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COMMUNICATION

Merging Molecular Recognition and Gold(I) Catalysis with Triphoscalix[6]arene Ligands

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Dedicated to Vincenzo Balzani on the occasion of his 85th birthday

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Abstract: We report the synthesis and characterization of novel triphosphine calix[6]arene ligands. These supramolecular wheels, with recognition features governed by the hydrogen-bonding domain, were employed to synthesize multitasking trinuclear gold(I) complexes as a new platform for the synthesis of interwoven (pseudo)rotaxanes species. Parallelly, the multivalent, metal-bonded upper-rim displayed catalytic features promoting highly selective gold catalyzed cycloisomerization reactions of 1,6-enynes.

Since many years, the versatility of the calix[6]arene scaffold has been exploited to construct heteroditopic synthetic receptors to design interlocked and interwoven species such as (pseudo)rotaxanes, with the aim to synthesize artificial nano-machines and devices.[1] A key feature of this class of compounds is represented by the hydrogen-bonding (HB) donor domain, present on the upper ring of the calix[6]arene, which is able to promote the threading of mono- and di-cationic species, in low polarity solvents.[2] This occurs by weak HB interactions able to separate the ion pair associated with an organic axle, for instance, a bipyridinium salt, promoting the threading inside the π-rich aromatic cavity of the host.[3] In this context, we recently developed a novel class of calix[6]arene-based heteroditopic receptors (TSA) that present three sulfonamide moieties at the macrocycle's upper rim.[4] Here, the HB domain was utilized to design ion-pair selective receptors for bipyridinium salts.[5] Particularly, while in the presence of weak ion-pairs, TSAs form pseudorotaxanes in a typical *cone* conformation, the use of tight ion-pairs led to a selective rearrangement that brings the calix[6]arene in a *partial cone* (*p*C) conformation. The reactivity of these systems is highly influenced by the reaction medium. In fact, in polar protic solvents, such as methanol or water, TSAs work as Brönsted acid catalysts, promoting a general Michael addition of indoles to nitroolefines.[6] Parallelly, another important goal that has been tackled in supramolecular chemistry is the synthesis of multivalent organometallic macrocycles for catalysis.[7] Inspired by nature's enzymes, many researchers aimed to devise artificial (metal-)catalysts for selective organic transformations.[8] In this context, cutting-edge contributions demonstrated the ability of calix[n]arene[9] and resorcinarene-based cavitands,[10] appropriately functionalized with phosphine ligands, to promote highly selective metal-catalyzed transformations. Although much progress has been recently reached using phosphine-based cavitands, particularly in the field of gold catalysis,[11-13] the working mode of these supramolecular species is limited to the catalytic event itself. Due to our recent interest in the synthesis of supramolecular multitasking objects able to perform different functions through the control of the space and binding sites, we now introduce a novel family of triphoscalix[6]arene derivatives. Remarkably, the selective functionalization of the scaffold allowed for the unprecedented synthesis of triphosphine ligands, eventually coordinated with three gold(I) nuclei, which were exploited for both molecular recognition and catalysis (Figure 1).

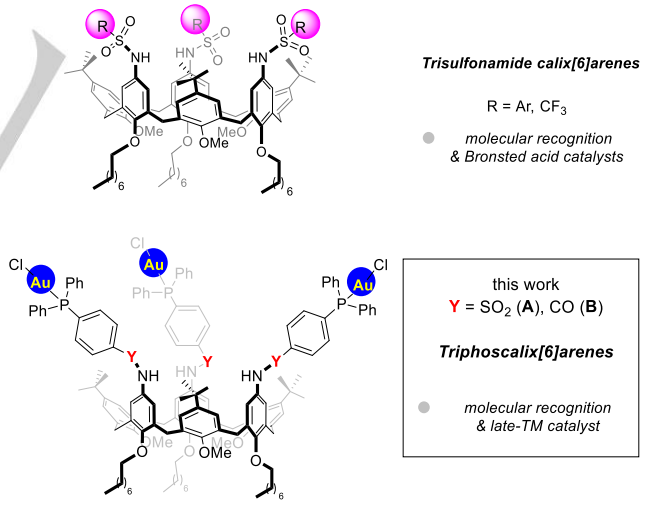

Figure 1. Comparing the reactivity of TSA Brönsted Acids with Triphosphine calix[6]arene Au(I) complexes.

