Propargyl calix[4]arenes and their complexes with silver(I) and gold(I)

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Abstract: A calix[4]arene 1*b* has been substituted at the lower rim by reaction with propargyl bromide to give either the 1,3- bis(propargyl) derivative 2*b*, which is formed regioselectively, or the tetrakis(*O*-propargyl)calix[4]arene 3 under different reaction conditions. The molecular structure of 2*b* has been characterized by X-ray analysis (monoclinic, space group $P2_1/c$, Z = 4, a = 10.960(1), b = 24.302(3), c = 10.673(1) Å, $\beta = 112.99(8)^\circ$, R = 0.0516). The molecules of 2*b* in the crystal are arranged in a "head-to-head, tail-to-tail" manner with a phenyl substituent of one molecule partly enclosed in the bowlic cavity of another. Since the two OCH₂C=CH groups are accessible, 2*b* can be polymerized by heating to 250°C and the polymerized propargyl calix[4]arene derivatives are stable up to 460°C. Compound 3 exists as a mixture of conformers, the ratio of partial cone to 1,3-alternate conformations being 4:1 or 2:1, dependent on the preparative conditions. These propargyl calix[4]arene derivatives can be further derivatized to form silver(I) or gold(I) alkynyl units by reaction with AgNO₃ or [AuCl(SMe₂)], respectively, and base. Further reaction of these transition metal complexes with phosphines yields calixarene derivatives with two metal-phosphine units at the lower rim of the calix[4]arene bowl.

Key words: calix[4]arene, propargyl, gold, silver, polymer.

Résumé : On a substitué un calix[4]arène. 1*b*, sur sa portion inférieure en le soumettant à une réaction avec du bromure de propargyle qui conduit au dérivé 1,3-bis(propargyle), 2*b*, qui se forme régiosélectivement, ou au tétrakis(*O*-propargyl)calix[4]arène, **3**, sous des conditions réactionnelles différentes. La structure moléculaire du composé 2*b* a été caractérisée par diffraction des rayons X (monoclinique, groupe d'espace $P2_1/c$, Z = 4, a = 10,960(1), b = 24,302(3) et c = 10,673(1) Å, $\beta = 112,99(8)^\circ$ et R = 0,0516). Dans le cristal, les molécules de 2*b* sont arrangées de façon « tête à tête, queue à queue » avec un substituant phényle d'une molécule partiellement entouré dans la cavité d'une autre. Puisque les deux groupes OCH₂C==CH sont accessibles, le produit 2*b* peut être polymérisé par chauffage à 250°C et les dérivés polymérisés propargyl calix[4]arène sont stables jusqu'à 460°C. Le composé **3** existe sous la forme de conformères pour lesquels le rapport des conformations à cône partiel/alterné-1,3 est de 4 : 1 ou de 2 : 1 suivant les conditions de préparation. On peut préparer de nouveaux dérivés de ces dérivés propargyl calix[4]arènes de façon à former des unités argent(I) ou or(I) alcynyles par réactions respectivement avec du AgNO₃ ou du [AuCl(SMe)₂] en présence de base. Des réactions ultérieures de ces complexes de métaux de transition avec des phosphines fournissent des dérivés de calixarène comportant deux unités métal-phosphine dans la partie inférieure du bol du calix[4]arène.

Mots clés : calix[4]arène, propargyle, or, argent, polymère.

[Traduit par la rédaction]

Introduction

Calix[4]arenes are useful building blocks for more complicated molecules with unusual properties (1) and the hydroxyl substituents that are usually present are very useful for chemical modification. General procedures have been developed for regio- and stereoselective functionalization at the lower rim of calix[4]arenes such as *tert*-butylcalix[4]arene, 1a (2–6). However, it has proved to be more difficult to study the regioand stereo-selectivity of reactions of the parent calix[4]arene, 1b. The derivative 1,3-bis(O-propargyl)-*tert*-butylcalix-

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¹ Author to whom correspondence may be addressed. Telephone: (519) 679-2111, ext. 6336. Fax: (519) 661-3022. E-mail:pudd@julian.uwo.ca [4]arene, 2a, has been reported (6) and such compounds are of interest as potential encapsulating ligands for transition metal ions by coordination to the alkynyl substituents (7). This paper reports the regioselective synthesis of a new 1,3-dipropargyl calix[4]arene derivative 2b and a tetrapropargyl calix[4]arene derivative 3, together with a study of their conformations, conformational mobility, thermal properties, and ability to form complexes with silver(I) and gold(I).

Results and discussion

Regioselective synthesis and structure of 1,3-bis(*O*propargyl)calix[4]arene, 2*b*

Calix[4]arenes are readily converted into a wide variety of derivatives at the lower ring by alkylation of the phenolic groups (8). In this way, the 1,3-bis(*O*-propargyl)calix[4]arene 2b was prepared regioselectively in high yield (92%) from propargyl bromide and calix[4]arene 1b in a 1:2 ratio in acetone solution in the presence of potassium carbonate as shown in Scheme 1. The ¹H NMR spectrum of 2b exhibited an AB

Scheme 1.



pattern for the bridging methylene groups at δ 3.40 and 4.40 ppm (${}^{2}J_{\text{HH}}$ = 14 Hz), a triplet for the acetylenic proton at 2.58 ppm (${}^{4}J_{\rm HH} = 4$ Hz), a doublet for the methylene groups of the propargyl units at 4.25 ppm (${}^{4}J_{HH} = 4$ Hz), an A₂B system for the aromatic protons at 6.66-7.08 ppm, and a singlet for the phenolic protons at 7.05 ppm (confirmed by D₂O exchange). These data, together with the ¹³C NMR evidence, show that 2b in solution exists in the cone conformation (1).

