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## Accepted Article

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# Isolation of Homo/Mixed Valence Ag<sub>12</sub>, Ag<sub>29</sub>, and Ag<sub>8</sub> Clusters Stabilized by Cyclic Alkyl(amino) Carbene-Anchored Monoanionic Phosphorus Ligand

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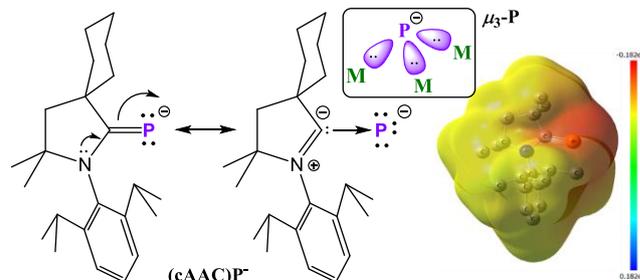
‡ Both authors contributed equally

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**Abstract:** Silver (Ag) clusters are attractive candidates for their promising optical properties, and biomedical activities. Herein, we report on the first syntheses, and isolation of three homo/mixed valence silver nano-clusters (NCs) with Ag<sub>12</sub>Cl<sub>3</sub>, Ag<sub>29</sub>, and Ag<sub>8</sub> cores; [((cAAC)P)<sub>6</sub>Ag<sub>12</sub>Cl<sub>3</sub>](OTf)<sub>3</sub> (**1**), [((cAAC)P)<sub>6</sub>Ag<sub>29</sub>] (**2**), and [((cAAC)P)<sub>4</sub>Ag<sub>8</sub>] (**3**) having three/two-fold symmetry, employing cyclic alkyl(amino) carbene (cAAC)-supported phosphinidenide (cAACP<sup>-</sup>) as the π-accepting stabilizing ligand. The average diameters of the two Ag NCs (**1**, **2**) are approximately of 1.6 to 2 nm. The redox non-innocent mono-atomic phosphorus anions (P<sup>-</sup>) anchored with cAAC ligands are *in situ* generated by the reaction of AgOTf with a boryl-phosphaalkene (cAAC)P-B(N<sup>i</sup>Pr)<sub>2</sub> via the cleavage of the P-B bond with the help of triflate anion (OTf<sup>-</sup>) as a weak nucleophile. The equivalent numbers of the *in situ* generated (cAAC)P<sup>-</sup> anions are oxidized to produce the corresponding bis-phosphinidene (cAAC)<sub>2</sub>P<sub>2</sub>, leading to the generation of Ag(0) ions in solution for the formation of the unprecedented mixed valence Ag NC **2**. Complex **3** is achieved by the reaction of potassium phosphinidenide cAACPK with AgNTf<sub>2</sub>. The ligand field, and the steric hindrance of the (cAAC)P units play a crucial role for stabilization of the complexes **1-3**, further providing a three (**1**, **2**)/two (**3**)-fold stand. The Ag<sub>12</sub>Cl<sub>3</sub> NC (**1**) with tri-cationic core [Ag(I)<sub>12</sub>Cl<sub>3</sub>] is found to be diamagnetic, and fluorescent, emitting green light at 563 nm when excited at 400 nm. Whereas, the neutral Ag<sub>29</sub> (**2**), and Ag<sub>8</sub> (**3**) clusters are found to be paramagnetic, and NMR silent showing characteristic EPR signals for Ag(0) at room temperature.

The development of the chemistry of main group elements taken a leap frog, and has provided the benefits to the other areas of chemistry,<sup>[1]</sup> physics,<sup>[2]</sup> and material science.<sup>[3]</sup> A careful utilization of main group compounds and/or fragments as ligands can often address the scientific challenges of the chemists, and physicists considering the syntheses and diverse properties of molecules with specific interest.<sup>[4]</sup> The stabilization, isolation, and characterization of low valent, low coordinate metal clusters, and the reactive singlet main group species, like carbenes,<sup>[5-6]</sup> nitrenes,<sup>[7]</sup> and phosphinidenes<sup>[8]</sup> were once the major challenges to the synthetic chemists. However, nowadays, those species are not only routinely synthesized in the laboratory, but also could find various applications in different areas of chemistry with expanding boundaries.<sup>[9]</sup> Finally, many of such molecules will be at the door steps of the new horizon/paradigm

of chemistry.<sup>[10-11]</sup> In this regard, cyclic alkyl(amino) carbene (cAAC)<sup>[12]</sup> has overcome many limitations, which were initially faced by employing other prominent σ-donor ligands.<sup>[1,9-11]</sup> So far, a few cAAC-Ag(I) complexes have been synthesized, isolated, characterized, and theoretically studied.<sup>13</sup> cAAC-Ag(I)-amide complexes are found to be luminescent with very high quantum yields, since they display thermally assisted delayed fluorescence (TADF) property.<sup>[10]</sup> This is a remarkable achievement with respect to the exciting optical properties of the cAAC containing metal complexes.<sup>[9-10]</sup> So far, many metal atoms of the periodic table have been stabilized in their zero oxidation state by employing cAAC as a significant π-accepting ligand.<sup>[14]</sup> However, among the three coinage metal atoms (Cu, Ag, Au), synthesis of only the (cAAC)Ag(0) complex could not be achieved till date, while the other two (cAAC)<sub>2</sub>Cu(0)/Au(0) complexes have been isolated in the laboratory.<sup>[14]</sup> Quantum chemical calculations have indicated the lower interaction energy between cAAC ligand and Ag atom as a reason for the non-isolability of such complex.<sup>[13b]</sup> However, we envisioned that a combination of cAAC and P<sup>-</sup> ligands could be an alternative stabilizing ligand system, considering the synthetic availability of cAAC-supported phosphinidenides cAAC=P<sup>-</sup> for the stabilization of Ag(0) species. While carbene is expected to be a harder donor (C), phosphorus (P) is a softer donor-ligand, which in principle can efficiently coordinate to the softer Ag center giving rise to the isolation of unusual Ag-based metal clusters.



