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$[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$: Two New Hydride and Phosphine Co-Protected Clusters and Their Fragmentation Leading to Naked Clusters, Ag_{13}^{++} and Ag_{25}^{+++}

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hexane) and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ (DPPB = 1,4-bis(diphenylphosphino)butane). The cluster composition was confirmed by high-resolution electrospray ionization mass spectrometric (HRESI MS) studies and also by other supporting data. To the best of our knowledge, the newly synthesized $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ clusters are the smallest and the largest known hydride and phosphine coprotected silver clusters, respectively, synthesized in the solution phase. Collision-induced dissociation (CID) was used to probe their fragmentation pattern in the gas phase, which also supported their compositions. During the CID experiment, naked clusters Ag_{13}^+ and Ag_{25}^+ got formed starting from the ligated Ag_{15} and Ag_{27} clusters, respectively, where the number of metal atoms remained nearly the same as in the parent clusters. Collision energy-dependent fragmentation pathways of the formation of



naked clusters have been explored in detail. We suggest that silver clusters protected by hydride and phosphine ligands may become useful precursors to make new naked clusters in the gas phase.

INTRODUCTION

New methods for the synthesis of atomically precise noble metal nanoclusters have been explored extensively in the past few decades due to the potential applications of these materials in catalysis, energy storage, sensing, drug delivery, optics, etc.¹⁻⁷ Their photophysical properties have also gained much attention.^{8,9} An atomically precise cluster is composed of a core (or arrangement of metal atoms) and its shell (arrangement of ligands and bonding between them and the metal core). Staple units are formed by the interaction of sulfur of the thiol commonly used as the ligand and the surface metal atoms, but this is not a general case and examples include phosphine-protected systems.^{10,11} The properties of nanoclusters can be manipulated either by changing the core or the ligand surface, which will in turn alter their total structure.^{12,13} Therefore, the introduction of new ligand results in a new cluster system, which can be a promising synthetic approach for a new class of materials. Liquid phase synthesis of noble metal nanoclusters has been investigated widely with classic ligands, namely thiols,^{14,15} phosphines,^{16,17} alkynyls¹⁸ and/or their combinations.¹⁹ The use of these organic ligands results in a wide range of nuclearities in nanoclusters which have been characterized as Au_{102} , ²⁰ Au_{25} , ²¹ Au_{18} , ²² Ag_{44} , ²³ Ag_{25} , ²⁴ Ag_{29} , ²⁵ etc., by varying ligands and synthetic methods.

In the context of increasing the global energy demand, metal hydrides, 26 complex hydrides, 27 and metal–organic frameworks (MOFs) 28 have been explored to discover new

hydrogen storage materials. For the last three decades, group 11 metal (copper, silver, gold) hydrides have become an emerging category of research in terms of their new molecular structures, interesting properties, and hydrogen related applications.²⁹ A series of copper hydride clusters have been explored by different research groups in view of their various applications, like energy storage and conversion.^{30,31} In contrast, inorganic ligands (H⁻ and OH⁻) have rarely been used for the synthesis of Au and Ag nanoclusters. Their use could have given us the opportunity to find different core sizes and enhanced properties. So far, reports of Ag clusters by using hydride as inorganic ligand are much fewer and should be further explored. Mass spectrometry-based investigations have identified low-nuclearity clusters with very few hydride ligands.³² For hydride protected clusters, the presence of coligands is necessary to give them adequate stability. In 2016, Bakr group reported a new class of silver clusters where hydrides are majority ligands in the presence of phosphines, the latter acted as coligands. They have synthesized hydride rich $[Ag_{18}H_{16}(TPP)_{10}]^{2+}$, $[Ag_{25}H_{22}(DPPE)_{8}]^{3+}$, and

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 $[Ag_{26}H_{22}(TFPP)_{13}]^{2+}$ clusters using TPP (triphenylphosphine), DPPE (1,2-bis(diphenylphosphine))ethane), and TFPP (tris(4-fluorophenyl)phosphine) coligands, respectively.³³ High resolution ESI mass spectra with distinct isotopic patterns helped them to identify the compositions of these hydride-protected clusters. In 2017, a report from our group showed that these clusters can be the starting materials to create naked silver clusters in the gas phase by collision-induced dissociation (CID).³⁴ We have also demonstrated that naked clusters can be formed outside the mass spectrometer by thermal desorption of hydrogen and phosphine ligands.³⁵ The formation of naked clusters with specific nuclearity was investigated further to understand their structures, fragmentation pathways, and reactivity in the gas phase.³⁶

