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Conformational control of nonplanar free base porphyrins: towards bifunctional catalysts of tunable basicity

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COMMUNICATION

Selective Formation of a Supramolecular Coordination Complex in the Nanometre Scale with a Ferrocene-based Phospholane Ligand†

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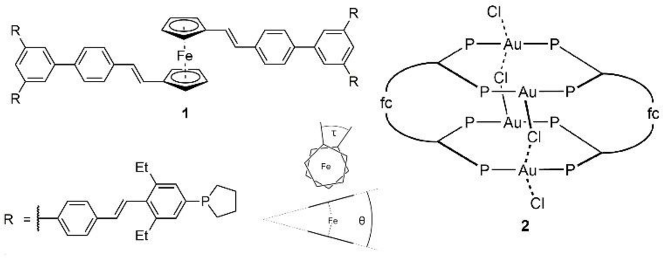
A straightforward synthesis of the tetradentate phospholane ligand 1 is reported. The 2:1 [M:L] reaction of 1 with [AuCl(tht)] (tht = tetrahydrothiophen) resulted in a 4:2 [M:L] supramolecular coordination complex 2 where two ligands 1 are bridging four gold(I) cations. The formation of 2 can be rationalised via a geometrical analysis of the ligand. The coordination mode of the gold atoms was evaluated based on a CSD search, revealing the geometrical changes for a transition from linear to trigonal planar coordination environment.

Supramolecular Coordination Complexes (SCCs), constructed from polydentate organic ligands and transition metals by reversible metal-ligand bonds, are a field of continuously growing interest since they provide a wide range of applications, such as in sensing,[1] inclusion,[2] and catalysis[3]. There are numerous examples for ferrocene-bearing SCCs, and a review on this topic has recently been published by Yang and co-workers, also giving a proposal for the classification of the different types of SCCs.[4] Even though there is a large variety of ligands available, there are only few examples for SCCs containing exclusively polyphosphine ligands. Phosphines require a higher synthetic effort in handling and, due to rotation around the P–C bond, various orientations of the phosphine ligand and its lone pair of electrons have to be considered, resulting in a lower predictability and selectivity of the formed coordination complexes. One possible attempt to limit this variety is to use gold(I) as metal cation, since it almost exclusively favours a linear coordination mode. Literature provides examples of selectively formed SCCs in the shape of macrocycles, tetrahedra, helices and polymeric structures based solely on phosphine ligands and gold(I).[5–9]

Even though phospholane ligands possess unique properties for chiral catalysis and are also referred to as privileged ligands,[10] their coordination chemistry with gold(I) remains largely unexplored. Recently, we have shown that highly flexible bis-phospholane ligands based on solely aliphatic alkylene backbones react selectively with [AuCl(tht)] (tht = tetrahydrothiophene) to give nanotubes, polymeric chains and 2:2 [M:L] dimetallamacrocycles, $[Au_2Cl_2\{\mu\text{-}(C_4H_8P)(CH_2)_n(PC_4H_8)\text{-}\kappa^2P,P'\}_2]$ (n = 5, 7, 9, 11).[11] Using a bis-phospholane, in which the central part of the alkylidene spacer had been replaced by a ferrocenylene moiety resulted in formation of macrocyclic 1:1 [M:L] complexes.[12] In both complexes, the gold(I) cation is in the usual linear coordination environment but additionally exhibits an interaction with the chloride counterion ([2+1] coordination). When the number of phospholane moieties is increased to three (tris-phospholane), a coordination polymer of gold(I) chloride instead of a molecular complex was obtained.[13] Nevertheless, molecular gold(I) complexes can be obtained with suitable tridentate phosphines, as we have recently shown.[14–16] To further explore the coordination chemistry of polyphospholane ligands, we have now expanded the ligand structure to a tetrakis-phospholane (**1**) and have studied its coordination chemistry with gold(I).



Scheme 1. Structural formula of ligand **1** and schematic representation of the observed supramolecular 4:2 [M:L] coordination complex **2**.

