Electronic Supplementary Material (ESI) for Dalton Transactions.

$Au_{54}(Et_3P)_{18}Cl_{12}$: A structurally related Cluster to $Au_{32}(Et_3P)_{12}Cl_8$ gives insight into the formation process

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Inhalt

1. Experimental Details

The reactions were partly conducted in an inert gas atmosphere performing standard Schlenk techniques. CH_2Cl_2 was pre-dried with CaH_2, Et_2O was pre-dried with Na. Ethanol and the solvents mentioned before were purified via distillation. Et_3PAuCl was synthesized as described by our group.[1]

Dynamic light scattering measurements were performed at a Malvern Zetasizer Nano ZS. UV/VIS spectra were recorded at a PG Instruments T60 UV/VIS Spectrophotometer. EDX analysis was performed using solid samples at a HITACHI SU8030 scanning electron microscope with Bruker EDX. NMR spectroscopic measurements were executed with a Bruker DRX-250 spectrometer. The chemical shifts are given in ppm against the external standards $SiMe_4$ (^1H, ^{13}C) and 85 % phosphoric acid (^{31}P). CD_2Cl_2 was used as received.

Synthesis of $Au_{54}(Et_3P)_{18}Cl_{12}$: Et_3PAuCl (0.71 g, 2.0 mmol) was dissolved in ethanol (20 ml) without employing Schlenk technique. Solid $NaBH_4$ (0.076 g, 2.0 mmol) was dispersed in ethanol (20 ml) and added dropwise to Et_3PAuCl. During the addition the colourless solution turned dark red and the mixture was stirred for one hour before the solvent was removed under reduced pressure.

All further steps were executed under inert conditions. The residual dark brown precipitate was dissolved in CH_2Cl_2 (30 ml), filtered and the organic solvent was removed. The precipitate was again dissolved in CH_2Cl_2 (15 ml), filtered and layered with three times the amount of Et_2O (45 ml). The solution was left in the dark for 3 weeks where it lost its colour completely. Black rectangular crystals of the composition $Au_{54}(Et_3P)_{18}Cl_{12}$ could be found on the glass wall. (yield: 42 mg; 2 µmol; 9,5 %)

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 1.92 (t, *J* = 8 Hz, 108 H, Et_3), 1.37 – 1.06 (m, 162 H, Et_3). ^{13}C{^{1}H} NMR (62.9 MHz, CD_2Cl_2): δ (ppm) = 18.15 (m, Et_3), 9.22 (s, Et_3). ^{31}P{^{1}H} NMR (101 MHz, CD_2Cl_2): δ (ppm) = 96.93 (s, $Au_{54}(Et_3\mathbf{P})_{18}Cl_{12}$).

2. Crystal data

Crystals were mounted on the diffractometer at 150 K. The data were collected on a Bruker APEX II DUO diffractometer equipped with an IμS microfocus sealed tube and QUAZAR optics for monochromated MoKα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems cryostat. A semiempirical absorption correction was applied using the program SADABS. The structure was solved by direct methods and refined against F^2 for all observed reflections. The H atom positions in all compounds were refined using a riding model. Programs used: SHELXS and SHELXL[2] within the Olex2 program package.[3]

During refinement, it becomes obvious, that the central Au_2 dumbbell, namely the Atom Au1 and its symmetry equivalent (1-x, 1-y, 1-z) could be best describes as less occupied with an occupation number of 94.96%. Additionally, some remaining electron density directly on the inversion centre could be assigned to another less occupied Au atom (Au1A) with an occupation number of 5.04%. This leads to the fact, that not a phase pure substance is present in the crystal, but a 95:5 mixture of $Au_{54}(Et_3P)_{18}Cl_{12}$ and $Au_{53}(Et_3P)_{18}Cl_{12}$. Orienting quantum chemical calculations show that both modifications are principally stable.

It was tried to verify if this 5 % occupation was just an artifact of the measurement via ESI-MS measurements. Unfortunately, it was not possible to obtain any data. Multiple attempts did not lead to any results. This is due to the low solubility of $Au_{53/54}(Et_3P)_{18}Cl_{12}$. It was neither possible to exchange the phosphines to increase the solubility, nor could any results be obtained by using weakly coordination anions, as well as $Au_{53/54}(Et_3P)_{18}Cl_{12}$ could not be ionized so that it would have been possible to find any signals. Other methods like NMR EDX or DLS measurements are not sensitive enough to distinguish between $Au_{53}(Et_3P)_{18}Cl_{12}$ and $Au_{54}(Et_3P)_{18}Cl_{12}$.

