# **Electronic Supplementary Information (ESI)**

# Synthesis of RhH-doped Au-Ag Alloy Nanoclusters and Dopant Evolution

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# **Experimental Section**

#### Materials

Silver nitrate (AgNO<sub>3</sub>, >99.9%) was purchased from Alfa Aesar. Rhodium chloride hydrate (RhCl<sub>3</sub>·xH<sub>2</sub>O, 99.98%), tetraphenylphosphonium bromide (PPh<sub>4</sub>Br, 97%), sodium borohydride (NaBH<sub>4</sub>, 99%), sodium borodeuteride (NaBD<sub>4</sub>, 98 atom% D), hydrogen tetrachloroaurate trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O, reagent grade) and chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, ACS reagent, >37.50% Pt basis) were obtained from SigmaAldrich. 2,4-Dimethylbenzenethiol (HSPhMe<sub>2</sub>, >96%) was purchased from Tokyo Chemical Industry. Ultrahigh-pure grade toluene, methanol, acetonitrile, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and tetrahydrofuran (THF) were purchased from Thermo Fisher Scientific. Water was purified using a Millipore Milli-Q system (18.2 MΩ·cm). All chemicals were used as received without further purification.

#### Methods

The molecular formulas of the synthesized nanoclusters (NCs) were determined by an ESI mass spectrometer (Agilent 6230 TOF LC/MS) in the negative ion mode. The NC samples were dissolved in CH<sub>2</sub>Cl<sub>2</sub> at a concentration of 0.1 mg mL<sup>-1</sup> and directly injected into the mass spectrometer. Absorption spectra of the NC solutions in CH<sub>2</sub>Cl<sub>2</sub> were recorded using a Shimadzu UV-Vis-NIR spectrophotometer (UV-3600). X-ray photoelectron spectroscopy (XPS) measurements were conducted using an XPS system (K-alpha, Thermo UK) with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV). Samples for analysis were deposited on a glass substrate, and their binding energies were calibrated against the C 1s peak centered at 284.8 eV. <sup>1</sup>H NMR spectra were obtained using a 400 MHz FT-NMR spectrometer (Avance III HD 400, Bruker Biospin) with chemical shifts reported relative to the residual deuterated solvent peak (CD<sub>2</sub>Cl<sub>2</sub> at 5.32 ppm). Continuous-wave electron paramagnetic resonance (EPR) experiments were conducted on a frozen NC solutions in CH<sub>2</sub>Cl<sub>2</sub> (1 mM) at 5 K using a Bruker EMX plus 6/1 spectrometer. EPR spectra were acquired with the following parameters: microwave frequency = 9.64 GHz; microwave power = 1 mW; modulation frequency = 100 kHz; modulation amplitude = 10.0 G. The EPR spectrum was fitted with anisotropic g-tensor ( $g_x$ ,  $g_y$ ,  $g_z$ ) by conducting EasySpin toolbox in MATLAB software (R2020b). The anisotropic hyperfine coupling of Rh and Au nuclei was not considered in simulation due to the narrow line width and absence of hyperfine splitting in experimental data.

# Synthesis of [RhHAg24(SPhMe2)18]<sup>2-</sup> NCs

[RhHAg<sub>24</sub>(SPhMe<sub>2</sub>)<sub>18</sub>]<sup>2-</sup> (abbreviated as [RhHAg<sub>24</sub>]<sup>2-</sup>) NCs were synthesized according to a procedure reported elsewhere with some modifications.<sup>1,2</sup> AgNO<sub>3</sub> (40 mg, 0.23 mmol) was dissolved in a 2:15 (v/v) mixture of water and THF (17 mL in total) with vigorous stirring in 30-mL vial. Subsequently, HSPhMe<sub>2</sub> (0.090 ml, 0.65 mmol) was added to the solution, after which its color rapidly changed to yellow. Next, RhCl<sub>3</sub>·xH<sub>2</sub>O (5mg, 0.024 mmol) dissolved in H<sub>2</sub>O (2 mL) was added to the yellow solution followed by PPh<sub>4</sub>Br (12 mg, 0.028 mmol) dissolved in methanol (1 mL). Freshly prepared NaBH<sub>4</sub> solution (15 mg, 0.4 mmol) with 0.5 mL ice-cold H<sub>2</sub>O was added to the reaction mixture. The color of the reaction mixture rapidly turned to dark brown. After 15 min of vigorous stirring, the solution was transferred to a 250-mL round-bottom flask and dried by rotary-evaporation. The dried product was washed with H<sub>2</sub>O and methanol at least 5 times. Then, the dried product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL)

