Supporting Information for

$Au_{70}S_{20}(PPh_3)_{12}$: An intermediate sized metalloid gold cluster stabilized by the Au_4S_4 ring motif and Au-PPh_3 groups

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1. Experimental Details

All reactions were done in an inert gas atmosphere performing standard Schlenk techniques. Toluene and diethylether were pre-dried with sodium, pentane was dried with CaH_2. All organic solvents were purified via distillation. $(Ph_3P)AuSC(SiMe_3)_3$ was synthesized as described in the literature.[1]

EDX analysis was performed at solid samples at a HITACHI SU8030 scanning electron microscope with Bruker-EDX. Dynamic light scattering measurements were performed at a Malvern Zetasizer Nano ZS. Single crystal measurements were performed at the synchrotron light source ANKA at the KIT (Karlsruher Institute of Technology).

NMR spectroscopic measurements were done at a Bruker DRX-250. The chemical shifts are given in ppm against external standards $SiMe_4$ (^1H) and 85% phosphoric acid (^{31}P). C_6D_6 was dried with 3 Å molecular sieves.

Synthesis of $Au_{70}S_{20}(PPh_3)_{12}$

$(Ph_3P)AuSC(SiMe_3)_3$ (0.72 g, 1 mmol) was dissolved in 25 ml Et_2O. The pale-yellow solution was contaminated with 25 ml distilled H_2O and stirred for 2 hours. The phases were separated and the organic phase was set under a nitrogen atmosphere and stirred. 0.7 ml of 1M $C_{12}H_{28}BLi$ (0.7 mmol) was added dropwise to the $(Ph_3P)AuSC(SiMe_3)_3$. The mixture reacted quickly from a pale yellow to red to brown to black. The solution was also bubbling and getting colder. After 4 hours of stirring a black precipitate had formed and the solution took on a slight brown colour. The mixture was dried under vacuum to give a greyish-black precipitate. The precipitate was washed with pentane and extracted with 30 ml of toluene, where 480 mg were dissolved. The black-coloured extract was stored at 40 °C for 12 to 14 weeks. This led to black moth-shaped and also hexagonal crystals of $Au_{70}S_{20}(PPh_3)_{12}$. EDX analysis of the crystals (figure S9) showed an elemental ratio of Au:S:P = 92.8 : 4.6 : 2.6 (calculated ratio for $Au_{70}S_{20}(PPh_3)_{12}$: Au:S:P = 93.2 : 4.3 : 2.5).

Up to now, in all experiments reproducibly 30 to 50 crystals of $Au_{70}S_{20}(PPh_3)_{12}$ are obtained, which leads to an isolated crystalline yield of about 6 - 8 mg (1 – 1.5 %). The by-products are $Ph_3PAuSC(SiMe_3)_3$, PPh_3S and PPh_3O which can be seen in the ^{31}P-NMr spectrum shown in figure S8. The cluster itself is not soluble in any of the conventional organic solvents like toluene, tetrahydrofuran, dichloromethane or acetonitrile. It is merely soluble in 1,3-Dimethyl-2-imidazolidinone which is an unfavourable solvent to continue the work in regard to the boiling point (225 °C), the melting point (8 °C) and the capability to recrystallize the dissolved substances. Because of the low yield and bad solubility of the crystalline compound it was actually not possible to do any additional measurements that needed more substance.