To explore the diversity of hydride and phosphine coprotected silver clusters, we have synthesized two new silver nanoclusters by varying the synthetic parameters like the phosphine ligand used, reaction time and rate of mixing. We find that by changing the phosphine from DPPH (1,6bis(diphenylphosphino)hexane) to DPPB (1,4-bis-(diphenylphosphino)butane), we get two different clusters, $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$. These clusters are thoroughly characterized by high-resolution electrospray ionization mass spectrometry (HRESI MS), optical spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM EDS) and transmission electron microscopy (TEM). The in situ gas phase fragmentation or CID of these newly synthesized clusters have also been studied in detail. Fragmentation study confirms the number of hydrogen and phosphine ligands and also results in naked clusters, Ag_{13}^{+} and Ag_{25}^{+} starting from Ag15 and Ag27 clusters, respectively. Further confirmation of hydride protection comes from deuterium labeling experiments.

EXPERIMENTAL SECTION

Reagents and Materials. Silver nitrate (AgNO₃, 99.9%) was purchased from Rankem India. 1,4-Bis-(diphenylphosphino)butane (DPPB) and 1,6-bis-(diphenylphosphino)hexane (DPPH) were purchased from Spectrochem. Sodium borohydride (NaBH₄, 98%) and sodium borodeuteride (NaBD₄, 98 atom % D) were purchased from Sigma-Aldrich. All solvents such as dichloromethane (DCM) and methanol (MeOH) were purchased from Rankem and were of analytical grade. CDCl₃ (99.8 atom % D) was purchased from Sigma-Aldrich for NMR measurements. All of the chemicals were used without further purification.

Synthesis of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (I). To synthesize cluster I, a reported method was used with some modifications.³³ In a typical synthesis method, 20 mg of AgNO₃ was dissolved in 5 mL of MeOH, followed by the addition of 75 mg of DPPH dissolved in 9 mL of DCM under constant stirring. After 20 min of stirring, 35 mg of NaBH₄ in 1 mL of ice-cold water was added. The addition of NaBH₄ imediately changed the color of the reaction mixture from colorless to light yellow. The reaction was vigorously stirred (~1000 rpm) under dark at room temperature. After 20 min of stirring, the color of the solution changed to green from light yellow. Then at 2 h of reaction, the green color changed to dark yellow, which indicated the formation of the cluster, $[Ag_{15}H_{13}(DPPH)_5]^{2+}$. The yellow solution was evaporated under vacuum and washed with cold deionized (DI) water.

Then the solid yellow material was dissolved in methanol and the solution was centrifuged for 5 min at 8000 rpm for 2 times to remove the excess phosphine ligands. The yellow supernatant containing cluster was vacuum evaporated and dissolved in 2 mL of methanol for further characterization. For mass spectrometric experiments, 100 μ L of the cluster solution was diluted to 1 mL by methanol. To synthesize the deuterated Ag₁₅ analogue, a similar method was followed by replacing NaBH₄ with NaBD₄.

Synthesis of [Ag_{27}H_{22}(DPPB)_7]^{3+} (II). For synthesis of cluster II, the above-mentioned procedure was followed only by exchanging DPPH with DPPB and keeping all other chemicals the same. After adding the NaBH₄ solution, the reaction mixture became light yellow immediately. Then the reaction was kept for vigorous stirring (~1000 rpm) at room temperature under dark condition. Over 3 h of continuous stirring, the color of the solution changed to blackish green which indicated the formation of the cluster, $[Ag_{27}H_{22}(DPPB)_7]^{3+}$. To synthesize the deuterated Ag_{27} analogue, a similar method was followed by replacing NaBH₄ with NaBD₄.

Instrumentation. UV-vis Absorption Spectroscopy. UV-vis spectra of nanoclusters were recorded using a PerkinElmer Lambda 25 UV-vis spectrometer. Absorption spectra were typically measured in the range of 200–1100 nm with a band-pass filter of 1 nm.

ESI MS. The electrospray ionization mass spectra (ESI MS) were measured using a Waters Synapt G2Si High Definition Mass Spectrometer. This mass spectrometer consists of an electrospray source, quadrupole ion guide/trap, ion mobility cell and TOF analyzer. Nitrogen gas was used as the nebulizer gas, and all of the mass spectra were collected in positive ion mode. Mass spectrometric measurements were made using the following conditions:

For Detecting the Hydride and Phosphine Coprotected Silver Nanoclusters (I and II). Flow rate, $30 \ \mu$ L/min; capillary voltage, 3 kV; cone voltage, 20 V; source offset, 20 V; source temperature, 100 °C; desolvation temp, 150 °C; desolvation gas flow, 400 L/h; trap gas flow, 5 L/h.