To obtain information about co crystallized solvents, the SQUEEZE[4] program routine was used to identify two voids of 405 Å³ volume in the unit cell (one per molecule) containing 190 electrons. This fits to 4.5 molecules of Et_2O.

3. Detailed view of $Au_{53}(Ph_3P)_{18}Cl_{12}$ and $Au_{54}(Ph_3P)_{18}Cl_{12}$

$Au_{53}(Et_3P)_{18}Cl_{12}$ and $Au_{54}(Et_3P)_{18}Cl_{12}$ differ only by one Au atom. In $Au_{54}(Et_3P)_{18}Cl_{12}$ the centre of the cluster is made up of an Au_2 dumbbell (Figure S1 a) while in $Au_{53}(Et_3P)_{18}Cl_{12}$ a single Au atom is positioned in the centre (Figure S1 b).

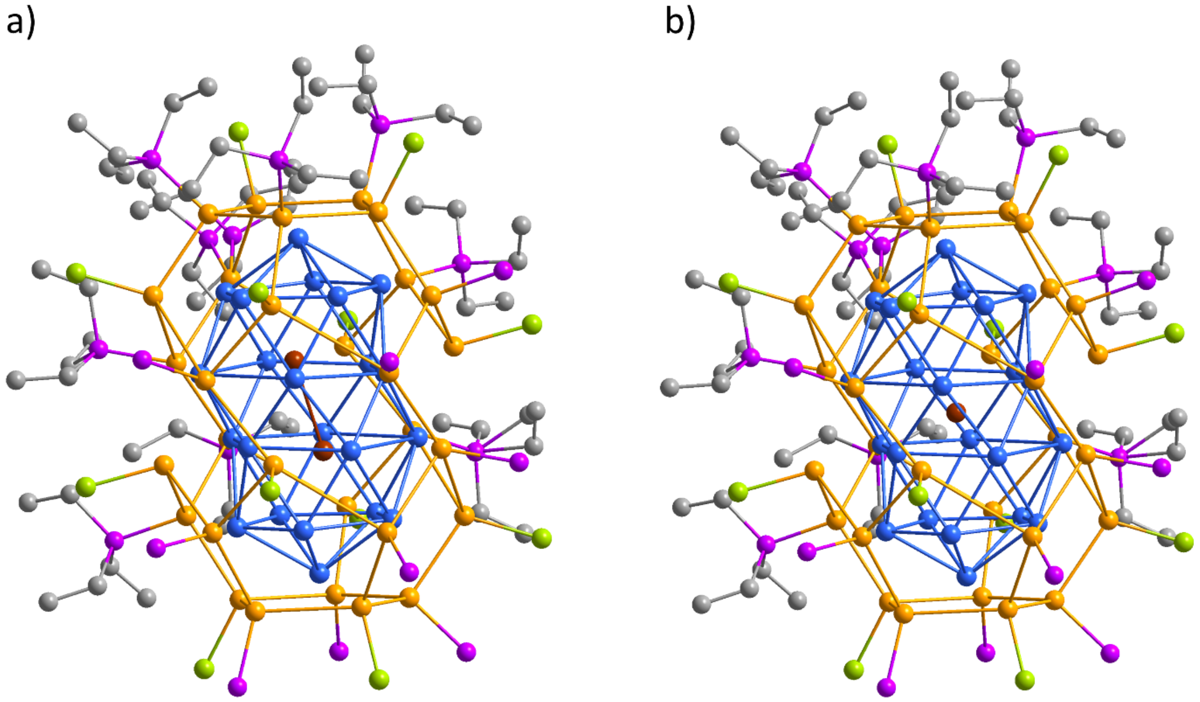


Figure S1: Comparison of a) $Au_{54}(Et_3P)_{18}Cl_{12}$ and b) $Au_{53}(Et_3P)_{18}Cl_{12}$. Au blue, gold and brown; P purple; Cl green; C grey.

Figure 2 in the main text showed the alternative structural discussion for $Au_{54}(Et_3P)_{18}Cl_{12}$. For clarity the phosphines and Cl atoms have been omitted. In Figure S2 the two alternatives are shown again with P and Cl atoms.

