Electronic Supplementary Material (ESI) for Chemical Science

Supporting information

A 58-electron superatom-complex model for the magic phosphine-protected gold clusters (Schmid-gold, Nanogold®) of 1.4-nm dimension

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Definition of the stabilization energy

The form of the stabilization energy used in this work can be rationalized as follows. We aim at an energetic comparison of the relative energies of different cluster sizes and compositions. We consider two species A (here gold) and L (here a ligand) which can occur in various clusters A_XL_Y. The formation energy of these compositions shall be compared to the energy of a reference reservoir of A and L. The reservoir shall be large enough to build a large number of the clusters. If we have N times A and M times L in our reservoir, particle conservation gives

$$K* A_XL_Y + (N-K*X) *A + (M-K*Y) *L = N*A + M*L \quad (1)$$

where we have built K clusters of composition A_XL_Y out of the reservoir. In the following, we assume that we completely consume all A in the reservoir to build the clusters while there is an excess of L. Then the number of clusters that can be build is given by

$$K = N / X \quad (2)$$

and depends on the cluster composition and the size of the reservoir for A. To arrive at the stabilization energy, we need to compare the energy of the clusters $E_{cluster}$ to the energy of the reservoir $E_{reservoir}=N*E_A+M*E_L$, where E_A and E_L are the energies of A and L in the reservoir per particle. The energy difference for the formation of K clusters out of the reservoir is

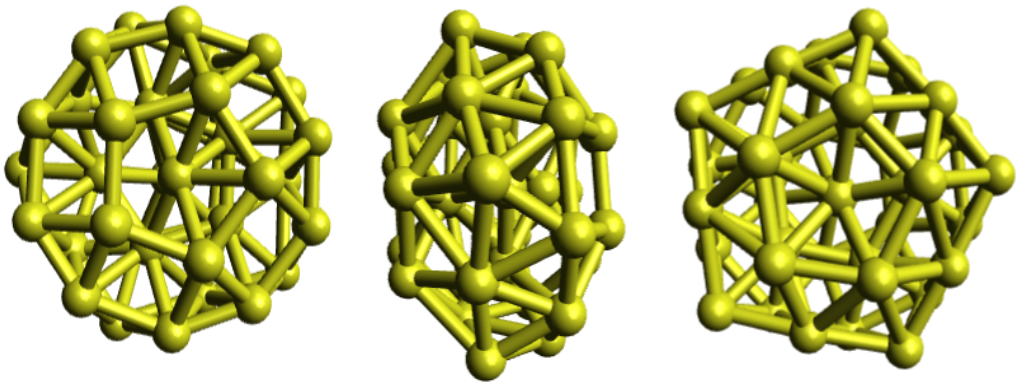
$$E_{diff} = K*E_{cluster} - K*X*E_A - K*Y*E_L = K* (E_{cluster} - X*E_A - Y*E_L) \quad (3)$$

and depends on the size of A's reservoir N. The number of L in the reservoir does not appear here anymore as the relevant quantity defining the reservoirs' size is the number of cluster K that can be build from it. In order to define energies that are comparable for different cluster sizes, we divide the energy difference through A's reservoir size and arrive at

$$E_{stab} = E_{diff}/N = (E_{cluster} - X*E_A - Y*E_L) / X \quad (4)$$

which is essentially the expression used in eq. (1) of the main text (we have used a single ligand type here). It represents the energy gained ($E_{stab}>0$) or needed ($E_{stab}<0$) to build clusters out of the reservoir per component A.

The Au_{37} gold core of structure 2



The Au_{37} gold core in the energetically best structure **2**. Compare for the presentation of the Ni_{39} III.W&D2 structure in reference 1.

Critical comparison with experiment

Here a more detailed critical comparison to the experiment than in the main text is given.

