Supporting Information

Hetero-biicosahedral $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^+$ nanocluster: selective synthesis and optical and electrochemical properties

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1. Additional Information for Experiments

Parameters used in mass spectrometry measurements.

***Specialized parameters for the 1+ region*:** End plate offset: −500 V, Capillary: −4500 V, Nebulizer: 1.0 Bar, Dry gas: 2.0 L/min, Dry temperature: 100°C, Capillary exit: 100.0 V, Hexapole 1: 20.0 V, Hexapole 2: 14.0 V, Transfer time: 98.0 µs, Lens 1 storage: 40.0 V, Lens 2: 7.0 V, Lens 4: 0.6 V, Detector: 0 V, Skimmer 1: 40.0 V, Skimmer 2: 20.0 V, Hexapole RF: 800.0 Vpp, Pre pulse storage: 25.0 µs, Lens 1 extraction: 20.3 V, Lens 3: −20.3 V, Lens 5: −29.6 V.

***Specialized parameters for the 2+ region*:** End plate offset: −500 V, Capillary: −4500 V, Nebulizer: 2.5 Bar, Dry gas: 2.0 L/min, Dry temperature: 100°C, Capillary exit: 100.0 V, Hexapole 1: 20.0 V, Hexapole 2: 18.0 V, Transfer time: 80.0 µs, Lens 1 storage: 40.0 V, Lens 2: 7.0 V, Lens 4: 0.6 V, detector: 0 V, Skimmer 1: 40.0 V, Skimmer 2: 20.0 V, Hexapole RF: 800.0 Vpp, Pre pulse storage: 25.0 µs, Lens 1 extraction: 20.3 V, Lens 3: −20.3 V, Lens 5: −29.6 V.

2. Additional Tables

Table S1. Occupancy of Pd in $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ ($Au_{24}Pd$−I and $Au_{24}Pd$−II).

Position	$Au_{24}Pd$−I		$Au_{24}Pd$−II	
	Au	Pd	Au	Pd
Site 1 [a]	50.9%	49.1%	51.0%	49.0%
Site 2 [a]	50.7%	49.3%	49.3%	50.7%

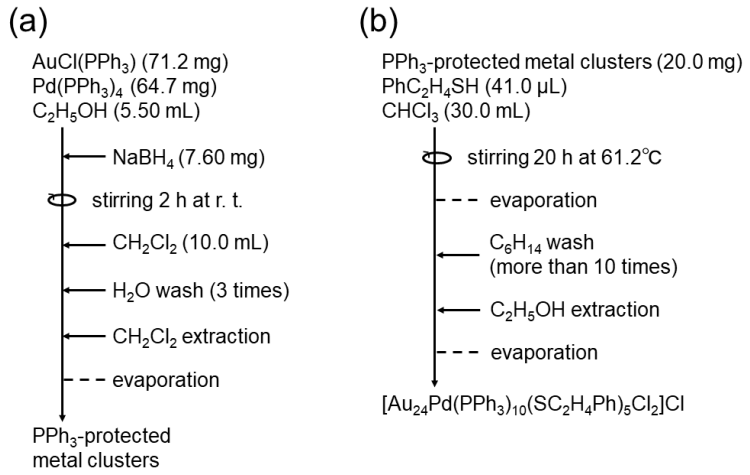
[a] see Figure 3(a).

Table S2. Au−P, Au−S, and Au−Cl Bond Lengths in $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ ($Au_{24}Pd$-I and $Au_{24}Pd$-II) and $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

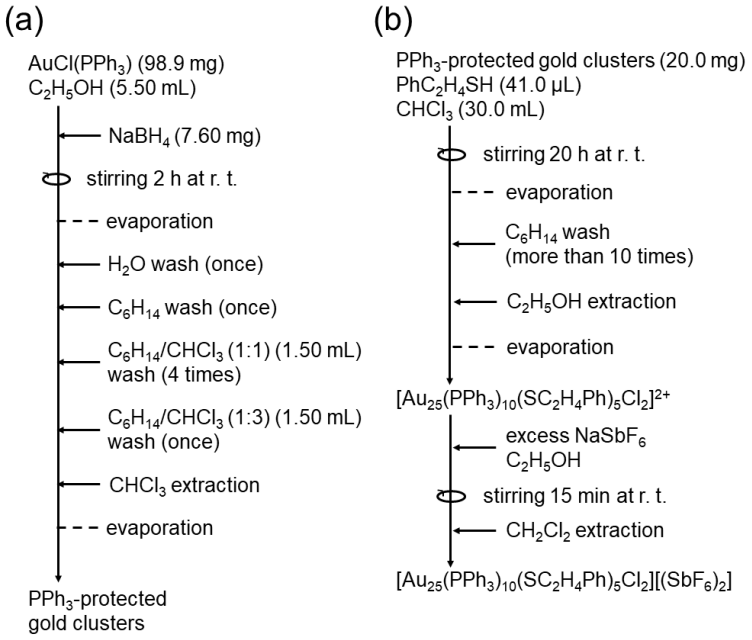
Bond Type [a]	$Au_{24}Pd$−I (Å)	$Au_{24}Pd$−II (Å)	Au_{25} (Å)
Au18, 41, 23−P9, 17, 191	2.285	2.284	2.291
Au38, 45, 19−P14, 18, 153	2.286	2.291	2.292
Au23, 25, 11−P1, 8, 207	2.292	2.294	2.292
Au15, 13, 18−P10, 6, 245	2.295	2.295	2.294
Au36, 46, 20−P12, 20, 172	2.295	2.295	2.294
Au39, 14, 13−P15, 5, 115	2.295	2.296	2.296
Au30, 43, 16−P13, 19, 77	2.298	2.301	2.298
Au35, 17, 9−P16, 3, 96	2.299	2.301	2.298
Au28, 4, 21−P11, 4, 134	2.306	2.301	2.299
Au20, 29, 22−P7, 2, 226	2.310	2.308	2.300
Au22, 34, 3−S10, 8, 35	2.373	2.374	2.362
Au12, 2, 15−S3, 2, 70	2.373	2.381	2.367
Au24, 3, 7−S10, 2, 44	2.374	2.384	2.368
Au8, 7, 12−S4, 9, 70	2.377	2.387	2.368
Au32, 16, 14−S1, 7, 53	2.378	2.387	2.372
Au21, 5, 6−S1, 9, 53	2.379	2.388	2.373
Au11, 31, 17−S5, 6, 54	2.388	2.389	2.375
Au19, 33, 8−S3, 8, 35	2.389	2.390	2.375
Au27, 26, 10−S5, 6, 44	2.391	2.393	2.376
Au9, 10, 5−S4, 7, 54	2.394	2.397	2.382
Au37, 40, 24−Cl1, 1A, 1	2.387	2.394	2.354
Au44, 42, 25−Cl2, 0A, 2	2.391	2.398	2.361

[a] see cif files.

3. Additional Schemes



Scheme S1. Protocol for isolating high-purity $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$.



Scheme S2. Protocol for isolating high-purity $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.[1]

4. Additional Figures

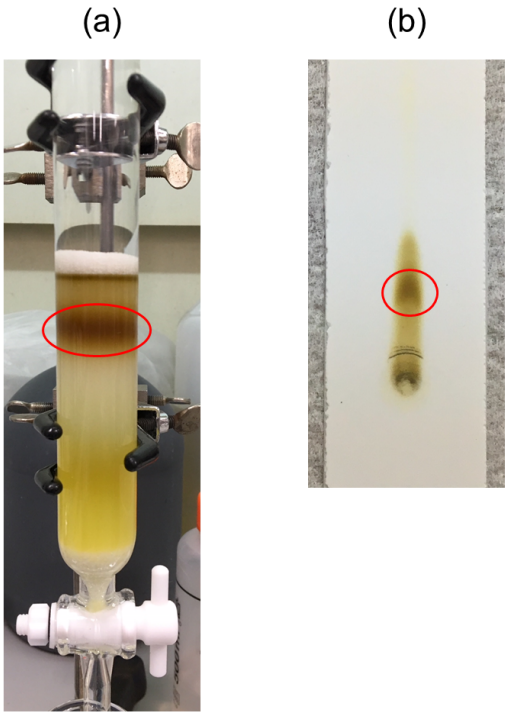


Figure S1. Purification of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ by (a) silica-gel column chromatography and (b) thin-layer chromatography to obtain high-purity samples. Red circles indicate $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$.