followed by the addition of methanol (8 mL) to remove large nanoparticles by precipitation. The supernatant was centrifugated after the addition of methanol (16 mL) to collect the synthesized NCs. The obtained precipitates included  $[RhHAg_{24}]^{2^-}$  NCs and  $[Ag_{25}(SPhMe_2)_{18}]^{1^-}$  NCs. Purification of  $[RhHAg_{24}]^{2^-}$  NC from the NC mixture was achieved by extracting  $[Ag_{25}(SPhMe_2)_{18}]^{1^-}$  NCs with toluene.  $[RhDAg_{24}(SPhMe_2)_{18}]^{2^-}$  NCs were synthesized using a similar procedure, except for the use of NaBD<sub>4</sub> and D<sub>2</sub>O. The  $[RhHAg_{24}]^{2^-}$  NCs were found to be stable at least 7 days in CH<sub>2</sub>Cl<sub>2</sub>. The NCs were also soluble in other solvents, such as THF, acetonitrile, and acetone. However, they were unstable and rapidly decomposed in these solvents within a day. Therefore, all the metal-exchange reactions and characterizations were performed in CH<sub>2</sub>Cl<sub>2</sub>.

#### **Preparation Au-SPhMe<sub>2</sub> Complex**

The Au-SPhMe<sub>2</sub> complex was synthesized according to a reported procedure.<sup>3</sup> For the synthesis of Au-SPhMe<sub>2</sub> complex, HAuCl<sub>4</sub> (393 mg, 1.0 mmol) was dissolved in acetonitrile (10 mL), and HSPhMe<sub>2</sub> (300  $\mu$ L, 2.2 mmol) was added to the solution with vigorous stirring. The color of the solvent gradually changed from brown to pink within 1h. After 12 h, a white powder precipitated. The obtained white powder was washed and centrifugated with methanol at least five times. The Au-SPhMe<sub>2</sub> complex was obtained in over 90 % yield (on the basis of Au) and used directly for the metal-exchange reaction.

## Metal Exchange Reaction of [RhHAg<sub>24</sub>(SPhMe<sub>2</sub>)<sub>18</sub>]<sup>2-</sup> with Au-SPhMe<sub>2</sub>

In a typical procedure,  $[RhHAg_{24}]^{2-}$  NCs (20mg, 3.8  $\mu$ mol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and Au-SPhMe<sub>2</sub> complex (10 mg, 30.0  $\mu$ mol) was added to the solution. The solution was kept in air under vigorous stirring for 2 h at room temperature. The color of the solution changed from green to dark brown. Then, the solvent was removed by rotary-evaporation. The obtained powder was washed several times with methanol and hexane. The [RhHAu<sub>x</sub>Ag<sub>24-x</sub>(SPhMe<sub>2</sub>)<sub>18</sub>]<sup>2-</sup> (x = 8–12) (abbreviated as [RhH(AuAg)<sub>24</sub>]<sup>2-</sup>) NCs were extracted with CH<sub>2</sub>Cl<sub>2</sub> from the powder . After removing the solvent by rotary-evaporation, the dried product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) to which toluene (20mL) was added to induce precipitation. After 30 min, the supernatant was removed by centrifugation, leaving high-purity [RhH(AuAg)<sub>24</sub>]<sup>2-</sup> NCs by the addition of a large amount of Au-SPhMe<sub>2</sub> complex (15 mg). However, the obtained NCs were unstable and rapidly decomposed. The upper limit was found to be x = 8–12 for producing stable [RhH(AuAg)<sub>24</sub>]<sup>2-</sup> NCs. [RhHAu<sub>x</sub>Ag<sub>24-x</sub>(SPhMe<sub>2</sub>)<sub>18</sub>]<sup>2-</sup> (x = 1–4) NCs were synthesized using a similar procedure, except for the use of a reduced amount the of Au-SPhMe<sub>2</sub> complex (3 mg, 9.0  $\mu$ mol).