Scheme 1 shows the structural formula of **1** which was prepared in a good overall yield starting from 1,3,5-tris{*p*-(diethoxyphosphonylmethyl)phenyl}benzene and 4-bromo-2,6-diethylbenzaldehyde (details in SI). In order to obtain an SCC where every gold atom is coordinated by two phosphorus atoms ([M:L] ratio 2:1), ligand **1** was reacted with two equivalents of [AuCl(tht)] in dichloromethane (DCM). Crystals of

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complex **2** could be obtained from the resulting dark red solution by gas-phase diffusion within a few days (details in SI). Complex **2** crystallised in the triclinic space group $P\overline{1}$ with one molecule in the unit cell (Z = 1) and is located on a crystallographic inversion centre. X-ray analysis revealed the formation of a 4:2 [M:L] coordination complex $[Au_4Cl_4(\mathbf{1})_2]$, in which two ligands **1** are bridging four gold(I) cations, thus resulting in a cage structure (Scheme 1, Figure 1). The complex has a remarkable size as demonstrated by diameters (distance between marginal atoms) of about 3.8 nm (Fe1···Fe1′) and 3.3 nm (Au2···Au2′). According to the classification of Yang et al.,[4] complex **2** represents an *exo*- as well as *edge*-functionalised bis-ferrocenyl-based metallacycle. Even though several complexes are known where two gold(I) atoms are coordinated by two identical bis-phosphine ligands (see discussion *vide infra*), to our knowledge **2** represents the first complex where two tetrakis-phosphine ligands are coordinating four gold(I) cations forming an SCC.

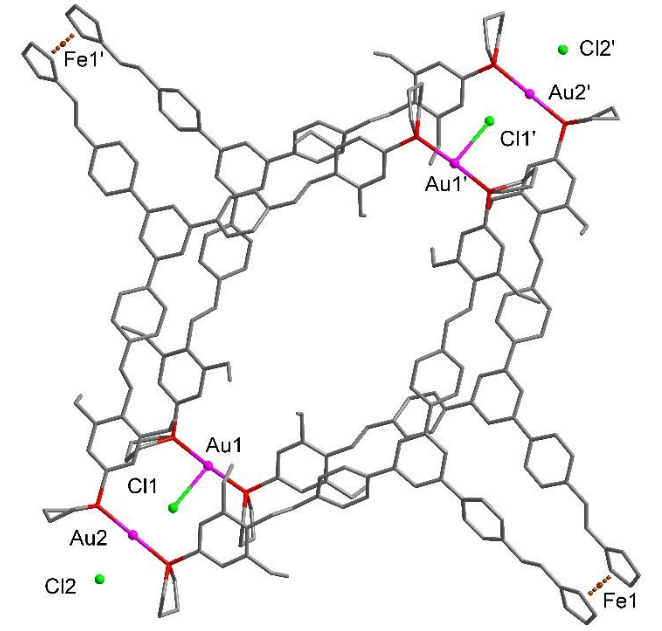

Figure 1. Molecular structure of **2**. Hydrogen atoms and disorders of ethyl groups as well as phospholane rings are omitted for clarity.

The close arrangement of the rigid Y-shaped branches of the ligand in **2** creates a large cavity inside the cage structure. These cavities form channels along the crystallographic [211] direction (Fig. S1) with an approximately rectangular size of about 2 Å x 5 Å. This arrangement in the crystal structure is stabilised by multiple intermolecular π-π-stacking interactions between the aromatic moieties of the supramolecular complexes. In these solvent-accessible channels, merely eight very poorly defined DCM molecules could be located during the X-ray structure refinement. Using the SQUEEZE routine implemented in PLATON for the final refinement (details in SI) indicated the presence of an additional 20 DCM molecules (thus 28 in total) which are completely disordered within these channels.

When removed from solution, crystals of **2**·28DCM rapidly lose the co-crystallised solvent, thereby also losing crystallinity within a few minutes, as confirmed by powder XRD measurements, showing only an amorphous phase. This amorphous substance was subsequently dried in vacuum and further analysed. Elemental analysis showed a C and H content which corresponds to complex **2** with 3 DCM molecules. This was also confirmed by MS-coupled TGA/DSC measurements (Fig. S6) which showed a mass loss of 5% until 198 °C (theoretical 5.3% for 3 DCM), and fragments with m/z 84, 86 and 88 (3 isotopic compounds due to presence of ^{35}Cl and ^{37}Cl) could be detected.

