

Gilded Chalice: Tetra-aurated Calix[4]arenes

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

5,11,17,23-Tetrakis(trimethylsilylethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**1**) was synthesised in two steps starting from 25,26,27,28-tetra-*n*-propoxycalix[4]arene, and the structure of **1** was determined by X-ray diffraction. Compound **1** was desilylated (K₂CO₃) to give 5,11,17,23-tetrakis(ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**2**), which was tetra-aurated under basic conditions (NaOEt, THF) with a series of phosphane-gold chlorides (*o*-Tol₃PAuCl, Ph₃PAuCl, Ph₂MePAuCl, PhMe₂PAuCl, Me₃PAuCl, Cy₃PAuCl, *t*-Bu₃PAuCl) to afford in good to excellent yields the tetra-aurated tetraethynylcalix[4]arene species **3–9** in one step [with phosphane ligands *o*-Tol₃P (**3**), Ph₃P (**4**), Ph₂MeP (**5**), PhMe₂P (**6**), Me₃P (**7**), Cy₃P (**8**), *t*-Bu₃P (**9**)]. All compounds were characterised by ¹H NMR and infrared spectroscopy, mass spectrometry and by elemental analyses, additionally **3**, **4**, **5**, **8** and **9** by ¹³C{¹H}, and **3–6**, **8** and **9** by ³¹P{¹H} NMR spectroscopy. The molecular structures of complexes **3** and **9** were determined by X-ray diffraction and show pinched-cone conformations, but neither intra- nor intermolecular attractive aurophilic Au...Au contacts. The acceptor ability of complexes **3** and **9** was investigated by complexation attempts with various phosphane-gold chlorides and xenon gas under pressure, but interactions could not be determined experimentally. The formation of a complex between xenon and gilded calix[4]arene could, however, be predicted for fluorine-substituted species and with very small phosphane ligands (PH₃) on the basis of quantum-chemical calculations; the energy of formation is 9.6 kJ mol⁻¹. The crystal structure of Ph₂MePAuCl was also determined and shows Au...Au-bonded dimers.

Key words: Gold, Xenon, Calix[4]arenes, Ethynes, Acceptor, Crystal Structure, Quantum-Chemistry

Introduction

Host-guest chemistry of macrocyclic ligands is an established part of macromolecular chemistry. It developed since Pedersen's reports on potassium crown-ether complexes in 1967 [1]. Today we know more than 5000 crown-type systems [2] and three-dimensional cryptands [3] and together with the myriad of polydentate ligands for metal complexation this comprises an immense body of polydonor molecules. The reverse situation, poly-Lewis acids, is much less well developed. Such systems typically contain a number of metal or other Lewis-acidic functions (*e.g.* based on boron, silicon *etc.*) arranged in a way to allow re-

verse complexation of a Lewis-basic entity. One of the reasons for the present paucity of variety in poly-Lewis acids can be seen in the fact that they require donor-free frameworks to carry the Lewis-acid functions, and such frameworks are practically restricted to hydrocarbons or organosilanes (and possibly boranes and carbaboranes). Despite the overwhelming dominance of poly-Lewis bases, a considerable number of known poly-Lewis acids include systems based on silicon [*e.g.* 4], tin [*e.g.* 5], mercury [*e.g.* 6–10] as well as boron [*e.g.* 9–16], aluminium [17–22], gallium [18–21] and indium [23] as Lewis-acid functions. Within this selection such compounds are of particular interest, in which the metal functions are placed

in a defined geometrical arrangement, *i. e.* where such functions are bonded to more or less rigid frameworks and ready to work as acceptors in a concerted way.

Besides classical donor-acceptor functionality, molecular recognition can also be based on other types of weak bonding, *e. g.* dispersive forces like the principle of metallophilicity. The main objects of study in this context are polynuclear gold(I) complexes. The phenomenon of aurophilicity has attracted multifaceted attention in recent years [24–30]. Isocyanide and alkynyl organogold(I) complexes are generally photoluminescent, and applications of these classes of compounds include the development of cluster compounds [31] as well as of mesogenic [32] and polymorphic materials [33]. They have also been used to construct new chemosensors [34]. This concept was used to construct metal-ion sensing compounds which are based on the principle to switch Au...Au interactions of dinuclear gold(I) complexes on and off, when bridging diphosphanes and crown ether-functionalised thiolate ligands complex metal ions [35, 36]. Calixarene compounds have also widely been employed in chemosensing work [37] and have already been envisaged as well-suited building blocks for the construction of oligo-nuclear gold(I) scaffolds that allow for selective chemosensing due to defined Au...Au distances [38].

Results and Discussion

Synthesis

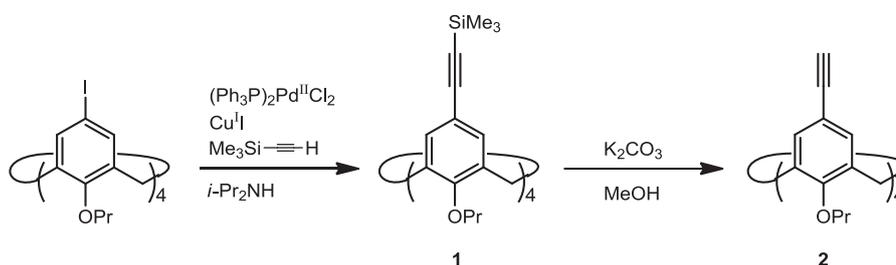
In order to place four metal atoms on one side of a molecule that point into the same direction, we chose calix[4]arenes with fixed conformations as backbones. The synthetic access to *cone*-5,11,17,23-tetraethynyl-25,26,27,28-tetra-*n*-propoxy-calix[4]arene is well

established. Starting with 25,26,27,28-tetrahydroxy-calix[4]arene, the OH function can be protected in a classical Williamson ether formation reaction [39, 40]. Tetra-iodation to *cone*-5,11,17,23-tetraiodo-25,26,27,28-tetra-*n*-propoxy-calix[4]arene was achieved by a protocol of Mattay *et al.* using iodine, sodium peroxodisulphate and tetramethylammonium iodide as reagents [41]. This tetraiodide was then subjected to a Sonogashira coupling reaction with trimethylsilylacetylene [42] (Scheme 1) resulting in 5,11,17,23-tetrakis(trimethylsilylethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**1**). Deprotection was achieved by treatment with base (K_2CO_3) in 91% yield. In this way tetraethynylcalix[4]arene (**2**) is available in a yield of 43% over all four steps of synthesis. Details of its characterisation are provided in the Experimental Section.

