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COMMUNICATION

Isolation of a Carbene-phosphaalkenide Supported Neutral Ag₁₀ Nanocluster Featuring Elusive Silver-sub-iodide Analogs, Ag₂I and Ag₆I₄

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Cyclic alkyl(amino)carbene (cAAC)-supported phosphalkenides [(cAAC=P)[−]] are successfully employed as ligands to stabilize two elusive silver sub-iodide analogs, Ag₂I and Ag₆I₄ within an atomically-precise silver(I)-nanocluster [(Me₂-cAAC=P)₄Ag₁₀I₆] (2), isolated and structurally characterized in the solid-state. 2 features a butterfly-like Ag₁₀I₆ metallic core stabilized by four monoanionic μ₃-cAAC=P[−] ligands. Quantum chemical calculations are performed to elucidate the nature of Ag–Ag and Ag–ligand bonding interactions.

Silver sub-halides (Ag_nX_m, n > m)^{1–2} represent an intriguing class of elusive inorganic molecules, featuring lower valence silver ions, in which halide deficiency could promote unusual Ag–Ag interactions. In 2005, Müller-Rösing et al. computationally investigated a series of silver halides, including Ag₂X, AgX, AgX₂, and AgX₃ (X = F, Cl, Br), employing density functional theory (DFT), which revealed possible stabilization of such molecular entities (Figure 1).¹ Their study further highlighted the influence of halides on bonding characteristics and structural arrangement of such systems, providing an important theoretical foundation for better understanding of silver-rich halides.

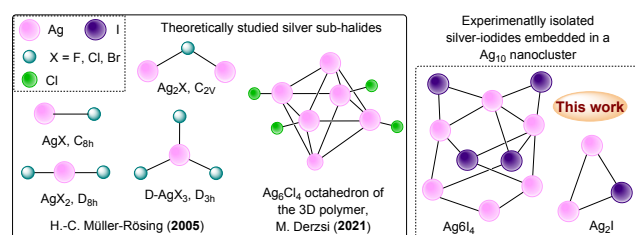


Figure 1. Previously reported representative silver sub-halides studied theoretically.

In 2021, Derzsi et al. theoretically predicted an unprecedented silver sub-chloride, Ag₆Cl₄; representing the first binary diamagnetic semiconducting Ag₆ cluster, exhibiting a distinct electronic structure, characterized by

Ag⁺-like cationic centers with significant metal–metal interactions (Figure 1).² Among various binary halides of silver, only silver sub-fluoride, Ag₂F has been successfully synthesized and structurally characterized in the solid state.³ The heavier sub-halides (Ag₂X, X = Cl, Br, I) remained elusive due to a marked decrease in their thermodynamic stability.

