Supplementary information for

$PtAg_{18}$ Superatoms Co-stabilized by Phosphines and Halides: Synthesis, Structure and Catalysis

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EXPERIMENTAL SECTION

Reagents: 1,3-bis(diphenylphosphino)propane (dppp, 99%) was purchased from J&K Scientific Ltd. (Beijing, China). Sodium hexafluoroantimonate ($NaSbF_6$, 98%) was purchased from Adamas. (Shanghai, China). Silver nitrate ($AgNO_3$, 98%), chloroplatinic acid hexahydrate (H_2PtCl_6•$6H_2O$, 99.9%), dichloromethane (CH_2Cl_2, A.R.), methanol (CH_3OH, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Water used in all experiments was ultrapure. All other reagents were used as received without further purification.

Synthesis of $[PtAg_{18}(dppp)_6Cl_8](SbF_6)_2$: $AgNO_3$ (2 mg, 0.012 mmol), dppp (8 mg, 0.019 mmol), and H_2PtCl_6 (1 mg, 0.0019 mmol) were dissolved in mixed solvents of CH_2Cl_2 and MeOH. The reducing agent, 1.1 mg $NaBH_4$ in 0.3 mL ethanol, was then added dropwise. After that, $NaSbF_6$ (5 mg, 0.019 mmol) was added, followed by stirring for 10 min. The reaction was aged for 1 h in the absence of light to obtain raw product. After that, the solution was subjected to diffusion of ether and hexane. Orange block crystals were obtained after two weeks (1.03 mg, 28.98 % yield based on Ag).

Characterizations

UV/Vis spectra were collected by JascoV-650 Spectrophotometer using a quartz cuvette of 1 mm path length. The scanning speed is 1000 nm min^{-1}. The spectra were recorded in diluted solutions of dichloromethane and the signal of the blank solvent was subtracted. The spectra were recorded in diluted solutions of dichloromethane and the signal of the blank solvent was subtracted.

Positive-ion electrospray ionization mass spectra (ESI-MS) were recorded using an Agilent 6224 time-of-flight mass spectrometer. The samples dissolved in dichloromethane were directly infused at a flow rate of 1.2 mL/h by a syringe pump. Typical parameters used for the measurements were as follows: capillary voltage: 4.0 kV; drying gas temp: 150℃; drying gas flow: 4 L/min; nebulizer pressure: 20 psi.

^{1}H and ^{31}P NMR spectra were recorded at room temperature on a Bruker AV-600 spectrometer with TMS and solvent residual signal as an internal reference. All NMR data were processed on MestReNova software.

X-ray photoelectron spectroscopy (XPS) data was collected on ESCALABXI+. The spectra were calibrated using the C 1s peak (284.6 eV).

The infrared spectrum was recorded on Nicolet iS50 FT-IR spectrometer.

X-ray single-crystal analysis: The diffraction data of the single crystals of cluster $PtAg_{18}$ was collected on a Rigaku Oxford Diffraction System X-ray single-crystal diffractometer using Cu Kα (λ= 1.54184 Å) at 293 K. The data was processed using $CrysAlis^{Pro}$.[1] The structure was solved and refined using Full-matrix least-squares

based on F2 using ShelXT,[2] ShelXL[3] in Olex2,[4] and Shelxle.[5] The thermal ellipsoids of the ORTEP diagram were done at 50% probability. Detailed crystal data and structure refinements for the compound is given in Table S1. CCDC 2077400 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Catalytic experiment

Preparation of $PtAg_{18}$/XC-72 catalysts

In the typical preparation,1.9 mg of $[PtAg_{18}(dppp)_6Cl_{l8}](SbF_6)_2$ was dissolved in 10 mL of dichloromethane. Then 190.0 mg of XC-72 in ethanol was mixed and the mixture was stirred at room temperature for three hours. The mixture was then centrifuged, and the obtained solids were separated out. The supported catalysts were then dried to give the final catalysts.