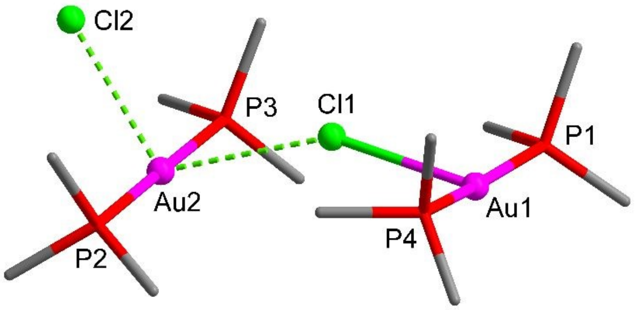

Figure 2. Detailed view of the coordination sphere of Au1 and Au2 in complex **2**. Hydrogen atoms and disorders in the phospholane units at P3 and P4 are omitted for clarity. Selected bond lengths and distances [Å] and angles [°]: Au1–P1 2.296(2), Au1–P4 2.295(2), Au2–P2 2.295(2), Au2–P3 2.306(2), Au1–Cl1 2.882(2), Au2···Cl1 3.309(2), Au2···Cl2 3.108(3), P1–Au1–P4 168.4(1), P2–Au2–P3 179.0(1), P1–Au1–Cl1 94.2(1), P4–Au1–Cl1 92.7(1), Cl1···Au2···Cl2 107.0(1).

Figure 1 displays the molecular structure of complex **2**. The cyclopentadienyl rings of the ferrocenylene (fc) moieties deviate significantly from coplanarity (Θ = 3.4°, Scheme 1) and furthermore show a slight torsional twist from an ecliptic conformation (τ = 4.2°) causing the two Y-shaped branches of the ligand (Scheme 1) to be slightly shifted and instead of being perfectly superimposed. Even though these conformational changes may be rather small they become substantial for the phospholane units due to the size of the branches of the ligand and thus set the right geometrical conditions for the coordination of the four gold(I) atoms. Both crystallographically independent gold(I) atoms are coordinated by two phosphorus atoms of two different ligands with Au–P bond lengths in the typical range of about 2.30 Å (Table 1).[11,12] Figure 2 shows a detailed view of the Au coordination sphere. The P–Au–P bond angles are 179.0(1)° and 168.4(1)° which clearly indicate a linear coordination environment of the gold(I) atoms but in case of the latter points to further interactions. In fact, the positions of the chloride ions show a correlation as the Au–Cl distance for the gold atom with the smaller P–Au–P bond angle is much shorter (Au1–Cl1 2.882(2)). This is conspicuously long, but was already observed for similar coordination compounds.[11,12] Conversely, the Au–Cl distance of the gold atom with almost perfectly linear P–Au–P bond angle is much longer (Au2···Cl2 3.108(3)) and can only be considered as an ionic interaction. A similar distance is observed to Cl1 (Au2···Cl1 3.309(2)) which thus bridges both gold atoms. The Au1···Au2 distance is about 6.0 Å and therefore clearly excludes the presence of aurophilic interaction.

This relationship between the P–Au–P bond angle and the Au–Cl distance is often observed in three-coordinate gold(I) bis-

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phosphine complexes. While the so-called *T-shaped* or [2+1] coordination mode of Au2 observed in **2** represents one end of the spectrum (with P–Au–P close to 180° and weak interaction with the halide), the *trigonal planar* coordination environment in compounds such as $[AuCl(PPh_3)_2]$[17] (with a P–Au–P bond angle far from 180° and a short gold-chloride bond) represents the other end. In contrast, the coordination environment of the second gold atom in **2** (Au1) and in fact of numerous other complexes reported in the literature lie between both these extremes. For example, Bowmaker *et al.*[18] described different polymorphs for complexes $[AuX(PCy_3)_2]$ (X = Cl, Br, and I) where the gold-halide bond length varies strongly. Based on their data, they proposed a linear dependency between the P–Au–P bond angle and the Au–X distance and furthermore explained the variation of the halide position with a stabilisation through weak interactions in the crystal structures, such as weak hydrogen bonds. As no such dependency is observed in compound **2**, we have conducted a comprehensive search in the Cambridge Structural Database (CSD) to ascertain to what extent these findings can be applied to related gold(I) bis-phosphine complexes with an $\{AuP_2\}$ motif involving a halide (X = Cl, Br, and I) as a third donor atom. The search and subsequent individual inspection of the results (comprehensive details in SI) gave 232 hits in 165 structures of which the P–Au–P bond angle, Au–X, Au–P as well as potential Au···Au distances were analysed.

