

# EurJIC

European Journal of Inorganic Chemistry

 **Chemistry  
Europe**

European Chemical  
Societies Publishing

## Accepted Article

**Title:** Reactivity Studies of Cyclic Alkyl(Amino) Carbene (cAAC)-Supported Phosphinidenide with AuCl

**Authors:** Ekta Nag, Maria Francis, and Sudipta Roy

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

**To be cited as:** *Eur. J. Inorg. Chem.* **2023**, e202300485

**Link to VoR:** <https://doi.org/10.1002/ejic.202300485>

# Reactivity Studies of Cyclic Alkyl(Amino) Carbene (cAAC)-Supported Phosphinidenide with AuCl

Ekta Nag,<sup>[a]</sup> Maria Francis,<sup>[a]</sup> and Sudipta Roy\*<sup>[a]</sup>

[a] E. Nag, M. Francis, Dr. S. Roy  
Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati,  
Tirupati 517507, India  
E-mail: [roy.sudipta@iisertirupati.ac.in](mailto:roy.sudipta@iisertirupati.ac.in)  
Homepage: <https://sudiptagroup.com/>

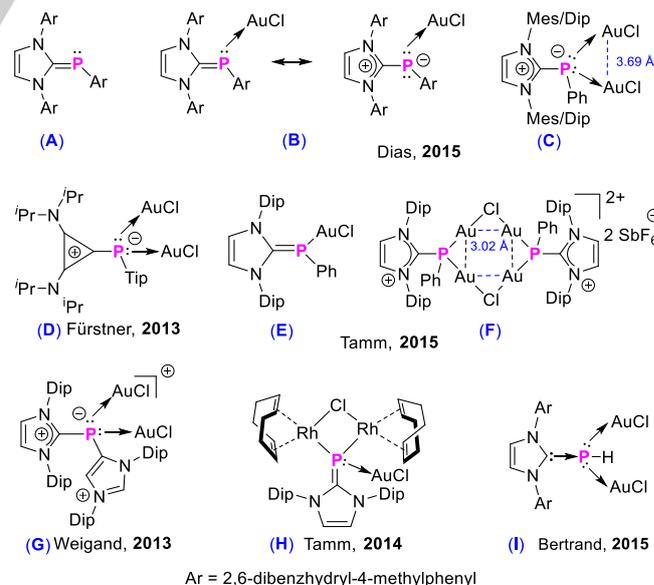
Supporting information for this article is given via a link at the end of the document.

**Abstract:** A neutral octa-nuclear Au<sup>I</sup>-cluster (**2**) with molecular formula [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] [Cy-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>)] has been isolated, and structurally characterized by single-crystal X-ray diffraction. **2** has been further studied by NMR and ESI-MS. The μ<sub>3</sub>-P bridged Au<sup>I</sup>-cluster **2** possesses a C<sub>2</sub> axis that passes through the two Au atoms positioned oppositely of the central Au(I)<sub>4</sub>P<sub>4</sub> core, and two carbene-P chromophores. The emission spectrum of **2** exhibited a broad band with λ<sub>em</sub> at 720 nm, and an average lifetime of 3.36 ns when excited at 388 nm in solid state at room temperature. Cyclic voltammetry (CV) studies revealed that **2** can undergo reversible one-electron oxidation at 0.76 V. The electronic transition in **2** has been further studied by computational methods.

## Introduction

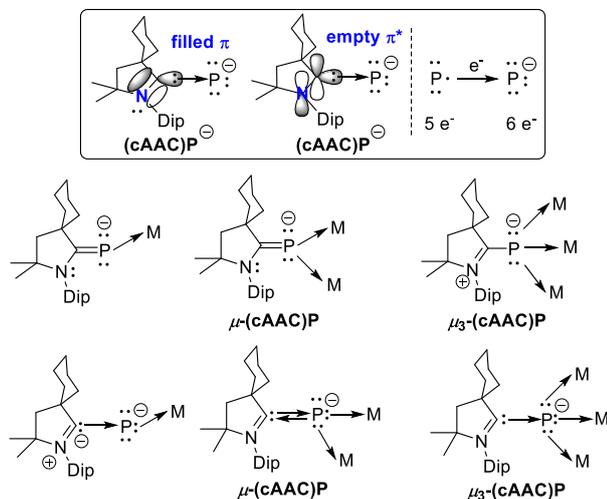
N-heterocyclic carbenes (NHCs) have been proven to be excellent ligands so far for the generation of two coordinate Au<sup>I</sup> complexes [1-11] consisting of mononuclear to polynuclear [2,4,7,9-10] metallic units with fascinating structural aspects, varied catalytic,<sup>[4]</sup> and photoluminescence (PL) properties.<sup>[7,10-11]</sup> The Au<sub>11</sub>-nanocluster reported by Narouz et al. showed an improved electrochemical reduction of CO<sub>2</sub> to CO with coordination of an NHC ligand.<sup>[6]</sup> The carbon-centered hexa-nuclear Au<sup>I</sup> cluster reported by Ube et al. showed green emission with a μ<sub>6</sub>-C atom at the centre.<sup>[9]</sup> There are several other Au-complexes reported, which have been stabilized by various ligands, and attracted the attention of chemists over the past few decades.<sup>[12-36]</sup> While carbenes and phosphines act as monodentate ligands; combination of a singlet carbene with a P-Ar (Ar = bulky aromatic group) unit or P<sup>-</sup> anion evolves a new class of ligand, called the carbene-phosphenidene/phosphenidene [NHC=P-(Ar) (**A**); Ar = Ph, Mes, Figure 1], which can possess two to three pairs of non-bonding electrons on each P-atom, and thereby, can have multiple bridging modes. A decade ago, Weigand, and Fürstner independently showed that a cationic, and neutral carbene-phosphenidene can coordinate to two AuCl molecules (**G**, **D**) (Figure 1). Dias,<sup>[16]</sup> and Tamm groups<sup>[8]</sup> separately isolated bis-AuCl adducts of NHC=P-(Ar) (Ar = 2,6-dibenzhydryl-4-methylphenyl, (**B**); Mes, Ph, (**C**)) with a Au...Au distance of 3.69 Å. Interestingly, Doddi et al. further showed that the dichlorination of NHC=P-(Ph)(AuCl)<sub>2</sub> can lead to the formation of a tetrameric Au<sub>4</sub>Cl<sub>2</sub> di-cation, stabilized by two NHC-phosphenidene (**F**).<sup>[8]</sup> In 2014, Tamm group reported the first example of an NHC-phosphenidene with a formal mono-anionic phosphorus ligand, bridging three metal atoms (**H**).<sup>[37a]</sup> In