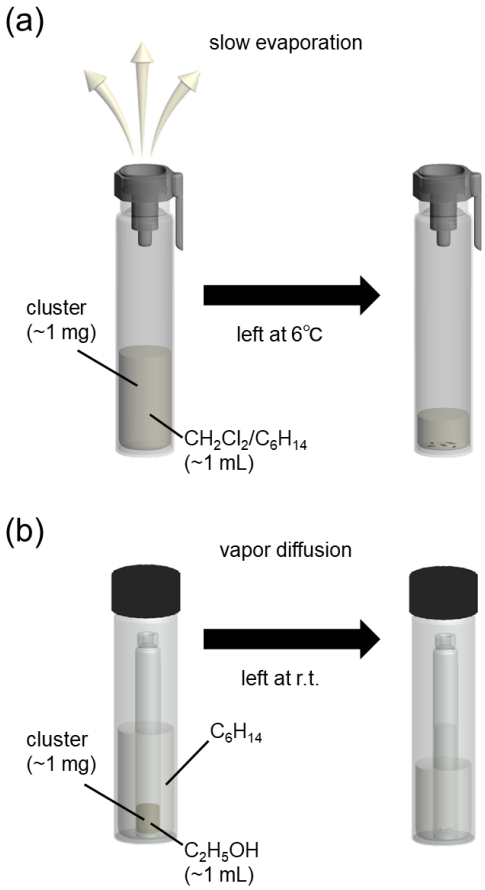


Figure S2. Schematic depiction of crystallization of (a) $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ (slow evaporation) and (b) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$ (vapor diffusion).

Figure S3. Photographs of single crystals of (a) $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ (block- and needle-like) and (b) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$ (block-like).

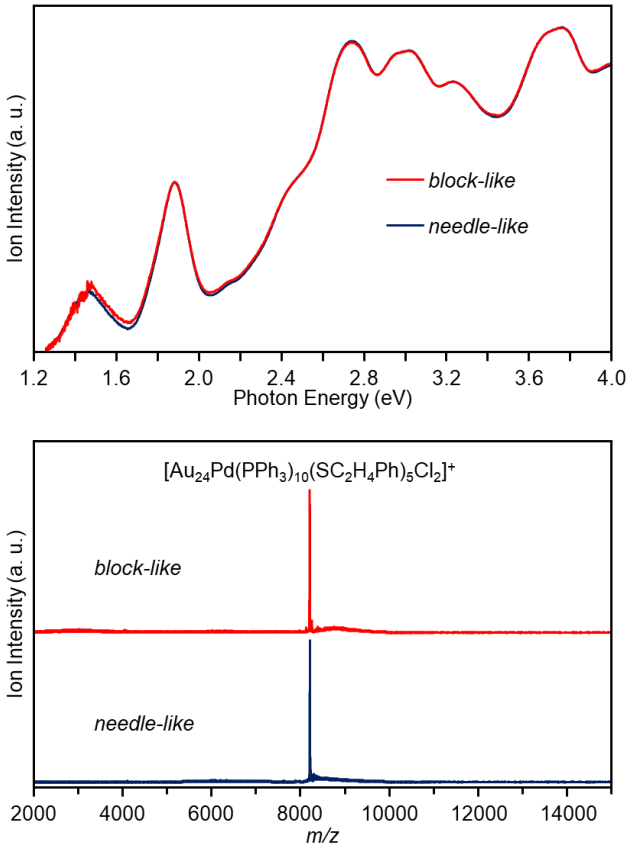


Figure S4. (a) Optical absorption spectra of dichloromethane solution and (b) positive-ion ESI mass spectra of block- and needle-like $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$.

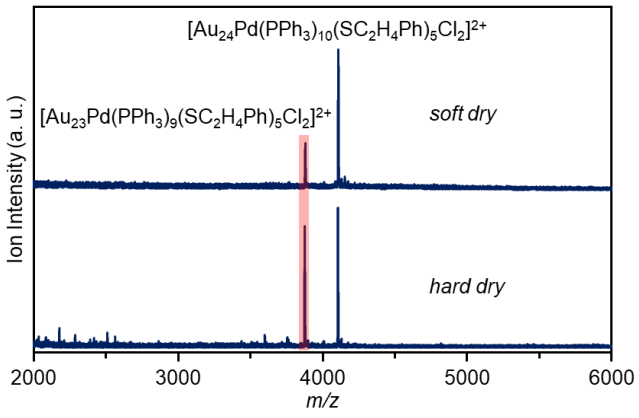


Figure S5. (a) Positive-ion electrospray ionization (ESI) mass spectra of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$ in the region around *m/z* 4000 depending on the ESI conditions. The relative intensity of $[Au_{23}Pd(PPh_3)_9(SC_2H_4Ph)_5Cl_2]^{2+}$ depended on the dry condition in the ESI process, suggesting that the $[Au_{23}Pd(PPh_3)_9(SC_2H_4Ph)_5Cl_2]^{2+}$ is fragment ion generated from $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$.

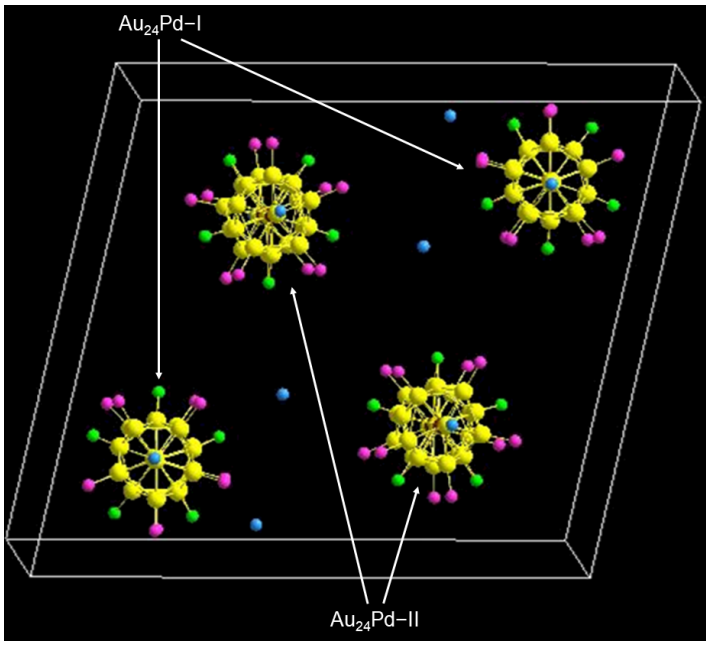


Figure S6. Unit cell of the crystal of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$.

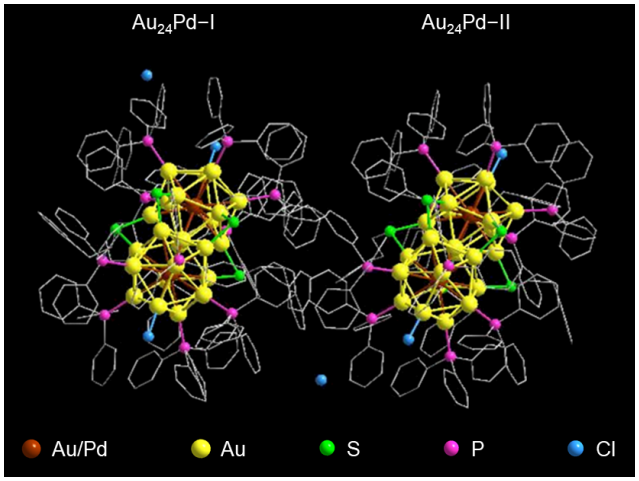


Figure S7. Full structures of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ ($Au_{24}Pd$−I and $Au_{24}Pd$−II). Hydrogen atoms are not shown for clarity. In this figure, the counteranion could be assigned as a chloride ion. However, the highest Q peak observed in the solvent sphere was ~6, whereas the Q peak corresponding to a chloride attached to the core structure (Au) was around 20. The low Q peak value is attributed to the disordered nature of chloride ions because they never order very well in the solvent sphere. The presence of other Q peaks with smaller values (2–3) around chlorides in the solvent sphere indicates the diffuse nature of the chloride counteranion.

