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Mobility of gold and silver ions around a macrocyclic polyphosphane. Supramolecular architecture of a digold–calix[4]arene complex

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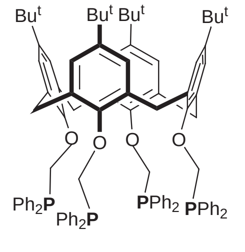
The calixarenes 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphinomethoxy)calix[4]arene (L^1) and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(1,3,5-trimethyl-4,6-dioxo-1,3,5-triaza-2-phosphorinan-2-yl)calix[4]arene (L^2), substituted at the lower rim, reacted with 4 equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) to yield respectively the tetragold complexes $[(AuCl)_4L^1]$ **1** and $[(AuCl)_4L^2]$ **2**, both adopting a cone conformation. The solid state structure of **1** has been determined by an X-ray diffraction study, which reveals crystallographic twofold symmetry. The reaction of L^2 with 2 equivalents of [AuCl(tht)] resulted in the formation of a mixture of two compounds. One, $[(AuCl)_2L^2]$ **3**, could be isolated and was characterised by an X-ray diffraction study. The gold atoms of **3** are tethered to two distal P atoms. Intermolecular Au · · · Au contacts are observed for each gold atom [3.2879(7) Å], resulting in a loose polymeric structure in the solid state. Reaction of L^1 with [AuCl(tht)] and $TlPF_6$ resulted in quantitative formation of the dinuclear complex $[Au_2L^1][PF_6]_2$ **4** where each gold atom is chelated by two proximal phosphino groups. Fast rotation of the gold atoms around the axis of the calixarene occurs in solution. In this co-operative intramolecular movement each gold atom switches from one pair of P atoms to an adjacent one ($\Delta G^\ddagger = 79.4$ kJ mol^{-1}). The silver analogue **5** was obtained by treating L^1 with $AgBF_4$.

The calix[4]arene matrix is a macrocyclic building block that possesses a remarkable structural versatility and may undergo controlled multiple functionalisation.[1–7] It has become a widely employed tool for engineering of highly sophisticated molecular and supramolecular systems.[8–12] Among the most striking developments in this area are sensors for the detection of neutral and anionic species,[13] selective complexants for the extraction of valuable metal ions,[14–18] novel metallomesogenic materials,[19] and molecular capsules for the entrapment of reactive organometallic fragments.[20,21] A topic of growing interest deals with the combination of calixarenes and transition metals.[22,23] Transition metals have notably been used for shaping calixarenes,[24] and generating molecular-sized cages from calixarenes.[25]

Recent investigations by us and others have shown that tethering of four P^{III}-containing units to the narrow rim of cone-shaped calix[4]arenes provides a complexation domain suitable for the binding of up to four transition metals.[26–31] Such preorganised assemblies are expected to possess important properties and, in particular, allow examination of co-operative interactions between metal centres maintained in close proximity. It may also be anticipated that these units are highly appropriate vehicles for studying dynamic processes involving metal fragments bound to a calixarene surface. This latter topic is relevant to the understanding of metal ion transport in multitopic molecular systems.[11,32,33]

In the present study we report on the synthesis and properties of multimetal species obtained from the previously reported tetrafunctionalised calixarenes L^1 and L^2.[30,34] These ligands, which contain four trivalent phosphorus atoms, adopt a cone-shaped structure in solution. X-Ray diffraction studies of a tetra- and a di-nuclear complex are described. We also report the *first* examples of dynamic processes involving two metal centres moving on a calixarene-subtended P_4 surface. The ability of ligand L^1 to form tetranuclear complexes with palladium has recently been outlined in a preliminary communication.[29]



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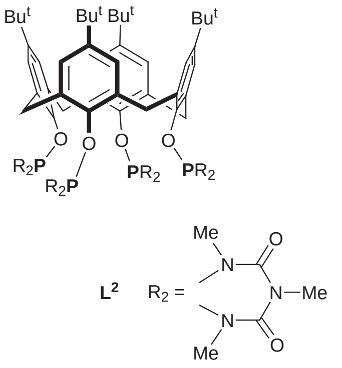

L²

Results and Discussion

Tetranuclear gold complexes

In order to investigate its multiple binding properties towards gold centres, L^1 was allowed to react with 4 equivalents of [AuCl(tht)] (tht = tetrahydrothiophene). This reaction led to the tetranulcear complex **1** (Scheme 1) in quantitative yield. The FAB mass spectrum of **1** shows an intense peak at *m/z* 2335, corresponding to the [M − Cl] cation. The NMR data (^{1}H, ^{31}P, ^{13}C) are consistent with a C_4-symmetrical structure in solution (sharp signals), but from many studies it now appears likely that such a symmetry is only virtual and reflects a fast C_{2v}–C_{2v}

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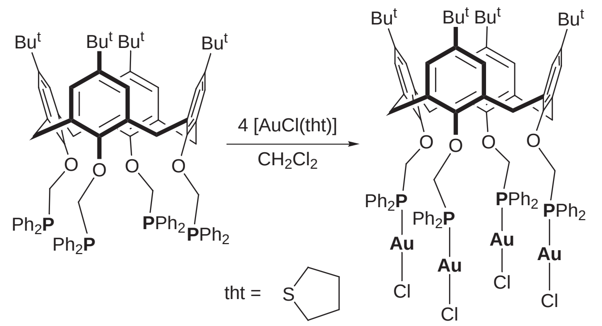