The conformation of 2b in the solid state was determined by an X-ray structure determination. The 1,3-bis(O-propargyl)calix[4] arene 2b adopts the cone conformation in a distorted form as shown in Fig. 1. The two benzene rings bearing propargyl groups are almost parallel to each other (interplanar angle $2.28(1)^{\circ}$, while the two phenolic rings have a relatively large interplanar angle $(77.7(1)^\circ)$ and are tilted to place the two hydroxy groups almost inside the cavity with a small O...O separation of 2.9 Å. This arrangement allows intramolecular hydrogen bond formation between proximal hydroxy and ether groups with OH..O distances of 2.0–2.3 Å. These hydrogen bonds are probably responsible for holding the molecule in the cone conformation (8a). There are a number of related dihydroxycalixarenes, which display similar hydrogen bonding, of which a bis(O-cyanomethyl) analog is particularly striking (6a). In addition to these intramolecular hydrogen bonds, there is structural evidence for weak intermolecular "tail-to-tail" hydrogen bonds between C=C-H..OH groups of adjacent molecules, leading to chains of molecules (Fig. 2b). These are examples of so-called "soft" CH..O hydrogen bonds (8b). Finally, a phenyl group of each calixarene molecule is partially enclosed in the bowlic cavity of a neighboring molecule (Fig. 2a), thus creating "head-to-head" association that leads to blocking of the entrance to the cavity. Small molecule inclusion, which has often been observed in 1,3-dialkylated *tert*-butylcalix [4] arenes, is therefore not present in 2b. Bond lengths and angles are unexceptional and are summarized in Table 1.

Synthesis and conformations of the tetrakis(Opropargyl)calix[4]arene 3

The calixarene 2b did not react with excess propargyl bromide and base at room temperature (7), but either 1b or 2b did react with excess propargyl bromide in refluxing acetone in the presence of K_2CO_3 to give the new tetrapropargyl calix[4] arene derivative 3. At short reaction times, a mixture of products representing various stages of alkylation were present but, after 1 day, complete conversion to the tetrakis(Opropargyl)calix[4]arene 3 occurred. After 24 and 48 h reflux,

Table 1. Selected interatomic distances (Å) and angles (°) in 2b (a) Bond lengths (Å)

$\begin{array}{c} O(1) & - C(16) \\ C(1) & - C(2) \\ C(3) & - O(3) \\ C(5) & - C(37) \\ C(10) & - C(11) \\ C(17) & - C(25) \\ C(22) & - C(23) \\ O(4) & - C(24) \\ C(30) & - C(31) \end{array}$	$\begin{array}{c} 1.374(3) \\ 1.154(5) \\ 1.442(3) \\ 1.522(4) \\ 1.515(4) \\ 1.509(4) \\ 1.471(4) \\ 1.405(3) \\ 1.520(4) \end{array}$	$\begin{array}{c} O(2) & - C(36) \\ C(2) & - C(3) \\ O(3) & - C(4) \\ C(9) & - C(10) \\ C(15) & - C(17) \\ C(21) & - C(22) \\ C(23) & - O(4) \\ C(29) & - C(30) \\ C(35) & - C(37) \end{array}$	$\begin{array}{c} 1.372(3)\\ 1.450(5)\\ 1.402(3)\\ 1.523(5)\\ 1.515(4)\\ 1.167(4)\\ 1.438(3)\\ 1.520(4)\\ 1.514(4) \end{array}$
(b) Bond angles (°)		and the second secon	
C(1)-C(2)-C(3)	178.6(4)	O(3)-C(3)-C(2)	112.7(3)
C(4)-O(3)-C(3)	116.4(2)	C(9)-C(4)-O(3)	119.6(3)
C(5)-C(4)-O(3)	117.8(3)	C(6)-C(5)-C(37)	119.4(3)
C(4)-C(5)-C(37)	122.2(3)	C(8)-C(9)-C(10)	120.6(3)
C(4)-C(9)-C(10)	122.2(3)	C(11)-C(10)-C(9)	113.1(3)
C(12)-C(11)-C(10)	121.6(3)	C(16)-C(11)-C(10)	120.9(3)
C(14)-C(15)-C(17)	121.1(3)	C(16)-C(15)-C(17)	120.6(2)
O(1)-C(16)-C(15)	121.2(2)	O(1)-C(16)-C(11)	116.9(2)
C(25)-C(17)-C(15)	112.1(2)	C(21)-C(22)-C(23)	177.0(3)
O(4)-C(23)-C(22)	113.1(2)	C(24)-O(4)-C(23)	114.3(2)
C(25)-C(24)-C(29)	123.0(2)	C(25)-C(24)-O(4)	117.7(2)
C(29)-C(24)-O(4)	119.2(2)	C(26)-C(25)-C(17)	120.0(3)
C(24)-C(25)-C(17)	122.9(2)	C(28)-C(29)-C(30)	120.1(3)
C(24)-C(29)-C(30)	122.5(2)	C(32)-C(31)-C(36)	117.8(3)
C(32)-C(31)-C(30)	122.2(3)	C(36)-C(31)-C(30)	119.9(2)
C(34)-C(35)-C(37)	120.8(3)	C(36)-C(35)-C(37)	122.2(3)
O(2)-C(36)-C(31)	116.2(2)	O(2)-C(36)-C(35)	121.4(2)
C(35)-C(37)-C(5)	113.3(2)		

the calix [4] arene 3 was present as a mixture of the partial cone and 1,3-alternate conformers in 2:1 and 4:1 ratios, respectively. Clearly, in the absence of hydroxyl groups to take part in hydrogen bonding, the cone conformation is no longer preferred and so there is a major difference from 2b in this respect.