2. Detailed view on $Au_{70}S_{20}(PPh_3)_{12}$

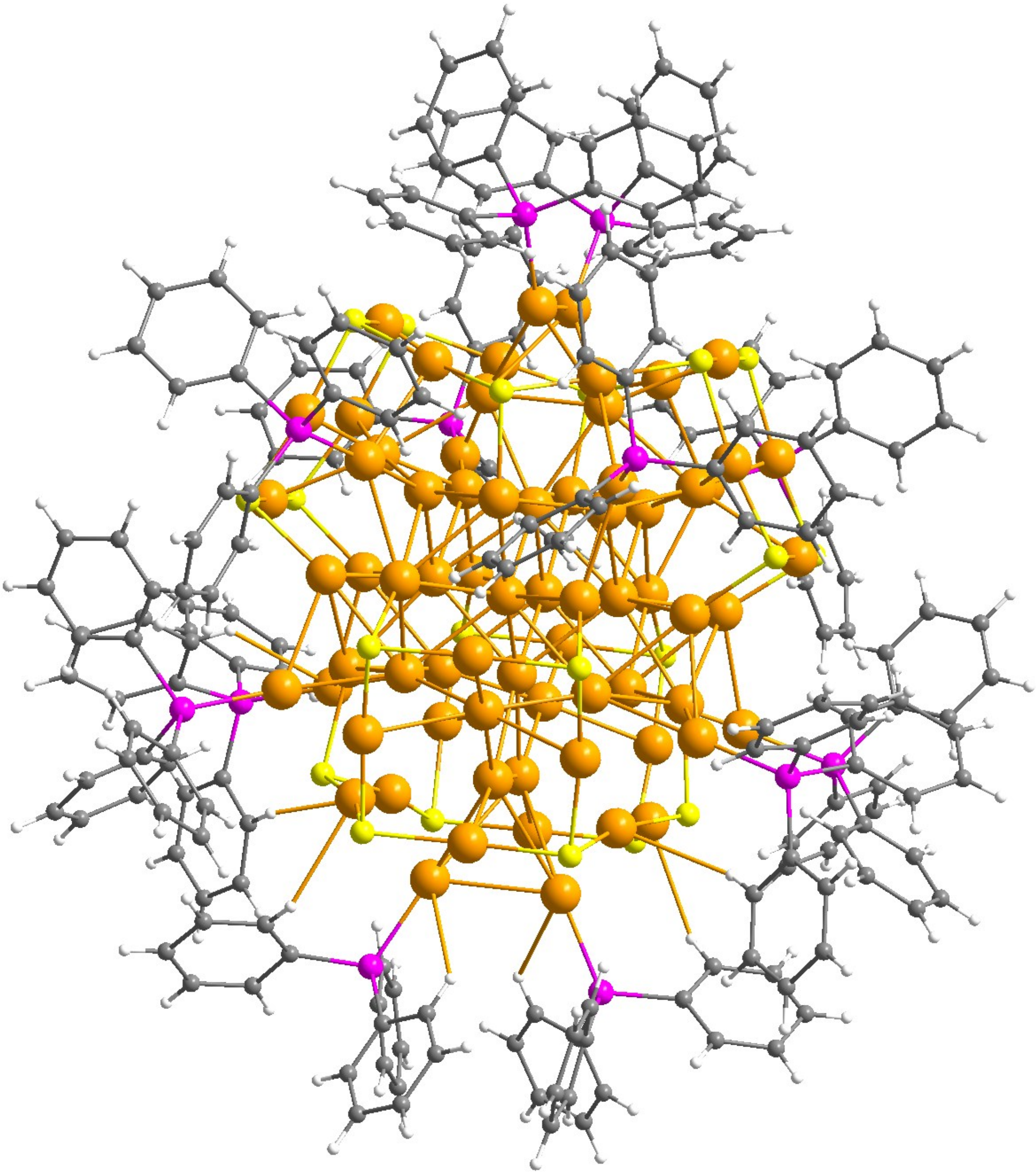

Figure S1: Ball and stick presentation of the complete molecular structure of $Au_{70}S_{20}(PPh_3)_{12}$ in the solid state.

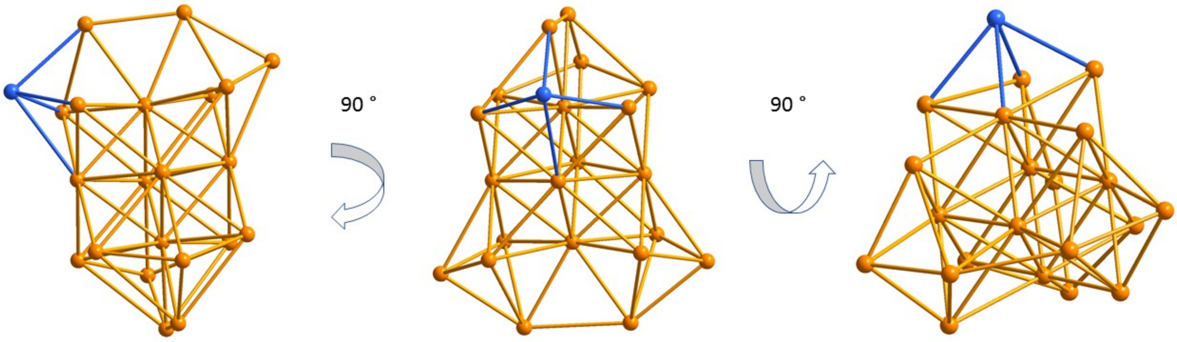

Figure S2: Different views of the Au_{22} core. One gold atom and the corresponding bonds are coloured blue for a better overview, Au blue and orange.

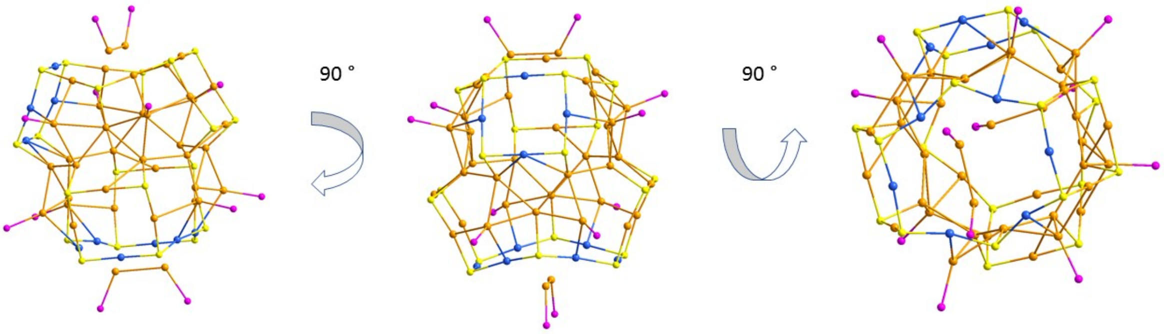

Figure S3: Different views of the $Au_{48}S_{20}(PPh_3)_{12}$ shell. The gold atoms of one Au_4S_4 ring motif and the Au_6S_6 ring are coloured blue for a better overview, Au blue and orange, S yellow, P violet.