2015, Bertrand and co-workers showed the coordination behaviour of the parent phosphenidene NHC-PH treating with two equiv of (tht)AuCl (tht = tetrahydrothiophene), which resulted in the formation of the bis-metal complex **I**, representing a formal μ<sub>3</sub>-P atom considering the isolobal relation between the H<sup>+</sup> and Au<sup>+</sup> ions.<sup>[37b]</sup> While a neutral carbene-phosphenidene can bind to only two Au<sup>I</sup> centres (Figure 1), an anionic carbene-phosphenidene ligand cAAC=P<sup>-</sup> (cAAC = cyclic alkyl(amino) carbene), possessing three pairs of electrons on the P-atom can bind up to three Au<sup>I</sup> ions.<sup>[38-39]</sup> However, the coordination chemistry of anionic cAAC-phosphenidenides (cAAC=P<sup>-</sup>) is yet to be explored. In this context, NHC-phosphenidenide stabilized molecular phosphorus-potassium clusters [K<sub>4</sub>(SiMesP)<sub>2</sub>(HMDS)<sub>2</sub>] (SiMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidine-2-ylidene, HMDS = N(SiMe<sub>3</sub>)<sub>2</sub>), and [K<sub>6</sub>(SiMesP)<sub>2</sub>(O<sup>t</sup>Bu)<sub>4</sub>] reported by the Hänisch group exhibiting μ<sub>3</sub>-bridging through P atoms is noteworthy.<sup>[40]</sup> In past one decade, while NHC=P-P(Ar) [Ar = Ph, Mes, Figure 1] has been shown to stabilize around six different Au<sup>I</sup> complexes (**B-C**, **E-G**), till now no neutral Au-cluster have been reported with the anionic cAAC=P<sup>-</sup> ligand. Moreover, for none of these Au<sup>I</sup> complexes (**A-G**), the corresponding redox, and photoluminescence properties have been reported.



**Figure 1.** Previously reported representative neutral and/or cationic carbene-phosphenidene complexes/clusters of Au (**B-I**). Dip = 2,6-diisopropylphenyl; Mes = 2,4,6-trimethylphenyl.

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  $C_{\text{carbene}}$  atom to form a comparatively stronger  $\sigma$ -bond by making the  $N=C$  bond as a formal double bond (Figure 2).<sup>[41]</sup>



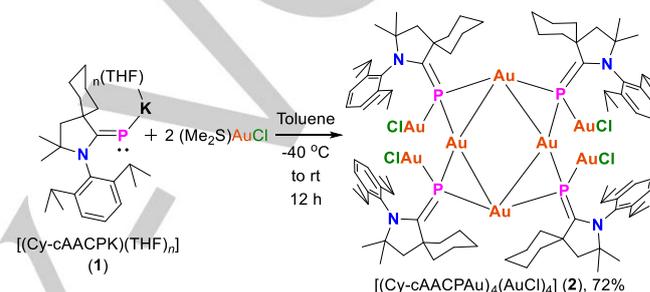
**Figure 2.** Bridging modes of the mono-anionic carbene-phosphinidenide ligand ( $cAAC=P^-$ ).

## Results and Discussion

We have performed the Natural Bond Orbital (NBO) analysis (at BP86/def2-TZVPP level of theory) of  $cAAC=P^-$  ligand to have a deeper understanding of the electron densities distribution, and nature of participating orbitals in complex formation. These studies showed the presence of two lone pairs of electrons on the P atom, one with 1.98e occupancy, having 77% of s- and 23% of p-character (HOMO-2); while the other with 1.79e occupancy and 99.9% of p-character (HOMO) (see SI for Computational details). To have a comparison between the present ligand system ( $Cy-cAAC=P^-$ ) with the already existing  $NHCP^-$  ligand, similar calculations have been performed at the same level of theory, which showed comparable results with respect to the electron occupancies (see SI for details). However as expected, the NPA charges on P are found to be greater in  $NHCP^-$  (-0.415) than that of  $Cy-cAAC=P^-$  (-0.342), whereas, the same on  $C_{\text{carbene}}$  is found to be significantly greater in case of  $Cy-cAAC=P^-$  when compared to that of  $NHCP^-$  (-0.079), which are in good agreement with the fact that cAACs are better  $\pi$  acceptors than the NHCs (see SI for Computational Details). However, when  $cAAC=P^-$  being used as a ligand for complex formation, the electron densities would be pushed over the P atom, facilitating the  $\mu_3$ -bridging with available metal ions.

We have previously shown that the neutral chloro-phosphinidene  $cAAC=P-Cl$ <sup>[42]</sup> can be quantitatively converted to the corresponding K-phosphinidenide  $cAAC=P-K$  (**1**) by reductive dehalogenation of the former in the presence of two equiv of K-metal under ambient temperature.<sup>[42]</sup> **1** can be inherently utilized as the source of the mono-anionic phosphorus ligand,  $cAAC=P^-$ ,<sup>[38-39]</sup> which can bridge between two or three

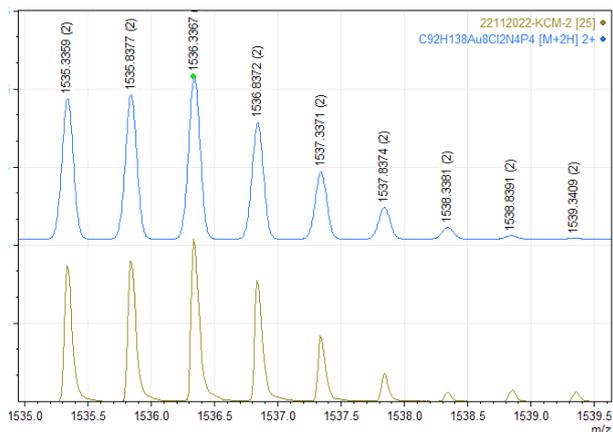
metal centres; where cAAC acts as the electron reservoir as illustrated in Figure 2. Herein, we report on the synthesis, and structural characterization of a neutral atomically precise, first cAAC-phosphinidenide-stabilized redox-active, fluorescent octa-nuclear  $Au^I$ -cluster **2** in excellent yield as an orange light emitter. The K-salt of  $Cy-cAAC$ -phosphinidenide ( $Cy-cAAC=PK$ )(THF)<sub>n</sub> (**1**) ( $Cy-cAAC = :C(N-2,6-Pr_2C_6H_3)(C_6H_{10})(CMe_2)(CH_2)$ ) was reacted with two equiv of  $(Me_2S)AuCl$  in toluene. The reaction was initiated at  $-40^\circ C$  (using isopropanol/liquid nitrogen bath), and stirred for 12 h at room temperature (rt) to obtain the crystalline, orange color precipitate of  $[(Cy-cAACPAu)_4(AuCl)_4]$  (**2**), which was filtered, and dissolved in DCM. The yellow-orange rod-shaped single crystals, suitable for single-crystal X-ray diffraction were obtained in 72% yield from the concentrated DCM solution at  $-20^\circ C$  from a freezer (Scheme 1).



