Coordination Chemistry of Calix-Phosphanes: Cooperativity in the Assembly of a Tetragold Calixarene Complex

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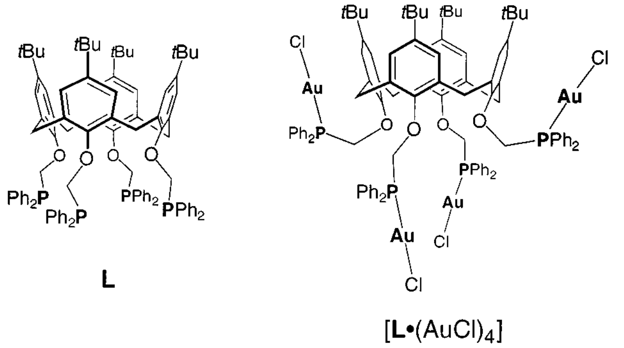
Assemblage of the tetragold complex [L·$(AuCl)_4$] from *p-tert*-butyl-calix[4]-$(OCH_2PPh_2)_4$ (L) and [AuCl(tetrahydrothiophene)] was investigated by NMR and UV/Visible spectroscopic titrations. Three steps could be resolved and are assigned, respectively, to addition of one, two and four AuCl units to the macrocyclic ligand. At each stage of metallation, symmetrical species persist on the NMR time scale since the bound AuCl fragments migrate between the different phosphorus centers via both intra- and intermolecular processes. The derived stability constants ($\log\beta_1 = 4.4 \pm 0.2$, $\log\beta_2 = 7.0 \pm 0.7$, and $\log\beta_4 = 14.5 \pm 2.0$) indicate both positive and negative cooperativity during build-up of the tetranuclear species. An X-ray diffraction study made with crystals obtained from an L:Au (1:2) mixture revealed the formation of an unusual binuclear complex whose solid state structure comprises a polymeric chain of [L·AuCl] units linked by pseudo-tetrahedral Au^+ ions, each generic unit containing a pendant linear PAuCl fragment. This polymeric species, with its two distinct binding modes, provides a simple rationale by which to explain the role of cooperativity in the overall assembly process.

Introduction

Calixarene-based polytopic ligands are attractive building blocks for the construction of molecules maintaining several *discrete* transition metal centers in close proximity.[1–8] Such intricate architectures provide important opportunities to study metal–metal cooperativity in polynuclear complexes and, inter alia, to extend our understanding of the mechanism of heavy-metal transport in biological systems.[9] As reported recently, the tetra-substituted calix[4]arene **L** possesses the necessary functionality to bind up to four metal centers at the lower rim. This ligand is also known to form bimetallic gold and silver complexes displaying unusual kinetic behavior in solution,[10] although the manner in which such metallo-calixarenes are assembled remains poorly understood. Following a recent study in which we reported the synthesis of the tetranuclear gold complex [**L**·$(AuCl)_4$][10] (Scheme 1) we now describe the stepwise formation of this complex by reaction of **L** with [AuCl(THT)] (THT = tetrahydrothiophene) under conditions that allow the mechanism to be resolved. During this study an unprecedented calixarene polymer could be isolated whose structure is detailed below.

Results and Discussion

As pointed out in a previous study, ^{31}P and ^{1}H NMR spectroscopy suggests that addition of sub-stoichiometric amounts of [AuCl(THT)] to **L** in $CDCl_3$ forms a mono-gold species[11] that co-exists with the free ligand. In fact, careful examination of the NMR spectra shows that excess **L** exchanges with coordinated ligand, since the broad signal due to the mono-gold complex moves upfield with increasing ligand concentration. Furthermore, the NMR spectra show the mono-gold complex to be symmetrical such that, in addition to bimolecular ligand exchange, it appears that the bound AuCl fragment migrates between the four P atoms attached to the calixarene platform. ^{31}P NMR spectra recorded at higher concentrations of [AuCl(THT)] (Au:**L** = 1–4; ligand concentration = 5×10^{-3} M) comprise a singlet whose chemical shift varies over the range 22–33 ppm,[12] while the corresponding ^{1}H NMR spectra confirm the presence of symmetrical species throughout the titration.[13]



