SUPPORTING INFORMATION

Palladium doping of magic gold cluster $Au_{38}(SC_2H_4Ph)_{24}$: formation of $Pd_2Au_{36}(SC_2H_4Ph)_{24}$ with higher stability than $Au_{38}(SC_2H_4Ph)_{24}$

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I. Experiments

A. Chemicals

All chemicals were commercially obtained and used without further purification. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4{\cdot}4H_2O$) was obtained from Tanaka Kikinzoku. Palladium sodium chloride trihydride ($Na_2PdCl_4{\cdot}3H_2O$), tetraoctylammonium bromide ($(C_8H_{17})_4NBr$), sodium tetrahydroborate ($NaBH_4$), methanol, acetonitrile, toluene, and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries. Phenylethanthiol (PhC_2H_4SH) was purchased from Tokyo Kasei. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was purchased from Santa Cruz Biotechnology. Deionized water with a resistivity of > 18.2 MΩ cm was used.

B. Isolation of $Pd_2Au_{36}(SC_2H_4Ph)_{24}$

A mixture of Pd-Au:SC_2H_4Ph clusters was prepared by a method similar to that for the preparation of Au:SC_2H_4Ph clusters[1], except that a mixture of Pd and Au salts was used as the starting material. 3.9 mmol of PhC_2H_4SH was added to 50 mL of a THF solution containing 0.364 mmol of Na_2PdCl_4 and 0.936 mmol of $HAuCl_4$, and the mixture was stirred for 30 min at room temperature. An aqueous solution of $NaBH_4$ (15 mmol, 10 mL) cooled to 0 °C was then quickly added to the mixture. The orange suspension soon became a black-brown solution, which was stirred for 4 h. The reaction mixture was then filtered to remove the black residue, which was insoluble in solvents such as toluene, THF, acetone, acetonitrile, and water. The filtered solution was concentrated in a rotary evaporator until only a mixture of black-brown solid and colorless liquid solution (residual H_2O from aq. $NaBH_4$) remained.[1] This mixture was washed with methanol (4-10 times) to remove PhC_2H_4SH and other byproducts. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry confirmed that the product contained Pd-Au:SC_2H_4Ph clusters with various chemical compositions (Fig. 1(a)).

The following two steps were used to isolate $Pd_2Au_{36}(SC_2H_4Ph)_{24}$ from the product. In the first step, $Pd_nAu_{38-n}(SC_2H_4Ph)_{24}$ (n = 1, 2) were separated from the mixture. After drying the product, acetonitrile was added and most $Pd_nAu_{25-n}(SC_2H_4Ph)_{18}$ (n = 0, 1) were dissolved and removed. The mixture was then separated into three fractions (**1**-**3**) (Fig. S1) using recycling size exclusion chromatography (SEC). The MALDI mass spectra of fractions **1**-**3** (Fig. S2) shows that **1**-**3** contain $Pd_nAu_{25-n}(SC_2H_4Ph)_{18}$ (n = 0, 1) clusters, which were not removed by washing, $Pd_nAu_{38-n}(SC_2H_4Ph)_{24}$ (n = 1, 2), and the large clusters [(Pd-Au)$_n$:SC_2H_4Ph cluster; n = 44, 68, 102], respectively, which confirms that $Pd_nAu_{38-n}(SC_2H_4Ph)_{24}$ (n = 1, 2) clusters were separated using this process. In the next step, $PdAu_{37}(SC_2H_4Ph)_{24}$ was preferentially decomposed in solution. 3.4 mg of $Pd_nAu_{38-n}(SC_2H_4Ph)_{24}$ (n = 1, 2) was dissolved in 40 mL of THF and the solution was stirred for eight days at 60 °C. According to the MALDI mass spectrum of the

solution after eight days, $PdAu_{37}(SC_2H_4Ph)_{24}$ was decomposed in the THF solution, and $Pd_2Au_{36}(SC_2H_4Ph)_{24}$ was isolated in high purity by this method (Fig. 1(c)).