**Scheme 1.** Canonical structures, and MEP plot (computed at M062x/def2-SVP with iso-density surface value of 0.0004 a.u.) of cAAC=P<sup>-</sup> anion.

Although, the carbene-stabilized phosphinidenides, e.g., NHC=P<sup>-</sup> (NHC = N-heterocyclic carbene) and cAAC=P<sup>-</sup>, have

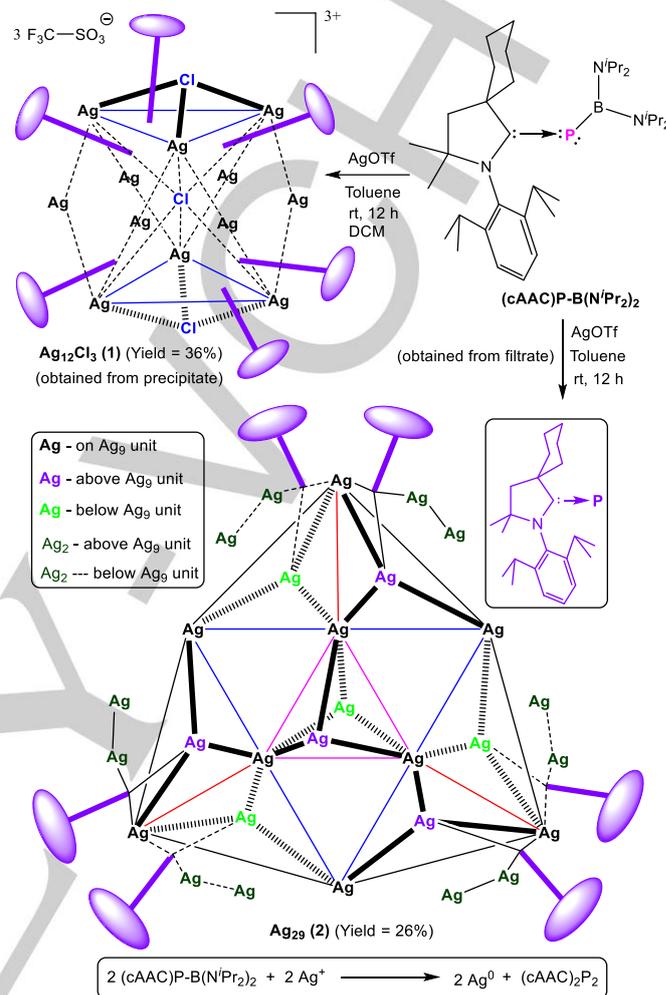
been isolated in the laboratory, their chemistry with transition metals is still at the infancy.<sup>[15]</sup> The cAAC is known to control its electron-pair quite well depending upon the requirement of the acceptor atoms.<sup>[14,16]</sup> It donates the lone pair of electrons on the C<sub>carbene</sub> atom to form a comparatively stronger  $\sigma$ -bond by making the N=C bond as a double bond (Scheme 1). We have performed the Natural Bond Orbital (NBO) analysis (at M06-2X/def2SVP level of theory) of cAACP<sup>-</sup> ligand to have a deeper understanding of the electron densities distribution and nature of participating orbitals in complex formation (see SI for Computational details), which showed two lone pairs of electrons on P atom, one with 1.98e occupancy having 77% s- and 23% of p-character (HOMO-2); while the other with 1.79e occupancy and 99.9% p-character (HOMO) (see SI for Computational details).

More than one and half decades ago, Manuel Pereiro et al. have theoretically shown that the Ag(0)<sub>n</sub> clusters (n = odd number) can have at least one unpaired electron until n = 11 with magnetic momentum of 1  $\mu_B$ .<sup>[17]</sup> Their studies showed that the magnetic momentum will be five times higher when n value is 13. The magnetic momentum slowly decreases to zero when n reaches 18, while it again increases to 3  $\mu_B$  for n = 23.<sup>[17]</sup> So far, NHC and P-SiMe<sub>3</sub> anchored diamagnetic Ag(1)<sub>12</sub> and Ag(I)<sub>26</sub> clusters have been isolated.<sup>[18]</sup> Also, several Ag(I) clusters have been reported utilizing thiol, phosphine, sulfide, selenide, alkyne, perchlorate, etc. as the bridging ligands.<sup>[19]</sup> These Ag(I)-clusters are often highly luminescent,<sup>[19]</sup> and some of them are also used as catalysts. In most of the cases, they are obtained by serendipitous synthetic routes.<sup>[19]</sup> Clusters of Ag-H moiety have been isolated,<sup>[20]</sup> and their corresponding bare Ag<sub>n</sub>H<sup>+</sup> cations have been studied by mass spectrometry.<sup>[21]</sup> Utilizing the unique electronic effects of cAAC and phosphorus, herein, we report on the first syntheses, isolation, and characterization of three air and moisture sensitive, mixed valence Ag<sub>8</sub>, Ag<sub>29</sub>, and homo valence Ag<sub>12</sub>Cl<sub>3</sub> nano-clusters (NCs) [((cAAC)P)<sub>6</sub>Ag<sub>12</sub>Cl<sub>3</sub>](OTf)<sub>3</sub> (**1**), ((cAAC)P)<sub>6</sub>Ag<sub>29</sub> (**2**), and ((cAAC)P)<sub>4</sub>Ag<sub>8</sub> (**3**) with three/two-fold symmetry having Ag(I)<sub>12</sub>, Ag(0)<sub>23</sub>, and Ag(0)<sub>4</sub> units, respectively, as yellow blocks/plates (Scheme 2). Complexes **2** (Ag<sub>29</sub>) and **3** (Ag<sub>8</sub>) are NMR silent and paramagnetic, which have been confirmed by EPR studies.