The synthesis of the novel multivalent calix[6]arene derivatives **A** and **B** (see Figure 1) was accomplished starting from the known trinitrotrioctyloxy derivative **TN**. Reduction of the nitro groups in the presence of hydrazine and catalytic amounts of Pd/C, led to the triaminoderivative that was subsequently reacted in the presence of *p*-iodobenzensulfonyl chloride or *p*-iodobenzoyl chloride to afford the corresponding tri(sulfon)amide scaffolds (83% and 75% respectively). Successively, these

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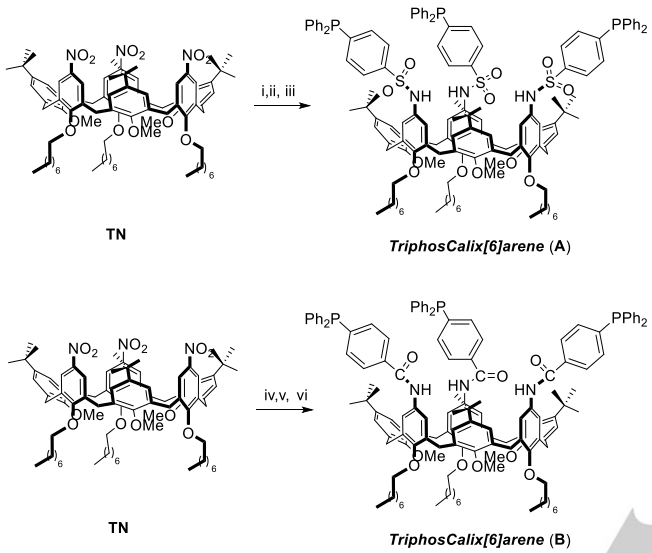
intermediates were submitted to typical cross-coupling conditions using $Pd(OAc)_2$ (20 mol %) as the catalyst and diphenylphosphine[14] to yield triphoscalix[6]arene ligands **A** and **B** in moderate yields (51% and 48%) (Scheme 1). Ligand **B** could be also delivered in a more convenient manner through a convergent approach based on an amide-coupling reaction using an excess of 4-diphenylphosphino benzoic acid (3.5 equiv.) in the presence of the triaminocalix[6]arene intermediate (see SI for more details).



Scheme 1. Synthesis of Triphosphinocalix[6]arene ligands **A** and **B**: i) Pd/C (cat.), N_2H_4 H_2O, EtOH, 100 °C, quant.; ii) 4I-$C_6H_4SO_2Cl$, TEA, CH_2Cl_2, 25 °C, 83%; iii) $Pd(OAc)_2$ (cat.), $PHPh_2$; TEA, DMF, 130 °C, 51%; iv) Pd/C (cat.), N_2H_4 H_2O, EtOH, 100 °C, quant.; v) 4I-C_6H_4COCl, TEA, CH_2Cl_2, 25 °C, 75%; vi) $Pd(OAc)_2$ (cat.), $PHPh_2$, TEA, DMF, 130 °C, 48%.

The conformation adopted by **A** and **B** in solution was analyzed by NMR spectroscopy. In $CDCl_3$, **A** is present in a typical *pseudo cone* conformation as reflected by the AX system of two doublets ($J \sim 15$ Hz) for the six bridging methylene groups and the up-field shift (~2.5 ppm) of the methoxy groups, which points inside the aromatic cavity of the calix[6]arene scaffold. Noteworthy, ^{31}P-NMR of triphosphine **A** was characterized by a single peak at -5 ppm, indicating the high symmetrical geometry of the calix[6]arene ligand. A more entangled situation was observed for **B**. Here, the major *pseudo cone* conformer is in equilibrium, at the NMR time scale (Fig. S1 in SI), with a second conformation that gives rise to six pair of doublets: three for the equatorial and three for the axial diasterotopic methylene protons (vide supra). Such a pattern is suggestive of a "distorted" *cone*. The presence of two species in equilibrium was further reflected by ^{31}P-NMR analysis that presents two close signals at -5.56 and -5.95 ppm (Figure 2).