L^1 1

Scheme 1

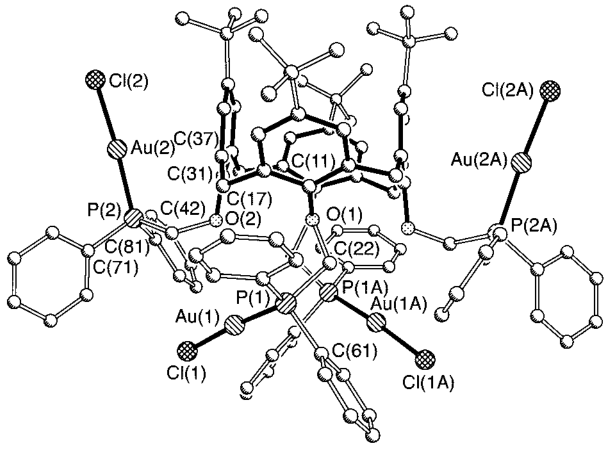


Fig. 1 Molecular structure of complex **1**

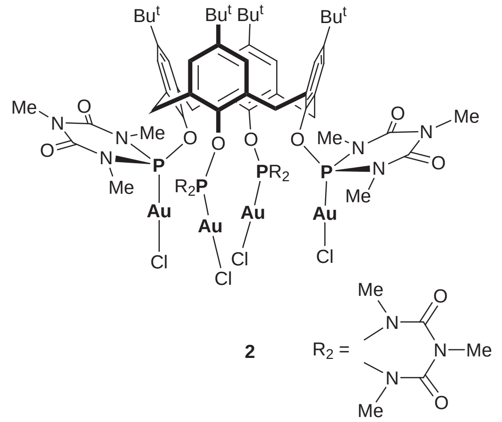
exchange process.[35] A single-crystal X-ray determination (Fig. 1 and Table 1) confirmed the presence of four gold atoms anchored to the calixarene ligand and revealed that the highest symmetry element in the solid state is actually a crystallographic C_2 axis.

The calixarene matrix adopts a distorted cone shape with two facing phenolic units almost parallel (interplane angle 4.2°) and the other two being essentially perpendicular (89.4°). The distance between the centroids of the two parallel rings is 5.37 Å and that between the other two rings is 7.40 Å. Two opposite P–Au–Cl units are oriented parallel to their appended phenoxy rings, whilst the other two lie roughly orthogonal to the calixarene axis. The particular alignment of the two PAuCl fragments adjacent to the corresponding phenoxy rings (see Fig. 1) is likely to minimise steric interactions between the phosphino groups and the calixarene backbone and is not considered to reflect any bonding interaction between the gold atom and the π system of the appended phenoxy rings [shortest Au···C contact 3.593(10) Å; Au(2)···C(36)]. The intramolecular Au(1)···Au(1) distance is 5.277(1) Å and the shortest intermolecular distance is Au(1)···Au(1) 5.269(1) Å (operator $1 - x$, $-y$, $1 - z$). Other structural parameters are given in Table 1.

The related tetranuclear gold complex **2** was obtained using a procedure similar to that outlined in Scheme 1 but starting from L^2. Its ^{13}C NMR spectrum shows that the cone shape of the calixarene is maintained upon complexation [$\delta(C_6H_2CH_2) = 31.44$]. Complex **2** shows a *broad* peak (δ 101.6 *vs.* 91.8 for the free calixarene) in its ^{31}P NMR spectrum, suggesting that the complex is either exhibiting dynamic behaviour in solution or exists as a mixture of structurally similar isomers. Careful examination of the ^1H NMR spectrum reveals that the resonances of the C(O)N*Me* groups display a complex pattern. A possible explanation for this observation is that rotation of the relatively bulky phosphorus heterocycles around the P–O bonds is restricted, so that the four phosphorinane fragments adopt various orientations with respect to the calixarene axis. Note that rotamers have neither been detected in **1** nor in the related 25,26,27,28-tetra(diphenylphosphinooxy)calix[4]arene tetragold complex recently reported by Puddephatt and coworkers.[28] Other characteristic data for **2** are given in the Experimental section.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Au(1)–P(1)	2.226(3)	Au(1)–Cl(1)	2.292(3)
Au(2)–P(2)	2.223(3)	Au(2)–Cl(2)	2.271(3)
P(1)–C(51)	1.805(11)	P(1)–C(61)	1.828(11)
P(1)–C(22)	1.845(10)	P(2)–C(81)	1.797(11)
P(2)–C(71)	1.817(12)	P(2)–C(42)	1.849(10)
P(1)–Au(1)–Cl(1)	175.35(11)	P(2)–Au(2)–Cl(2)	176.28(14)
C(51)–P(1)–Au(1)	116.1(4)	C(61)–P(1)–Au(1)	108.1(3)
C(22)–P(1)–Au(1)	115.0(3)	C(81)–P(2)–Au(2)	114.7(3)
C(71)–P(2)–Au(2)	111.9(4)	C(42)–P(2)–Au(2)	115.7(3)



2

Non-exhaustive auration of L^1 and L^2: formation of neutral complexes

Since compound L^1 contains four discrete binding sites we surmised that it would also allow formation of complexes with a lower gold content. As an approach to this subject, NMR spectroscopy was used to monitor the addition to L^1 of 1, 2 and 3 equivalents of [AuCl(tht)]. For each experiment the room temperature ^1H NMR spectrum, recorded 0.5 h after the reaction was completed, virtually corresponded to that of a new single species distinct from L^1 and **1** and having a highly symmetrical structure (one Bu^t signal, a single AB quartet for the $C_6H_2CH_2$ groups, one peak for the *m*-H; see Experimental section). These spectra were identical to those obtained upon reaction of the tetranuclear complex **1** with 3, 2 or 1 equivalent of L^1, respectively. These findings unambiguously indicate that (i) partially aurated compounds must be formed during the addition experiments, and (ii) the resulting species undergo dynamic processes. The latter may be inter- or intra-molecular, or both. Similar observations arose from investigations of the reaction mixtures of L^2 with various amounts of [AuCl(tht)]. Despite variable temperature studies on each of the above-mentioned reaction mixtures, the exact number of species formed in each of the gold addition (or displacement) experiments could not be determined. Neither was it possible to determine whether these reaction mixtures correspond to equilibria between species of *different* nuclearity.