C. Size exclusion chromatography (SEC)

A recycling high performance liquid chromatography (HPLC) system (Japan Analytical Industry Co., Ltd, LC-9201) equipped with a stainless steel column (Waters Co., Ultrastyragel^{TM}) was used. The upper limit of size fraction, *total exclusion limit*, for the Ultrastyragel^{TM} column was 3×10^4. Toluene was used as the eluent with a flow rate set to 2.4 mL/min. The UV-Vis absorbance detector was operated at 290 nm.

D. Characterization

MALDI mass spectra were collected on a linear-mode time-of-flight (TOF) mass spectrometer (Applied Biosystem, Voyager Linear RD VDA 500) using a nitrogen laser (337 nm). DCTB was used as the MALDI matrix. To minimize dissociation of the clusters caused by laser irradiation, a cluster-to-matrix ratio of 1:1000 was used. The laser fluence was decreased to the lowest value that enabled detection of the ions. Electrospray ionization (ESI) mass spectrometry was performed using a Fourier transform (FT)-mass spectrometer (Bruker, Solarix). A 1:1 (v/v) toluene/acetonitrile solution of $Pd_2Au_{38}(SC_2H_4Ph)_{24}$ with a concentration of 1 mg/mL was electrosprayed at a flow rate of 800 μL/hour. Thermogravimetric analysis (TGA; Bruker, TGA2000SA) was performed using 3.4 mg of $Pd_2Au_{38}(SC_2H_4Ph)_{24}$ at a heating rate of 5 °C/min in the temperature range of 25–500 °C. X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010MC) was conducted using a chamber at a base pressure of *ca*. 2×10^{-8} Torr and X-rays from the Mg-Kα line at 1253.6 eV were used for the excitation. Transmission electron microscopy (TEM; Hitachi, H-7650) images were recorded using an electron microscope operated at 100 kV; typical magnification of the images was 100,000×. UV-Vis/near-IR absorption spectrum of $Pd_2Au_{36}(SC_2H_4Ph)_{24}$ was recorded at ambient temperature using a spectrometer (Jasco, V-670). The raw spectral data, $I(w)$, which are functions of wavelength, were converted to energy-dependent data, $I(E)$, according to the following relation, such that the integrated spectral areas were conserved:

$$I(E) = I(w)/(\partial E/\partial w) \propto I(w) \times w^2$$

E. Stability against decomposition in THF solution

To investigate the stability of the clusters against decomposition, an organic synthesizer (Eyela, PPS-2510) was employed to precisely and reproducibly control the reaction temperature. THF solution (40 mL) containing 2.0 mg (totally *ca*. 0.2 μmol) of a mixture of $Pd_2Au_{36}(SC_2H_4Ph)_{24}$ and $PdAu_{37}(SC_2H_4Ph)_{24}$, and 1.0 mg (*ca*. 0.1 μmol) of $Au_{38}(SC_2H_4Ph)_{24}$ was placed in the organic synthesizer and heated to 60 °C while stirring at 1000 rpm. The resulting solution was washed with methanol to remove byproducts prior to characterization.

F. Stability against thiol etching

To investigate the stability of the clusters against thiol etching, an organic synthesizer was also employed. In this experiment, 1.0 mg (totally *ca*. 0.1 μmol) of a mixture of $Pd_2Au_{36}(SC_2H_4Ph)_{24}$ and $PdAu_{37}(SC_2H_4Ph)_{24}$, and 0.5 mg (0.05 μmol) of $Au_{38}(SC_2H_4Ph)_{24}$ were incubated in pure PhC_2H_4SH (2.0 mL) at 80 °C under vigorous stirring in air. The resulting solution was washed with methanol to remove PhC_2H_4SH and byproducts prior to characterization.