For MS/MS Studies of I and II. For MS/MS or collisioninduced dissociation (CID) studies, the molecular ion peaks were at first selected in the quadrupole and then were fragmented inside the trap by changing the collision energy (CE).

Flow rate, 30 μ L/min; capillary voltage, 3 kV; cone voltage, 20 V; source offset, 20 V; trap collision energy, 2–110 (variable); source temperature, 100 °C; desolvation temperature, 150 °C; desolvation gas flow, 400 L/h; trap gas flow, 5 L/h.

NMR Spectroscopy. Nuclear magnetic resonance (NMR) spectroscopy measurements were done at room temperature by using a Bruker 500 MHz NMR spectrometer. Pure ligands (DPPH and DPPB) and the clusters I and II were dissolved in CDCl₃ to collect ¹H and ³¹P NMR spectra.

XPS. X-ray photoelectron spectroscopy (XPS) of nanoclusters was performed by using an ESCA Probe TPD spectrometer of Omicron Nanotechnology. A monochromatic Al K α (1486.69 eV) X-ray source was used. Samples were drop casted on a sample stub and measurements were carried out with a constant analyzer energy of 50 eV for the survey scans and 20 eV for the specific regions. Binding energies in the spectra were calibrated with respect to the C 1s peak at 284.8 eV.



Figure 1. (A) UV–vis absorption spectrum of I. Inset: Photograph of the cluster in methanol. (B) HRESI MS of I in positive mode which shows an intense peak at m/z 1951.8, corresponding to $[Ag_{15}H_{13}(DPPH)_5]^{2+}$. Inset: schematic of the $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ cluster. (C) Comparison of the experimental and calculated isotopic distributions of I.

SEM EDS. Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM EDS) analysis were performed using a FEI QUANTA-200 SEM. Samples were prepared by dropcasting methanolic solutions of nanoclusters on an ITO plate, which were dried under room temperature.

TEM. Transmission electron microscopy (TEM) was performed using a JEOL 3010, 300 kV instrument at an accelerating voltage of 200 kV. The accelerating voltage was kept low to reduce beam-induced damage. Samples were prepared by drop casting the methanol solution of the clusters on carbon-coated copper grids and dried under ambient conditions.

RESULTS AND DISCUSSION

Both the clusters, $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (I) and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ (II), were synthesized by reducing the silver-phosphine complexes in the presence of NaBH₄, which act as a reducing agent as well as the source of hydride ligands (a detailed synthetic procedure is given in the Experimental Section). For the synthesis of cluster I, at first Ag-DPPH complex was made in MeOH/DCM solvent and then it was reduced by ice-cold NaBH₄ solution under vigorous stirring at ~1000 rpm. After 2 h of reaction, the solution became dark yellow in color (inset of Figure 1A), which shows a small peak at 370 nm in the optical absorption spectrum, as presented in Figure 1A. To probe the molecular composition, highresolution electrospray ionization mass spectrometry (HRESI MS) has been performed using the yellow methanolic solution. The positive mode HRESI MS data (Figure 1B) show a sharp peak at m/z 1951.8, which suggests the formation of a monodispersed cluster, and there was no other cluster peak up to m/z 10 000. The expanded spectrum shows the difference between two successive peaks in the isotopic distribution of cluster as m/z 0.5, which implies that the cluster is in +2 charge state. The peak was assigned as $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ where the isotopic pattern, which is made by the different isotopic abundances of the constituent elements, was used to assign the accurate composition. Figure 1C presents a comparison between the experimental spectrum (blue trace)

and the calculated spectrum (black trace), which matched perfectly. The presence and number of hydrogens in the cluster were further confirmed by synthesizing cluster I with NaBD₄ instead of NaBH₄ and keeping all other conditions the same. The deuterated analogue shows an ESI MS peak at m/z 1958.3, due to $[Ag_{15}D_{13}(DPPH)_5]^{2+}$. An exact match of experimental (pink trace) and calculated (black trace) isotopic pattern is shown in Figure S1A, which validates the composition of the cluster as $[Ag_{15}D_{13}(DPPH)_5]^{2+}$. Hence, 13 hydrogen ligands were confirmed by the mass shift of $\Delta m/z = 6.5$ in between $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ clusters ($\Delta m = 13$, z = 2), shown in Figure S1B.