**Scheme 1.** Synthesis of  $[(Cy-cAACPAu)_4(AuCl)_4]$  (**2**).  $Cy-cAAC = C_{23}H_{35}NP$ .

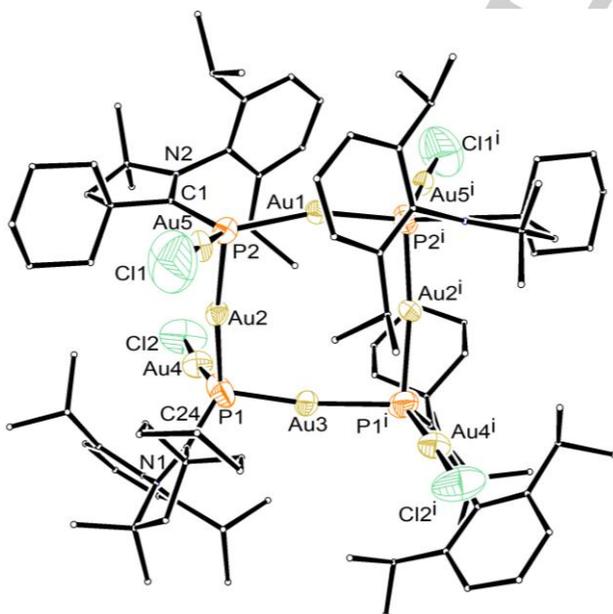
Reaction of **1** with one equiv of  $(Me_2S)AuCl$  in toluene under similar reaction conditions produced **2** with a reduced yield of 10% along with the formation of the bis-phosphinidene  $Cy-cAAC_2P_2$  as the major product, which was characterized by NMR spectroscopy.<sup>[43]</sup> The orange crystalline solid of **2** was found to be stable in air for about a week, and for more than a year under argon atmosphere at rt. The powder of **2** was found to be thermally stable up to  $208^\circ C$  under an inert atmosphere, and then decomposed to a brown liquid. The crystals of **2** were soluble in polar organic solvents, like THF and DCM, but not in non-polar solvents, e.g., toluene and hexane. The DCM solution of **2** was found to be stable for months at rt under an argon atmosphere. Moreover, upon exposure of the same solution to air under humid conditions for 12 h at rt, no decomposition was observed, which was subsequently proved by the  $^{31}P$  NMR spectroscopic analysis, showing the resonances characteristic of only cluster **2**.

The octa-nuclear  $Au^I$ -cluster **2** was characterized by ESI-MS (in DCM solution), showing the presence of the di-cation ( $2-2Cl$ )<sup>2+</sup>  $[(Cy-cAACPAu)_4(Au_4Cl_4) - 2Cl]^{2+}$  (Figure 3). For other representative dicationic fragments of cluster **2**, see SI (Figures S20-21).



**Figure 3.** Experimental (bottom) and simulated (top) ESI-MS spectra of [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub> - 2Cl]<sup>2+</sup> di-cation (2-2Cl)<sup>2+</sup> in DCM. Cy-cAACP = C<sub>23</sub>H<sub>35</sub>NP. ESI-MS: m/z calculated for C<sub>92</sub>H<sub>140</sub>Au<sub>8</sub>Cl<sub>2</sub>N<sub>4</sub>P<sub>4</sub> as [M - 2Cl]<sup>2+</sup>: 1535.3359 (Molecular Weight: 3072.6865); found: 1535.3357.

X-ray single-crystal diffraction of **2** showed the formation of a charge-neutral, octa-nuclear Au-phosphinidenide cluster [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] (**2**), which crystallizes in monoclinic C2/c space group (Figure 4). **2** contains four μ<sub>3</sub>-P bridging Cy-cAAC=P<sup>-</sup> anions, four Au<sup>I</sup> ions, and four AuCl units having a centre of inversion within the molecular structure of **2**. The four Au<sup>I</sup> ions in the middle have been bridged by μ<sub>3</sub>-P<sub>Cy-cAAC=P</sub> to form a nonplanar Au<sub>4</sub> unit at the centre of cluster **2**. Each P atom of the Cy-cAAC=P<sup>-</sup> ligands is coordinated to one AuCl molecule, leading to the formation of a nonplanar Au(I)<sub>4</sub>P<sub>4</sub> core in the middle with two AuCl molecules above, and two below the average plane of Au<sub>4</sub>P<sub>4</sub> unit. The structure of **2** is found to be quite unique when it is compared with those of the previously reported Au-complexes (Figure 1).<sup>[1-10]</sup>

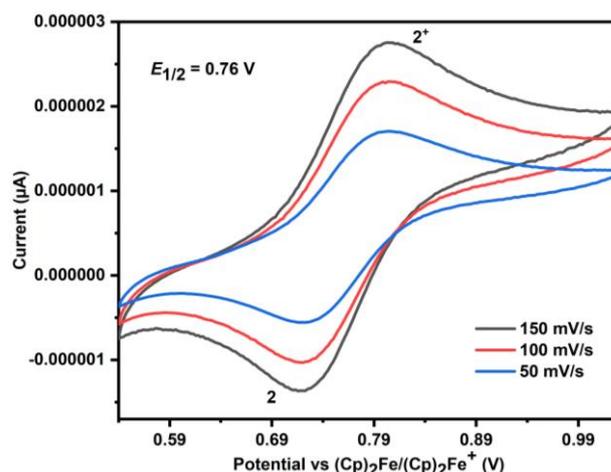


**Figure 4.** Molecular structure of [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] (**2**). The ellipsoids are shown at the 50% probability level. The occupancies of Au1 and Au3 are 0.5. Hydrogen atoms, and disordered atoms are omitted for clarity. Metal atoms Au1, Au2, Au4, Au5, Cl1, and Cl2 are disordered with occupancies of major counterpart 0.8, 0.62, 0.53 and 0.51 and 0.51 and 0.53, respectively.

Selected experimental bond lengths [Å], and bond angles [°]: P2-C1 1.789(11), N2-C1 1.323(15), P1-C24 1.820(11), N1-C24 1.399(14), Au5-Cl1 2.17(2), P2-Au1 2.325(3), Au4-P1 2.404(4), Au5-P2 2.304(3), P2-Au2-P1 171.2(3), P2-Au5-Cl1 177.7(7), Au4-P1-Au2 107.1(2). Symmetry code: (i) -x+1, y, -z+3/2.