The development by Weare et al.[2] of a convenient and versatile synthesis employing quaternary ammonium-bromide agent has stimulated much new work. They reported an average composition of 100:21 (*Au:P*) for a sample incorporating also clusters larger than 1.4-*nm*. An improved characterization by Sharma et al.[3] of a similarly prepared sample gave a composition of 100:24:12 (*Au:P:total halide*), which is quite close to the 69:20:12, considering again the presence of a minor fraction of larger (therefore Au-rich) clusters. These authors also discovered a facile exchange reaction with solution-phase 'monomers' — $Au(PPh_3)Cl$ — and interpreted the exchange dynamics (observed by NMR spectroscopy) in terms of an invariant gold "core surrounded by Au complexes containing both PPh_3 and Cl^- ligands", such labile complexes dissociating exclusively as intact monomers (t*o repeat*: both the known $[Au_{39}(PR_3)_{14}Cl_6]^{(-)}$ and the newly proposed Au_{69} structures contain such adatom complexes and removing of a complete $Au(PR_3)Cl$ unit does not change the delocalized electron count). Finally, Schaaff[4] described the electrospray ionization (ESI) of size-purified sample of Nanoprobes' product Nanogold® yielded very highly (+)-charged gas-phase clusters, whose subsequent electron-transfer reactions with perfluoro anions yields mainly the (+1, +2, +3)-charged clusters in the mass spectrum. The well defined intensity onsets at a mass of 14,7 kDa suggests a minimal fragmentation-resistant compound $[Au_{57}(PPh_3)_8]^{(-1)}(H+)_{2\text{-}4}$, as the end-product of the reaction:

$$[Au_{69}(PPh_3)_{20}Cl_{12}]^{-1} = 12\ Au(PPh_3)Cl + [Au_{57}(PPh_3)_8]^{-1}$$ *i.e. the loss of up to 12 "monomers"*

[Note that $(57 \times 197) + (8 \times 433) = 14{,}693$]

where the 197 Da and 433 Da are the masses of a gold atom and a PPh_3 unit, respectively. An earlier MALDI-MS investigation[5] of the Nanoprobes' Greengold product attributed the mass peak at 21,7-*kDa* to a single globular 75-atom cluster, which is inconsistent both with its elution order (smaller than Nanogold) and the expected brown color implied by Fig. 3 in the main text, which is a well known characteristic of the Schmid / Nanogold clusters[6]. It should more likely be attributed to a linked dimer of the smaller Au_{39} cluster (cf. ref. 6 of the main text). The reported[15] mass-difference (22,0 kDa – 14,8

kDa = 7,2 kDa) separating the 'intact' (MALDI) from the 'minimal' (LDI-fragmented) cluster-ions corresponds approximately to 11 $Au(PPh_3)Cl$ units (0,66 kDa each), whereas two unlinked $[Au_{39}(PR_3)_{14}Cl_6]^{(-)}$ clusters contain 12 Cl.

References

1 E. K. Parks, K. P. Kerns, and S. J. Riley , *J. Chem. Phys.*, 1998, **109**, 10207 -10216

2 W. W. Weare, S. M. Reed, M. G. Warner, and J. E. Hutchison , *J. Am. Chem. Soc.*, 2000, **122**, 12890-12891

3 R. Sharma, G. P. Holland, V. C. Solomon, H. Zimmermann, S. Schiffenhaus, S. A. Amin, D. A. Buttry and J. L. Yarger, *J. Phys. Chem. C*, 2009, **113**, 16387–16393

4 T. G. Schaaff, *private communication*

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6 U. Kreibig and M. Vollmer, *"Optical properties of metal clusters"*, 1995, Springer Berlin, pp. 227-9, 250, 353-7

Coordinates of structure 2

Positions are given in Å.