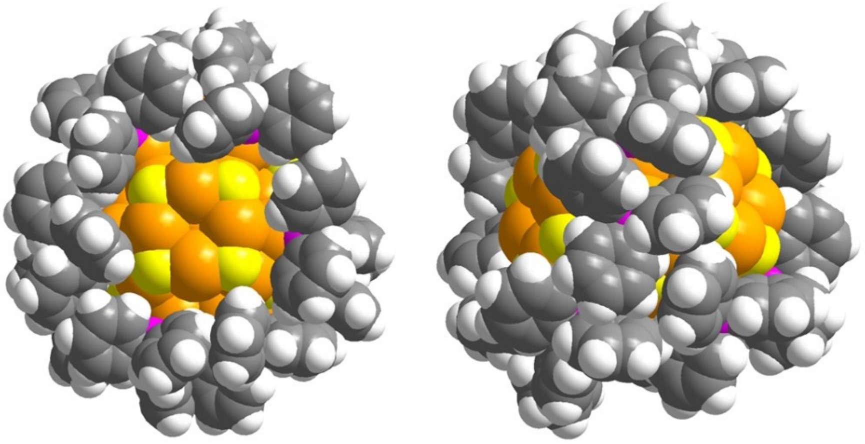

Figure S4: Space-filling model of $Au_{70}S_{20}(PPh_3)_{12}$ from two points of view. Left side: Au_4S_4 ring. Right side: 2 $Au(PPh_3)$ groups cover the Au_6S_6 ring.

3. NMR spectra

All ^1H NMR spectra were calibrated to the solvent residual signal at 7.16 ppm.

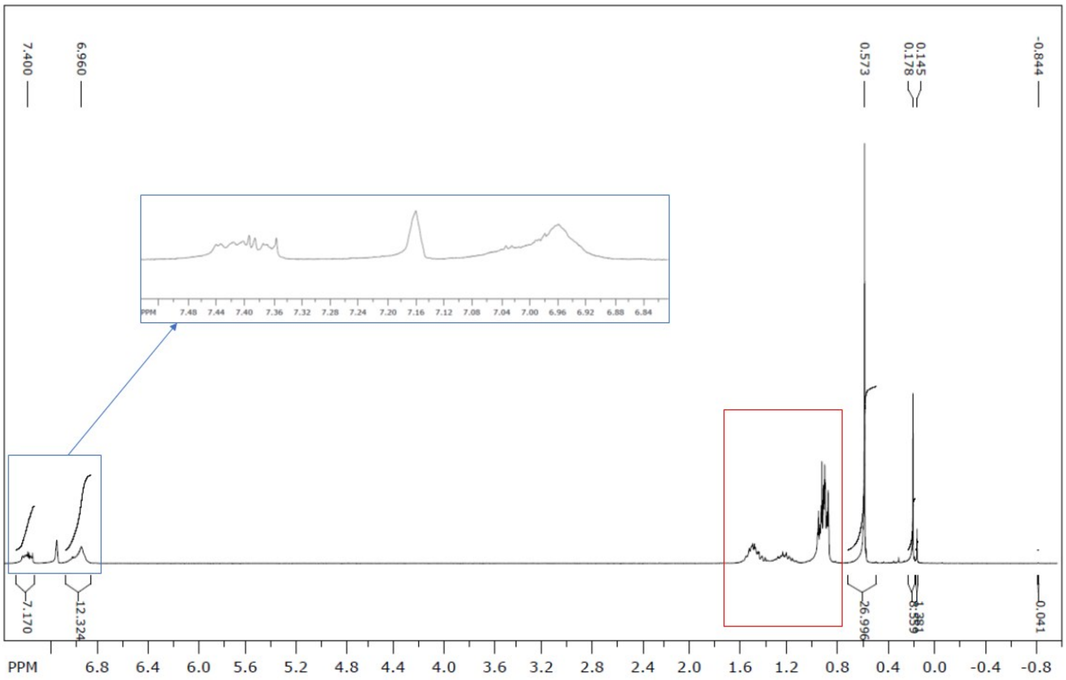

Figure S5: ^1H NMR spectrum of the pentane extract. The signals at 7.40, 6.96 and 0.57 belong to $Ph_3PAuSC(SiMe_3)_3$. PPh_3S is also in the range of 7.40 and 6.96. The signal at 0.18 belongs to $HSC(SiMe_3)_3$. Normally, one would find a much smaller signal at 0.90 for the HS proton. However, this singal is overlayed by the signals of L-Selectride® (red framed area). The signal at 0.15 together with the extremely small signal at -0.84 belong to $HC(SiMe_3)_3$.