It is noteworthy that during the synthesis of cluster I, within 20 min of addition of NaBH4, the color of the solution changed to green from light yellow. Then the green solution became dark yellow upon 2 h of continuous stirring resulting the final product $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (I). Hence, to know the actual composition of the intermediate green solution, we studied the UV-vis and ESI MS. To collect the green solution, the stirring was stopped after 1 h when the solution was green in color. However, as soon as the stirring was stopped, the green color changed to yellowish green within 5 min, and after 15 min, it became fully dark yellow. Figure S2 shows the timedependent UV-vis spectrum of these three differently colored solutions with their corresponding photographs, which show a visible change in their optical spectrum. We have also checked the time-dependent ESI MS, which is shown in Figure S3. The mass spectrum of the pure green solution exhibits the presence of $[Ag_{22}H_{21}(DPPH)_6]^{2+}$ cluster, whereas the yellowish green solution shows higher abundance of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ compared to [Ag₂₂H₂₁(DPPH)₆]²⁺. After 15 min of stopping stirring, the green solution becomes dark yellow and the entire composition becomes $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (I), which is shown in Figure 1. From these results, we can conclude that the synthesis of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (yellow) involves the formation of an intermediate cluster, $[Ag_{22}H_{21}(DPPH)_6]^{2+1}$ (green). This observation suggests the formation of a stable cluster through an etching process, where the rate of this step



Figure 2. MS/MS spectra of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (I) with increasing CE from 5 to 110 (in instrumental units). Ligand DPPH is represented by "L". Due to the increase in CE, detachment of hydrogens, DPPH and $[AgDPPH]^+$ happened from the parent nanoclusters which resulted in formation of the naked cluster, Ag_{13}^+ . The ions written in brown are involved in the formation of naked cluster Ag_{13}^+ . Schematic illustrations of the protected parent cluster and the naked cluster are shown in the inset.

is also dependent on the stirring speed.³⁷ Due to the instability of the intermediate green cluster, it was not possible to characterize it further.

Both the clusters $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ were stable for about 1 month if stored at ~4 °C. However, they tend to degrade or become unstable after complete removal of excess phosphines from the solution by centrifugation. Crystallization demands removal of excess ligands and byproducts. As a result, obtaining crystals of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ has been challenging due to their instability after cleaning. We have tried to remove excess phosphines by precipitating them at lower temperature during crystallization, but the effort was not successful until now.

For the characterization of cluster I, ¹H and ³¹P NMR spectroscopy has been done and the data are compared with those of the ligand DPPH (Figures S4 and S5). In Figure S6A, the XPS survey spectrum confirms the presence of C, O, P, and Ag. The specific regions of Ag and P are deconvoluted in Figure S6B,C, respectively. The XPS peak corresponding to Ag $3d_{5/2}$ appears at 368.0 eV, which confirms Ag in zero oxidation state. SEM EDS analysis also confirms the presence of Ag and P in cluster I. The atomic ratio of Ag and P obtained from this analysis is close to the atomic ratio of Ag and P in cluster I (Figure S7). TEM image of cluster I reveals that the average particle size is 1.46 ± 0.13 nm (Figure S8).