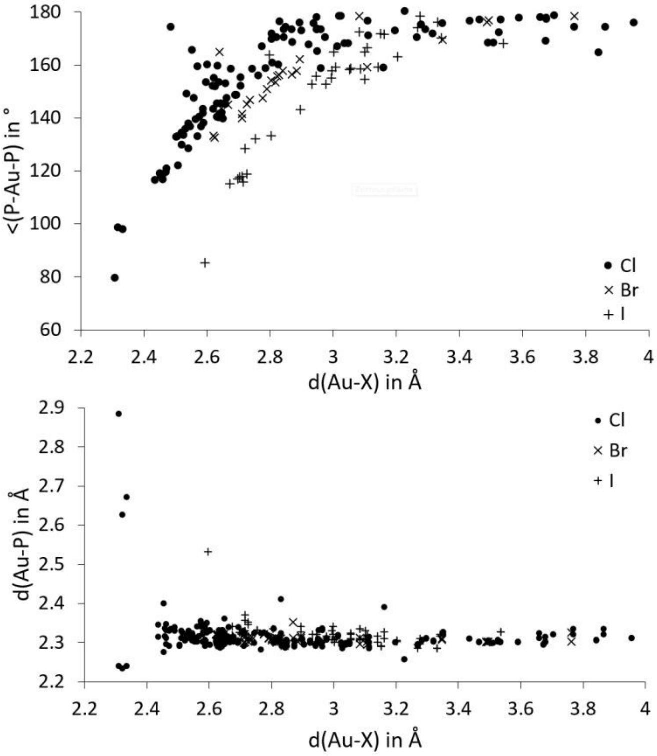

Figure 3. Results of the CSD search. Plot of the P–Au–P bond angles versus the Au–X distances (top) and plot of the Au–P bond lengths versus the Au–X distances (bottom).

In Figure 3 (top), the plot of Au–X distances versus P–Au–P bond angles demonstrates that the P–Au–P angle approaches 180° for longer Au-X bonds or distances. This dependency deviates significantly from linearity as was also speculated previously.[18] When examining individual structures, it seems in fact that intermolecular interactions, namely hydrogen bonds, are responsible for stabilising a halide position further away from the Au atom.[18–20] This is also true for the molecular structure of **2**·28DCM where the remote halide Cl2 forms two weak hydrogen bonds of type CH–Cl with H atoms of the phospholane groups. Furthermore, due to its vicinity to the void filled with solvent molecules, interactions with the DCM molecules can also be assumed.

In Figure 3 (bottom), the Au–X distance is plotted versus the respective Au–P distances. Obviously, there is neither any dependency at all between the two geometrical parameters nor any influence of the type of halide. The Au–P distances vary within a close range about 2.3 Å. The reason could be relativistic effects of gold[22–24] as suggested by ^{197}Au Mößbauer spectroscopy of selected complexes;[21] the Au–P bonding orbitals have largely s-character, Au–X mainly p-character, involving only negligible π-acceptor interactions.

Interestingly, when the Au–X distance falls below a critical value lying between 2.334 and 2.437 Å for Cl (no cases for Br and I), the coordination environment rearranges to a distorted T-shaped or distorted trigonal-planar mode involving one very long Au–P distance. This is observed for merely three complexes[25,26], [AuCl(L)] with L = 1,2-bis[bis(2-methylphenyl)phosphino]benzene (VIJHAA) and $[(AuCl)_n(\{cyclo\text{-}(P_4tBu_3)\}_2)]$ with n = 2, 3 (SUCYOH, SUCYUN) even though more results can be found when other atoms than halides are included as a third donor[27,28]. For all the findings mentioned here, there seems to be no systematic influence of aurophilic interactions, although commonly present (Section S5, Fig. S2 and S3, SI).