To date most studies demonstrating the lability of gold fragments have been carried out on cluster compounds.[36] Very recently scrambling of $Au(PPh_3)^+$ units between two phosphorus(III) centres of a unique diphosphine was demonstrated by Assmann and Schmidbaur.[37] In this case, intermolecular exchange occurs in competition to a bimolecular process. Thus,

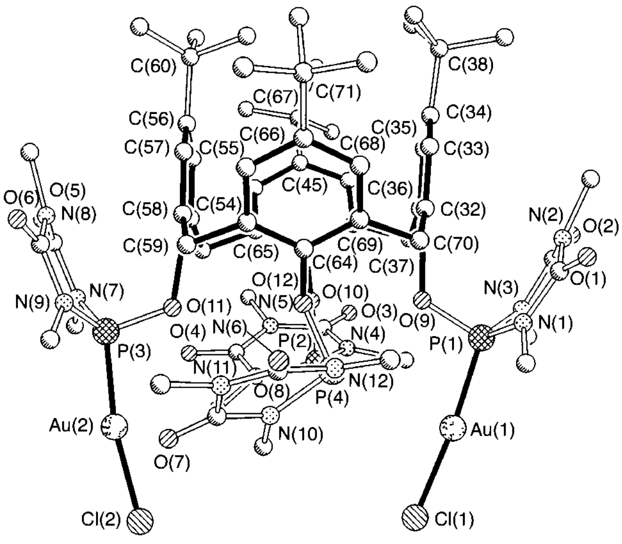
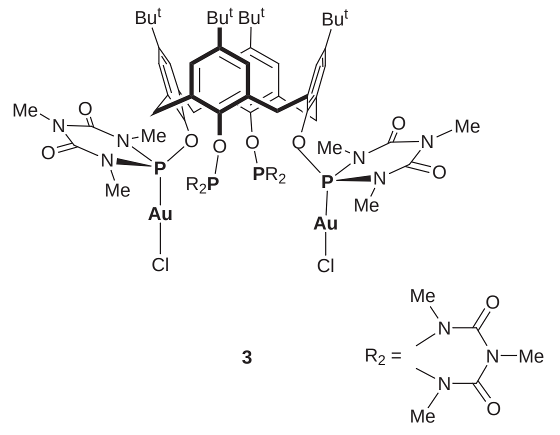


Fig. 2 Molecular structure of complex **3**

it is conceivable that, when a partially aurated complex is formed with L^1 or L^2 in one of the reactions described above, the AuCl units jump between molecules, so as to form species of differing nuclearity. On the other hand, partially aurated species may also undergo intramolecular fluxional processes in which the gold atoms migrate between phosphorus sites.

Addition of 0.5 equivalent of free L^1 to a 1 : 1 Au : L^1 reaction mixture caused the appearance of signals of free L^1 besides those of the original dynamic species (see above), both in the ^{1}H and ^{31}P NMR spectra. This result shows that among the compounds formed in the 1 : 1 mixture there is at least one species in which intramolecular gold scrambling is favoured over intermolecular exchange. The probability of intermolecular gold transfer in an L^1 complex was deduced from the [AuCl(tht)]-addition experiments described above, starting from the tetranuclear gold complex **1**.

The conclusive proof for the formation of partially aurated species was provided on crystallising a dichloromethane–toluene solution containing L^2 with 2 equivalents of [AuCl(tht)]. Careful analysis of the single crystals formed revealed that at least two types of gold-containing species were present. The molecular structure of one of them, namely the digold complex **3**, was established by a single crystal X-ray diffraction study (Fig. 2). For the other isolated crystals the presence of gold atoms was established, but disorder problems prevented a precise analysis (see Experimental section). Compound **3** crystallised as a solvate with toluene and adventitious water (1 : 1.5 : 1).



3

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Au(1)–P(1)	2.209(2)	Au(1)–Cl(1)	2.270(2)
Au(1)···Au(2^{I})	3.2879(7)	Au(2)–P(3)	2.206(2)
Au(2)–Cl(2)	2.272(2)		
P(1)–Au(1)–Cl(1)	174.40(8)	P(1)–Au(1)–Au(2^{I})	106.04(6)
Cl(1)–Au(1)–Au(2^{I})	79.37(6)	P(3)–Au(2)–Cl(2)	170.12(8)
P(3)–Au(2)–Au(2^{II})	110.69(6)	Cl(2)–Au(2)–Au(1^{II})	78.51(6)
O(9)–P(1)–Au(1)	105.2(2)	N(3)–P(1)–Au(1)	118.9(2)
N(1)–P(1)–Au(1)	116.3(2)	O(11)–P(3)–Au(2)	104.9(2)
N(9)–P(3)–Au(2)	118.1(3)	N(7)–P(3)–Au(2)	117.9(3)

Symmetry transformation used to generate equivalent atoms: I $x, 1-y, -\frac{1}{2}+z$; II $x, 1-y, \frac{1}{2}+z$.