We next evaluated the ability of **A** and **B** to work as supramolecular receptor for viologen salts derivatives. Hence, we equilibrated a solution of **A** with 1.5 equivalents of DOV•2OTs in $CDCl_3$ at room temperature. The formation of a deep yellow mixture suggested the presence of charge-transfer interactions indicative of the formation of a pseudorotaxane complex. ^{1}H-NMR analysis was subsequently performed. We first observed an extensive up-field shift of the aromatic CH and N-CH_2 protons of the guest, which thus confirmed the formation of an interwoven species, along with two new downfield-shifted signals for the methoxy groups ($ and £) in a 1:2 ratio (Figure 3). Similarly, the three protons of the NH groups of the host, suffered a splitting (1:2 ratio) and a downfield shift to 10.2 and 9.5 ppm as a consequence of their engagement in HB interactions with the tosylate counterions (Figure 3).[15] A different pattern for the methylene groups, analogous to what is usually observed with this family of heteroditopic TSA receptors, revealed a fair selective formation (~ 3:1) of a pseudorotaxane in a *partial cone* conformation. 2D NMR techniques confirmed this finding, and, particularly, HSQC analysis revealed a significant shift of the ^{13}C-NMR resonances to δ = 35.7 ppm for the a/a' couple.[16] This shift, typical of an anti-orientation of the methylene bridging protons, is the prerogative of an inversion point associated with a ring bearing a methoxy group ($) (see figure S1 in supporting information). Differently, triphosamide derivative **B** was not able to host any bipyridinium guest, probably due to the low efficiency of the NH amide moieties to separate the ion pairs associated with the viologen-based salts.

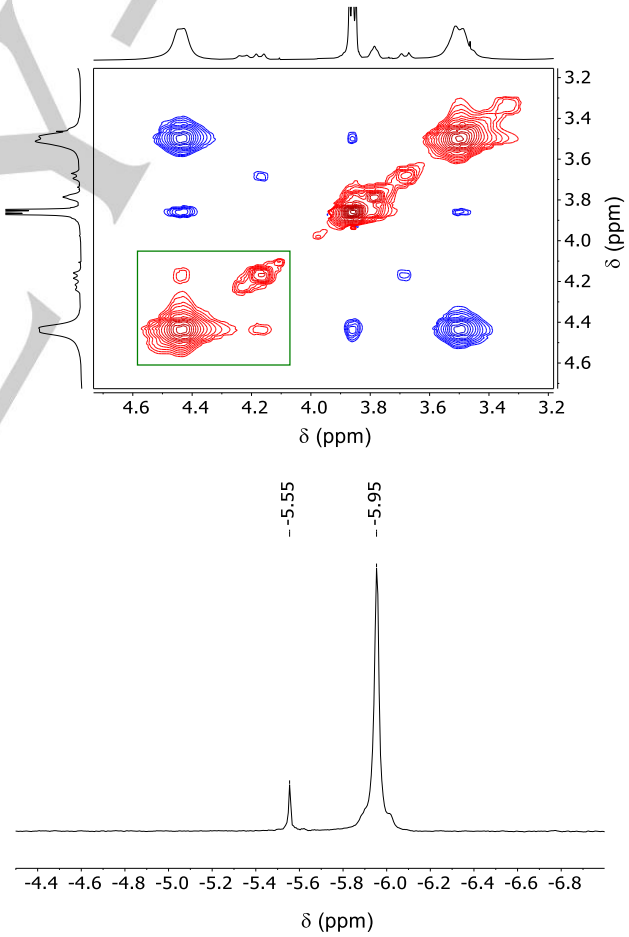


Figure 2. ^{1}H-ROESY spectra of **B** showing interchanges (highlighted in green) between axial methylene protons of "distorted" cone and pseudo-cone conformation (left); detailed ^{31}P-NMR of **B** (right).