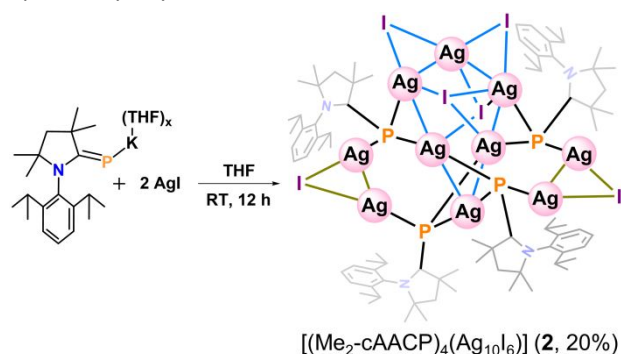
Atomically precise silver nanoclusters (NCs) are rapidly emerging as versatile nanomaterials with unique, molecular traits, such as, discrete HOMO-LUMO transitions, photoluminescence, etc., which largely depend on their geometry and composition.^{4–7} Diverse anionic ligands, ranging from thiolates, halides and alkynyls to neutral organophosphorus compounds are noteworthy in stabilizing silver NCs.⁸ However, iodide-based neutral silver NCs are scarce in the literature. However, noteworthy to mention that Liu and co-workers reported a few cationic silver NCs with multi-coordinated iodide centres,^{9–11} such as the luminescent Ag₁₁ clusters, [Ag₁₁(μ₉-I)(μ₃-I)₃{E₂P(O[−]Pr)₂}]₆(PF₆) (E = S, Se), featuring μ₉-iodide in a tricapped trigonal-prismatic coordination environment, which exhibited bright orange-to-red emissions with microsecond-range lifetimes.⁹ In 2014, the same group reported three halide-centered Ag₈ clusters [Ag₈(X){S₂P(CH₂CH₂Ph)₂}]₆(PF₆) (X = F, Cl, Br), followed by the isolation of a strong yellow-luminescent Ag₁₂ cluster [Ag₁₂(μ₁₂-I)(μ₃-I)₄{S₂P(CH₂CH₂Ph)₂}]₆(I), containing a μ₁₂-I motif at the center of a cuboctahedral silver(I) atom cage.¹⁰ Xu et al. reported a silver iodide metal–organic framework (MOF), {[Ag₁₄I₁₆(HDABCO)₂}·(DABCO)}_n containing an anionic [Ag₁₄I₁₆]^{2−} cluster, assembled through edge-sharing of twelve AgI₄ tetrahedra, and two AgI₃ triangular units.¹² However, structurally well-defined silver NCs, featuring elusive silver sub-iodide analogs with fewer iodides remain unprecedented.² In this context, it is worth mentioning that synthetic main group chemists have very often witnessed the superiority of carbenes over other σ-donor ligands; more specifically, of cyclic alkyl(amino) carbenes (cAACs) addressing various synthetic challenges. Moreover, considering the unique combination of the soft and hard donor sites present in cAAC-supported mono-anionic phosphorus anion (cAAC=P[−]),¹³ we decided to probe its applicability as the stabilizing ligand for the synthesis of

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structurally well-defined novel silver iodide-based NCs, which could be of potential interest as the electrochemical energy-storage materials,¹⁴ and herein, we successfully report on the first stabilization, and structural characterizations of two elusive silver sub-iodide analogs, Ag₂I and Ag₆I₄ within an atomically-precise silver(I) NC [(Me₂-cAAC=P)₄Ag₁₀I₆] (**2**), featuring Ag₁₀I₆ core.

The reaction of a 1:2 molar ratio of cAAC-supported potassium phosphalkenide, Me₂-cACPK (**1**)¹³ (Me₂-cAAC = :C(N-2,6-*i*-Pr₂C₆H₃)(CMe₂)₂(CH₂)), and AgI in THF at room temperature resulted in an immediate color change of the reaction mixture from dark red to yellow colored decanuclear Ag(I)-NC [(Me₂-cAAC)₄(Ag₁₀I₆)] (**2**) in 20% isolated yield after one week (**Scheme 1**). The ³¹P {¹H} NMR spectrum of **2**, recorded in DCM-d₂ at -50 °C exhibited multiple resonances at -70.33 to -86.17 ppm region (see ESI, **Figure S3**), indicating the presence of chemically non-equivalent phosphorus environments in **2**. These resonances are slightly downfield shifted relative to the triplet observed for the previously reported Ag(I)₇ NC (δ = -127.3 ppm), while remaining substantially upfield of the triplet obtained for the Ag(I)₅-cluster [(Cy-cAAC)₄(Ag)₅]NTf₂ (δ = -23.3 ppm), reported by Roy et al.¹⁵



Scheme 1. Synthesis of carbene-phosphinidenide stabilized NC [(Me₂-cAAC)₄(Ag₁₀I₆)] (**2**).