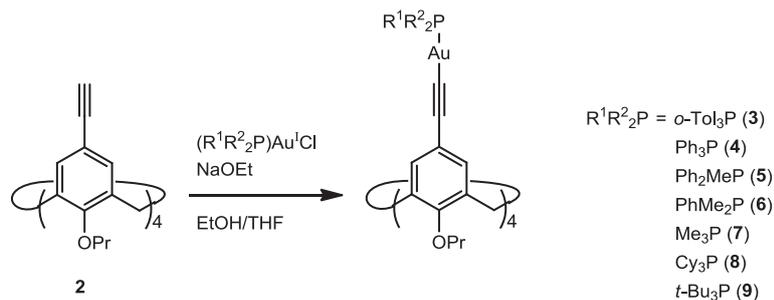
The de-protected 5,11,17,23-tetrakis(ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**2**) was subsequently reacted in the presence of sodium ethoxide as a base with a series of phosphane-gold chlorides of different steric demand at the phosphorus function (Scheme 2). The reactions proceeded generally in good to excellent yields to afford the tetra-aurated species **3–9** in one step.

Some of the compounds are of extremely low solubility in common organic solvents, which restricted their analysis by solution-based methods. The tetrakis-gold(I)acetylide compounds were characterised by 1H (**3–9**), $^{13}C\{^1H\}$ (**3, 4, 5, 8, 9**) and $^{31}P\{^1H\}$ NMR (**3–6, 8, 9**) spectroscopy, by infrared spectroscopy (**3–9**), mass spectrometry (**3–9**), elemental analyses (**3–9**), and by X-ray diffraction of single crystals (**3** and **9**).

The presence of a cone conformation, *i. e.* the conformational stability during auration, follows from the occurrence of a single set of resonances in the 1H NMR spectra. The hydrogen atoms of the methylene groups



Scheme 1.



Scheme 2.

bridging the arene units in the calix[4]arene skeletons result in two doublets for each the equatorial and axial atoms of this geminal pair, *e. g.* for compound **3** at 3.00 ppm for H_{eq} and at 4.26 ppm for H_{ax} . The corresponding coupling constant in this case is 12.4 Hz. Other characteristic spectroscopic data for the compounds are the $^{31}\text{P}\{^1\text{H}\}$ resonances at 24.5 (**3**), 42.6 (**4**), 26.9 (**5**), 12.1 (**6**), 56.2 (**8**), and 91.5 (**9**) ppm, and the resonances of the gold-bound ethynyl carbon atoms at 126.8 (**3**), 134.8 (**8**) and 133.7 (**9**) ppm as well as their extraordinarily large $^2J_{\text{P,C}}$ coupling constants of 143 (**3**), 134 (**8**) and 130 (**9**) Hz.

Crystal structures

During these studies we obtained single-crystalline material suitable for structure determination by X-ray diffraction of the tetra-gold complexes **3** and **9** as well as of the synthetic intermediate tetrakis(silylethynyl)calixarene **1** and the phosphane-gold chloride precursor $(\text{Me}_2\text{PhP})\text{AuCl}$, which we report here.

Tetrakis(silylethynyl)calixarene **1**

The molecular structure of the trimethylsilyl precursor **1** was determined by single-crystal X-ray diffraction (Fig. 1) and proves, besides spectroscopic evidence, the presence of the *cone*-conformation. Some

selected structure parameters are provided in Table 1. Most of them are of standard values and deserve no detailed comments. Notable are the deviations from linearity in the C–C–Si units, which is more pronounced for the units involving Si(1) and Si(3), which belong to trimethylsilyl groups that are forced into close proximity by the conformation of the calix[4]arene skeleton.

In order to describe the conformation of calix[4]arenes quantitatively in terms of structural parameters we have defined a tilt angle τ between the mean plane of a benzene ring and the mean plane defined by the *O*-bound (*ipso*) and *para*-positioned carbon atoms of its neighbouring benzene rings (Fig. 1) [43]. Planes intersecting above the wide rim define negative tilt angles τ , those intersecting below are positive. For symmetric conformations, τ is half the interplanar angle between the planes defined by two opposing benzene rings. The pseudo-symmetry of the *cone*-conformation of **1** is therefore described by pairwise similar tilt angles τ of -11.3 and -8.4° for the benzene rings containing C(6) and C(20), and 50.4 and 51.5° for those containing C(13) and C(27).

$(\text{Ph}_2\text{MeP})\text{AuCl}$

The reported structures of the phosphane-gold chlorides with sterically demanding substituents at phosphorus, for example $(o\text{-Tol}_3\text{P})\text{AuCl}$ [44], $(\text{Ph}_3\text{P})\text{AuCl}$

Table 1. Selected bond lengths and angles of 5,11,17,23-tetrakis(trimethylsilylethynyl)-25,26,27,28-tetra-*n*-propoxy-calix[4]arene (**1**).

	d (Å)		\angle (deg)		τ (deg)
Si(1)–C(30)	1.827(4)	C(29)–C(30)–Si(1)	173.2(3)	Ar at O(1)	-11.3
Si(2)–C(35)	1.832(4)	C(34)–C(35)–Si(2)	177.1(3)	Ar at O(2)	50.4
Si(3)–C(40)	1.827(4)	C(39)–C(40)–Si(3)	169.8(3)	Ar at O(3)	-8.4
Si(4)–C(45)	1.836(3)	C(44)–C(45)–Si(4)	178.9(3)	Ar at O(4)	51.5

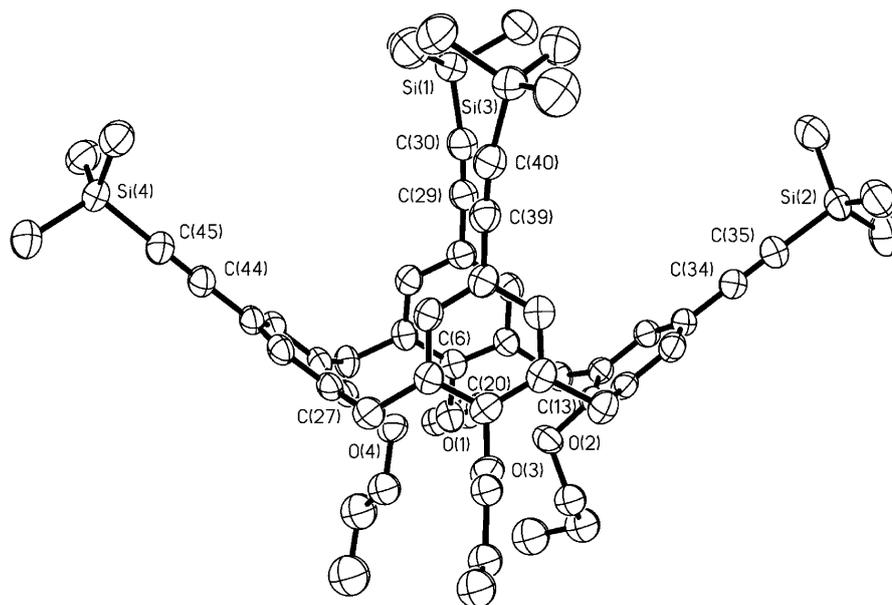


Fig. 1. Molecular structure of 5,11,17,23-tetrakis(trimethylsilyylethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**1**) in the solid state. Hydrogen atoms, solvent molecules and minor-occupied disordered atom positions are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