ÓR.

3: $R = CH_2C \equiv CH$

C1C26 035 Scheme 2. **ÓR** ÓR RÒ ÓR ÓΒ RÒ **Partial Cone** Cone RO OR

1,3-Alternate

1.2-Alternate

ÓR

OR

OR

OR

Many tetrakis(O-alkyl)calix[4]arene derivatives (though only if the alkyl group is smaller than propyl) are conformationally flexible at room temperature. A schematic representation of the four possible conformers of tetrakis(O-propargyl) calixarene with the different orientations of the phenyl rings of the cyclic tetramer is shown in Scheme 2. It has been established that the conformations of calix[4]arenes can be determined by the splitting pattern of the ArCH₂Ar methylene protons in the ¹H NMR spectra and by the number of peaks in the ¹³C NMR spectra (6, 8). The conformational isomerism of **3** is demonstrated from the observation that the ratio of 1,3alternate to partial cone conformer is dependent on the conditions of formation, and this observation also shows that the interconversion between conformers is very slow at room temperature. In agreement with the latter conclusion, the ¹H NMR spectrum of 3 recorded at room temperature at 300 MHz showed sharp signals with no evidence of exchange broadening (Fig. 3). The ¹H NMR spectrum in the methylene region is particularly informative (Fig. 3). The minor 1,3-alternate conformer has higher symmetry and gives rise to single resonances of equal intensity due to the CH₂ groups of the propargyl (H¹, 4.08 ppm, d, J(HH) = 4 Hz) and CH₂Ar₂ (H²,

3.76 ppm, s) groups. The major partial cone conformer has lower symmetry and its spectrum is correspondingly more complex. There are two nonequivalent CH₂Ar₂ groups and each has nonequivalent protons CH^aH^b, thus giving rise to four resonances labelled H^{3a}, H^{3b}, H^{4a}, H^{4b}. There are three nonequivalent propargyl groups in a 1:1:2 ratio, and the CH₂ protons of the last propargyl groups are also nonequivalent. Each CH₂ resonance appears as a doublet due to the coupling ⁴J(CH₂CCH). Hence there are four resonances, two appearing as doublets (H^5, H^6) and two (H^{7a}, H^{7b}) as more complex multiplets due to the extra coupling ${}^{2}J(H^{7a}H^{7b})$. The ratio of partial cone to 1,3-alternate conformer was 4:1 as determined by integration of the spectra, and the spectral assignments are in agreement with those for similar compounds (8). The ^{13}C NMR spectra in both the ArCH₂Ar and OCH₂CCH regions (Experimental section) provided a further diagnostic tool to confirm that the only conformations present are the partial cone and 1.3-alternate at room temperature (9).

It has previously been reported that the conformation of Oalkylated calixarenes can be frozen as a single conformation, the partial cone, by complexation with the silver cation, which binds to two arene groups and one ether group (10). In agreement, addition of silver(I) trifluoroacetate to a solution of 3gave the tetrakis(O-propargyl)calix[4]arene-silver(I) complex 4, which was shown by its ¹H NMR spectrum to exist only as the partial cone conformer. Hence weak binding of the silver cation probably occurs as shown in 4 and not by binding to the C \equiv C bonds of the propargyl substituents (11).



Polymerization of the propargyl calix[4]arene derivatives It is known that the dipropargyl derivatives of bisphenols are attractive building blocks for resins for use as advanced composites, adhesives, coatings, and electronics applications (12). Hence polymerization of the propargyl calix[4]arenes was studied (13). The polymerization of 2a or 2b was performed by heating in diphenyl ether for 6 h at 120°C and then for 2 h at 150-160°C without a catalyst (12, 13). The polymerization proceeded without evolution of any volatiles and produced a solid thermoset resin 5. The polymer 5 is soluble in many organic solvents and is neither hygroscopic nor moisture sensitive. The molecular weight of 5a, as estimated by gel permeation chromatography (GPC) with THF as eluent and using polystyrene standards, was $M_w = 56\ 000$ with a polydispersity $(M_w/M_p = 3.2)$. Differential scanning calorimetry (DSC) measurements of the poly(1,3-(O-propargyl)-tert-butylcalix[4]arene), 5a, shows an exceptionally high glass transition temperature, T_{g} , of the polymer at 250°C (14). TGA of the polymer 5a in air (Fig. 4) shows that decomposition with weight loss occurs above 460°C, which is slightly higher than for its

Fig. 1. A view of the molecular structure of 2b, showing the cone conformation and intramolecular OH..O hydrogen bonding.

C12

Fig. 2. Intermolecular interactions in 2*b*: (*a*) The head-to-head arrangement, showing mutual aryl group inclusion. (*b*) The tail-to-tail association involving C≡CH..O hydrogen bonding.



precursor 2*a* (440°C). Clearly, the propargyl calix[4]arene polymer has excellent thermal stability. The polymer is formed through opening of the triple bonds of the propargyl groups. Thus, 5*a* gave broad ¹H NMR resonances at $\delta = 1.0$, 2.1 and 3.7, 6.3, and 7.0 which are assigned to the *t*-Bu, CH₂, ==CH, and aromatic protons, respectively. In agreement, the FTIR showed the absence of alkyne groups, with no bands corresponding to the bands of 2*a* due to $\nu_{CC-H} = 3289 \text{ cm}^{-1}$ (s) or $\nu_{C==C} = 2120 \text{ cm}^{-1}$ (w).