Compared to the phosphalkenide precursor **1** (δ = 206.9 ppm),¹³ the substantial upfield shift of the ³¹P resonances reflects the enhanced electron density at the phosphorus atoms upon coordination to the Ag(I) centers, consistent with their retained anionic phosphinidenide character. The pure crystals and powders of **2** were found to be stable for at least six months under an argon atmosphere, whereas exposure to air resulted in gradual decomposition to a brown residue within two days. **2** is thermally stable up to 200 °C, and finally decomposes to Ag₁₀ at 800 °C (**Figure S4**). The NC **2** was structurally characterized by X-ray single-crystal diffraction, which revealed that **2** crystallizes in monoclinic *P*2₁ space group. The molecular structure shows an Ag(I)₆I₄ core in **2** has been corrected to two Ag(I)₂I units via μ_3 monoanionic (Me₂-cAAC=P⁻) (**Figure 2a**). The Ag(I)₆I₄ and Ag(I)₂I cores were displayed in **Figure 2** (b), showing a rational fusion of them leading to the formation of three μ_3 -bridged Ag(I)₁₀I₆. Two μ - (I1, I3) and μ_3 -iodides (I2, I4) connect six Ag(I) ions of Ag(I)₆I₄ in **2**. Each of three Ag(I) centres (Ag4, Ag7, Ag8) is connected to two P-atoms of Me₂-

cAAC=P ligands. DFT calculation showed that LUMO is located around these three Ag-ions. The resulting Ag-P framework is further capped by a distorted Ag₆I₄ sub-halide unit, which occupies the upper region of the metallic core and contributes to the overall structural rigidity of the cluster. The peripheral Ag1 and Ag3 centers are connected through Ag2, generating a trinuclear Ag₃ cap that is additionally supported by the two iodide ligands I1 and I3. This arrangement gives rise to two Ag₂I sub-halide motifs, interconnected through the central Ag2 atom, with the sub-halide unit incorporating two μ - and two μ_3 -bridging iodide ligands. The Ag...Ag separations in **2** span from 2.85 to 3.03 Å, with an average distance of 2.93 Å, comparable to those reported for the previously reported Ag₄ core of the Ag₇ cluster [2.8668(5)–2.8816(4) Å] and the Ag₅ cluster (average Ag...Ag distance = 2.96 Å),¹⁵ while being slightly shorter than those reported for Ag₁₀ (2.90–3.20 Å),¹⁶ Ag₁₂ (2.92–3.20 Å), Ag₈ NCs (2.97–3.41 Å),¹⁷ and the luminescent Ag₂I₂ cluster (2.998 Å).¹⁸