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161

Au    13.4783    11.4903    10.7923
Au    10.6871     9.3247    14.5930
P     10.1457     8.5572    16.7156
H     10.9942     9.0753    17.7249
H     10.1859     7.1862    17.0883
H      8.8837     8.9213    17.2566
Au    14.8716    11.9857    13.9031
Au    13.3845    11.3019     7.7224
Au    13.5119     8.5013     7.1956
P     13.3038     8.0369     4.9189
H     14.4709     7.5208     4.2956
H     13.0493     9.1307     4.0565
H     12.3288     7.1275     4.4369
Au    15.1906     9.5938    12.2009
Au    13.6910     9.4127    14.6646
Cl    13.7023     7.6537    16.3443
Au    13.6996     8.7744     9.8815
Au    15.9164    10.5053     6.8159
Cl    16.9969     9.1088     5.1519
Au    12.1980     9.3903    12.1996
Au    13.8931     7.1916    12.2814
P     13.5488     5.2195    13.4169
H     14.5578     4.6998    14.2688
H     13.2135     4.0111    12.7424
H     12.4829     5.2466    14.3502
Au    16.0769    10.7038     9.6071
Au    15.8910     7.9241     8.5993
P     17.9710     7.1596     7.9701
H     18.9658     8.1213     7.6656
H     18.0746     6.3595     6.8028
H     18.7297     6.3362     8.8511
Au    13.2042    13.8120    12.4215
Au    13.2669    13.8136     9.1207
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Au	13.2083	13.8080	15.4015
Au	13.3050	13.8041	6.2803
Cl	13.3932	13.8678	3.9198
Cl	13.3927	13.8960	17.7457
Au	15.5345	13.3126	10.8130
Au	16.6739	9.9371	14.5889
P	17.2974	9.2565	16.7166
H	17.0598	10.2378	17.7104
H	18.6301	8.9121	17.0685
H	16.6010	8.1576	17.2882
Au	15.4748	14.7884	13.8809
Au	15.7046	13.1187	7.7947
Au	18.3994	12.4904	7.1282
P	18.7273	12.1413	4.8439
H	19.5585	13.0828	4.1802
H	17.5730	12.2390	4.0280
H	19.2633	10.9264	4.3467
Au	17.8780	14.3272	12.1938
Au	17.5323	12.8726	14.6203
Cl	19.2042	12.3013	16.3017
Au	18.1992	12.6772	9.8539
Au	17.1935	15.3251	6.8734
Cl	18.8499	15.9252	5.1953
Au	17.1933	11.4038	12.1913
Au	19.7993	12.3919	12.1945
P	21.5467	11.4756	13.3726
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H	22.6257	10.8011	12.7324
H	21.1507	10.4578	14.2748
Au	17.0089	15.5762	9.6136
Au	19.5998	14.5903	8.6041
P	21.0099	16.2970	7.9698
H	20.4480	17.5614	7.6662
H	21.7827	16.1097	6.7952
H	22.0520	16.7280	8.8410
Au	14.4255	15.8563	10.8315
Au	17.9207	15.8889	14.6023
P	18.7780	16.2390	16.7296
H	17.7823	16.3297	17.7332
H	19.5375	17.3870	17.0779
H	19.5981	15.2294	17.2997
Au	12.9943	16.2539	13.8772
Au	14.6042	15.9311	7.7326
Au	16.1125	18.2927	7.1954
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H	15.8932	19.6263	4.2828
H	16.1384	17.4866	4.0546
H	17.8693	18.7176	4.4420
Au	14.1943	18.4037	12.1962
Au	15.4255	17.6101	14.6185
Cl	16.4802	19.0738	16.2761
Au	15.8852	18.2126	9.8921
Au	13.0003	18.0953	6.8780
Cl	12.9074	19.8941	5.2518
Au	16.7839	16.8070	12.1942
Au	16.6767	19.5909	12.2695
P	18.0766	20.9980	13.4340
H	17.5398	21.9864	14.2989
H	19.0500	21.8116	12.7849

H	18.9277	20.3504	14.3623
Au	12.7965	17.9963	9.6171
Au	14.5917	20.1846	8.6070
P	13.3044	21.9932	7.9865
H	11.9381	21.7576	7.6951
H	13.6652	22.7075	6.8160
H	13.1519	23.1029	8.8676
Au	11.6689	15.5990	10.7254
Au	12.7054	18.9197	14.5988
P	12.6431	19.8820	16.7119
H	12.2837	18.9632	17.7284
H	11.7619	20.9401	17.0633
H	13.8561	20.3773	17.2614
Au	10.8140	14.3277	13.9013
Au	11.6730	15.8007	7.7054
Au	9.8137	17.9864	7.2069
P	9.7689	18.4576	4.9232
H	8.5411	18.1675	4.2708
H	10.6520	17.7245	4.0936
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Au	9.1457	16.0884	12.1832
Au	10.2869	17.1076	14.6039
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Au	9.8223	17.7050	9.9090
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Cl	7.4747	15.4723	5.1249
Au	11.4864	18.0702	12.1791
Au	8.8051	18.7986	12.3911
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H	8.7355	21.2928	14.3618
Au	9.1215	14.6782	9.6039
Au	7.5986	16.9949	8.5996
P	5.4584	16.4179	7.9722
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H	4.9367	17.0338	6.8052
H	4.3600	16.6661	8.8458
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Au	8.1577	14.8915	14.5660
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H	5.9815	14.6630	17.0696
H	7.2174	16.4453	17.2474
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Au	8.2990	11.9113	7.2015
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H	7.6200	10.7087	4.3007
H	8.7384	12.5412	4.0547
H	6.6212	12.6476	4.4590
Au	9.7936	10.6168	12.1910
Au	9.1912	12.0023	14.6104
Cl	7.5253	11.4794	16.3240
Au	8.5072	11.8052	9.9068
Au	10.9285	10.3089	6.8198
Cl	9.9275	8.8756	5.1277
Au	8.6158	13.4193	12.1888
Au	7.1062	11.1048	12.3867