Catalytic experiments

For the catalytic test, a vial with the volume of 20 mL was used as the reactor. The catalytic reaction was carried out in air at room temperature. Typically, 0.05 mg of 4-nitrophenol dissolved in 0.5 mL of H_2O was added into the vial, followed by freshly prepared $NaBH_4$ aqueous solution (1.0 mg per 2 mL). To the solution, 25.0 mg of catalysts ($PtAg_{18}$/XC-72 catalysts) were added once and kept stirring. UV-Vis absorption spectroscopy was employed to monitor the total catalytic process. The conversion from 4-nitrophenol to 4-aminophenol was calculated from the absorbance intensity using the following equation:

$$Conversion = \frac{A(initial) - A(final)}{A\ (\ initial\ )} \times 100\%$$

Computational details

The adsorption energy was evaluated based on DFT calculations by performing with the quantum chemistry program Gaussian 9. Structural optimization at the b3lyp/genecp (6-31G(d) for C, H, Cl, N, O, P, and lanl2dz for Pt and Ag) level were first performed, and the final electronic energy at the pbe/tzvp level was calculated based on optimized structure. The adsorption energy is defined as the difference in energy between the adsorbed system and the combined energies of the bare cluster and isolated adsorbate molecule. A negative value indicates a favorable interaction.

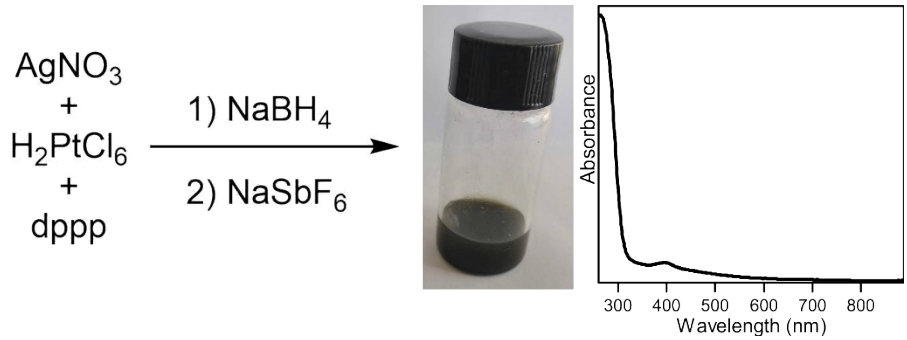

Figure S1. Synthetic prototype and characterization of raw product of $PtAg_{18}$ clusters.

Figure S2. Photographs of single crystals of $PtAg_{18}$ clusters.

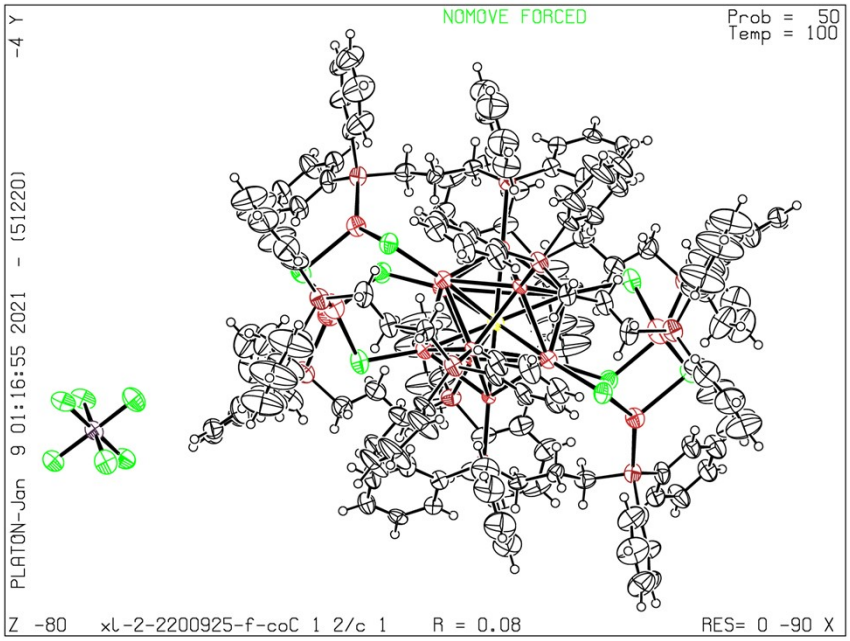

Figure S3. The thermal ellipsoids of the ORTEP diagram of $PtAg_{18}$ clusters.