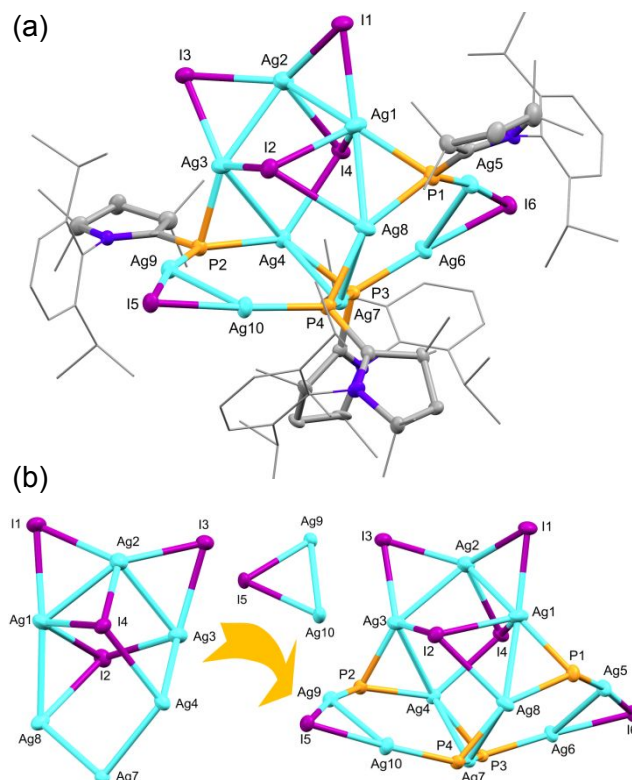


Figure 2. (a) Molecular structure of [(Me₂-cAAC)₄(Ag₁₀I₆)] (**2**). The anisotropic displacement parameters are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected experimental [calculated at B3LYP-D3(BJ)/def2-SVP] bond lengths [Å] and bond angles [°]: Ag1–I1 2.8325(13) [2.8518], I4–Ag1 3.1400(13) [2.8938], Ag2–Ag3 2.9139(15) [2.9945], Ag9–Ag10 2.9467(12) [2.9752], Ag10–P4 2.375(3) [2.4082], Ag1–Ag8 2.9231(14) [2.9881], Ag8–P1 2.420(3) [2.4585], Ag1–P1 2.499(3) [2.5445], P1–C10 1.755(12) (1.7589), Ag9–I5–Ag10 67.52(34) [66.27], Ag1–Ag2–Ag3 86.93(4) [98.02], Ag2–I3–Ag3 63.80(34) [65.13]. (b) The Ag₂I and Ag₆I₄ submerged into the structural core of **2**.

The Ag–P bond distances in **2** range from 2.360–2.511 Å, indicating broadly comparable Ag–P interactions throughout the cluster; these distances are slightly shorter than those reported for the Ag₇ [2.3977(10)–2.5635(10) Å] and the Ag₅ cluster (~2.54 Å),¹⁵ comparable to those of the Ag₂I₂ cluster

(2.51–2.52 Å),¹⁸ but longer than those reported for the dodecanuclear Ag cluster (2.379–2.455 Å).¹⁷ The Ag–I bond distances fall in the ranges of 2.717–2.833 Å for the μ -bridging iodides and 2.823–3.140 Å for the μ_3 -bridging iodides, comparable to those reported for the luminescent $\text{Ag}_2\text{I}_2(\text{dppb-Ac})_2$ cluster (average Ag–I = 2.824 Å).¹⁸ The Ag...Ag separation within the Ag_2I_2 subunit is 2.893 Å, which is shorter than that reported for $\text{Ag}_2\text{I}_2(\text{dppb-Ac})_2$ (2.998 Å),¹⁸ but comparable to the Ag...Ag distance observed in the $(\text{Ag}^{\text{I}}_3)_4\text{L}_4$ metal–organic cages (2.89 Å).¹⁹ The Ag_6I_4 subunit in **2** adopts a distorted hexagonal arrangement of Ag atoms supported by two μ - and two μ_3 -bridging iodide ligands. The Ag...Ag distances within this subunit range from 2.872 to 3.036 Å, slightly exceeding those reported for the octahedral Ag_6Cl_4 cluster (2.68–2.87 Å).² The Ag_2I_2 subunit in **2** exhibits an Ag...Ag separation of 2.872 Å, which is comparable to those of Ag_2F system (2.811–2.990 Å) (Figure 2b).³

The redox behavior of NC **2** was investigated by cyclic voltammetry (CV) studies in THF containing 0.1 M [*n*-Bu₄N]PF₆ as the electrolyte, which exhibited a quasi-reversible reduction at $E_{1/2} = -0.93$ V (referenced against (Cp)₂Fe/(Cp)₂Fe⁺) (Figure S7), suggesting the *in situ* generation of the corresponding radical anion **2**^{•−}. Further, **2** was chemically reduced by K₂C₈ in a 1:1 molar ratio using THF, probing the generation of the radical anion [(Me₂-CAAC=P)₄Ag₁₀I₆]^{•−} (**2**^{•−}) *in situ*. The X-band EPR spectrum of the resulting reaction solution displayed a broad, isotropic resonance, centered at ~335.6 mT, with a *g* value of 2.0115, which was consistent with the formation of a metal-centered radical, and further supported by the Mulliken spin density calculations on **2**^{•−} (Figures S8–S9).

The high-resolution TEM images of **2** revealed the formation of well-defined, spherical particles with a crystalline nature, exhibiting an average diameter in the range of 14.23–17.93 nm with an average diameter of 15.67 nm (Figure 3, (a)), displaying distinct lattice fringes with an interplanar spacing of 0.2511 nm.