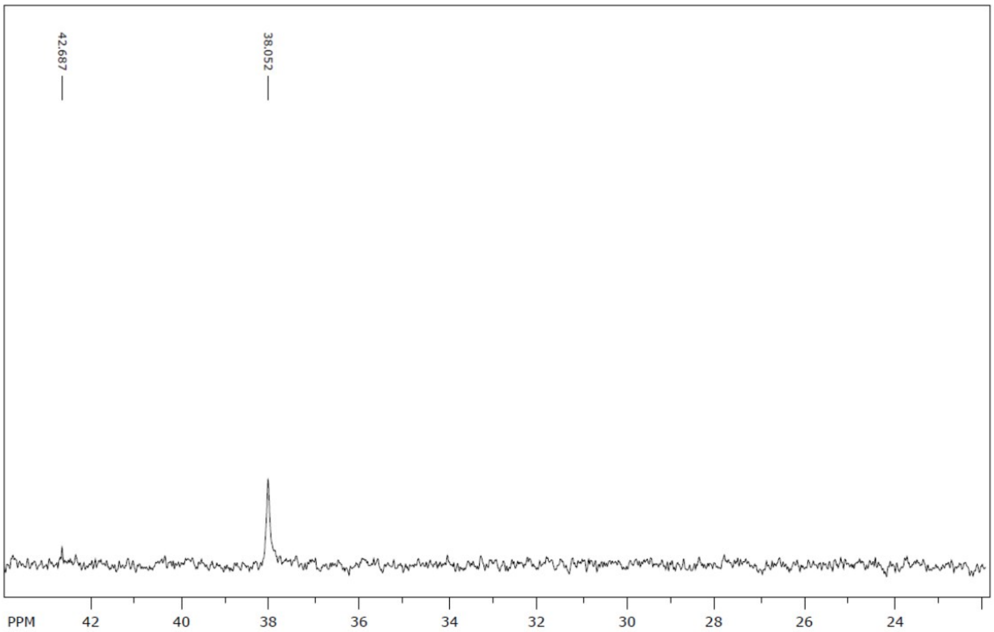

Figure S6: ^{31}P NMR spectrum of the pentane extract. Two signals can be seen whereas the signal at 42.69 belongs to PPh_3S and the signal at 38.05 to $Ph_3PAuSC(SiMe_3)_3$.

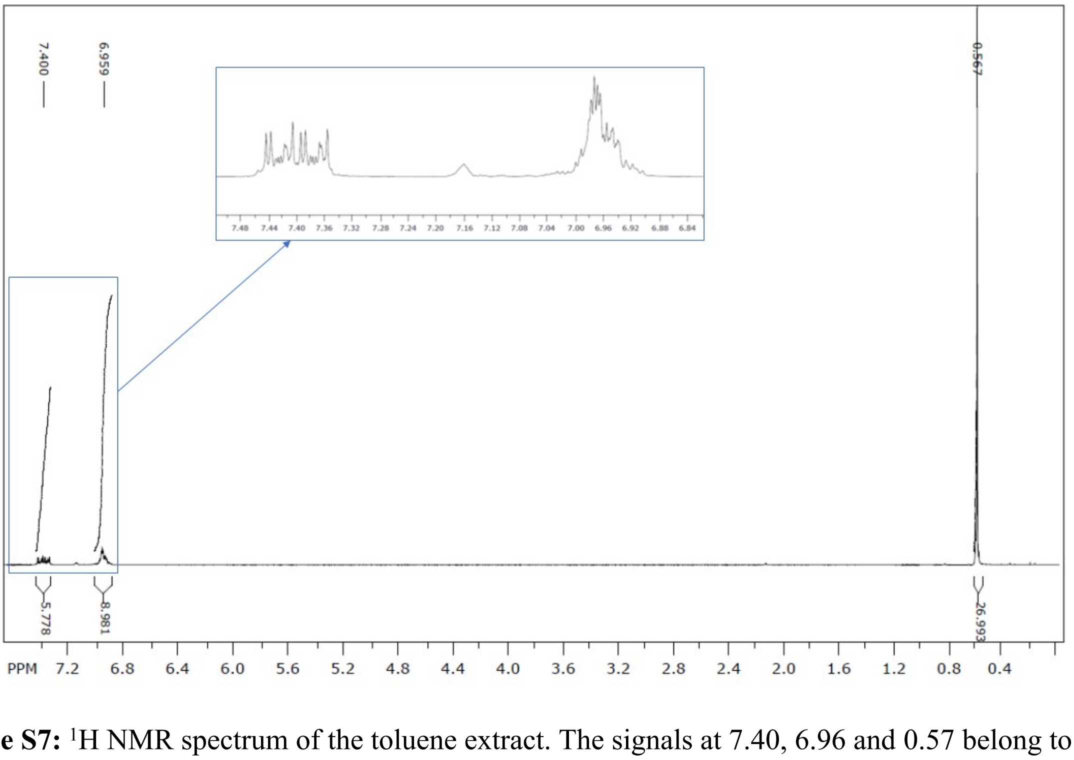

Figure S7: ^{1}H NMR spectrum of the toluene extract. The signals at 7.40, 6.96 and 0.57 belong to $Ph_3PAuSC(SiMe_3)_3$. The signals between 1.6 and 0.8 have completely disappeared indicating that L-Selectride® as well as $HSC(SiMe_3)_3$ and $HC(SiMe_3)_3$ have been removed by the washing step with pentane.