### Isolation of [Rh(AuAg)24]<sup>2-</sup>NCs

The  $[RhH(AuAg)_{24}]^{2^{-}}$  NCs underwent a structural transformation into  $[Rh(AuAg)_{24}(SPhMe_2)_{18}]^{1^{-}}$  (abbreviated as  $[Rh(AuAg)_{24}]^{1^{-}}$ ) NCs in CH<sub>2</sub>Cl<sub>2</sub> (20 mg in 10 mL) within 3 days. The intermediate  $[Rh(AuAg)_{24}]^{2^{-}}$  NC was obtained from the mixture of NCs at the end of the hydride desorption process (after 70 h) by the solubility difference in toluene; the dianionic NCs, such as  $[RhH(AuAg)_{24}]^{2^{-}}$  and  $[Rh(AuAg)_{24}]^{2^{-}}$ , are practically insoluble in toluene, whereas monoanionic  $[Rh(AuAg)_{24}]^{1^{-}}$  NCs are highly soluble. Reasonably pure  $[Rh(AuAg)_{24}]^{2^{-}}$  NCs were isolated by removing  $[Rh(AuAg)_{24}]^{1^{-}}$  NCs using toluene extraction at the end of the hydride desorption process.

## SC-XRD of [RhHAu10Ag14(SPhMe2)18]<sup>2-</sup> NCs

Single crystals of  $(PPh_4^+)_2[RhHAu_{10}Ag_{14}(SPhMe_2)_{18}]^{2-}$  NCs were grown at room temperature by layering hexane over the CH<sub>2</sub>Cl<sub>2</sub> solution of NCs. Diffraction data were obtained according to a previously reported method<sup>1, 4-8</sup> using the BL2D-supramolecular crystallography beamline at the Pohang Accelerator Laboratory (PAL), Pohang, Republic of Korea. The single-crystal Xray diffraction structure of (PPh4<sup>+</sup>)<sub>2</sub>[RhHAu<sub>10</sub>Ag<sub>14</sub>(SPhMe<sub>2</sub>)<sub>18</sub>]<sup>2-</sup> was deposited at the Cambridge Crystallographic Data Centre (CCDC) with deposition number CCDC-2180274. The CheckCIF program generated A-level and B-level alerts. The A-level alert was related to the low value of diffraction data caused by the damage to the air-sensitive crystal and disorder of protecting ligands. Some observed HSPhMe<sub>2</sub> ligands were disordered; for this reason, AFIX constraints and DFIX, SADI, DELU, SIMU, and ISOR restraints were applied. Minor issues that caused B and C-level alerts were mainly related to the HSPhMe<sub>2</sub> ligands in the crystal structure. They originated from the disordered nature of the cluster ligands, but did not affect the angles and bond lengths of the Rh(AuAg)<sub>12</sub> icosahedral core framework. The Au and Ag atoms were initially treated as partially occupied Au/Ag with the same coordination and anisotropic displacement using EXYZ. The Au/Ag occupancies for kernel Au atoms and staple Ag atoms are converged after refinement.

### **Computational Methods**

Geometric optimization, molecular energetic properties, and associated orbital composition analysis were performed using DFT calculations. For all NCs, constrained geometric optimization was performed only for the C and H atoms based on the experimental crystal structure backbone at the TPSS/def2-SV(P),<sup>9</sup> level of theory as implemented in ORCA v5.0.1.<sup>10,11</sup> The resolution-of-identity approximation to the Coulomb term was applied with the def2/J<sup>12</sup> auxiliary basis set to accelerate the computation of the two-electron integral. Molecular energetic information was then calculated with revTPSS/jorge-TZP-DKH<sup>13,14</sup> using the G16<sup>15</sup> package version RevA.03 with the Douglas-Kroll-Hess 2nd order scalar relativistic calculation.<sup>16</sup> Gaussian NBO v3.1 was used for natural atomic orbital analysis. For clarity, the contribution of the atomic orbital to the molecular orbital below 0.1% was omitted. Numerical grids were plotted for every 0.20 Bohr (190, 200, and 207 points in the x-, y-, and z-directions, respectively) to calculate the AIM charge.

