Activating gold catalysts by encapsulation in a self-assembled cage

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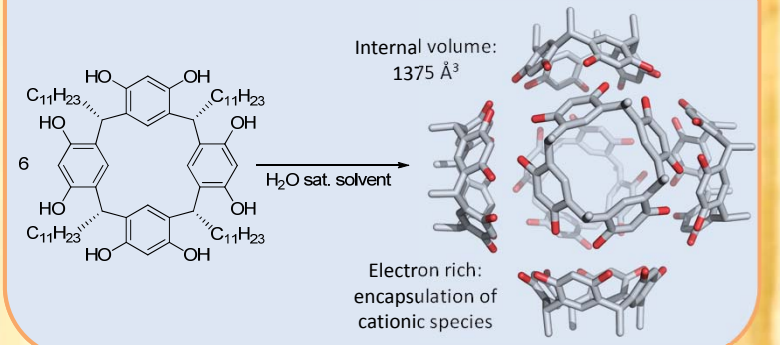
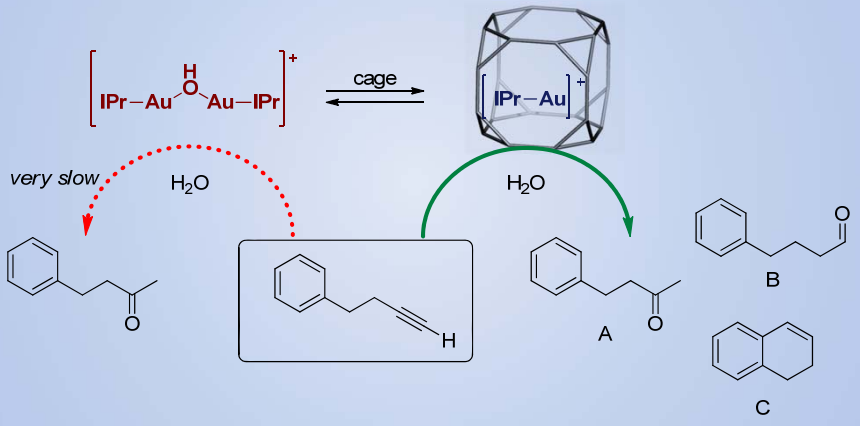
1. Introduction

Enzymes show very high activities and selectivities by using a confined space around the active center. Many natural active sites only display activity (and/or selectivity) when present in the confined space generated by the surrounding protein. These principles can be mimicked by encapsulation of transition metal complexes in a synthetic capsule. In this contribution, a self-assembled hexameric resorcin[4]arene capsule is used to activate gold catalysts by encapsulation, hereby shifting the equilibrium from the inactive dimer to the active monomer.

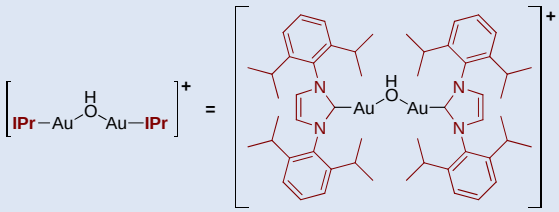
2. Self-assembled hexameric cage



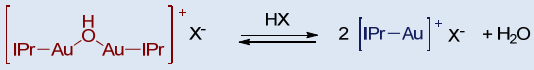
3. Influence of the cage in catalysis



4. Gold catalyst



5. Activation of the catalyst



Outside cage *Inside cage*

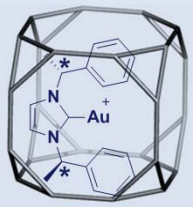
- The dimeric complex is too large to be encapsulated
- Monomeric complexes outside the cage react with water to form the inactive dimer
- Confirmed by ^{1}H NMR

6. Hydration reaction

		Without cage		With cage	
X^-	Reaction time (h)	Conversion	A : B : C	Conversion	A : B : C
BF_4^-	27	12%	100 : 0 : 0	69%	44 : 0 : 56
SbF_6^-	27	50%	97 : 3 : 0	88%	73 : 7 : 21
OTf^-	27	5%	100 : 0 : 0	89%	73 : 8 : 18
NTf_2^-	27	6%	100 : 0 : 0	65%	71 : 10 : 19

7. Conclusion & Outlook

- It was shown that the cage can activate the dinuclear gold carbene. This leads to a changed product distribution in catalysis.
- This concept will be extended to asymmetric catalysis. A chiral dimeric complex will be used to study the asymmetric hydration of allenes.



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