As these hydride and phosphine coprotected silver nanoclusters can create naked silver clusters in the gas phase, the process of dissociation was investigated in detail. The newly synthesized cluster $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (I) was selected by a quadrupole mass filter in the G2Si mass spectrometer and was subjected to collision induced dissociation (CID) with Ar gas inside the trap. Figure 2 presents a detailed study of CID of cluster I, which helps in understanding the fragmentation pathway as well as naked cluster formation. At first, the parent ion peak at m/z 1951.8 was mass selected, and then with increase in collision energy (CE), fragmentation of the parent ion started to appear. The major peak of the parent ion was seen up to CE 5, whereas, at CE 10 onward, the extent of fragmentation increased with continuous decrease in parent ion intensity. Up to a CE of 30, the parent ion $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (m/z 1951.8) underwent a loss of two DPPH and 13 hydrogens to produce $[Ag_{15}(DPPH)_3]^{2+}$ $(m/z)^{2+}$ 1490.9). After that at CE 50, doubly charged $[Ag_{15}(DPPH)_3]^{2+}$ becomes singly charged $[Ag_{14}(DPPH)_2]^+$ (m/z 2418.8) by losing one [AgDPPH]⁺. Then there were losses of one Ag and one DPPH from $[Ag_{14}(DPPH)_2]^+$, creating $[Ag_{13}(DPPH)_2]^+$ $(m/z \ 2310.2)$ and $[Ag_{14}(DPPH)]^+ (m/z \ 1963.9)$, respectively. Next, by increasing the CE to 70, $[Ag_{14}(DPPH)_2]^+$, $[Ag_{13}(DPPH)_2]^+$, and $[Ag_{14}(DPPH)]^+$ got further dissociated to $[Ag_{13}(DPPH)]^+$ (m/z 1855.9) by consecutive steps. At CE 90, $[Ag_{13}(DPPH)]^+$ started losing the remaining DPPH ligand and formed the naked cluster, Ag_{13}^+ (m/z 1401.7). All of the ligands were completely desorbed from the parent cluster, $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ at CE 110 and resulted in Ag_{13}^+ with other possible smaller naked clusters due to the application of higher CE. There is a second possible fragmentation pathway of parent ion for the formation of Ag_{13}^{+} . In this second pathway, at first, parent ion $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (m/z1951.8) lost one DPPH and generated $[Ag_{15}H_{13}(DPPH)_4]^{2+}$ $(m/z \ 1724.3)$ at CE 20. Then at CE 30, it underwent an $[AgH_2(DPPH)_2]^+$ loss to produce singly charged $[Ag_{14}H_{11}(DPPH)_2]^+$ (*m*/*z* 2430.1). Next, $[Ag_{14}H_{11}(DPPH)_2]^+$



Figure 3. Expanded ESI MS of $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (blue trace) and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ (pink trace) at different CE during the formation of naked cluster Ag_{13}^+ . The mass shift $(\Delta m/z)$ in between the blue and pink trace confirms the presence of hydrogen in the fragmented ions. The isotopic distribution of Ag_{13}^+ confirms the absence of hydrogen atoms, which also matches with the calculated pattern (black trace).

was fragmented again to give $[Ag_{13}(DPPH)]^+$ (*m*/*z* 1855.9) and ultimately it produced naked cluster Ag_{13}^+ (*m*/*z* 1401.7).

To confirm the complete removal of hydrogens from the parent cluster [Ag₁₅H₁₃(DPPH)₅]²⁺, the fragmentation pathway was compared with its deuterated analogue, $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ (Figure 3). In Figure 3, we have compared the first fragmentation pathway of the parent ion which is described in Figure 2. The second fragmentation method is compared in Figure S9. In Figure 3, the expanded ESI MS of blue and pink traces correspond to the parent or fragmented ions generated from [Ag₁₅H₁₃(DPPH)₅]²⁺ and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ clusters, respectively. The mass shift $(\Delta m/z)$ in between the blue and pink traces happened due to the replacement of hydrogen atoms with the deuterium atoms in the deuterated analogue. At CE 5, the mass shift is m/z = 6.5in-between $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (m/z 1951.8) and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ (m/z 1958.3) clusters, which refers to the presence of 13 hydrogen atoms ($\Delta m = 13$, charge state z = 2) in the parent cluster. At CE 10, due to one DPPH loss, the fragmented ions were generated at m/z 1724.3 (blue trace) and m/z 1730.8 (pink trace). These generated ions show the same mass shift of $\Delta m/z = 6.5$ ($\Delta m = 13$, z = 2), which confirms that there was no hydrogen losses in this step. In the next step at CE 30, the mass shift in between m/z 1718.8 (blue trace) and m/z 1719.3 (pink trace) is $\Delta m/z = 0.5$ ($\Delta m = 1, z$ = 2), which tells about the existence of one hydrogen in the daughter ion, after the desorption of 12 hydrogens and the formation of $[Ag_{15}H(DPPH)_4]^{2+}$. At the same CE 30, $[Ag_{15}H(DPPH)_4]^{2+}$ further underwent fragmentation and generated a peak at m/z 1490.9 (blue trace), which shows a mass shift of $\Delta m/z = 0$ ($\Delta m = 0, z = 2$) with its deuterated counterpart (pink trace). This step confirms the complete removal of hydrogens from the parent cluster and the generation of $[Ag_{15}(DPPH)_3]^{2+}$. Next, $[Ag_{15}(DPPH)_3]^{2+}$ was fragmented by [AgDPPH]⁺, Ag, and DPPH consecutively to produce singly charged $[Ag_{13}(DPPH)]^+$ (*m*/*z* 1855.9) with no mass shift, and finally at CE 90, the naked cluster Ag_{13}^+ was generated after losing the last DPPH. Expanded peak shapes of Ag_{13}^{+} (*m*/*z* 1401.7), generated from $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ (blue trace) and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ (pink trace), merged with each other $(\Delta m/z = 0)$ and also their isotopic distributions match with the calculated one (black trace). These observations confirm the formation of the naked cluster, Ag_{13}^{+} . By the same way, complete hydrogen desorption from cluster I has been confirmed for the second fragmentation pathway, which is shown in Figure S9. Here at CE 5 and 10,