To reduce the computational cost, simplified model NCs, composed of the Rh(H)Au<sub>12</sub> core protected by six Ag<sub>2</sub>(SCH<sub>3</sub>)<sub>3</sub> staple motifs ligands, were employed. Geometric optimization was performed using the single crystal structure of [RhHAu<sub>x</sub>Ag<sub>24-x</sub>(SPhMe<sub>2</sub>)<sub>18</sub>]<sup>2-</sup> and replacing the RuAu<sub>10</sub>Ag<sub>2</sub> alloy kernel and SPhMe<sub>2</sub> ligands with the RhAu<sub>12</sub> kernel and SCH<sub>3</sub> ligands, respectively. Spin density and 3D orbital surfaces were obtained from the model [RhAu<sub>12</sub>Ag<sub>12</sub>(SCH<sub>3</sub>)<sub>18</sub>]<sup>2-</sup> NC. The geometric optimization of the [RhAu<sub>12</sub>Ag<sub>12</sub>(SCH<sub>3</sub>)<sub>18</sub>]<sup>1-</sup> NC was achieved from the initial structure adopted from the [PtAu<sub>24</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>]<sup>0</sup> NC with the superatomic 6-electron configuration (1S<sup>2</sup>1P<sup>4</sup>).<sup>17</sup>



**Figure S1.** (a) Negative-mode ESI mass spectrum of the purified cluster product,  $[RhHAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x=8–12). (b) Comparisons between the experimental data (black) in (a) and the simulated isotope patterns (red).



**Figure S2.** (a) UV-Vis absorption spectra of  $[RhHAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 8–12, black) and  $[RhDAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 8–12, blue) NCs. The wavelength-scale absorption spectrum,  $Abs(\lambda)$ , was converted to the energy-scale spectrum, Abs(E), according to the relation  $Abs(E) \propto [Abs(\lambda)]\lambda^2$ . (b) ESI mass spectrum of  $[RhDAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 8–12). The inset shows the comparison between the most intensive peak (\*) of the experimental data (black) and the simulated isotope pattern (blue).



**Figure S3.** Temporal evolution of (a) ESI mass and (b) <sup>1</sup>H-NMR spectra monitored during the metal-exchange reaction between  $[RhHAg_{24}(SPhMe_2)_{18}]^{2-}$  and Au–SPhMe<sub>2</sub> complex for 120 min. The highly shielded resonance of the doped hydride is observed in the region from -4 to -11 ppm. (c) <sup>1</sup>H-NMR spectrum of purified  $[RhHAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 8–12) NCs in CD<sub>2</sub>Cl<sub>2</sub>. The inset shows the hydride peak centered at approximately -7.5 ppm. The signals produced by the in- and out-SPhMe<sub>2</sub> ligands of the staple motif are highlighted in blue and green, respectively.<sup>18</sup>

(a)	RhH(AuAg) <sub>24</sub> NC				•			Rh					
				+			M <sub>12</sub> kernel						
(b)		4				•	T M., Kerne	X	6	M′2	(SR) <sub>3</sub> :	staple	
- 1		M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	 M12
	Δ	78 %	76 %	73 %	78 %	74 %	75 %	69 %	73 %	74 %	72 %	69 %	73 %
	Ag	22 %	24 %	27 %	22 %	26 %	25 %	31 %	27 %	26 %	28 %	31 %	27 %
1	6 M' <sub>2</sub> (SR) <sub>3</sub> Staple Motifs												
-		M'1	M'2	M'3	M'4	M'5	M'6	M'7	M'8	M'9	M'10	M'11	M'12
	Au	3 %	5 %	8 %	3 %	8 %	7 %	12 %	11 %	12 %	10 %	7 %	8 %
	Ag	97 %	95 %	92 %	97 %	92 %	93 %	88 %	89 %	88 %	90 %	93 %	92 %

**Figure S4.** (a) Crystal structure of the  $[RhHAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 8–12) NC, which consists of Rh-centered M<sub>12</sub> icosahedron protected by six-M'<sub>2</sub>(SR)<sub>3</sub> dimeric staple motifs. (b) Results of chemical occupancy analysis performed on the crystal structure of  $[RhHAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 8–12) NC. Each metal atom site is labeled with a different number (Mx / M'x, x = 1–12). The M<sub>12</sub> kernel atoms in this NC are mainly composed of Au atoms, whereas the metal atoms in the staple motifs (M') are predominantly Ag atoms.