P	5.0872	10.8141	13.4570
H	4.8752	9.7172	14.3334
H	3.8641	10.7274	12.7324
H	4.7262	11.8581	14.3462
Au	11.1895	10.2067	9.6014
Au	8.5120	9.4786	8.5941
P	8.3912	7.2658	7.9539
H	9.5911	6.5573	7.6901
H	7.6906	6.9534	6.7596
H	7.7697	6.3128	8.8120

Coordinates of structure 3

Positions are given in Å

141

Au	13.1960	11.6393	11.1313
Au	10.7094	9.6486	15.0575
P	10.1486	8.6418	17.0694
H	10.9060	9.0834	18.1820
H	10.2686	7.2411	17.2624
H	8.8404	8.8457	17.5803
Au	14.9137	12.1453	14.1446
Au	13.4910	11.4988	8.0776
Au	13.5858	8.8483	7.3205
P	13.2889	8.1061	5.1360
H	14.3527	7.4209	4.4860
H	13.0480	9.0890	4.1380
H	12.2348	7.2149	4.7994
Au	15.1431	9.7746	12.5431
Au	13.7306	9.5484	14.9578
Cl	13.6504	7.8430	16.6720
Au	13.7124	9.0705	10.0624
Au	16.1133	10.6424	7.4137
Cl	17.6593	6.6613	8.2277
Au	12.1988	9.5195	12.6229
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H	14.7721	4.8973	14.2458
H	13.3470	4.1195	12.8321
H	12.6830	5.3750	14.4653
Au	16.2367	10.6475	10.1343
Au	15.9194	8.1343	8.7412
Au	13.2059	14.0286	12.7399
Au	13.3216	13.9483	9.5232
Au	13.3283	13.9567	15.7375
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Cl	13.6493	14.0118	4.1696
Cl	13.4444	14.0188	18.0709
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H	18.8243	9.0796	17.2117
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Au	15.7410	13.2766	8.2568
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P	18.8845	12.1787	5.1264
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H	17.8663	12.2675	4.1399
H	19.4227	10.9169	4.7543
Au	17.9162	14.5114	12.5369
Au	17.6202	13.0512	14.9413
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H	22.3654	12.6630	14.3332
H	22.7631	11.1076	12.8927
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Au	17.3993	15.7699	10.0692
Au	19.7107	14.6478	8.6587
Au	14.6831	15.8800	11.1323
Au	18.0019	16.0274	14.9363
P	18.9443	16.4681	17.0072
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H	19.8754	15.5282	17.5239
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Au	14.7228	15.9662	8.1386
Au	16.0556	18.2485	7.3406
P	16.7245	18.7364	5.1605
H	16.2618	19.9303	4.5397
H	16.3356	17.8222	4.1452
H	18.0980	18.8487	4.8132
Au	14.2525	18.4634	12.5506
Au	15.6067	17.8580	14.9435
Cl	16.6404	19.2165	16.6658
Au	15.8214	18.2606	10.1182
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Cl	14.1471	22.5206	8.2301
Au	16.8396	17.0218	12.5329
Au	16.6898	19.7581	12.5074
P	18.0400	21.2780	13.5862
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H	18.9132	22.1723	12.9056
H	18.9708	20.7008	14.4878
Au	12.8253	18.4883	10.1432
Au	14.6178	20.2760	8.7303
Au	11.9154	15.9440	10.9462
Au	12.8384	19.0768	14.9552
P	12.7325	20.1708	16.9967
H	12.4795	19.2930	18.0787
H	11.7548	21.1598	17.2756
H	13.8928	20.8278	17.4839
Au	10.9108	14.5538	14.3405