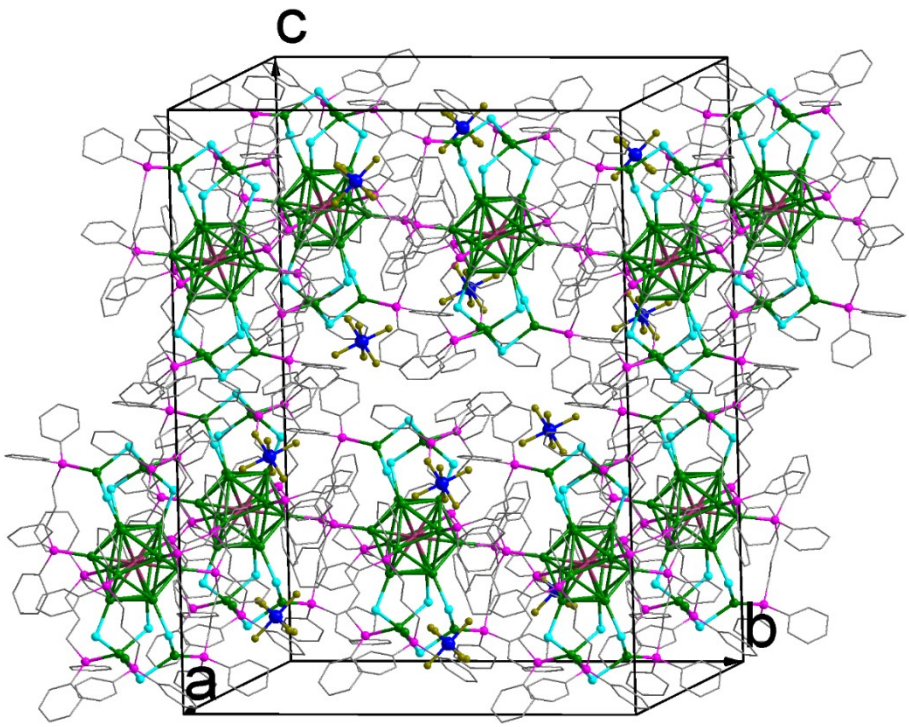

Figure S4. The packing structure of $PtAg_{18}$ clusters in their single crystals. Color legend: green spheres, Ag; magenta spheres, Pt; pink spheres, P; turquoise spheres, Cl; dark yellow spheres: F; blue spheres: Sb; gray spheres, C. All hydrogen atoms are omitted for clarity.

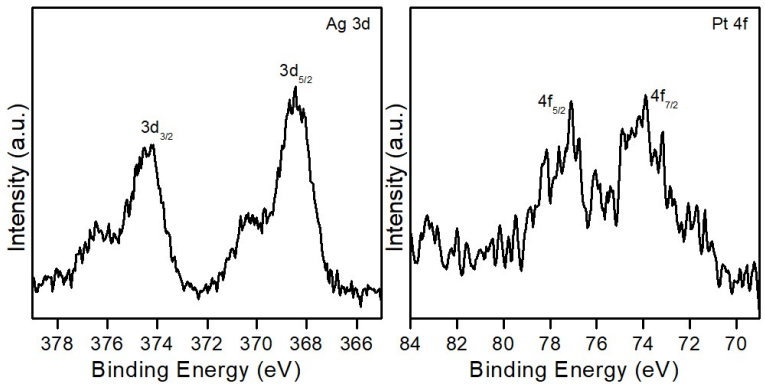

Figure S5. XPS spectra of $PtAg_{18}$ clusters (left: Ag; right: Pt).