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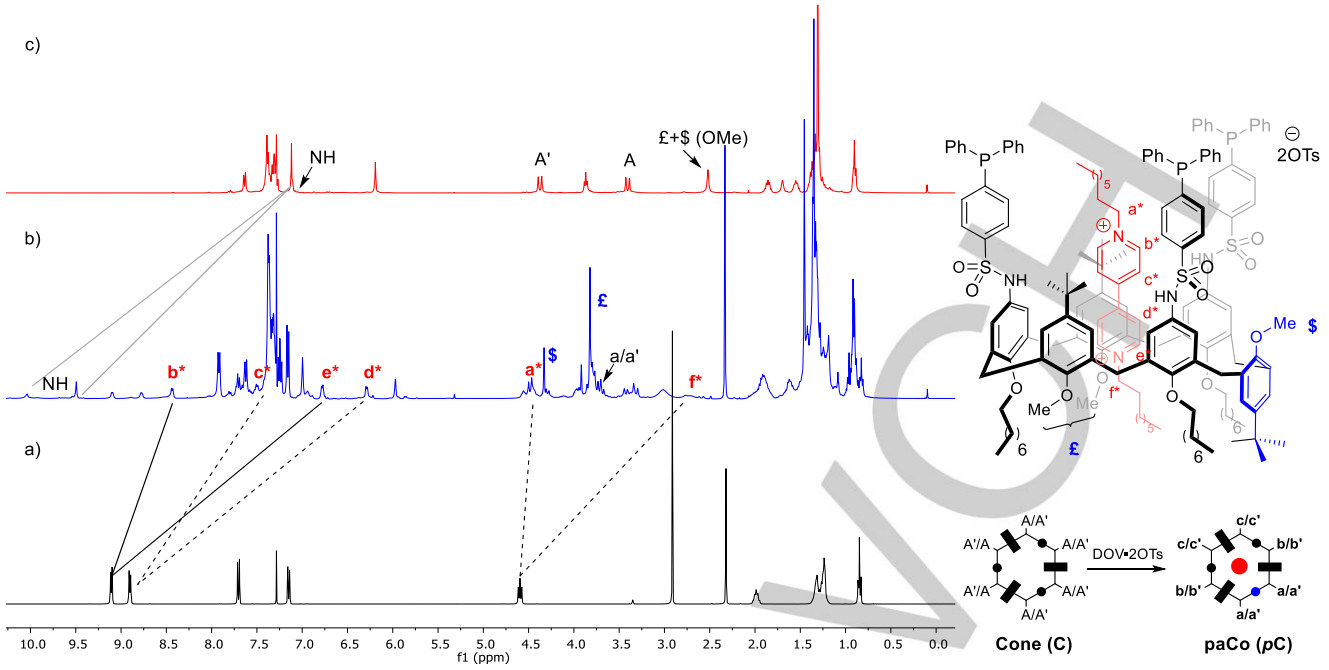

Figure 3. ^{1}H-NMR spectra (400 MHz, 298 K) of a) DOV•2OTs in CD_3CN, b) pseudorotaxane P[**A**(*p*C)⊃DOV]2OTs in $CDCl_3$, c) calixarene **A** in $CDCl_3$. Down-right, schematic representation of P[**A**(*p*C)⊃DOV]2OTs. The color of the ovals/rectangles indicate the relative position of the phenolic substituent with respect to the plane defined by the bridging methylene groups (hexagon), i.e. black upward, blue downward. The rectangle identifies the phenolic ring substituted with the octyloxy chains, while the circle those with the methoxy groups.