**Figure S5.** Au 4f, Ag 3d, and Rh 3d XPS profiles of  $[RhH(AuAg)_{24}]^{2-}$  NC. The experimental data (black dots) are shown with envelopes (red line) and fitted curves. The Au 4f and Ag 3d spectra were fitted with two Gaussian curves, representing Au<sup>0</sup> (Ag<sup>0</sup>) and Au<sup>I</sup> (Ag<sup>I</sup>), respectively.



**Figure S6.** (a) Crystal structures of  $[RhHAg_{24}]^{2-}$  NC (left) and  $[RhH(AuAg)_{24}]^{2-}$  NC (right) Color legend: red, Rh; green, Ag; blue, S; orange, Au-rich kernel. The PhMe<sub>2</sub> is omitted for clarity. (b) Bond distances (denoted by color) in the RhAg<sub>12</sub> and Rh(AuAg)<sub>12</sub> kernels of the  $[RhHAg_{24}]^{2-}$  NC (left) and  $[RhH(AuAg)_{24}]^{2-}$  NC (right). Black dashed line indicates the broken Ag-Ag bond (3.50 Å) in the RhAg<sub>12</sub> kernel.



**Figure S7.** (a) Negative-mode ESI mass spectrum of the  $[RhAu_xAg_{24-x}(SPhMe_2)_{18}]^{1-}$  (x = 8–12) NCs. (b) Comparisons between the experimental data (blue) in (a) and the simulated isotope patterns (red).



**Figure S8.** Temporal evolution of (a) UV-Vis and (b) ESI mass spectra of  $[RhH(AuAg)_{24}]^{2-}$  NCs monitored after the addition of dilute H<sub>2</sub>O<sub>2</sub> solution (1.4 wt%) to the CH<sub>2</sub>Cl<sub>2</sub> solution of NCs. The reaction time is denoted on the spectra.



**Figure S9.** (a) Toy model of RhH with a bond distance of 1.68 Å. (b) Relative orbital energies and 3D orbital surfaces of the molecular orbital of RhH. The relative contributions of the atomic orbitals (Rh and H) to the molecular orbitals are expressed by the bar lengths (blue, H 1s; green, Rh 4d; red, Rh 5s).



**Figure S10.** (a) UV-Vis absorption and (b) ESI mass spectra of the  $[RhHAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  NC (x = 1–4) recorded after 0 and 72 h in CH<sub>2</sub>Cl<sub>2</sub>. The inset shows the comparison between the most intensive peak (\*) of experimental isotope patterns with the simulated isotope pattern (red) of  $[RhHAu_2Ag_{22}(SPhMe_2)_{18}]^{2-}$ .



Figure S11. UV-Vis absorption spectra of  $[Rh(AuAg)_{24}]^{1-}$  NCs recorded at 0 and 5 days in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S12.** (a) DFT optimized structure of the  $[Rh(AuAg)_{24}(SCH_3)_{18}]^{1-}$  NC and its kernel structure (b). The bond lengths are denoted by color. (c) Calculated orbital energy levels and 3D orbital surfaces of the  $[Rh(AuAg)_{24}(SCH_3)_{18}]^{1-}$  NC.



**Figure S13.** (a) ESI mass spectrum of  $[RhAu_xAg_{24-x}(SPhMe_2)_{18}]^{2-}$  (x = 7–11) NCs separated at the end-stage of the hydride desorption process (after 70 h). Dianionic NCs were obtained after the removal of  $[Rh(AuAg)_{24}]^{1-}$  NCs by toluene extraction. (b) Comparisons of representative experimental data with the simulated isotope patterns of  $[RhAu_8Ag_{16}(SPhMe_2)_{18}]^{2-}$  and  $[RhAu_9Ag_{15}(SPhMe_2)_{18}]^{2-}$ .



**Figure S14.** Schematic of the two-step kernel evolution from  $[RhH(AuAg)_{24}]^{2-}$  to  $[Rh(AuAg)_{24}]^{1-}$  NC. (a) DFT-optimized structure of  $[RhH(AuAg)_{24}]^{2-}$  (left),  $[Rh(AuAg)_{24}]^{2-}$  (middle), and  $[Rh(AuAg)_{24}]^{1-}$  (right) NCs and (b) their corresponding Rh(H)Au<sub>12</sub> kernel structures. The bond lengths are denoted by color.



