Self-assembly of metal complexes with cyclophane or polymeric chain structures about a 1,3,5-tris(diphenylphosphino)benzene core

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Two very different molecular shapes are formed using the ligand 1,3,5-tris(diphenylphosphino)benzene (L); polymeric chains form through Au···Au contacts in the crystals of [(ClAu)$_3$L], while the metallocyclophane [(PtCl$_2$)$_3$L$_2$] self assembles from five components when L and [PtCl$_2$(cod)] are combined in a 2:3 molecular ratio.

Supramolecular chemistry embodies the study of molecular assemblies through weak interactions and apparent concerted reactions of multiple molecules to form complex structures through self-assembly techniques.[1] Studies in this area of chemistry have yielded interesting guest–host complexes with large cyclophanes,[2] and novel molecular architecture such as molecular squares[3] and cantenanes.[4] Through judicious ligand choice and design, self-assembly techniques have helped produce complex molecules with intramolecular metal–metal interactions.[5]

The ligand 1,3,5-tris(diphenylphosphino)benzene[6] (L), with its potential for C_{3v} symmetry, is an attractive ligand for producing transition-metal complexes with intriguing geometries. The rigid aromatic bridge makes it impossible for this ligand to chelate to one metal centre or for metal centres on one ligand to directly interact. However, there is the potential for extended networks to form through multiple ligand coordination to one metal centre, or by intermolecular metal–metal interactions. L is also attractive as the centre for the formation of a three-armed transition-metal based dendrimer. The dendrimer could then grow through the addition of a multitude of different ligands depending on the desired properties. Cyclophane hosts could also arise when appropriate metal centres or metal complexes are used as the cyclophane straps to hold two ligands together. This cyclophane geometry could create a cavity ready to accept guests either through π interactions with the ligands or through ligation to the metal centres.

We have characterized two dramatically different transition metal complexes of L. The first is the metallocyclophane [(PtCl$_2$)$_3$L$_2$] which forms as colourless crystals, [(PtCl$_2$)$_3$L$_2$]·5CH$_2$Cl$_2$, in 32.4% yield when a dichloromethane solution of [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene) is allowed to diffuse slowly into a dichloromethane solution of the ligand. Unfortunately, [(PtCl$_2$)$_3$L$_2$] has negligible solubility in common organic solvents, and consequently we have not been able to obtain spectroscopic data for the complex in solution. Analysis by X-ray crystallography revealed that the complex has the structure shown in Fig. 1.† The molecule consists of two L ligands which are held together by three *cis*-PtCl$_2$ straps. Thus in a single reaction, the five separate components have undergone self assembly to form this metallocyclophane. Individual molecules of [(PtCl$_2$)$_3$L$_2$] have a helical twist as seen in Fig. 1(*b*), but these have crystallized in a centrosymmetric space group. Thus the crystal contains a racemic mixture. The centre-to-centre benzene–benzene separation is 3.12 Å which produces closer contact than in the purely organic [3.3]paracyclophane where the corresponding distance is 3.25 Å.[7] The closest (non-bonded) C···C separation between the two rings is 3.133 Å. The P···P separations (3.525, 3.558, 3.558 Å) are larger than the centre-to-centre benzene-benzene separation. As expected the Pt···Pt separations (7.701, 7.893, 7.893 Å) are too long to accommodate any direct interactions between the P$_2$PtCl$_2$ units. Recently the synthesis and structure of a related metallocyclophane that incorporates six Cu^{I} units has been reported.[1]

Mixing Me$_2$SAuCl and L in a 3:1 molar ratio in dichloromethane solution produces [(ClAu)$_3$L] which may be isolated as a colourless solid in 86% yield by adding methanol to the mixture. In dichloromethane solution at 23 °C, [(ClAu)$_3$L] exhibits a single ^{31}P NMR resonance at δ 34.2. On cooling this resonance remains a singlet down to −80 °C. This behaviour suggests that the complex remains monomeric in solution and that there is free rotation of the ClAuPPh$_2$ groups about the benzene core of the ligand.[8]

The structure of [(ClAu)$_3$L] has been determined by a X-ray crystallographic study† and the results are shown in Fig. 2. Three linear P–Au–Cl groups are present with normal bond