The cyclic alkyl(amino) carbene (cAAC)-supported borylphosphaalkene, (cAAC)P-B(N<sup>i</sup>Pr)<sub>2</sub> (cAAC = :C(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(C<sub>6</sub>H<sub>10</sub>)(CMe<sub>2</sub>)(CH<sub>2</sub>))<sup>[22]</sup> has been employed for the first time as the precursor for the *in situ* generation of (cAAC)P<sup>-</sup> under ambient reaction condition as a redox non-innocent anion. The reaction of (cAAC)P<sup>-</sup> with AgOTf in 1:1 molar ratio at room temperature in anhydrous toluene for 12 h resulted in the formation of a brownish-red reaction mixture with brown precipitate, which was isolated upon filtration, and dissolved further in anhydrous dichloromethane (DCM) to obtain a brownish-red clear solution. The reddish-yellow filtrate was concentrated to dryness under vacuum, and further dissolved in DCM for crystallization. The bright yellow plate shaped crystals of the Ag NC [((cAAC)P)<sub>6</sub>Ag<sub>12</sub>Cl<sub>3</sub>](OTf)<sub>3</sub> (**1**), and ((cAAC)P)<sub>6</sub>Ag<sub>29</sub> (**2**) were obtained after 3-5 days from the precipitate and the corresponding filtrate, respectively.

Both **1**, and **2** have been separately crystallized from the concentrated DCM solutions kept at -40 °C in pure forms in about 26-36% yield (see SI). The respective redox reaction of

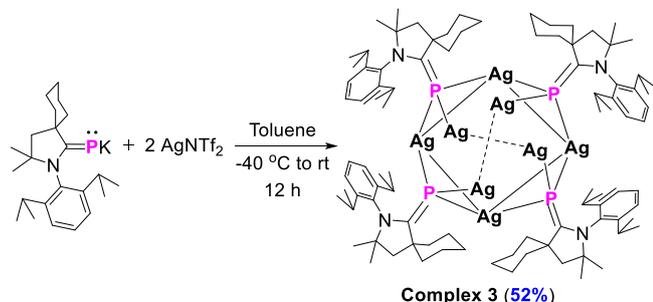
partial Ag(I) to Ag(0) generation has been shown in Scheme 2 (bottom). The formation of the by-product (cAAC)<sub>2</sub>P<sub>2</sub> has been confirmed by the NMR spectroscopic analysis.<sup>[15]</sup>



**Scheme 2.** Synthesis route of clusters [((cAAC)P)<sub>6</sub>Ag<sub>12</sub>Cl<sub>3</sub>](OTf)<sub>3</sub> (**1**; side view), and [((cAAC)P)<sub>6</sub>Ag<sub>29</sub>] (**2**; top view), represented by Ag<sub>n</sub> core only. Each cluster contains six cAAC and six P<sup>-</sup> ligands.

To explore the role of the counter anion a different silver salt, viz. AgNTf<sub>2</sub> has been employed in the similar reaction with phosphosphaalkene ((cAAC)P-B(N<sup>i</sup>Pr)<sub>2</sub>),<sup>[22]</sup> which could not produce any desired Ag cluster. However, a 1:1.5 molar ratio of the potassium phosphinidene ((cAAC)P-K) and AgNTf<sub>2</sub> reacted in toluene at -40 °C to room temperature, affording the greenish-brown colored residue after 12 h, which was filtered to give a reddish-brown filtrate, and dissolved further in anhydrous DCM to get a light brownish-yellow color solution. The concentrated DCM solution (1-2 mL) kept at -40 °C resulted in the formation of yellow block shaped single crystals of a new Ag cluster ((cAAC)P)<sub>4</sub>Ag<sub>8</sub> (**3**) in 52% yield (Scheme 3). The initially obtained reddish brown filtrate was concentrated to dryness, and then dissolved further in DCM and kept for crystallization at -40 °C freezer. After 4-5 days colorless block shaped crystals of the by-product **4** [(KNTf)<sub>n</sub>] were obtained, which was characterized by single-crystal X-ray diffraction (see SI).