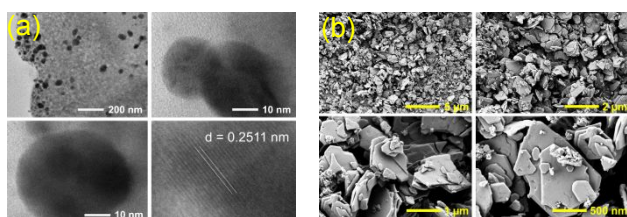


Figure 3. (a) High resolution TEM images, (b) Scanning electron microscopy (SEM) images of the NC [(Me₂-CAACP)₄(Ag₁₀I₆)] (**2**). The particle sizes, and interplanar distances were determined using ImageJ software.²⁰

The morphology and elemental composition of **2** were further investigated by field-emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 3 kV, which exhibited predominantly block-shaped aggregated particles with well-defined sharp edges, clearly visible at the higher magnification of 500 nm, with observed features spanning length scales from 5 μm to 500 nm (Figure 3 (b)).

Geometry optimization of the Ag₁₀I₆ NC **2** was performed at the B3LYP-D3(BJ)/def2-SVP^{21–23} level of theory in its singlet

ground state. To gain a deeper insight into the electronic structure and bonding characteristics, natural bond orbital (NBO) analysis was performed, which reveals that the occupied orbitals are predominantly localized on the Ag and I atoms, whereas the unoccupied orbitals are mainly distributed over the ligand framework. Notably, the LUMO+4 orbital exhibits significant delocalized π character, which is primarily localized on the Dipp substituent attached to the carbene carbon (C_{CAAC}). The Kohn–Sham (K-S) orbital analysis indicates the presence of π back-donation from C_{CAAC} to the π orbital of the phosphorus atom in both the HOMO and HOMO–1 (Figure 4). In addition, an orbital interaction between the Ag d_{xy} orbital and the π orbital of the phosphorus atom is observed, highlighting the contribution of Ag–P orbital overlap to the overall electronic structure and bonding within the cluster. The Ag–I bonding is characterized by a significant polarization toward the I atom (89–92%), indicating that the electron density is predominantly localized on the I atom. This highly polarized bond is consistent with a donor–acceptor interaction, where the I atom acts as an electron donor to the Ag centre. The corresponding bond occupancy values range from 1.79–1.87, suggesting strong but partially polarized Ag–I bonding. Additionally, the presence of 3c–2e bonding is observed in **2**, involving two Ag atoms and one P atom with significant polarization toward the P atom, indicating the dominant role of the P centre in electron density distribution within the Ag–P–Ag framework.

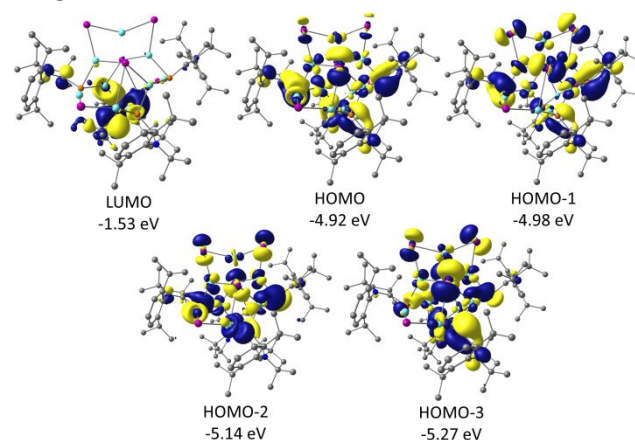


Figure 4. Representative K-S orbitals of the NC [(Me₂-CAACP)₄(Ag₁₀I₆)] (**2**), calculated at the B3LYP-D3(BJ)/def2-SVP level of theory in singlet spin ground state.