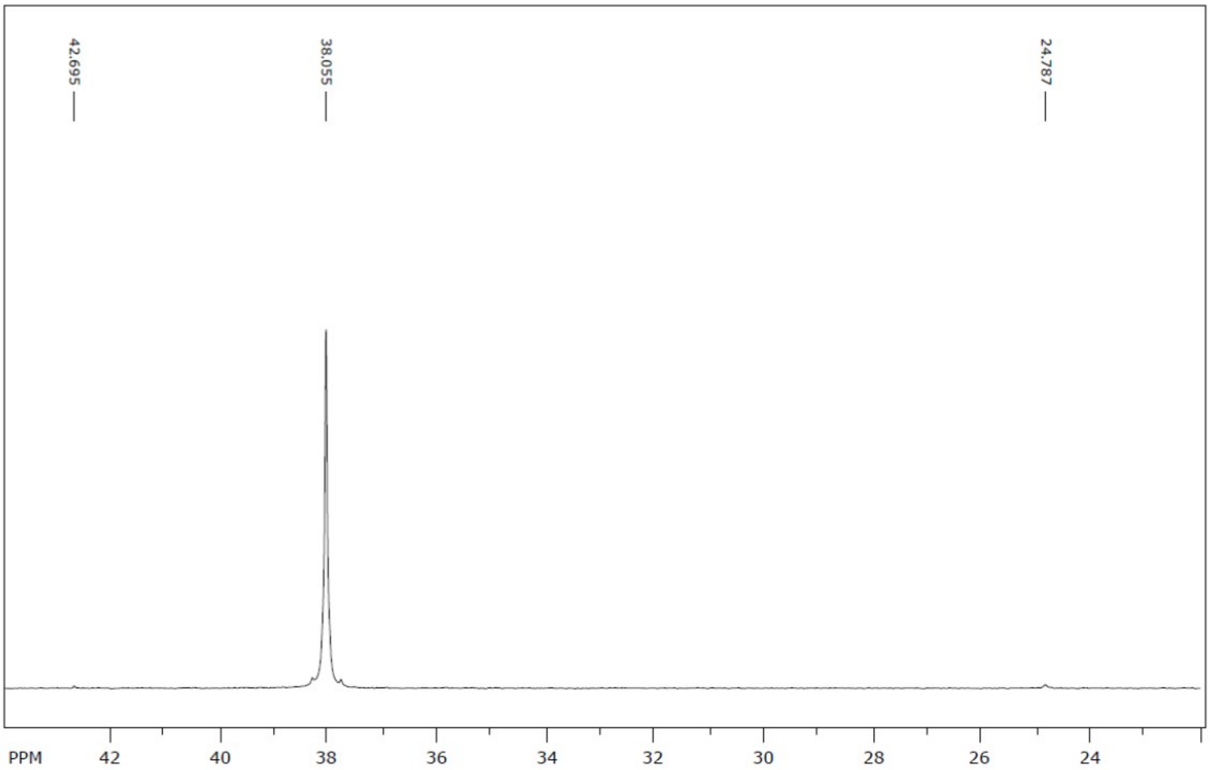

Figure S8: ^{31}P NMR spectrum of the toluene extract. Three signals can be seen whereas the signal at 42.69 belongs to PPh_3S, the main signal at 38.05 belongs to $Ph_3PAuSC(SiMe_3)_3$ and the signal at 24.79 to PPh_3O. Consequently, the main compound within the toluene extract observable via ^{31}P-NMR is the educt $Ph_3PAuSC(SiMe_3)_3$ which might explain the low yield of $Au_{70}S_{20}(PPh_3)_{12}$. The absence of any visible signal of $Au_{70}S_{20}(PPh_3)_{12}$ can be due to the bad solubility of this cluster while PPh_3S and PPh_3O are side products during cluster formation.

4. EDX measurements of crystals of $Au_{70}S_{20}(PPh_3)_{12}$

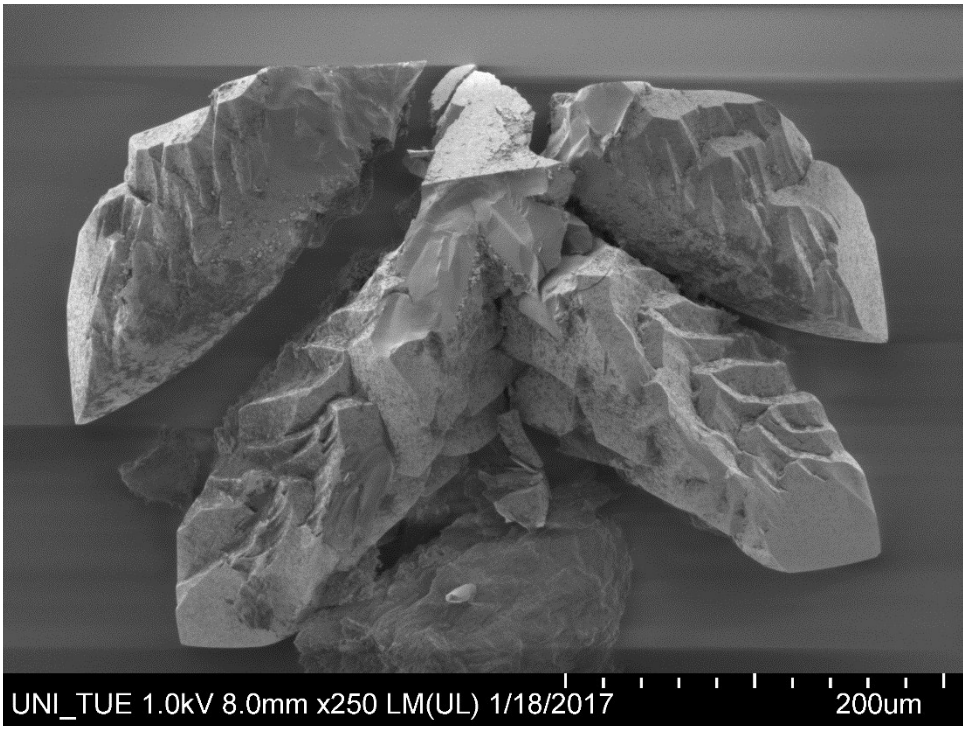

Figure S9: SEM-Image of a moth shaped single crystal of $Au_{70}S_{20}(PPh_3)_{12}$. Most single crystals had this moth-like form. The EDX measurements were performed at 5 different areas and 3 spots.