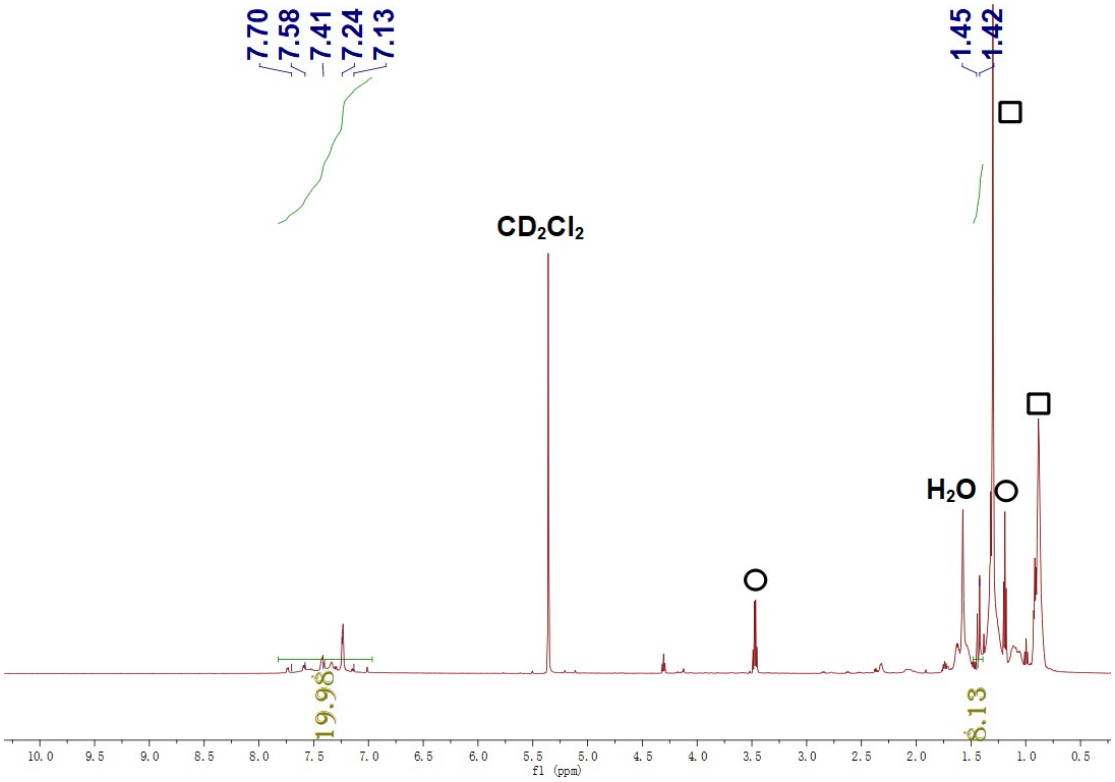

Figure S6. ^{1}H NMR spectrum of $PtAg_{18}$ clusters (CD_2Cl_2). □ hexane; ○ ether.

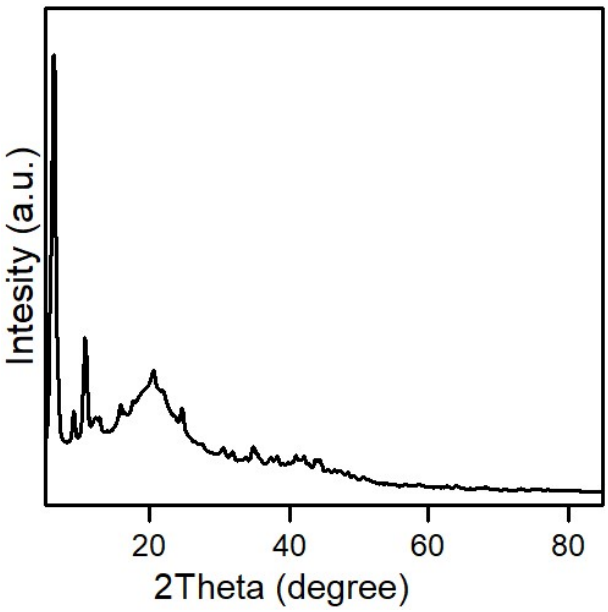

Figure S7. Powder X-ray diffraction spectrum of $PtAg_{18}$ clusters.