Complexes of 2 and 3 with transition metals

There is much current interest in the properties of calix[4]are-

nes as ligands (13, 15–18) and so the synthesis of alkynylmetal complexes from the propargylcalix[4]arenes was studied. Treatment of **2***a* with [AuCl(SMe₂)] in the presence of sodium acetate as base gave the digold(I) complex **6***a*. The ¹H NMR spectrum of **6***a* is broad but the observation of only two broad signals due to the methylene protons of the calixarene at 3.4 and 4.2 ppm, one broad resonance due to the methylene protons of the propargyl groups at 4.3 ppm, and one broad Bu¹ resonance at 1.1 ppm indicates that **6***a* is primarily in the cone conformation. The FTIR spectrum showed the absence of a CC-H proton (disappearance of the band due to ν_{CCH} at 3275 cm⁻¹) and the presence of a new weak band due **Fig. 3.** The ¹H NMR spectrum of compound **3** in the methylene region.



Fig. 4. (a) TGA of 2a; (b) TGA of polymeric 2a.



to $\nu_{C=CAu}$ at 1988 cm⁻¹. Alkynylgold(I) complexes are usually oligometric or polymetric (RC=CAu)_n to allow the gold(I) centres to be linear 2-coordinate. Complex **6***a* could be of this type or each gold(I) centre could be weakly ligated by oxygen donors present in the calixarene skeleton; since **6***a* is soluble in organic solvents it is probably not polymetric (19). In similar ways, **2***a* reacted with silver nitrate and ammonia to give **6***b*, and **3** reacted with [AuCl(SMe₂)] and sodium acetate to give complex **7** as shown in Scheme 3.

Further reaction of these propargylmetal complexes 6 and 7 with either monodentate or bidentate phosphine ligands gave

the corresponding complexes 8 and 9 as shown in Scheme 3. The complexes 8a-8d are in the cone conformation and have C_2 symmetry, with the two metal-phosphine units at the lower rim of the calix[4]arene. The resonances in the ¹H NMR spectra due to the CH₂ groups serve as spectroscopic probes, and clearly indicate the cone conformation. The complexes 9a and 9b give similar ¹H NMR resonances as for their precursor 3, indicating that the complexation of the propargyl groups does not change the conformation and that there is still a mixture of the partial cone and 1,3-alternate conformations, which do not easily interconvert. The complexes 8 and 9 do not exhibit the inclusion behaviour that is typical of other calixarenes (1), perhaps because the bulky metal-phosphine substituents at the lower rim cause the aryl rings to which they are bound to tilt in such a way as to close access to the top of the bowl (20).

Conclusion

This work has shown that the calixarene 1b can be functionalized with two or four propargyl groups at the lower rim and that the reaction to give the dipropargyl derivative is regioselective. Preliminary studies indicate that silver(I) can be incorporated into the propargylcalix[4]arenes either by weak π bonding to the arene groups or, in the presence of base, by forming σ -bonded propargylsilver(I) groups. Gold(I) also forms propargyl derivatives containing two or four gold atoms. Clearly there is potential for further derivatization of these propargylcalix[4]arenes with metal substituents but it may prove difficult to develop useful inclusion chemistry. In this sense, the incorporation of propargyl groups at the upper rim is preferred and the synthesis and coordination chemistry of such compounds is planned.

Experimental section

compounds 5,11,17,23-tetra-tert-butyl-The precursor calix[4]arene, 1a (21), calix[4]arene 1b (22), 5,11,17,23-tetra*tert*-butyl-25,27-bis(propargyl)calix[4] arene, 2a (7), and [AuCl(SMe₂)](19) were prepared by literature methods. Molecular modeling was carried out using PCMODEL.² NMR spectra were collected by using a Varian Gemini 300 spectrometer. ¹H and ¹³CNMR chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. ³¹P NMR chemical shifts were determined relative to 85% H₃PO₄ as external standard. IR spectra were recorded as Nujol mulls using a Bruker IFS32 FTIR spectrometer. The molecular weights of poly[1,3-(O-propargyl)-tertbutylcalix[4]arene] and of poly[1,3-(O-propargyl)calix[4]arene] were measured by GPC using THF as solvent and polystyrene standards for calibration. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Mass spectra were recorded by using a Finnegan mat 8230 mass spectrometer.

1,3-Di-O-propargyIcalix[4]arene, 2b

A solution of calix[4]arene 1*b* (0.5 g, 1.18 mmol) and BrCH₂CCH (0.5 g, 4.2 mmol) in acetone (100 mL) and K_2CO_3 (1.2 g, 8.7 mmol) were stirred for 12 h at 20°C. The solvents

² PCMODEL Molecular Modeling Software, version 4.2, Serena Software, 1992.