II. Calculation

We have carried out DFT calculations of geometry optimization for $[Pd_2Au_{36}(SC_2H_4Ph)_{24}]^{2-}$ without assuming any

molecular symmetry. In the calculations we adopted a model cluster system in which PhC_2H_4S was replaced with CH_3S. Such a simplification of the ligand has frequently been used in previous calculations and appears to be reasonable.[2,3] The calculations were performed starting from the initial guess structure constructed on the analogy of the structure of $Au_{38}(SC_2H_4Ph)_{24}$ determined by XRD experiment[4]. All the calculations were carried out using the TURBOMOLE package of *ab initio* quantum chemistry programs.[5] Geometry optimizations were performed at the level of Kohn-Sham density functional theory (KS-DFT), employing the Becke three-parameter hybrid exchange functional with the Lee-Yang-Parr correlation functional (B3LYP).[6,7] The double-ζ valence-quality plus polarization basis from the TURBOMOLE basis set library was used in all calculations, along with 60-electron and 28-electron relativistic effective core potentials[8] for the gold and palladium atoms, respectively.

III. Results

A. Characterization

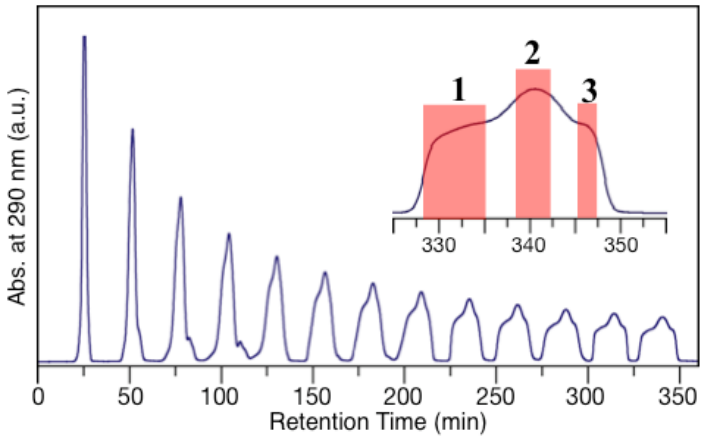

Fig. S1 Chromatogram of recycling SEC for the Pd-Au:SC_2H_4Ph clusters.

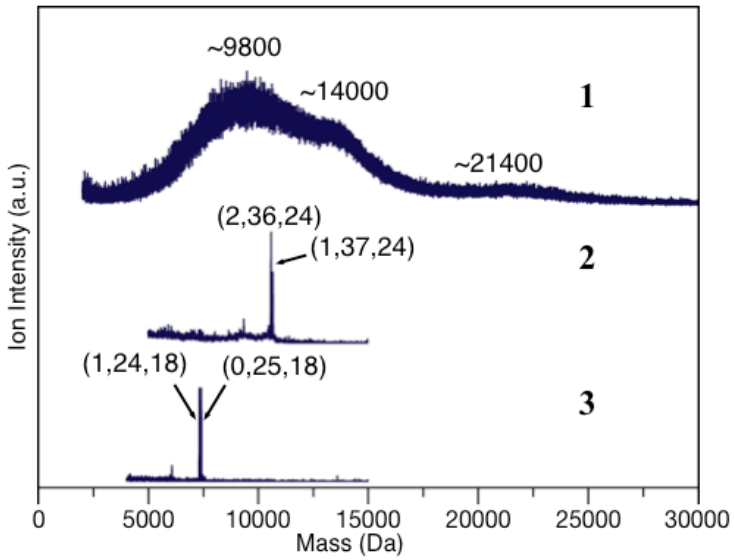

Fig. S2 MALDI mass spectra of fractions **1**-**3**. The notation (*N*, *M*, *L*) represents $[Pd_NAu_M(SC_2H_4Ph)_L]^-$. In the mass spectrum of fraction **1**, only fragment ions of $(Pd\text{-}Au)_n$:SC_2H_4Ph clusters (n = 44, 68, 102) were observed (*ca*. 9800 Da, *ca*. 14,000 Da, *ca*. 21,400 Da, respectively).