Complex **2** possesses 2-fold rotation axis of symmetry, where the rotation axis passes through Au1 and Au3 and hence the occupancy of these atoms is 0.5. The Au<sup>I</sup> ions are slightly disordered around the mean Au<sub>4</sub> plane with an average Au-Au, and Au-P distances of 3.54, and 2.33 Å, respectively.<sup>[11-18]</sup> The Au...Au distance at the central Au<sub>4</sub> ring (3.54 Å) is significantly higher than that of the tetrameric dicationic chloride-bridged Au(I)<sub>4</sub> complex (3.02 Å).<sup>[8]</sup> The previously reported Au-Au distances of bis-carbene-Au<sub>2</sub> complexes are found to be comparatively shorter (3.3955(5)/3.362(1) Å), indicating the presence of auriphilicity between the two gold ions.<sup>[11]</sup> Thus, the auriphilicity in **2** could be said as weaker in magnitude, which might be the reason why the Au-ions in **2** are slightly disordered. The C-N, and C-P bond distances of Cy-cAAC=P unit of **2** are 1.323(15)/1.399(14), and 1.789(11)/1.820(11) Å. The P1-Au2, and P1-Au4 bond lengths are in the range of 2.353(5)-2.404(4) Å, and are significantly longer when compared with the reported tetranuclear dicationic NHC-diphenylphosphinidene [(IPr-PPH)<sub>2</sub>Au<sub>4</sub>Cl<sub>2</sub>](X)<sub>2</sub> complexes [2.239(10) Å].<sup>[8]</sup> The <sup>31</sup>P NMR spectrum of **2** exhibits multiple resonances in the range of -39.6-45.6 ppm. The observed chemical shifts are found to be upfield shifted when compared to that of the corresponding Cy-cAAC=P<sup>-</sup> ligand ((Cy-cAAC=PK)(THF)<sub>n</sub> (**1**); 207 ppm), and the tetrameric chloride bridged dicationic Au<sub>4</sub> complex (-28.17 ppm) reported by Doddi et al.,<sup>[8]</sup> but similar to that of the cationic complex isolated by Weigand et al. (-40.4 ppm).<sup>[17]</sup>

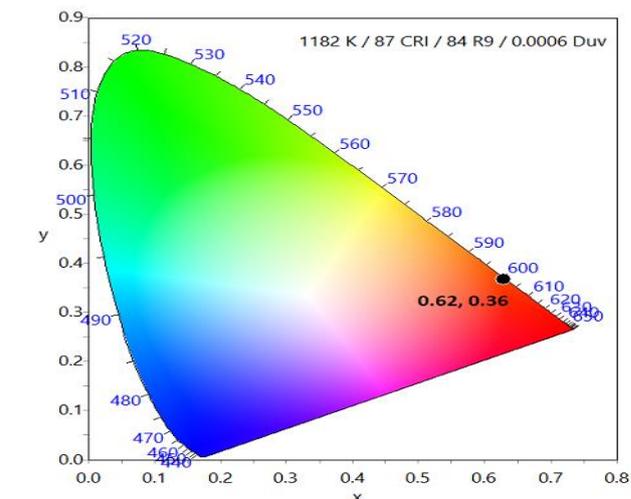
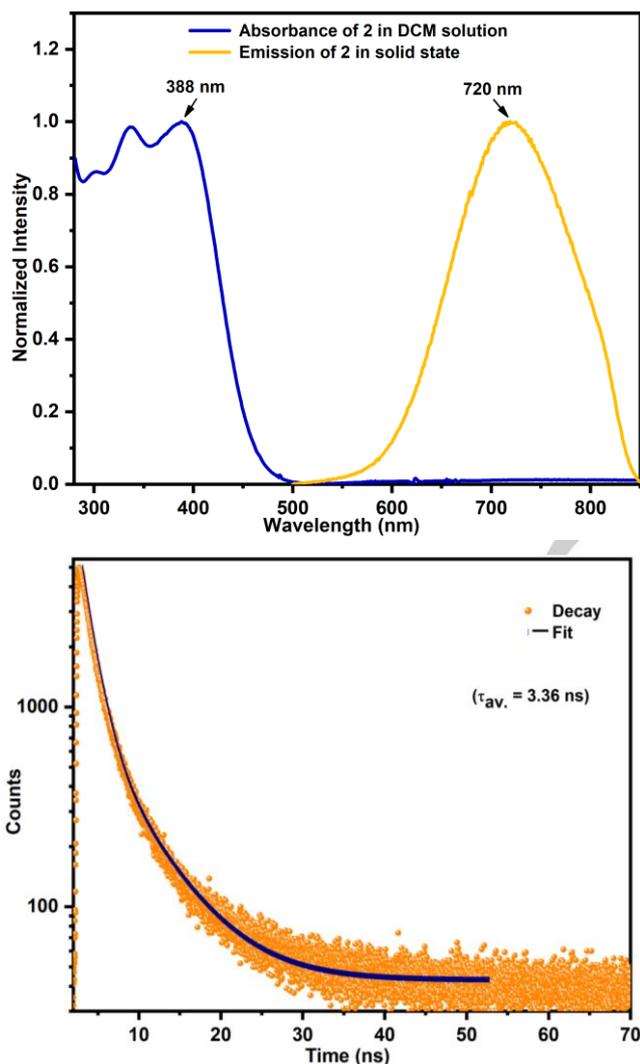
Complex **2** was found to be redox active. The cyclic voltammetry (CV) studies of **2** showed that [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] (**2**) can undergo an one electron reversible oxidation above E<sub>1/2</sub> = 0.76 V (Figure 5) in DCM, suggesting the formation of the corresponding cation [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>]<sup>+</sup> (**2**<sup>+</sup>) with the peak to peak potential difference of 70, and 300 mV, respectively. However, several attempts to isolate the cation **2**<sup>+</sup> in the solid state were failed.



**Figure 5.** Cyclic voltammograms of complex [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] (**2**) in DCM containing 0.1 M [n-Bu<sub>4</sub>N]PF<sub>6</sub> as the electrolyte employing silver as a reference electrode, glassy carbon as a working electrode, and platinum as counter electrode. cAAC = Cy-cAAC.

## Photophysical Studies

The UV-vis studies of **2** showed three strong absorption bands at 310, 336, and 388 nm in DCM (Figure 6, top). The previously reported dark green color cationic carbene-Au<sup>I</sup> complex with a two-coordinate Au<sup>I</sup> ion showed similar UV-vis absorption bands at 312, 401, 435, and 642 nm.<sup>[13]</sup> The absorption at 642 nm has been assigned due to the electronic transition from HOMO to the 5d orbital of Au<sup>I</sup>.<sup>[13]</sup> The excitations with the wavelengths ranging from 250-470 nm led to a broad emission band<sup>[7]</sup> of **2** in the range of 550-850 nm with a maximum ( $\lambda_{\text{max}}$ ) at 720 nm in the solid state at rt (Figure 6, top).