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Figure 4. (A) UV–vis absorption spectrum of **II**. Inset: Photograph of the cluster in methanol. (B) HRESI MS of **II** in positive mode which shows an intense peak at m/z 1973.2 corresponding to $[Ag_{27}H_{22}(DPPB)_7]^{3+}$. Inset: Schematic of the $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ cluster. (C) Comparison of the experimental and calculated isotopic distribution of **II**. The * peaks refer to unidentified species.

the same kind of fragmentation and mass shift happened, which was observed in Figure 3. At CE 30, the fragmented peaks were generated at m/z 2430.1 (blue trace) and m/z2441.2 (pink trace) showing a mass shift of $\Delta m/z = 11$ ($\Delta m =$ 11, z = 1), which confirms the presence of 11 hydrogens in the $[Ag_{14}H_{11}(DPPH)_2]^+$ ion. At the same CE 30, $[Ag_{14}H_{11}(DPPH)_2]^+$ further created a fragmented peak at m/*z* 2322.2 (blue trace), which shows the same mass shift of $\Delta m/$ z = 11 ($\Delta m = 11$, z = 1) with its deuterated counterpart (pink trace, m/z 2333.3). This step confirms that there was only one Ag loss and no hydrogen loss. The newly generated $[Ag_{13}H_{11}(DPPH)_2]^+$ ion again lost 11 hydrogens and one DPPH to create $[Ag_{13}(DPPH)]^+$ (m/z 1855.9) and it did not show any mass shift with its deuterated counterpart. Finally at CE 90, naked cluster Ag_{13}^+ (*m*/*z* 1401.7) was formed with no mass shift $(\Delta m/z = 0)$ in between the blue and pink traces and confirms the removal of all hydrogens from the parent cluster I. The CE dependent full range MS/MS spectra of $[Ag_{15}D_{13}(DPPH)_5]^{2+}$ cluster are given in Figure S10. The fragmentation pathway of cluster I, confirmed by the MS/MS experiments of $[Ag_{15}H_{13}(DPPH)_{5}]^{2+}$ and $[Ag_{15}D_{13}(DPPH)_5]^{2+}$, has been represented as a flowchart in Figure S11.

As the size of nanoclusters is very much dependent on phosphine's structure in the ligand shell, here we have used another diphosphine with shorter chain length, DPPB. The cluster synthesis is similar to the previous Ag_{15} method, where only DPPH is replaced by DPPB ligand (details are in the Experimental Section). In this synthesis, we get a blackish green solution (inset of Figure 4A) after 3 h of continuous stirring at ~1000 rpm. It is important to mention that for the synthesis of both the clusters (DPPH and DPPB protected) stirring at higher rpm (~1000) is very much necessary and complexes are formed otherwise, instead of nanoclusters. The reason can be that faster reduction kinetics is required to facilitate the formation of higher mass clusters compared to lower mass complexes.

The DPPB protected silver cluster II exhibits similar kinds of optical features like Ag₁₈ cluster, and the latter was reported

before.³³ However, here both the optical peaks are red-shifted compared to Ag₁₈ and appeared at 550 and 620 nm, which can be due to the formation of differently sized cluster core (Figure 4A). The positive mode HRESI MS data (Figure 4B) of the methanolic blackish green solution (cluster II) shows a peak at m/z 1973.2 with peak separation of m/z 0.33, which confirms the charge state of +3. Along with this +3 charge state cluster, there were some +1 charge state peaks, which are unidentified and can be due to the byproduct of the reaction. The m/z 1973.2 peak was assigned as $[Ag_{27}H_{22}(DPPB)_7]^{3+}$, where the isotopic pattern of the experimental spectrum (olive trace) matches exactly with the calculated one (black trace), shown in Figure 4C. The number of hydrogens in cluster II was confirmed by synthesizing the cluster with NaBD₄ instead of NaBH₄.

