Ar)(cAPA)N⁻] (Ar = dipp; Li, **5**). Quantum chemical calculations showed that both the rearrangements are spontaneous. **3a** has been further utilized as the source of an excellent chelating ligand with dual donor sites. **3a** upon reaction with CuCl (1:2), and AgOTf (1:1) produced two novel clusters with $Cu(I)_4$ (**6**), and $Ag(I)_8$ (**7**) cores stabilized by the newly developed bidentate mono-anionic ligand [(Ar)(cAl)P⁻] with a harder N-, and a softer P-donor sites. Moreover, complexes **3a–3c** reacted with 1-bromo-N,N,N',N'-tetraisopropylboranediimine, affording the first syntheses of cyclic alkyl(aminoboryl) phosphalkenes **8a–8c** in good yields.

Experimental Section

See Supporting Information for the detailed syntheses and characterizations of complexes **2a–4b**, **5–7**, and compounds **8a–8c**.

Deposition Numbers 2267433 (for **2a**), 2267496 (for **3a**), 2268456 (for **4a**), 2168489 (for **5**), 2267793 (for **6**), 2267705 (for **7**), 2248956 (for **8a**), 2258444 (for **8b**), 2269056 (for **8c**) contain

the supplementary crystallographic data for this paper. The Crystallographic Information Files for **2a-4a**, **5-7**, **8a-8c** can be obtained from the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service via www.ccdc.cam.ac.uk/structures/.

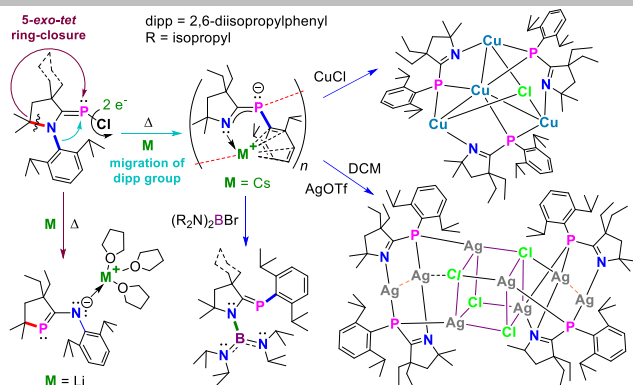
Acknowledgements

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Keywords: Coinage metal clusters • Cyclic alkyl(amino) carbenes (cAACs) • Cyclic alkyl(aminoboryl) phosphalkenes • Phosphinidenide rearrangement • Structure and bonding

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COMMUNICATION



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1 – 8
Isolation of (Aryl)- (Imino) Phosphide, and (Phosphaalkene) Amide Complexes of Alkali Metals from Carbene-Phosphinidenes under Reductive-Thermal Rearrangements

Carbene-anchored chloro-phosphinidenes have undergone unprecedented rearrangements under reductive-thermal condition in presence of alkali metals to afford the corresponding complexes of (aryl)- (imino)phosphides, and (phosphaalkene)amide. The former proved to be an excellent precursor for a novel chelating ligand with dual PN-donor sites, which provided direct synthetic routes for Cu(I)₄, Ag(I)₈ clusters, and cyclic alkyl(aminoboryl) phosphalkenes.