Intrigued by these features, we next carried out the synthesis of the corresponding trinuclear gold(I) calix[6]arene complex. Hence **A**$(AuCl)_3$ was obtained by simply mixing triphosphine **A** with 3 equivalents of Au(DMS)Cl precursor in CH_2Cl_2 and characterized by NMR and HR-MS spectroscopy. Interestingly, ^{31}P NMR analysis revealed a significant shift to 33 ppm upon exhaustive complexation of the phosphines with Au(I) nuclei. This value, equal to that of PPh_3AuCl, suggested that the electronic and steric properties of **A**$(AuCl)_3$ are not influenced by the calix[6]arene scaffold and so could be somehow related to the ones of the well-established gold(I) catalyst. Furthermore, NMR analysis of **A**$(AuCl)_3$ did not show any notable variation in the geometry of the calix[6]arene macrocycle, which is still present in a *pseudo-cone* conformation in low-polarity solvents. For the sake of comparison, we evaluated the ability of **A**$(AuCl)_3$ to work as a host in the presence of bipyridinium salts. We thus operated as previously described by mixing **A**$(AuCl)_3$ with an excess of DOV•2OTs and analyzed the mixture by NMR. In solution, we observed the formation of an interwoven structure, which could be easily assigned to the pseudorotaxane in a *partial cone* conformation P[**A**$(AuCl)_3$(*p*C)⊃DOV]2OTs, in slow exchange, on the NMR timescale, with the "empty" host. This could be deduced by the presence of a residual signal at ~2.6 ppm for the methoxy groups inside the aromatic cavity (Figure 4 and SI for a complete characterization). The described situation could be attributed to a steric effect, operated by the presence of three gold(I) nuclei, which depletes somehow the ability of the wheel **A**$(AuCl)_3$ to perform hydrogen-bonding interactions with the counterions of the salt and promoting the threading of the axle from the upper-rim of the macrocycle. Hence, the results collected so far indicates that the selective (*partial cone vs cone*) complexation features of trisulfonamide calix[6]arene derivatives are completely in charge of the HB domain of the wheel, independently by the presence of coordinating substituents, such as a phosphine, present at the upper rim of the calix[6]arene unit.

We thus wanted to analyze the eventual reactivity of the novel trinuclear gold(I) calix[6]arene complexes in a model catalytic reaction. To this end, we chose a gold(I)-catalyzed cycloisomerization of 1,6-enynes.[17-18] By submitting an *N*-tethered enyne **1a** to **A**$(AuCl)_3$ (0.5 mol %) in the presence of catalytic amounts of $AgSbF_6$ as the chloride scavenger,[19] we observed complete consumption of the starting material after 30 min (91% yields, entry 1, Table 1). NMR analysis of the crude reaction mixture revealed a quite remarkable selectivity (14:1) toward the formation of the 6-*endo*-dig rearranged diene **2a** with respect to **2a'**, which is instead formed through an initial 5-*exo*-dig cyclization.[20] Comparable results were obtained by running the catalysis with loading as low as 0.25 mol % for **A**$(AuCl)_3$. The reaction, although slower, yielded product **2a** after 1 h with 85% yields (entry 2).

We finally tested calixphos amide **B** as a catalyst. Hence, a reaction performed by forming *in-situ* **B**$(AuCl)_3$ (0.5 mol %) led to **2a** in high yields and close selectivity (88%, 13:1 *endo*:*exo* entry 3). The results collected so far were compared with data reported in the literature for mononuclear PPh_3AuCl (**C**) and JohnPhosAuCl (**D**) catalysts.[21] Indeed, while **A/B**$(AuCl)_3$ showed a reactivity similar to the one of the triphenylphosphine gold(I) catalyst **C**, the selectivity was closer to the one of the sterically more encumbered **D** (entries 4,5 Table 1).