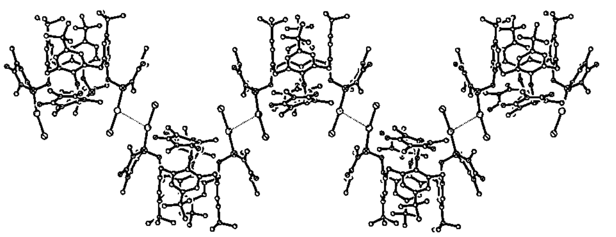
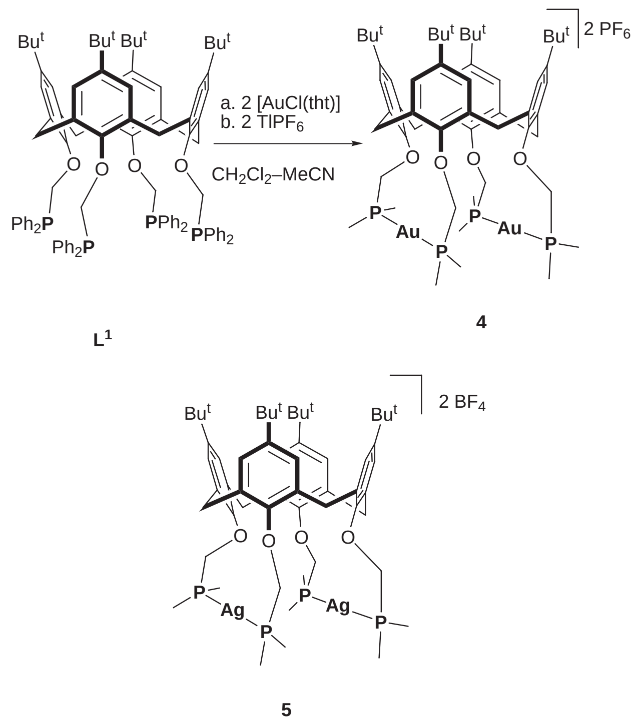


Fig. 3 View showing the supramolecular structure of the dinuclear gold complex **3** [intermolecular Au···Au distance 3.2879(7) Å]

As expected, the calix[4]arene framework is present in the cone conformation (Fig. 2), with interplanar angles between the aromatic rings of the macrocycle and the calixarene reference plane (average plane defined by the four bridging methylene carbon atoms) of 84 [C(31) ring], 53 [C(42) ring], 86 [C(53) ring] and 53° [C(64) ring]. The gold-bearing aromatic rings are essentially parallel (interplanar angle 2°) whereas the other two subtend an angle of 74°. The distances between the centres of the two pairs of opposite phenolic rings are 5.47 and 7.60 Å. The 3-NMe vectors of all the 1,3,5-trimethyl-4,6-dioxo-1,3,5-triaza-2-phosphorinan-2-yl groups point away from the calix[4]arene cavity, thus minimising the steric interactions with the neighbouring heterocycles. These heterocycles adopt orientations with respect to the corresponding phenolic rings that are best described by the following torsion angles: N(2)···P(1)–O(9)···C(34) 5, N(5)···P(2)–O(10)···C(45) −24, N(8)···P(3)–O(11)···C(56) −3 and N(11)···P(4)–O(12)···C(67) 71°. Thus, heterocycles P(1) and P(3) (linked to the Au–Cl fragments) tend to ‘overlap’ with the corresponding phenolic rings, resulting in an ‘eclipsed’ arrangement, whereas heterocycles P(2) and P(4) are staggered with respect to the corresponding phenolic rings (Fig. 2). The partial superposition of the heterocycles P(1) and P(3) and the two corresponding phenol rings ensures minimum steric interaction between the PAuCl fragments and the uncomplexed heterocycles. π-Stacking between the two rings can be ruled out. Interestingly, the P(2) and P(4) doublets point roughly in the same direction, so that the two P–Au–Cl fragments become formally inequivalent. Note that the absence of a symmetry element in the solid-state structure of **3** is reminiscent of the NMR peculiarities (several signals for the NMe groups) described above for complex **2**. The six-membered heterocycles display a typical[30] half-boat conformation in which the phosphorus atoms lie 0.56–0.60 Å outside the plane formed by the remaining atoms. The P–Au–Cl groups are almost linear [P(1)–Au(1)–Cl(1) 174.40(8) and P(3)–Au(2)–Cl(2) 170.12(8)°]. Intermolecular Au···Au contacts of 3.2879(7) Å are observed, so that a loose polymeric structure emerges in the solid state (Fig. 3). Such gold–gold (aurophilic) interactions are well known.[38–41] The intramolecular Au(1)···Au(2) distance is 7.800(1) Å. See Table 2 for further structural details.

Cationic digold and disilver complexes

From molecular models[42] it is apparent that the phosphorus–phosphorus separation between neighbouring phosphino



Scheme 2

groups in L^1 is suitable for linear P–M–P co-ordination. Such ligating behaviour was indeed found in complex **4**, which was obtained quantitatively according to the reaction sequence outlined in Scheme 2. Note that **4** was also formed as the sole product when L^1 was treated with an excess of [Au(tht)(MeCN)]$^+$. Complex **4** is stable upon standing in solution. It is worth mentioning that chloride abstraction from complex **1** (with 4 equivalents of AgBF$_4$) followed by addition of 1 equivalent of L^1 afforded the BF$_4$ analogue of **4** as the sole product. These findings illustrate the strong tendency of L^1 to behave as a strong double chelator towards Au$^+$, rather than as a bridging ligand.