Table S1: Results of the EDX measurements of the crystallite at 5 different areas:

Element	Norm. Wt. %	Norm. Wt. % calculated	Norm. At. %	Norm. At. % Calculated
Au	92,5 ± 0,3	93,2	66,5 ± 0,9	68,6
S	4,9 ± 0,2	4,3	19,6 ± 0,9	19,6
P	2,6 ± 0,0	2,5	13,9 ± 0,1	11,8

Table S2: Results of the EDX measurements of the crystallite at 3 different spots:

Element	Norm. Wt. %	Norm. Wt. % calculated	Norm. At. %	Norm. At. % Calculated
Au	92,8 ± 0,2	93,2	67,5 ± 0,6	68,6
S	4,6 ± 0,1	4,3	20,2 ± 0,5	19,6
P	2,6 ± 0,0	2,5	12,3 ± 0,1	11,8

5. DLS measurements

All Dynamic light scattering (DLS) measurements were performed at a Malvern Zetasizer Nano ZS. The following table shows DLS measurements of the solution where cluster **1** crystallized later. The measurements were done at different temperatures from 25 °C to 40 °C. Therefore a program of the Malvern Zetasizer Nano ZS was used which equilibrated the sample for 10 minutes, conducted the measurement and then repeated this procedure in 5 °C steps. The PdI was calculated as recommended by Malvern (PdI = (Standard deviation/Size)^2). In this case a low PdI means that the solution is monodisperse. A PdI of 0.0 can be seen as uniform, 0.0-0.1 can be seen as narrow, everything above can be seen as polydisperse.

Table S3: Results of the DLS measurements:

measurement	size (d. nm)	St dev (d. nm)	PdI
25 °C	2.319	0.413	0.03
30 °C	2.739	0.441	0.03
35 °C	2.663	0.400	0.02
40 °C	2.502	0.422	0.03

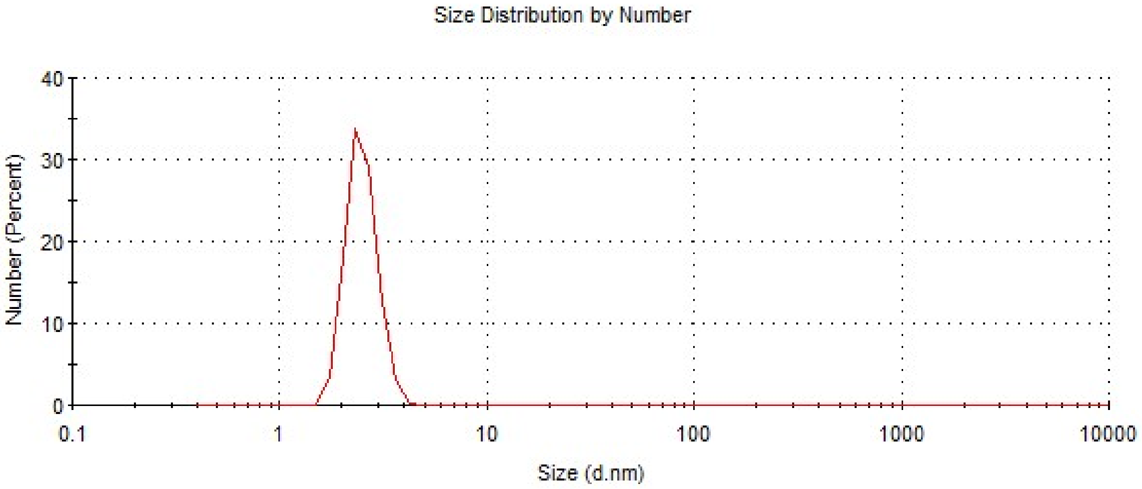

Figure S10: The Graph of the DLS measurement at 35 °C.

6. Computational Details

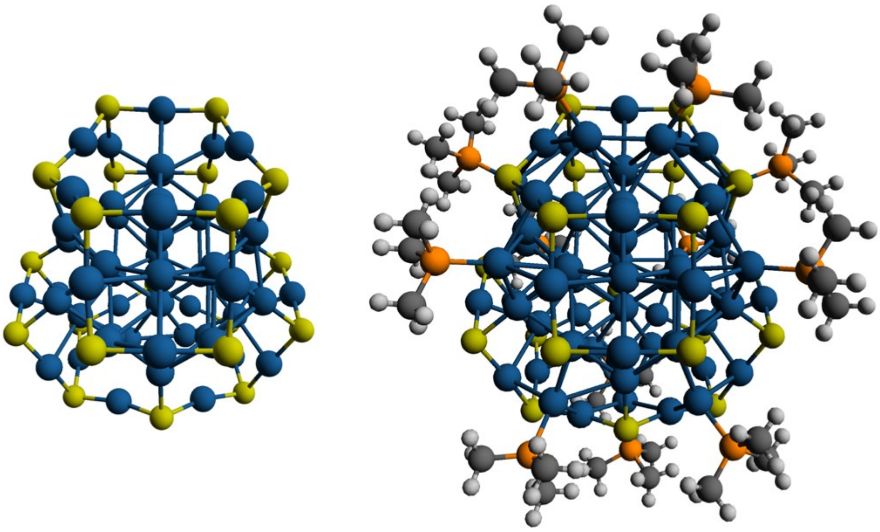

Figure S11: Ball and stick presentation of $Au_{58}S_{20}$ and $Au_{70}S_{20}[P(CH_3)_3]_{12}$ respectively.