Scheme 3. AuCl(SMe₂)/NaOAc or Ag(NO₃)/NH₃ 'nн ÒН CH₂C=CH CH₂C=CM $2a: \mathbf{R} = \mathbf{Bu}^{t}$ 6a: M = Au; 6b: M = AgPR'3 'nн CH₂C=CMPR₃ $8a: M = Au, PR'_3 = PPh_3$ $8b: M = Au, PR_3 = PPh_2Me$ $8c: M = Au, PR_3 = 1/2dppm$ 8d: $M = Ag, PR_3' = PPh_3$ AuCl(SMe₂) NaOAc CH₂C=CH CH2C=CAuPR'3 CH₂C=CAu 3 7 9a: PR'₃ = PPh₃ 9b: PR'₃ = PPh₂Me

were removed under vacuum and the residue was extracted using chloroform (20 mL). **2***b* can be further purified by crystallization, by slow diffusion of methanol into a chloroform solution. The light yellow crystals of **2***b* (0.54 g, 92%) were collected by filtration, washed with hexane (3 × 20 mL), and dried under vacuum, mp 182–184°C. Spectroscopic data for **2***b*: FTIR: ν_{OH} = 3423 cm⁻¹ (s), ν_{CCH} = 3275 cm⁻¹ (s), ν_{CC} = 2118 cm⁻¹ (w). NMR in CDCl₃, $\delta(^{1}H)$: 2.58 (t, ⁴*J*_{HH} = 4 Hz, 2H, CCH), 3.40, 4.40 (ABq, ²*J*_{HH} = 13 Hz, 8H, ArCH₂Ar), 4.80 (d, ⁴*J*_{HH} = 4Hz, 4H, OCH), 6.66–6.73 (m, 4H, ArH), 6.85 and 6.82 (s, 4H, ArH), 7.08 and 7.06 (s, 4H, ArH), 7.05 (s, 2H, OH). $\delta(^{13}C)$: 63.46 (CH₂CCH), 31.85 (ArCH₂Ar), 78.32 (CH₂CCH), 153.03, 151.37, 133.42, 129.01, 128.56, 128.26, 125.75, 119.25 (Ar). EI-MS, *m/e*: 500; calcd. for C₃₄H₂₈O₄: 500.

Single crystal X-ray analysis of 2b

Single crystals of complex 2*b* were obtained as described above. A suitable crystal with dimensions of $0.42 \times 0.35 \times$ 0.22 mm was selected, mounted at the end of a glass fibre, and used for the experiments. The diffraction experiments were carried out using a Siemens P4 diffractometer with the xscANs software package³ using graphite monochromated Mo K radiation at 23°C. The cell constants were obtained by centering 25 high-angle reflections (20.7 $\leq \Theta \leq 21.7^{\circ}$). The Laue symmetry 2/*m* was determined by merging symmetry

equivalent reflections. A total of 5666 reflections were collected in the Θ range 2.0–25.0° (-13 \leq h \leq 1, -1 \leq k \leq 28, $-12 \le l \le 12$) in Θ -2 Θ scan mode at variable scan speeds (2-10 deg/min). Background measurements were made at the ends of the scan range. Three standard reflections were monitored at the end of every 297 reflections collected. An empirical absorption correction was applied to the data. The maximum and minimum transmission factors are 0.956 and 0.939, respectively. The space group $P2_1/c$ was determined from the systematic absences (h0l, l = 2n + 1 and 0k0, k = 2n + 1). The data processing, solution, and the initial refinements were done using the SHELXTL-PC programs (23). The final refinements were performed using SHELXL-93 software programs (24). Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms were not directly located but were included in the calculated positions for the purpose of structure factor calculations only. In the final least-squares refinement cycles on F^2 the model converged at $R_1 = 0.0516$, $wR_2 = 0.1046$, and GOf = 1.008 for 2659 observations with $F_o^2 \ge 4\sigma(F_o)$, 366 parameters, and $R_1 = 0.1101$, $wR_2 = 0.1288$ for all 4612 data. In the final difference Fourier synthesis the electron density fluctuates in the range 0.17 to -0.17 e Å⁻³, of which the top peak was associated with O(1) at a distance of 1.06 Å. There is no shift in the mean or the maximum shift/esd in the final cycles. A secondary extinction coefficient was refined to 0.0035(5). Experimental detail and crystal data are summarized in Table 2. The positional and thermal parameters, bond distances and angles, the anisotropic thermal parameters,

³ "XSCANS", Siemens Analytical X-Ray Instruments Inc., Madison, 1990.

Table 2. Crystal data and experimental details.

Empirical formula	C ₃₄ H ₂₈ O ₄	
Formula weight	500.56	
Temperature	23°C	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.960(1) Å	
	b = 24.302(3) Å	
	c = 10.673(1) Å	
	$\beta = 112.99(8)^{\circ}$	
Volume	2177.6(4) Å ³	
Ζ	4	
Density, calculated, observed	1.270, 1.29(5) g cm ⁻³	
Absorption coefficient	0.082 mm^{-1}	
<i>F</i> (000)	1056	
Independent reflections	$4613 \ (R(int) = 0.0231)$	
Refinement method	Full-matrix least squares on F^2	
Data/restraints/parameters	2659/0/366	
Goodness-of-fit (GOF) on F^2	1.022	
Final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.0516, wR2 = 0.1046	
<i>R</i> indices (all data)	R1 = 0.1101, wR2 = 0.1288	

 $R1 = \sum (||F_o| - |F_c||) / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2};$ GOF = $[\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined.

hydrogen atom coordinates, and selected torsion angles have been deposited as supplementary material.⁴

