

Homogeneous Catalysis

Encapsulated Cobalt–Porphyrin as a Catalyst for Size-Selective Radical-type Cyclopropanation Reactions

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Abstract: A cobalt–porphyrin catalyst encapsulated in a cubic M_8L_6 cage allows cyclopropanation reactions in aqueous media. The caged-catalyst shows enhanced activities in acetone/water as compared to pure acetone. Interestingly, the M_8L_6 encapsulated catalyst reveals size-selectivity. Smaller substrates more easily penetrate through the pores of the "molecular ship-in-a-bottle catalysts" and are hence converted faster than bigger substrates. In addition, *N*-tosylhydrazone sodium salts are easy to handle reagents for cyclopropanation reactions under these conditions.

Bio-inspired supramolecular cage catalysts, sometimes referred to as molecular flasks, attracted much attention in recent years.^[1] The aim of these fascinating man-made architectures is to translate some of the operational modes of enzymes-nature's catalysts-to synthetic systems. One of their main characteristics is that catalyzed transformations take place in confined spaces. Unfortunately, the design of such molecular flasks is very challenging while offering mostly only a very limited scope of substrates for catalysis. Recently, we have reported the synthesis of the Nitschke-type M₈L₆ cubic cage 1 through self-assembly (Scheme 1).^[2,3] Furthermore, we showed that 1 is suitable to encapsulate tetra(4-pyridyl)metalloporphyrins (M(TPyP) (2) with M = Zn, Co) to give the $M_8L_6P_1$ cubic cages [2-Zn@1] and [2-Co@1] (P=porphyrin guest). In particular, the encapsulation of a cobalt-porphyrin is interesting, because these complexes are known for their catalytic activity in radical-type reactions.^[4,5] Indeed, we were able to show that [2-Co@1] is a catalytically active molecular flask. However, reactions catalyzed by the cubic cage were limited to DMF as solvent to date. Furthermore, the substrate scope

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remained unexplored. In addition, and most importantly with respect of the content of the present paper, it remained unclear if size-selective transformations are possible with encapsulated catalysts, such as [**2-Co**@1].

Shape and size selectivity plays a tremendously important role in several enzymatic processes,^[6] as well as a plethora of catalytic reactions with zeolites,^[7] zeolite-like "ship-in-a-bottle" catalysts,^[8] metal-organic frameworks,^[9] and related systems.^[10] In marked contrast, homogeneously catalyzed processes with soluble, caged (supramolecular) catalysts or "molecular ship-in-a-bottle" systems showing shape or size selectivity are extremely rare.^[11] The development of such systems is of importance for, among others, the advancement of selective tandem catalytic processes and/or one-pot, multicomponent reactions with complex mixtures of catalysts and substrates.

Herein, we present, to the best of our knowledge, the first example of a soluble "molecular ship-in-a-bottle catalyst" capable of size-selective radical-type cycplopropanation reactions. In addition, an unexpected beneficial effect of water on the rate and selectivity of cobalt-porphyrin-catalyzed cyclopropanation reactions is reported.

We started our investigations by improving the solubility of cage 1, aiming for a cage that is soluble in different organic solvents or solvent mixtures. Because modification of the aldehyde or porphyrin structure might interfere with the cage formation, we decided to manipulate the counterion.^[12] Replacing $Fe(OTf)_2$ with $Fe(NTf_2)_2$ resulted in cage compound 3 in 97% yield (see the Supporting Information for characterization). Cage compound 3 proved to be soluble in acetone, acetonitrile, and DMF, as well as in solvent mixtures, for example, 1,2dichlorobenzene/acetonitrile or water/acetone. In addition, high-resolution mass spectrometry showed that the stoichiometry of the assemblies does not change in different solvents (see the Supporting Information). Analogous to compound 1, cage 3 is also able to encapsulate metalloporphyrins 2-Zn and 2-Co to give [2-Zn@3] and [2-Co@3] in good yields (Scheme 1 and the Supporting Information). Furthermore, compound 3 and [2-Zn@3] were studied by using ¹H NMR diffusion-orderedspectroscopy (DOSY) techniques revealing that both compounds behave as single, intact supramolecular entities in solution (see the Supporting Information).