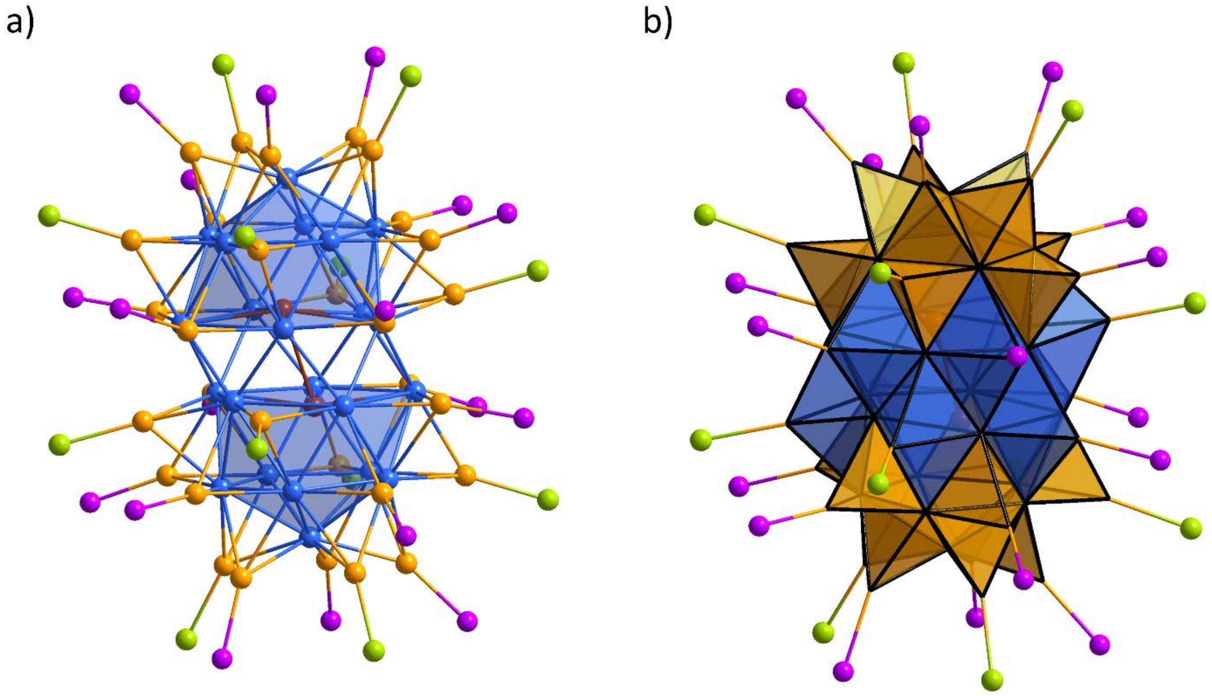


Figure S2: Alternative structural description for $Au_{54}(Et_3P)_{18}Cl_{12}$. a) inner Au_{22} shell with Au_2 dumbbell in the centre and 30 Au atoms binding on the exterior and b) inner Au_2 dumbbell surrounded by 20 tetrahedral Au_4X and ten rectangular pyramidal Au_5X units. Au blue, gold and brown; P purple; Cl green.

4. EDX measurements

EDX spectroscopy for $C_{108}H_{270}Au_{53.94}Cl_{12}P_{18}$. The data is shown in wt. %.

calculated Au : Cl : P = 91.5 : 3.7 : 4.8

found Au : Cl : P = 92.1 : 3.6 : 4.3

The data only shows minor differences. The difference of the ratio of Au : Cl : P between $C_{108}H_{270}Au_{53}Cl_{12}P_{18}$ and $C_{108}H_{270}Au_{54}Cl_{12}P_{18}$ is so small, that it was not possible to verify or prove false the aforementioned 6 % occupation of $Au_{53}(Et_3P)_{18}Cl_{12}$.

5. DLS measurements

For DLS measurements it has to be taken into account, that the Intensity of the measured signal is proportional to the diameter of the particle to the power of 6 ($I \alpha d^6$). This means for example that one particle with a diameter of 10 nm shows the same intensity as one million particles with a diameter of 1 nm. The concentration of 1 nm particles in this example is much bigger than the concentration of 10 nm particles.

The DLS measurements of $Au_{54}(Et_3P)_{18}Cl_{12}$ were performed in CH_2Cl_2. A filter with a pore size of 0.25 µm was used. The hydrodynamic diameter is 2.3 ± 0.3 nm. This is in good accordance with the end to end diameter of 2.2 nm derived from the molecular structure.

