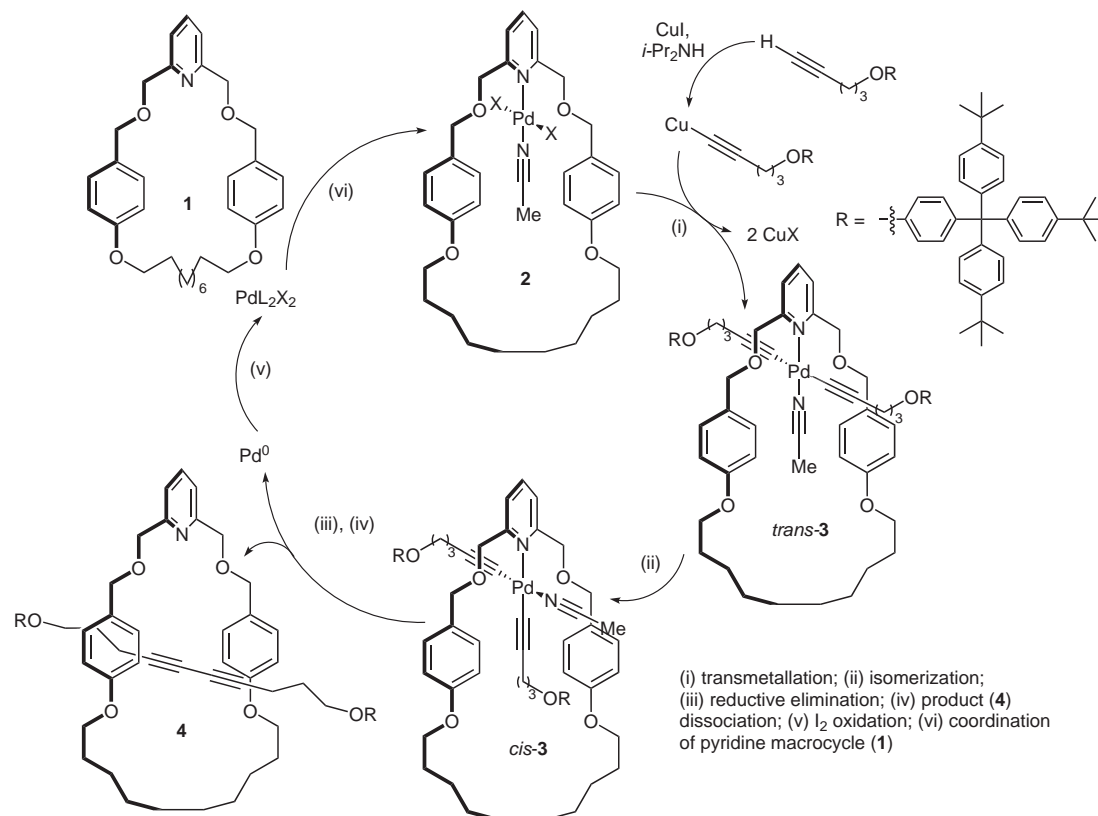


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A Catalytic Palladium Active-Metal Template Pathway to [2]Rotaxanes

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Palladium-Catalyzed Synthesis of Rotaxanes



Significance: The authors describe a means by which to assemble rotaxanes using catalytic palladium. A catalytic amount of preformed **2** ($X = Cl$) undergoes transmetalation with an alkynyl cuprate. This occurs with retention of stereochemistry at Pd(II), to give *trans*-**3**, thus threading the macrocycle. Isomerization to the *cis*-isomer, followed by reductive elimination and dissociation liberates **4**. Pd(0) is re-oxidized with iodine to the active Pd(II) species, coordination of **1** then completes the catalytic cycle.

Comment: There is a general preference for catalytic reaction systems since the use of stoichiometric metal generates significant waste and can increase the cost of a reaction. For the assembly of rotaxanes, there exist few such substoichiometric techniques. Although the authors had previously described one such method in the catalytic synthesis of rotaxanes using 'click' chemistry (*J. Am. Chem. Soc.* **2006**, *128*, 2186), this work is significant since it extends the scope to palladium-catalyzed reactions. Therefore, this work provides an excellent foundation for the development of other catalytic assemblies of macromolecular structures, by way of reductive elimination of the termini from an encapsulated metal.

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