With [2-Co@3] in our hands, we explored its ability to catalyze the cyclopropanation of styrene (4) with ethyl diazoacetate (5) in different solvents (Table 1). These experiments showed that the change of counterion has little effect on the catalytic synthesis of **6** (Table 1, entries 1 and 2, turnover

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Scheme 1. Synthesis of cubic cages 1 and 3 with subsequent encapsulation of 2-M. [2-M@1] is shown as a model (Spartan 08, MM SYBYL FF; hydrogen atoms and counterions are omitted for clarity).

Table 1. Cobalt-catalyzed cyclopropanation of styrene.								
+		O U N ₂ OEt —	cat. (0.25 mol%) Solvent, 70°C, 1h					
4 (*	I.0 equiv)	5 (1.0 equiv)	1			6		
Entry	Catalyst	Solvent ^[c]		Yield [%]	d.r. ^[d]	TON		
1 ^[a]	[2-Co @1]	DMF		28	65:35	33		
2 ^[a]	[2-Co@3]	DMF		25	65:35	30		
3	[2-Co@3]	DMF		6	65:35	27		
4	[2-Co@3]	acetone		19	65:35	77		
5	[2-Co@3]	acetone/water	1:5	46	66:34	182		
6	3	acetone/water	1:5	_	_	_		
7	2-Co	acetone/water	1:5	3	83:17	10		
8	7	acetone/water	1:5	_	—	—		
9	8	acetone/water	1:5	_	—	—		
10	9	acetone/water	1:5	75	73:27	302		
11	9	acetone		63	78:22	252		
12	10	acetone/water	1:5	64	79:21	255		
13 ^[b]	[2-Co@3]	acetone/water	1:5	73	65:35	292		
14 ^[b]	[2-Co @ 3]	acetone/water	1:5	76	66:34	304		
[a] Catalyst loading (0.8 mol%), 4 (1.2 equiv). [b] Reaction time 24 h. [c] $[D_6]$ acetone was used. [d] d.r.=diastereomeric ratio.								

number (TON) = 33 and 30, respectively).^[13] Reducing the catalyst loading to 0.25 mol% resulted in a decreased yield of only 6% and a similar TON of 27 (entry 3). However, employing [D₆]acetone as solvent increased the yield to 19% (Table 1, entry 4, TON = 77). Remarkably, the reactivity of [**2-Co@3**] increased further by carrying out the reaction in a 5:1 mixture of water and [D₆]acetone giving 46% **6** (Table 1, entry 5, TON = 182).^[14]

Control experiments showed that the empty cage 3 is not catalytically active at all (Table 1, entry 6). Importantly, [2-Co@3] is substantially more active than the free tetra-(4-pyridyl)porphyrin catalyst 2-Co (entry 7, 3%, TON = 10). Furthermore, watersoluble 5,10,15,20-tetra-(4-Nmethylpyridyl)-porphyrin cobalt(II) tetraiodide (Co-TMePy-P*4I, 7, Figure 1) and tetrasodium 5,10,15,20-tetra(4-sulfonyl)porphyrin cobalt(II) (Co-TPPS*4Na (8), Figure 1) showed no activity at all under the applied conditions (entries 8 and 9). It has to be noted that [2-Co@3] (although soluble in acetone/water mixtures) can migrate to some extend into the water-insoluble substrate phase. This means that [2-Co@3] may act as a phase-transfer catalyst (with the cyclopropanation catalyst embedded). On the other