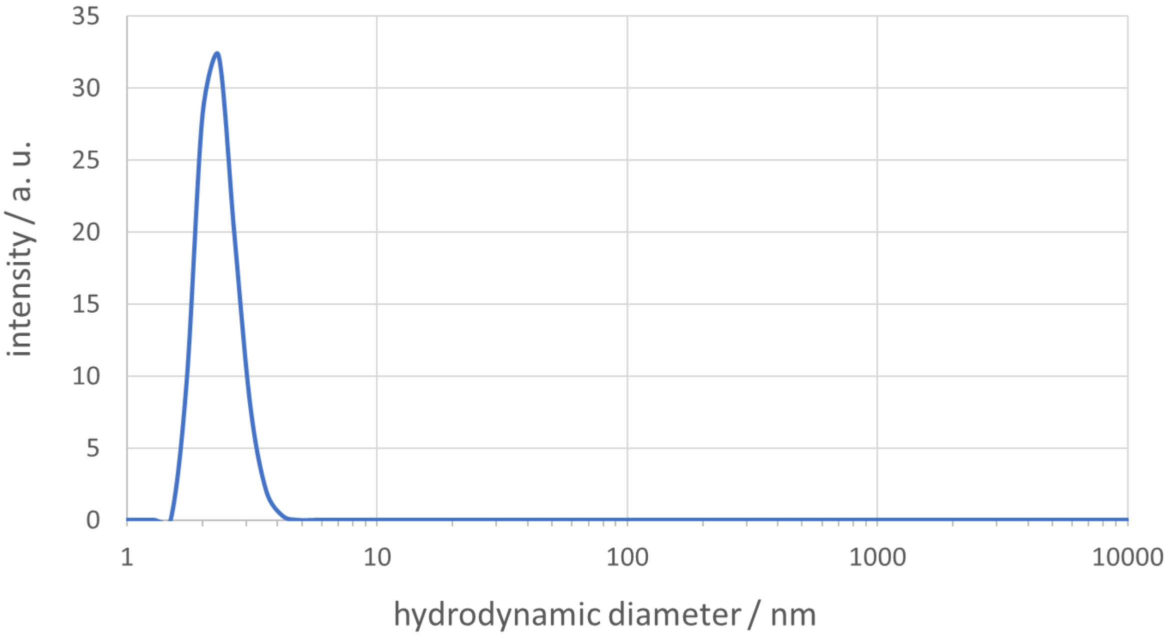
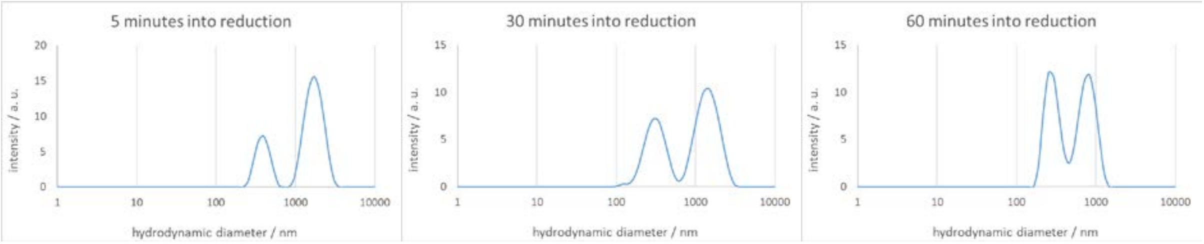


Figure S3: DLS spectrum of $Au_{54}(Et_3P)_{18}Cl_{12}$.

The following three measurements were conducted during the reduction. EtOH was used as a solvent. There was taken a sample after 5, 30 and 60 minutes. A filter with a pore size of 0.45 µm was used. As it can be seen there is no signal at small sizes between 1 and 10 nm but only a change in intensities between the two main signals. The bigger signals over 500 nm could be caused by the reduction process because it is very likely that the reduction is still going on.