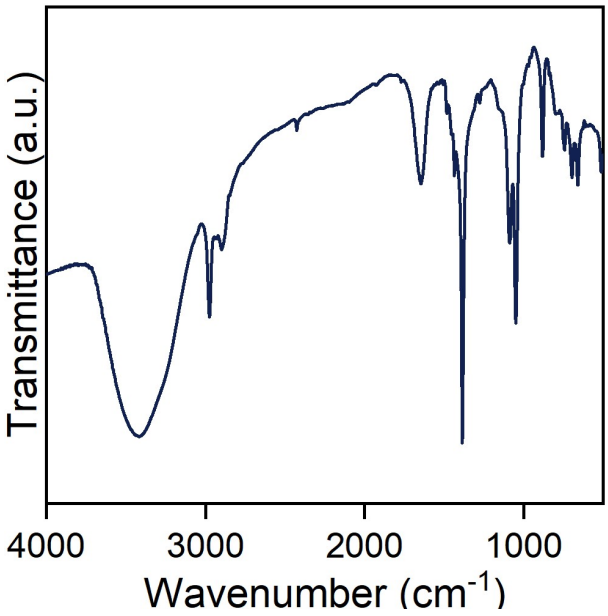

Figure S8. Infrared spectrum of $PtAg_{18}$ clusters.

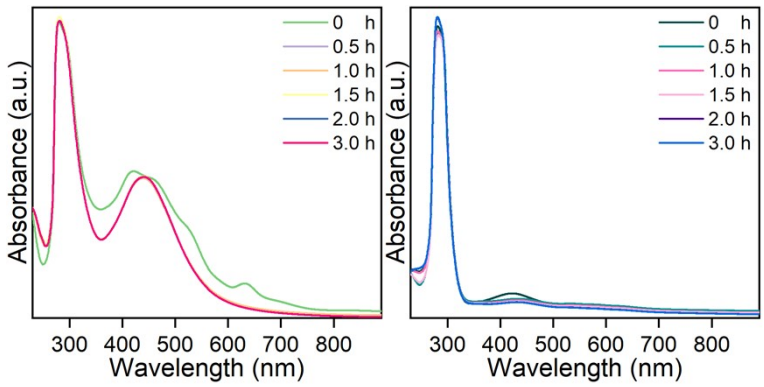

Figure S9. Time-dependent UV–vis absorption spectra of $Ag_{44}(SR)_{30}$ (left) and $[Ag_9Cu_6(^tBuC{\equiv}C)_{12}]^+$ (right) at 50 °C.

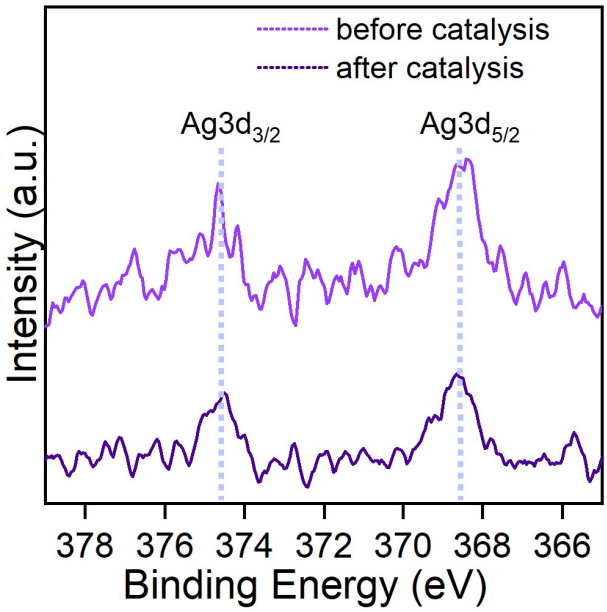

Figure S10. Ag XPS spectra of $PtAg_{18}$/XC-72 before and after catalytic hydrogenation reaction.