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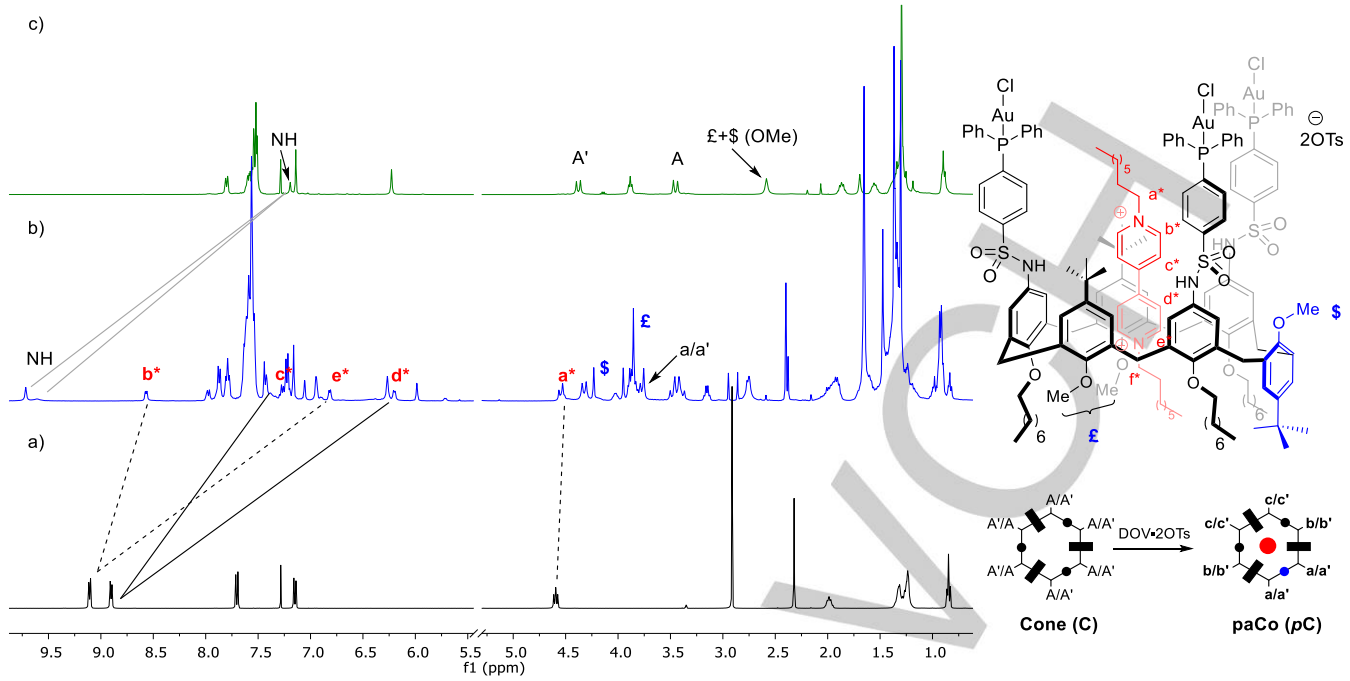
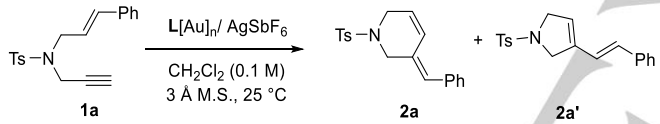


Figure 4. ^{1}H-NMR spectra (400 MHz, 298 K) of a) DOV•2OTs in CD_3CN, b) pseudorotaxane P[**A**$(AuCl)_3$(*p*C)⊃DOV]2OTs in CD_2Cl_2, c) calixarene **A**$(AuCl)_3$ in $CDCl_3$. Down-right, schematic representation of P[**A**$(AuCl)_3$(pC)⊃DOV]2OTs. The color of the ovals/rectangles indicate the relative position of the phenolic substituent with respect to the plane defined by the bridging methylene groups (hexagon), i.e. black upward, blue downward. The rectangle identifies the phenolic ring substituted with the octyloxy chains, while the circle those with the methoxy groups.

Table 1. Ligand effect in gold-catalyzed cycloisomerization of **1a**.



Entry	L[Au]$_n$	min	2a/2a'	2a [%]
1[a]	**A**$(AuCl)_3$ (0.5 mol %)	30	14:1	91
2[b]	**A**$(AuCl)_3$ (0.25 mol %)	60	--	85
3[c]	**B**$(AuCl)_3$ (0.5 mol %)	30	13:1	87
4[d]	PPh_3AuCl (2.0 mol%) (**C**)	5	1:0	100
5[d]	JohnPhosAuCl (2.0 mol %) (**D**)	120	7:1	87

[a] Reaction conditions: **1a** (0.2 mmol), $AgSbF_6$ (1.5 mol %), isolated yields. [b] **1a** (0.2 mmol), $AgSbF_6$ (0.75 mol %). [c] **1a** (0.2 mmol), **B** (0.5 mol %), Au(DMS)Cl (1.5 mol %), $AgSbF_6$ (1.5 mol %). [d] Reported data, see ref. 20. Ts = 4-Toluensulfonyl.