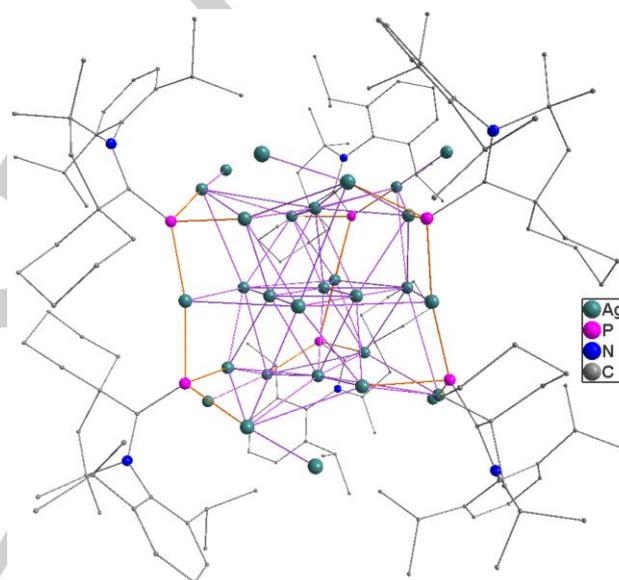
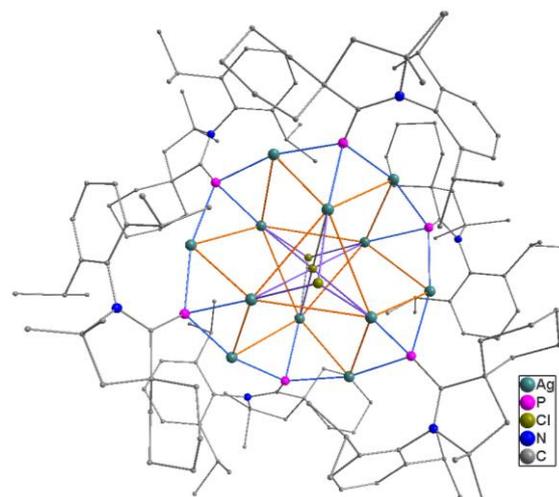
Complexes **1-3** are found to be air and moisture sensitive. The crystals of **1-3** are stable at room temperature for more than six months under an inert atmosphere. The yellow color  $\text{Ag}_{29}$  crystals after exposing to air turned to red in color after 4-5 h, and then slowly turned to colorless powder. Whereas, the golden yellow crystals of  $\text{Ag}_{12}\text{Cl}_3$  slowly turned light yellow to colorless powder after 8-10 h.



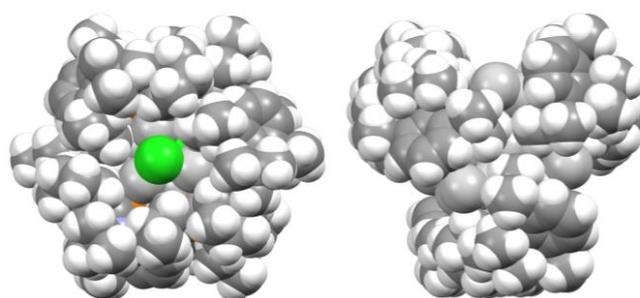
**Scheme 3.** Synthesis of complex  $[(\text{cAAC})\text{P}]_4(\text{Ag})_8$  (**3**).

Complexes **1-3** are only sparingly soluble in THF, but completely soluble in DCM. The DCM solutions of **1**, and **2** are found to be stable at room temperature for 3-4 days under an inert atmosphere. The light-yellow color DCM solution of  $\text{Ag}_{12}\text{Cl}_3$  NC (**1**) starts changing the color after 30 min to a colorless solution with the formation of a brown precipitate. The powder of **1-3** decomposed to brown liquids at 210-212 °C, 211-213 °C, and 205-207 °C, respectively. The  $^{13}\text{C}$  spectrum of a DCM- $d_2$  solution of **1** exhibited doublet at 230.1 ppm ( $J_{\text{C-P}} = 88.2$  Hz), which is downfield shifted when compared with that of the corresponding  $[\text{cAAC}=\text{PK}(\text{THF})_x]_n$  (206.8 ppm,  $J_{\text{C-P}} = 80.64$  Hz),<sup>[15a]</sup> but upfield shifted when compared with those of the corresponding free carbene (309.4 ppm).<sup>[12]</sup> The  $^{19}\text{F}$  spectrum exhibited a sharp singlet at -78.7 ppm. The  $^{31}\text{P}$  spectrum exhibited a triplet at -132.2 ( $J_{31\text{P}-109\text{Ag}} = 749.16$  Hz) ppm. The DCM- $d_2$  solutions of **2**, and **3** did not show any resonances in the respective  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  spectra at room temperature or at a lower temperature (measured at different temperatures starting from room temperature to -60 °C).

The molecular structures of both the NCs **1**, and **2** are shown in Figure 1. The space-filling views of both of these metal clusters (**1-2**) have been shown in Figure 2. Both complexes **1**, and **2** have crystallized in a center-symmetric space group with the near-3-bar (**1**) /3-bar (**2**) symmetry element, which passes through the central Cl (**1**) / Ag (**2**) atoms. Six (cAAC)P ligands act like two sets of three-fold stands from the top and bottom of the periphery of  $\text{Ag}_{12}\text{Cl}_3$  unit, both having the  $\text{Ag}_6\text{Cl}_3$  (**1**) /  $\text{Ag}_9$  (**2**) unit as common. The cluster **1** possesses a non-planar, rather a 3D  $\text{Ag}_6\text{Cl}_3$  unit, while **2** has a planar  $\text{Ag}_9$  sheet in the middle of the cluster (Figures 3-4).



**Figure 1.** Molecular structures of  $[(\text{cAAC})\text{P}]_6\text{Ag}_{12}\text{Cl}_3(\text{OTf})_3$  (**1**) (top), and  $(\text{cAAC})\text{P}]_6\text{Ag}_{29}$  (**2**) (bottom). Three  $\text{OTf}^-$  anions (**1**) and H atoms (**1-2**) were omitted for clarity.<sup>[23]</sup> See SI for crystallographic bond parameters of complexes **1**, and **2**.