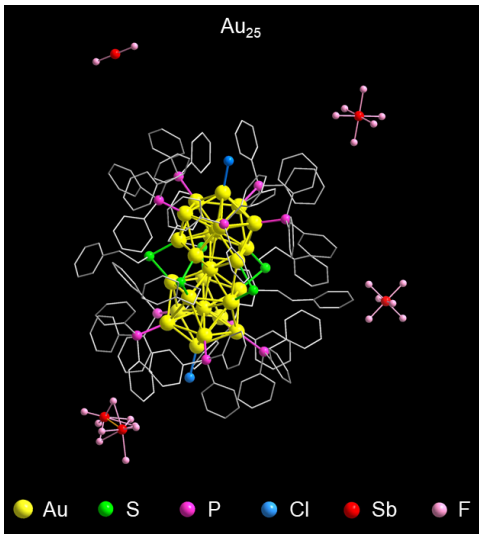


Figure S8. Full structure of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$. Hydrogen atoms are not shown for clarity. Although this cluster has two SbF_6 anions, one SbF_6 was disordered over 4 position and they were refined using SUMP command. At one such position, SbF_6 anion with occupancy (0.2662) could be fully assigned whereas remaining part was of the $[SbF_6]^-$ was partially assigned in additional three positions. Finally, four positions were refined using SUMP command in Olex2.

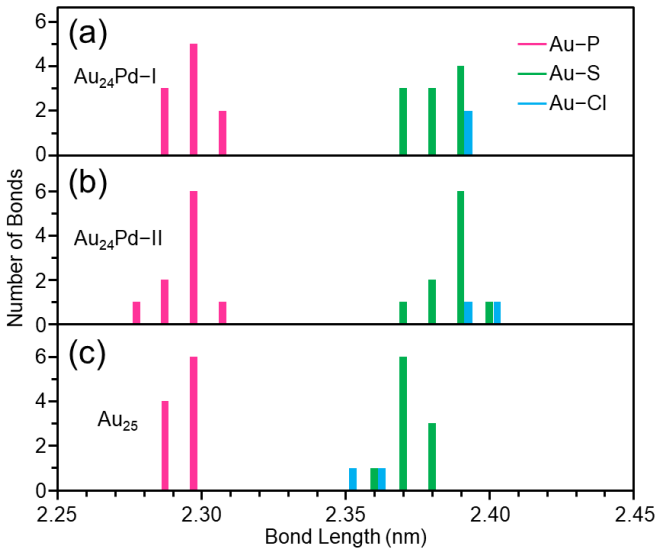


Figure S9. Au−P, Au−S, and Au−Cl bond lengths in (a) $Au_{24}Pd$−I, (b) $Au_{24}Pd$−II, and (c) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

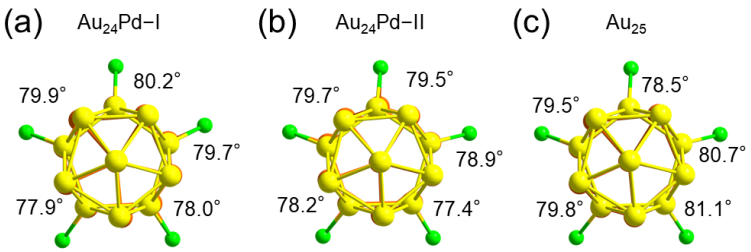


Figure S10. Au–S–Au angles in (a) $Au_{24}Pd–I$, (b) $Au_{24}Pd–II$, and (c) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

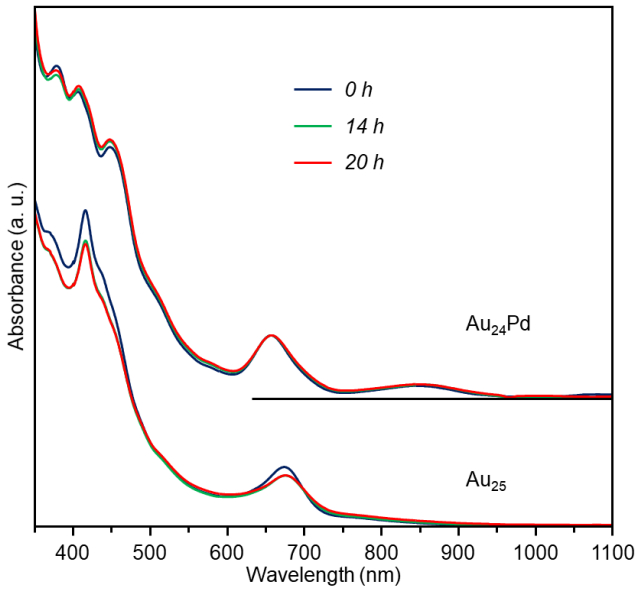


Figure S11. Time dependence of optical absorption spectra of chloroform solution of (a) $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ and (b) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

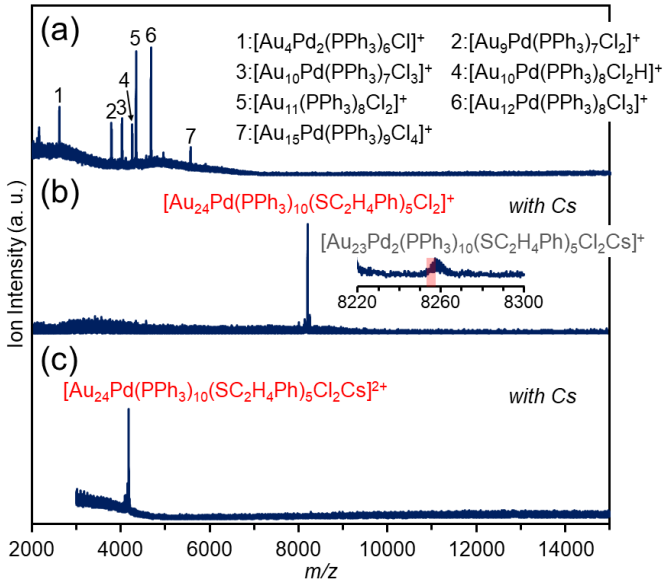


Figure S12. Positive-ion electrospray ionization mass spectra of (a) the precursor $Au_{n-x}Pd_x$ clusters obtained by increasing the quantity of Pd salt by three times in the synthesis and (b), (c) the products obtained from the reaction between the precursor $Au_{n-x}Pd_x$ clusters shown in (a) and PhC_2H_4SH at 61.2°C. In the experiments in (b) and (c), Cs salt was added to the solution to observe the neutral cluster as a cation. The parameters of the measurement were optimized to monitor the mass peaks around 8000 with strong intensity in (b) and those around 4000 with strong intensity in (c).

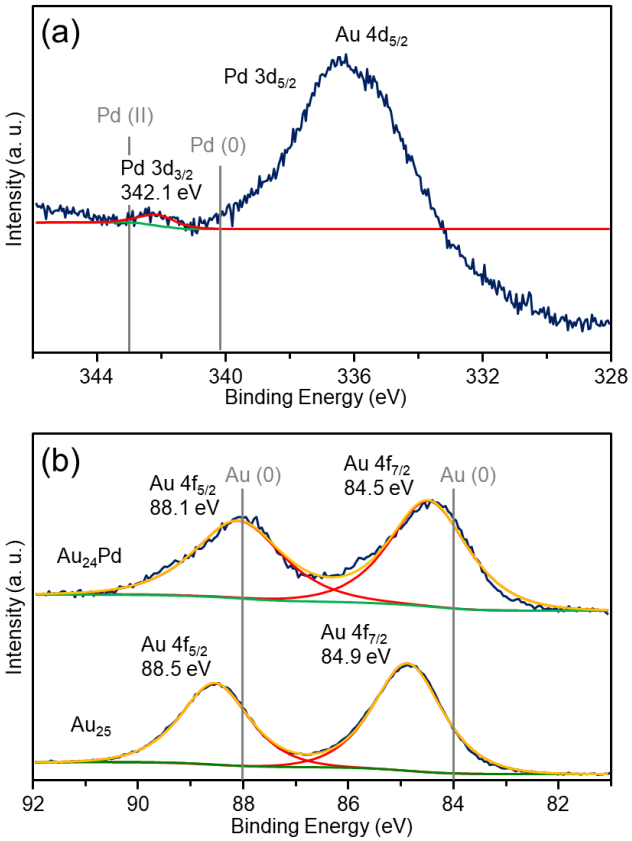


Figure S13. (a) Pd $3d_{3/2}$ spectrum and (b) Au 4f spectrum of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$. In (b), Au 4f spectra of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$ is also shown for comparison.