[45], (Cy₃P)AuCl [46] and (*t*-Bu₃P)AuCl [47] do not show significant Au⋯Au interactions. In contrast, the structure of (PhMe₂P)AuCl [48] features such attractive aurophilic Au⋯Au interactions with a distance of 3.262 Å. Similarly the arrangement of the molecules of (Me₃P)AuCl in the solid phase is governed by Au⋯Au interactions, leading to the formation of helical chains with Au⋯Au distances of 3.271, 3.356 and 3.386 Å. In the context of this work we obtained crystals of (Ph₂MeP)AuCl by slow evaporation of the solvent of a solution in CDCl₃ of this compound (in an NMR tube) and thus were able to determine its crystal structure (Fig. 2).

(Ph₂MeP)AuCl crystallises in the triclinic space group *P* $\bar{1}$ with two independent molecules in the asymmetric unit. The structure is shown in Fig. 2. The distance of 3.080(1) Å between Au(1) and Au(2) is shorter than those in (PhMe₂P)AuCl and (Me₃P)AuCl. Considering the steric demand of the phosphane ligand, (Ph₂MeP)AuCl is intermediate between (Ph₃P)AuCl (no Au⋯Au interactions) and (Me₂PhP)AuCl (with longer Au⋯Au interactions).

The Au–P bonds at 2.239(1) Å for Au(1)–P(1) and 2.233(1) Å for Au(2)–P(2) are of comparable lengths to those in (Ph₃P)AuCl (2.235(3) Å). Shorter Au–P

distances were found in (Me₂PhP)AuCl at 2.214(6) and 2.205(5) Å. The Au–Cl bonds are 2.316(1) Å (Au(1)–Cl(1)) and 2.305(1) Å (Au(2)–Cl(2)) and thus longer than in both reference compounds (2.279(3) Å in (Ph₃P)AuCl and 2.276(6)/2.273(6) Å in (Me₂PhP)AuCl). Apparently, the gold-gold interaction leads to steric stress, so that steric repulsion between the ligands occurs. This leads to P–Au–Cl angles of 175.0(1)° (P(1)–Au(1)–Cl(1)) and 172.5(1)° (P(2)–Au(2)–Cl(2)), which are smaller than in the almost linear (Ph₃P)AuCl (P–Au–C: 179.7(1)°) and also smaller than in (Me₂PhP)AuCl (P–Au–C: 177.2(3)° and 175.4(2)°). However, based on these purely structural data we cannot exclude intra-molecular hydrogen bridges (methyl-H⋯Cl(1) 2.84 Å, *o*-H⋯Cl(2) 2.80(1) Å) to be an alternative explanation.

*5,11,17,23-Tetrakis(tri-*o*-tolylphosphane-gold-ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (3)*

The molecular structure of (*o*-Tol)₃PAu-CC-calix[4]areneOPr (**3**) was determined by X-ray diffraction of a single crystal belonging to the triclinic space group *P* $\bar{1}$ and is shown in Fig. 3, selected struc-

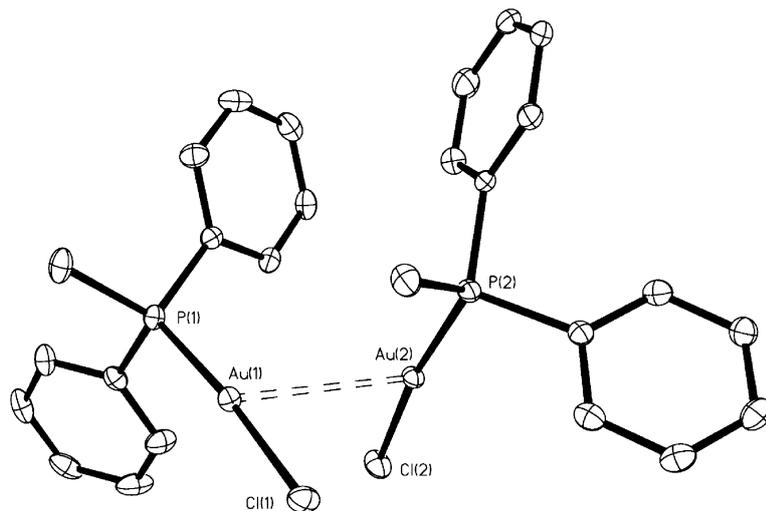


Fig. 2. Molecular structure and aggregation of diphenylmethylphosphane-gold(I) chloride in the crystal. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