hand, due to encapsulation in the hydrophobic cavity of [2-Co@3], substrates might be pulled into the aqueous phase. Inspired by this, we tested 5,10,15,20-tetra(phenyl)-porphyrin cobalt(II) (Co-TPP (9), Figure 1). Interestingly, by using catalyst 9 in acetone/water, high yields (75%) of product 6 were obtained already after one hour (d.r.=73:27, TON=302; Table 1, entry 10). Again, a positive influence of water on the reaction outcome has been observed when the reaction in pure acetone gave 6 only in 63% (Table 1, entry 11). A possible explanation for this result might be a stabilization of intermediates through hydrogen bonding from water. Catalyst 10 developed by Zhang and co-workers is known to be superior to 9 in dichloromethane (Figure 1).^[15,16] However, in acetone/water the simpler complex 9 actually outperforms catalyst 10 in terms of activity (64%, d.r. = 79:21, TON = 255; Table 1, entry 12). The reactions using the apolar catalyst 9 and 10 probably did not take place in the aqueous phase. Phase separation of the catalyst into the organic-substrate layer might well play a role in the observed rate enhancements. However, generally reactions in strongly concentrated solutions (organic solvents) typically led to lower yields due to enhanced carbene dimerization. Hence, water does have a true beneficial effect on these reactions. A detailed study of these results is beyond the scope of the current work. Given these data, explaining the enhanced rates and higher TONs obtained with [2-Co@3] in acetone/ water mixtures compared with pure acetone is not so straightforward, and the effect of water on these reactions requires more research in the near future. For now, it suffices to state that the optimal reaction conditions of [2-Co@3] were obtained by performing the reactions in acetone/water mixtures, by using catalyst loadings of 0.25 mol %.

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Figure 1. Structures of catalysts Co-TMePyP*4I (7), Co-TPPS*4Na (8), CoTPP (9), and 10.

Using [2-Co@3] as catalyst for a prolonged reaction time of 24 h resulted in a higher TON of 292 and gave 73% **6** (Table 1, entry 13). Reducing the temperature to 50 °C gave similar results, showing that the reaction can be performed under milder conditions (entry 14, 76%, TON = 304).



Scheme 2. Substrate scope of alkenes suitable for [**2-Co**@**3**]-catalyzed cyclopropanation with **5**. [a] [D_6]acetone/water (2:5).

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With the above-described reaction conditions optimized for the caged catalyst [2-Co@3], we explored the scope of suitable alkenes as substrates (Scheme 2). We started our investigations testing diverse styrene derivatives. Styrenes with electron-donating groups gave the corresponding cyclopropanes in high yields (11, 75%, TON = 302, d.r. = 77:23; 12, 88%, TON = 351, d.r. = 76:24). Styrenes with electronwithdrawing substituents also react smoothly, giving cyclopropanes 13 and 14 in good to high yields (13, 78%, TON=320, d.r.=82:18; 14, 66%, TON=265, 80:20). 2-Vinylnaphtalene is also a suitable substrate leading to 15 in 69% yield, whereas sterically demanding cyclopropane 16 was only obtained in 18% yield. The lower yield could be an indication that it is more challenging to assemble the bulky styrene and 5 in the cavity of [2-Co@3]. Another possible reason might be a substrate or product inhibition due to π stacking. However, compound [2-Co@3] still reached

a TON of 73. Cyclopropanation of other alkenes by using catalyst [**2-Co@3**] was less successful. Using phenyl or methyl methacrylate as substrates gave **17** and **18** in moderate yields (**17**, 25%, TON=100, d.r.=82:18; **18**, 20%, TON=82, d.r.=53:47). Unsubstituted acrylates, such as *n*-butyl acrylate reacted through a [3+2]-cycloaddition giving 1*H*-pyrazoles (not shown). Simple olefins, such as 1-octene and allylbenzene gave cyclopropanation products in low yields of 5% or less (see **19** and **20**).

Next, we focused on studying the scope of diazo compounds in the cyclopropanation of styrene **4** (Scheme 3).



Scheme 3. Substrate scope of diazo compounds suitable for [2-Co@3]-catalyzed cyclopropanation of 4.

Benzyl diazoacetate gave cyclopropane **21** in 72% yield. This result is similar to ethyl diazoacetate **5**, which gave **6** under the same conditions in 76% yield. Using the bulky *tert*-butyl diazoacetate (**27**) resulted in the formation of **22** in only 22%. This matches the results described in Scheme 2, in which the bulky 4-benzhydrylstyrene gave low yield of **16** in comparison to other substrates. Disubstituted diazo compounds seem to be unreactive towards **[2-Co@3]**.