We carried out first principle density functional calculations using GPAW.[2] This method utilizes the frozen core approximation and uses soft pseudo valence wavefunctions. [3,4] The electron wavefunctions are projected onto a real-space grid with a grid spacing of 0.2Å, using the finite-difference mode. The exchange and correlation effects were accounted for through the Perdew, Burke, and Ernzerhof (PBE) functional. [5] The structure optimization calculations were performed with a maximal force of 0.05 eV/Å for any atom to achieve the lowest energy configuration. It should be noted that the protecting $P(Ph_3)$ ligands were reduced to $P(CH_3)$ ligands to reduce computational cost. The electronic charges on individual atoms were calculated using a Bader analysis. [6,7,8] This method uses zero flux surfaces to find the maximum and minimum on the charge density surface; in which, the minimum charge density is perpendicular to the surface. Y_{lm} analysis was performed as described previously.[9]

7. Crystal packing

Compound **1** crystallizes in the trigonal crystal lattice in the space group R-3c with 18 molecules in the unit cell. This leads to a very huge unit cell of 133.000 Å³ volume. Thereby the clusters are arranged as layers along the crystallographic c-axis. These layers could be described as a defect structure of a classical hexagonal layer. Here, 25% of the lattice positions in this layer is missing in that way, a trihexagonal layer is formed, as found e.g. in the Kagomé lattice (figue S12). These trihexagonal layers are stacked in an ABC type, as shown in figure S13. One unit cell is thereby part of 6 Kagomé lattices in an ABC ABC stacking.

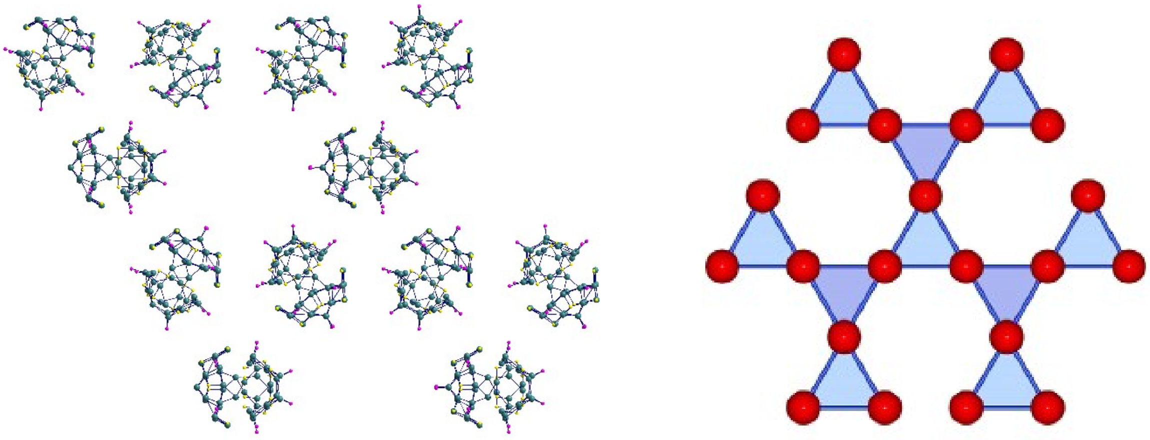

Figure S12: Left: Schematic view along the crystallographic c axis. All carbon, hydrogen and „naked“ gold atoms are omitted for clarity. Right: Cut-out of the trihexagonal „Kagomé“ lattice.