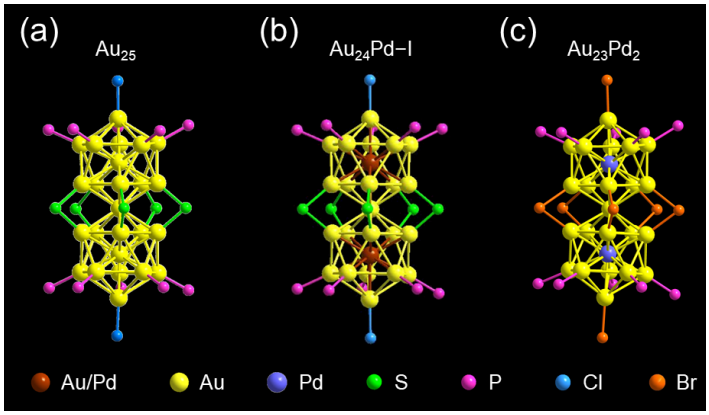


Figure S14. Comparison of the framework structures of (a) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$, (b) $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ ($Au_{24}Pd–I$), and (c) $[Au_{23}Pd_2(PPh_3)_{10}Br_7]^0$ (ref. 2).

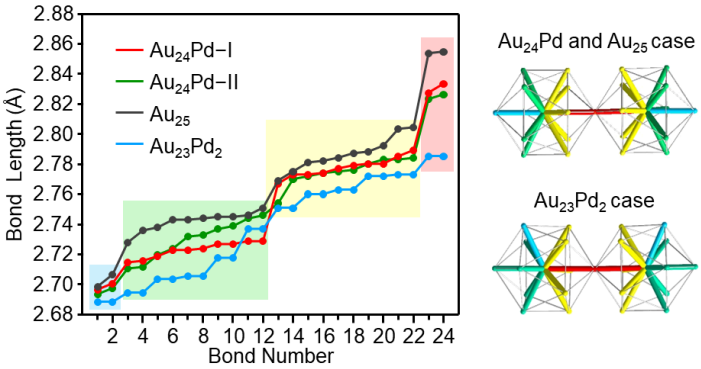


Figure S15. Comparison of bond lengths between the central atom and surface atoms among $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$, $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ ($Au_{24}Pd–I$ and $Au_{24}Pd–II$), and $[Au_{23}Pd_2(PPh_3)_{10}Br_7]^0$ (ref. 2). The metal core of $[Au_{23}Pd_2(PPh_3)_{10}Br_7]^0$ is most contracting in these clusters.

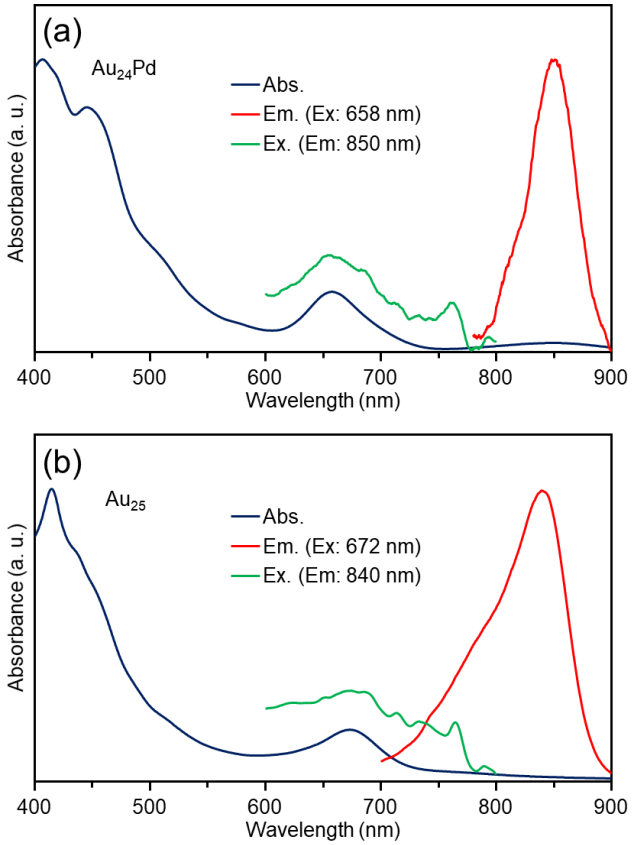


Figure S16. Photoluminescence (PL) spectra of (a) $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^+$ and (b) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$. The estimated PL quantum yields of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^+$ and (b) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$ were 2.4×10^{-5} and 1.0×10^{-3}, respectively. These results indicate that the single Pd substitution increases the PL quantum yield of the cluster only a little, different from the effect of Ag doping. It has been reported that substitution with 13 Ag atoms markedly increased the PL quantum yield of the cluster.[3] In this case, the 13th Ag atom could be located in the position that connects the two icosahedral 13-atom clusters. This position is related to the lowest unoccupied molecular orbital of the cluster and thereby this substituent strongly affects the relaxation from the photoexcited state. In contrast, a Pd atom was substituted in the central position of each icosahedral 13-atom core in $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^+$. This substituent should affect the lowest unoccupied molecular orbital of the cluster only a little. This would be the reason why Pd substitution did not increase the PL quantum yield of the cluster.

5. Additional Crystal Structure Information

5.1. Crystal Data

Crystal data and some of the important structural refinement parameters for cluster (**1-2**) are given below.

$[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$: $C_{220}H_{194.5}Au_{24.0125}Cl_3P_{10}Pd_{0.9875}S_5$; M_w. 8249.32 g/mol; triclinic, P-1 (No. 2); a = 20.474(2) Å, b = 31.755(4) Å, c = 36.216(4) Å, α = 75.3930(10)°, β = 74.9100(10)°, γ = 84.0290(10)°; V = 21981(4) Å^3 ; T = 100 K; Z = 4; μ (Mo K_α) = 16.236 mm^{-1}; Total 244227 reflections measured (2.452° ≤ 2Θ≤ 53.44°) and unique reflections are 92330 (R_{int} = 0.0620) which were used in all calculations. Then Final *wR2* of all data was 0.1364 and *R1* was 0.0594 (I > 2σ (I)).

$[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$: $C_{220}H_{195}Au_{25}Cl_2F_{10.6225}P_{10}S_5Sb_{2.0225}$; M_w. 8751.88; monoclinic, $P2_1/n$ (no. 14); a = 20.44900(14) Å, b = 35.9379(2) Å, c = 31.80647(19) Å, β = 91.1204(6)°; V = 23369.9(3) Å^3 ; T = 113(2) K; Z = 4; μ(CuKα) = 32.178 mm^{-1}; Total reflections measured 250020 (4.972° ≤ 2Θ ≤ 147.276°) and unique reflections are 46597 unique (R_{int} = 0.0612) which were used in all calculations. Then Final *wR2* of all data was 0.1195 and *R1* was 0.0416 (I>2σ (I)).

All the details of crystal data and structural refinement parameters are tabulated in the followings.

