Binding of a TICl Entity by a Tetrarod Tetrathiacalixarene Metalloligand via Metallophilic Interactions


Dedicated to Professor Heinrich Lang on the occasion of his 65th Birthday

Abstract: The successive auration of p-tert-butyltetramercap-totetraethylcalix[4]arene, H₂(MTC[4]), with gold(I) phosphine units was investigated. Through deprotonation with NaOMe, followed by salt metathesis reactions with (PR₃)AuCl (R = Me, Ph) complexes with two and three [(PR₃)Au]⁺ moieties could be prepared and isolated, namely [(Ph₃PAu)₂H₂(MTC[4])] and [(Me₃PAu)₂H₂(MTC[4])]. In [(Me₃PAu)₃H(MTC[4])] two gold atoms already come close enough to undergo aurophilic interactions. To introduce a fourth [(PR₃)Au]⁺ entity TIOEt had to be used for the deprotonation, which led to the finding that four gold atoms organised by the (MTC[4])⁺ coordination platform are able to bind and stabilize a TICl entity, yielding [(Me₃PAu)₄TICl(MTC[4])]. As evidenced by structural and theoretical investigations the binding occurs through strong metallophilic interactions, which lead to photoluminescence at low temperatures.

Introduction

Calixarenes have a lot of potential in various different areas of research and they have also raised significant interest in the field of coordination chemistry.[1,2] The parent calix[4]arene features four phenol units linked by four methylene bridges to result in the typical chalice structure. In 1999 a variant was reported – p-tert-butyltetramercaptopotetraethylcalix[4]arene (H₂(MTC[4])) – where the methylene units are replaced by S atoms (leading to additional coordination sites) and the OH by SH functions.[3–5] However, thus far this representative has only rarely been employed in coordination chemistry, presumably because the synthesis is much more demanding and the thiol units are prone to oxidation. Hence, only a hexanuclear mercury complex,[6] dinuclear iridium/rhodium complexes with a 1,2-alternate conformation[6] and dinuclear tungsten/molybdenum complexes[6] have been reported until now.

Recently, we investigated the copper(I) chemistry of H₂(MTC[4]) and found that [(Ph₃PCu)₄(MTC[4])] complexes are rather stable entities and are formed independently of the stoichiometry between ligand and metal precursor.[7] In the absence of phosphine co-ligands [Cu₄(MTC[4])] units are formed as well and subsequently stabilize by aggregation to a hexamer with a hollow ball structure.[7]

Gold(I) ions also have a high affinity towards S donors and at the same time they are known to undergo aurophilic interactions. Hence, we were interested to investigate, whether in this case it is possible to control the number of Au⁺ ions coordinated by H₂(MTC[4]) by using different amounts of gold(I) precursor, and what the consequence with regard to metal-metal interactions would be.

Results and Discussion

As gold precursors we initially tested (Me₃S)AuCl, (OC)AuCl and AuCl. AuCl acted as an oxidant for the thiol groups converting them into disulfide units. The reactions with (Me₃S)AuCl and (OC)AuCl led to the precipitation of white solids, which due to their low solubility could not be identified.

Finally, (Ph₃P)AuCl was chosen as the precursor, bearing a strongly binding phosphate ligand that was envisaged to reduce the oxidation potential of the gold(I) ions (thus avoiding disulfide formation) and to stabilize at the same time the gold complexes, once formed.

In first attempts a dinuclear gold(I) complex was targeted. Hence, H₂(MTC[4]) was deprotonated with two equivalents of NaOMe and subsequently treated with two equivalents of (Ph₃P)AuCl in THF. After removal of all volatiles, extraction with CH₂Cl₂ and addition of n-pentane, led to crystals of the product, which could be investigated by X-ray diffraction, revealing the structure of [(Ph₃PAu)₂H₂(MTC[4])] (Figure 1 and Scheme 1). The calixarene ligand has adopted a pinched-cone structure, where the two aryl thiolate units, which coordinate the gold atoms,
It turned out to be difficult to completely remove the NaCl that was concomitantly formed in the reaction depicted in Scheme 1. Therefore, the elemental analysis shows some deviations, however, the $^{31}P(1^1H)$-NMR spectrum of ([Ph$_3$PAu]$_2$H$_2$(MTC[4])) exhibits a single signal at 36.6 ppm, excluding contamination by other complexes.