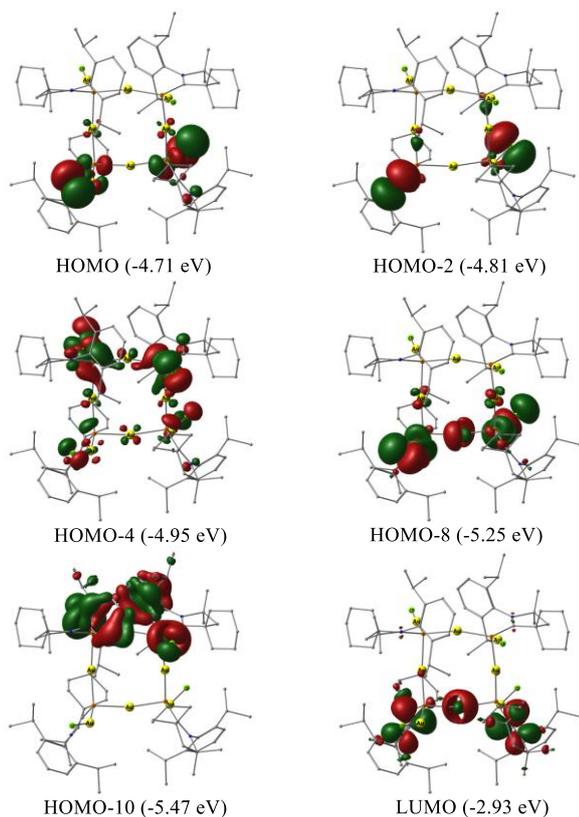


**Figure 6.** Top: UV-vis absorption (blue curve,  $\lambda_{\text{max}} = 388$  nm) and Emission (orange curve,  $\lambda_{\text{em}} = 720$  nm) spectra of [(Cy-cAACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] (**2**) in solid state at rt. Middle: Lifetime decay plot of **2** at rt. The exciting pulsed and emission shown in orange color ( $\tau_{\text{av.}} = 3.36$  ns at 720 nm during excitation with a light source EPL of 375 nm) and fitting in blue curve. Bottom: Photoluminescence color coordinates of **2** plotted in the CIE 1931 chromaticity diagram. The black dot corresponds to the coordinates attributed to pure orange light emission (0.62, 0.35).

The previously reported carbene-Au<sup>I</sup>-complexes with Au...Au interactions display emission bands of 400-600 nm upon excitation in the range of 300-400 nm.<sup>[14]</sup> A trinuclear carbene-Au<sup>I</sup>-amide complex with Au...Au distances of 3.6660(5), 3.7296(5), and 3.7526(3) Å showed emission band at 722 nm (orange emission) upon excitation at 296 nm.<sup>[15]</sup> **2** possesses an average emission lifetime of 3.36 ns (at  $\lambda_{\text{em}} = 720$  nm) when it is excited with the light source EPL of 375 nm (Figure 6, bottom). The photoluminescence quantum yield (PLQY)  $\Phi_{\text{PL}}$  of **2** has been experimentally estimated to be nearly 1% (0.89%). The lower value could be rationalized by the higher thermal motion of Au<sub>4</sub> unit leading to the facile dissipation of absorbed photons via non-radiative decay.

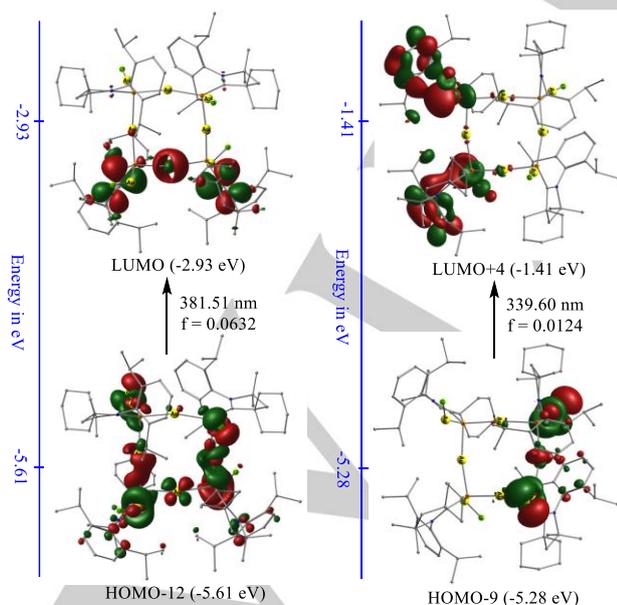
**2** possesses two chemically different Au<sup>I</sup> ions from central Au(I)<sub>4</sub> unit, and two different terminally coordinated AuCl molecules (Figure S4 in SI). It also contains two different Cy-cAAC=P moieties, which possess the N-C-P unit as the electron accepting chromophore ( $\pi^*_{\text{N-C-P}}$ ). The filled d-orbitals of Au<sup>I</sup> centre are expected to involve in the electronic conjugation/cross-conjugation of this complex.

The natural bond orbital (NBO) analysis of **2**, calculated at BP86/LanL2DZ level of theory showed that the HOMO, and HOMO-2 represent the d-orbitals of Au, and p-orbitals of Cl of the two AuCl units of **2** (Figure 7). HOMO-129 illustrates the  $\sigma$  interaction between the C<sub>cAAC</sub> and P atom. HOMO-104 exhibits an extended electron delocalization of a  $\pi$ -type nature between the (Cl)Au-P-Au moiety. Whereas, HOMO-14 and HOMO-6 signify the interactions involving the P atom and the Au atoms. The former displays a  $\sigma$ -type interaction encompassing both types of Au atoms, whereas the latter portrays an interaction between the P atom and Au(Cl) (see SI).



**Figure 7.** NBOs of **2** calculated at BP86/LanL2DZ level of theory (all energy values given above are in eV).

The time dependent density functional theory (TD-DFT) calculation on **2**, performed at BP86/LanL2DZ level of theory showed that the transitions at 381.5, and 339.6 nm correspond to HOMO-12→LUMO, and HOMO-9→LUMO+4 transitions (Figure 8).



**Figure 8.** Calculated absorption maxima of excitation energies, oscillator strengths of **2** at BP86/LanL2DZ in solvent (DCM) phase. Electronic transition from the electron pairs on P/Cl to  $\pi^*_{\text{N=C-P}}$  of Cy-cAAC=P unit of **2**.