Table S3. Details of Crystal Data and Structural Refinement Parameters in $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ and $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

Cluster	$[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$	$[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$
Empirical formula	$C_{220}H_{194.5}Au_{24.01}Cl_3P_{10}Pd_{0.99}S_5$	$C_{220}H_{195}Au_{25}Cl_2F_{10.62}P_{10}S_5Sb_{2.02}$
Formula weight	8249.32	8751.88
Temperature/K	100	113(2)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	20.474(2)	20.44900(14)
b/Å	31.755(4)	35.9379(2)
c/Å	36.216(4)	31.80647(19)
α/°	75.3930(10)	90
β/°	74.9100(10)	91.1204(6)
γ/°	84.0290(10)	90
Volume/Å^3	21981(4)	23369.9(3)
Z	4	4
ρ_{calc}g/cm^3	2.493	2.487
μ/mm^{-1}	16.236	32.178
F(000)	14952.0	15811.0
Crystal size/mm^3	0.22 × 0.18 × 0.09	0.2 × 0.16 × 0.08
Radiation MoKα	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	2.452 to 53.44	4.972 to 147.276
Index ranges	-25 ≤ h ≤ 25, -40 ≤ k ≤ 40, -45 ≤ l ≤ 45	-25 ≤ h ≤ 23, -44 ≤ k ≤ 44, -37 ≤ l ≤ 39
Reflections collected	244227	250020
Independent reflections	92330 [R_{int} = 0.0620, R_{sigma} = 0.0918]	46597 [R_{int} = 0.0612, R_{sigma} = 0.0382]
Data/restraints/ parameters	92330/9498/4198	46597/2848/2504
Goodness-of-fit on F^2	1.049	1.072
Final R indexes [I>=2σ(I)]	R_1 = 0.0594, wR_2 = 0.1158	R_1 = 0.0416, wR_2 = 0.1158
Final R indexes [all data]	R_1 = 0.1148, wR_2 = 0.1364	R_1 = 0.0489, wR_2 = 0.1195
Largest diff. peak/hole/ eÅ^{-3}	4.06/-2.54	3.58/-2.59

5.2. Structure Quality Indicators and Refinement Details

SADABS-2016/2[4] (Bruker 2016/6) was used for absorption correction for the crystal $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ and CrysAlisPro version 1.171.39.20a was used for $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

First initial model of each structure of all the clusters containing heavy atoms (metal, sulfur, coordinated chloride and phosphorous atoms) and most of the carbon atoms of phosphine and few carbon atoms of thiolates were solved by Shelxt using intrinsic phasing method[5] (for $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$) and SIR-92 using direct method[6] (for $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$). Total structures of all the clusters were refined by full-matrix least-squares method against F^2 by SHELXL-2018/3[7] using Olex2 software.[8] Some high Q peaks appearing inside or near to cluster cores are artifacts derived from Fourier truncation errors. In $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$, one of the counter chloride anions was refined isotropically. Some Q peaks (value around 2-3) around chloride anion were kept unassigned as to give reviewers and as well as readers a view of the situation where chloride ions are disordered over the solvent sphere. Due to that unassigned Q peaks and as well as unassigned Q peak near to the metal, an alert "VERY LARGE Solvent Accessible VOID(S) in Structure" comes in the check cif file. Also, $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$ has few disordered $-C_2H_4Ph$ of thiolate and –Ph of phosphine ligands which were modeled (using PART command) and refined (details of occupancies are given in cif file). Finally, positions and extent of Pd were determined by substitutional disorder refinement (detail results are summarized in the following table S4). In $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$, although it has two SbF_6 anions, however, one SbF_6 was disordered over 4 position and they were refined using SUMP command. At one such position, SbF_6 anion with occupancy (0.2662) could be fully assigned whereas remaining part was of the $[SbF_6]^-$ was partially assigned in additional three positions (Table S5). Over all four positions was refined using SUMP command in Olex2. In both the structure, the hydrogen atoms were placed at calculated positions with the exception of disordered H atoms, and their positions were refined with a riding model. During overall refinement, several restrain and constrain (EXYZ, ISOR, RIGU, SIMU, DFIX, AFIX 66 and EADP) have been used.

Table S4. Atomic Occupancy (Au/Pd) of $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$.

	molecule 1 of the asymmetric unit		molecule 2 of the asymmetric unit	
	Atom position	Occupancy	Atom position	Occupancy
Icosahedron core central	Au47	0.510(6)	Au49	0.494(6)
	Pd47	0.490(6)	Pd49	0.506(6)
	Au48	0.508(6)	Au50	0.511(6)
	Pd48	0.492(6)	Pd48	0.492(6)
Icosahedron shared vertex	Au6	1	Au1	1
Each icosahedron surface metal	Au	1	Au	1
	Pd	0	Pd	0
Metallic occupancy of individual molecule	$Au_{24.01}Pd_{0.99}$			
Molecular formula from crystallography	$[Au_{24.01}Pd_{0.99}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$			

Table S5. Occupancy Detail of Disordered SbF_6 Anion of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Sb2	0.267(3)	F11	0.267(3)	F8	0.267(3)
F7	0.267(3)	F12	0.267(3)	F10	0.267(3)
F9	0.267(3)	Sb3	0.377(4)	Sb4	0.261(4)
Sb5	0.237(9)	F18	0.377(4)	F14	0.377(4)
F17	0.377(4)	F15	0.377(4)	F13	0.377(4)
F104	0.261(4)	F121	0.261(4)	F178	0.261(4)
F290	0.261(4)	F125	0.095(4)		

5.3. Additional Refinement Detail of Each Cluster

5.3.1. $[Au_{24}Pd(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl$

5.3.1.1. Fixed Uiso

At 1.2 times of: All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups

5.3.1.2. Shared sites

{Au47, Pd47}{Au48, Pd48}{Au49, Pd49}{Au50, Pd50}

5.3.1.3. Restrained distances

C419-C385, 1.52 with sigma of 0.02 C419-C417, 1.52 with sigma of 0.02 C471-C477,1.52 with sigma of 0.02 C346-C477, 1.52 with sigma of 0.02 C427-C353, 1.47 with sigma of 0.02 C418 C353,1.55 with sigma of 0.02

5.3.1.4. Restrained planarity

C381, C380, C379, C384, C383, C382 with sigma of 0.1, C367, C366, C368, C369, C370, C371 with sigma of 0.1

5.3.1.5. Uiso/Uaniso restraints and constraints

All non-hydrogen atoms have similar U: within 1.7A with sigma of 0.01 and sigma for terminal atoms of 0.02 Uanis(C397) ≈ Ueq, Uanis(C398) ≈ Ueq, Uanis(C399) ≈ Ueq, Uanis(C400) ≈ Ueq, Uanis(C401) ≈ Ueq, Uanis(C402) ≈ Ueq, Uanis(C367) ≈ Ueq, Uanis(C368) ≈ Ueq, Uanis(C369) ≈ Ueq, Uanis(C370) ≈ Ueq, Uanis(C371) ≈ Ueq, Uanis(C366) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02 Uanis(C417) ≈ Ueq, Uanis(C419) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02 Uanis(C392) ≈ Ueq, Uanis(C393) ≈ Ueq, Uanis(C394) ≈ Ueq, Uanis(C395) ≈ Ueq, Uanis(C396) ≈ Ueq, Uanis(C391) ≈ Ueq, Uanis(C465) ≈ Ueq, Uanis(C466) ≈ Ueq, Uanis(C467) ≈ Ueq, Uanis(C468) ≈ Ueq, Uanis(C469) ≈ Ueq, Uanis(C470) ≈ Ueq: with sigma of 0.005 and sigma for terminal atoms of 0.001 Uanis(C418) ≈ Ueq, Uanis(C353) ≈ Ueq, Uanis(C427) ≈ Ueq, Uanis(C426) ≈ Ueq, Uanis(C431) ≈ Ueq, Uanis(C428) ≈ Ueq, Uanis(C429) ≈ Ueq, Uanis(C430) ≈ Ueq, Uanis(C346) ≈ Ueq, Uanis(C477) ≈ Ueq, Uanis(C471) ≈ Ueq, Uanis(C472) ≈ Ueq, Uanis(C473) ≈ Ueq, Uanis(C474) ≈ Ueq, Uanis(C475) ≈ Ueq, Uanis(C476) ≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02 Uanis(C327) ≈ Ueq, Uanis(C328) ≈ Ueq, Uanis(C461) ≈ Ueq, Uanis(C326) ≈ Ueq, Uanis(C459) ≈ Ueq, Uanis(C460) ≈ Ueq, Uanis(C329) ≈ Ueq, Uanis(C462) ≈ Ueq, Uanis(C330) ≈ Ueq, Uanis(C463) ≈ Ueq, Uanis(C325) ≈ Ueq, Uanis(C464) ≈ Ueq: with sigma of 0.005 and sigma for terminal atoms of 0.001, Uanis(Au49) = Uanis(Pd49), Uanis(Au50) = Uanis(Pd50), Uanis(Au47) = Uanis(Pd47), Uanis(Au48) = Uanis(Pd48)