Attempts to increase the number of gold atoms on the thiol/thioether framework of H$_4$(MTC[4]) from two to three by offering three equivalents of (Ph$_3$P)AuCl led to a mixture of ([Ph$_3$PAu]$_2$H$_2$(MTC[4])) and the desired trinuclear complex ([Ph$_3$PAu]$_3$H(MTC[4])), likely because there is steric repulsion between the bulky phosphine ligands. Hence, (Me$_3$P)AuCl was employed as the gold precursor, which was added to a solution of H$_4$(MTC[4]) in THF after deprotonation with three equivalents of NaOMe. After the removal of all volatiles the residue was extracted with CH$_2$Cl$_2$ to remove the formed NaCl and single crystals suitable for diffraction analysis could be grown by layering a toluene solution with n-pentane. This provided the structure of ([Me$_3$PAu]$_2$H(MTC[4])) as shown in Figure 2 and Scheme 1.

As before, the calixarene ligand adopts a pinched-cone conformation. Three thiolate groups coordinate gold atoms, which are additionally ligated by one phosphate ligand each. Au1 and Au3 additionally interact with a thioether group weakly (2.8686(13) and 2.9917(14) Å), so that again a T-shaped coordination sphere results, while Au2 is coordinated linearly. However, Au2 undergoes an aurophilic interaction with Au3 at a typical distance of 3.0667(3) Å. This is interesting, as in principle Au2 would also have the opportunity to interact with a thioether function, similar to the other two gold atoms, if it dismisses the aurophilic interaction. Apparently, even this very weak bonding stabilizes the system to the larger extent than a thioether contact would. The $^{31}P(1^1H)$-NMR spectrum of ([Me$_3$PAu]$_2$H(MTC[4])) dissolved in THF-$d_8$ showed two signals at -7.7 and -8.6 ppm in the ratio 2:1. Considering that the aurophilic interaction is more prominent than the interaction with the thioether groups, this suggests that the structure persists in solution and leads to one resonance corresponding to the two phosphine ligands bound to the two gold atoms involved in the aurophilic interaction (P1 and P2) and one for the remaining one (P3).

![Figure 1. Molecular structure of ([Ph$_3$PAu]$_2$H$_2$(MTC[4]))](image1)

All hydrogen atoms, apart from those connected to sulfur, as well as co-crystallized molecules of DCM have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–P1 2.262(2), Au2–P2 2.252(2), S4–H4 1.27(8), S8–H8 1.17(8), Au1–S2 2.3112(18), Au1–S1 2.920(2), Au2–S6 2.3045(19), Au2–S5 2.986(2); P1–Au1–S2 165.23(7), P2–Au2–S6 170.22(7), P1–Au1–S1 113.54(8), C5–S4–H4 100(4), C29–S9–H9 86(4).
Aiming at a tetranuclear complex it was obvious to deprotonate $H_4[MTC(4)]$ now with four equivalents of NaOMe followed by treatment with (Me$_3$PAu)Cl. However, the deprotonation led to a turbid solution, probably as the resulting [Na$_4$MTC(4)] is only sparingly soluble and precipitates partly. The subsequent reaction of the suspension with the gold precursor only led to a product mixture. Consequently, the deprotonation was performed with four equivalents of TIOEt, which resulted in a clear, yellow solution. Subsequently, four equivalents of (Me$_3$PAu)Cl were added and after workup [(Me$_3$PAu)$_2$TICI(MTC(4))] could be isolated in 40% yield (Scheme 2). The molecular structure in the solid-state was revealed by single crystal X-ray diffraction (Figure 3).

As in the di- and trinuclear complexes, discussed above, two of the aryl rings are oriented almost parallel to each other, while the other two are almost orthogonal (85.6°), so that the thiolate groups are pointing toward the interior of the complex. Each of the four gold atoms is coordinated by two thiolate functions, a thioether donor as well as a phosphine ligand, similarly as in the case of the Cu ions in the compound [(Ph$_2$PCu)$_3$(MTC(4))].

However, while in the latter the Cu atoms have a tetrahedral coordination sphere with Cu-S distances that were all similar, in [(Me$_3$PAu)$_2$TICI(MTC(4))] a see-saw type arrangement is found. Each thiolate unit exhibits one short (2.3257(15)–2.3558(17) Å) and one long (2.9427(15)–3.0083(17) Å) contact to the surrounding gold atoms, which undergo only weak interactions with the thioether units (2.9084(16)–3.0772(15) Å). A unique feature of the structure is the thallium(I) chloride moiety, which – after formation in course of the salt metathesis reaction as shown in Scheme 2 – is bound on top of the gold platform through metallophilic interactions with three gold atoms.