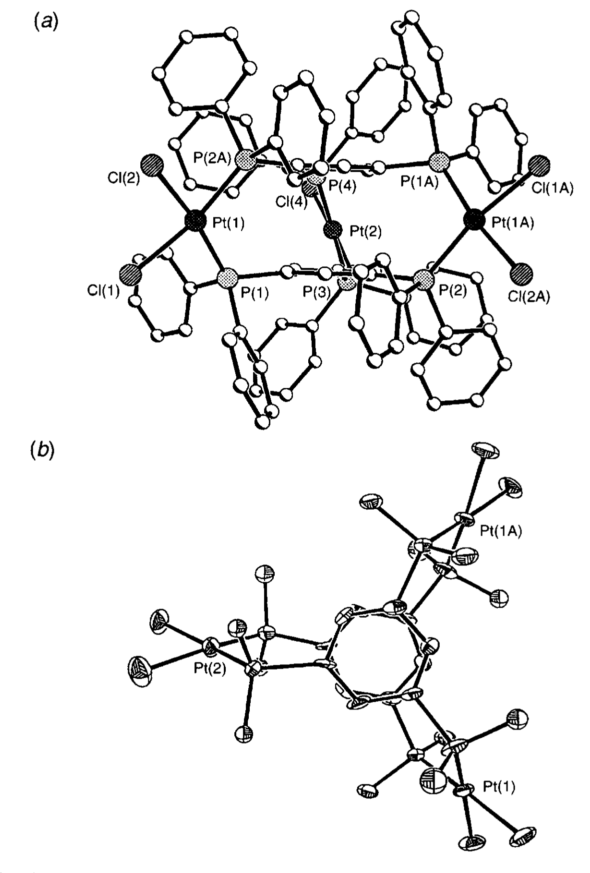

Fig. 1 Two nearly orthogonal perspective views of [(PtCl$_2$)$_3$L$_2$] showing only one of two similar core structures. (*a*) Shows the molecule as viewed down the twofold rotation axis and (*b*) shows the molecule with 50% thermal contours for all atoms and only the *ipso* carbon atoms of each phenyl ring. Selected bond distances (Å) and angles (°), Pt(1)–P(1) 2.244(4), Pt(1)–P(2A) 2.255(5), Pt(1)–Cl(1) 2.345(4), Pt(1)–Cl(2) 2.346(4), Pt(2)–P(3) 2.235(13), Pt(2)–P(4) 2.251(12), Pt(2)–Cl(3) 2.358(9), Pt(2)–Cl(4) 2.344(10); P(1)–Pt(1)–P(2A) 104.5(2), Cl(1)–Pt(1)–Cl(2) 88.2(2), P(3)–Pt(2)–P(4) 103.6(3), Cl(3)–Pt(2)–Cl(4) 87.3(4).

distances. Two of these [those involving Au(1) and Au(3)] lie near the plane of the central benzene ring, while the third, which involves Au(2), protrudes away from the ligand plane. As expected, the intramolecular Au···Au separations are too long for any intramolecular interactions between these units. Since gold(I) centres are attracted to one another, sometimes in solution,[8] and often within crystals,[9] intermolecular Au···Au contacts were also examined. Polymeric chains are formed through intermolecular Au···Au interactions [Au···Au distance 3.1421(11) Å] as shown in Fig. 2(*b*). The chain structure is generated through simple translation. This interaction involves the two gold atoms that are almost co-planar with the central benzene ring. The other Au(2)–Cl(2) arm, which juts above this plane, is not involved in any Au···Au contact. This arm is tilted towards Cl(3a). This tilt may be due to a weak interaction between Au(2) and Cl(3A) on the neighbouring molecule; since the distance between these two atoms (3.38 Å) is slightly less than the sum of their van der Waals radii (3.41 Å).[10] Thus, the solid contains linear chains of [(ClAu)$_3$L] molecules rather than the three-dimensional net that could form if all three P–Au–Cl groups were to display intermolecular bonding through Au···Au contacts. A number of related, two-dimensional chain structures have been observed for complexes of the type, {(ClAu)$_2$(ditertiaryphosphine)}. Further studies of the utility of L in the construction of polynuclear arrays of transition metal complexes are in progress.