Scheme 1. Drawing of **L** and [**L**·$(AuCl)_4$]

X-ray diffraction studies made with crystals isolated from a concentrated **L**:Au (1:2) mixture (CH_2Cl_2, 0.025 M) indicate formation of a binuclear complex whose solid-state structure[14] consists of a polymeric chain of [**L**·AuCl] units linked by trigonal Au^+ ions (Figure 1). The basic motif contains a pendant P–Au–Cl fragment while each linking Au cation is bound to three phosphorus atoms, two of which originate from the same calixarene. A chloride anion is ap-

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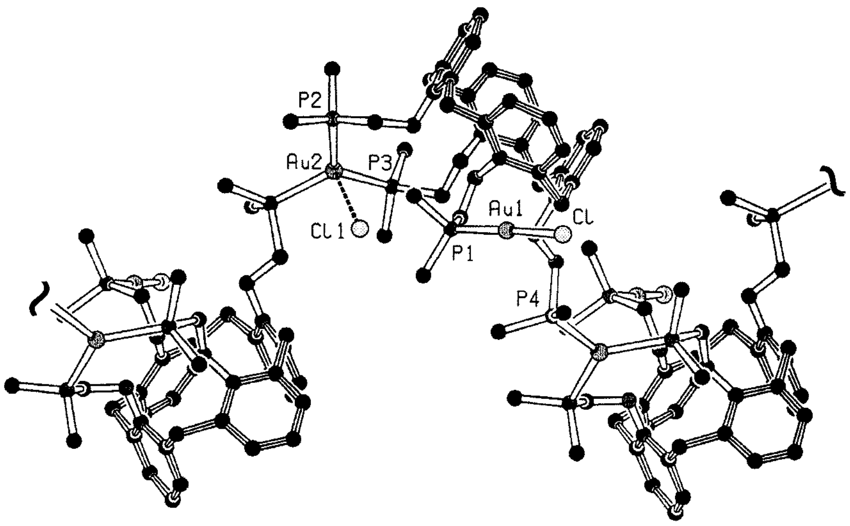


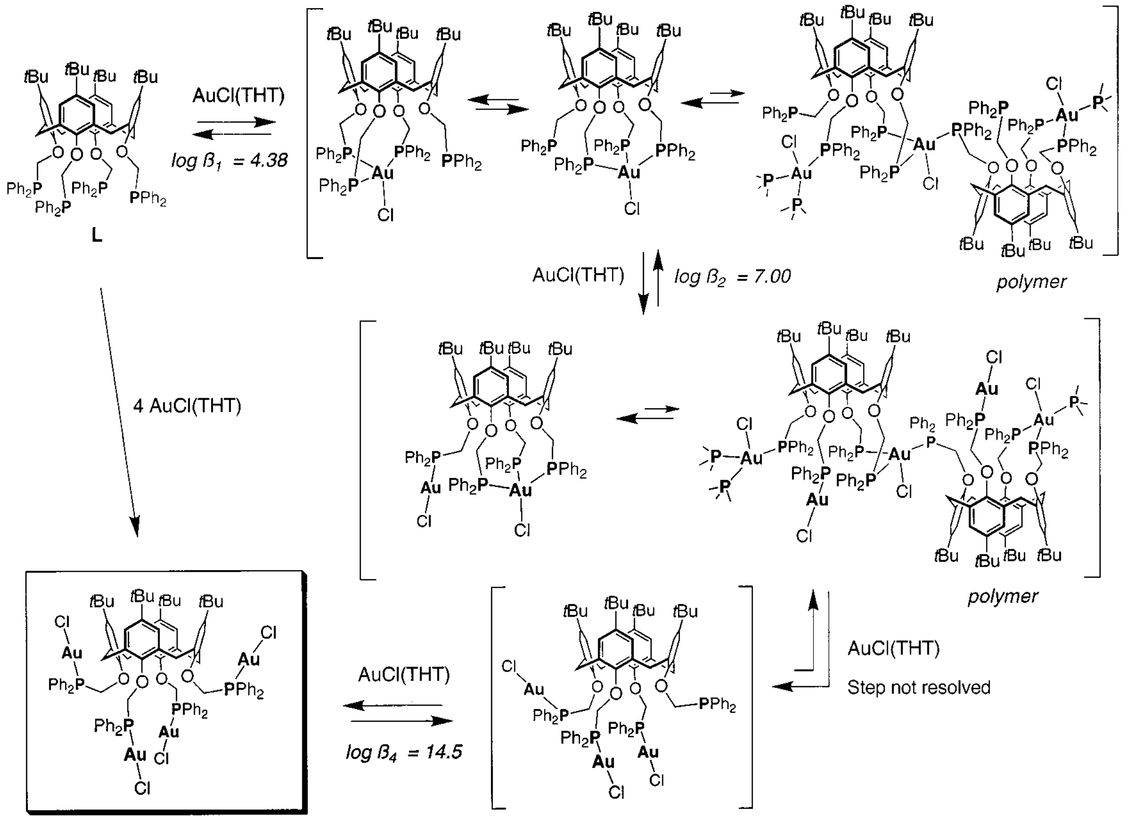
Figure 1. PLATON view of polymeric [**L**·Au_2Cl_2]$_\infty$; for clarity the *t*Bu groups have been omitted and only the *ipso* carbon atoms of the PPh_2 aryl rings are shown; selected bond distances (Å) (standard deviations in parentheses): Au(1)–Cl 2.283(7), Au(1)–P(1) 2.254(7), Au(2)–P(2) 2.371(6), Au(2)–P(3) 2.379(6), Au(2)–P′(4) 2.384(6), Au(2)–Cl(1) 3.012(6); dihedral angles between the facing aryl rings of the calixarene matrix: 80.3(7)° and 1.6(7)°