In most known structures with gold(I)-thallium contacts, a basic gold(I) complex entity binds an acidic (sometimes naked) thallium(I) ion, based on the atomic distances which are shorter than the sum of the atomic radii. Laguna and coworkers pioneered the synthesis of a variety of coordination polymers based on these metallophilic interactions and further groups made important contributions to the development of the field; studies concerning the structures and properties in dependence on the ligation of the metals revealed valuable insights. However, the number of non-polymeric structures in the CCDC data where a thallium(I) ion is bound through strong metallophilic bonds by two (or even more) gold atoms is still quite limited.

Notably, binding of a neutral, intact TIX unit (X = monovalent anion) as in [(Me$_3$PAu)$_2$TICI(MTC(4))] via the Tl atom and with a terminal X ligand, is to our knowledge unique. Disordering of the Tl and the Cl atoms (see Supporting Information, Figure S5) suggests that the TICI entity is quite mobile between the gold atoms and can readily move from one side (Au3) to the other side (Au4) (and the observation of just
two signals of equal intensity in the $^{31}$P($^1$H)-NMR spectrum (see Supporting Information, Figure S3) is consistent with this). In the following, only the structure with Tl1a and Cl1a in the positions as shown in Figure 3 (main occupancy) is discussed further.

The lengths of the bonds between the Tl atom and the gold centres that are involved in the metallophilic interactions (Au1–Tl1A 3.0892(12), Au2–Tl1A 2.9556(13), Au3–Tl1A 3.225(5) Å) are shorter than the van-der-Waals radii between Au(I) and Tl(I) (3.62 Å), while the distance to Au4 is longer than that. The contacts to Au1 and Au2 are even shorter than the metallic radii (3.14 Å), which points to strong metallophilic interactions, while the one with Au3 has medium strength. This is in agreement with the analysis of other structures with Au–Tl interactions.

The UV/Vis spectrum of [(Me$_3$PAu)$_4$TlCl(MTC[4])] does not show any distinct features and the onset of absorption (see Supporting Information, Figure S4) at approximately 425 nm corresponds to the yellow colour of the complex. In the past, some of the compounds featuring strong Au–Tl interactions were found to exhibit interesting bright visible luminescent products. In order to investigate the interaction between the TlCl entity and the Au atoms more closely, theoretical investigations were performed. The calculations were carried out using the Molpro code. The details of the calculations, obtained data and related discussion are provided in the Supporting Information.

At the PBE0-D3 level, the overall interaction energy between the TlCl entity and [(Me$_3$PAu)$_4$TlCl(MTC[4])] is $\Delta E_{\text{int}} = -32.5$ kcal/mol. It consists of the intermolecular interaction energy between the fixed-structure entities $\Delta E_{\text{int}}$ of $-44.5$ kcal/mol and the relaxation energy $\Delta E_{\text{relax}}$ of +12 kcal/mol (see Eqs. (S1)–(S3) in the Supporting Information for definition). This value is in accord with what one expects from a metallophilic bond energy, which, for example, for gold atoms usually falls in the range of 5–15 kcal/mol per bond. The PBE0-D3 optimized structure closely resembles the experimental one: the four optimized Tl–Au bond lengths are Tl–Au1: 2.98 Å, Tl–Au2: 3.00 Å, Tl–Au3: 3.11 Å, and Tl–Au4: 3.66 Å, which nicely matches the trend of the experimental structure, though the distances on average are slightly shorter. However, the potential seems to be quite shallow here, as the PBE–D3 intermolecular interaction energies $\Delta E_{\text{int}}$ (which reflects the pure interaction between the individual entities, see Eq. (52) for definition) based on the experimental and computationally relaxed structures differ only in the sub-kcal/mol region (see Table S2). This is in line with the experimental observation of high mobility of the TlCl entity with respect to the gold atoms, as noted above. The PBE0-D3 estimate for $\Delta E_{\text{int}}$ is in a very good agreement with the local CCSD(T) value, which suggests that this method provides a reliable description for this system.

In the following we analyse, which physical effects contribute to bonding in this system. In metallophilic interactions, van der Waals dispersion is known to play a substantial role. This system is no exception: the intermolecular local MP2 correlation contribution is as much as $-40$ kcal/mol, $-21$ kcal/mol of which can be associated with the dispersion interaction between the Tl and Au atoms (see Table S3).