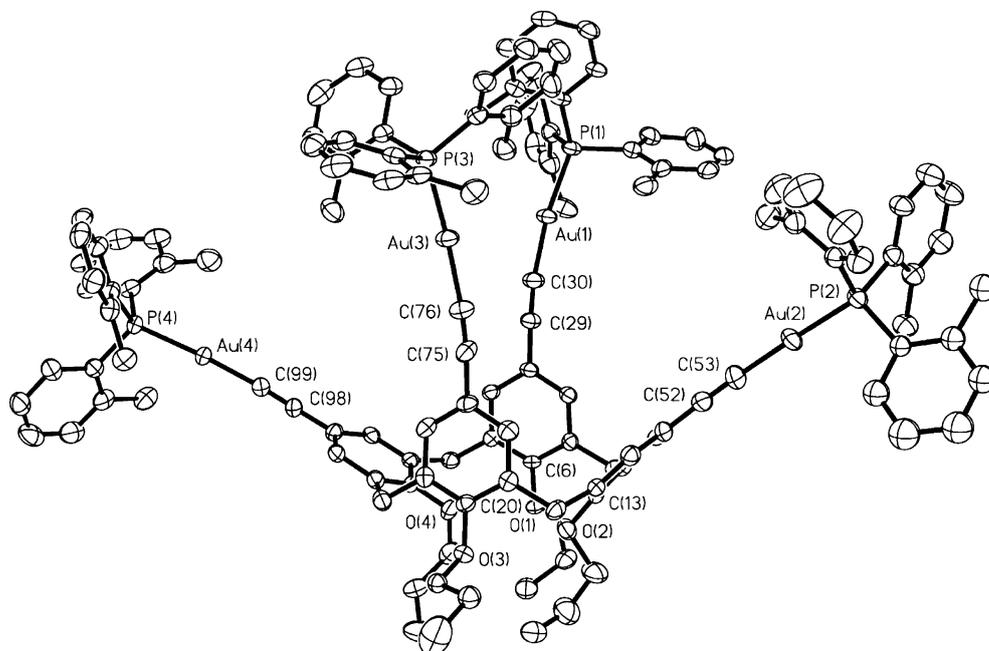


Fig. 3. Molecular structure 5,11,17,23-tetrakis(tri-*o*-tolylphosphane-gold-ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**3**) in the crystal. Hydrogen atoms, solvent molecules and minor-occupied disordered atom positions are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

ture parameter values are listed in Table 2. The crystal contains molecules with pinched-cone conformation, characterised by two different pairs of tilt angles τ : whereas the benzene rings bound to the oxygen atoms

O(1) and O(3) show tilt angles of $\tau = -0.8^\circ$ and $\tau = -9.0^\circ$, the tilt angles for the rings bonded to the oxygen atoms O(2) and O(4) measure $\tau = 46.8^\circ$ and $\tau = 59.1^\circ$, respectively. Similar to the structure of the

Table 2. Selected bond lengths and angles of 5,11,17,23-tetrakis(tri-*o*-tolylphosphane-gold-ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**3**).

	<i>d</i> (Å)		\angle (deg)		τ (deg)
Au(1)–C(30)	2.000(6)	C(29)–C(30)–Au(1)	170.0(6)	Ar at O(1)	–0.8
Au(1)–P(1)	2.291(2)	C(30)–Au(1)–P(1)	171.4(2)		
Au(2)–C(53)	1.994(7)	C(52)–C(53)–Au(2)	175.1(6)	Ar at O(2)	46.8
Au(2)–P(2)	2.293(2)	C(53)–Au(2)–P(2)	175.3(2)		
Au(3)–C(76)	2.009(6)	C(75)–C(76)–Au(3)	174.8(6)	Ar at O(3)	–9.0
Au(3)–P(3)	2.279(2)	C(76)–Au(3)–P(3)	174.6(2)		
Au(4)–C(99)	2.015(6)	C(98)–C(99)–Au(4)	176.2(6)	Ar at O(4)	59.1
Au(4)–P(4)	2.292(1)	C(99)–Au(4)–P(4)	174.1(2)		

silylated calixarene **1** described above, the structural parameters reflect the steric repulsion between the opposing AuP(*o*-Tol)₃ groups: the expected approximate linearity of the C≡C–Au units is – on average – more distorted for those units bonded to the coarsely parallel benzene rings with C(29)–C(30)–Au(1) 170.0(6)°, C(75)–C(76)–Au(3) 174.8(6)°, while – on average – the other two angles (C(52)–C(53)–Au(2) 175.1(6)°, C(98)–C(99)–Au(4) 176.2(6)°) are wider.

None of the Au...Au distances, intra- or intermolecular, provides evidence for aurophilic attractive interactions. The shortest Au...Au separation between the two closer lying gold atoms Au(1) and Au(3) is 6.291(1) Å, the longest between Au(2) and Au(4) 17.894(1) Å. The shortest intermolecular Au...Au distance is 6.490(1) Å,

*5,11,17,23-Tetrakis(tri-*t*-butylphosphane-gold-ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (9)*

The molecular structure of (*t*-Bu)₃PAu-CC-calix[4]areneOPr (**9**) was determined by X-ray diffraction of a single crystal belonging to the tetragonal space group *I*4₁/*a* and is shown in Fig. 4, and selected structure parameter values are listed in Table 3.

The crystal contained highly disordered different solvent molecules (one C₆H₅F, two CHCl₃ and two

C₆H₁₄) the scattering contributions of which were treated by the SQUEEZE method [49]. Furthermore, there was a disorder of C(20) resolved on two positions (72 : 28). The overall quality of the crystal, reflected in part by this solvent disorder, did not allow a refinement to a good *R* factor (*R* [*I* > 2 σ (*I*)] = 9.42%), but the obtained structural parameters are consistent with those of the structure of the analogous complex **3**, which adds to their validity.

As in complex **3**, the molecules of **9** are of pinched-cone conformation, characterised by two different pairs of tilt angles τ , but here, due to exact C₂ symmetry, the pairs have identical values. The benzene rings bound to the oxygen atoms O(1) (and O(1')) show tilt angles of $\tau = -0.8^\circ$, the tilt angles for the other two rings bonded to the oxygen atoms O(2) and O(2') measure $\tau = 46.8^\circ$. Again there is a deviation from the expected approximate linearity of the C≡C–Au units, but in the case of **9** the values for the two distinguishable C≡C–Au units are identical within experimental error (C(14)–C(15)–Au(1) 174.6(9)° and C(16)–C(17)–Au(2) 173.3(11)°).

As in **3** none of the Au...Au distances, intra- or intermolecular, is short enough to provide evidence for attractive aurophilic interactions. The shortest intramolecular Au...Au separation Au(1) and Au(1') is 7.610(1) Å, the shortest intermolecular Au...Au distance is 5.817(1) Å.

Table 3. Selected bond lengths and angles of 5,11,17,23-tetrakis(tri-*t*-butylphosphane-gold-ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**9**).