Au	11.8998	15.8514	7.8441
Au	10.1293	18.0098	7.4486
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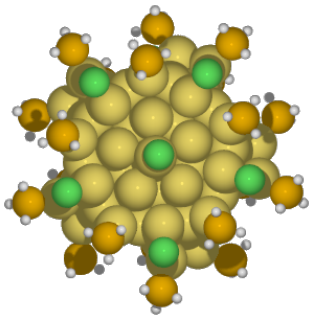
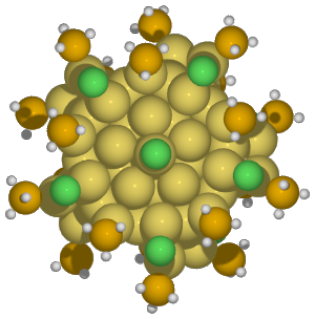
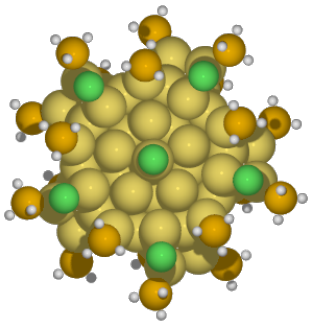
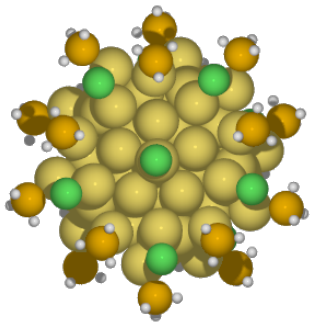
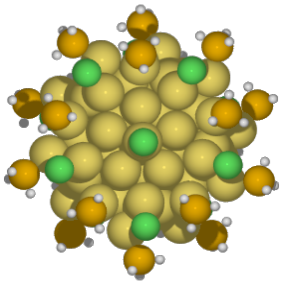
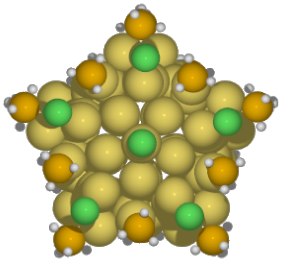
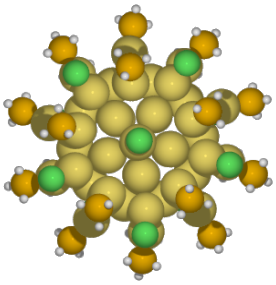
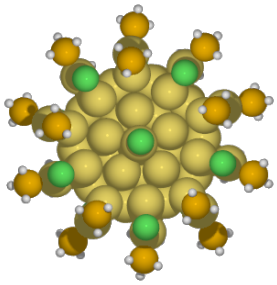
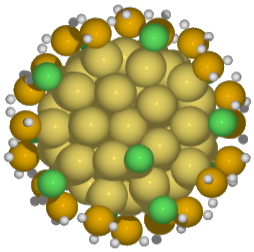
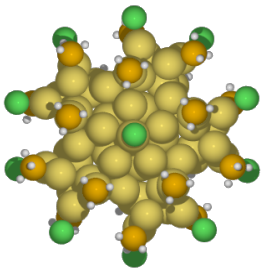
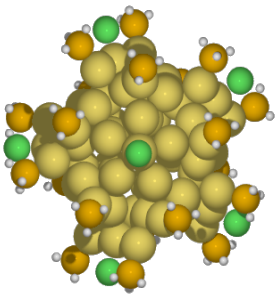
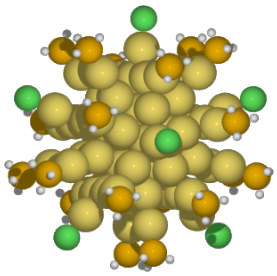
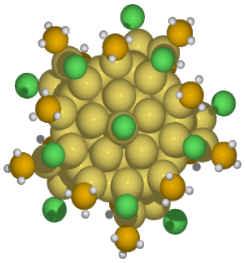
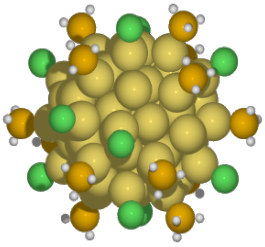
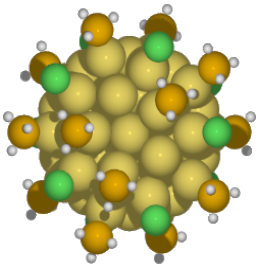
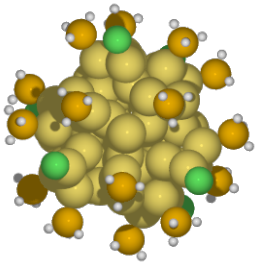
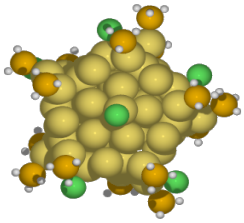
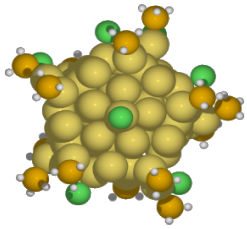
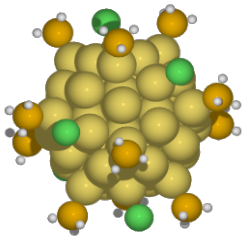
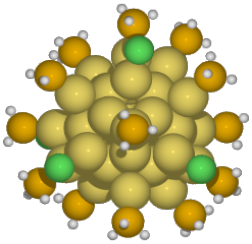
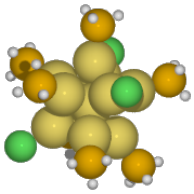
H	8.5855	18.6861	4.6628
H	10.6042	18.1011	4.2387
H	10.1830	20.1040	4.8793
Au	9.3412	16.2771	12.6322
Au	10.3173	17.4171	15.0194
Cl	9.4253	18.6643	16.8783
Au	9.9232	17.7439	10.1580
Au	9.2428	15.0826	7.5359
Cl	5.4579	17.2028	8.0340
Au	11.5084	18.2186	12.5946
Au	8.8280	18.9464	12.6135
P	7.7939	20.7488	13.5911
H	6.7145	20.4874	14.4747
H	7.2223	21.8366	12.8766
H	8.6183	21.4842	14.4815
Au	8.7933	14.9522	10.2243
Au	7.7075	17.1527	8.7164
Au	10.9901	13.3358	11.0255
Au	8.2631	15.1504	15.0242
P	7.2122	15.3897	17.0760
H	7.9588	14.8619	18.1567
H	5.9596	14.7839	17.3502
H	6.9664	16.6964	17.5736
Au	12.0282	11.9325	14.2461
Au	11.1287	13.1395	7.9237
Au	8.5208	12.2550	7.4686
P	7.7126	12.2898	5.2763
H	7.3317	11.0526	4.6873
H	8.5907	12.7268	4.2479
H	6.5733	13.0505	4.8963
Au	9.8307	10.9450	12.6530
Au	9.1270	12.2334	15.0555
Cl	7.6110	11.8273	16.8871
Au	8.6380	11.9566	10.2282
Au	11.0096	10.4109	7.5331
Cl	7.7221	7.6080	8.0078
Au	8.7065	13.6188	12.6482
Au	7.1276	11.3437	12.7243
P	5.0843	10.9634	13.6998
H	4.9765	9.8588	14.5839
H	3.8769	10.7741	12.9712
H	4.6455	11.9833	14.5832
Au	10.9169	10.0472	10.2286
Au	8.4643	9.7281	8.6655