Tetrakis(O-propargyl)calix[4]arene, 3

A mixture of 1b (0.5 g, 1.18 mmol) and BrCH₂CCH (1 g, 8.4 mmol) in acetone (100 mL) and K₂CO₃ (2 g, 14.5 mmol) was stirred and heated to reflux for 48 h. The cooled reaction mixture was processed exactly as described in preparation of 2b to afford a tetrakis(O-propargyl)calix[4]arene 3 (5.6 g, 82%). Spectroscopic data of **3**: NMR in CD₂Cl₂: 1,3-alternate con*former*, $\delta({}^{1}\text{H}, \text{ppm})$: 2.43 (t, 4 H, ${}^{4}J_{\text{HH}} = 4$ Hz, CCH), 4.00 (d, ${}^{4}J_{\text{HH}} = 4$ Hz, 4H, OCH₂), 3.76 (8H, ArCH₂Ar), 7.42–6.33 (m, ArH of both 1,3-alternate and partial cone conformers). δ (¹³C, 74.1 (OCH₂CCH), 59.2 (OCH₂C*C*H), 80.6 ppm): (OCH₂CCH), 37.6 (ArCH₂Ar), 154.4 (OAr), partial cone conformer, $\delta({}^{1}\text{H}, \text{ppm})$: 2.52 (\tilde{t} , 1H, ${}^{4}J(\text{HH}) = 4$ Hz, CCH), 2.49 (t, $^{4}J(HH) = 4$ Hz, CCH), 2.19 (t, 1H, $^{4}J(HH) = 4$ Hz, CCH), 4.3 and 3.1 (AB q, 4H, ${}^{2}J_{HH} = 14$ Hz, ArCH₂Ar), 3.85 and 3.77 $(AB q, 4H, {}^{2}J_{HH} = 14 Hz, ArCH_{2}Ar), 4.52 and 4.44 (AB q, 4H, ArcH_{2}Ar), 4.52 and 4.44 (AB q, 4H, ArcH_{2}Ar), 4.52 and 4.44 (ArcH_{2}Ar), 4.52 and 4.44 (ArcH_{2}Ar), 4.52 arcH_{2}Ar), 4.52 arcH_{2$ ${}^{4}J_{\text{HH}} = 4 \text{ Hz}, {}^{2}J_{\text{HH}} = 14 \text{ Hz}, \text{ OCH}_{2}, 4.42 \text{ (d, } {}^{4}J_{\text{HH}} = 4 \text{ Hz}, 2\text{H},$ OCH_2), 4.04 (d, ${}^4J_{HH}$ = 4 Hz, 2H, OCH_2). $\delta({}^{13}C, ppm)$: 75.1 (OCH₂CCH), 58.4 (OCH₂CCH), 59.9 (OCH₂CCH), 61.3 (OCH₂CCH), 81.6 (OCH₂CCH), 80.8 (OCH₂CCH), 80.3 (OCH₂CCH), 32.2 (ArCH₂Ar), 36.4 (ArCH₂Ar), 156.6 (OAr), 156.0 (OAr), 155.5 (OAr), 138.00, 134.76, 134.32, 133.97, 133.19, 131.48, 131.31, 130.72, 130.59, 129.34, 129.08, 128.76, 123.68, 1213.57, 123.20, 122.98, 122.75, 122.51, 122.40 (Ar). The ratio of the two conformers was determined from the integration of resonances due to the C=CH protons to be 4:1. FTIR: $\nu_{\rm CCH} = 3289 \text{ cm}^{-1}$ (s), $\nu_{\rm CC} = 2120 \text{ cm}^{-1}$ (w), EI-MS, *m/e*: 576, 537; calcd. for C₄₀H₃₂O₄: 576, M – CH₂CCH: 537. Anal. calcd. for C₄₀H₃₂O₄: C 83.3, H 5.6, found: C 83.5, H 5.2%.

Tetrakis(O-propargyl)calix[4]arene-Ag(CF₃COO), 4

A mixture of **3** (0.2 g, 0.35 mmol) and Ag(CF₃COO) (0.08 g, 0.36 mmol) in acetone (100 mL) was stirred for 2 h at room temperature. The product **4** (0.26 g, 93%) was precipitated by adding methanol (10 mL). Spectroscopic data of **4:** FTIR: $v_{CCH} = 3289 \text{ cm}^{-1}$ (s), $v_{CC} = 2120 \text{ cm}^{-1}$ (w). ¹H NMR in CDCl₃: δ : 2.20 (t, 1H, ⁴J_{HH} = 4 Hz, CCH), 2.50 (t, 2H, ⁴J_{HH} = 4 Hz, CCH), 2.54 (t, 1H, ⁴J_{HH} = 4 Hz, CCH); 4.29 and 3.12 (AB q, 4H, ²J_{HH} = 21 Hz, ArCH₂Ar), 3.82 (AB q, 4H, ²J_{HH} = 21 Hz, ArCH₂Ar), 4.48 (AB q, 4H, ⁴J_{HH} = 4 Hz, ²J_{HH} = 24 Hz, OCH₂), 4.46 (d, ⁴J_{HH} = 4 Hz, 2H, OCH₂), 4.04 (d, ⁴J_{HH} = 4 Hz, 2H, OCH₂); 6.46–7.42 (m, 12H, ArH). Anal. calcd. for C₄₂H₃₂AgO₆F₃: C 63.3, H 4.0; found: C 63.0, H 3.8%.