	<i>d</i> (Å)		\angle (deg)		τ (deg)
Au(1)–C(15)	1.954(8)	C(14)–C(15)–Au(1)	174.6(9)	Ar at O(1)	–0.8
Au(1)–P(1)	2.266(2)	C(15)–Au(1)–P(1)	176.5(3)		
Au(2)–C(17)	2.034(8)	C(16)–C(17)–Au(2)	173.3(11)	Ar at O(2)	55.3
Au(2)–P(2)	2.300(2)	C(17)–Au(2)–P(2)	177.4(3)		

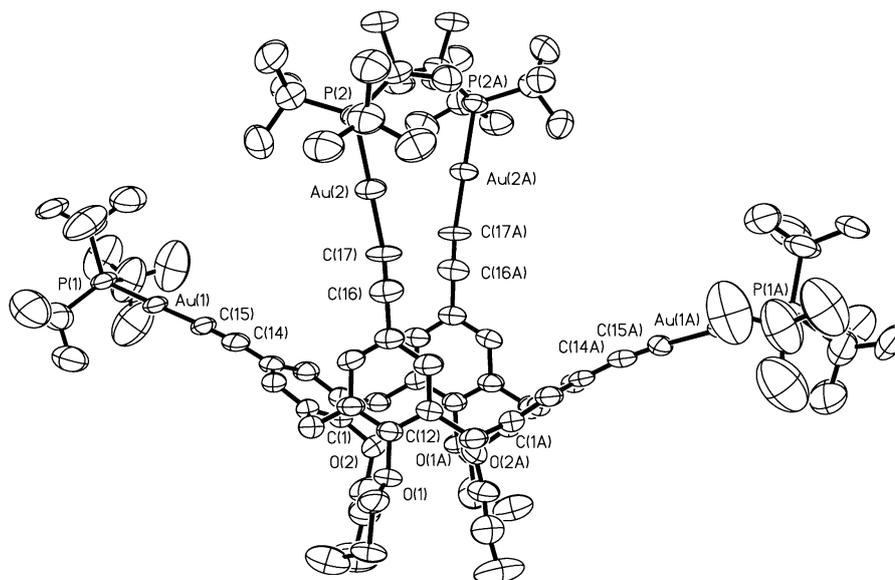


Fig. 4. Molecular structure 5,11,17,23-tetrakis(tri-*t*-butylphosphane-gold-ethynyl)-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**9**) in the crystal. Hydrogen atoms, solvent molecules and minor-occupied disordered atom positions are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

Evaluation of receptor properties

Due to the fact that in the crystal structures of both, compounds **3** and **9**, the gold atoms are placed at the upper rim of a chalice-like tetraethynyl-calix[4]arene and are held at a distance, so that they do not interact aurophilically with one another, there is an unquenched potential of acceptor quality for aurophilic, or generally metallophilic, or other dispersive interactions. Although each of them might be weak, the concerted action of four of them plus the pre-orientation of the system, made it worthwhile investigating the possibility of receptor properties of such compounds.

To cut a long story short, all experimental attempts in this direction failed so far. We tried to offer small triorganylphosphane-gold chlorides, in the expectation, that their gold atoms would be interspersed between those of the gilded calixarenes, but did not observe significant changes in the NMR spectra of solutions of mixtures relative to those of the individual components in the same solvents, neither could we isolate any solid material from such experiments other than the starting materials. In this context we employed phosphane-gold chlorides with sterically demanding substituents at phosphorus, which are known not to be stabilised by aurophilic Au...Au con-

tacts in the solid [(*o*-Tol₃P)AuCl, (Ph₃P)AuCl and (*t*-Bu₃P)AuCl], so they could gain energy by formation of Au...Au interactions with the gilded calixarenes, but also (Ph₂MeP)AuCl (structure see above, by interspersing the number of Au...Au interactions could be doubled) and (Me₃P)AuCl (an equal number of Au...Au interactions would be formed on interspersing of four molecules into one gilded calixarene).

As these experiments were unsuccessful, we turned to a different kind of closed-shell interaction to be explored. Namely, a formal $d^{10}-p^6$ interaction between a coordinatively saturated and an uncharged Au(I) species and the noble gas xenon. Gold-xenon interactions have been in the focus of both theoretical and experimental investigations previously. In 1995 Pyykkö has reported a strong bonding potential between Xe and ionic Au⁺ which predicts an energetic minimum species showing a largely covalent bond type [50]. Some years after this prediction in 1998 clear experimental evidence for the existence of XeAu⁺ was found [51]. After some time, a whole series of various Au–Xe compounds was prepared and characterised by Seppelt and co-workers, containing gold atoms in formal oxidation states of +I or +II and xenon atoms bound in a largely covalent manner [52–54]. To the best of our knowledge there are no theoretical or ex-

perimental studies about purely closed-shell type interactions between a coordinatively saturated and uncharged Au species and Xe published as yet. Due to its four Au atoms the here reported gilded calixarene complexes appear to be well-suited candidates to act as chelating tetradentate acceptors for one xenon atom. To test the plausibility of such a coordination mode we have undertaken high-level *ab-initio* calculations on a closely related model compound. We have chosen PH_3 as a sterically and computationally less demanding ligand for Au, and the ether substituents were replaced by fluorine atoms (**10**). Due to its higher electronegativity compared to alkoxy substituents we expect to get an upper estimation for the interaction energy between gold and xenon atoms, since the interaction energy will increase with increasing positive polarisation of Au. A geometry optimisation has yielded a minimum structure shown in Fig. 5 where two gold atoms are approaching a xenon atom by 3.937 Å (the sum of the van der Waals radii of gold and xenon with 3.82 Å is only slightly below this value), while the other two gold atoms appear to interact not significantly with the xenon atoms ($d(\text{Au}\cdots\text{Xe}) = 9.623$ Å). In the optimised structure the basic conformational properties of the gilded calixarenes are still retained –

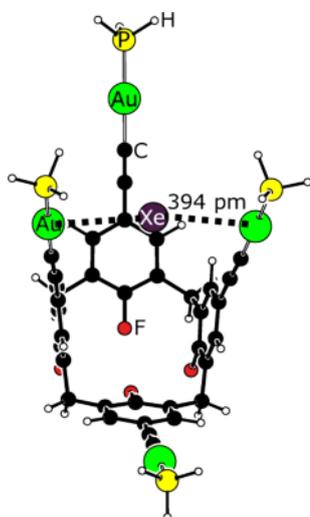


Fig. 5 (color online). Predicted structure of a complex of a xenon atom to a tetra-aurated calixarene molecule with four $-\text{C}\equiv\text{C}-\text{Au}-\text{PH}_3$ groups and fluorine substituents (**10**). The Xe–Au distance found is 3.937 Å, and the energy of formation amounts to 9.6 kJ mol⁻¹. The overall molecular symmetry is C_{2v} .

a pinched cone conformation, *i. e.* the molecule acts as a bidentate chelating acceptor rather than a tetradentate one. The gain of energy by formation of the Xe-(gilded calixarene) complex is calculated to be 9.6 kJ mol⁻¹. A similar gain could be expected for the other two gold atoms, if bonded to xenon as well, but obviously the change in conformation is more costly in energy than the resulting gain. Weak closed-shell van der Waals complexes between xenon and metal-free calixarene complexes have been investigated in solution with ¹²⁹Xe NMR spectroscopy using hyperpolarised Xe [55]. This method appears to be well suited for a future experimental characterisation of the proposed $d^{10} - p^6$ Au–Xe interaction.