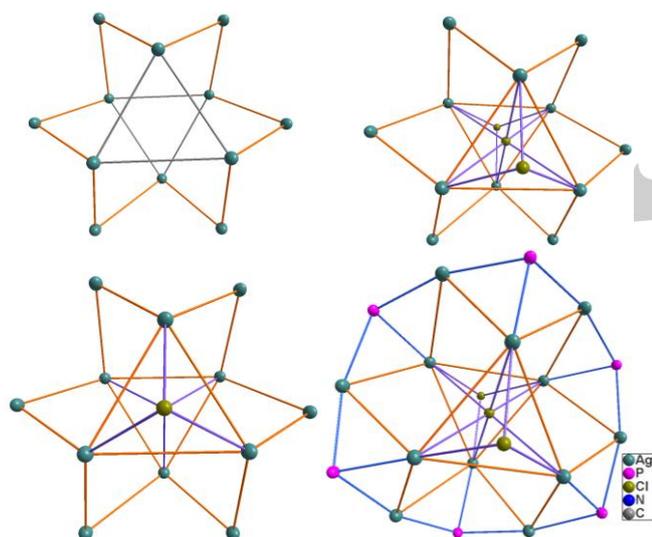


**Figure 2.** Space-filling views of  $[(\text{cAAC})\text{P}]_6\text{Ag}_{12}\text{Cl}_3(\text{OTf})_3$  (**1**) (left), and  $[(\text{cAAC})\text{P}]_6\text{Ag}_{29}$  (**2**) (right). Average diameter of both **1**, and **2** is 2 nm.

Crystallographic refinements revealed that  $[(\text{cAAC})\text{P}]_6\text{Ag}_{12}\text{Cl}_3(\text{OTf})_3$  (**1**) possesses twelve  $\text{Ag}(\text{I})$ , three chloride ( $\text{Cl}^-$ ), and  $(\text{cAAC})\text{P}^-$  anions, leading to the formation of a tri-cationic  $\text{Ag}_{12}\text{Cl}_3$  cluster **1**. The  $\text{Ag}_6\text{Cl}_3$  unit of the NC **1** can be

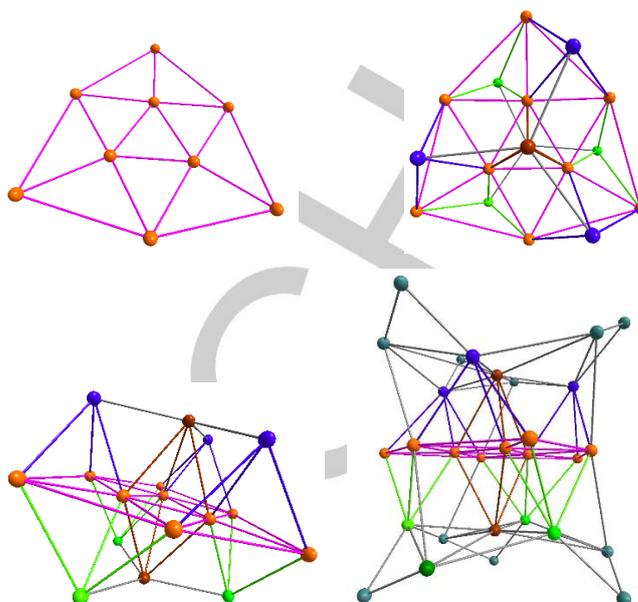
considered as a *trans*-bicapped octahedron (Figure 3; Top). Two  $\text{Ag}_3$ -triangular faces of central  $\text{Ag}_6\text{Cl}$  octahedron (Figure 3, middle) can be connected via six Ag atoms in a zig-zag manner (indicated by yellow bonds; Figure 3, middle). The six  $\mu_3$ -P(cAAC) units (Figure 1, top; Figure 3, bottom) have prevented the further growth of the  $\text{Ag}_{12}\text{Cl}_3$  unit of NC 1. Three (cAAC) $\text{P}^-$  ligands from top/bottom are in gauche orientation/arrangement with respect to each other.

The distances from the  $\text{Ag}_4/\text{Ag}_5/\text{Ag}_6$  to the plane of the aromatic ring of the Dip group (Dip = 2,6-diisopropylphenyl) in **1** are 3.22/3.11/3.16 Å, respectively. The distances between the central  $\mu_6$ -Cl2 of  $\text{Ag}_{12}\text{Cl}_3^{3+}$  core of **1** to the six neighboring Ag(I) ions are 2.71 (Ag2), 2.82 (Ag1) and 2.88 (Ag3) Å. The distances from  $\mu_3$ -Cl1 of **1** to the nearest three neighboring Ag(I) ions are 2.64 (Ag1), 2.70 (Ag2) and 2.73 (Ag3) Å. The Ag-Ag distances within the  $\text{Ag}_{12}\text{Cl}_3^{3+}$  core are in the range of 2.92 to 3.20 Å. The P-Ag distances in **1** are in the range of 2.39 to 2.43 Å (see SI). The  $\text{C}_{\text{cAAC}}\text{-N}$  and  $\text{C}_{\text{cAAC}}\text{-P}$  bond distances in **1** are in the range of 1.30 to 1.31 Å, and 1.78 to 1.80 Å, respectively, which are in line with the  $\text{cAAC}\rightarrow\text{P}^-$  dative bond ( $\text{Ag}_{12}$  (**1**); Scheme 1).<sup>[14-16]</sup>