Formation of the rather bulky products, such as **22**, showed that the large cavity of [**2-Co@3**] is still accessible for rather large substrates, but the rather low yields obtained also suggest that the cage may well allow size-selective reactions. We

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further investigated this aspect through competition experiments between different styrenes (Table 2). Initially, we chose styrene **4** and 4-benzhydrylstyrene **24** as substrates and employed the optimized reaction conditions while using same amounts of alkenes (in total, 2 equiv) and one equivalent of **5**. Indeed, [**2-Co@3**] clearly favors the formation of **6** over **16** (70:30; Table 2, entry 1). Changing the bulky styrene to **25** gave cyclopropanes **6** and **26** in a similar ratio (64:36; entry 2). However, using the bulky diazo compound **27** as substrate resulted in an increased selectivity towards the less bulky product **22** (Table 2, **22/28** 79:21; entry 3). To the best of our knowledge, these are the first reported size-selective cobalt–porphyrin-catalyzed cyclopropanation reactions. Furthermore, it is a rare example of a size-selective homogeneous catalysts.

Earlier reports, using different diazo substrates, showed that catalytic substrate activation took place inside the cavity of these type of molecular flasks, thus leading to different selectivities compared to similar but non-encapsulated catalysts.^[3]





In good agreement, the results described in this paper show that [**2-Co@3**] allows size-selective substrate transformations. This is most easily explained by a slower migration of larger substrates through the pores of the cage compared to smaller substrates (Figure 2).^[17] As such, the pores of the molecular flask surrounding the cobalt catalyst in [**2-Co@3**] make it possible to distinguish between substrates of similar reactivity but different size. It is important to note that Co-TPP (**9**) is not able to distinguish between these same substrates (Table 2, entries 4–6).

Because the number of stable diazo compounds is limited, and since diazo compounds are partly toxic and explosive, we further became interested in using precursors, which are safe to handle. *N*-Tosylhydrazone sodium salts seemed promising to us, because they are easily accessible from aldehydes while being water soluble. Indeed, styrene **4** could be cyclopropanated by using *N*-tosylhydrazone **29** giving **30** in moderate yield (Scheme 4; 33 %, TON = 132, d.r. = 73:27).



Scheme 4. Cyclopropanation of 4 with *N*-tosylhydrazone sodium salt 29.

In conclusion, we have synthesized a new molecular flask [2-Co@3], soluble in different solvents and solvent mixtures, including water/acetone. Employing water/acetone mixtures as the solvent increased the catalytic performance of [2-Co@3] in styrene cyclopropanation reactions dramatically. The caged catalyst [2-Co@3] showed a preference for cyclopropanation of styrenes over other vinylic substrates. While exploring the substrate scope, it became clear that [2-Co@3] is a size-selective catalyst showing preference for cyclopropanation of smaller styrene and diazo substrates. Bulky substrates reacted slower than smaller ones, thus allowing size-selective competition reactions. To the best of our knowledge, [2-Co@3] is the first well-documented homogeneous catalyst capable of size-selective radical-type cycplopropanation reactions. Furthermore, it is a rare example of a "molecular ship-in-a-bottle" catalysts. Fi-

> nally, we showed that *N*-tosylhydrazone sodium salts are useful diazo precursors in [**2-Co@3**]-catalyzed reactions in aqueous media.

Experimental Section

To an oven-dried Schlenk flask were added [2-Co@3] (35 mg, 2.5 μ mol), [D₆]acetone (0.50 mL), and deionized water (2.50 mL). Argon was bubbled 3 min through



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the reaction mixture. Compounds **4** (1.0 mmol; 104 mg) and **5** (1.0 mmol; 114 mg) were added, and the reaction mixture was stirred for 24 h in an oil bath at 50 °C. The mixture was cooled to RT, and acetone (5 mL) was added. The solvents were removed under reduced pressure, and the crude product was purified by column chromatography to give **6** (145 mg, 760 μ mol, 76%, d.r. (*trans/cis* 66:34).

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Encapsulated Cobalt-Porphyrin as a Catalyst for Size-Selective Radicaltype Cyclopropanation Reactions



Molecular ship-in-a-bottle: A cobalt– porphyrin catalyst encapsulated in a cubic M_8L_6 cage allows cyclopropanation reactions in aqueous media. The caged catalyst showed enhanced activities in acetone/water as compared to pure acetone. Most remarkably, the M_8L_6 -encapsulated catalyst acts as a soluble, size-selective homogeneous "molecular ship-in-a-bottle" catalyst (see scheme).

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