Conclusion

We have successfully demonstrated that molecules with four gold atoms pre-oriented to one side of a semi-rigid calix[4]arene skeleton can be synthesised with a variety of different triorganylphosphane groups. Two of these compounds could be crystallised and their structure determined by X-ray diffraction. Both show the presence of a pinched-cone conformation of the calix[4]arene skeleton leading to a shorter and a longer Au \cdots Au distance across the molecule, but all Au \cdots Au distances are too long to be attributable to attractive aurophilic interactions. The resulting unquenched receptor potential by means of the formation of four (or more) weak dispersive type interactions with suitable guest molecules have been explored by reacting the described gilded calix[4]arenes with a variety of phosphane gold chlorides and also elemental xenon under elevated pressure. Because in none of these experiments interactions between guest molecules and gilded calix[4]arene hosts could be observed, although high-level calculations for a model xenon complex with small phosphane ligands at the receptor suggest the possibility of formation and stability of the product, it seems likely that the steric repulsion of the larger substituents used in the experiments energetically overrules the complexation energies. Further work is therefore necessary either to reduce the steric bulk and use compounds such as **7** with Me_3P substituents in the complexation experiments or to use different skeletons for binding the gold atoms, which have smaller Au \cdots Au spacings and do not have to change their conformation too much.

Experimental Section

All manipulations were carried out under dry nitrogen with standard Schlenk and high-vacuum techniques or an MBraun UNILab glove box operated under argon. Solvents were purified and dried by standard methods immediately prior to use. 5,11,17,23-Tetraiodo-25,26,27,28-tetra-*n*-propoxycalix[4]arene was prepared according to a literature procedure [40]. Tri-*o*-tolylphosphane-gold chloride [56–58], triphenylphosphane-gold chloride [59], diphenylmethylphosphane-gold chloride [60], tricyclohexylphosphane-gold chloride [61], and tri-*t*-butylphosphane-gold chloride [47, 62] were prepared along the lines of established protocols. All other chemicals were obtained from commercial sources and used without further purification. NMR spectra were recorded in CDCl₃ with a Bruker DRX 500 spectrometer. All NMR shifts were referenced to the residual peaks of the used solvents except ²⁹Si which was referenced to SiMe₄, and ³¹P which was referenced to 85% H₃PO₄ as external standard. Mass spectra were recorded with a Bruker Esquire 3000 spectrometer. Melting points were determined with a Büchi 545 instrument and are uncorrected. IR spectra were recorded from samples prepared as KBr pellets on Bruker Vector 22 and Shimadzu FT-IR 8400S instruments. Elemental analyses were performed using a LECO CHNS 932 instrument.

General procedure for the synthesis of tetra-aurated calix[4]arenes

To a solution of 5,11,17,23-tetraethyl-25,26,27,28-tetra-*n*-propoxycalix[4]arene (1 eq., usually: 0.1–0.3 mmol) and the phosphane gold(I) precursor (R¹R²P)AuCl (4.2 eq., R¹R²P = *o*-Tol₃PAuCl, Ph₃PAuCl, Ph₂MePAuCl, PhMe₂PAuCl, Me₃PAuCl, Cy₃PAuCl, *t*-Bu₃PAuCl) in 40 mL thf was added a freshly prepared solution of sodium ethanolate in 15 mL ethanol (5 eq. Na). After stirring overnight the solvent was removed and the residue extracted with dichloromethane. The organic phases were combined, dried over Na₂SO₄ and concentrated. Upon addition of *n*-hexane the product precipitated as a yellowish powder which was then dried in a vacuum.

5,11,17,23-Tetrakis[(tri-*o*-tolylphosphane)goldethynyl]-25,26,27,28-tetra-*n*-propoxy-calix[4]arene (5)

Yield: 96%. M.p.: 230°C (decomp.). – ¹H NMR (500.1 MHz, CDCl₃): δ = 0.90 (t, 12 H, CH₂CH₃), 1.91 (tq, 8 H, CH₂CH₃), 2.69 (s, 36 H, PArCH₃), 3.00 (d, ²J_{H,H} = 12.4 Hz, 4 H, Ar₂CHH_{eq}), 3.74 (t, 8 H, OCH₂), 4.26 (d, ²J_{H,H} = 12.4 Hz, 4 H, Ar₂CHH_{ax}), 6.90 (dd, br, ³J_{P,H} = 12.0 Hz, ³J_{H,H} = 7.9 Hz, 12 H, PC_{Ar,6}H), 6.94 (s, 8 H, ArH), 7.14 (t, br, ³J_{H,H} = 7.5 Hz, 12 H, PC_{Ar,5}H), 7.25 (m, br, 12 H, PC_{Ar,3}H), 7.38 ppm (t, br, ³J_{H,H} = 7.5 Hz, 12 H, PC_{Ar,4}H).

– ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ = 10.2 (CH₂CH₃), 23.0 (CH₂CH₃), 23.9 (d, ³J_{P,C} = 11.0 Hz, PArCH₃), 30.9 (Ar₂CH₂), 76.8 (OCH₂), 104.8 (d, ³J_{P,C} = 27 Hz, AuC≡C), 118.9 (d, ⁴J_{P,C} = 2.9 Hz, C_{Ar}C≡C), 126.2 (d, ³J_{P,C} = 9.1 Hz, PC_{Ar,5}), 126.8 (d, ¹J_{P,C} = 53.3 Hz, PC_{Ar,1}), 126.8 (d, ²J_{P,C} = 143 Hz, AuC≡C), 131.1 (d, br, ⁴J_{P,C} = 1.8 Hz, PC_{Ar,4}), 132.0 (d, ³J_{C,P} = 8.5 Hz, PC_{Ar,3}), 132.6 (C_{Ar}H), 133.4 (d, ²J_{P,C} = 8.5 Hz, PC_{Ar,6}), 133.5 (C_{Ar}CH₂), 143.6 (d, ²J_{P,C} = 13.2 Hz, PC_{Ar,2}), 155.1 ppm (C_{Ar}O). – ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ = 24.5 ppm (s, *o*-Tol₃P). – IR (KBr): ν = 2108 cm⁻¹ [vw, ν(C≡C)]. – MS ((+)-ESI): *m/z* = 2690.9 [M+H]⁺, 2886.4 a. u. [M+Au]⁺. – Anal. for C₁₃₂H₁₂₈Au₄O₄P₄: calcd. C 58.93, H 4.80; found C 58.89, H 5.02.