The FAB mass spectrum of complex **4** displays an intense peak at 1980, with the profile exactly as expected for the [(Au$_2$L^1)PF$_6$] monocationic species. Note that there was no indication for formation of oligomeric species. The ^{1}H NMR spectrum of **4** recorded at 20 °C displays two AB quartets (intensity 1 : 1) for the C$_6$H$_2$CH_2 groups and one sharp peak for the Bu^t groups, whereas the ^{31}P NMR spectrum shows a single peak. These observations are fully consistent with the C_{2v}-symmetrical structure as drawn. A remarkable feature of one of the two C$_6$H$_2$CH$_A$H$_B$ quartets is the large separation between the corresponding A and B parts (Δδ 2.5 *vs.* 0.78 for the other one). We tentatively assign this AB system to the methylene groups that form a 12-membered metallomacrocycle with the gold atoms. In these methylene groups one CH bond probably comes very close to the metal atom and it is likely that this creates high anisotropy around the CH$_2$ group. On heating a solution of **4** in C$_2$D$_2$Cl$_4$ the C$_6$H$_2$CH_2 signals first broaden, then coalesce to a single non-resolved AB system. The original spectrum reappeared upon cooling the solution to room temperature (Fig. 4). These findings can be interpreted in terms of a fast equilibration of the type shown in Scheme 3 (homomerisation), in which the gold ions move between the different pairs of neighbouring phosphorus centres.

To rule out intermolecular gold transfer, we repeated the variable temperature study at a 10-fold lower concentration and verified that this has no influence on the coalescence temperature. The observed intramolecular dynamics, in which the two metal atoms move simultaneously (both clockwise or counterclockwise), is reminiscent of those found in some recently reported Li$_2$ complexes.[43] The experimentally determined thermodynamic data reveal that there is no important entropic contribution to this process ($\Delta S^\ddagger = -0.008$ kJ K^{-1} mol^{-1}, $\Delta H^\ddagger = 76.020$ kJ mol^{-1}). It appears therefore very likely that the migration of the gold ions from one site to the other does not involve a significant structural change. The related silver complex **5**, which was prepared by treating L^1 with 2 equivalents of AgBF$_4$, displayed similar dynamic behaviour. In the temperature range 273–330 K the ^{31}P NMR spectra showed a single signal with the expected J(AgP) coupling constants. As for **4**, the ^{1}H NMR spectrum of **5** displays two AB systems for the C$_6$H$_2$CH_2C$_6$H$_2$ hydrogen atoms. Again one AB separation is rather large (Δδ 2.23) compared to the other one (0.85).

The dynamics observed in complexes **4** and **5** involves two metal ions and four phosphorus centres. The exact nature of the

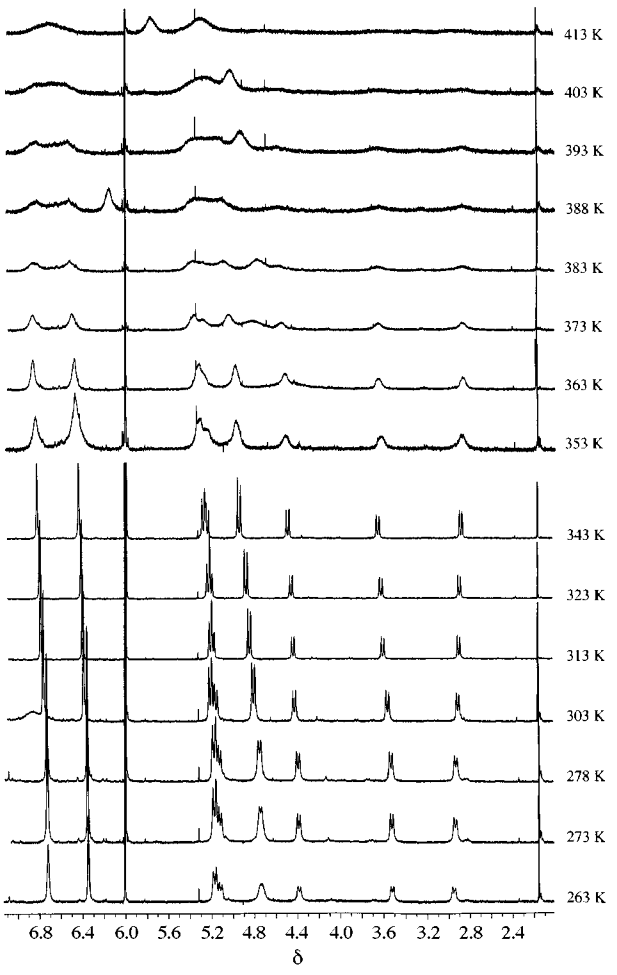
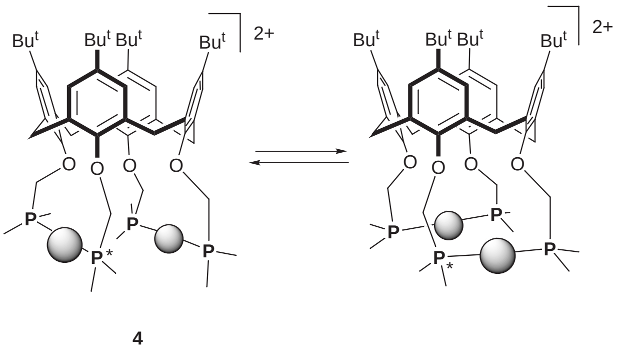


Fig. 4 Variable temperature ^{1}H NMR spectra (500 MHz, C$_2$D$_2$Cl$_4$) for complex **4**



Scheme 3 Rotation of the gold atoms around the C_2 axis of the calixarene in complex **4**

driving force which allows metal migration is not known, but it is likely that the M–P bond cleavages that must occur during this process are favoured by the strain existing within the two 12-membered metallomacrocycles. Dissociation of phosphine ligands in gold complexes are not unusual and have been observed in a number of mononuclear complexes of the type $[Au(phosphine)_2]^+$.[44]

In summary, we have shown that cone-shaped calix[4]arenes substituted at the lower rim by four phosphorus(III) centres behave as a small binding surface for four AuCl units. In the dinuclear complexes **4** and **5** a unique motion of two metal ions along the P_4 surface could be established. Further investigations are needed to assess which factors will allow the introduction of similar dynamics in the solid state.