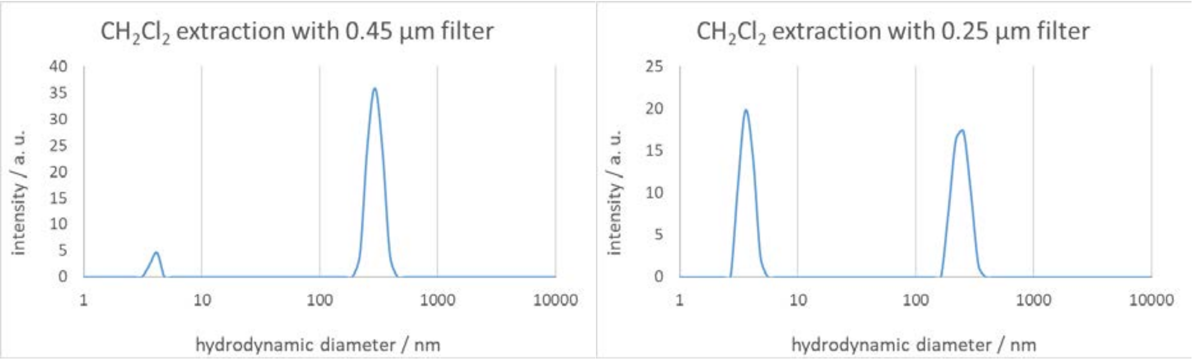
392.1 ± 77.0
1765 ± 447

319.6 ± 97.0
1476 ± 473

291.7 ± 66.5
795 ± 194

Figure S4: DLS spectra taken during reduction after 5 minutes (left), 30 minutes (middle) and 60 minutes (right). Beneath the spectra the different sizes (in nm) are shown.

The next two measurements were conducted after the end of the reaction. The solvent was removed and the remaining solid dissolved in CH_2Cl_2. Two different filter sizes, namely 0.45 µm and 0.25 µm, were used to see if the pore size of the filters is affecting the results. The different filters seem to only show minor effects.

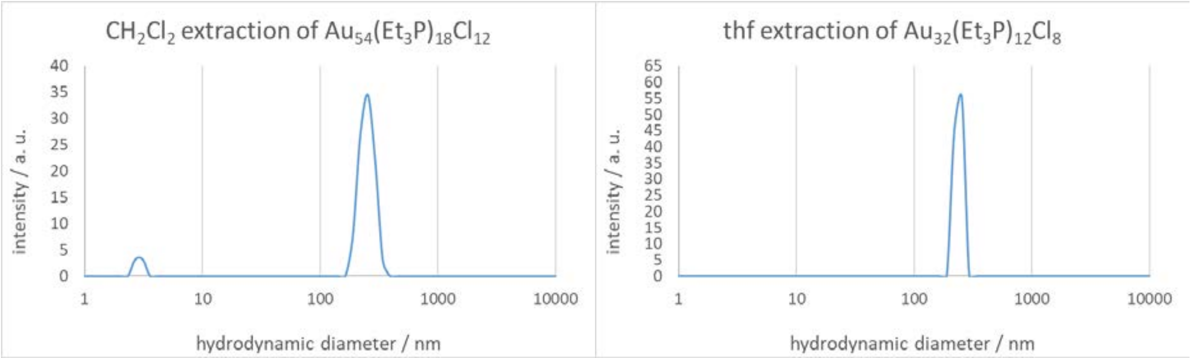


4.00 ± 0.27
297.7 ± 41.2

3.74 ± 0.47
244.8 ± 37.2

Figure S5: DLS spectra after reduction and the first extraction with CH_2Cl_2 using filters of a pore size of 0.45 µm (left) and 0.25 µm (right). Beneath the spectra the different sizes (in nm) are shown.

The last two measurements show the CH_2Cl_2 and thf extract where $Au_{54}(Et_3P)_{18}Cl_{12}$ and $Au_{32}(Et_3P)_{12}Cl_8$ could be found. A filter with a pore size of 0.45 µm was used. Whereas for $Au_{54}(Et_3P)_{18}Cl_{12}$ small and bigger particles can be found in the case of $Au_{32}(Et_3P)_{12}Cl_8$ only bigger particles can be found.



2.91 ± 0.21

251.9 ± 36.0

239.4 ± 17.3

Figure S6: DLS spectrum of the CH_2Cl_2 extract where after two weeks $Au_{54}(Et_3P)_{18}Cl_{12}$ could be found (left) and DLS spectrum of the thf extract where after two weeks $Au_{32}(Et_3P)_{12}Cl_8$ could be found (right).

6. UV/VIS measurements

To support the DLS measurements UV/VIS spectra were recorded to see if any changes in the optical properties were happening. The following three measurements were conducted during the reduction. EtOH was used as a solvent. There was taken a sample after 5, 30 and 60 minutes. As it can be seen there is one absorption band at around 510 nm for all three measurements.