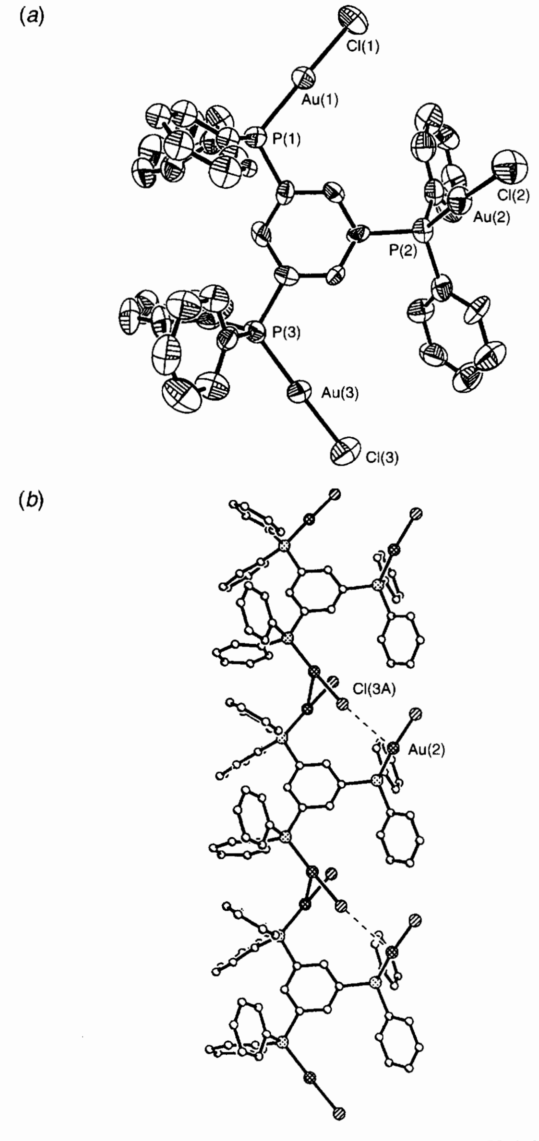

Fig. 2 (*a*) A view of an individual molecule of [(ClAu)$_3$L] with 50% thermal contours for all atoms. Selected bond distances (Å), Au(1)–P(1) 2.231(5), Au(1)–Cl(1) 2.300(5), Au(2)–P(2) 2.228(5), Au(2)–Cl(2) 2.275(5), Au(3)–P(3) 2.233(5), Au(3)–Cl(3) 2.291(5); (*b*) a drawing of a chain of molecules of [(ClAu)$_3$L] that form through Au···Au contacts. The dashed line emphasizes the close Au(2)···Cl(3A) contact.

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Footnote

† *Crystal data*: colourless plates of $C_{84}H_{66}Cl_6P_6Pt_3{\cdot}5CH_2Cl_2$, that were obtained by diffusion of a CH_2Cl, solution of [$PtCl_2$(cod)] into a CH_2Cl_2 solution of L, form in the monoclinic space group *C*2/*c* with *a* = 24.389(14), *b* = 19.212(6), *c* = 20.836(8) Å, β = 104.83(3)° at 133 K with *Z* = 4 with the use of graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. A 3% decay in two standard reflections was observed over the course of the data collection. Refinement of 8323 reflections, 25 restraints, and 335 parameters yielded wR_2 = 0.153 and a conventional R_1 = 0.079 based on observed data with $I > 2\sigma(I)$. Disorder in the structure involves two clearly resolved sites for Pt(2) and the phosphorus and chlorine atoms that are connected to it. These sites reside on either side of a crystallographic twofold rotation axis. Additionally two alternate sites exist for eight of the phenyl rings on the periphery of the molecule. However, the important features of the core structural unit described here are similar in the two molecular orientations that are present. The largest peak in the final difference map (1.10 e Å^{-3}) is 0.94 Å from Pt(2) and results from Fourier ripples from that heavy atom.

Colourless plates of $C_{42}H_{33}Au_3Cl_3P_3$ that were obtained by diffusion of diethyl ether through methanol into a CH_2Cl_2 solution of the compound form in the triclinic space group $P\bar{1}$ with *a* = 10.104(2), *b* = 12.448(2), *c* = 17.237(3) Å, α = 91.25(1), β = 104.29(2), γ = 105.00(1)° at 133 K with Z = 2 with the use of graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Refinement of 8800 reflections and 364 parameters yielded wR_2 = 0.149 and a conventional R_1 = 0.072 based on observed data with $(I) > 2\sigma(I)$. The largest peak in the final difference map (1.3 e Å^{-3}) is 0.90 Å from Au(1) and results from Fourier ripples from that heavy atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/286.

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