Experimental

Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. Solvents were dried over suitable reagents and freshly distilled under dry nitrogen before use. All reactions were carried out using modified Schlenk techniques under a dry nitrogen atmosphere. Routine ^{1}H ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.1, 50.3 and 81.00 MHz, respectively. The ^{1}H chemical shifts are reported relative to residual protiated solvents ($CDCl_3$, δ 7.26; CD_2Cl_2, δ 5.32), the ^{13}C chemical shifts relative to deuteriated solvents ($CDCl_3$, δ 77.00; CD_2Cl_2, δ 53.8) and the ^{31}P NMR data relative to external H_3PO_4. Mass spectra were recorded on a ZAB HF VG or a KRATOS MS 50 RF analytical spectrometer using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed by the Service de Microanalyse, Centre de Recherche Chimie, Strasbourg, and by the Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig. Melting points were determined with a Büchi capillary melting-point apparatus and are uncorrected.

Compounds L^1,[34] L^2[30] and [AuCl(tht)][45] were synthesized according to published procedures.

Preparations

$[(AuCl)_4L^1]$ 1. To a stirred solution of compound L^1 (0.300 g, 0.21 mmol) in CH_2Cl_2 (10 cm^3) was added a solution of [AuCl(tht)] (0.268 g, 0.84 mmol) in CH_2Cl_2 (10 cm^3). After 0.5 h the solution was filtered over a bed of Celite, concentrated to *ca.* 5 cm^3, and addition of pentane precipitated complex **1** as a colourless powder which was dried *in vacuo*. Yield 0.438 g, 88%; m.p. 158–163 °C (decomp.). ^{1}H NMR (200 MHz, 293 K, $CDCl_3$): δ 7.82–7.25 (m, 40 H, PPh_2), 6.52 (s, 8 H, *m*-H), 5.30 (s br, 8 H, OCH_2PPh_2), 4.16 and 2.79 (AB quartet, *J* = 13 Hz, 4 H each, $C_6H_2CH_2$) and 1.01 (s, 36 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, $CDCl_3$): δ 151.75, 146.04, 134.61, 131.79, 127.93 and 125.87 (quaternary aryl C), 134.36, 134.10, 132.08, 129.21, 129.04 and 125.87 (aryl CH), 71.75 (d, J_{PC} = 42 Hz, OCH_2PPh_2), 33.85 [s, $C(CH_3)_3$], 32.01 (s, $C_6H_2CH_2$) and 31.35 [s, $C(CH_3)_3$]. ^{31}P-{^{1}H} NMR (81 MHz, 293 K, $CDCl_3$): δ 22.7 (s). FAB mass spectrum: *m*/*z* 2335 (M^+ − Cl, 100%) (Found: C, 48.76; H, 4.52. Calc. for $C_{96}H_{100}Au_4Cl_4O_4P_4$: C, 48.62; H, 4.25%).

$[(AuCl)_4L^2]$ 2. To a stirred solution of compound L^2 (0.255 g, 0.19 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of [AuCl(tht)] (0.244 g, 0.76 mmol) in CH_2Cl_2 (10 cm^3). After 0.5 h a precipitate was formed and the solvent was evaporated to dryness, yielding a colourless residue. Analytically pure complex **2** was obtained by recrystallisation from toluene–CH_2Cl_2 (1:1). Yield 0.318 g, 55%; m.p. 140 °C (decomp.). ^{1}H NMR (200 MHz, 293 K, CD_2Cl_2): δ 6.82 (s br, 8 H, *m*-H), 3.91 and 3.25 (AB quartet, *J* = 13 Hz, 8 H, $C_6H_2CH_2$), 3.60 (m, 24 H, PNMe), 2.78 {m, 12 H, $CH_3N[C(O)]_2$} and 1.07 (br s, 36 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, CD_2Cl_2): δ 150.79–127.90 (aryl C), 37.60 [d of complex m, PNMe, ^{3}J(PMe) ≈ 15 Hz], 37.50 (m, NMe), 34.66 [s, $C(CH_3)_3$], 31.44 [$C(CH_3)_3$ and $C_6H_2CH_2$] and 30.88 [s, $NCH_3(CO)_2$]. ^{31}P-{^{1}H} NMR (81 MHz, 293 K, CD_2Cl_2): δ 101.6 (s). FAB mass spectrum: *m*/*z* 2235.3 (M^+ − Cl, 100%) (Found: C, 32.44; H, 3.82. Calc. for $C_{64}H_{88}Au_4Cl_4N_{12}O_{12}P_4 \cdot 2CH_2Cl_2$: C, 32.47; H, 3.79%).

Partially aurated species derived from L^1 and L^2 (the signals arising from tht have been omitted). L^1:[AuCl(tht)] = 1:1. ^{1}H NMR (200 MHz, 293 K, $CDCl_3$): δ 7.37–7.12 (40 H, PPh_2), 6.71 (br s, 8 H, *m*-H), 5.17 (br s, 8 H, OCH_2PPh_2), 4.24 and 3.02 (AB quartet, *J* = 12 Hz, 4 H each, $C_6H_2CH_2$) and 1.05 (s, 36 H, *tert*-butyl). ^{31}P-{^{1}H} NMR (81 MHz, 293 K, $CDCl_3$): δ 16.6 (br s).