Poly[1,3-(O-propargyl)calix[4]arene), 5

A solution of **2** (0.5 g) in Ph₂O (10 mL) was heated to 120°C for 6 h and then heated to 150–160°C for another 2 h under nitrogen atmosphere, to give an orange-brown hard resin (0.5 g) after evaporation of the Ph₂O. The polymer was purified by dissolving the solid obtained above in THF (2 mL) and then precipitating with MeOH (20 mL). The precipitate **5** was a yellow solid, which was dried under vacuum. Spectroscopic data of *poly[1,3-(O-propargyl)-tert-butylcalix[4]arene,* **5***a*: FTIR: ν_{OH} = 3370 cm⁻¹ (s). ¹H NMR in CDCl₃: δ : 1.1 (br, Bu¹), 2.1 (br, ArCH₂Ar), 3.2 (br, ArCH₂Ar) 3.4 (br, OCH₂), 6.3 (br, ==CH), 7.0 (br, Ar and OH). Spectroscopic data of *poly(1,3-(O-propargyl)calix[4]arene)*, **5***b*: FTIR: ν_{OH} = 3370 cm⁻¹ (s). ¹H NMR in CDCl₃; δ : 2.2 (br, ArCH₂Ar), 3.3 (br, 8H, ArCH₂Ar), 3.4 (br, 4H, OCH₂), 6.1 (br, ==CH), 7.0 (br, 10H, Ar and OH).

1,3-Bis(O-propargylsilver)tetra-tert-butylcalix[4]arene, 6b A solution of 2a (0.5 g, 0.69 mmol) in THF (5 mL) was mixed with a solution of AgNO₃ (0.235 g, 1.38 mmol) in ammonia (10 M, 5 mL) and the mixture was stirred for 3 h. The product precipitated as the volume of solvent was reduced, and was purified by dissolving in CH_2Cl_2 (5 mL) and then precipitating by addition of MeOH (20 mL). The yellow product was filtered, washed with MeOH, and dried under vacuum. FTIR: $\nu_{\rm CC} = 2058 \text{ cm}^{-1}$ (w). ¹H NMR in CDCl₃, δ : 1.1 (br, m, 36H, Bu^t), 3.4 (br, ArCH₂Ar), 4.2 (br, 4H, ArCH₂Ar), 4.2 (br, 4H, OCH_2), 7.0 (br, 10H, Ar and OH). Anal. calcd. for $C_{50}H_{58}Ag_{2}O_{4}$: C 64.0, H 6.2; found: C 63.7, H 5.9%. Complex 6a was prepared in a similar way but using [AuCl(SMe₂)] with NaOAc as base. Spectroscopic data for 1,3-bis(O-propargylgold)tetra-tert-butylcalix[4]arene, 6a: FTIR: $v_{CC} = 2015$ cm^{-1} (w). ¹H NMR in CDCl₃, δ : 1.1 (br, m, 36H, Bu^t), 3.4 (br, 4H, ArCH₂Ar), 4.2 (br, 8H, ArCH₂Ar and OCH₂), 7.0 (br, 10H, Ar and OH). Anal. calcd. for $C_{50}H_{58}Au_2O_4$: C 53.8, H 5.2; found: C 54.0, H 5.3%. Complex 7 was prepared in a similar way from the calixarene 3. Spectroscopic data for

⁴ These supplementary data can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Structure factor amplitudes are no longer being deposited and may be obtained directly from the author. Tables of positional parameters, bond distances and angles, and hydrogen atom coordinates have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

tetrakis(O-*propargylgold*)*calix*[4]*arene*, **7**: FTIR: $\nu_{CC} = 2002$ cm⁻¹ (w). ¹H NMR in CDCl₃, δ : 1.1 (br, m, 36H, Bu^t), 3.4 (br, 4H, ArCH₂Ar), 4.2 (br, 4H, ArCH₂Ar), 4.3 (br, 8H, OCH₂), 7.0 (br, 8H, Ar). Anal. calcd. for C₄₀H₂₈Au₄O₄: C 35.3, H 2.1; found: C 35.0, H 2.0%.

1,3-Bis{O-propargyl(triphenylphosphine)gold}tetra-tertbutylcalix[4]arene, 8a

Triphenylphosphine (0.094 g, 0.36 mmol) was added to a solution of complex **6***a* (0.2 g, 0.18 mmol) in CH₂Cl₂ (10 mL) and the mixture was stirred for 1 h. The product was precipitated by adding MeOH (20 mL), then filtered, washed with MeOH, and dried under vacuum. FTIR: $\nu_{CC} = 2147 \text{ cm}^{-1}$ (w). NMR in CDCl₃: $\delta(^{1}\text{H}, -40^{\circ}\text{C})$: 0.86 (s, 18H, Bu^t), 1.28 (s, 18H, Bu^t), 3.30 and 4.53 (AB q, 8H, ²J_{HH} = 13 Hz, ArCH₂Ar), 4.87 (d, 4H, ⁴J_{PH} = 2 Hz, OCH₂), 6.66, 6.80, 7.02 (8H, Ar), 7.57–7.24 (m, 30H, PPh), 9.5 (s, 2H, OH); $\delta(^{31}\text{P}, -40^{\circ}\text{C})$: 39.2 (s, PPh₃). Anal. calcd. for C₈₆H₈₈Au₂O₄P₂: C 62.9, H 5.4; found: C 62.6, H 3.8%.