5.3.1.6. Rigid body (RIGU) restrains

All non-hydrogen atoms with sigma for 1-2 distances of 0.002 and sigma for 1-3 distances of 0.002

5.3.1.7. Others

Sof(Pd47)=1-FVAR(1), Sof(Au47)=FVAR(1), Sof(Pd48)=1-FVAR(2), Sof(Au48)=FVAR(2), Sof(Pd49)=1-FVAR(3), Sof(Au49)=FVAR(3), Sof(Pd50)=1-FVAR(4), Sof(Au50)=FVAR(4), Sof(C433)=Sof(C434)=Sof(H434)=Sof(C435)=Sof(H435)=Sof(C436)=Sof(H436)=Sof(C437)=Sof(H437)=Sof(C438)=Sof(H438)=1-FVAR(5),
Sof(C360)=Sof(H360)=Sof(C361)=Sof(H361)=Sof(C362)=Sof(H362)=Sof(C363)=Sof(H363)=Sof(C364)=Sof(H364)=Sof(C365)=FVAR(5),
Sof(C420)=Sof(C421)=Sof(H421)=Sof(C422)=Sof(H422)=Sof(C423)=Sof(H423)=Sof(C424)=Sof(H424)=Sof(C425)=Sof(H425)=1-FVAR(6),
Sof(C439)=Sof(C440)=Sof(H440)=Sof(C441)=Sof(H441)=Sof(C442)=Sof(H442)=Sof(C443)=Sof(H443)=Sof(C444)=Sof(H444)=FVAR(6),
Sof(H37C)=Sof(H37D)=Sof(C445)=Sof(H445)=Sof(C446)=Sof(H446)=Sof(C447)=Sof(H447)=Sof(C448)=Sof(H448)=Sof(C449)=Sof(H449)=Sof(C450)=Sof(C452)=Sof(H45C)=Sof(H45D)=1-FVAR(7),
Sof(H37A)=Sof(H37B)=Sof(C410)=Sof(C411)=Sof(H411)=Sof(C412)=Sof(H412)=Sof(C413)=Sof(H413)=Sof(C414)=Sof(H414)=Sof(C415)=Sof(H415)=Sof(C451)=Sof(H45A)=Sof(H45B)=FVAR(7),
Sof(C453)=Sof(C454)=Sof(H454)=Sof(C455)=Sof(H455)=Sof(C456)=Sof(H456)=Sof(C457)=Sof(H457)=

Sof(C458)=Sof(H458)=1-FVAR(8),
Sof(C347)=Sof(H347)=Sof(C348)=Sof(H348)=Sof(C349)=Sof(H349)=Sof(C350)=Sof(H350)=Sof(C351)=
Sof(H351)=Sof(C352)=FVAR(8),
Sof(C459)=Sof(H459)=Sof(C460)=Sof(H460)=Sof(C461)=Sof(H461)=Sof(C462)=Sof(H462)=Sof(C463)=
Sof(H463)=Sof(C464)=1-FVAR(9),
Sof(C325)=Sof(C326)=Sof(H326)=Sof(C327)=Sof(H327)=Sof(C328)=Sof(H328)=Sof(C329)=Sof(H329)=
Sof(C330)=Sof(H330)=FVAR(9),
Sof(C465)=Sof(C466)=Sof(H466)=Sof(C467)=Sof(H467)=Sof(C468)=Sof(H468)=Sof(C469)=Sof(H469)=
Sof(C470)=Sof(H470)=1-FVAR(10),
Sof(C391)=Sof(C392)=Sof(H392)=Sof(C393)=Sof(H393)=Sof(C394)=Sof(H394)=Sof(C395)=Sof(H395)=
Sof(C396)=Sof(H396)=FVAR(10)

5.3.1.8.a Secondary CH_2 refined with riding coordinates

C234(H23A,H23B), C235(H23C,H23D), C236(H23E,H23F), C237(H23G,H23H), C239(H23I,H23J), C240(H24A,H24B), C253(H25A,H25B), C260(H26A,H26B), C274(H27A,H27B), C299(H29A,H29B), C338(H33A,H33B), C346(H34A,H34B), C353(H35A,H35B), C378(H37A,H37B), C378(H37C,H37D), C403(H40A,H40B), C417(H41A,H41B), C418(H41E,H41F), C419(H41C,H41D), C451(H45A,H45B), C452(H45C,H45D), C477(H47A,H47B)

5.3.1.8.b Aromatic/amide H refined with riding coordinates

C2(H2), C3(H3), C4(H4), C5(H5), C6(H6), C8(H8), C9(H9), C10(H10), C11(H11), C13(H13), C14(H14), C15(H15), C16(H16), C17(H17), C19(H19), C20(H20), C21(H21), C22(H22), C23(H23), C25(H25), C26(H26), C27(H27), C28(H28), C29(H29), C32(H32), C33(H33), C34(H34), C35(H35), C37(H37), C38(H38), C39(H39), C40(H40), C41(H41), C43(H43), C44(H44), C45(H45), C46(H46), C47(H47), C49(H49), C50(H50), C51(H51), C52(H52), C53(H53), C55(H55), C56(H56), C57(H57), C58(H58), C59(H59), C61(H61), C62(H62), C63(H63), C64(H64), C65(H65), C67(H67), C68(H68), C69(H69), C70(H70), C71(H71), C73(H73), C74(H74), C75(H75), C76(H76), C77(H77), C79(H79), C80(H80), C81(H81), C82(H82), C83(H83), C85(H85), C86(H86), C87(H87), C88(H88), C89(H89), C91(H91), C92(H92), C93(H93), C94(H94), C95(H95), C97(H97), C98(H98), C99(H99), C100(H100), C101(H101), C103(H103), C104(H104), C105(H105), C106(H106), C107(H107), C109(H109), C110(H110), C111(H111), C112(H112), C113(H113), C115(H115), C116(H116), C117(H117), C118(H118), C119(H119), C121(H121), C122(H122), C123(H123), C124(H124), C125(H125), C127(H127), C128(H128), C129(H129), C130(H130), C131(H131), C133(H133), C134(H134), C135(H135), C136(H136), C137(H137), C139(H139), C140(H140), C141(H141), C142(H142), C143(H143), C145(H145), C146(H146), C147(H147), C148(H148), C149(H149), C151(H151), C152(H152), C153(H153), C154(H154), C155(H155), C157(H157), C158(H158), C159(H159), C160(H160), C161(H161), C163(H163), C164(H164), C165(H165), C166(H166), C167(H167), C169(H169), C170(H170), C171(H171), C172(H172), C173(H173), C175(H175), C176(H176), C177(H177), C178(H178), C179(H179), C181(H181), C182(H182), C183(H183), C184(H184), C185(H185), C187(H187), C188(H188), C189(H189), C190(H190), C191(H191), C193(H193), C194(H194), C195(H195), C196(H196), C197(H197), C199(H199), C200(H200), C201(H201), C202(H202), C203(H203), C205(H205), C206(H206), C207(H207), C208(H208), C209(H209), C211(H211), C212(H212), C213(H213), C214(H214), C215(H215), C217(H217), C218(H218), C219(H219), C220(H220), C221(H221), C223(H223), C224(H224), C225(H225), C226(H226), C227(H227), C229(H229), C230(H230), C231(H231), C232(H232), C233(H233), C238(H238), C242(H242), C243(H243), C244(H244), C245(H245), C246(H246), C248(H248), C249(H249), C250(H250), C251(H251), C252(H252), C255(H255), C256(H256), C257(H257), C258(H258), C259(H259), C262(H262), C263(H263), C264(H264), C265(H265), C266(H266), C269(H269), C270(H270), C271(H271), C272(H272), C273(H273), C276(H276), C277(H277), C278(H278), C279(H279), C280(H280), C282(H282), C283(H283), C284(H284), C285(H285), C286(H286), C288(H288), C289(H289), C290(H290), C291(H291), C292(H292), C294(H294), C295(H295), C296(H296), C297(H297), C298(H298), C300(H300), C302(H302), C303(H303), C304(H304), C305(H305), C306(H306), C308(H308), C309(H309), C310(H310), C311(H311), C312(H312), C314(H314), C315(H315), C316(H316), C317(H317), C318(H318), C320(H320), C321(H321), C322(H322), C323(H323), C324(H324), C326(H326), C327(H327), C328(H328), C329(H329), C330(H330), C332(H332), C333(H333), C334(H334), C335(H335), C336(H336), C337(H337), C339(H339), C341(H341), C342(H342), C343(H343), C344(H344), C345(H345), C347(H347), C348(H348), C349(H349), C350(H350), C351(H351), C355(H355), C356(H356), C357(H357), C358(H358), C359(H359), C360(H360), C361(H361), C362(H362), C363(H363), C364(H364), C366(H366), C368(H368), C369(H369), C370(H370), C371(H371), C373(H373), C374(H374), C375(H375), C376(H376), C377(H377), C379(H379), C380(H380), C382(H382), C383(H383), C384(H384), C386(H386), C387(H387), C388(H388), C389(H389), C390(H390), C392(H392), C393(H393), C394(H394), C395(H395), C396(H396), C398(H398), C399(H399), C400(H400), C401(H401), C402(H402), C405(H405), C406(H406), C407(H407), C408(H408), C409(H409), C411(H411), C412(H412), C413(H413), C414(H414), C415(H415), C416(H416), C421(H421), C422(H422), C423(H423), C424(H424), C425(H425), C426(H426),