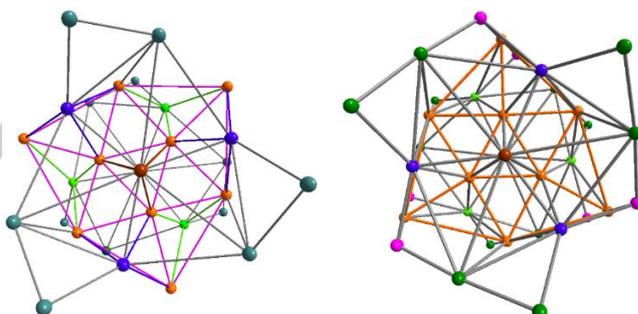
**Figure 3.**  $\text{Ag}_6$  unit at the center of NC  $[(\text{cAAC})\text{P}]_6\text{Ag}_{12}\text{Cl}_3(\text{OTf})_3$  (**1**) (top, left). Two Cl-atoms are *trans*-bicapped over  $\text{Ag}_6\text{Cl}$ -octahedron (top, right). Two triangular  $\text{Ag}_3$  units of  $\text{Ag}_6\text{Cl}$ -octahedron are connected by six Ag-atoms from periphery in a zig-zag fashion shown by yellow-orange lines (bottom, left). Two Ag-atoms from this peripheral site and one Ag-atom from a triangle which has been bridged by a P-atom in  $\mu_3$ -fashion (blue lines; bottom, right).

The  $\text{Ag}_{29}$  NC **2** possesses an  $\text{Ag}_9$  planar sheet in the middle, which is made of ten  $\text{Ag}_3$  sub-triangles (Figure 4, top left). There are two Ag atoms (Figure 4, brown ball) above and below the central  $\text{Ag}_3$  plane (marked pink; Scheme 1, bottom). There is no Ag atom above and below the three  $\text{Ag}_3$  sub-triangles, adjacent to the central inner triangle (marked blue; Scheme 1, bottom). There are six peripheral triangles, which are alternatively capped by the three Ag atoms from top, and three atoms from bottom (marked green; Scheme 1; Figures 4-5). These two sets of Ag atoms (violet and blue colored) are related by 3-bar symmetry operation. Three Ag atoms at the edges of the planar  $\text{Ag}_9$  sheet is further connected by three sets of  $\text{Ag}_2$  units from above and below the  $\text{Ag}_{17}$  unit ( $\text{Ag}_4 + \text{Ag}_9 + \text{Ag}_4$ ).



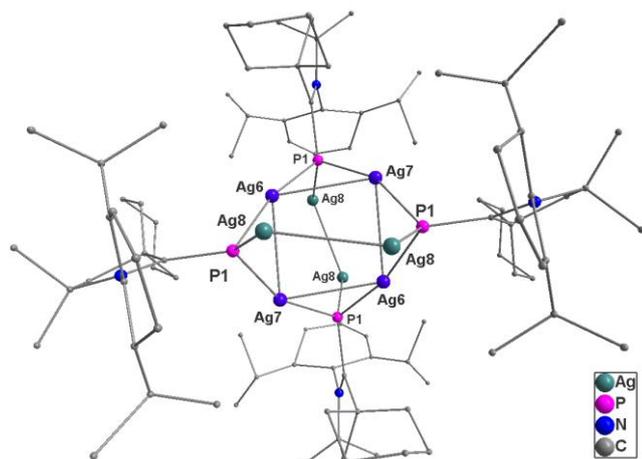
**Figure 4.**  $\text{Ag}_{29}$  core of the NC **2**. The brown colored Ag-atoms are above/below the central  $\text{Ag}_3$  triangle. The violet and green colored Ag atoms are above and below the  $\text{Ag}_9$  sheet, respectively. Three sets of  $\{\text{Ag}_2\}$  units are at the periphery of the violet/bright-green Ag atoms in a propeller fashion with a pseudo three-fold symmetry.

Finally, the  $\text{Ag}_{29}$  core of the NC **2** can be considered as two crowns connected via a common base (Figure 5). Six triangular peripheral faces of  $\text{Ag}_{29}$  cluster are bridged by six  $\mu_3$ -P(cAAC) units (Scheme 1; Figures 1, and 5). The  $\text{C}_{\text{cAAC}}\text{-N}$  and  $\text{C}_{\text{cAAC}}\text{-P}$  bond distances in **2** are 1.34 and 1.75 Å, respectively (see SI).



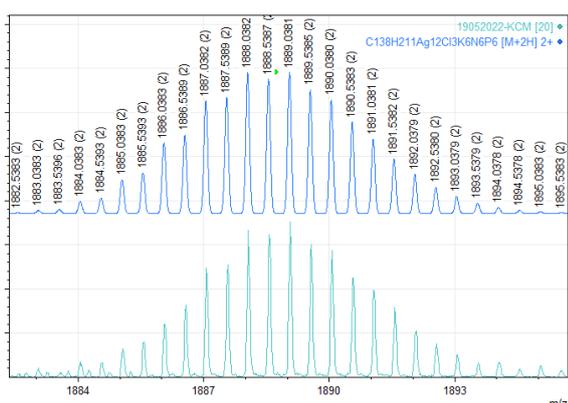
**Figure 5.** Top view of  $\text{Ag}_{29}$  core of the NC  $[(\text{cAAC})\text{P}]_6\text{Ag}_{29}$  (**2**) with P atoms (top) and without P atoms (pink ball, bottom). Six P atoms acting as a  $\mu_3$ -bridging atom among  $\text{Ag}_3$  triangle (violet/bright-green, orange, dark green colored Ag atoms; bottom).