Previous computational studies of Au–Tl model clusters at the HF/MP2 level revealed quite a wide range of interaction energies: from 3 kcal/mol to more than 100 kcal/mol, depending on the cluster. The main reason for such a scatter is variation in the electrostatic interaction. On the one hand, for some clusters a charge transfer was observed, leading to formation of an ionic bond. In these cases, the HF part of the interaction energy, which contains the electrostatic effects, is strongly attractive and constitutes up to 90% of the overall interactions.

The UV/Vis spectrum of [(Me$_3$PAu)$_4$TlCl(MTC[4])] dissolved in 2-methyltetrahydrofuran (MeTHF) at temperatures between 77 K and 295 K. While at temperatures above 110 K there is hardly any emission visible, two broad emission bands start to emerge around 550 nm and 700 nm at 100 K.

Upon further cooling both shift to lower wavenumbers and gain intensity; finally, at 77 K the most prominent band is found at 520 nm. Such a temperature dependence is not unusual for heterometallic gold compounds of this type, but the origin is difficult to ascertain. We did not determine the quantum yield, as the complex in solution is not inert towards the surroundings under such dilute conditions and partly decomposes to non-luminescent products.

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Interaction energy. In other systems, the electrostatic component is weaker. Then due to the exchange repulsion, the HF contribution is only slightly attractive or even repulsive, and binding becomes dispersion dominated. This is what is also observed in our case. According to DFT-SAPT (see Supporting Information for details), the electrostatic interaction in our system is attractive and with ~84 kcal/mol quite prominent, but this attraction is completely compensated by the exchange repulsion: +91 kcal/mol.

In addition to the electrostatic and dispersion effects, there seems to be a weak covalent interaction in our system, most likely involving the lone-pair electrons of Tl. This follows from the drop in the kinetic energy at larger Tl–Au distances (see Figure S8), which is an indication of an onset of a covalent bond.[26] Finally, we note that the four Me₃P groups "hold" the TICI entity by means of the exchange repulsion (see Figure S7).

Conclusion

In summary, we have shown here that a successive introduction of gold ions onto the tetracaptothiocarboxylarene coordination platform is possible. The tetranuclear gold complex formed upon using four equivalents of gold precursor was found capable of acting as a metalloligand for a molecular TlCl entity upon using four equivalents of gold precursor was found capable of acting as a metalloligand for a molecular TlCl entity formed during the metalation process through salt metathesis. The TICI entity is bound via comparatively strong metallophilic interactions, which lead to photoluminescence at low temperatures.

Experimental Section

General Considerations: All manipulations were carried out under an argon atmosphere using Schlenk techniques or in gloveboxes under argon atmosphere maintained below 1 ppm of O₂. Solvents were purified in an MBraun solvent purification system and stored under argon atmosphere over activated molecular sieves. H₃[MTCl(4)] was synthesized according to literature procedures.[3b,21] Instead of column chromatography, recrystallization from dichloromethane was employed to purify the compounds formed during the metalation process through salt metathesis. ATR-IR spectra were recorded on a Bruker Alpha spectrometer with an ATR sampling unit under argon atmosphere. ATR-IR spectra were recorded on a Bruker Alpha spectrometer with an ATR sampling unit under argon atmosphere. ATR-IR spectra were recorded on a Bruker Alpha spectrometer with an ATR sampling unit under argon atmosphere.

Deposition numbers 2012942, 2012941 and 2012943 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the CCDC Cambridge Crystallographic Data Centre.

Synthesis of [(Me₃P)Au]₂[H₃[MTC(4)]]: H₃[MTC(4)] (100.0 mg, 127 μmol, 1 equiv.) was dissolved in 5 mL THF and NaOMe (13.7 mg, 254 μmol, 2 equiv.) was added. The solution was stirred for 5 min, thus changing color to light yellow. (Ph₂)₂P=Cl (125.9 mg, 254 μmol, 2 equiv.) was added yielding in a clear light yellow solution, which was stirred for 2 h in the dark. Subsequently, the volatiles were removed under vacuum and the residue extracted with 60 mL of dichloromethane. The solution was reduced to ca. 8 mL, and afterwards subjected to a centrifugation and decantation. Again, the volatiles were removed and the residue dried under vacuum. 152.0 mg (89 μmol, 70%) of [(Me₃P)Au]₂[H₃[MTC(4)]] were thus isolated as a colorless powder. Single crystals for X-ray diffraction were grown through layering of a concentrated solution in dichloromethane with n-pentane.