Pictures of the structures

Pictures of all the structures considered in this study; Au: gold, Cl: green, P: yellow, H: white. The stabilisation energies (as defined in the main text, eV) and the masses corresponding to PPh_3 ligands (amu) are given. Compare for fig. 2 in the main text. The coordinates can be obtained on request from to the corresponding author.

 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=0.01, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=0, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=0, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.01, m=19262
 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.01, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.02, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.03, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.03, m=19262
 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.04, m=19262	 $[Au_{69}(PH_3)_{20}Cl_{12}]^{-1}$ E_{stab}=-0.05, m=19262	 $[Au_{64}(PH_3)_{20}Cl_7]^{-1}$ E_{stab}=-0.14, m=18100	 $[Au_{64}(PH_3)_{20}Cl_7]^{-1}$ E_{stab}=-0.25, m=18100
 $[Au_{69}(PH_3)_{15}Cl_{12}]^{-1}$ E_{stab}=-0.06, m=17950	 $Au_{69}(PH_3)_{15}Cl_{11}$ E_{stab}=-0.09, m=17915	 $Au_{69}(PH_3)_{15}Cl_{11}$ E_{stab}=-0.09, m=17915	 $[Au_{63}(PH_3)_{18}Cl_6]^{-1}$ E_{stab}=-0.23, m=17344

 $[Au_{64}(PH_3)_{15}Cl_7]^{-1}$ E_{stab}=-0.18, m=16789	 $[Au_{64}(PH_3)_{14}Cl_8]^{-2}$ E_{stab}=-0.17, m=16562	 $[Au_{55}(PH_3)_{12}Cl_6]^{-1}$ E_{stab}=-0.18, m=14193	 $[Au_{39}(PH_3)_{14}Cl_6]^{-1}$ E_{stab}=-0.03, m=11566
 $Au_{11}(PH_3)_7Cl_3$ E_{stab}=-0.14, m=4109			