**Figure S15.** (a) Total spin density map of the  $[Rh(AuAg)_{24}]^{2-}$  model NC (isosurface value = 0.0004). (b) 3D orbital surfaces of the singly occupied molecular orbital (SOMO) and the degenerate LUMO of the  $[Rh(AuAg)_{24}]^{2-}$  NC (isosurface value=0.01).

## **Supplementary Tables S1-S6**

NCs	Rh-M <sub>kernel</sub> (Å)	M <sub>kernel</sub> -M <sub>kernel</sub> (Å)	Longest M <sub>kernel</sub> -M <sub>kernel</sub> (Å)	M <sub>kernel</sub> -S <sub>staple</sub> (Å)
[RhHAg <sub>24</sub> ] <sup>2-</sup>	2.77 (0.03)	* <mark>2.92 (</mark> 0.14)	3.50	2.47 (0.03)
[RhH(AuAg) <sub>24</sub> ] <sup>2-</sup>	2.76 (0.02)	2.90 (0.07)	3.14	2.42 (0.01)

**Table S1.** Average bond lengths of the  $[RhHAg_{24}]^{2-}$  and  $[RhH(AuAg)_{24}]^{2-}$  NCs.

\* Average bond distance includes the longest  $M_{kernel}$ - $M_{kernel}$  bond (3.50 Å).

**Table S2**. Bond lengths and Wiberg bond orders of the  $[RhHAg_{24}]^{2-}$  and  $[RhH(AuAg)_{24}]^{2-}$  model NCs.

Bond Length (Å)	* [RhHAg <sub>24</sub> ] <sup>2–</sup>	[RhH(AuAg) <sub>24</sub> ] <sup>2–</sup>
Rh-H	1.62	1.68
Longest M <sub>kernel</sub> -M <sub>kernel</sub>	3.50	3.14
M <sub>kernel</sub> -H	1.81, 2.18, 2.27, 2.62	1.73, 1.75, 1.94, 2.66
Average M <sub>kernel</sub> -H	2.22	2.02
** M-M in M <sub>kernel</sub>	3.01, 3.14, 3.20, 3.36	2.86, 2.88, 2.89, 2.92
Average M-M in M <sub>4, kernel</sub>	3.18	2.89
<sup>‡</sup> Wiberg bond order	* [RhHAg <sub>24</sub> ] <sup>2–</sup>	[RhH(AuAg) <sub>24</sub> ] <sup>2–</sup>
Rh-H	0.74	0.71
M <sub>kernel</sub> -H	0.39, 0.18, 0.15, 0.08	0.52, 0.50, 0.32, 0.06
Average M <sub>kernel</sub> -H	0.20	0.35

\* Bond lengths from reference S1.

\*\* M-M in  $M_{kernel}$  represents the bond distances between four nearest  $M_{kernel}$  atoms from H.

 $\ddagger$  Wiberg bond orders calculated for the [RhHAg<sub>24</sub>]<sup>2-</sup> NC are different from ref S1 because of the inclusion of the relativistic effect (recalculated using jorge-TPZ-DKH basis set).

NC	[Rhł	I(AuAg) <sub>24</sub> ]²−	[Rh(AuAg) <sub>24</sub> ] <sup>1–</sup>		
	Label	Orbital Energy (eV)	Label	Orbital Energy (eV)	
LUMO+4	D	1.95	D	2.10	
LUMO+3	D	1.79	D	1.94	
LUMO+2	D	1.71	D	1.52	
LUMO+1	D	1.50	D	1.49	
LUMO	D	1.44	Р	0.22	
*HOMO	Р	0	Р	0	
HOMO-1	Р	-0.05	Р	-0.04	
HOMO-2	Р	-0.22		-0.21	
HOMO-LUMO gap		1.44		0.22	

Table S3. Relative orbital energies of the [RhH(AuAg)<sub>24</sub>]<sup>2-</sup> and [Rh(AuAg)<sub>24</sub>]<sup>1-</sup> model NCs

\* The HOMO level energies for both NCs were normalized to 0 eV for comparison.