1H-NMR (500 MHz, THF-d₈): δ = 7.73–7.48 (m, 16H, Ar–H), 7.48–7.28 (m, 17H, Ar–H), 7.27–7.05 (m, 3H, Ar–H/SH), 6.92 (s, 3H, Ar–H), 6.42 (s, 1H, –SH), 1.35 (s, 18H, –C(CH₃)₂), 0.88 (s, 18H, –C(CH₃)₃) ppm. 13C-NMR (75 MHz, THF-d₈): The 13C NMR data were derived as far as possible from the HSQC and HMBC spectra. However, in particular the resonances of the quaternary C atoms belonging to the aryl rings could not be determined, also due to the low solubility in THF. δ = 146.6 (Ar–C), 144.5 (Ar–C), 135.0 (PPh₃–C), 134.8 (PPh₃–C), 131.7 (Ar–C), 130.6 (Ar–C), 129.6 (PPh₃–C), 129.5 (PPh₃–C), 34.8 (–C(CH₃)₂), 34.3 (–C(CH₃)₃), 31.5 (–C(CH₃)₂), 31.4 (–C(CH₃)₃), 31.3 (–C(CH₃)₂) ppm. 31P{1H}-NMR (202 MHz, THF-d₈): δ = 36.57 (s ppm). ATR-IR (solid): ν = 3056 (w), 2958 (w), 2413 (w, v–H), 1574 (w), 1478 (m), 1461 (w), 1435 (m), 1391 (m), 1375 (m), 1359 (m), 1248 (m), 1181 (w), 1151 (m), 1098 (m), 1028 (m), 998 (w), 873 (m), 785 (w), 745 (s), 709 (s), 691 (vs), 637 (w), 618 (w), 603 (w), 556 (w), 536 (vs), 501 (vs), 446 (m) cm⁻¹. An elemental analysis showed that despite the extraction with dichloromethane and subsequent crystallization, still two equivalents of NaCl remained in the bulk substance. C₉₉H₆₅Au₂Cl₄Na₃P₃S₆ (M = 18187.70 g/mol): Calc. C 50.19%; H 4.21%; S 14.10%; Found C 50.66%; H 4.31%; S 14.03%.

Synthesis of [(Me₃P)Au]₂[H₃[MTC(4)]]: [(Me₃P)Au]₂[H₃[MTC(4)]] (150.0 mg, 191 μmol, 1 equiv.) was dissolved in 40 mL THF and NaOMe (30.9 mg, 573 mmol, 3 equiv.) was added. After stirring for 5 min the solution was cloudy and light yellow. The addition of solid (Me₃P)AuCl led to a clearing within 5 min. Subsequent to further stirring for one hour in the dark the volatile components were removed in vacuo. The residue was extracted with 4 mL DCM and the resulting suspension centrifuged. The supernatant was decanted and all volatiles removed. 89.3 mg (41.2 μmol, 22%) of [(Me₃P)Au]₂[H₃[MTC(4)]] were isolated in form of a colorless powder. Crystals suitable for X-ray diffraction were grown through layering of a concentrated solution in toluene with n-pentane.
466 (m) cm⁻¹. C₇H₂₅AuP₅S₅ (M = 1601.44 g/mol): Calcd.: C 36.75%; H 4.53%; S 16.02%. Found: C 37.03%; H 4.47%; S 15.70%.

**Synthesis of [(Me₅P)Au(TICI(MT4))]:** H₄(TICI(4)) (50.0 mg, 63 μmol, 1 equiv.) was dissolved in THF. Thalliummethanolate (63.5 mg, 254 μmol, 4 equiv.) was added while stirring the solution, which thus changed color to yellow. A suspension of (Me₅)PAlCl₃ (78.55 mg, 254 μmol, 4 equiv.) in THF was added. A suspension of a colorless precipitate in a yellow solution resulted, which was stirred for 16 h in the dark. This led to the additional precipitation of a yellow solid. Solution and solid were separated by decanting and the yellow part of the solid extracted with 30 mL of THF. The resulting solution was combined with the decanted solution and all volatiles were removed in vacuo. The residue was recrystallized by Projekt DEAL.

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Conflict of Interest

The authors declare no conflict of interest.

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