The former is the electronic excitation from the d-orbital of Au atoms, and lone pair of electrons of Cl atoms into the  $\pi^*$  of  $\text{C}=\text{N}_{\text{cAAC}}$ , while the latter from the d-type orbital on Au-atom with Cl lone pairs type orbitals to  $\pi^*$  orbital extended over phenyl ring of diisopropylphenyl group (Dip). The corresponding oscillator strengths are (f) 0.0632, and 0.0124, respectively. Notably, the Au1–C<sub>Dip-ring</sub> distance in **2** is found to be 3.36(2) Å, while the Au2/Au3 centres are surrounded by cyclohexyl/Pr groups of cAAC. The Au4–C<sub>Dip-ring</sub> distance is found to be 3.30(1) Å.

## Conclusion

In conclusion, we have utilized the potassium salt of cyclic alkyl(amino) carbene-anchored mono-anionic phosphorus atom (Cy-cAAC=P<sup>-</sup>) as the ligand to react with AuCl to stabilize, and isolate the octa-nuclear Au<sup>I</sup>-cluster (**2**) in high yield. **2** possesses a square like nonplanar Au<sub>4</sub> ring whose all four vertices have been bridged by  $\mu_3$ -P<sub>Cy-cAAC=P</sub> atoms to additional four terminal AuCl molecules. Cyclic voltammetry studies showed that **2** can be reversibly oxidized to its mono-cation in DCM solution at 0.76 V. The average lifetime of fluorescence transition of **2** has been experimentally estimated to be 3.36 ns in solid state with a photoluminescence quantum yield of 0.89%. TD-DFT calculations showed that **2** possesses two electron-donor orbitals (PAuCl, AuCl), and two low-lying  $\pi^*$  orbitals as the acceptors (N=C-P, and the aromatic ring of the Dip group of cAAC) corresponding to two different electronic transitions, which are also supported by the experimentally observed UV-vis absorption spectrum of **2**.

## Experimental Section

All manipulations were carried out using either standard Schlenk line techniques under argon atmosphere or in an argon-filled glove box, where O<sub>2</sub> and H<sub>2</sub>O levels were kept below 0.1 ppm at all times using oven-dried (150 °C) glassware. Solvents obtained from the Solvent Purification System were further dried by refluxing with Na/K alloy for two days, followed by vacuum distillation over 4 Å molecular sieves. Commercially purchased deuterated solvent CD<sub>2</sub>Cl<sub>2</sub> was further purified by stirring over anhydrous CaH<sub>2</sub> for two days, followed by 12 h of reflux, and vacuum distillation.

**Synthesis of complex [(Cy-cACPAu)<sub>4</sub>(AuCl)<sub>4</sub>] (**2**):** In an oven dried Schlenk flask, Cy-cAAC=PK (**1**) (150 mg, 0.37 mmol, 1 equiv), and anhydrous (Me<sub>2</sub>S)AuCl (218.3 mg, 0.74 mmol, 2 equiv) were taken. Freshly distilled and precooled (-40 °C using isopropanol/liquid nitrogen bath) toluene (15 mL) was added to the same flask to obtain a yellowish-orange solution. The reaction mixture was stirred overnight at room temperature (rt) in the absence of light. An orange color precipitate was formed after overnight stirring. The reaction mixture was filtered through a frit to obtain a light orange color residue of complex **2**, which was further washed with cold *n*-hexane (0 °C), and dissolved in anhydrous DCM. The DCM solution was concentrated up to 1-2 mL, and stored at -20 °C to obtain the needle shaped, golden

yellow single-crystals of complex **2** (210 mg, 72%) suitable for X-ray single-crystal diffraction.

**<sup>1</sup>H NMR** (400 MHz, 298 K, DCM-*d*<sub>2</sub>)  $\delta$ : 7.88 (d, *J* = 6.5 Hz, 1H, -ArH), 7.63-7.54 (m, 4H, -ArH), 7.40-7.29 (m, 6H, -ArH), 7.05 (d, *J* = 6.3 Hz, 1H, -ArH), 3.48-3.28 (m, 4H, -(cyclohexyl)), 3.21-3.08 (m, 2H, -(cyclohexyl)), 3.04-2.93 (m, 2H, -(cyclohexyl)), 2.76 (septet, *J* = 12.8, 6.4 Hz, 2H, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.61-2.50 (m, 6H, -CH(CH<sub>3</sub>)<sub>2</sub>), 2.46-2.39 (m, 2H, -(cyclohexyl)), 2.38-2.32 (m, 2H, -(cyclohexyl)), 2.21 (d, *J* = 6.9 Hz, 8H, -CH<sub>2</sub>), 2.00 (d, *J* = 13.1 Hz, 6H, -(cyclohexyl)), 1.94-1.84 (m, 8H, -(cyclohexyl)), 1.81-1.73 (m, 6H, -(cyclohexyl)), 1.67 (d, *J* = 6.6 Hz, 4H, -(CH<sub>3</sub>)<sub>2</sub>), 1.65-1.55 (m, 8H, -(cyclohexyl)), 1.57 (d, *J* = 6.6 Hz, 4H, -(CH<sub>3</sub>)<sub>2</sub>), 1.39 (d, *J* = 6.9 Hz, 12H, -(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, *J* = 5.3 Hz, 12H, -(CH<sub>3</sub>)<sub>2</sub>), 1.33-1.24 (m, 28H, -(CH<sub>3</sub>)<sub>2</sub>), 1.20-1.13 (m, 12H, -(CH<sub>3</sub>)<sub>2</sub>) ppm; **<sup>13</sup>C** **{<sup>1</sup>H}** **NMR** (101 MHz, 298 K, DCM-*d*<sub>2</sub>)  $\delta$ : 224.0 (*C*<sub>carbene</sub>), 145.8, 144.8, 143.4, 133.3, 132.0, 131.0, 130.3, 126.9, 126.7, 126.6, 125.9, 179.0, 78.3, 58.6, 58.3, 46.3, 45.8, 42.2, 41.6, 39.8, 33.0, 32.2, 31.9, 31.3, 30.8, 29.8, 29.2, 29.0, 28.5, 27.8, 27.0, 25.4, 25.2, 25.0, 24.8, 24.1, 23.8, 23.3, 23.0, 22.7, 14.2 ppm.

**Decomposition Point:** 208-210 °C.

**Photophysical studies of 2:** All measurements have been performed under argon atmosphere using standard quartz cuvettes (1 cm × 1 cm cross-section) or quartz holder. The UV-Vis absorption spectrum for **2** has been recorded using Agilent Cary Series UV-Vis-NIR spectrophotometer. The photoluminescence (PL) spectrum, lifetime, and absolute quantum yield for **2** have been measured in the solid state or in solution (DCM) in an EDINBURGH FLS1000 photoluminescence spectrometer at rt. The DCM solution of **2** showed the absorption maximum at 388 nm, and emission maximum at 715 nm, whereas, in solid-state emission maximum was observed at 720 nm on excitation at 400 nm. The lifetime of **2** was found to be 3.36 ns at 720 nm during excitation with a light source EPL of 375 nm.