The deuterated analogue shows an ESI MS peak at m/z1980.6 due to $[Ag_{27}D_{22}(DPPB)_7]^{3+}$. The exact match of experimental (red trace) and calculated (black trace) isotopic pattern is shown in Figure S12A, which validates the composition of $[Ag_{27}D_{22}(DPPB)_7]^{3+}.$ The mass shift in between the $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ and $[Ag_{27}D_{22}(DPPB)_7]^{3+}$ clusters was $\Delta m/z = 7.3$ ($\Delta m = 22, z = 3$) which confirms the presence of 22 hydrogens in cluster II, shown in Figure S12B. $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ was further characterized with ¹H and ³¹P NMR by comparing with ligand DPPB (Figures S13 and S14). The XPS survey spectrum (Figure S15A) confirms the presence of C, O, P, and Ag elements in the cluster and the deconvoluted spectra of Ag 3d and P 2p regions are shown in Figure S15B,C, respectively. The XPS peak due to Ag 3d_{5/2} appears at 368.2 eV, which confirms that Ag is in zero oxidation state. The presence of Ag and P were also confirmed by SEM EDS and their ratio (Ag:P) obtained from EDS analysis was close to the atomic ratio of Ag and P in cluster II (Figure S16). The average particle size of cluster II is 1.72 \pm 0.14 nm, which is obtained from the TEM image of the cluster (Figure S17).

Formation of naked cluster was also investigated from $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ (II) by doing CID of the parent cluster, inside the trap of the G2Si mass spectrometer. Figure 5



Figure 5. MS/MS spectra of $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ (II) with increasing CE from 2 to 70 (in instrumental units). Ligand DPPB is represented by "L". Due to the increase in CE, detachments of hydrogens, DPPB, and $[AgDPPB]^+$ happened from the parent nanoclusters forming the naked cluster, Ag_{25}^+ . The ions labeled in brown are involved in the formation of naked cluster Ag_{25}^+ . Schematic illustrations of the protected parent cluster and naked cluster are shown in the insets.

represents a detailed study of the CID of cluster II, which helps us to understand the CE-dependent fragmentation pathway and formation of naked cluster. For that, the parent ion $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ (m/z 1973.2) was mass selected and then CE was increased slowly to get the fragmented ions. At CE 2, there was a major peak of the parent ion. Here also we observed two fragmentation pathways for the formation of the naked cluster. In the first way, at CE 10, the parent ion (m/z)1973.2) undergoes one DPPB ligand loss and forms $[Ag_{27}H_{22}(DPPB)_{6}]^{3+}$ (m/z 1830.8). Next, $[Ag_{27}H_{22}(DPPB)_6]^{3+}$ undergoes the loss of 20 hydrogens and forms $[Ag_{27}H_2(DPPB)_6]^{3+}$ (m/z 1824.1) at CE 30. The expanded ESI MS of these 20 hydrogen losses is shown in Figure 5 inset (left column, down). At the same CE, some of the $[Ag_{27}H_2(DPPB)_6]^{3+}$ got fragmented to $[Ag_{27}(DPPB)_5]^{3+}$ $(m/z \ 1681.4)$ after one DPPB and two hydrogen losses. This $[Ag_{27}(DPPB)_5]^{3+}$ ion also can be formed from $[Ag_{27}H_{22}(DPPB)_6]^{3+}$ by one DPPB and 22 hydrogen losses. At CE 40, $[Ag_{27}H_{22}(DPPB)_6]^{3+}$ and $[Ag_{27}H_2(DPPB)_6]^{3+}$ were fully converted to $[Ag_{27}(DPPB)_5]^{3+}$, and it further undergoes one DPPB loss at CE 40 to form $[Ag_{27}(DPPB)_4]^{3+}$ (m/z)1539.4). At CE 50, by losing one [AgDPPB]⁺, triply charged $[Ag_{27}(DPPB)_4]^{3+}$ got converted to doubly charged $[Ag_{26}(DPPB)_3]^{2+}$ (m/z 2041.9). Next, at CE 60, there was one DPPB and one [AgDPPB]⁺ loss and formation of singly charged $[Ag_{25}DPPB]^+$ ion (m/z 3122.7). Finally, at CE 70, the