In order to verify the general applicability of the transformation, we synthesized a small family of 1,6-enynes **1** with different sulfonamide-based *N*-tethering moieties (Scheme 2, a) and cinnamyl fragments (Scheme 2, b) and submitted to optimal conditions. Electron-rich groups such as for **1b,c** performed with comparable high efficacy delivering the corresponding 1,3-dienes **2b**,**c** in high yields (91-87%). Contrarily, for halogen and nitro-substituted arylsulfonamides **1d**-**f**, we observed a general decreased performance probably due to the higher affinity of such FGs toward the gold(I) catalyst. The reaction never reached full conversion despite a prolonged stirring (up to 2 hours). Nevertheless, **2d**-**f** could be isolated in synthetically useful yields (78-60%). Substitution at the *ortho*-position of the cinnamyl fragment with a methyl group did not impact the catalysis with product **2g** isolated with high yields. Interestingly, in the presence of electron-withdrawing groups such as fluoride, chloride and trifluoromethyl, the catalysis required additional time to reach full conversion. After 1 h, product **2h**-**j** were delivered in very good yields (79-85%). The reactivity was also preserved in the presence of isoprenyl-substituted enynes. However, while in the case of **1k**, a simple 1,3-diene **2k** was isolated with 94% yields, a different outcome was observed for the geranyl-substituted **1l**. Here, the 5-*exo*-dig cyclization pathway became more predominant, and the formation of gold(I)-carbene intermediates led to a diastereoselective cascade bis-cyclopropanation to form tetracycle **2l** in valuable yields of 79% (Scheme 2, c).[22] This shift in the selectivity was also observed for enynes bearing a tri-substituted cinnamyl fragment **1m,n**. In accordance with the literature,[20] the 6-*endo* pathway became unfavorable, leading to the formation of dienes **2m,n** in 73% and 65% yields, respectively (Scheme 2, d).

Finally, the role of the calix[6]arene scaffold was investigated running the model catalytic reaction with a monomeric sulfonamide-based phosphine **E** and in the presence of a competitive binder such as DOV •2OTs (Table 2). In the first case, we observed a slight drop in the regioselectivity (**2a**/**2a'** = 11:1, entry 1) which highlighted the cooperative role of three phosphines implanted in the calix[6]arene ligand in controlling the selectivity of the catalysis. Contrarily, the reaction with an *in situ*-formed pseudorotaxane (entry 2) did not display any substantial variation with respect to the model one. Although just preliminary results, this led us to conclude that the catalytic event occurs outside the aromatic cavity of the trinuclear gold catalyst **A**$(AuCl)_3$.[23]