C428(H428), C429(H429), C430(H430), C431(H431), C432(H432), C434(H434), C435(H435), C436(H436), C437(H437), C438(H438), C440(H440), C441(H441), C442(H442), C443(H443), C444(H444), C445(H445), C446(H446), C447(H447), C448(H448), C449(H449), C454(H454), C455(H455), C456(H456), C457(H457), C458(H458), C459(H459), C460(H460), C461(H461), C462(H462), C463(H463), C466(H466), C467(H467), C468(H468), C469(H469), C470(H470), C472(H472), C473(H473), C474(H474), C475(H475),C476(H476)

5.3.1.8.c Fitted hexagon refined as free rotating group

C1(C2,C3,C4,C5,C6), C12(C13,C14,C15,C16,C17), C18(C19,C20,C21,C22,C23), C24(C25,C26,C27,C28,C29), C30(C31,C32,C33,C34,C35), C36(C37,C38,C39,C40,C41), C42(C43,C44,C45,C46,C47), C48(C49,C50,C51,C52,C53), C54(C55,C56,C57,C58,C59), C60(C61,C62,C63,C64,C65), C66(C67,C68,C69,C70,C71), C72(C73,C74,C75,C76,C77), C78(C79,C80,C81,C82,C83), C84(C85,C86,C87,C88,C89), C90(C91,C92,C93,C94,C95), C96(C97,C98,C99,C100,C101), C102(C103,C104,C105,C106,C107), C108(C109,C110, C111,C112,C113), C114(C115,C116,C117,C118,C119), C120(C121,C122,C123,C124,C125), C126(C127,C128,C129,C130,C131), C132(C133,C134,C135,C136,C137), C138(C139,C140,C141,C142,C143), C144(C145,C146,C147,C148,C149), C150(C151,C152, C153,C154,C155), C156(C157,C158,C159,C160,C161), C162(C163,C164,C165,C166,C167), C168(C169,C170,C171,C172,C173), C174(C175,C176,C177,C178,C179), C180(C181,C182,C183,C184,C185), C186(C187,C188,C189,C190,C191), C192(C193,C194,C195,C196,C197), C198(C199,C200,C201,C202,C203), C204(C205,C206,C207,C208,C209), C210(C211,C212,C213,C214,C215), C216(C217,C218,C219,C220,C221), C222(C223,C224,C225,C226,C227), C228(C229,C230,C231,C232,C233), C241(C242,C243,C244,C245,C246), C247(C248,C249,C250,C251,C252), C254(C255,C256,C257,C258,C259), C261(C262,C263,C264,C265,C266), C268(C269,C270,C271,C272,C273), C275(C276,C277,C278,C279,C280), C281(C282,C283,C284,C285,C286), C287(C288,C289,C290,C291,C292), C293(C294,C295,C296,C297,C298), C301(C302,C303,C304,C305,C306), C307(C308,C309,C310,C311,C312), C313(C314,C315,C316,C317,C318), C319(C320,C321,C322,C323,C324), C325(C326,C327,C328,C329,C330), C331(C332,C333,C334,C335,C336), C340(C341,C342,C343,C344,C345), C347(C348,C349,C350,C351,C352), C354(C355,C356,C357,C358,C359), C360(C361,C362,C363,C364,C365), C366(C367,C368,C369,C370,C371), C372(C373,C374,C375,C376,C377), C379(C380,C381,C382,C383,C384), C385(C386,C387,C388,C389,C390), C391(C392,C393,C394,C395,C396), C397(C398,C399,C400,C401,C402), C404(C405,C406,C407,C408,C409), C410(C411,C412,C413,C414,C415), C420(C421,C422,C423,C424,C425), C426(C427,C428,C429,C430,C431), C433(C434,C435,C436,C437,C438), C439(C440,C441,C442,C443,C444), C445(C446,C447,C448,C449,C450), C453(C454,C455,C456,C457,C458), C465(C466,C467,C468,C469,C470), C471(C472,C473,C474,C475,C476)

5.3.2. $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2][(SbF_6)_2]$

Number of restraints - 2848, number of constraints - unknown.

5.3.2.1. Fixed Uiso

At 1.2 times of: All C(H) groups, All C(H,H) groups

5.3.2.2. Restrained distances

Sb2-F11 ≈ Sb2-F8 ≈ Sb2-F7 ≈ Sb2-F12 ≈ Sb2-F10 ≈ Sb2-F9 with sigma of 0.02, F11-F8 ≈ F11-F7 ≈ F11-F12 ≈ F11-F10 ≈ F8-F7 ≈ F8-F10 ≈ F8-F9 ≈ F7-F12 ≈ F7-F9 ≈ F12-F10 ≈ F12-F9 ≈ F10-F9 with sigma of 0.04

5.3.2.3. Uiso/Uaniso restraints and constraints

C1 ≈ C2 ≈ C3 ≈ C4 ≈ C5 ≈ C6 ≈ C7 ≈ C8 ≈ C9 ≈ C10 ≈ C11 ≈ C12 ≈ C13 ≈ C14 ≈ C15 ≈ C16 ≈ C17 ≈ C18 ≈ C19 ≈ C20 ≈ C21 ≈ C22 ≈ C23 ≈ C24 ≈ C25 ≈ C26 ≈ C27 ≈ C28 ≈ C29 ≈ C30 ≈ C31 ≈ C32 ≈ C33 ≈ C34 ≈ C35 ≈ C36 ≈ C37 ≈ C38 ≈ C39 ≈ C40 ≈ C41 ≈ C42 ≈ C43 ≈ C44 ≈ C45 ≈ C46 ≈ C47 ≈ C48 ≈ C49 ≈ C50 ≈ C51 ≈ C52 ≈ C53 ≈ C54 ≈ C55 ≈ C56 ≈ C57 ≈ C58 ≈ C59 ≈ C60 ≈ C61 ≈ C62 ≈ C63 ≈ C64 ≈ C65 ≈ C66 ≈ C67 ≈ C68 ≈ C69 ≈ C70 ≈ C71 ≈ C72 ≈ C73 ≈ C74 ≈ C75 ≈ C76 ≈ C77 ≈ C78 ≈ C79 ≈ C80 ≈ C81 ≈ C82 ≈ C83 ≈ C84 ≈ C85 ≈ C86 ≈ C87 ≈ C88 ≈ C89 ≈ C90 ≈ C91 ≈ C92 ≈ C93 ≈ C94 ≈ C95 ≈ C96 ≈ C97 ≈ C98 ≈ C99 ≈ C100 ≈ C101 ≈ C102 ≈ C103 ≈ C104 ≈ C105 ≈ C106 ≈ C107 ≈ C108 ≈ C109 ≈ C110 ≈ C111 ≈ C112 ≈ C113 ≈ C114 ≈ C115 ≈ C116 ≈ C117 ≈ C118 ≈ C119 ≈ C120 ≈ C121 ≈ C122 ≈ C123 ≈ C124 ≈ C125 ≈ C126 ≈ C127 ≈ C128 ≈ C129 ≈ C130 ≈ C131 ≈ C132 ≈ C133 ≈ C134 ≈ C135 ≈ C136 ≈ C137 ≈ C138 ≈ C139 ≈