**Measurement of the absolute quantum yield ( $\Phi_f$ ) of 2:** The absolute quantum yield for cluster **2** was measured using an integrating sphere for both the powder form, and the DCM solution of cluster **2** utilizing the Edinburgh FLS1000 photoluminescence spectrometer. The absolute method obtains the quantum yield directly by capturing all fluorescence emitted by the sample via the integrating sphere. The measurements were performed starting with the blank measurement followed by the sample measurement for both the solid and solution samples of **2** at rt.

## Supporting Information

Deposition Number 2194542 (for **2**) contains the supplementary crystallographic data for this paper. The Crystallographic Information File for **2** can be obtained from the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service via

[www.ccdc.cam.ac.uk/structures/](http://www.ccdc.cam.ac.uk/structures/). The authors have cited additional references within the Supporting Information.<sup>[45-60]</sup>

## Acknowledgements

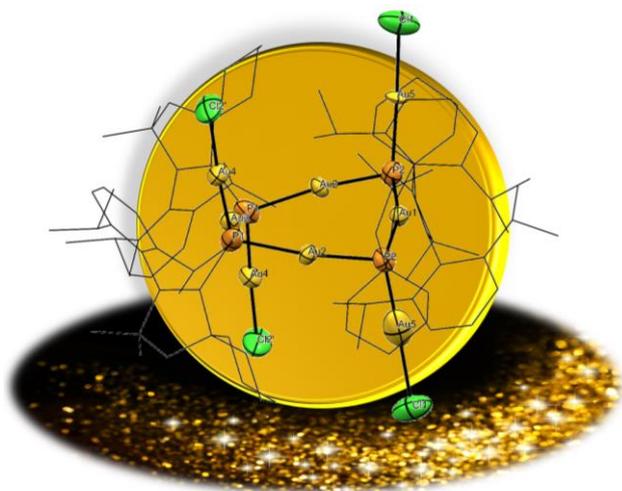
SR gratefully acknowledges SERB, New Delhi for the POWER grant (SPG/2021/003237), and IISER Tirupati. EN, and MF thank IISER Tirupati, and CSIR respectively for their respective SRFs. We thank Dr. PSG, Bruker India, for initial structure refinement of **2**.

**Keywords:** Au<sub>3</sub>-cluster • Cyclic alkyl(amino) carbene • Phosphinidenide • Redox and fluorescence • Structure and bonding

- [1] R. S. Ramon, S. Gaillard, A. Poater, L. Cavallo, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2011**, *17*, 1238-1246.
- [2] T. J. Robilotto, J. Bacsá, T. G. Gray, J. P. Sadighi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12077-12080.
- [3] G. D. Frey, R. D. Dewhurst, S. Kousar, B. Donnadieu, G. Bertrand, *J. Organomet. Chem.* **2008**, *693*, 1674-1682.
- [4] L. Jin, D. S. Weinberger, M. Melaimi, C. E. Moore, A. L. Rheingold, G. Bertrand, *Angew. Chem. Int. Ed.* **2014**, *53*, 9059-9063.
- [5] M. Joost, N. S. Merceron, A. Amgoune, D. Bourissou, *Organometallics* **2019**, *38*, 3494-3497.
- [6] M. R. Narouz, K. M. Osten, P. J. Unsworth, R. W. Y. Man, K. Salorinn, S. Takano, R. Tomihara, S. Kaappa, S. Malola, C. -T. Dinh, J. D. Padmos, K. Ayoo, P. J. Garrett, M. Nambo, J. H. Horton, E. H. Sargent, H. Häkkinen, T. Tsukuda, C. M. Crudden, *Nature Chem.* **2019**, *11*, 419-425.
- [7] P. A. Lummis, K. M. Osten, T. I. Levchenko, M. S. A. Hazer, S. Malola, B. Owens-Baird, A. J. Veinot, E. L. Albright, G. Schatte, S. Takano, K. Kovnir, K. G. Stamplecoskie, T. Tsukuda, H. Häkkinen, M. Nambo, C. M. Crudden, *JACS Au* **2022**, *2*, 875-885.
- [8] A. Doddi, D. Bockfeld, A. Nasr, T. Bannenberg, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2015**, *21*, 16178-16189.
- [9] H. Ube, Q. Zhang, M. Shionoya, *Organometallics* **2018**, *37*, 2007-2009.
- [10] M. R. Narouz, S. Takano, P. A. Lummis, T. I. Levchenko, A. Nazemi, S. Kaappa, S. Malola, G. Yousefzaladeh, L. A. Calhoun, K. G. Stamplecoskie, H. Häkkinen, T. Tsukuda, C. M. Crudden, *J. Am. Chem. Soc.* **2019**, *141*, 14997-15002.
- [11] A. A. Penney, V. V. Sizov, E. V. Grachova, D. V. Krupenya, V. V. Gurzhiy, G. L. Starova, S. P. Tunik, *Inorg. Chem.* **2016**, *55*, 4720-4732.
- [12] D. Fenske, F. Simon, *Angew. Chem. Int. Ed.* **1997**, *36*, 230-233.
- [13] M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, *Angew. Chem. Int. Ed.* **2014**, *53*, 9372-9375.
- [14] T. Lu, C.-F. Yang, C. A. Steren, F. Fei, X.-T. Chen, Z.-L. Xue, *New J. Chem.* **2018**, *42*, 4700-4713.
- [15] J. Ruiz, D. Sol, M. A. Mateo, M. Vivanco, R. Badía-Laiño, *Dalton Trans.* **2020**, *49*, 6561-6565.
- [16] V. A. K. Adiraju, M. Yousufuddin, H. V. R. Dias, *Dalton Trans.* **2015**, *44*, 4449-4454.
- [17] K. Schwedtmann, M. H. Holthausen, K.-O. Feldmann, J. J. Weigand, *Angew. Chem. Int. Ed.* **2013**, *52*, 14204-14208.
- [18] M. Alcarazo, K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, *Chem. Commun.* **2013**, *49*, 3140-3142.
- [19] E. Zeller, H. Bernda, H. Schmidbaur, *Inorg. Chem.* **1993**, *32*, 3203-3204.
- [20] S. Thompson, J. Eng, T. J. Penfold, *J. Chem. Phys.* **2018**, *149*, 014304.
- [21] M. Peters, A. Doddi, T. Bannenberg, M. Freytag, P. G. Jones, M. Tamm, *Inorg. Chem.* **2017**, *56*, 10785-10793.
- [22] M. R. Narouz, K. M. Osten, P. J. Unsworth, R. W. Y. Man, K. Salorinne, S. Takano, R. Tomihara, S. Kaappa, S. Malola, C. T. Dinh, J. D. Padmos, K. Ayoo, P. J. Garrett, M. Nambo, J. H. Horton, E. H. Sargent, H. Häkkinen, T. Tsukuda, C. M. Crudden, *Nature* **2019**, *11*, 419-425.
- [23] P. Bellon, M. Manassero, M. Sansoni, *Cryst.* **1965**, *318*, 2423-2427.
- [24] T.-H. Huang, F.-Z. Zhao, Q.-L. Hu, Q. Liu, T.-C. Wu, D. Zheng, T. Kang, L.-C. Gui, J. Chen, *Inorg. Chem.* **2020**, *59*, 16027-16034.