ically sited on each AuP_3 plane, the Au–Cl contact being 3.012(6) Å.[15] This structure differs markedly from known arrangements where AuCl units bound to three P^{III} atoms involve tetrahedral gold atoms.[16–19] It is also noteworthy that this structure contrasts with the numerous gold-linked inorganic polymers for which the gold(I) connector has a coordination number two.[20] The present X-ray structure, which provides a rationale for the bimolecular ligand exchange processes inferred from the NMR studies, is the first indication that gold(I) centers of coordination number two and four co-exist in a single molecule.

The processes leading to formation of [**L**·$(AuCl)_4$] were examined by spectrophotometric titrations with progressive addition of [AuCl(THT)] to **L** (5×10^{-5} M) in acetonitrile at 25 °C. Global analysis of the titration data exposed three discrete steps in the overall assembly. The first step, which corresponds to formation of [**L**·(AuCl)], involves a stability constant of $\log\beta_1 = 4.4 \pm 0.2$ while addition of a second AuCl fragment is characterized by $\log\beta_2 = 7.0 \pm 0.7$. Remarkably, addition of further AuCl fragments to [**L**·$(AuCl)_2$] proceeds easily and, in fact, the individual steps leading to attachment of the third and fourth metallic centers could not be resolved. The tetranuclear species [**L**·$(AuCl)_4$], which dominates the equilibrium mixture at high molar ratios of [AuCl(THT)] regardless of total concentration, is formed with $\log\beta_4 = 14.5 \pm 2.0$.

The observed trend in stability constants is best explained by reference to the X-ray structure where two different types of bound AuCl fragments can be seen. Thus, at low molar ratios of Au:**L** the incoming AuCl fragment binds to the calixarene platform with a *pseudo*-tetrahedral geometry by coordinating to three phosphane groups.[21] These phosphanes might be provided by one or two molecules of **L**, according to the total concentration, while the NMR results require that the structure is labile with facile exchange between the various phosphane groups (Scheme 2). This *pseudo*-tetrahedral arrangement is more stable than the corresponding linear P–Au–Cl geometry by ca. 10 kJ mol^{-1}.[22] Attachment of a second AuCl fragment to [**L**·(AuCl)] must produce a species having both linear and *pseudo*-tetrahedral P–Au–Cl units, which equilibrate on the NMR timescale, with both monomeric and oligomeric species being possible (Scheme 2).[23] In order to accommodate a third AuCl fragment the more stable *pseudo*-tetrahedral complex must dissociate to allow the formation of two linear P–Au–Cl units. This process involves a small decrease in the Gibbs free energy ($\Delta G^\circ \approx -4$ kJ mol^{-1}) whilst facilitating attachment of the fourth AuCl fragment by providing a vacant phosphane ligand. Therefore, formation of [**L**·$(AuCl)_4$],[10] which is known to possess four linear P–Au–Cl units, proceeds smoothly (Scheme 2).

