

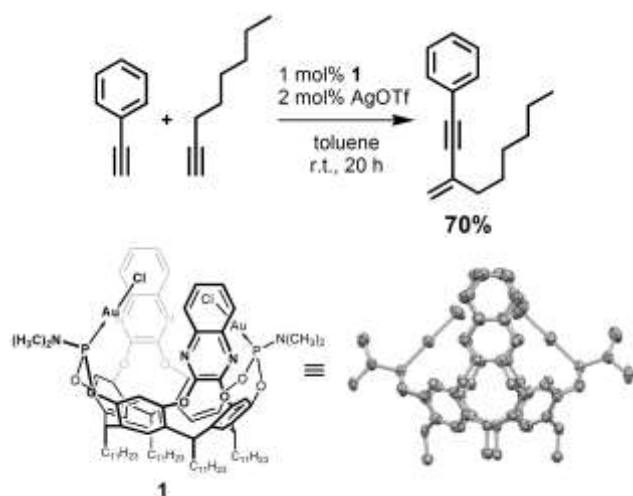
Evaluation of Metallo-catalytic Cavities of Introverted Bis-Au Complexes through Cross-dimerization of Terminal Alkynes

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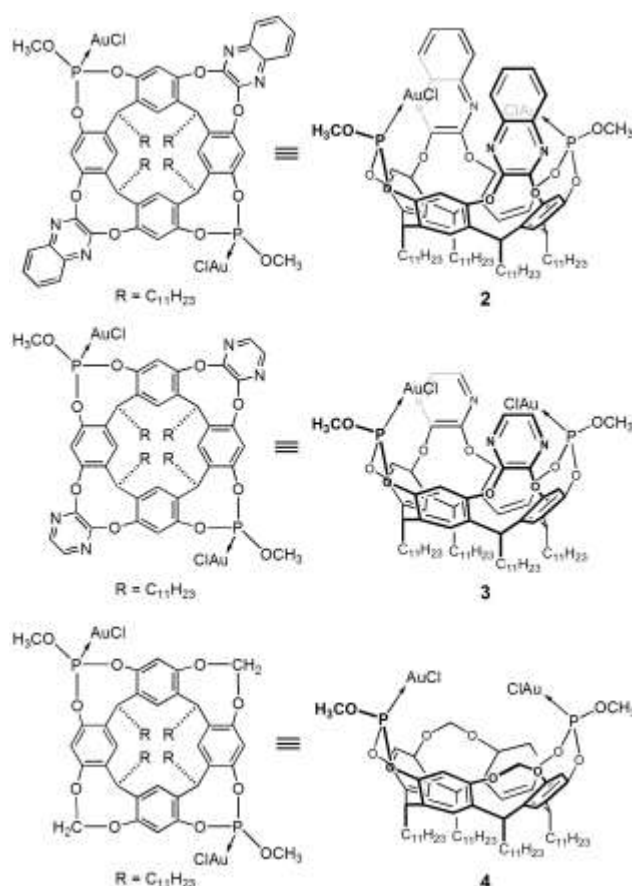
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The development of introverted metal cavitands for catalytic use has attracted much attention, because the enforced cavities allow enzymatic catalysis to be mimicked. Recently our group synthesized inwardly oriented phosphoramidite-Au dinuclear cavitand complex **1** that was flanked by two quinoxaline walls and a resorcin[4]arene base. The molecular structure was determined by crystallographic analysis, which disclosed that the phosphoramidite P-N bonds point outside placing the two Au atoms inside. We explored its catalytic proclivity and found it enables the selective direct dimerization of terminal alkynes to afford conjugated enynes (**Scheme 1**).¹ We already demonstrated several control experiments in which an introverted mono-Au cavitand, AuCl·PPh₃, and AuCl·S(CH₃)₂ had no catalytic activity; however, the effect of its cavity space surrounded by quinoxaline walls was not yet verified, because bis-Au model complexes that removes two walls didn't exist.

Herein, we present the synthesis of bis-Au complex **2** and corresponding models **3** and **4**, including a comparison of their reactivities in dimerization reactions (**Scheme 2**).² In models **3** and **4**, for which the former equips the space with two pyrazine walls and the latter lacks two walls of its parent **2**, the two Au atoms are directed towards the appended resorcin[4]arene core. We anticipated that evaluation of the reactivities of **2**, **3**, and **4** in the previously reported dimerization reactions would unveil the role of the cavity space and the origin of the supramolecular catalysis. The results are summarized in **Table 1**, in which, cross-adduct **5** and homo-adduct **6** were the only products obtained, and **5** were predominantly formed. Bis-Au **2** catalyzed the reactions to provide yields of 58 % with molar ratios of **5** to **6** of 3.0:1 (entry 1). In contrast, pyrazine-type bis-Au **3** gave markedly lower yields of 6 % with molar ratios of **5** to **6** of 4.3:1 (entry 2). Surprisingly, model bis-Au **4** did not catalyze any reaction (entry 3). These results explained that the larger compartment exhibits much more catalytic-activity. The two quinoxaline moieties proved to be quintessential for the catalytic event.



Scheme 1. An introverted bis-Au cavitand **1** catalyzed cross-dimerization of terminal alkynes.



Scheme 2. Introverted bis-Au phosphite cavitand **2** and corresponding models **3** and **4**.

Table 1. Comparison between **2**, **3**, and **4** in the dimerization reactions

Entry	Catalyst	Yield [%] of	
		5	6
1	2	58	19
2	3	6	1
3	4	0	-

References

- Endo, N.; Kanaura, M.; Schramm, M. P.; Iwasawa, T. *Eur. J. Org. Chem.* **2016**, 2514-2521.
- Kanaura, M.; Endo, N.; Schramm, M. P.; Iwasawa, T. *Eur. J. Org. Chem.* **2016**, 4970-4975.