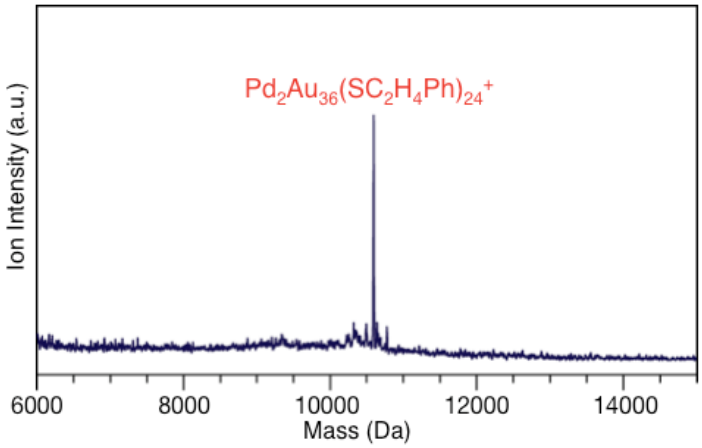

Fig. S3 Positive-ion MALDI mass spectrum of the product.

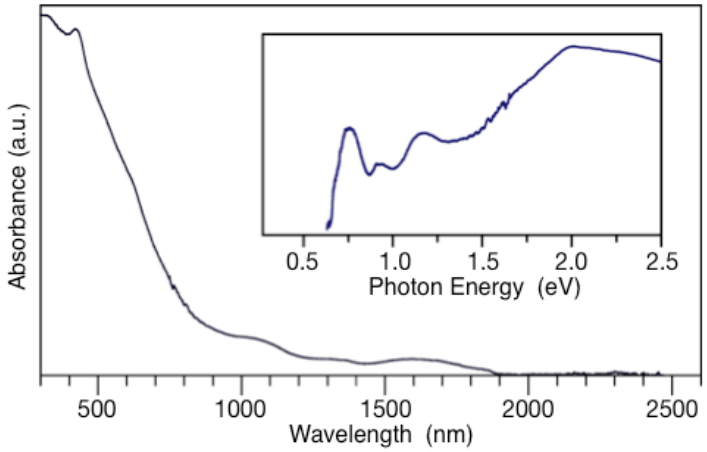

Fig. S4 Absorption spectrum of the product. Inset: optical absorbance vs. photon energy.

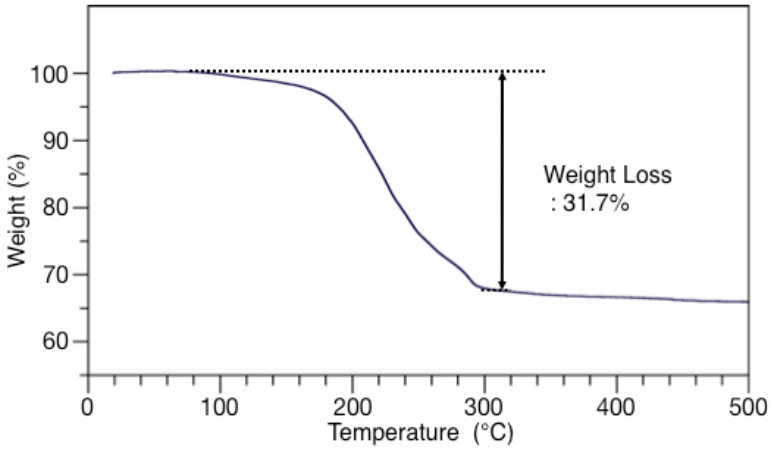

Fig. S5 TGA pattern of the product. The weight ratio of metal to ligand (68.3%, 31.7%) was consistent with that for $[Pd_2Au_{36}(SC_2H_4Ph)_{24}]Na_2$ (69.1%, 30.9%) within the experimental error.

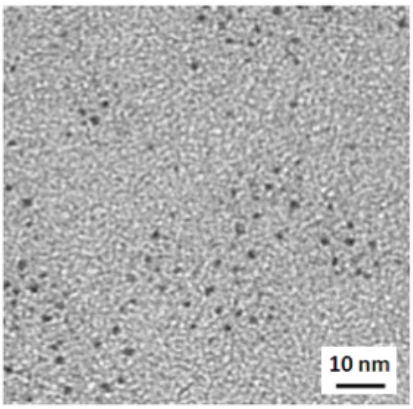

Fig. S6 TEM image of the product.