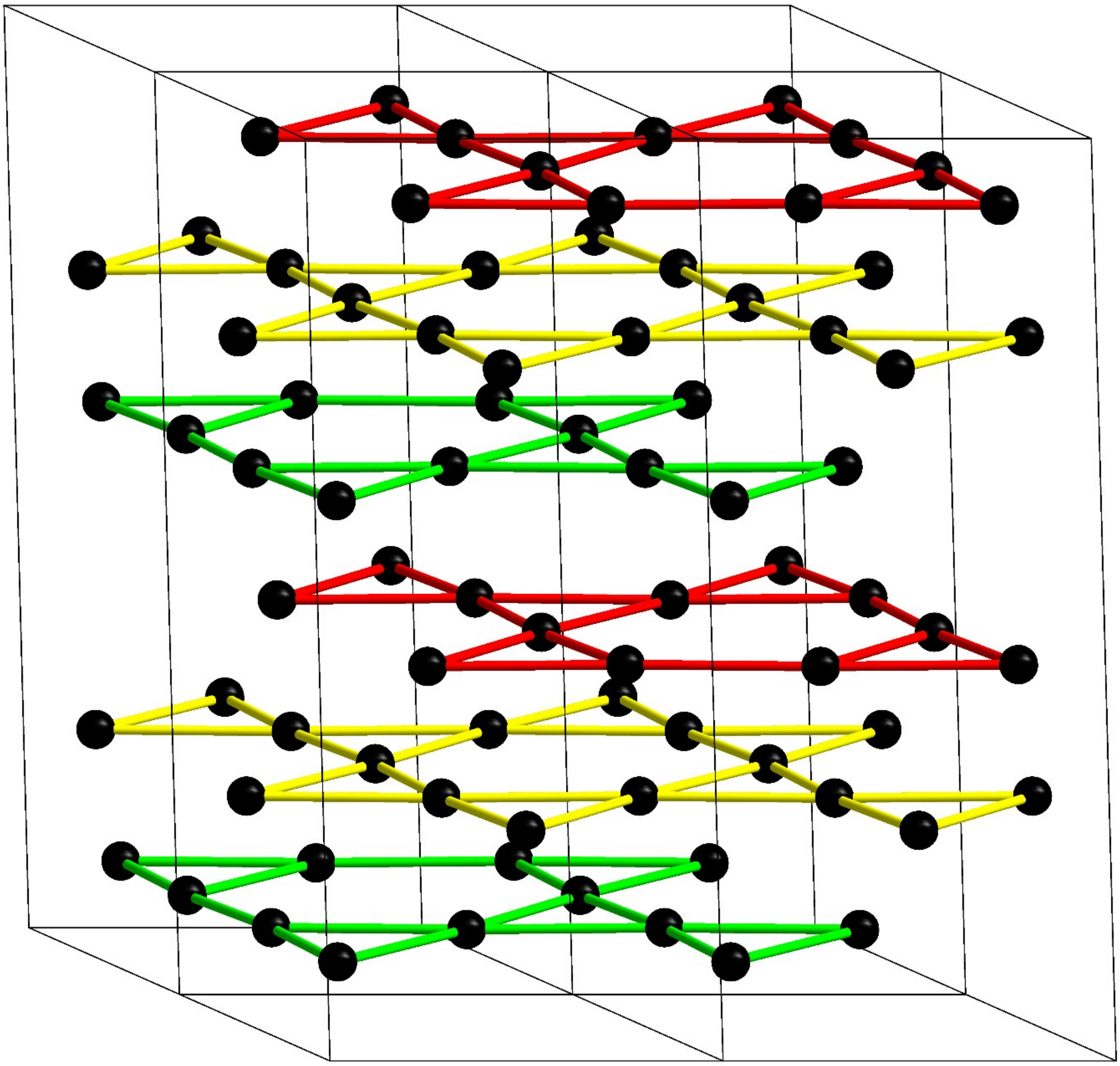

Figure S13: View on 4 unit cells (doubled in a and b) with schematic presentation of the cluster centers as black balls. The ABC stack is illustrated as colored layers A (red) B (yellow) C (green)

Having a closer look at the Kagomé stack, one can easily find large voids, i.e. in all hexagons. Looking along the crystallograpic c axis (figure S14), one can find tubes parallel to the c axis. Furthermore, a very huge void is formed as a distorted cuboctahedron with a diameter of around 3 nm! The content of this void could not be resolved with the crystal data in hand. Due to the good accordance of the EDX spectra on **1** with the calculated values of Au, S, and P atoms, we could exclude further heavier atoms than carbon. Thus we assume heavily disordered solvent molecules, like toluene or thf, which could not be located due to symmetry operations. Furthermore, using the PLATON crystal structure analyzing program, even the SQUEEZE algorithm could not handle such large voids, so we got no idea about the amount of disordered solvents and the content is still unknown.

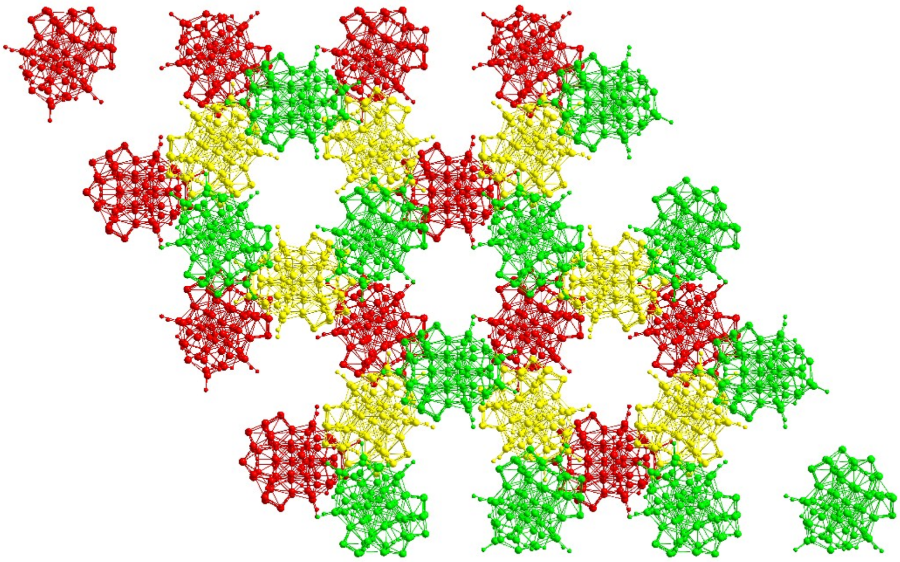

Figure S14: View of the ABC stack along the c axis. Different layers are shown in different colors.

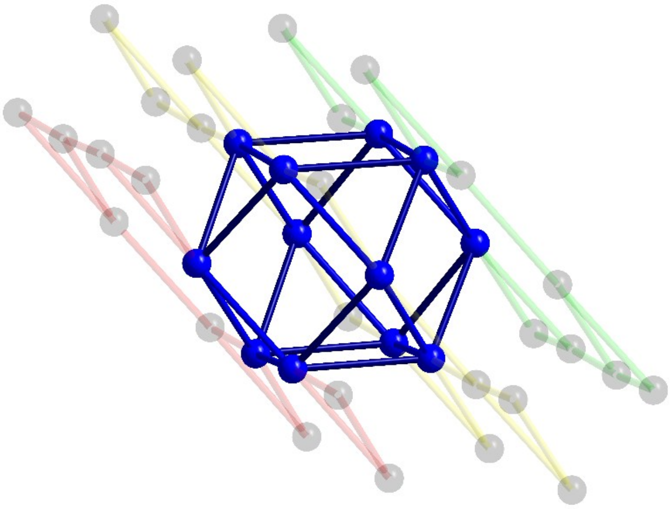

Figure S15: Illustration of the very huge cuboctahedral void formed by the ABC stack of Kagomé layers

References:

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