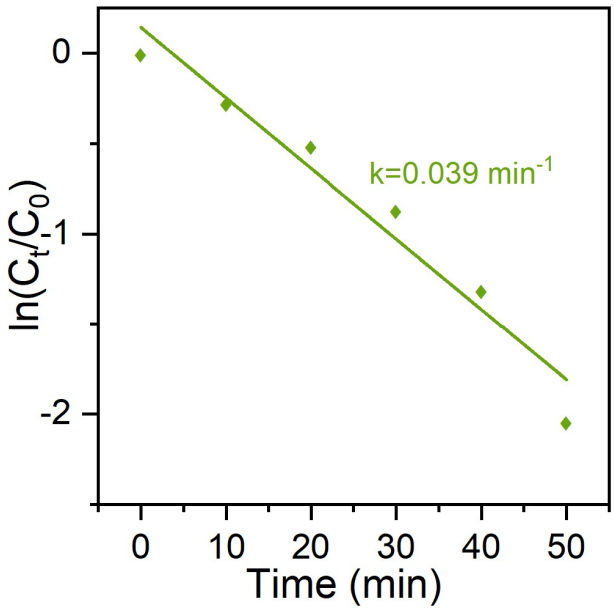

Figure S11. Time-dependent ln(C_t/C_0) for $PtAg_{18}$/XC-72.

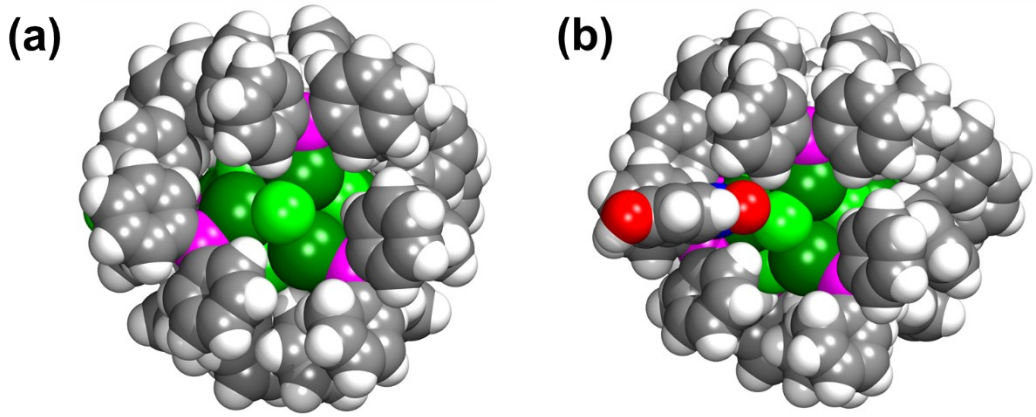

Figure S12. (a) Diagram of three of the six exposed silver atoms of $PtAg_{18}$; the other three open silver sites are located on the opposite side. (b) Diagrams of the adsorption of 4-nitrophenol on the surface of $PtAg_{18}$.

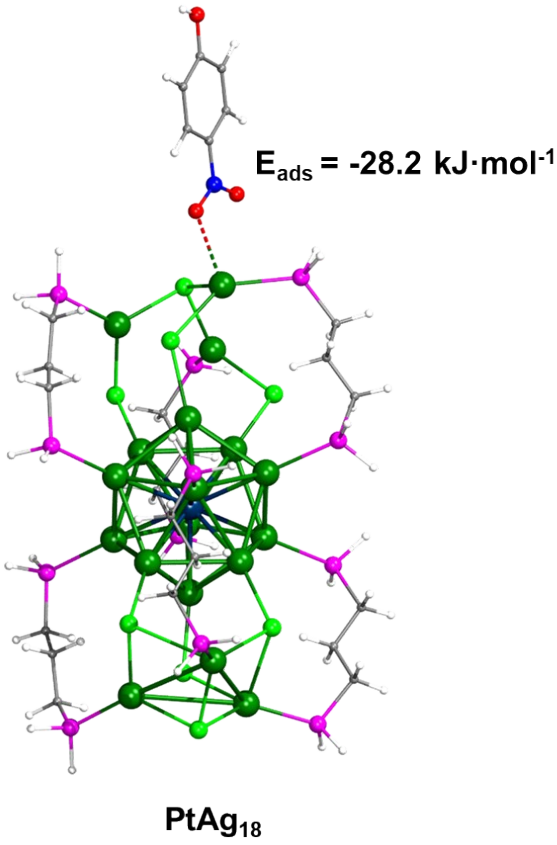

Figure S13. Optimized structures of 4-nitrophenol adsorbed on the $PtAg_{18}$.

Table S1. Crystal data and structure refinement for $[PtAg_{18}(dppp)_6Cl_8](SbF_6)_2$.