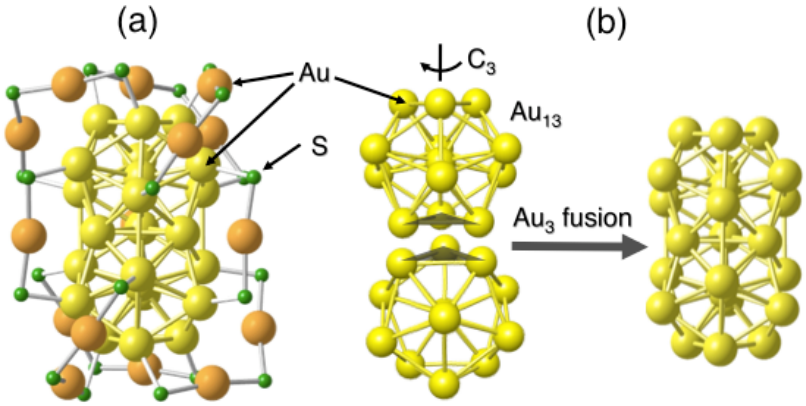

Fig. S7 (a) Structural representation and (b) anatomy of the Au_{23} core structure of $Au_{38}(SC_2H_4Ph)_{24}$ [4]. In (a), the PhC_2H_4 moieties is omitted for clarity.

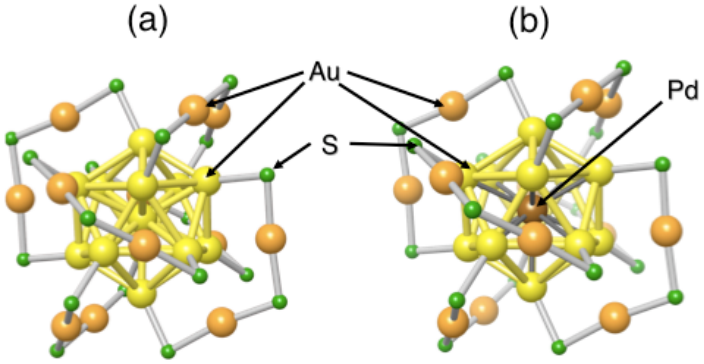

Fig. S8 Structural representation of (a) $Au_{25}(SR)_{18}$ [9,10] and (b) $PdAu_{24}(SR)_{18}$ [11]. (The R moieties are omitted for clarity in both figures.)

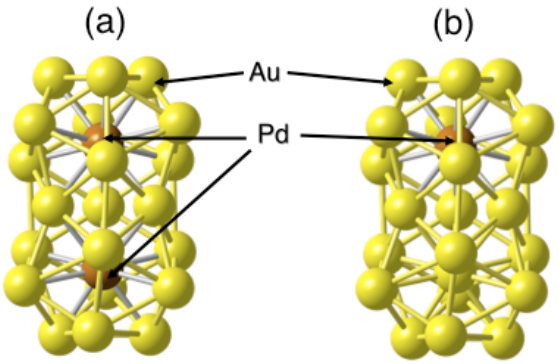

Fig. S9 (a) Pd_2Au_{21} core structure of the optimized structure for $Pd_2Au_{36}(SCH_3)_{24}$ (Fig. 2(d)). (b) Proposed metal core structure for $PdAu_{37}(SC_2H_4Ph)_{24}$.