C140 ≈ C141 ≈ C142 ≈ C143 ≈ C144 ≈ C145 ≈ C146 ≈ C147 ≈ C148 ≈ C149 ≈ C150 ≈ C151 ≈ C152 ≈ C153 ≈ C154 ≈ C155 ≈ C156 ≈ C157 ≈ C158 ≈ C159 ≈ C160 ≈ C161 ≈ C162 ≈ C163 ≈ C164 ≈ C165 ≈ C166 ≈ C167 ≈ C168 ≈ C169 ≈ C170 ≈ C171 ≈ C172 ≈ C173 ≈ C174 ≈ C175 ≈ C176 ≈ C177 ≈ C178 ≈ C179 ≈ C180 ≈ C181 ≈ C182 ≈ C183 ≈ C184 ≈ C185 ≈ C186 ≈ C187 ≈ C188 ≈ C189 ≈ C190 ≈ C191 ≈ C192 ≈ C193 ≈ C194 ≈ C195 ≈ C196 ≈ C197 ≈ C198 ≈ C199 ≈ C200 ≈ C201 ≈ C202 ≈ C203 ≈ C204 ≈ C205 ≈ C206 ≈ C207 ≈ C208 ≈ C209 ≈ C210 ≈ C211 ≈ C212 ≈ C213 ≈ C214 ≈ C215 ≈ C216 ≈ C217 ≈ C218 ≈ C219 ≈ C220: within 1.7A with sigma of 0.02 and sigma for terminal atoms of 0.04, Sb2 ≈ F11 ≈ F8 ≈ F7 ≈ F12 ≈ F10 ≈ F9: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08, Uanis(Sb5) ≈ Ueq: with sigma of 0.005 and sigma for terminal atoms of 0.002, Uanis(Sb4) ≈ Ueq: with sigma of 0.005 and sigma for terminal atoms of 0.002, Uanis(F125) ≈ Ueq: with sigma of 0.005 and sigma for terminal atoms of 0.002, Uanis(C113) = Uanis(C116)

5.3.2.4 Rigid body (RIGU) restrains

C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, C11, C12, C13, C14, C15, C16, C17,C18, C19, C20, C21, C22, C23, C24, C25, C26, C27, C28, C29, C30, C31, C32, C33,C34, C35, C36, C37, C38, C39, C40, C41, C42, C43, C44, C45, C46, C47, C48,C49, C50, C51, C52, C53, C54, C55, C56, C57, C58, C59, C60, C61, C62, C63, C64,C65, C66, C67, C68, C69, C70, C71, C72, C73, C74, C75, C76, C77, C78, C79,C80, C81, C82, C83, C84, C85, C86, C87, C88, C89, C90, C91, C92, C93, C94, C95,C96, C97, C98, C99, C100, C101, C102, C103, C104, C105, C106, C107, C108,C109, C110, C111, C112, C113, C114, C115, C116, C117, C118, C119, C120, C121,C122, C123, C124, C125, C126, C127, C128, C129, C130, C131, C132, C133, C134,C135, C136, C137, C138, C139, C140, C141, C142, C143, C144, C145, C146, C147,C148, C149, C150, C151, C152, C153, C154, C155, C156, C157, C158, C159, C160,C161, C162, C163, C164, C165, C166, C167, C168, C169, C170, C171, C172, C173,C174, C175, C176, C177, C178, C179, C180, C181, C182, C183, C184, C185, C186,C187, C188, C189, C190, C191, C192, C193, C194, C195, C196, C197, C198, C199,C200, C201, C202, C203, C204, C205, C206, C207, C208, C209, C210, C211, C212,C213, C214, C215, C216, C217, C218, C219, C220 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004, Sb2, F11, F8, F7, F12, F10, F9 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

5.3.2.5. Others

1*[Sof(Sb2)+Sof(F11)+Sof(F8)+Sof(F7)+Sof(F12)+Sof(F10)+Sof(F9)]+1*[Sof(Sb3)+Sof(F18)+Sof(F14)+Sof(F17)+Sof(F15)+Sof(F13)]+1*[Sof(Sb4)+Sof(F104)+Sof(F121)+Sof(F178)+Sof(F290)]+1*[Sof(Sb5)+Sof(F125)]=1 with esd of 0.001, Sof(Sb2)=Sof(F11)=Sof(F8)=Sof(F7)=Sof(F12)=Sof(F10)=Sof(F9)=FVAR(1), Sof(Sb3)=Sof(F18)=Sof(F14)=Sof(F17)=Sof(F15)=Sof(F13)=FVAR(2), Sof(Sb4)=Sof(F104)=Sof(F121)=Sof(F178)=Sof(F290)=FVAR(3), Sof(F125)=FVAR(4), Sof(Sb5)=1.25*FVAR(5)

5.3.2.6.a Secondary CH2 refined with riding coordinates

C3(H3A,H3B), C9(H9A,H9B), C28(H28A,H28B), C78(H78A,H78B), C80(H80A,H80B), C81(H81A,H81B), C117(H11A,H11B), C143(H14A,H14B), C153(H15A,H15B), C154(H15C,H15D)

5.3.2.6.b Aromatic/amide H refined with riding coordinates

C5(H5), C10(H10), C15(H15), C17(H17), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26), C27(H27), C30(H30), C31(H31), C32(H32), C33(H33), C36(H36), C37(H37), C38(H38), C39(H39), C97(H97), C187(H187), C209(H209), C136(H136), C34(H34), C42(H42), C43(H43), C44(H44), C45(H45), C46(H46), C48(H48), C49(H49), C51(H51), C52(H52), C55(H55), C56(H56), C57(H57), C58(H58), C60(H60), C61(H61), C62(H62), C63(H63), C64(H64), C65(H65), C66(H66), C67(H67), C68(H68), C69(H69), C70(H70), C71(H71), C72(H72), C73(H73), C76(H76), C77(H77), C79(H79), C82(H82), C83(H83), C84(H84), C86(H86), C87(H87), C88(H88), C89(H89), C90(H90), C91(H91), C92(H92), C93(H93), C94(H94), C95(H95), C96(H96), C98(H98), C99(H99), C100(H100), C101(H101), C102(H102), C104(H104), C105(H105), C106(H106), C107(H107), C110(H110), C112(H112), C113(H113), C114(H114), C115(H115), C116(H116), C118(H118), C119(H119), C120(H120), C121(H121), C122(H122), C123(H123), C124(H124), C126(H126), C127(H127), C128(H128), C129(H129), C130(H130), C131(H131), C132(H132), C133(H133), C135(H135), C137(H137), C138(H138), C139(H139), C140(H140), C141(H141), C142(H142), C144(H144), C145(H145), C148(H148), C149(H149), C150(H150), C151(H151), C152(H152), C155(H155), C156(H156), C157(H157), C158(H158), C160(H160), C161(H161), C162(H162), C163(H163), C164(H164), C165(H165), C166(H166), C167(H167), C168(H168), C169(H169), C170(H170), C171(H171), C173(H173), C174(H174), C175(H175), C176(H176), C177(H177), C178(H178), C179(H179), C180(H180), C181(H181), C182(H182), C183(H183), C184(H184), C185(H185), C186(H186), C188(H188), C189(H189), C190(H190), C191(H191), C192(H192), C193(H193), C194(H194), C195(H195), C196(H196), C197(H197), C198(H198), C199(H199), C200(H200), C201(H201), C202(H202), C203(H203), C204(H204), C205(H205), C206(H206), C207(H207), C208(H208), C210(H210), C211(H211), C212(H212), C213(H213), C214(H214), C215(H215), C216(H216), C217(H217), C218(H218), C219(H219), C220(H220)

5.3.2.6.c Fitted hexagon refined as free rotating group

C41(C97,C187,C209,C136,C34), C111(C112,C113,C114,C115,C116), C125(C126,C127,C128,C129,C130),

C159(C160,C161,C162,C163,C164)

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