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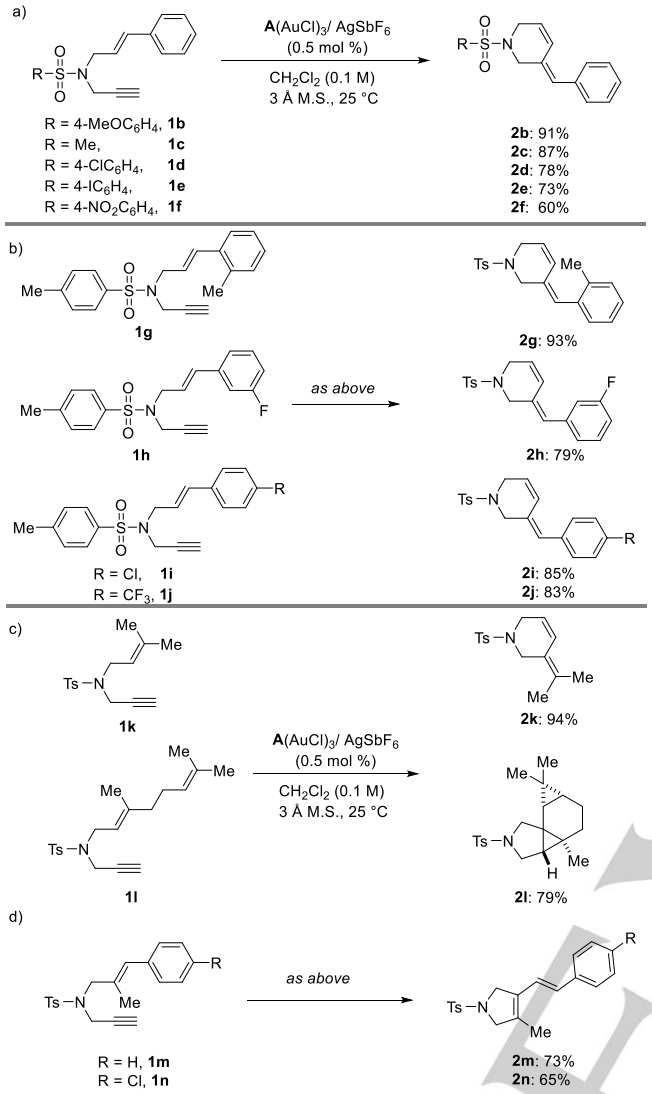
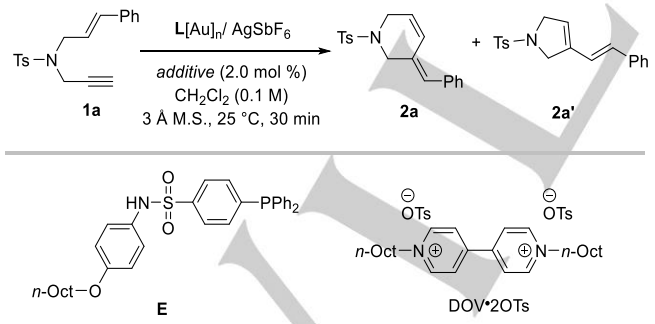


Scheme 2. Catalysis with enynes **1**.

Table 2. Probing the role of the calix[6]arene scaffold.



Entry	L[Au]$_n$	additive	2a/2a'	2a [%][a]
1[a]	**E**AuCl (2.0 mol %)	--	11:1	93
2[b]	**A**(AuCl)$_3$ (0.5 mol %)	DOV•2OTs	14:1	89

[a] Yields determined using 1,3,5-trimethoxybenzene as the internal standard.

In conclusion, we reported on the synthesis of a novel family of multitasking calix[6]arene-based phosphine ligands that were employed to construct trinuclear gold(I) complexes. While these species are both able to perform as catalysts for general cycloisomerizations of 1,6-enynes, their ability as guests is highly influenced by the HB domain that promotes the threading of viologen-based axles inside the aromatic cavity of the wheel. This study paves the way for more investigations on the reactivity of these complexes and their (pseudo)rotaxane analogues particularly on the control of regio- and stereoselectivities in established gold-catalyzed cascade reactions.[24]

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Keywords: phosphines • calix[6]arenes • pseudorotaxanes • molecular recognition • gold catalysis

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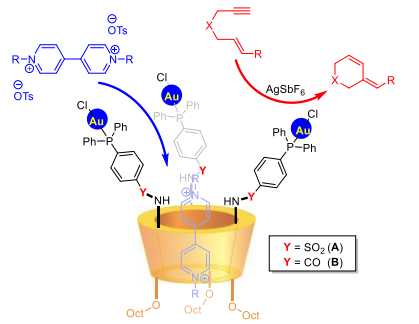
Triphoscalix[6]arene for molecular recognition & gold catalysis



We report the synthesis of novel trinuclear triphosphine-gold(I)-calix[6]arene complexes **A**,**B**. These multitasking supramolecular wheels, which could be employed as a platform for the synthesis of interwoven (pseudo)rotaxanes species, displayed catalytic features promoting highly selective cycloisomerizations of 1,6-enynes.

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