- [25] A. S. Romanov, C. R. Becker, C. E. James, D. Di, D. Credgington, M. Linnolahti, M. Bochmann, *Chem. Eur. J.* **2017**, *23*, 4625-4637.
- [26] P. J. Conaghan, C. S. B. Matthews, F. Chotard, S. T. E. Jones, N. C. Greenham, M. Bochmann, D. Credgington, A. S. Romanov, *Nat. Commun.* **2020**, *11*, 1758.
- [27] R. Jazzar, M. Soleilhavoup, G. Bertrand, *Chem. Rev.* **2020**, *120*, 4141-4168.
- [28] M. Bevilacqua, M. Roverso, S. Bogialli, C. Graiff, A. Biffis, *Inorg. Chem.* **2023**, *62*, 1383-1393.
- [29] S. M. van de Looij, E. R. Hebels, M. Viola, M. Hembury, S. Oliveira, T. Vermonden, *Bioconjugate Chem.* **2022**, *33*, 4-23.
- [30] M. Zhou, C. Zeng, Q. Li, T. Higaki, R. Jin, *Nanomaterials* **2019**, *9*, 933.
- [31] A. S. Romanov, M. Bochmann, *Organometallics* **2015**, *34*, 2439-2454.
- [32] J. Wei, S. Kahlal, J.-F. Halet, J.-Y. Saillard, A. Muñoz-Castro, *J. Phys. Chem. A* **2022**, *126*, 536-545.
- [33] H. Hirai S. Ito, S. Takano, K. Koyasu, T. Tsukuda, *Chem. Sci.* **2020**, *11*, 12233-12248.
- [34] F. Chotard, V. Sivchik, M. Linnolahti, M. Bochmann, A. S. Romanov, *Chem. Mater.* **2020**, *32*, 6114-6122.
- [35] Y. Yang, P. R. Sharp, *J. Am. Chem. Soc.* **1994**, *116*, 6983-6984.
- [36] A. M. Polgar, F. Weigend, A. Zhang, M. J. Stillman, J. F. Corrigan, *J. Am. Chem. Soc.* **2017**, *139*, 14045-14048.
- [37] a) A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2014**, *53*, 13568-13572; b) L. L. Liu, D. A. Ruiz, F. Dahcheha, G. Bertrand, *Chem. Commun.* **2015**, *51*, 12732-12735.
- [38] E. Nag, S. Battuluri, B. B. Sinu, S. Roy, *Inorg. Chem.* **2022**, *61*, 13007-13014.
- [39] E. Nag, S. Battuluri, K. C. Mondal, S. Roy, *Chem. Eur. J.* **2022**, *28*, e202202324.
- [40] M. Balmer, F. Weigend, C. von Hänisch, *Chem. Eur. J.* **2019**, *25*, 4914-4919.
- [41] K. C. Mondal, H. W. Roesky, A. C. Stückl, F. Ehret, W. Kaim, B. Dittrich, B. Maity, D. Koley, *Angew. Chem. Int. Ed.* **2013**, *52*, 11804-11807.
- [42] A. Kulkarni, S. Arumugam, M. Francis, P. G. Reddy, E. Nag, S. M. N. V. T. Gorantla, K. C. Mondal, S. Roy, *Chem. Eur. J.* **2021**, *27*, 200-206.
- [43] O. Back, B. Donnadiou, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369-373.
- [44] a) G. A. Bowmaker, C. L. Brown, R. D. Hart, P. C. Healy, C. E. F. Rickard, A. H. White, *J. Chem. Soc., Dalton Trans.* **1999**, 881-890; b) S. K. Mallisery, D. Gudat, *Dalton Trans.* **2010**, *39*, 4280-4284; c) L. E. Marbella, S. E. Crawford, M. J. Hartmann, J. E. Millstone, *Chem. Commun.* **2016**, *52*, 9020-9023.
- [45] V. Lavallo, Y. Canac, C. Präsang, B. Donnadiou, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705-5709.
- [46] S. Roy, K. C. Mondal, S. Kundu, B. Li, C. J. Schürmann, S. Dutta, D. Koley, R. Herbst-Irmer, D. Stalke, H. W. Roesky, *Chem. Eur. J.* **2017**, *23*, 12153-12157.
- [47] Bruker (2021). APEX4. Bruker Nano, Inc., Madison, WI, USA.
- [48] 'SAINT V8.40B (Bruker AXS LLC, 2019).
- [49] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.
- [50] G. M. Sheldrick, *Acta Cryst. Section A: Foundations and Advances*, **2015**, *71*, 3-8.
- [51] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1429-1437.
- [52] a) P. Pyykkö, *Angew. Chem.* **2006**, *118*, 28-29; b) G. Frenking, *The Chemical Bond*, **2014**, 25-48.
- [53] E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comp. Chem.* **2013**, *34*, 1429-1437.
- [54] Y. Ge, A. Le, G. J. Marquino, P. Q. Nguyen, K. Trujillo, M. Schimelfenig, A. Noble, *ACS Omega* **2019**, *4*, 18809-18819.
- [55] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
- [56] R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454-464.
- [57] C. Van Caillie, R. D. Amos, *Chem. Phys. Lett.* **1999**, *308*, 249-255.
- [58] S. Miertuš, E. Scrocco, J. Tomasi, *J. Chem. Phys.* **1981**, *55*, 117-129.
- [59] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999-3094.
- [60] R. L. Martin, *J. Chem. Phys.* **2003**, *118*, 4775-4777.

## Entry for the Table of Contents



A neutral, redox-active  $\text{Au}_8$  cluster has been stabilized and isolated in the solid state by employing cyclic alkyl(amino) carbene (cAAC)-supported mono-anionic phosphorus (cAAC=P<sup>-</sup>) as the ligand. The novel  $\text{Au}_8$  cluster has been observed to exhibit orange emission with an average lifetime of 3.36 ns and photoluminescence quantum yield of 0.89% (in solid state).

Institute and/or researcher Twitter usernames: @liserTirupati; @ekta\_nag