

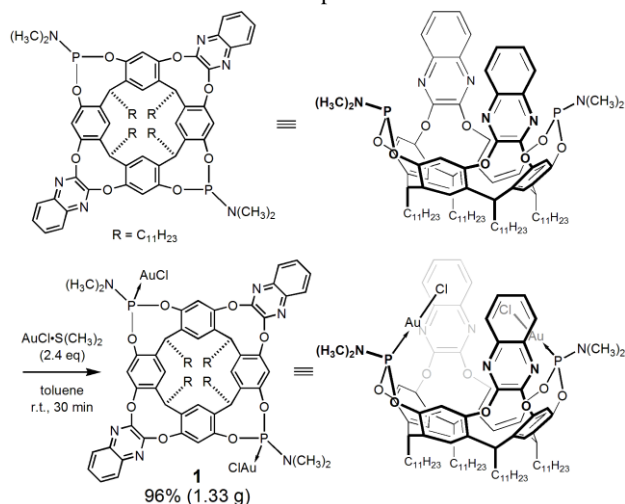
An Introverted Bis-Au Cavitaand and Its Catalytic Dimerization of Terminal Alkynes

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A preparative synthesis of an inwardly oriented phosphoramidite-Au dinuclear resorcinarene cavitaand complex is described, including a description of potent catalytic dimerization.¹ A cavitaand scaffold of di-quinoxaline-spanned resorcin[4]arene reacted with a commercially available precursor of P(NMe₂)₃ to form a single bis-phosphoramidite. This phosphorus ligand tethered to the cavitaand platform was explored to make a complex with transition metals; upon reaction of the ligand with AuCl•S(CH₃)₂, a new bis-Au complex was prepared quantitatively in 1.33 gram scale (Scheme 1). The molecular structure was determined by crystallographic analysis, which disclosed that the phosphoramidite P-N bonds point outside placing the two Au atoms inside (Figure 1). We explored its catalytic proclivity and found it capable for the selective direct dimerization of terminal alkynes to prepare conjugated ene-yne (Scheme 2). In examining the **1**-mediated Conia-ene reaction we were surprised to find no evidence of cyclization – instead, **1** brought two alkynes together to result in a dimerization event. In addition, we examined the dimerization of commercially available 1-octyne; **1** catalyzed the homo-dimerization to give a single isomeric enyne in head-to-tail fashion with 83% yield. Furthermore, we were excited to find that ethynylbenzene and 1-octyne were preferentially coupled to give a cross-dimer as the predominant product in 70% yield. A homo-dimer was also formed under the reaction conditions but only fractionally so (17%). We conducted thorough control experiments: (1) utilizing the mono-Au complex,² (2) using commercially available AuCl(PPh₃), (3) using phosphorus-free AuCl(SMe₂), and (4) using the gold-free host. Dimers were not observed in any case. These suggest that the substructure of dinuclear **1** is indispensable for producing cross-dimers. This carbon-carbon bond forming reaction enables us to construct a nine-membered ring structure (Scheme 3). Thus, mixed dimerizations give rise to chemoselective products and large ring formation via intramolecular dimerization complements this new reaction.



Scheme 1. Synthesis of an introverted bis-Au cavitaand **1**.

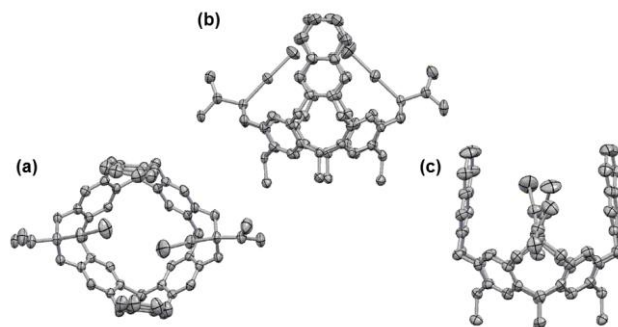
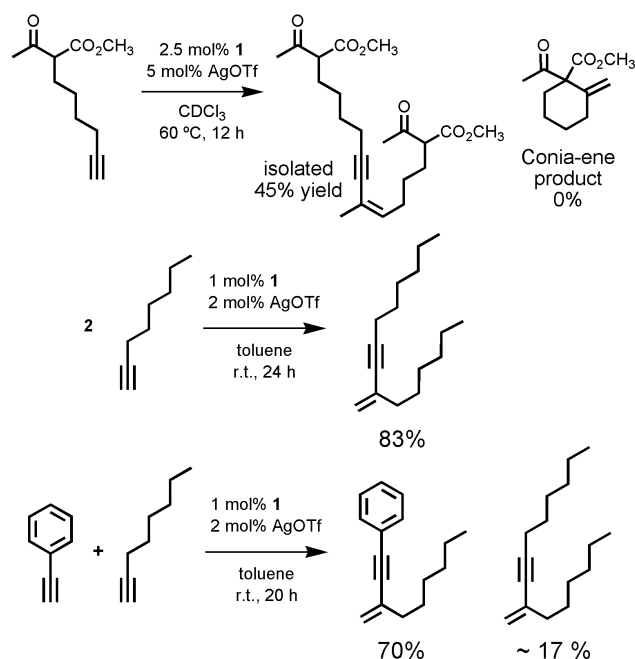
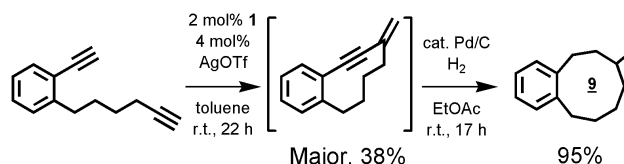


Figure 1. ORTEP drawing of **1** with thermal ellipsoids at the 50% probability level: (a) top view; (b) side view from a quinoxaline wall; (c) side view from a phosphoramidite moiety. The interior CH₂Cl₂ is deleted for ease of viewing, and hydrogen atoms are omitted for clarity.



Scheme 2. Catalytic dimerizations of terminal alkynes.



Scheme 3. Cross-dimerization between intramolecular aryl- and alkyl alkyne.

References

- Endo, N.; Kanaura, M.; Schramm, M. P.; Iwasawa, T. *Eur. J. Org. Chem.* **2016**, 2514-2521.
- Schramm, M. P.; Kanaura, M.; Ito, K.; Ide, M.; Iwasawa, T. *Eur. J. Org. Chem.* **2016**, 813-820.