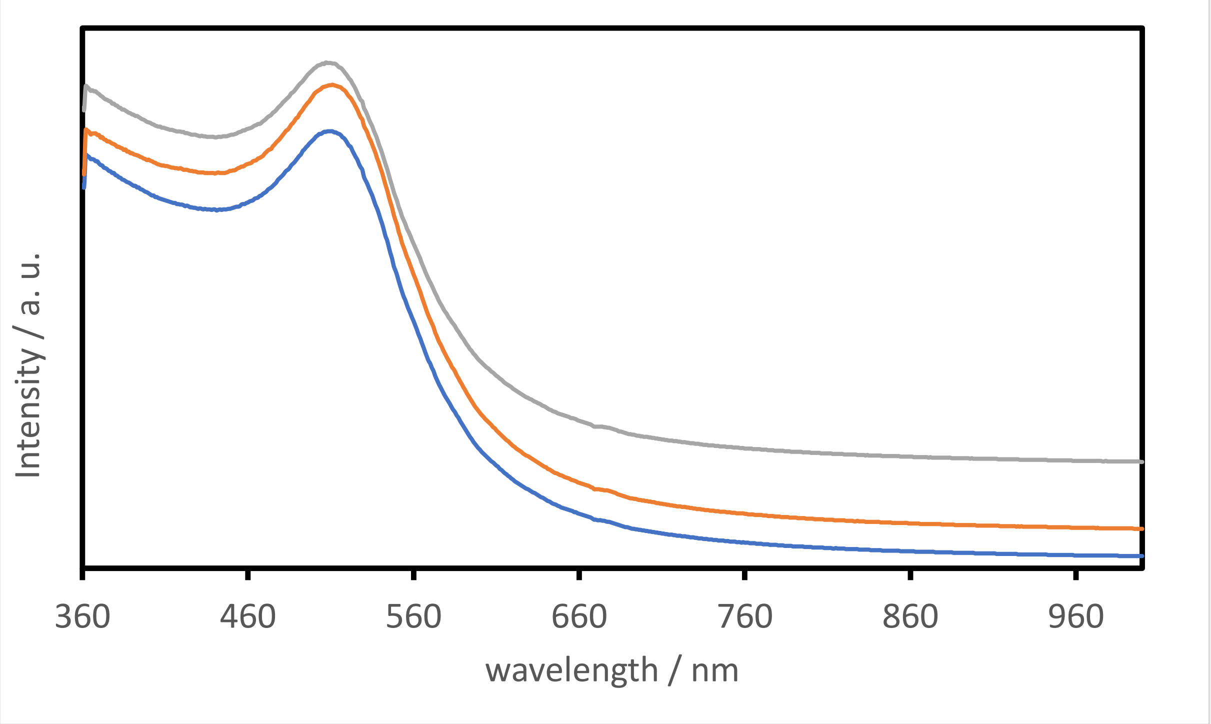


Figure S7: UV/VIS spectra taken during reduction after 5 minutes (blue), 30 minutes (orange) and 60 minutes (green) with an absorption band around 510 nm.

The next measurement was conducted after the end of the reaction (orange in figure S8). The solvent was removed and the remaining solid was dissolved in CH_2Cl_2 (blue in figure S8). The absorption band of the CH_2Cl_2 is still around 510 nm, but the shape of the spectrum changes after the extraction.