5,11,17,23-Tetrakis[(triphenylphosphane)goldethynyl]-25,26,27,28-tetra-*n*-propoxy-calix[4]arene (6)

Yield: 85%. M.p.: 230°C (decomp.). – ¹H NMR (500.1 MHz, CDCl₃): δ = 0.94 (t, 12 H, CH₂CH₃), 1.96 (tq, 8 H, CH₂CH₃), 3.06 (d, ²J_{H,H} = 12.4 Hz, 4 H, Ar₂CHH_{eq}), 3.80 (t, 8 H, OCH₂), 4.33 (d, ²J_{H,H} = 12.4 Hz, 4 H, Ar₂CHH_{ax}), 7.03 (s, 8 H, ArH), 7.28–7.36 (m, 24 H, PC_{Ar,m}H und PC_{Ar,p}H), 7.53 ppm (dd, ³J_{H,P} = 12.2 Hz, ³J_{H,H} = 7.5 Hz, 36 H, PC_{Ar,o}H). – ¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ = 10.2 (CH₂CH₃), 23.0 (CH₂CH₃), 30.9 (Ar₂CH₂), 76.8 (OCH₂), 104.8 (br d, ³J_{P,C} = 26 Hz, AuC≡C), 118.9 (C_{Ar}C≡C), 128.9 (d, ³J_{P,C} = 11.2 Hz, C_{Ar,m}), 130.3 (d, ¹J_{P,C} = 54.7 Hz, C_{Ar,i}), 131.1 (s, br, C_{Ar,p}), 132.7 (C_{Ar}H), 133.6 (C_{Ar}CH₂), 134.4 (d, ²J_{P,C} = 13.9 Hz, C_{Ar,o}), 155.3 ppm (C_{Ar}O). – ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ = 42.6 ppm (s, Ph₃P). IR (KBr): ν = 2102 cm⁻¹ [vw, ν(C≡C)]. – MS ((+)-ESI): *m/z* = 2522.6 a. u. [M+H]⁺. – Anal. for C₁₂₀H₁₀₄Au₄O₄P₄: calcd. C 57.15, H 4.16; found C 57.62, H 4.40.

5,11,17,23-Tetrakis[(diphenylmethylphosphane)goldethynyl]-25,26,27,28-tetra-*n*-propoxy-calix[4]arene (7)

Yield: 71%. – ¹H NMR (500.1 MHz, CDCl₃): δ = 1.01 (t, 12 H, CH₂CH₃), 2.00 (tq, 8 H, CH₂CH₃), 2.01 (d, ²J_{P,H} = 8.1 Hz, 12 H, PCH₃), 3.09 (d, ²J_{H,H} = 12.7 Hz, 4 H, Ar₂CHH_{eq}), 3.86 (t, 8 H, OCH₂), 4.37 (d, ²J_{H,H} = 12.7 Hz, 4 H, Ar₂CHH_{ax}), 6.92 (s, 8 H, ArH), 7.41–7.55 and 7.66–7.73 ppm (m, 40 H, PArH). – ¹³C{¹H} NMR (75.5 MHz, CDCl₃, partially from 2D spectra): δ = 9.7 (CH₂CH₃), 13.4 (PCH₃), 22.8 (CH₂CH₃), 30.4 (Ar₂CH₂), 76.7 (OCH₂), 128.7, 131.0, 132.2, 132.7 ppm (C_{Ar}H). – ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ = 26.9 ppm (s, Ph₂MeP). – IR (KBr): ν = 2093 cm⁻¹ [w, ν(C≡C)]. – MS ((+)-ESI): *m/z* = 2274.5 a. u. [M+H]⁺. – Anal. for C₁₀₀H₉₆Au₄O₄P₄: calcd. C 52.83, H 4.26; found C 52.30, H 4.32.

Table 4 (color online). Crystallographic data of **1**, Ph₂MePAuCl, **3** and **9**.

Compound	1	Ph ₂ MePAuCl	3	9
Empirical formula	C ₆₀ H ₈₀ O ₄ Si ₄ , C ₆ H ₅ F	C ₁₃ H ₁₃ AuCIP	C ₁₃₂ H ₁₂₈ Au ₄ O ₄ P ₄ , 6 C ₆ H ₅ F, 1/2 C ₆ H ₁₄	C ₉₆ H ₁₅₂ Au ₄ O ₄ P ₄ , (one C ₆ H ₅ F, two CHCl ₃ , two C ₆ H ₁₄ squeezed)
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD	AXS X8 Prospector Ultra with APEX II
λ, Å	0.71073	0.71073	0.71073	1.54178
T, K	200(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic	tetragonal
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> ₄ /a
a, Å	13.6876(3)	8.8882(7)	17.2487(2)	29.6529(13)
b, Å	15.4533(4)	11.0425(4)	18.8592(2)	29.6529(13)
c, Å	17.6466(3)	14.9281(6)	25.4673(4)	28.4624(12)
α, deg	106.39(1)	109.76(4)	92.99(1)	90
β, deg	102.94(1)	91.74(6)	109.78(1)	90
γ, deg	105.78(1)	107.96(5)	107.02(1)	90
V, Å ³	3257.95(12)	1296.80(12)	7348.75(16)	25026.8(19)
Z	2	4	2	8
ρ _{calcd.} , g cm ⁻³	1.10	2.22	1.50	1.48
μ, mm ⁻¹	0.1	11.6	4.1	10.6
θ range, deg	2.9–25.0	3.0–30.0	2.9–27.5	8.9–72.1
Completeness to θ _{max} , %	94.3	99.8	99.5	98.3
hkl ranges	–15 ≤ h ≤ 16 –18 ≤ k ≤ 18 –17 ≤ l ≤ 20	–12 ≤ h ≤ 12 –15 ≤ k ≤ 15 –20 ≤ l ≤ 20	–22 ≤ h ≤ 22 –24 ≤ k ≤ 24 –33 ≤ l ≤ 33	–36 ≤ h ≤ 33 –36 ≤ k ≤ 36 –35 ≤ l ≤ 33
Refl. measd./unique/R _{int}	30 474/10 825/0.036	64 184/75 57/0.0484	138 130/33 598/0.067	118 609/12 142/0.1188
Data/restraints/parameters	10 825/154/664	7557/0/291	33 598/0/1694	12 142/405/492
Goof on F ²	1.035	1.073	1.041	1.037
R [I > 2 σ(I)]/wR2	0.069/0.1772	0.0187/0.0353	0.0469/0.1139	0.0942/0.2599
R(all data)/wR2	0.0927/0.1945	0.0261/0.0370	0.0709/0.1256	0.0990/0.2698
Δρ _{fin} (max/min), e Å ⁻³	0.48/–0.45	0.82/–1.32	2.08/–1.23	7.13/–1.56
Disordered atoms	all propyl groups, F(1) on two positions (occupation 51 : 49)		one propyl group, one tolyl group	highly disordered solvent was squeezed.; sum formula contains solvent, disorder of C(20) on two positions (72 : 28).
CCDC numbers	1 012 529	1 012 530	1 012 531	1 012 528