The present study reveals that formation of [**L**·$(AuCl)_4$] is a stepwise process where both negative and positive cooperativity between the metal centers can take place. The key feature of the overall assembly mechanism involves the interplay between *pseudo*-tetrahedral and linear P–Au–Cl geometries, with the former being more stable but more demanding in the number of phosphane groups. Consequently, the reaction is driven towards the less-stable linear geometry as more metal centers become attached to the platform. This mechanism explains all the known aspects of the reaction, including why [**L**·$(AuCl)_2$] crystallizes and why [**L**·$(AuCl)_3$] is not detected, and is made possible by having X-ray structural data for both [**L**·$(AuCl)_2$] and [**L**·$(AuCl)_4$]. Clearly, such switching between different binding geometries within the same molecule is highly unusual and it should be stressed that interconversion is uniquely controlled by the molar ratio. Complexes possessing either of the extreme *pseudo*-tetrahedral or linear geometries can be generated and it will be interesting to determine whether



Scheme 2. Proposed stepwise formation of $[\mathbf{L}\cdot(AuCl)_4]$; intramolecular migrations of the bound AuCl fragments have not been fully detailed

the exchange processes that occur during the formation of $[\mathbf{L}\cdot(AuCl)_4]$ involve gold–gold interactions.

Experimental Section

Synthesis of Polymeric $[\mathbf{L}\cdot(AuCl)_2]$: To a solution of **L** (0.361 g, 0.25 mmol) in CH_2Cl_2 (5 mL) was added a solution of [AuCl(tetrahydrothiophene)] (0.160 g, 0.50 mmol) in CH_2Cl_2 (5 mL). The solution was filtered through Celite. Crystals of $[\mathbf{L}\cdot Au_2Cl_2]_\infty$ were obtained by slow diffusion of hexane into this solution. Yield: 0.290 g, 60%. – ^{31}P NMR (81 MHz, 293 K, CD_2Cl_2): δ = 31.4 (br s). – ^{1}H NMR (200 MHz, 293 K, $CDCl_3$): δ = 7.90–7.28 (40 H, PPh_2), 6.61 (br s, 8 H, *m*-ArH), 4.97 (br s, 8 H, PCH_2O), 4.53 and 2.92 (AB q, ^2J = 12 Hz, 2 × 4 H, $ArCH_2$), 1.04 (s, 36 H, *t*Bu). – $C_{96}H_{100}Au_2Cl_2O_4P_4\cdot 2H_2O$ (1943): calcd. C 59.36, H 5.40; found C 59.30, H 5.20.