naked cluster Ag_{25}^+ (m/z 2696.6) was formed from [Ag25DPPB]⁺ with other smaller size naked clusters, Ag2⁺ and Ag_{23}^{+} due to the application of higher CE. In the second fragmentation method, at first the parent ion $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ (m/z 1973.2) loses one $[Ag(DPPB)_2]^+$ unit and gets converted to doubly charged $[Ag_{26}H_{22}(DPPB)_5]^{2+}$ (m/z 2479.2) at CE 10. Then at CE 30, it loses 18 hydrogens and forms $[Ag_{26}H_4(DPPB)_5]^{2+}$ $(m/z)^{2+}$ 2470.2), followed by the formation of $[Ag_{26}H_4(DPPB)_4]^{2+}$ $(m/z \ 2257.1)$ after one DPPB loss. Expanded view of the loss of 18 hydrogens is shown in Figure 5 inset (left column, up). Next, $[Ag_{26}H_4(DPPB)_4]^{2+}$ again loses four hydrogens and forms $[Ag_{26}(DPPB)_4]^{2+}$ (m/z 2255.0) at CE 40. Expanded views of the mass shift due to the loss of four hydrogens is shown in Figure 5 inset (right column, down). After all of the hydrogens are lost, there was two consecutive losses of DPPB from $[Ag_{26}(DPPB)_4]^{2+}$ making $[Ag_{26}(DPPB)_2]^{2+}$ $(m/z)^{2+}$ 1828.9). Next, after one [AgDPPB]⁺ loss singly charged $[Ag_{25}(DPPB)]^+$ (m/z 3122.7) was formed, which was further fragmented to the naked cluster Ag_{25}^+ (m/z 2696.6) at CE 70. To confirm the removal of all DPPB and hydrogen ligands, we have compared the experimentally obtained isotopic patterns (olive trace) of Ag_{25}^+ with the calculated one (black trace), which shows the exact match between them (Figure S18). Due to the lower intensity of the ESI MS peak of $[Ag_{27}D_{22}(DPPB)_7]^{3+}$, we were not able to fragment that ion

to compare the hydrogen atom loss with the deuterium atoms. We hope that the detailed study of all of the ligand losses in Figure 5 will be sufficient to understand and prove the formation of naked cluster Ag_{25}^+ . The full fragmentation pathway of cluster II, confirmed by the MS/MS experiments, is presented in a flowchart and shown in Figure S19.

According to the electron counting rule, $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ possesses zero free electron (geometric stability) and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$ possesses two free electrons (electronic stability). The silver naked clusters generated from the reported hydride and phosphine coprotected silver clusters were Ag_{17}^+ , Ag_{21}^+ , and Ag_{19}^+ . Here, we are reporting the formation of Ag_{13}^+ and Ag_{25}^+ from $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$, respectively. As diphosphines are more strongly bonded to the metal core compared to monophosphines, here CE-dependent fragmentation has been performed instead of cone voltage-dependent fragmentation to make naked clusters. As of now, Ag_{13}^+ is the smallest and Ag_{25}^+ is the largest known naked clusters of silver which could be created from monolayer protected silver nanoclusters.

CONCLUSIONS

In conclusion, we have reported two new hydride and diphosphine coprotected silver nanoclusters, $[Ag_{15}H_{13}(DPPH)_5]^{2+}$ and $[Ag_{27}H_{22}(DPPB)_7]^{3+}$. These weakly ligated silver clusters can be used as the source of hydrogen and as a reagent for chemical transformations. The naked clusters Ag_{13}^{+} (12 valence electrons) and Ag_{25}^{+} (24 valence electrons) were created from parent hydride and phosphine coprotected clusters, Ag15 and Ag27, respectively, in their cationic form by CID experiments. The favored formation and stability of these odd numbered cationic silver naked clusters can be correlated to the odd-even effect which refers the higher stability of the closed electronic shells. A detailed study of the fragmentation steps during the formation of naked clusters can help to elucidate the cluster structures, though the determination of crystal structure is very much needed to understand the process in detail. Here we have demonstrated that tuning the size of monolayer protected clusters gives us the opportunity to explore the various sizes of silver naked clusters in the gas phase. We hope that our results will provide new insights into ion-molecule reactions, gas phase unimolecular chemistry and soft landing of metal clusters. We note that $M_{25}L_{18}^{-}$ (M = Au, Ag; L = SR) clusters are the most thoroughly investigated clusters in the family of atomically precise noble metal clusters and Au₂₅ naked cluster has been seen only in the dissociation of protein protected clusters.38

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c05867.

Characterization of clusters by UV-vis, ESI MS, NMR, XPS, SEM EDS and TEM; complete fragmentation pathway of clusters (PDF)

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Notes

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