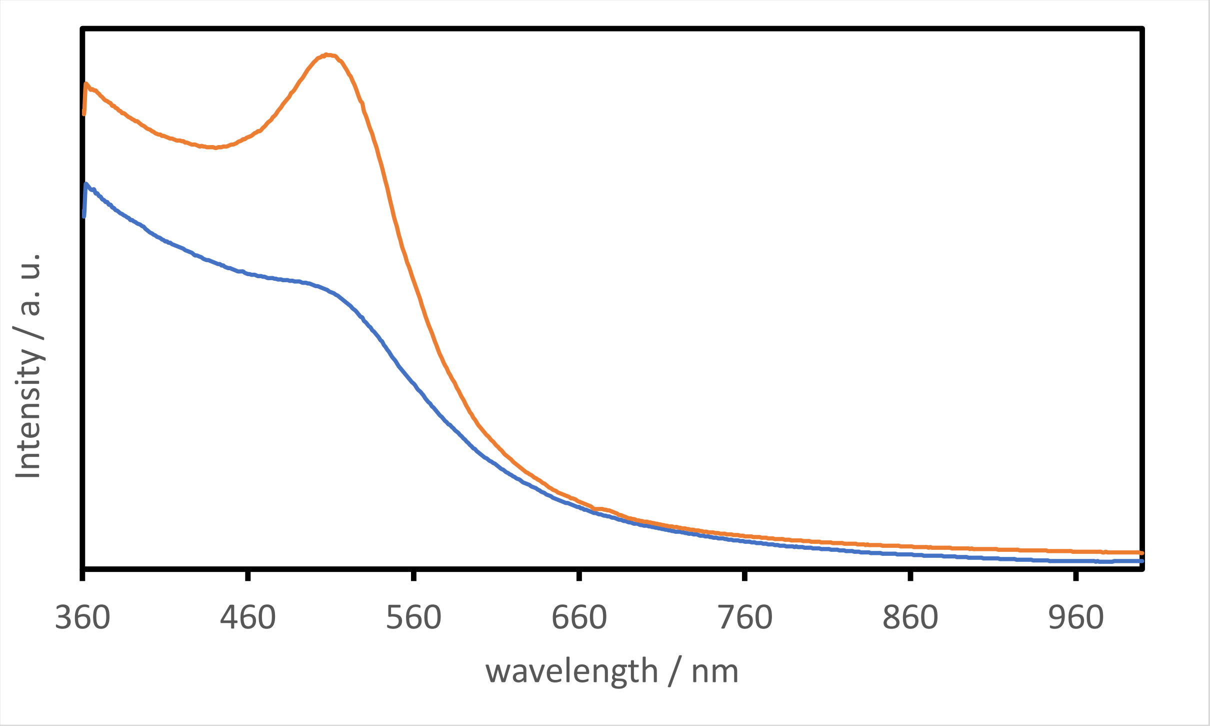


Figure S8: UV/VIS spectrum of the reaction solution after 60 minutes reaction time (orange) and UV/VIS spectrum of the reaction residue dissolved in CH_2Cl_2 (blue).

The following measurement (figure S9) shows the UV/VIS spectrum of the CH_2Cl_2 extract from which $Au_{54}(Et_3P)_{18}Cl_{12}$ could be isolated in crystalline form. For comparison the spectrum of dissolved crystals of $Au_{54}(Et_3P)_{18}Cl_{12}$ in CH_2Cl_2 is added (orange in figure S9). The absorption band of the CH_2Cl_2 extract shows an absorption band around 534 nm which is also found in the spectrum of dissolved crystals of $Au_{54}(Et_3P)_{18}Cl_{12}$. However, the other absorption band e.g. at 450 nm are not found in the spectrum of the extract.