Furthermore, the bonding interaction between C_{CAAC} and P atoms is represented by double occupancy, while one bonding orbital is predominantly localized on C_{CAAC}, reflecting π back-donation from the C_{CAAC} to the P atom. In contrast, the second bonding orbital is polarized toward the P atom, corresponding to σ -electron donation from the P atom to C_{CAAC}. These complementary donor–acceptor interactions highlight the synergistic nature of the C_{CAAC}–P bonding and underscore the importance of bidirectional charge transfer in stabilizing the electronic structure of the cluster. The Bader's quantum theory of atoms in molecules (AIM) was employed to perform topological analysis of the

electron density ($\rho(r)$) of ligands,^{24a-b} at the B3LYP-D3(BJ)/def2-SVP level of theory on the optimized geometry of **2**. The highest electron density, $\rho(r)$, was observed for the Ag–I interaction, accompanied by a positive value of $\Delta^2\rho(r)$ and the lowest ellipticity among the investigated interactions, indicating a predominantly closed-shell bonding character (Figure 5).

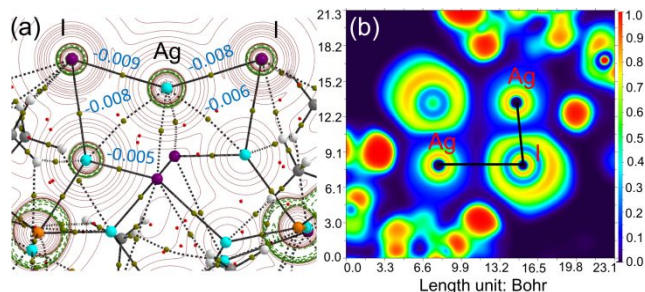


Figure 5. (a) Contour plot of the Laplacian distribution [$\nabla^2\rho(r)$] across I3–Ag8–I1 plane of the NC [(Me₂-CAACP)₄(Ag₁₀I₆)] (**2**). Solid maroon lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$), while dotted green lines denote charge depletion ($\nabla^2\rho(r) > 0$). Solid lines connecting atomic nuclei (grey) are bond paths, and cyan spheres on bond paths indicate BCPs. Blue numbers represent total energy densities at respective BCPs. (b) ELF plot of **2**. The left colour bar indicates the increasing localization.

Furthermore, the total energy density, $H(r)$, was found to be negative ($H(r) < 0$) for all the interactions, suggesting that each interaction is energetically favourable and contributes to the stabilization of the molecular system. To investigate the extent of electron localization and delocalization within the system (**2**), Electron Localization Function (ELF)²⁵ analysis was performed at the B3LYP/def2-SVP level of theory, which revealed the presence of di-, tri-, tetra-, penta-, and nona-synaptic basins, indicating diverse modes of electron localization involving Ag and I centers. The tri-synaptic basins exhibit the highest electron population of 4.1869 e, highlighting significant electron localization across the Ag–I–Ag framework. Notably, the most highly populated basins predominantly involve both Ag and I atoms, suggesting substantial multi-center electron accumulation. The nona-synaptic basin, comprising eight Ag atoms and one I atom, is identified with an electron population of 3.5946 e. The presence of such a highly populated multi-center basin provides evidence for extensive electron delocalization across the Ag–I framework and highlights the potential contribution of multi-center interactions to the overall electronic structure of cluster **2**.

In conclusion, we have successfully stabilized cAAC-phosphaalkenide-supported atomically precise Ag(I)₁₀I₆ NC [(Me₂-CAAC=P)₄Ag₁₀I₆] (**2**), encapsulating the two silver-iodide subunits, Ag₂I and Ag₆I₄ for the first time ever. Single-crystal X-ray diffraction revealed the presence of a butterfly-like Ag₆I₄ core present in **2**. Detailed quantum chemical calculations provided detailed insights into the nature of Ag–Ag and Ag–I interactions in present molecular architecture.

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Data availability

The data supporting this article (Experimental details, UV-vis, XPS, single-crystal X-ray data, computational details) have been included as part of the ESI. †Crystallographic data for **2** has been deposited at the CCDC (2529298†), and can be obtained from <https://www.ccdc.cam.ac.uk/>.

Conflicts of interest

There are no conflicts to declare.

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Data Availability Statement

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