L^1:[AuCl(tht)] = 1:2. ^{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*-H), 4.97 (br s, 8 H, OCH_2PPh_2), 4.53 and 2.92 (AB quartet, *J* = 12 Hz, 4 H each, $C_6H_2CH_2$) and 1.04 (s, 36 H, *tert*-butyl). ^{31}P-{^{1}H} NMR (81 MHz, 293 K, $CDCl_3$): δ 31.4 (br s).

L^1:[AuCl(tht)] = 1:3. ^{1}H NMR (200 MHz, 293 K, $CDCl_3$): δ 7.66–7.19 (40 H, PPh_2), 6.58 (br s, 8 H, *m*-H), 4.96 (br s, 8 H, OCH_2PPh_2), 4.46 and 2.90 (AB quartet, *J* = 12 Hz, 4 H each, $C_6H_2CH_2$) and 1.01 (s, 36 H, *tert*-butyl). ^{31}P-{^{1}H} NMR (81 MHz, 293 K, $CDCl_3$): δ 34.5 (br s) and 25.2 (br s).

L^2:[AuCl(tht)] = 1:1. ^{1}H NMR (200 MHz, 293 K, CD_2Cl_2): δ 6.76 (br s, 8 H, *m*-H), 3.38 and 3.19 (AB quartet, *J* = 13 Hz, 4 H each, $C_6H_2CH_2$), 3.44 (br d, 24 H, PNMe), 2.64 {br s, 12 H, $[C(O)]_2NMe$} and 1.03 (s, 36 H, *tert*-butyl). ^{31}P-{^{1}H} NMR (81 MHz, 293 K, CD_2Cl_2): δ 96.8 (br s) and 91.0 (br s). ^{31}P-{^{1}H} NMR (81 MHz, 203 K, CD_2Cl_2): δ 107.2 (br s) and 89.2 (s).

L^2:[AuCl(tht)] = 1:2. ^{1}H NMR (200 MHz, 298 K, CD_2Cl_2): δ 6.81 (br s, 8 H, *m*-H), 3.89 and 3.23 (AB quartet, *J* = 13 Hz, 4 H each, $C_6H_2CH_2$), 3.53 (br d, 24 H, PNMe), 2.70 {br s, 12 H, $[C(O)]_2NMe$} and 1.04 (br s, 36 H, *tert*-butyl). ^{31}P-{^{1}H} NMR (81 MHz, 293 K, CD_2Cl_2): δ 99.1 (br s) and 96.0 (br s).

L^2:[AuCl(tht)] = 1:3. ^{1}H NMR (200 MHz, 298 K, CD_2Cl_2): δ 6.5 (br s, *m*-H), 3.90 and 3.33 (AB quartet, *J* = 13 Hz, 4 H each, $C_6H_2CH_2$), 3.70 (br s, 24 H, PNMe), 2.75 {br s, 12 H, $[C(O)]_2NMe$} and 1.00 (br s, 36 H, *tert*-butyl). ^{31}P-{^{1}H} NMR (81 MHz, 293 K, CD_2Cl_2): δ 106.2 (br s).

$[Au_2L^1][PF_6]_2$ 4. To a solution of compound L^1 (0.151 g, 0.10 mmol) in CH_2Cl_2 (10 cm^3) was added a solution of [AuCl(tht)] (0.067 g, 0.21 mmol) in CH_2Cl_2 (10 cm^3). After 0.5 h the solution was added to a suspension of thallium hexafluorophosphate (0.073 g, 0.21 mmol) in acetonitrile (2 cm^3). After stirring for 5 min the white precipitate was filtered through a bed of Celite, and the filtered solution concentrated to *ca.* 5 cm^3. Addition of pentane yielded complex **4** as a colourless precipitate. Yield 0.209 g, 94%; mp 120–123 °C (decomp.). ^{1}H NMR (200 MHz, 293 K, $CDCl_3$): δ 7.79–7.25 (40 H, PPh_2), 6.82 and 6.33 (AB quartet, *J* = 2, 4 H each, *m*-H), 5.23 and 2.73 (AB quartet, *J* = 13, 2 H each, $C_6H_2CH_2$), 5.14 and 4.88 (AB quartet, *J* = 13, 4 H each, OCH_2PPh_2, $J_{PA} = J_{PB} \approx 0$), 4.48 and 3.70 (AB quartet, *J* = 13 Hz, 2 H each, $C_6H_2CH_2$) and 0.98 (s, 36 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, $CDCl_3$): δ 152.65–125.14 (aryl C), 73.00 (vt, J_{PC} + $^{3}J_{PC}$ = 46 Hz, OCH_2PPh_2), 33.93 [s, $C(CH_3)_3$], 32.00 and 31.70 (2s, $C_6H_2CH_2$) and 31.31 [s, $C(CH_3)_3$]. ^{31}P-{^{1}H} NMR (81 MHz, 293 K, $CDCl_3$): δ 40.6 (br s). FAB mass spectrum: *m*/*z* 1980.4 ($[M - PF_6]^+$, 20%) (Found: C, 54.30; H, 4.88. Calc. for $C_{96}H_{100}Au_2F_{12}O_4P_6$: C, 54.25; H, 4.74%).