Identification code	$[PtAg_{18}(dppp)_6Cl_8](SbF_6)_2$
Empirical formula	$C_{162}H_{158}Ag_{18}Cl_8F_{12}P_{12}PtSb_2$
Formula weight	5368.36
Temperature/K	100
Crystal system	monoclinic
Space group	C1 2/c1
a/Å	16.4557(4)
b/Å	30.7351(6)
c/Å	37.4768(10)
α/°	90
β/°	97.714(2)
γ/°	90
Volume/Å^3	18783.0(8)
Z	4
ρ_{calc}g/cm^3	1.898
μ/mm^{-1}	20.723
F(000)	10320.0
Crystal size/mm^3	0.2 × 0.1 × 0.3
Radiation	CuK\a (λ = 1.54184)
2Θ range for data collection/°	3.420 to 61.168
Index ranges	-15 ≤ h ≤ 18, -34 ≤ k ≤ 34, -42 ≤ l ≤ 42
Reflections collected	9531
Independent reflections	14428 [R_{int} = 0.1045, R_{sigma} = 0.0832]
Data/restraints/parameters	14428/657/933
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0826, wR_2 = 0.2206
Final R indexes [all data]	R_1 = 0.1239, wR_2 = 0.2627
Largest diff. peak/hole / e Å^{-3}	5.50/-1.63

Table S2. Selected bond lengths in $PtAg_{18}$.

Bond	Bond length (Å)	Bond	Bond length (Å)
Pt-Ag	2.738	Ag_{core}-Cl	2.44
Ag_{core}-Ag_{core}	2.879	Cl-Ag_{shell}	2.638
Ag_{core}-P	2.37	Ag_{shell}-P	2.3735

Table S3. Selected bond lengths (Å) for cluster $PtAg_{18}$.

Parameter	value	Parameter	value
Pt00-Ag1	2.7236(10)	Pt00-Ag2	2.7248(13)
Pt00-Ag3	2.7182(13)	Pt00-Ag4	2.7512(13)
Pt00-Ag5	2.7543(14)	Pt00-Ag6	2.7565(14)
Ag1-Ag2	2.8783(14)	Ag1-Ag3	2.8329(14)
Ag1-Ag4	2.8709(17)	Ag1-Ag5	2.8572(17)
Ag1-Ag6	2.9688(17)	Ag1-P00D	2.373(5)
Ag2-Ag1	2.8783(14)	Ag2-Ag2	2.835(2)
Ag2-Ag4	2.8494(16)	Ag2-Ag5	2.9185(17)
Ag2-Ag5	2.9102(17)	Ag2-P00F	2.369(5)
Ag3-Ag1	2.8329(14)	Ag3-Ag3	2.874(2)
Ag3-Ag4	2.9261(16)	Ag3-Ag6	2.8657(17)
Ag3-Ag6	2.8886(17)	Ag3-P00G	2.369(5)
Ag4-Ag1	2.8709(17)	Ag4-Ag5	2.8724(18)
Ag4-Ag6	2.8406(18)	Ag4-Cl3	2.425(5)
Ag5-Ag2	2.9185(17)	Ag5-Ag6	2.8567(18)
Ag5-Cl00	2.449(5)	Ag6-Ag3	2.8887(17)
Ag6-Cl1	2.446(5)	Ag7-Cl00	2.527(5)
Ag7-Cl2	2.592(5)	Ag7-P00I	2.370(5)
Ag8-Cl1	2.570(6)	Ag8-Cl2	2.580(6)
Ag0B-Cl2	2.545(5)	Ag8-P00L	2.393(6)
Ag0B-P00K	2.354(6)	Ag0B- Cl3	2.532(6)

References:

1. CrysAlis^{Pro} Version 1.171.35.19. (2011). *Agilent Technologies Inc. Santa Clara,* CA, USA.
2. Sheldrick, G. M. *Acta Cryst. A* **2015,** *71,* 3.
3. Sheldrick, G. M. *Acta Cryst. A* **2008,** *64,* 112.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009,** *42,* 339.
5. Huebschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Cryst.* **2011,** *44,* 1281.