The complex 1,3-bis/O-propargyl(methyldiphenylphosphine)gold]tetra-tert-butylcalix[4]arene, 8b was prepared in a similar way: FTIR: $v_{CC} = 2129 \text{ cm}^{-1}$ (w). NMR in CDCl₃, $\delta(^{1}\text{H}): 0.88 \text{ (s, 18H, Bu}^{t}), 1.29 \text{ (s, 18H, Bu}^{t}), 2.02 \text{ (d, 6H, }^{2}J_{\text{PH}} = 8 \text{ Hz, PMe}), 3.32 \text{ and } 4.54 \text{ (AB q, 8H, }^{2}J_{\text{HH}} = 13 \text{ Hz, ArCH}_{2}\text{Ar}),$ 4.87 (s, 4H, OC H_2), 6.68, 6.89, 7.04 (8H, Ar), 7.62–7.38 (m, 20H, PPh), 8.76 (s, 2H, OH); $\delta(^{31}P)$: 22.4 (s, PMePh₂). Anal. calcd. for C₇₆H₈₄Au₂O₄P₂: C 60.2, H 5.6; found: C 59.9, H 5.8%. The complex [1,3-bis(8O-propargyl)[µ-bis(diphe*nylphosphinomethane*)*digold*])*tetra*-tert-*butylcalix*[4]*arene*, 8c, was prepared similarly. FTIR: $v_{CC} = 2129 \text{ cm}^{-1}$ (w). NMR in CDCl₃, $\delta({}^{1}H, -40^{\circ}C)$: 1.10 (s, 18H, Bu^t), 1.20 (s, 18H, Bu^t), 3.35 and 4.54 (AB q, 8H, ${}^{2}J_{HH} = 14$ Hz, ArCH₂Ar), 3.77 (t, 4H, $^{2}J_{PH} = 8$ Hz, PCH₂P), 4.72 (s, 4H, OCH₂), 7.63–6.5 (m, 28H, Ar and PPh), 8.76 (s, 2H, OH); $\delta(^{31}P, -40^{\circ}C)$: 29.7 (s, dppm). Anal. calcd. for C₇₅H₈₀Au₂O₄P₂: C 60.0, H 5.4; found: C 59.6, H 5.7%. The complex 1,3-bis/O-propargyl(triphenylphosphine)silver]tetra-tert-butylcalix[4]arene, 8d was prepared similarly. FTIR: $\nu_{CCH} = 2101 \text{ cm}^{-1}$ (w). NMR in CDCl₃, $\delta(^{1}\text{H})$: 0.95 (s, 18H, Bu^t), 1.32 (s, 18H, Bu^t), 3.36 and 4.40 (AB q, 8H, ${}^{2}J_{\text{HH}} = 14 \text{ Hz}, \text{ArCH}_{2}\text{Ar}), 4.75 \text{ (s, 4H, OCH}_{2}), 7.42-6.33 \text{ (m,}$ 38H, Ar, PPh and OH); $\delta(^{31}P, 22^{\circ}C)$: 29.0 (s, br); $\delta(^{31}P,$ -60° C): 7.0 (m, ¹J(AgP) = 67 Hz). Anal. calcd. for C₈₆H₈₈Ag₂O₄P₂: C 70.6, H 4.4; found: C 70.2, H 4.6%. The complex tetrakis{O-propargyl(triphenylphosphine)gold]calix-[4]arene, 9a was prepared similarly. FTIR: $v_{CC} = 2131 \text{ cm}^{-1}$ (w). NMR in CDCl₃: 1,3-alternate conformer, $\delta({}^{1}H)$: 4.29 (s, 8H, OCH₂), 3.70 (8H, ArCH₂Ar), 7.6–6.2 (m, ArH of both 1,3alternate and partial cone conformers); $\delta(^{31}P, 22^{\circ}C)$: 42.7 (s, br, PPh₃); $\delta({}^{31}P, -80^{\circ}C)$: 41.0 (s, PPh₃); *partial cone con-*former: 3.07 and 4.20 (AB q, 4H, ${}^{2}J_{HH} = 14$ Hz, ArCH₂Ar), 3.83 and 4.49 (AB q, 4H, ${}^{2}J_{HH} = 14$ Hz, ArCH₂Ar), 4.51 and 4.98 (AB q, 4H, ${}^{2}J_{HH} = 14$ Hz, OCH₂), 4.59 (s, 2H, OCH₂), 4.67 (s, 2H, OCH₂); $\delta({}^{3}P, -80^{\circ}C)$: 42, 43, 44 (s, PPh₃), Anal. calcd. for C₁₁₂H₈₈Au₄O₄P₄: C 55.8, H 3.7; found: C 55.5, H 3.8%. The complex tetrakis{O-propargyl(methyldiphenylphosphine)gold/calix[4]arene, 9b was prepared similarly. FTIR: $v_{CC} = 2131 \text{ cm}^{-1}$ (w). NMR in CDCl₃: 1,3-alternate conformer, δ(¹H): 4.28 (s, 8H, OCH₂), 3.70 (8H, ArCH₂Ar), 7.7– 6.22 (m, ArH of both 1,3-alternate and partial cone conformers); *partial cone conformer*: 3.00 and 4.50 (AB q, 4H, ${}^{2}J_{HH} =$ 14 Hz, ArCH₂Ar), 3.84 and 4.38 (AB q, 4H, ${}^{2}J_{HH} =$ 14 Hz, ArCH₂Ar), 4.50 and 4.90 (AB q, 4H, ${}^{2}J_{HH}$ = 14 Hz, OCH₂), 4.58 (s, 2H, OCH₂), 4.67 (s, 2H, OCH₂); $\delta({}^{31}P, 22^{\circ}C)$: 40.1 (s, br, PMePh₂). Anal. calcd. for C₉₂H₈₀Au₄O₄P₄: C 51.1, H 3.0; found C 50.7, H 2.6%.

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