5,11,17,23-Tetrakis[(tricyclohexylphosphane)gold-ethynyl]-25,26,27,28-tetra-*n*-propoxy-calix[4]arene (**8**)

Yield: 76%. M. p.: 200°C (decomp.). – ¹H NMR (500.1 MHz, CDCl₃): δ = 0.92 (t, 12 H, CH₂CH₃), 1.22–1.28 [m, 36 H, PCH(CH₂CH₂)₂CHH_{eq} and PCH(CH₂CHH_{eq})₂CH₂], 1.42–1.54 [m, 24 H, PCH(CHH_{eq}CH₂)₂CH₂], 1.63–1.74 [m, 12 H, PCH(CH₂CH₂)₂CHH_{ax}], 1.76–1.86 [m, 24 H, PCH(CH₂CHH_{ax})₂CH₂], 1.92 (tq, 8 H, CH₂CH₃), 1.94–2.04 [m, 36 H, PCH(CHH_{ax}CH₂)₂CH₂ and PCH_{ax}(CH₂CH₂)₂CH₂], 3.01 (d, ²J_{H,H} = 12.4 Hz, 4 H, Ar₂CH₂), 3.76 (t, 8 H, OCH₂), 4.28 (d, ²J_{H,H} = 12.4 Hz, 4 H, Ar₂CH₂), 6.98 ppm (s, 8 H, ArH). – ¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ = 10.2 (CH₂CH₃), 23.0 (CH₂CH₃), 25.9 [PCH(CH₂CH₂)₂CH₂], 27.2 [d, ²J_{P,C} = 11.7 Hz, PCH(CH₂CH₂)₂CH₂], 30.5 [PCH(CH₂CH₂)₂CH₂], 30.6 (Ar₂CH₂), 33.1 [d,

¹J_{P,C} = 27.4 Hz, PCH(CH₂CH₂)₂CH₂], 76.8 (OCH₂), 104.1 (br d, ³J_{P,C} = 25 Hz, AuC≡C), 119.2 (C_{Ar}C≡C), 132.6 (C_{Ar}), 133.4 (C_{Ar}), 134.8 (d, ²J_{P,C} = 134 Hz, AuC≡C), 155.0 ppm (C_{Ar}O). – ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ = 56.2 ppm (Cy₃P). – IR (KBr): ν = 2091 cm⁻¹ [vw, ν(C≡C)]. – MS ((+)-ESI): m/z = 2595.2 a. u. [M+H]⁺, 2617.1 [M+Na]⁺, 2790.8 [M+Au]⁺. – Anal. for C₁₂₀H₁₇₆Au₄O₄P₄: calcd. C 55.55, H 6.84; found C 55.61, H 6.84.

5,11,17,23-Tetrakis[(tri-*t*-butylphosphane)goldethynyl]-25,26,27,28-tetra-*n*-propoxy-calix[4]arene (**9**)

Yield: 77%. – M. p.: 200°C (decomp.). – ¹H NMR (500.1 MHz, CDCl₃): δ = 0.92 (t, 12 H, CH₂CH₃), 1.50 (d, ³J_{H,P} = 13.1 Hz, 108 H, CCH₃), 1.93 (tq, 8 H, CH₂CH₃), 3.01 (d, ²J_{H,H} = 12.5 Hz, 4 H, Ar₂CH_{eq}), 3.75 (t, 8 H, OCH₂), 4.27 (d, ²J_{H,H} = 12.5 Hz, 4 H, Ar₂CH_{ax}), 6.99 ppm

(s, 8 H, ArH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): $\delta = 10.3$ (CH_2CH_3), 23.0 (CH_2CH_3), 30.9 (Ar_2CH_2), 32.4 (br s, CCH_3), 38.9 (d, $^1J_{\text{P,C}} = 17.3$ Hz, CCH_3), 76.8 (OCH_2), 103.9 (br d, $^3J_{\text{P,C}} = 24$ Hz, $\text{AuC}\equiv\text{C}$), 119.2 ($\text{C}_{\text{Ar}}\text{C}\equiv\text{C}$), 132.7 (C_{Ar}), 133.4 (C_{Ar}), 133.7 (d, $^2J_{\text{P,C}} = 130$ Hz, $\text{AuC}\equiv\text{C}$), 154.9 ppm ($\text{C}_{\text{Ar}}\text{O}$). – $^{31}\text{P}\{^1\text{H}\}$ NMR (202.4 MHz, CDCl_3): $\delta = 91.5$ (*t*- Bu_3P). – IR (KBr): $\nu = 2091$ cm^{-1} [w, $\nu(\text{C}\equiv\text{C})$]. – MS ((+)-ESI): $m/z = 2283.1$ a. u. [$\text{M}+\text{H}$] $^+$, 2304.1 [$\text{M}+\text{Na}$] $^+$, 2479.1 [$\text{M}+\text{Au}$] $^+$. – Anal. for $\text{C}_{96}\text{H}_{152}\text{Au}_4\text{O}_4\text{P}_4$: calcd. C 50.53, H 6.71, found C 49.91, H 6.67.

Crystal structure determinations

Single crystals suitable for X-ray diffraction measurement were suspended in a paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. The structures were solved by Direct Methods and refined by full-matrix least-squares cycles (programs SHELXS-97 and SHELXL-97 [63]). The structures are represented using the program ORTEP-III. Further details on the crystallographic measurements can be found in Table 4.

CCDC 1012528–1012531 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details

All calculations have been performed with the TURBO-MOLE program package (version 6.3) [64]. The geometry optimisation was carried out at the SCS-MP2 level of theory using the *ricc2* routine [65, 66]. C_{2v} symmetry was detected and used throughout. Ahlrichs def2-TZVPP basis sets were employed for all elements (this implies relativistic electron core potentials for gold and xenon), and the corresponding fitting basis sets for the RI approximation were used. The interaction energy was corrected for a basis set superposition error (BSSE) with the standard counterpoise correction (CP). Cartesian coordinates for the optimised complex can be found in the Supporting Information.

Supporting information

Quantum-chemically calculated Cartesian coordinates of **10** are given as Supporting Information (2 pages) available online (DOI: 10.5560/ZNB.2014-4149).

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