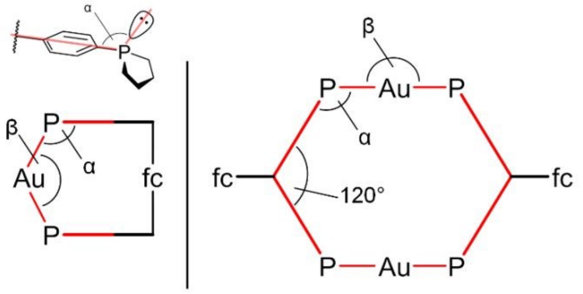

Figure 4. Schematic representation of the angles α and β in the two different coordination modes – left: intramolecular, *side view* of the ligand; right: intermolecular, *top view* onto the plain constructed by two bridging ligands. Only one half of the ligand backbone is shown.

The comprehension of the Au coordination environment also allows to better understand why of all theoretical possibilities the SCC with the M:L [4:2] stoichiometry is formed. Accordingly, the ligand geometry and the possible orientations of the lone pairs of electrons at the phosphorus atom of the phospholane moieties must be taken into account. Coordination of the gold(I) atoms occurs along the direction of the lone pairs of electrons of the donor atoms (Figure 4, top). Therefore, the C_{aryl}–P–Au bond angle α is typically found in the range of 113 to 114° (in **2** 115.31° and 118.81°) if no steric hindrance is present. The

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thermodynamically most favoured P–Au–P angle β is expected to be 180°. Even though several complexes with trigonal-planar coordination environment are known, a linear coordination mode is still by far the most favoured for gold(I).[24,29,30] As can be understood from Figure 4 (left), in a hypothetical M:L [2:1] complex both arms of ligand **1** at 1,1´-position of the ferrocene unit would be oriented in parallel fashion to each other to bind the single Au atom (*intra*molecularly) thus resulting in an angle β of around 132° (180° – 2·|α–90°|, internal angle sum triangle‡). The ligand backbone of **1** allows no free conformational changes (e.g., a rotation of the fc unit, dihedral angle *Θ*) that would change this coordination angle on gold(I) which is far from the favoured linear arrangement and therefore highly unfavourable. In contrast, this is avoided in the M:L [4:2] complex **2** by coordinating the gold atoms by two separate ligands (*inter*molecularly). The coordinating arms of the ligand backbone would ideally be branched at 120° (1,3,5-substituted benzene core); including the angles α results in P–Au–P bond angles β of 168° (180°–2·|α–120°|, ‡), which deviates much less from ideal linearity. Furthermore, the two independent ligands in **2** can additionally compensate this deviation by slight conformational changes such as the angle *Θ*, leading to angles β closer to 180° as is in fact observed for P3–Au2–P2. Accordingly, only the formation of the SCC with M:L [4:2] (**2**) is observed.

Conclusions

In conclusion, a new tetradentate tetrakis-phospholane ligand **1** was synthesised and used to create a new M:L [4:2] SCC (**2**) with gold(I) in the nanometre scale with Au in a linear coordination environment. The realisation of the M:L [4:2] stoichiometry instead of [2:1] can be rationalised by careful consideration of the geometrical parameters of the ligand. Furthermore, a comprehensive CSD search on related gold(I) complexes has shown that with increasing gold-halide distances, the P–Au–P bond angles approach 180° while the Au–P bond lengths are usually unaffected. These results are generally applicable for three-coordinated gold(I) halide complexes.

Notes and references

‡ For calculation of the P–Au–P bond angle β, an isosceles triangle between these three atoms is considered. The sum of angles (always 180°) is composed of β and two identical angles γ. In case of the hypothetical M:L [2:1] complex the P–C bond is perpendicular to the P···P connection line and therefore, γ can be obtained by subtracting 90° from α. Instead, in the idealised M:L [4:2] complex the trigonal arrangement of the ligand causes a relative angle of 120° between these two elements and thus necessitates subtracting 120° from α to obtain γ.

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