$[Ag_2L^1][BF_4]_2$ 5. To a stirred solution of silver(I) tetrafluoroborate (0.027 g, 0.14 mmol) in tetrahydrofuran (2 cm^3) was added a solution of compound L^1 (0.100 g, 0.07 mmol) in tetrahydrofuran (10 cm^3). After 5 min the solvent was evaporated to dryness, yielding a colourless residue. The latter was dissolved in CH_2Cl_2 (5 cm^3) and the resulting solution filtered over a bed of Celite. Addition of hexane precipitated complex **5** as

Table 3 Crystallographic data for complexes **1** and **3***

	1	**3**·$1.5C_6H_5CH_3·H_2O$
Formula	$C_{96}H_{100}Au_4Cl_4O_4P_4$	$C_{74.5}H_{104}Au_2Cl_2N_{12}O_{13}P_4$
M	2371.31	1964.41
Crystal colour, habit	Colourless prism	Colourless tablet
Crystal dimensions/mm	0.50 × 0.40 × 0.25	0.70 × 0.30 × 0.15
a/Å	29.370(4)	37.230(6)
b/Å	22.809(3)	27.211(4)
c/Å	18.807(3)	21.269(4)
β/°	114.79(2)	126.671(10)
U/Å^3	11 438(3)	17 721(5)
Z	4	8
D_c/g cm^{-3}	1.377	1.473
μ/mm^{-1}	5.30	3.57
No. reflections measured	12 264	23 002
No. independent reflections	9932	15 517
R_{int}	0.048	0.091
R [$F > 4\sigma(F)$]	0.050	0.049

* Details in common: monoclinic, space group *C*2/*c*; 173 K; $(\Delta/\sigma)_{max} < 0.001$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

a colourless powder. Yield 0.102 g, 80%; mp 141–143 °C (decomp.). ^{1}H NMR (200 MHz, 293 K, $CDCl_3$): δ 7.70–7.26 (br m, 40 H, PPh_2), 6.76 and 6.30 (2 br s, 4 H each, *m*-H), 5.13 and 4.56 (AB quartet, J = 11, 4 H each, OCH_2PPh_2), 4.40 and 2.17 (AB quartet, J = 12, 2 H each, $C_6H_2CH_2$), 4.22 and 3.37 (AB quartet, J = 12 Hz, 2 H each, $C_6H_2CH_2$) and 0.98 (s, 36 H, *tert*-butyl). ^{13}C-{^{1}H} NMR (50 MHz, 293 K, $CDCl_3$): δ 152.63–124.66 (aryl C), 73.57 (vt, $J_{PC} + {}^3J_{PC} = 30$ Hz, OCH_2PPh_2), 33.66 [s, $C(CH_3)_3$], 31.64 and 29.95 (2s, $C_6H_2CH_2C_6H_2$) and 31.09 [s, $C(CH_3)_3$]. ^{31}P-{^{1}H} NMR (81 MHz, 293 K, $CDCl_3$): δ 4.6 [2d, $J(^{107}Ag–P)$ = 509 Hz, $J(^{109}Ag–P)$ = 585 Hz, PPh_2]. FAB mass spectrum: *m*/*z* 1743 ($[M - BF_4]^+$, 8) (Found: C, 63.16; H, 5.69. Calc. for $C_{96}H_{100}Ag_2B_2F_8O_4P_4$: C, 62.97; H, 5.50%).

Variable temperature NMR experiments

The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra for the variable temperature studies were recorded on a Bruker ARX-500 spectrometer (^{1}H, 500.1 MHz) for L^1 complexes and an AC-200 spectrometer (^{1}H, 200.1; ^{31}P, 81.0 MHz) for L^2 complexes. All temperatures were corrected to the ethylene glycol spin temperature, and are estimated to be reliable at ±5 K. The spectra were recorded every 10 K for each experiment to determine the coalescence temperature T_c/K. The free energy barrier for the observed process ($\Delta G^‡ = 79.4$ kJ mol^{-1}) is derived from the Eyring equation: $\Delta G^‡ = 10^{-3}RT_c[22.96 + (\ln T_c/\Delta\nu)]$ kJ mol^{-1}.[46] The calculations for the determination of $\Delta H^‡$ and $\Delta S^‡$ are based on the two exchange processes $PCH_2 \longleftrightarrow PCH'_2$ and *m*-H $\longleftrightarrow$ *m*-H′.

Crystallography

Crystallographic data for complexes **1** and **3** are given in Table 3. Colourless crystals of **1** suitable for diffraction were obtained by slow diffusion of hexane into a chlorobenzene solution of the pure complex. Single crystals of **3** were obtained by addition of toluene to a dichloromethane solution (1 : 1, v/v) containing a 2 : 1 mixture of [AuCl(tht)] and L^2. Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 with LT-2 low temperature attachment). The orientation matrices for **1** and **3** were refined from setting angles of 64 (81) reflections in the 2θ range 5–25° (monochromated Mo-Kα radiation). Absorption corrections were based on ψ scans. Both structures were solved by direct methods and refined aniostropically on F^2 (program SHELXL 93[47]). Hydrogen atoms were included using a riding model or rigid methyl groups. Weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ were employed, with $P = (F_o^2 + 2F_c^2)/3$.

Special features of refinement. In compound **1** various regions of poorly resolved electron density indicate the presence of disordered solvent, but no appropriate model could be refined. In the crystal data, values for M_r, D_c, *etc.* do not include this extra solvent. In **3** the *tert*-butyl group C(61)–C(63) is disordered over two positions and one toluene is disordered over an inversion centre.

From the experiment leading to **3** {1 equivalent [AuCl(tht)] + 2 equivalents L^2} further crystals were collected. An X-ray determination of ligand L^2 with 1.5 'AuCl' was conducted: we found one AuCl site to be fully occupied and the neighbouring one half-occupied; the latter represents alternative (overlapping) sites in neighbouring molecules. The calixarene system displayed a cone conformation. One solvent molecule and the half occupied Au atom also overlapped; in view of these disorder problems, the full data of this compound will not be presented. Crystal data: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 17.783(4)$, $b = 19.528(4)$, $c = 28.508(6)$, $\beta = 107.573(12)°$.

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See http://www.rsc.org/suppdata/dt/1998/2115/ for crystallographic files in .cif format.

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