Crystal Data for Polymeric $[LAu_2Cl_2]\cdot 2H_2O$: $C_{96}H_{100}Au_2Cl_2O_4P_4\cdot 2H_2O$, M = 1943, orthorhombic, space group $P2_12_12_1$, colorless crystals, a = 17.0365(5), b = 23.3634(8), c = 29.038(1) Å, V = 11558(1) Å^3, Z = 4, D_c = 1.12 g·cm^{-3}, μ = 2.670 mm^{-1}, $F(000)$ = 3920. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-K_α radiation, 0.71073 Å) at –100 °C. 59120 reflections collected ($2.5 \leq \varphi \leq 26.3°$), 5916 data with $I > 3\sigma(I)$. The structure was solved using the Nonius OpenMoleN[14] package and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms except for one water molecule. The absolute structure was determined by refining Flack's x parameter. Final results: $R(F)$ = 0.058, $wR(F)$ = 0.084, GOF = 1.653, 981 parameters, largest difference peak = 1.084 eÅ^{-3}. Structure graphics were performed with the program PLATON.[24] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137702. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Determination of the Binding Constants: The global binding constants log β_n were determined by UV/Visible spectrophotometric titration in acetonitrile (spectroscopic grade). For these measurements, 50 flasks were filled under N_2 atmosphere with a solution of tetraphosphane **L** in acetonitrile (3 mL, 5×10^{-5} M) to which were added variable amounts of [AuCl(THT)] as multiples of 10 μL of a 3×10^{-4} M acetonitrile solution. The Au:L ratios ranged from 0 to 7. The solutions were left for 12 h before measurement. The spectra were recorded between 190 and 310 nm using a quartz cell (1 cm path length) that was thermoregulated at 25 ± 0.5 °C. The absorbance changes monitored were significant enough to be exploited by multiwavelength numerical treatment based on a Benesi–Hildebrandt type equation (program SPECFIT©[25]), which yielded the desired global binding constants log β_n.

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[11] For Au:L ≈ 0.5, the ^{31}P NMR spectrum displays a very broad peak at $\delta \approx 10$ corresponding to the "mono-gold" species and a sharper peak at $\delta = -21$ due to the free ligand.

[12] The chemical shift of the ^{31}P NMR signal varies with Au:L ratio: $\delta = 16.6$ (1:1 ratio); 31.4 (2:1 ratio); 25.2 (3:1 ratio); 22.7 (4:1 ratio). For the free ligand, $\delta = -20.4$.

[13] All room-temperature ^{31}P NMR spectra display a single peak. On cooling the 2Au:1L solution, the phosphorus signal broadens before splitting into several signals (202 MHz, 183 K). These observations indicate that dynamic processes occur in solution, but the exact nature of the interconverting species could not be inferred from these data. Note, there is no indication of exchange reactions occurring with [L·(AuCl)$_4$] over the temperature range –80 °C/+25 °C.

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[15] Because of the particular position of Cl(1), exactly apically sited above the AuP$_3$ plane and hence indicative of a bonding interaction, we favor an AuP$_3$Cl formulation rather than $[\mathrm{AuP_3}]^+\mathrm{Cl}^-$.

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[21] P$_3$-coordination of **L** to a single metal center has been established recently. See: C. B. Dieleman, C. Marsol, D. Matt, A. Harriman, N. Kyritsakas, J.-P. Kintzinger, *J. Chem. Soc., Dalton Trans.* **1999**, 4139–4148. Molecular mechanics computer simulations confirm that intramolecular pseudo-tetrahedral binding is possible.

[22] We assume that β_2 corresponds to formation of the binuclear species possessing both pseudo-tetrahedral and linear AuCl fragments, whereas β_1 refers to formation of the pseudo-tetrahedral geometry. Consequently, ignoring statistical factors, free-energy changes for formation of pseudo-tetrahedral [$\Delta G^\circ = -RT\ln(\beta_1) = -24.5$ kJ mol^{-1}] and linear [$\Delta G^\circ = -RT\ln(\beta_2 - \beta_1) = -14.4$ kJ mol^{-1}] sites can be estimated from the titration data. Attaching a third AuCl fragment, assumed to give three linear appendages, corresponds to a crude free-energy change of $\{\Delta G^\circ \approx -RT\ln[3(\beta_2 - \beta_1) - \beta_2]\}$ of –4.4 kJ mol^{-1}. Finally, the free energy change for attachment of four linear AuCl fragments $\{\Delta G^\circ \approx -RT\ln[4(\beta_2 - \beta_1) \approx -58$ kJ mol$^{-1}\}$ can be compared to the experimental value ($\Delta G^\circ = -RT\ln(\beta_4) = -80 \pm 12$ kJ mol^{-1}).

[23] Linear P–Au–P coordination occurs in [LAu$_2$](PF$_6$)$_2$ but it is most unlikely that such species are formed in the present study. Indeed, $[\mathrm{LAu_2}]^{2+}$ does not react with "AuCl" fragments to afford compounds of higher nuclearity.

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