The molecular structure of silver NC **3** has been shown in Figure 6. Complex **3** crystallizes in orthorhombic  $F222$  space group having three two-fold axes. The planar  $\text{Ag}(0)_4$  core ( $\text{Ag}_6\text{Ag}_7\text{Ag}_6\text{Ag}_7$ ; Ag-Ag 2.97 Å violet colored in Figure 6) of **3** has been kept in an *anti*-prismatic fashion by two  $\text{Ag}(I)_2$  units ( $\text{Ag}_8\text{Ag}_8$ ; Ag-Ag  $\sim 3.41$  Å) from above and below the planes of central  $\text{Ag}(0)_4$  unit. The  $\text{cAAC}=\text{P}$  ligand displays  $\mu_3$ -bridging mode (Figure 6). It has been also characterized by ESI-MS mass spectrometry in DCM solution [ $m/z = 2541$  (left) for  $[(\text{cAAC})\text{P}]_4\text{Ag}_8 + 3(\text{CH}_2\text{Cl}_2) - 3\text{H}]^+ = [\mathbf{3} + 3(\text{CH}_2\text{Cl}_2) - 3\text{H}]^+$ ] (see Figure S29).



**Figure 6.** Molecular structures of  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**). H atoms were omitted for clarity.<sup>[23]</sup> See SI for crystallographic bond parameters of **3**.

The stability of  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**) in DCM solution was further confirmed by ESI-MS as shown in Figure 7. ESI-MS technique is known to retain the composition of **1** in solution with addition of  $K^+$  and  $H^+$  under well accepted mass spectrometric condition. In addition, complex **1** has been further studied by DFT calculations (for NBO analyses, see Figure S26, Table S10), and TD-DFT analyses (see SI).

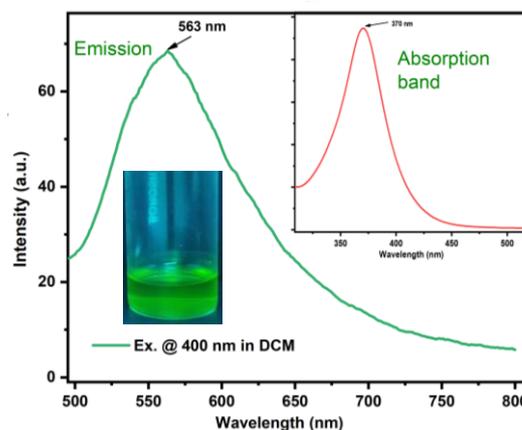


**Figure 7.** Experimental (bottom) and simulated (top) ESI-MS spectra of  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**) in DCM solution. (top;  $m/z = [(cAAC)P_6Ag_{12}Cl_3 + 6K + 3H]^2+$ ;  $M = [(cAAC)P_6Ag_{12}Cl_3 + 6K + H]$ ).

The photophysical properties of complexes **1-3** were investigated (see SI, Figures S1-S6). The UV/vis spectrum of  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**) was recorded in DCM under an inert atmosphere, which showed a broad (310-450 nm) absorption band with  $\lambda_{max}$  at 370 nm (Figure 8, inset). The cluster  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**) was found to be fluorescent, emitting at 563 nm when excited at 400 nm (Figure 8). The fluorescence lifetime ( $\tau_{av}$ ) of complex  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**) in DCM solution at room temperature was found to be 1.75 ns at 563 nm ( $\lambda_{em}$ ) at an excitation of 375 nm (Figure S4). The relative quantum yield ( $\phi_F$ ) of complex **1** in DCM solution was found to be 4.39% at room temperature (see SI).

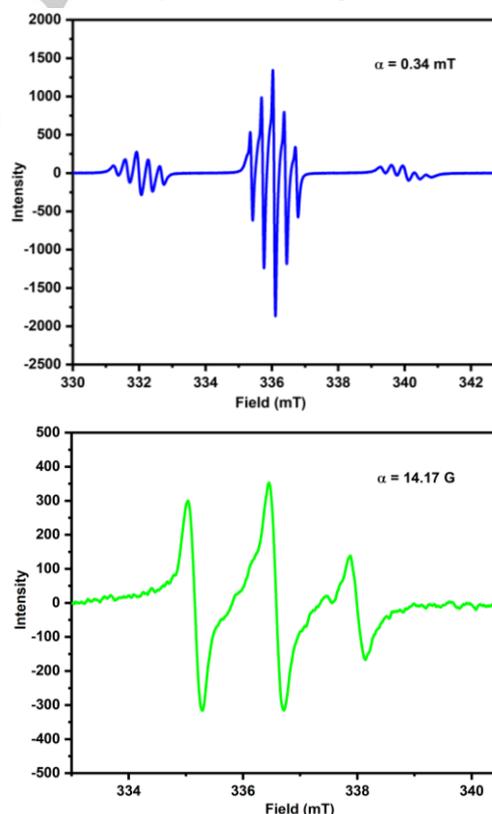
The UV/vis spectra of complexes **2**, and **3** were recorded in DCM under inert atmosphere, which showed absorption maxima,

$\lambda_{max}$  at 439 and 371 nm, respectively (See SI, Figures S5-S6). Complexes **2**, and **3** were found to be non-emissive.



**Figure 8.** Emission, UV/vis (inset) bands of DCM solution of the NC  $[(cAAC)P_6Ag_{12}Cl_3](OTf)_3$  (**1**). The DCM solution of **1**, appearing green (inset) under short UV-light.