B. Optimized Coordination for $[Pd_2Au_{36}(SCH_3)_{24}]^{2-}$

S	4.7697006	-2.2784622	1.7647436
S	-1.2625297	-2.6380664	6.4664077
Au	4.0285806	-3.1149948	3.8796882
S	3.2570269	-4.1388431	5.9172942
Au	1.0008456	-3.3427255	6.1294873
S	-4.4274668	-3.1526119	2.2166291
S	-1.5396083	2.3925229	6.4164465
Au	-4.8049972	-1.8929050	4.2062144
S	-5.2907409	-0.5734263	6.1550740
Au	-3.3906245	0.9022152	6.1984382
S	-0.5235959	5.2035609	1.7176773
S	3.0917276	0.3572449	6.1662307
Au	0.4869355	5.0823779	3.8682273
S	1.4946956	4.8774579	6.0412942
Au	2.3669553	2.6334793	5.9864603
S	4.6781511	-1.7875252	-2.7867546
S	0.0149660	2.8117927	-6.6247795
Au	4.5889414	-0.2487462	-4.6114710
S	4.5285403	1.1898869	-6.5440313
Au	2.2719423	2.0141352	-6.5139614
S	-3.9773314	-3.9452776	-2.0286789
S	1.5658200	-2.0375699	-6.8400926
Au	-2.9378338	-4.5677631	-4.0873584
S	-1.9170016	-5.2576392	-6.1526673
Au	-0.1387686	-3.6592209	-6.4011288
S	-2.0274152	4.8438597	-1.8814893
S	-3.3590754	-1.0589300	-6.4383960
Au	-3.1449652	4.2540639	-3.9067973
S	-4.4621015	3.5646722	-5.7981582
Au	-3.8617361	1.2459622	-6.0448141
S	-4.8034400	2.2557078	2.3453194
S	-5.3941447	1.4339823	-2.3335337
Au	-5.0956064	1.7536407	0.0214768
S	0.8522205	-5.3205261	2.2607865
S	0.8472408	-5.3399423	-2.5278628
Au	0.8342035	-5.2701710	-0.1333090
S	4.3404894	2.7708399	2.0447197
S	3.7648094	3.3053157	-2.6781240
Au	4.0103175	3.0355943	-0.3117308
C	-3.6717082	4.3364751	-7.2727705
H	-4.2405217	4.0265506	-8.1653545
H	-2.6229583	4.0202801	-7.3825772
H	-3.7269572	5.4328038	-7.1667597
C	-0.8235997	6.1696266	-2.2906918
H	-1.3693502	7.0903329	-2.5583552
H	-0.1610156	5.8798283	-3.1202449
H	-0.2241863	6.3489794	-1.3822377
C	-2.3204516	-0.9884494	-7.9581072
H	-2.9640071	-0.7272491	-8.8149374
H	-1.8812910	-1.9882201	-8.1118189
H	-1.5115085	-0.2491043	-7.8610951
C	0.1558108	4.5642834	-6.0774634
H	0.6234908	5.1590731	-6.8803554
H	0.7517332	4.6453481	-5.1565432
H	-0.8612801	4.9404156	-5.8752280
C	5.5534263	2.6376688	-6.0475612
H	5.4624427	3.4095751	-6.8298924
H	6.6028020	2.3050267	-5.9804821
H	5.2280619	3.0403097	-5.0752313