**Table S4.** Coefficients of the fragment orbitals determined for the frontier orbitals of the  $[RhHAg_{24}]^{2-}$ ,  $[RhH(AuAg)_{24}]^{2-}$ , and  $[Rh(AuAg)_{24}]^{1-}$  NCs.

NC	Label	Dopant		M <sub>12</sub> kernel	Staple Motifs
[RhHAg <sub>24</sub> ] <sup>2–</sup>		Rh	н	Ag <sub>12</sub>	6 Ag <sub>2</sub> (SR) <sub>3</sub>
НОМО	Р	17.7 %	0 %	31.5 %	50.8 %
HOMO-1	Р	15.7 %	0 %	30.4 %	53.9 <b>%</b>
HOMO-2	Р	9.4 %	3.1 %	30.0 %	57.5 %
Average		14.3 %	1.0 %	30.6 %	54.1 %
[RhH(AuAg) <sub>24</sub> ] <sup>2–</sup>		Rh	н	Au <sub>12</sub>	6 Ag <sub>2</sub> (SR) <sub>3</sub>
НОМО	Р	9.3 %	0 %	38.1 %	52.6 %
HOMO-1	Р	9.5 %	0 %	39.3 %	51.2 %
HOMO-2	Р	5.8 %	1.0 %	35.0 %	58.2 %
Average		8.2 %	0.3 %	37.4 %	54.0 %
[Rh(AuAg) <sub>24</sub> ] <sup>1–</sup>		Rh	н	Au <sub>12</sub>	6 Ag <sub>2</sub> (SR) <sub>3</sub>
LUMO	Р	12.5	0	40.2	47.3
НОМО	Р	10.8	0	38.0	51.2
HOMO-1	Р	8.3	0	33.4	58.3
Average		10.5 %	0 %	37.2 %	52.3 %

**Table S5.** Bader charge analyses conducted on Rh and H atoms in the  $[RhHAg_{24}]^{2-}$ ,  $[RhH(AuAg)_{24}]^{2-}$ , and  $[Rh(AuAg)_{24}]^{1-}$  model NCs.

Bader Charge	<sup>‡</sup> [RhHAg <sub>24</sub> ] <sup>2–</sup>	[RhH(AuAg) <sub>24</sub> ] <sup>2–</sup>	[Rh(AuAg) <sub>24</sub> ] <sup>1–</sup>
Rh	-0.09	-0.16	-0.27
н	-0.20	-0.13	-

 $\frac{1}{2}$  Bader charges of the [RhHAg<sub>24</sub>]<sup>2-</sup> NC were calculated using jorge-TZP-DKH basis set which includes the relativistic effect.



Crystallographic data obtained for (PPh4<sup>+</sup>)2[RhHAu10Ag14(SPhMe2)18]<sup>2-</sup> (CCDC 2180274)

Empirical formula	$C_{6.43}H_{6.89}Ag_{0.39}Au_{0.39}Cl_{0.26}P_{0.07}Rh_{0.03}S_{0.59}$			
Formula weight	237.68			
Temperature/K	100(2)			
Crystal system	triclinic			
Space group	P-1			
a/Å	19.803(4)			
b/Å	19.885(4) b/Å			
c/Å	32.507(7)			
α/°	86.42(3)			
$\beta/^{\circ}$	73.32(3)			
$\gamma/^{\circ}$	62.20(3)			
Volume/Å <sup>3</sup>	10808(5)			
Ζ	61			
$\rho_{calc}g/cm^3$	2.228			
$\mu/mm^{-1}$	9.505			
F(000)	6794.0			
Crystal size/mm <sup>3</sup>	$? \times ? \times ?$			
Radiation	synchrotron ( $\lambda = 0.8000$ )			
2\Overlap range for data collection/\overlap	2.324 to 52.084			
Index ranges	$-24 \le h \le 24, -24 \le k \le 24, -40 \le l \le 40$			
Reflections collected	69644			
Independent reflections	$35829 [R_{int} = 0.0537, R_{sigma} = 0.0653]$			
Data/restraints/parameters	35829/0/2275			
Goodness-of-fit on F <sup>2</sup>	1.068			
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0916$ , $wR_2 = 0.2592$			

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