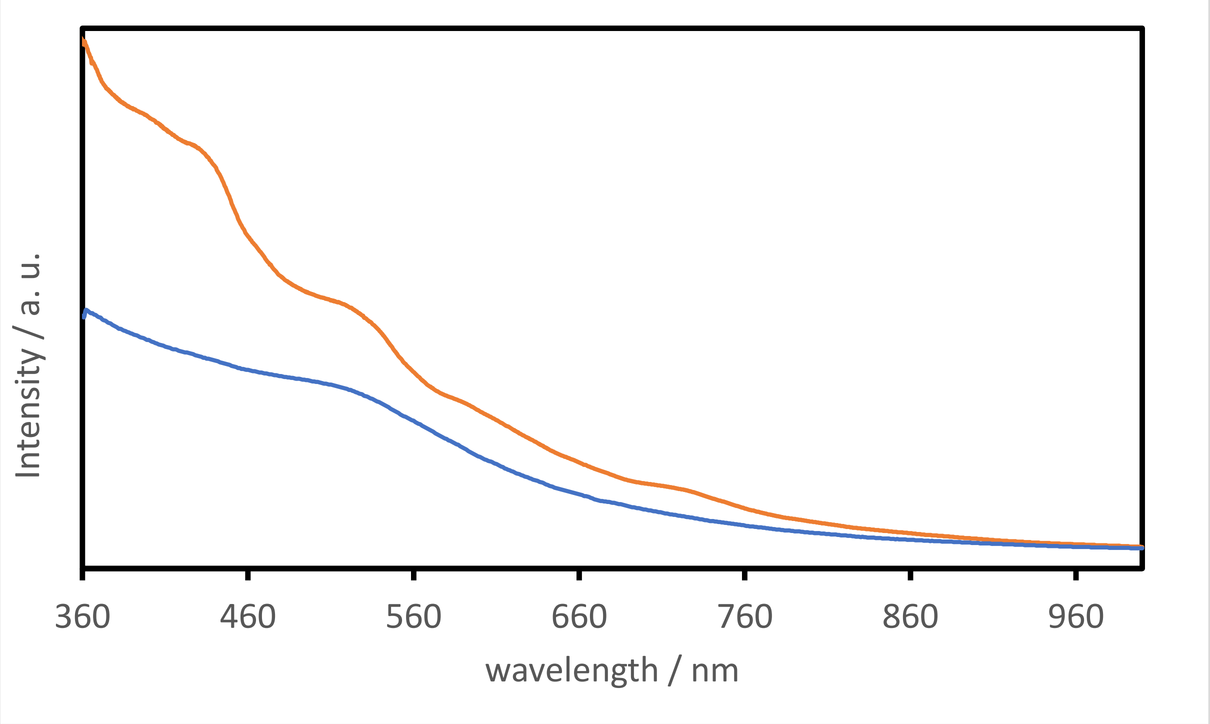


Figure S9: UV/VIS spectrum of the CH_2Cl_2 extract (blue) from which after two weeks $Au_{54}(Et_3P)_{18}Cl_{12}$ could be isolated in crystalline form. UV/VIS spectrum of dissolved crystals of $Au_{54}(Et_3P)_{18}Cl_{12}$ in CH_2Cl_2 (orange).

The last measurement shows the thf extract from which $Au_{32}(Et_3P)_{12}Cl_8$ could crystallized (blue in figure S10). For comparison the spectrum of dissolved crystals of $Au_{32}(Et_3P)_{12}Cl_8$ in CH_2Cl_2 is shown (orange in figure S10), showing significant differences.

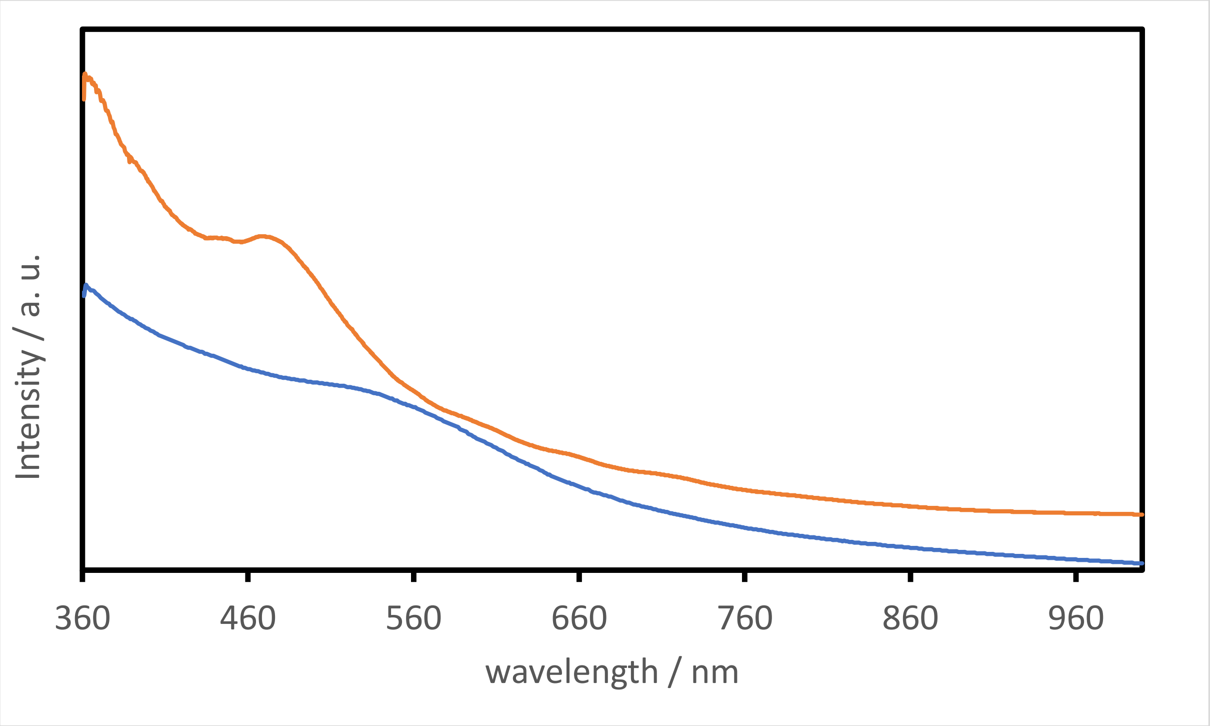


Figure S10: UV/VIS spectrum of the thf extract (blue) from which after two weeks $Au_{32}(Et_3P)_{12}Cl_8$ could be isolated in crystalline form. UV/VIS spectrum of dissolved crystals of $Au_{32}(Et_3P)_{12}Cl_8$ in CH_2Cl_2 (orange).

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[1] S. Kenzler, M. Kotsch, A. Schnepf, *Eur. J. Inorg. Chem.* **2018**, 3840-3848.

[2] (a) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122. (b) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3−8.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339−341.

[4] A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148 - 155.