C	2.6332454	-5.3997043	-2.9726005
H	3.0672174	-6.3419449	-2.5987722
H	3.1852640	-4.5426925	-2.5572357
H	2.7037509	-5.3749271	-4.0731505
C	-2.2449856	-4.1345541	6.0337083
H	-2.1197345	-4.8915256	6.8263172
H	-3.3049490	-3.8380187	5.9617437
H	-1.9304653	-4.5502375	5.0658591
C	-0.6422498	1.6410047	7.8399631
H	-1.2413738	1.7919552	8.7535356
H	-0.4663593	0.5660214	7.6841061
H	0.3263304	2.1581712	7.9412666
C	-4.9778116	-1.6707088	7.6015071
H	-5.1647166	-1.0867580	8.5180733
H	-5.6815659	-2.5183203	7.5559353
H	-3.9407351	-2.0398772	7.6086937
C	-6.2815274	1.5218898	3.1576879
H	-6.3708593	0.4454866	2.9451995
H	-7.1831501	2.0478179	2.8009032
H	-6.1793080	1.6646468	4.2460532
C	-6.2626098	-0.1811963	-2.5071966
H	-5.7249839	-0.9909685	-1.9908810
H	-6.3158213	-0.4132343	-3.5838599
H	-7.2833893	-0.0879405	-2.1005095
C	4.8241087	0.4218651	5.5519370
H	5.4566648	0.9063209	6.3152234
H	5.1655534	-0.6143178	5.3887763
H	4.8901269	0.9807278	4.6060124
C	2.9353932	6.0205783	6.0766066
H	3.4854694	5.8587746	7.0185943
H	3.6101881	5.8608990	5.2231193
H	2.5503761	7.0536118	6.0500671
C	2.9714200	4.9593363	-2.8238144
H	2.0395391	5.0074809	-2.2407825
H	2.7452568	5.1337817	-3.8891831
H	3.6711010	5.7345073	-2.4691320
C	-1.0465304	-6.8139078	-5.6855017
H	-0.4249437	-7.1323631	-6.5389662
H	-1.8096797	-7.5830055	-5.4798569
H	-0.4183427	-6.6661664	-4.7928513
C	5.9535885	-1.1067739	-1.6521799
H	5.9687077	-1.7585176	-0.7634995
H	5.7135544	-0.0760077	-1.3481981
H	6.9369579	-1.1307058	-2.1512848
C	6.0146458	-0.9844439	2.1689303
H	6.8819806	-1.4539473	2.6628780
H	6.3387684	-0.5250779	1.2212485
H	5.5944152	-0.1998511	2.8127425
C	4.3714027	4.4916819	2.6919083
H	5.2163725	5.0402637	2.2426230
H	4.5127702	4.4274408	3.7834969
H	3.4271557	5.0179043	2.4825236
C	-3.4041161	-5.2530119	-0.8633311
H	-3.7546755	-4.9818739	0.1463245
H	-2.3054668	-5.3299966	-0.8547405
H	-3.8449554	-6.2182844	-1.1629318
C	3.1343603	-2.9890039	-6.6933304
H	3.1964580	-3.5239726	-5.7340179
H	3.9707901	-2.2737340	-6.7563896
H	3.1941795	-3.7071975	-7.5284588
C	-2.2692577	5.7153187	2.0059289
H	-2.2880558	6.7494694	2.3886066

H	-2.7748249	5.6681104	1.0271475
H	-2.7787534	5.0421857	2.7113842
C	-0.7506693	-6.1140429	2.6989044
H	-1.6080688	-5.5205014	2.3446373
H	-0.7921687	-6.1968784	3.7978368
H	-0.7900850	-7.1241647	2.2587529
C	4.1438788	-3.2533763	7.2674596
H	3.7976067	-3.6634393	8.2308032
H	5.2244969	-3.4427170	7.1553408
H	3.9440569	-2.1708321	7.2364383
C	-5.7010757	-2.4903829	1.0605203
H	-5.6168548	-1.3965287	0.9595796
H	-5.5348660	-2.9555434	0.0748238
H	-6.7026243	-2.7594342	1.4350319
Au	-1.7821160	-1.2694010	-4.5035081
Au	-0.6740839	1.6190873	-4.5251381
Au	1.2442636	-0.8219075	-4.6560039
Au	1.8630130	1.6435679	-2.9576928
Pd	-0.2946660	-0.1443448	-2.3646115
Au	1.1961600	1.0116724	-0.2075479
Au	-1.8831491	0.4587050	-0.0574086
Au	-0.5754419	2.6676281	1.5375980
Au	-0.3591492	1.6681552	4.3126902
Pd	-0.0871224	-0.0961249	2.1014085
Au	1.7393841	-0.6068773	4.2283548
Au	-1.3063159	-1.2469246	4.3663863
Au	-2.7484058	0.8471586	2.7097220
Au	-0.7735755	2.6342375	-1.7754915
Au	-2.9796219	0.8262156	-2.7238877
Au	-2.4065722	-1.9776785	-1.6904251
Au	0.1394914	-1.9050619	-0.1286612
Au	-2.2695026	-1.9101418	1.6689847
Au	2.3809418	-1.1210116	-1.9349649
Au	0.1432082	-2.9414995	-2.8779232
Au	0.5082223	-2.8472263	2.6175521
Au	2.5600849	-1.0598846	1.4021804
Au	2.0663517	1.7604950	2.4845138

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