The  $Ag_{29}$  NC **2** having odd number of  $Ag(0)$  atoms ( $Ag(0)_{23}$ ) is expected to have at least one unpaired electron or more, depending upon the organization of the  $Ag$  atoms in the three dimensional space of the core.<sup>[17]</sup> Both complexes **2**, and **3** are found to be NMR silent ( $^1H$ ,  $^{13}C$ ,  $^{31}P$ ) in the range of room temperature to  $-60^\circ C$  in  $CD_2Cl_2$ , suggesting the presence of unpaired electron as expected. Complexes **2**, and **3** have been further characterized by EPR studies (Figure 9).



**Figure 9.** Top: X-band EPR spectrum of the NC  $[(cAAC)P_6Ag_{29}]$  (**2**) in DCM at 293 K. Bottom: X-band EPR spectrum of the NC  $[(cAAC)P_4Ag_8]$  (**3**) in DCM at 293 K.

The NC  $[(\text{cAAC})\text{P}]_6\text{Ag}_{12}\text{Cl}_3(\text{OTf})_3$  (**1**) did not show any EPR signal at room temperature or at a lower temperature, while  $[(\text{cAAC})\text{P}]_6\text{Ag}_{29}$  (**2**) displayed characteristic hyperfine EPR lines at  $g = 2.0012$  with the hyperfine coupling constant of 3.4 G due to  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  isotopes of both  $I = -1/2$  at 293 K (Figure 9).<sup>[24]</sup> The neutral NC  $[(\text{cAAC})\text{P}]_4\text{Ag}_8$  (**3**) is NMR silent even at  $-40^\circ\text{C}$ , and shows three hyperfine EPR lines at  $g = 2.0033$  with a hyperfine coupling constant of 14.17 G (see SI). The electrochemical properties of the complexes **1-3** were studied by cyclic voltammetry (CV) in DCM solution of 0.1 M [*n*-Bu<sub>4</sub>N]PF<sub>6</sub> (see SI, Figures S7-S15). The cyclic voltammograms of tri-cationic NC **1**, and neutral NC **3** showed irreversible e<sup>-</sup> transfer processes in the range of -1.10 V to -1.95 V at the scan rate of 100 mV/s (Figures S8, S12). NC **2**, and **3** display an irreversible oxidation processes over +1.25 V (Figure S13). The nature of nano-size of this class of complexes has been proven by the TEM image of complex **1** (~2 nm; see SI, Figure S26).

In conclusion, we have synthesized three unprecedented homo/mixed valence Ag-based NCs (Ag<sub>12</sub>Cl<sub>3</sub>, **1**; Ag<sub>29</sub>, **2**; Ag<sub>8</sub>, **3**) employing carbene-phosphinidenide ligands. Both **1**, and **2** possess a three-fold symmetry with an inversion center within these clusters. Complex **3** possesses three two-fold symmetry. The Ag<sub>12</sub>Cl<sub>3</sub> core is composed of a *trans*-bicapped Ag<sub>9</sub> unit, while Ag<sub>29</sub> contains a planar Ag<sub>9</sub> sheet in the middle. Six (cAAC)P<sup>-</sup> ligands appear to be two sets of three-fold stands to the Ag<sub>12</sub>Cl<sub>3</sub>/Ag<sub>29</sub> cores. The NC **2** (Ag<sub>29</sub>), and NC **3** (Ag<sub>8</sub>) are NMR silent, paramagnetic clusters, which have been proven by EPR studies at room temperature. Complexes **1**, and **3** have been further studied by ESI-MS technique. The tri-cationic Ag<sub>12</sub>Cl<sub>3</sub> cluster (**1**) is a green light emitter with the λ<sub>em</sub> of 563 nm when excited at 400 nm. We assume that the unusual ligand field of (cAAC)P<sup>-</sup> unit might be the key for the stabilization and isolation of such unusual mixed valence silver containing species in the laboratory. Our result brings yet another new horizon to the basket of cAAC chemistry.

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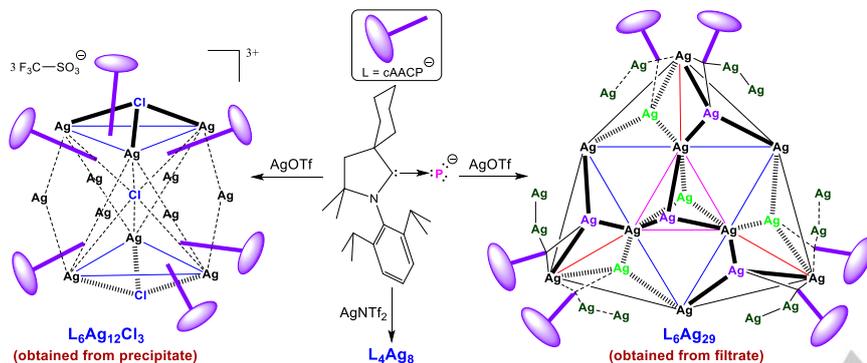
**Keywords:** Ag(I)/Ag(I)-Ag(0) nano-clusters • Cyclic alkyl(amino) carbene • Phosphaalkene reactivity • Phosphinidenide • Three/two fold symmetry

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## Entry for the Table of Contents



We have demonstrated the first syntheses, and solid state isolation of three unprecedented silver clusters  $[(cAAC)P]_6Ag_{12}Cl_3(OTf)_3$  (**1**),  $[(cAAC)P]_6Ag_{29}$  (**2**), and  $[(cAAC)P]_4Ag_8$  (**3**) by employing *in situ* generated cyclic alkyl(amino) carbene (cAAC)-supported phosphinidenide ( $cAACP^-$ ) as the stabilizing ligand from the corresponding phosphalkene and potassium phosphinidenide, respectively.

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